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FORWORD

For every country, scientific activities are important and covering each and all of them internationally. These activities provide more vivid scientific environment, more common benefits and opens up a new dimension to innovations.

For this reason, one of the most important subjects in recent years is polymeric composites and technologically every field has brought innovations and found great uses. At our country there has been studied on this subject for about 25 years as well.

Scientific and applied studies in this field provided a more beneficial environment with the scientific meetings (Symposium, panel, workshop etc.). Because of the exchange of information and the related sectors getting together provided more useful and creative composites and will continue to do so in the future.

For the first time in 2006, an event was organized in the form of symposiums, exhibitions and workshops in Izmir with the support and the contributions of the relevant institutions in our country. Up to today, these activities as two international and one national symposiums have been continued to carry out, once at every two years.

Even though the position of the countries may be difficult under certain conditions, the scientific activities are indispensable. For the same reason, in spite of facing a few difficulties such activities have been carried out continuously in our country. This year our colleagues who are participating from abroad, in spite of having some difficulties did their best to come and attend our symposium, this is giving us a great strength. We hope that these challenges do not limit the scientific field.

Two important areas (defense industry and renewable energy) included as needed for the discussions in this year's activity, each of which will be of great benefit because of the large application areas. At each events, the workshops were organized as per participants' requests.

As participants we all hope, the expected and desired benefits of the subjects such as sharing the scientific and technological information, monitoring the innovations, discussing the topics and efficiency of the workshops, in a good environment can be provided.

As the field of polymer composite is known and developed both in the world and in our country with increasing interest in the scientific and sectoral areas, because of the variety of the environmental problems and the economic positions some difficulties are arising and with the correct solutions evolving to a healthier development.

The effectiveness of these activities, with the presence of the relevant parties and as well as with the debates and the common sense, will be of great benefit. In order to carry out the workshop with the proposed applications the necessary studies have been implemented. For this purpose, the specialists from the industry, universities and abroad will provide the institutional and experimental contributions. For this workshop, we would like to thank Herkim and Kosse Composite, for the identification of the subject and for the preparation of the practical workshop together with those concerned.

After these events, the documents of participation will be given to the symposiums and workshop participants. Symposium book will cover all the abstracts of the presentations and the full manuscripts will be published in our website.

Oral presentations will be held in eleven sessions, including the symposium, in parallel with the next sessions on November 3rd, 2017. The workshop will take place at 3rd and 4th of November 2017. Most of the participants are valuable experts within our country. However in spite of all the difficulties, those who were coming from abroad as invited participants or applicants, will added to the value of this activity. We would like to thank all of the participants for their valuable contributions.

One of the biggest challenges in the realization of the scientific activities is the need for support. For this reason, we would like to thank all the organizations and persons who are supportive. Our main sponsorship in this year's event is PETKİM, the largest and most qualified chemical organization in our country. We would like to thank Mr. Hasan Ömer from HERKİM POLYMER CHEMISTRY INDUSTRY INC. for his suggestions and support from the start, and the institutions IZMIR METROPOLITAN MUNICIPALITY , AEGEAN REGION CHAMBER OF INDUSTRY , IZMIR CHAMBER OF COMMERCE , ISTANBUL CHEMICAL AND CHEMICAL PRODUCTS EXPORTERS' ASSOCIATIONS , AEGEAN EXPORTERS' ASSOCIATIONS , TURKISH COMPOSITE MANUFACTURERS ASSOCIATION, PETKİM PETROCHEMICALS HOLDING INC.(MAIN SPONSOR), HERKİM POLYMER CHEMISTRY INDUSTRY INC. (SPECIAL SPONSOR), BOYTEK RESINS, GELCOATS, PIGMENT PASTES, KOSSE COMPOSITE MARKETING , LITERATUR CHEMICALS, POLUTEK POLYESTER AND POLYURATHANE LIMITED COMPANY, TILA COMPOSITE AGENCY LIMITED COMPANY, OCSiAl, ŞİŞECAM INDUSTRY INC., AKKIM CONSTRUCTION CHEMICALS INC. for their contributions.

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ÖNSÖZ

Bilimsel etkinlikler her ülke için önemli olduğu gibi uluslararası düzeyde tüm ülkeleri kapsamaktadır ve bilimsel ortamı daha canlı daha ortak yarar sağlayan, yeniliklere ufuk açan bir nitelik kazandırmaktadır.

Bu nedenle, son yılların önemli uğraşı konularından biri de polimerik kompozitlerdir ve teknolojik olarak her alanda yenilikler getirmiş ve büyük kullanım alanları bulmuştur. Bizim ülkemizde de yaklaşık 25 yıldır çalışmalar yapılmaktadır.

Bu alanın bilimsel ve uygulamalara yönelik çalışmaları, bilimsel toplantılarla da (Sempozyum, panel, çalıştay vb.) daha yararlı bir ortamı, bilgi alışverişini ve malzemeyi oluşturan kesimler ve alanlar bir araya gelerek daha yararlı kompozitlerin oluşmasını sağlamış ve sağlamaktadır.

2006'da İzmir'de ilk kez sempozyum, sergi ve çalıştaylar biçiminde bir etkinlik yapılmış, ülkemizdeki ilgili kuruluşların desteği ve katkıları ile gerçekleşmiş ve günümüze kadar iki yılda bir olmak üzere ilki ulusal diğerleri uluslarası olarak devam etmektedir.

Ülkelerin konumu kimi şartlarda zorlansa da bilimsel etkinliklerin yapılması vazgeçilmez nitelik taşımaktadır. Bu nedenle, bizim ülkemizde de bazı zorluklar yaşansa da bu tür etkinlikler sürmektedir. Bu yıl, yurt dışı katılımında meslektaşlarımızın kimi sorunları olsa da gelmeye çalışmaları bizlere büyük güç vermektedir. Umarız bu tür zorluklar bilimsel alanı kısıtlamaz.

Uygulama alanının çok geniş olması büyük yarar sağlamış bu yıl ki etkinliğimizde de gereksinim duyulan önemli iki alan (savunma sanayi ve yenilenebilir enerji) tartışmaya uygun görülmüştür. Her etkinlikte katılımcıların isteklerine yönelik çalıştaylar da düzenlenmiştir.

Umarız katılımcılar olarak hepimiz iyi bir ortamda bilimsel ve teknolojik bilgi paylaşımı, yeniliklerin izlenmesi, konuların tartışılması ve çalıştayın verimliliği beklenilen ve istenilen yararı sağlayabilir. Polimerik kompozit alanı bilindiği gibi dünyada ve ülkemizde bilimsel ve sektörel olarak giderek artan ilgi ile çalışılıp gelişirken özellikle çevresel sorunlar ve ekonomik konumların değişken olmaları sonucu zorluklar ortaya çıkarmakta ve bunların doğru çözümleri ile daha sağlıklı bir gelişmeye evrilmektedir.

Bu etkinliklerin ortak akıl ve tartışmalarla, ilgili kesimlerin varlığında, daha iyiye ulaşmada yararı büyük olacaktır. Çalıştayın uygulamalı biçimde gerçekleşmesi önerilerine yönelik çalışmalar yapılmıştır. Bu amaç için sanayiden, üniversitelerimizden ve yurtdışından uzmanlaşmış değerli elemanlar kuramsal ve deneysel katkı vereceklerdir. Bu çalıştay da konuyu

saptayarak uygulamalı biçimde çalıştayı ilgililerle hazırlayarak gerçekleştiren Herkim ve Kosse Kompozit'e çok teşekkür ederiz.

Bu etkinlikler sonrası sempozyum ve çalıştay katılımcılarına katılım belgeleri verilecektir. Sempozyum ve çalıştayda sunulan bildiri özetleri özet kitapçığında toplanmış, tam metinler odamızın web sitesinde yayınlanacaktır.

Sözlü sunumlar 3 Kasım öğleden sonraki oturumlar paralel olmak üzere (Sempozyum) 11 oturum da toplanmıştır. Çalıştay ise 3 ve 4 Kasım olarak gerçekleşecektir. Katılımcıların çoğu yurtiçinden değerli uzmanlardır. Ancak yurtdışından tüm zorluklara karşın gerek çağrılı gerek başvuru ile gelenler bu etkinliğe değer katacaklardır. Tüm sunum yapan katkı veren katılımcılarımıza çok teşekkür ederiz.

Bilimsel etkinliklerin gerçekleştirilmesinde en büyük zorluklardan biri de, gereksinim duyulan desteğin bulunmasıdır. Bu nedenle, destek vermeyi esirgemeyen tüm kuruluş ve kişilere teşekkür ederiz. Bu yıl ki etkinliğimizde ana sponsorluğu ülkemizin en büyük ve nitelikli kimya kuruluşu olan PETKİM'dir. Bu etkinliğin ilk başlatılmasında konunun önemini dikkat çekerek fikir veren, katkılarını tüm etkinlikler sırasında esirgemeyen özel sponsor Herkim (Sayın Hasan Ömer) aynı şekilde bu etkinliklerin sürdürülmesine katkılarıyla sağlayan *İZMİR BÜYÜKŞEHİR BELEDİYESİ*, *EGE BÖLGESİ SANAYİ ODASI, İZMİR TİCARET ODASI, İSTANBUL KİMYEVİ MADDELER ve MAMÜLLERİ İHRACATÇILARI BİRLİĞİ, EGE İHRACATÇI BİRLİKLERİ*, *KOMPOZİT SANAYİCİLERİ DERNEĞİ*, *PETKİM PETROKIMYA HOLDING A.Ş. (ANA SPONSOR)*, *HERKİM POLİMER KİMYA SANAYİ VE TİCARET A.Ş. (ÖZEL SPONSOR)*, *BOYTEK REÇİNE BOYA VE KİMYA SAN. TİC. A.Ş.*, *KOSSE KOMPOZİT MÜHENDİSLİK VE PAZARLAMA LTD. ŞTİ.*, *LİTERATÜR KİMYA*, *AKKİM YAPI KİMYASALLARI SAN. VE TIC. A.Ş.*, *TİLA KOMPOZİT TEMSİLCİLİK İÇ VE DIŞ TİC. LTD.ŞTİ.*, *OCSiAl*, *ŞİŞECAM SANAYII A.Ş.*, *POLÜTEK POLYESTER VE POLİÜRETAN LTD.ŞTİ.*'ya teşekkür ederiz.

Ayrıca bu etkinliğin gerçekleşmesinde KMO Yönetimi ve koordinatör olarak görevi üstlenen Ege Bölge Şubesi Yönetim Kurulu'na emeği ile gece gündüz çalışan sekreterya görevini yürüten meslektaşlarımıza, oda çalışanlarımıza ve destek veren tüm üyelerimize kurum ve kuruluşlarımıza teşekkür ederiz.

Saygılarımızla,

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FULL PAPERS / TAM METİNLER

FILAMENTS SPUN FROM THERMOTROPIC POLYESTERS

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Abstract: Use of strong and stiff reinforcement elements that are chemically and thermally stable, unaffected by water, uv radiation, etc. at correct geometry with suitable binders are major key factors for the formation of successful composites. These prerequisites are met to varying degees by synthetic filaments like aromatic polyamides (Aramids) and carbon fibres which are reffered to as high strength and high modulus (HSHM) filaments.

Success of aramids is a direct result of high molecular anisotropy along the fibre axis easily achieved by their lyotropic liquid crystalline behaviour. Nearly all of the molecules in the filament crossection are load bearing elements. Carbon fibres also owe their success to their molecular structure which consists of axially oriented turbo stratified layers of graphite sheets held by Van Der Waal forces. Another form consists of axial micro tubes configured by graphite like organisation on tubular surfaces along the fibre axis. Either route gives tremendous rise to its tensile properties.

However, these HSHM fibres gets destroyed when bent around small radii. It limits their utilisation to stiff composite articles. Carbon fibres additionally suffer from premature rupture when subjected to even small torsional deformations.

Rubber matrix reinforcement that may be needed in a variety of demanding applications is not possible with these otherwise very highly sucessful materials. The task is currently met by conventional flexible filaments with aliphatic origin. Aliphatic molecular morphology permits only few load bearing chains across the fibre axis due to whic they are mechanically poor performers They also suffer from high degree of shrinkage at elevated service temperatures. There exists a need to a high performing flexible filament that will not rupture when flexed or torsioned or shrink at service temperatures. Aramids are not very dependable if used in wet environments, composites reinforced by them needs to be protected against effects of water and humidity.

Aromatic polyesters are themotropic liquid crystalline counterparts of aramids. They are synthesized and converted to filaments with relative ease and are naturally impervious to wet conditions which increased the interest in them. However, it turned out that they also suffer from premature rupture when flexed as well as being comparatively somewhat poor tensile performers. Further more, heat treatment needed to improve their mechanical performance is too long to permit commercial production easily.

Thermotropic homo-polyesters due to their planar rigid rod like molecular geometry crystallise into near perfect crystallites that melt at temperatures well above their thermal stability limit. To rendrer them processable molecular regularity is disrupted by the intoduction of various molecular forms at random. Consequently the crystallite perfection and hence the melting temperature is lowered for processability. However, the mechanical performance is also lowered!

To solve the problems assciated with HSHM filaments new macromolecule design philosophies and new process aproaches are needed.

One approach envisaged may open the gate to processing thermotropic polyesters into filaments with flawless molecular orientation oblivating the need for lengthly heat treatment while another approach may allow a flexible filament to be produced in exchange for some acceptable loss in mechanical performance.

Some pioneering studies showed that thermotropic random co-polyesters lend themselves to processing manupulations leading to selective formation of liquid and/or solid domains with interesting properties that may open new processing horizons. Polymer alloys, insitu composites, pico fillers and novel processing techniques may be explored for further improvements.

Introduction:

Conventional synthetic filaments spun from aliphatic molecules has long being deserted in challenging applications as composite reinforcing elements. This is due to their low number of load bearing elements along the fibre axis leading to poor mechanical performance. Carbon fibres, aramids, super drawn polyolefins, and few other approaches has been quite satisfactory so far where high tensile strength is needed. However, they all have certain drawbacks. High tensile strength requires high molecular anisotropy but it also limits flexibility leading to premature rupture when bent around small radii or subjected to torsional deformations. Some types also cannot be exposed to high temperatures or allowed to become wet. Hence there is a need to a high performing filament that can endure to being flexed, impervious to wet conditions and has ability to withstand relatively high temperatures.

Backgrund:

Aliphatic chains of polyester varieties such as PET are very flexible due to thetraheadral bonds of carbon atoms found in ethylene structures. It leads molecules to assume a random coil configuration in liquid form whether they are liquified by heat or by solvent action.

The rapid acceletation of the molten polymer jet to takeup speed upon exit from the spinneret orefice leads to attenuation (thinnig) of the filaments creating a considererable stress on the molecular chains. This is the basis of extensional deformation leading to axial orientation.

The molecular parallelism gained by such mechanical forcing is rapidly lost when the attenuating stress is removed before the oriented mass sets solid. Stress removal takes place upon the solidification of the filament external surface. As now this extremely thin solid layer supports the axial stess of spinning the internal still liquid mass becomes stress free. Molecules in the core

rapidly relax into a random coil configuration. The driving force is of thermodynamic origin brought about by high chain polarity.

As can be seen on the shematic representation of PET repeat unit in Fig 1. opposite polarities are abundant and are in close proximity. Release of stress on these chains allows them to buckle on themselves to form crystalls by chain folding. This is made possible by the presence of the highly flexible teraheadral conformers. It takes about three repeat units to form a crystallite by chain folding.

Thus filaments with oriented outer layer and disoriented core is produced. This is the feed for the production of fully drawn fibres. The second step is a drawing process carried out above the glass transition temparature.

Although the term referring to the final state of filament is “fully drawn” in reality there are only a few load bearing elements that tie the cristallites creating the achievable ultimate tensile strength which is as low as 0.4 GPa for PET and PA varieties. The filament consists of oriented crystallites interconnected by few tie molecules and amorphous sites that alternate along its long axes. This fibre morphology imparts flexibility to the filaments much needed in textile processes like yarn spinning, weaving, knitting, etc.

It was hoped that increased attenuating stress by increasing the acceleration of the filament stream excessively will lead to fully drawn yarn (FDY) to be produced in one step[1]. Unfortunately this commercial attempt failed.

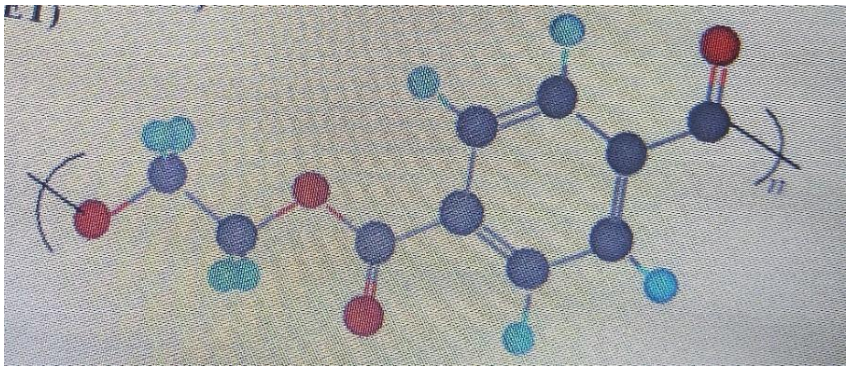


Fig 1: PET repeat unit: Light blue spheres represent positively charged hydrogen atoms and red spheres srepresent negatively charged oxygen atoms.

Polymers with non polar chains or chains with considerable stearic hindrance cannot form high melting polymeric crstallites in filament form. If filaments spun from low density PE are considered there is not much chance of them to crystallise appreciably no matter how oriented their chains may be. Hence these filaments loose their integrity at relatively low temperatures. This is the major drawback of Spectra fibres produced by incremental super drawing. Despite their respectable tensile performance they cannot retain their integrity at all if the service temperature appoaches to around 90 ^{o}C.

Wet spun systems also require to a two step process but they are done tandemly and a similar tensile performance is obtained. However, a skin - core structure is developed during coagulation. The the molecular parallelism in the core is increased by tandemly applied stetch during slow progressing coagulation which improves the tensile strength to acceptable levels for conventional textile applications.

Production of polyacrylonitrile (PAN) which is a precurser for carbon fibres is a good example to wet spun systems.

Major Breakthroughs:

Carbon Fibres:

Early ninteen seventies also witnessed the PAN filaments being converted into carbon fibres by some oxidation followed by a pyrolysis treatment to drive all of the atoms except carbon. A third final step above 2000 o C is conducted for graphitization. Accompanying stretch ensures the formation of turbo stratified graphite layers bound by Van Der Waal forces which gives remarkable strength and stiffness to these fibres[5].

Lyotropics:

Flory[2] in ninteen fifties predicted that rod like chains that consist of aromatic sub units connected in para form would act as liquid crystals (LC). Stephanie Kwolek[3] of DuPont followed this prediction to come up with p-paraphenylenethrepthalamide chains that form anistropic domains when dissolved in strong polar solvents at a critical temprature, critical concentration and critical molecular weight. Such systems are termed lyotropic to denote that the LC behaviour is generated by solvent action.

These anisotropic local domains would orient along the flow direction upon elongational deformation of spinning leading to 100 % oriented structures.

This is the explanation behind the commercial success of Kevlar achieved in early ninteen seventies. Kevlar is about twice as strong as steel at the same weight and approximately 5 times stronger at the same diameter with less than a fift of its density.

It is worth mentioning at this stage that liquid crystals are divided into three groups[4]. Amongst the smectic, nematic and cohelesteric forms filament world is interested in the least constrained form of nematic variety.

Rod like stiff molecules form nematic phase upon melting and are birefringent due to the one dimensional order preserved, its loss would render the melt isotropic. The temperature at which extinction may ocur depends on the features of the molecule. The higher the randomisation and the disruption of regularity and the lower the molecular weight nematic temperature range is small. In certain cases the nematic range can be so large that extinction temperature may exceed that of thermal stability.

Thermotropics:

Aromatic polyesters are themotropic liquid crystalline counterparts of aramids. They are synthesized and converted into filaments with relative ease and are naturally impervious to wet conditions which increased the interest in them. However, it turned out that they also suffer from premature rupture when flexed as well as being comparatively somewhat poor tensile performers. Further more, heat treatment needed to improve their mechanical performance is too long to permit commercialisation.

Thermotropic homo-polyesters due to their planar rigid rod like molecular geometry crystallise into near perfect crystallites that melt at temperatures well above their thermal stability limit. To rendrer them processable molecular regularity is disrupted by the intoduction of various molecular forms at random. Consequently the crystallite perfection and hence the melting temperature is lowered for processability. However, the mechanical performance is also lowered!

Kantor and Holub[6] in 1962 at New York Scottia trying to increase the melting temperature of plastics for General Electric reacted therepthalic acid with p-phenylene diacetate. The description of the observations on the patent is a clear evidence that they actually synthesized an LC system but did not recognise it as polymeric liquid crystals were not known then.

In 1976 Jerome Jackson[7] a researcher at Eastman Kodak laboratories wanted to increase Tg of PET used for the medicinal x -ray film substrate so that it can be processed at high temperatures for fast photographic image development without affecting the dimensional stability. He added p-acetoxy benzoic acid to PET and co-polymerised. The test bars were four times higher in tensile strength at around 40 to 50 mole % additions of the co-monomer. He infact like Kantor and Holub had made the accidental discovery of thermoropics.

Upon the announcement made by Jakson on four fold iprovement of PET by random co-polymerisation, DuPont with polymeric LC experience gained on lyotropic systems realised that LC behaviour can be brought forward by heat also. The new class was termed thermotropic systems with polyesters on the lead.

The rod like chains do not have the chance of folding or assuming random coil configuration. They have to stay as a rod naturally. Thermodynamic forces due to polarity would keep them lying next to each other in liquid state whether achieved by heat or solvent action. Since it is not possible for the entire polymer mass to lie in parallel due to a number of external influences like gravity container surface contact, etc. What is termed as “local domain” is thus formed. The long axes of molecules in the domain point to approximately in the same direction and have one dimensional order. Neigbouring domains in the same polymer mass at rest may point to different directions and despite the micro level anisotropy present within a domain, at macro level the domains are perfectly isotropic.

This arrangement first of all gets rid of all of the complications due to chain folding and entaglements. The macroscopic isotropy of local domains rapidly vanishes when an attenuating flow deformation is applied. The entire mass undergoes an extensional deformation leading to 100 % orientation of the polymer chains.

Thermotropic polyesters are rendered processable by means of melting temperature depressions as previously mentioned. This is the major limiting factor in the manufacturing of high strength filaments.

First of all the high molecular weight will present a viscosity problem so a lower molecular weight polymer is spun into highly oriented filaments. The molecular weight is then inreased by a solid state polycondensation (SSP) in filament form. If the molecular structure is semi crystalline the improvement of molecular weight by solid stating is limited simply because the oriented chains are bound physically to their neigbours and lack the necessary segmental mobility for polymerisation. Crystallinity is therefore a drawback for an SSP treatment.

A non crstallisable thermotropic polymer is commercialised under the name Vectran. It does not have a melting temperature. As temperature is increased beyond Tg which seems to be around 125 ^{o} C polymer starts flowing. Vectran is a copolyester of two phenolic acids. One of them is a benzene ring residue the other is a napthalane residue. Along the molecule repeat unit length staggering as well as the ester link direction variation at random eliminates crystallinity. Filaments spun from such a low melting copolymer may not allow even moderately high temperature applications.

Remnant Problems

Although the problems created by conventional aliphatic polymers are overcome to a certain extent by LC systems, there still are some problems to be solved.

High molecular anisotropy and stifness combination gives high tensile strength and high youngs modulus under tension but due to the lack of radial cohesion these systems invariably lack compressive strength and torsional strength. These structures are highly akin to tree branches and rupture in a similar way by delamination when bent excessively Fig 2.

This behaviour may be traced to the existence of local domains for random copolymers. The chains that constitute a domain reach to an internal thermodynamic stability by exclusion of other chains and coher radially.

During filament formation these domains simply align in the filament direction but no radial attraction is generated. After the heat treatment molecules that already lie along the axis with ends near each others react and become longer and give rise to tensile strength but, still no radial cohesion is generated. Infact they are hidden fibrils thsat become apparent upon mechanical failure as indicated by the excessive fibrillation of the small knot in Fig. 2.

However, it must be stressed that if there could be sufficient radial coherence the stiff rod would probably have an appreciable compressive and torsional strengths but flexibility would still not be had in the sense of bending without rupture. The material would simply be stiff and resiliant.

As regards thermotropics three main problems persist in the path that may lead to a commercially successful filament yarn. First one is the lengtly heat treatment, second one is the other is loss of tenacity at relatively low service temperatures with final one being the low achievable ultimate tenacity due to disruption of polymer chain.

As mentioned before crystallinity is the main reason for all problems.

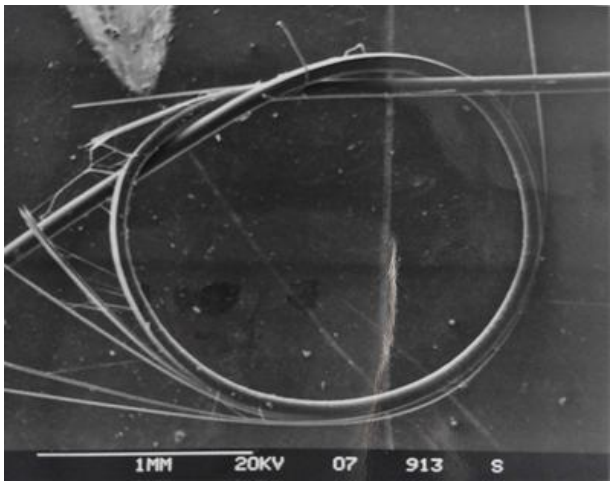


Fig 2: Destruction of a thermotropic filament by delamination and fibrillation

Filaments obtained by dry jet wet spinning of lyotropic homo-polymers also lack radial strength. Study conducted on structure of Kevlar by Dobb[8] *et al* revealed that fibre consists of radially distributed pleated sheets. The bent specimens delaminate and rupture due to excessive axial orientation and lack of radial strength.

In short, high stifness, effect of water, low melting temperature, are the major problems to be solved. Some new approaches may be useful in these respects.

Experimental:

Studies are conducted on poly p-phenyleneisopthalate co-p-oxybenzoate compositions. Hydroquinone di acetate (HQ) (m.p. 124 ^{o} C) and isopthalic acid (IA) (m.p. 347 ^{o} C) were charged in equimolar quantities for stochiometric reasons against a certain mole percent of p-acetoxy benzoic acid (PABA) (m.p. 187 ^{o} C) and polymerised by melt acidolysis tecnique to form the basic series of polymers. Details of monomer and polymer preparation are described elsewhere[9]. Further analysis for novel aproaches are made on 67B co-polymer where p-acetoxy benzoic acid constitutes the 67 mole percent of the composition.

HQ and IA both have two functional groups, reaction of which yields a molecule of acetic acid that condenses out as by product. PABA also has two functional groups that also yields an acetic acid molecule upon reaction with natural stochiomeric balance. All three are reacted simultaneously to yield a random wholly aromatic co-polyester. Rapid heating and widely different melting temperatures of the starting materials ensured random co-polymerization.

Filaments were obtained on a ram extruder below and above335 o C. Those extruded below 335 o C were heat treated at 270 o C under nitrogen atmosphere for 48 hours and subjected to cold drawing and characterised.

Polymer characterisation:

Wide angle x-ray diffraction studies were conducted on a flat plate camera. A Hilger and Watts x-ray generator equipped with a sealed off type x-ray tube was used to obtain nickel filtered CuKα monochromatic radiation at 1.54 Angstrom wavelength at an acceleration voltage of 40 kV and a tube current of 16 mA.

Inter planar spacings were calculated by data taken from the waxs patterns using the relation for Bragg angle:

$2Ø = \text{Arctan}(R/2L)$ Where:

R is the Radius of the reflection directly measured from the film,
L is the camera length.

The interplanar spacing was then calculated using the Bragg equation;

$n\lambda = 2d \sin Ø$ Where:

n is an integer denoting the order of reflection,
λ is the wavelength of the monochromatic x-rays.
d is the interplanar spacing
Ø is the angle between the atomic plane and both the incident and reflected beams.

Differential scanning calorimetic measurements of polymers were determined on a DuPont thermal analyser 990 coupled to a DuPont DSC cell 910. Calibrations were done by high purity metal standards.

TGA analysis were carried out by a model 951 DuPont TGA instrument coupled to model 990 thermal analyser. As onset of thermal decomposition 5 % weight loss which occurs arund 455 ^{o} C was accepted.

Hot stage microscopic examinations were carried on a Reichert – Thermovar hot stage microscope for visual determination of LC behaviour.

Discussion of the results:

Waxs pattern of as made 67B composition (Fig 3a) indicates that crystallinity exists by some weak but sharp reflections imposed on a halo which is believed to be due to pseudohexagonal gathering of hihly disrupted rodlike chains. The polymer structure consistsof co-existing two phases. The crystal phase and a further disrupted pseudo hexagonal phase where the average interplanar distance is considerably higer than 6 Angstroms. Various heat treatments were conducted for enhancement of these phases.

DSC studies conducted on the am heat treated powder samples supported the evidence of these co-exsting phases amply by the data presented in Fig 7b. There is a melting endotherm at 280 ^{o} C with onset at 250 ^{o} C for the crystalline phase and another shallow endothermic peak with onset at around 350 ^{o} C for the weak halo representing the distupted pseudo hexagonal phase.

Melt extrusion of 67B at 270 ^{o}C and at 350 ^{o}C resulted with extrudates that exibit remarkably different waxs patterns Figs 3a & 3b.

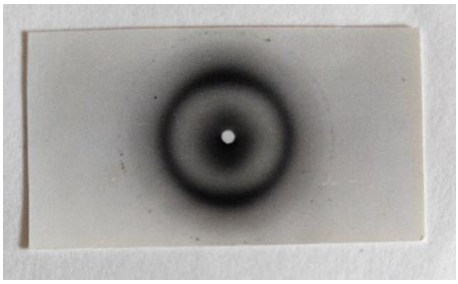


Fig 3a. Extrusion made at 270 ^{o}C exhibiting transverse orientation.

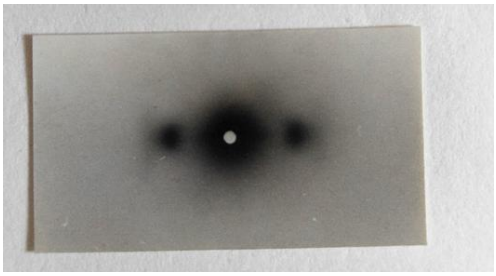


Fig 3b. 67B melt extrudate showing longitudional orientation.

Fibres spun st 270 ^{o}C were cold extrudates and exibited transverse orientation (Fig 3a). It is thought that local domains that consist of pseudo hexagonal phase that soften at 350 ^{o}C were mobilised by ram pressure and subjected to shear deformation in molten steam of the crystalline phase. Since shear causes tumbling of local domains in the flow direction[10] with long axes of molecules at right angles to the flow direction transverse orientation is achieved.

Conversely, the fibres spun at 350 ^{o}C were longitudionally oriented as both phases were molten at this temperature (Fig 3b). The mechanical behaviour of these filaments were same as other examples of hihly oriented structures. Considerable tensile strength could be achieved but premature rupture upon flexing could not be eliminated.

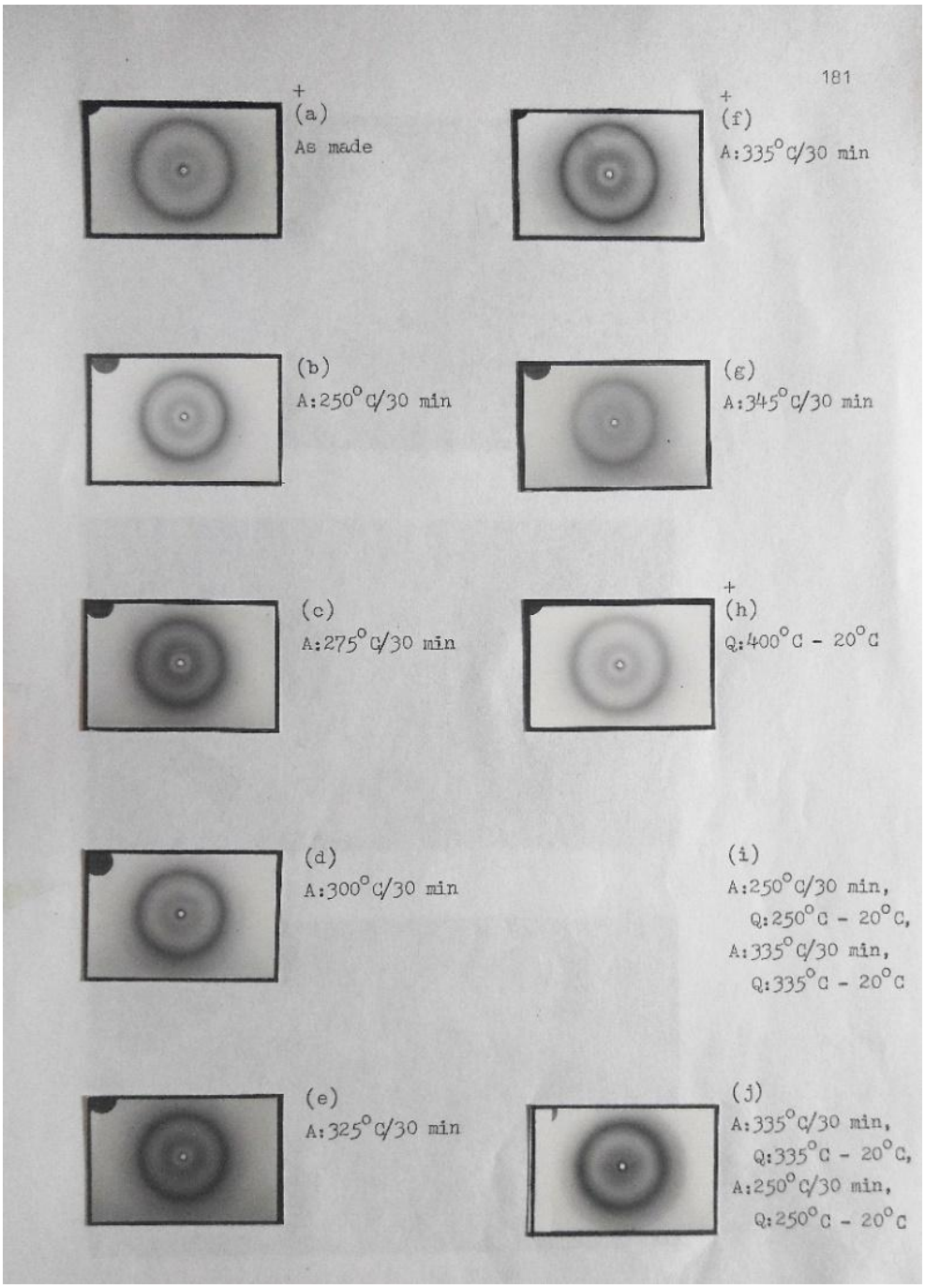


Fig 4a. Powder waxs patterns of as made and heat treated 67B.

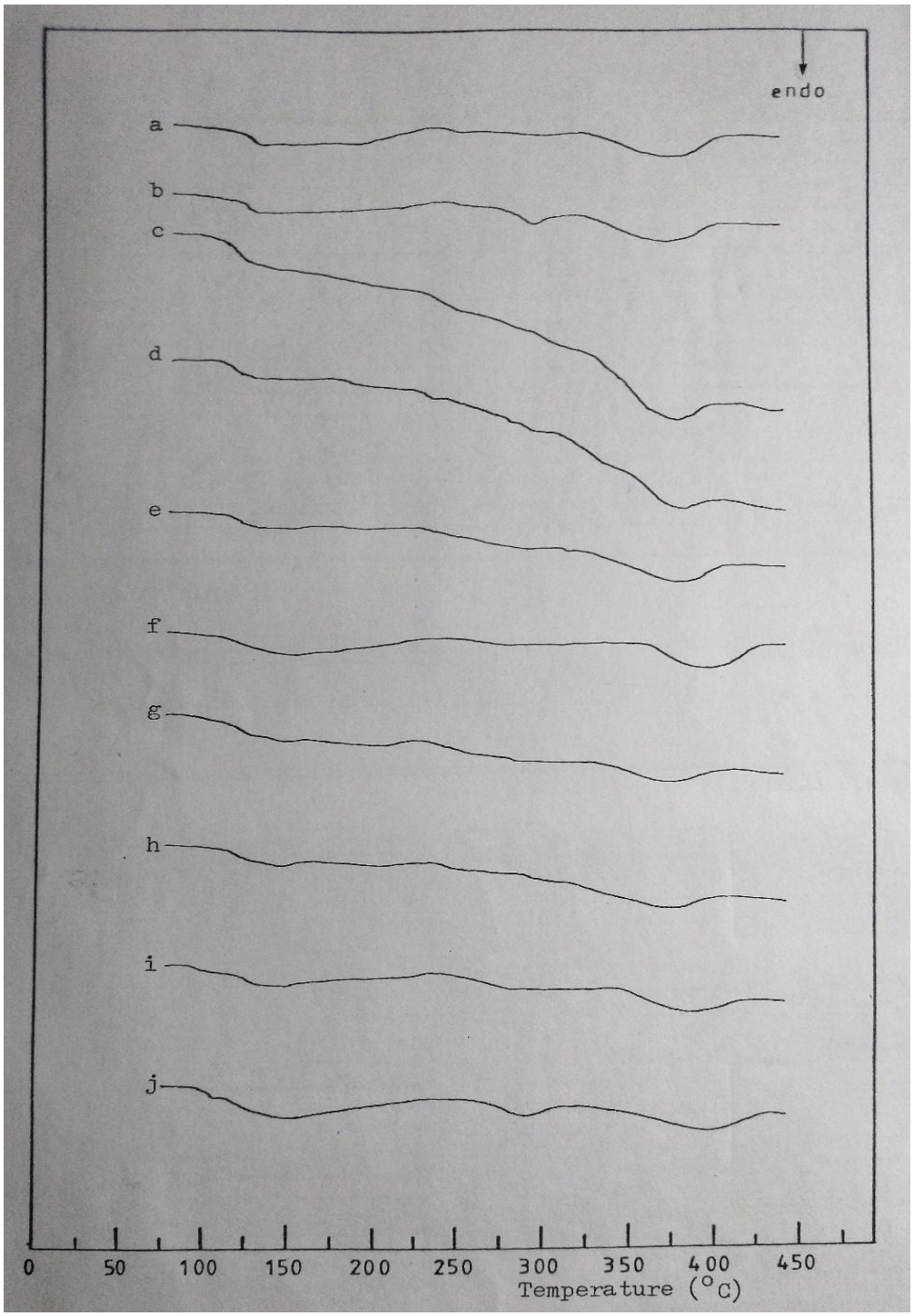


Fig 4b. The corresponding DSC traces of the 67B waxs patterns.

A further study on 67B cold extrudate was conducted. Heat treatment of these filaments at 270 ^{o} C for 48 hours under nitrogen atmosphere showed that the internal structure has undergone two major changes.

The molecular weight has increased considerably as indicated by disappereance of filament brittlenes (dissolution was not possible for viscosity measurements) and crystallinity was

increased as indicated by the waxs pattern (Fig 5). Further more, cold drawing of heat treated fibres by 100 % showed that transversely oriented structures has become almost totally longitudionally oriented (Fig 6). Filamets were stronger and considerably more flexible after heat treatment and drawing. A further evidence of shift of orientation from transverse to longitudional can be seen directly on the SEM micrograph of the cold drawn extrudate fracture face on Fig 7.

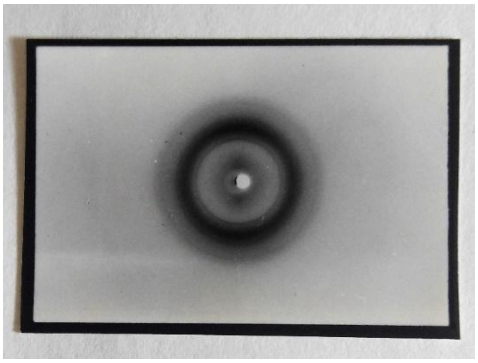


Fig 5. Waxs pattern of heat treated cold extrudates of 67B.

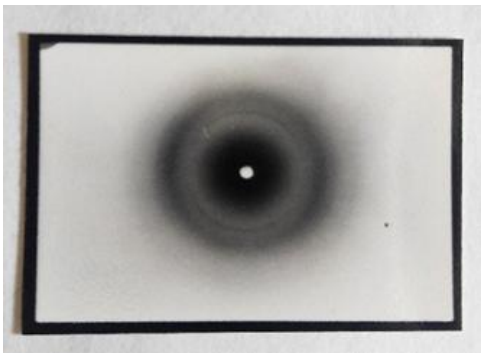


Fig 6. 67B cold extrudate after heat treatment and cold drawing.

The fact that the molecular chains are not fully oriented is responsible for loss of filament brittleness together with the increased chain length by SSP.

It is also worth mentioning that a very considerable percentage of molecules act as load bearing elements at the filament cross section in contrast to conventional filaments of aliphatic origin where only a few tie molecules bear the load.

Production of a wholly aromatic fibre that may have a flexible behaviour seems to be possible by this two stage process where a transversely oriented fibre is spun first later drawn for longitudional orientation following a solid state polymerization. This may be the basis of reinforcing material production for demanding flexible composite applications. As these wholly aromatic filaments will be considerably stronger than conventional aliphatic filaments and yet be flexible to reinforce rubber matricees.

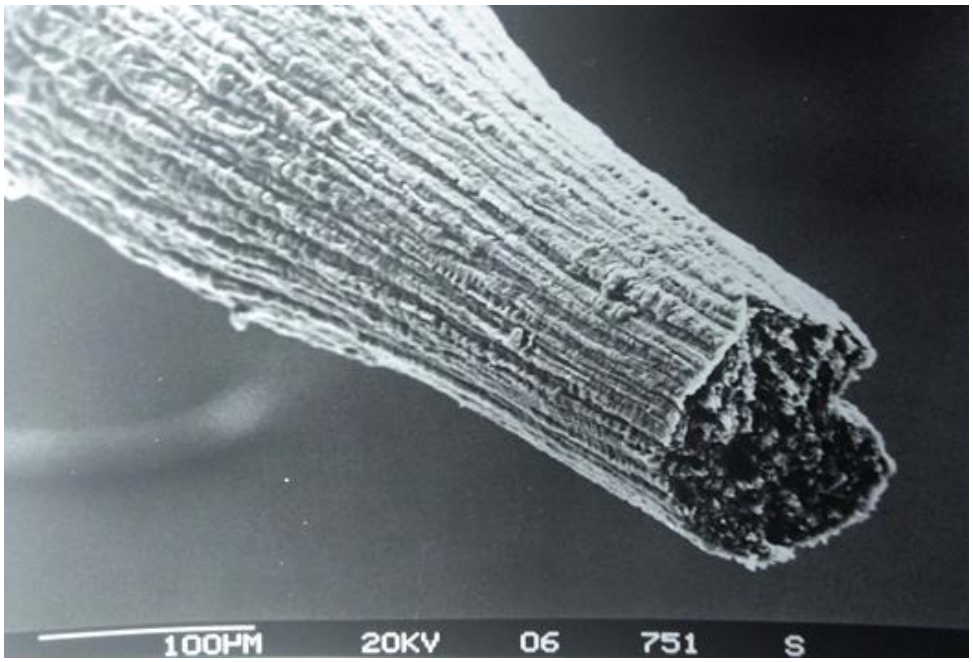
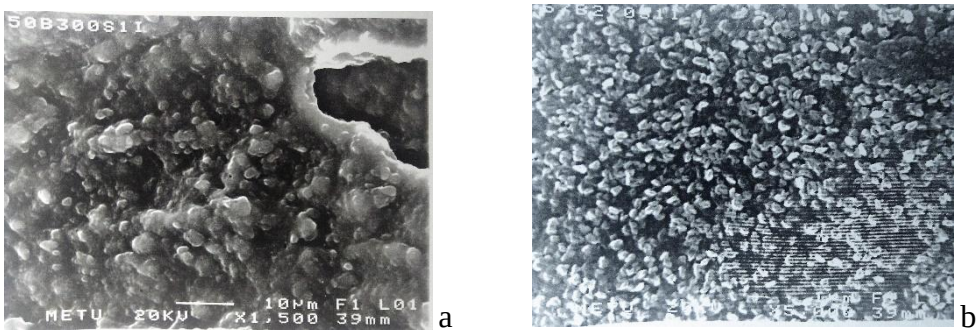


Fig 7. Fracture face of cold drawn 67B exrudate.

A different study[10] conducted on 50B and 67B revealed that upon shear in a shear cell continuosly for about 30 to 120 seconds small polymer bundles were seperated from the polymer bulk probably in solidified form. The effect of shearing was arrested by rapid quenching of the shear cell.

Surfaces where the shear instrument was in contact were examined by SEM and waxs patterns were obtained to determine the direction of molecular axes of domains in relation to the shear direction.



a b

Fig 8. SEM micrographs of two quenched polymer surfaces in contact to the shearing steel rod. a) 50B sheared at 300 ^{o} C at 66 s^{-1} shear rate. b) 67B sheared at 270 ^{o} C at 66 s^{-1} shear rate.

Fig 8 b shows the quenched polymer surface in contact with the shearing steel rod. Where polymer bundles were created.

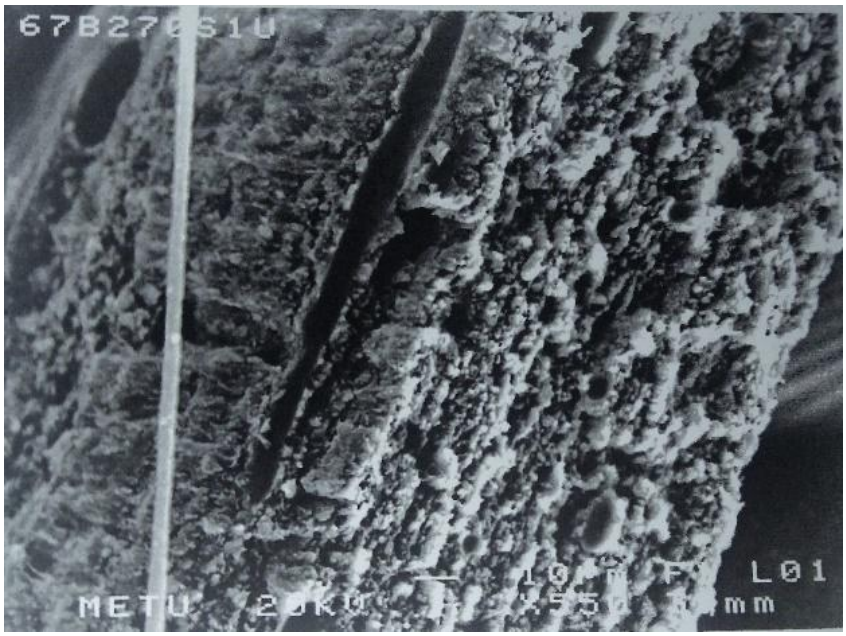


Fig 9. 67B sheared at 270 o C at 66 s-1 shear rate

Polymer	Shear Temperature °C	Shear Rate (s^{-1})	Intrinsic Viscosity (dl/g)	Direction of Shear	WAXS Patterns
67B	270	82	1.10	↑	
67B	270	225	1.10	↑	
67B	270	365	1.10	↑	

Fig 10. Waxs data taken on the sheared samples showing transverse orientation of molecules.

Fig 9 shows the micrograph of the polmer facture face which is at right angles to the shear plane. The curved inner part (shear surface) is towards RHS of the micrograph where the polymer bundles stick out. It is an indication that bundles were tumbling during the shear.

Another supporting evidence is provided by waxs patterns taken on the shared samples shown in Fig 10. X-ray beam was perpendicular to the shear surface. Resulting waxs data shows transverse orientation in agreement with the SEM data

It is envisaged that polymer alloys that bear such grouped wholly aromatic bundles could first spun to obtain transverse orientation of the aromatic bundles followed by heat treatment and

drawing for production of high tenacity low shrinkage yarns much seeked for reinforcing special composites for flexible applications.

Further Work:

Field of thermotropics is not new but, despite the time passed realisation of high tenacity filament yarns of wholly aromatic nature by melt spinning of thermotropics has not reached to a commercial success.

Production of flexible composite reinforcing fiament yarns may be possible by manuplating co existing different structures or creating polymer alloys which may act as insitu composites to constitude a reinforcing element that can be flexed. This approach is proposed to be the basis of further work.

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SCALING EFFECT ON TENSILE PROPERTIES OF CROSS-PLY GLASS NCF/EPOXY COMPOSITES

ÇAPRAZ-KATLI KIVRIMSIZ CAM ELYAF/EPOKSİ KOMPOZİT PLAKALARIN ÇEKME MUKAVEMETİ ÜZERİNDE ÖLÇEK ETKİLERİ

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ÖZET

Yüksek mekanik özellikleri ve basit üretim süreçleri nedeniyle kıvrımsız elyaf (KE) takviyeli kompozit malzemeler yat/tekne ve rüzgâr türbini kanatları üretiminde yaygın olarak kullanılmaktadır. Kompozit malzemelerinin mekanik özellikleri uluslararası standartların rehberliğinde belirli numune ölçüleri kullanılarak laboratuvar ortamında belirlenmektedir. Standart deney numuneleriyle elde edilen mekanik özellikler ise gerçek yapıların mekanik özelliklerini tam olarak yansıtmayabilir. Örneğin bir deney numunesinde genellikle 8-10 kat elyaf bulunurken, gerçek mühendislik yapıları yüzlerce kat elyaf içerebilir. Diğer yandan gerçek mühendislik yapılarının mekanik özelliklerini bu yapıları test ederek belirlemeye çalışmak ise büyük miktarda zaman, para ve iş gücü harcanmasını gerektirmekte olduğundan ekonomik değildir. Dolayısıyla, laboratuvar ölçeğindeki test numunelerinin mekanik özelliklerinin numune ölçeği ile olan ilişkisinin belirlensmesi büyük önem taşımaktadır. Bu çalışmada, cam KE/epoksi malzemeyle üretilmiş üç farklı ölçeğe sahip deney numunelerinin mekanik özellikleri incelenmiştir. Numune kalınlığı, uzunluğu ve genişliği, tab kalınlığı ve uzunluğu, deney hızı gibi parametreler ölçeklendirilerek ASTM D-3039 standardına göre testler gerçekleştirilmiştir. Kullanılan tabaka dizilimleerine sahip farklı ölçeklerdeki numunelerde mukavemet ve rijitlik değerlerinde büyük bir değişim gözlenmezken, hasar mekanizmalarının numune ölçeğiyle birlikte değiştiği görülmüştür.

ABSTRACT

In the marine, automotive and wind turbine blades the non-crimp fabric (NCF) composites are widely used due to their sufficient mechanical properties and simple production methods such as vacuum assisted resin transfer moulding. Thus, the mechanical behaviour of those materials under various types of loading must be well understood. In laboratories experiments are done to address this need. Generally, the experiments are completed under the guidance of a specific standard. In these standards the test conditions, specimen size, analysis of results etc. are described in detail. Still, these laboratory data may not be sufficient to predict the mechanical behaviour of real structures because the real life structures may have over a hundred of layers while standard laboratory specimens have lesser layers depending on the laboratory facilities. On the other hand, the testing of real life structure consumes a high amount of time, money and labour work. In this study, a series of coupon tests were carried out for glass

NCF/epoxy specimens as a function of specimen scale. Three different scales (full, three-quarter and half scales) based on the ASTM D-3039 standard test coupon were tested where the thickness, length and the width of the specimen, tab thickness, tab length and testing speed were scaled accordingly. The results were recorded and compared for all scales. The results indicate that the stiffness and strength of the material system used is relatively insensitive to the scaling effects. Finite element models are currently under development in order to explain this insensitivity in detail.

Giriş

Farklı kompozit malzeme sistemlerinde ölçek etkisini incelemek için çeşitli çalışmalar yapılmıştır. Bullock [1], iki farklı grafit/epoksi kompozit malzemeyle çekme ve eğilme testleri yapmıştır. Çekme numuneleri 6 kat elyaftan oluşurken, eğilme numuneleri 15 katlı olarak üretilmiştir. Sonuçlar, eğilme mukavemetinden yola çıkarak çekme mukavemetinin belirlenmesinde Weibull dağılımının kullanılabileceğini göstermiştir. Jackson ve diğ. [2, 3] ölçeğin grafit/epoksi kompozitlerde çekme ve eğilme davranışına etkisini incelemişlerdir. 1/6'dan tam ölçeğe kadar, farklı elyaf sıralamalarına sahip numuneler test edilmiştir. Farklı ölçeklerdeki numunelerin rijitlikleri hemen hemen aynı çıkmasına karşın, normalize edilmiş maksimum kuvvet, numune boyutları büyüdükçe azalmıştır. Yaygın kullanılan hasar kriterleri sonuçları tahmin etmekte başarısız olurken Weibull istatistiksel modeli başarılı sonuçlar vermiştir. Kellas and Morton [4] dört farklı elyaf sıralaması ve dört farklı ölçek kullanarak ölçeğin grafit/epoksi kompozit malzeme üzerindeki etkisini incelenmişlerdir. Sonuçlara göre, numune boyutu arttıkça malzemenin çekme mukavemeti azalmıştır. Green ve diğ. [5] delikli numuneler üzerinde ölçek etkisini incelemişlerdir. Delik çapı-genişlik oranı bütün numunelerde sabit tutulmuştur. Tabaka ve alt-laminat seviyelerinde ölçeklendirilerek oluşturulan numuneler test edilmiştir. Artan numune boyutlarıyla birlikte çentikli mukavemetin %64 civarında düştüğü gözlemlenmiştir. Tabaka seviyesinde ölçeklendirilen numunelerde ise bazı durumlarda tam tersi bir eğilim görülmüştür. Bütün numuneler göz önüne alındığında üç farklı hasar türü gözlemlenmiştir; fiber hasarıyla birlikte yoğun delaminasyon, fiber hasarıyla birlikte sınırlı delaminasyon ve tam kesit hasarı. Wisnom ve Atkinson [6] E-cam/epoksi tek-yönlü numunelerde çekme ve eğilme davranışına ölçeklendirmenin etkisini incelemişlerdir. Hasarın cihazın çenelerinden uzakta oluşmasını sağlamak için eğimli bir tab kullanmışlardır. Genel olarak, numune boyutu arttıkça hasar geriniminin azaldığı gözlemlenmiştir. Lavoie ve diğ. [7] karbon fiber prepreg kullanılarak üretilen tek-yönlü, çapraz-katlı ve yarı-izotropik plakalarda ölçeklendirmenin çekme davranışı üzerine etkisini çalışmışlardır. Ölçek arttıkça $[+45_n/-45_n/90_n/0_n]_s$ düzenine sahip plakaların çekme mukavemeti düşmüş ve hasar cihaz çenesine yakın oluşmaya başlamıştır. Benzer şekilde $[0]_{8n}$ ve $[0_{2n}/90_{2n}]_s$ plakalar da çenelere yakın hasara uğramıştır.

Bu çalışmanın amacı numune ölçeklendirmesinin KE kompozitlerdeki mukavemet ve rijitliğe olan etkisini incelemektir. Üç farklı ölçek için çekme testleri ASTM D-3039 [8] standardına göre tamamlanmış ve sonuçlar değerlendirilmiştir.

Malzeme ve Yöntem

Kompozit malzeme sisteminde takviye fazı olarak 300g/m^2 alan ağırlığına sahip yarı tekyönlü E-cam kıvrımsız elyaf kullanılmıştır. Oda sıcaklığına kürleşebilen bir epoksi reçine ise matris fazı olarak kullanılmıştır. Düzlemsel kompozit plakalar vakum destekli reçine transfer yöntemiyle üretilmiş ve karbür freze ile numune boyutlarında kesilmiştir. Yarım ölçekli numune standart ASTM D-3039 numunesi boyutlarında seçilmiştir. Bunun dışındaki diğer ölçekler ise ¾ ve tam ölçek olarak belirlenmiştir. Ölçeklendirme işlemi çekme hızı ve tab boyutlarına da uygulanmıştır. Bütün numunelerde $[\pm 45°]_{ns}$ elyaf düzenine sahip tablar kullanılmıştır. Tam ölçekli numunelerin tabları ASTM D-3039'a göre 7° eğim açısına sahipken ¾ ve ½ ölçekli numunelerin tabları eğimli değildir. Numune ve tab boyutları, deney hızlarıyla birlikte Tablo 1'de gösterilmiştir.

Tablo 1: $[90°/0°]_{ns}$ numunelerin ölçekleri ve boyutları.

Ölçek	n	Tabaka sayısı	Uzunluk (mm)		Genişlik (mm)		Kalınlık (mm)		Test hızı (mm/dak)
			Numune	Tab	Numune	Tab	Numune	Tab	
½	2	8	250	50	25	25	2.5	2.5	2
¾	3	12	375	75	37.5	37.5	3.75	3.75	3
Tam	4	16	500	100	50	50	5	5	4

Çekme deneyleri Zwick-Roell marka mekanik test cihazıyla yapılmış, ölçüm için mekanik ekstansometre kullanılmıştır. Gerilme-uzama eğrileri bütün numuneler için kaydedilmiştir.

Tablo 2'de bütün ölçekler için test edilen numunelerin deney sonuçları ve hasar konumları listelenmiştir. Dört adet yarım ölçekli (n=2) numune hasar konumlarını ve mekanik değerlerini gözlemlemek için çekme yükü altında hasara maruz bırakılmıştır. İki tanesi istenildiği gibi ölçüm aralığında hasara uğrarken, diğer ikisi çenelerin yanında (taba bitişik) hasara uğramıştır. Hasar konumlarından bağımsız olarak mukavemet ve rijitlik değerleri %5.06 standart sapma ile tutarlı şekilde ölçülmüştür. Bu sonuçtan yola çıkarak hasar konumlarının deney sonuçları üzerindeki etkisinin sınırlı olduğu ifade edilebilir. Diğer bir deyişle, çene kenarındaki hasar, numunenin son hasarını aldığı ana yakın ortaya çıkmıştır.

Tablo 2: Çekme deneyi sonuçları.

Numune kodu	F_{max} [N]	σ_{max} [MPa]	E [MPa]	Ortalama (% Sapma)			Hasar konumu
				F_{max} [N]	σ_{max} [MPa]	E [GPa]	
n2_1	21685	346.9	21387	19974 (5.06)	370.36 (5.06)	199.74 (5.06)	Taba bitişik
n2_2	23992	383.8	19058				Taba bitişik
n2_3	23573	377.2	19486				Ölçüm aralığında
n2_4	23340	373.4	19966				Ölçüm aralığında
n3_1	57566	409.4	20484	55247 (3.91)	392.87 (3.91)	198.52 (4.55)	Tabın içinde
n3_2	54883	390.3	20255				Çeneden ¼ tab boyu uzaklıkta
n3_3	53292	379	18816				Çeneden ½ tab boyu uzaklıkta
n4_1	99265	397	20185	100340 (1.51)	401.36 (1.51)	202.40 (0.38)	Çeneden ½ tab boyu uzaklıkta
n4_2	101415	405.6	20295				Çeneden ½ tab boyu uzaklıkta

Üç-çeyrek ölçekli (n=3) numunelerin çekme deneyi sonucundaki mukavemet ve rijitlik değerleri de tutarlı sonuçlar vermiştir. Yine de, çene kenarlarında oluşan gerilme yığılmaları hasar şeklini etkilemiştir. Numuneler tabın içinden veya taba yakın bölgeden hasar almıştır. İlginç bir şekilde, hasar çeneden uzaklaştıkça mukavemet ve rijitliğin azaldığı da görülmüştür. Bunun sebebi, hasar başlangıcını takiben çene bölgesinde oluşan gerilme gevşemesi olabilir. Tam ölçekli (n=4) numunelerin de mukavemet ve rijitlik değerleri de yakın olarak belirlenmiştir. Tablardaki eğim sayesinde de hasar çeneden yarım tab boyu (50 mm) kadar uzakta oluşmuştur. Bütün ölçeklerdeki numuneler göz önüne alındığında maksimum standart sapma %5.06 olarak görülmektedir. Bu da deney öncesinde yapılan üretim ve numune hazırlama ile testler sırasında izlenen işlemlerin uygun olduğunu göstermektedir. Şekil 1'de bütün ölçekler için tipik gerilme-uzama eğrileri gösterilmiştir.



Şekil 1: Farklı ölçekler için tipik gerilme uzama eğrileri.

Sonuçlar

Bu çalışmada E-cam yarı tek-yönlü kıvrımsız elyaf/epoksi malzeme sistemi kullanılarak üretilen farklı ölçeklerdeki çapraz-katlı ($[90°/0°]_{ns}$) plakaların çekme davranışına ölçeklendirmenin etkisi incelenmiştir. Sonuçlara göre mevcut malzeme sisteminin çekme mukavemeti ve rijitliğinin görece olarak ölçeklendirmeden etkilenmediği görülmüştür. Ölçeklendirme etkisine karşı duyarsızlığı açıklamak adına sonlu eleman modellerinin geliştirilmesi devam etmektedir.

Teşekkür

Bu çalışma Balıkesir Üniversitesi Bilimsel Araştırma Projeleri Birimi tarafından BAP-2017-160 numaralı proje kapsamında desteklenmektedir.

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DESIGN AND MANUFACTURING OF SMALL SCALE WIND TURBINES: FIBER REINFORCED POLYMER COMPOSITE APPLICATION

KÜÇÜK ÖLÇEKLİ RÜZGAR TÜRBİNİ TASARIM VE İMALATI: FİBER TAKVİYELİ POLİMER KOMPOZİT UYGULAMASI

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Özet

Bu çalışmada küçük ölçekli bir rüzgâr türbini üretilerek yerleşim yerinden uzak sahalar için elektrik enerjisi üretimi amaçlanmıştır. Bu amaca ulaşmak için öncelikle, gerekli hesaplamalar, modelleme çalışmaları, türbin parçalarının kompozit malzemeden üretim çalışmaları ve sahada elektrik enerjisi üretim kapasitesinin incelenmesi aşamaları planlanmıştır.

Bu amaçla ilk olarak Türkiye Rüzgar Enerjisi Potansiyeli Atlasından Kütahya için 8 m/sn rüzgar hızı seçilmiştir. Kanat uzunluğu 40 ± 2 cm sınır şartlarına göre gereken hesaplamalar yapılmış ve bir kanat profili belirlenmiştir. Yapılan mukavemet hesaplamaları ile belirlenen kanat profili SolidWorks yazılımında modellenerek olası hataların giderilmesi için 3D yazıcı ile Akrilonitril Bütadien Stiren (ABS) polimer malzemeden kanat prototipi üretimi yapılmıştır. Kanat profili üzerinde gerekli görülen iyileştirmelerin ardından yine SolidWorks programı ile hazırlanan kalıplar Kestamid (dökme Poliamid, PA) malzemeden CNC dik işlem merkezinde üretilmiştir. Burun kısmı için gerekli kapağa ait kalıbın üretilmesi ile kompozit malzemeden türbin kanadı ve burun üretimine geçilmiştir. Kompozit kanatlar 6'şar kat halinde 300 gr/m^2 ağırlıklı twill cam elyaf kumaş ve epoksi reçine sistemi kullanılarak vakum infüzyon yöntemi ile üretilmiştir. Oda sıcaklığında 24 saat kürlenen kompozit kanatlar ve burun parçası, alüminyum malzemeden yapılan arka kanat ve Poliamid (PA) malzemeden üretilen gövde üzerinde bir araya getirilerek türbinin montajı tamamlanmıştır.

Üretim faaliyetlerinin ardından yapılan saha çalışmalarında yaklaşık 4 m/sn rüzgar hızında harekete geçebilen ve sürekli düzgün bir dönüş sergileyen rüzgar türbini ile 20.4 Volt gerilim ve yaklaşık olarak 1-1.4 Amper akım elde edilmiştir. Bu çalışma imalat mühendisliği öğrencilerinin bitirme tezi olarak 2.5 ay içerisinde tamamlanmıştır. Elde edilen bulgulara göre daha büyük ölçekli türbinlerin üretilebileceği ve enerji üretim kapasitelerin arttırılabileceği görülmüştür.

Anahtar Kelimeler: Rüzgâr Türbini Kanadı, Fiber Takviyeli Polimer Kompozit, Yenilenebilir Enerjisi

Abstract

In this study, a small scale wind turbine was produced and it was aimed to produce electric energy for remote areas from the settlement. In order to achieve this goal, firstly, the necessary calculations, modeling studies, the production of turbine parts from composite materials and the examination of the production capacity of electric energy are planned.

For this purpose, firstly wind speed of 8 m / s was selected for Kütahya from Potential Atlas of Turkey Wind Energy. The wing length was calculated according to the boundary conditions of 40 ± 2 cm and a wing profile was determined. Wing profile determined by performed strength calculations was modeled in SolidWorks software and a wing prototype was produced from acrylonitrile butadiene styrene (ABS)

polymer material with 3D printer to eliminate possible errors. After the necessary improvements on the wing profile, the molds prepared with the SolidWorks program were produced in the CNC vertical machining center using cast polyamide, PA. With the production of the necessary mold for the nose part, production of turbine wing and nose has been started from composite material. Composite wings were produced by vacuum infusion method using 6 layers of 300 g / m^2 twill glass fiber fabric and epoxy resin system. Composite wings and nose pieces cured at room temperature for 24 hours were assembled on the body made of polyamide (PA) material and the rear wing made of aluminum material and assembly of the turbine was completed.

After the production activities, 20.4 Volt voltage and about 1-1.4 Amperes current were obtained with the wind turbine which can move at a wind speed of about 4 m / sec and exhibit a steady smooth return. This work was completed within 2.5 months as a graduation thesis for the students of manufacturing engineering. According to the findings, larger scale turbines could be produced and energy production capacities could be increased.

Keywords: Wind Turbine Wing, Fiber Reinforced Polymer Composite, Renewable Energy

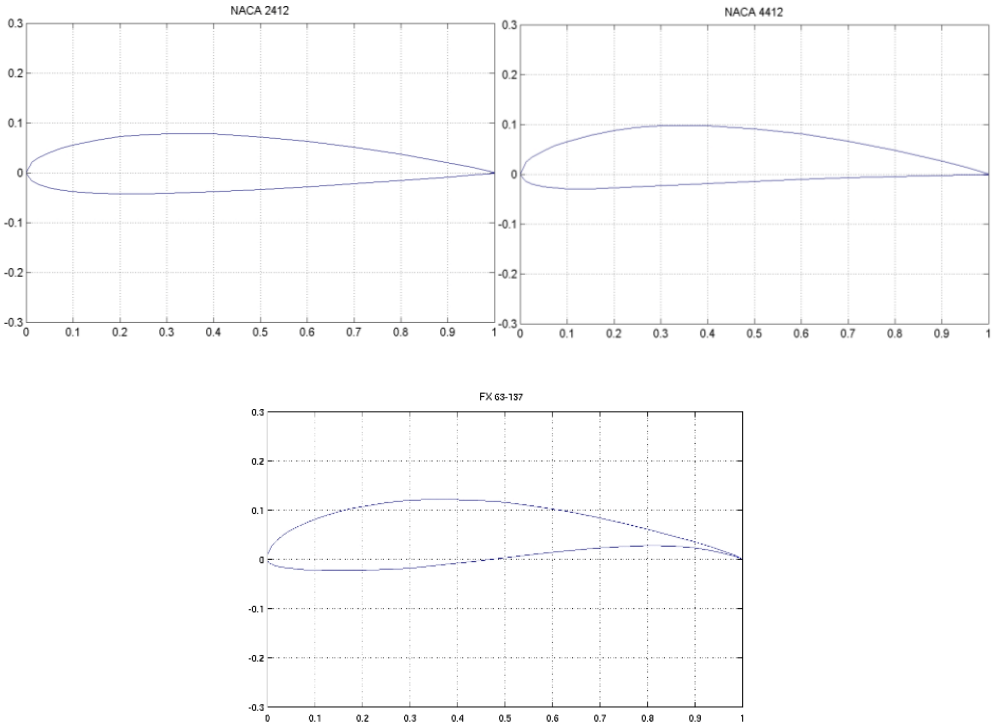
Giriş ve Amaç

Rüzgâr enerjisi; doğal, yenilenebilir, temiz ve sonsuz bir güç olup kaynağı güneştir. Güneşin dünyaya gönderdiği enerjinin %1-2 gibi küçük bir miktarı rüzgâr enerjisine dönüşmektedir. Rüzgârın özellikleri, yerel coğrafi farklılıklar ve yeryüzünün homojen olmayan ısınmasına bağlı olarak, zamansal ve yöresel değişiklik gösterir. Rüzgâr hız ve yön olmak üzere iki parametre ile ifade edilir. Rüzgâr hızı yükseklikle artar ve teorik gücü de hızının küpü ile orantılı olarak değişir [1]. Temiz bir enerji kaynağıdır. Çevre dostudur. Yenilenebilirdir, bitmesi gibi bir durum güneş var olduğu sürece olmayacaktır ve hiçbir atık madde içermez. Bu yüzden sera gazları dolayısıyla asit yağmurlarına neden olmaz. En önemli dezavantajı rüzgârların düzenli olmayışıdır, bu durum enerji üretiminde dalgalanmaya sebebiyet verecektir [2-4]. Rüzgâr enerjisi, kullanımı giderek artan ve potansiyeli yeni keşfedilmiş tükenmez bir enerji kaynağıdır. Dünya rüzgâr enerji potansiyelini belirleyebilmek amacıyla Uluslararası Enerji Ajansı (IEA) tarafından çeşitli araştırmalar yapılmıştır. Bu araştırmalarda, 5.1 m/s üzerinde rüzgâr kapasitesine sahip bölgelerin, uygulamaya dönük ve toplumsal kısıtlar nedeni ile %4'ünün kullanılacağı öngörüsüne dayanarak, dünya teknik rüzgâr potansiyeli 53000 TWh/yıl olarak hesaplanmıştır. Rüzgâr potansiyeli bakımından zengin olan bölgelerimiz Ege, Marmara ve Doğu Akdeniz kıyılarıdır. Elektrik İşleri Etüd idaresi tarafından hazırlanan "Türkiye Rüzgâr Atlası" na göre yerleşim alanları dışında 50m yükseklikteki rüzgar hızları, Marmara, Batı Karadeniz, Doğu Akdeniz kıyılarında 6.0 – 7.0 m/sn, iç kesimlerde ise 5.5 – 6.5 m/sn civarında, Batı Akdeniz kıyılarında 5.0 –6.0 m/sn iç kesimlerde 4.5 – 5.5 m/sn, Kuzey –Batı Egede ise kıyılarda 7.0-8.5 m/sn, iç kesimlerinde ise 6.5-7.0 m/sn dir [5-11]. Rüzgâr türbini, rüzgârdaki kinetik enerjiyi önce mekanik enerjiye daha sonra da elektrik enerjisine dönüştüren sistemdir [12]. Bir rüzgâr türbini genel olarak kule, kanatlar, rotor, dişli kutusu, jeneratör (alternatör), elektrik-elektronik elemanlardan oluşur. Rüzgârın kinetik enerjisi rotorda mekanik enerjiye çevrilir. Rotor milinin devir hareketi hızlandırılarak gövdedeki jeneratöre aktarılır. Jeneratörden elde edilen elektrik enerjisi aküler vasıtasıyla depolanarak veya doğrudan alıcılara ulaştırılır [11]. Rüzgar türbini kanatları günümüzde kompozit teknolojisi kullanılarak üretilebilmektedir. Bunun dışında metalik malzemeler, polimer mühendislik malzemeleri de kullanılmaktadır. Bu çalışmada küçük ölçekli bir rüzgâr türbini üretilerek yerleşim yerinden uzak sahalar için elektrik enerjisi üretimi amaçlanmıştır. Bu amaca ulaşmak için öncelikle, gerekli hesaplamalar, modelleme çalışmaları, türbin parçalarının 2D cam elyaf kumaştan kompozit malzeme esaslı üretim çalışmaları ve sahada elektrik enerjisi üretim kapasitesinin incelenmesi aşamaları planlanmıştır.

Materyal Metot

Tasarım ve modelleme

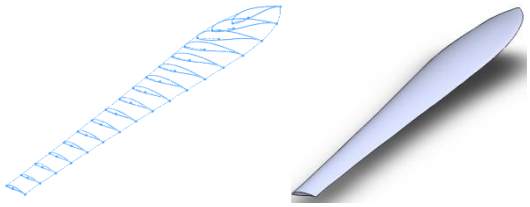
400 mm kanat uzunluğa sahip, 4 kanatlı türbin için kanat katı modelinin oluşturulması için Solidworks programı kullanılmıştır. Modelin Solidworks' te oluşturulması için öncelikle bazı parametrelerin belirlenmesi gerekmektedir. Bunun için ilk olarak elde edilecek güç hesaplanır. Gücü bulmak için öncelikle, kanat Sayısına göre uç-hız oranı ($\lambda_{D)}$) seçiminin yapılması gerekmektedir. Mukavemet şartları göz önünde bulundurularak λ_D = 3.5 seçilmiştir. Kütahya ili için ortalama 8m/s olarak sabit kabul edilmiştir. Yapılan hesaplamalara göre güç (P) = 99 W bulunmuştur. Kanat profili için daha önceden yapılmış araştırmalar ve uygulamalar ışığında NACA-2412 kanat profili seçildi. Ancak, bu kanat profiline uygun üretilen prototipte bu profil yapısının üretilecek kanat ölçülerine göre çok mukavim olamayacağı ön görülerek kanat profili önce NACA-4412 ve son olarak WORTMANN FX 63-137 olarak belirlenmiştir (Şekil 1). Düz, yaptığı çalışmada, bu kanadın ince geometride olması performansının hücum açısı ile olan değişimlerini yüksek derecede etkilendiğini ve bu değişimlerin çok yüksek eğimlerde olduğunu belirtmiştir [13].



Şekil 1. Kanat profillerinin iki boyutlu kartezyen gösterimi [14]

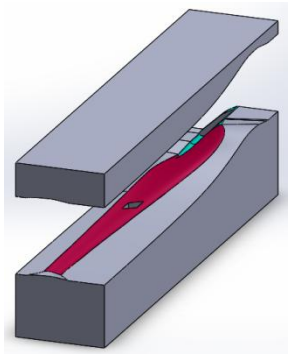
Kort uzunluğu kanat üzerinde ilerledikçe değişeceğinden her istasyondaki kort uzunluğu ve bağlama açısı hesaplanması gerekmektedir. Burada **λ**=3,5 olarak seçilmiştir. (4 kanatlı rüzgâr türbinlerinde kanat uç hız oranı 1-5 arasında seçilebilir.) Kanat boyunca (400 mm) 16 istasyon olduğunu kabul edilmiştir. İlk istasyon rotordan 68mm ileride başlatılmıştır (kanat elemanının rotora bağlanması için 68 mm'lik bir uzunluk bırakılması istenmiştir.). Kanat kort uzunluğu ve bağlanma açısı hesaplandıktan sonra *UIUC Airfoil Data Site* sitesinden WORTMANN FX 63-137 için koordinat datası alınarak, bu datalar Microsoft Excel programında hesaplanan kort uzunluklarıyla çarpılmasıyla her bir düzlem için gerekli profil dataları elde edilir (Elde edilen datalar Solidworks programında Eğriler komutuyla düzlem yüzeyine çekilir. Çekilen datalar her düzleme, hesaplanan kort uzunlukları ve bağlanma açısına uygun olarak atanır ve Loft

komutuyla katı model oluşturulur. Daha sonra belirlenen her istasyon için o istasyonda olması gereken bağlama açısı ve kort uzunluğuna göre çizimler yapılmıştır (Şekil 2).



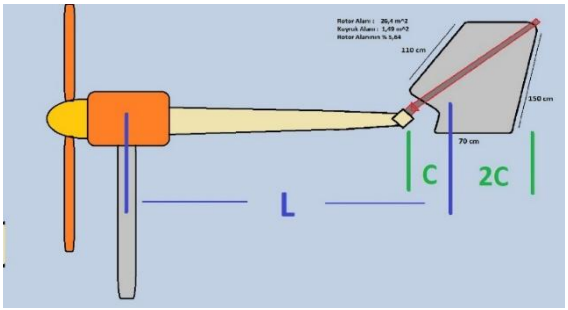
Şekil 2. Kanat profilinin modellenmesi

Model tamamlandıktan sonra kanadı kompozit yapıya uygun şekilde imal edebilmek için kalıp seti oluşturulur. Kanat modeline draft analizi ve ters açı analizi uygulandıktan kalıp ayrım hattı tanımlanır. Kalıp ayrım çizgileri tamamlandıktan sonra ayrım yüzeyleri tanımlanır. Ayrım yüzeyleri oluşturulduktan eksik kalan yüzeyleri yüzey komutlarıyla tamamlanır. Ayrım yüzeyleri tamamlanmış kanat modelinin kalıp araçlarıyla kalıp setinin oluşturulabilmesi için çekme düzlemine kalıp ölçülerine uygun dikdörtgen çizilerek kalıp sınırları belirlenir (Şekil 3).

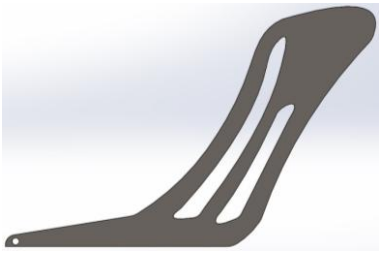


Şekil 3. Kalıp setinin tamamlanmış hali.

Kuyruk palasının alanı rotor alanının %5'inden daha küçük %10'undan daha büyük olmamalı. Şekil olarak oku andıran palalar daha etkindir. Pala ebatları olarak uzunluğu h olan bir palanın yüksekliği 2h olduğunda en iyi verim alınmaktadır. Kuyruk direğinin uzunluğu ise rotor çapının %60'ında olmalı ve bu uzunluğa palanın uzunluğunun %33'ü dâhil olmalıdır (Şekil4). Kuyruk direğinin uzunluğu Ana türbin direğinin merkez noktası temel alınarak hesaplandı [15]. Tasarım Şekil 5'teki gibidir. Kuyruk hafif ve mukavemetli olması için alüminyum sandviç plakadan üretilmiştir. Çıkarılan şablonla şekil verilmiştir.



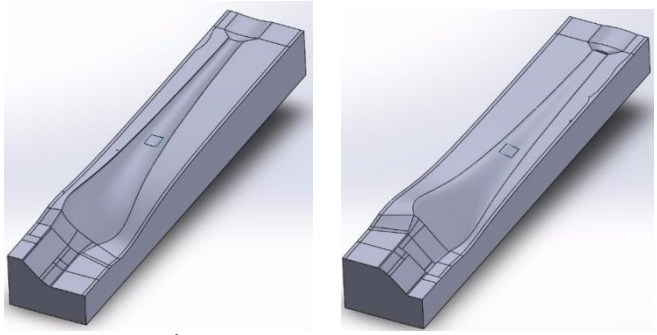
Şekil 4. Kuyruk palasının Rotor alanına oranı [15]



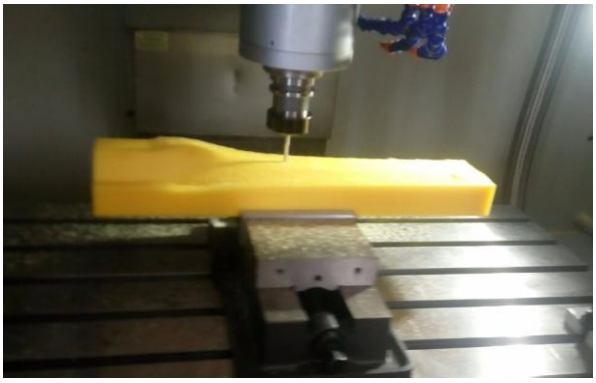
Şekil5. Kuyruk parçası

Üretim

Hazırlanan kalıp setinin iki parçası için ayrı ayrı (Şekil 6) CAM hazırlığı yapılarak CNC dik işlem merkezinde döküm polyamid malzemeden işlenmiştir (Şekil 7). Alt ve üst kalıba uygulanan CAM operasyonları birbiriyle aynı olacak şekilde yapılmıştır, sebebi CNC dik işlem tezgâhında üretim sırasında oluşabilecek yüzey pürüzlülük farkını en aza indirerek üretim sonrası uygulamalarda oluşabilecek kalite farklarını minimize etmektir. Aynı şekilde rotor ve kapağı kalıbı işlenmiştir.



Şekil 6. Bilgisayar Destekli İmalat (CAM) için hazırlanan alt ve üst kalıp yarımları



Şekil 7. Kalıp yarımının CNC dik işlem tezgâhında işlenmesi

Rüzgâr Türbini Kanatlarından en büyük beklenti; uzun sürede dayanıklılığını koruması, aerodinamik olarak türbinin enerji verimliliğine ilave katkı sağlaması, tüm dış etkenlere karşı bütünlüğünü ve yüzey kalitesini kaybetmemesi gibi özelliklerdir. Bu özelliklerin sağlamak için de yapılan tüm çalışmalar ve denemeler sonucunda Rüzgâr Türbinleri Kanatlarının kompozit teknolojisi ile üretilmesinin en uygun yöntem olduğu ve kullanılan malzemelerde de günden güne gelişim yaşanması ile bunun desteklendiği görülmüştür. Rüzgâr türbinlerinin yapımında çok çeşitli malzemeler kullanılmaktadır. Rüzgâr

türbinlerinden yüksek verim elde edilmesi, her birim için uygun malzemenin seçilmesiyle mümkündür. Bu nedenle, tüm koşullarda malzeme gelişim ve davranışları incelenmektedir. Genellikle tüm durumlarda malzeme seçimi için beş metot tercih edilmektedir. Bu metotlar: ekonomik ve performans karakteristikleri, özellik ölçüm değerleri, değerlerin analizi, hasar analizi, ekonomik ve fayda analizi olarak adlandırılır [16] . Bu çalışmaya konu olan rüzgar türbini kanatlarının kompozit olarak üretimi için vakum infüzyon tekniği kullanılmıştır. Vakum infüzyon işlemi; reçine ile cam fiberin yapışması esnasında vakum ile beraber reçinenin sürülmesi güçlü ve uniform bir tabaka oluşturur. Bu esnada önemli olan şey hava kabarcıklarının yüzeyin altına geçişinin engellenmesidir. Kum noktalar ve hava kabarcıkları yüzeyin altında kaldığı zaman kanat mukavemetini ve güvenilirliğini zayıflatmaktadır. Bu yüzden çok önemli bir işlemdir. Reçinenin vakumlanması işlemine vakum infüzyon denilir. Rüzgar türbini kalıpla vakum infüzyon tekniği ile üretimi aşağıdaki aşamalardan oluşmaktadır.

- Kalıp yüzeyine kalıp ayırıcı sürülmesi
- Epoksi reçinenin hazırlanması
- Cam fiber, soyma kumaşı ve reçine yayılma ağının hazırlanması
- Kalıba Cam Elyaf Serilmesi ve Epoksi reçinenin sürülmesi
- Kalıbın vakum torbası içine yerleştirilmesi
- Kanadın kalıptan alınması ve kanat geometrisinin kesilmesi
- Kanat yarımlarının yapıştırılması ve ara malzeme olarak Poliüretan (PU) takviye edilmesi

Kalıp yüzeyine kalıp ayırıcı sürülmesi

Kalıp Ayırıcılar, epoksi ile kalıp arasında film oluşturarak kanat yarımlarının kalıptan kolay ve deforme olmadan ayrılmasını sağlayan kimyasal karışımlardır. Bu kimyasal karışım her kanat üretiminde kalıp yüzeyine 10’ar dakika zaman aralığında 5 kat sürülmüştür (Şekil 8).



Şekil 8. Kalıp Yüzeyine Kalıp Ayırıcı Sürülmesi

Epoksi reçinenin hazırlanması

Çekmenin az oluşu iç gerginliğin ve dolaysısıyla yapısal çatlakların oluşumunun engellenmesine yardımcı olmaktadır. Yüksek mukavemetli, kimyasallara, ısıya, elektrik ve hava şartlarına karşı oldukça dayanıklıdırlar. Güçlü yapısal özellikleriyle beraber hassas ve özel kompozitlerin üretiminde tercih edilirler. Uzay, havacılık, otomotiv ve savunma sanayi gibi sektörlerde kullanılan epoksi reçinelerin daha üstün yapısal özellikler elde etmek için ikincil kürlenme (post curing) uygulanabilmektedir. Epoksi reçineler özellikle vakum torbalama, otoklav, vakum infüzyon, elyaf sarma ve el ile tabakalama gibi kompozit üretim yöntemlerinde kullanılmaktadırlar [17]. Optimum ağırlık ve yüzey kalitesi elde edilmesi

amacıyla dört deneme yapılmıştır. Bu yapılan denemeler sonucunda en iyi sonucu 4.üncü deneme olan 80 gr epoksi, 28 sertleştirici kullanıldığında alınmıştır.

Cam fiber, soyma kumaşı ve reçine yayılma ağının hazırlanması

Üretilecek kanatların mukavim olması amacıyla her bir kanat yarımının altı kat cam elyaf kullanılarak üretilmesi uygun görülmüştür. Soyma kumaşı infüzyon uygulamaları için geliştirilmiştir ve uygulama sonucunda çıkan yüzey üzerine zımpara atma ihtiyacını ortadan kaldırır. Reçine yayılma ağı, **v**akum destekli infüzyon esnasında reçine akışına yardımcı olmak amacıyla kullanılır (Şekil 9).



Şekil 9. Cam Elyaf, Soyma Kumaşı ve Reçine Yayılma Ağı Hazırlanması

Kalıba cam elyaf serilmesi ve epoksi reçinenin sürülmesi

Kesilen cam elyaflar kalıba serilir. Her serilen katta epoksi reçine cam elyafa bir sünger yardımıyla sürülür. Tüm elyaflar epoksi reçine ile ıslandıktan sonra soyma kumaşı ve reçine yayılma ağı kalıp üzerine serilerek vakum infüzyon işlemine hazır hale getirilir (Şekil 10).



Şekil 10. Cam Elyafın Kalıba Serilmesi ve Epoksi Reçinenin Sürülmesi

Kalıbın vakum torbası içine yerleştirilmesi

Uygun ölçülerde vakum torbası kesilip (75 cm x 65 cm), hava sızdırmazlığı sızdırmaz bant kullanılarak sağlanmıştır. Daha sonra epoksi reçinenin akışını sağlayacak reçine hattı kurulur. Reçine hattı için spiral hortum ve normal şeffaf hortum kullanılır. Şeffaf hortum bir ucundan spiral hortuma bağlanır. Spriral hortumun vakum torbası çıkışındaki kısmı sızdırmaz bant ile sarılır ve çözülmesin diye yapıştırılır. Hazırlanan vakum torbası içerisine Kalıp yerleştirilir. Kalıp vakum torbasına yerleştirildikten sonra vakum pompası ile vakum torbası içerisindeki bütün hava çekilir. Vakum pompasını kapatmadan hemen önce vakum hortumu katlanır ve zipper ile katlı halde sabitlenir. Daha sonra reçinenin kuruması için kalıp vakum torbası içinde 8 saat kadar bekletilir (Şekil 11).



Şekil 11. Kalıbın vakum torbasına yerleştirilmesi ve vakumlanarak bekletilmesi

Vakum İnfüzyon işlemi bittikten sonra kalıptan alınan kanat yarımları kanat profiline ve geometrisine uygun şekilde kesilir ve ölçüsüne getirilir (Şekil 12).



Şekil 12. Kanat Yarımlarının Kesilmesi

Kesilerek ölçüye getirilen kanat yarımları, kanat geometrisine uygun biçimde yapıştırılır. Yapıştırılan kanat yarımları Poliüretan ile dolduruldu. Son olarak yapıştırılıp poliüretanla doldurulan kanatlar

zımparalanarak kanat geometrisine uygun hale getirildi. Ara malzemeler; sandviç yapıdaki kompozit ürünlerde kullanılan dolgu malzemeleridir. Özellikle eğilme dayanımını arttırmaları, kompozit ürünlerin kullanım yerlerinin artmalarına sebep olmuştur. Ara malzeme kullanımı nedeniyle, yaklaşık %3 oranında bir ağırlık artışı ile eğilme dayanımının 3.5 kat, rijitliğin ise 7 kat dolaylarında artırılması mümkündür [18]. Ara malzeme olarak, yatay ve düşey zeminlerde rahatlıkla uygulanabilirliği ve uygulandığı yüzeyi fiziki darbelere karşı güçlendirmesi yanı sıra uygulama hızını oldukça yüksek olmasından dolayı poliüretan kullanılmıştır.

Burun üretimi

Türbin motoruna etki eden eksenel yükü azaltabilmek için burun kısmının kompozit malzemeden üretilmesi uygun görülmüştür. Burun üretiminde kanatlarda da olduğu gibi vakum infüzyon yöntemi kullanılmıştır. Üretimi tamamlanan burun kısmı rotora uygun şekilde kesilip boyanarak montaj için son haline getirilmiştir. Hazırlanan tüm parçalar daha sonra bir araya getirilerek montaj tamamlanmıştır (Şekil 13).



Şekil 13. Montaj tasarım ve saha çalışma görüntüsü.

Sonuçlar

Bu çalışmada dört kanatlı bir rüzgâr türbininin tasarımı ve imalatı gerçekleştirilmiştir. Türbin gücü ve diğer türbin elemanlarının hesaplamaları gerçekleştirilmiştir. Kanat profili olarak WORTMANN FX 63-137 seçilmiştir. Tasarım hesaplamalarında kanat boyu belirlenip güç ve kanat hesaplamaları gerçekleştirilmiştir. Rüzgâr türbin kanadının performansı, kanat profilinin doğru seçilmesi ile birlikte kanat imalatındaki hassasiyet ve kanat malzemesinin seçimi ile yakından ilgilidir. Bu sebeple kanat imalatında cam elyaf kullanılarak kompozit yapı elde edilmiştir. İçi boş olarak imal edilen kanat yarımlarını birleştirdikten sonra mukavemet ve hafiflik için kanat içi poliüretan köpükle dolduruldu. Kanatların uygun pitch açısıyla bağlanabilmesi için özel açılı rotor üretildi. Rüzgâr türbininin rüzgârda en verimli şekilde yararlanması kanatların rüzgâra dik konuma gelmesi gerekir. Türbin ağırlık merkezine düzlemsel rulman ile montaj edilmiş ve uygun boyutta kuyruk üretilerek türbinin kule ekseninde serbest dönmesi sağlanmıştır. 12 m/sn rüzgâr hızında 22 V gerilim üretimi elde edilmiştir.

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POLİMERİK KOMPOZİTLERDE ALEV GECİKTİRİCİ OLARAK KULLANILAN ÇİNKO BORATIN ($2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$) ÜRETİMİ VE KARAKTERİZASYONU

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Özet

Çinko borat, PVC, poliolefinler, elastomerler, poliamidler ve epoksi reçinelerde alev geciktirici bir ajan olarak kullanılmaktadır. Bu yaygın etkisinin yanında çinko borat kömürleştirme hızlandırıcı, damlama önleyici, duman giderici, kızarma baskılayıcı, elektriksel ve optik özelliklerin modifikatörü olarak da işlev görmektedir. Çinko borat üretimi esnasında, B_2O_3/ZnO mol oran, elde edilen ürünlerin fiziksel ve kimyasal özelliklerini önemli ölçüde etkilemektedir. 70 °C ve 90 °C 'de, B_2O_3/ZnO mol oranı 2, 5 saat reaksiyon süresi ve 3,0 mol/lt borik asit konsantrasyonunda farklı türde çinko borat numuneleri hazırlanmıştır. FTIR ve XRD sonuçlarına göre, 70 °C ve 90 °C 'de elde edilen çinko boratların kimyasal yapısı, $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ ve $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ karışımı olduğu tespit edilmiştir. TGA analizine göre ise, numunelerdeki kütle kaybının, teorik olarak yapıda bulunan hidrat miktarına eş değer olduğu sonucuna varılmıştır. Reaksiyon sıcaklığının artması ile de parçacıkların ortalama çapı azaldığı belirlenmiştir. Borik asit konsantrasyonu 4,7 mol/lt değerine çıkarıldığında elde edilen borat türünün değiştiği tespit edilmiştir. Bu konsantrasyonda ultrasonik uygulama sonucu elde edilen çinko boratın kimyasal yapısının $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ olduğu FTIR ve XRD spektrumlarından belirlenmiştir. TGA analizi ile belirlenen kütle kaybı miktarının teorik olarak hesaplanan çinko borattaki hidrat miktarına eşit olduğu bulunmuştur. Ultrasonik uygulama ile hazırlanan numunelerin tanecik boyutunun küçüldüğü SEM analizi ile belirlenmiştir.

Abstract

Zinc borate can be used as a fire retardant in PVC, polyolefins, elastomers, polyamides and epoxy resins. Besides this widespread effect, it also serves as char promoter, anti-drip agent, smoke suppressant, afterglow suppressant, modifier of electrical and optical properties. During the production of zinc borate, the molar ratio of B_2O_3/ZnO significantly affects the physical and chemical properties of the products obtained. Different types of zinc borate samples were prepared at 70 °C and 90 °C, with B_2O_3/ZnO molar ratio of 2, reaction time of 5 h and a 3.0 mol/lt of boric acid concentration. According to FTIR and XRD results, the chemical structure of zinc borates obtained at 70 °C and 90 °C was found to be a mixture of $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ and $ZnO{\cdot}B_2O_3{\cdot}2H_2O$. According to the TGA analysis, the loss of mass in the samples was theoretically equivalent to the amount of hydrate in the structure of zinc borates. It was determined that the average particle size decreased as the reaction temperature increased. The structure of zinc borate structure changed when the boric acid concentration was increased to 4.7 mol/lt. It was determined that the chemical structure of the zinc borate obtained using ultrasonic application at this concentration is found to be $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ from FTIR spectrum and XRD pattern. The mass loss determined by TGA

analysis was found to be equal to the theoretical amount of hydrate in the zinc borate structure. It was determined from SEM analysis that the particle size of the samples prepared by ultrasonic treatment was decreased.

1. Giriş

Bor bileşikleri, seramik, kâğıt, cam, deterjan, plastik, tekstil ve metal endüstrisinde yaygın olarak kullanılmaktadır. Bu alanlarda kullanılan metal boratlar, doğada bulunan veya sentetik yollarla hidratlı ya da hidratsız olarak elde edilmektedir [1]. Metal boratların en önemli bileşiklerinden birisi olan çinko borat, sentetik, hidratlı bir metal borattır ve kristal formda çeşitli bileşikleri ($ZnO \cdot B_2O_3 \cdot 1.12H_2O$, $ZnO \cdot B_2O_3 \cdot 2H_2O$, $6ZnO \cdot 5B_2O_3 \cdot 3H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$, $4ZnO \cdot B_2O_3 \cdot H_2O$, $3ZnO \cdot 5B_2O_3 \cdot 14H_2O$ ve $ZnO \cdot 5B_2O_3 \cdot 4.5H_2O$) vardır. Bu bileşiklerin fiziksel ve kimyasal özelliklerini 0,25-5 aralığındaki (B_2O_3/ZnO) mol oranı belirlemektedir [2]. Çinko boratlar, poliolefinler, elastomerler, PVC, poliamidler ve epoksi reçinelerde alev geciktirici ajan olarak kullanılmaktadır. Alev geciktirici özelliğine ek olarak çinko boratlar, polimerlerde, damlama önleyici ajan, kömürleştirme hızlandırıcı, kızarma baskılayıcı, duman giderici olarak, elektriksel ve optik özelliklerin iyileştirilmesinde de kullanılmaktadır.

Baltacı ve ark.'nın yapmış olduğu çalışmada kümen varlığında ve yokluğunda çinko oksit ve borik asitten çinko borat elde etmişlerdir. Karakterizasyon çalışmaları sonucunda, elde edilen çinko boratın düzensiz yassı tanecikler halinde olduğu ve kimyasal formülünün $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$ şeklinde olduğu sonucuna varılmıştır. Aynı araştırmacılar ürettikleri çinko boratları, polietilen tereftalat üzerinde alev geciktirici olarak kullanmışlardır. Sınırlayıcı oksijen indeksi ve basınç dayanım testine göre, elde edilen sonuçlardan kompozitin dayanımını arttırdığı gözlemlenmiştir [3]. Fang ve ark., polivinil klorür içine katkı materyali ekleyerek elde edilen polivinil klorür kompozitinin mekanik, yangın geciktirme ve termal bozunma özelliklerini araştırmıştır. Polimerin içine kattıkları çinko borat ve tahta tozunun termal bozunmayı etkilediği rapor edilmiştir. Tahta tozunun termal bozunmayı geciktirdiği; çinko boratın ise bozunma sıcaklığını yükselttiği sonucuna varılmıştır. Çinko borat katkısı ile elde edilen kompozitlerin mekanik mukavemet özelliklerinin çinko borat ilavesi ile olumsuz etkilendiği bildirilmiştir [4]. Gao ve ark., poliüretanın alev geciktiriciliğini arttırmak için polimerizasyon (in-situ) aracılığı ile poliüretan/çinko borat nano kompozitleri hazırlamışlardır [5]. Çalışmada kullanılan çinko boratın kimyasal yapısı polifosfat ester ve oleik asitle modifiye edilmiştir. Çalışmada çinko boratın yüzey modifikasyonu, üretilen nano kompozitlerin özellikleri ve mikroyapısı araştırılmıştır. Az miktardaki oleik asit ilavesinin çinko borat nano tanecikleri dağılımını geliştirdiği ayrıca oleik asitle modifiye edilmiş çinko boratın, poliüretanın termal kararlılığı üzerine önemli etkilere sahip olduğu rapor edilmiştir [5].

Bu çalışmada, borik asit ve çinko oksitten çinko borat üretiminde B_2O_3/ZnO mol oranı, reaksiyon sıcaklığı ve ultrasonik uygulamanın çinko borat özellikleri üzerine etkisinin araştırılması hedeflenmiştir.

2. Deneysel Çalışmalar

Kullanılan Malzemeler: Çalışmanın başlangıcında çinko borat sentezi için hammadde olarak borik asit $B(OH)_3$ ve çinko oksit (ZnO), titrasyon deneylerinde D-Mannitol Sigma-Aldrich 'den (% 99.9) temin edilmiştir. Tüm deneylerde de-iyonize su kullanılmıştır.

Çinko borat ($2ZnO \cdot 3B_2O_3 \cdot 3H_2O$) sentezi: Borik asit ve çinko oksitten çinko borat üretiminde manyetik karıştırıcılı cam reaktör kullanılmıştır. Borik asit ile çinko oksit arasındaki reaksiyon, 70 °C ve 90 °C 'de 5 saat boyunca ve B_2O_3/ZnO molar oranı 2,0 [6] kullanılarak ve borik asidin farklı konsantrasyonlarında, 155 dev/dak. karıştırma hızında yürütüldü. Oluşan üründen reaksiyona girmemiş borik asidi uzaklaştırmak için, çökelti deiyonize su kullanılarak birkaç kez yıkandı. Ana sıvının ve yıkama suyunun pH 'ı ve Zn, $B(OH)_3$ içeriği ölçüldü. Elde edilen çinko borat kristallerinin, diborontrioksit (B_2O_3) ve çinko oksit (ZnO) içerikleri sırasıyla NaOH ve EDTA kullanılarak analitik titrasyon ile belirlendi. Çinko oksit ile borik asit arasındaki reaksiyonda ultrasonik uygulamın etkisi incelemek için 600 W 'lık ultrasonik dalgalar üretilirken 20 kHz sonik jeneratör (Ace Glass Inc) ve titanyum rod (Sonic and Materials Inc) kullanıldı. Reaksiyon maksimum genliğin %30 unda gerçekleştirildi.

***Karakterizasyon*:** Çinko borat numunesinin karakterizasyonunda Fourier dönüşümü kızılötesi spektroskopi (FTIR, Shimadzu 8601) , X-Işını kırınımı (XRD, Philips Xpert-Pro), Termal gravimetrik analiz (TGA, Shimadzu TGA-51), parçacık boyut dağılımı (Malvern Mastersizer 2000) ve Taramalı elektron mikroskopu (SEM, Philips XL30 SFEG) kullanıldı.

3. Sonuçlar ve Tartışma

Borik asit ve çinko oksitten çinko borat üretiminde, reaksiyon sıcaklığındaki borik asidin çözünürlüğü, reaktiflerin konsantrasyonunu belirleyen önemli parametrelerden biridir. Reaksiyonda borik asitin oluşturduğu asitlikten dolayı çinko oksit reaksiyon ortamında çözünür [7]. Bu noktada, çinko oksidin tanecik boyutu, reaksiyon ortamında çözünme hızını veya reaksiyon hızını etkileyen parametredir.

Reaksiyon mekanizması: Borik asit ve çinko oksitten çinko borat üretimi sırasında meydana gelen reaksiyonlar aşağıdaki gibidir. Denklem 2 'de, borik asit, borat anyonu oluşturmak için su ile reaksiyona girer ve asidik karakter sağlayan bir H^+ protonu oluşturur. -1 ve -2 yüklü olan poliborat anyonları sırasıyla denklem 3 ve 4 'te verildiği gibidir.

$$B(OH)_{3(s)} \longrightarrow B(OH)_{3(aq)} \quad (1)$$

$$B(OH)_{3(aq)} + H_2O_{(l)} \rightleftharpoons B(OH)_4^-{}_{(aq)} + H^+{}_{(aq)} \quad (2)$$

$$2B(OH)_{3(aq)} + B(OH)_4^-{}_{(aq)} \rightleftharpoons B_3O_3(OH)_4^-{}_{(aq)} + 3H_2O \quad (3)$$

$$B_3O_3(OH)_4^-{}_{(aq)} + H_2O \rightleftharpoons B_3O_3(OH)_5^{-2}{}_{(aq)} + H^+{}_{(aq)} \quad (4)$$

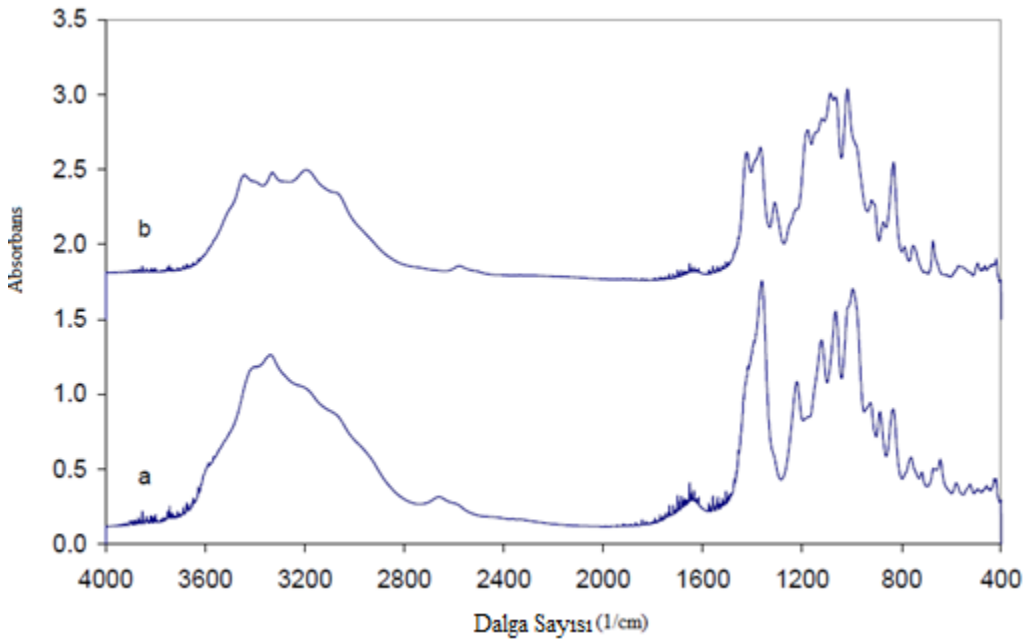
$$ZnO_{(s)} + 2H^+{}_{(aq)} \longrightarrow Zn^{+2}{}_{(aq)} + H_2O \quad (5)$$

$$Zn^{+2}{}_{(aq)} + B_3O_3(OH)_5^{-2}{}_{(aq)} + H_2O \longrightarrow Zn[B_3O_3(OH)_5]\cdot H_2O_{(s)} \quad (6)$$

$$Zn[B_3O_3(OH)_5]\cdot H_2O_{(s)} \longrightarrow Zn[B_3O_4(OH)_3]_{(s)} + 2H_2O \quad (7)$$

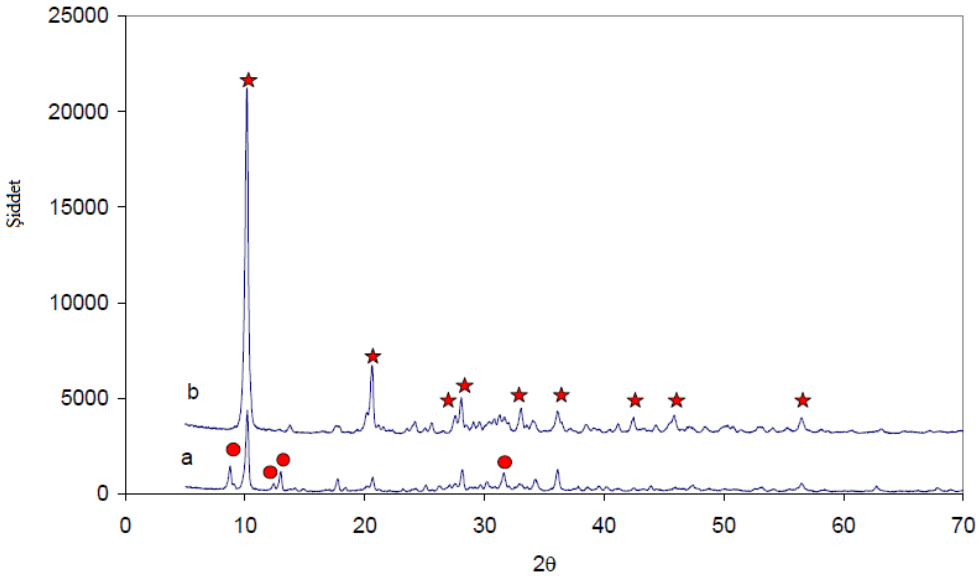
Denklem 5 'te, ZnO, sulu çözeltide Zn^{+2} katyonları oluşturmak üzere protonların (H^+) varlığında suda çözünür. Denklem 6 'da Zn^{+2} katyonları, çözünmeyen katı $Zn[B_3O_3(OH)_5].H_2O$ oluşturmak için $B_3O_3(OH)_5^{-2}{}_{(aq)}$ poliborat anyonuyla reaksiyona girer. Başlangıçta çinko borat kümeleri oluşur ve konsantrasyonu, aşırı doygunluğa ulaşana kadar artar. Denklem 7 'de gösterildiği gibi $Zn[B_3O_3(OH)_5]\cdot H_2O_{(s)}$ den yapısındaki OH gruplarının polimerizasyonu ve kristalizasyon suyunun serbest bırakılmasıyla, $Zn[B_3O_4(OH)_3]_{(s)}$ üretilir.

Reaksiyon sıcaklığının etkisi: 3 mol/lt, 50 mL borik asit çözeltisi ile eşdeğer miktarda çinko oksit arasındaki reaksiyon, B_2O_3/ZnO: 2 molar oranında, 70 °C ve 90 °C 'de 5 saat yürütülmüştür. 70 °C 'de borik asit ve çinko oksitten elde edilen çinko boratın FTIR spektrumu Şekil 1a 'da gösterilmiştir. 3400 cm^{-1} dalga boyundaki pik, üründeki OH gruplarını, 1650 cm^{-1} üründeki kristalizayon suyunun varlığını, 1360 ve 1230 cm^{-1} 'deki pikler sırasıyla BO_3 ve B-O-H gruplarını, 1130 ve 1000 cm^{-1} arasındaki pikler $\nu_{as}(BO_4)$ 'ü ve 839 cm^{-1} 'deki pik ise $\nu_s(BO_4)$ grubunu temsil etmektedir. Şekil 1b 'de ise 90 °C 'de borik asit ve çinko oksitten elde edilen çinko boratın FTIR spektrumu gösterilmiştir. Bu spektrumdan, tamamen farklı bir tür çinko borat olduğu düşünülmektedir. Yani elde edilen bu ürün $2ZnO\cdot 3B_2O_3\cdot 7H_2O$ ve $2ZnO\cdot 3B_2O_3\cdot 3H_2O$'ya benzememektedir. 2900 ile 3400 cm^{-1} dalga boyu arasındaki pikler, OH gruplarının ana borat zincirine farklı şekilde bağlandığını göstermektedir. 1650 cm^{-1} dalga boyundaki pik yapıdaki kristalleşme suyuna aittir. Bor ve oksijen arasındaki koordinasyonda yer alan pikler, 1400 ile 400 cm^{-1} dalga bölgesi arasında gözlenmiştir. 1430-1317 cm^{-1} ve 925 cm^{-1} 'deki pikler sırasıyla trihedral (BO_3) bor oksijen koordinasyonunun asimetrik ve simetrik gerilme titreşimleri ile 1182-1020 cm^{-1} ve 835 cm^{-1} 'deki pikler, tetrahedral (BO_4) yapının asimetrik ve simetrik gerilme titreşimleriyle ilişkilidir.



Şekil 1. Borik asit derişimi 3 mol/lt, mol oran 2, reaksiyon süresi 5 saat, 70 °C (a) ve 90 °C (b) 'de üretilen çinko boratların FTIR spektrumları

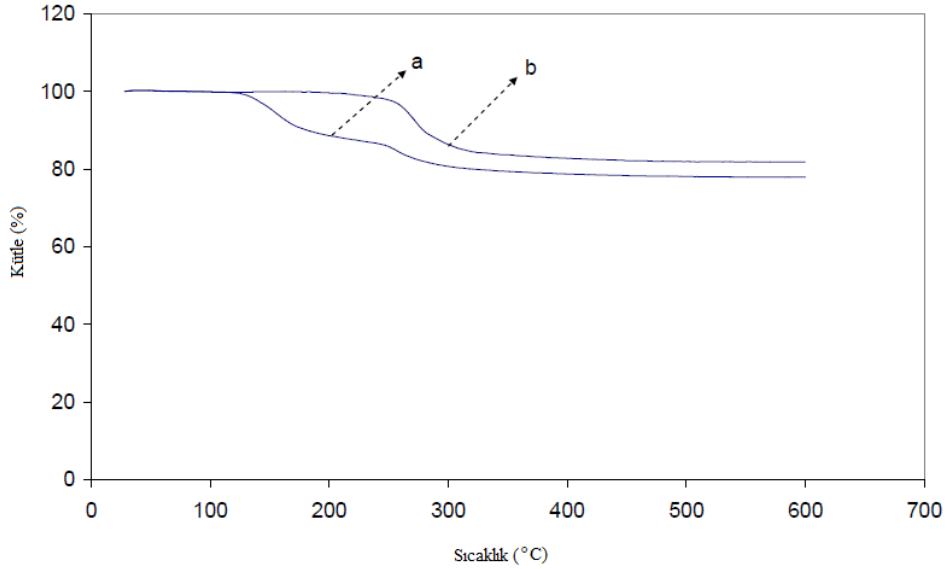
Reaksiyon süresi 5 saat ve 70 °C ve 90°C reaksiyon sıcaklığında üretilen çinko boratların x ışını kırınımı diyagramları (XRD) Şekil 2 'de verildiği gibidir. Şekil 2 'de iki ana pik grubu vardır. Yıldız ile işaretli ilk grubun açıları 10,2°, 20,6°, 28,1°, 33,1°, 36,2°, 45,9° ve 56,7, daire ile işaretli ikinci grubun açıları 8,8°, 12,8°, 13,0°, ve 31,7°'dir. Bu piklerden, bu ürünün $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ (Sawada et al., 2004) ve $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ 'nun bir karışımı olduğu belirlenmiştir (JCPDS 75-0766).



Şekil 2. Borik asit derişimi 3 mol/lt, molar oran 2, reaksiyon süresi 5 saat, 70 °C (a) ve 90 °C (b) 'de üretilen çinko boratların x ışını kırınımı diyagramları

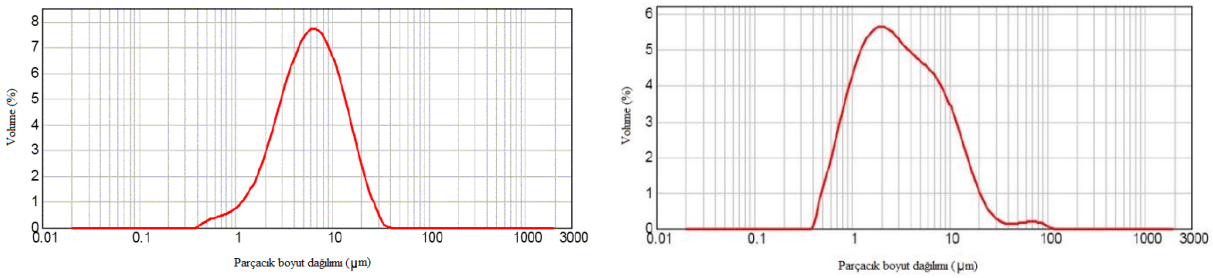
Şekil 3 'de 70 °C ve 90 °C reaksiyon sıcaklığında ve 5 saat reaksiyon süresi ile elde edilen çinko boratın termal davranışı verilmektedir. Şekil 3a 'da, farklı çinko borat türlerine ait iki ayrışma aşaması

vardır. Çinko boratlar, $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ ve $ZnO{\cdot}B_2O_3{\cdot}2H_2O$, 130 °C 'den 250 °C 'ye ısıtıldığında, su ve hidroksil gruplarını kaybettikleri gözlenmektedir. Kütle kaybının yaklaşık 130 °C 'de meydana geldiği ilk adım $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ çinko borat türüne ve 240 °C civarında kütle kaybının başladığı ikinci adımda ise $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ çinko borat türüne aittir. Numunenin 600 °C 'ye kadar ısıtılması ile kütle kaybı yaklaşık olarak %22,14 olmuştur. Şekil 3b 'de ise, 90 °C 'de 5 saat reaksiyon süresi ile üretilen çinko borata ait TGA eğrisi gösterilmektedir. Elde edilen bu çinko borat 600 °C 'ye ısıtıldığında toplam kütle kaybı yaklaşık olarak %18,16 olarak ölçülmüştür. Numunede ilk kütle kaybı 240 °C civarında başlarken 400 °C'nin üstünden 600 °C 'ye kadar başka kütle kaybı gözlemlenmemiştir.



Şekil 3. 3 mol/lt borik asit, mol oranı 2, reaksiyon süresi 5 saat, 70 °C (a) ve 90 °C (b) 'de üretilen çinko boratların TGA eğrileri

70 °C ve 90 °C 'de elde edilen çinko borat numunelerine ait parçacık boyut dağılımı grafikleri Şekil 4 görülmektedir. 70 °C ve 90 °C 'de üretilen çinko boratların hacim-ağırlıklı ortalama parçacık çapı, sırasıyla, 7,6 µm ve 5,9 µm 'dir. Reaksiyon sıcaklığının 70 °C 'den 90 °C 'ye artmasıyla parçacıkların ortalama çapı azalmıştır.

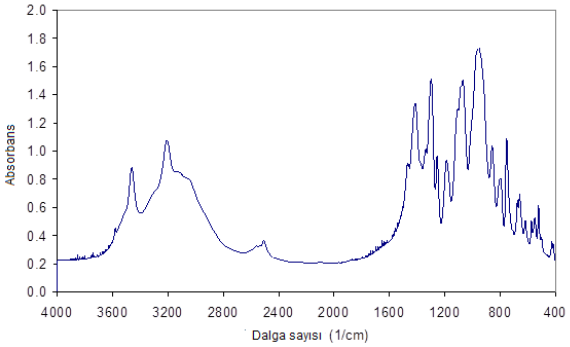


(a) (b)

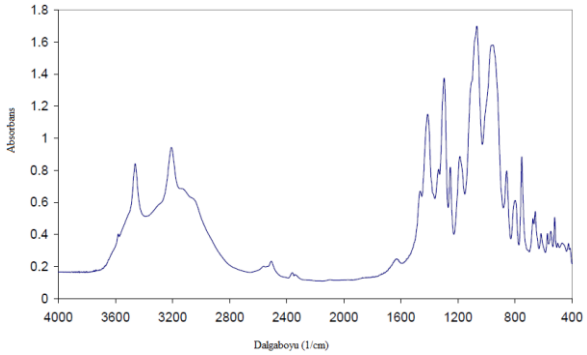
Şekil 4. 3 mol/lt borik asit, mol oran 2, reaksiyon süresi 5 saat, 70 °C (a) ve 90 °C (b) 'de üretilen çinko boratların parçacık boyut dağılımları

Ultrasonik uygulama etkisi: Borik asit ve çinko oksit reaksiyonunda ultrasonik uygulamanın nihai ürünün tanecik boyutunu kontrol edebileceği düşünülmüştür. Çinko oksit ile borik asit arasındaki reaksiyonda ultrasonik uygulama, 4,7 mol/lt borik asit konsantrasyonunda ve 90 °C 'de 5 saat reaksiyon süresi ile

B_2O_3/ZnO 2,0 mol oranına göre, yeterli miktarda çinko oksit kullanılarak çalışılmıştır. Ultrasonik uygulama olmadan ve ultrasonik uygulama ile hazırlanan çinko boratın FTIR spektrumları ve XRD diyagramları sırasıyla Şekil 5 ve Şekil 6 'de verildiği gibidir. Ultrasonik uygulaması olmadan ve ultrasonik uygulaması ile 5 saat ısıtılarak elde edilen örneklerin FTIR spektrumları ve x-ışını kırınımı diyagramları, $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ çinko borat üretildiğini göstermiştir. $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ kristal suyu içermediğinden Şekil 5 deki FTIR spektrumlarında 1650 cm^{-1} de H_2O bükülme titreşimi gözlenmemektedir. Şekil 6'daki x-ışını kırınımı diyagramı da $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ ait JCPDS 32-1464 [6]'de verilen yansımalara sahiptir. Örneklerin TGA eğrileri Şekil 7 kütle kaybının 290 °C de başladığını, 600 °C 'ye kadar % 12,69 kütle kaybı olduğunu göstermektedir. Bu değer, kimyasal formülü $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ olan çinko boratın teorik su içeriğine karşılık gelmektedir.

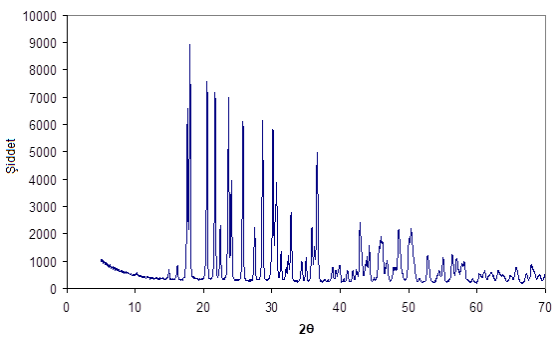


(a)

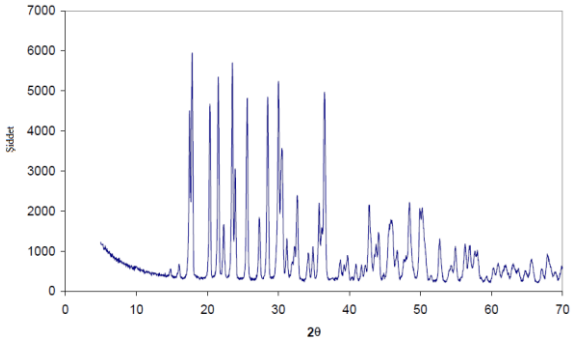


(b)

Şekil 5. (a) Borik asit derişimi 4,7 mol/l, reaksiyon süresi 5 saat, mol oranı 2, 90 °C 'de üretilen (b) aynı koşullarda ultrasonik uygulama kullanarak üretilen çinko boratların infrared spektrumları

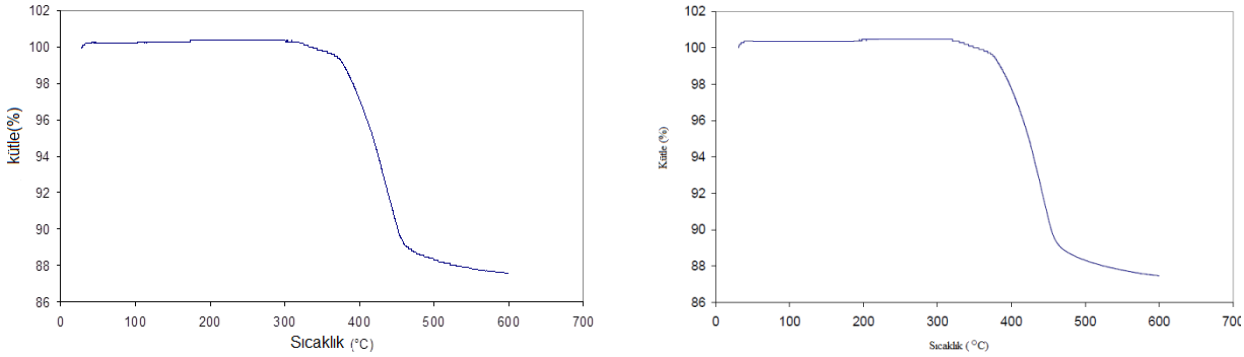


(a)



(a)

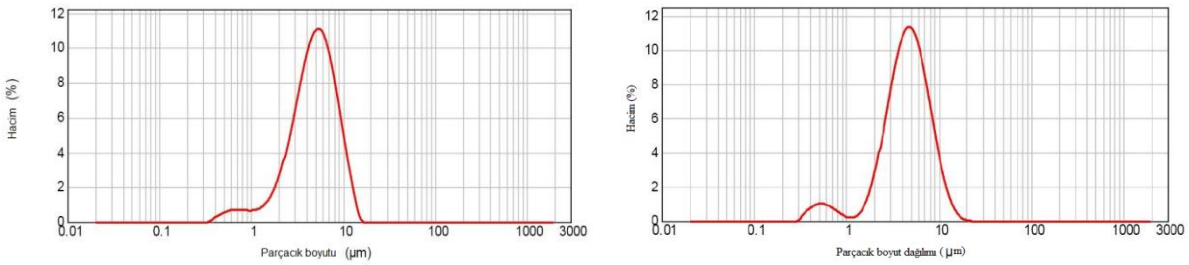
Şekil 6. (a) Borik asit derişimi 4,7 mol/l, reaksiyon süresi 5 saat, mol oranı 2, 90 °C 'de üretilen (b) aynı koşullarda ultrasonik uygulama kullanarak üretilen çinko boratların XRD diyagramları



(a) (b)

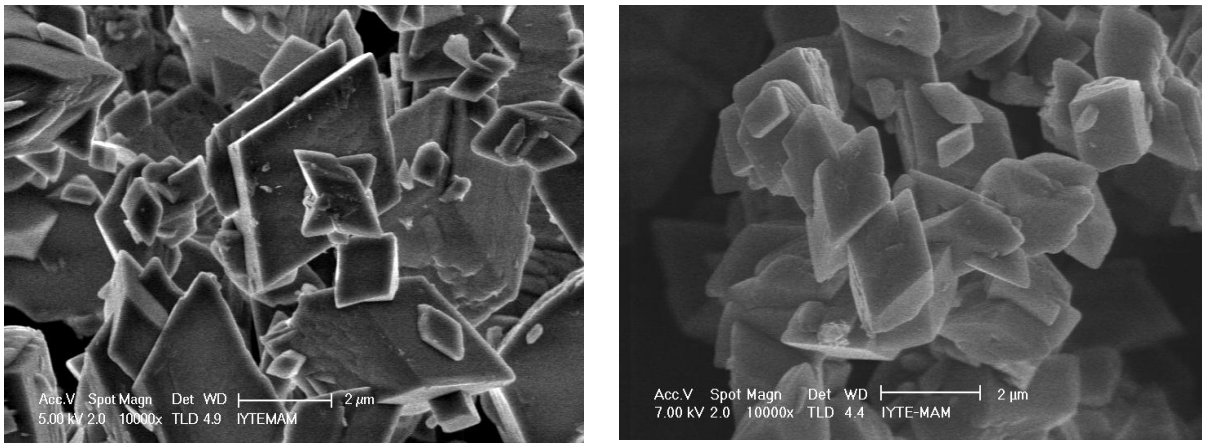
Şekil 7. (a) Borik asit derişimi 4,7 mol/lt, reaksiyon süresi 5 saat, mol oran 2, 90 °C 'de üretilen (b) aynı koşullarda ultrasonik uygulama kullanarak üretilen çinko boratların TGA eğrileri

Ultrasonik uygulama olmadan ve ultrasonik uygulama kullanılarak elde edilen çinko boratların parçacık boyut dağılımları Şekil 8 'de gösterilmiştir. Her iki örnekte de bimodal tane boyutu dağılımı gözlenmektedir. Ultrasonik uygulama ile tane boyutu dağılımının daha küçük boyutlara kaydığı gözlenmektedir. Ultrasonik uygulama ile 1,0 μm altı tanecik hacim kesrinde artış vardır. Ultrasonik uygulama ile ortalama tane boyutu 5,7 μm den 5,1 μm'ye düşmüştür. Gürbüz ve ark., [8] ve Ersan ve ark. [9] ultrasonik uygulama ile daha düşük sıcaklık ve sürelerle aşı kristali olmadan $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ elde edilebileceğini göstermiştir. Bu çalışmada ise ultrasonik uygulama ile tane boyutu dağılımının daha küçük değerlere kaydığı gösterilmiştir. Şekil 9'da görülen SEM mikrograflarında ultrasonik uygulama ile tane boyutunda çok daha büyük oranda azalma olduğu gözlenmektedir. Parçacıkların aglomere olmaları nedeniyle su içinde yapılmış tane boyutu analizinde bu fark yeteri kadar gözlenmemiştir.



(a) (b)

Şekil 8. (a) Borik asit derişimi 4,7 mol/lt, reaksiyon süresi 5 saat, mol oranı 2, 90 °C 'de üretilen (b) Aynı koşullarda ultrasonik uygulama kullanarak üretilen çinko boratların parçacık boyut dağılımı



(a) (b)

Şekil 9. Borik asit derişimi 4,7 mol/lt, reaksiyon süresi 5 saat, mol oranı 2, 90 °C 'de üretilen (b) aynı koşullarda ultrasonik uygulama kullanarak üretilen çinko boratların SEM mikrofotoğrafları

4. Sonuçlar

Bu çalışmada borik asitin 3 mol/lt derişiminde 70°C ve 90°C da elde edilen çinko borat ürünlerinin farklı olduğu bulunmuştur. Reaktörde borik asit ve çinko oksidin reaksiyonunda ultrasonik uygulama olmadan ve uygulama ile çinko boratlar elde edilmiştir. FTIR spektrumları ve X-ışını kırınımı diyagramları 70 °C'de $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ ve 90 °C'de $ZnO{\cdot}B_2O_3{\cdot}2H_2O$ (JCPDS 75-0766) türlerinin elde edildiğini göstermiştir. TGA analizi ile hesaplanan kütle kaybının, bu iki çinko boratın yapısında bulunan hidratların teorik olarak hesaplanan su miktarına eşit olduğu tespit edilmiştir. 70 °C ve 90 °C 'de hazırlanan çinko boratların parçacık boyut dağılımında farklılıklar gözlenmiştir. Reaksiyon sıcaklığının 70 °C ve 90 °C yükselmesi ile ortalama parçacık çapı 7,6 µm'dan ve 5,9 µm'na küçülmüştür. 4,7 mol/lt derişimde borik asitle ultrasonik uygulama olmadan veya ultrasonik uygulama ile $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ (JCPDS 75-0766) elde edilmiştir. Yapıda bulunan teorik olarak hesaplanan hidratın miktarının, TGA sonucu yaşanan kütle kaybına yaklaşık olarak eşit olduğu sonucuna varılmıştır. Ultrasonik uygulama ile daha küçük tane kesrinde artış ve ortalama tane boyutunda 5,7 µm den 5,3 µm azalma olmuştur. Taramalı elektron mikroskobu mikrofotoğrafları tane boyutundaki azalmanın çok daha fazla olduğunu göstermiştir.

Reaksiyon koşullarına bağlı olarak elde edilen çinko borat türlerinin fiziksel ve kimyasal özellikleri birbirlerinden farklı olduğundan polimerlerdeki alev geciktirici katkı uygulamalarında polimer özellikleri ile uyumlu çinko borat türünün seçimi göz önünde bulundurulması gereken bir husustur.

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DEVELOPING NEW LIGHTWEIGHTED PLASTIC and STEEL ALLOYED (HYBRID) TOW HOOK FOR AN AUTOMOBILE

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ABSTRACT

In our fast-paced-world, especially for our current decade, automobile producers have already turned their faces to new materials and production solutions because of environmental and ecological irregularities and forces. To take under control of fuel consumptions and carbon emissions, it becomes necessary to produce more light weighted and environmentalist automobile. On the other hand, it requires without structural, security and comfort lack to respond customers 'wishes. With this approach, a typical steel alloy tow hook is converted to hybrid.

In this study, an automobile still on production line, is selected. Hybrid tow hook is designed according to sustain of structural stiffness, strength, geometrical and vehicle homologations. New required design volumes are generated by free-shape optimization. After design work, hybrid tow hook is analyzed under specified loads and boundary conditions using Finite Element Method. In spite of weight reduction and material changing, it is clearly seen that structural requirements still keep their performance if it compares to totally steel alloy tow hooks.

Keywords
Tow Hook, Thermoplastics, Glass Fiber, Composite

ÖZET

Hızla gelişen dünyamızda, özellikle son on yılda otomobil üreticileri çevre ve ekolojik düzensizlikler ve baskılar sebebiyle yeni malzeme ve üretim metotlarına yönelmişlerdir. Yakıt tüketimi ve karbon emisyon gazı salınımını kontrol altına almak için, daha hafif ve çevreci araçların üretmek gerekli hale gelmiştir. Diğer açıdan, yapısal, güvenlik ve konfor kaybı olmadan, müşterilerin beklentilerinin karşılanması gerekmektedir. Bu yaklaşımla, bir tipik çelik alaşım malzemeden çeki kancası, hibrit malzeme kullanımı ile cam elyaf takviyeli termoplastik ve çelik alaşım olacak şekilde dönüştürülmüştür. Bu sebeple, ürün ağırlığı azaltılması amaçlanmıştır.

Bu çalışmada, hâlihazırda üretim hattında olan bir otomobil seçilmiştir. Direngenlik, yapısal dayanım, geometrik ve homologasyon gereklilikleri sağlanacak şekilde hibrit çeki kancası tasarlanmıştır. Gerekli tasarım hacimleri serbest şekil optimizasyonu yardımı ile belirlenmiştir. Modelleme çalışması sonrası hibrit çeki kancası Sonlu Elemanlar Metodu kullanılarak gerekli yük ve sınır koşulları altında analiz edilmiştir. Ağırlık azaltımı ve malzeme değişikliği çalışmasına rağmen, tamamen çelik alaşım çeki kancaları ile benzer performansı göstermektedir.

Anahtar Kelimeler

Çeki Kancası, Termoplastik, Cam Elyafı, Kompozit

1. INTRODUCTION

According to decrease emissions and reach legislation limits, automobile manufacturers all over the world deal with new ways and solutions On the other hand, a lightweight automobile must be safe in every crash scenarios, should be comfortable to satisfy the expectation of customers. There is a challenging balance with satisfying whole requirements and keeping costs minimum.

This paper aims designing and developing studies of a light weighted plastic and steel alloy (hybrid) tow hook according to structural, homologation and test norm requirements.

2. GENERAL

2.1. Technical Terms

Technical Terms is used during the study are listed below at **Table 1**.

Terms	**Expression**
On the road towing	To transport a breakdown vehicle for a short distance on the public road
Gross Vehicle Weight	The maximum loaded (cargo and passengers included) vehicle weight
Tow Hook	An apparatus fixed to vehicle for towing operation
Thermoplastic	A plastic which becomes moldable above a specific temperature and returns to a solid when cooling
Polyamide	A type of polymer which is repeating of amides

Table 1 - Technical Definitions

2.2. Tow Hook Strength Test

A designed tow hook has to be evaluated for structural level on active and passive towing operations. Tow Hook Strength Test ensures that a tow hook and it is attached or related components remain without failure or not excessive permanent damage according to test norms and procedures. According to test norm, for every loading has to be equal to minimum load (**F**) that is formulated below;

$$\boldsymbol{F = 50\% \, x \, Gross \, Vehicle \, Weight} \quad (1)$$

2.2.1. Loading Conditions

Testing contains both longitudinal and angular loading conditions simulates of normal customer usage during towing operations. All cases shown in **Figure 1** and listed below.

- **Longitudinal Tensile load**, horizontally along the longitudinal axis of the vehicle, labelled **"A"**

- **Angular Lodings**, ±5° vertically, ±25° horizontally to the longitudinal axis of vehicle numbered loadings conditions from 1 to 8 according to **Figure 1**.

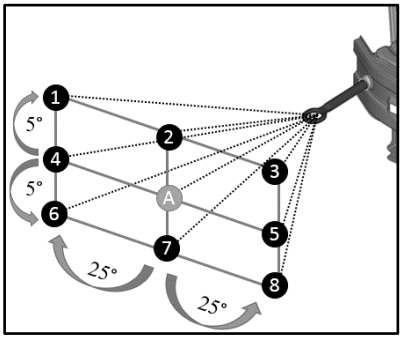


Figure 1 - Loading Conditions

3. DEVELOPMENT STUDY

Developing a new hybrid tow hook processes are expressed and evaluated in this context.

3.1. Minimum Loading

Still on production line vehicle is selected for this case study to assume the minimum load. Gross Vehicle Weight is defined for1800 kg included the most heavy engine option, accessories, 5 passengers and 50 kg baggage. According to formulation,

$$\boldsymbol{F = 50\% \, x \, 1800\,,} \quad \textbf{(1)}$$

$$\boldsymbol{F = 900 \, kg\,,} \quad \textbf{(2)}$$

With 9.81 m/s^2 gravity;

F≒8830 N is applied**.** **(3)**

3.1. Free-Shape Optimization

In this development study, free-shape optimization method is applied on solid tow hook. The objective of this optimization is to minimize volume of tow hook despite increasing of von mises stress as a constraint under every longitudinal and angular load steps. Design volume is shown with yellow at **Figure 2**. Whole volume is assumed as steel alloy. According to definitions, minimum volume of steel alloy to sustain all constraints is obtained. Altair Optistruct 13.0 performs optimization with Free-Shape Optimization module.

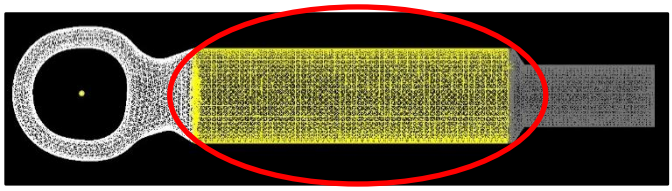


Figure 2 - Optimization Design Volume

The optimization problem is structured as,

- **Responses**: Volume, Static Stress
- **Constraints**: Maximum defined Von Mises Stress
- **Objective**: Minimize Design Volume
- **Design Variable:** nodes move normal to surface

After 15 steps converging of this optimization, volume-changing value for only design volume is plotted by magnitude from 0 to maximum 9.9 mm, shown with variable axial side at **Figure 3**. Only steel alloy volume of tow hook is defined by optimization study.

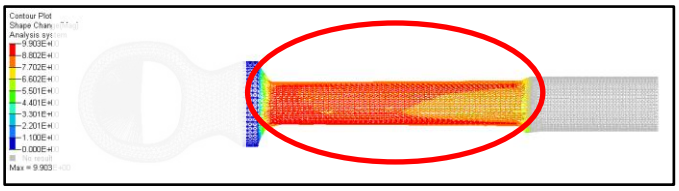


Figure 3 - Free Shape Optimization Result

Optimized volume, that is steel alloy, and other remained volume for thermoplastic are used for redesigning work of tow hook. After six steps nonlinear loading implicit analysis, residual portion of volumes are revealed and sculptured manually, shown at **Figure 4**.

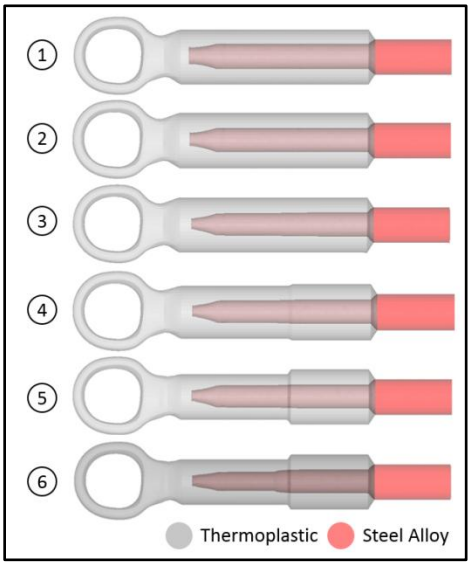


Figure 4 – Sculpturing Steps of Design Volume

At the end of the 3D modelling of final shape design is obtained, is shown at **Figure 5**. Final design solid is re-meshed and analyzed for loading conditions according to test norm finally.

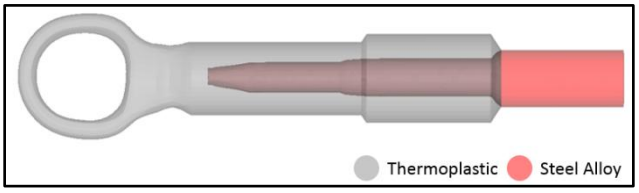


Figure 5 - Final Design

3.1. Boundary Conditions and Mesh Structure

The tow hook, mounting and structural supports and nearby contactable components are included to Finite element Model. Instead of full vehicle body, sliced and trimmed FE model is used in virtual analyses to decrease computational duration. End nodes of boundaries have 6-dof fixed constraints.

To determine structural performance of final design, a Finite Element Model is created to perform a nonlinear static analysis. For pre-processor in this study, *Altair Hypermesh 13.0* is used. Sheet plate surfaces are modelled with 2D shell elements, adhesives; volume-based elements are modelled with 3D solid elements. Beam and spot-welds are modelled with 1D elements. For whole FE Model, element types and quality criteria of mesh structure are listed below at **Table 2**. The loading and unloading simulations are performed by *ABAQUS 6.13* Software. The nonlinear implicit solver is used.

	Criteria			**Accepted**	
	1D	**2D**	**3D**	**Shell Elements**	**Tetra Solid Elements**
Number of Elements	28	67,835	44,483	-	-
Number of Nodes	56	283,971	232,558	-	-
Maximum Warpage	-	14,65	4.97	≤ 15.0	≤ 10.0
Aspect Ratio	-	3.89	6.73	≤ 5.0	≤ 10.0
Skewness	-	0.56	0.78	≤ 0.60	≤ 0.60
Jacobian	-	0.49	0.74	≤ 0.60	≤ 0.60

Table 2. Element Quality List

3.2. Material Properties

According to remained solid volumes and stress responses during optimization, the steel alloy insert requires minimum 200 Gpa Modulus of Elasticity, 600 Mpa Yield Strength and around 800 Mpa or over Tensile Strength for a secure design. To sustain these requirements, mostly used for machinery parts, quenched and tempered 8.8 quality of fastener material, C35 (DIN norm) medium carbon steel alloy is selected.

Thermoplastic cover is assumed in the simulations for high strength and stiffness, minimum 200 Mpa Tensile Strength and 15 Gpa modulus of Elasticity. According to properties, a long glass fiber reinforced Polyamide, PA66 GF50 is selected. Warpage of the fibers are neglected because of mostly longitudinally shrinkage and all materials both steel alloy and thermoplastic cover are modelled as an isotropic material behavior.

3.3. Results

After all loading points are singularly converged, nodal displacements; von Mises Stress and Equivalent Plastic Strains are plotted from model. Nodal displacements at global axis are written from force-applied point, shown at **Table 3.** Finite Element Simulations shows that, new designed tow hook is suitable for structural strength. For every loading case, total and plastic deformation results against evaluation criteria according to test norm and regulations.

Point	**Total Deformation [mm]**				**Plastic Deformation [mm]**				**Target**	
	X	**Y**	**Z**	**Mag**	**X**	**Y**	**Z**	**Mag**	**Plastic Def. [mm]**	**No Damage**
A	-0.893	-0.316	0.849	**1.273**	-0.049	-0.030	-0.069	**0.090**	≤ 5 mm	without failure, rupture etc.
1	-0.524	8.275	2.941	**8.798**	-0.010	2.083	0.251	**2.098**		
2	-0.948	-0.326	2.848	**3.019**	-0.055	-0.036	0.114	**0.132**		
3	-0.793	-8.933	2.910	**9.428**	-0.063	-2.191	0.278	**2.210**		
4	-0.474	8.261	0.502	**8.290**	-0.013	2.080	-0.177	**2.088**		
5	-0.734	-8.979	0.432	**9.020**	-0.062	-2.206	-0.194	**2.216**		
6	-0.398	8.279	-1.928	**8.510**	-0.024	2.100	-0.585	**2.180**		
7	-0.817	0.323	1.748	**1.956**	-0.062	-0.033	-0.472	**0.477**		
8	-0.660	-8.942	-2.035	**9.194**	-0.071	-2.212	-0.649	**2.307**		

Table 3 - Finite Element Model Results

As nodal displacement results are examined, point 8 is observed as the most critical loading because of 2.307 mm magnitude Plastic deformation value. Total Displacement contour of loading Point-8 is shown below at **Figure 6**. Maximum Von Mises Stress Values are under tensile stress of assigned material according to **Figure 7.**

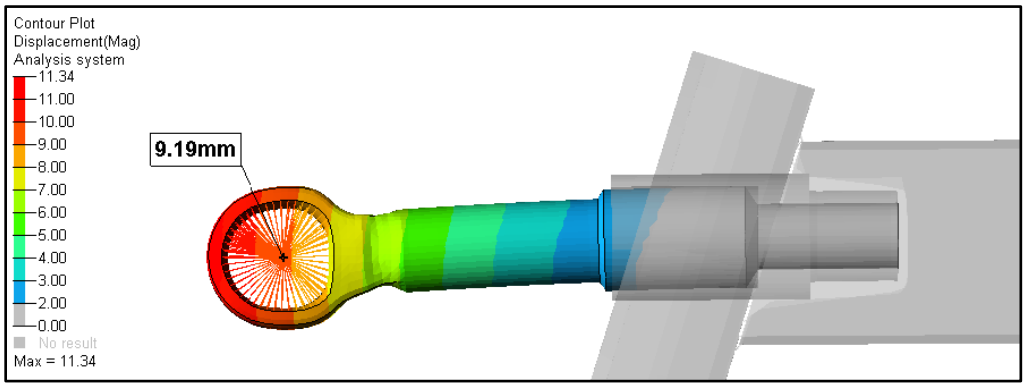


Figure 6 – Total Displacement Contour @ Point-8

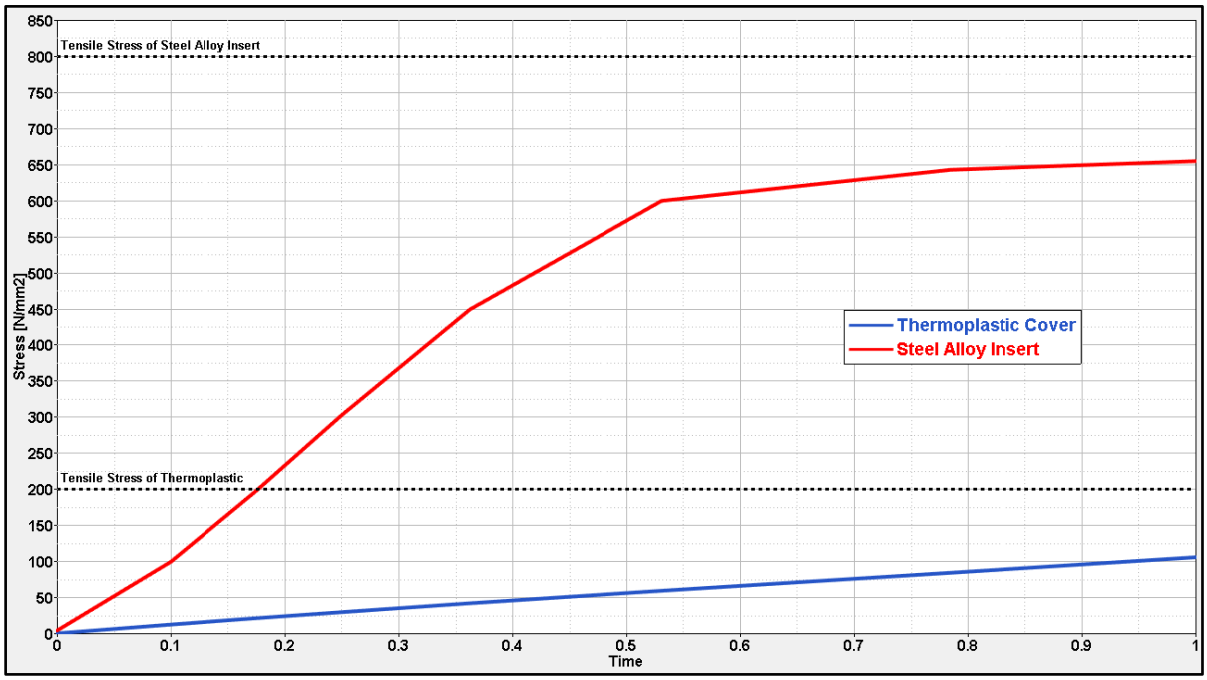


Figure 7 - Max. Von Mises Stress Level @ Point-8

4. CONCLUSION

In the automotive industry, usage of polymeric material provides various advantages. To express the main advantages, weight reduction, cost reduction, design flexibility, cost reduction and corrosion are the most called ones. In parallel with weight reduction, there is a significant decrease in fuel assumption and emissions. Polymeric materials have also much better corrosion performance against any metals. Because of all these important positive factors, usage of polymeric materials in the automotive industry has improved over the years.

In this study, a totally steel allow tow hook has been converted to hybrid with thermoplastic and steel alloy insert reinforced. Using with polymers weight and cost reduced and corrosion avoided an innovative tow hook design has been obtained.

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EVALUATING LIGNIN AS A CO-AGENT FOR NITRILE RUBBER VULCANIZATION

LİGNİNİN NİTRİL KAUÇUK VULKANİZASYONUNDA KOAJAN OLARAK DEĞERLENDİRİLMESİ

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Abstract

Lignin is a natural polymer derived from renewable resources. It has great potential as a reinforcing material in polymeric materials; because it is non-toxic, inexpensive, available in large amounts as a waste from cellulose production. Lignin has a resin-like structure and it is able to accompany vulcanization reaction by affecting the network structure of rubber matrix. In this study, possible co-agent effect of lignin in nitrile rubber vulcanization has been evaluated in terms of rheological and dynamic properties. Rheological properties were measured from their respective cure curves, which were obtained by using a moving die rheometer (MDR, Alpha MDR 2000R). Cure curves were processed to get listed time-torque data for calculating kinetic parameters using Isayev and Deng nonlinear kinetic model. Dynamic measurements were performed by using a rubber process analyzer (RPA, Montech RPA 3000) for determining *G'* values for different oscillation frequencies, which are used to estimate before and after cure crosslink densities according to Pawlowski's model.
Keywords: Crosslink density, Cure kinetics, Lignin, Nitrile rubber

Özet

Lignin, yenilenebilir kaynaklardan elde edilen doğal bir polimerdir. Toksik olmaması, ucuzluğu ve selüloz üretiminde atık olarak çıkması nedeniyle kolay ve bol bulunuyor olması nedenleriyle polimerik malzemelerde takviye edici malzeme olarak kullanımı ilgi çekmektedir. Lignin, reçine benzeri bir yapıya sahiptir ve kauçuk matrisinin ağ yapısını etkileyerek vulkanizasyon tepkimesine eşlik edebilir. Akrilonitril bütadien kauçuğu (nitril kauçuk, NBR), agresif maddelere karşı yüksek dayanıklılığından dolayı, özel amaçlı endüstriyel kauçuk ürünleri üretmek için yaygın olarak kullanılan bir kauçuk tipidir. Bununla birlikte NBR'nin çiğ dayanımı göreceli olarak düşüktür; mekanik özellikleri ve ısıl yaşlanma direnci zayıftır. Bütünüyle bakıldığında, nitril kauçuğun özelliklerinin geliştirilmesi akademi ve endüstri için önemli bir konudur. Bu çalışmada, nitril kauçuk vulkanizasyonunda ligninin olası ko-ajan etkisi, reolojik ve dinamik özelliklerin ölçümü yoluyla araştırılmıştır. Lignin varlığında gerçekleştirilen NBR vulkanizasyonunun reaksiyon kinetiği doğrusal olmayan bir vulkanizasyon kinetik modeli kullanılarak değerlendirilmiştir.

Hamur hazırlamada kullanılan nitril kauçuğun ticari kodu KNM 40M'dir ve Elkim Kauçuk firmasından satın alınmıştır. Lignin, Zonguldak Çaycuma OYKA Kâğıt Ambalaj Sanayi ve Ticaret A.Ş. tesislerinden % 76 kuru madde içeriğinde ham olarak temin edilmiştir. Takviye edici dolgu maddesi ve proses yağı olarak sırasıyla HAF N330 karbon karası ve Petrol Ofisi firmasının PO SK-10 kodlu aromatik yağı kullanılmıştır.

Reolojik özelliklerin değerlendirilmesiyle, lignini, kükürtlü vulkanizasyon sisteminde hızlandırıcı reaksiyonlarını önemli ölçüde etkilediği görülmüştür. Hamur dinamik ölçümleri, kükürt varlığında ligninin ko-ajan olarak görev yaptığını, hem fiziksel hem de kimyasal çapraz bağların miktarını artırdığını göstermiştir. Bununla birlikte, lignin hamur içinde dağılımının iyileştirilmesi ile etkinliğinin artabileceği de düşünülmektedir. Reaksiyon kinetiği çalışmalarından elde edilen bulgular, reolojik ve dinamik özelliklerinden elde edilen sonuçları destekler niteliktedir.

Anahtar kelimeler: Çapraz bağ yoğunluğu, Lignin, Nitril kauçuk (NBR), Vulkanizasyon kinetiği

1. INTRODUCTION

Nitrile Rubber is commonly considered the workhorse of the industrial and automotive rubber products industries. By selecting an elastomer with the appropriate acrylonitrile content in balance with other properties, NBR can be used in a wide variety of application areas requiring oil, fuel, and chemical resistance. On the other hand, NBR has relatively low green strength and mechanical properties as well as poor aging resistance. Improving its overall properties is an important issue for academy and also industry.

An important factor effecting the physical properties of cured rubbermaterials is crosslink density [1]. Several methods such as swelling, application of Mooney-Rivlin theory on the stres-strain curves, evaluating Young's modulus, dynamic-mechanical analysis, and solid nuclear magnetic resonance (NMR) can be used to determine the crosslink density of cured rubber [2]. A novel method, developed by Lee and Pawlowski, estimates physical and chemical crosslink densities seperately by using Rubber Process Analyser (RPA) [3].

According to Pawlowski's method, the chemical crosslink density can be calculated by using Equation 1.

$$X_{chem} = [G'_{cured}(0.5\ Hz) - G'_{uncured}\ (5\ Hz)]/2RT \quad (1)$$

where,

X_{chem} = Chemical crosslink density (mol/m^3),
G'_{cured} = Storage modulus of cured rubber @ 0.5 Hz (kPa),
$G'_{uncured}$ = Storage modulus of uncured rubber at 5 Hz (kPa),
R = Gas constant (J/molK),
T =Absolute temperature (K).

Here, $[G'_{cured}(0.5\ Hz)]/2RT$ value is evaluated to be appearent crosslink density of the rubber, whereas $[G'_{uncured}(5\ Hz)]/2RT$ value is related to physical crosslink density. Theraby, X_{chem} states directly the amount of crosslinks constituted by vulcanization reaction.

There are lots of mathematical models for evaluating vulcanization kinetics. These can be classified in two major topics: mechanistic and empirical (phenomenological). In mechanistic approach, amount of consumed and produced species during vulcanization reaction is a tool for mathematical models whereas

vulcanization experimental data is fitted to nonlinear kinetic models in empirical approach. nth order vulcanization kinetics approach (Isayev and Deng model) is the most common kinetic model for vulcanization and given with Equation 2. It correlates total vulcanization reaction rate with isothermal reaction temperature and instant vulcanization time, in the curing region of the cure curve (between minimum and maximum torque) [4].

$$\alpha = \frac{k(t-t_0)^n}{1+k(t-t_0)^n} \quad (2)$$

where, α = state of cure, k = reaction rate constant (min-1), t = instant time (min), n = reaction order, and t_0= induction time in minutes. In this model, it is assumed that vulcanization rate is maximum at the beginning of the reaction [5]. Calculated k values for various reaction temperatures are used to determine activation energy of the reaction (E_a) by means of Arrhenius equation. Reaction order does not depend on vulcanization temperature; it is varied only by compound formulation.

In this study, the effect of lignin on the rheological properties, physical and chemical crosslink densities of NBR based rubber compounds was investigated. Cure kinetics of the compounds was also evaluated for correlating the lignin's reinforcing mechanism.

2. EXPERIMENTAL

2.1 Materials

Commercial code of NBR was Krynac 330 and was purchased from Elkim Kauçuk, Turkey. Lignin was kindly obtained from Zonguldak Çaycuma OYKA A.Ş. as raw and with 76% dry content. Carbon black (HAF N330) and aromatic oil (Petrol Ofisi, PO SK-10) was used in compounding step as reinforcing filler and process oil, respectively. The other compounding ingredients were commercially used chemicals in rubber and tyre industries.

2.2 Methods

Rubber compounds were prepared in a banbury mixer and laboratory two-roll mill, subsequently. Six different formulations which contain various amount of lignin are given in Table1 .

Table1.Rubber compound formulations

	NBR-Ref	**NBR-SL05**	**NBR-SL1**	**NBR-SL3**	**NBR-SL5**	**NBR-SL10**
	Composition (phr)					
NBR	100	100	100	100	100	100
C/B (N330)	40	40	40	40	40	40
Napthenic oil	6	6	6	6	6	6
Activator-1	5	5	5	5	5	5
Activator-2	1.5	1.5	1.5	1.5	1.5	1.5
Stabilizer	1	1	1	1	1	1
Accelerator	1	1	1	1	1	1
Lignin	-	0.5	1	3	5	10
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5

In order to calculate cure kinetic parameters(k, n, E_a), listed time-torque data were measured from the cure curves, obtained by using a moving die rheometer (MDR, Alpha Pioneer). Test temperatures were selected as 150°C, 160ºC, 170ºC, 180ºC, and 190º. Data points of the cure curves (torque versus time) were

converted to state of cure (α, between 0 and 1) versus time (t) table. OriginPro 8.0® software was used to evaluate t-α data by means of Isayev and Deng kinetic model. Cure curves obtained at 180ºC were used to determine rheological properties.

Dynamic measurements were performed by using a rubber process analyzer (RPA, Montech RPA 3000). Frequency sweep measurements between 0.1 and 10 Hz were evaluated for calculating appearent and chemical crosslink densities according to Pawlowski's approach.

3. RESULTS AND DISCUSSION

3.1 Reological Properties

Cure curves of all the compounds are shown in Figure 1 and selected rheological properties are given in Table 2.

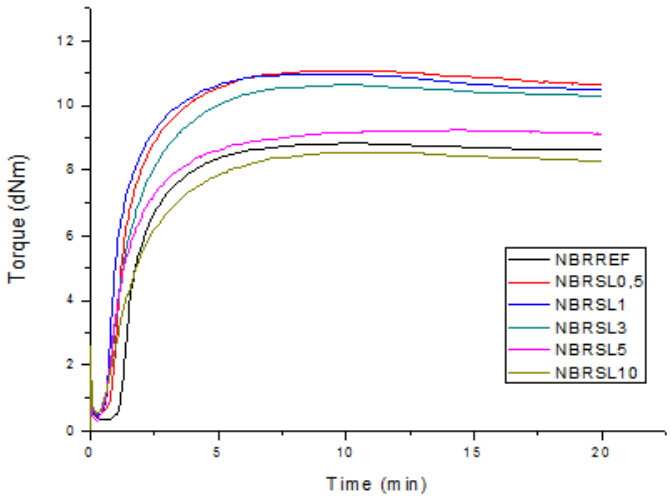


Figure 1. Cure curves of all the compounds

As clearly seen from the Table that, most impressive changes in rheological properties are poor scorch safety and improved cure extent values for lignin containing compounds. Moderate and relatively high lignin contents gave distinct effects in NBR. Up to 3 phr lignin loading, cure extent, which can be successfully correlated to crosslink density for rubber vulcanizates, was measured almost 25% higher than the reference NBR compound. However, after 3 phr lignin content, drop in cure rate was revealed. Improved cure extent without a significant change in cure rate indicates co-agent effect of lignin during vulcanization. Poor scorch safety is counted among the adjustable cure behaviour in rubber compounds; therefore, it was not evaluated as a disadvantage of lignin.

Table 2. Important rheological properties

	NBR-Ref	NBR-SL05	NBR-SL1	NBR-SL3	NBR-SL5	NBR-SL10
ML (dNm)	0.33	0.48	0.44	0.49	0.30	0.55
MH (dNm)	8.84	11.08	10.98	10.63	9.32	8.56
ts2 (min)	1.37	0.99	0.77	0.87	0.85	0.99
t90 (min)	4.03	3.86	3.39	4.18	4.74	4.76
Cure rate index	37.59	34.84	38.17	30.21	25.71	26.53
Cure extent (dNm)	8.51	10.60	10.54	10.14	9.02	8.01

3.2. Crosslink Density Measurements

Physical, chemical and total (apparent) crosslink densities are given in Table 4. In carbon black containing rubber compounds, physical crosslink density can be correlated to bound rubber content. Therefore, high physical crosslink density values indicate good rubber-filler interaction. Here, it was concluded that lignin incorporation did not have a significant effect on filler dispersion and rubber-filler interface up to a specific ratio (3 phr). Higher level of lignin containing compounds thought to be negatively affected during mixing stage due to possible difficulties on lignin dispersion at mixing temperatures. Chemical crosslink density represents amount of crosslinks that occur during vulcanization and directly indicatesefficiency of the vulcanization system. As clearly seen from Table 4 that, lignin incorporation considerably increased the chemical crosslink density for all cases. Thus, apparent crosslink densities are also quite higher relative to NBR reference vulcanizate. This improvement was much more pronounced for low lignin concentrations (0.5 and 1 phr). Higher amount of crosslinks was attributed to possible co-agent activity of lignin on NBR vulcanization by altering the crosslinking reaction mechanism.

Table 4. Apparent and chemical crosslink densities of the compounds (mol/m^3)

	NBR-Ref	NBR-SL05	NBR-SL1	NBR-SL3	NBR-SL5	NBR-SL10
X_{phy}	34.49	39.14	37.49	37.67	26.73	43.67
X_{chem}	78.80	104.49	103.38	96.29	83.77	88.59
X_{app}	113.29	143.49	140.88	133.96	113.50	132.26

3.3. Vulcanization Kinetics

Nonlinear regression results, which were obtained fitting cure data to Isayev and Deng kinetic model, are given in Table 3. Vulcanization activation energies were calculated through Arrhenius equation and are depicted in Figure 2.

Table 3. Reaction kinetic parameters *n* and *k*(min^{-1}) through Isayev and Deng model

	150°C		**160°C**		**170°C**		**180°C**		**190°C**	
	n	**k**	**n**	**k**	**n**	**k**	**n**	**k**	**n**	**k**
NBR-Ref	2.42	0.008	2.71	0.025	2.66	0.140	2.74	0.604	2.05	1.847
NBR-SL05	2.86	0.008	2.80	0.050	3.05	0.171	2.22	0.780	2.68	3.401
NBR-SL1	2.09	0.042	2.32	0.103	2.36	0.462	2.49	1.273	2.50	3.118
NBR-SL3	1.84	0.046	1.93	0.112	1.88	0.359	1.80	0.727	2.18	2.353
NBR-SL5	1.67	0.082	1.59	0.241	1.65	0.515	1.67	1.385	1.79	3.339
NBR-SL10	1.52	0.096	1.67	0.166	1.66	0.388	1.81	0.930	1.87	2.721

Isayev and Deng model submits that reaction order may has various values different than 1 and expresses that rubber main chain is not the only kind reacting in vulcanization. When we compare the order of reactions given in Table 3, we can see that after a certain level of lignin concentration (1 phr), SL compounds have lower reaction order than the reference compound (2 or lower than 2). Only 0.5 phr lignin containing compound has a higher reaction order for all the vulcanization temperatures. The order of reaction decreases with increasing lignin content. This can be explained by altered reaction stoichiometry caused by altered reaction kinetics in lignin containing compounds as a result of its accompanying to the reaction mechanism. Reaction rate constant tends to increase in SL compounds especially for higher curing temperatures. The reaction rate is always higher than that of the reference compound, but does not change systematically with increasing lignin content.

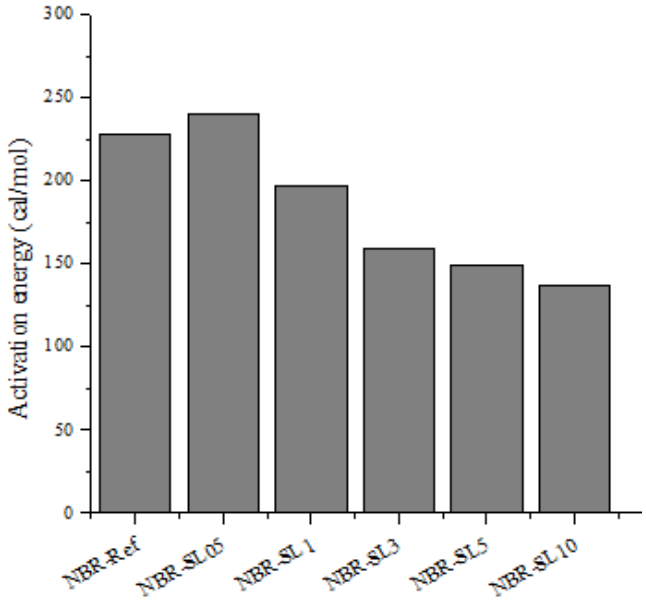


Figure 2. Reaction activation energies through Isayev and Deng model

Lignin incorporation exhibits a decreasing trend in activation energy, also with some small experimental variations. Lower activation energy means easier crosslinking. Here, when we consider the amount of chemical crosslink density mentioned above, lower activation energy could also lead higher crosslink concentration during vulcanization. In vulcanization reactions, it is very well-known that competing reactions occur during rubber vulcanization. Some of these result with efficient crosslink formation and the minor rest does with unexpected termination on crosslink precursors. In such cases, co-agent activity is one of the most preferred solution to increase crosslinking efficiency between rubber chains. Here, lignin has been revealed to be an effective co-agent in NBR vulcanization, considering low activation energy, higher cure extent and higher chemical and apparent crosslink density.

4. CONCLUSION

In this study, the effect of lignin on the rheological properties, physical and chemical crosslink densities of NBR based rubber compounds was investigated. Cure kinetics of the compounds was also evaluated for correlating the lignin's reinforcing mechanism.
In the presence of lignin, rheological properties of the NBR based compounds were almost stable whereas cure extent was improved. Evaluating low activation energy, higher cure extent and higher chemical and apparent crosslink density together, lignin has been concluded to be an effective co-agent in NBR vulcanization.

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PHTHALATE FREE PLASTICIZER SYNTHESIS FRIENDLY FOR HUMAN HEALTH AND ENVIRONMENT

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Abstract

Environmentally friendly products good for the environment and safer for customers. With the increasing environmental awareness, some chemicals have been limited both in terms of environment and human health. Phthalates are the most widely used plasticizers for many years. They increase the softness and flexibility of the products. Some phthalates have been added to the 'cancerable product' list and they are in the category of hazardous substances. In the near future, the use and production of phthalates and phthalate based products are foreseen to be completely prohibited. In this respect, it is aimed to develop a phthalate free product having high content of solid and low content of solvent that can be used as a primary plasticizer for solvent-based and water-based coating systems. It is envisaged that the product can be utilizable in many sectors because of the usability in solvent-based and water-based systems.

Introduction and Objective

According to the latest data, 5 million tons of plasticizer is produced annually in the world and it is used in different sectors. Dioctyl phthalate (DOP, DEHP), a phthalic acid ester, has been used for years to give flexibility to products [1]. After 1980s, some restrictions were introduced for the use of phthalate products due to the carcinogenic effects on human health [2]. Diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) with less carcinogenic effect have been proposed for use as plasticizer [3]. In recent years, researchers have begun to work on plasticizers, which can reduce the proportions of phthalates in formulations as secondary plasticizer or completely remove the phthalates from the formulas being an alternative to phthalates [4]. These studies show that plasticizers are selected from compounds having low VOC (volatile organic compound) value , low molecular weight and they are used as additive materials in the polymer industry. Use of dicarboxylic glycols, adipates, polyhydroxybutyrates, polylacticacids, urea, polyols, citrates as plasticizer and integration of them into water-based and solvent-based systems are being studied. In general, plasticizers have high boiling point. Low-mass plasticizers may penetrate resin systems more easily, but may adversely affect performance permanence, and they may easily deteriorate from polymer matrix in very low molar mass [5]. When plasticizers are incorporated into the resin, they reduce the mechanical stress, hardness, viscosity, glass transition temperature (Tg) value of the resin [6]. The compound that forms the plastifiant resin can have 14-40 carbons with a straight carbon chain or cyclic structure [7,8]. The main parameters affecting the performance of plasticizers in resin and paint systems are resin-

plasticizer compatibility, permanence of flexibility, chemical and water resistance, mechanical strength [9,10,11].

Material-Method

Different types of glycols, alone or in mixtures, are used in the esterification reaction with benzoic acid in the presence of a suitable catalyst and at a certain temperature. If there is a color problem in the final product, a second process can be used to remove the color. In this study, in order to avoid color problem in the synthesis process, the addition of the appropriate color removal agent to the reaction environment is an important step of the project. The color and solid content of the plasticizer was determined according to the standards of Gardner and TS EN ISO 3251, respectively. Viscosity measurements were done according to DIN 53211, ASTM D 1200 standards.

Results and Discussion

The temperature range for the synthesis is selected 200-240 ^{0}C. The type and amount of the catalyst was differentiated and the reaction was carried out until the acidity was lowered to 1 % (as benzoic acid).Time-acid value chart is given in Figure 1 for optimum conditions. The solid content of the product was found to be 96 %. Viscosity was in the range of 80-100 cps. As a result of the laboratory tests and optimization studies, the amount of plasticizer in final formulation of water based product, was determined as 8 % and the amount of plasticizer in final formulation of solvent based product was determined as 2 %. Some performance test results of standard water and solvent based products with and without plasticizer are given in Table 1 Table 2. One of the main difficulties that can be experienced in transition from laboratory work to serial production on an industrial scale is excess of the reaction period. The choice of the appropriate catalyst and optimize the quantity are the subjects that will study for gain energy.

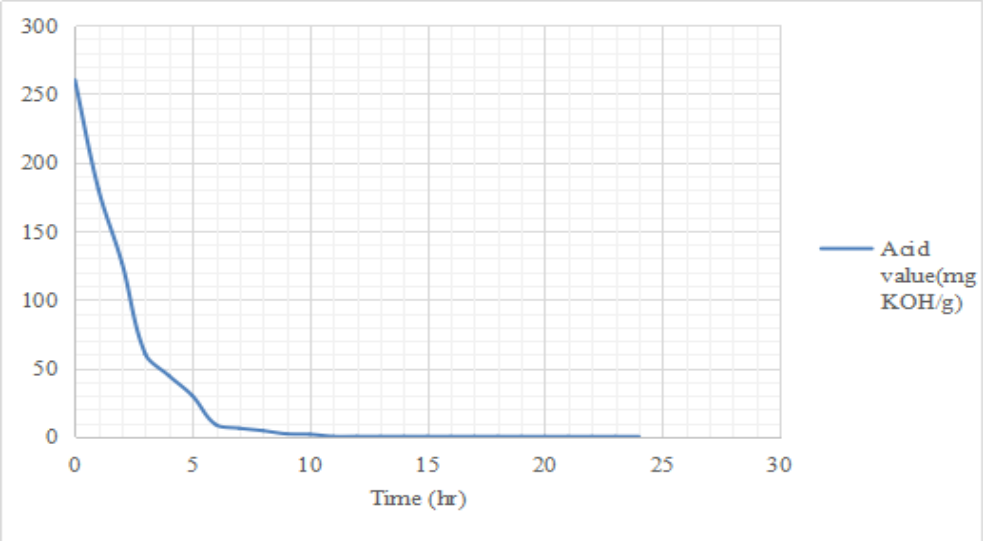


Figure 1. Time-Acid value chart

Table 1. Paint film properties of a standard solvent based product with and without plasticizer

Plasticizer wt., %	**MEK Chemical Resistance (rub)**	**Impact Resistance (joule)**	**Pencil Hardness**	**Gloss (at 60 °C)**	**T-bend**
-	>100	14	H	10	1,0
2,0	>100	15	F	10	0,5

Table 2. Paint film properties of a standard water based product with and without plasticizer

Plasticizer, wt., %	**Gloss (at 85 °C)**	**Film Hardness, (König)**	**Alcali and Water Resistance (spot)**	**Heat Resistance (80 °C,7 day)**
-	6,6	42	OK	OK
7,0	6,6	20	OK	OK

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ANTIOXIDANT EFFECT OF HENNA FOR VARIOUS SULPHUR CURING SYSTEMS

KINANIN FARKLI KÜKÜRTLÜ VULKANİZASYON SİSTEMLERİNDEKİ ANTİOKSİDAN ETKİSİ

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Özet

Doğal kauçuk (NR), yüksek elastikiyet ve iyi mekanik özelliklerin beklendiği çok sayıda uygulamada vazgeçilmez bir hammaddedir. Bununla brlikte, düşük oksijen ve ozon dayanımı, doğal kauçuğun kullanımını sınırlayan en önemli eksikliğidir. Doğal kauçuğun kullanım ömrünün hamur hazırlama aşamasında çeşitli antioksidan maddelerin eklenmesi yoluyla artırılması en yaygın yöntemdir. Kauçuk eşya ve araç lastiği sektörlerinde bu amaçla en çok kullanılan antioksidanlar fenolik ve amin bazlı sentetik antioksidanlar ve 2,2,4-trimetill-1,2-dihidrokinolindir (TMQ). Bununla birlikte sentetik antioksidanlar, üretimleri sırasında bazı çevresel problemlere neden olmaktadırlar ve bu nedenle doğal alternatifleri ile değiştirilmeleri üzerine çok sayıda çalışma yapılmaktadır. Bu çalışmada, doğal bir antioksidan olan kınanın doğal kauçuktaki antioksidan etkisi, etkin (EV) ve konvansiyonel (CV) vulkanizasyon sistemleri için karşılaştırmalı olarak incelenmiştir.

Kına içeren hamurlar reolojik, mekanik ve yaşlanma özellikleri açısından değerlendirilmiştir. Sıcaklık taramalı gerilme-durulma (TSSR) testleri ile antioksidan tipi ve pişirme sisteminin değerlendirilmesinde malzemenin çaprazbağ yoğunluğu ve durulma davranışlarından yararlanılmıştır. Kına, kükürtlü vulkanizasyon sistemi ile pişirilen doğal kauçuk esaslı malzemelerde başarılı bir alternatif antioksidan olarak kullanılabilmiştir. Malzemenin kısa ve uzun dönem yaşlanma davranışları üzerinde pişirme sisteminin oldukça etkili olduğu görülmüştür. Bu etki, farklı vulkanizasyon sistemleri için çaprazbağ kararlılığında gerçekleşen değişkenliğe bağlanmıştır.

Anahtar kelimeler: Antioksidan, Doğal kauçuk, Kına, Yaşlanma

Abstract

Natural Rubber (NR) has been used in lots of applications which require high flexibility and good mechanical properties. However, poor resistance against to ozone and oxygen is a drawback for NR. Oxidative aging of NR leads to the deterioration in the physical and mechanical properties. Using various antioxidants during compounding is common way to improve the aging resistance and so service life of NR. In rubber and tire industries, the most widespread used antioxidants are phenolic and amine based synthetic antioxidants and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ). However, synthetic antioxidants cause some environmental problems during their production processes; like the other rubber compounding ingredients, antioxidants tend to be replaced by natural alternatives. In this study, henna has been

evaluated as a natural antioxidant in NR based rubber compounds for efficient (EV) and conventional (CV) vulcanization systems.

Natural rubber (SVR20) was purchased from Elkim Kauçuk, Turkey. Henna was obtained from domestic market with 4.67% humidity. Carbon black (HAF N660) and naphtenic oil (Petroyağ Octopus N821) was used in compounding step as reinforcing filler and process oil, respectively. The other compounding ingredients were commercially used chemicals in rubber and tyre industries. 2 L capacity of a laboratory type internal mixer and two-roll mill were used subsequently for preparing the rubber compound formulations, which were designed by replacing traditional antioxidants with henna. Performance of henna was evaluated in terms of rheological, mechanical and aging properties of henna containing compounds. Aging properties were also investigated for short and long term thermal aging experiments. Temperature scanning stress relaxation (TSSR) tests were performed for understanding the relation between antioxidant type and vulcanization system by means of crosslink density and relaxation behaviour of the materials.

It has been concluded that, henna can be used as an alternative antioxidant for sulphur vulcanization of natural rubber matrix, compansating little deterorations in mechanical properties. Short and long term performances of henna were also found to be related to vulcanization system. This variation has been attributed to crosslink stability for different vulcanization systems.

Keywords: Aging, Antioxidant, Henna, Natural Rubber

1. GİRİŞ

Doğal kauçuk (NR), yüksek elastikiyet ve iyi mekanik özelliklerin beklendiği çok sayıda uygulamada vazgeçilmez bir hammaddedir [1,2]. Bununla brlikte, düşük oksijen ve ozon dayanımı, doğal kauçuğun kullanımını sınırlayan en önemli eksikliğidir. Doğal kauçuğun oksidatif yaşlanması, zaman içinde fiziksel ve mekanik özelliklerinin bozulmasına, malzemenin kullanıldığı noktada performansını kaybetmesine neden olur [3]. Doğal kauçuğun kullanım ömrünün hamur hazırlama aşamasında çeşitli antioksidan maddelerin eklenmesi yoluyla artırılması en yaygın yöntemdir. Kauçuk eşya ve araç lastiği sektörlerinde bu amaçla en çok kullanılan antioksidanlar fenolik ve amin bazlı sentetik antioksidanlar ve 2,2,4-trimetill-1,2-dihidrokinolindir (TMQ). Bununla birlikte sentetik antioksidanlar, üretimleri sırasında bazı çevresel problemlere neden olmaktadırlar ve bu nedenle doğal alternatifleri ile değiştirilmeleri üzerine çok sayıda çalışma yapılmaktadır [4-8]. Bu çalışmada, doğal bir antioksidan olan kınanın doğal kauçuktaki antioksidan etkisi, etkin (EV) ve konvansiyonel (CV) vulkanizasyon sistemleri için karşılaştırmalı olarak incelenmiştir.

2. DENEYSEL YÖNTEM

2.1 Malzeme

Kauçuk matris olarak kullanılan doğal kauçuk (SVR20), Elkim Kauçuk firmasından satın alınmıştır. %4,67 nem içeren kına, aktardan temin edilerek doğrudan kullanılmıştır. Takviye edici dolgu maddesi ve proses yağı olarak sırasıyla karbon karası (HAF N660) ve Petroyağ firmasından Octopus N821 ticari kodu ile satın alınan naftenik yağ kullanılmıştır. Diğer hamur bileşenleri kauçuk ve lastik sektöründe yaygın olarak kullanılan ticari kimyasallardır.

2.2 Yöntem

Her iki pişirme sisteminde de referans olarak, TMQ içeren hamurlar alınmış, bu hamurlara TMQ yerine farklı oranlarda kına eklenerek yeni hamurlar hazırlanmıştır. Çalışılan hamur formülasyonları Tablo 1'de

verilmiştir. Kauçuk hamurları önce 2 L kapasiteli Banbury tipi dâhili bir karıştırıcı, daha sonra ise iki silindirli bir laboratuvar mili kullanılarak hazırlanmıştır. Hamurların reometre eğrileri Alpha Pioneer marka hareketli kalıp reometresi (MDR) kullanılarak ASTM D2084 standardına uygun olarak çekilmiş, bu eğrileri kullanarak hamurların optimum pişme süreleri ve önemli reolojik özellikleri belirlenmiştir. Vulkanizasyon işlemi, seçilen sıcaklık ve optimum pişme süresi dikkate alınarak ısı ve basınç altında hidrolik preste gerçekleştirilmiştir. Preste levha haline getirilen vulkanize olmuş hamurlardan, standart kesme bıçakları yardımıyla örnekler hazırlanmıştır. Örneklere çekme (ASTM D412) ve kalıcı deformasyon (ASTM D395) testleri uygulanmıştır. Çekme ve kalıcı deformasyon ölçümleri, vulkanizatlar farklı süreler boyunca 70°C'de hava sirkülasyonlu etüvde ısıl yaşlandırmaya (ASTM D573) tabi tutulduktan sonra da gerçekleştirilmiştir. Ayrıca sıcaklık taramalı gerilme-durulma (TSSR) testleri ile antioksidan tipi ve pişirme sisteminin değerlendirilmesinde malzemenin çaprazbağ yoğunluğu ve durulma davranışlarından yararlanılmıştır.

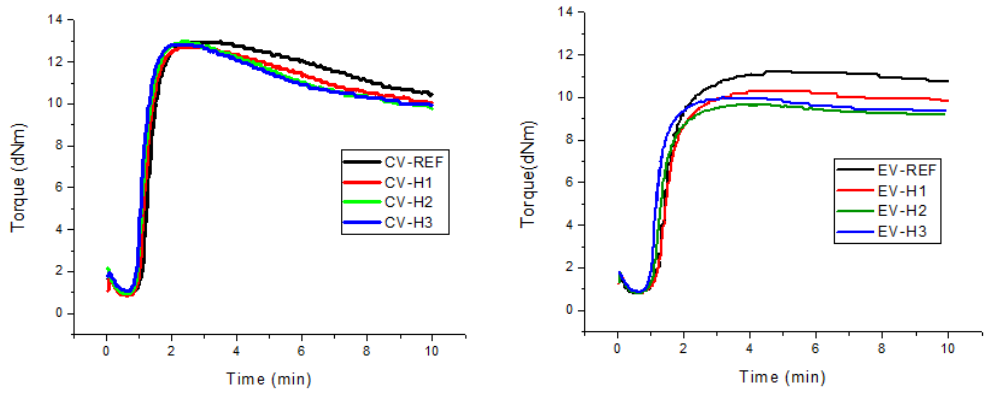
Tablo 1. Kauçuk hamur formülasyonları

	CV-Ref	**CV-H1**	**CV-H2**	**CV-H3**	**EV-Ref**	**EV-H1**	**EV-H2**	**EV-H3**
	Bileşim (phr)							
NR (SVR 20)	100	100	100	100	100	100	100	100
C/B (N660)	40	40	40	40	40	40	40	40
Proses yağı	6	6	6	6	6	6	6	6
Kına	-	H1	H2	H3	-	H1	H2	H3
Çinko oksit	5	5	5	5	5	5	5	5
Stearik asit	2	2	2	2	2	2	2	2
TMQ	2	-	-	-	2	-	-	-
CBS	0.5	0.5	0.5	0.5	1.5	1.5	1.5	1.5
TMTD	0.75	0.75	0.75	0.75	2.25	2.25	2.25	2.25
Kükürt	2.5	2.5	2.5	2.5	0.5	0.5	0.5	0.5

3. BULGULAR ve TARTIŞMA

3.1 Reolojik Özellikler

Tüm karışımların reometre eğrileri Şekil 1'de, önemli reolojik özellikleri ise Tablo 2'de verilmiştir.



(a) (b)

Şekil 1. Hamurların reometre eğrileri (a) CV kodlu hamurlar, (b) EV kodlu hamurlar

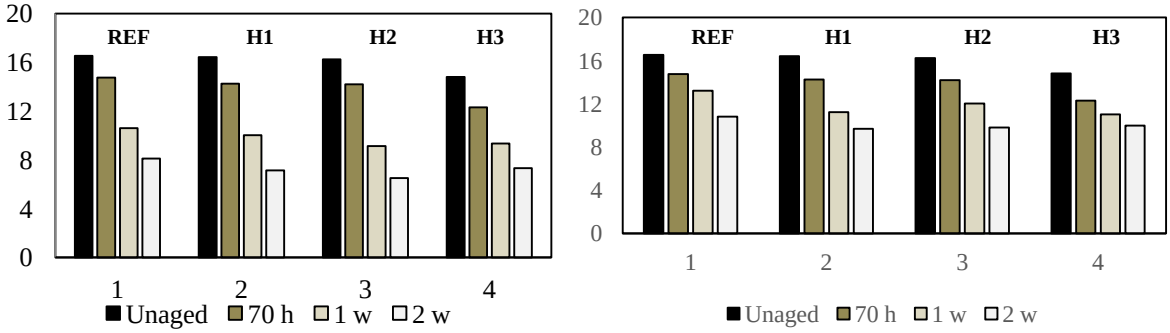
Tablo 2. Hamurların önemli reolojik özellikleri

	CV-Ref	CV-H1	CV-H2	CV-H3	EV-Ref	EV-H1	EV-H2	EV-H3
MH-ML (dNm)	11.8	11.9	12.0	11.7	10.4	9.37	8.8	9.1
CRI	151	167	166	184	86	92	112	127
ts2 (min)	1.12	1.04	0.98	0.95	1.34	1.30	1.17	1.05

Tablo 2'de konvansiyonel ve etkin vulkanizasyon sistemleri için, maksimum ve minimum tork değerlerinin arasındaki farkı ifade eden pişme genliği, pişme hız indisi (CRI) ve ön pişme süresi (ts2) değerleri yer almaktadır. Pişme genliği değerleri incelendiğinde, yüksek oranda kükürt kullanılarak gerçekleştirilen konvansiyonel pişirme sistemi referans hamurunda %10 kadar daha yüksek çaprazbağ düzeyinin elde edildiği, kına içeren hamurlarda da elde edilen çaprazbağ düzeylerinin aynı kaldığı görülmüştür. Etkin vulkanizasyon sisteminde ise kına varlığında çaprazbağ düzeylerinde azalma göze çarpmaktadır. EV sisteminde, CV sistemine kıyasla oldukça yüksek oranda hızlandırıcı kullanılmaktadır. EV'de kına kullanımında sistematik olmayan çaprazbağ düzeyi değişimi, kınanın, vulkanizasyon sırasında oluştuğu bilinen aktif hızlandırıcı kompleksleri ile tepkimeye girerek çaprazbağlanma mekanizmasını değiştirmesine bağlanmaktadır. Bununla birlikte, muhtemel tepkimelerin gerçekleştiğinin ispatlanması ve mekanizmalarının ortaya koyulması için ilave karakterizasyon tekniklerine ihtiyaç bulunmaktadır. Kınanın vulkanizasyon hızı üzerindeki etkisini hem CRI, hem de ts2 verileri ile değerlendirmek mümkündür. Her iki vulkanizasyon sisteminde de kınanın etkisinin, tepkimeyi hızlandırma yönünde olduğu görülmüştür. EV sisteminde hız artışı, artan kına oranlarında CV sistemine göre daha belirgindir. Bu bulgu, EV sisteminde gözlenen düşük çaprazbağ düzeyi ile örtüşmektedir. Her iki vulkanizasyon sistemi için de, antioksidan olarak kına kullanımının, reolojik özellikler üzerinde oldukça düşük ve müdehale edilebilir değişikliklere neden olması, kınanın yüksek kullanım potansiyelini işaret etmesi nedeniyle olumlu bir bulgu olarak değerlendirilebilir.

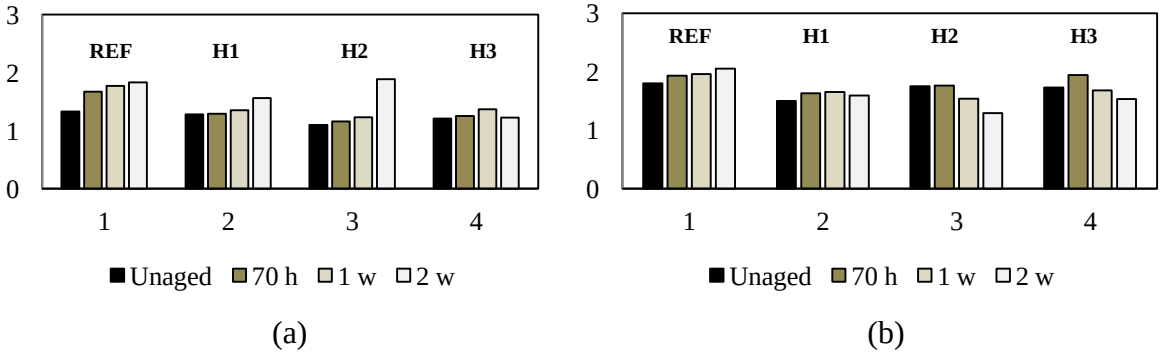
3.2. Mekanik Özellikler

Vulkanizatların mekanik özellikleri, 70°C'de kısa ve uzun dönem yaşlanma etkilerini değerlendirebilmek amacıyla, yaşlanma öncesi ve sonrası birlikte raporlanmıştır. Kopma dayanımı, %100 gerilme modülü ve kalıcı deformasyon özellikleri, her iki pişirme sistemi için ayrı ayrı olmak üzere, sırasıyla Şekil 2-4 arasında verilmiştir.



Şekil 2. Vulkanizatların yaşlanma öncesi ve sonrası kopma dayanımları (MPa) **(a)**CV **(b)**EV

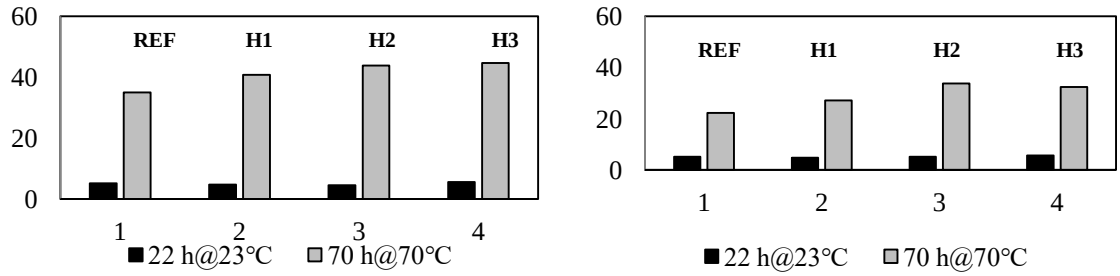
Vulkanizatların yaşlanma öncesi kopma dayanımı değerleri incelendiğinde, hamur içinde kına varlığının, bu özellik üzerinde kaydadeğer bir etkisi olmadığı görülmektedir. Ancak artan kına oranlarında (H3 hamurları) inert dolgu etkisi nedeniyle mekanik özelliklerde düşüş eğilimi gözlenmeye başlamıştır. Referans formülasyonların yaşlanma dayanımları incelendiğinde CV sisteminin, beklendiği gibi EV sistemine göre ısıl ve oksidatif yaşlanmaya karşı çok daha hassas olduğu görülmektedir. Mekanik özellikler açısından değerlendirildiğinde, kına içeren CV vulkanizatlarının yaşlanma dayanımları, TMQ ile korunan vulkanizatlarınkine çok yakındır. Bununla birlikte H kodlu vulkanizatlarda artan yaşlanma sürelerinde kopma dayanımındaki düşüşün %5-10 kadar daha yüksek olduğu da görülmektedir.



Şekil 3. Vulkanizatların yaşlanma öncesi ve sonrası %100 gerilme modülü değerleri (MPa) (a)CV (b)EV

Vulkanizatların yaşlanma dayanımını belirlemede kopma dayanımına kıyasla daha ayırdedici bir özellik olan gerilme modülü değerleri, tüm vulkanizatlar için Şekil 3'te görülmektedir. CV ve EV sistemleri için referans vulkanizatlar kıyaslandığında, EV sistemi ile pişirilen örneklerin daha yüksek modül değerleri sergiledikleri ve kopma dayanımlarına benzer olarak ısıl yaşlanma ile modül değişimlerinin de CV kodlu örneklere kıyasla düşük olduğu görülmüştür. CV örneklerinde, kına varlığında modül artışının TMQ ile korunan vulkanizatlara göre, bazı sapmalar dışında, daha az olduğu göze çarpmaktadır. Buna göre, kınanın CV vulkanizasyon sistemi için, 70°C gibi ortalama yaşlanma sıcaklıkları ve kısa-orta dönem yaşlanma süreleri söz konusu olduğunda, TMQ'ya alternatif doğal bir antioksidan olarak başarılı bir şekilde

kullanılabileceği söylenebilir. EV sistemi ile pişirilen örneklerde yaşlanma ile modül artışı ise tüm yaşlanma süreleri için TMQ ile korunan örneklerle kıyasla oldukça azdır. Bu durum, tüm kına oranları için benzerdir.



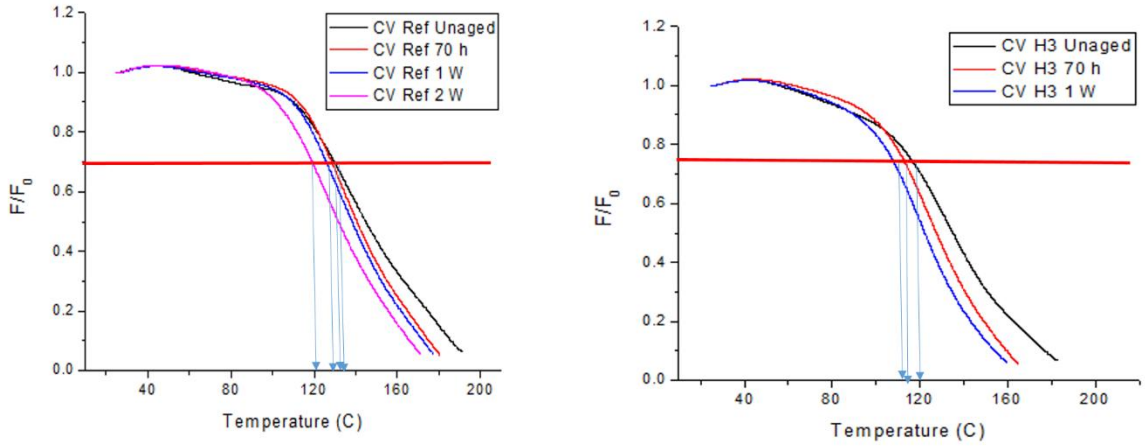
(a) (b)

Şekil 4. Vulkanizatların oda sıcaklığında ve 70°C'de ölçülen kalıcı deformasyonları (%) (a)CV, (b)EV

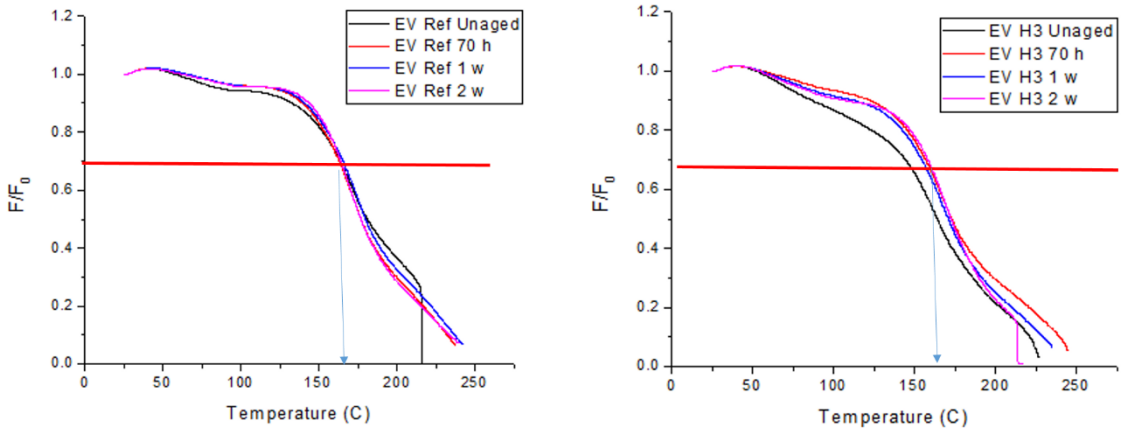
EV ve CV sistemlerine ait referans vulkanizatlar kıyaslandığında, özellikle yüksek sıcaklıkta uzun süre yaşlanma ile kalıcı deformasyon düzeylerinin CV sisteminde belirgin şekilde yüksek olduğu görülmektedir. Bu durum, CV sisteminde ağırlıklı olarak oluştuğu bilinen uzun kükürt çaprazbağlarının göreceli olarak zayıf kararlılığına bağlanmaktadır. Kına kullanılan CV formülasyonlarında diğer mekanik özelliklerdeki yaşlanma kaybı, TMQ ile korunan formülasyonlar ile neredeyse aynı iken kalıcı deformasyon düzeylerindeki artış, kına varlığında hızlandırıcı reaksiyon mekanizmasında gerçekleşen muhtemel değişime bağlanmıştır. Bu değerlendirmeye yönlendiren bir başka bulgu da formülasyon içindeki kına miktarının artmasıyla EV sistemi için sıcakta kalıcı deformasyon artışının CV sistemine kıyasla daha belirgin olmasıdır. Bölüm 3.1'de bahsedildiği gibi, EV sisteminde yüksek oranda hızlandırıcı kullanımı H kodlu formülasyonlarda çaprazbağlanma düzeyinde düşüşü beraberinde getirmektedir. Çaprazbağ düzeyinin düşük olması vulkanizatın elastic özelliklerinden de kayıp anlamına gelmektedir. Bu durumda kalıcı deformasyonun da artması, sözkonusu bulguyu destekler niteliktedir.

3.3. Sıcaklık Taramalı Gerilme Durulma (TSSR) Değerlendirmeleri

CV ve EV vulkanizasyon sistemleri için, antioksidan olarak 2 phr TMQ kullanılarak hazırlanan REF kodlu vulkanizatlar ile yüksek oranda kına kullanılarak hazırlanan H3 kodlu vulkanizatların izotermal olmayan durulma davranışları sırasıyla Şekil 5 ve Şekil 6'da verilmiştir.



Şekil 5. CV vulkanizasyon sistemi için REF ve H3 kodlu vulkanizatların izotermal olmayan durulma (TSSR) eğrileri



Şekil 6. EV vulkanizasyon sistemi için REF ve H3 kodlu vulkanizatların izotermal olmayan durulma (TSSR) eğrileri

Şekil 5'ten görüldüğü gibi, referans CV vulkanizatının yarı modülüne ulaştığı karakteristik sıcaklık (T50) 150°C civarında iken, H3 vulkanizatı için T50 değeri 120°C'ye düşmektedir. Bununla birlikte, 1 hafta yaşlanma sonrasında T50 değeri referans vulkanizatta %20 azalırken (120°C'ye), H3 için bu azalma %5 civarında (115°C'ye) kalmıştır. 2 hafta yaşlanma sonrasında da durulma özelliklerinde benzer bir değişim söz konusudur; fakat H3 için T50 değerinin REF vulkanizatına kıyasla 5°C kadar düşük olduğu da görülmektedir. Şekil 6'dan açıkça görüldüğü gibi, EV sistemi için TMQ ile kınanın, vulkanizatın yaşlanma sonrası izotermal olmayan durulma davranışı üzerinde oldukça benzer bir etkiye sahip olduğu

söylenebilir. Elastomerlerin gerilme-durulma davranışları üzerinde en etkili olan parametreler arasında çaprazbağ yoğunluğu ilk sırayı almaktadır. Hazırlanan tüm hamur bileşimlerine ait orjinal (yaşlanma öncesi) çaprazbağ yoğunlukları Tablo 3'te, Şekil 5 ve 6'da verilen durulma eğrilerinin kalkış eğimlerinden elastisite teorisi uyarınca hesaplanan çaprazbağ yoğunlukları, tüm vulkanizatların farklı süreler boyunca yaşlandırıldıkları durumlar da değerlendirilerek, Tablo 4'te, verilmiştir.

Tablo 3'ten görüdüğü üzere, CV sistemi ile göre pişirilen vulkanizatlarda orjinal çaprazbağ yoğunluğu, kına varlığında bir miktar artış göstermiştir. Bu artış, Tablo 2'de görülen pişme genliği artışı ile de örtüşmektedir. EV kodlu vulkanizatlar için ise kına varlığının çaprazbağ yoğunluğunda bir miktar düşüşe neden olduğu görülmektedir. Tablo 3'ten ayrıca, CV sistemi ile elde edilen çaprazbağ yoğunluğunun EV sistemine kıyasla belirgin şekilde yüksek olduğu da görülmektedir. İzotermal olmayan gerilme-durulma davranışını, örneklerin oda sıcaklığından 300°C'ye kadar sabit hızda ısıtıldığı koşullarda ölçüldüğünden, yaşlanma sonrası çaprazbağ yoğunluğu ile ilişkilendirmek daha doğru bir yaklaşımdır. Tablo 4'ten, CV sisteminde, referans vulkanizatın çaprazbağ yoğunluğu yaşlanma ile azalmaktadır. Uzun kükürt çaprazbağlarının ısı etkisiyle parçalanması, kısa kükürt bağlarına kıyasla daha kolay olduğundan, bu, beklenen bir durumdur. CV-H3 için ise, yaşlanma süresi uzadıkça bu parçalanmanın daha fazla olduğu görülmektedir. Böylelikle, Şekil 5'teki değişimin, çaprazbağ yoğunluğu düşüşü ile açıklanması mümkündür. Bununla birlikte, vulkanizatların ellik kayıplarının belirlenmesinde uygulanan test sıcaklığı 70°C iken, TSSR testinde ulaşılan sıcaklık çok daha yüksek düzeylerdedir (300°C). Çalışılan kauçuk matrisin NR olduğu düşünülürse, 90°C'den sonra gerçekleşen hızlı nominal gerilme düşüşünün önemli bir diğer nedeninin de polimerdeki ana zincir degradasyonu olduğu söylenebilir. EV kodlu vulkanizatlarda ise hem referans hamurda, hem de H3 hamurunda ısıl yaşlanmanın çaprazbağ yoğunluğunu artırıcı yönde etki gösterdiği görülmektedir.

Tablo 3. Hazırlanan tüm formülasyonlar için orjinal çaprazbağ yoğunlukları (mol/m^3)

CV-Ref	**CV-H1**	**CV-H2**	**CV-H3**	**EV-Ref**	**EV-H1**	**EV-H2**	**EV-H3**
127.3	136.7	136.9	137.2	107.1	99.0	98.5	98.9

Tablo 4. Orjinal ve yaşlanmış vulkanizatların çaprazbağ yoğunlukları (mol/m^3)

	CV-Ref	**CV-H3**	**EV-Ref**	**EV-H3**
Unaged	127.3	137.3	107.2	98.9
70 h	125.4	131.3	98.6	82.9
1 w	123.5	111.4	115.8	101.8
2 w	118.6	66.7	117.0	133.0

4. SONUÇ

Kına, kükürtlü vulkanizasyon sistemi ile pişirilen doğal kauçuk esaslı malzemelerde başarılı bir alternatif antioksidan olarak kullanılabilmiştir. Malzemenin kısa ve uzun dönem yaşlanma davranışları üzerinde pişirme sisteminin etkili olduğu görülmüştür. Bununla birlikte, ortalama ve yüksek sıcaklık koşullarına olan dayanımı ayırdetmek için izotermal olmayan gerilim-durulma eğrileri ve aynı yöntem ile hesaplanan çaprazbağ yoğunlukları değerlendirilmiştir. Kınanın, ortalama sıcaklık koşullarında yaşlanma dayanımında CV ve EV sistemleri için etkisi benzer iken, artan yaşlanma sıcaklıklarında EV sistemi ile pişirilen vulkanizatlarda avantajlı bir antioksidan olduğu sonucuna varılmıştır. Bu etki, farklı vulkanizasyon sistemleri için çaprazbağ kararlılığında gerçekleşen değişkenliğe bağlanmıştır.

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A COMBINED EXPERIMENTAL-NUMERICAL APPROACH FOR EFFICIENT PERMEABILITY MEASUREMENT

GEÇİRGENLİK ÖLÇÜMÜNÜN ETKİNLİĞİNİN ARTTIRILMASINA YÖNELİK BİRLEŞİK DENEYSEL-SAYISAL YÖNTEM

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ABSTRACT

Introduction

In composite materials processing with Liquid Composite Molding techniques (e.g., Resin Transfer Molding, Vacuum Assisted Resin Transfer Molding, etc.), permeability characterization of porous fiber preforms is crucial since it is used in the mold design stage to predict the flow pattern, mold filling time, and to determine the inlet and vent locations through mold-filling simulations. However, experimental permeability characterization is a tedious process, requiring many measurements in a domain of fiber volume fraction. A common and significant variation in permeability is due to human factor and material irregularity, which in turn increases the number of required measurements to observe statistical variation. If fluid flow is disturbed by the presence of zones of higher or lower permeability mainly due to race-tracking or irregularity of the fabric, the experimental data is often discarded.

Aim

Our goal is to develop a methodology to correctly estimate the permeability of a fabric preform in the presence of race-tracking by integrating experimental and numerical solution of two-dimensional resin flow based on Darcy law and conservation of mass and assess the capabilities of the developed method through several case studies.

Materials and Methods

In-plane permeability of a random glass mat (areal density of 450 g/m^2) is characterized by 1D permeability measurements using samples with dimensions of 250 mm × 60 mm. An aqueous solution of polyethylene glycol (M_w = 35 kDa and colored by a water based food dye to increase the contrast) is used as the test fluid and by following the Squared Flow Front approach [1], using the following data: (i) the flow front propagation (recorded by a video camera, Canon EOS 650D, 1920×1080 pixels resolution, at 30 frames per second) and (ii) inlet pressure (recorded by a pressure transducer, Keller S35X, 0 – 10 bar operation range, 0.02 bar accuracy). For each experiment, fluid temperature is measured at the inlet, and the correct fluid viscosity for permeability calculation is taken from viscosity-temperature curve obtained through viscosity measurement using a Couette rheometer (AR 2000ex, TA Instruments).

In another set of experiments, race-tracking is introduced by intentionally cutting portions of fabric layers smaller than the mold width of 60 mm. Flow front propagation, inlet pressure and fluid temperature are

recorded throughout the experiments. In the post-processing stage, flow front location is tracked at each frame of the video, the top surface area of the specimen surface is discretized into a grid of square elements and saturation of each square element and its fill time are recorded.

A mold-filling simulation tool based on Control Volume Finite Element Method is implemented assuming saturated incompressible flow in a rigid porous medium. In addition to using the experimental parameters (fluid viscosity and inlet pressure) as inputs, simulation tool also has the capability to take into account the spatially varying permeability. Levenberg-Marquardt method [2,3] is used for minimizing the difference between the simulated and experimental fill times of elements and thus finding the permeability of each element.

Results

Figure 1 shows the results of one of the experiments with intentional race-tracking. In this experiment, the first 150 mm sides of fabric layers along both top and bottom edges ($0 < x < 150$ mm) are cut 3 mm smaller than the remaining part of the fabrics (150 mm $< x < 250$ mm). Figure 1a shows the permeability map at the last iteration of the optimization routine: permeability is significantly higher in the regions where race-tracking was introduced intentionally than the bulk region. Figure 1b shows the histogram of the permeability values and it is divided into two classes, one corresponding to the regular fabric zones and the other corresponding to race-tracking zones, using Otsu's Method [4] as will be detailed in the presentation. Median permeability values of the two classes are plotted along with the results of experiments with no race-tracking in Figure 1c. The median value of the bulk zone (denoted by K_{bulk} in that figure) is in good agreement with the results of experiments in which no race-tracking is allowed.

During the presentation, the details of experiments, simulations and optimization algorithm will be introduced with a focus on interpretation of permeability map results.

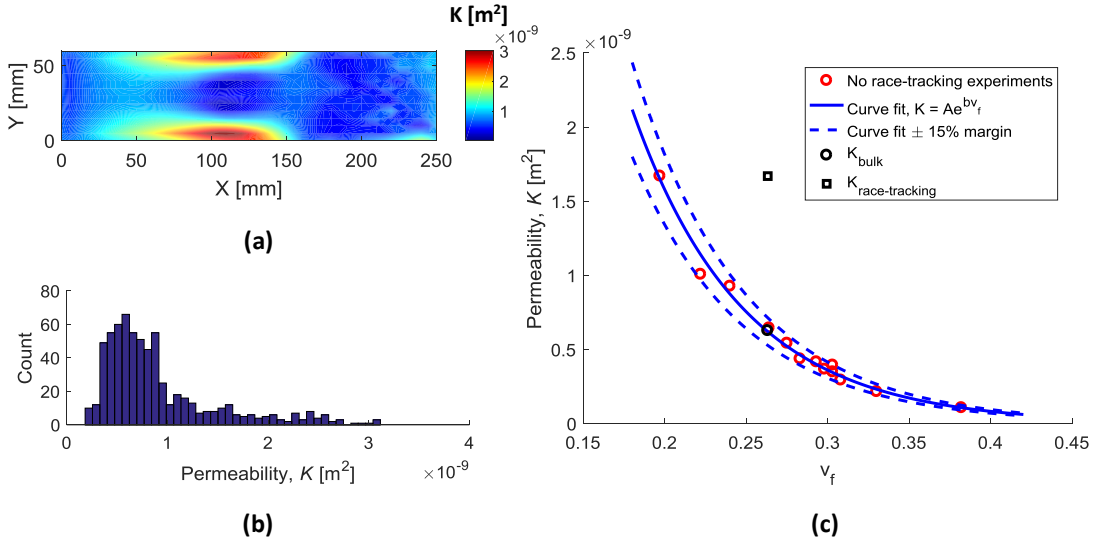


Figure 1: *Results of an experiment with a race-tracking channel introduced intentionally. (a) estimated permeability map, (b) histogram of the estimated permeability values, (c) permeability of bulk (K_{bulk}) and race-tracking ($K_{race\text{-}tracking}$) zones along with the results of experiments without race-tracking. Dashed lines show ±15%*

margins of the curve fit and indicate that results of experiments without race-tracking (red circles) fall within that range.

Keywords
Liquid composite molding, permeability, material characterization

ÖZET

Giriş
Kompozit malzemelerin Sıvı Kompozit Kalıplama yöntemleri (Reçine Transfer Kalıplama, Vakum Destekli Reçine Transfer Kalıplama v.b.) ile üretiminde, gözenekli elyaf kumaşın geçirgenliğinin karakterizasyon sonuçları, kalıp tasarım aşamasında kalıp dolum simülasyonlarına girdi olarak kullanılmakta ve kalıp dolum süresi ve akış ilerleyişinin öngörülmesine ve giriş ve çıkışların belirlenmesine yardımcı olmaktadır. Ancak, geçirgenliğin deneysel karakterizasyonu, belirli bir elyaf hacim oranı aralığında birçok ölçüm gerektirmektedir. Bu ölçümler sırasında karşılaşılan en yaygın sorunlar işçilik (malzeme hazırlama) ve malzeme bozukluklarından kaynaklanmakta ve istatistiksel varyasyonu görebilmek için gerekli deney sayısını daha da arttırmaktadır. Ek olarak, deneysel ölçümler sırasında akışın düşük veya yüksek geçirgenlikli bölgelerden etkilenmesi, sonuçların güvenilirliğini azaltmakta ve testlerin tekrarlanmasına sebep olmaktadır.

Amaç
Hedefimiz, elyaf kumaş ile kalıp duvarları arasındaki kanal boyunca yüksek geçirgenliğe sahip bölgelerin akış üzerinde belirgin etkiye sahip olduğu deneylerin sonuçlarının doğru yorumlanmasını sağlayan, deneysel ve sayısal yöntemlerin bir arada kullanıldığı bir yöntem geliştirmek ve bu yöntemin kabiliyetlerini çeşitli örnek vakalar yoluyla incelemektir.

Malzeme ve Yöntemler
450 g/m^2 yüzeysel yoğunluğa sahip bir cam elyaf keçenin geçirgenliği bir boyutlu akış deneyleri ile ölçülmüştür. Bu deneylerde, 250 mm × 60 mm boyutlarında numuneler ve test sıvısı olarak sulu polietilen glikol çözeltisi (M_w = 35 kDa ve gıda boyası kullanılarak renklendirilmiş) kullanılmıştır. Deneyler sırasında, akış ilerleyişi (kamera ile kaydedilmiş, Canon Eos 650D, 1920×1080 çözünürlük, 30 saniyelik görüntü sayısı) ve kalıp girişindeki sıvı basıncı (basınç algılayıcısı ile kaydedilmiş, Keller S35X, 0 – 10 bar operasyon aralığı, 0.02 bar doğruluk) kaydedilmiş ve geçirgenlik Squared Flow Front yöntemi [1] kullanılarak hesaplanmıştır. Sıvı sıcaklığı kalıp girişinde ölçülmüş ve sıvı viskozitesi, daha önce Couette reometre (AR 2000ex, TA Instruments) ölçümleri ile elde ettiğimiz viskozite-sıcaklık eğrisi kullanılarak hesaplanmıştır.

Başka bir ölçüm setinde ise, elyaf katmanlarının bazı kısımlarını, kasıtlı olarak, olması gerekenden daha dar keserek yüksek geçirgenlikli bölgeler oluşturulmuş; ve akış ilerleyişi, girişteki sıvı basıncı ve sıcaklığı deneyler boyunca kaydedilmiştir. Elde edilen görüntüler işlenerek, her karede akış ön safhasının konumu belirlenmiş ve görüntülerde numunenin yüzeyinde kare elemanlardan oluşan ağda her bir kare elemanın doluluk oranı ve dolum anı kaydedilmiştir.

Gözenekli rijit maddelerde doymuş sıkıştırılamaz akış prensibine dayanan, konuma bağlı değişiklik gösteren geçirgenliği hesaba katan ve deneysel parametreleri (sıvı viskozitesi ve girişteki sıvı basıncı) girdi olarak kullanan, Kontrol Hacmi Sonlu Eleman Metodu temelli bir kalıp dolum simülasyonu

geliştirilmiştir. Levenberg-Marquardt yöntemi [2,3] kullanılarak, elemanların deneysel ve sayısal dolum sürelerinin aralarındaki farkın enazlanması yoluyla elemanların en uygun geçirgenlik değeri bulunmuştur.

Sonuçlar

Şekil 1, kasıtlı olarak yüksek geçrigenlikli bölge oluşturduğumuz deneylerden birine ait sonuçları göstermektedir. Bu deneyde, numunenin alt ve üst kenarında ilk 150 mm boyunca ($0 < x < 150$ mm) numunenin geri kalanına kıyasla (150 mm $< x < 250$ mm) 3 mm daha dar kesilmiştir. Şekil 1a'da eniyileştirme rutininin son adımında elde edilen geçirgenlik haritası sunulmuştur ve dar kesilmiş bölgelerde geçirgenliğin, numunenin geri kalanına kıyasla oldukça yüksek olduğu görülmektedir. Geçirgenlik değerlerinin histogramı Şekil 1b'de verilmiş ve sunum sırasında detaylandırılacağı üzere, Otsu Metodu kullanılarak, biri normal kısımlara diğeri yüksek geçirgenlikli kısımlara karşılık gelen iki sınıfa ayrılmıştır. Şekil 1c'de, her iki sınıfın medyan değerlerine ek olarak, normal deneylerin (yüksek geçirgenlikli bölge içermeyen numuneler) sonuçları verilmiştir. Görüldüğü üzere, bu deneydeki normal kısımların medyan geçirgenlik değeri (şekilde K_{bulk} şeklinde gösterilmiş), normal deneylerin sonuçlarıyla uyum içerisindedir.

Sunum sırasında, deneysel ve sayısal yöntemler ve eniyileştirme algoritması anlatılacak ve geçirgenlik haritasının yorumlanmasına odaklanılacaktır.

Anahtar Kelimeler

Sıvı Kompozit Kalıplama, geçirgenlik, malzeme karakterizasyonu

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OPTIMAL DESIGN OF COMPRESSED HYDROGEN STORAGE VESSELS USING MULTİ-OBJECTİVE GENETIC ALGORITHM

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Abstract

In this study, a 139-L (nominal working pressure; $P_{working}$=350 bar, L/D ratio=3.0) carbon fiber overwrapped pressure vessel (Type III) with geodesic dome ends was modeled and analyzed by using ANSYS Workbench with the ACP module. Netting analysis was used to estimate the thicknesses of the helical and hoop layers. The aluminum liner (thickness=7.5 mm) was wrapped by 39 carbon plies (16 helical and 23 hoop) and the total thickness of the vessel was 27.0 mm. The Von Mises stress criterion was used for the aluminum liner while the maximum stress failure criterion was used to predict the burst pressure of the vessel. The MOGA method (Multi-Objective Genetic Algorithm) was utilized to obtain the optimum helical angles to maximize the burst pressure of the pressure vessel.

Introduction

Whether for vehicular onboard or stationary storage, composite overwrapped pressure vessels (COPVs) have been considered as the most effective solution for high pressure storage of liquid and gaseous fluids. COPVs have been in use for decades and are currently used in many applications from giant solid rocket motor cases to tiny paint-ball gun pressure reservoirs. They are found most frequently in the applications where component weight is critical. Compared with metallic solutions, they offer significant weight reduction up to 75%, better corrosion and fatigue resistance and overall safety by utilizing the high strength and stiffness of composite materials. COPVs have been classified based on their construction; metallic liner hoop-wrapped with composite (Type II), metallic liner (generally made of aluminum) fully overwrapped with composite (Type III), polymer-lined composite vessel (Type IV) and linerless composite pressure vessel (Type-V). For many high-pressure applications -requiring cylinders operated at 350 bars or greater- carbon fiber reinforced Type III and Type IV vessels represent the most practical solution. In order to achieve widespread acceptance today, it is vital to have accurate and reliable knowledge about structural behavior of COPVs [1, 2].

COPVs are composed of a cylindrical portion and dome parts. The dome is the most critical section which strongly affects the overall COPV's performance. The reasons are as follows: (i) liner thickness changes in the dome section due to the deep drawing of aluminum, (ii) composite layup over this region is characterized by continuously changing angles in each ply, and (iii) the end zones of each layer may vary significantly, having different stiffening profiles [2]. Therefore, the dome section may have higher stress levels depending on the implemented design. The desired parameters for a good dome shape are higher burst pressure, internal volume and lower weight [3]. Optimum design of dome contours for pressure vessels has been studied by several researchers [4-6]. Geodesic shape is the most commonly applied profile for pressure vessels and considered to be the optimum deformed shape of the dome.

The finite element method has been the most effective numerical tool for modeling of pressure vessels. Li et al. [7] established the design model of the composite vessel using ANSYS-APDL (Ansys Parametric

Design Language) and VC++ language. Park et al. [8] determined the filament wound patterns using semi-geodesic path equations for an arbitrary surface, and established the finite element model of the composite vessel using ABAQUS software package. Son and Chang [9] investigated the stress distributions in the composite layers of a Type III hydrogen pressure vessel composed of a thin aluminum liner (5 mm) and a thick composite laminate (45 mm) by using three different modeling techniques. The authors showed that the full ply-based modeling technique was necessary to design of a Type III hydrogen pressure vessel and determine stress distributions in both the metal liner and the composite layers accurately. Liu and Zheng [10, 11] established parametric finite element model for the cylinder part using ANSYS finite element code. The optimal design attempts were also made to reach the minimum weight and highest strength under the constraint of safety coefficient which specified by the CGH2R Draft Revision 10 of European Union and the ISO/DIS 15869.2 as 2.35 and 2.25 respectively. Several algorithms have been used to optimize COPVs design (weight, strength, reliability, life time) by changing the winding angles and thickness. One of the most popular algorithms is the genetic algorithm. Messager et al. [12] developed a genetic algorithm-based optimization method to increase the buckling pressure of the composite vessel. Kim et al. [13] proposed an optimal design method of the composite vessel by combining the finite element analysis and the genetic algorithm. Liu et al. [14] proposed an adaptive genetic algorithm and an immune algorithm, respectively, to perform the optimal design of the composite vessel which aims to obtain the minimum weight under the constraints of safety coefficient and processing parameters. Liu et al. [15] published a comprehensive review on numerical simulation and optimal design for COPVs.

In this study, the design and analysis of a Type-III pressure vessel rated at 35 MPa were performed using ANSYS Workbench with the ANSYS Composite PrepPost (ACP) module. The Von Mises stress criterion was used for the aluminum liner while the maximum stress failure criterion used for the composite section of the vessel. The MOGA method (Multi-Objective Genetic Algorithm) was utilized to optimize helical winding angles to improve the burst pressure of the pressure vessel. This study aims to provide knowledge and better understanding of the finite element modeling of COPVs.

Design of Type-III composite pressure vessel

A cylindrical pressure vessel with geodesic dome ends under working pressure of 35 MPa with overall length of 1257.15 mm and inner radius (R_0) of 206 mm was considered in this study. L/D ratio was 3.05. End cap opening radius (r) was 85 mm (Figure 1).

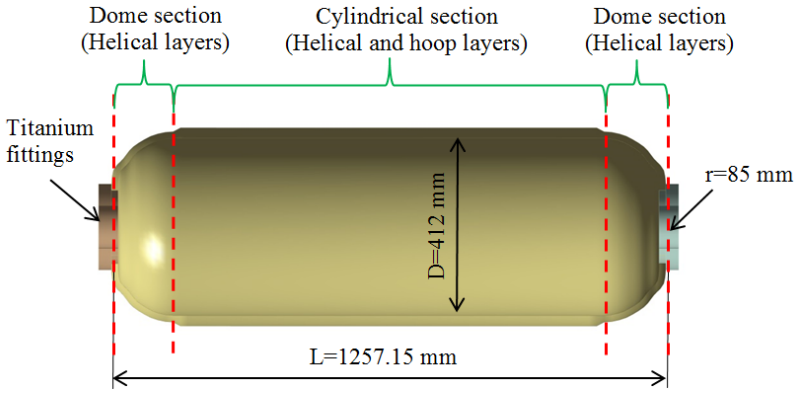


Figure 1. Cross-sectional view of composite pressure vessel

The helical winding angle (α_0) at the cylinder was calculated as 24.3° using Eq. (1);

$$\alpha_0 = \arcsin\left(\frac{r}{R_o}\right) \quad (1)$$

where r is the radius of the polar axis and R_0 denotes the inner radius of the vessel. The netting theory was used to calculate the thickness of each composite layer and the longitudinal in situ fiber strength. The strength value is inversely solved by the burst pressure of composite vessel. The thickness of helical plies $(t_{f,\alpha})$ was calculated using Eq. (2) [15]:

$$t_{f,\alpha} = \frac{R_0 P_i}{2\sigma_a \cos^2 \alpha_0} \tag{2}$$

where σ_a is in-situ fiber strength calculated by dividing maximum fiber tensile strength by factor of safety. P_i is the applied pressure. Factor of safety (F.S.) was taken as 2.35 as stated in the CGH2R Draft Revision 10 of European Union. The thickness of hoop plies $(t_{f,90})$ was calculated as follows [15]:

$$t_{f,90} = \frac{p_i R_0 (2 - \tan^2 \alpha_0)}{2\sigma_a} \tag{3}$$

The numbers of helical and hoop plies (n_α and n_{90}) was calculated by using Eq. (4):

$$n_\alpha = \frac{t_{f,\alpha}}{t_{ply,helical} V_f}, n_{90} = \frac{t_{f,90}}{t_{ply,hoop} V_f} \tag{4}$$

where V_f is the fiber volume fraction and assumed to be as 0.6. The ply thicknesses of helical ($t_{ply,\ helical}$) and hoop layer ($t_{ply,\ hoop}$) were considered as 0.5 mm. From the netting theory, number of helical and hoop plies were calculated as 16 and 23 respectively. The total thickness of the composite was 19.5 mm.

Finite element modeling

The vessel was composed of an aluminum liner (7075-T6) and a carbon/epoxy composite. The thickness of aluminum liner was 7.5 mm. The material properties used in the finite element analysis are listed in Table 1. The finite element model of the composite pressure vessel was created using ANSYS Workbench with ACP module. First step was to create 2D geometric model of the vessel. Then the material properties of the carbon/epoxy composite were entered. Second step involves meshing of 2D surface and the entering of the number of plies, the thickness and the orientation of each ply using ACP-module. As the last step, the 3D finite element models of the vessel and titanium fittings were created.

Table 1. Material properties of titanium, aluminum alloy (Al7075-T6) and carbon/epoxy composite.

Aluminum	**Value**	**Titanium**	**Value**
E	71.7 GPa	E	96 GPa
υ	0.33	υ	0.36
σ_{yield}	503 MPa	σ_{yield}	930 MPa
$\sigma_{ultimate}$	572 MPa	$\sigma_{ultimate}$	1070 MPa
Carbon/epoxy composite	**Value**		
E_1	121 GPa	X_t	2231 MPa
E_2, E_3	8.6 GPa	X_c	1082 MPa
G_{12}, G_{13}	4.7 GPa	Y_t	29 MPa
G_{23}	3.1 GPa	Y_c	100 MPa
υ_{12}, υ_{13}	0.27	S	60 MPa
υ_{23}	0.40		

Figure 2 shows the mesh structure of the vessel. In total, 137,260 solid layered elements with 211,743 nodes were used. The applied boundary and loading conditions are shown in Figure 3. Frictionless support was applied to the fittings' surfaces (translation in the x direction is fixed, all other free. An internal pressure of 35 MPa was applied to the inner surfaces of the vessel.

Design optimization of Type-III composite pressure vessel using genetic algorithm

Genetic Algorithm (GA), a category of stochastic search methods, can be defined as search algorithms, based on the mechanics of natural selection and genetics. Genes and chromosomes are the paramount elements in GAs. A chromosome is a strand of genes. In a real-case problem, genes are the variables that should be optimized, and a chromosome is a solution to the problem. Genetic Algorithms search for the optimal solution from populations of chromosomes. Multi-objective optimization deals with solving optimization problems which involve multiple objectives. Most real-world application and optimization problems involve multiple objectives and should be ideally formulated and solved as a multi-objective optimization problem. The processing steps of multi-objective genetic algorithm (MOGA) are shown in Figure 4.

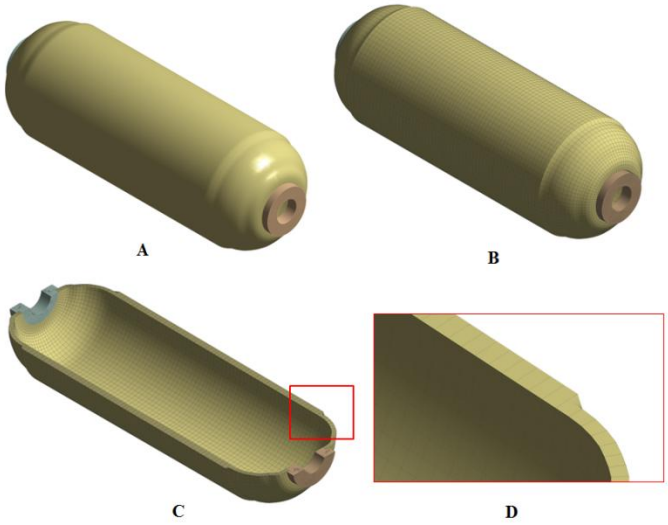


Figure 2. Modeling of the pressure vessel (a) geometric, (b) 3D finite element model, (c) mesh details and (d) the transition at the junction of geodesic domes.

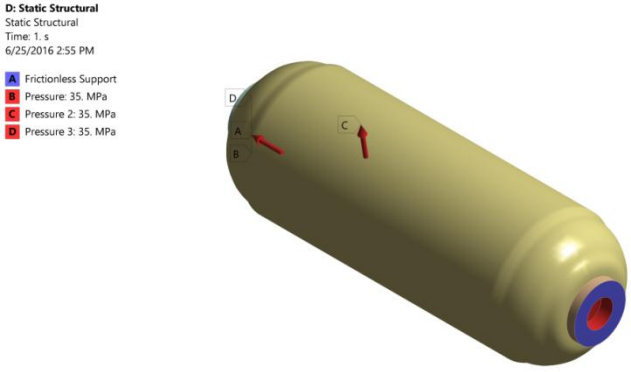


Figure 3. Boundary and loading conditions

The initial population is randomly created, and then fitness function evaluation, selection, crossover and mutation are performed. The elitism concept is introduced in order to obtain the best parents for children reproduction. When the criteria are not satisfied, the algorithm returns to initial population. And finally, the Pareto solutions are obtained. Table 2 shows the MOGA parameters used in this study. Once the static

structural analysis was done, the parameters were defined using ACP module. Then, Response Surface Optimization was initiated. The first step was to create a design of experiments (DOE). A Central Composite Design (CCD) based DOE was setup, which created 289 Design Points for the sixteen input design parameters. These 289 Design Points were then run automatically to generate output data at these points. A Mathematical formula was fitted to the data, which is called a "response surface". The parameters with significant influence on the outputs were determined from this formula, with which new response surfaces were created. The MOGA method (Multi-Objective Genetic Algorithm) was utilized to obtain the optimum filament winding angles ranges from ±10 to ±55. The objective was to minimize the delamination and fiber failure indices and keep them below 1/2.35=0.42 which satisfies the safety condition of the pressure vessel.

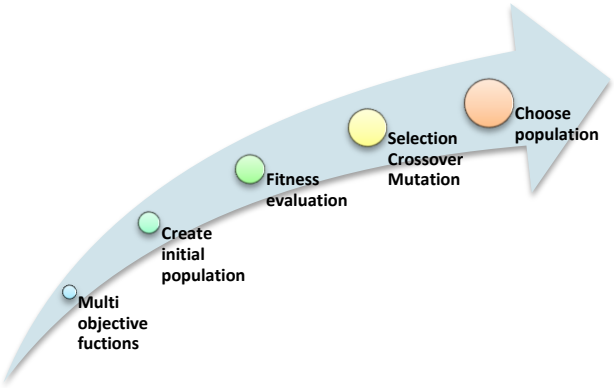


Figure 4. The processing steps of MOGA

The MOGA was done with an initial sampling size of 10000 samples, and with 100 samples per iteration. It converged after 11,286 evaluations and found 3 possible candidates that matched given objectives.

Table 2. MOGA parameters used in this study

Parameters	
Number of initial samples	10,000
Number of samples per iteration	100
Maximum allowable Pareto percentage	70
Converge stability percentage	2
Maximum number of iteration	50
Mutation probability	0.01
Crossover probability	0.98

Results and discussion

The deformation in the radial direction for the internal pressure of 35 MPa was found to be maximum in the transition region from the cylindrical part to dome section i.e. highlighted in red, and the minimum is found at the fixed position i.e. shown in blue color (Figure 5). This section can be considered as one of the critical section of the pressure vessel.

Figure 6 shows the equivalent Von-Mises stress distribution in the aluminum liner. The maximum Von-Mises stress was 367 MPa which was lower than the tensile yield strength of the aluminum. The maximum stress values was observed close to the openings of the vessel. This section of the aluminum was the most critical section in terms of liner's safety. Therefore, in real-life applications, the aluminum liner thickness is increased in these regions. In the cylindrical section of the liner, the maximum von-Mises stress was determined as 298 MPa. This value was less than the yield strength of the aluminum. Autofrettage process is applied to increase the pressure capacity of the vessel in real-life scenario. A little

plastic deformation is allowed for better performance. Autofrettage pressure for 35 MPa working pressure is about 52.5 MPa (generally 1.5 times of working pressure). The Von-Mises stress value was calculated as 550 MPa under autofrettage pressure. This value is little higher than the yield strength of the aluminum. It could be said that this pressure vessel would show very little plastic deformation.

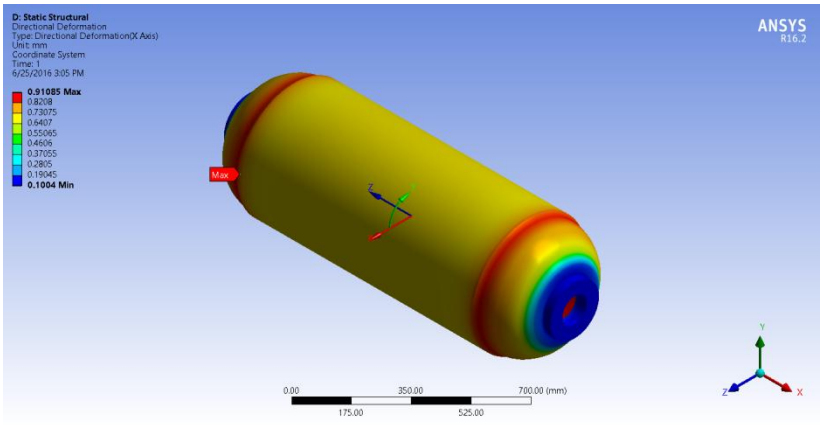


Figure 5. Radial deformation in the pressure vessel

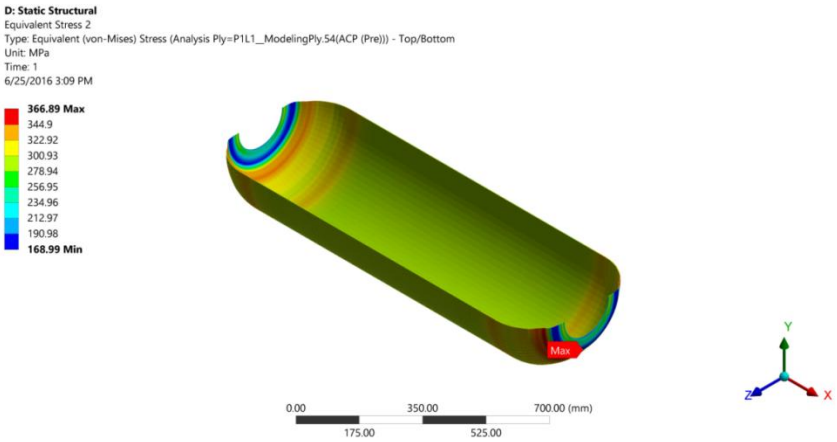


Figure 6. von-Mises stress distribution in the pressure vessel

In this study, a ply-by-ply modeling strategy was adopted to capture 3D stress state and failure in each ply. Stress distribution in the cylindrical section of the composite vessel is shown in Figure 7. As expected, the equivalent Von-Mises showed a decrease from the inner to outer surface of the vessel. It was also observed that the Von-Mises were almost remained constant through the liner thickness then started to decrease in the helical layers. The Von-Mises stress reached to its maximum value in the transition section where the hoop layers were introduced. The normal stress in the x-direction values (σ_x) decreased from the inner from the inner to outer surface of the vessel.

In the literature, different of failure criteria were used to study for predicting failure and its location in the pressure vessel. In this study, the maximum stress failure criterion was used to study how the winding angles affect the burst pressure of the composite pressure vessel. Figure 8 shows the maximum stress failure index contour plots for different failure modes. The red contour shows the possible failure locations where the failure index greater than 1.0. Matrix failure index value was the highest (e_{max}=1.4492). This means the pressure vessel may fail because of the crack propagation in the matrix

under repetitive pressurization. However, the fatigue is not the topic of this study. The delamination failure index was the second highest index calculated over the pressure vessel (e_{max}=0.4472). The maximum delamination index was obtained in the locations very close to the openings of the vessel. This is due to the higher stress concentrations in the dome section and the contact stresses between the pressure vessel and the fittings. The fiber failure possibility seemed to be lower than the delamination failure (failure index was about 0.21417). Therefore, delamination failure was considered as the dominant failure mode for the safety of the pressure vessel. The burst of the pressure vessel will occur close to the end openings due to delamination failure. The predicted burst pressure was estimated by dividing applied pressure by the maximum delamination failure index. The predicted burst pressure was calculated as 78.25 MPa.

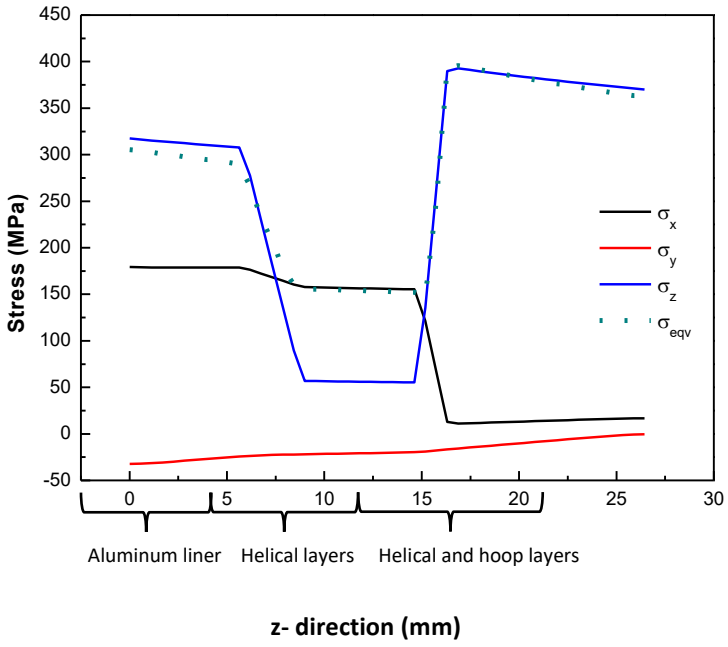


Figure 7. Stress distribution in the cylindrical section along the z-direction

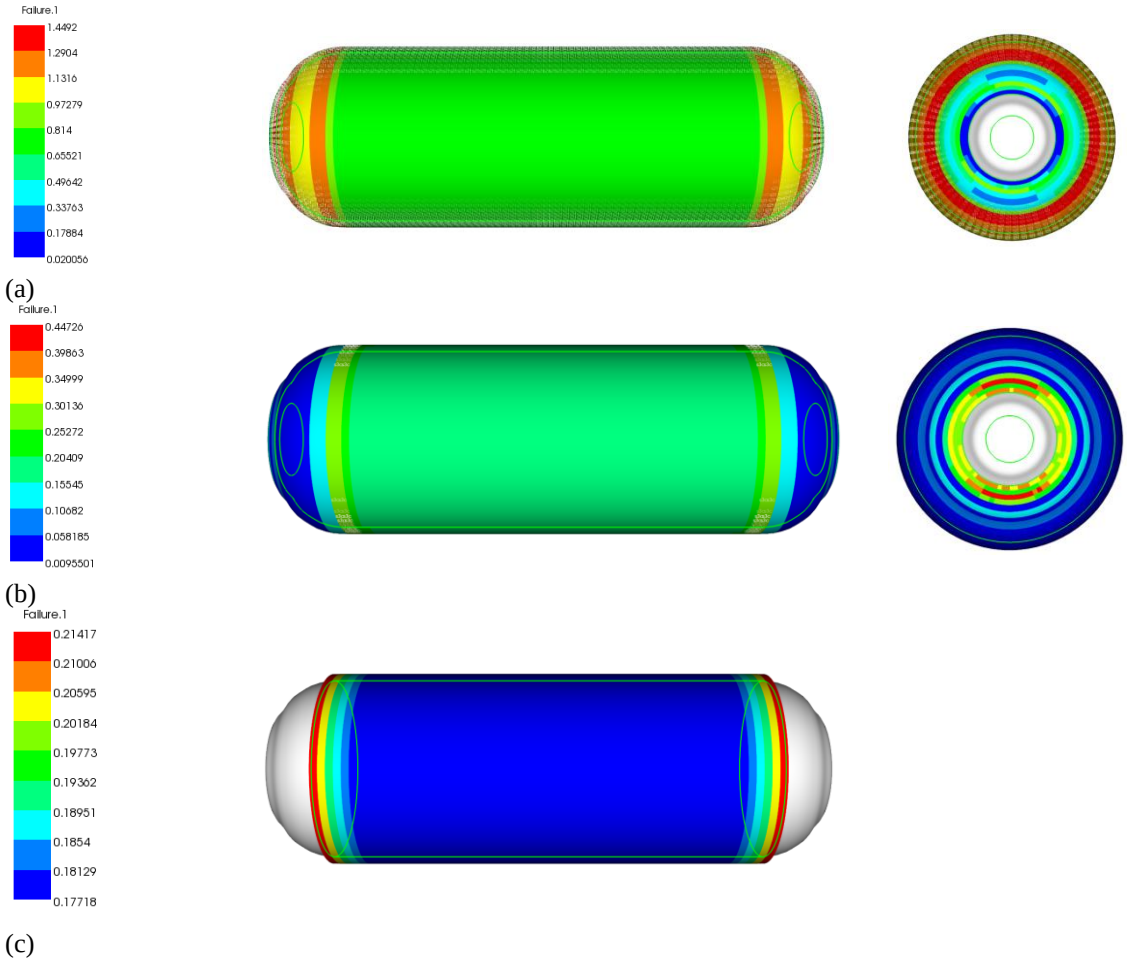
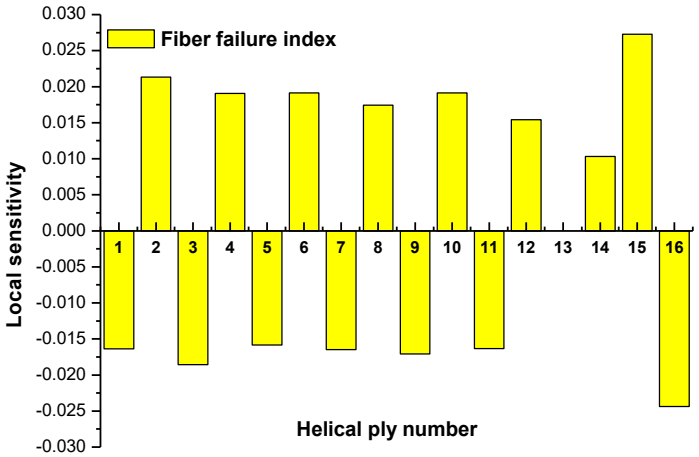
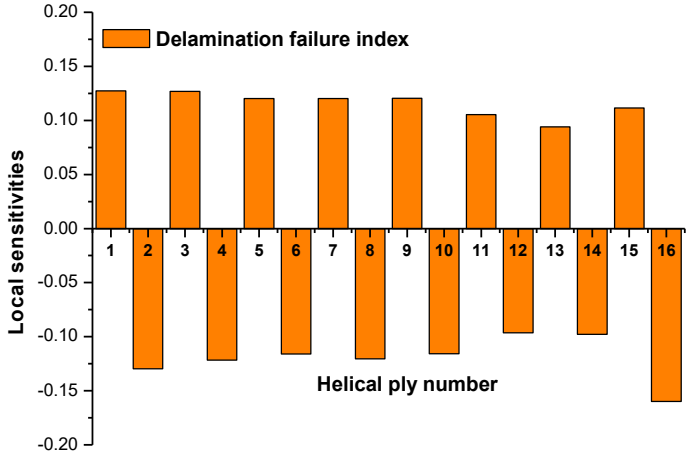


Figure 8. Failure index contour plots for different failure modes; (a) delamination, (b) matrix tension failure and (c) fiber failure.

The Min-Max Search determines the entire output parameter space from the Response Surface to approximate the minimum and maximum values of each output parameter. Table 3 shows the helical winding for minimizing the failure indices for different failure modes. Minimum fiber and delamination failure indices were found to be as 0.1966 and 0.3850; respectively. Figure 9 shows the local sensitivities among input and output parameters. As seen in the figure, the effects of helical winding angles on the delamination failure index were more pronounced than fiber failure index.



(a)



(b)

Figure 9. Local parameters sensitivities for (a) fiber failure and (b) delamination failure index

Tablo 4 shows the three candidate points that satisfy the following objectives; (i) minimize the delamination and fiber failure indices and (ii) keep them below 1/2.35=0.42. By using the winding angles defined in Candidate Point-1, the maximum delamination index was determined as 0.3901. The predicted burst pressure was calculated as 89.72 MPa. After optimization, the burst pressure of the pressure vessel was increased about 15%.

Table 3. Helical angles for minimum failure indices for different failure modes

Failure mode	**Helical ply number** *Helical angles (^{o})*								**Minimum value**
Fiber failure	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	0.1966
	10	-10	10	-55	10	-55	55	-55	
	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**	
	10	-10	10	-10	10	-10	10	-55	
Delamination	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	0.3850
	25.15	-22.65	24.88	-25.95	24.83	-28.80	25.74	-27.97	
	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**	
	26.07	-28.88	29.36	-32.11	32.32	-28.09	20.34	-17.30	

Table 4. Results from MOGA

Candidate points	**Helical ply number** *Helical angles (^{o})*								**Fiber failure index**	**Delamination failure index**
Candidate point-1	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	0.2111	0.3901
	26.07	-24.50	24.14	-27.66	24.47	-26.55	29.81	-25.67		
	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**		
	26.27	-31.98	30.74	-28.88	30.33	-34.39	20.22	-19.43		
Candidate point-2	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	0.21123	0.3908
	26.44	-24.51	24.01	-25.16	24.44	-27.21	29.93	-25.03		
	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**		
	26.99	-31.95	30.74	-28.84	30.33	-34.37	20.20	-23.77		
Candidate point-3	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	0.20987	0.39179
	26.88	-20.03	25.30	-23.95	27.71	-27.39	29.72	-24.54		
	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**		
	26.28	-30.21	28.65	-28.97	38.95	-34.23	20.49	-21.71		

Concluding remarks

In this study, design optimization of a Type-III composite pressure vessel was described. Netting analysis was used to estimate the thicknesses of the helical and hoop layers. The Von Mises stress criterion was used for the aluminum liner while the maximum stress failure criterion was used to predict the burst pressure of the vessel. MOGA method was utilized to optimize the helical winding angles to obtain maximum burst pressure. Through this optimization, the best combination of the helical winding angle was obtained to reach the maximum burst pressure. The results showed that MOGA method is robust and effective to optimize the winding angles for improving the structural safety of the composite pressure vessel.

Acknowledgments
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AZ91 MG ALAŞIMI ÜZERİNE YAPILAN HİDROKSİAPATİT/PEG KOMPOZİT KAPLAMALARA AĞIRLIKÇA YÜZDE PEG MİKTARININ ETKİSİ

INVESTIGATION INTO EFFECT OF WEIGHT PERCENTAGE OF PEG ON HYDROXYAPATITE/PEG COMPOSITE COATED ON AZ91 MG ALLOY

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ÖZET

Ti esaslı alaşımlar ve paslanmaz çelikler gibi metalik biyomalzemeler günümüzde sıkça kullanılmasına rağmen, yoğunluklarının çok yüksek olması nedeniyle doku-implant arayüzey uyuşmazlığı, gerilim bariyer etkisi yaratması gibi sınırlayıcı etkilere sahiptir. Literatürde yapılan çalışmalarda biyomalzeme olarak kullanıma uygun görülen AZ91 Mg alaşımı ise düşük yoğunluğu nedeni ile bu tür problemlere neden olmadığı bilinmektedir. AZ91 düşük yoğunluğa ve ağırlığa sahiptir ve kolayca şekillendirilebilir. Bütün bu avantajlarına rağmen AZ91 Mg alaşımı, vücut sıvıları ile temas halinde iken stabil kalamamakta ve korozyona uğramaktadır. Bu durum literatürde mevcut çalışmalarda çoğunlukla vücut içinde çözünen alaşımın yerini sağlıklı dokuya bırakması için kullanılmıştır. Korozyonun engellenmesi durumunda uzun süreli uygulamalarda kullanım için mükemmel bir potansiyele sahip olan bu alaşım çeşitli yüzey işlemleri ile geliştirilebilir. Bu çalışmada, bahsedilen üstünlükler sebebi ile altlık malzemesi olarak seçilen AZ91 magnezyum alaşımı üzerine, sol-jel yöntemi ile hidroksiapatit (HA) / polietilen glikol (PEG) kompozit kaplamalar yapılmıştır. Yapılan kaplamalar ile AZ91 Mg alaşımının vücut içinde çözünme hızının minimize edilmesi planlanmaktadır. AZ91 Mg alaşım tozları 325 °C sıcaklık ve 275 MPa basınçta preslenerek toz metalurji yöntemi ile üretilmiştir. Kaplamalar sol-jel metoduyla, ağırlıkça yüzde oranları değiştirilerek, hazırlanan HA/PEG çözeltilerine daldırılarak yapılmış ve daha sonra 300 °C' de sinterlenmiştir. Çözeltilerdeki PEG miktarının kaplama yüzey kalitesine ve sürekliliğine etkisi taramalı elektron mikroskobu (SEM) ve X-ışını kırınımı (XRD) kullanılarak incelenmiştir.

Anahtar kelimeler: Sol-jel metodu, Hidroksiapatit, PEG, AZ91 Mg alaşımı

ABSTRACT

Objective

Biomedical alloys which are used today such as Ti alloys and stainless steels have high density and fracture toughness. Moreover these alloys give stress-shielding effect because of their high fracture toughness compared with bone, and they require additional surgery most of the time. AZ91 Mg alloys do not cause of these problems. They have low density, lightness and easy procesability. But unfortunately, AZ91 Mg alloy is not stable in human body alone. AZ91 Mg alloy should be improved if it is used as a stable implant. These possible improvements are surface treatments, functional coatings and several reinforcements.

Hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$, HA) which forms inorganic structure of natural bone, usually is used for promote cell growth in biomedical applications. HA is logical coating for biomedical applications because of their biocompatibility and similarities to bone. However due to sol-gel method disadvantages, HA

layers are not adequate to totally protect corrosion alone. Crack-free coating is an essential property for this method. Thermal expansion mismatch between coating and substrate cause cracks when sintering process of coating layer. This work aims at a crack-free coating on surface. For this purpose, well known synthetic polymer Polyethylene Glycol (PEG) is used as reinforcement.

In this paper, AZ91 Mg alloy is coated with HA/PEG by sol-gel and dip coating method. Parameters are determined according to weight percentage of PEG. Surface morphology and coating thickness are analyzed by scanning electron microscope (SEM) and the phase structure is investigated by X-ray diffraction (XRD).

Material - Method

AZ91 Mg alloys powders were pressed with unidirectional hot press. Produced AZ91 Mg plates were cut, mechanically ground and clean. For HA solution preparation, calcium nitrate tetra hydrate ($Ca(NO_3)_2.4H_2O$) and di phosphorus penta oxide (P_2O_5) which provide Ca and P are used. They were solubilized in ethanol and mixed. For PEG solutions preparation, 0,05g, 0,1g and 0,2g PEG were solubilized in 10 ml distilled water different beakers. After that 10 ml HA solution was added into each one of PEG solution beaker Prepared AZ91 Mg alloy samples were dipped into solutions. Then they were pulled out at the same speed after keeping them in solution during 5 s. After first dip they were aged 3 h at room temperature and dried at 45˚C during 21 h. This cycle was applied 2 more times. After completion of coating they were sintered at 300˚C with 5˚C/min heating rate.

Pre Assessment

According to obtained datas, solutions did not cause formation of cracks on the surface of samples. Thicknesses of layers on the surface varies between 0,2 μm and 1 μm. However, according to EDS and XRD results, it is seen that the obtained layer is not HA. The layer formed on the surface could be the MgO layer. Probable reason the formation of this MgO layer is distilled water which used for preparing the solutions. HA precipitates on the surface of this formed layer were emerged. As a result, it was thought that the formed layer could not be sufficient to allow the AZ91 Mg alloy to remain stable in the human body.

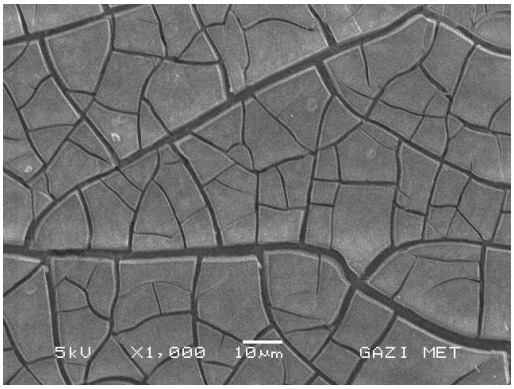
Keywords: Sol-Gel method, Hydroxyapatite, PEG, AZ91 Mg alloy

GİRİŞ VE AMAÇ

Mg alaşımları düşük yoğunluk ve özgül ağırlık değerlerinden dolayı ortopedik ve dental uygulamalar için kullanılmaya oldukça müsait alaşımlardır. Ağırlık ve yoğunluk değerlerinin düşük ve kemiğe yakın değerlerde olması biyomalzemeler için önemli bir kriterdir [1, 2]. Çünkü günümüzde kullanılan titanyum alaşımları ve paslanmaz çelikler gibi yüksek yoğunluklu, özgül ağırlıkları ve kırılma toklukları yüksek malzemeler, implante edildiği kemik dokusuna zarar verebilmekte, kemiğin aşınmasına veya vücudun tepki göstermesine neden olabilmektedir. Gerilim Bariyer Etkisi (GBE) olarak adlandırılan bu etki sonucunda hasar görmüş dokunun ek işlemler görmesi veya implantın çıkartılması gerekebilir [3]. AZ91 Mg alaşımı kemiğe yakın yoğunluk ve kırılma tokluğu değerlerine sahip olduğu için vücutta implant ve doku arasındaki bu uyuşmazlıktan kaynaklanan bir GBE yaratmaz [4]. Ayrıca biyouyumluluğu yüksek, vücutta toksik etki yaratmayan, üretimi kolay, maliyeti Ti alaşımlara kıyasla oldukça düşük olan bir biyomalzemedir [4]. Bütün bu avantajlarına rağmen AZ91, tek başına vücut içinde kullanıldığında stabil kalamamakta ve vücut sıvısının içinde korozyona uğrayarak çözünmektedir [5, 6]. Eğer AZ91 Mg alaşımı kalıcı implant uygulamalarında kullanılmak istenirse geliştirilmesi gerekmektedir. Bu alaşımın korozyon dayanımını arttırabilecek muhtemel işlemler çeşitli takviyeler, yüzey işlemleri ve fonksiyonel kaplamalardır [6–10].

Hidroksiapatit ($Ca_{10}(PO_4)_6OH_2$, HA) genellikle biyomedikal uygulamalarda hücre büyümesini teşvik etmek ve hücre tutunmasını kolaylaştırmak amacı ile kullanılan doğal kemik yapısının inorganik formudur. HA biyouyumluluğu ve kemik yapısına benzerliği sebebi ile implant ve protez uygulamalarında

hem tek başına hem de kaplama malzemesi olarak kullanılabilen nitelikli bir biyomalzemedir [6, 11–13]. Yazarlar tarafından daha önce AZ91 Mg alaşımı üzerine yapılan HA kaplamalarda karşılaşılan en büyük problem sol-jel yönteminin de dezavantajlarından olan kaplama tabakasında çatlak oluşumu problemidir [14]. Çözelti hazırlanırken kullanılması gereken çözücü kimyasallar, kurutma ve sinterleme işlemleri sırasında buharlaşmakta, altlık ve kaplama tabakası arasındaki ısıl genleşme farkının da etkisiyle kaplama tabakasının çatlamasına neden olmaktadır (Şekil 1) [6, 15]. Bu çatlaklar korozyona karşı sağlanacak olan dayanımı düşüreceği için çatlaksız kaplama elde edilmesi gerekmektedir. HA kaplama tabakasının tek başına yeterli olmadığı görülmüş ve çatlaksız kaplama eldesi için sentetik polimerlerden PEG, katkı malzemesi olarak seçilmiştir. Kullanılan PEG malzemesinin buradaki işlevi, HA'yı bir arada tutarak kaplamanın çatlaksız olmasını sağlamaktır. Kaplama yapılıp sinterleme aşamasına geçildiğinde PEG'in buharlaşarak sistemden uzaklaşması beklenmektedir [16, 17].



Şekil 1. AZ91 Mg alaşımı üzerine sol-jel ve daldırmalı kaplama yöntemi ile uygulanan HA kaplamanın SEM görüntüsü [14].

Bu çalışmada AZ91 Mg alaşımı sol-jel ve daldırmalı kaplama yöntemi kullanılarak HA/PEG ile kaplanmıştır. Çözeltiler hazırlanırken ağırlıkça yüzde PEG miktarı değiştirilmiş ve bu değişimin etkileri incelenmiştir. Yüzey morfolojisi incelemeleri için SEM cihazı ve faz yapı analizi için XRD cihazı kullanılmıştır.

MATERYAL VE METOT

AZ91 Mg alaşım tozları tek yönlü sıcak pres ile 275 MPa basınç ve 325 ˚C sıcaklıkta 1 saat preslenmiştir. Preslenen bulk numune hassas kesme cihazı kullanılarak 60 x 10 x 4 mm parçalara ayrılmış ve bu parçaların yüzeyi SiC zımpara kağıtları kullanılarak mekanik olarak zımparalanmıştır. Sonrasında numuneler sırasıyla 10 dakika ve 20 dakika sürelerde aseton ve etanol ile ultrasonik temizleyici ile temizlenmiştir.

HA solüsyonu hazırlanırken; Ca ve P öncüleri olarak seçilen kalsiyum nitrat tetra hidrat ($Ca(NO_3)_2.4H_2O$) ve di fosfor penta oksit (P_2O_5) kullanılmıştır. 35 ml etanol içinde stokiyometrik oranları molce 1,67:1 (Ca/P) olacak şekilde çözündürülmüş daha sonra Ca içeren solüsyon P içerikli solüsyon içine damlatılarak eklenmiştir. Solüsyon oda sıcaklığında manyetik karıştırıcı ile 5 saat düşük hızda karıştırılmıştır.

PEG solüsyonları hazırlığı için; 10 ml distile su bulunan farklı beherler içinde 5, 10 ve 20 g/L olacak şekilde PEG eklenerek ayrı ayrı 1 saat süre ile karıştırılmıştır. Daha sonra her bir PEG çözeltisi içine, 10 ml HA çözeltisi eklenmiş ve 0,5 saat daha karıştırılmıştır.

Hazırlanan AZ91 Mg alaşım numuneleri 200 mm/dk sabit hız ile çözelti içine daldırılıp 5 s çözelti içinde bekletilmiş daha sonra aynı sabit hız ile çözeltiden çıkartılmıştır. Numuneler 1 kat kaplandıktan sonra 3 saat oda sıcaklığında yaşlandırma ve 21 saat, 45 ˚C sıcaklıkta kurutma işlemi görmüştür. Her numune üzerindeki katman 3 kat olana kadar bu çevrim ilerletilmiştir. 3'er kat kaplanan ve kurutulan numuneler

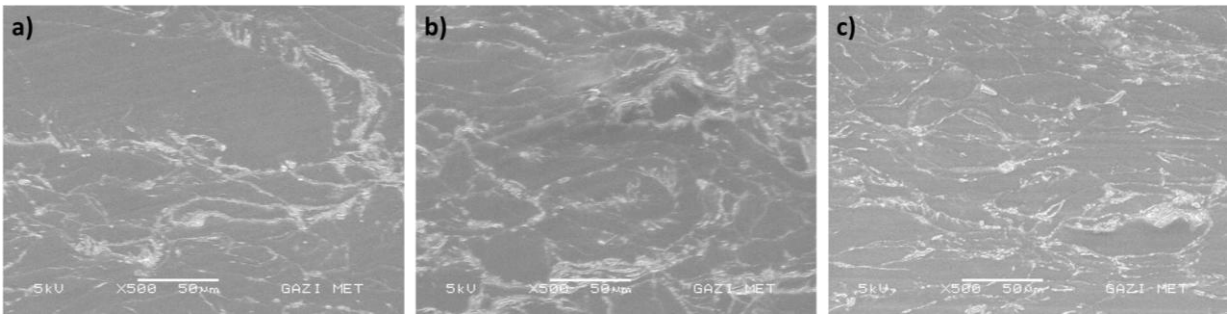
sinterleme işlemi için fırına konulup, ortam atmosferinde 5 ˚C/dk hız ile ısıtılan fırında 300 ℃ sıcaklıkta sinterlenmiştir.

Kaplama kalitesini ve yüzey topografisini gözlemlemek amacıyla JEOL JSM marka 6060LW, 0,5-30 kV ve 15X - 300.000X büyütme yapabilen SEM cihazı kullanılmıştır. Elementel analiz için EDS cihazı kullanılmıştır.

Hazırlanan numunelerin yapısal analizleri Bruker D8 Advance marka, Lynxeye dedektörlü XRD cihazı kullanılmıştır. Bakır hedefli X- ışını tüpü (1,5418 Å) kullanılarak 40 V voltaj ve 30 mA akım ile 2Θ değeri 8˚-92˚arasında ve adım aralığı 0.02 °/s olacak şekilde tarama yapılmıştır.

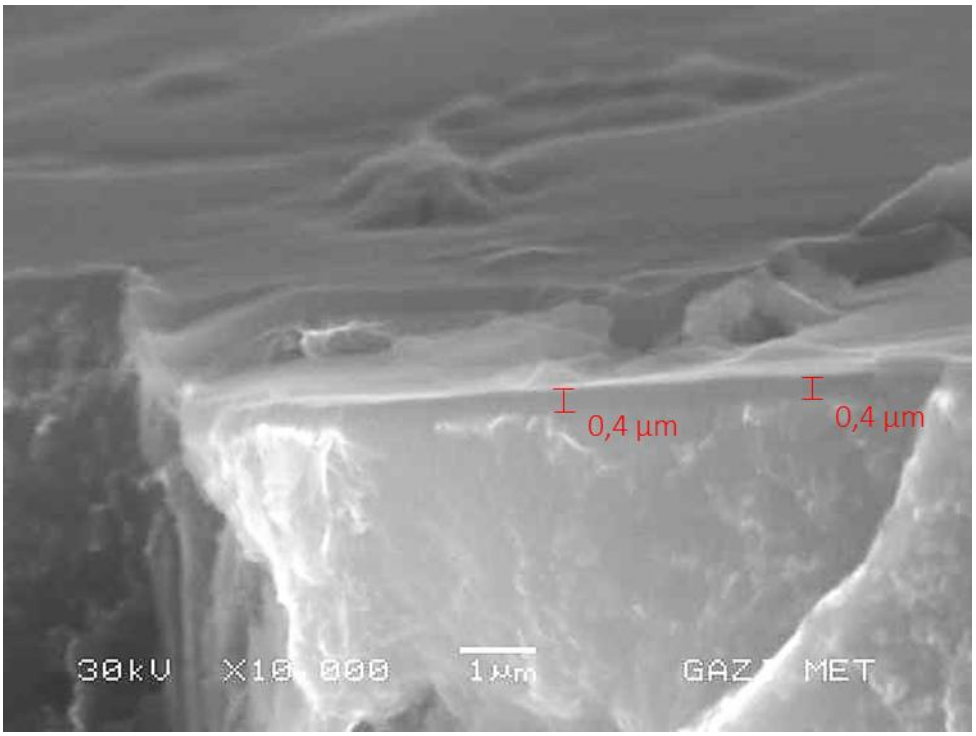
BULGULAR

AZ91 Mg alaşımı üzerine yapılan HA/PEG kompozit kaplamaların yüzey morfolojileri incelendiğinde, Şekil 1'de görülen çatlaklı kaplamanın, çözeltiye PEG eklenerek engellenmiş hali Şekil 2'de görülmektedir.



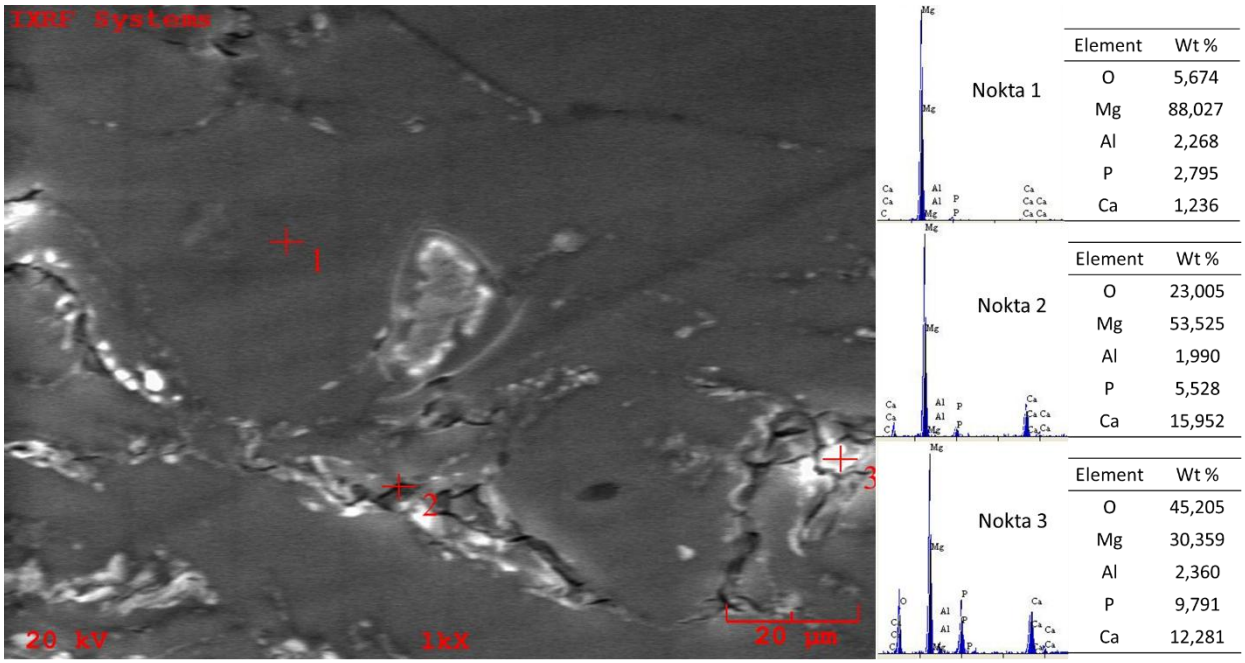
Şekil 2. AZ91 Mg alaşımı üzerine yapılan HA/PEG kompozit kaplamaların 500X büyütmede SEM görüntüleri a) 0,05 g/L PEG+HA, b) 0,1 g/L PEG+HA ve c) 0,2 g/L PEG+HA.

Elde edilen kaplamaların kırık yüzeylerinden alınan SEM görüntülerine göre (Şekil 3) kaplama kalınlıkları her numune için yaklaşık 0,4 µm olarak ölçülmüştür. Bu değer, daha önce aynı koşullarda PEG katkısı kullanılmadan yapılan HA kaplamaların kalınlıklarına göre (4-6 µm) bir hayli düşüktür. Çözeltiye eklenen PEG katkısının çatlakları giderdiği ancak kaplama kalınlığını azalttığı görülmüştür. Bu durumun, iki farklı çözeltinin (HA ve PEG) karıştırılması sonucunda nihai HA çözeltisinin normalden daha seyreltik olmasından kaynaklandığı düşünülmektedir.



Şekil 3. AZ91 Mg alaşımı üzerine yapılan HA/PEG kompozit kaplamaya ait kalınlık ölçümü.

Yapılan noktasal EDS analizleri incelendiğinde (Şekil 4), Nokta 1 ve benzeri bölgelerde yüksek miktarda Mg ve O elementlerine rastlanmıştır. Kaplama tabakasının çok ince oluşu altlık malzemenin de görülmesine neden olduğu düşünülmektedir. Nokta 2 ve Nokta 3'te HA öncüleri olan Ca ve P oranları Nokta 1'e göre daha fazladır. Bu bölgelerde çökelti halinde HA bulunduğu düşünülmektedir.



Element	Wt %
O	5,674
Mg	88,027
Al	2,268
P	2,795
Ca	1,236

Element	Wt %
O	23,005
Mg	53,525
Al	1,990
P	5,528
Ca	15,952

Element	Wt %
O	45,205
Mg	30,359
Al	2,360
P	9,791
Ca	12,281

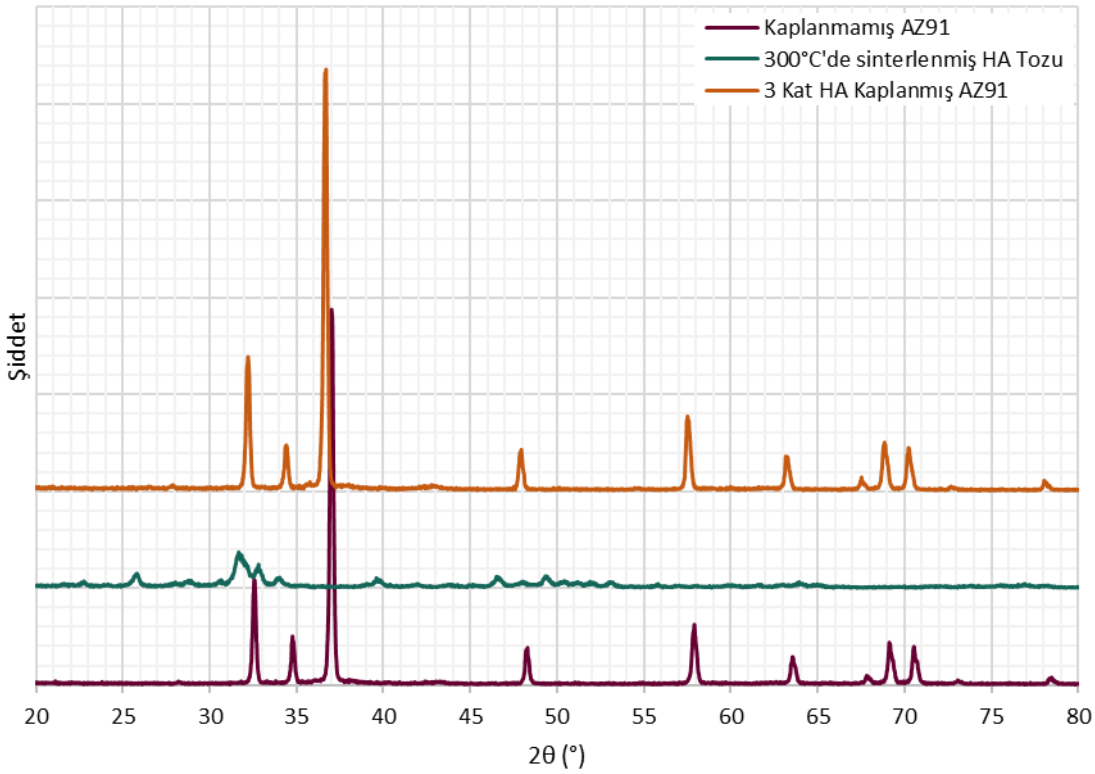
Şekil 4. AZ91 Mg alaşımı üzerine yapılan HA/PEG kompozit kaplamaya ait noktasal EDS analizleri.

Yapılan genel EDS analizleri sonucunda oluşturulan Tablo 1'de numunelerde bulunan O, Mg, Al, P ve Ca'nın ağırlıkça yüzde miktarları verilmiştir. PEG miktarı arttıkça yüzdece Mg ve O element miktarlarının azaldığı ve HA oluşumunda etkili P miktarının arttığı görülmüştür.

Tablo 1. AZ91 Mg alaşımı üzerine yapılan HA/PEG kompozit kaplamaya ait genel EDS analizi.

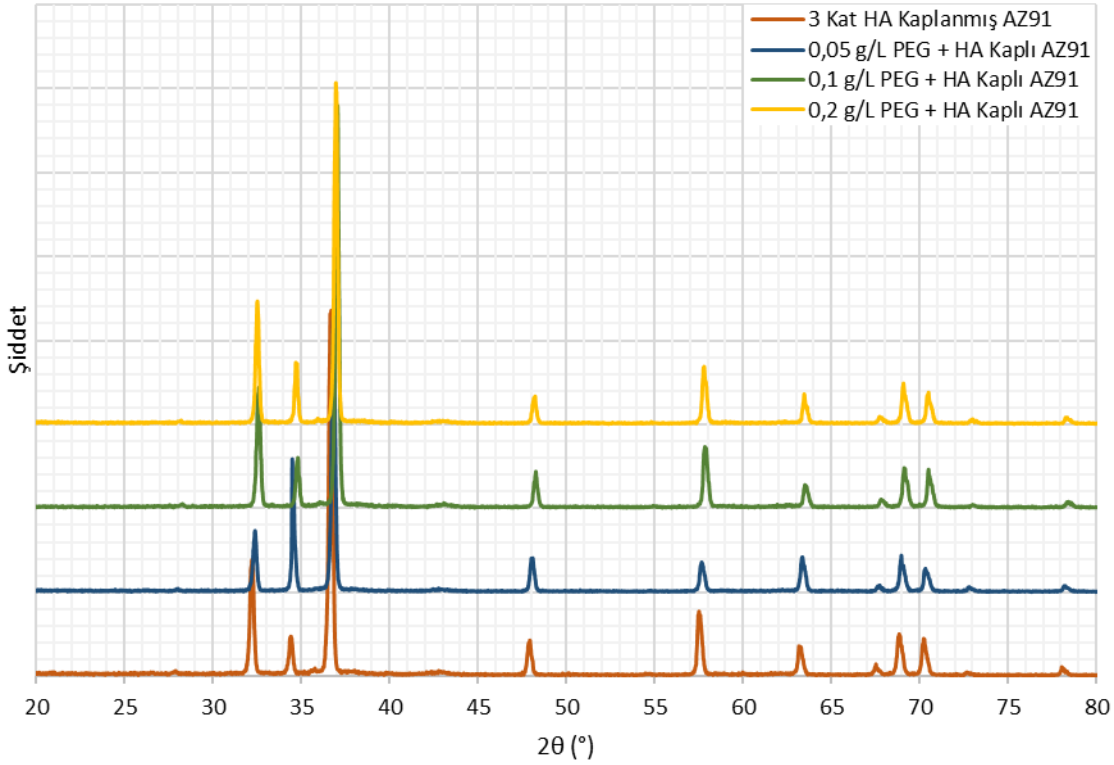
Element	Wt% (0,05 g/L PEG)	Wt% (0,1 g/L PEG)	Wt% (0,2 g/L PEG)
O	7,654	10,160	13,128
Mg	85,430	81,205	79,059
Al	2,194	3,458	2,926
P	2,364	3,047	3,267
Ca	2,357	2,131	1,619

Şekil 5'te Kaplanmamış AZ91 Mg alaşımı, 300 °C'de sinterlenerek üretilmiş HA tozu ve 3 kat HA kaplanmış AZ91'e ait XRD grafikleri verilmiştir. Kaplanmamış AZ91 Mg alaşım pikleri ICDD 00-001-1141 kart numaralı AZ91'e karşılık gelmektedir. 300 °C'de sinterlenmiş HA tozu incelendiğinde, piklerin literatürdeki ICDD 00-009-432 HA pikleri ile eşleştiği görülmektedir. AZ91 Mg alaşımı üzerine kaplanan HA'nın etkisi, kaplama tabakasının ince olması nedeni ile çok net görülememekle birlikte, kaplanmış numunenin pikleri için, 33°,35° ve 37°'deki piklerin kaymasına ve 33°' deki pikin şiddetinde artmaya neden olmuştur (Şekil 5).



Şekil 5. Kaplanmamış AZ91 Mg alaşımı, 300 °C'de sinterlenerek üretilmiş HA tozu ve 3 kat HA kaplanmış AZ91'e ait XRD grafikleri.

0,05, 0,1 ve 0,2 g/L'lik PEG + HA ile kaplanan AZ91 Mg alaşımlarına ait XRD grafikleri, sadece 3 kat HA kaplı AZ91 alaşımına ait XRD grafiği ile karşılaştırıldığında (Şekil 6), piklerde herhangi bir değişiklik olmadığı görülmektedir. PEG polimerik bir malzemedir ve sinterleme sıcaklığı olan 300 °C'de buharlaşması beklenmektedir. XRD piklerinde bir farklılık gözükmemesi ise bu buharlaşmanın gerçekleştiğini doğrulamaktadır.



Şekil 6. AZ91 Mg alaşımı üzerine yapılan HA/PEG kompozit kaplamaya ait XRD grafikleri.

SONUÇ VE TARTIŞMA

Çalışmada, hazırlanan çözeltiler, daldırmalı kaplama yöntemi ile AZ91 Mg alaşım numuneler üzerine kaplanmıştır. Yapılan incelemelerden elde edilen bulgulara göre; kurutma ve sinterleme sonucunda numune yüzeylerinde oluşan ve engellenmek istenen çatlaklara rastlanmamıştır. Çözeltiye eklenen PEG ile bu çatlaklar engellenebilmiştir ve yüzeydeki tabakanın kalınlığı yaklaşık 0,4 µm olarak ölçülmüştür. Hazırlanan çözelti kaplama kalınlığını inceltmiş ve yer yer HA çökeltilerinin oluşmasına neden olmuştur. XRD sonuçları incelendiğinde eklenen PEG miktarının piklerde herhangi bir değişim meydana getirmediği gözlemlenmiştir. PEG, beklenildiği gibi sinterleme sırasında buharlaşmıştır ve dolayısıyla farklı oranlarda çözeltiye eklenen PEG miktarının pik şiddetlerine bir etkisi olmamıştır.

Sonuç olarak oluşan tabakanın beklenenden ince olması sebebi ile biyomalzeme uygulamalarında AZ91 Mg alaşımının vücut içerisinde stabil kalmasını sağlamak için yeterli olmayacağı düşünülmektedir. Bu durumun sol jel prosesindeki jelleşme adımı süresinin uzatılması ile kaplama kalınlığının artırılarak çözülmesi planlanmaktadır. Üretilen malzemenin performansının daha iyi değerlendirilebilmesi için, sonraki çalışmada yapay vücut sıvısı içinde korozyon deneyleri yapılması planlanmaktadır.

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ENHANCEMENT OF PRODUCT PROPERTIES OF ORIGINAL AND WASTE POLYVINYL BUTYRAL (PVB) / POLYVINYL CHLORIDE (PVC) COMPOSITES WITH NANO-ADDITIVES

NANO-KATKI MADDELERİ İLE ORİJİNAL VE ATIK POLİVİNİL BUTİRAL (PVB) / POLİVİNİL KLORÜR (PVC) KOMPOZİTLERİNİN ÜRÜN ÖZELLİKLERİNİN GELİŞTİRİLMESİ

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ÖZET

Plastikleştirilmiş PVB ve plastikleştirilmiş PVC'den çeşitli konsantrasyonlarda Polivinil Butiral (B) / Polivinil klorür (P) kompozitlerinin hazırlanması ve karakterizasyonu üzerine çalışılmıştır. PVB'nin en önemli kullanım alanı güvenlik camları olup, geri dönüşüme giren güvenlik camından kazanılan PVB tekrar kullanılabilir ve PVC gibi benzer özellikteki polimerlerle harmanlanabilir. Polimerik kompozit filmleri hazırlamak için çift gidiş gelişli W50 ve sürtünme oranı 2:3 olan Brabender yoğurucu cihazı kullanılmıştır. Öncelikle, PVB/PVC kompozitlerde yer alan PVB'nin orijinal (OB) ve geri dönüştürülmüş (RB) kaynaklı olmasının etkisi araştırılmıştır. Daha sonra, bu kompozitlere, iki nano katkı maddesinin (Kil (C) ve Kalsit-$CaCO_3$ (K)) ve bunların değişen konsantrasyonlarının etkisi değerlendirilmiştir.

Üretilen filmlerin farklı uygulama alanlarında yeni bir ürün olarak değerlendirilebilmesi için kimyasal, mekanik ve termal özellikleri FTIR, Mekanik, XRD, DSC, TGA, Optik Mikroskop, SEM ve Renk Ölçümü cihazları ile karakterize edilmiştir. Fourier Dönüşümlü Kızılötesi (FTIR) analizi ile her kompozit film için beş farklı pozisyonda fonksiyonel gruplar belirlenmiştir. Kompozit filmler oldukça üniform yapıda olup yeni bir fonksiyonel grubun oluşumu gözlenmemiştir. Polimerik kompozit filmlere ağırlıkça %5 Kalsit (K) ilavesi, mekanik özellikler açısından, ağırlıkça % 5 kil (C) ilavesinden daha iyi sonuçlar vermiştir. Ancak, orijinal OB90_P10 ve geri dönüşümlü RB90_P10 kompozit filmlerine ağırlıkça % 0,1 kil eklenmesiyle, en yüksek gerilme mukavemeti ve kopmada uzama değerleri elde edilmiştir. Çünkü az miktarda kil ilavesi, kristallenme, kristal yapısı ve kristallenme kinetikleri üzerinde bir etkiye sahiptir, bu nedenle bu filmin, ticari olarak kullanılan PVC malzemelerden daha iyi gerilme mukavemetine sahip olduğu görülmektedir. Ayrıca, XRD Analizinden görüldüğü gibi ağırlıkça % 5 kil ilavesi, mekanik özelliklerin azalmasına neden olan kristallik derecesini düşürmüştür. DSC analizi ile orijinal PVB'nin camsı geçiş sıcaklığının (Tg) yaklaşık 18 °C olduğu ve geri dönüşümlü PVB'nin yaklaşık 22 °C olduğu belirlenmiştir. PVC'nin camsı geçiş sıcaklığı -26 °C civarında bulunmuştur. Camsı geçiş sıcaklığı, PVB'ye PVC eklenmesiyle daha düşük değer göstermemiş, polimerlerin kompozit yapısındaki özellik değişimleri nedeniyle yüksek değerler görülmüştür. Renk ölçüm testinden, polimerik kompozit filmlerin renkleri, ağırlıkça %0,1 ve %1 kil miktarı ilavesi ile değişmediği, fakat ağırlıkça %5 kil miktarı ilavesi ile sarılık değerinin arttığı gözlenmiştir. Filmlerde ağırlıkça %5 Kalsit ilavesi ile renk değişikliği gözlenmemiştir. Sonuç olarak, az miktarda kil içeren (%0,1) geri dönüştürülmüş PVB / PVC esaslı kompozit filmler orijinal PVC yerine önerilebilir. Bu çalışma, atık camın neden olduğu çevre sorunlarının

çözümüne yönelik bir girişim olup, elde edilen malzemeler döşeme, tutkal üretimi, inşaat mühendisliği gibi farklı uygulamalarda kullanılabilir.

Anahtar kelimeler: *polivinil butiral, güvenlik camı, geri dönüşüm, polivinil klorür, kompozit malzeme*

ABSTRACT

The aim of this study is the preparation and characterization of Polyvinyl Butyral (B)/Polyvinyl chloride (P) blends consisting of plasticized original and waste PVB and plasticized PVC at various concentrations. The common usage area of PVB is the safety glass and waste PVB obtained from recycled safety glass could be utilized again in blends with similar polymers such as PVC. The Brabender kneader device which is contained two blungers W50 and a friction ratio of 2:3 was used to prepare polymeric composite films. The properties of the original and recycled PVB, used as constituents of the blend was analyzed and compared. The contribution of two nano-additives (Clay (C) and $CaCO_3$ (K)) into the composites was evaluated. The obtained materials can be employed in diverse applications such as flooring, production of glue and in civil engineering. This study is an attempt to resolve environmental problems caused by the waste windshield.

In order to evaluate the films as a new product for other application areas, their chemical, mechanical, thermal properties have been characterized by using FTIR, Mechanical, XRD, DSC, TGA, Optical Microscopy, SEM and Color Measurement devices. The Fourier Transform InfraRed (FTIR) analysis has been used to determine the composite films functional groups on five different positions for each film. The composite films are uniform and no formation of a new functional group is observed. Although, in mechanical test results show that the addition of 5 wt% $CaCO_3$ (K) into polymeric composite films have given better results than addition of 5wt% clay, but 0.1% (wt/wt) clay (C) added original OB90_P10 and recycled RB90_P10 composite films showed the highest tensile strength and elongation at break values. Because, the addition of small amount of clay has an impact on the crystallization, crystal structure and crystallization kinetics, therefore, this film has better tensile strength than commercially used PVC materials. Clay addition of 5 wt% has decreased the degree of crystallinity and caused the mechanical properties decreased. The DSC analysis determined that a glass transition temperature (Tg) of original PVB was almost 18 °C and recycled PVB was around 22 °C. The glass transition temperature of PVC was around -26 °C which has a lower glass transition temperature than PVB. The addition of PVC into PVB polymeric composite films on glass transition temperature did not decrease but it was found to increase because the composite structure property change of the polymers. From the color measurement test, for 0.1 wt% and 1 wt% clay amount, the effect on the color is not really obvious but yellowness increased with addition of 5wt% clay amount. No color change was observed for the films with the addition of 5 wt% of $CaCO_3$. After thermal degradation, surface properties and color changes have been fully examined, only recycled or PVB/PVC with small amount of clay (0.1 wt%) based composite films can be recommended instead of original PVC. This study is an attempt to solve environmental problems caused by waste windshield, and the materials obtained can be used in different applications such as flooring, glue production, civil engineering.

Key words: *PVB, safety glass, recycling, PVC, clay, calcium carbonate*

1. INTRODUCTION

Increasing of raw material prices, environmental aspects and still growing landfill places have increased the need for plastic waste recycling. Polymer recycling is a way to reduce environmental problems caused by polymeric waste accumulation generated from day-to-day applications of polymer materials. The recycling of polymeric waste helps to conserve natural resources.

Polyvinyl butyral (PVB) is a resin usually used for applications that require strong binding, optical clarity, adhesion to many surfaces, toughness and flexibility. PVB resins are consumed in wood coatings, wash primers, structural adhesives, inks/dry toners and as a binder for ceramics and composite fibers. But, PVB is pioneer as the key ingredient for automotive safety glass interlayers. Therefore, the total amount of PVB sheet produced by automotive industry and civil engineering is estimated around 120 million kg per year in worldwide [1]. However, the indisputable advantage of PVB is that the interglassed PVB is not degraded. This is very important because PVB is not essentially exposed to UV radiation (up to 320 nm), mechanical stress, elevated temperature, oxygen and any corrosive damaging substances [2, 3]. Therefore, the interglassed PVB sheets should possess physical properties very similar to those of the extruded material before the lamination process.

Due to this knowledge, PVB may be used again, for example in blends with similar polymers such as poly(vinyl chloride) (PVC). PVB/PVC blends can be applied in applications in PVC industry like flooring, sheathing of wires, production of carpets, drainage, window profiles, waterproofing membrane and sheets, sewer pipes, automotive applications, adhesives and synthetic leather [4]. Other important information is that PVC and PVB are typical polymers which are plasticized in order to achieve high toughness. PVB and PVC systems have very similar macromolecules polarity, which is also the case for the plasticizers used. Due to the similar polarity, it is assumed that some blends of PVB and PVC could have good miscibility [5,6]. This study will have an impact on the re-use of wastes of PVB as the main component in blends with PVC for industry applications.

2. MATERIALS AND METHODS

Original PVB sheets were obtained from DuPont (USA) and under the trade name Butacite B5. The Original PVB sheet contains approx. 28% (w/w) of plasticizer triethylene glycol bis(2-ethylhexanoate) (labeled 3GO). The average molecular weight (MW) of PVB is 410 kg/mol and the PVB polydispersity is 4.0. Recycled PVB particles which were obtained from windshields were provided by Praktik group in Czech Republic. The particles of recycled PVB contain less than 0.03% (w/w) of impurities such as glass and sand etc.

PVC powder was supplied from Fatra in Czech Republic. A suspension type of PVC polymer which is Ongrovil S 5070 with K value 70 contains 38% of plasticizer diisononyl phthalate (DINP) in a ratio of 3:2 (w/w). Thermal stabilizer is also used (0.5% w/w to PVC) in the mixture. The material obtained is PVC powder with adsorbed additives. The molecular weight of PVC was estimated according to K value to be 75 kg/mol.

The following nano-additives were used: commercially organic modified montmorillonite (methyl, Tallow, bis-2-hydroxyethyl, quaternary ammonium) and Calcit-$CaCO_3$. Cloisite 30B

was supplied from Southern Clay Products. Inc. Particle size is between 2 and 13μm. Calcium Carbonate is namely micromilled calcite OMYA EXH 1sp which is obtained from Calplex and average particle size is 1.4μm.

2.1 Preparation of Polymeric Composite Films

Four different groups of polymeric composite films have been prepared. The first group with original PVB (OB) with the amount of PVC (P) has been increased from 10% to neat PVC is obtained. The second group has been prepared at the same compositions with recycled PVB (RB). The third group has the nano-clay (C) addition in PVB/PVC composites with the addition of clay as 0.1, 1, and 5 wt%. The same compositions of composites have also been prepared using Recycled PVB. The forth group includes 5 wt% calcite (K) additions. Finally, forty-two polymeric composite films have been obtained including OB, RB, P, C and K

The Brabender kneader device which is contained two blungers W50 and a friction ratio of 2:3 was used to prepare polymeric composite films. A constant amount of 40g input materials (PVB/PVC/Nano-additives) were placed in the chamber and processed for 10 minutes at 160 °C with a rotation speed of 25 rpm. The blends which are in the form of pellets were placed between two PET sheets preventing the contact with air and thus oxidative degradation. After that, they were placed in a table press and hold them at 160 °C for 5 min. Lastly, polymeric composite films were cooled in a cold press. Steps of polymeric composite film preparation can be seen in **Figure 1.0.**

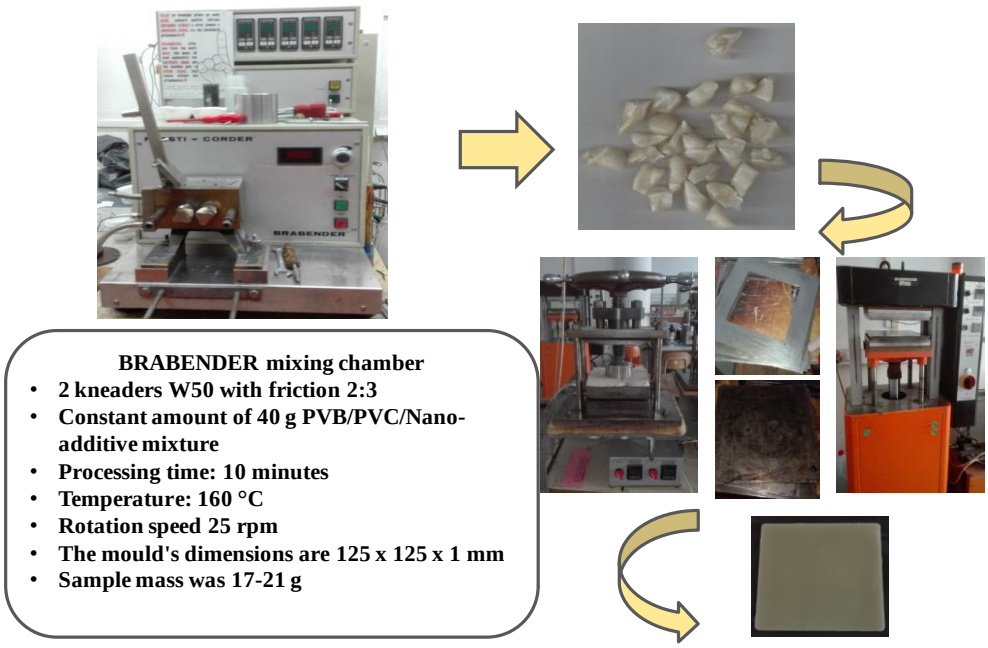


Figure 1.0 Experimental procedure of original and recycled PVB polymeric composite films with PVC, Clay and Calcium Carbonate addition

2.2 Experiments and Measurements

In order to evaluate the films as a new product for other application areas, their chemical, mechanical, thermal properties have been characterized by using following test methods:

- Fourier Transform Infrared Spectroscopy (FT-IR) (Thermo Nicolet Avatar FTIR model 320) analysis was used to specify functional groups.
- The mechanical properties of the samples prepared were determined by Galdabini Quasar 25 with a 2 stages displacement rate. The 1st stage had speed configuration of 1 mm/min up to strain of 600 µm while the 2nd stage had a speed configuration of 100 mm/min till the sample was broken. The measurement was carried out at room temperature at 23 °C.
- XRD, PANalytical X´Pert PRO diffractometer with a Cu tube source (λ = 0.1540 nm) operated at 1.2 kW was used to determine the degree of crystallinity of produced composite films.
- DSC (1 STARe System METTLER TOLEDO) was used to determine glass transition temperatures.
- Thermal degradation behavior of composite films is analyzed from TGA (TA TGA-SDT Q600) thermograms.
- Optical Microscopy (Leica DFC 295) was used to observe the crystallinity and surface structure.
- SEM (Carl Zeiss 300VP) was used to determine the surface morphology.
- Spectrophotometer CM 2600d Konica Minolta was used to determine L, a, b values of films.

3.RESULTS AND DISCUSSION

Polymeric composites have been characterized by FT-IR, Mechanical, XRD, DSC and TGA analyses and they are given below under subsections.

3.1 FT-IR Analysis

The Fourier Transform InfraRed (FT-IR) analysis has been used to determine the composite films functional groups on five different positions for each film. The composite films are uniform and no formation of a new functional group is observed as shown **Figure 2.0.**

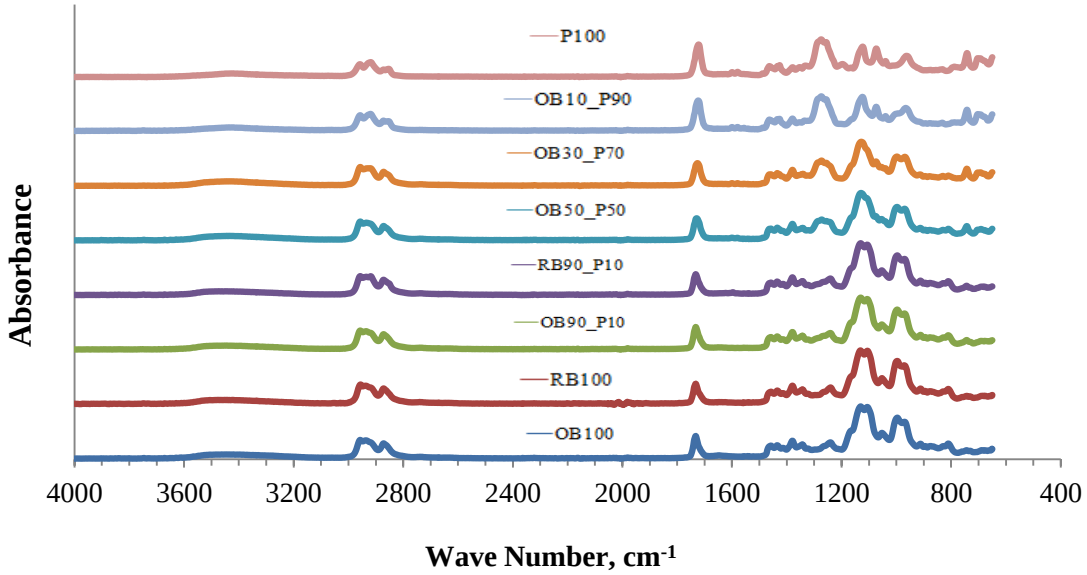


Figure 2.0 FT-IR spectra of selected samples

3.2 Mechanical Results

The mechanical results can be seen in **Figure 3.0**. Although, the addition of 5 wt% $CaCO_3$ (K) into polymeric composite films have given better results than addition of 5wt% clay, 0.1% (wt/wt) clay (C) added original OB90_P10 and recycled RB90_P10 composite films showed the highest tensile strength and elongation at break values. Because, the addition of small amount of clay has an impact on the crystallization, crystal structure and crystallization kinetics, therefore, this film has better tensile strength than commercially used PVC materials.

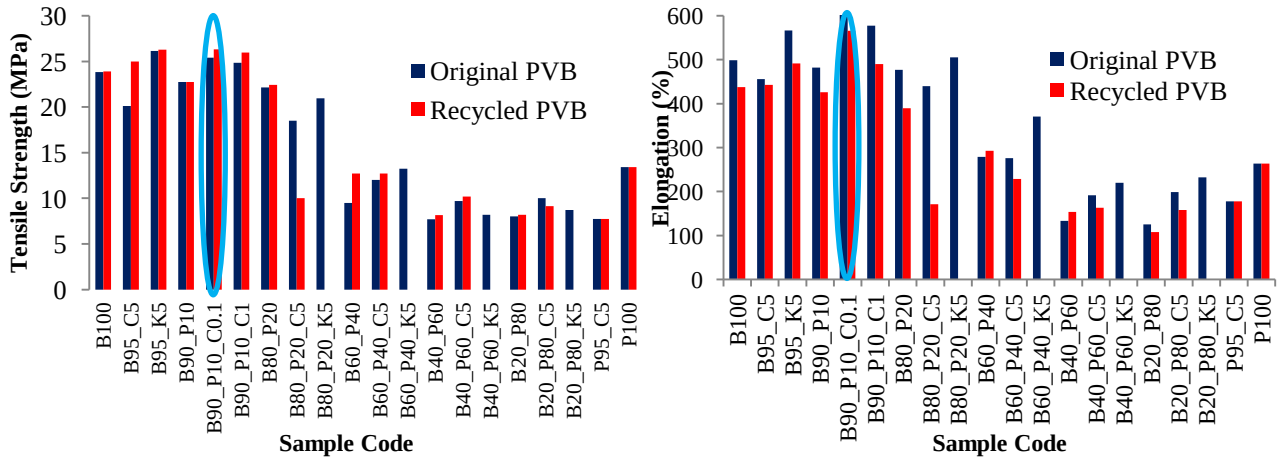


Figure 3.0 Comparison of mechanical results of original and recycled PVB in blend with PVC Calcite and Clay.

3.3 XRD Analysis

Crystal structures of all original and recycled PVB composite films in blend with PVC, Clay and Calcite obtained are identified by XRD analysis. In **Figure 4.0**, the XRD analysis of neat polymeric films, nano-clay (Closite 30B) and polymeric composite films can be seen. Clay has a peak around 2θ degrees at 4.7. This peak of clay has disappeared in the polymeric composite films, because clay has fully exfoliated in the structure.

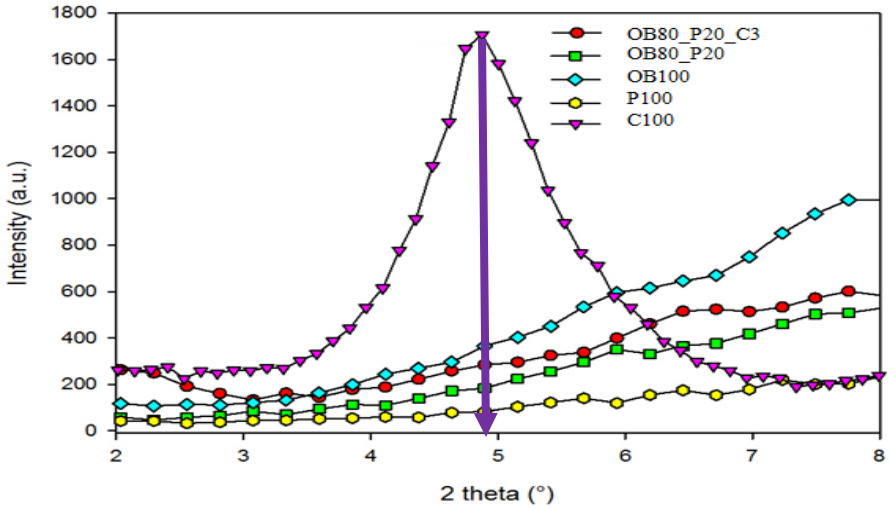


Figure 4.0 XRD pattern of neat clay, PVB, PVC and composite films

Figure 5.0 shows the maximum peak observed at 2θ degrees of 20 for all composite films which is the characteristic peak of both PVB and PVC. Clay addition of 5 wt% has decreased the degree of crystallinity that can be seen from XRD analysis and caused the mechanical properties decreased (Figure 3.0). It can also be seen in Figure 5.0 that calcite added polymeric composite has chracteristic peaks of calcium carbonate.

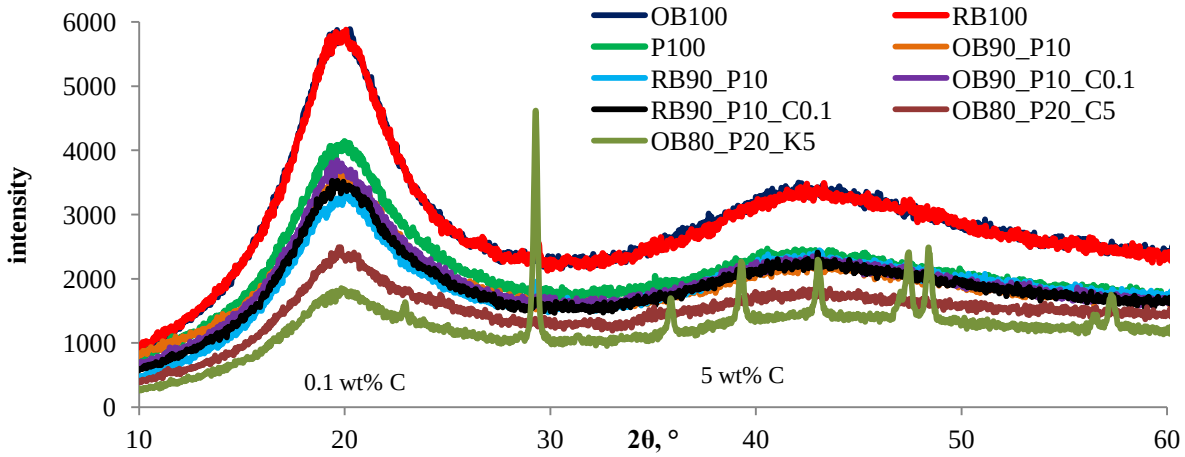


Figure 5.0 XRD profiles of original and recycled PVB with PVC, Clay and Calcite addition

3.4 DSC Analysis

The DSC analysis determined that the glass transition temperature (Tg) of original PVB was almost 18 °C and recycled PVB was around 22 °C as increased (Table 1.0). The glass transition temperature of PVC was around -26 °C which has a lower glass transition temperature than PVB. The addition of PVC into PVB polymeric composite films of glass transition temperature, actually expected that it should be shown lower value but it was found in increased value because the changing properties of polymeric composite structure.

Table 1.0 Results of DSC analysis for original and recycled PVB/PVC composite films

	Original PVB			Recycled PVB		
Sample Name	**Weight, mg**	**T_{Onset},°C**	**Tg, °C**	**Weight, mg**	**T_{Onset},°C**	**Tg, °C**
B100	6.97	5.73	17.77	6.95	9.28	22.75
B80_P20	7.67	7.67	18.06	7.78	29.99	38.44
B50_P50	6.73	18.18	26.76	7.47	20.03	28.93
B20_P80	6.73	30.04	34.19	7.46	13.29	25.21
P100	6.36	-44.50	-25.69	6.36	-54.05	-25.84

3.5 TGA Analysis

Thermal degradation behavior of polymeric composite films is analyzed by TGA thermograms which are given in Figures 6.0. The thermal decomposition was carried out under nitrogen atmosphere from 30°C to 1200°C at a heating rate of 10°C/min but PVB and PVC are completely thermally decomposed (in nitrogen) before 600°C. Remaining weight % of original PVB (OB100) and recycled PVB (RB100) were found as 1.30 % and 3.16 at 600 °C. Remaining weight % of PVC (P100) was found 12.16 % at 600°C. The amounts of ash % values at 600 °C are given in Figure 7.0.

Weight loss of PVB occurs in two distinct regions between 200–300 and 300–500 °C and corresponding to about 20 and 80% mass loss. The PVB was primarily losing plasticizer in the temperature volatilization process between 200-300 °C. The major products of the decomposition above 300 °C were initially butyraldehyde and butenal produced by the elimination of butyral groups followed by acetic acid above 380 °C from the elimination of acetate groups. The thermal degradation of PVC occurs through two degradation steps between 230-330 °C and 330-500 °C. The temperatures at the maximum weight losses of PVC were observed at 330 and 500 °C. The first step corresponds to the weight loss caused by the dehydrochlorination of PVC, while the second step presents the total weight loss resulted from the degradation of the dehydrochlorinated residuals. As can be seen from Figure 6.0 that the thermal stabilities of the original and recycled PVB films are better than the composite films with PVC, clay and calcium carbonate additions. The addition of PVB into PVC has improved the thermal stability of plasticized PVC.

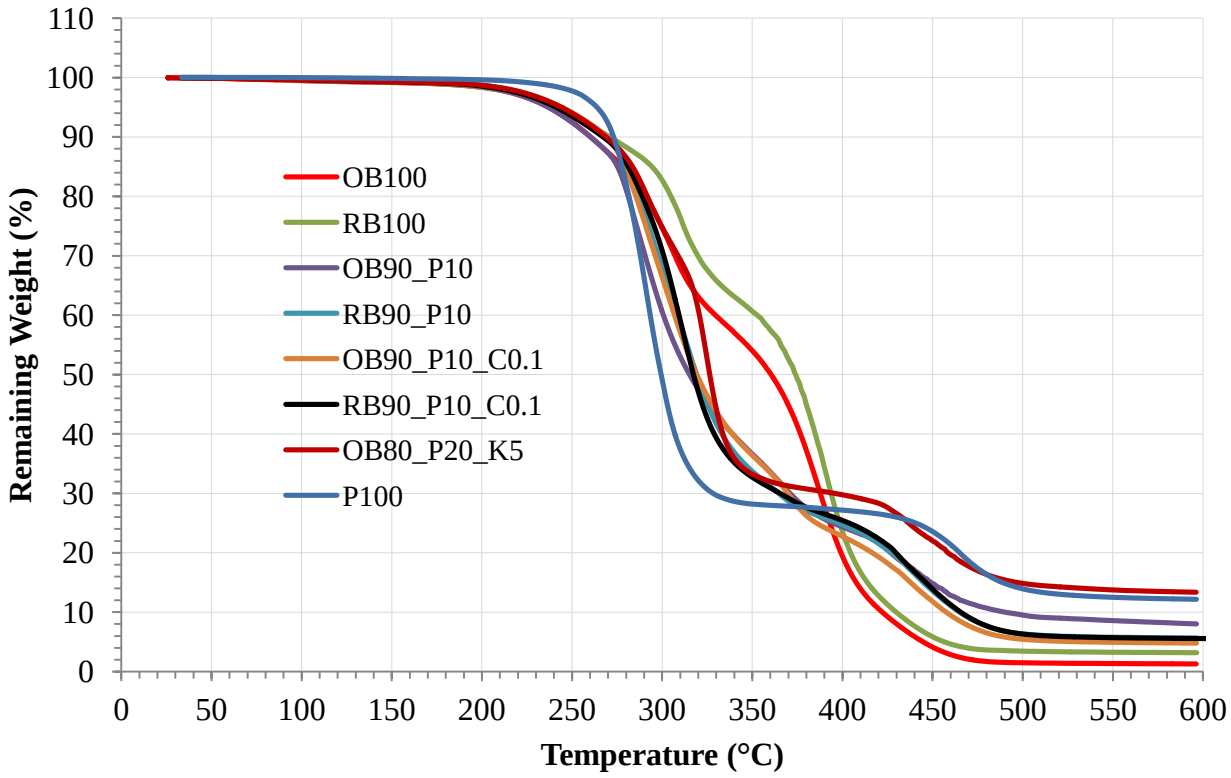


Figure 6.0 Thermograms of selected polymeric composite films

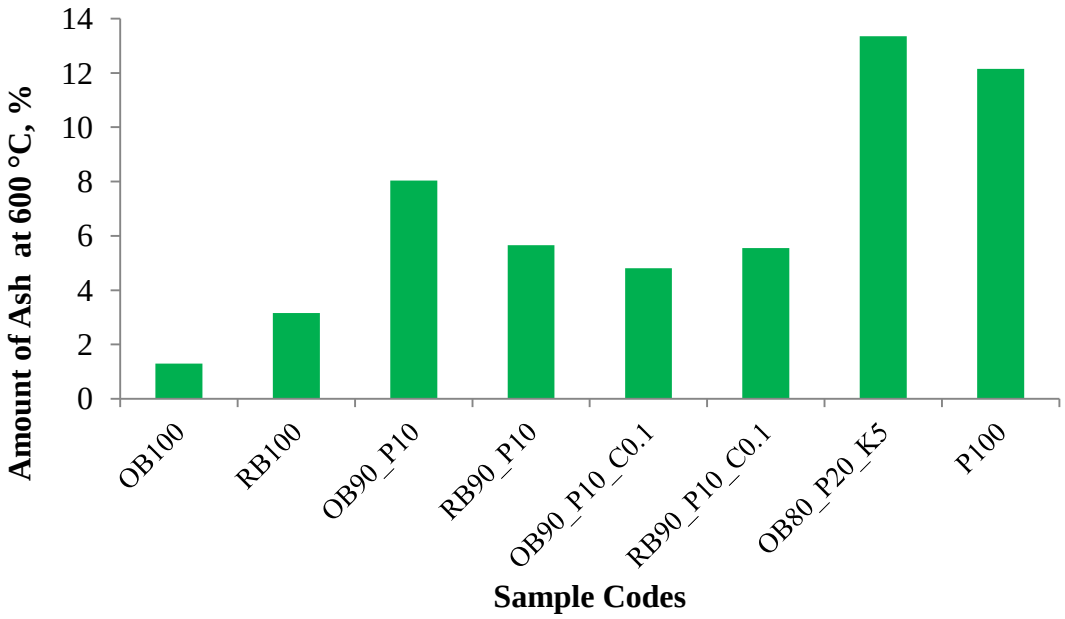


Figure 7.0 The amount of ash % at 600 °C

4. CONCLUSION

In conclusion, investigating the possibility of new applications of recycled PVB will help to solve a major environmental problem and decrease the price of traditional PVB and PVC as obtained good product properties of polymeric composite films:

- The recycled inter-glassed PVB sheets possess physical properties very similar to those of the original extruded material.
- It can be mentioned that as 0.1% (wt/wt) Clay added OB90_P10 and RB90_P10 composite films showed the highest tensile strength and highest elongation at break as well compare to the other additive and amounts based composites. It has obtained that the recycled PVB composite film has good tensile strength than commercially used PVC materials.
- Additions of 5 wt% $CaCO_3$ into polymeric composite films have given better mechanical results than addition of 5wt% clay.
- From the color measurement test, for 0.1 wt% and 1 wt% clay amount, the effect on the color is not really obvious but yellowness increased with addition of 5wt% clay amount. No color change was observed for the films with the addition of 5 wt% of $CaCO_3$.
- Addition of 0.1% clay has decreased the degree of crystallinity of the composite films but it has given very good mechanical properties.
- The thermal stabilities of the original and recycled PVB films are better than the composite films with PVC, clay and calcium carbonate additions. The addition of PVB into PVC has improved the thermal stability of plasticized PVC.

- Consequently, recycled PVB/PVC/Clay based composites film can be recommended as a new material instead of PVC.

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POLİMER ESASLI KOMPOZİTLERDEN KALIP YAPIMI VE ÜRÜN TASARIMINA UYGULANMASI

MOLDING FROM POLYMER-BASED COMPOSITES AND ITS APPLICATION TO PRODUCT DESIGN

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Özet

Bu çalışmada SolidWorks programında hazırlanan ayna gövdesi tasarımı Pepakura Designer isimli program kullanılarak, tekrar en küçük birime indirgenmiş ve 2D hale getirilmiştir. 2D üretim resmine dönüştürülen tasarım 1,6 mm kalınlığındaki mukavvaya çıktı alınmış ve solvent bazlı yapıştırıcı ile birleştirilerek model haline getirilmiştir. Elle yatırma yöntemiyle, mukavva model yardımıyla % 40 cam elyaf ve polyester reçine malzeme kullanılarak döküm kalıbı oluşturulmuştur. Kalıp yüzeylerine kalıp ayrıştırıcı uygulanmış olan döküm kalıbına, mermer tozu/polyester kütlece 3 oranında olacak şekilde karıştırılarak eklenmiştir. Karışıma % 0,1 oranında hızlandırıcı (kobalt tuzu) ve sertleştirici (%30 oranında seyreltilmiş metil etil keton peroksit) ilave edilmiştir. Kuruma sonrası parçalar kalıptan çıkartılmış, tasarlanan ayna için gerekli olan tekrar sayısına ulaşılıncaya kadar işlem tekrar edilmiştir. Tüm parçaların döküm işlemi bittikten sonra parçalar, yapıştırıcı kullanılarak polimerlerin yapıştırılmasında kullanılan yüzey hazırlama vb. işlemlere uygun olacak şekilde birleştirilmiştir. 24 saat süreyle kurumaya bırakılan ayna gövdesi sonrasında renklendirme işlemine tabi tutulmuştur. Hazırlanan kalıpla işlemlerin tekrarlanabilir olduğu ve Bilgisayar destekli tasarım programlarıyla hazırlanan ve %40 cam elyaf ve polyester reçineden üretilen kalıpların kullanılabilir olduğu görülmüştür. Gelecekte seri üretimi olmayan ya da prototipi yapılacak ürünler için bu tür kalıplama uygulamalarının ve tasarım programlarının yoğun bir şekilde kullanılacağı düşünülmektedir.

Anahtar Kelimeler: Bilgisayar destekli tasarım (CAD), polimer kompozitler, cam elyaf, kalıp tasarımı, ürün tasarımı

Abstract

In this study, the mirror stem design prepared in SolidWorks program was reduced to the smallest unit once again by using the program named Pepakura Designer and it was made 2D. The design converted into a 2D production drawing was printed on cardboard 1.6 mm in thickness and it was made a model by joining by the solvent-based adhesive. With the hand lay-up method, a casting mold was created by using 40% fiberglass and polyester resin material with the help of a cardboard model. Marble powder/polyester were mixed in a way that they would be at 3-ratio by mass and were added to the casting mold to the mold surface of which a mold release agent was applied. Accelerator at the rate of 0.1 % (cobalt salt) and hardener (diluted methyl ethyl ketone peroxide at the rate of 30%) were added to the mixture. After drying, the pieces were taken out of the mold, the procedure was repeated until the repetition number necessary for the designed mirror was achieved. After the casting process of all pieces had been completed, the pieces were joined by using an adhesive in a way which would be suitable for the surface preparation and similar processes employed in the adhesion of polymers. The mirror stem put for drying

for 24 hours was later subjected to the coloring process. It was observed that the processes were repeatable in the mold prepared and the molds prepared by computer-aided design programs and produced from 40 % fiberglass and polyester resin were usable. It is considered that this type of molding applications and design programs will be intensively used in the future for products without mass production or for products the prototype of which will be created

Key Words: Computer Aided Design (CAD), polymer composite, fiberglass, mould design, product design

1. Giriş

Tasarım, S. Hilav tarafından, "-Zihinde canlandırılan biçim, tasavvur." olarak ifade edilmiştir [1]. 554 sayılı Endüstriyel Tasarımların Korunması hakkındaki kanun hükmündeki kararnamede tasarım, bir ürünün tümü veya benzeri bir parçası üzerinde süslemenin çizgi, şekil, biçim, renk, doku, malzeme veya esneklik gibi insan duyuları ile algılanan çeşitli unsur veya özelliklerinin oluşturduğu bütün şeklinde tanımlanmıştır [2]. Tasarım ile mevcut teknolojiler ya da yeni geliştirilen teknolojiler kullanılarak mamul ya da yarı mamul şeklinde, ürünler üretilir. Genel anlamda tasarım, tüketicinin ihtiyaç duyduğu özellikleri bünyesinde barındıran ve tüketicinin beğenisini kazanacak bir biçimde çizimlerin yapılması ile başlayan bir süreçtir [3]. Mevcut tanımlardan yola çıkarak tasarımı "Bir ürünü zihinde canlandırma (tasavvur etme), mühendislik çizimleri ve iş akış sürecine bağlı olarak üretilebilecek şekilde oluşturma ve geliştirme faaliyetleri olarak tanımlayabiliriz.Günümüzde tasarımlarda, Bilgisayar Destekli (CAD-Computer Aided Design) ve Ortaklaşa Mühendislik (Concurrent Engineering) denilen sistemlerden yoğun bir şekilde faydalanılmaktadır [4,5]. Parça (ürün) tasarımında pek çok faktör etkili olmaktadır. Ancak genel bir sınıflandırma yapılacak olursa, parça tasarımına etki eden faktörler aşağıdaki gibi sınıflandırılabilir [4,6]:

1- **Tasarlanacak parça hakkında genel bilgiler:** Kullanım amacı ve yeri, daha önce tasarlanmış ve üretilmiş uygulamalar vb.
2- **Tasarımdan beklenen fonksiyonel özellikler:** Mekanik ve fiziksel özellikler, kullanım ömrü, çalışacağı ortam sıcaklığı, nem, kimyasallara karşı dayanım, ultraviyole kararlılığı vb.
3- **Estetik Özellikler:** Renk, şeffaflık, temas yüzeyleri, yüzey işlemler vb.
4- **Ekonomiklik ve üretilebilirliği:** Üretim, malzeme ve işçilik maliyetleri, mevcut makine, ekipman ve teknolojiyle üretilebilirlik, son işlemler vb.

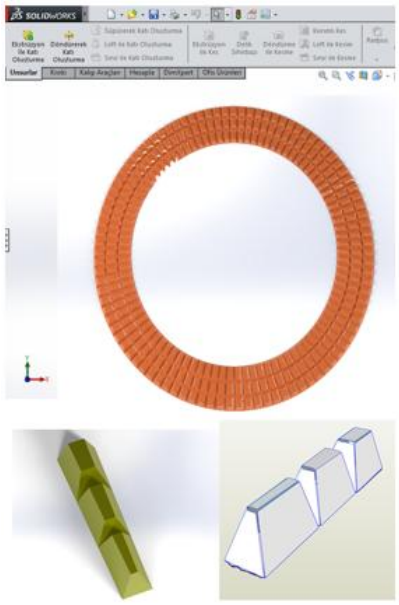
Tasarım sonucunda ortaya çıkan ürünün üretiminde metaller, seramikler, plastikler ve kompozit malzemeler gibi çok farklı malzemeler kullanılmaktadır [4,7]. Kompozit malzemeler nispeten diğer malzeme türlerine göre yeni bir malzeme türü olmasına rağmen endüstrideki kullanım oranları giderek artmakta ve havacılıktan, uzay ve uçak sanayine, deniz taşıtlarından inşaat ve otomotive kadar çok geniş bir yelpazede, yeni ürün geliştirme çalışmaları yoğun bir şekilde yapılmaktadır [7]. Kompozit malzemeler, iki veya daha fazla sayıdaki farklı malzemenin, en iyi özelliklerini bir araya toplamak ya da ortaya yeni bir özellik çıkarmak amacıyla malzemelerin makro seviyede birleşmeleriyle oluşturulan malzemeler şeklinde tanımlanabilir [7,8]. Kompozit malzemeler, matris olarak isimlendirilen sürekli bir faz ve sürekli fazdan daha dayanıklı ve sert olan takviye malzemesinden oluşurlar. Matris malzemesi olarak genellikle metaller, polimerler veya seramikler kullanılır. Kompozitler kullanılan matris malzemesine göre, *1-Metal kompozitler, 2-Seramik kompozitler, 3-Polimer Kompozitler* şeklinde sınıflandırılmaktadır. Takviye malzemesi olarak elyafların kullanımı, malzemelerin mekanik özelliklerini önemli oranda arttırmaktadır. Polimer kompozitlerin üretiminde cam elyaf, karbon elyaf, aramit elyaf en çok kullanılan takviye malzemeleri olarak öne çıkmaktadır [4,7,8]. Mermer tozu, kalsit, bentonit, kil gibi pek çok malzemede dolgu amacıyla kullanılmaktadır [4].

Mermer tozlarının dolgu şeklinde kullanımı ve polyester matrisli kompozit malzeme üretimi ile ilgili Hirostova ve ark. ürettikleri kompozit malzemede mermer dolgunun fiziksel yaşlanmasına olan etkisini incelemişlerdir [9]. Epoksi reçine ve mermer tozlarından oluşan kompozit malzemenin deformasyon özelliklerini inceleyen Kristova ve ark. epoksi reçine ve mermer tozlarının etkileşim bölgelerinde deformasyona uğradığını ifade etmişlerdir [10].

Bu çalışmada, *SolidWorks* ortamında 3D (üç boyutlu) olarak tasarlanan ayna çerçevesi *Pepakura Designer* isimli program yardımıyla tekrar eden en küçük birime indirgenmiş ve 2D (iki boyutlu) hale getirilmiştir. 2D haline getirilen tasarım, mukavva ve yapıştırıcı kullanılarak modellenmiş ve cam elyaf takviyeli polimerik kompozitten elle yatırma yöntemi kullanılarak döküm kalıbı yapılmıştır. Döküm kalıbında, reçine, mermer tozu, çimento gibi malzemeler kullanılarak tasarım ürüne dönüştürülmüş ve renklendirme işleminden sonra ürün hazır hale getirilmiştir. Bu çalışmada, 3D olarak tasarlanan bir ürünün, bilgisayar destekli programlar yardımıyla 2D haline getirilmesi, tasarım ve üretim süreçlerinde bilgisayar destekli programların ve modelleme yöntemlerinin kullanımın endüstriyel olarak yaygınlaştırılması amaçlanmıştır. Genel anlamda bu çalışmada tasarımdan üretime bir sonuç hedeflendiği için, nihai ürünün sahip olması gereken mekanik özelliklerin belirlenmesinde kullanılan mekanik testler bu çalışmanın kapsamının dışında tutulmuştur.

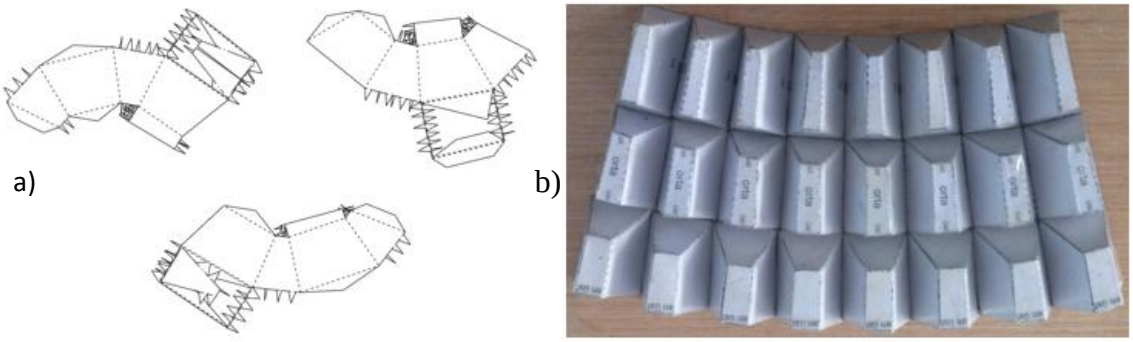
2. Malzeme ve Metot

Bu çalışmada, ürünün 3D olarak tasarlanmasında, bir tasarım fikrinin çizime dönüştürülmesi, parça üzerinde farklı değişiklikler ve ölçülendirmeler yapılması, modeller ve detaylı çizimlerin oluşturulmasını sağlayan SolidWorks mekanik tasarım otomasyon uygulaması kullanılmıştır. 3D tasarımın tekrar eden en küçük birime indirgenmesi ve 2D (iki boyutlu) hale getirilmesi, *Pepakura Designer* programında yapılmıştır. Tasarımın son şekli ve tekrar eden birime indirgenmiş hali Şekil 1.' de verilmiştir.



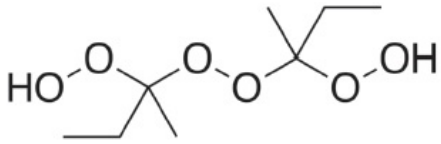
Şekil 1. Tasarımın son şekli ve tekrar eden en küçük birime indirgenmiş hali

İmalat resimleri yekpare olarak Şekil 2.' de gösterildiği gibi yapıştırma kulakçıklarıyla birlikte çıktı alınmış ve döküm modelinin yapımında 1,6 mm kalınlığında mukavva karton ve yapıştırma içinde solvent bazlı sıvı yapıştırıcı kullanılmıştır. Hazırlanan modelin döküm esnasında malzeme ile yapışmaması için kâğıtların üzeri bantlanmış ve kalıp ayırıcı görevi yapacak olan vaks çok katlı olarak sürülmüştür. Her bir uygulama sonrası bir saat süreyle vaksın kuruyarak tabaka oluşturması beklenmiştir.



Şekil 2. Döküm Modeli a) Tekrar eden birimin *Pepakura Designer* programında CAD' ten açılım haline getirilmiş hali b) Yapıştırıcı ile birleştirilerek oluşturulan döküm modeli

Kalıbın jelkont kısmını oluşturacak yüzey için, polyester karışıma %0,1 hızlandırıcı görevinde kobalt ve sertleştirici etki yapması amacıyla da % 0,1 (% 30 oranında seyreltilmiş) metil etil keton peroksit (mekp) eklenmiştir. Mekp doymamış polyester reçinenin soğuk proseste (oda sıcaklığında) kürleşmesi amacıyla karışıma eklenmiştir. Mekp kimyasal bileşimi Şekil 3.' de gösterilmiştir.



Şekil 3. Metil etil keton peroksitin yapısı

Karışım homojen haline gelinceye kadar karıştırılmış ve model yüzeyine birkaç kat uygulayarak kurumaya bırakılmıştır. Kurutma işleminden sonra, kalıp yüzeyine uygulamak amacıyla polyester ve % 40 cam elyaftan oluşan ikinci bir karışım hazırlanmıştır. Karışımın viskozitesini arttırmak ve maliyeti düşürmek amacıyla karışıma çimento ilave edilmiştir. Hazırlanan karışım fırça yardımıyla kalıbın son katına işlenmiş ve Kompozit malzemeden hazırlanan kalıbın son şekli verilmiştir. Kalıp tamamen kuruduktan sonra mukavvadan hazırlanan model kalıptan çıkartılmış, kalıp üzerindeki hatalar ve boşluklar macun ile düzeltilmiştir. 180 nolu zımpara kâğıdı kullanılarak kalıbın tesviyesi gerçekleştirilmiş ve kalıp Şekil 4.' de gösterildiği gibi üretime (döküme) hazır hale getirilmiştir.



Şekil 4. Model kullanılarak hazırlanan polimer kompozit döküm kalıbı

Polimer kompozitten hazırlanan kalıbın ayrım yüzeylerine kalıp ayırıcı uygulanmış, ürünün dökümünde kullanılacak olan polyester ve mermer tozundan oluşan karışım kalıba dökülerek kurumaya bırakılmıştır. Karışıma toplam kütlenin %0,1 oranında hızlandırıcı olarak kobalt tuzu ve %0,1 oranında mekp sertleştirici olarak ilave edilmiştir. Kuruma sonrası dökülen parça kalıptan çıkartılmış, tasarlanan ayna çerçevesi için gerekli olan tekrar sayısına ulaşılıncaya kadar işlem tekrar edilmiştir. Döküm sonrası kalıptan çıkartılan parça Şekil 5.' te gösterilmiştir.



Şekil 5. Döküm parçanın son hali

Tüm modelin dökümü tamamlandıktan sonra parçalar plastiklerin yapıştırma işlemi ile birleştirilmesinde kullanılan yüzey hazırlama yöntemlerine göre [11,12] hazırlanmış ve yapıştırıcı kullanılarak birleştirilmiştir. Birleştirilen parçalar 24 saat süreyle oda sıcaklığında kurumaya bırakılmıştır. Model kullanıcıların/tüketicilerin istediği renk ve özelliklerde olacak şekilde renklendirilmiş ve tasarım ve üretim süreci tamamlanmıştır.



Şekil 6. Birleştirme ve renklendirme işlemiyle bitmiş ürün

3. Sonuçlar ve Tartışma

3D tasarımlar ile farklı özellikle ve geometride ürün tasarlamak mümkündür. Ürün üzerindeki revizyonlar küçük değişikliklerle tasarıma uygulanabilmektedir. Farklı revizyon kodları ile sisteme kaydedilen parçalar üzerinde yapılan değişiklikler takip edilebilmekte ve geçmiş dönemde yapılan çalışmalara ulaşılabilmektedir. CAD-Cam programlarının eksik kaldığı noktalarda, SolidWorks - *Pepakura Designer* programlarında olduğu gibi farklı CAD-Cam programlarından faydalanılmaktadır. Ürünün 3D olaraks SolidWorks programında tasarımı ve 2D (iki boyutlu) hale getirilmesi, *Pepakura Designer* programında başarılı bir şekilde gerçekleştirilmiştir. Karton mukavva üzerine alınan çıktıda yapıştırma kulakçıklarının *Pepakura Designer* programında etkin şekilde oluşturulduğu gözlemlenmiştir. Modelin yapıştırıcı ile birleştirilmesinde bu kulakçıklardan faydalanılmıştır.

Hazırlanan karışımın model yüzeyine uygulanmasında fırça kullanılmış ve katman oluşturmak amacıyla her bir uygulama arasında 30-60 dakika arasında değişen bekleme sürelerinin uygulanması model hazırlama sürecinin başarısını arttırmıştır. Kalıp jelkot kısmının üzerine kalıp gövdesini oluşturmak amacıyla polyester ve % 40 cam elyaftan oluşan karışıma ilave edilen çimentonun viskoziteyi arttırdığı gözlemlenmiştir. Özellikle büyük kütleli parçaların model ve kalıp oluşturma aşamalarında çimento kullanımının maliyeti azaltıcı olarak kullanılabileceği düşünülmektedir. Jelkot kısmında polyester içerisine katılan mekp' in kürleşmeyi hızlandırdığı ve kobal tuzu ile birlikte sertliği arttırdığı gözlemlenmiştir.

Model oluşturma sonrası kalıp yüzeyindeki hataların macun ile kapatılması ve sonrasında zımpara ile bu yüzeylerin tesviye edilmesi işlemi, döküm sonrası parçaların yüzey kalitesini arttırmıştır. Özellikle polyester ve cam elyafın birlikte kullanıldığı polimer kompozit ürünlerde, belli bir üretim sayısından sonra bu işlemin tekrarlanması, üretilen parçaların yüzey kalitelerinin sürekliliğinin sağlanması açısından önemli olacağı düşünülmektedir. Düşük yüzey enerjisine sahip oldukları için plastiklerin yapıştırma yöntemiyle birleştirilmesinde çok farklı problemlerle karşılaşılmaktadır. Plastikerin yapıştırılması ve istenilen mukavemetin elde edilebilmesi için yapıştırma işlemi öncesi yüzeylere farklı yüzey işlemleri uygulanmalıdır [11,12]. Döküm sonrası parçaların birleştirilmesinde uygun yapıştırıcının seçimi ve

yapıştırılan yüzeylerin doğru şekilde hazırlanmasının ürünlerin dayanıklılığı ve birleştirme işleminin başarısı açısından oldukça önemli olduğu tespit edilmiştir.

4. Sonuçlar

Deneysel çalışmalar kısmında verilen malzemeler kullanılarak SOLIDWORKS programında katı modeli oluşturulan ve *Pepakura Designer* programında 2D ye dönüştürülerek modellenen ürün için kompozit malzemelerden başarılı bir şekilde kalıp yapılmıştır. Oluşturulan kalıba hazırlanan karışım dökülmüş ve ürüne ait parçaların üretimi gerçekleştirilmiştir. Parçaların birleştirilmesiyle ayna çerçevesinin tamamı oluşturulmuş ve renklendirme işlemine tabi tutulmuştur. Hazırlanan kalıpla yapılan işlemlerin tekrarlanabilir olduğu ve bu tür ürünlerin üretiminde kompozit malzemeden tasarlanan ve üretilen kalıpların kullanılabilir olduğu görülmüştür.

Gelecekte seri üretim olmayan ya da prototipi yapılacak ürünler için bu tür kalıpların yoğun bir şekilde kullanılacağı düşünülmektedir. Aynı şekilde kompozit kalıp sektörünün gelişmesiyle birlikte, kalıpların ağırlığının azalacağı ve karışıma katılan farklı malzemelerle kalıp maliyetlerlerinin büyük oranda azalacağı düşünülmektedir. Plastiklerin birleştirilmesinde kullanılan yapıştırma tekniğinin, gelecekte yapıştırma mühendisliği olarak bir bilim dalına dönüşeceği özellikle otomotiv, deniz ve raylı taşıtlarda kompozit ve plastikten yapılan parçaların hem aynı türden malzemelerle hem de metal, seramik diğer malzemelerle birleştirilmesinde yoğun bir şekilde kullanılacağı öngörülmektedir.

Kaynaklar

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DEVELOPMENT OF ANTIBIOTIC LOADED CHITOSAN COMPOSITE NANOSPHERES FOR BONE TISSUE ENGINEERING APPLICATIONS

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Abstract
Recently, drug carrier nanospheres were come into prominence to obtain controlled release in tissue transplantation operations. Chitosan/nanoclay composite antibiotic carrier nanospheres were fabricated to overcome the burst release problems by controlling the rate and enhancing the stability of the nanospheres. In this study, antibiotic releasing chitosan/clay nanocomposite spheres were fabricated with electrospray method. The nanospheres were characterized with SEM, FT-IR and zeta potential analysis. In addition, the antimicrobial activity of nanoparticles against *S. aureus* and *E. Coli* was investigated. The drug release profile was studied as a function of time. It was indicated that the prepared nanospheres diameters were around 166nm with narrow size distrubutions. Slower and controlled release profile was obtained with the chitosan/nanoclay composites. Drug carriers showed antimicrobial activity against *S. aureus* in correlation with their release profiles.

1. Introduction
The bone tissue transplantation operations are generally followed by antibiotic treatment to prevent the possible inflammation at the defect site. The poor circulation of blood in the osseous tissue makes necessary the supply of great amount of antibiotics to reach the adequate therapeutic level in the affected region. In conventional methods, these antibiotics were generally given to patients by oral, intravenous or intramuscular administration. However, to achieve the therapeutic level without causing any side effect is an extremely challenging issue. For this reason, localised control systems for antibiotic releasing is needed in the bone tissue transplantations to prevent the infection. The controlled drug delivery systems avoid the side effects, overdosing and toxicity of the antibiotics while releasing desired amount of drug. Releasing the active agents within a polymeric matrix is an effective way to achieve the goal as the polymer can act as the rate-controlling structure to obtain the desired controlled release profile **[1]**. While a variety of devices have been used for controlled release drug delivery, biodegradable polymeric micro/nano-scaled spheres are one of the most common types. Among natural polymers, chitosan has been commonly used in biomedical applications. It is composed of 2-amino-2-deoxy-D-glucose ($GlcNH_2$) residues with a variable number of randomly located *N*-acetyl-glucosamine groups (GlcNAc). Inflammatory responses in implantation models, induced infections and incidence of immunological reactions are prevented with chitosan based biomaterials **[2]**. Chitosan based drug carrier systems have been developed for bone tissue engineering applications **[3-5]**. However, the low stability and the faster degradation profile of the chitosan needs using cross-linking agents or fillers to obtain more stable form with enhanced properties. Chitosan/nanoclay composite structures can be alternative to synthetic crosslinkers. Polymer/clay based nanocomposites have also been proposed for drug delivery applications in biomedical field **[6]**. Montmorillonite (MMT), one of the mostly used layered silicate for polymer, has a 2:1 structure, consisting of triple layer sandwich structure that consists central octahedral sheet dominated by alumina, bonded to two silica tetrahedral sheets by oxygen ions that belong to both sheets **[7]**. Chitosan/MMT based systems are evaluated for drug delivery applications according to regulate the release rate of the active agent **[8-10]**.
In this study, it is proposed to fabricate antibiotic releasing chitosan/clay nanocomposite spheres for bone tissue engineering applications. Vancomycin is selected as a model drug which is broad-spectrum antibiotic against Gram-positive bacteria that is used for osteomyelitis treatment **[11]**. The aim of the study is to prevent the initial burst release of the drug within the nanocomposite matrix.

2. Materials-Method

2.1. Materials

High molecular weight chitosan, acetic acid (Sigma-Aldrich) and montmorillonite (OMMT) (Cloisite 10A, Southern Clay Products Inc.) as were used for. Vancomycin (Anko-L 500mg, Mustafa Nevzat) was selected as model drug.

2.2. Fabrication of antibiotic loaded spheres

2% (w/w) chitosan was dissolved in 90% acetic acid and mixed overnight. 3% (w/w chitosan) clay and vancomycin with a polymer: drug ratio of 10:1 were added to polymeric solution for antibiotic loaded composite nanospheres production. Homogeneous distribution of clay and antibiotic in polymeric solution was achieved with microfluidizer (Microfluidics). Nanospheres were obtained with the electrospraying method with operating conditions of 10cm distance between collector and syringe; voltage of 20kV and solution flowrate of 5ml/h.

2.2. Characterization

2.2.1. Particle size and morphology

The size and morphology of the chitosan/clay nanospheres were determined with SEM analysis with Quanta FEG 250 ($7x10^{-2}$ mbar and 15 mA). Before the analysis, samples were coated with Argon (Emitech K550X). Sphere diameters were calculated with ImageJ software. In addition, the hydrodynamic size of chitosan/clay nanospheres were determined with dynamic light scattering (DLS).

2.2.2. Chemical characterization

Chemical characterization and the interaction between drug-polymer were observed with FT-IR (ATR) (Shimadzu FTIR-8400S) at wavelengths ranging from 4000–650 cm^{-1}.

2.2.3. Zeta potential

The surface charges of chitosan/clay composite nanospheres were analysed with Nanoplus Zeta Sizer (Particulate System).

2.2.4. Antimicrobial activity

Disc diffusion method was used to determine the antimicrobial activity of the antibiotic loaded composite nanospheres. *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) were used as model bacteria. The frozen bacteria stocks were activated at 37ºC for overnight. The turbidity of cultured microorganisms in peptone solution was adjusted to McFarland 0.5. Nanospheres attached on blank discs were sterilized under UV cabinet for 30min. $3.4x10^7$ cfu/ml of early mid-log phase culture of *S. aureus* in tryptic soy broth and $2.5x10^7$ cfu/ml of *E. coli* in nutrient agar were incubated at 37°C for 24 h. The nanospheres attached on the surface of the discs gently put on the surface of inoculated agar with *E. coli* and *S. aureus*. Ampicillin and amoxicillin antibiotic discs were used as control groups. Petri dishes were incubated at 37°C overnight and the clear zones around the discs were recorded as inhibition zone which indicates antimicrobial activity.

2.2.5. Release profile

Antibiotic loaded nanospheres fabricated with electrospraying method were collected on a surface. The release studies of Vancomycin loaded nanospheres in powder form were performed at 37°C, in phosphate buffer saline (PBS, pH=7.4) with 60 rpm. Samples were taken in specific time intervals and the quantitation was determined with UV-VIS spectrophotometer (Varioskan). The amount of vancomycin in release media was determined according to the previously prepared calibration curve at a wavelength of 282 nm.

3. Results and Discussions

3.1. Particle size and morphology

The morphology and the particle sizes of fabricated nanospheres were determined with the SEM analysis. According to the images, perfectly spherical shape was obtained for both groups with the electrospraying method (Fig. 1).

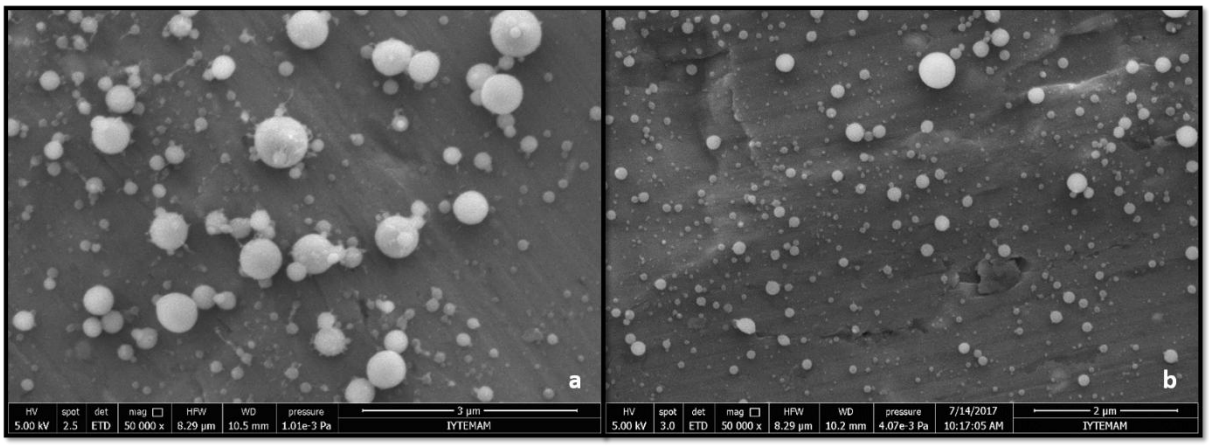


Figure 4. SEM images of chitosan (a) and chitosan-clay composite (b) nanospheres.

The particle diameters of chitosan nanospheres (301nm) decreased with the clay addition into polymer matrix (166nm) as indicated in Table 1. Besides, uniform size distribution was obtained with the composite groups (Figure 2).

Table 2. Particle sizes of chitosan and chitosan/clay nanospheres

Groups	Particle size (nm)
Chitosan-VC	301±6
Chitosan/Clay-VC	166±4

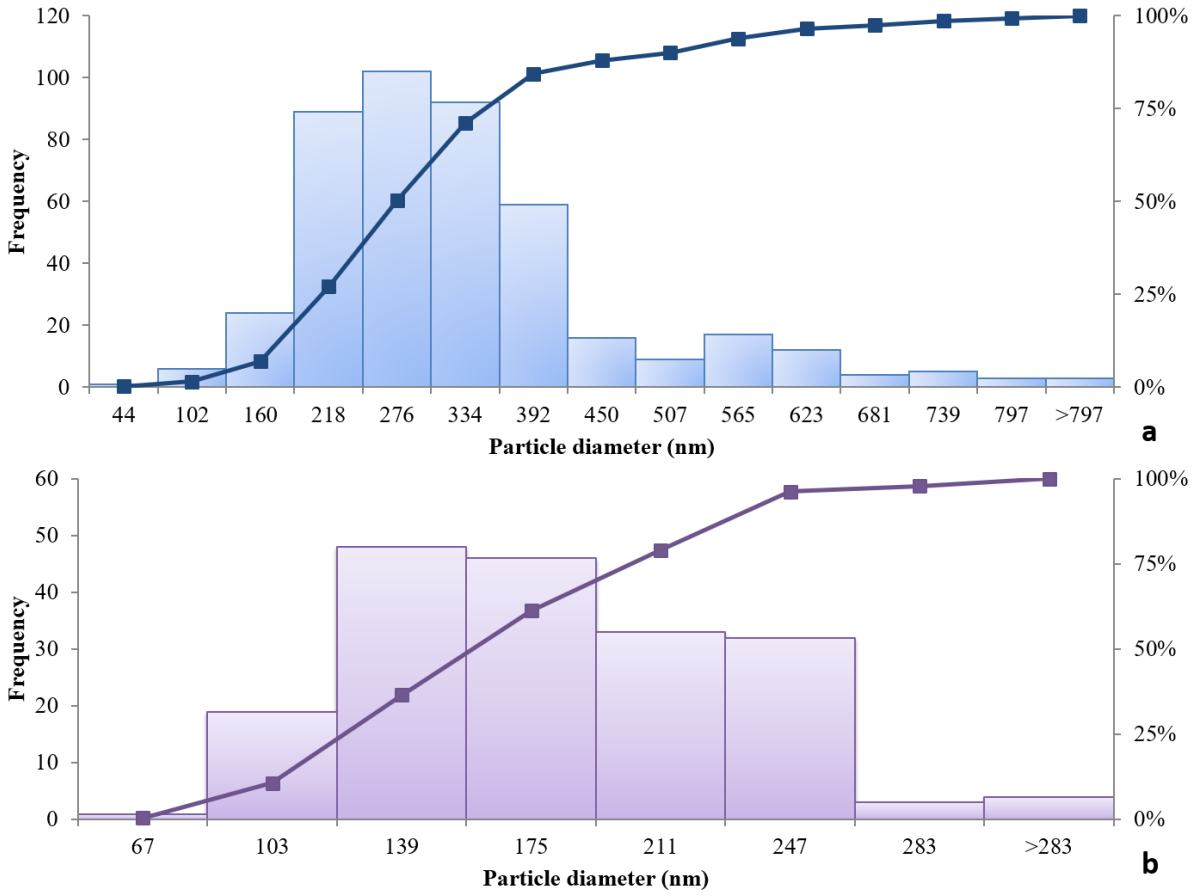


Figure 5. Particle size distributions of chitosan (a) and chitosan/clay (b) nanospheres according to SEM imaging.

The hydrodynamic size of the chitosan nanospheres using Zetasizer cannot be measured because of the rapid degradation and agglomeration of spheres in aqueous media. The clay addition provided more stable form without any crosslinker. The hydrodynamic size distribution of the chitosan-clay spheres was depicted in Figure 3. Narrow distribution was observed with the DLS analysis. The 96.3% of spheres were around 101.1nm where only 3.7% of spheres has a diameter of 366 nm. This small amount of larger nanospheres can be attributed with collapsed and precipitated particles during the measurement.

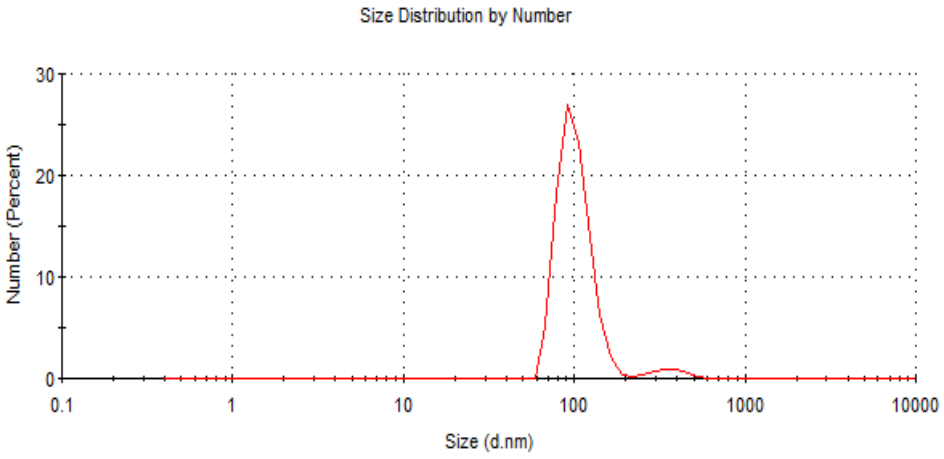


Figure 6. Number size distribution of chitosan-clay composite nanospheres by DLS analysis.

3.2. Chemical characterization

The IR spectra of chitosan/clay composite was depicted in Figure 4. The main characteristic bands of chitosan and clay were given in the Table 2. The peak at 2990cm^{-1} due to OH stretching is shifted to 2934 cm^{-1} and overlapped with the characteristic peak of MMT due to -CH_2- vibration at 2916 cm^{-1} at the composite group.

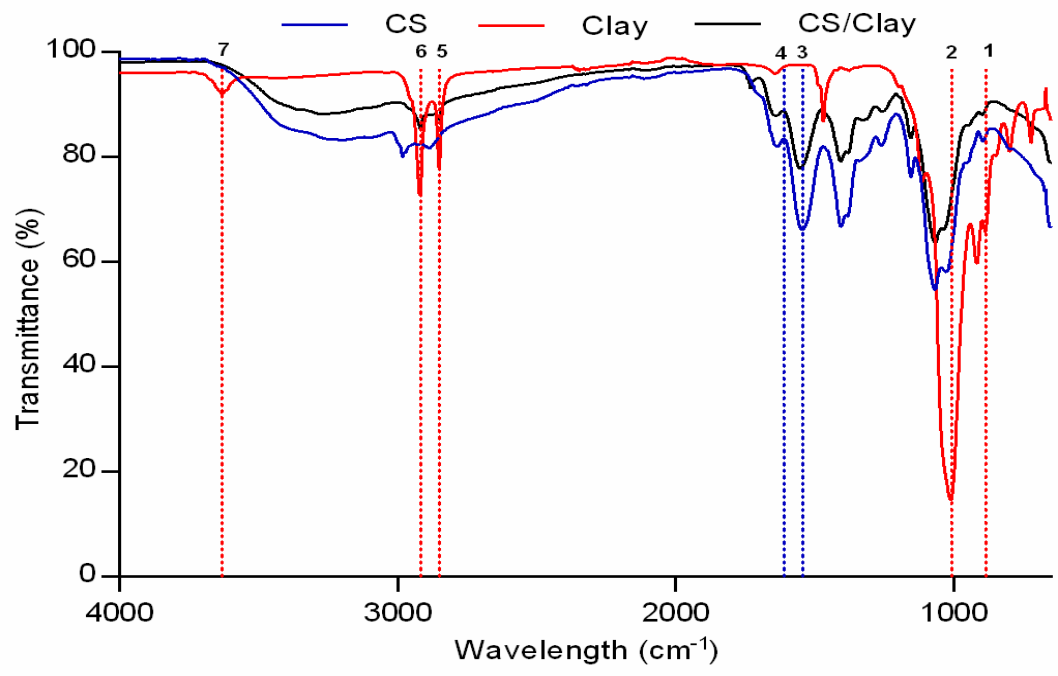


Figure 7. IR Spectra of chitosan (CS), clay and CS/Clay nanocomposite.

Table 3. Main spectral bands of chitosan and clay (MMT)

No	Wavenumber (cm^{-1})	Band	Formulation	Reference
1	913	Al-Al-OH stretching	MMT CS/MMT	**[12]**
2	1020	Si-O stretching	MMT	**[13]**
3	1560	N-H bending	Chitosan (amine)	**[14]**
4	1655	C=O stretching	Chitosan (amide I)	
5	2852	-CH- stretching	MMT CS/MMT	**[15]**
6	2916	-CH2 vibration	MMT CS/MMT	
7	3667	AlOH and SiOH stretching	MMT	**[12]**

Vancomycin loaded chitosan and chitosan/clay nanospheres were chemically characterized by FT-IR analysis and depicted in Figure 5. The characteristic peak of vancomycin due to R-CO-NH_2 functional group at 1632cm^{-1} was observed in both chitosan and chitosan/clay groups **[16]**. In addition, the organic groups of the drug were found at 3340 cm^{-1} (OH), 1664 cm^{-1} (C=O stretching) and 1494 cm^{-1} (C=C stretching) for both groups **[17]**. The hydrogen bonding between chitosan and glycopeptide antibiotic only caused a slight shift in the peak position since there is no major chemical interaction between the polymer matrix and the drug.

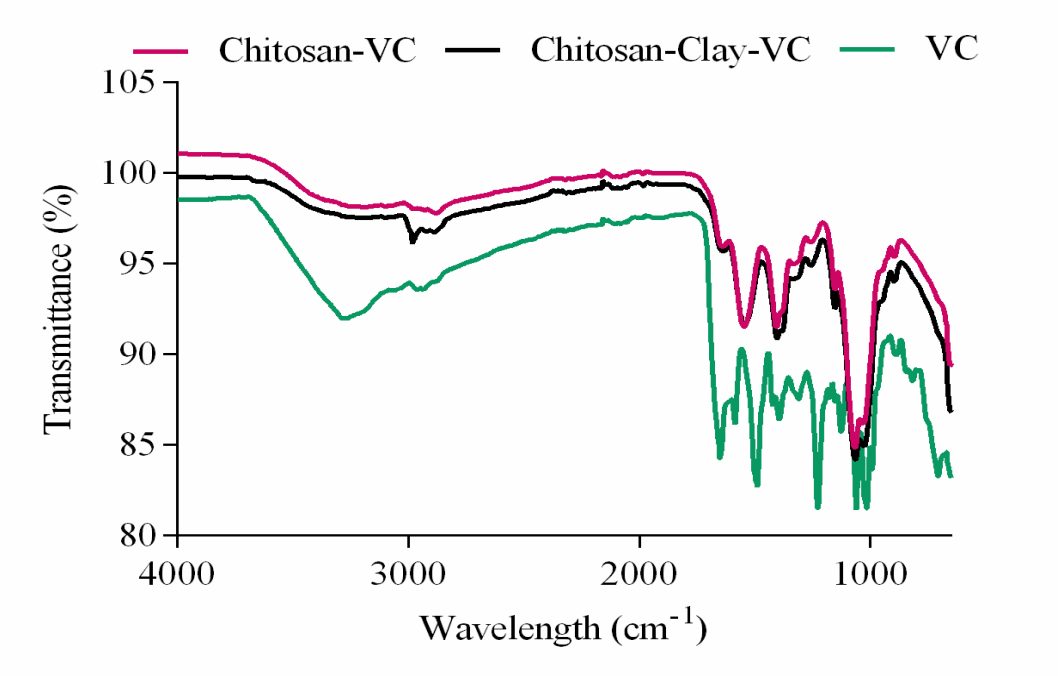


Figure 8. IR Spectra of drug loaded chitosan (CS), and CS/Clay nanocomposite.

3.3. Zeta potential

The zeta potential of the drug loaded chitosan and chitosan/clay nanospheres were measured to determine their surface charges (Table 3). Positively charged nanospheres were obtained with the vancomycin addition. The findings were in accordance with expected results, a decrease in the surface negativity due to interaction of carboxyl groups and the cationic drug on the particle surface **[18]**. Also, the composite groups have higher charge value that means increase in stability. The positive charge of zeta potential increases the nanosphere interaction with cell surface.

Table 4. Zeta potentials of drug loaded chitosan and chitosan/clay nanospheres

Groups	Zeta potential (mV)
Chitosan-VC	+13.02
Chitosan/Clay-VC	+19.15

3.4. Antimicrobial activity

The antimicrobial activity of drug loaded composite nanospheres were investigated for two different pathogens; gram-positive *S. aureus* and gram-negative *E. coli*. Studies reported that vancomycin loaded natural polymer based materials showed bactericidal properties against *Staphylococci* strains **[19,20]**. Similarly, antimicrobial activity was observed only against *S. aureus* since vancomycin is an antibiotic against gram-positive bacteria (Fig. 6). The decrease in inhibition zone compared to control group can be attributed to gradual release of antibiotic due to electrostatic interactions between chitosan and clay. The

chitosan nanospheres released the antibiotic faster than composite groups resulted with the higher antimicrobial activity at 24h incubation period. The results indicate that the antibiotic is released to the media and caused antimicrobial effect on *S. aureus*. In addition, higher antibacterial activity is expected in real case since optimum condition for bacteria growth (temperature, pH, nutrient) is supplied in experimental conditions **[21]**.

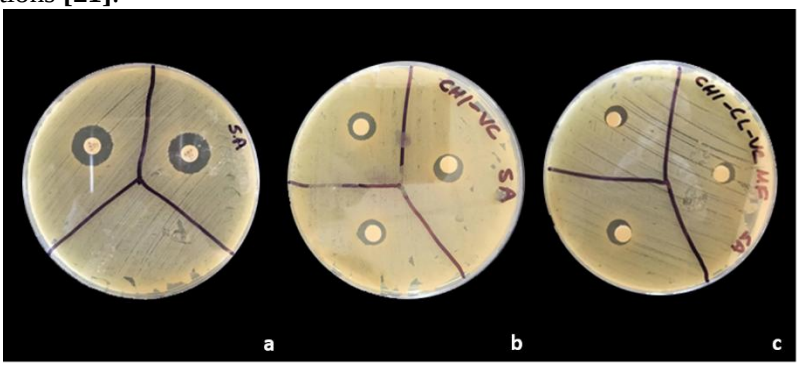


Figure 9. Antimicrobial activity of control discs (a), chitosan-VC nanospheres (b) and chitosan/clay-VC nanospheres, respectively.

3.5. Release profile

The *in vitro* release behaviour of drug loaded monolayer and bilayer films were depicted in Figure 9. The release behaviour of nanospheres after 6 h from implantation is critical to prevent the bacterial adhesion on implant surface **[22]**. The burst release at the initial period can be attributed to dissolution of vancomycin from the spherical surface. Figure 7 indicates the cumulative vancomycin release% for chitosan and chitosan/clay composite nanospheres for the early incubation period (72h). Slower release profile was obtained within the nanocomposite spheres. Control group showed a second peak at the 48 h that can be attributed with the degradation of the polymer. The nanocomposite group showed an initial burst release at 6h, following controlled release at 24h of incubation.

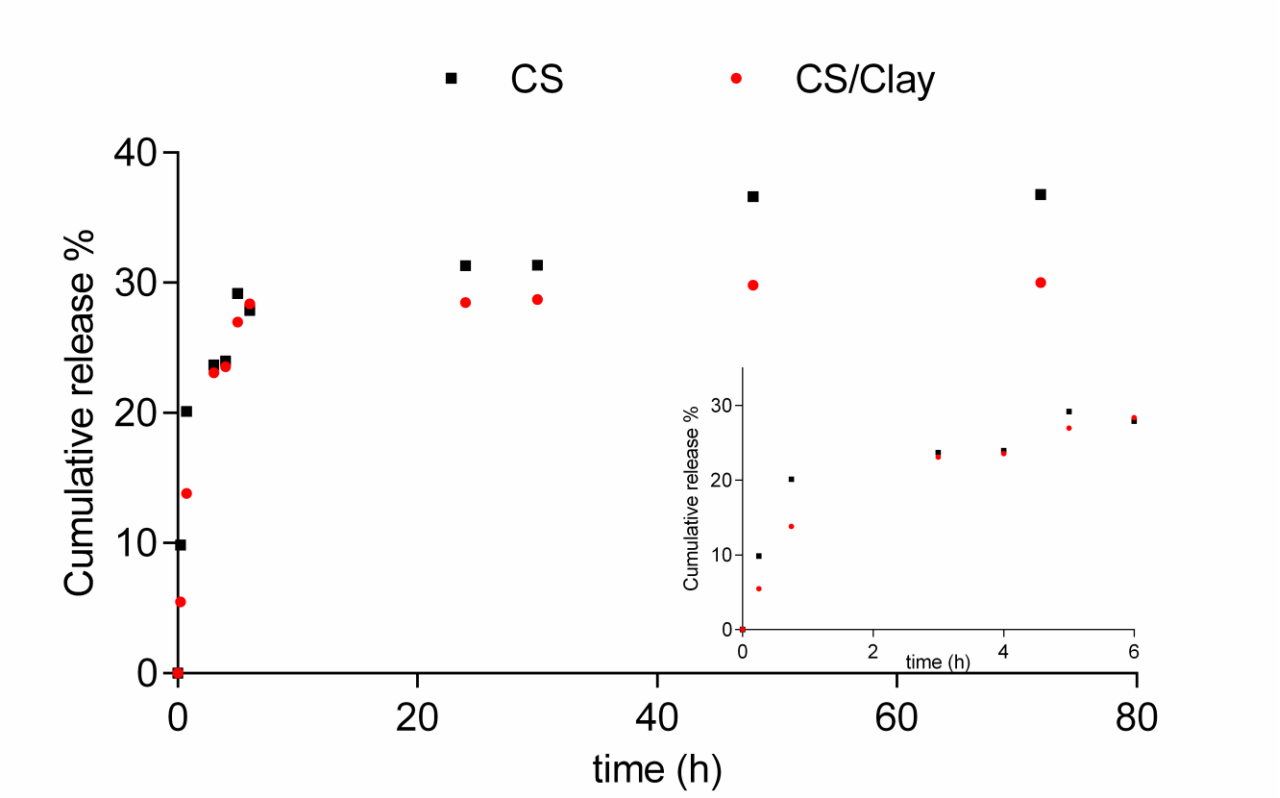


Figure 10. Cumulative drug release% of chitosan and chitosan/clay nanocomposite groups for 72 h incubation.

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ANTISTATIC ZINC OXIDE /POLYETHYLENE COMPOSITES

ANTİSTATİK ÇİNKOOKSİT /POLİETİLEN KOMPOZİTLER

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Abstract

The electrostatic charging of polyethylene can be prevented by adding conductive additives. One of these additives is zinc oxide (ZnO). In the present study the effects of surface modification of nano ZnO powder that was used to improve the electrical conductivity and mechanical property of the linear low density polytethylene (LLDPE) on properties of composites was aimed to be investigated.ZnO was modified by mixing with aminopropyltriethoxisilane (AMPTES) and polyethylene glycol 4000 (PEG 4000) in aqueous ethanol solutions and then drying. Different amounts (5-20%) of modified and unmodified zinc oxide powders and LLDPE were mixed using a Haake Rheomixer at 50 rpm for 10 minutes at 160 ^{o}C. The mixtures were pressed to 15x15x0.1 cm sheets in Carver Hot press at 160^{o}C under 6800 kg load with a 10 min hold. The electrical conductivity and stress-strain properties of the sheets were measured.

The electrical conductivity of the sheets prepared in Carver hot press increased with the volume fraction of unmodified ZnO. However the conductivities of sheets made from modified ZnO were lower than that of the composites from unmodified ZnO. Modifed ZnO particles did not create a sufficiently conductive path in polyethylene. However their conductivity was lower than that pure polyethylene. The tensile strength of the composite decreased with increasing of ZnO volume fraction Surface modification of composites enhanced the tensile strength of the composites but did not affect their elongation at break up to 15% ZnO. Composites from ZnO modified with PEG 4000 had lower modulus of elasticity than that of composite from unmodified ZnO. Composite made with 3% AMTES modified composite had higher modulus of elasticity indicating better interfacial adhesion.

Özet

Amaç

Polietilenin statik elektrikle yüklenmesi içine iletken katkılar katılarak önlenebilir. Bu katkılardan biri de çinkooksit (ZnO) dur. Bu çalışmada polietilenin elektrik iletkenliğini ve mekanik özelliklerini geliştirmek için katılan nano ZnO tozunun yüzey modifikasyonunun kompozit özelliklerine etkisinin araştırılması amaçlanmıştır.

Materyal ve Metod

ZnO aminopropiltrietoksisilan (AMPTES) ve polietilen glikol 4000 (PEG 4000) in etil alkolün sulu çözeltilerinde karıştırılarak bekletilip kurutularak ile modifiye edilmiştir. Farklı oranlarda (% 5-20) değiştirilmemiş veya değiştirilmiş çinko oksit ve polietilen karışımı Haake Rheomixer'de 160 ^{o}C 50 devir/dak 10 dakika karıştırılmış ve karışımlardan Carver Sıcak presde 160^{o}C de ve 6800 kg yük altında 15x15x0.1 cm boyutunda levhalar elde edilmiştir. Levhaların yoğunluğu, su temas açısı, elektirik iletkenliği ve germe-uzama özellikleri ölçülmüştür.

Bulgular ve Tartışma

Levhaların elektrik iletkenliği değiştirilmemiş ZnO hacim oranı ile artmıştır. Çinko oksit katkısı ile yalıtkan LLDPE statik elektriği boşaltan (statically dissipated) bir malzemeye dönüşmüştür. LLDPE e

bu özelliği kazandırmak için kullanılan % 15 veya % 20 ZnO katkısı malzemenin mekanik özelliklerinde aşırı bir kayba neden olmuştur. Bu nedenle çinko oksit AMTES ve PEG400 ile hidrofobik bir yapı kazandırmak amacı ile modifiye edilmiştir. ZnO modifikasyonu sırasında tanecikler birbirine yapışarak aglomere olmuş ve bu nedenle kompozit özelliklerinde önemli iyileşmeler elde edilememiştir. Tablo 1 katkısız ve %20 ZnO veya modifiye çinko oksit içeren kompozitlerin yoğunlukları, su temas açısı, hacimsel elektrik özdirenç değerleri, çekme dayanımı, kopma uzaması ve elastic modül değerleri verilmiştir. Kompozitlerin ölçülen yoğunluklarından %2-3 oranında boşluk hacmine sahip oldukları anlaşılmıştır. Modifiye ZnO ten hazırlanan levhalarla değiştirilmemiş ZnO dan hazırlanan levhalar birbirine yakın su temas açısı değerlerine sahiptir. Modifiye ZnO içeren filmlerin elektrik öz direnci değiştirilmemiş ZnO içeren filmlerden yüksek bulunmuştur. Modifiye çinko oksit taneciklerinin LLDPE içinde topaklar halinde dağıldığından yeteri kadar iletken bir yol yaratmamıştır. Kompozitlerin çekme dayanımı ZnO hacim oranı arttıkça azalmıştır. Çinko oksitin yüzey modifikasyonu ile biraz daha yüksek çekme gerilimi elde edilmiş ama kopma uzamasında önemli bir değişiklik olmamıştır. ZnO yüzeyi %3 PEG 4000 veya %6 AMPTES ile modifitye edildiğinde hem kopma dayanımı hem kopma uzaması artmıştır. PEG 4000 modifikasyonu ile elastic modül azalırken AMPTES modifikasyonu ile artmıştır.

Tablo 1. %20 değiştirilmemiş ve değiştirilmiş çinko oksit içeren kompozitlerin özellikleri

ZnO %	Mofifikasyon	Teorik yoğunluk g/cm^3	Arşimet yoğunluğu, g/cm^3	Kontak açısı, ^{o}	Hacimsel elektrik resistivite, Ω cm	Çekme dayanımı, N/mm^2	Kopma uzaması, %	Elastik modül, N/mm^2
20.0	Yok	1.86	1.85	93.8	$2.06x10^{10}$	9.9	12.3	216.0
20.0	1% PEG 4000	1.86	1.82	87.6	$5.43x10^{10}$	10.2	15.0	159.3
20.0	2% PEG 4000	1.86	1.88	86.6	$1.97x10^{11}$	8.7	12.0	154.3
20.0	1 % AMPTES	1.86	1.82	89.0	$1.78x10^{11}$	11.0	11.9	291.9
20.0	2 % AMPTES	1.86	1.79	86.4	$1.30x10^{13}$	10.0	12.9	201.8

Sonuç

Yalıtkan LLDPE % 15-20 oranında ZnO katılarak statik elektriği boşaltan bir malzemeye dönüştürülmüştür. Bu derece yüksek oranda ZnO katkısı mekanik özellikler de aşırı bir kayba neden olmuştur. Mekanik özellikleri geliştirmek amacı ile ZnO nun LLDPE içinde tek taneler halinde dağılmasını sağlıyacak yüzey modifikasyonları yapılmıştır. ZnO in bu modifikasyonlar sırasında topaklanması ile mekanik özelliklerde çok az bir gelişme olmuştur. ZnO taneciklerinin topaklanmasını önliyecek bir yüzey modifikasyonu üzerinde çalışmalar devam etmalidir.

Introduction and aim

Polymeric materials are generally insulating materials in nature and likely to accumulate the electrostatic discharge [1]. The application of conductive particles/nanoparticles to a polymer matrix is expected to induce electrical conductivity. Polymers are insulators but conductivity of them can be increased by the introduction of conducting fillers. Increments in conductivity of polymers depend on the volume fraction of filler used to increase the electrical conductivity. With the increasing of volume fraction of filler, filler particles in polymer starts to contact with each other and creates a continuous path for electron to pass electric current. This theory is called as percolation theory [2]. Introduction of this conducting filler into polymer may not give good results in terms of electrical properties since the properties of conducting filler is not suitable to have good mixing. Modifications are applied to have a proper mixing to increase the conductivity of polymer with filler. There are lots of study shows that modified fillers gives better results in terms of conductivity compared to filler without modification.

Zinc oxide is a most common semiconductive material that has a large surface area, high ultraviolet (UV) absorption, and long life-span, and widely used as gas sensor, active filler for rubber and plastic, UV absorber in cosmetics and anti-virus agent in coating. ZnO have also the properties such as dielectric, piezoelectric, pyroelectric , semiconducting, acousto-optic, optical, electrooptical, nonlinear optical, photoelectrochemical and electrical properties [3].

Linear Low Density Polypropylene (LLDPE) is a substantially linear polymer, with significant numbers of short branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins with density range of 0.915 to 0.925 g/cm^3 [3].

To improve or change the distribution of the nanoparticles, and the compatibility between the nanoparticles and other materials, physical or chemical methods are needed to change the physical, chemical, mechanical properties, and the surface structure of nanoparticles. Surface chemical modification of nanoparticles plays a very important role to reduce the agglomeration. Due to modifier adsorption or bonding on the particle surface, which reduces the surface force of hydroxyl groups, the hydrogen bonds between particles are eliminated to prevent the formation of oxygen bridge bonds when nanoparticles are drying, so preventing the agglomeration [4].

To reduce the aggregation among nanoparticles and to improve the congruity between ZnO filler and the polyethylene, ZnO nanoparticles are treated with some modifier such as Aminopropyltriethoxysilane(AMPTES) and polyethylene glycol(PEG) to provide well dispersion on surface. AMPTES) and PEG are examples of surface modifiers for ZnO. In the case of AMTES pH≈10.5 condensation into siloxane (Si-O-Si) polymer and the hydrolysis of silane into silanol are observed. However at this pH the ZnO surface is negatively charged and a high condensation is observed and after heating the aminosilanoltriols forms aggregates and later these aggregates are adsorbed onto ZnO surface [5]. The surface modification of ZnO by previous investigators [5, 6] indicated that Zn-O-Si bonds were formed on the surface and maximum two of the four Si-O bonds of AMPTES could react with ZnO due to steric hinderences. Regarding to PEG and ZnO relation, PEG macromolecules bond with the solid surface of the ZnO by the aid of –OH end group and may interact with the PEG through hydrogen bonding. However the pH of the solution affects the mechanism of the bonding since in low pH values the concentrations of $–ZnOH_2^+$ group and –ZnOH group increase and –ZnO group decrease. At low pH more polymers could be adsorbed on the surface of the ZnO particles due to the presence of –OH groups in the solution [7, 8]. Posthumus et al. modified various oxide nanoparticles using 3-methacryloxypropyl trimethoxysilane and investigated the grafting [9]. Tang et al. used polymethacrylic acid for nZnO modification and dispersionof nZnO in aqueous system was improved [10]. Hong et al. modified nZnO by oleic acid and better compatibility was gained between inorganic nanoparticle and organic matrix [11]. Hong et al. used poly methyl methacrylate for grafting nZnO and applied it in nanocomposite preparation with styrene and better thermal behavior was obtained [12]. Ma et al. modified nZnO surface by KH570 silane coupling agent and the dispersion was improved [13].

Chang et al. studied the silane modified ZnO-UHMWPE (ultra high molecular weight polyethylene) composites.The elongation at break and tensile strength of modified and unmodified ZnO-filled UHMWPE was decreased with increasing of ZnO filler loading compared to pure UHMWPE [14]. Li et al. investigated the mechanical properties of silane modified nano ZnO-LLDPE composites. They found that, the elongation at break and the tensile strength of the composite films was increased firstly and then was decreased with increasing ZnO content. The optimal ZnO content was found 0.3 wt % and the maximum tensile strength, elongation at break were found to be 43.2% and 39.4% higher than pure LLDPE's respectively**[**15]. Hong et al. studied addition of nanosized and micron sized ZnO to low molecular weight polyethylene. The percolation threshold value for ZnO-polyethylene composites were found approximately at 30 vol% and addition of 40 vol% ZnO decreased the resistivity to 10^{11} ohm cm. In another investigation the particle size effect was studied by using nano and micron sized ZnO particles and the electrical resistivity was found at the order of 0.3x 10^{13} ohm cm after the addition of 60 vol% ZnO[16]. In contrast, Hong et al. reported the lowest resistivity as 10^{9} ohm cm upon the addition of 30 vol% ZnO [12]. In fact Hong et al. studied ZnO particles and linear low density polyethylene (LDPE) composites to investigate the particle size affect. Micron sized (300 nm) and nanosized (49 and 24 nm) powders were used as fillers in their study. The percolation limit decreased as the particle size of zinc oxide was decreased. When the interparticle distance was decreased to below 40 nm, tunneling began to occur. The percolation onset occurred at a lower volume fraction as the particle size was decreased, due to decrease in interparticle spacing. The neat polymer volume resistivity was 10^{19} ohm cm and the lowest volume resistivity found was 10^{9} ohm cm for 24 nm powder at above 30 vol% [17].

Ozmihci and Balköse [18] investigated the effects of particle size and electrical resistivity of zinc oxide (ZnO) on mechanical properties, electrical and thermal conductivities of composites made with linear low density polyethylene (LLDPE). Micron sized (mZnO), submicron sized (sZnO), and nano sized (nZnO) powders having resistivities of 1.5 x 10^{6}, 1.5x 10^{9}, and 1.7 3 x10^{8} were used to prepare composites with 5–20 vol % filler. The tensile strength was lowered and the modulus of elasticity of the composites was increased with ZnO addition. Rather than the particle size of the ZnO, its initial resistivity and aspect ratio affected the resistivity of composites. The resistivity of the LLDPE was lowered from 2.3 x 10^{16} Ω cm down to 1.4 x10^{10} Ω cm with mZnO addition. Thermal conductivity of the composites was increased with ZnO addition 2.5–3 times of the polymer matrix. The composites can be used for electrostatically dissipating applications due to their decreased electrical resistivity .

In this paper composites with better electrical and mechanical properties were aimed to be prepared from pure m-ZnO and LLDPE that were used by Ozmihçi and Balkose [18]by modifying ZnO with AMPTES and PEG 4000. The ZnO-polymer composites plates were prepared by mixing ZnO and polyethylene in a rheometer and the mixture was pressed in hot press. Morphology, density, water contact angle, electrical conductivity, modulus of elasticity, elongation at break and the tensile strength of composites were measured.

Materials and methods

ZnO powder (Ege Kimya AŞ) that was used in our previous study [18]was used in experiments.It has 3.86 μm particle size and 1.6x10^{6} Ωcm volumetric resistivity.

The surface modification of ZnO powders (was performed with 3-aminopropyltriethoxysilane (AMPTES) (Fluka) and PEG 4000 (Aldrich). 1.08 g PEG was dissolved in 9 cm^3 1:1 v/v ethanol and water solution by mixing with magnetic stirrer with a constant stirring rate by 20 minute at 25 ^{o}C. This solution was mixed with 30 g of ZnO in a porcelain mortar and pestle by 15 minute. For drying, this sample was left in fume hood at 25 ^{o}C for 24 hours and the sample was placed into an air circulating oven at 40 ^{o}C for 24 hours. The same procedure was repeated with 2.16 g PEG with 9 cm^3 solution.

Modified ZnO particles having AMTES in the same proportions were prepared similarly. The modified zinc oxide were called as 1% and 2 % PEG4000 and AMPTES samples.

Linear low density polyethylene(LLDPE) from Sigma Aldrich was used for preparation of the composites. ZnO particles and polyethylene were mixed using a Haake Rheomixer at 50 rpm for 10 minutes at 160 ^{o}C. Unmodified ZnO and polymer composites were prepared in volume % of 5, 10, 15 and 20. Composites with polyethylene matrix containing 20 volume % modified ZnO were prepared by using surface modified ZnO powders. The mixtures were then uniaxially pressed and well-shaped with dimensions of 15x15x0.1 cm by using Carver hot press at 6800 kg force and 160 ^{o}C with a 10 min hold.

The SEM (Philips XL-30S FE) and FTIR (Shimadzu FTIR-8201) were performed to modified ZnO powders to understand the morphology and modification performance. The morphology of composites were characterized by using SEM (Philips XL-30S FE). Composites were broken after immersing in liquid N_2 at 77 K and fracture surfaces were examined by using SEM. Density of the composites was measured by using density kit apparatus (Sartorious). Contact angle of the composites were measured 3 times (Attension theta optical tensiometer) with attached camera of KSU CAM 101 and the average data were reported as the contact angle.

Electrical resistivity of the composites were measured by using Keithley 6517A Electrometer/High Resistance meter connected to 8009 Resistivity Text Fixture sample holder. The resistivity was measured according to ASTM D257.

The tensile tests of the samples were conducted by Shimadzu AG-I 250kN using 5 mm/min stretching rate at room temperature according to ASTM standard 638 for PE matrix composites. Dog bone samples were cut from composite plates by using Ceast Automatic hollow die punch for the determination of mechanical properties of the composites.

Results and discussion

Zinc oxide is a white and fluffy powder which is insoluble in water and alcohol but soluble in acid and alkali. The purity of ZnO was given as 99.8% and the average particle particle size was 3.86 μm [18]. Each particle of ZnO has a unique shape. Tripot, bar, cube and needle shaped particles were dispersed in the medium. ZnO was agglomerated during surface modification with PEG and AMTES as seen in Figure 1. It was not possible to disperse the agglomerates by grinding with mortar and pestle, since they were very strongly bound to each other .The mixing of ZnO with PEG and AMPTES in 1:1 ethanol water solution and then drying may be the reason of agglomeration. Using higher ethanol concentration or another solvent with low surface tension would prevent the agglomeration of ZnO particles due to capillary action of water in solid water interface.

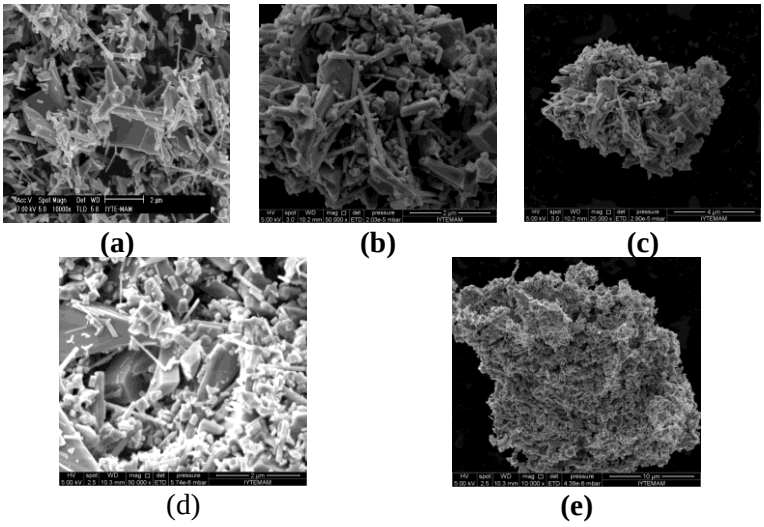
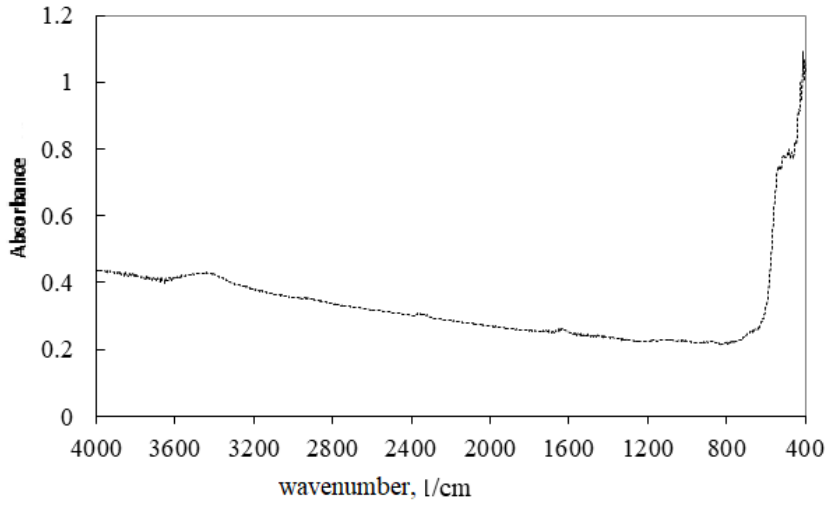


Figure 1. SEM micrographs of a. ZnO (b, c) %1 AMTES modified ZnO (d, e)%1 PEG Modified ZnO

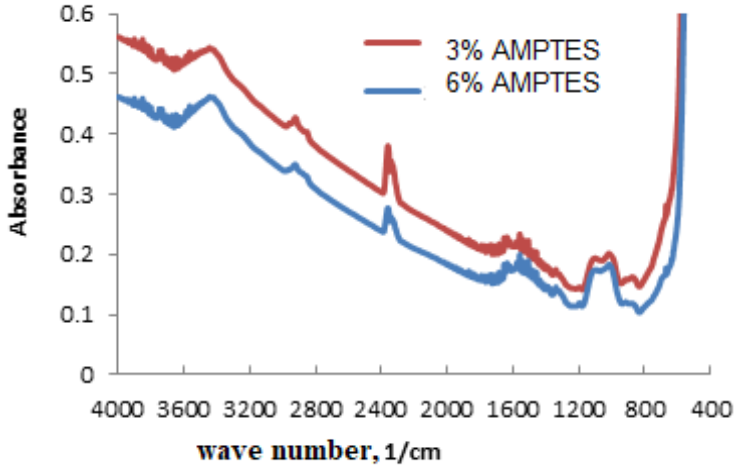
FTIR spectra of ZnO, AMPTES and PEG modified ZnO are given in Figure 2. Characteristic peaks of (Zn-O) 473cm^{-1} and 532 cm^{-1} are seen in the spectra of ZnO and modified ZnO. All ZnO samples had hydrogen bonded OH groups as indicated by the band at 3400 cm^{-1}. The 2800 cm^{-1} C-H stretching, 1100 cm^{-1} C-O-C stretching, 1300 cm^{-1} CH_2 bending and 1200 cm^{-1} CH_2 twisting vibration, are present PEG 4000 modified ZnO [19]. 1591 cm^{-1} belonging to amine groups, 1030 cm^{-1} Si-O-C_2H_5 and silylester of AMPTES are seen in FTIR spectrum of AMPTES modified ZnO [6].

Micrographs of fracture surfaces of unmodified and Modified ZnO-LLDPE composites are seen In Fig 3. While composite made with unmodified ZnO showed brittle fracture at the liquid nitrogen temperature (-190^{o}C), the composites made form AMPTES and PEG modified ZnO

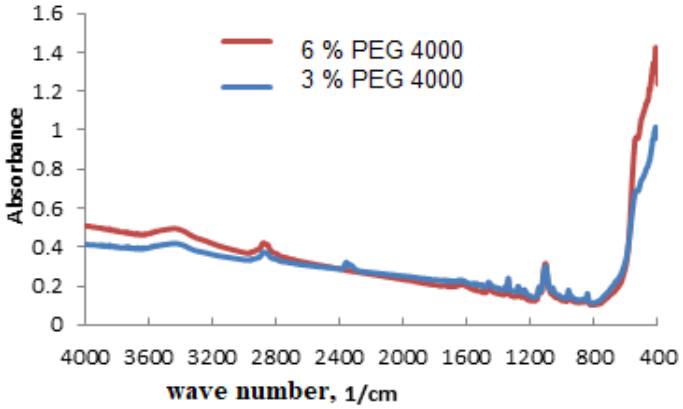
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(a)



(b)



(c)

Figure 2. FTIR spectra of a. unmodified b. AMTES c. PEG modified zinc oxide

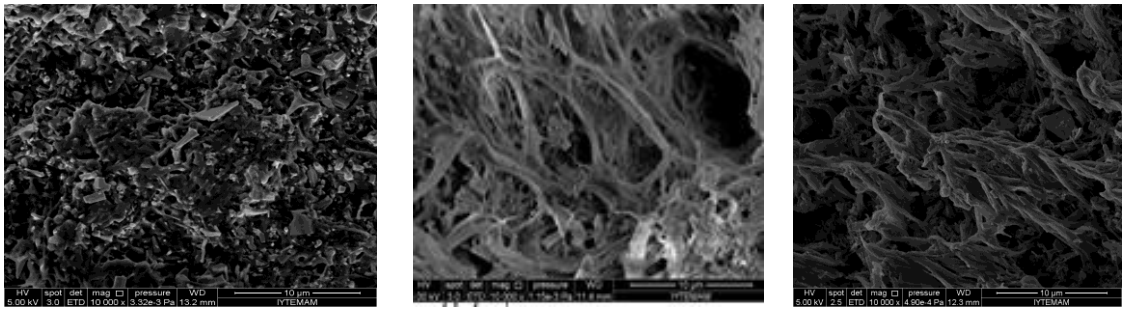
showed ductile fracture with a fibrillated structure indicating deformation of polymer phase during fracture. Also big agglomerates of modified ZnO are seen in their composites indicating that during melt mixing of modified ZnO and LLDPE the agglomerates were not disintegrated and dispersed evenly in polymer melt.

Theoretical density of the composites was calculated by using density (ρ) for ZnO powders (5.6 g/cm^3) and LLDPE (0.92 g/cm^3) matrix materials. The theoretical density calculation of composites was made with this equation:

$$\rho_{Theoretial} = \rho_{PE}(1-\phi) + \rho_{ZnO}\phi$$

Where Φ is volume fraction of ZnO. The calculated density values and the measured density values were not identical but they were close to each other as seen in the Table 1. However for composites having modified ZnO lower density values were observed accept for 2 % PEG modified composite. Lower experimental density indicated the composite sample had empty spaces (2-3 %) and higher intensity indicated higher crystallinity in polymer phase.

Contact angle of water droplet on the surface of the composites were measured to investigate the treatment of the surface modifier. To make the polymer and ZnO surface compatible the hydrophilic ZnO surface was modified with an organic compound (AMPTES and PEG) to make the ZnO surface hydrophobic. The contact angle of on the surface of LLDPE was found 87°. The contact angles of the composites with different volume fraction of unmodified ZnO and 20 vol % modified zinc oxide are shown in the Table 1. They were in the range of 85.2-92.0^o showing that ZnO or modified ZnO had no significant effect on the wettability of LLDPE with water.



(a) (b) (c)

Figure 3. SEM micrographs of fracture surfaces of polyethylene 20 vol % ZnO composites a. Unmodified b. Modified with 3 % AMTES c. Modified with 3% PEG

The volume resistivity of LLDPE was 4.57x10 16 Ω cm as seen in Table 1. For the addition of 5 vol% ZnO to the polymer the volume resistivity value decreased to 1.02x10^{16} Ω cm. The volume resistivity of polyethylene decreased to 3.16x10^{14}, 1.26x10^{12} and 2.06x10^{10} Ω cm for 10%, 15% and 20% ZnO respectively in Table 1. When the concentration of filler increased and reached the percolation threshold value the resistivity of the composites decreased dramatically. After reaching threshold value, electron passing through the composite started to make hopping and resistivity of the composite decreased. The resistivity of the LLDPE was lowered from 2.3 x 10^{16} Ω cm down to 1.4 x10^{10} Ω cm with ZnO addition in our previous study [17] which are very close to the present study showing the reproducability of our work. The composites should have an electrical conductivity in the range of 10^{-12} and 10^{-8} S/cm for electrostatic dissipation applications, 10^{-8} and 10^{-2} S/cm for moderately conductive applications 10^{-2} S/cm and higher for shielding applications [18]. Thus the composites prepared in the present study are electrostically dissipating materials at 15 vol % ZnO and 20% ZnO loading levels as

seen in Figure 4. ZnO filler with $1.6x10^6$ Ω cm resistivity decreased the resistivity of electrically insulating LLDPE to the level of statically dissipating material.

The resistivity values of LLDPE composites prepared from surface modified ZnO are also given in given in Table 1 and Figure 5. The resistivity of the composites from PEG and AMPTES modified ZnO composites were higher than that of the unmodified composite but still in the range of statistically dissipating materials.

Table 1. Density, contact angle, electirical resistivity, tensile strength,elastic modulus, and elongation at break values of modified and unmodified composites.

ZnO %	Modification	Theoretical density, g/cm^3	Archimedes Density, g/cm^3	Contact Angle, ^{o}	Electrical Resistivity, Ω cm	Tensile strength, N/mm^2	Elongation at break, %	Elastic modulus, N/mm^2
0.0	None	0.92	1.01	86.8	$4.57x10^{16}$	18.3	1190.9	125.6
5.0	None	1.15	1.14	85.2	$1.02x10^{16}$	17.0	1140.1	118.9
10.0	None	1.39	1.38	87.6	$3.16x10^{14}$	17.7	1165.5	122.3
15.0	None	1.62	1.61	92.2	$1.26x^{12}$	14.4	1105.9	171.5
20.0	None	1.86	1.85	93.8	$2.06x10^{10}$	9.9	12.3	216.0
20.0	3% PEG 4000	1.86	1.82	87.6	$5.43x10^{10}$	10.2	15.0	159.3
20.0	6% PEG 4000	1.86	1.88	86.6	$1.97x10^{11}$	8.7	12.0	154.3
20.0	3 % AMPTES	1.86	1.82	89.0	$1.78x10^{11}$	11.0	11.9	291.9
20.0	6 % AMPTES	1.86	1.79	86.4	$1.30x10^{13}$	10.0	12.9	201.8

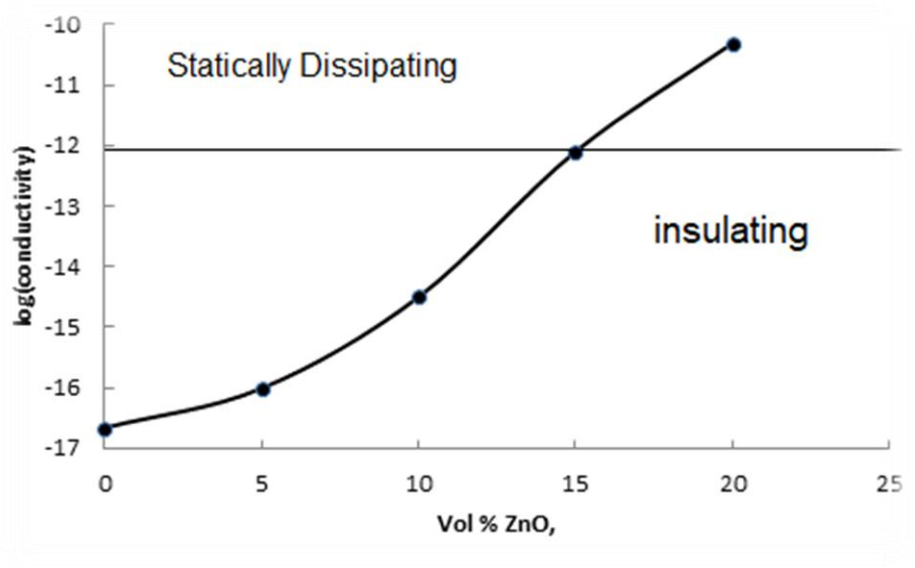


Figure 4. Change of Log conductivity with Volume % of Filler

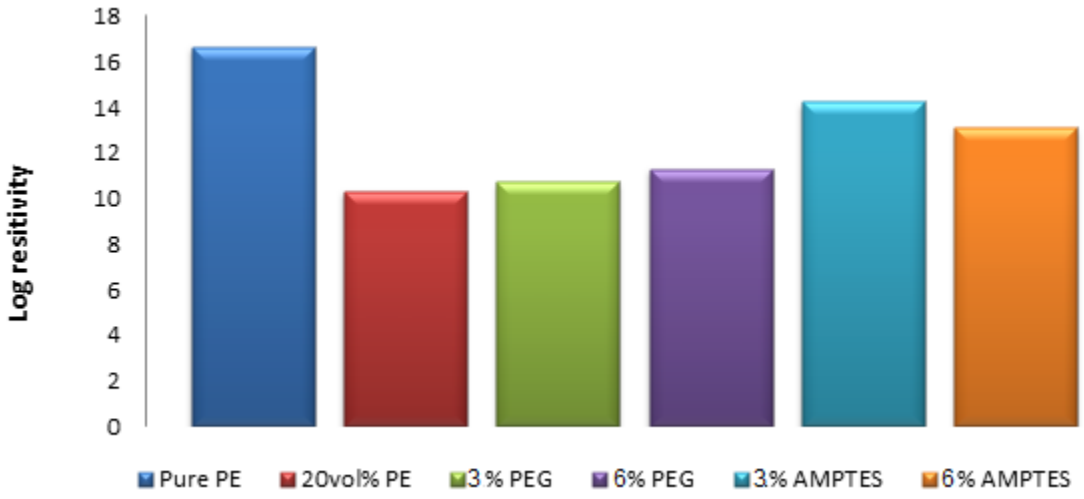


Figure 5. Log resistivity comparison of LLDPE , 20 vol% composites

The mechanical properties of the composites are also reported in Table 1. Tensile strength of LLDPE decreased from 18.3 kg/cm^2 down to 9.9 kg/ cm^{2}with ZnO addition up to 20 % in volume. The elongation at break of the composites with up to 15 % of ZnO were above 1100 %, but it decreased to 12.3 % when 20% ZnO was added. The elastic modulus of the composites increased with ZnO volume fraction. When the surface of ZnO was modified with 3% PEG or 6 % AMPTES both tensile strength and elongation at break was improved. While the elastic modulus was lowered with PEG modification, it was increased with AMPTES modification.

In the present study it was aimed to get statically dissipating material with sufficient mechanical properties. Composite with 20% zinc oxide is statistically dissipating but does not have sufficient tensile strength. Thus ZnO was surface modified with AMPTES and PEG 4000 to make a better dispersion of

ZnO particles at this high loading. However the improvement obtained was not sufficient to make the material to be used in applications where high tensile strength is required. Other modification methods such as treating zinc oxide with AMPTES in toluene [5] or in water in acidic and basic conditions [6] should be used in further studies.

Conclusion

Zinc oxide powder was used to improve the electrical conductivity and mechanical property of the polyethylene matrix composites. To increase the homogeneity of ZnO particle in polyethylene two different modifier AMPTES and PEG 4000 were used with two different percentages 1% and 2%. Rheometer was used to have dispersed polymer composites. 5%, 10%, 15% and 20% ZnO-polyethylene composites were prepared. Only 20% composites were modified with modifiers.

When amount of zinc oxide powders were increased, the density values of the composites were also increased. However the surface modification caused agglomeration of ZnO particles giving hard to grind large particles. This resulted in composites 2-3 % empty volume. Unmodified zinc oxide and modified ZnO did not have a significant effect on contact angle of composites. Addition of AMPTES and PEG 4000 modifiers did not also improved significantly the mechanical properties on contrary to expectations. This was caused by the agglomeration formation during surface modification of zinc oxide.

The electrical conductivity of the composites increased from insulating to statistically dissipating material by addition of conducting ZnO. When the surface of ZnO was modified with 3% PEG or 6 % AMPTES both tensile strength and elongation at break was improved. While the elastic modulus was lowered with PEG modification, it was increased with AMPTES modification. Further studies on ZnO surface modification should be made to improve electrical and mechanical properties.

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RESEARCH ON DRUG RELEASE PERFORMANCE OF HYDROXYAPATITE-GELATIN COMPOSITES PRODUCED IN SBF MEDIUM

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Abstract: In most of drug treatments, initial burst releases from drug release systems can cause side effects. It is possible to limit these effects by applying drug carriers that provides controlled relase of the drugs. In this study, hydroxyapatite-gelatin composites are produced in the presence of SBF (Simulated Body Fluid) and spray dryer is used for obtaining drug loaded composites. Composites are produced by wet precipitation method at pH 7.4 and 37°C implementing glutaraldehyde (GA) as a cross-linking agent. By running experiments with different amounts of gelatin and glutaraldehyde, their effects on encapsulation efficiency and drug release profiles are studied. Drug encapsulation experiments are performed with 5-Fluorouracil (5-FU) as a selected drug. Drug loading process is performed by using spray drier with an inlet temperature of 80°C and feed rate of 5 ml/min. Drug release of 5-FU from the HAp-GEL comosites are determined in phosphate buffer solution (PBS) at pH 7.4 and 37°C. Different mathematical models are used to obtain release mechanism of the drug. Compites are analyzed by XRD, FTIR, SEM and TGA to observe morphology and structure. It is concluded that drug loaded HAp-GEL composites can be used in drug delivery applications.

Keywords : Hydroxyapatite, gelatin, drug release, composite, polymer

Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is a bioseramic material found in bone and teeth composition which has apatite-like structure [1]. In spite of its biocompatibility, bioactivity and nontoxicity, hydroxyapatite has been used for sentetic bone material production, bone and teeth implants and drug delivery applications [2]. However, highly fragile and hard structure of hydroxyapatite limited its usage in clinical applications [3]. The mechanical disadvantages of hydroxyapatite can be overcomed by using a polymer in order to produce a hydroxyapatite-polymer composite. In recent years, studies aiming to use ceramic/polymer materials as drug carrier have gained importance. By adding biodegradable polymers with different degradation rate and mechanism to ceramic materials, variety of release profiles can be obtained. One of the polymers used in drug release systems is gelatin which can be used alone or constituent of a composite. Gelatin is obtained by partial hydrolysis of collagen and widely used in food and medicine. Not only being biocompatible, biodegradable and nontoxic, but also economic made gelatin a preferable polymer in drug release studies [4]. In addition, gelatin has an efficient sweelling-releasing characteristic, does not produce antigen and does not have a negative effect on cell viability [3]. In the current study, hydroxyapatite-gelatin (HAp-GEL) composites are produced in the presence of SBF (Simulated Body Fluid) and spray dryer is used for obtaining drug loaded composites. 5-FU, which is widely used for the treatment of colon, rectal, breast, ovary, pancreas, stomach, brain and skin cancer, is selected as drug [5]. Composites are produced by wet precipitation method implementing glutaraldehyde (GA) as a cross-linking agent. By running experiments with different amounts of gelatin and

glutaraldehyde, their effects on encapsulation efficiency and drug release profiles are studied. Drug encapsulation experiments are performed with 5-FU as a selected drug. Drug release profiles are evaluated according to four different kinetic models including Zero Order, First Order, Higuchi and Korsmeyer-Peppas. The obtained composites are characterized by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Thermogravimetric Analysis (TGA) and X-Ray Diffraction (XRD).

Materials

Materials used for HAp-GEL composites preparation including gelatine, calcium hydroxide ($Ca(OH)_2$, %96), phosphoric acid (H_3PO_4 , %85) and gluteraldehyde were purchased from Merck. Reactants used for SBF preparation are listed in Table 1. Sodium chloride (NaCl), sodium hydrogen carbonate ($NaHCO_3$), potassium chloride (KCl), di-potassium hydrogen phosphate trihydrate ($K_2HPO_4.3H_2O$), magnesium chloride hexahydrate ($MgCl_2.6H_2O$), calcium chloride ($CaCl_2$), sodium sulfate (Na_2SO_4) and hydrochloric acid (HCl) were obtained from Merck and tris (hydroxymethyl) aminomethane ($(CH_2OH)_3CNH_2$) was provided from Sigma. Potassium phosphate dibasic (K_2HPO_4) and potassium phosphate monobasic (KH_2PO_4) which were used for PBS preparation were obtained from Merck and Carlo Erba respectively.

Methods

In order to obtain SBF, reactants in Table 1 were added to 750 ml deionized water in the given order and dissolved under constant stirring at 37°C. To prevent instant pH increase, $(CH_2OH)_3CNH_2$ was dissolved slowly. Following the addition of reactants, 1 M HCl was used for pH adjustment to 7.4. Solution was rested for 1 day and completed to 1 L afterwards.

Table 1. Reactants used for SBF preparation

Reactant	Quantity
NaCl	7,996 g.
$NaHCO_3$	0,350 g.
KCl	0,224 g.
$K_2HPO_4.3H_2O$	0,228 g.
$MgCl_2.6H_2O$	0,305 g.
1M HCl	40 ml
$CaCl_2$	0,278 g.
Na_2SO_4	0,071 g.
$(CH_2OH)_3CNH_2$	6,057 g.

80.2 ml 1 M K_2HPO_4 and 19.8 ml 1 M KH_2PO_4 were prepared and mixed to prepare PBS solution. The mixture was completed to 1 L with deionized water and adjusted to pH 7.4 with 1 M HCl solution. For hydroxyapatite-gelatin composite preparation, $Ca(OH)_2$-SBF and H_3PO_4 (%85)-GEL-SBF solutions were

prepared and mixed for two hours at about 37°C and 400 rpm. H_3PO_4 (%85)-GEL-SBF solution was feeded to $Ca(OH)_2$-SBF with peristaltic pump at a feding rate of 5 ml/min leading to the formation of HAp crystals in the solution. pH was adjusted to 7.4 with 1M NaOH or HCl if necessary. Obtained solution was mixed at 37°C and 400 rpm for another 2 hours and left rested. After 24 hours of aging for the completion of HAp crystals growth, GA-deionized water solution was added to solution for crosslinking. At the end of 3 hours of stirring, solution was filtered and precipitated composites were washed with sodium bisulfate and de-iyonized water several times. Finally, obtained precipitates were dried in incubator at 40°C for 24 hours and collected afterwards. Three different HAp-GEL composites with 1:1, 1:2 and 1:4 HAp/GEL weight ratio were obtained and crosslinked with 2% (v/v) GA-deionized water solution. In order to observe the crosslinking agent effect, one of the composites (HAp-GEL 1:1) was chosen and crosslinked with another GA-deionized water concentration of 5% (v/v). 5-FU loaded HAp-GEL composites were prepared with spray dryer under the operation conditions including 80°C inlet temperature of hot air, 5 ml/min inlet flow of feeding solution and 0,1 MPa atomizer pressure. Inlet solution was prepared by adding 75 mg 5-FU and 3 g composite to 300 ml deionized water respectively.
In order to obtain the encapsulation efficiency, 50 mg drug loaded composites were added to 50 ml deionized water at 37°C while mixing at 250 rpm. After mixing, mixture was filtrated, 1 ml. was taken from the liquid part and diluted to 25 ml with deionized water. Absorbance value of the solution was obtain by Uv-vis (Jenway 6305) spectra and calibration curves was evaluated to calculate the drug concentrations. The same procedure was repeated for HCl and pH 7.4 PBS solvents. In order to obtain the encapsulation efficiency, Equation 1 was used.

$$\text{Encapsulation efficiency (\%)} = \frac{\text{Theorical drug amount}}{\text{Drug amounts in composites}} \text{X100} \qquad (1)$$

In vitro release studies were carried out in shaking water bath at 200 rpm, composites suspended in PBS medium at 37°C and pH 7,4 conditions. At predetermined time intervals samples taken from the solution and centrifuged for several minutes. Each time after removing samples, fresh PBS was added to solution. 5-FU concentration in the release medium was evaluated by UV spectrophotometer at the wavelength of 266 nm in triplicate essays. The crystallinities of the composites were analyzed by X-ray diffraction (XRD) (Bruker D-8 Advance). Thermogravimetric analysis (TGA)(Perkin Elmer Diamond) was performed in order to predict the mass ratio of gelatin content and to observe thermal behaviour of the composites at the temperature interval of 25-550°C. By Fourier transform infrared spectroscopy (FTIR) (Shimadzu), characteristic functional groups were identified in the wavenumber range of 800-4000 . The morphology of the spray-dried HAp-GEL composites with different gelatin and GA content were observed by scanning electron microscopy (SEM).

Results and Discussion

XRD analysis of HAp-GEL composites

The X-ray diffraction patterns of the HAp-GEL composites crooslinked with %2 GA solution are shown in Fig. 1. and XRD patterns of composites crosslinked with different amount of GA (%2 and %5 GA solution) are given in Fig. 2. For all three samples in Fig.1, characteristic HAp peaks were observed confirming the formation of HAp crystals and calcium phosphate phases other than HAp were not detected. Some studies have revealed that increasing gelatin content supresses the growth of HAp crystals and cause XRD peaks with lower intensities [6]. However, Fig. 1 shows that increasing gelatin content does not lead to a distinctive difference of peak intensities in this study.

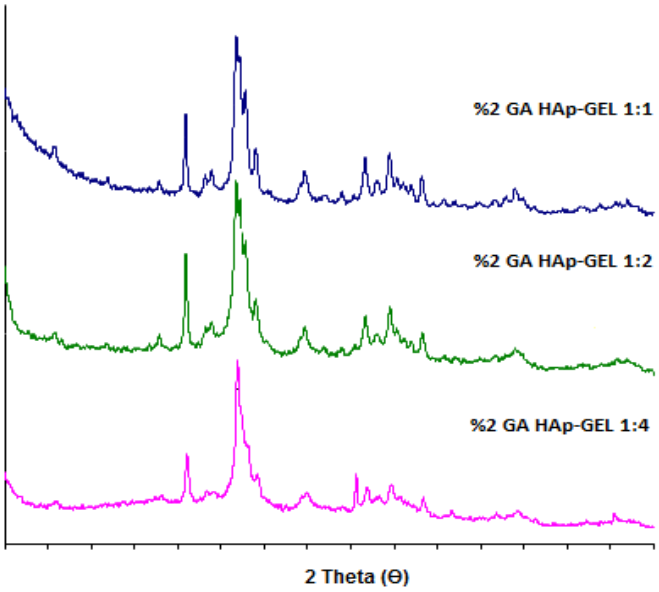


Fig.1. Comparison of XRD patterns of HAp-GEL composites with various HAp/GEL weight ratios

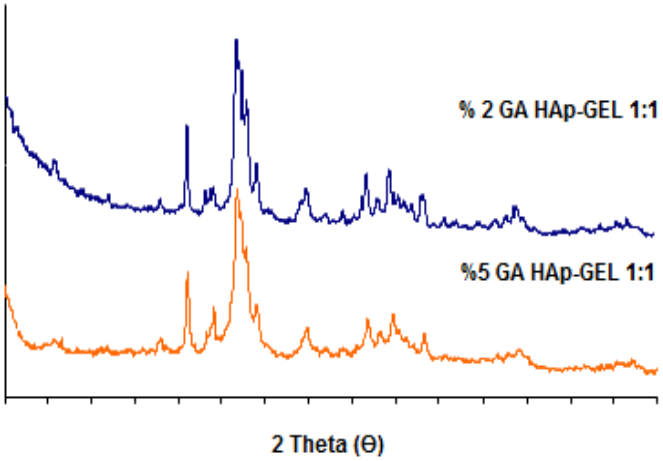


Fig.2. Comparison of XRD patterns of HAp-GEL composites crosslinked with different amount of GA

As seen in both Fig. 1 and Fig.2, composites with different gelatin amounts have similar intensities in their XRD patterns, which proves that gelatin amount do not have a distinctive effect on HAp crystallization size.

TGA analysis of HAp-GEL composites

Fig. 3 illustrates the TGA analysis of HAp-GEL composites with different HAp/GEL weight ratios.From the data in Fig.3., weight loss of the composites increase as the gelatin content increase as expected. However, it is concluded that the actual ratio of HAp-GEL in the composites diverge from the theoretical ratios. In Fig. 4, Theoretical HAp/GEL ratios calculated from the precipitation reactions and the experimental ratios derived from the TGA results are shown comparatively. Experimental values are

calculated approximately by assuming organic phase includes only gelatin while inorganic phase includes hydroxyapatite only and organic phase is completely burnt until the temperature reaches to 550°C.

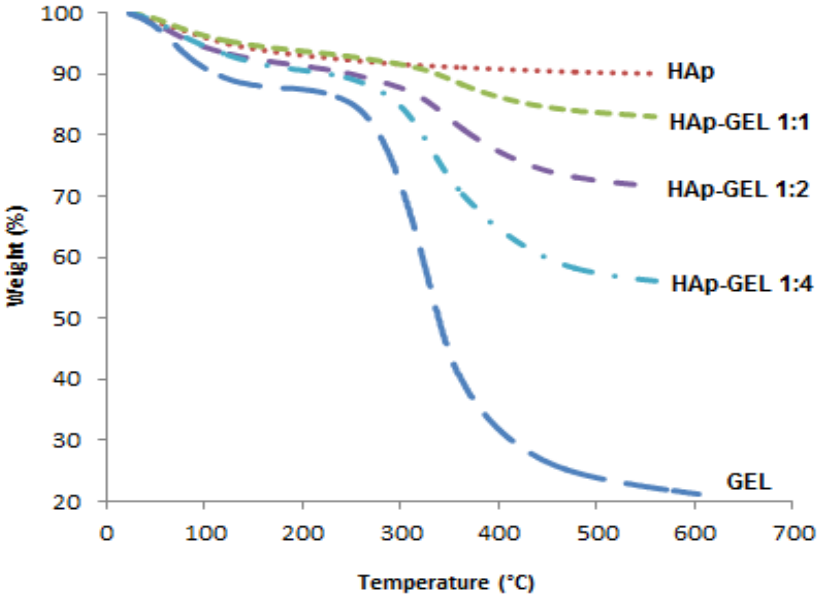


Fig. 3. TGA patterns of HAp-GEL composites, HAp and gelatin

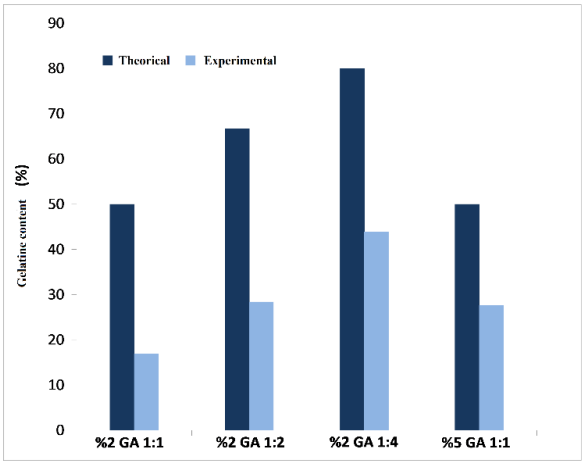


Fig. 4. Comparison of theoretical and experimental weight ratios of HAp/GEL composites

FTIR analysis of HAp-GEL composites

Fig. 5 shows the FTIR patterns of HAp-GEL composites with different HAp/GEL weight ratios. In all three samples, PO_4 bands were observed around 1020 cm^{-1}. 1020,39 cm^{-1}, 1019,42 cm^{-1}, 1020,39 cm^{-1} bands at υ3 mode and 961,56 cm^{-1}, 959,63 cm^{-1}, (950-960) cm^{-1} bands at υ1 mode which determined in HAp-GEL 1:1, HAp-GEL 1:2 and HAp-GEL 1:4 composites respectively are the evidence for the presence of HAp phase. The bands between 3000 cm^{-1} and 3600 cm^{-1} are caused by O-H stretch as well as being one of the characteristic HAp peaks. As the gelatin amount increases, intensities of O-H strecth bands were also increased. Typical H-O-H bands were observed between 3680 cm^{-1} and 3840 cm^{-1}

in all composites, which can be caused by binding energies of free water molecules on HAp surface [6]. 1422,56 cm^{-1} , 1422,56 cm^{-1} , 1416,78 cm^{-1} υ3 vibration bands and 873,79 cm^{-1} , 873,79 cm^{-1} ve 871,86 cm^{-1} υ2 vibration bands seen in HAp-GEL 1:1, HAp-GEL 1:2 and HAp-GEL 1:4 composites respectively are indications of CO_3 ions. As observed in Fig. 5, intensities of υ3 CO_3 bands increase as the gelatin content increase in composites. It is known that in smaller HAp crystals , CO_3 ve H_2O groups can join PO_4 regions more effectively [6]. Also gelatine can limit the growth of HAp crystals by

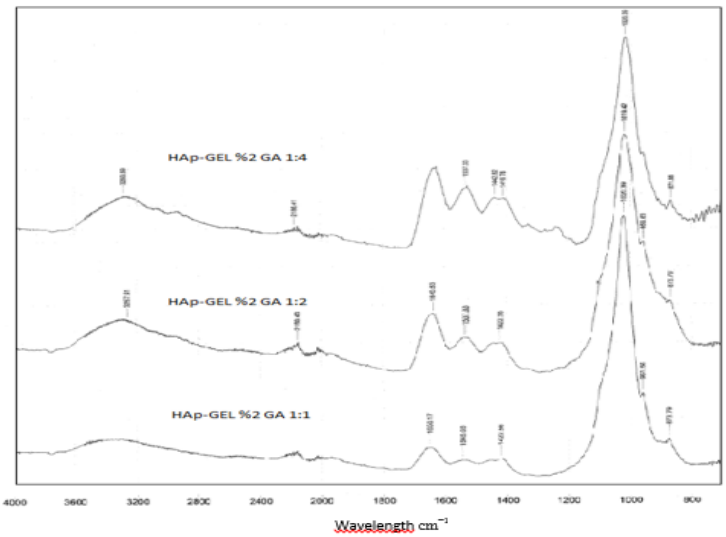


Fig. 5. Comparison of FTIR Spectrums of HAp-GEL composites with various HAp/GEL weight ratios

surrounding them [6], therefore the increase of CO_3 band intensities can be related to formation of smaller HAp crystals at higher gelatine contents. Amide I and amide II bands are observed in between 1600-1700 cm^{-1} and 1500-1600 cm^{-1} band gap respectively. Amide bands shows an increase in intensity with increasing gelatine amount which can be interpreted as higher organic-inorganic interaction. Existing peaks between 1200 cm^{-1} and 1300 cm^{-1} at higher gelatine containing composites can be related to P-O-H stretches, reflecting the organic conection between HAp and gelatin phases. On the other hand, peaks shown at 1345 cm^{-1} were confirmed to be caused by the interaction of Ca ions from HAp and COO- groups from gelatin [7]. For this reason, peaks between 1200-1300 cm^{-1} bands can be sign of Ca-COO bondings. In all composites, peaks that can be related to C-H bondings were formed between 2000 cm^{-1} and 2400 cm^{-1} band gap. These peaks can be formed between gelatin and amino acid chains by GA molecules, as C_3H_3 molecules occuring as a result of crosslinking reactions can be the source of C-H bondings.

EDS analysis of drug loaded HAp-GEL composites

EDS analysis and Ca/P ratios of HAp-GEL composites are given in Fig. 6 and Table 2 respectively. It is observed that Ca/P ratio increases with increasing gelatin content and decrease with increasing crosslinking agent content. The Ca/P ratio of 1,67 which is the Ca/P ratio of pure hydroxyapatite were not obtained in produced composites [8]. This can be caused by production in SBF medium, as it is known that calcium phosphate precipitation in SBF medium can be similar with biological mineralization, leading to non-stoichiometric ratios of Ca/P [9]. During precipitation reactions in production steps, different calcium phosphate compounds can occur and cause various Ca/P ratios. Ph change in production steps can be the reason occuring different calcium phosphate compounds [9].

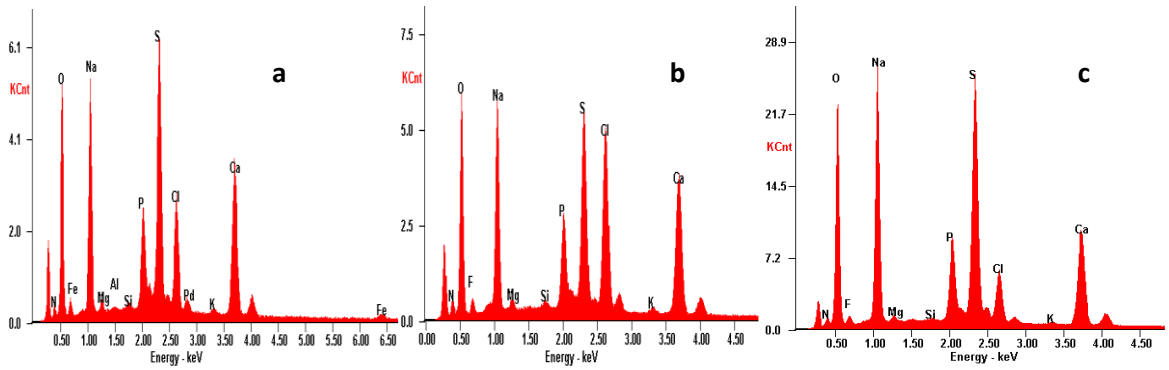


Fig. 6 EDS analysis of HAp-GEL composites (a)%2 GA HAp-GEL-5-FU 1:1, b) %2 GA HAp-GEL-5-FU 1:2, c) %5 GA HAp-GEL-5-FU 1:1.

SEM analysis of drug loaded HAp-GEL composites

SEM analysis of drug loaded HAp-GEL composites are illustrated in Fig. 7. In all composites, drug loaded spherical particules are observed. However, similar to pure gelatine morphology, adjacent spherical particules are also observed. Agglomerated irregular shapes can be caused by impurities [10]. In general, a regular particule size distribution was not observed.

Encapsulation efficiencies of drug loaded HAp-GEL composites

Encapsulation efficiencies of HAp-GEL composites loaded by absorption method are illustrated in Table 3. In all composites, drug loading efficiencies are observed to be higher in asidic media. Among the %2 GA crosslinked composites, HAp-GEL 1:2 shows the highest efficiencies in each media. In addition, drug loading efficiency increase as the GA amount increase.

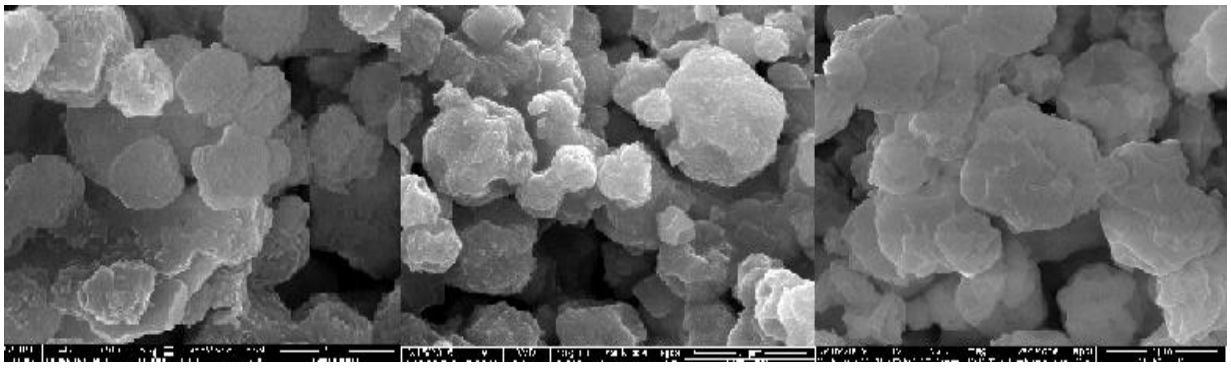


Fig. 7. a) %2 GA HAp-GEL 1:1, b) %2 GA HAp-GEL 1:2, c) %5 GA HAp-GEL 1:1

Table 2. Ca/P ratios of various HAp-GEL composites

Samples	Ca/P ratio
%2 GA HAp-GEL 1:1	1,88
%2 GA HAp-GEL 1:2	1,91
%5 GA HAp-GEL 1:1	1,49

Table 3. Encapsulation efficiencies of HAp-GEL composites loaded by absorption method

Samples	Deionized water (%)	HCl (%)	PBS (%)
%2 GA HAp-GEL 1:1	2,82	5,16	2,37
%2 GA HAp-GEL 1:2	3,88	7,79	3,05
%2 GA HAp-GEL 1:4	2,49	3,51	2,26
%5 GA HAp-GEL 1:1	3,75	6,01	3,62

Table 4. Encapsulation efficiencies of HAp-GEL composites loaded with spray dryer

Samples	Deionized water (%)	HCl (%)	PBS (%)
%2 GA HAp-GEL 1:1	308,01	264,73	215,00
%2 GA HAp-GEL 1:2	428,26	399,67	278,00
%2 GA HAp-GEL 1:4	175,67	178,80	166,70
%5 GA HAp-GEL 1:1	379,25	308,01	307,50

Encapsulation efficiencies of HAp-GEL composites loaded with spray dryer are illustrated in Table 4.
In all composites, drug loading efficiencies are observed to be higher in deionized water media. As in absorption method, %2 GA HAp-GEL 1:2 shows the highest efficiencies in each media and drug loading efficiency increase as the GA amount increase.

Drug release profiles of HAp-GEL composites

Drug release profiles of HAp-GEL composites loaded by spray dryer are evaluated for four different kinetic models. In Fig. 8, drug release profiles of %2 GA HAp-GEL 1:1, %2 GA HAp-GEL 1:2 and %2 GA HAp-GEL 1:4 composites evaulated against Zero Order, First Order, Higuchi and Korsmeyer-Peppas kinetic models are illustrated. As seen in Fig. 8, biphasic release profile is observed in all composites and initial burst is increased as the gelatin content increases. Initial burst increase with polymer content can be related to polar nature of 5-FU and HAp [1]. In this study, water solvent used during 5-FU loading with spray dryer may cause the 5-FU and HAp molecules to be accumulated on the composite surface. In composites with more HAp content, Hap molecules may have substituted the 5-FU molecules which are closer to the surface. It is known that initial burst cause side effects in the body and decrease the effectiveness of drugs [1]. For this reason, composites with less gelatin content can be more appropriate for drug release applications.

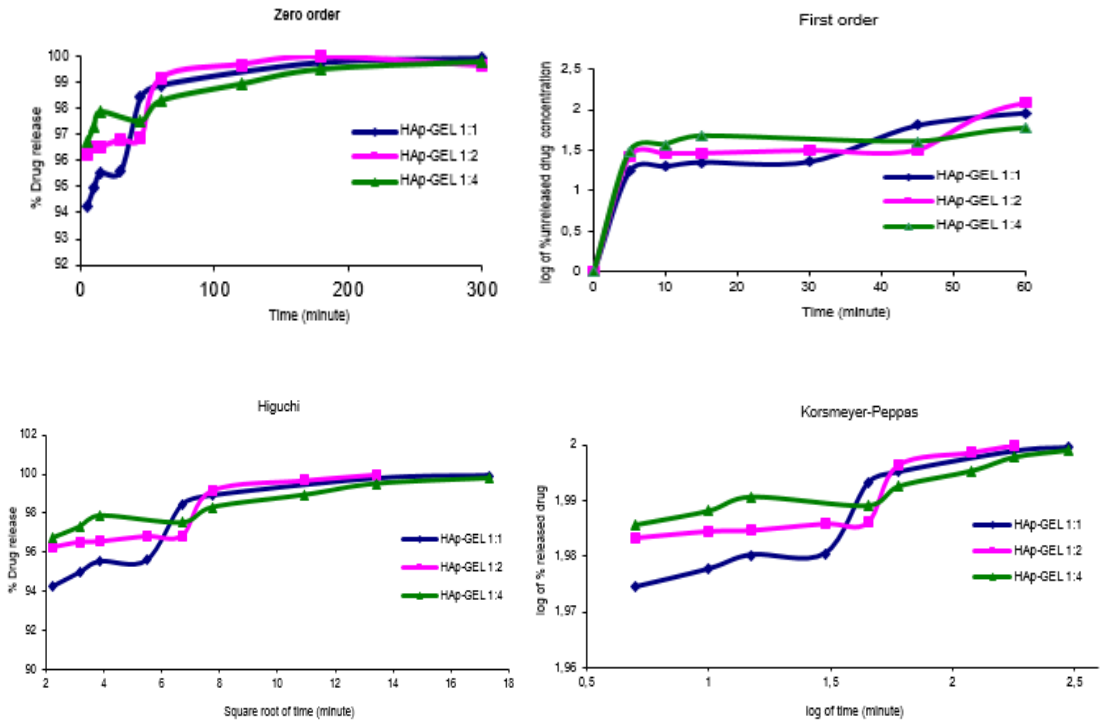


Fig. 8. Drug release profiles of %2 GA HAp-GEL(1:1, 1:2, 1:4) composites

In Table 5, drug release rates of the HAp-GEL composites are given. It is observed that total release rate is decreasing with increasing gelatine content, as opposed to initial burst values. It is thought that drug release is occured in a way of absorption of PBS through composite pores, dissolving of drugs in PBS and release of drug with PBS through composite pores. High HAp content may speed up the absorption of PBS through the pores and decomposition of gelatin, therefore accelerating the drug release. In addition, polar HAp molecules can pull the water molecules inside the composite pores speed up the polymer degradation. In Fig. 9, drug release profiles of %2 GA HAp-GEL 1:1, and %5 GA HAp-GEL 1:1 composites evaulated against Zero Order, First Order, Higuchi and Korsmeyer-Peppas kinetic models are illustrated.

Table 5. Drug release rate of HAp-GEL composites

Sample	Release rate (%release/hour)
%2 GA HAp-GEL 1:1	1,35
%2 GA HAp-GEL 1:2	0,89
%2 GA HAp-GEL 1:4	0,73
%5 GA HAp-GEL 1:1	1,19

As seen in Fig. 9, initial burst increases as the GA content increases. It was reported that increasing crosslinking agent amount decrease the initial burst as the crosslinking strengthen the polymeric bonds and cause the drug to be released slower [11, 12]. However, in this study it is concluded that crosslinking agent amount affects also polymer content in the composites. In TGA analysis, different gelatin content is observed in %2 GA HAp-GEL 1:1 and %5 GA HAp-GEL 1:1 to composites. This can lead gelatine's effect to overcome GA's effect on drug release rate.

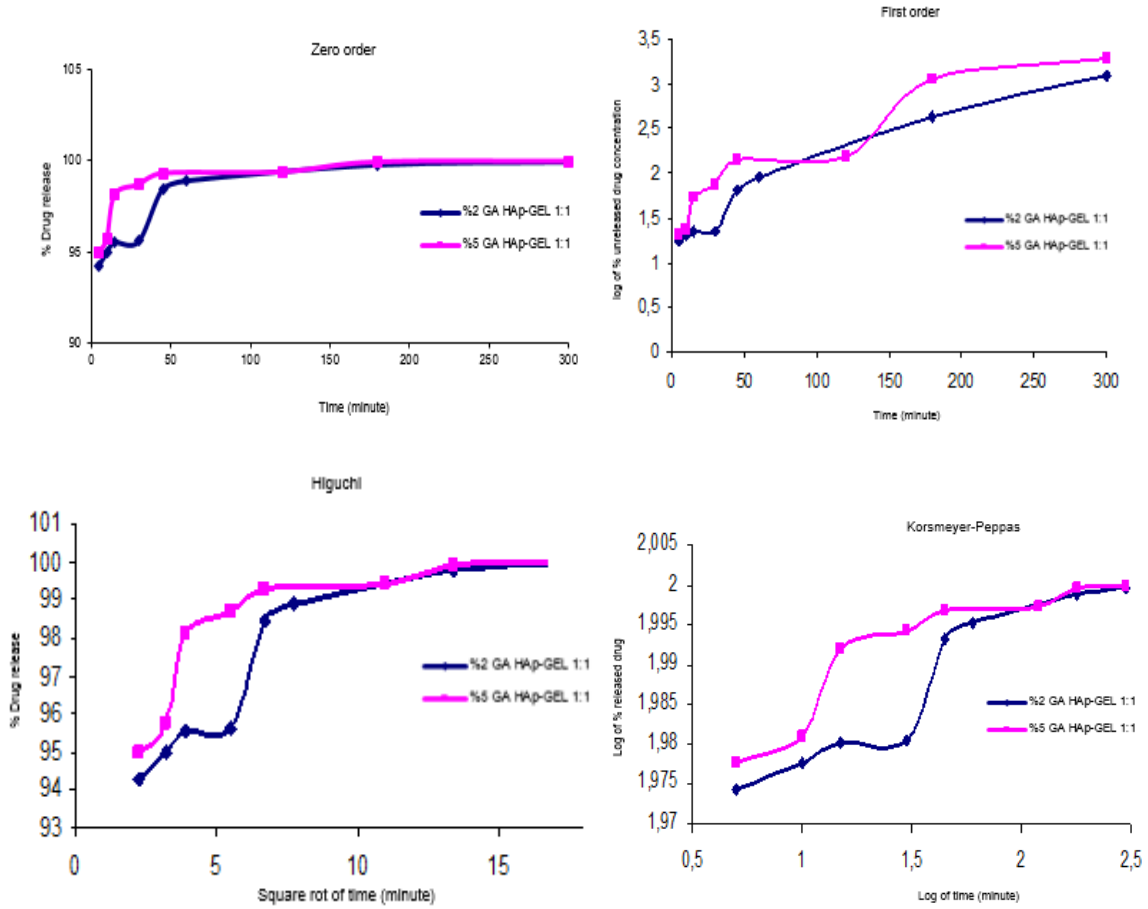


Fig. 9. Drug release profiles of %2 GA HAp-GEL(1:1, 1:2, 1:4) composites

Conclusion

Current study focused on production of HAp-GEL composites in the presence of SBF, 5-FU loading via spray dryer, observing encapsulating efficiency and evaluating drug release mechanism. To understand the effect of HAp/GEL weight ratio and GA amount on encapsulation efficiency and drug relase mechanism, different weight ratios and GA amounts are selected. The produced composites show higher encapsulation efficiencies with spray dryer as opposed to loading with absorption method. As a result of drug relase studies, it is determined that initial burst values are affected by the gelatin content of composites. High initial burst values are observed with greater gelatin content. However, total release rate decreases as the gelatin content increases. Considering GA, it is observed that initial burst values increase with increasing GA amounts. Among the four studied kinetic models, produced HAp-GEL composites fit best to first order kinetic model.

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EFFECTS OF PROCCESSING PARAMETERS AND MATERIAL COMPOSITION ON THE PROPERTIES OF PP COMPOUNDS

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ÖZET

Son yıllarda artan çevresel duyarlılık, gelecek için öngörülen düşük CO_2 emisyon hedefleri ve yakıt tasarrufu gibi ekonomik kaygılar otomotiv imalatçılarını daha hafif araçlar üretmeye itmektedir [1,14]. Bu kapsamda gerek metallere göre daha hafif olmaları gerekse ucuz olmaları sebebi ile otomotiv içerisinde polimer malzemelerin kullanım alanları gün geçtikçe artmaktadır. Polipropilen ve polietilen gibi polyolefinler, güçlü mekanik özellikleri, kolay proses edilebilirlikleri ve düşük yoğunluklu olmaları sebebi ile otomotivde kullanılan polimerler arasında önemli bir paya sahiptir [3,4,6]. Polyolefinler genellikle katkısız olarak kullanıldıklarında düşük fiziksel, mekanik ve termal özelliklere sahip olurlar. Bununla birlikte göreceli ucuz da değillerdir. Bu yüzden polyolefinler fiziksel, mekanik ve termal özelliklerin iyileşmesi ve aynı zamanda ucuzlatma sağlamak için hammadde üreticilerince genellikle katkılı olarak üretilirler. Son zamanlarda polyolefin malzeme üreticileri arasında artan trend daha az katkı oranlarında aynı fiziksel, mekanik ve termal özelliklerin sağlanabildiği ve dolayısıyla daha az yoğunluklu malzemelerin üretimidir [2,5,7,8,9,10,11,12]. Bu malzemelerin laboratuvar ortamından sanayiye taşınması için farklı proses parametrelerinin ya da farklı katkıların son ürüne etkisinin bilinmesi ciddi önem arz etmektedir [15,16,17,18].

Bu sebeple bu çalışmada araç hafifletme ve ucuzlatma hedefi kapsamında tampon, rüzgarlık, bagaj paneli gibi yüksek hacimli araç dış trim parçalarında mevcutta yoğun kullanım alanı bulan yüksek talk katkılı polipropilen bazlı hammaddelerde daha düşük talk oranı ile ya da nonokil katkısı ile aynı özelliklerin elde edilip edilemeyeceği incelenmiştir.

ABSTRACT

In recent years, increasing environmental sensitivity, low CO2 emission targets and economic concerns such as fuel economy have pushed automotive manufacturers to produce lighter vehicles [1,14]. In this context, being lighter and cheaper than metal have increased the usage areas of polymer materials in automotive industry day by day. Polyolefins such as polypropylene and polyethylene have a significant share among automotive polymers due to their strong mechanical properties, easy processability and low density. Polyolefins generally have low physical, mechanical and thermal properties when used without additives [3,4,6]. Moreover, they are relatively not inexpensive. Due to this reason, by raw material producers, polyolefins are mostly produced with cheaper additives which also improve their physical, mechanical and thermal properties. The recent increasing trend amongst polyolefin material manufacturers is the production of less dense materials with the same physical, mechanical and thermal properties at lower add-on rates [2,5,7,8,9,10,11,12]. It has crutial importance to know the effect of different process parameters or different additives on the final product in order to transfer these materials from the laboratory environment to the industrial applications [15,16,17,18].

For this reason, in this study it has been investigated whether the same characteristics can be achieved with low talc content or with nanoclay additive instead of high-talc-doped polypropylene-based raw

materials that are used now in serial productions of some big-size exterior trim parts such as bumpers, spoilers and trunk pannels.

MATERIAL AND METHOD

A kind of polypropylene (PP) copolymer T30 with 30% talc content which is commercially available and being used for the productions of exterior automotive parts for years was taken as a first and reference material. Then, two different PP copolymer B30 with %30 and B20 with %20 talc content were taken as alternatives. These two alternative materials are still under development and never used for the production of any exterior trim part in automotive industry. So, their process behaviours are unknown.
These 3 materials were molded at different mold temperatures and different barrel temperatures by an injection machine to investigate the effects of process parameters on the mechanical and thermal properties.
Moreover, it was aimed to investigate the effect of different additive ratios on mechanical and thermal properties with addition of 1wt.%, 3wt.% and 5wt.% nanoclay in 20wt.% talc filled polypropylene by Twin Screw Extruder. Then, these nanocomposites were molded at fixed mold temperature and barrel temperatures by an injection machine.
All the samples were characterized physically, mechanically and thermally by several techniques which are Thermogravometric Analysis (TGA), Melt Flow Index (MFI), Tensile Test, Bending Test, Izod and Charpy Impact Test, Heat Deflection Temperature (HDT) and Vicat Softening Point (VST), Differential Scanning Calorimeter (DSC), X-Ray Diffraction (XRD).

RESULTS

Effects of Different Talc Content

S1, S2 and S3 samples were injected from different materials T30, B30 and B20 respectively by a fixed mold temperature (15°C) and barrel temperature (200°C-210°C -220°C -225°C -230°C) and subjected to MFI, TGA, tensile, 3 point bending , impact, HDT – VST, DSC analyses in order to determine how different talc content affected to their mechanical and thermal behaviors.

Comparison of MFI results

#	Material	Talc Content (wt.%.)	MFI (g/10min)
S1	T30	30	15
S2	B30	30	20
S3	B20	20	23

Comparison of TGA results

#	Weight loss (%) between 250-550°C
S1	66
S2	65
S3	75

Comparison of DSC analysis

#	T_m (°C)	T_c (°C)	ΔH_m J/g	X_m (%)	ΔH_c J/g	X_c (%)
S1	165,2	130,1	17,5	6	21,0	7
S2	163,5	130,9	31,0	10	36,0	11
S3	164,3	132,5	22,0	8	26,7	10

Comparison of Tensile and Flexural properties

#	T. Strength (σ_m) (MPa)	F. Strength (σ_{fM}) (MPa)	T. Modulus (E_t) (MPa)	F. Modulus (E_f) (MPa)
S1	20	32	2670	2670
S2	24	38	3250	3020
S3	26	39	3000	2790

Comparison of Impact Properties

#	Notched Izod Impact (kJ/m²)	Notched Charpy Impact (kJ/m²)
S1	20	21
S2	12	10
S3	9	8

Comparison of Softening Points

#	HDT-B (°C)	VICAT-B (°C)
S1	112	142
S2	118	146
S3	114	145

Effects of Different Mold Temperatures

Samples which were injected with different mold temperatures were subjected to tensile, 3 point bending , impact, HDT – VST and DSC analyses in order to determine how different mold temperatures affected to their mechanical and thermal behaviors.

#	Material	Mold Temperature (°C)
S1	T30	15°C
S16	T30	50°C
S17	T30	80°C
S2	B30	15°C
S4	B30	50°C
S6	B30	80°C
S3	B20	15°C
S5	B20	50°C
S7	B20	80°C

Comparison of DSC Analysis

#	T_m (°C)	T_c (°C)	ΔH_m J/g	X_m (%)	ΔH_c J/g	X_c (%)
S1	165,2	130,1	17,5	6	21,0	7
S16	164,6	130,3	42,4	14	48,2	15
S17	163,0	130,3	62,0	20	71,5	23
S2	163,5	130,9	31,0	10	36,0	11
S4	164,5	130,3	27,0	8	32,7	10
S6	163,9	130,4	25,1	8	30,0	9
S3	164,3	132,5	22,0	8	26,7	10
S5	164,5	133,2	29,3	11	36,5	13
S7	164,1	131,8	26,2	9	31,2	11

Comparison of Tensile and Flexural Properties

#	T. Strength (σ_m) (MPa)	F. Strength (σ_{fM}) (MPa)	T. Modulus (E_t) (MPa)	F. Modulus (E_f) (MPa)
S1	20	32	2670	2670
S16	20	32	2740	2650
S17	20	31	2750	2650
S2	24	38	3250	3020
S4	24	35	3260	2830
S6	23	38	3230	3090
S3	26	39	3000	2790
S5	25	38	3000	2730
S7	25	37	3000	2610

Comparison of Impact Properties

#	Notched Izod Impact (kJ/m²)	Notched Charpy Impact (kJ/m²)
S1	20	21
S16	18	19
S17	16	16
S2	12	10
S4	11	9
S6	11	9
S3	9	8
S5	9	9
S7	9	8

Comparison of Softening Points

#	HDT-B (°C)	VICAT-B (°C)
S1	112	142
S16	116	142
S17	117	142
S2	118	146
S4	116	148
S6	114	147
S3	114	145
S5	110	145
S7	111	141

Effects of Different Barrel Temperatures

Samples which were injected from material B20 with different barrel temperatures were subjected to tensile, 3 point bending , impact, HDT – VST and DSC analyses in order to determine how different barrel temperatures affected to their mechanical and thermal behaviors.

#	Material	Barrel Temperature (°C)
S10	B30	185-195-205-210-215
S2	B30	200-210-220-225-230
S8	B30	215-225-235-240-245
S11	B20	185-195-205-210-215
S3	B20	200-210-220-225-230
S9	B20	215-225-235-240-245

Comparison of DSC analysis

#	T_m (°C)	T_c (°C)	ΔH_m J/g	X_m (%)	ΔH_c J/g	X_c (%)
S10	163,5	131,4	23,4	7	25,3	8
S2	163,5	130,9	31,0	10	36,0	11
S8	163,8	133,5	41,3	13	48,9	15
S11	162,6	131,0	17,6	6	23,3	8
S3	164,3	132,5	22,0	8	26,7	10
S9	165,2	132,2	20,6	7	24,3	9

Comparison of Tensile and Flexural Properties

#	T. Strength (σ_m) (MPa)	F. Strength (σ_{fM}) (MPa)	T. Modulus (E_t) (MPa)	F. Modulus (E_f) (MPa)
S10	24	39	3190	3070
S2	24	38	3250	3020
S8	23	36	3040	2830
S11	25	38	2900	2670
S3	26	39	3000	2790
S9	25	38	2940	2680

Comparison of Impact Properties

#	Notched Izod Impact (kJ/m²)	Notched Charpy Impact (kJ/m²)
S10	14	11
S2	12	10
S8	13	12
S11	10	10
S3	9	8
S9	9	8

Comparison of Softening points

#	HDT-B (°C)	VICAT-B (°C)
S10	112	147
S2	118	146
S8	116	146
S11	108	145
S3	114	145
S9	119	144

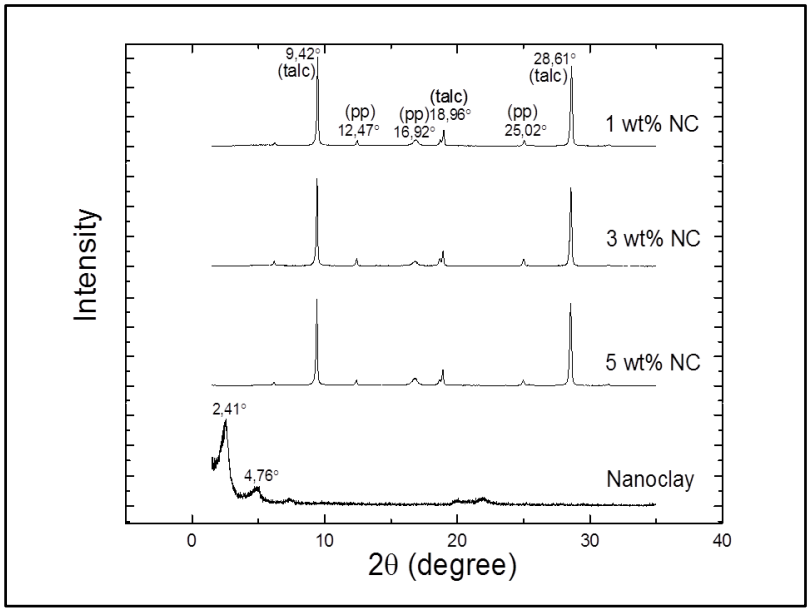
Effects of Nanoclay Addition

Samples S12, S13, S14, S15 which were prepared as compounds of B20 material with different nanoclay contents respectively 0 wt.%, 1 wt.%, 3 wt.% and 5 wt.% by Twin Screw Extruder , then injected by fixed mold temperature (15°C) and barrel temperature (200-210-220-225-230), were subjected to MFI, XRD, tensile, 3 point bending , impact, HDT – VST and DSC analyses in order to determine how different nanoclay contents affected to their mechanical and thermal behaviors.

Comparison of MFI results

#	MFI (g/10min)
S15	17
S12	18
S13	19
S14	18

Comparison of XRD results



Comparison of DSC Analysis

#	T_m (°C)	T_c (°C)	ΔH_m J/g	X_m (%)	ΔH_c J/g	X_c (%)
S15	164,5	128,5	16,0	6	17,8	6
S12	163,8	129,2	32,8	12	40,4	15
S13	164,6	128,7	25,3	9	29,7	11
S14	164,4	130,1	31,4	11	36,0	13

Comparison of Tensile and Flexural Properties

#	(σ_m) (MPa)	F. Strength (σ_{fM}) (MPa)	T. Modulus (E_t) (MPa)	F. Modulus (E_f) (MPa)
S10	23	35	2540	2400
S2	25	38	2780	2700
S3	24	37	2810	2590
S9	26	38	2960	2610

Comparison of Impact Properties

#	Notched Izod Impact (kJ/m²)	Notched Charpy Impact (kJ/m²)
S15	8	8
S12	10	9
S13	10	9
S14	10	9

Comparison of Softening Points

#	HDT-B (°C)	VICAT-B (°C)
S15	97	139
S12	104	144
S13	95	142
S14	112	146

Discussions and Recommendations

By comparing the effects of talc content on PP compounds, it was found that talc addition decreased the MFI so the material's easy to processability but increased the degree of crystallinity due to talc's tendency to act as a nucleating agent and to promote nucleation. Talc content also expanded the modulus so the

stiffness due to talc's platy structure which had tendency to orient flow direction during injection. Moreover, talc addition decreased the impact resistance.
Mold temperature changes affected the materials which have higher molecular weight more than the lower ones because it caused an extension on mobility of the molecules. During injection, higher mold temperature supplied more time to material to get in an ordered from, so crystallinity values also swelled by mold temperature On strength and modulus values, any obvious effect of mold temperature was observed. On impact resistance, a reduction was observed by mold temperature most probably due to the raise on degree of crystallization.
Barrel temperature changes diminished the materials viscosity so slight increase wasobserved on degree of crystallinity values. On strength and modulus values, effects of barrel temperature was not so obvious but their impact resistances reduced most probably due to the increase on degree of crystallization
PP compound including %20 talc content also extruded in a TSE with different nanoclay contents (0 wt.%, 1 wt.%, 3 wt.%, 5 wt.%). XRD results showed that most probably due to the surface modification of nanoclay any agglomeration of nanoclay was observed in PP matrix. In a contrast with literature, nanoclay addition extended MFI An interaction may be occured between the polymer matrix and the surfactants of the nanoclay or clay particles have disturbed chain entanglemenents by high aspect ratio of clay layers. DSC analyses show that nanoclay addition increased the degree of crystallinity by nearly 50% due to the nucleation effect of nanoclay. The melting temperature (T_m) remained nearly unaltered after the addition of nanoclay, which means that the crystal size of PP did not change. Nanoclay also had a positive effect on stiffness , ultimate strength and impact resistance but obtained impact resistance values are still not sufficient for a material that became a canditate for an extrior automotive part

CONCLUSION

Using lower talc contents of PP compounds on exterior automotive parts could benefit weight reduction, cost reduction and process efficiency but lower impact resistance than requirement could be risky for final product / automobile tests. Process paramaters could have positive effects but could not be sufficient. Further studies in order to increase impact resistance could be performed first at compounding phase like impact modifiers addition or any other nano filler addition.

FOREWORD

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GERİ DÖNÜŞÜM CAM ELYAF TAKVİYELİ POLİMER (CTP) ATIK ORANININ SICAK PRES KALIPLAMA BİLEŞİMİNİN (BMC) MEKANİK ÖZELLİKLERİNE ETKİLERİNİN İNCELENMESİ

INVESTIGATION OF THE EFFECTS OF RECYCLED GLASS FIBER REINFORCED POLYMER (GFRP) WASTE RATIO ON MECHANICAL PROPERTIES OF BULK MOULDING COMPOUND (BMC)

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Özet

Bu çalışmada, termoset esaslı cam elyaf takviyeli polimer (CTP) plakaların mekanik geri kazanımı işlemi ve tekrar kullanımı araştırılmıştır. Geri dönüşüm ürünleri kütlesel olarak % 4, 8, 12, 16 oranlarında sıcak pres kalıplama bileşiminde (BMC) orijinal fiberlerin yerine kullanılmıştır. Geri dönüşüm cam fiber içeren numunelerin çekme test sonuçlarındaki düşme miktarı, referans numune ile karşılaştırıldığında %5'in altında kalmıştır. %4 geri dönüşüm içeren numunenin en düşük eğilme dayanımına sahip olduğu gözlenmiştir. Kütlece % 8, 12, 16 geri dönüşüm takviyeli numunelerin eğilme test sonuçları ise, referans numune ile kıyaslandığında eğilme özelliklerinde düşme miktarları %10-12 civarında belirlenmiştir. Kütlece %4 geri dönüşüm ürünü içeren numune hariç, diğer numuneler kabul edilebilir mekanik performans göstermiştir.

Anahtar kelimeler: Mekanik geri dönüşüm, cam elyaf takviyeli polimer (CTP), sıcak pres kalıplama bileşimi (BMC)

Abstract

Sheet Molding Compound (SMC) and Bulk Molding Compound (BMC) composite manufacturers are making the highest volume consuming products in the automotive industry. SMC and BMC production lines constitute 6% of total composite production volume in Turkey and 20% of total production volume in Europe. This data shows that SMC and BMC manufacturers should increase their market shares and production capacities in Turkey in the near future. Increased production capacity will lead to an increase in raw material and energy costs. In this study, it was aimed to obtain recycled thermoset glass fiber reinforced polymer (GFRP) materials known with grain size and chemical content which were a result of mechanical recycling process from GFRP wastes, and evaluate these qualified recycled materials in the sustainable quality of the molding for the production of composite parts in BMC dough.

Mechanical recycling of GFRP waste materials was conducted by a laboratory-type cutting-mill recycling machine. The virgin glass fibers with an average size of 12 mm were used in the BMC prescription.

Recycling products were classified through 11.7, 9.5, 6.7, 5.6, 4, 3.35, 2 and 1 mm sieves. Recycled products having sizes of 1 mm, 2 mm and 3.35 mm with a weight of 36%, 18% and 16% constitute 70% of the total product mass. The average particle size distribution of 1 kg of recycled products was calculated from three samples. The average size of the coarse recycled glass fibers is 3 mm. The heat treatment process was carried out on the recycled glass fibers in order to determine the resin content on the fibers. The chemical content of recycled GFRP products was determined by Fourier Transform Infrared spectroscopy (FTIR) analysis. The recycled glass fibers, were used by 4, 8, 12, and 16 percent in weight instead of/with the virgin fibers in the BMC dough. In the production of the samples, 24 kg of chopped glass fibers were used 12% by mass in 200 kg BMC dough. In 24 kg chopped E-glass fibers, 1, 2, 3, 4 kg of recycled products, with the order of 4, 8, 12 and 16 percent by weight, replaced original fibers. Recycled glass fiber reinforced BMC dough was manufactured in Literatür Kimya Ltd. Co. in Balıkesir. The BMC plates weighing 300 grams, 250 × 150 × 4 mm in size were produced under the pressure of 150 bar at 145˚C for 3 minutes. Tensile and flexural static tests according to ISO 527-1 and ISO 178 standards were applied to the samples cut from the BMC plates. Mechanical tests were carried out on a 250 kN Zwick Roell Z250 electromechanical test device. The results were compared with reference samples containing 100% virgin fibers. The crack and fracture surfaces of samples were analyzed by using optical microscope.

The amount of reduction in the values of tensile test results of samples containing recycled materials remained less than 5% of the reference sample results. The samples with 4% recycled materials had the lowest bending strength. The reduction of bending properties of the samples including 8, 12, 16% recyclates was found be approximately 10-12% of the results of the reference sample. Except for sample containing 4% wt. of recyclates; others exhibited an acceptable mechanical performance. It was thought that using recycles containing shorter glass fiber content resulted in a decrease in the mechanical strength of product. The recycled products added to the BMC dough were used instead of and in combination with the virgin glass fibers. However, it was determined that the recycled products contained an average of 47% wt. glass fiber as a result of the heating and holding processes in ash furnace. Therefore, the use of recycled products in the BMC prescription resulted in a reduction in mass % of glass fiber in the final product. As a result, another reason for the decrease in strength values; this can be explained by the reduction in the amount of total mass of glass fibers used in the BMC product prescription. In the future work, it is aimed that the mechanical recycled powder filler material will be used instead of calcite ($CaCO_3$) in the BMC dough as qualified filler. In addition, the production parameters: mixing time and speed, mold temperature etc., need to be investigated.

Keywords: Mechanical recycling, glass fiber reinforced polymer (GFRP), bulk molding compound (BMC)

1. Giriş

Kompozit malzemeler özellikle otomotiv ve havacılık sanayinde, enerji maliyetlerini ve dolayısıyla CO_2 emisyonu değerlerini düşürmeleri sebebiyle geniş uygulama alanına sahiptirler. Örnek olarak kompozit malzeme uygulamaları, binek otomobil üretiminde ortalama 200 kg düzeylerinde hafiflik sağlamaktadır [1]. Avrupa'da her yıl 17 milyon binek araç üretildiği düşünülürse, konstrüksiyonda sağlanan hafiflik miktarı büyük miktarda yakıt tüketimi tasarrufu anlamı taşımaktadır. Avrupa'da üretilen binek araçlarda tüketilen ortalama 120 kg plastik malzemenin, ağırlıkça %20'si kompozit malzeme içermektedir [2]. Ülkemizde kompozit malzemelerin ağırlıklı olarak yapı/inşaat, otomotiv ve boru/tank sektörlerinde kullanıldığı rapor edilmiştir. Bu sektörlerin toplamı kompozit malzeme tüketim pastasının yaklaşık %85'ni oluşturmaktadır. Türkiye'de taşımacılık ve otomotiv sektörü kompozit malzeme tüketiminde toplam hacmin %20' sini oluşturmaktadır Taşımacılık ve otomotiv sektöründe kompozit uygulamalarına: ön taraf taşıyıcıları, tampon kirişleri, tampon ve çamurluklar, kaput, davlumbazlar, kapı panelleri, ön panel, iç tavan, supap kapağı, karter, far muhazaları, frigorifik kamyon kasaları, oto makasları (kompozit

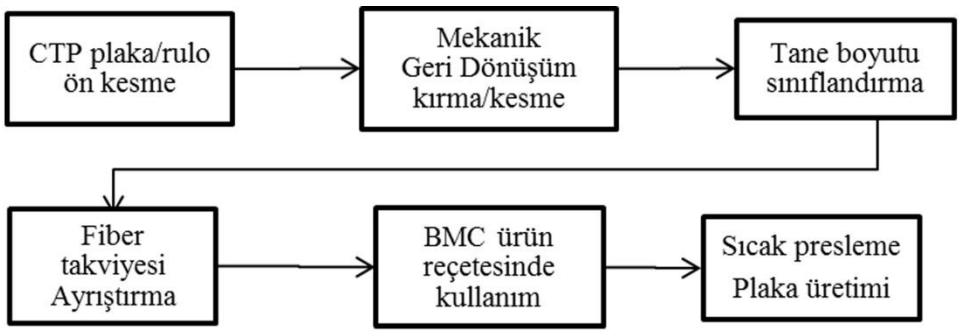
yaprak ve parabolik yaylar), kamyonet kabinleri, rüzgâr deflektörleri, tren/metro koltukları vb. örnek gösterilebilir. Otomotiv sektöründe yoğun olarak kullanılan SMC ve BMC sıcak presleme hatları ülkemizde toplam kompozit üretim hacminin %6'sını, Avrupa'da ise toplam üretim hacminin %20 sini oluşturmaktadır. Avrupa'da SMC-BMC endüstrisinin %40'lık hacmi ise taşımacılık ve otomotiv sektörüne hizmet etmektedir [3]. Bu veriler önümüzdeki dönemde SMC ve BMC üreticilerinin Türkiye'deki pazar paylarını ve üretim kapasitelerini arttırmaları gerektiğini göstermektedir. Artan üretim kapasitesi ise hammadde ve enerji giderlerinin artışına neden olacaktır. SMC ve BMC sıcak pres kalıplanması, kırpılmış cam elyaf ve dolgulu polyester içeren pestil ve hamur haline getirilmiş karışımların yüksek sıcaklık (120^{o}C -160^{o}C) ve basınç altında (100-150 bar) kalıplanma yöntemleridir. Dolgulu polyester içerisinde polyester reçine, inhibitör, sertleştirici, styrene, dolgu, kalınlaştırıcı, kalıp ayırıcı ve pigment bulunmaktadır. Örnek seçilen bir BMC hamurunda; kırpılmış cam elyaf %17, reçine %18, dolgu ($CaCO_3$) %55-60, çinko stearate %1,8, TBPB %0,5, pigment %2,5, styrene %3.1oranında ve %9.2 polystyrene düşük çekme katkısı bulunmaktadır. Kırpılmış cam elyaf boyutları; BMC hamurunda 3.175 mm-12.5mm (1/8″-1/2″), SMC pestilinde ise 12,5 mm-25 mm (1/2″-2″) aralığında değişmektedir. Cam elyaf içeriği, BMC hamurunda toplam karışımın ağırlıkça %10-%30'nu, SMC pestilinde ise ağırlıkça %10-%60'nu oluşturur [4]. BMC ve diğer üretim sektörleri (CTP, Flaman sarma boru üretimi) açısından bakıldığında, dolgu (kalsit) miktarı ise ortalama %60 düzeyinde kullanılmaktadır. Yurtdışında, SMC ve BMC endüstrisinde hammadde girdilerini azaltmak ve üretim firesi ürünlerin bertaraf edilmesine yönelik geri dönüşüm odaklı teknolojiler geliştirilmektedir.

Literatürde, SMC- BMC hatlarından çıkan atıklar kapalı devre (closed loop) üretim hattında tekrar cam içeriği ve dolgu malzemesi olarak kullanılmıştır [5-7]. Atıkların orjinal takviye ve dolgu malzemeleri ile birlikte kullanıldığı gözlenmiştir. Ayrıca, sektörde otomotiv firmalarına SMC mekanik geri dönüşüm ürünü fiber ve dolgu materyali üreten ve pazarlayan, ERCOM (Almanya) ve Phoenix Fiberglass (Kanada) firmalar bulunmaktadır [8, 9]. SMC atıklardan elde edilen 0,2 mm altı toz ve 0.5mm ile 1.25mm aralığında cam içeriğinin ağırlıkça %20 değerinin altında kalsit dolgusu ve orijinal fiberler yerine SMC ve BMC ürünlerinde kullanılması olumlu sonuçlar vermiştir. Yapılan bir pilot çalışmada; SMC hatlarında ağırlıkça %10 değerinde 0,2 mm altı ve 0,2-0,5 mm aralığında SMC toz atığın kalsit dolgusu yerine kullanılması çekme, eğilme ve darbe dayanım değerlerini artmasını sağladığı görülmüştür. Ağırlıkça % 30 oranında aynı toz atığın karışıma eklenmesi ise çekme ve eğilme dayanımı değerlerinde düşüşe sebep olduğu gözlenmiştir [10]. Diğer bir çalışmada, SMC toz atıktan kütlece %50/%50 yarı yarıya hazırlanan 0,2-0,5 mm toz ve 0,5-1,25mm cam içeriğin ağırlıkça % 50 değerinde kalsit yerine SMC hattında karışıma katılması nihai ürünün eğilme dayanım değerlerinde yine artış sağlamıştır [11]. Araştırmalarda; 1,25 mm altı dolgu materyali, tekrar SMC ve BMC ürünlerinde başarılı şekilde uygulanmıştır. Inoh vd. [12], SMC ürünlerinde, $CaCO_3$ dolgu malzemesi yerine kullanılan SMC geri dönüşüm dolgu malzemesinin özgül ağırlık değerinin %25 oranında düşük olduğunu bu nedenle, geri dönüşüm dolgusunun % kütlece kullanılmasının, fazla atık girdisinin (%25) karışıma katılmasına neden olabileceğini vurgulamıştırlar. Karışım viskozite değerlerinin kontrol edilebilir kalması için geri dönüşüm dolgu malzemesinin ağırlıkça %30'un altında olması gerektiği vurgulanmıştır. Derosa R. vd. [13], SMC geri dönüşüm ürünü cam fiberleri, BMC hamurunda orijinal cam fiberler yerine kullanmıştır. Araştırmada, 12,7 mm, 12,7&6.35 mm, 6.35 mm, 3.175 mm boyutlarında orijinal fiber takviyeli, ağırlıkça %100 geri dönüşüm fiber (3.175 mm) içeren ve takviye elemanı içermeyen numunelerin eğilme dayanım ve rijitlik değerleri karşılaştırılmıştır. Tamamen geri dönüşüm ürünü fiber içeren numunelerin eğilme dayanım değerleri, 12.7 mm boyutunda orijinal fiber içeren numunelere kıyasla %75 oranında azalmıştır. Ağırlıkça %11.5 geri dönüşüm fiber içeren numunelerin eğilme dayanım ve rijitlik değerlerinde ise, ağırlıkça %11.5 ve 6.35 mm boyutunda orijinal fiber içeren numunelere kıyasla %70 ve %51 azalma gözlenmiştir. Yapılan çalışmalarda, hasar alan BMC numunelerinde çatlak ilerlemesinin, geri dönüşüm fiber- matris ara yüzeyinde oluştuğu mikroskobik görüntüler ile tespit edilmiştir. Geri kazanım ürünü fiber ve matris arasında oluşan bağ kuvvetinin zayıf olduğu ortaya çıkmıştır [14, 15].

Bu çalışmada, CTP fire malzemelerden sağlanan mekanik geri dönüşüm ürünü toz atığın tekrar değerlendirilmesi amaçlanmaktadır. Çok yüksek üretim kapasitelerine sahip ilgili sektörlerden atık niteliğindeki CTP plaka-rulo fire malzeme tedariki rahatlıkla sağlanmıştır. CTP ürünler, genelde doymamış polyester (izoftalik/ortoftalik), 500-1550 gr/m^2 birim alan ağırlığında E-cam elyaf ve dolgu malzemesi (kalsit, silika, kil) içermektedirler. Bu yüzden, CTP toz atığın SMC-BMC parça imalatında kullanılabilirliği teknik açıdan uygun görülmektedir. Çalışma kapsamında öncellikli olarak üretilecek yeni geri dönüşüm materyalinin BMC hazır kalıplama hamurunda kullanılması hedeflenmiştir. Ayrıca, sürekli kompozit üretimi yapan hatların atıklarının temiz ve hep aynı kalitede olmasından dolayı ham madde tedarikinde kalite anlamında sürdürülebilirlik sağlanabilmektedir. Çalışma kapsamında üretilen menşei ve içeriği belirlenen toz atığın farklı sektörlerde kullanım potansiyeline sahip olması nedeniyle; rögar, ızgara, pis su kapak üretimi, plastik kirişler vb. yapı uygulamalarında, CTP geri kazanım ve tekrar kullanım uygulamasının yaygınlaşması öngörülmektedir.

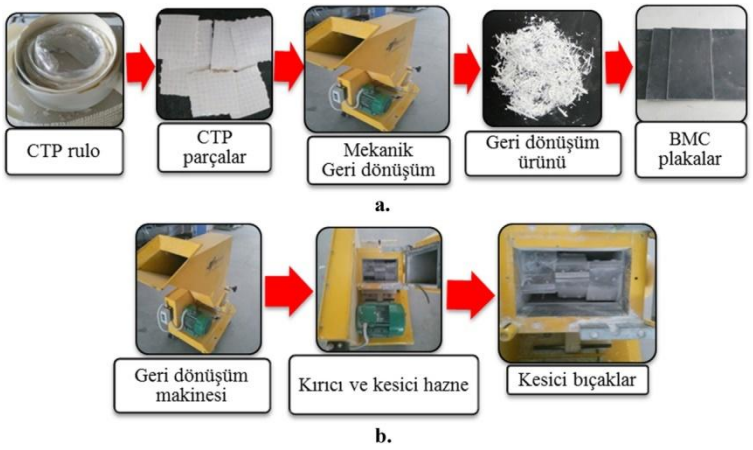
2. Materyal-Yöntem

Çalışmada, fire CTP plaka ve rulo malzemelere mekanik geri dönüşüm prosesi uygulanmıştır. CTP fire malzemeler ilk olarak bıçaklı kırıcı makine haznesine uygun şekilde 50x50 mm boyutlarında parçalar halinde hazırlanmıştır. Kırma ve kesme işlemleri sonrasında cam fiber, reçine ve dolgu içeren toz atık elde edilmiştir. Fiber ve dolgu malzemesi içeren ürünlerin tane boyutu sınıflandırılması elek ile eleme yöntemi ile yapılmıştır. Geri dönüşüm ürünü cam fiberler, BMC hamurunda orijinal fiberler ile birlikte kullanılmıştır. Çalışmada takip edilen aşamalar Şekil 1' de şematik olarak verilmiştir.



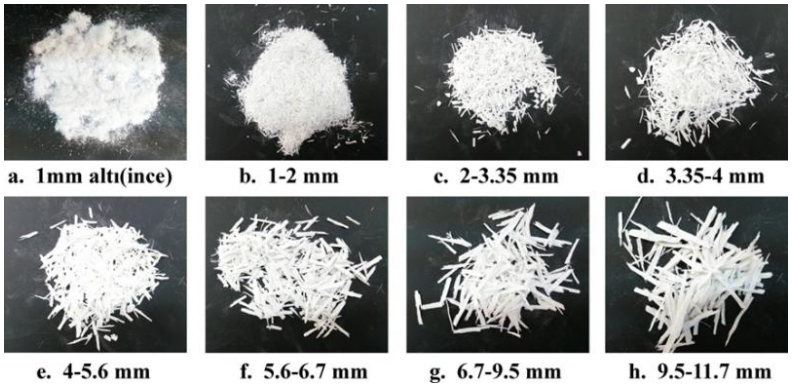
Şekil 1. CTP plaka geri dönüşüm işlemi

CTP plaka ve rulo fire malzemelerin mekanik geri dönüşümü için kırma ve kesme amaçlı tasarlanan laboratuvar tipi bıçaklı kırıcı geri dönüşüm makinesi kullanılmıştır. Kırıcı öğütücü makine 50 mm × 50 mm parça besleme boyutuna sahiptir. Mekanik geri dönüşüme uğrayacak CTP malzemelere, rotor üzerinde bıçaklar ve öğütme duvarı arasında parçalama (kırma) işlemi uygulanmaktadır. Mekanik geri dönüşüm işlem sıralaması ve bıçaklı kırıcı makinesine ait detaylar Şekil 2'de verilmiştir.

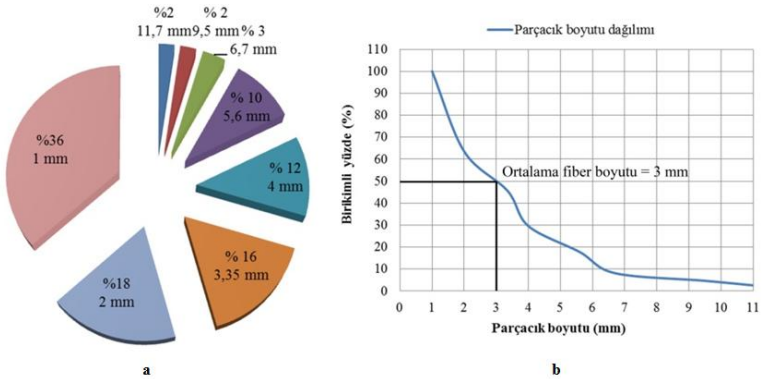


Şekil 2. a. Geri dönüşüm işlem sıralaması, b. Bıçaklı kırıcı/kesici makine detayları

Geri dönüşüm ürünleri tane boyutu 1 mm'den küçük (<1mm) ise ince taneli ve 1 mm'den büyük eşit (≥1 mm) ise kaba taneli olarak ayrılmıştır. Geri dönüşüm ürünlerine 11.7, 9.5, 6.7, 5.6, 4, 3.35, 2 ve 1 mm eleklerden geçirilerek sınıflandırma yapılmıştır. Tane boyutu sınıflandırılması yapılan atıkların resimleri Şekil 3'de verilmiştir. Geri dönüşüm ürünlerinin 1kg kütlesindeki ortalama tane boyutu dağılımı 3'er örnek üzerinden hesaplanmıştır (Şekil 4 a). Ağırlıkça % 36 ,% 18 ve % 16 oranlarına sahip, 1 mm, 2 mm ve 3.35 mm boyutlara sahip geri dönüşüm ürünleri, toplam ürün kütlesinin %70'ni oluşturmaktadır. Parçacık boyutu birikimli yüzde (% kütle) tane boyutu grafiği çıkarılmış, neticesinde ortalama geri dönüşüm tane boyutu 3 mm olarak belirlenmiştir (Şekil 4 b).



Şekil 3. CTP geri dönüşüm ürünü, a. İnce tane (<1 mm), b, c, d, e, f, g, h. kaba tane (>1 mm)

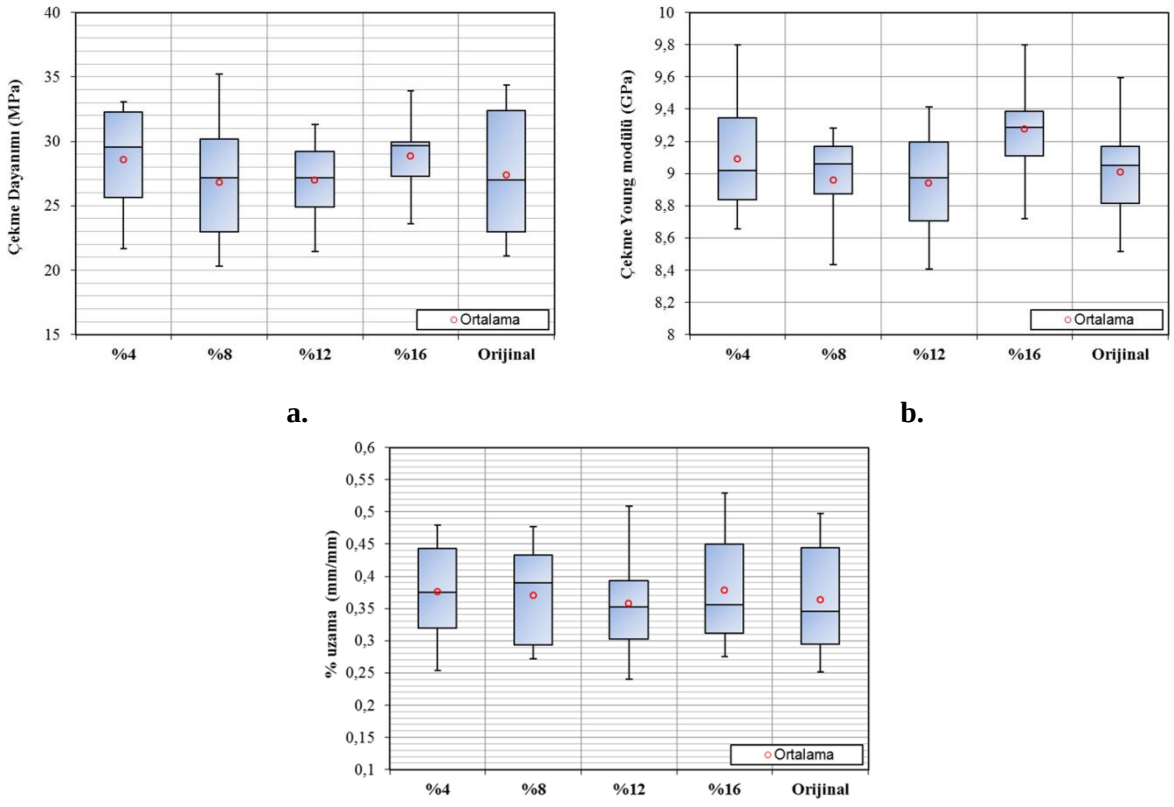


Şekil 4. a. Geri dönüşüm ürünlerinin tane boyutu dağılımı (% kütlece), b. Geri dönüşüm ürünü birikimli yüzde/parçacık boyutu grafiği

Geri dönüşüm ürünleri tane boyut sınıflandırılması işleminden sonra BMC hamur içerisinde orijinal fiberler (kullanılmamış) ile birlikte takviye elemanı olarak kullanılmıştır. Numunelerin üretiminde, 200 kg BMC hamur içerisinde kütlece %12 oranında 24 kg, orijinal ve geri dönüşüm ürünü kırpık cam elyaf kullanılmıştır. Orijinal cam fiber boyutu 12 mm'dir. 24 kg fiber takviyesi içerisinde kütlece % 4, 8, 12 ve 16 oranında sırası ile 1, 2, 3, 4 kg geri dönüşüm ürünleri, orijinal fiberlerin yerini almıştır. 300 gram ağırlığında, 250×150×4 mm ebatlara sahip test plakaları 3 dakika sürede, 145˚C'de, 150 bar basınç altında üretilmiştir. Aynı zamanda, 24 kg orijinal cam fiberin kullanıldığı referans plakalar da üretilmiştir. Hazırlanan plakalardan kesilen numunelerin mekanik performansları, referans numuneler ile karşılaştırılmıştır.

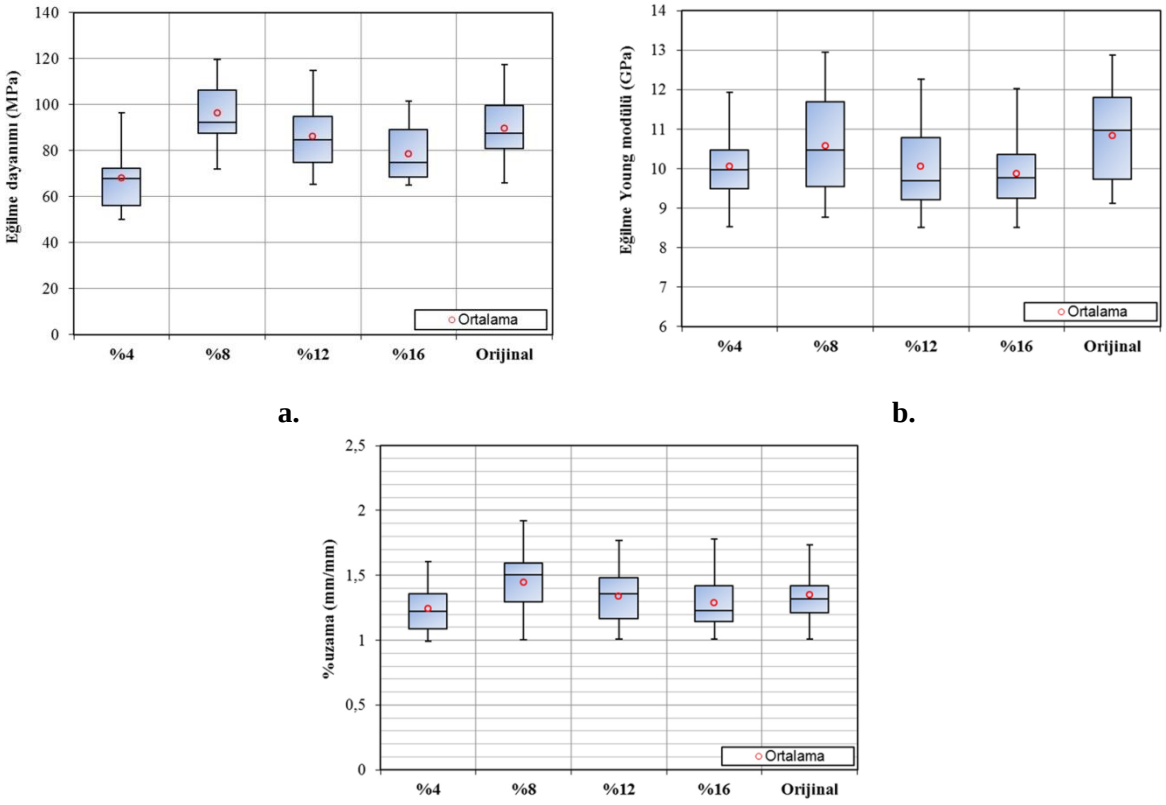
3. Bulgular

Üretilen BMC plakalardan kesilen numunelerin ISO 527-1 (çekme) ve ISO 178 (eğilme) standartlarına uygun şekilde statik mekanik testleri yapılmıştır. Çekme testi numuneleri 25 mm × 250 mm × 4 mm, eğilme test numuneleri ise 10 mm × 80 mm × 4 mm boyutlarında standartlara uygun şekilde hazırlanmıştır (genişlik × uzunluk × kalınlık). Mekanik testler 250 kN Zwick Roell Z250 elektromekanik çekme–basma cihazında yapılmıştır. Numunelerin statik mekanik test sonuçları kutu-bıyık diyagramları şeklinde Şekil 5 ve 6'da verilmiştir. Kutu bıyık diyagramlarında mekanik özelliklerin maksimum, minimum, ortalama ve medyan değerleri verilmiştir. Statik mekanik çekme testleri için 15'er, eğilme testleri için ise 30'ar adet numune test edilmiştir. Orijinal olarak isimlendirilen referans numunedir. Geri dönüşüm içeren numunelerin çekme dayanımı, Young modülü ve % uzama değerlerinin ±%5 sınırlar dâhilinde ve kabul edilebilir olduğu gözlenmiştir. Kütlece %16 geri dönüşüm cam fiber içeren numune en yüksek çekme dayanımı, Young modülü ve % uzama değerlerine sahiptir.



Şekil 5. Kütlece % 4, 8, 12, 16 geri dönüşüm ürünü içeren BMC test numunelerinin a. çekme dayanımı, b. Young Modülü, c. % uzama değerleri

Eğilme test sonuçları kütlece %4, %12 ve %16 geri dönüşüm cam fiber içeren numunelerin eğilme dayanımı azalma göstermiştir. Kütlece %12 geri dönüşüm cam fiber içeren numunenin eğilme dayanımında %10'un altında (kabul edilebilir) düşme gözlenmiştir. %8 atık içeren numunenin orijinal numuneye kıyasla eğilme dayanımı değeri artmıştır.



Şekil 6. Kütlece % 4, 8, 12, 16 geri dönüşüm ürünü içeren BMC test numunelerinin a. eğilme dayanımı, b. Young Modülü, c.% uzama değerleri

Geri dönüşüm takviyeli ürünlerin ortalama dayanım, Young modülü ve % uzama değerleri Çizelge 1 ve 2'de verilmiştir. Geri dönüşüm ürünü içeren numunelerin mekanik dayanım değerlerinde %10 düşme kabul edilebilir görülmüştür [8].

Çizelge 1. Çekme deneyi test sonuçları

Geri dönüşüm ürünü (% kütlece)	%4	%8	%12	%16	Orijinal
Çekme dayanımı (MPa)	**28.575**	**26.772**	**26.948**	**28.839**	**27.345**
Std. sapma	4.070	4.667	3.129	2.774	4.753
Young Modülü (GPa)	**9.09**	**8.957**	**8.94**	**9.277**	**9.008**
Std. sapma	352.145	326.743	311.337	306.297	292.602
% uzama	**0.375**	**0.370**	**0.358**	**0.378**	**0.363**
Std. sapma	0.0762	0.0771	0.0824	0.0798	0.0843

Çizelge 2. Eğilme deneyi test sonuçları

Geri dönüşüm ürünü (% kütlece)	%4	%8	%12	%16	Orijinal
Eğilme dayanımı (MPa)	**67,912**	**96,099**	**86,111**	**78,543**	**89,695**
Std. sapma	14,245	13,986	13,171	11,527	13,172
Young Modülü (GPa)	**10.054**	**10.566**	**10.055**	**9.867**	**10.839**
Std. sapma	945,455	1245,521	1023,262	954,842	1113,922
% uzama	**1,240**	**1,446**	**1,337**	**1,289**	**1,350**
Std. sapma	0,163	0,236	0,210	0,212	0,213

Geri dönüşüm ürünü malzeme ağırlıkça en çok polimerik reçine ve cam fiber takviyesinden meydana gelmektedir. Bunların dışında çok az miktarlarda da olsa inorganik kısım (başlatıcılar, katalizörler, $CaCO_3$ vb.) bulunabilmektedir. Cam fiberler ve inorganik malzemeler ısıya karşı oldukça dayanıklı iken polimerik reçineler 200˚C'den sonra bozunmaya başlarlar. Bu yüzden geri dönüşüm ürünündeki cam fiber oranı belirli bir ısıtma düzeni sonucunda kalan ürün miktarlarından yola çıkılarak, gravimetrik olarak kabaca tayin edilebilmektedir [16]. Çalışmada; 3 farklı geri dönüşüm ürününün (ham ürün, 1 mm elek üstü ve 1 mm elek altı) yaklaşık 3-4 gramı porselen krozede tartıldıktan sonra, Protherm PLF 120/10 marka kül fırını içerisinde aşağıda takip edilen ısıtma ve bekletme aşamalarından geçirilmiştir:

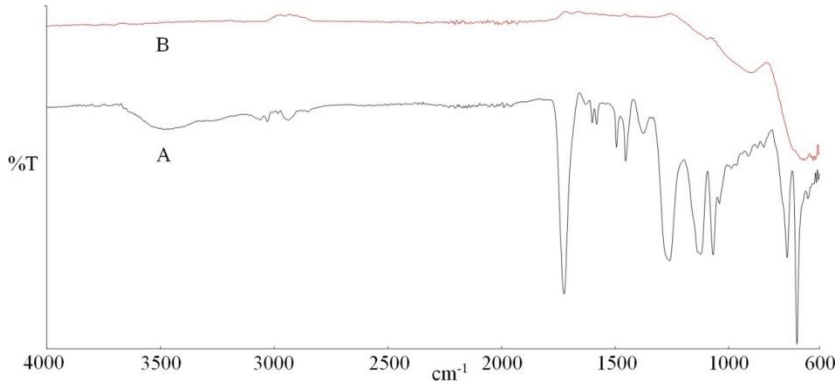
a) 2.25°C/dk. ısıtma hızıyla 300°C ye çıkarma,
b) 300°C de 30 dk. bekletme,
c) 1.16°C/dk. ısıtma hızıyla 300°C den 650°C ye çıkarma
d) 650°C de 40 dk. bekletme,
e) Oda sıcaklığına soğutma

Soğuyan ürünlerin yüzeylerinde polimerik atıklar kalabilmektedir, bunları uzaklaştırmak için krozedeki ürün saf su ile yıkanmış ve süzgeç kâğıtlarına alınmıştır. Son olarak 40°C etüvde, 1 gün kurutulmuştur. Kurutulan örnekler sabit tartıma gelene kadar birkaç kez tartılmış ve ısıtma sonrası kalan ürün miktarları kaydedilmiştir. Sonuçların doğruluğunu artırmak için analizi yapılacak her ürünün farklı noktalarında 3 kez ısıtma için örnek alınmış böylece her ürün için 3 örnek analizi yapılmıştır. Elde edilen sonuçlar Çizelge 3'de özetlenmiştir.

Çizelge 3. Geri dönüşüm ürünlerinin kütlece fiber oranları

	1mm elek üstü			Ham ürün			1 mm elek altı		
Alınan miktar (g)	3.993	3.992	3.341	3.201	4.039	3.072	3.546	2.722	2.911
Kalan miktar (g)	1.815	1.817	1.684	1.478	1.544	1.331	1.503	1.237	1.268
% Cam fiber	**45.45**	**45.51**	**50.40**	46.17	38.22	43.32	42.38	45.44	43.55

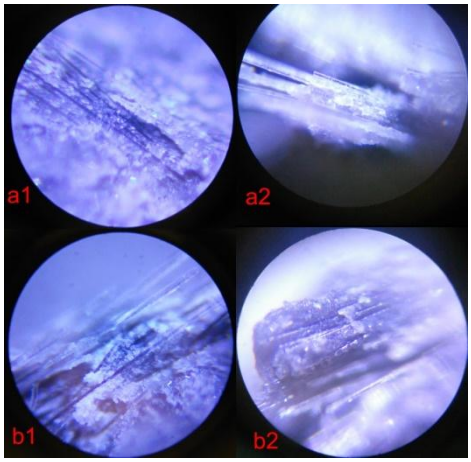
BMC hatlarında kullanılan geri dönüşüm ürünün yapısını daha iyi analiz edebilmek için Perkin Elmer 65 model (Fourier transform infrared spectroscopy) FT-IR cihazı 600-4000 cm^{-1} aralığında kullanılmıştır.



Şekil 7. BMC hamurunda kullanılan geri dönüşüm ürünün (A) ve 650°C ye ısıtma sonucu oluşan ürünün (B) FT-IR spektrumu

Şekil 7 (A) da görüldüğü gibi geri dönüşüm ürünü olarak kullanılan malzemede 3500 cm^{-1} civarında geniş OH bandı vardır ve bu moleküller arası hidrojen bağından kaynaklanan bir titreşimdir. 3000 cm^{-1} de orta şiddette C-H bağları görünürken 1723 cm^{-1} de şiddetli bir C=O piki ortaya çıkmaktadır. 1580-1625 cm^{-1} arasında orta şiddette N-H grupları, 1400-1500 arası yine orta şiddete C-H grupları vardır. 1260 ve 1068 cm^{-1} görülen iki şiddetli pik yapıda C-O bağlarını göstermektedir. 1123 cm^{-1} de görülen şiddetli pik yapıdaki cam fiberden kaynaklanan O-Si-O titreşimlerini göstermesi bakımından önemlidir [17]. Son olarak 700-750 cm^{-1} arasında görülen iki şiddetli pikin ise $CaCO_3$ (kalsit) ait olduğu düşünülmektedir. Çalışmada, cam fiber oranını bulmak için yaptığımız 650°C'ye kadar ısıtma ve yıkama işleminden sonra çıkan ürünün de FT-IR spektrumu alınmıştır. Şekil 7 (B)' de görüldüğü gibi yapıda sadece Si-O (1091), Si-OH(897) ve Ca-O(667) [18] titreşimleri gözlenirken polimerik reçineye ait bütün fonksiyonel gruplar kaybolmuştur. Böylece kalan ürünün bir SiO_2-CaO karışımı olduğu ortaya çıkmış ve geri dönüşüm ürününde hesaplanan cam fiber oranı doğrulanmıştır.

Geri dönüşüm takviyeli ve orijinal ürünlerin ışık 'mikroskobundaki analizi Gazer ES-2000-SC model cihaz ile 300 büyütmede yapılmış ve Şekil 8' de gösterilmiştir. Cam fiberlerin plaka içerisindeki yerleşimleri ve kırılma noktalarındaki yapıları değerlendirildiğinde her iki ürünün de benzer yapıda olduğu görülmektedir.



Şekil 8. Geri dönüşüm ürünü cam fiber ile yapılan plaka (a1,a2) ve orijinal plakaların (b1,b2) ışık mikroskobu görüntüleri (x300 büyütme)

4. Sonuç-Tartışma

Çalışmada, CTP plaka ve rulo üretim firesi malzemelere mekanik geri dönüşüm prosesi uygulanmış ve geri dönüşüm ürünleri BMC ürün reçetesinde fiber takviyesi (1mm<tane boyutu≤11.7mm) olarak kullanılmıştır. Ortalama cam fiber boyutu kısa olan geri dönüşüm ürünlerinin BMC hamurunda kullanılması, mekanik dayanım değerlerinin genel olarak düşmesine sebep olmuştur. BMC hattında kullanılan geri dönüşüm ürünleri % kütlesel olarak orijinal fiberler yerine/birlikte kullanılmıştır. Fakat geri dönüşüm ürünlerinin kül fırını analiz neticesinde ortalama kütlesinin %47'sinin cam fiber olduğu belirlenmiştir. Geri dönüşüm ürünlerinin BMC hattında kullanılması nihai üründe % kütlesel olarak cam fiber miktarının azalmasına neden olmuştur. Netice olarak dayanım değerlerinde düşmenin bir diğer nedeni; BMC ürün reçetesinde toplam kütlece % fiber miktarının düşmesi ile açıklanabilir. İlerleyen çalışmalarda, CTP mekanik geri dönüşüm çıktısı toz dolgu malzemesinin BMC hamurunda kalsit ($CaCO_3$) yerin ve birlikte nitelikli dolgu olarak kullanılması hedeflenmektedir.

5. Teşekkür

Literatür Kimya Elektrik İnş. İthalat İhracat San. Tic. Ltd. Şti. şirketine çalışmanın tamamlanmasında üretim hatlarını açtıkları, test numunelerinin üretilmesinde emek ve zaman ayırdıkları için teşekkür ederiz.

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KATI YAĞLAYICI KATKILI KARBON ELYAF/PA6 POLİMER KOMPOZİTLERİN TRİBOLOJİK ÖZELLİKLERİNİN İNCELENMESİ

INVESTIGATION Of The TRIBOLOGICAL PROPERTIES Of SOLID LUBRICANT FILLED CARBON FIBER/PA6 POLYMER COMPOSITES

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Bu çalışmada, katı yağlayıcı olarak kullanılan politetrafloretilen (PTFE) ve Wax (vaks) katkıların, %20 karbon elyaf katkılı PA6 (PA6/20KE) polimer kompozitlerin tribolojik özelliklerine etkisi incelenmiştir. Çalışmada, PTFE katkı oranı %10, vaks katkı oranı ise %4 oranında kullanılmıştır. Aşınma ve sürtünme testleri 10-40N yük ve 0.4-1.2m/s kayma hızı aralıklarında, kuru ortamda, pin-on-disk sistemi kullanılarak gerçekleştirilmiştir. Çalışma sonucunda, artan yük ve kayma hızına bağlı olarak sürtünme katsayısı ve aşınma oranı artmıştır. %20Karbon elyaf katkılı PA6 polimerine ilave edilen PTFE ve vaks katkıları sürtünme katsayısını ve aşınma oranını önemli oranda azaltmıştır. En düşük sürtünme katsayısı ve aşınma oranı %4vaks katkılı PA6 numunede elde edilmiştir.

Anahtar Kelimeler: PA6, Karbon elyaf, Sürtünme katsayısı, Aşınma oranı

Aim of the Study

In this study, the influence of PTFE and wax on the tribological properties of polyamide 6 composite filled with 20% wt. carbon fiber was investigated.

Materials and Methods

The PTFE and wax filler contents of the composite were by 10 and 4 wt.%, respectively. Wear and friction tests were carried out in a dry environment using a pin-on-disc system at 10-40 N load and 0.4-1.2 m/s sliding speed.

Results

As a result of the study, the coefficient of friction and wear rate increased with increasing load and sliding speed. PTFE and wax additives significantly reduced the friction coefficient and wear rate of 20% carbon fiber filled PA6 polymer composites. The lowest coefficient of friction and wear rate were obtained on the 4% wax filled PA6 composites.

Keywords: PA6, Carbon fiber, Coefficient of friction, Wear rate

1. Giriş Ve Amaç

Partikül veya fiber formundaki katkılar polimerik malzemelerin rijitliğini ve dayanımını geliştirmek için yoğun bir şekilde kullanılmaktadır. İkinci faz olarak ilave edilen katkı, aynı zamanda, polimer kompozitin aşınma direncini önemli oranda etkilemektedir. Karbon fiber, cam fiber ve aramit fiber en fazla tercih edilen ve kullanılan katkı elemanlarıdır [1]. karbon fiber katkının yüksek performans uygulamalarında, düşük yoğunluk ve yüksek mekanik özellikleri nedeniyle tercih edildiğini belirtmiştir. Yapılan

çalışmalarda, karbon elyaf takviyeli termoplastiklerin cam elyaf takviyeli olanlara göre daha iyi sürtünme ve aşınma özellikleri gösterdiği belirtilmiştir. Bunun sebebinin ise karbon elyafın cam elyafa göre yüksek modüle ve kendini yağlama özelliğine sahip olmasına bağlamışlardır [2,3].

Fiber takviyeli polimer kompozitlerin tribolojik özelliklerini anlamak için uygulanan kayma hızı, yük, ve kayma mesafesi gibi proses şartlarının yanında katı yağlayıcı olarak kullanılan katkıların da etkilerinin incelenmesi gerekmektedir. Literatürde proses şartlarının ve katkı türü ile miktarının tribolojik özellikler üzerine etkilerinin incelendiği birçok çalışma mevcuttur. Tang ve arkadaşları [4] aramit fiber katkılı PA6 polimerinin tribolojik özellikleri üzerine nano-MoS_2 katkısının etkisini incelemişlerdir. Çalışma sonucunda, nano-MoS_2 katkının ilave edilmesi ile disk yüzeyinde çok katmanlı laminar film tabakasının oluştuğunu ve sürtünme katsayısı ile aşınma oranının azaldığını belirtmiştir. Katı yağlayıcı olarak -CH_2-CH_2- moleküler zincir yapısıyla çok yüksek yoğunluklu polietilen (ÇYYPE) diğer önemli katkı türüdür. Hasmi ve arkadaşları [5] koton fiber takviyeli poliester kompozitlerde ÇYYPE katkının tribolojik özellikleri önemli oranda geliştirdiğini belirtmiştir. Politetrafloretilen (PTFE) ve grafit katkılar transfer film tabakasının oluşumuna katkı sağladığı için sürtünme katsayısı ve aşınma oranı azalmaktadır. Dolayısıyla fiber takviyeli polimerlerin tribolojik özelliklerini geliştirmek için geniş bir şekilde kullanılmaktadır. Du-Xin [6] %15 karbon elyaf takviyeli PA6 polimerine ilave ettikleri farklı oranlardaki PTFE ve çok yüksek yoğunluklu polietilen (ÇYYPE) katkıların tribolojik performansı incelemişlerdir. PA6/15KE polimerinde artan yük ve kayma hızına bağlı olarak sürtünme katsayısı azalırken aşınma oranı artmıştır. PA6/15KE polimerine ilave edilen PTFE ve ÇYYPE katı yağlayıcıları sürtünme katsayısının önemli oranda azalmasını sağlamıştır. Çalışma sonucunda PTFE ve ÇYYPE karışımının tribolojik özellikler üzerine en etkili malzeme grubu olduğunu belirtmişlerdir. Jia ve arkadaşları [7] ise %15 karbon elyaf katkılı poliimit (PI) polimerine ilave ettikleri grafit, MoS_2 ve PTFE gibi katı yağlayıcıların sürtünme ve aşınma davranışlarını inceledikleri çalışmada katı yağlayıcıların sürtünme katsayısını ve aşınma oranını önemli oranda azalttıklarını belirtmişlerdir. Bijwe ve arkadaşları [8] PA12 polimerine farklı oranlarda ilave ettikleri karbon fiber ve PTFE katkının aşınma davranışlarını inceledikleri çalışmada, yükün artması ile birlikte sürtünme katsayısının azaldığını aşınma oranının ise arttığını belirlemişlerdir. Ayrıca karbon fiber ve PTFE katkılar sürtünme katsayısı ve aşınma oranının azalmasına sebep olmuştur. Kumar ve Kanagaraj [9] grafit katkılı Pa6 polimerinin tribolojik özelliklerini inceledikleri çalışmada yükün artması ile birlikte sürtünme katsayısının azaldığını ancak aşınma oranının arttığını belirlemişlerdir. Tribolojik özellikler açısından en verimli numunenin %20 grafit katkılı PA6 olduğunu belirtmişlerdir. Cai ve Wang [10] katkısız PA66 ve karbon fiber katkılı PA66 kompozitlerin kuru ve sulu ortam şartları altında tribolojik özelliklerini inceledikleri çalışma sonucunda, artan yüke bağlı olarak sürtünme katsayısı ve aşınma oranının arttığını, kayma hızının artması ile sürtünme katsayısının azalırken aşınma oranının arttığını belirlemişlerdir. Li ve Xia [1] farklı oranlarda karbon elyaf katkılı PA6 polimerinin tribolojik özelliklerini inceledikleri çalışmada, artan yüke ve kayma hızına bağlı olarak sürtünme katsayısının ve aşınma oranının arttığını belirtmişlerdir. PA6 polimerine ilave edilen karbon fiberin aşınma oranının azalmasına katkı sağladığını belirtmişlerdir. Luo ve arkadaşları [11] ise %15 PTFE katkılı polifenilen sülfit (PPS) polimerine ilave ettikleri farklı oranlardaki karbon elyafın aşınma özelliklerini inceledikleri çalışmada, yüke bağlı olarak sürtünme katsayısının ve aşınma oranının arttığını belirtmişlerdir.

Bu çalışmada, katı yağlayıcı olarak kullanılan politetrafloretilen (PTFE) ve Wax (vaks) katkıların, %20 karbon elyaf katkılı PA6 (PA6/20KE) polimer kompozitlerin tribolojik özelliklerine etkisi incelenmiştir. Çalışmada, PTFE katkı oranı %10, vaks katkı oranı ise %4 oranında kullanılmıştır. Aşınma ve sürtünme testleri 10-40N yük ve 0.4-1.2m/s kayma hızı aralıklarında, kuru ortamda, pin-on-disk sistemi kullanılarak gerçekleştirilmiştir.

2. Deneysel Çalışmalar

Deneysel çalışmalarda, matris malzemesi olarak 1.12 g/cm^3 yoğunluğa sahip Emaş Plastik/Türkiye firmasından temin edilen Poliamit 6 polimeri kullanılmıştır. Takviye elemanı olarak kullanılan kırık karbon fiberler ise DowAksa firmasından temin edilmiştir. %20 oranındaki karbon fiber, %10 PTFE ve %4 vaks takviyeli PA6 polimer granüllerin üretilmesinde 11 sıcaklık bölgesine sahip çift vidalı ekstruder (vida çapı 26 mm, L/D oranı 46) kullanılmıştır. Sıcaklık dağılımı, besleme hunisinden kalıba doğru 80-80-120-220-220-230-230-235-235-240-240^{o}C olacak şekilde ayarlanmıştır. 2mm silindirik çubuk formundaki flamentler su banyosundan geçirildikten sonra granül haline getirilmiştir. Elde edilen granüller 100^{o}C'de 4 saat boyunca kurutulmuştur. Standartlara uygun test numuneleri enjeksiyon kalıplama (Hastek-Borche Model) yöntemi ile üretilmiştir. Üretimlerde, 110 bar enjeksiyon basıncı ve 250-255-260-265-270-270^{o}C enjeksiyon sıcaklıkları kullanılmıştır.

Aşınma deneyleri, kuru ortam şartları altında, oda sıcaklığında ve pim-disk (pin-on-disc) aşınma sistemi kullanılarak gerçekleştirilmiştir. Karşı disk olarak ise 1040 çeliği kullanılmıştır. Şekil 1'de, bu çalışma için tasarlanan pim-disk aşınma cihazı verilmiştir. Her bir test öncesi pim ve disk yüzeyleri alkol ile temizlenmiş ve kurutulmuştur. Tablo 1'de bu çalışmada kullanılan malzemeler ve deney şartları (uygulanan yük, kayma hızı ve ortam sıcaklığı) verilmiştir. Her bir aşınma deneyinden önce ve sonra pimlerin ağırlıkları ölçülmüş ve ağırlık kaybı (Δm) tespit edilmiştir. Aşağıdaki formül kullanılarak test numunelerinin aşınma oranları (K_0) hesaplanmıştır.

$$K_0 = \Delta m / L \cdot \rho \cdot F \ (m^2/N)$$

Burada; Δm: ağırlık kaybı (g), L: kayma mesafesi (m), ρ: malzemenin yoğunluğu (g/cm^3), F: uygulanan yük (N).



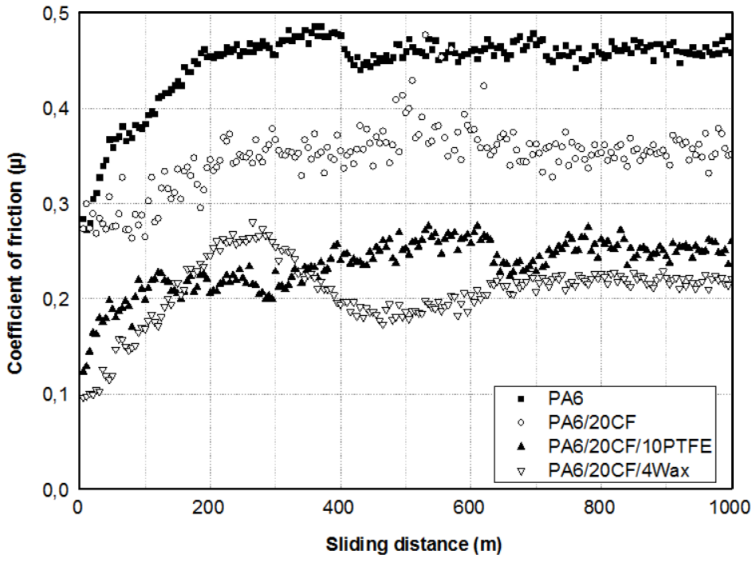
Şekil 1. Pim-disk aşınma cihazı

Tablo 1. Aşınma ve sürtünme deneylerinde kullanılan polimer malzemeler ve deney şartları

Malzeme	Yoğunluk (g/cm^3)	Ortam Sıcaklığı (^{o}C)	Kayma Mesafesi (m)	Yük (N)	Kayma hızı (m/s)
PA6	1.123	22±2	1000	10	0.4 0,8 1.2
PA6/20KE	1.205			20	
PA6/20KE/10PTFE	1.329			30	
PA6/20KE/4Vaks	1.218			40	

3. Deney Sonuçları

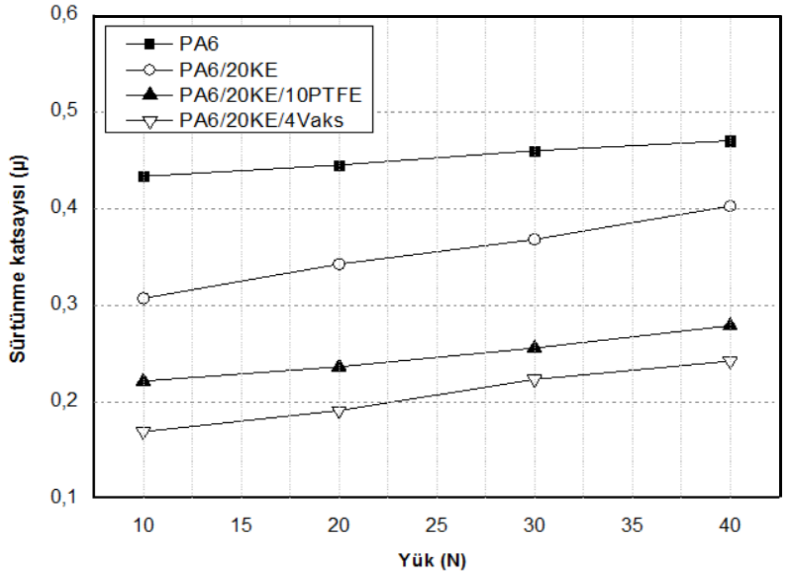
Şekil 2'de, 0.8m/s kayma hızında ve 30N yük altında, katkısız PA6 ile %20 karbon elyaf, %10 PTFE ve %4 vaks katkılı PA6 polimer kompozit malzemelerin sürtünme katsayısı-kayma mesafesi ilişkileri verilmiştir. Şekilde görüldüğü gibi PA6 ve kompozitlerinin sürtünme katsayısı değişimi başlangıç aşaması ve kararlı hal aşaması olmak üzere iki aşamada meydana gelmiştir. Sürtünme katsayıları başlangıç aşamasında hızlı bir şekilde artmış ve 400m gibi bir mesafede kararlı hal aşamasına ulaşmıştır. Hem PA6 polimeri hem de PA6 polimer kompozitleri için sürtünme katsayısı benzer değişim göstermiştir. PA6 polimerine ilave edilen karbon elyaf ve katı yağlayıcı olarak ilave edilen PTFE ve vaks katkıları sürtünme katsayısını önemli oranda azaltmıştır. Bunun sebebi ise çelik disk yüzeyinde oluşan transfer film tabakası ve katkı miktarına bağlı olarak transfer film tabakası kalınlığının değişmesine bağlanmıştır. Oluşan transfer film tabakası polimer pim ile çelik disk yüzeyi arasında ince bir film tabakası oluşturarak pim ve disk yüzeylerinin temasını kesmiş ve sürtünme katsayısının önemli oranda azalmasına sebep olmuştur. Jia ve arkadaşları [7] yaptıkları çalışmada poli-imid (PI) polimerine ilave ettikleri karbon elyaf ve katı yağlayıcıların (PTFE veya grafit) hem kuru hem de sulu ortam şartlarında sürtünme katsayısını azalttığını tespit etmişlerdir. Benzer şekilde, Bahadur ve Polineni [12] cam elyaf takviyeli ve CuO katkılı naylon kompozitlere ilave ettikleri PTFE katkının disk malzeme üzerinde oluşturduğu transfer film tabakası nedeniyle aşınma oranının önemli oranda azaldığını belirtmişlerdir. Ozsoy ve arkadaşları [13] ise vaks katkılı naylon6 kompozitlerinin sürtünme katsayısının, katkısız naylon6 malzemesinin katsayısından daha düşük olduğunu belirtmişlerdir. Sürtünme katsayısındaki azalmanın sebebinin ise; vaks malzemesinin yağlayıcı olarak davranarak numune ile çelik disk arasındaki temas bölgesini düşürmesi ve aşınan yüzeyde daha az sıcaklık artışına sebep olması olarak açıklamışlardır.



Şekil 2. PA6 ve PA6 polimer kompozit malzemelerin sürtünme katsayısı-kayma mesafesi ilişkisi

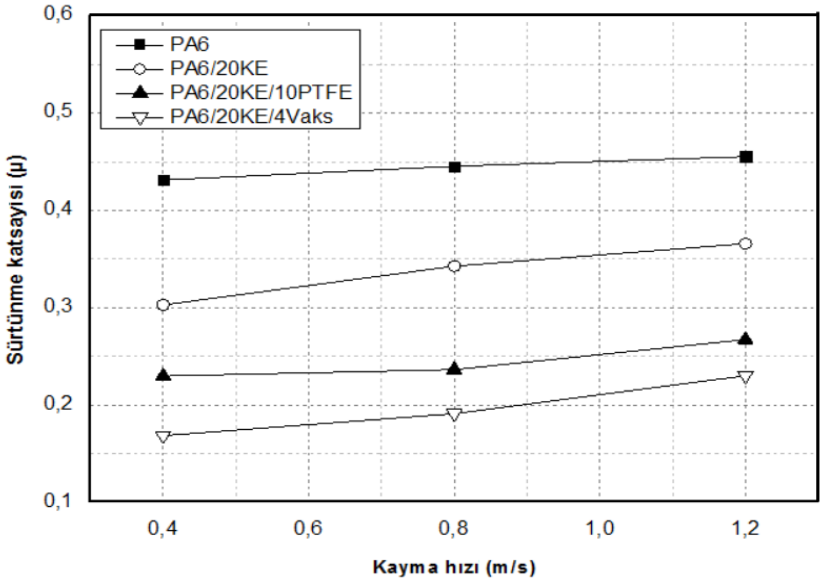
Şekil 3'de, katkısız PA6 ile %20KE, %10PTFE ve %4Wax katkılı PA6 polimer kompozit malzemelerin, 0.8m/s kayma hızında uygulanan yüke karşı sürtünme katsayısındaki değişimi verilmiştir. Şekilden de görüldüğü gibi, PA6 polimerine ilave edilen karbon elyaf ve katkı yağlayıcı olarak kullanılan PTFE ve vaks katkıları sürtünme katsayısını azaltmıştır. 0.8m/s kayma hızı ve 40N yük altında PA6 polimerinin sürtünme katsayısı 0.4704 iken %20 oranında karbon elyaf ilave edilmesi ile sürtünme katsayısı 0.4028'e düşmüştür. Sürtünme katsayısındaki azalma, yaklaşık olarak %16.78 oranındadır. PA6/20KE polimerine %10 PTFE eklendiğinde ise kompozitin sürtünme katsayısı %44.42 oranında azalmıştır. PA6/20KE polimerine %4 oranında vaks katkısı ilave edildiğinde sürtünme katsayısı %66.30 oranında azalmıştır. Uygulanan yükün sürtünme katsayısı üzerine etkisi incelendiğinde ise genel olarak uygulanan yükün artmasıyla, sürtünme katsayısının arttığı gözlenmiştir. Uygulanan yükün 10N'dan 40N'a artırılması ile PA6, PA6/20KE, PA6/20KE/10PTFE ve PA6/20KE/4Vaks polimer kompozitlerinin sürtünme katsayıları

sırasıyla, %8.4, %31.1, %25.9 ve %43.2 oranlarında artmıştır. En düşük sürtünme katsayısı, 10N yük altında, PA6/20KE/4vaks polimer kompozit numunesinde elde edilmiştir. Benzer sonuçlar Li [1] ve Cai [10] tarafından yapılan çalışmalarda da elde edilmiştir.



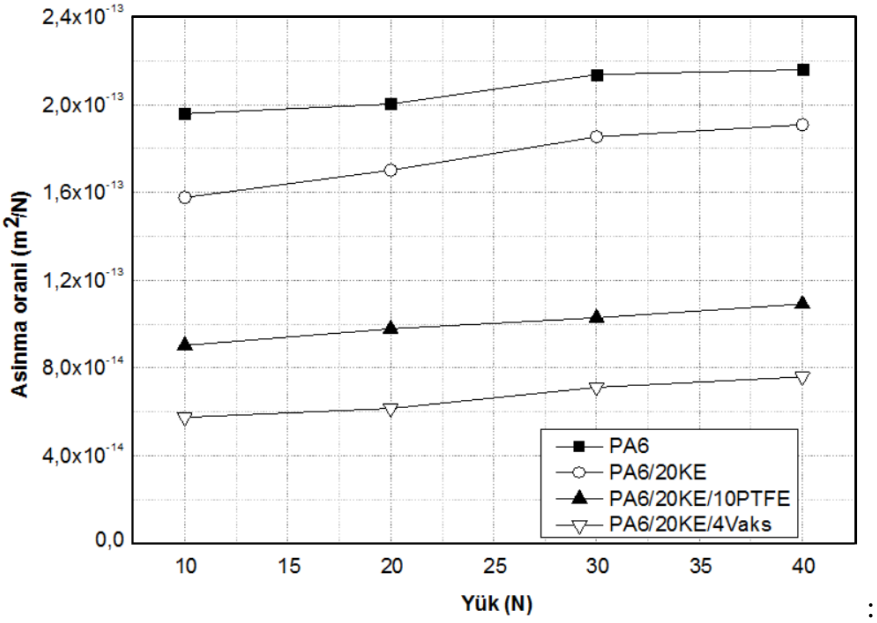
Şekil 3. Sürtünme katsayısı-yük değişimi (Kayma hızı: 0.8m/s)

Şekil 4'te ise 20N yük altında PA6 polimeri ile PTFE ve Vaks katkılı PA6 polimer kompozitlerinin kayma hızına bağlı olarak sürtünme katsayılarındaki değişim verilmiştir. Şekil incelendiğinde artan kayma hızına bağlı olarak sürtünme katsayısının arttığı gözlenmiştir. Bu artış PA6 polimeri için %5.58 oranında elde edilirken PA6/20KE polimeri için %20.77 oranında, PA6/20KE/10PTFE polimeri için %16.32 oranında ve PA6/20KE/4Vaks polimeri için %36.5 oranında elde edilmiştir. Uygulanan kayma hızı aralıklarında, PA6 polimerine ilave edilen %20 oranındaki karbon elyaf sürtünme katsayısını %24.5 oranında azaltmıştır. PA6/20KE polimerine ilave edilen PTFE ve Vaks katkıları ise sürtünme katsayısını %36.8 ve %59.0 oranlarında azaltmıştır. Uygulanan yük ve kayma hızı aralıklarında sürtünme katsayısını etkileyen en önemli parametrenin yük olduğu görülmektedir.



Şekil 4. Sürtünme katsayısı-kayma hızı değişimi (Yük: 20N)

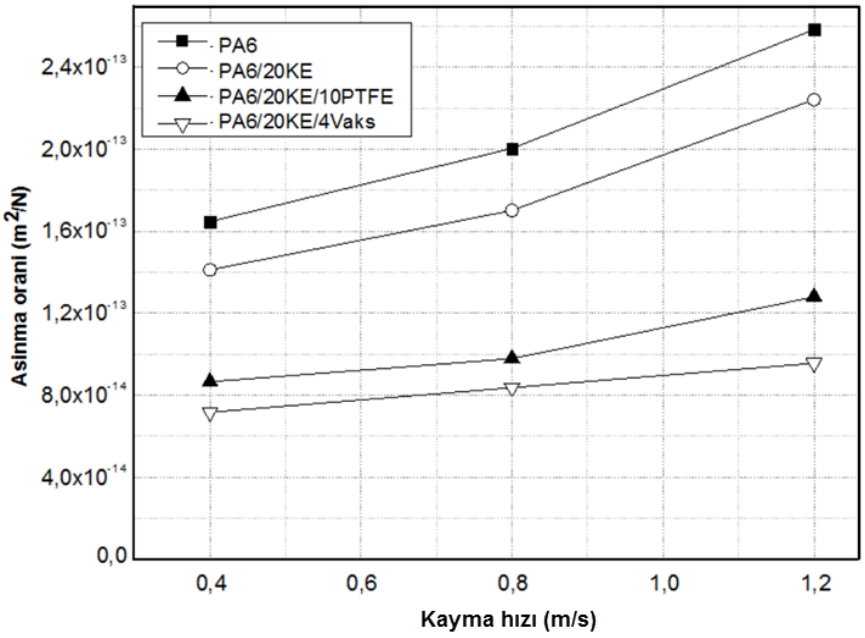
Şekil 5'de katkısız PA6, %20 karbon elyaf , PTFE ve Vaks katkılı kompozit malzemelerin 0.8m/s kayma hızında, uygulanan yüke karşı aşınma oranlarındaki değişim verilmiştir. Şekilde görüldüğü gibi, tüm malzemelerde uygulanan yükün artmasıyla, spesifik aşınma oranının arttığı gözlenmiştir. Genel olarak, PA6 polimeri ve %20 karbon elyaf katkılı PA6 polimer kompozitlerin aşınma oranları 10^{-13} m^2/N civarlarında elde edilirken PTFE ve Vaks katkılı numunelerde 10^{-14} m^2/N civarlarında elde edilmiştir. 0,8 m/s hız-40N yük altında, katkısız PA6'nın aşınma oranı $2.15x10^{-13}$ m^2/N iken; PA6'ya %20 oranında karbon elyaf eklenmesiyle aşınma oranının $1.90x10^{-13}$ m^2/N değerine düşmüştür. Aşınma oranındaki bu düşüş, yaklaşık olarak %13,13'tür. Aynı zamanda katkısız PA6'ya sırasıyla %10 oranında PTFE ve %4 oranında Vaks eklendiğinde, elde edilen kompozitlerin aşınma oranlarının $1.09x10^{-13}$ m^2/N ve $7.59x10^{-14}$ m^2/N değerlerine düştüğü, gerçekleşen bu düşüşlerin ise sırasıyla %74,9 ve %151,33 civarında olduğu gözlenmiştir. Şekilde görüldüğü gibi, 0,8m/s kayma hızı-40N yük altında, en yüksek aşınma oranını $2.159x10^{-13}$ m^2/N değeri ile katkısız PA6 sergilerken; en düşük aşınma oranını ise $5.147x10^{-14}$ m^2/N değeri ile PA6/20KE/4Vaks kompoziti sergilemiştir. Zhao ve arkadaşlarının [14] yaptıkları çalışmada, karbon elyaf takviyeli poliimid kompozitlerinin aşınma oranlarının, katkısız poliimid malzemesinin aşınma oranından daha düşük olduğunu belirtmişlerdir. Karbon elyafın, aşınma oranını düşürmesinin sebebinin; yüksek mukavemetli olan karbon fiberin, yükün çoğunu paylaşması ve böylelikle PI matrisini aşınmadan koruması olduğunu vurgulamışlardır. Rao ve arkadaşları [15] ise yaptıkları çalışmada, PA66 matrisine PTFE eklenmesiyle, aşınma oranında düşüş gözlendiğini ve bunun sebebinin de, PTFE'in temas yüzeylerinde ince film tabakası oluşturması olduğunu belirtmişlerdir.



:

Şekil 5. Aşınma oranı-yük değişimi (Kayma hızı: 0.8m/s)

Şekil 6'da katkısız PA6, %20 karbon elyaf , PTFE ve Vaks katkılı kompozitlerin 20N yük altındaki aşınma oranı-kayma hızı ilişkisi verilmiştir. Şekilden görüldüğü gibi kayma hızının 0.4 m/s'den 1.2 m/s'ye artırılması ile hem saf PA6 polimerinin hem de PTFE ve Vaks katkılı PA6 kompozit malzemelerinin aşınma oranlarında artış gözlenmiştir. Bu artış sırasıyla katkısız PA6, PA6/20KE, PA6/20KE/10PTFE ve PA6/20KE/4Vaks kompozit malzemeleri için sırasıyla %28, %31, %30 ve %26 oranında elde edilmiştir**.** Cai ve Wang [10] ile Dickens ve Sullivan [16] yaptıkları çalışmalar sonucunda artan kayma hızı ile birlikte aşınma oranının arttığını belirlemişlerdir.



Şekil 6. Aşınma oranı-kayma hızı değişimi (Yük: 20N)

Şekil 7'de PA6 polimeri ve PA6 polimer kompozit numuneler ait disk resimleri verilmiştir. Şekillerde görüldüğü gibi tüm numuneler için çelik disk yüzeyinde transfer film tabakasının oluştuğu gözlenmiştir. Oluşan bu film tabakası ise PA6 polimerinin hem sürtünme katsayısının hem de aşınma oranının şekillenmesinde önemli rol oynamıştır.



PA6 PA6/20KE PA6/20KE/10PTFE PA6/20KE/4Vaks

Şekil 7. PA6 polimeri ve PA6 polimer kompozit numuneler ait disk resimleri

4. Sonuçlar

PA6 polimerine ilave edilen %20 karbon elyaf ve katı yağlayıcı olarak ilave edilen %10PTFE ve %4Vaks katkılarının tribolojik özelliklere etkisinin incelendiği çalışmada aşağıdaki sonuçlar elde edilmiştir:

1. Uygulanan yükün artmasıyla, sürtünme katsayısının arttığı gözlenmiştir.
2. En düşük sürtünme katsayısı, 10N yük altında, PA6/20KE/4vaks polimer kompozit numunesinde elde edilmiştir.
3. PA6 polimerine ilave edilen karbon elyaf ve katkı yağlayıcı olarak kullanılan PTFE ve vaks katkıları sürtünme katsayısını azaltmıştır.
4. Artan kayma hızına bağlı olarak sürtünme katsayısı artmıştır.

5. Uygulanan yük ve kayma hızı aralıklarında sürtünme katsayısını etkileyen en önemli parametrenin yük olduğu belirlenmiştir.
6. En yüksek aşınma oranını katkısız PA6 polimerinde elde edilirken en düşük aşınma oranı PA6/20KE/4Vaks polimer kompozitinde elde edilmiştir.
7. Kayma hızının artırılması ile PA6 kompozit malzemelerinin aşınma oranları artmıştır.
8. Disk yüzeylerinde oluşan film tabakası ise PA6 polimerinin hem sürtünme katsayısının hem de aşınma oranının şekillenmesinde önemli rol oynamıştır.

Teşekkür

Yazarlar, Dumlupınar Üniversitesi, Bilimsel Araştırma Projeleri Başkanlığına desteklerinden dolayı teşekkür eder. (Proje No: DPÜ-BAP 2016-90)

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EFFECT OF CHEMICAL MODIFICATIONS ON COCONUT WASTE SHELL/EPOXY COMPOSITES PROPERTIES

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Abstract

In this study, coconut shell waste (CW) was used as raw material to obtain bio-based epoxy composite materials. The chemical modifications of CW with alkali and acetic anhydride were performed. The composites were prepared with CW in varied per cent values (10-50 wt%) using the casting technique. Modified CW particles were characterized by FTIR. Effects of CW amounts and chemical modification procedures on the mechanical properties of the composites were investigated. Modification with NaOH or acetic anhydride remarkably enhanced the tensile strength of the composites materials, but slightly decreased the e-modulus. Elongation of composites were observed to decrease with the CW content in the composite. Tensile strength of all composites are higher than that obtained with neat epoxy.

Keywords : biocomposite, epoxy resin, mechanical properties

1. Introduction

Biocomposites are composite materials made from natural filler and petroleum-derived non-biodegradable polymers or biopolymers. The interest on development of "green products" based on natural resources for both matrices and reinforcements has been increasing in recent years [1]. One of the most important properties of green materials is their biodegradability, because the problem of the solid waste generated by plastic materials after their final use increases the importance of biodegradable polymers/composites. Green materials have been successively used in many sectors including packaging, automotive and construction **[**1-3]. The natural plant-derived filler materials include many waste plant shells such as coconut, nut, walnut etc. due to their low costs they are potential biofillers. The advantages of using natural plant fibers over traditional glass fibers are their good specific strengths and modulus, low density and good biodegradability [4]. Coconut shell filler (80–85% of the gross weight of the coconut is considered waste) is a potential candidate for the development of new generation composites [5, 6]. In literature, many studies were carried out on preparation of various polymer composites, such as polyester, polyurethane, polypropylene, epoxy etc. using coconut fiber (coir) [7-10].

Surface modification which is usually made on solid materials is the act of modifying the surface of a material by bringing new physical, chemical or biological characteristics. Various treatments have been used to improve the properties of the natural fibers. A number of investigations have been conducted on chemical treatment (such as alkali, alcohol, hydrogen peroxide) of natural fibers to modify their surface chemical groups and to study the effect of treated fibers on mechanical properties of composite materials [11-13]. Chemical treatments were carried out using NaOCl, NaOH and H_2O_2 on coconut fiber surfaces by Brigida and coworkers [14]. Oxygen plasma treatment of coconut fiber has a positive effect on the tensile strength of poly(lactic acid) composites because of introduced chemical groups such as carboxylic acid and ester onto fiber surface [15].

In this study coconut waste (coconut shell together with coir) particles (CW) were chemically modified with NaOH and acetic anhydride and used as fillers. In our opinion, composites with these-type fillers can be used in the broad range of applications as building materials or other household appliances.

2. Experimental

2.1. Materials

A commercially available bisphenol F-type epoxy resin NPEF 170 called as ER, (EEW 160-180 g/eq, Konuray Chemical Co.) was used during the experimental studies. m-Xylene diamine and 2,4,6-tris(dimethylaminomethyl)phenol (Sigma-Aldrich) were used as the curing agent and epoxy embedding medium accelerator, respectively. Coconut as imported product was obtained from nearby local market and the shell with coir powder were obtained by grinding in IKA A11 basic mill and sieved.

2.2. Methods

2.2.1. Alkali modification

The natural fibers are lignocellulosic in nature. The purpose of chemical treatment is to remove a certain amount of lignin, oil and wax from coir fiber**,** thereby increasing surface roughness:

$$\text{Fiber - OH} + \text{NaOH} \rightarrow \text{Fiber - O - Na} + H_2O$$

The CW particles were strred with 5% NaOH solution and stirred for 24 h. The washing was repeated several times by adding fresh quantities of water. The alkali modifed CW particles then were dried.

2.2.2. Modification with acetic anhydride (AA)

The alkaline-treated CW was treated in glacial acetic acid for 1 h at 30 C; it was decanted and soaked in acetic anhydride containing one drop of concentrated H_2SO_4 for 5 min.

2.2.3. Composite preparation

The CW (particle size<63 μm) and neat ER mixed at varying per cent values (10-50 wt% for CW) were mechanically stirred at 1200 rpm and room temperature for 3 hours. Then the mixture was ultrasounded for an hour at 60°C to obtain a good dispersion. Following that, 30 wt% epoxy hardener and 1 wt% epoxy accelerator were added into the blend. The mixture was degassed for 60 min. at 40ºC and transferred into the mould. Composite specimens were prepared according to the ASTM D 638 standard. The curing procedure was carried out in an oven at 100ºC for 24 hours and then the samples were post-cured at 120ºC for another 24 hours.

2.3. Analysis and testing

2.3.1. FTIR analysis

The FTIR spectra of the modified CWs were obtained with Bruker-Platinum ATR- vertex 70 (Germany) between 500 and 4000 cm^{-1} wavenumbers at a resolution of 4 cm^{-1} using an attenuated total reflectance (ATR) accessory.

2.3.2. SEM analysis

Scanning electron microscopy (SEM) analyses were performed using a *Philips* XL30 SFEG instrument to investigate the interface between LW filler and the polymeric matrix.

2.3.3. Mechanical test

The resistances to stretch properties were determined by Stretch and Pressing Equipment TST-Mares/TS-mxe.

3. Result and Discussion

FTIR spectra of untreated, NaOH treated and AA modified CW particles are given in Fig.1. SEM images of composites are shown in Figs.2-4.

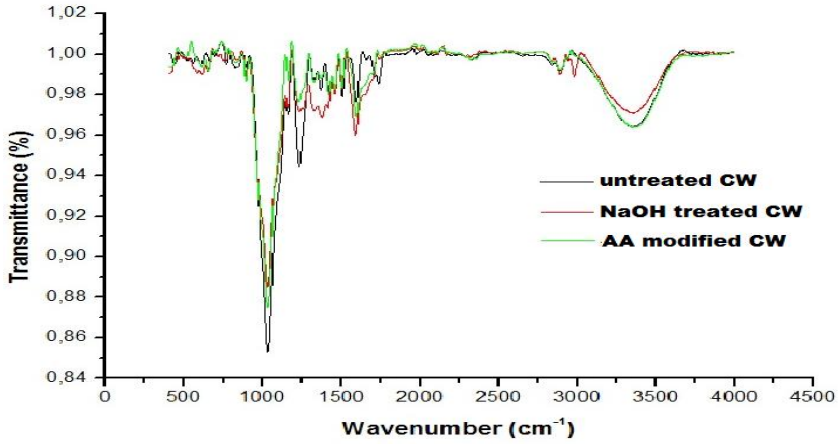


Fig.1. FTIR spectra of untreated, alkali treated and AA modified CWs

According to Fig. 1, for neat CW the following peaks were observed: the O-H stretching at 3349 cm^{-1}, aromatic C=C stretching at 1595 and 1515 cm^{-1}, stretching of unconjugated CO groups present in polysaccharides and xylans at 1731 cm^{-1}. In the FTIR spectrum of NaOH treated CW disappeared the hemicellulose ketone/aldehyde C=O peak at 1731 cm^{-1}. The intensity of the C-H stretching band at 2927 cm^{-1} and C-O stretching of the lignin guaicyl ring at 1265 cm^{-1} decreased compared to untreated CW, which proves that reduction of the lignin amount [16].

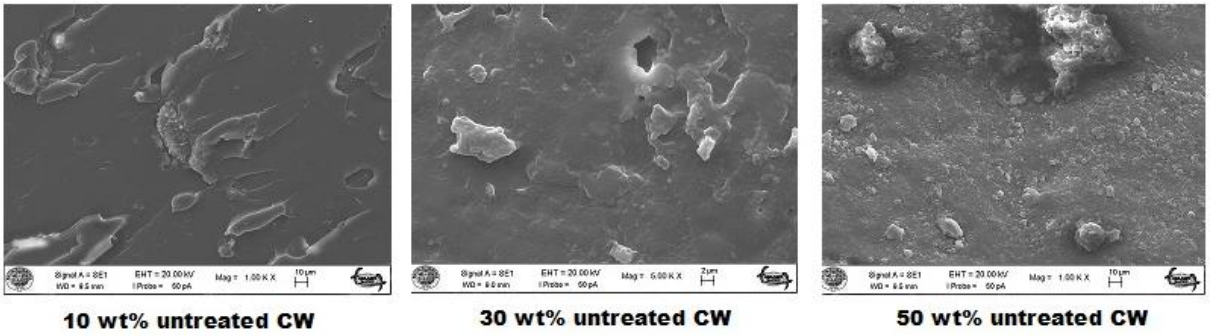


Fig. 2. SEM images of ER/untreated CW composites

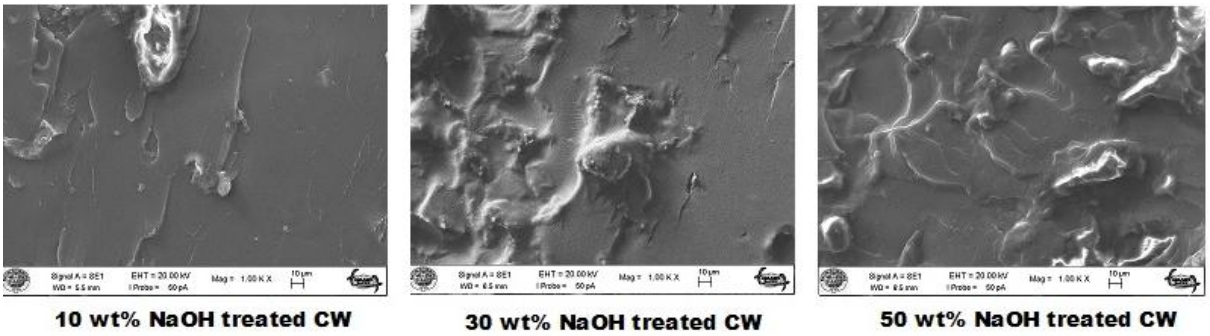


Fig. 3. SEM images of ER/NaOH treated CW composites

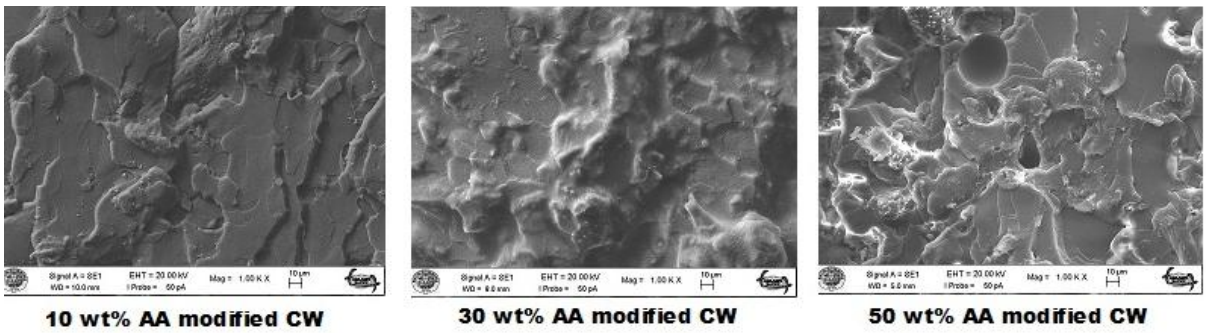


Fig. 4. SEM images of ER/AA modified CW composites

Table 1. Mechanical properties of composites

CW (wt%)	Elongation at break (%)	Tensile strength (MPa)	E-modulus (GPa)
NPEF-170 (ER)			
-	**1.067**	**108**	**9.0**
ER/untreated CW composites			
10	1.234	114	9.3
20	0.974	132	9.5
30	0.921	134	9.4
40	0.666	98	9.7
50	0.659	104	9.9
ER/NaOH treated CW composites			
10	1.010	133	6.8
20	1.002	154	7.2
30	0.958	134	8.8
40	0.942	134	9.5
50	0.515	137	8.9
ER/AA modified CW composites			
10	1.250	151	9.3
20	1.160	160	9.5
30	0.958	140	8.6
40	0.931	137	8.1
50	0.622	137	8.6

Morphological analysis using SEM clearly shows difference in the morphology of the composites (Figs. 2-4). Composites prepared with NaOH treated and AA modified CWs were more homogeneous than composites prepared with untreated CW. For all of the composites, the heterogeneity increased most beyond 30 wt% CWs loading, and that showed itself in the slightly weakening of the mechanical properties (see Table 1). Further, modification of CW with AA more improved the filler-matrix interaction.

As seen from Table 1, the chemical modification significantly affected the tensile strength and modulus values of the CW composites. The tensile strength and elongation of the composites increased in the order of untreated CW <NaOH treated CW <AA modified CW. The most appropriate filler amount were determined as 30%, 20% and 20 wt% for untreated CW, NaOH treated CW and AA modified CW, respectively.

Acknowledgement

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DEVELOPMENT OF HYDROXYL TERMINATED POLYETHER BASED COMPOSITE ROCKET PROPELLANT FOR INSENSITIVE MUNITION APPLICATIONS AND ITS CHARACTERIZATION

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Abstract

The aim of the present study is the development of a new generation hydroxyl terminated polyether (HTPE) based composite rocket propellant and its characterization in terms of mechanical, ballistic and thermal properties. HTPE binders are developed and used in certain composite rocket propellant formulations as less sensitive alternatives to hydroxyl terminated polybutadiene (HTPB) which is the most common polymer used in propellant formulations. It is claimed that HTPE propellants give a less severe response than HTPB propellants in Insensitive Munition (IM) tests. In the first part of this study, HTPE based networks were synthesized to investigate the structure-property relationships in segmented polyurethane structures. They were prepared by hand mixing and applying vacuum for degassing of the resulting mixtures. After curing at constant temperature, the mixtures were characterized in terms of mechanical (Uniaxial tensile test, hardness test), structural (Swelling test, X-ray diffraction) and thermal (Differential scanning calorimeter (DSC), thermal gravimetric analysis (TGA), vacuum stability) properties. In the second part, the propellant samples were prepared by incorporating energetic components such as oxidizer, energetic plasticizer, burning rate catalyst to HTPE based elastomers in a 1-pint size vertical mixer. Ballistic characterization of propellant samples were made by strand burner tests. They were also characterized by DSC, TGA, and vacuum stability tester for thermal properties. The third part of this study was focused on the manufacturing and characterization of the candidate HTPE based propellant in larger scale. It was characterized again in terms of the mechanical, ballistic and thermal properties. Results showed that the propellant that was developed has good mechanical and ballistic properties with well characterized thermal properties. These features indicate that it can be a good alternative for tactical missile systems, which are especially used in naval platforms.

Introduction

Propellants can be defined as materials that generate a large number of gaseous molecules at high temperature during combustion and can self-sustain combustion without the presence of ambient oxidizers. Since combustion is a self-sustaining exothermic rapid-oxidizing reaction, both oxidizers and fuels are needed to form a propellant. A new family of rocket propellants designed to fulfil IM requirements has emerged. They are based on crosslinked Hydroxy Terminated Polyether (HTPE) binders and are being used in certain composite rocket propellant formulations as alternatives to HTPB which is the most common polymer used in propellant formulations. Although, HTPE has been described as a new type of binder [1], polyether binders have been used in formulations since the mid-1950s [2], prior to the development of HTPB propellants. HTPE based copolymer consists of a block copolymer of poly-1,4-butanediol and polyethyleneglycol in a molar ratio of approximately 1 to 1 [3]. HTPE propellants were developed as less sensitive replacements for HTPB/Ammonium Perchlorate (AP) propellants currently used in several tactical missile rocket motors [4]. It is claimed that HTPE propellants give a less severe response than HTPB propellants in Insensitive Munitions (IM) tests especially in slow cook-off and

bullect impact [5]. This type of propellant was developed to reduce solid loading by using an energetic plasticizer that is compatible with HTPE binder. In this way, the specific impulse is maintained at or above that of a comparable HTPB, and also the sensitivity is reduced by replacing a percentage of AP by Ammonium Nitrate (AN) [6].

Objective

The study presented herein described the design of a new generation HTPE based composite propellant in order to meet the challenging insensitive munition requirement of solid rocket motors.

Experimental

First, HTPE based networks were synthesized in order to understand the structure-property relationships in segmented polyurethane structures. HTPE networks were obtained by the end-linking process of the HTPE chains via its terminal OH groups with isocyanate containing molecules. The properties of networks can be changed by using different types of isocyanate containing curing agents, curing catalysts and chain extenders with the corresponding HTPE binder. In addition, by manipulating the curative/binder equivalent ratio (NCO/OH ratio-R value) and weights of the network's ingredients, various kinds of polymeric structures were obtained.

Then, propellant samples were prepared by incorporating energetic components to HTPE based elastomers. The main ingredients of any propellant formulations are composed of polymeric binder, oxidizer, energetic as well as non energetic plasticizer, burning rate catalyst, curing catalyst or catalyst system, and some additives like combustion stabilizer and antioxidant stabilizer. The same procedure stated in propellant samples was followed for the large scale production of candidate propellant. However, the weight of the propellant prepared was increased by ten fold in this case.

Finally, in order to investigate the effects of propellant ingredients on the inert polyurethane matrix structure, mechanical, morphological and thermal analyses were performed. Furthermore, propellant samples prepared were characterized in terms of ballistic and thermal properties. A candidate propellant whose formulation was finalized after these analyses was subjected to mechanical, ballistic and thermal characterization.

Results and Discussion

The mechanical properties of the rocket propellant are mainly determined by the mechanical properties of the polymeric network. The propellant must be able to expand and contract within the rocket shell without cracking or detaching itself from the inner walls of the casing. The fundamental mechanical properties such as tensile strength, percent elongation at break and Young's modulus of both the polymeric network and the propellant should be characterized for use in a rocket motor. Tensile tests were performed in order to determine these properties. Below you can find the test results.

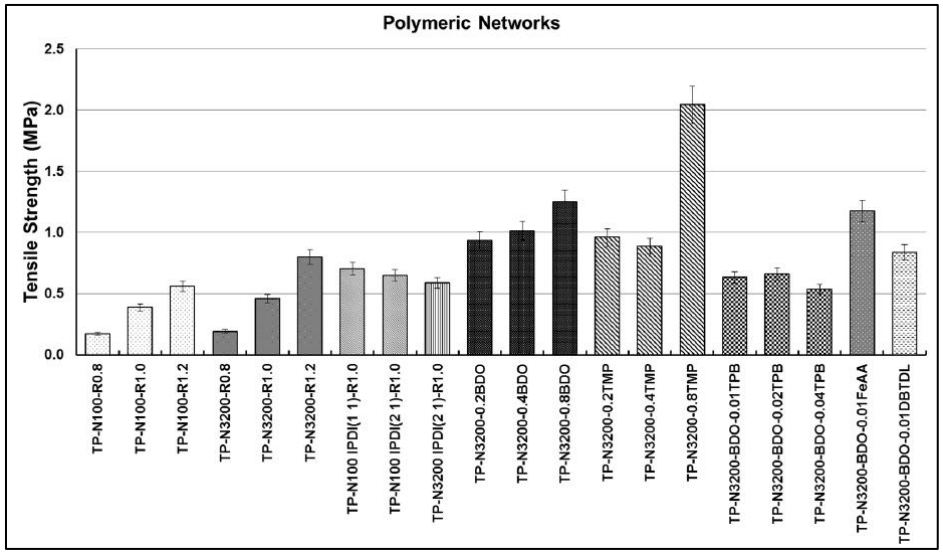


Figure 11 Tensile strength data of non-energetic polyurethane network structures

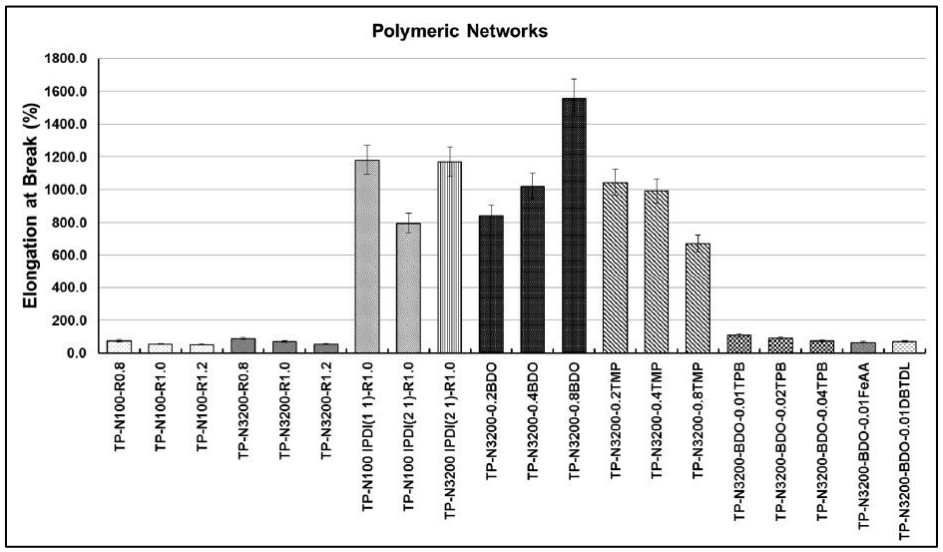


Figure 12 Percent elongation at break data of non-energetic polyurethane network structures

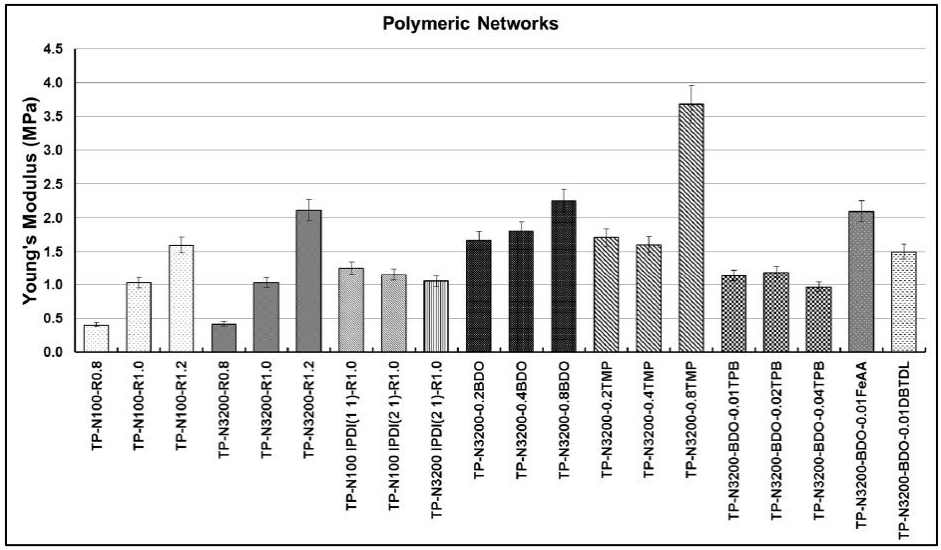


Figure 13 Young's modulus data of non-energetic polyurethane network structures

The best mechanical strengths were obtained with Desmodur type of isocyanates like N-100 and N-3200. They enabled the formation of organized structures leading to phase segregation which resulted from high intermolecular interactions between urethane linkages due to high hydrogen bonding through the nitrogen atoms on isocyanate and amide functionalities with TPEG and other polar urethane groups. The use of chain extenders 1,4-butandiol (BDO) and trimethylolpropane (TMP) as diol and triol, respectively, also upgraded the mechanical properties such that tensile strength and Young's modulus increased. However, elongation at break values showed different tendencies with the increase in the chain extender content. The increase in BDO content also increased the elongation values, on the other hand, TMP decreased the elongation values. Ferric acetyl acetonate (FeAA) and dibutyltindilaurate (DBTDL) showed higher catalytic activities to urethane reactions in comparison to triphenylbismute(TPB) and this resulted in higher tensile strength and Young's modulus.

Uniaxial tensile tests were performed at three different temperatures of -40^{o}C, 25^{o}C and 60^{o}C with 50 mm/min. crosshead speed using the microtensile test specimen for the propellant developed. The average stress-strain properties of three specimens are shown in Figure 4. Two different types of stress-strain behavior can be stated. The homogeneous (neckless) streching in which slightly linear stress-strain relationships were established and kept up to the point of maximum tensile strength, and sample fracture was observed at 60 ^{o}C and 25 ^{o}C. As cooling from 60 ^{o}C and 25 ^{o}C to -40^{o}C took place, the stress-strain curves showed a transition from a neckless stretching into an inhomogeneous stretching with a characteristic necking at low elongations and pronounced ductile behavior, actually resulting in an increased overall elongation at break at -40 ^{o}C when compared to the stress-strain curves at 60 ^{o}C and 25 ^{o}C.

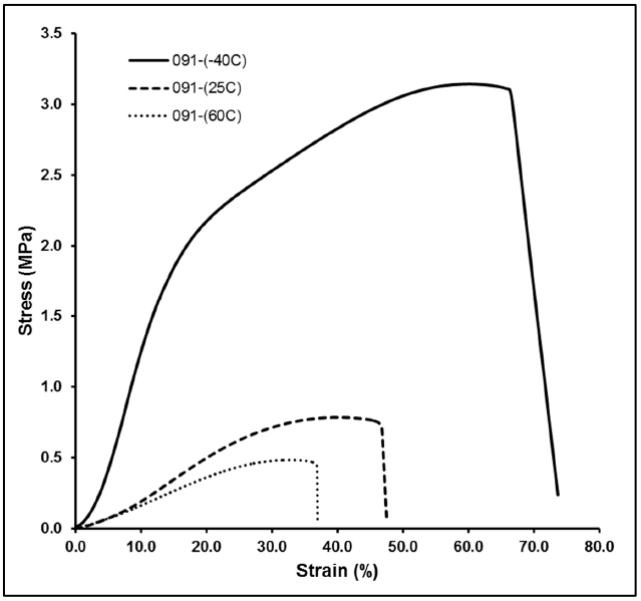


Figure 14 The stress-strain curves of propellant manufactured at three different temperatures

Structural analysis of polymeric network structures showed that the increase in NCO/OH ratio increased the hard segment content which led to lower extent of swelling and higher crosslinking for the samples prepared with N-3200 in both aniline and THF. Polyurethane samples showed mainly three diffraction peaks which were resulted from the crystallization of the soft-segment phase at about 11^o, 20.5^o and 43^o degrees. The broad diffraction profiles may be resulted from the soft segment-hard segment phase mixing which could also led to formation of small crystals. It was realized that as the degree of crosslinking increased, crystal perfection decreased and the intensity of diffraction peak in X-Ray diagrams tended to decrease. The diffraction patterns of HTPE-N3200 polymeric networks with different NCO/OH ratios are shown below.

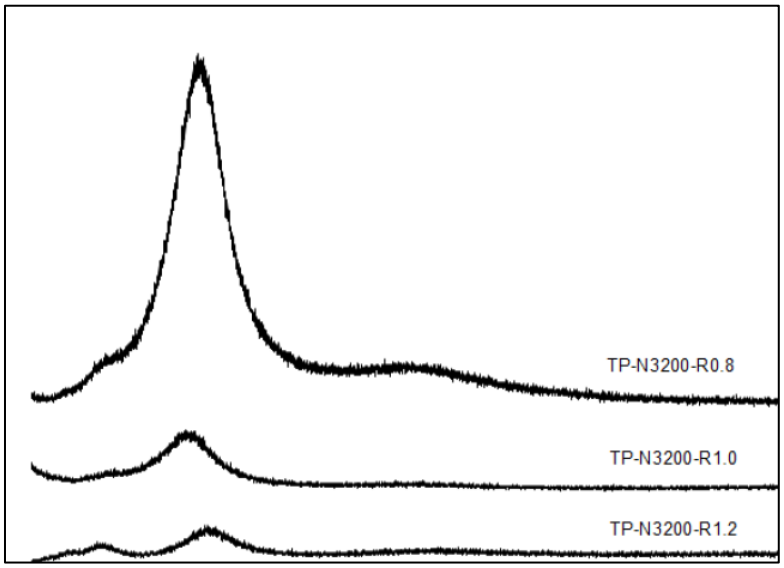


Figure 15 The diffraction patterns of HTPE-N3200 samples with different NCO/OH ratios

DSC allows the determination of glass-rubber transition temperature, melting – recrystallization temperature and their corresponding heat transitions which give information about the characteristics of microphase separation or phase mixing of polymeric structures. Three endotherms and one exotherm were mainly observed in the DSC thermograms of polymeric networks. The lowest temperature endotherm can be attributed to the glass transition temperature which was determined as about -73^{o}C. It is known that HTPE has a glass transition temperature of about -80^{o}C [7]. The next endotherm was between the temperatures of 0-10^{o}C which is the crystalline melting point. It involves a change from the crystalline solid state of the soft segment into the melt form. The last broad endotherm can be seen between the temperature range of 200-450^{o}C. This high temperature endotherm can be ascribed to the melting of microcrystalline regions within hard microdomains [8]. The low temperature intense exotherm at around -30^{o}C can be linked to soft segment crystallization of ordered regions. Figure 6 shows the DSC thermogram of HTPE-N3200 polymeric sample with NCO/OH ratio of 1.0.

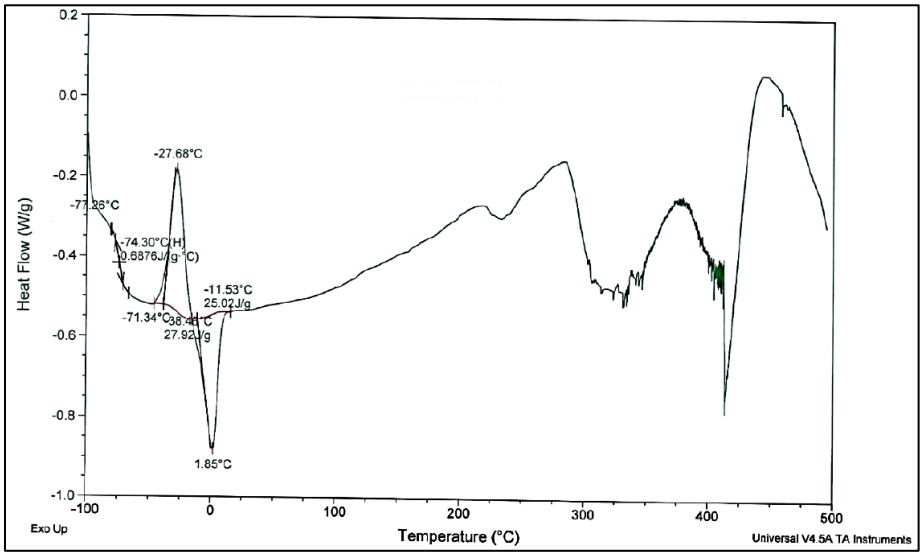


Figure 16 DSC thermogram of HTPE-N3200 polymeric sample with R:1.0

The quantification of thermal degradation of polymeric networks was investigated by TGA. Results show that two stage degradation processes can be proposed for all the polymeric networks. The first degradation occurred at the maximum temperature of about 300^{o}C which can be related to decomposition of urethane links. The second degredation is observed at around 360^{o}C which reaches a maximum temperature of about 400^{o}C as shown in Figure 7.

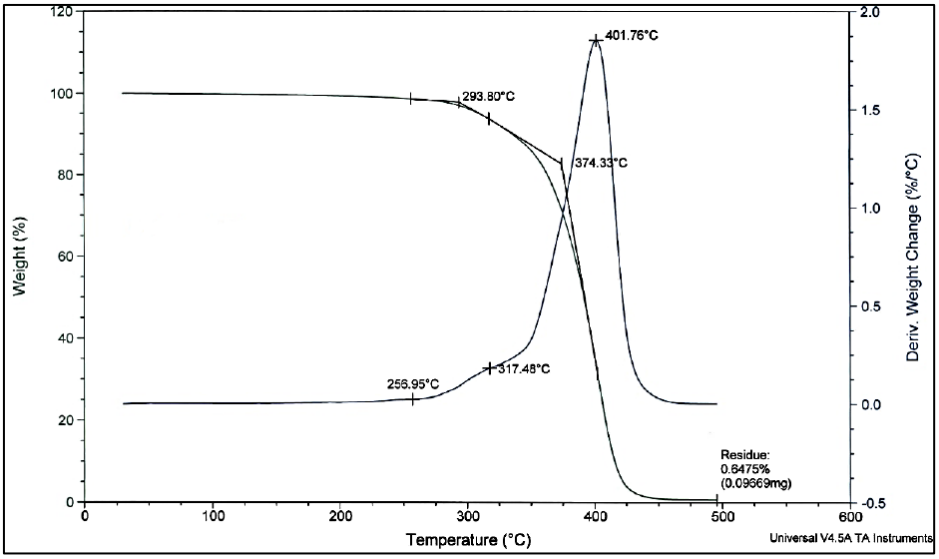


Figure 17 TGA thermogram of HTPE-N3200 polymeric sample with R:1.0

Thermal characteristics of propellant samples were also investigated by DSC in order to evaluate phase transitions, decomposition temperatures and corresponding heat transfers.The thermal analysis showed that the Tg of the propellant samples was only influenced by the type of energetic plasticizer. The particle size of AP, the modality of AP, the type of burning rate catalyst, the use of different energetic oxidizers like HMX, AN and Al as metallic fuel, respectively, did not affect the molecular mobility and crystallization nature of the propellants. In fact, the different energetic ingredients possessed different decomposition patterns. DSC analysis showed that propellant samples were completely decomposed between 350^{o}C and 400^{o}C by giving the highest exothermic response. The weight loss patterns depicted from TGA analysis mainly illustrated three stages of decomposition. The onset temperature of weight loss of stages were recorded approximately as 130^{o}C, 230^{o}C and 300^{o}C.

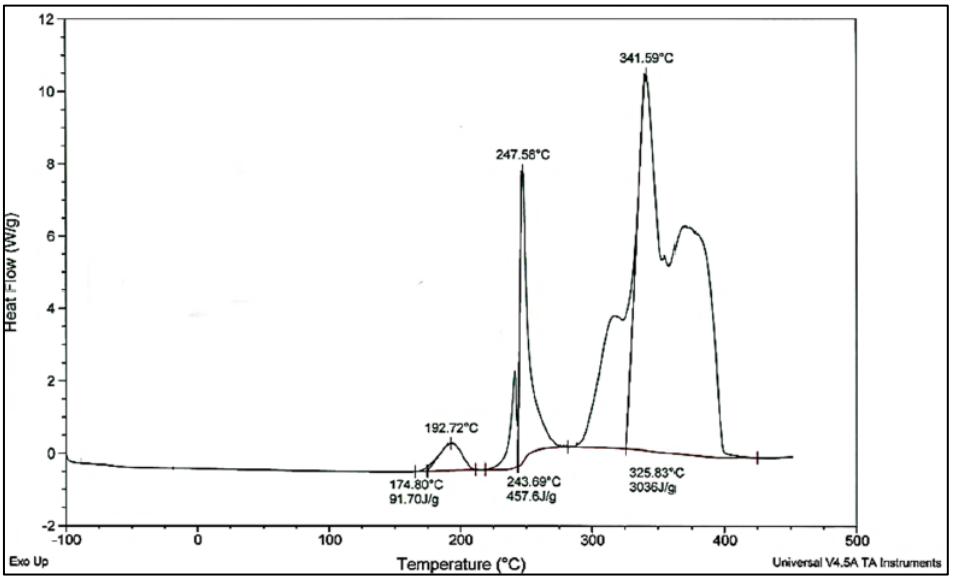


Figure 18 DSC thermogram of HTPE-AP based propellant sample

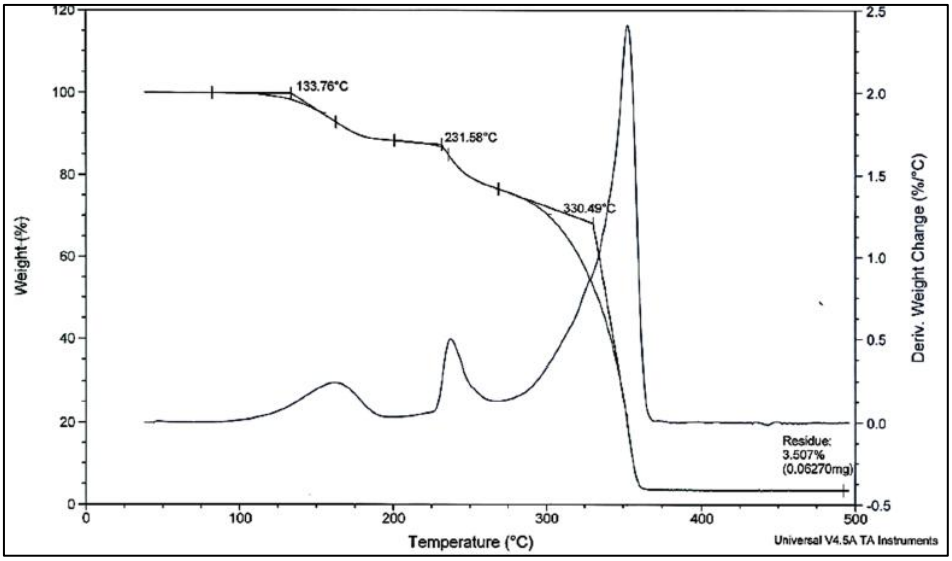


Figure 19 TGA thermogram of HTPE-AP based propellant sample

Burning rate and related burning rate pressure exponent are the critical ballistic results that can be experimentally determined. They are functions of the propellant composition and can be changed by changing the propellant characteristics by manipulating the type and weight of propellant ingredients. The burning rate and pressure exponent of propellant samples were determined by strand burner measurements for the pressure range of 6.9 – 13.8 MPa at constant temperature of 20^{o}C according to related military standard. In general, the burning rate of a composite solid propellant depends on the pressure, initial temperature, and particle size of energetic solid components, the presence or absence of a metal in the composition of the propellant, the oxidizer to fuel ratio, and the chemical nature of the propellant [9]. Results showed that the decrease in average particle size of energetic particles led to increase in the burning rate. Further, the use of different energetic particles with different particle sizes resulted in different burning rate and burning rate exponent. The oxide form iron seemed to be the best efficient burning rate enhancer giving high burning rate values.

Rocket test motor firings were performed to verify the calculated specific impulse and to determine the pressure exponent and the burning rates at different pressures of the propellant developed. The variations of combustion pressure and thrust with time are shown in Figures 10 and 11, respectively. It is clear that the maximum thrust level tends to increase with an increase in combustion pressure.

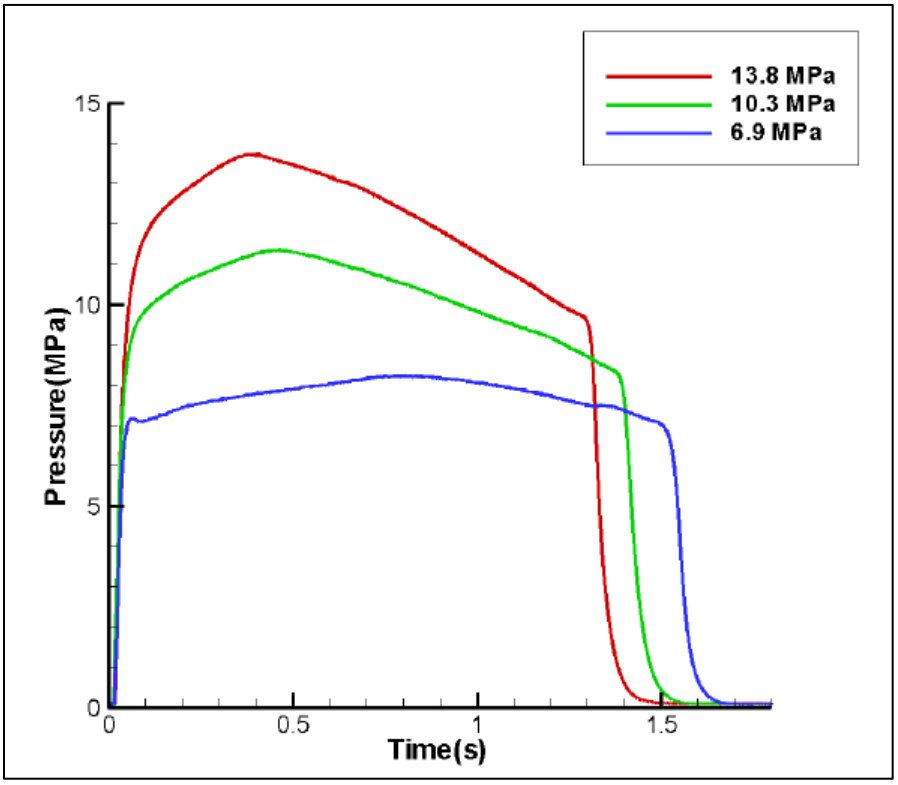


Figure 20 The variation of combustion pressure with time during test firings at three different pressures

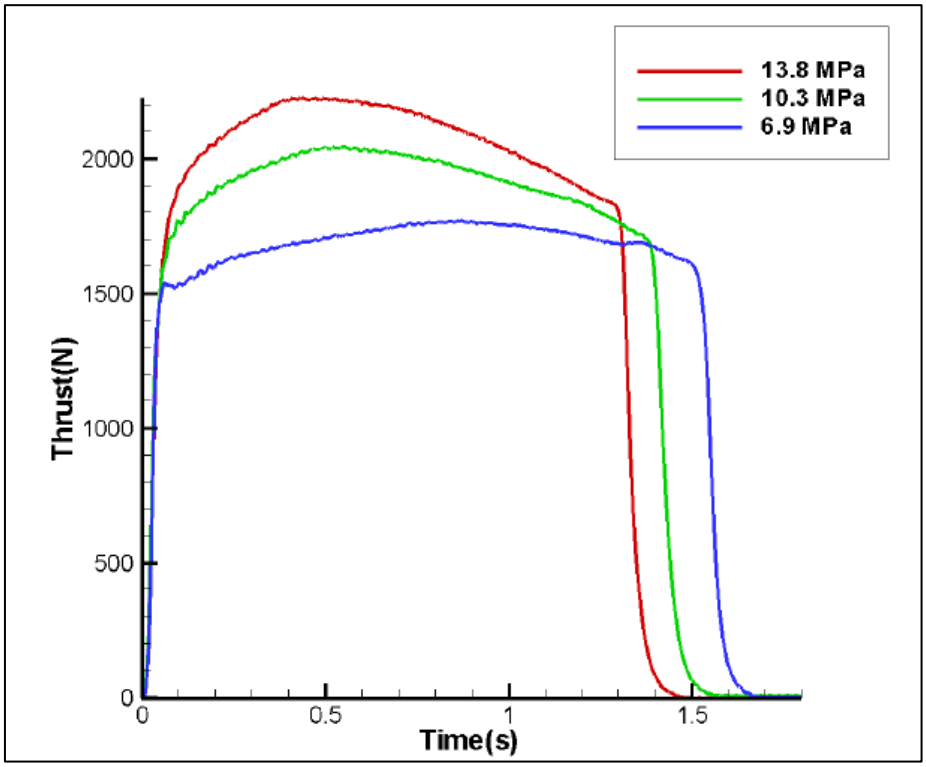


Figure 21 The variation of thrust with time during test firings at three different pressures

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THE EFFECT OF FLEXURAL STRAIN RATES ON THE FLEXURAL BEHAVIOR OF 4/3 GLARE FIBER METAL LAMINATED COMPOSITES

4/3 CETA FİBER METAL TABAKALI KOMPOZİTLERİN EĞİLME DAVRANIŞLARINA EĞİLME HIZININ ETKİSİ

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Özet

Amaç: Fiber Metal Tabakalar (FMT), ince metal levhalar ve kompozit tabakaların sıralı katmanlarından oluşan hibrid sandviç yapılardır. FMT malzemenin ağırlık kazancı açısından sağladığı %15-30'luk verim, yorulma mukavemeti, darbelere karşı gösterdiği direnç ve gelişmiş hasar toleransı gibi özellikleri sayesinde özellikle havacılık alanında büyük bir rağbet görmüş ve kullanımı her geçen gün artmıştır. Günümüzde üretilen yolcu ve savaş uçaklarında ağırlıkça %25'lere varan oranlarda FMT malzeme kullanılmaktadır. Bu çalışmanın amacı; THY Teknik A.Ş. kompozit atölyesinde üretilen 4/3 formasyonlu FMT malzemesinin üç nokta eğilme testleri altında eğilme davranışını incelemektir.

Materyal-Yöntem: Bu çalışmada, askeri ve sivil havacılıkta yoğun olarak kullanılan bir FMT türü olan CETA malzeme (Cam Elyaf Takviyeli Alüminyum), THY Teknik A.Ş. kompozit atölyesinde otoklav yöntemiyle üretilmiştir. FMT üretimi sırasında, 3 kat sürekli cam fiber takviyeli epoksi prepreg ve 4 kat Al 2024-T3 kullanılmıştır. Al 2024-T3 sac levhalar ve cam fiber takviyeli epoksi prepreg malzemesinden üretilen GLARE, 55 cm x 55 cm ebatında hazırlanarak vakum torbasına alınmıştır. Hot Bounder cihazı ile otoklav işlemi, 121 °C'de ve 40-50 psi vakum basıncı altında 2 saatte gerçekleşmiştir. Daha sonra vakumdan çıkarılan GLARE malzeme, ASTM D790–15 standardına uygun eğilme numuneleri olacak şekilde lazer kesme cihazında istenen boyuta getirilmiştir. Eğilme testleri 1 mm/dk ve 10 mm/dk eğilme hızlarında gerçekleştirilmiştir.

Ön değerlendirmeler: GLARE malzemelere Zwick Z-250 cihazında farklı hızlarda üç nokta eğilme testleri uygulanmış ve eğilme modülü, eğilme dayanımı ve maksimum kuvvetteki sehim değerlerinin değişimi tespit edilmiştir. Test hızının artması ile eğilme dayanımı ve eğilme modülü değerlerinde artış sehim değerlerinde ise hızlı bir düşüş gözlenmiş olup numunelerde oluşan hasar mekanizmalarının bölgesel ezilme hasarından delaminasyon hasarına doğru kaydığı belirlenmiştir. Eğilme testleri sonrasında GLARE malzemesinde oluşan hasar mekanizmaları dijital kamera görüntüleri ile tespit edilmiştir.

Anahtar kelimeler: *FMT, CETA, Eğilme özellikleri, Hasar Mekanizmaları*

Abstract

Aim: Fiber Metal Laminates (FMLs) are hybrid sandwich materials consisting of ordered layers of fine metallic sheets and composite laminates. The usage of FML has been increasing in the aircraft applications due to the its 15-30% efficiency in terms of weight gain, fatigue resistance, resistance to impact and improved damage tolerance. Currently FML material is used up to 25% by weight of manufactured passenger aircraft and fighter aircraft. The aim of this study is to examine the flexural behavior of 4/3 configurated FML material which is produced in Turkish Airlines Technic Inc. composite workshop under three point bending tests.

Materials-Methods: In this study, GLARE (Glass reinforced aluminium) which is an FML type that is used extensively in military and civil aviation is manufactured by Turkish Airlines Technic Inc. composite workshop with autoclave method. During FML production, 3 layers of continuous glass fiber reinforced epoxy prepreg and 4 layers of Al 2024-T3 are used. GLARE which consists of Al 2024-T3 sheet metals and glass fiber reinforced epoxy prepreg material is prepared with a size of 55 cm x 55 cm. It is taken to vacuum bag in an autoclave with a Hot Bounder device at 121 ° C and under 40-50 psi pressure for 2 hours. The GLARE material is then removed from the vacuum bag and brought to the desired size in accordance with ASTM D790-15 standard in the laser cutting device. Flexural tests are applied to the GLARE samples under 1 mm/min and 10 mm/min flexural strain rates.

Preliminary evaluations: GLARE is subjected to three point bending tests at bending rates at a Zwick Z-250 device. The variation on the flexural modulus, flexural strength and maximum strength values is determined. From test results, the flexural strength and flexural modulus values increased with the increase of the bending rates. Beside this, the deflection of maximum load values decreased rapidly. It is also determined that the damage mechanisms change local crushing damages to delamination damages. After the bending tests, damage mechanisms which are occurring in the GLARE are detected by digital camera images.

Keywords: FLM, GLARE, Flexural properties, Damage Mechanisms

1.Introduction

Fibre metal laminates (FMLs) are metallic materials consisting of a laminate of several thin metal layers bonded to plies of composite material. This combination allows the material to behave much as a simple metallic structure, but with specific advantages such as a high mechanical properties and weight-savings [1]. GLARE (Glass Laminate Aluminum Reinforced Epoxy) is a type of FMLs based on glass fibers. GLARE typically consists of several layers of thin aluminum alloy sheets especially 2024 or 7075 interspersed with layers of unidirectional or woven glass fiber reinforced epoxy composite materials [2]. GLARE takes advantages of both metals and fiber-reinforced composites, providing superior mechanical properties that cannot be achieved by either of its constituents. Major advantages of GLARE include low density, high fracture toughness and strength and fatigue resistance [2]. Because of these advantages, GLARE is being sought after for more applications in the aerospace industry. For instance, GLARE is selected for the fabrication of the Boeing 777 bulk cargo floor [3] and the upper fuselage panels of Airbus A380 [4].

From literature surveys, researchers have focused on the mechanical properties such as fatigue properties and impact properties of FMLs relative to their constituent materials [5-8]. Also the interfacial properties and tensile behavior of FML materials were also performed [9]. On the other hand, few studies have been found about the flexural properties of GLARE. During flight, structural parts of the wings are subjected to the bending loads. Especially, wings of a new generation of passenger aircraft consist of FMLs material. By this way, flexural properties of GLARE based FMLs shall be investigated. Rajkumar et al.[10] focused on the effect of strain rate and lay-up configuration on mechanical behavior such as tensile and flexural

properties of four different combinations of 3/2 FMLs (Al 6061/bidirectional glass fiber/carbon fiber reinforced epoxy resin). The results showed that the tensile strength increased with increasing of strain rate. On the other hand, the flexural strength values decreased at higher strain rates. Hassan et al. [11] investigated the mechanical behavior of various lay-up layered FMLs which consisted of 1, 2, 4, 6, and 8 layers of woven fiber sandwiched between two thin sheets of aluminum. Tension and flexural tests were carried out to measure both tensile and flexural strength for different layup specimens. The results illustrated that as the number of woven layer increased as both strengths increased. The failure mode for bending FMLs appeared as delamination. Carrillo and Cantwell [12] studied on the mechanical properties of a novel FML based on a polypropylene composite. Two stacking arrangements were used as $[Al/0/90]_s$ and $[Al/\pm 45]_s$. Four point flexural samples were loaded according to the ASTM D790-80 standard. Results showed that flexural tests on $[Al/0/90]_s$ and $[Al/\pm 45]_s$ configurations showed that the fiber orientation had only a secondary effect on the properties of the FML, with the maximum stress and the strain at failure being similar in both cases.

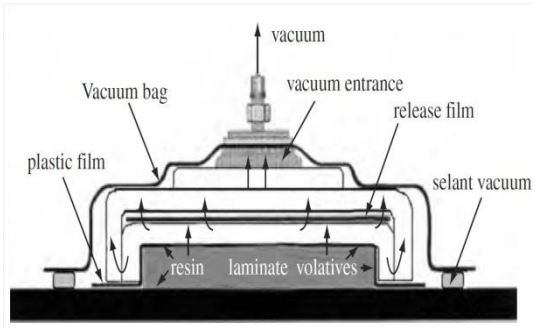
From literature survey, it is easily determined that there is not any study found which is about the flexural properties of 4/3 configurated GLARE material under various strain rates. This study presents the variation of flexural strength, flexural modulus and flexural strain of 4/3 configurated GLARE under 1 mm/min and 10 mm/min strain rates. First of all, the manufacturing process which is done in Turkish Airlines Technic Inc. of GLARE material is described. After manufacturing process, three point bending test results are given in detail. At last, damage mechanisms of flexured GLARE materials are shown with digital camera observations.

2. Materials and Methods

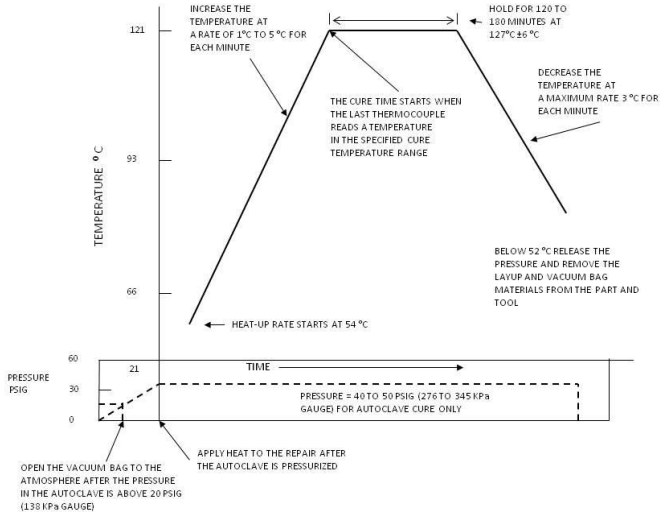
2.1. Materials and Manufacturing Technique

FMLs used in this experimental investigation are manufactured in Composite Laboratory at Turkish Airlines Technic Inc. by using vacuum bag technique. 4/3 configurated GLARE consist of four layers of 2024-T3 Al sheets and three layers of class III, style 1581 (Glass Fiber Reinforced Plastic (GFRP) fabric) laminate. BMS 8-79 Style 120 38" CL3 is a fiberglass pre-preg style that contains HexPly® F155 resin system. It's an advanced modified epoxy formulation designed for autoclave curing to offer very high laminate strengths, coupled with increased fracture toughness and adhesive properties.

Schematic representation of vacuum bag system is shown in Fig.1-a. The cure preparation step involves primarily the bagging of the part and the placement of many ancillary materials. The common cure preparation arrangement, including the part, the tool, the bagging and the ancillary materials are shown in Fig 1-a. The function of these various components are: vacuum bag (the envelope parts and the tools for vacuum can be made by nylons, polymer blends, some metals or silicone rubbers); plastic and release films (release composite from tools, can be made by fluorinated ethylene propylene; halohydrocarbon polymers; PTFE; polyimides; polyamides or polytetramethylene terephthalamide) and bleeder (absorbs the excess of resin, it can be made by woven fabrics, felts [13]. During the autoclave process, it is necessary a previous knowledge involving the temperature and the pressure requirements, for the composite layer consolidation and cure. In general, GLARE is processed up to 121 °C in order to avoid damages in the aluminum 2024-T3 alloys. At this temperature the resin viscosity is reduced and resin flows easily. Adequate temperature levels to be used during the consolidation process can be determined by using Boeing 737-800 Structural Repair Manual 51-70-05 [14]. Pressure is needed to press and to consolidate the plies and suppress voids. Thermal and rheological techniques are appropriate to study the events that take place in the composite layer, and so optimized curing cycles can be obtained, as exemplified in Fig. 1-b.



a.Schematic representation of vacuum bag technique [13]



b.Autoclave process steps for 4/3 configurated GLARE [14]

Figure 1. 4/3 configurated GLARE process system and manufacturing procedure

2.2. Mechanical Tests and Evaluation of Damage Mechanisms

The three point bending test according to the ASTM D790–15 standard was applied to the prepared 4/3 configurated GLARE samples to measure the flexural properties such as flexural strength, flexural modulus and flexural strain. The experimental samples in this study were prepared in 125 mm x 12.7 mm x 3.2 mm by cutting out from the panel of 550 mm x 550 mm x 3.2 mm by using a laser cut. Beside this, support span of 16 times the depth of the GLARE samples is used for three point bending tests. Three rigid rollers having 12 mm of diameter have been used as loading and supporting devices. Rubber pressure pads of 12 mm width were placed between the bars and specimen to prevent local damage to the face skins. At least five samples of GLARE were tested under 1 mm/min and 10 min/min strain rates and flexural load/strain values were recorded using Zwick Z-250 universal test machine. After three point bending tests, GLARE samples are examined optically with a digital camera in order to elucidate the damage mechanisms during flexural loading.

3. Results and Discussions

The effect of flexural strain rate on the flexural strength of 4/3 congifurated GLARE is presented in Fig.2. From Fig.2-a and b, the estimated of maximum flexural strength values are found to be nearly at 657 MPa and 676 MPa for 1 mm/min and 10 mm/min strain rates, respectively. Flexural strength is the maximum stress which is calculated by using Eq. 1 [15].

$$\sigma_f = \frac{3.P.L}{2.b.d^2} \quad (1)$$

Where;
σ = stress in the outer fibers at midpoint, MPa, *P* = load at a given point on the load-deflection curve, N, *L* = support span, mm, *b* = width of beam tested, mm and *d* = depth of beam tested, mm. It is clearly said

that the variation of the flexural strain rate has not been a cause for a significant change on the flexural strength of 4/3 configurated GLARE. The flexural strength/flexural strain behavior for both arrangements is very similar, highlighting the strong influence of the aluminum in these samples as similar to Ref [12]. Beside this, the GLARE samples have not failed after reaching the first peak load (Fig.2-a). A closer examination shows that the constituents in the GLARE remained well bonded as similar to Ref [11]. This result indicates that the manufacturing process of 4/3 GLARE is appropriate. Another important result is flexural strain values shift from 8.19 mm to 7.27 mm for 10 mm/min. The damage formation of GLARE samples begins earlier due to higher strain rates.

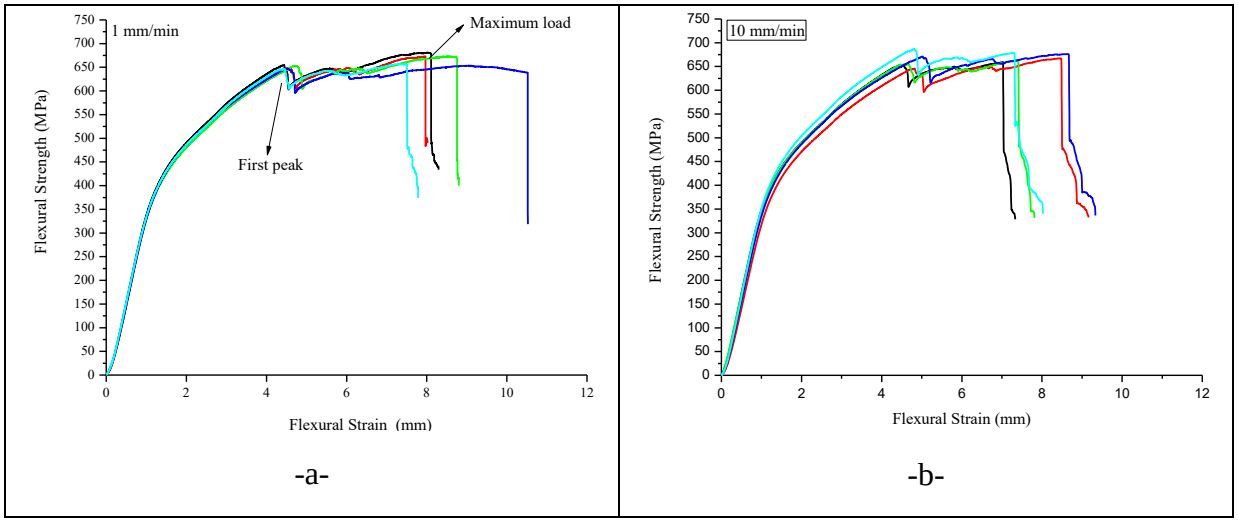


Figure 2. Flexural strength versus flexural strain curves of 4/3 configurated GLARE under different flexural strain rates

Flexural modulus is defined as a tendency of material to bend and determined from the slope of stress-strain curve. Flexural modulus also can be calculated using Eq. 2 [15-16]. Then, the mean values of flexural properties are calculated and given at Table 1.

$$E_B = \frac{L^3 m}{4bd^3} \qquad (2)$$

Where;
E_B = modulus of elasticity in bending, MPa, L = support span, mm, b = width of beam tested, mm, d = depth of beam tested, mm, and m = slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm of deflection.

Table 1. Flexural modulus of 4/3 configurated GLARE under various strain rates

Sample	1 mm/min strain rate	10 mm/min strain rate
1	54695 MPa	55284 MPa
2	53946 MPa	55497 MPa
3	54508 MPa	55941 MPa
4	51903 MPa	55627 MPa
5	54847 MPa	58073 MPa
Mean values	***53980 MPa***	***56084 MPa***

From Table 1, it is determined that the flexural modulus increases with the increment of flexural strain rate. The flexural modulus values improve approximately 4% for 10 mm/min strain rates according to 1 mm/min. It is again apparent that higher strain rates (10 mm/min) offer a modulus value that is higher than those associated with the lower strain rates (1 mm/min).

Fig.3 illustrates the main damage modes of three point bended GLARE samples. It is clear that the delamination damage mode is only extended along the bi-material interfaces that are between rear metallic layer and composite layer. This can be attributed to local tensile stresses induced in the rear surface of GLARE samples. On the other hand, samples have not failed up to maximum flexural load reaching the maximum flexural load. A closer examination shows that the constituents in the GLARE (i.e., the aluminum and the composite layers) remained well bonded. The width of the delamination are very nominal for both GLARE samples which are tested at 1 mm/min and 10 mm/min and the central part of the rear metallic layer and composite layer act as a single entity due to heterogeneous fibers as similar to Ref.[10]. Beside this, cracks also occur at the rear metallic layer of GLARE samples at 10 mm/min. Due to high strain rates, metallic layer crack can be seen hence the strength of individual layers have higher integrity, thus it can bear higher load and higher tendency of delamination.

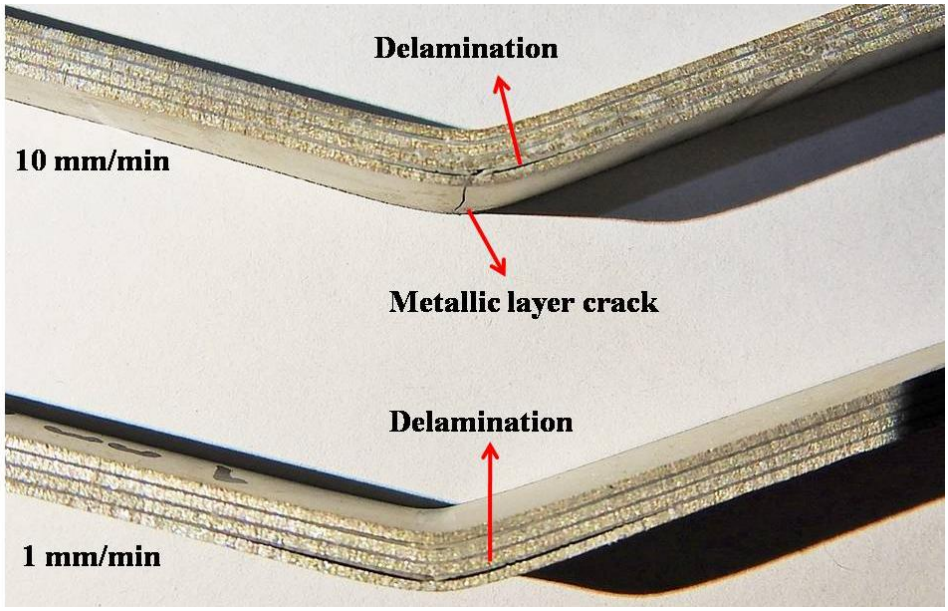


Figure 3. Digital damage observations of 4/3 configurated GLARE samples after three point bending tests

4. Conclusions

Flexural properties such as flexural strength, flexural modulus and flexural strain of 4/3 configurated GLARE samples which were manufactured by using autoclave technique were investigated under the terms of different strain rates. From experimental results, it is worth nothing that the change of strain rates did not affect the flexural strength values. On the other hand, flexural modulus values of GLARE samples were increased nearly 4% at higher strain rates with lower flexural strain. From damage observations, it is determined that delamination was the main damage mechanism for all GLARE samples. Delamination occurred at only the center of the rear face of the GLARE samples. In addition, metallic layer crack also observed at 10 mm/min strain rates due to integrity of individual layers.

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STACKING SEQUENCES DESIGN OF COMPOSITE HYDROGEN STORAGE TANKS USING OPTIMIZATION ALGORITHMS

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Keywords: pressured gas storage tanks, optimum design, first-ply failure theory, classical lamination theory

Özet

Basınçlı gaz depolama tankları hidrojen gibi gazların taşınması ve kullanılması esnasında tercih edilmektedir. Mobil uygulamalarda (hidrojen yakıt hücresi ile çalışan araçlar ve otobüsler), mukavemet ve hafifliği birlikte sunan Tip III, Tip IV (polimer iç gömlek) ve Tip V (iç gömleksiz) kompozit depolama tankları tercih edilmektedir. Bunların içinden, Tip III basınçlı hidrojen depolama tankları, temel takviye bölümü olarak kompozit ve tank kalıbını oluşturan metal iç gömlekten meydana gelir. İç gömlek, depolama tankına binen yükün bir miktarını taşırken, çoğunu kompozit bölüme aktarır. Literatüre bakıldığında, Tip III depolama tankları, bazı araştırmacılar tarafından hem teorik hem de deneysel yöntemlerle, ağırlık azaltma ve patlama basıncını arttırma yönünden incelendiği görülmektedir. Yapılan çalışma silindirik Tip III hidrojen depolama tanklarının optimum tasarımı ve kırılma analizi ile ilgilidir. Malzemeler olarak, kompozit yapı karbon fiber/epoksi den oluşurken, iç gömlek 6061-T6 alüminyumdan seçilmiştir. Optimizasyon öncesinde, geliştirilen bilgisayar kodunun literatürden faydalanarak doğrulaması yapılmıştır. Ardından, Tip III ve Tip V tankların birbirlerine göre mekanik performansı ve ağrılıkları karşılaştırılmıştır. Gerilme ve gerinimler, Klasik Laminasyon Teorisi kullanılarak belirlenmiştir. Elde edilen sonuçlar ise, Tsai-Wu kırılma kriterine göre karşılaştırılmıştır. Optimizasyon bölümünde, 8, 12 ve 16 tabakadan oluşan dizaynların optimum açı ve patlatma basınçları elde edilmiştir. Optimum açıların tespiti Tsai-Wu, Tsai-Hill, Maksimum Stres ve Hashin kırılma kriterleri indekslerinin minimizasyonu ile gerçekleştirilmiştir. Bu esnada Differensiyel Evrim ve Nelder-Mead optimum tasarımların elde edilmesinde kullanılan optimizasyon algoritmaları olmuştur. Optimizasyon için seçilen algoritmalar, optimal tasarımların patlama basıncındaki mekanik performansları ve sonuç bulma hızları bakımından karşılaştırılmıştır.

Abstract

In this study, maximization of burst pressure of a cylindrical laminated composite tank including metal liner (Type III pressure tank) with certain material properties has been aimed. An analytical approach based on Classical Lamination Theory (CLT) has been studied according to the first-ply failure strength

on symmetrically laminated composite tank. Optimum fiber angle orientations of laminated symmetric and balanced composites have been investigated to provide maximum possible stiffness in order to increase the burst pressure. Three designs having symmetric and balanced stacking sequences with different number of layers have been examined. As materials, carbon fiber reinforced epoxy has been chosen for the composite region and 6 series T6 heat treated aluminum liner has been preferred. Before optimization, developed computer code has been verified from literature. Then, mechanical performances and weights of Type III and Type V storage tanks have been compared. After this, in optimization part, optimum stacking sequences and maximum burst pressure have been obtained using failure evolutions predicted by Tsai-Wu, Tsai-Hill, Maximum Stress and Hashin failure theories. Stochastic search algorithm "Differential Evolution (DE)" and direct search algorithm "Nelder-Mead (NM)" has been used to obtain optimal designs. Results obtained by optimization algorithms have been compared in the aspect of mechanical performance and CPU time.

1. Introduction

Pressured gas storage tanks are preferred in certain industries which require to store more gas in a tank. Recently, hydrogen has been a type of fuel for electrical vehicles (i.e. fuel cell vehicles). Therefore, composite storage tanks having higher strength and lightweight have been preferred to store hydrogen. Besides, mobile applications, in aero-space and defense industry, these storage tanks are also expected to have critical specifications such as high working pressure capability (around 700 bar), lightweight and cost efficiency.

Type III storage tanks are built by composite as the main reinforcement part and inner metal liner named as mold of the tank. The liner carries minor amount of the loads that tank undergoes and transmits most of the loads to the composite part. This type storage tanks can be designed to have desired mechanical performance and lightweight, similar to composite tank with polymer liner (Type IV) and composite tank without liner (Type V).

Recently, Type III tanks have been studied by some researchers in the aspect of weight minimizations and maximization of burst pressures both theoretically and/or experimentally. In these studies, the main objective is generally about increasing the overall stiffness while decreasing the required weight of the storage tank.

Xu Ping et. al (2009), used Adaptive Genetic Algorithm method to maximize burst pressure, minimize weight and also provided the advantages of this method compared to Standard Genetic Algorithm and Monte-Carlo optimization methods [1]. Peletier and Vel (2006) studied multi-objective optimization to increase strength, stiffness while minimizing mass of the pressure vessel [2]. In another study, Chang (2000) modelled three different Type V storage tanks having same curvature radius and length using NASTRAN [3]. Fiber angle orientations of 8-layered, 12-layered and 16-layered designs were in angle-ply formations. Chang obtained burst pressures based on first-ply failure of laminated composite pressure vessel using NASTRAN and compared the results with experimental ones. In their study, Zheng and Liu (2008) examined burst strength evaluation of Type III composite cylindrical laminates with theoretical and experimental approaches [4]. They used universal numerical algorithm in MATLAB to optimize inner radius, winding angles, total layer number and thickness of metal liner and a layer.

2. Theoretical Background

2.1. Classical Lamination Theory

In classical lamination theory, each composite layer is assumed as thin, homogenous, linear-elastic, anisotropic and perfectly bonded [5]. Q, $\overline{Q}$ stiffness values and A-B-D matrices for composite and liner are found to obtain the relationship between global/local strains and global/local stresses [6].

$$\overline{Q}=\begin{bmatrix}\overline{Q}_{11} & \overline{Q}_{12} & \overline{Q}_{16}\\ \overline{Q}_{12} & \overline{Q}_{22} & \overline{Q}_{26}\\ \overline{Q}_{16} & \overline{Q}_{26} & \overline{Q}_{66}\end{bmatrix} \quad \text{for laminated composite} \tag{1}$$

$$Q_{liner}=\begin{bmatrix}Q_{11,liner} & Q_{12,liner} & 0\\ Q_{12,liner} & Q_{22,liner} & 0\\ 0 & 0 & Q_{66,liner}\end{bmatrix} \quad \text{for metal liner} \tag{2}$$

Global stress and strain components can be expressed in below where "c" is the number of a layer counted from the bottom;

$$\begin{bmatrix}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{bmatrix}_c=\begin{bmatrix}\overline{Q}_{11} & \overline{Q}_{12} & \overline{Q}_{16}\\ \overline{Q}_{12} & \overline{Q}_{22} & \overline{Q}_{26}\\ \overline{Q}_{16} & \overline{Q}_{26} & \overline{Q}_{66}\end{bmatrix}_c\begin{bmatrix}\epsilon_x\\ \epsilon_y\\ \gamma_{xy}\end{bmatrix}_c \tag{3}$$

Extensional [A], stretching-coupling [B] and flexural rigidity stiffness [D] matrices have been expressed as

$$A_{ij}=\begin{bmatrix}A_{11} & A_{12} & A_{16}\\ A_{12} & A_{22} & A_{26}\\ A_{16} & A_{26} & A_{66}\end{bmatrix},\quad B_{ij}=\begin{bmatrix}B_{11} & B_{12} & B_{16}\\ B_{12} & B_{22} & B_{26}\\ B_{16} & B_{26} & B_{66}\end{bmatrix},\quad D_{ij}=\begin{bmatrix}D_{11} & D_{12} & D_{16}\\ D_{12} & D_{22} & D_{26}\\ D_{16} & D_{26} & D_{66}\end{bmatrix} \tag{4}$$

$$\text{where } A_{ij}=\left(\sum_{c=1}^{n}[\overline{Q}_{ij}]_c\,(h_c-h_{c-1})+Q_{i,j,liner}\right),\ i=1,2,6\ ;j=1,2,6 \tag{5}$$

The relationship between global strain and in-plane loads have been determined as

$$\begin{bmatrix}\epsilon_x\\ \epsilon_y\\ \gamma_{xy}\end{bmatrix}=\begin{bmatrix}A_{11} & A_{12} & A_{16}\\ A_{12} & A_{22} & A_{26}\\ A_{16} & A_{26} & A_{66}\end{bmatrix}^{-1}.\begin{bmatrix}N_x\\ N_y\\ N_{xy}\end{bmatrix} \tag{6}$$

Consequently, local stress components can be obtained using Eq. (3) and Eq. (5) as

$$\begin{bmatrix}\sigma_1\\ \sigma_2\\ \tau_{12}\end{bmatrix}_c=\begin{bmatrix}\cos^2\theta_c & \sin^2\theta_c & 2\cos\theta_c\sin\theta_c\\ \sin^2\theta_c & \cos^2\theta_c & -2\cos\theta_c\sin\theta_c\\ -\cos\theta_c\sin\theta_c & \cos\theta_c\sin\theta_c & \cos^2\theta_c-\sin^2\theta_c\end{bmatrix}\begin{bmatrix}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{bmatrix}_c \tag{7}$$

2.2. Failure Criteria

Laminated composite materials are anisotropic. Hence, failure theories developed for isotropic materials are not suitable to use for composite materials. Failure theories used to predict failure behaviors for laminated composite are based on the stresses in the material or local axes caused due to different properties at different angles and axes [7]. In this study, failure theories being benefited for the optimization are provided.

Maximum Stress Failure Theory

According to this theory, laminated composite is failed, if one of the condition below is not ensured [7];

$$\begin{aligned} &-(\sigma_1^C)_{ult} < \sigma_1 < (\sigma_1^T)_{ult} \text{ , or} \\ &-(\sigma_2^C)_{ult} < \sigma_2 < (\sigma_2^T)_{ult} \text{ , or} \\ &-(\tau_{12})_{ult} < \tau_{12} < (\tau_{12})_{ult} \end{aligned} \quad (8)$$

Tsai-Hill Failure Theory

This theory is procured on distortional energy yield criterion for isotropic materials of Von-Mises failure theory being applied to orthotropic materials [7].

$$(\sigma_1/\sigma_{1\,ult}^T)^2 - (\sigma_1\sigma_2/(\sigma_{1\,ult}^T)^2) + (\sigma_2/\sigma_{2\,ult}^T)^2 + (\tau_{12}/\tau_{12,ult})^2 < 1 \quad (9)$$

If the condition given in above is violated, material is assumed as failed. It should be noted that the condition above has been given for two dimensional laminated composite materials.

Tsai-Wu Failure Theory

Tsai-Wu applied the total strain energy failure theory of Beltrami to a lamina in plane stress to determine this failure theory [8]. A lamina of a composite is assumed to be failed, if the condition given in below is not provided[6].

$$H_1\sigma_1 + H_2\sigma_2 + H_6\tau_{12} + H_{11}\sigma_1^{\,2} + H_{22}\sigma_2^{\,2} + H_{66}\tau_{12}^{\,2} + 2H_{12}\sigma_1\sigma_2 < 1 \quad (10)$$

Hashin Failure Theory

This failure theory is related to fiber and matrix failures and consist of four failure modes being tensile fiber failure, compressive fiber failure, tensile matrix failure, compressive matrix failure, interlaminar tensile failure and interlaminar compression failure [9]. It should be noted that only tensile fiber and tensile matrix failure modes are given. If one of the conditions below is violated, material is assumed to be failed.

Tensile fiber failure mode

$$(\sigma_1/\sigma_{1\,ult}^T)^2 + j(\tau_{12}/\tau_{12,ult})^2 < 1 \quad (11)$$

Tensile matrix failure mode

$$(\sigma_2/\sigma_{2\,ult}^T)^2 + (\tau_{12}/\tau_{12,ult})^2 < 1 \quad (12)$$

2.3. Optimization Algorithms

In this study, optimization algorithms Differential Evolution and Nelder-Mead, are used to determine the optimum stacking sequences of the tank. These algorithms are briefly explained below:

Differential Evolution (DE)

Being one of the stochastic search methods, DE are used to achieve optimum designs for given parameters. DE consists of four main steps; initialization, mutation, crossover and selection, and checked by the parameters being scaling factor, crossover and population. Though DE is known as computationally expensive, it has the robustness and efficiency in finding global optimum [10].

The algorithm sustains a population of m points, $\{x_1, x_2,\ldots,x_j,\ldots,x_m\}$, where typically m is larger than *n*, with n being the number of variables.

Nelder-Mead Algorithm (NM)

This optimization method is a direct search method and also known as an efficient algorithm for multidimensional unconstrained optimization without derivatives. The algorithm sustains as set of n+1 points which forms the vertices of a polytope in n-dimensional space.

NM is not described as global optimization algorithm; however, it has reasonable efficiency for problems which don't have many local minima [11].

3. Problem Definition

Type III cylindrical tank is subjected to internal pressure P, axial N_x and hoop loads N_y. In-plane transverse load N_{xy} is zero. Inner radius R, thickness of a layer t, and angle of fiber θ are taken as geometrical dimensions. Critical parameters for calculations are shown in Figure 1.

$$N_x = P.R/2 \qquad N_y = P.R \qquad N_{xy} = 0 \qquad (13)$$

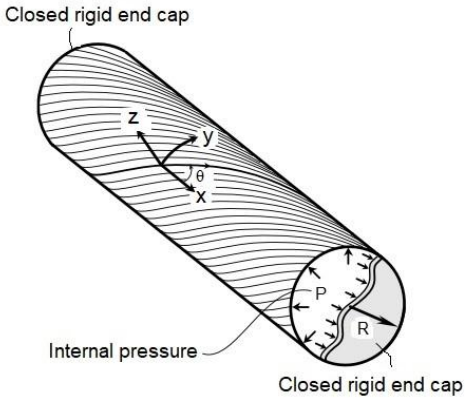


Figure 1: Parameters shown on the cylindrical tank [2]

This study consists of two main parts; mechanical analysis and optimization. The classical lamination theory and failure theories are used to determine mechanical behavior of the Type III cylindrical storage tank designs. Mechanical and geometrical properties of composite and liner given in Table 1 and Table 2, respectively, have been taken the study of Chang [3]. Table 3 shows the performance and verification of the developed computer code compared with the study of Chang [3].

Table 1. Mechanical properties used for Carbon/epoxy composite and Aluminum 6061-T6

Material	**Properties**									
	E_1 (GPa)	E_2 (GPa)	G_{12} (GPa)	ν_{12}	ν_{21}	$\sigma^{ult}_{1,t}$ (MPa)	$\sigma^{ult}_{1,c}$ (MPa)	$\sigma^{ult}_{2,t}$ (MPa)	$\sigma^{ult}_{2,c}$ (MPa)	τ^{ult}_{12} (MPa)
Carbon/Epoxy composite	142.5	9.79	4.72	0.27	0.018	2193	2457	41.3	206.8	61.28
Aluminum liner	70	70	26	0.33		310	280	310	280	207

Table 2. Geometrical features of composite and liner parts of the storage tank

Parts of Tank	**Inner radius (mm)**	**Thickness (mm)**	**Length (mm)**
Composite	50	0.125 (one layer)	300
Liner	49.75	0.125	

Table 3. Verification of developed computer code using the study of Chang

Fiber orientation[3]	Burst Pressure[3] (MPa) – Tsai-Wu (Numerical)	Burst Pressure[3] (MPa) (Experimental)	Burst Pressures (MPa)– Tsai-Wu (present study)
$[54/-54/54/-54]_s$	5.26	5.39	5.49
$[54/-54/54/-54/54/-54]_s$	7.28	7.6	8.24
$[54/-54/54/-54/54/-54/54/-54]_s$	9.22	9.61	10.97

In optimization part, DE and NM have been associated with Classical Lamination Theory and failure criteria. Then, these optimization algorithms have been used to obtain the optimum fiber orientation angles (θ) without changing layer thickness.

The laminates are subjected to symmetry and balance constraints. Moreover, Tsai-Wu, Tsai-Hill, Hashin Failure and Maximum Stress criteria are individually used to check whether the first ply failure is obtained in the laminates. The optimization problems can be defined as:

Find: $\{\theta_p, n\}, \theta_p \in [\theta_1, -\theta_1, \dots, \theta_n, -\theta_n]_s, \theta_p \in$ Integers,

p=1,2…,n where n=2,4 and 6 for separated designs

Minimize: Failure Criteria Index - Tsai-Wu, Tsai-Hill, Hashin, and Maximum stress

Constraints: Tsai-Wu≤ 1, Tsai-Hill ≤ 1, Hashin ≤ 1,

Maximum stress ≤ 1

$-90 \leq \theta_p \leq 90$

Symmetry

Balance

Methods: Differential Evolution, Nelder -Mead

4. Results and Discussion

In the current study, the optimum stacking sequences of composite part of Type III storage tank has been investigated. Before taking optimization into account, Type III and Type V storage tanks are compared as from the view point of the effect of liner on the mechanical performances. In this regard, burst pressures of Type III storage tanks using same angle orientations with the study of Chang have been higher compared to Type V storage tanks as shown in Table 4.

Table 4: Comparison of Type III (present study) with Type V [3] storage tanks

Fiber Orientations[3]	Burst pressure obtained for Type III storage tank (MPa)-Tsai-Wu (present study)	Burst pressure difference compared to Type V results[3] (%)	Weight of Type V tank[3] (gr)	Weight of Type III tank (gr) (present study)	Weight difference (%)
$[54/-54/54/-54]_s$	6.58	19.8	76.9	92.8	20
$[54/-54/54/-54/54/-54]_s$	9.46	14.8	117	132.9	13.6
$[54/-54/54/-54/54/-54/54/-54]_s$	12.35	12.5	156.8	172.7	10

According to the results, liner has positive effect on mechanical performance through failure progression for a storage tank. However, addition of each composite layer to Type III storage tank decrease the additional performance provided by aluminum liner. Since, substantial portion of stress accumulated on storage tank have been getting to be supported more by composite part for each layer added. The performance enhancement procured by liner has resulted in weight penalty with respect to storage tank without liner. From data obtained, if one designs a storage tank, addition of a metal liner improves burst pressure compared to Type V storage tanks having same number of layers. Yet, it is important to remember that the main objective of a liner is not to increase mechanical performance achieved at burst pressure.

Optimization results for 8-layered (Design I), 12-layered (Design II) and 16-layered (Design III) laminated Type III storage tanks have been given respectively in Table 5.

Table 5: Optimum solutions obtained using algorithms and CPU times for each optimization methods

Design	Failure Constraint	Optimum orientation - Differential Evolution	Burst Pressure (MPa) - Differential Evolution	Optimum orientation- Nelder Mead	Burst Pressure (MPa) – Nelder Mead	CPU time (sec) - Differential Evolution	CPU time (sec) – Nelder Mead
I	Tsai-Wu	$[55/ -55/ 54/ -54]_s$	9.67	$[62/ -62/ 47/ -47]_s$	8.91	5.8	4.7
	Tsai-Hill	$[54/ -54/ -54/ 54]_s$	9.59	$[54/ -54/ -53/ 53]_s$	9.52	6.3	4.6
	Hashin Failure	$[54/ -54/ 54/ -54]_s$	9.94	$[54/ -54/ 53/ -53]_s$	9.8	5.7	5.1
	Maximum Stress	$[52/ -52/ 52/ -52]_s$	11.1	$[52/ -52/ -52/ 52]_s$	11.1	6.4	5.1
II	Tsai-Wu	$[54/ -54/ 55/ -55/ 55/ -55]_s$	13.77	$[- 90/ -90/ 42/ -42/ -42/ 42]_s$	12.1	23.2	16.7
	Tsai-Hill	$[54/ -54/ 54/ -54/ -54/ 54]_s$	13.73	$[-52/ 52/ 59/ -59/ 52/ -52]_s$	13.3	19.6	16.5
	Hashin Failure	$[54/ -54/ -54/ 54/ -53/ 53]_s$	14.19	$[-54/ 54/ 53/ -53/ 53/ -53]_s$	14.24	13.6	9.5
	Maximum Stress	$[-51/ 51/ 51/ -51/ 51/ -51]_s$	16.5	$[-51/ 51/ 51/ -51/ 51/ -51]_s$	16.5	25.7	21.2
III	Tsai-Wu	$[-55/ 55/ -56/ 56/ 53/ -53/ -56/ 56]_s$	17.5	$[-61/ 61/ -54/ 54/ -46/ 46/ -53]_s$	16.3	35.2	39.9
	Tsai-Hill	$[-56/ 56/ 55/ -55/ -51/ 51/ -53/ 53]_s$	17.38	$[-53/ 53/ -50/ 50/ -60/ 60/ -53/ 53]_s$	17.1	27.8	26.3
	Hashin Failure	$[55/ -55/ 52/ -52/ 57/ -57/ -52/ 52]_s$	18.09	$[-56/ 56/ -49/ 49/ -52 52/ -55/ 55]_s$	17.4	17.5	14.1
	Maximum Stress	$[-50/ 50/ -51/ 51/ -51/ 51/ 51/ -51]_s$	21.28	$[-48/ 48/ -52/ 52/ -52/ 52/ -53/ 53]_s$	19.8	38.3	37.7

Optimum angles and corresponding burst pressures obtained through DE method have been similar for Tsai-Wu and Tsai-Hill overall. However, this similarity has disrupted from Tsai-Wu while using NM

algorithm. On the other side, results obtained through Tsai-Hill, Hashin and Maximum Stress as a constraint have been relatively more consistent in both algorithms. The deviation between the results of the optimization algorithms has been highest while using Tsai-Wu as failure constraint. Consequently, if one sets up constraints in the form of failure theories being especially Tsai-Wu in order to find optimum orientation and corresponding higher burst pressures, it would be better to use DE instead NM method.
Comparing CPU time, NM has showed better performance than DE giving an exception to third design optimized using Tsai-Wu as a constraint. In the aspect of failure constraints, Hashin failure criterian has been the quickest to give optimal results for both optimization algorithms. It should be noted that this observation might come true due to relatively brief theoretical formulation of Hashin failure criterion which lessens the workload on CPU.

5. Conclusion

In this study, single-objective optimal designs and stress analysis via certain optimization algorithms for the fiber reinforced symmetric-balanced laminated composite cylindrical storage tanks have been presented. The orientation of fiber angles has been chosen as design variable. DE and NM methods have been used to obtain the optimal designs. In order to obtain optimum results in analytical perspective, Classical Lamination Theory, Failure Theories and Optimization Algorithms have been utilized. In all designs, algorithms have been set to consider maximizing burst pressures while failure theories have been main constraints. Consequently, optimal fiber angle orientations obtained using DE over NM method have provided higher burst pressures but required more CPU time.

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COMPARISON OF ONE- AND TWO-DIMENSIONAL (RADIAL) PERMEABILITY MEASUREMENT METHODS ON E-GLASS FABRICS

E-CAM ELYAFLARI İÇİN BİR VE İKİ BOYUTLU (RADYAL) GEÇİRGENLİK ÖLÇÜM METODLARININ KARŞILAŞTIRILMASI

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Abstract

Permeability of a random fabric preform was measured both in 1D and 2D (radial) resin flow configurations under the same constant-injection pressure boundary conditions to illustrate the advantages of both approaches as well as their issues. Only one 1D experiment on a single specimen could allow measuring both unsteady (unsaturated) and steady (saturated) permeabilities which had 23% difference between them. However, this 1D measurement method requires another experiment to be conducted on another specimen to measure the permeability along the other principal direction. Radial resin flow configuration allows measuring the two principal measurements simultaneously using only one specimen. However, our setup allows measurement of unsteady permeability only, not for steady permeability.

Özet

E-cam elyaflı keçenin geçirgenliği, sabit enjeksiyon basıncı sınır koşullu bir ve iki boyutlu reçine akış düzeninde ölçülerek her iki düzenin de avantajları ve sorunları incelenmiştir. Kararsız ve kararlı geçirgenliğin bir boyutlu deney düzeneğinde tek bir numune ile tek bir deneyle ölçümü mümkün olmuştur ve kullanılan elyaf türü için %23 varyasyon gözlenmiştir. Bu bir boyutlu deney metodunun bir mahsuru, diğer asal yöndeki geçirgenliğin ölçümü için bir başka numune ile yapılacak ikinci bir deneye ihtiyaç duyulmasıdır. Tek bir numune ile yapılan iki boyutlu radyal reçine akışlı deneyde, her iki asal yöndeki geçirgenliğin aynı anda ölçümü mümkündür. Ancak, bu çalışmada kullanılan radyal deney düzeneği, sadece kararsız geçirgenliğin ölçümüne uygundur, kararlı geçirgenliğin ölçümüne uygun değildir.

Introduction

Mold filling simulations for liquid composite molding (LCM) processes are used to design a mold (decide on the locations of resin inlet and exits, distribution medium, boundary conditions, etc.) for a complete mold filling and thus reduce the rejection rate and cost in composite material manufacturing. Permeability tensor (***K***) of a fabric preform is a key parameter in the Darcy Law which relates resin velocity to pressure gradient and replaces the momentum equation of fluid mechanics for porous media flows. To determine the permeability of a fabric specimen, permeability measurement experiments are used. Some research studies discussed alternative approaches and their issues [1,2].

In-plane permeability measurement experiments can be divided into two groups as one- (linear) and two-dimensional (radial) resin flow generated in a mold. Another classification is based on the flow regime: unsteady (an initially dry fabric specimen is impregnated with resin) or steady (fabric is already wet). Constant-injection pressure and constant-injection flow rate are two different injection boundary conditions used in these material characterization experiments.

The aims of this study are to (1) compare the linear and radial permeability measurement methods by briefly reviewing the advantages and disadvantages of the two methods, (2) measure and compare in-

plane permeability values of a fabric using these two methods under the same injection boundary condition and flow regime.

Materials and Methods

A fabric preform was made by stacking ten plies of a random fabric (short fiber tows oriented randomly during fabric manufacturing). Linear and radial permeability measurement experiments were conducted on specimens. The experiments were done under constant-injection pressure boundary condition, and unsteady flow regime for both linear and radial resin flow experiments, and steady regime for only linear resin flow. The detailed information about the materials and boundary conditions is given in Table 1.

Table 1. Material properties

Resin	Type (test fluid)	Silicone oil
	Viscosity, μ [Pa.s]	0.100
	Density, ρ_{resin} [g/cm^3]	0.964
Random Fabric (Fibroteks)	Superficial density (mass per layer), ρ_{sup} [g/m^2]	450
	Number of layers, *n*	10
	Bulk density of glass fiber, ρ_{bulk} [kg/m^3]	2540
	Dimensions (width & length) for 1D flow [m]	0.10 & 0.30
	Dimensions (injection hole diameter & width of a square specimen) for radial flow [m]	0.012 & 0.26
	Thickness (compacted), *h* [m]	0.045
Boundary Conditions	Constant pressure line injection, P_{in} [kPa]	80 kPa
	Flow Regimes	Unsteady & Steady

One-Dimensional (Linear) Permeability Experiment

In linear permeability experiment with unsteady flow regime, initially dry 10 layers of random fabric specimen was placed on the flat metal mold and covered with a flexible vacuum bag. After sealing the mold, vacuum pressure was set to a constant gage value of 80 kPa by using a digital regulator for two purposes: (1) to compact the specimen and (2) to generate pressure gradient for driving resin from the inlet to the exit. A glass lid was placed on top of the vacuum bag to compact the fabric specimen uniformly. The gap between the glass lid and the lower mold was measured along all edges of the mold by using dial gages (see Fig. 1). After this gap and thus thickness of the fabric specimen was set to a constant value of ~4.50 mm by using four bolts-nuts, resin infusion was started. Flow front propagation was recorded by using a camera until the fabric specimen was fully impregnated with resin.

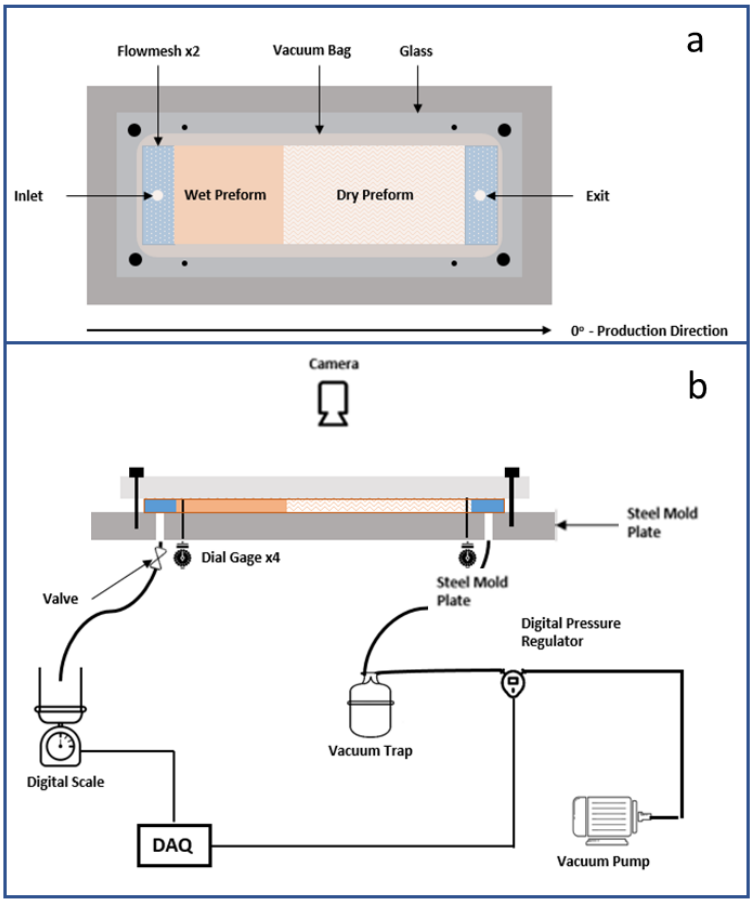


Fig. 1. Schematic of linear permeability measurement setup with an unsteady flow regime: (a) top view and (b) side view.

After the fabric specimen was fully impregnated with resin and resin coming out of the exit had an almost constant flow rate, permeability measurement experiment with steady flow regime was conducted (see Fig. 2). Mass of the injected resin was measured using a digital scale and recorded for 120 seconds (see Fig. 1).

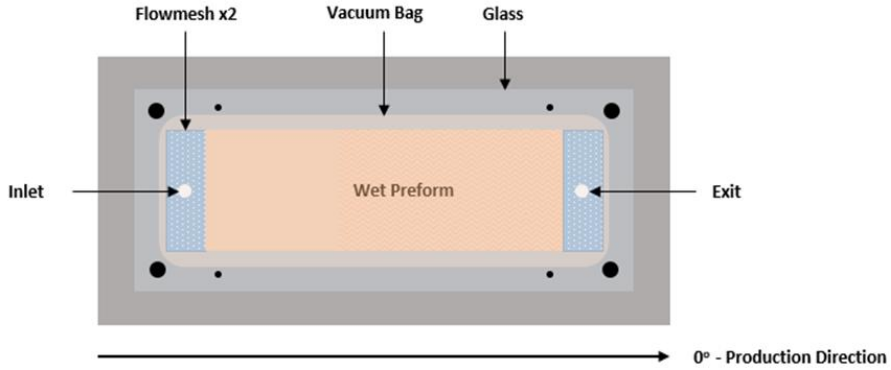


Fig. 2. Schematic of linear permeability measurement setup with a steady flow regime (i.e., resin infusion is continued even after complete mold filling).

One-Dimensional (Linear) Permeability Calculations

1D unsteady permeability (K_{uns}) under constant-injection pressure boundary condition is calculated by using the following formula:

$$K_{uns} = \frac{C\,\mu\,\phi}{2P_{in}} \qquad (1)$$

where μ, ϕ and P_{in} are viscosity of the resin, porosity of the fabric specimen and injection pressure (gage), respectively [3]. C is determined as 2.00×10^{-4} m^2/s by curve fitting to the experimental data (flow front position versus time) with least square method (see Fig. 3 for one sample case).

$$x_f(t) = \sqrt{C\,t} \qquad (2)$$

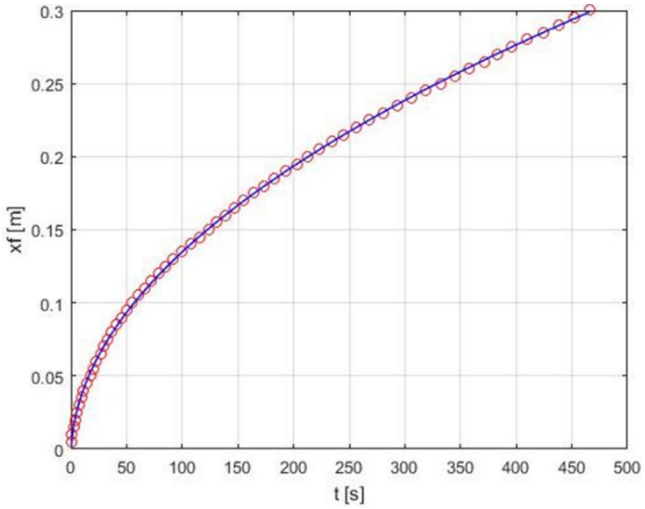


Fig. 3. Experimental data for the flow front position versus time (red circles) and curve fit using Equation (2) (blue line).

1D steady permeability (K_s) under constant-injection pressure boundary condition is calculated by using the following formula:

$$K_s = \frac{Q\,\mu\,L}{w\,h\,\Delta P} \qquad (3)$$

where L, w, h and ΔP are length, width and thickness of the fabric specimen and pressure difference between the exit and inlet, respectively. The mass flow rate, $\dot{m}$, is determined by curve fitting a 1st order polynomial to the experimental data (negative of the rate of change of resin mass in the storage tank with respect to time) using the least square method (see Fig. 4). Volumetric flow rate, Q is calculated as 7.35×10^{-8} m^3/s by dividing $\dot{m}$ by ρ_{resin}.

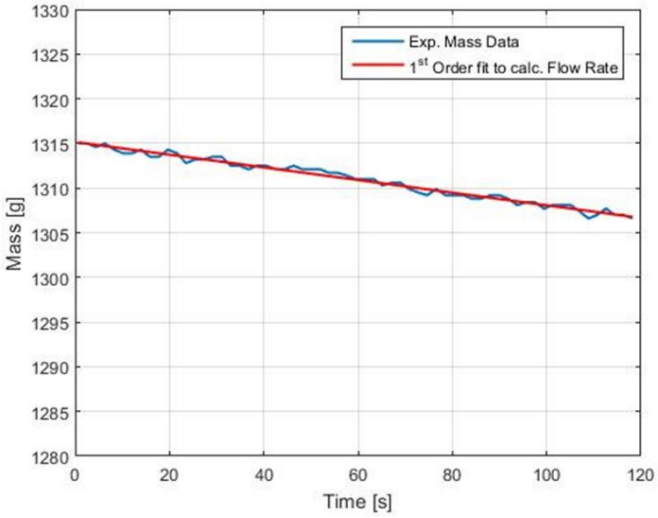


Fig. 4. Mass of resin (blue) and 1st order curve fit (red) versus time.

The parameters listed in Table 2 and the computed value of $C = 2.00\times10^{-4}$ m^2/s are substituted in Equation (1) to calculate the unsteady permeability:

$$K_{uns} = \frac{\left(2.00\times10^{-4}\ \mathrm{m^2/s}\right)(0.100\ \mathrm{Pa.s})(0.631)}{2\,(8.00\times10^{4}\mathrm{Pa})}$$

$$K_{uns} = 7.90\ \times\ 10^{-11}\ \mathrm{m^2}.$$

$Q = 7.35\times10^{-8}\mathrm{m^3/s}$ and other parameters are substituted in Equation (3) to calculate the steady permeability:

$$K_s = \frac{(7.35\times10^{-8}\ \mathrm{m^3/s})(0.100\ \mathrm{Pa.s})(0.3\ \mathrm{m})}{(0.1\ \mathrm{m})(0.0045\ \mathrm{m})(8.00\times10^{4}\mathrm{Pa})}$$

$$K_s = 6.12\ \times\ 10^{-11}\ \mathrm{m^2}.$$

which deviates –23% from the unsteady measurement.

Two-Dimensional (Radial) Permeability Experiment with Unsteady Flow Regime

Ten layers of random fabric are stacked to prepare a specimen with in-plane dimensions of 26 cm x 26 cm. A metal spacer with a constant thickness of ~4.50 mm was placed along the edges of a flat rigid mold to adjust the specimen thickness in this gap. The metal upper mold half with flow front monitoring channels was placed on the metal spacer and the mold was closed. The test fluid (silicone oil) in the pressure pot was pressurized using compressed air for a constant-pressure injection (see Fig. 5). Resin injection pressure was regulated by using a pressure regulator (placed on the pressure pot) and recorded by a pressure sensor (Keller PAA 35 with a resolution of 0.002 bar). The resin injection was started by opening the valve. Flow front propagation was monitored along the two orthogonal axes (named as 0° and 90°) by using a digital camera.

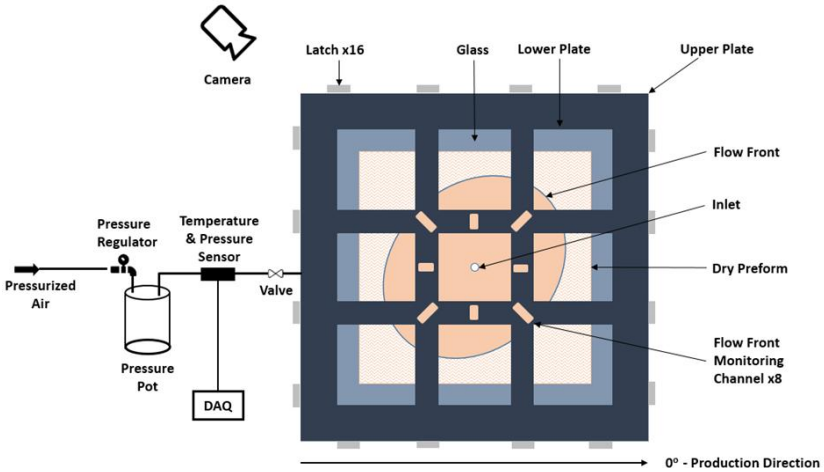


Fig. 5. Schematic of the radial permeability measurement setup.

2D unsteady permeability (K_{uns}) of a fabric specimen for isotropic flow under constant-injection pressure is calculated by using the following formula:

$$K_{uns} = \frac{\mu\,\phi}{4P_{in}}\left\{r_f^2\left(2\,ln\left(\frac{r_f}{r_0}\right)-1\right)+r_0^2\right\}\frac{1}{t} \qquad (4)$$

where r_f, r_0, t, μ, ϕ and P_{in} are the radius of the flow front, the radius of the inlet hole (0.006 m), time, viscosity, porosity and the injection pressure at the inlet, respectively [5].

The following sample calculation belongs to only one data point (at t = 253 s) along the production direction (0°):

$$K_{uns} =$$

$$\frac{(0.0973\ \text{Pa.s})\ (0.610)}{4\ (8.02\ \times\ 10^4\text{Pa})}\left\{(0.121\ \text{m})^2\left(2\ln\left(\frac{0.121\ \text{m}}{0.006\ \text{m}}\right)-1\right)+(0.006\ \text{m})^2\right\}\frac{1}{(253\ \text{s})}$$

$$= 5.37\ \times\ 10^{-11}\ \text{m}^2$$

Using least square method on all data points, the principal permeability components were computed as $K_{uns,0} = 5.35\times10^{-11}\text{m}^2$ and $K_{uns,90} = 5.35\times10^{-11}\text{m}^2$ along the two orthogonal axes (0° and 90°), respectively. A circular flow front and thus equal principal permeability components are a proof that the fabric used here has an isotropic permeability which is actually expected for a random fabric.

Results and Discussion

The results of the experiments are given in Table 2. More experiments will be conducted and presented later to study the statistical variation of the fabric used.

As an advantage of the radial permeability measurement experiment, both of the orthogonal permeability components, $K_{uns,0}$ and $K_{uns,90}$ could be determined by conducting only one experiment on a single fabric specimen. Although not observed for the isotropic fabric used here, any potential rotation of the principal axes is observed during the experiment and calculated in the post-processing. Both components were the same for the random fabric used here, which is the case for an isotropic porous medium. The flow regime was unsteady under a constant-injection pressure boundary condition. The unsteady permeability was calculated by recording the resin flow front propagation and post-processing the data.

The permeability of the same fabric specimen was also calculated in a one-dimensional permeability measurement setup only along the production direction. The setup allowed the measurement of unsteady

and steady permeabilities by recording the resin flow front propagation and flow rate with time in the former and latter, respectively. Thus, this setup has the advantage of measuring both unsteady and steady permeabilities, but requires more experiments than radial setup (two instead of one) for the measurement of in-plane principal permeability components (although not required for the isotropic fabric used here, it is needed for anisotropic fabrics in general).
Using transparent lids allowed monitoring if the assumptions are valid. For example, the resin flow was 1D as assumed by noticing that the front was almost a line verifying that no racetracking channel was created along the specimen and mold walls.
As a future work, different numerical fit approaches and their effects on the results of radial experiments will be investigated.

Table 2. Results of the experiments

	Porosity(ϕ)	V_f (%)	Fabric Stack Weight (g)	μ (Pa.s)	ΔP (kPa)	$K_{uns,0}$ (m^2)	K_s (m^2)	$K_{uns,90}$ (m^2)
1D sat.	0.631	36.9	126.6	0.100	80.0	-	6.12E-11	-
1D uns.	0.631	36.9	126.6	0.100	80.0	7.90E-11	-	-
2D uns.	0.610	39.0	301.1	0.0973	80.2	5.35E-11	-	5.35E-11

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MECHANICAL PROPERTIES OF CARBON–E-GLASS REINFORCED POLYESTER HYBRID COMPOSITES

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ABSTRACT

Fiber reinforced composite materials are used in various applications in aviation, maritime, sport, automotive, and defense industry due to their several advantages. Beside this, they have some disadvantages. The behaviour of hybrid composites is a weighed sum of the individual components in which there is a more favorable balance between the inherent advantages and disadvantages. The aim of this study is to determine the mechanical properties of glass-carbon/polyester hybrid composites. The carbon fiber fabrics and E-glass fiber fabrics were used with different orientation for hybridization. The results show that hybrid composites exhibit optimum performances as compared to the composites made of individual carbon or glass fabrics.

GENİŞLETİLMİŞ ÖZET

Fiber takviyeli kompozit malzemeler sahip oldukları birçok avantaj sayesinde havacılık, denizcilik, otomotiv, spor ve savunma sanayii gibi birçok alanda kullanılmaktadır. İki ya da daha fazla elyafların tek bir matriks içerisinde birlikte kullanılmasıyla hibrit kompozitler elde edilmektedir. Bu hibritleme sayesinde kompozitin özellikleri daha da iyileştirebilmektedir. Çalışmanın amacı, cam-karbon elyaf takviyeli polyester matriksli hibrit kompozitlerin mekanik özelliklerinin belirlenmesidir. Charpy darbe testi, çekme testi, üç nokta eğme testi ve dinamik mekanik analiz üzerinde çalışılmıştır.

Çalışmada matris olarak polyester reçine (Polipol-335, Poliya), takviye elemanı olarak tek yönlü karbon (500 gsm) ve cam elyaf (675 gsm) kumaşlar kullanılmıştır. Kobalt oktoat hızlandırıcı, metil etil keton peroksit ise sertleştirici olarak sırasıyla ağırlıkça % 0.5 ve 1.5 ilave edilmiştir. Kompozit plakalar vakum infüzyon yöntemiyle üretilmiştir. Bu makalede, C ve E sırasıyla karbon ve cam kumaşlarını, sayılar ise tekrarlanan birim sayısını temsil edecek şekilde; C_6, E_6, C_4E_2, $(CE)_{3S}$, $(EC)_{3S}$ olarak denemeler adlandırılmıştır. Denemelerde elyaf yönlenmesi $0^o/90^o$ olarak belirlenmiştir. Charpy darbe, çekme ve üç nokta eğme testleri standartlara uygun bir şekilde yapılmıştır. Dinamik mekanik analiz (DMA) ile numunelerin camsı geçiş sıcaklıkları (T_g) belirlenmiştir.

Çekme testi sonuçlarına göre $(CE)_{3S}$ denemesinin çekme mukavemeti diğer hibritlere kıyasla daha yüksektir. Bu konfigürasyonda, yüksek mukavemetli karbon elyaflar yük yönüne paraleldir. Karbon elyafların yük yönüne paralel olması mukavemeti arttırmaktadır. Charpy darbe testi sonuçlarına göre $(EC)_{3S}$ denemesinin darbe enerji değerleri diğer hibritlere kıyasla daha yüksektir. Bu konfigürasyonda, cam elyaflar darbe yönüne diktir. Daha esnek olan cam elyafların darbe yönüne dik olması kırılma enerjisini arttırmaktadır. Üç nokta eğme testi sonuçlarına göre, $(EC)_{3S}$ denemesinin eğme mukavemeti diğer hibritlere kıyasla daha yüksektir. Bu konfigürasyonda, cam elyaf yük yönüne diktir. Ayrıca, elyaf yönlerinin mukavemete etkisini incelemek için $(CE)_{3S}$ denemesi 0^o ve 90^o yönlerinde hazırlanmıştır. 0^o yönü ile elde edilen numunede karbon elyaflar yük yönüne diktir. 90^o yönüyle elde edilen numune de ise cam elyaflar yük yönüne diktir. Eğme testi sırasında numune üzerinde oluşan basma gerilmesine karşı karbon elyaflar daha dayanıksız olduğu görülmektedir. Bu sebeple, 0^o yönünde hazırlanan numunelerin eğme mukavemeti daha düşüktür. Denemelerin camsı geçiş sıcaklıkları (T_g) dinamik mekanik analiz (DMA) ile belirlenmiştir.

Test sonuçları, tek tip elyaf içeren karbon ve cam elyaf takviyeli kompozitlerle hibrit kompozitler karşılaştırıldığında, hibrit kompozitlerin daha optimum mekanik özelliklere sahip olduğunu göstermektedir.

1.INTRODUCTION

Composite materials are finding increasing applications in various engineering fields because of their superior inplane properties [1]. Fiber composites with a range of the mechanical properties can be fabricated through hybridization of two or more different fibers in a matrix material [2]. Hybridization in composites can lead to benefits in cost and enhancement of mechanical properties [3]. By mixing different fibres, it is possible to combine the advantages of different fibres while simultaneously mitigating their less desirable qualities [1]. Hybrid polymer composite material offer the designer to obtain the required properties in a controlled considerable extent by the choice of fibers and matrix. The properties are tailored in the material by selecting different kinds of fiber incorporated in the same resin matrix [4]. Hybrid composites are attractive structural materials, because the composite properties can be tailored to requirements. Other characteristics of hybrid composites are: cost effective utilisation of different fibre materials, possible weight saving, reduced notch sensivity, improved fracture toughness, longer fatigue life and improved impact resistance. Hybrid composites can be classified into two main categories: intermingled or intraply and interlaminated or interply [1]. In most cases, the purpose of hybridization is to obtain a new material retaining the advantages of its constituents, and hopefully overcoming some of their disadvantages. Another desired achievement is related to the cost, with one of the two components being generally cheaper than the other one. There are several types of hybrid composites, depending on the way the constituent materials are mixed, ,ie: (i) interply hybrids where layers of the two (or more) homogeneous reinforcements are stacked; (ii) intraply hybrids in which tows of the two (or more) constituent types of fibres are mixed in the same layer; (iii) intimately mixed (intermingled) hybrids where the constituent fibres are mixed as randomly as possible so that no concentrations of either type are present in the mareria; (iv) selective placement in which reinforcements are placed where additional strength is needed, over the base reinforcing laminate layer; (v) superhybrid composites which are composed of metal foils or metal composite plies stacked in a specified orientation and sequence [5]. In this study, interply carbon-glass fiber reinforced hybrid composite laminates were manufactured by

vacuum infusion technique and an experimental study was performed to investigate the effect hybridization on the mechanical properties.

2.EXPERIMENTAL

2.1. Materials

Unidirectional carbon (500 gsm) and E-glass (675 gsm) fabrics were used as reinforcement materials. The fiber orientation was selected as $0/90^{o}$. Polyester resin (Polipol-335, Poliya) together with cobalt octoat and methyl ethyl ketone peroxide were used as resin, resin accelerator and hardener with a weight ratio of 0.5 and 1.5 %, respectively.

The test samples were designated as C_6, E_6, C_4E_2, $(CE)_{3S}$, $(EC)_{3S}$ where C, E and numbers denote carbon, E-glass fabrics and repeated layers, respectively.

2.2. Method

The vacuum infusion technique was used to manufacture the composite laminates. This process is becoming more widespread within the composites industry. It is a type of closed mold processes. The vacuum infusion process utilizes vacuum to infuse resin into the laminates. The first step is to load the fabric and other processing aid materials into the mold. Then the dry material is sealed using a vacuum bag. A high vacuum pump is used to remove all of air in the cavity. Under vacuum, the resin is infused into the mold cavity to wet out the fabric fibers. In this study, the composites were cured in mold for 24 hours at room temperature. After curing, the laminates were removed from the mould. The post-curing was completed at 100 ^{o}C for 2 hours. The laminates were cut in required pieces according to ASTM standards for analyses.

The advantages of vacuum infusion include high quality, high fiber-to-resin ratio, high strenth and stiffness, good consistency, minimal shrinkage, good outside and inside surfaces, great process control, fast cycle time and low cost.

2.3. Mechanical Tests

Charpy impact, tensile and flexural tests were carried out in accordance with ASTM standards. Dynamic mechanical analysis (DMA) were used to determine the glass transition temperature (T_g) of the specimens.

3.RESULTS AND DISCUSSION

3.1. Tensile Test Results

Experiments were carried out according to ASTM D3039 standards by SHIMADZU AG-IC equipment. Tensile test results showed that $(CE)_{3S}$ specimens exhibit the highest tensile strength as compared to the other hybrid configurations as can be seen in the Figure 3.1. Due to stiffer carbon fibers that are parallel to the loading direction, tensile modulus and strength values were observed to increase.

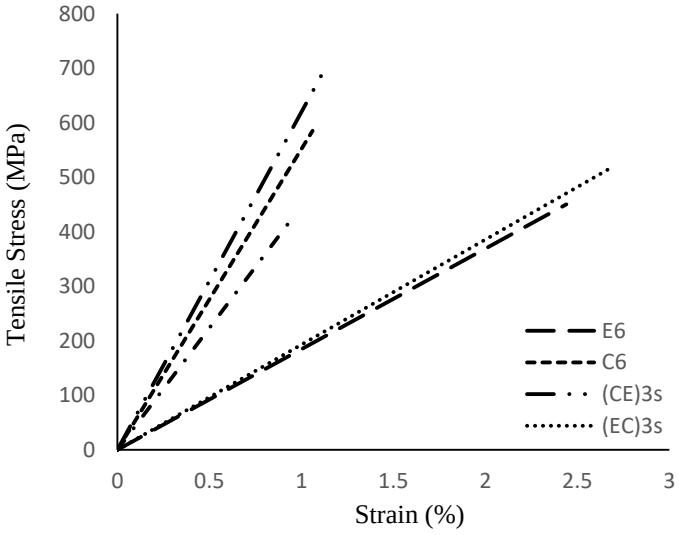


Figure 3.1: Tensile strength of specimens

3.2. Charpy Impact Test Results

The experiments were carried out according to ASTM D6110 standards by CEAST Resil Impactor. Charpy impact test results showed that E_6 specimens that include only E-glass fibers exhibit the highest impact strength as can be seen in the Figure 3.2. $(EC)_{3S}$ specimens has the higher impact strength as compared than the other hybrids. Due to higher fracture energy of E-glass fibers that were perpendicular to the loading direction, impact strength increases. Carbon fibers reduce the impact energy.

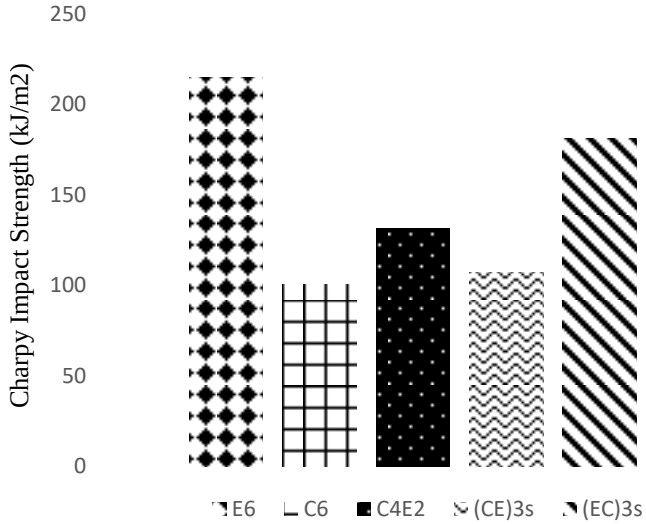


Figure 3.2: Impact strength of specimens

3.3. Three Point Bending Test Results

Experiments were carried out according to ASTM D790-03 standards by MTS - 100 kN load cell equipment. Flexural test results showed that $(EC)_{3S}$ specimens had the highest impact strength as compared to the other hybrids as can be seen in the Figure 3.3. In this configuration, E-glass fibers were perpendicular to the load direction. In order to determine the effects of fiber orientation on the flexural properties of the composites, $(CE)_{3S}$ were prepared in both 0^o and 90^o directions. For 0^o direction, the carbon fibers were perpendicular to the loading direction while for 90^o direction, the E-glass fibers were perpendicular to the loading direction. The load carrying capacity of the carbon fibers are lower than E-glass fibers in compression. Therefore, the specimens which were prepared in 0^o direction had the lower flexural properties.

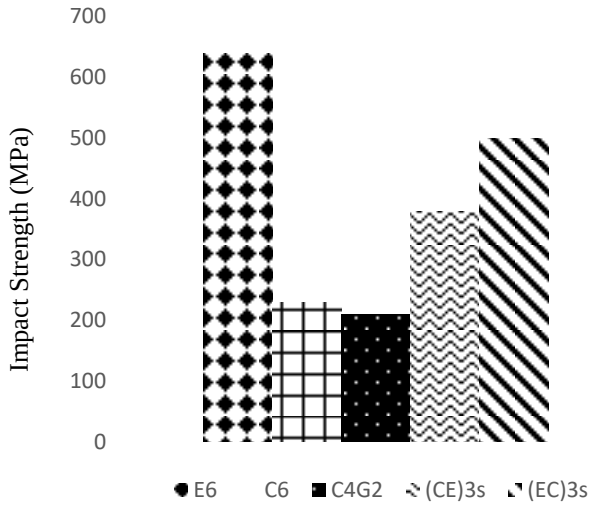


Figure 3.3: Flexural strength of specimens

3.4. Dynamic Mechanical Analysis Results

Dynamic Mechanical Analysis (DMA) is a technique where a low stress is applied to a sample in a cyclic manner. This allows the materials response to stress, temperature, frequency and other values to be studied. Storage modulus, loss modulus, glass transition temperatures (T_g) were determined by DMA. Graphs of all specimens were showed in Figures 3.4. and 3.5. respectively. Tg values were obtained from peak point of the 'tan delta – temperature' graph.

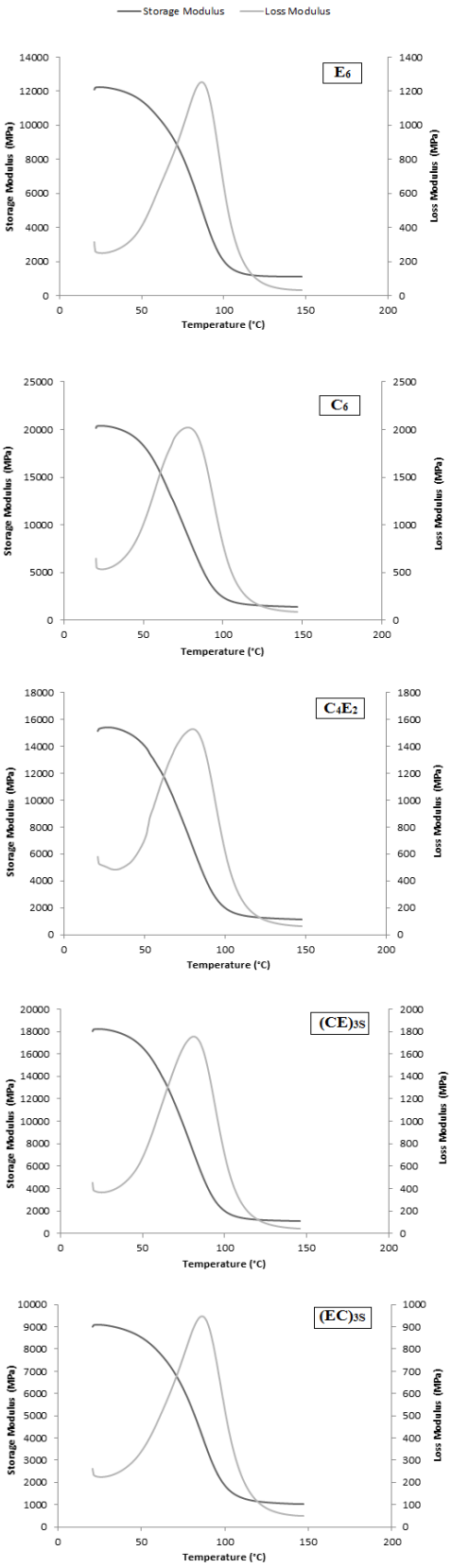


Figure 3.4: DMA graphs of specimens

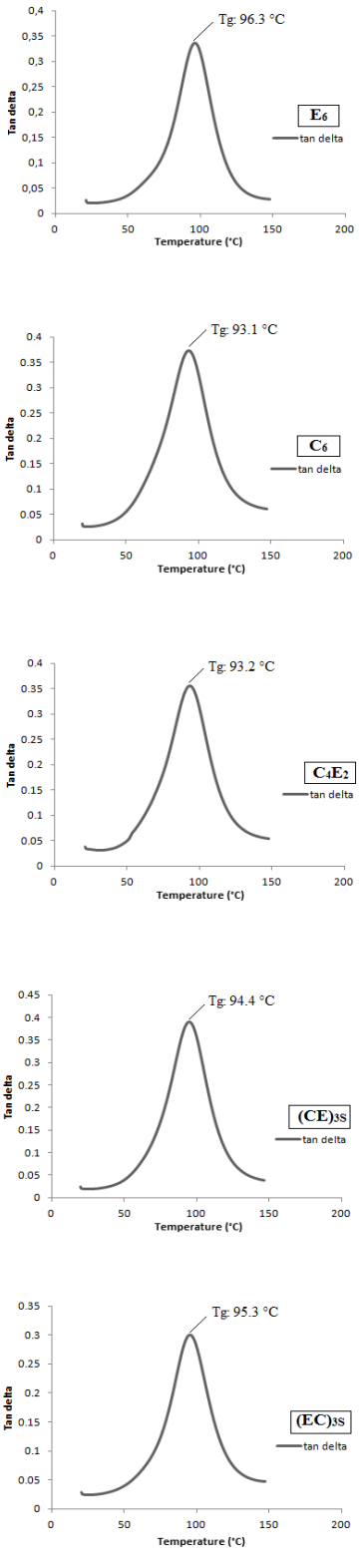


Figure 3.5: Tg values of specimens

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THE INVESTIGATION OF IMPACT RESPONSES OF BASALT FIBER REINFORCED EPOXY COMPOSITES AT CORROSION CONDITION

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ABSTRACT

In this paper, the low velocity impact behaviors of Basalt Fiber Reinforced(BFR) epoxy composites were investigated at sea water corrosion condition. Sea water (Mediterranean Sea) was determined as corrosion condition. Corrosion periods to determine the impact responses of BFR/Epoxy composites were determined as 0, 10, 20 and 40 days in terms of literature related in corrosion of composites. 6 laminated 400 tex basalt fiber fabrics and Bisphenol A (DGEBA) epoxy resin were used as reinforcement and matrix materials respectively. Basalt/Epoxy composites which were exposed sea water the during 0, 10, 20 and 40 days were applied to the low velocity impact test at 10j and 20j energy levels according to ASTM D 7136M. As results of low impact tests of all composites, when corrosion periods have been increased, the peak (Maximum) loads decreased and displacements increased. In addition, the rebound energy of basalt/epoxy composites decreased by increasing corrosion days and absorption energy increased by increasing corrosion day. It was observed that the increasing corrosion day caused to increase the delamination failures on the Basalt/Epoxy composites

Keywords: Sea water corrosion, basalt fiber reinforcement, low velocity impact behavior, composites

INTRODUCTION

Basalt fibers as an alternative reinforced material for composites have similar chemical composition of E-Glass fibers. However, The quantitis of Fe_2O_3, K_2O, MgO, TiO_2 ve Na_2O of chemical compositions is higher than E-glass fiber. The high amount of these elements for basalt fiber provides to higher mechanical properties than E-Glass Fiber[1].

Zhu et al. (2012) carried out the impact tests. As result of test, they emphasized the elongations of composites to determine the mechanical responses. In additioni they reported to become alternative fiber to e-glass for ranges of wide of usages[2]. Wang and Wu (2010) studied the hybridization of basalt and aramid fibers and tested the impact behaviors of low velocity impact tests at 2m/s and 3m/s. They found that basalt fiber increased the impact absorption [3]. Wei et al. (2011) reported the corrosion sea water behavors of E-Glass and Basalt/Epoxy exposed the 10, 20, 30 and 50 days. They found that after 10 day, it was observe the significant losses of mechanical properties of all composites. They reported that chemical composition(MgO, Na_2O, TiO_2, Fe_2O_3) of played important role for lossing mechanical properties [4].

This study, the low velocity impact behaviors of basalt fiber reinforced epoxy composites (BFR) have been investigated at sea water corrosion conditions. The losses of maximum forces and increasing displacements of BFR/Epoxy composites were determined at changing days of corrosion condition.

METHOS

The VARTM process in order to manufacturing of BFR/Epoxy composites was applied to 6 layers stacked symmetrically 400 tex basalt fiber fabrics by using median viscosity bisphenol A (DGEBA) epoxy as amatrix material.The specimens of 6 laminated BFR/Epoxy composites were produced as required specimen size according to ASTM D7136/7136M. The corrosion condition was defined as Mediterranean sea water for 10, 20 and 40 days of corrosion days. The low velocity impact tests (Figure 1.) were applied at 10j and 20j of energy levels in respect of ASTM D7136/7136M [5].

At the 10j and 20j of energy levels, the low velocity impact tests by repeating three times were executed to BFR/Epoxy composites to elaborate the impact responses like maximum forces (peak load), displacements. The low velocity impact test machine has been shown in Figure 1 [5].

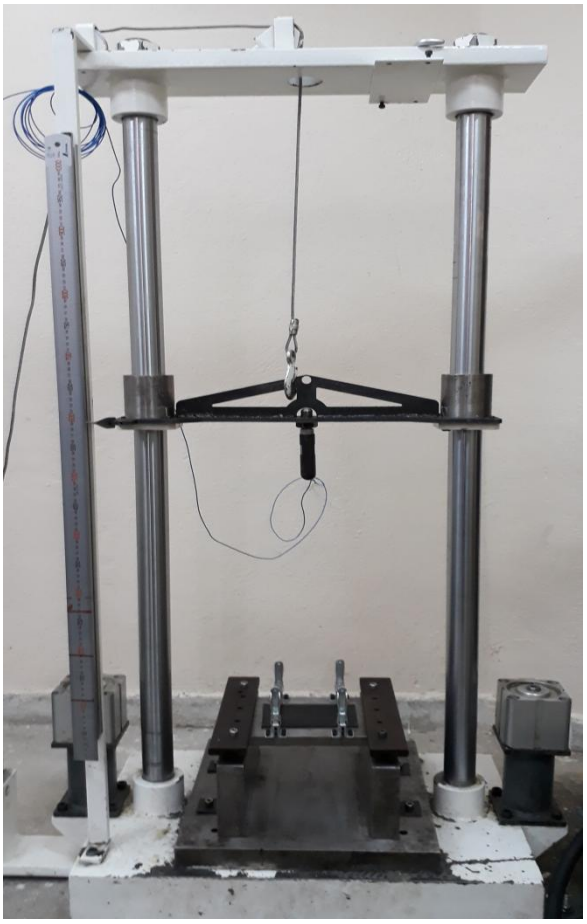


Figure 1. The low velocity impact tests of BFR/Epoxy composite [5].

RESULTS AND FINDINGS

BFR/Epoxy composites which exposed sea water during 0, 10, 20 and 40 days were applied to the low velocity impact tests to assess the impact responses at 10j and 20j of energy levels according to ASTM D7136/7136M standard. In terms of different energy levels (10j and 20j), the results of low impact tests of sea water corrosion exposed BFR/Epoxy composites have been presented in Figure 2. and Figure 3.

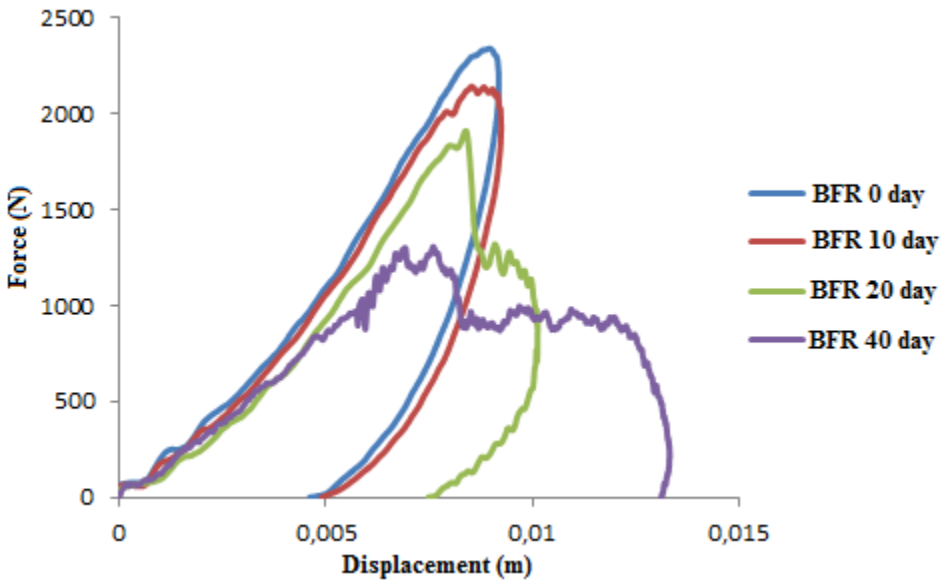


Figure 2. Low velocity impact responses of BFR/Epoxy composites at sea water condition at energy level of 10j [5].

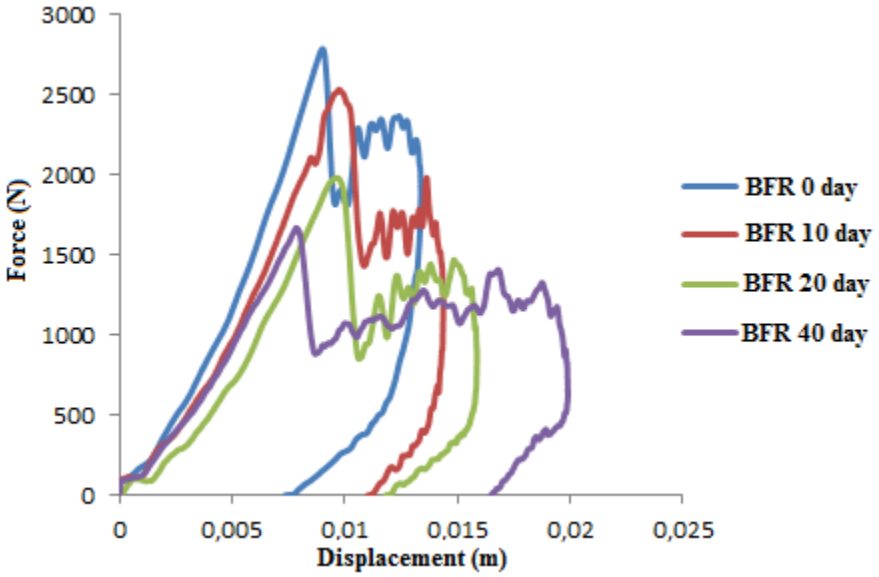


Figure 3. Low velocity impact responses of BFR/Epoxy composites at sea water condition at energy level of 20j [5].

When Figure 1. and Figure 2. have been investigated, maximum force(peak load) have decreased as sea water corrosion day has been increase. However, it has been clearly seen that as sea water corrosion day has been increase, the displacement of BFR/Epoxy composite has been increase. As the maximum force reached the maximum value, force sudden dropped and got floating values at 20j of energy level for all corrosion periods. But, the suddenly force dropping of BFR/Epoxy for 0 day and 10 day of corrosion periods has not seen at 10j of energy level. It has probably meant that BFR/Epoxy composites have been saved their structure integrity. After 0 and 10 days of corrosion periods of BFR/epoxy composites, the sudden dropped forces have been observed for 20 and 40 days of corrosion periods. In addition, the

increasing corrosion periods increased the losses of the bending stiffness of BFR/Epoxy by extending and raising failures of delamination, fiber breakage, debonding and matrix cracks[5-6]. It was considered that the increasing sea water absorption periods affected the bending stiffness and their impact responses [4-5].

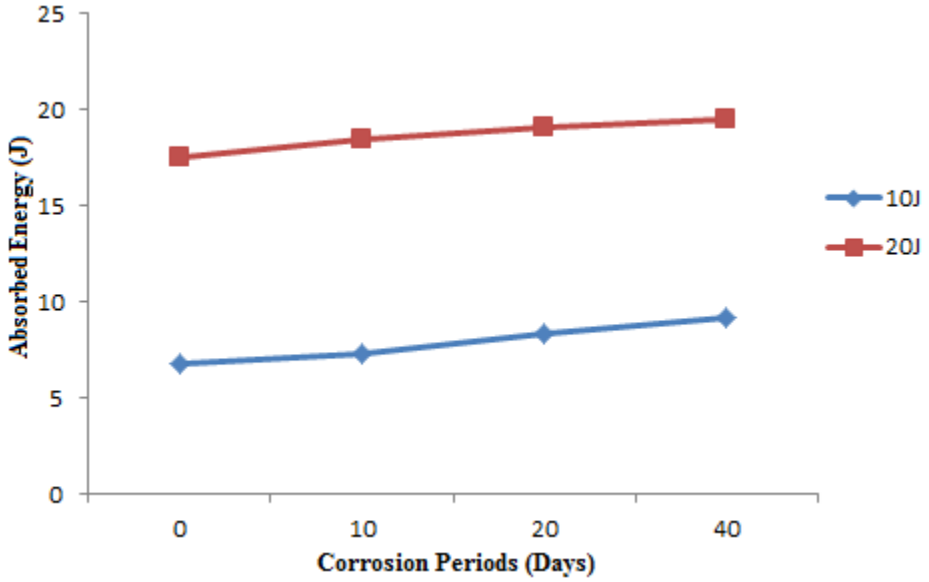


Figure 4. Absorbed Energies of BFR/Epoxy Composites in terms of corrosion periods [5].

Figure 4 shows the absorbed energies of BFR/Epoxy composites during 0,10, 20 and 40 days of corrosion periods. It was observed from Figure 4. that as the corrosion day raised, the absorbed energy increased. When investigated the microscope images of 40 day of sea water exposed BFR/Epoxy composite, it was seen that the delamination failure, fiber breakages and debonding enlarged almost in all layers. It was thought that the increasing corrosion period affected by decreasing the bending stiffness as result of increasing displacement because of the fact that sea water weakened between fiber and epoxy as well as interlayers[4-6].

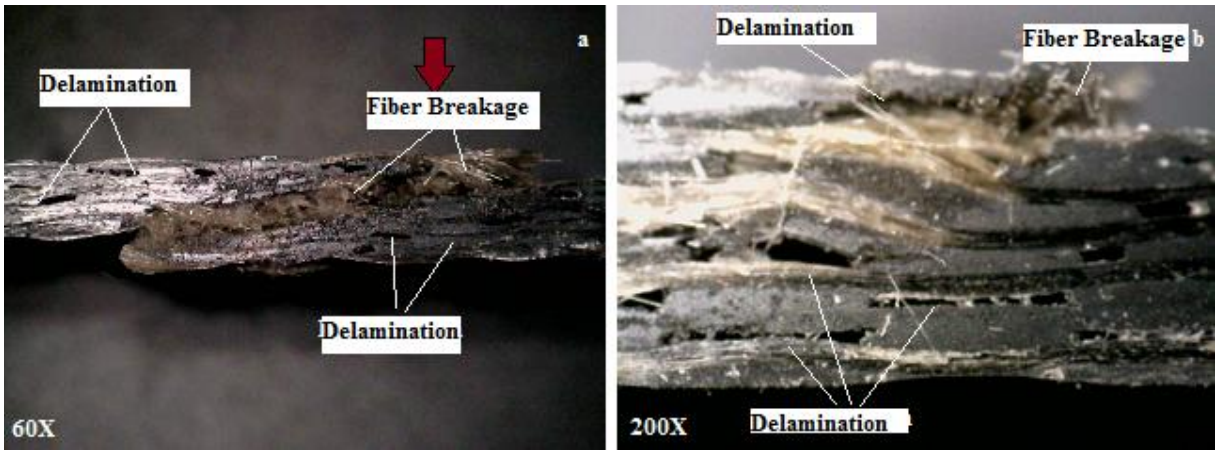


Figure 5. The failures of BFR/Epoxy composites during 40 days of corrosion periods [5].

CONCLUSION

The low velocity impact tests were applied to sea water exposed BFR/Epoxy composites during 10, 20 and 40 corrosion days and unexposed BFR/Epoxy composites at energy levels of 10j and 20j. As results of tests, When the energy levels increased, the maximum force raised. The maximum force decreased and displacement increased while exposure corrosion days of sea water (Mediterranean Sea) increased 0 day to 40 days. It was observed that the failures of delamination, debonding and fiber breakage enlarged by increasing corrosion days because of decreasing bending stiffness of BFR/Epoxy composites. The absorbed energies of BFR/Epoxy composites increased while corrosion days were raised.

ACKNOWLEDGEMENT

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TENSILE BEHAVIORS OF BASALT/EPOXY COMPOSITES AT SEA WATER CORROSION CONDITION

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ABSTRACT

There are many studies and applications about Glass Fiber and Carbon Fiber Reinforced Polymer composites. However, there are not sufficient wide ranges of studies in literature about Basalt Fiber Reinforcement (BFR). In addition, the effects of nanoparticle addition into polymer matrix by reinforcing BFR to composites have not been researched enough especially corrosion conditions. In this research, the effects of SiO_2 nanoparticle addition into Basalt/Epoxy composite have been researched at the sea water (mediterrian sea) corrosion condition. %4 wt. SiO_2 nanoparticles have been filled into epoxy polymer matrix and stirring by ultrasonic mixture process. %4 wt. SiO_2 nanoparticles filled and unfilled Basalt/Epoxy composites have been exposed to sea water during 0, 10, 20 and 40 days. At the end of corrosion waiting periods, SiO_2 nanoparticles filled and unfilled Basalt/Epoxy composites have been applied to the tensile tests according to ASTM D 3039/D 3039M. The tensile strengths of nanoparticle filled and unfilled Basalt/Epoxy composites have been found and compared with each other according to corrosion periods. The decreases of tensile strength of nanoparticle filled and unfilled Basalt/Epoxy composites exposed to 0, 10, 20 and 40 corrosion days and the contributions of SiO_2 nanoparticle were determined. The decreases of tensile strength of SiO_2 nanoparticle filled Basalt/Epoxy composites was found as lower than unfilled Basalt/Epoxy composites. In addition, same cases of SiO_2 nanoparticle filled BFR/Epoxy composites were defined for sea water absorption. It was observed that sea water absorption of Basalt/Epoxy composites related in and affected the mechanical properties of them.

Keywords: Basalt fiber reinforcement (BFR), sea water corrosion, mechanical properties, SiO_2 nanoparticle, nanocomposite.

INTRODUCTION

E-Glass and Carbon fiber reinforcements have been used in many industrial applications. In industry e-glass fiber reinforcement have been preferred generally, however carbon fibers as reinforcement material based on polymer matrix usage have better mechanical characteristics than e-glass fiber .Although carbon fiber shows better mechanical behaviors than e-glass fiber, it has high cost and difficult adhesion that is between matrix and carbon fiber[1-2]. Therefore, researchers have studied new alternative fiber reinforcements instead of e-glass and carbon fibers. Recently, the basalt fiber reinforcement has been concentrated to investigate their mechanical behaviors and its different conditions. The features of basalt fiber is recycling, natural long life, fire safety, chemical resistance, thermal and electrical insulation and

working in high-low temperatures, high mechanical properties [2-6]. In order to increase the mechanical properties of composite materials, researchers have been applied to modify the matrix materials by filling nanoparticles. These nanoparticle generally used in applications are carbon nanotube, nano clay, SiO_2, alimuna, TiO_2 nanoparticles. The most preferred nanoparticle is SiO_2 nanoparticle because of their specific surface area, low cost, the bonding ability, improving strength, modulus, fracture toughness[6-10]. In order to increase mechanical behaviors of polymer matrix by using SiO_2 nanoparticle addition in literature. Deng et al. (2007), Phonthammachi et al. (2013), Sadej-Bajerlain et al. (2011) studied about SiO_2 nanoparticle addition into polymer matrix to improve mechanical behaviors and found the fine findings[11-13]

In this study, the tensile strengths of SiO_2 nanoparticle filled and unfilled BFR/Epoxy composites were investigated at sea water conditions during 0, 10, 20 and 40 days of corrosion periods.

METHODS

SiO_2 nanoparticle filled and unfilled BFR/Epoxy composites were manufactured by two steps. In first step, bisphenol A (DGEBA) epoxy matrix material was modified by 4%wt SiO_2 nanoparticle addition. 4%wt SiO_2 nanoparticles were poured into epoxy matrix and then firstly, stirred by a mechanical stirrer during 10 min. and then, an ultrasonic probe stirrer (Bandelin HD2200) was used for 15 min. After that, the harder was poured into mixture and stirred mechanical mixing for 5 min and the degassed process of the mixture in vacuum oven was applied. The VARTM process in order to production of nanocomposites was applied to 6 layers stacked symmetrically 400 tex basalt fiber fabrics with 4%wt SiO_2 filled bisphenol A (DGEBA) epoxy and unfilled bisphenol A (DGEBA). The specimens of 6 laminated SiO_2 nanoparticle filled and unfilled BFR/Epoxy composites were prepared according to ASTM D3039/ D3039 M-08. The corrosion condition was determined as Mediterranean sea water and 10, 20 and 40 days of corrosion periods. The tensile tests (Figure 1.) were carried out at 2mm/min speed of tests according to ASTM D3039/ D3039 M-08 [6].



Figure 1. The tensile tests of SiO_2 nanoparticle filled and unfilled BFR/Epoxy Composites[6].

RESULTS AND FINDINGS

4%wt SiO_2 nanoparticle filled and unfilled BFR/Epoxy nanocomposites have been applied to tensile tests to determine the tensile strengths at sea water corrosion during 0, 10, 20 and 40 days according to ASTM D3039/ D3039 M-08. The reductions of tensile strengths of 4%wt SiO_2 nanoparticle filled and unfilled BFR/Epoxy nanocomposites which were kept in sea water corrosion during 10, 20 and 40 days have been determined and compared each other. The tensile strengths and reductions of tensile strengths of 4%wt SiO_2 nanoparticle filled and unfilled BFR/Epoxy nanocomposites have been given in Figure 2 and Figure 3. In addition, the sea water absorptions (%mass gain) of 4%wt SiO_2 nanoparticle filled and unfilled BFR/Epoxy nanocomposites have been shown in Figure 4. Figure 1 shows tensile strengths and elongations of sea water corrosion unexposed nanoparticle filled and unfilled BFR/Epoxy nanocomposites. It was observed from Figure 2 that while the average tensile strength for 4%wt SiO_2 nanoparticle filled BFR/Epoxy nanocomposite have was found as 603.3 MPa, the average tensile strength was 465.3 MPa for unfilled BFR/Epoxy nanocomposites. SiO_2 nanoparticle addition has provided to 27.7-29% increase of tensile strength[6]. In literature; Demirci et al. (2017) has been found 30.3% increase in tensile strength by adding SiO_2 nanoparticles for BFR/epoxy composites[14]. Ustun et al. (2016) has attained to improve the tensile strength of CFR/Epoxy composite by filling 0.3%MWCNT, 0.5%BN nanoparticles and hybrid of MWCNT/BN nanoparticles with 11%, 26.2% ve 31% increase[15]. Kuzmin et al.(2017) has found about 23% incerase in the tensile strength of composites by adding SiO_2 nanoparticle addition[16].

The tensile strengths of corrosion exposed 4% SiO_2 filled and unfilled BFR/Epoxy composites were 585.2 MPa, 434.1MPa for 10 days, 560.8 MPa, 390.7 MPa for 20 days and 518.8 MPa, 341.8 MPa respectively. It was observed that corrosion exposed 4% SiO_2 filled and unfilled BFR/Epoxy composites were 3.1%, 6.7% decreases in tensile strengths respectively for 10 days, 7.1%, 16.1% decreases in tensile strengths respectively for 20 days and 14%, 26.5% decreases in tensile strength for 40days. When investigated the decreases in tensile strengths exposing sea water corrosion during 10, 20 and 40 days, it was considered that SiO_2 nanoparticle addition have provided the retarding effects over decreasing the tensile strengths of BFR/Epoxy composites. This cases it can be investigated from curves of sea water absorptions of nanoparticle filled and unfilled BFR/Epoxy composites given in Figure 4. This curves present that SiO_2 nanoparticle addition decreases the absorption of sea water in composite structure. It was thought from these results that SiO_2 nanoparticle addition increased the tensile behavior besides with improving adhesion between fibers and epoxy matrix material. In addition, it was assumed that SiO_2 nanoparticles in epoxy matrix played the blocking role along the absorption (intake channels) ways which was occurred accumulations of cracks and voids in composite structures[17]. It has been opined about the reason of the increasing of the tensile strength of BFR/Epoxy that SiO_2 nanoparticles provide the retarding effects of fast crack propagation including crack blocking, blunting, bowing, forming secondary cracks and then crack branching with dissipation of fracture energy under loading[6].

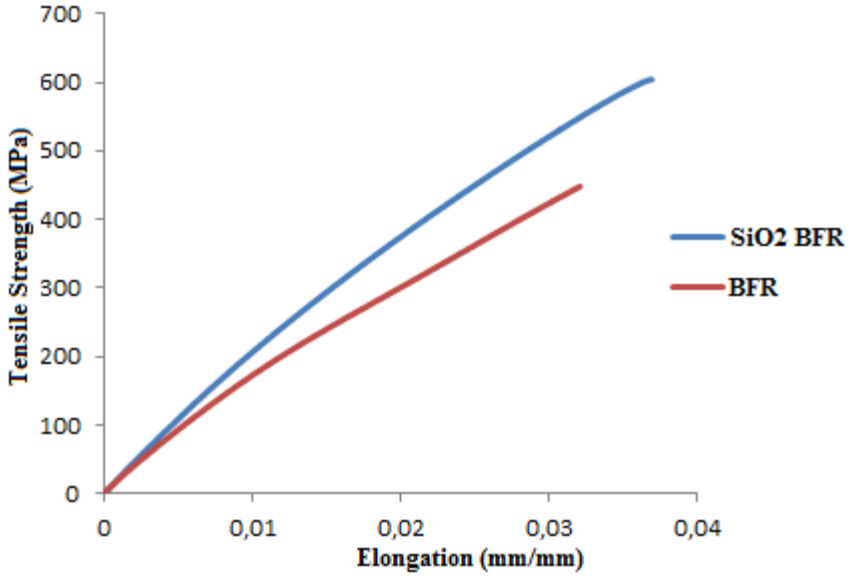


Figure 2. Tensile Strengths of sea water corrosion unexposed SiO_2 nanoparticle filled and unfilled BFR/Epoxy nanocomposites [6].

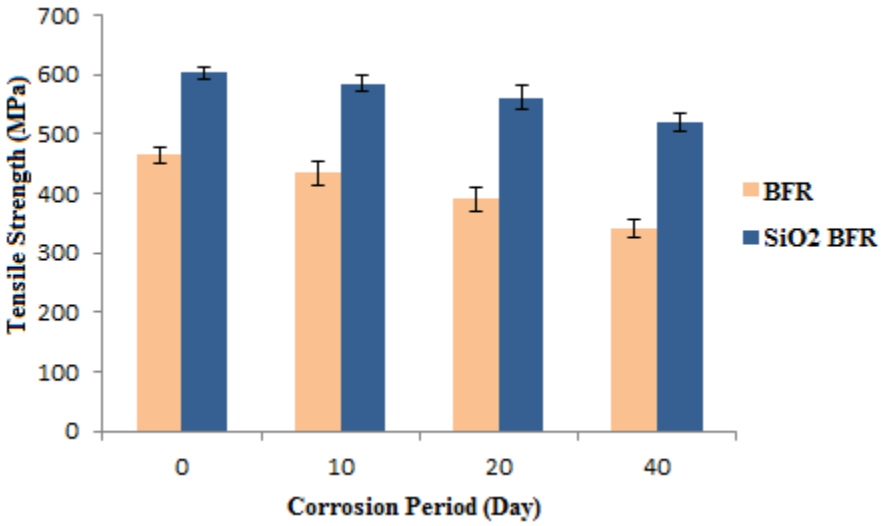


Figure 3. Tensile Strengths of SiO_2 nanoparticle filled and unfilled BFR/Epoxy composites according to the different corrosion days [6].

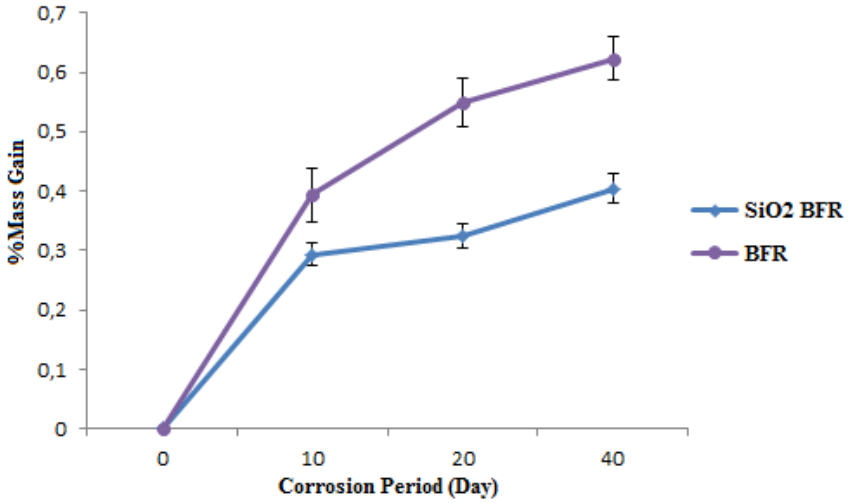


Figure 4. Sea water absorptions (mass gain %) of nanoparticle filled and unfilled BFR/Epoxy composites [6].

CONCLUSION

In this paper, The tensile behaviors of SiO_2 nanoparticle filled and un filled BFR/Epoxy composites has been investigated at sea water corrosion conditions during 0, 10, 20 and 40 days and results are given below briefly as items [6].

- SiO_2 nanoparticle addition into epoxy matrix has been contributed the increments about 27.7-29% to BFR/Epoxy nanocomposites.
- SiO_2 nanoparticle addition provided to retard the degradation of tensile behaviors of BFR/Epoxy composites. The degradation of tensile behaviors of SiO_2 nanoparticle filled BFR/Epoxy has been found lower than unfilled BFR/Epoxy composites. The losses of tensile strength of SiO_2 nanoparticle filled BFR/Epoxy composites have been defined as 3.1%, 7.1% and 14% respectively

for 10, 20 and 40 corrosion days. The losses of tensile strength of unfilled BFR/Epoxy composites have been found as 6.7%, 16.1% and 26.5% for 10, 20 and 40 days respectively.

- SiO_2 nanoparticles addition has been provided to lower absorptions of sea water. It was thought that SiO_2 nanoparticle showed the blocking effect along the absorption ways in composite structure and caused to retardant the crack propagations by fracture mechanism including crack bowing, blocking, blunting, branching and plastic deformation.

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A TEXTILE BASED LIGHTWEIGHT COMPOSITE WITH ELECTROMANGNETIC SHIELDING (EMI) and ELECTRICAL CONDUCTIVITY PROPERTIES

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Özet

Uçak dahil, pek çok savunma sanayi uygulamalarda, kullanılan malzemenin hafifliğinin yanı sıra elektromanyetik kalkanlama özelliğinin de mevcut olması oldukça önemlidir. Uygulama alanı olarak uçak sanayisi dikkate alındığında, gerek yıldırım çarpmaları, gerekse oluşacak elektromanyetik etkileri kontrol altında tutabilmek için çoğunlukla alüminyum ve benzeri metal yapılı malzemeler kullanılmaktadır. Bu çalışmada, alüminyum gibi metallere alternatif olmak üzere, daha hafif, elektrik iletkenliği ve elektromanyetik kalkanlama özelliği olan karbon yapılı tekstil tabanlı hafif kompozit ürün geliştirmek amaçlanmıştır. Çalışmada, epoksi reçine, karbon kumaş, karbon nanotüp (CNT) ve grafen oksit lifi kullanılmıştır. Epoksi reçine içerisine CNT katılarak ve karbon kumaş üzerine grafen oksit lifleri yerleştirilerek, tekstil tabanlı hafif, karbon kompozit üretilmiştir. Üretilen kompozit yapıların elektrik iletkenliği ve elektromanyetik kalkanlama özellikleri ölçülmüştür. Elde edilen tekstil tabanlı hafif karbon kompozitlerin yarı iletken sınıfında elektrik iletkenliğinin olduğu (10^{-4} S/cm mertebelerinde) ve orta derecede elektromanyetik kalkanlama (EMI) özelliğinin olduğu (32 dB) , bunun yanı sıra oldukça hafif olduğu (1.1 gr/cm^3) görülmüştür.

Abstract

In many defense applications including aircrafts, it is significant that the materials used need have electromagnetic shielding properties in addition to being lightweight. When aircrafts are considered as an application area, frequently aluminum and similar metals are used to control electromagnetic effects and lightening. In this study, design of textile based carbon lightweight composite structure that have reduced weight, electrical conducticity and electromagnetic shielding properties as an alternative to aluminum, is aimed. In the study, expoxy resin, carbon fabric, carbon nanotube (CNT) and graphene oxide fiber were are used. The textile based lightweight composites were manufactured with addingg CNT in epoxy resin and coating the surface of carbon fabric with grabene oxide fibers. Electrical conductivity and electromagnetic shielding properties of the composites were measured. The textile based lightweight carbon composites were found to be in semi-conductor range (around 10^{-4} S/cm) and have middle range electromagnetic shielding (EMI) properties (32 dB), and additionally lightweight (1.1 g/cm^3) .

Introduction

In terms of aerospace applications, weight has become a major concern. Composites, mainly carbon fiber composites, glass fiber reinforced compostes and aramide fiber reinforced composites govern the composites market which aims the reduction of weight while ensuring the properties desired. Use of composites exponentially increase in the last two decades with the developments in weight reduction, reducing fuel cost with this reduction and environmental concerns [1-3].

Fiber reinforced composites are being used in many different areas including aerospace due to their reduced weight and high mechanical performance. Some of other technical advantages of the fiber reinforced composites are good thermal stability, corrosion reduction, good damage tolerance, good strength and stiffness, etc. Fiber reinforced composites in aerospace applications consist a low-density matrix such as expoxy / phenolic resins in along with embedded fibers such as carbon, glass, etc. In these composites the weight reduction is governed by the matrix component, whereas; the fiber reinforcement provides the mechanical performance desired [4-7].

Electromagnetic interference (EMI) in aerospace caused several fatal accidents in 1980's and being reduced by the use of metal componets. However; the increased cost, weight and environmental concerns gave rise to the reserarches focusing on development of new materials suitable for use without those disadvantages [3,8].

In this study, a fiber reinforced composite that consists of glass fiber fabric, MWCNT (multi-walled carbon nanotube) and epoxy resin is investigated in terms of electrical conductivity and shielding effieciency for a potential use in aerospace applications.

Material and Methods

Materials

Expandable Graphite – GIC that is 300 μm in diameter was obtained from Grafen Chemical Industries (Grafen Co). $NaNO_3$ was obtained from Zag LTD and HCl, H_2SO_4 and $KMnO_4$ was supplied from Merck. Epoxy resin, carbon fiber woven fabric, hardner and curing agents was supplied from Fibermak Composites. MWCNT is obtaibed from Schenzen Nanotech Port Co. Ltd.

Methods

Electrical resistance values were measured with Microtest LCR Meter 6370, and electrical conductivities were calculated with the equation given below:

$$\kappa = L / (R \times A) \quad [9]$$

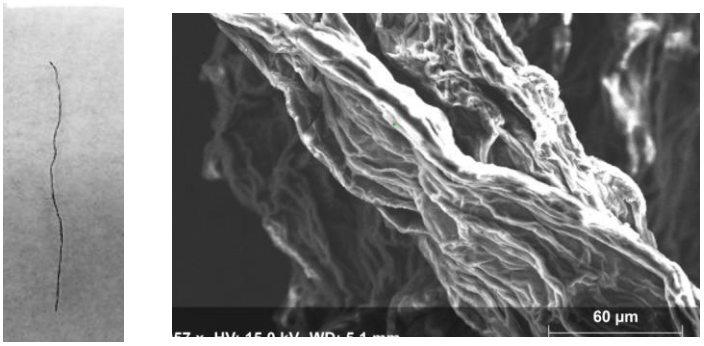
Where,
κ = Electrical conductivity coefficient (S/cm)
L= Thickness (cm)
R= Electrical resistance (Ω)
A= Area (cm^2)
The densities of the composites were calculated considering the mass and volume of the structures and found to be around 1 g/cm^3.
ASTM 4935-99 was used to measure shielding effectiveness (SE) values of the composites with a test device connected to a computer that transfers the measured results for the calculation of SE. 1 GHz test frequency was selected. The shielding effectivenesses are calculated by the computer according to the formula given below.

$$SE = (dB)_R - (dB)_L \quad [10]$$

In which;
$(dB)_R$ corresponds to the shielding efficiency of the reference (without sample)
$(dB)_L$ corresponds to the shielding efficiency of the sample load

Preparation of Graphene Oxide fiber and Reduced Graphene Oxide Fiber

GO filaments were obtained by Modified Hummer's Method followed by wet spinning [9-11]. The GO solution was processed through three coagulation baths in which the first coagulation bath consisted 30 ml / 70 ml EtOH /water and 5 % by wt $CaCl_2$, the second coagulation bath contained 40 ml / 60 ml EtOH /water, and the third coagulation bath had 50 ml / 50 ml EtOH /water. The filaments were dried for 24 hours at room temperature after the wet spinning process. The coagulated GO fiber and SEM image of GO fiber are shown in Figure 1.



a b

Figure 1: a. - Coagulated GO fiber b- SEM of GO fiber (longitudinally)

Integration of MWCNT into the Epoxy Matrix
15% by wt of MWCNT nanoparticles were added to expoxy resin by using an ultrasonic homogenizer.

Fabrication of composite fiber fabric composites

At first , hardner was added to MWCNT/epoxy composite, and a mixture was obtained. Afterwards, a layer of carbon fiber fabric was laid. On the top of the carbon fiber fabric, GO fibers were placed. Epoxy matrix was poured on the top of GO fibers. The second fabric layer, and additional epoxy matrix were placed at the top at last. The composites dried for 48 hours at room temperature and cut at a diameter of 20.5 mm and a thickness of 1 mm with a CNC cutting machine.
There are three sets of composites manufactured in this study. An expoxy composite (abbreviated as EPC) which consists of double ply carbon fabric and epoxy resin, a MWCNT incorporated composite (abbreviated as EPC/15CNT) that contains double ply carbon fabric in along with epoxy resin and 15wt.% MWCNT, and a GO fiber incorporated form of EPC/15CNT (abbreviated as EPC/15CNT/GO) that contains double ply carbon fabric, epoxy resin, single layer of GO fiber fillers and 15wt.% MWCNT.

Results and Discussion

The electrical conductivities of the composites are sho wn in Table 1. As can be seen in Table 1, all composites are in the semi-conductor range with. EPC has electrical conductivity in semiconductor range because of carbon fabric. However, 15% MWCNT incorporation resulted as decrease in electrical conductivity due to agglomeration of high loaded CNT and voids that may occur between resin matrix and CNT because of agglomeration. On the other hand, when GO was added to MWCNT incorporated composites, increase in electrical conductivity was observed due to an increase of electrical conductivity network (electrical conductivity path).

Composite	Electrical conductivity (S/cm)
EPC	$1.7\ 10^{-5}$
EPC/15CNT	$1.0\ 10^{-7}$
EPC/15CNT/GO	$1.2\ 10^{-4}$

Table 1. Electrical conductivity results of the composites

The EMI SE of the composites are shown in Table 2. As shown in Table 2, the SE results of the composites correspons to moderate shield effectiveness. Addition of MWCNT increased the SE, wheras, addition of GO to the composite reduced SE values.

Composite	EMI SE (dB)
EPC	12.3
EPC/15CNT	32.0
EPC/15CNT/GO	12.3

Table 2. EMI SE results of the composites

GO fiber results to decrease of EMI-SE (electromagnetic shielding) , this may be due to multiple reflection between and within conductive fibers, since it has been pointed out that multiple reflection mostly occurs when there are numerous and large surface areas or interfacial areas and multiple reflection decreases the shielding as pointed out by Al-Saleh et.al [12-14]. As can be seen from the SEM image in Figure 1, GO fiber has very rough surface which can lead to multiple reflection. Even though graphene flakes can have capacity for EMI SE [15-16] , graphene oxide fiber is disruptive for SE, due to highly rough surface leading to distruptive multiple reflection.
As known, CNT nanoparticles have higher electrical conductivity compared to the GO flakes [17]. Thus, resin with MWCNT provides better and higher SE than resin with GO fiber due to conductivity of MWCNT particles and highly rough surface of GO fiber.

Conclusion

The composites manufactured were observed to have lower densities (around .1 gr/ cm^3) then the commercial metal materials for shielding. When the electrical conductivities are compared, addition of highly loaded MWCNT (15%) reduced the electrical conductivity. Oppositely, GO fiber incorporated composites were observed to have increased electrical conductivity due to increased electrical conductivity path. The electromagnetic shielding of the MWCNT incorporated composite was measured as 32 dB. Graphene fiber decrease the EMI-SE due to highly rough surface leading to distruptive multiple reflection.

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DOKUMA CAM ELYAFLARIN FARKLI KATLARININ SMC KOMPOZİTLERİN MEKANİK ÖZELLİKLERİNE ETKİSİNİN İNCELENMESİ

INVESTIGATION OF THE EFFECTS OF DIFFERENT LAYERS WOVEN GLASS FIBERS ON MECHANICAL PROPERTIES OF SMC COMPOSITES

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ÖZET

Günümüzün modern imalat süreçlerinde ihtiyaç duyulan yüksek mekanik ve teknolojik özellikler geleneksel malzemelerle sağlanamaz. Yüksek mukavemet ve hafiflik talepleri birbiri ile çelişen iki mühendislik isteği olup ancak kompozit malzemelerle hayata geçirilebilirler. Bu nedenle, kompozit malzemelerin endüstride kullanımları giderek zorunlu hale gelmiştir. Sheet Molding Compounds (SMC), yüksek mukavemetli parçaların seri olarak üretildiği, başta otomotiv olmak üzere bir çok alanda kullanılan termoset bir polimer kompozit yöntemidir.

Bu çalışmada, öncelikle takviye malzemesi olarak farklı sayıda katlarda dokuma cam elyaflar kullanılarak SMC plakalar elde edilmiştir. Bu dokuma cam elyafların mekanik özelliklere etkisini incelemek için çekme ve eğilme deneyleri gerçekleştirilip sonuçları yorumlanmıştır.

Anahtar kelimeler: Sheet Molding Compound (SMC), Polimer kompozit, Dokuma cam elyaf

ABSTRACT

Objective

The high mechanical and technological features required in today's modern manufacturing processes cannot be achieved with conventional materials. The requirements such as high strength and lightweight are two contradictory engineering demands, but composite materials can be passed on. For this reason, industrial use of composite materials has become increasingly necessary. Sheet Molding Compounds (SMC) is a thermosetting polymer composite method which is used in many areas, mainly automotive, where high strength parts are produced in series.

In this study, firstly SMC plates were obtained by using woven glass fibers as reinforcement material in different number of layers, then experiments were carried out in which mechanical properties were obtained and the results were interpreted.

Material and Methods

The mechanical properties of the finished product obtained by the SMC method are generally directly dependent on the type of reinforcing materials, their volume ratio, and their distribution in the matrix. In this study, a special formulation was used for the prepregs. This formulation contains approximately 36% polyester, 10% thermoplastic resin, 30% calcite ($CaCO_3$), 20% fiber reinforcement material and 4% other additives. The obtained pesticide material was placed in SMC mold and processed at 140-150ºC temperature and appropriate pressure to obtain test plates. The test plates were tested by cutting them according to ISO 527 for tensile test specimen and ISO 178 for bending test specimen.

Discussions and Recommendations

The most important material that influences mechanical values is reinforcement materials. The type, proportion and distribution of the fiber materials used as reinforcing material significantly affect the material strength values. Strength increases considerably because the orientation of the force axis is made possible by the touch of the fibers. In addition, the mechanical properties of the SMC composite material are also increased because the fiber ratio increases as the weaving areas increase.

Key words: Sheet Molding Compound (SMC), polymer composite, woven glass fiber

1. GİRİŞ

Teknolojik gelişmeler sayesinde üstün malzemelere olan ihtiyaç kompozit malzemelere olan talebi beraberinde arttırmıştır. Sheet Molding Compounds (SMC), yüksek mukavemetli parçaların seri olarak üretildiği, başta otomotiv olmak üzere birçok alanda kullanılan termoset bir polimer kompozit yöntemidir.

SMC temel olarak, termoset reçine, takviye malzemeleri (elyaflar), dolgular ve katkı maddeleri olmak üzere 4 ana malzemeden oluşur [1]. İki aşamada üretilen bu yöntemin birinci adımında özel olarak hazırlanan reçine, elyaf, dolgu ve katkı maddeleri bir araya getirilip karıştırılarak pestil (prepreg) biçiminde malzemeler hazırlanır. İkinci adımda da olgunlaşması için bir süre bekletilen pestiller yüksek basınçlı ısıtmalı kalıplarda istenen şekle getirilir [2-3].

SMC üretim aşamalarını başarılı bir şekilde tamamlamak için prosesin hem kimyasal hem de mekanik olarak kontrolünün sağlanması gerekmektedir. Bu da ancak üretim süreci hakkında çok iyi bilgi birikimi olduğunda mümkündür. Örneğin üretim süreci esnasındaki hatalardan dolayı malzeme yüzeyinde ya da içerisinde boşluk oluşursa bu hem yüzey kalitesini düşürecek aynı zamanda mekanik özelliklerini olumsuz etkileyecektir [4-5]. Yine matris ve elyaf arasındaki etkileşimler ile elyaf oranı ve homojen dağılımı düzgün sağlanamazsa mekanik özellikler ve yüzey kalitesi olumsuz etkilenecektir [5-8]. Üretim süreci uygun şekilde gerçekleştirildiğinde ise üstün nitelikli malzemeler elde edilir. Daha iyi mekanik özellikler, kısa çevrim süresi, mükemmel yüzey kalitesi, estetik, korozyon dayanımı, düşük maliyet gibi özellikler SMC ile üretimin tercih edilmesinin nedenlerinden yalnızca bir kaçıdır. Bu özelliklerinden dolayı özellikle otomotiv sanayiinde saç malzeme yerine kullanımı giderek artmaktadır [4, 9-11].

Kompozit malzemelerde mukavemeti arttıran en önemli bileşen elyaflardır. Daha önce yapılan çalışmalarda farklı kompozit üretim yöntemleri ile elyaf oranları arasındaki ilişki ortaya konulmuştur. Elyaf oranı ile mukavemet artışı doğru orantılıdır. Kompozit malzemelerin kullanımındaki en önemli engellerden biri izotrop malzeme özellikleri göstermemesidir. Kuvvet tek taraftan etkiyorsa tek yönlü sürekli elyafların kullanımı uygun olabilir. Fakat gerçek tasarımlarda genelde malzeme farklı yönlerde kuvvetlere maruz kalmaktadır. Kompozit malzemenin farklı yönlerde mukavemetini artırmak için elyaf dokumalar kullanılmaktadır.

Bu çalışmada genellikle yüksek mekanik özelliklerin istendiği termoset kompozit parçaların üretiminde kullanılan SMC yöntemi ile, farklı katlarda cam dokuma elyaflar kullanılarak mekanik özelliklere etkisi incelenmiştir.

2. MATERYAL VE YÖNTEM

SMC yöntemi ile kalıplama sonucu elde edilen nihai ürünün mekanik özellikleri genellikle takviye malzemelerinin cinsine, hacimsel oranına, matris içerisindeki dağılımına doğrudan bağımlıdır. İki aşamada üretilen SMC kompozitlerin ilk aşamasında pestil biçimindeki malzemeler bir miktar bekletilerek olgunlaştırılır. Bu çalışmada hazırlanan pestil için Çizelge 2.1.'de verilen özel bir formülasyon kullanılmıştır.

Çizelge 2.1. Dokuma cam elyaf pestil için kullanılan formülasyon

Malzeme	Ağırlıkça (%)
Doymamış Polyester (Polipol 347)	35
Termoplastik Reçine	10
Polimerizasyon Katalisti	0,5
İç Kalıp Ayırıcı Zn-Çinko Stearat	1,3
İnert Dolgu (CaCO3) Kalsit	30
Diğer katkılar	3,2
Dokuma Cam Elyaf	20
Toplam	100

Bu çalışmada Poliya A.Ş. Türkiye firmasından temin edilen ve SMC kalıplama yöntemi için özel olarak üretilmiş Polipol-347 SMC-BMC tip doymamış polyester kullanılmıştır. Dokuma cam elyaf için, birim ağırlık/alan değeri 500 g/m^2, elyaf yönü [0/90°] olan düz cam elyaf dokuma Fibroteks A.Ş Türkiye firmasından temin edilmiştir.

SMC Pestiller üretilirken takviye malzemesi olarak ilk önce tek kat dokuma elyaf olacak şekilde ve sadece SMC reçinenin bulunduğu pestiller hazırlandıktan sonra olgunlaşması için bekletilmiştir (Şekil 2.1.).



Şekil 2.1. Dokuma SMC pestillerin hazırlanması

Daha sonra tek kattan altı kata kadar dokuma pestiller elde edildi. Altı kat dokuma pestil referans olarak seçilerek diğer pestillerin aynı ağırlıkta kalıpta basılması sağlandı. Bunun için basım esnasında aynı özelliklere sahip içeriğinde elyaf olmayan SMC reçine malzeme, üst üste yerleştirilen dokuma elyaf katların her iki tarafına tartılarak yerleştirildi ve böylelikle tüm pestillerin aynı ağırlığa sahip olması sağlandı. Örneğin tek kat dokuma elyaf kalıba uygun olarak kesilip tartıldıktan sonra eksik kalan miktar,

elyafsız SMC reçine ile tamamlanarak kalıp içine yerleştirilip pestiller basılmıştır. Aynı işlem altı kata kadar devam etmiştir.

Elde edilen pestil malzeme SMC kalıp içerisine yerleştirilerek, 140-150ºC sıcaklık ve uygun basınç altında işlenerek deney plakaları elde edilmiştir (Şekil 2.2.).



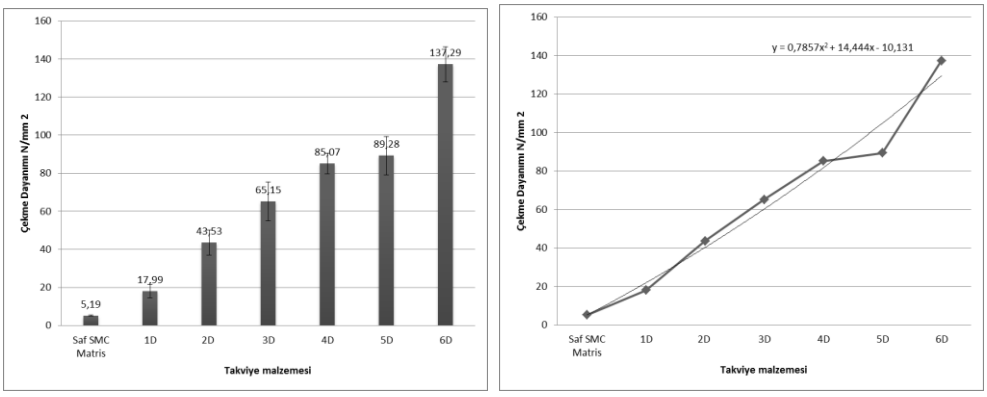
Şekil 2.2. Üretilen SMC plakalar.

Üretilen bu plakalar, çekme deneyi numunesi için ISO 527, eğilme deneyi numunesi için ise ISO 178 standartlarına uygun şekilde kesilerek test edilmiştir.

3. SONUÇLAR

Kompozit malzemelerin kullanımındaki en önemli engellerden biri izotrop malzeme özellikleri göstermemesidir. Kuvvet tek taraftan etkiyorsa tek yönlü sürekli elyafların kullanımı uygun olabilir. Fakat gerçek tasarımlarda genelde malzeme farklı yönlerde kuvvetlere maruz kalmaktadır. Kompozit malzemenin farklı yönlerde mukavemetini artırmak için elyaf dokumalar kullanılmaktadır. Dayanımı artıran bir diğer önemli özellik ise elyaf oranını artırmaktır. Bu sebeple de birden fazla dokuma kat üst üste yerleştirilir. Farklı sayıda cam elyaf dokuma katları kullanılarak üretilen SMC kompozitler daha sonra bu elyafların, parçanın mekanik özelliklerine olan etkisi incelenmiştir.

Çalışmada 1 kattan 6 kata kadar cam elyaf dokuma kullanılarak üretilen SMC kompozitlerin çekme deneyi sonuçları elde edilerek Şekil 3.1. ve Çizelge 3.1.'de verilmiştir. Çizelge ve grafik incelendiğinde dokuma kat sayısı ile dolayısıyla elyaf oranı arttıkça mekanik özellikler iyileşmiştir [12].



Şekil 3.1. Farklı katlardaki dokuma cam elyaflı SMC numunelerin ortalama çekme deneyi sonuçları

Bu konuda yapılan literatür çalışmaları bu durumu desteklemektedir. Elyaf oranı artışı malzemenin elastisite modülünü ve birim deformasyonunu arttırmıştır. Normalde kompozitlerde elastisite modülü arttıkça malzeme daha gevrek olmakta ve birim deformasyon değeri düşmektedir. Birim deformasyonun

artması demek aynı zamanda kompozitin tokluk değerinin de artması demektir ki bu da mühendislik tasarımlarında en çok istenen durumdur. Sonuç olarak SMC kompozit malzeme daha sert ve dayanıklı hale gelmiştir.

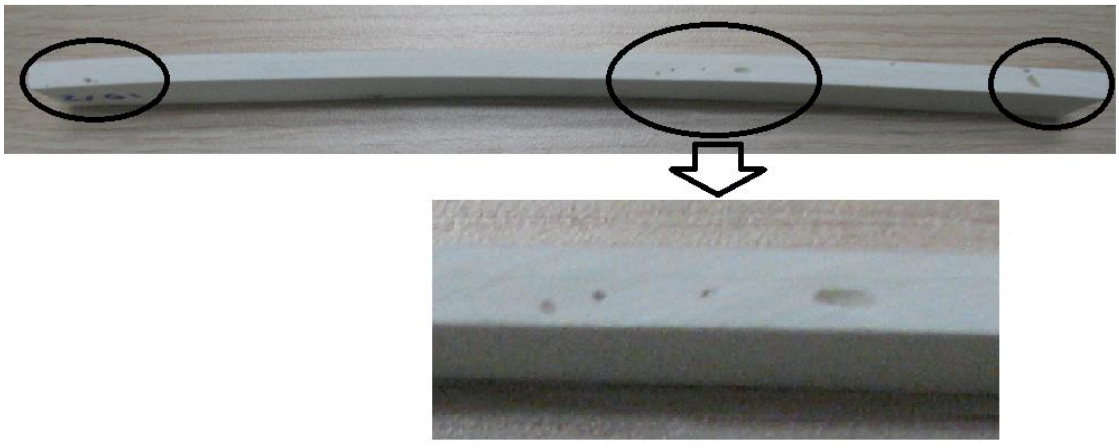
Çizelge 3.1. Farklı katlardaki dokuma cam elyaflı SMC numunelerin çekme deneyi sonuçları

Malzeme*	Çekme gerilmesi N/mm^2 (MPa)	Standart Sapma	Uzama %	Elastisite Modülü N/mm^2 (MPa)
Saf SMC reçine	5,19	0,28	-	-
1 D	17,99	3,54	-	1738,28
2 D	43,53	6,66	2,70	2483,11
3 D	65,15	10,33	3,46	3741,40
4 D	85,07	5,52	3,60	4160,62
5 D	89,28	10,14	3,91	4277,85
6 D	137,29	9,25	4,44	5601,93

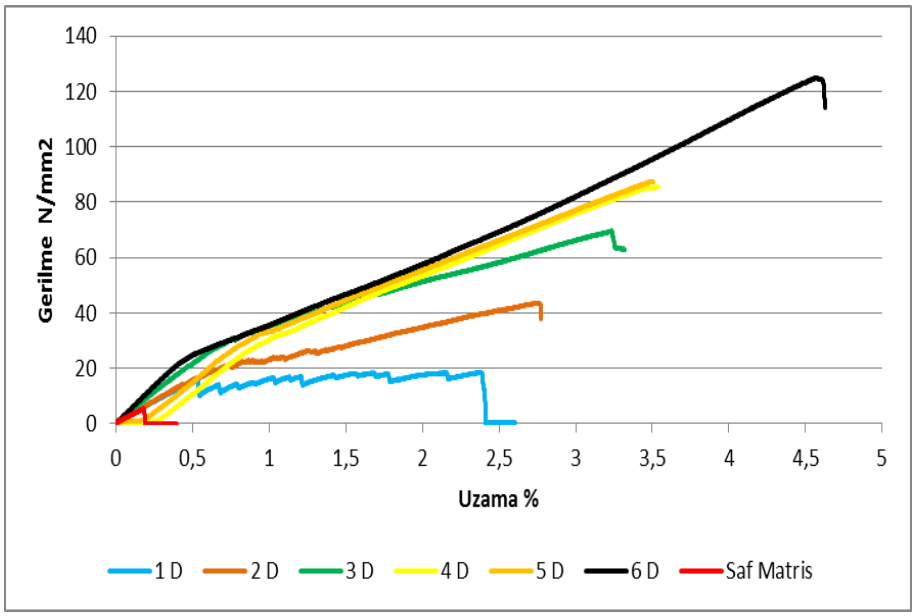
*Tüm sonuçların ortalama değerleri verilmiştir

Şekil 3.1. incelendiğinde elyaf oranı ile kompozitin çekme dayanımının lineer bir şekilde arttığı daha açık görülmektedir. Çizelge 3.1'deki sonuçlar incelendiğinde tek katlı dokuma ile altı kat dokuma arasında %700 fark gözükmektedir. Tek kat dokuma ile elde edilen kompozitin çekme dayanımının çok düşük çıkmasının tek sebebi elyaf oranı değildir.

Basınçlı bir kalıplama yöntemi olan SMC'de malzeme içerisinde yeterli miktarda elyaf yoksa, kalıp kapanması esnasında reçine kalıp boşluklarından taşarak kalıp içerisinde yeterli miktarda malzeme kalmamaktadır. Bu durum ise Şekil 3.2'de görüldüğü gibi malzeme içerisinde boşluklara yani poroziteye neden olmaktadır. Böylelikle mekanik özellikleri azaltmaktadır. SMC kompozit malzemelerin mukavemetini etkileyen en önemli unsurlardan birisi içindeki boşluk yapısının fazla olmasıdır [4-6, 13]. Bu boşluklar malzeme üzerinde matris çatlaklarına sebep olarak küçük gerilme etkilerinde malzemenin hasara uğramasına neden olur. Elyaf oranı düşük ve ara yüzey bağları zayıf olan numuneler de çok düşük kuvvetlerde belli bir yerinden kırılma eğilimindedirler.



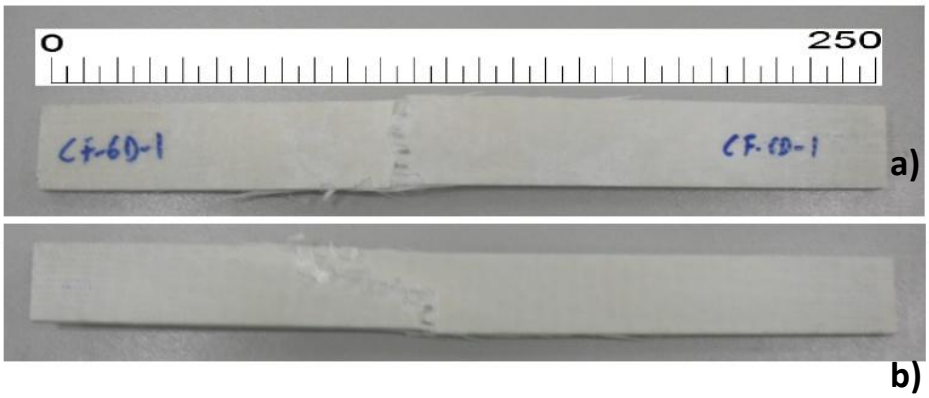
Şekil 3.2. Elyaf oranı düşük olan 2 kat cam dokumalı SMC plakada oluşan porozite



Şekil 3.3. Farklı katlardaki dokuma cam elyaflı SMC numunelerin çekme gerilmesi-birim deformasyon eğrileri

Çekme deney numunelerin ortalama değerleri alındığında malzemeyi temsil eden bir numunenin gerilme birim deformasyon eğrileri Şekil 3.3'de çizilmiştir. Sonuçlar incelendiğinde en fazla birim deformasyon altı kat dokuma elyafla üretilen SMC kompozitte bulunmaktadır. Ayrıca buna bağlı olarak en yüksek çekme gerilmesi ve elastisite modül değeri de yine bu kompozite aittir.

Dokuma elyaflı SMC kompozitin hasar mekanizması incelenirse; elyaflar numune boyunca sıra ile dizildiği için yük numune kesiti boyunca dağılmakta matris belli bir noktadan kırılmaktan çok uzunluk boyunca çatlak oluşturma eğilimli olmaktadır. Uygulanan kuvvet etkisi ile elyaflara normal yönünde gerilme oluştururken aynı zamanda kayma gerilmeleri etkisinde enine çatlaklar da oluşturmaktadır. Bu durum Şekil 3.4'de daha açık görülmektedir.



Şekil 3.4. Hasara uğramış çekme deneyi numuneleri, dokuma cam elyaf SMC'nin a) ön ve b) arka görünümü

Ayrıca dokuma elyaftaki bağlantı noktalarında reçine havuzları, boşluklar ve düşük ıslanma eğilimi vardır. Gerilme etkisi altında normal ve kayma gerilmeleri etkisi altında ilk önce matris çatlakları oluşacaktır. Bahsedilen kusurlardan dolayı matris ile elyaf arasında lokal ayrılmaların yanında ara yüzey dayanımı kötü olan elyaflar sıyrılacak (pull-out) ve iyi olanlar kopacaktır. Bunların dışında üst üste yerleştirilen

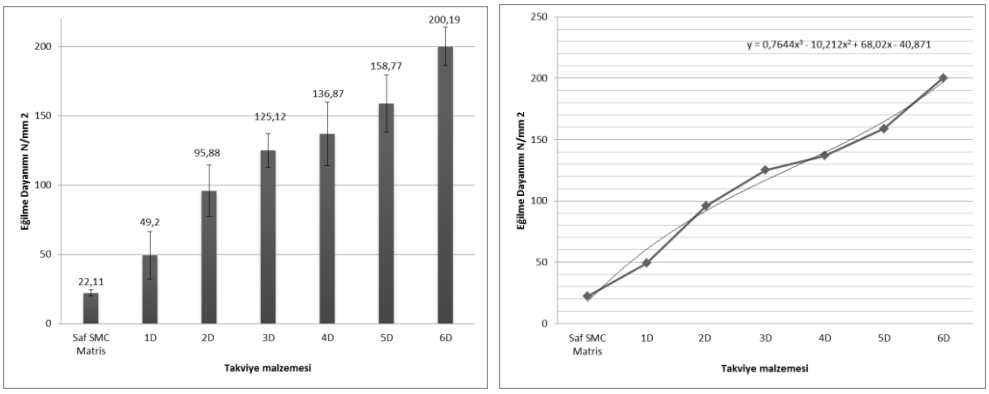
dokuma elyaf tabakaları arasında hem reçine havuzlarının olması hem de eğilme cevabı uyumsuzluğu sebebiyle tabakalar arası ayrılma (delaminasyon) gerçekleşerek en son malzeme hasara uğrayacaktır.

Dokuma kat sayısının artmasının doğal bir sonucu olarak kompozit elyaf oranı da artmaktadır. Çekme deney sonuçlarına benzer bir eğilim eğilme dayanımı sonuçlarında da Çizelge 3.2. ve Şekil 3.5'de açıkça görülmektedir. Tek katlı dokuma elyaf takviyeli SMC kompozit ile altı kat dokuma kompozitin eğilme gerilmesi değerleri arasında ise yaklaşık %308 artış vardır fakat bu fark çekme gerilmesi değerinden çok daha düşüktür.

Çizelge 3.2. Farklı katlardaki dokuma cam elyaflı SMC numunelerin eğilme deneyi sonuçları

Malzeme*	**Eğilme gerilmesi N/mm^2 (MPa)**	**Standart Sapma**	**Elastisite Modülü N/mm^2 (MPa)**
Saf SMC reçine	22,11	2,27	-
1 D	49,2	17,21	11742,95
2 D	95,88	18,45	18269,37
3 D	125,12	12,03	18925,63
4 D	136,87	22,92	19411,80
5 D	158,77	20,56	23928,49
6 D	200,19	13,94	30624,51

*Tüm sonuçların ortalama değerleri verilmiştir



Şekil 3.5. Farklı katlardaki dokuma cam elyaflı SMC numunelerin ortalama eğilme deneyi sonuçları

Ayrıca dokuma kat sayısı arttıkça gerilme dayanımının da yaklaşık olarak lineer arttığı Şekil 3.5.'de gösterilmiştir. Bu durum literatürde verilen değerlerle uyum içindedir. Yapılan birçok çalışmada kompozite dayanımını veren en önemli faktörlerden birinin malzemenin elyaf oranı olduğu belirtilmiştir.

4. TARTIŞMA VE ÖNERİLER

Mekanik değerleri etkileyen en önemli malzeme takviye malzemeleridir. Takviye malzemesi olarak kullanılan elyaf malzemelerinin cinsi, oranı ile parça içindeki dağılımı ve yönelimi malzeme mukavemetini önemli ölçüde etkilemektedir. Elyafların dokunması sayesinde kuvvet ekseninde yönlenmeleri mümkün hale geldiği için mukavemet önemli ölçüde artmaktadır. Ayrıca dokuma katları arttıkça elyaf oranı da arttığı için SMC kompozit malzemenin mekanik özellikleri de yükselmektedir.

Farklı kat sayılarında yapılan dokuma cam elyaf takviyeli SMC kompozit sonuçları incelendiğinde en fazla birim deformasyon altı kat cam dokuma elyafla üretilen SMC kompozitte bulunmaktadır. Ayrıca buna bağlı olarak en yüksek çekme gerilmesi ve elastisite modül değeri de yine bu kompozite aittir. Dokuma elyaflı SMC kompozitin hasar mekanizması incelenirse; elyaflar numune boyunca sıra ile dizildiği için yük numune kesiti boyunca dağılmakta matris belli bir noktadan kırılmaktan çok uzunluk boyunca çatlak oluşturma eğilimli olmaktadır. Uygulanan kuvvet etkisi ile elyaflara normal yönünde gerilme oluştururken aynı zamanda kayma gerilmeleri etkisinde enine çatlaklar da oluşturmaktadır. Ayrıca dokuma elyaftaki bağlantı noktalarında reçine havuzları, boşluklar ve düşük ıslanma eğilimi vardır. Gerilme etkisi altında normal ve kayma gerilmeleri etkisi altında ilk önce matris çatlakları oluşacak. Bahsedilen kusurlardan dolayı matris ile elyaf arasında lokal ayrılmaların yanında ara yüzey dayanımı kötü olan elyaflar sıyrılacak (pull-out) iyi olanlar kopacaktır. Bunların dışında üst üste yerleştirilen dokuma elyaf tabakaları arasında hem reçine havuzlarının olması hem de eğilme cevabı uyumsuzluğu sebebiyle tabakalar arası ayrılma (delaminasyon) gerçekleşerek en son malzeme hasara uğrar.

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FORMATION AND MORPHOLOGY OF CELLULOSE ACETATE MICROCAPSULES FOR SELF-HEALING COMPOSITES

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Abstract

Microcapsules containing various types of liquid resin and cure agent have possible usage in self-healing applications. These two components are released from microcapsules when a local damage is induced and from a new, cured matrix in the damaged area. The aim of this study is to prepare cellulose acetate (CA) microcapsules with two different epoxy resins (EPON 813 and EPON 828) and with various carbon nanotube (CNT) content. Epoxy resin and CA are dissolved in acetone/dichloromethane (DCM) mixture and CNT is added into resin as a second component and dispersed in resin by using an ultrasonicator. This mixture is added in sodium dodecyl sulfate (SDS) solution and CA microcapsules are obtained after evaporation of acetone and DCM at 40 ºC and 1200 rpm. For preparation of EPON 828 microcapsules with different shell thickness, carbon nanotube content (1.0% wt) is kept constant at the beginning, while core:shell ratio is changed between 1:1 and 4:1 by weight. After determining optimum core:shell ratio, CNT percentage of EPON 828 microcapsules is changed between 0.25 and 2.0%. Also various acetone and DCM ratios are used to adjust the core content of microcapsules. Shell thickness and core:shell ratio of EPON 813 microcapsules are adjusted by changing EPON 813:CA ratio between 1:0.25 and 1:1 by keeping CNT content (1.0% wt) and mixing rate (1200 rpm) constant. Different acetone:DCM ratios are applied to change the core:shell ratio of EPON 813 microcapsules. Synthesized microcapsules are characterized by FTIR, TGA, and SEM techniques. FTIR and TGA results confirm that CA microcapsules can in fact encapsulate epoxy resin. SEM results reveal that the shell thickness can be reduced by the increasing core:shell ratio. However, thinner shell structure often causes shell to collapse inward during the evaporation of DCM. Therefore, it is necessary to use a core:shell ratio over 1:1 to obtain intact spherical microcapsules. Microcapsules with average particle diameters between 12 and 24 microns can be obtained by changing the viscosity of the mixture used in the encapsulation process.

Keywords: Microcapsules, self-healing applications, cellulose acetate, carbon nanotube.

1. Introduction

Self-healing polymers and composites are expected to provide additional durability and reliability with autonomous crack repairing ability. The number of publications on self-healing materials has increased considerably in recent years because of their growing importance [1-3]. Self-healing materials based on microcapsules are more likely to be commercialized in the near future compared to other techniques [4], as microencapsulation is a mature technique which has been utilized for various purposes since 1960 [5-6]. Moreover, microcapsules can be easily incorporated into the polymer matrix using existing blending techniques. Microencapsulation is a technique in which solids, liquids, or gases can be enclosed in a sphere with diameters between a few micrometers to millimeters to be used in various industries such as pharmaceuticals, adhesives, feed additives, pesticides and herbicides, powder perfumes, textiles, thermochromic dyes, and self-healing materials.

Many self-healing agent systems that can be loaded as a core material and resin/hardener or monomer/initiator systems have been extensively studied in the literature [7-11]. Styrene/benzoyl peroxide and epoxy/diamin combinations are examples of two-component self-healing systems. In microcapsule based approach, core material can accommodate these two components together or they can

be placed in two separate capsules. More recently, nanomaterials such as carbon nanotubes have been added into microcapsules as the second component. For example, Caruso et al. [12] synthesized microcapsules containing CNTs using an *in situ* emulsification polymerization of urea-formaldehyde for damage sensing. Autonomic restoration of electrical conductivity using polymer-stabilized carbon nanotube and graphene microcapsules has been studied by Odom et al. [13]. Liquid-filled microcapsules via co-encapsulation of CNTs as optothermal-triggering element using interfacial polymerization technique have also been investigated [14]. Fereidoon et al. [15] reported the effect of nanoparticles on the morphology and thermal properties of self-healing poly(urea-formaldehyde) microcapsules. They employed carbon nanotubes to modify the physical properties of the PUF shell walls of microcapsules filled with dicyclopentadiene. Wei et al. [16] prepared CNT/poly(urea-formaldehyde) composites for electrochemical sensors by *in situ* polycondensation.

It is known that the addition of reinforcement material either in fiber or fabric form into a polymeric material may have a significant favorable effect on the mechanical properties of the polymer. However, CNTs often entangle together, forming bundles of micro-scale aggregates which do not disperse in conventional solvents because of strong van der Waals interactions between individual nanotubes. Thus, improved dispersion can be achieved in relatively few, custom-prepared solvents or polymer solutions.

Various epoxy resins can be used for dispersion of reinforcement materials and can be encapsulated into microcapsules using different strategies. Solvent evaporation is one of these techniques to obtain epoxy containing microcapsules. In this approach, epoxy and shell forming polymer is dissolved in an organic solvent and dispersed in water phase. A hard shell is obtained on epoxy droplets after evaporation of solvent. It has been shown in numerous publications that shells can be made from a variety of polymeric materials, such as poly(urea formaldehyde), poly(ethylene glycol)s, poly(methacrylate)s, poly(styrene)s, cellulose, poly(lactide)s, poly(lactide-co-glycolide)s, gelatin, polyetherimide and ethyl cellulose [17-22].

Cellulose acetate, cellulose acetate phthalate, cellulose acetate butyrate and ethyl cellulose are among cellulose based polymers that are commonly used in microencapsulation. It is possible to use solvent evaporation technique to form a hard shell on different liquid cores by using this approach. Phase change liquids, drugs, free radical scavengers, and dairy products among others have already been loaded into microcapsules [23-27]. While there are several studies on encapsulation of liquids in cellulose based microcapsules, there have not been detailed studies on encapsulation of resins for self-healing applications.

The aim of this study is to investigate the possible usage of solvent evaporation technique to prepare CA microcapsules containing epoxy and carbon nanotubes. Isolated microcapsules was attempted to be obtained by changing epoxy/CA ratio at a constant evaporation temperature. Effects of epoxy/CA ratio and carbon nanotube content on microcapsule morphology were investigated and particle size distribution of microcapsules was correlated with these parameters.

2. Materials and Methods

EPON 813 and EPON 828 were purchased from Miller Stephenson Chemical Co. Dichloromethane (DCM), Acetone, Cellulose Acetate [Mw~50000], sodium dodecyl sulfate (SDS) and multi-walled carbon nanotube (MWNT) [>90% carbon basis, D × L 110-170 nm × 5-9 μm] were obtained from Sigma Aldrich Co. and used without any further processing or purification.

2.1 Preparation of Microcapsules

In this study, CA microcapsules with CNT and EPON828 were prepared by using solvent evaporation approach. CNT free EPON 813 microcapsules were also prepared by changing core:sell ratio and solvent content. Encapsulation process was carried out at 1200 rpm mixing rate and at 40 ºC. Acetone was used together with DCM as co-solvent. For preparation of EPON 828 microcapsules, four different CNT contents (0.25, 0.5, 1.0, 2.0% w. nanotube/w. epoxy) were used to prepare the microcapsules. MWNT, EPON 828 and CA weighed in appropriate ratios and mixed in DCM/acetone solution on a magnetic

stirrer until EPON 828 and CA completely get dissolved in DCM. This mixture was sonicated by using a Vibra-Cell high intensity ultrasonic processor for 10 minutes to get better CNT dispersion. 40 ml of this mixture was added on 50 ml 1% w/V SDS solution drop by drop in 90 minutes to get organic phase/water emulsion at the desired mixing rate. After stabilization of emulsion, mixture was added onto 200 ml 1% w/V SDS solution and temperature of mixture was raised to 40 ºC. After 4 hours, mixture was cooled to room temperature and filtered by using Whatman Grade 93 filter paper. Solid product was washed with excess distilled water and dried at room temperature under the fume hood. A similar approach was adopted for preparation of CNT free CA microcapsules. Since CNT's were not used in this sets of experiments, sonication was not applied the EPON 813 solution. Figure 1 depicts the preparation procedure of microcapsules.

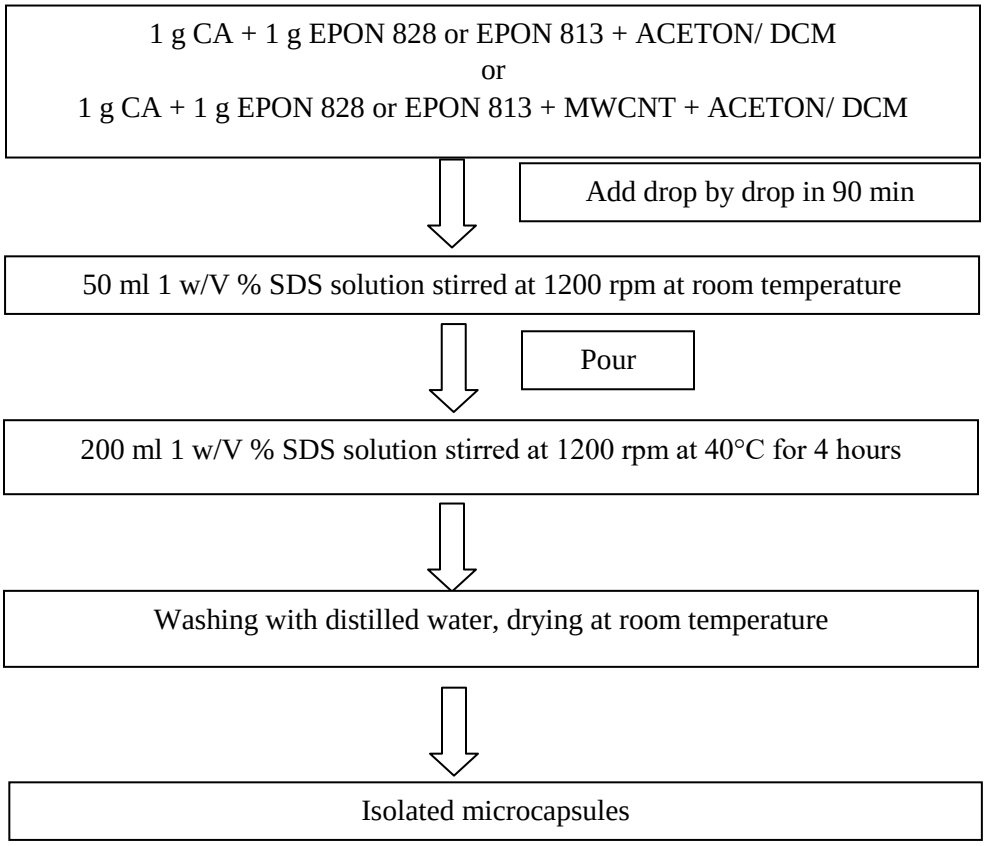


Figure 1. Preparation procedure of carbon nanotube containing CA microcapsules with EPON 828 and EPON 813 content

2.2 Characterization of Microcapsules

Chemical analyses of microcapsules were carried out by Bruker IFS 66/S Fourier Transform Infrared Instrument. Microcapsules were mixed with KBr, ground and pellets were prepared under the press. NEON 40 EsB scanning electron microscope (SEM) was used to characterize both surface and shell morphology of the microcapsules. Test samples were prepared on a glass side and coated by using Hummer VI Triode Sputter Coater. Thermal stability of microcapsules was determined by using TG-DSC instrument [TA Instruments Q50] at 10 ºC/min heating rate. Particle size distribution of the microcapsules was determined by analysis of SEM images at 50X magnification.

3. Results and Discussion

3.1 Size Distribution of Microcapsules

Viscosity of the oil mixture used in encapsulation process determines the size distribution of microcapsules. Viscosity of this mixture depends on many factors such as, molecular weight of shell forming polymer, viscosity of resin, amount of carbon nanotube and the solvent. In case of high viscosity mixture, oil droplets formed in surfactant solution come together and form millimeter size spherical particles. EPON 828 has higher viscosity compared to EPON 813 and larger amount of acetone/DCM mixture is need to overcome this problem. 10:30 ml (V/V) acetone/DCM mixture is ideal for getting spherical micron size microcapsules at 1:1 (w:w) resin/CA ratio for EPON 828 microcapsules. Increasing resin resin/CA ratio over 1:1 causes two changes. First, the amount of resin accommodated by each microcapsule increases. Second, shell thickeness of microcapsules becomes smaller. However, the shell of these microcapsules collapses inward during evaporation of aceton/DCM due to the thinner CA shell and this prevents formation of spherical microcapsules. By keeping resin:CA ratio 1:1, it is possible to change the CNT content of microcapsules. While microcapsules with 23 micron average diamater are obtained in the presence of 2.0% w/w CNT at 1200 rpm, average size of microcapsules drop to 12 microns when 0.25% w/w CNT is used.

In the case of EPON 813 microcapsules, it is possible to get spherical microcapsules by using just 5:15 ml (V/V) acetone/DCM mixture at 1:1 resin:CA ratio. When less amount of acetone/DCM mixture was employed, average microcapsule size is increase from 17 microns to 35 microns. Similar to EPON 828 microcapsules, thinner shells are formed when epoxy:CA ratio changed from 1:1 to 1:0.5 and 1:1 to 1:0.25. However, unlike EPON 828 microcapsules, spherical microcapsules can be obtained at :0.75 epoxy/CA ratio with an average size of 12 microns. Table 1 lists the codes used for nine different types of microcapsule batches produced with various combinations of mixing speed and nanotube content.

Table 1: Codes and average particle sizes and morphology of spherical microcapsules

Sample Code	Acetone/DCM ratio (V / V)	Core content	CNT percentage (%w/w)	Core:shell ratio (w / w)	Average Particle Size (Microns)
CA1	10 ml/ 10 ml	EPON 828	1.00	1:1	Collapsed
CA2	5 ml/ 10 ml	EPON 828	1.00	1:1	Collapsed
CA3	10 ml/ 30 ml	EPON 828	1.00	1:1	20
CA4	10 ml/ 30 ml	EPON 828	1.00	2:1	Non spherical
CA5	10 ml/ 30 ml	EPON 828	1.00	3:1	Non spherical
CA6	10 ml/ 30 ml	EPON 828	1.00	4:1	Non spherical
CA7	10 ml/ 30 ml	EPON 828	2.00	1:1	23
CA8	10 ml/ 30 ml	EPON 828	0.50	1:1	16
CA9	10 ml/ 30 ml	EPON 828	0.25	1:1	12
CA10	5 ml/ 15 ml	EPON 828	1.00	1:0.25	Collapsed
CA11	5 ml/ 15 ml	EPON 813	1.00	1:1	17
CA12	5 ml/ 15 ml	EPON 813	1.00	1:0.25	Non spherical
CA13	5 ml/ 15 ml	EPON 813	1.00	1:0.50	Non spherical
CA14	5 ml/ 15 ml	EPON 813	1.00	1:0.75	12
CA15	10 ml / 5 ml	EPON 813	1.00	1:1	35
CA16	10 ml/ 10 ml	EPON 813	1.00	1:0.75	24

3.2 Effect of Process Parameters on Microcapsule Morphology

Figure 2 shows the effect of epoxy content on surface morpholgy of EPON 828 microcapsules. Shell thickness of microcapspsules decreases with increasing epoxy content. During evaporation of volatile solvent (acetone:DCM mixture), a negative pressure is formed inside the microcapsules which results in the inward collapse of the shell, if the shell thickness is not sufficient. When 1:1 epoxy:CA ratio is used, microcapsules with rough surface is obtained and most microcapsules have regular shapes. Increased and excessive shell deformation is also observed with decreasing shell thickness.

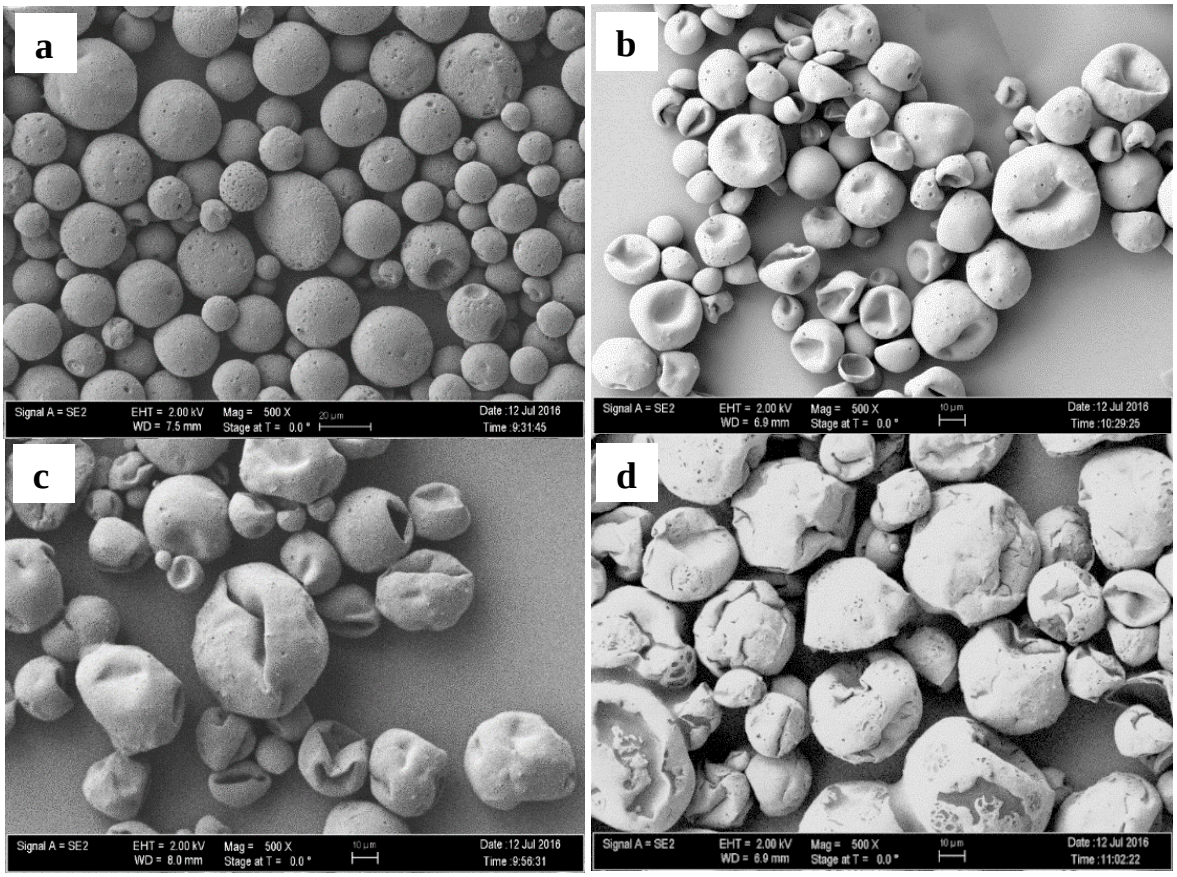


Figure 2. SEM images of EPON 828 microcapsules a) CA3, b) CA4, c) CA5, and d) CA6

Particle size distribution of EPON 828 microcapsules increases with increasing CNT content (Figure 3). Also there is an increase in surface roughness with increasing CNT ratio, and microcapsules have mostly spherical shape when 1:1 epoxy:CA ratio was used.

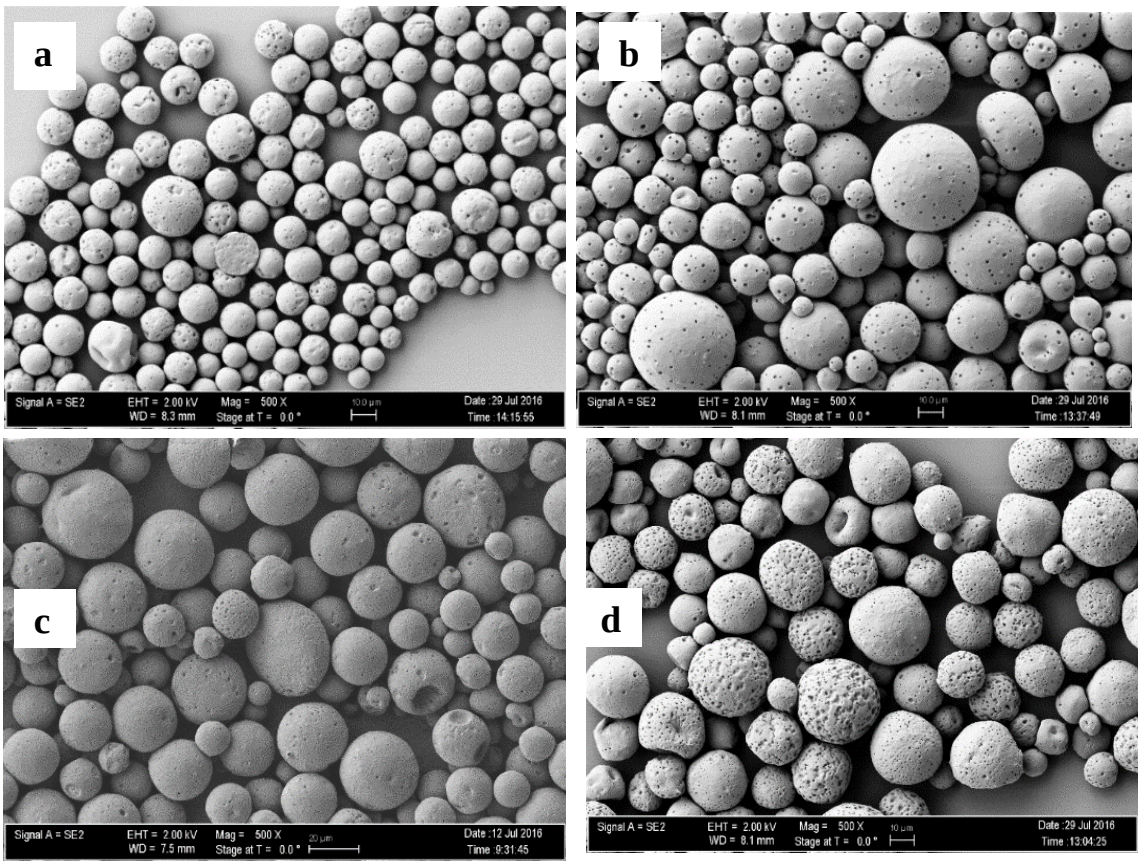


Figure 3. SEM images of EPON 828 microcapsules a) CA9, b) CA8, c) CA3, and d) CA7

Crater type formations are closed so that microcapsules can host liquid resin without creating any leakage. Presence of CNT can be observed on the shell either sticking out or lying flat on the surface (Figure 4).

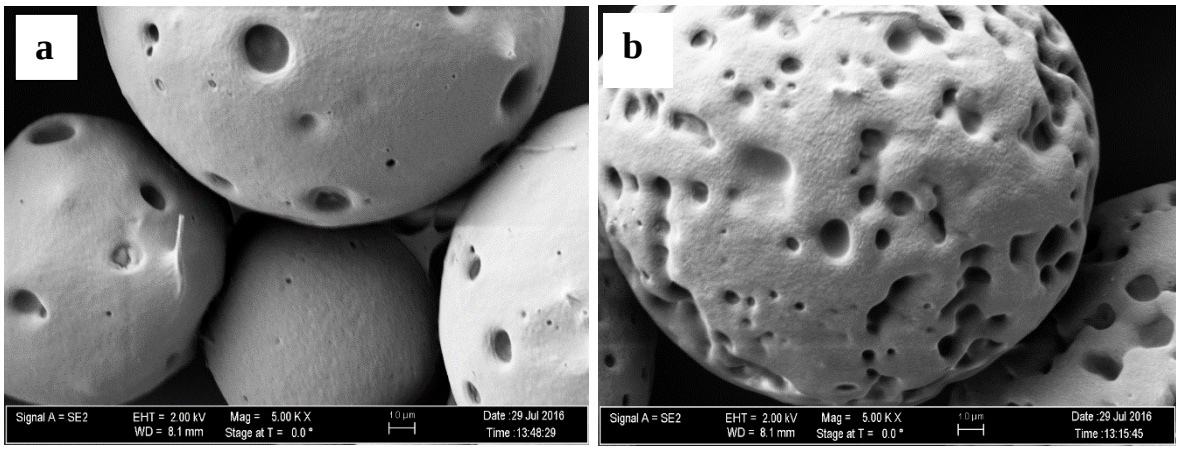


Figure 4. SEM images of EPON 828 microcapsules a) CA8 and b) CA7

Figure 5 shows the SEM images of EPON 813 microcapsules with 1:1 and 1:0.75 epoxy:CA ratio. Decrease in particle size distribution with decreasing CA amount is apparent in SEM images. Even if EPON 813 microcapsules have more irregular shapes, the roughness of shell surface is less than that of EPON 828 microcapsules. This could be influenced by the amount of volatile solvent used in encapsulation process.

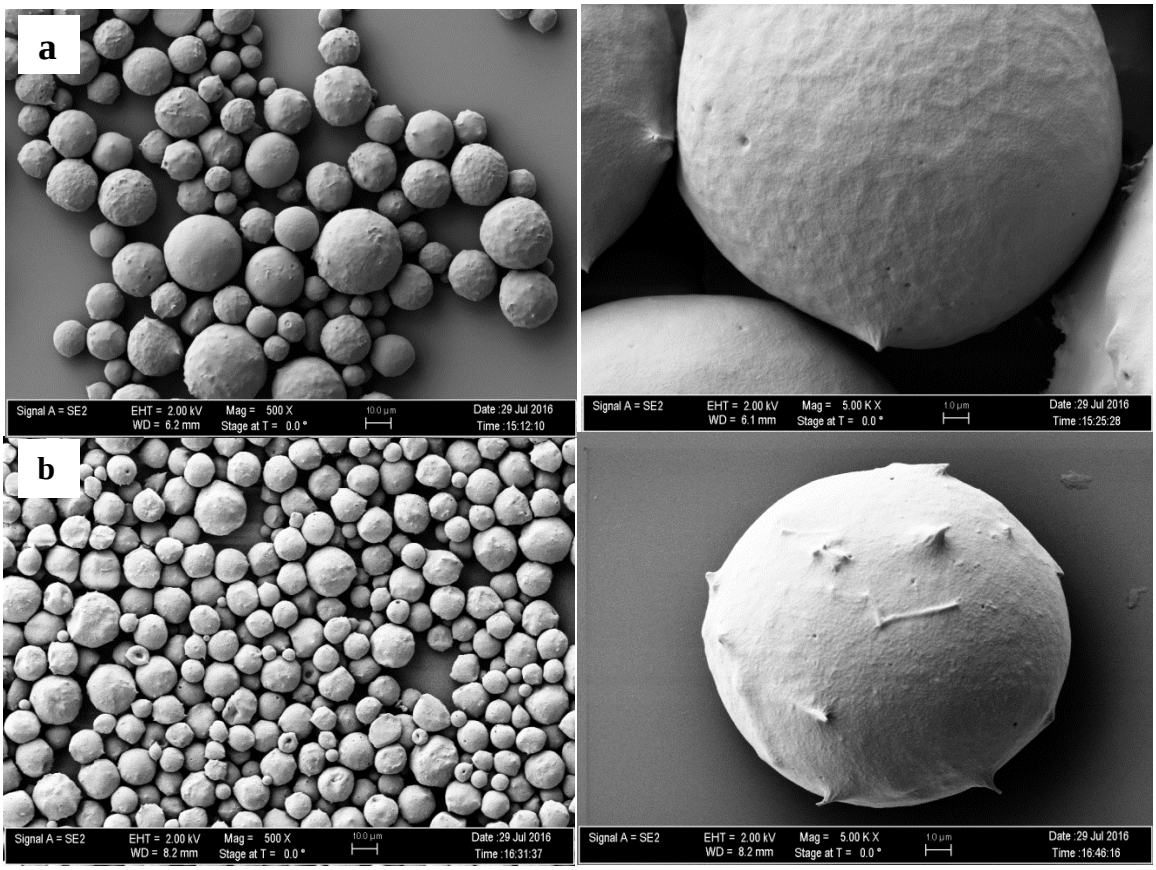


Figure 5. SEM images of 813 microcapsules a) CA11 (500X, 5000X), b) CA14 (500X, 5000X)

3.3 Thermal Analysis of CA Microcapsules

Figure 6a shows the typical TGA thermograms of EPON resin and CA. Thermal decomposition of CA starts at 360 ^{o}C and 80% of polymer degradades at around 380 ºC. The rest of the degradation product continue to decompose at higher temperatures. EPON resin starts to decompose at 240 °C and shows a two-stage degradation. After first decomposition, 85% of resin burns out and no residue is observed after 600 ºC.

Figure 6b shows the TGA curves of CNT and resin containing CA microcapsules. Decomposition starts at around 200 ºC and second degradation observed at 340 ºC. Both EPON and CA continue to degrade at higher temperatures above 400 ºC. Presence of EPON resin and CA is evident in microcapsules.

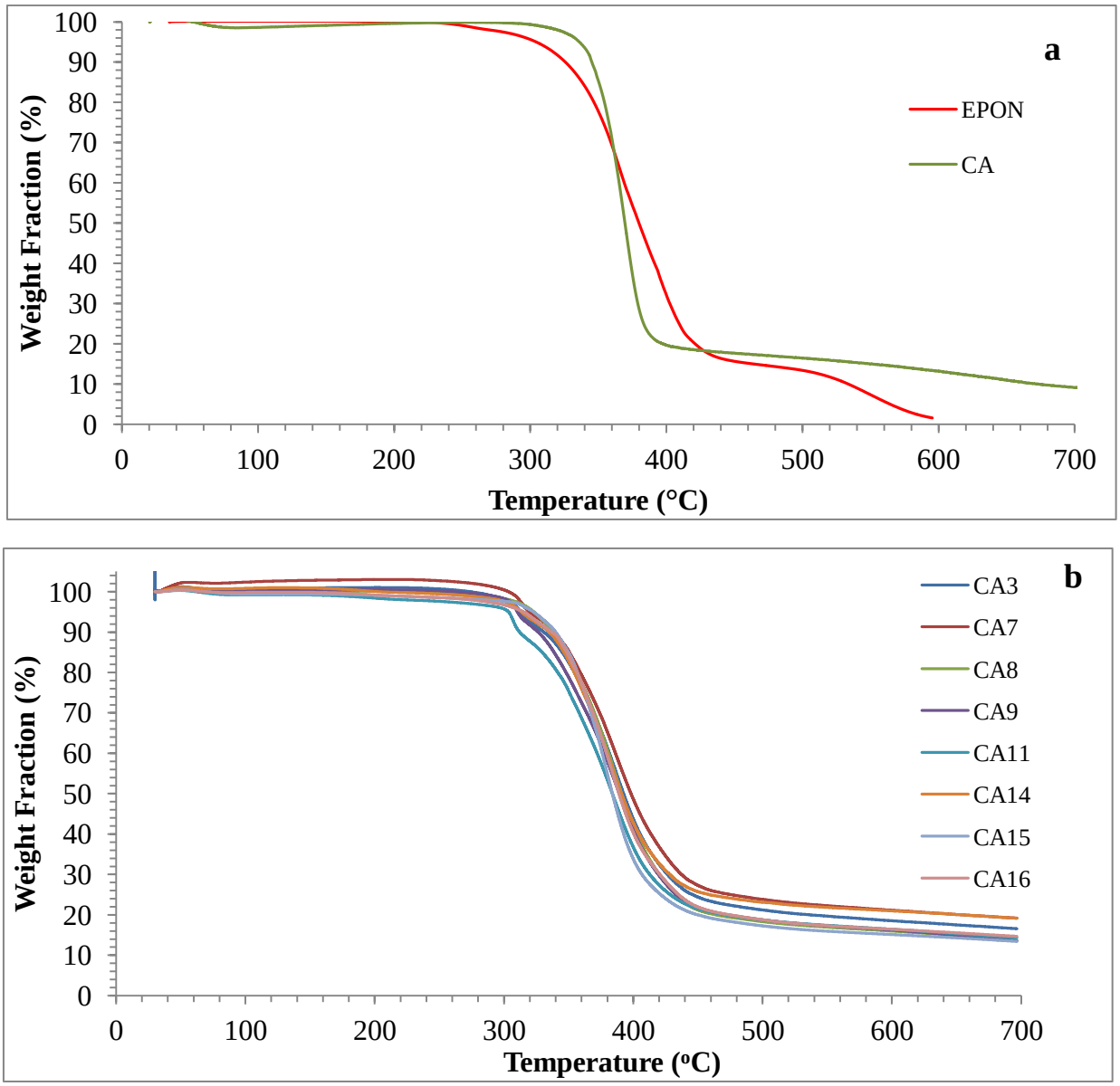


Figure 6. TGA thermograms of a) EPON resin and CA, b) CA microcapsules

3.4 FTIR Spectrums of Microcapsules with Different Carbon Nanotube Content

Figure 7 shows FTIR spectrum of microcapsules prepared in various nanotube content. CA shows a C=O stretching vibration at 1734 cm-1 and there is an absorption band at 1364 cm^{-1} which can be attributed to CH_3 groups. The band at 1213 cm^{-1} shows the presence -CO groups. The band at 1027 cm^{-1} corresponds to C-O-C stretching frequencies. Epoxy resin shows bands in the C=C phenyl ring stretching region (1620 and 1462 cm^{-1}) and the symmetric stretching band of epoxy ring can be seen at 1250 cm^{-1}. The asymmetric ring stretching band of epoxy ring is located at 922 cm^{-1} and the out-of-plane bending band of p-substituted phenyl ring appears at 825 cm^{-1}. Presence of epoxy resin and CA in microcapsules is evident in all the samples.

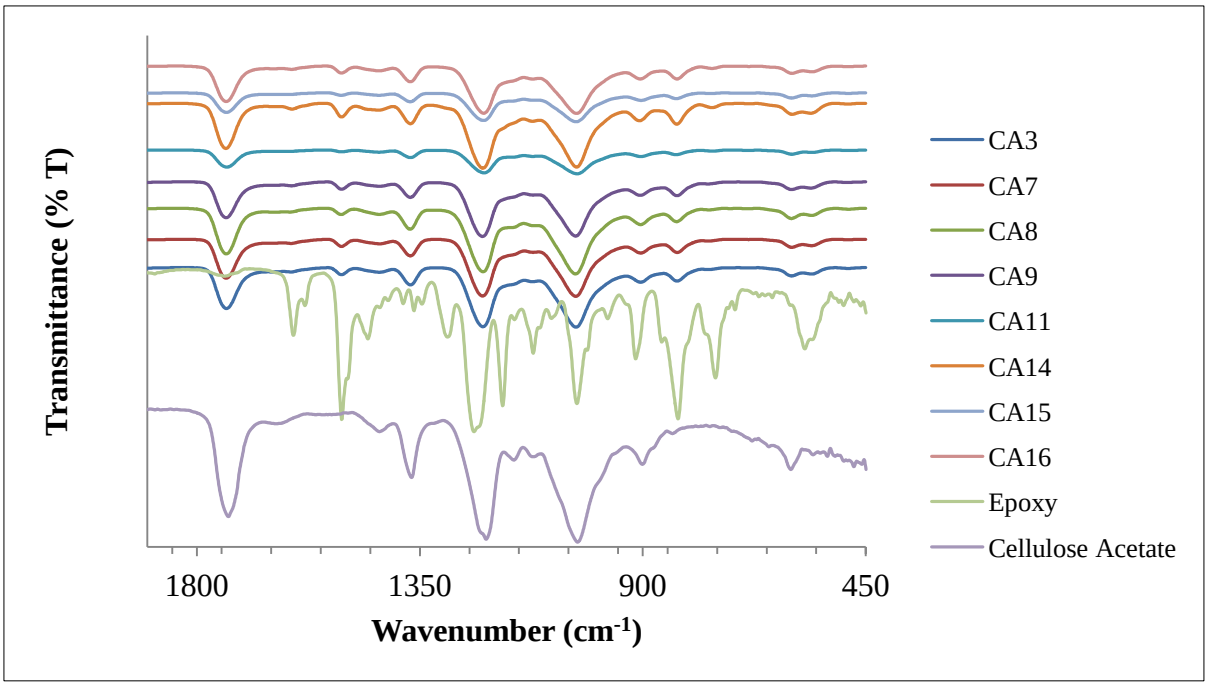


Figure 7. FTIR spectrums of EPON 828 and 813 CA microcapsules

4. Conclusion

Epoxy and carbon nanotube containing CA microcapsules were prepared by using solvent evaporation technique. Studies showed that spherical microcapsules cannot be obtained over 1:1 epoxy/CA ratio. Microcapsule surfaces with small dents is formed at 40 ºC evaporation temperature. Viscosity of oil part used in droplet formation plays an important role on overall morphology of microcapsules. Viscosity can be lowered by decreasing amount of CNT and by using a resin with a lower viscosity. Also amount of volatile solvent used to dissolve CA and resin effects the viscosity. However, using large amount of volatile solvent decreases the amount of resin entrapped in the microcapsules and shell starts to collapse inward more with the increased solvent amount. For self-healing applications, it is necessary to host as much resin as possible inside the microcapsules. Therefore, CA and EPON 813 combination is a good candidate to prepare the low viscosity mixture during droplet formation by using a small amount of volatile solvent.

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LOW VELOCITY IMPACT BEHAVOIRS OF SiO_2 NANOPARTICLE FILLED $\pm[55]_6$ BFR/EPOXY FILAMENT WOUND COMPOSITE PIPES

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ABSTRACT

Basalt fiber reinforcement (BFR) materials have been used in many industrial applications in last decade. Basalt fiber has higher mechanical properties than E-Glass Fiber reinforcement (GFR) as well as lower cost than Carbon Fiber reinforcement (CFR) material. However, Carbon Fiber reinforcement provides higher mechanical behaviors than Basalt Fiber reinforcement. Nowadays, nanoparticle filled polymer based material composite have been studied in many research areas for increasing the mechanical performances of matrix materials. In addition, the nanoparticle addition into matrix materials contributes the well combination between fibers and matrix by increasing the adhesion and improving fracture mechanisms. Therefore, in this study SiO2 nanoparticles has been filled into epoxy matrix and then SiO_2 nanoparticle (filled + and - directed fiber band) $\pm[55]_6$ filament wound BFR/Epoxy composite pipes was produced via CNC filament winding machine.SiO_2 nanoparticle filled and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes was carried out the low velocity impact tests according toASTM D7136/7136M standard at 15J energy level. As results of tests, SiO_2 nanoparticle addition into $\pm[55]_6$ filament wound BFR/Epoxy composites has been improved the responses of impact behaviors. It was observed that while the maximum load of low velocity impact was incrased but, displacement was decreased. In addition it was seen that, SiO_2 nanoparticle addition decreased the delamination failure of $\pm[55]_6$ filament wound BFR/Epoxy composite pipes.

INTRODUCTION

A new alternative basalt fibers have been become to forefront because of better mechanical characteristics which including tensile strengths, elongation, impact resistance, fracture toughness than glass fibers as well as lower cost than carbon fibers. Other advantages of basalt fibers than E-Glass are recycling, natural long life, fire safety, chemical resistance, thermal insulation, electrical insulation and working in high-low temperatures. The usage of basalt fibers in filament pipes and tanks have been used range of wide nowadays especially in natural gas tanks, fire tubes, diver tubes, hydrogen tubes, medical applications except military sectors all trade sectors[1-5].

Sfarra et al.carried out the low-speed impact tests to determine impact behaviors. They defined that the failures of delamination areas impacted BFR composites are larger than CFR composites[7]. Manikandan et al. performed the tests of shear, tensile and Izod impact in order to investigate the mechanical behaviors

of BFR/polyester and CFR/polyester composites and they found that BFR composites have fine shear, tensile and impact responses. They observe that BFR composites have high energy absorption due to having better adhesion than glass fibers[7]. Dehkordi et al. assessed at the end of low velocity impact tests that while the failure of fiber breakage was a dominant failure for BFR composites, the failures of pull-out and delamination of basalt/nylon hybrid composites were dominant failure[8].

METHODS

Before the low velocity impact tests, in order to investigate the effects of SiO_2 nanoparticle over filament wound BFR/epoxy composite, it should be modify epoxy and then produced the BFR/Epoxy composite pipes by integrated with nanoparticle modified epoxy matrix material. For modifying the epoxy, SiO_2 nanoparticles (Mknano, Canada) have features of a specific surface area of 650 m2/g and an average primary particle diameter of 15 nm as a filling material, a medium Bisphenol A (DGEBA) epoxy resin as a matrix material and 400 tex basalt fiber (Kammany Vek) as reinforcement material were used to get composite pipe structures[4-5]. According to pre-experiments and literature related in the mechanical behaviors of SiO_2 nanoparticle filled epoxy composites, 4%wt SiO_2 nanoparticles were added into epoxy and then firstly, applied to mechanical mixture process via mechanical stirrer during 10min. Secondly, the ultrasonic mixture process was carried out via via an ultrasonic probe stirrer (Bandelin HD2200) during 15 min, after that this mixture was stirred with harder during 5 min. As a result of mixture processes, SiO_2 nanoparticle modified epoxy was ready to produce the filament wound composite pipes. For producing the filament wound BFR/Epoxy composite pipes, the filament winding and specimen's parameters and were determined as 10 N fiber tension, average 11 mm bandwidth and 60 ^{o}C resin bath and ±6 layer, 72 mm internal diameter, average 2.63 mm thickness and ± 55 winding angle respectively. Nanoparticle filled and unfilled BFR/Epoxy composite pipes were manufactured via CNC filament winding machine in terms of the defined parameters. End of the winding process, pre-curing and curing processes were applied to semi products on the mandrel in oven at 135 ^{o}C and at 150 ^{o}C respectively for 3 hours [4-5]. The burn-off tests to determine the fiber volume fraction were carried out the 4% SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR and $\pm[55]_6$ filament wound BFR composite pipes in terms of ASTM-D2584-11. The fiber volume fraction was found as average of 0.61±1.5 for all composite pipes [4-5]. According to ASTM D7136/7136M standard at the energy level of 15j, the low velocity impact tests by repeating three times were performed to SiO_2 nanoparticle filled and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes to investigate the impact behaviors. The low velocity impact test machine has been shown in Figure 1.

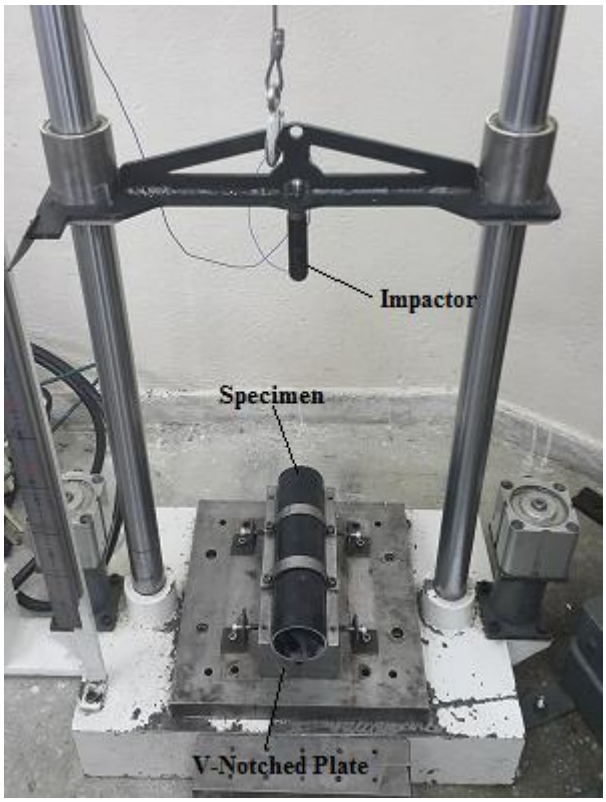


Figure1. The low velocity of impact test machine.

RESULTS AND FINDINGS

According to ASTM D7136/7136M standard, the low velocity impact tests by repeating three times at the energy level of 15j were performed to 4%wt SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes in order to investigate the impact behaviors. End of the low velocity impact tests of all $\pm[55]_6$ filament wound BFR/Epoxy composite pipes, the peak forces, displacements have been found and the impact failures have been investigated as well as the comparison of SiO_2 nanoparticle filled and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes each other.

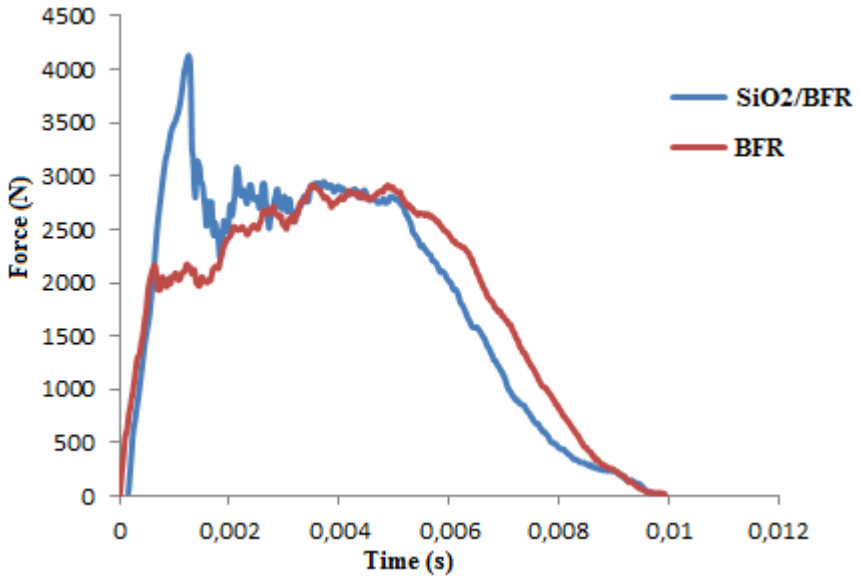


Figure 2. Force(N)-Time(s) curves of 4%wt SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes.

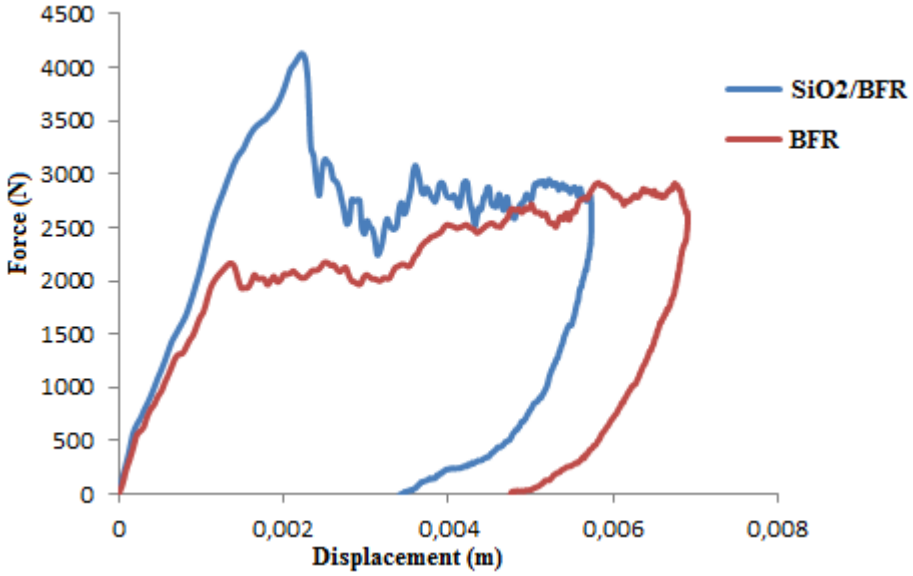


Figure 3. Force(N)-Displacement(s) curves of 4%wt SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes.

Figure 2 and Figure 3 show the contact-time and force-displacement curves for SiO_2 nanoparticle filled and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes at energy level of 15J. When observed two curves of SiO_2 nanoparticle filled and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes, it was clearly seen that the maximum force of SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy composite have presented higher value than unfilled unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite. But, the displacement of unfilled unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite has shown upper value than SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy composite. It probably means that SiO_2 nanoparticle addition into epoxy matrix contribute the strong

structure integrity to $\pm[55]_6$ filament wound BFR/Epoxy composite pipe by providing to increase the contact and bending stiffness[9-10]. When observed the curves, SiO_2 nanoparticle increased the contact and bending stiffness. It was thought that SiO_2 nanoparticle caused to retardant the crack propagation by providing fracture mechanism schematized in Figure 4. during contact time of impactor [10-13].

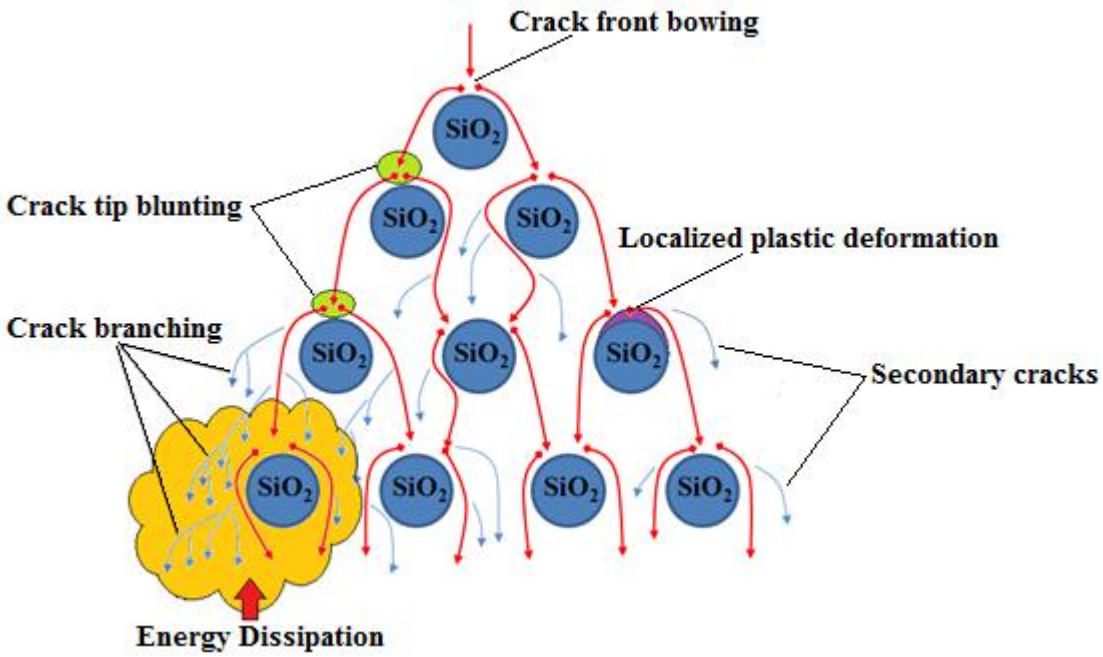


Figure 4. Fracture mechanisms of SiO_2 nanoparticle filled and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composites[4-5].

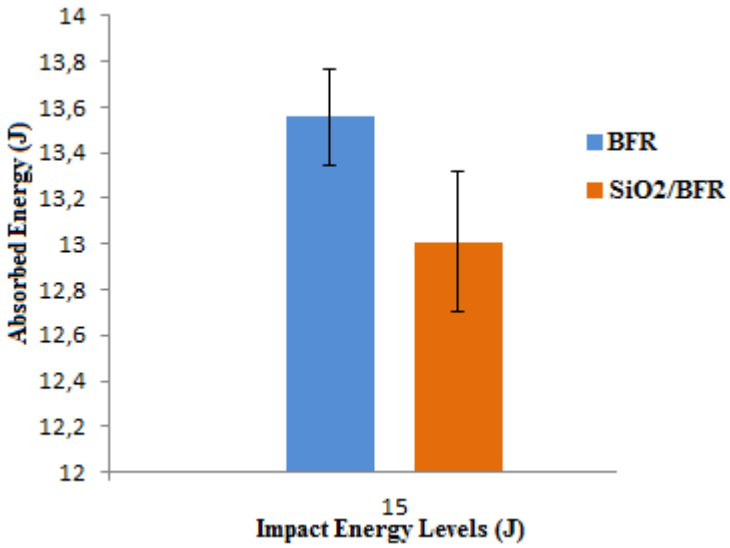


Figure 5. Absorbed energies of SiO_2 nanoparticle filled and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composites.

The absorbed at energy level of 15j was given in Fig.5. When the absorbed energy was observed, it was seen that the average absorbed impact energy level of unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipe attained higher value than SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy

composite pipes. It probably meant that SiO_2 nanoparticle addition into matrix decreased the failures of BFR/Epoxy composites (delamination, debonding and matrix cracks) by increasing bending stiffness and decreasing displacement during the impact time of impactor.

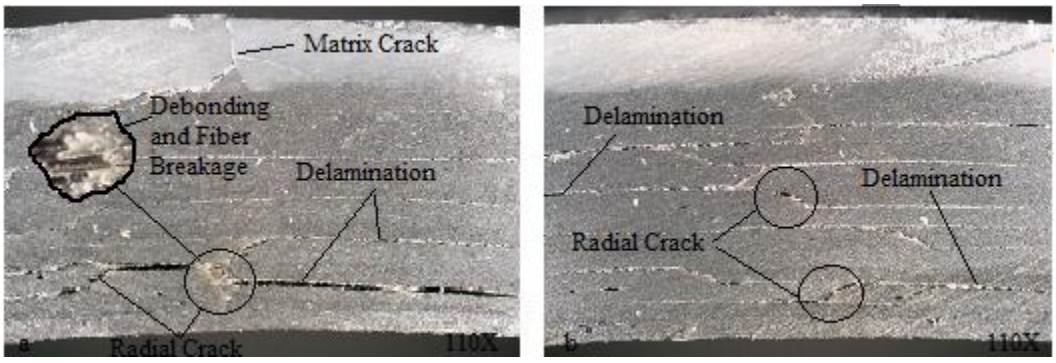


Figure 6. Microscope images of a) unfilled and b) SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy composites.

The failures of SiO_2 nanoparticle filled and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes have been seen on Figure 6. When investigated the image of unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes shown in Figure 6a, it can be seen matrix cracks, debonding, fiber breakage and delamination. However, for SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy composites, the failures of delamination and matrix crack has been seen in Figure 6b. The delamination failures of unfilled $\pm[55]_6$ filament wound BFR/Epoxy composites were observed almost all layers, whereas for SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy composites, the delamination failures were seen less than. It was considered about less delamination failures of SiO_2 nanoparticle filled $\pm[55]_6$ filament wound BFR/Epoxy composites that it was stemmed from the increasing bending and contact stiffness[11-13].

CONCLUSION

The results of the low velocity impact tests of SiO_2 nanoparticle filled and unfilled $\pm[55]_6$ filament wound BFR/Epoxy composite pipes have been summarized in below.

- SiO_2 nanoparticle addition into epoxy matrix increased the maximum impact force of $\pm[55]_6$ filament wound BFR/Epoxy composite pipes.
- SiO_2 nanoparticle addition into epoxy matrix decreased the displacement of $\pm[55]_6$ filament wound BFR/Epoxy composite pipes.
- SiO_2 nanoparticle addition into epoxy matrix increased the bending and contact stiffness of $\pm[55]_6$ filament wound BFR/Epoxy composite pipes.
- SiO_2 nanoparticle addition into epoxy matrix decrased the failures of matrix cracks, fiber breakage, debonding and especially delamination. It was thought that SiO_2 nanoparticle addition provided the fracture mechanisms in matrix containing crack blunting, bowing, occurring secondary cracks, crack branching and increasing adhesion between basalt fiber and epoxy matrix.

ACKNOWLEDGMENT

In this study, Composite pipes have been produced by benefiting from Selcuk University Scientific Research Projects (B.A.P) under grant number 11101030.

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DEVELOPMENT OF ALUMINUM HONEYCOMB CORED CARBON FIBER REINFORCED EPOXY COMPOSITE BASED SANDWICH STRUCTURES AND CHARACTERIZATION OF THEIR FATIGUE LIFE

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Abstract

Sandwich composite structures are commonly used in marine, aerospace and defence industry due to their high strength to weigth ratio and energy absorbtion capacity. Sandwich structures are composed of composite structures that are laminated between thin stiff facesheets bonded to a thicker lightweight core. Fatigue life of these structures have been critical parameter in recent years due to their application areas. Fatigue life is the performance of the material that is working under cyclic loads.
In this study, aluminum honeycomb cored carbon fiber reinforced epoxy composite based sandwich structures were developed. Carbon fiber reinforced epoxy composites were manufacturing via vacuum infusion method with four layers of unidirectional non-woven fabrics alligned in the orientation of [0^o/90^o]. Sandwich structures were manufactured by bonded aluminum honeycomb core and CFRP face by an adhesive. Static flexural behavior of sandwich structures were determined by three point bending test. Fatigue tests were carried out to sandwich structures in order to determine the fatigue failure modes and low cycle SN curve.

Introduction and objective

Usage of sandwich structures increases rapidly in wide application areas such as satellites, aircraft, marine, automotive, wind energy systems and bridge constructions due to their high stiffness and stregth to weight ratios [1,2]. Sandwich structures consist of two metallic or composite thin sheets which have high elastic modulus and strength bonded to thicker but lightweight cellular core materials such as honeycomb cells or foams [3,4]. The face material caries the bending stress and provide the structure a hard wearing surface whereas light core material carries the shear stress generated by loads and distrıbute the over a large area [5].
Due to their wide range of application area, fatigue behavior of sandwich structures should been investigated. The behavior of these structure under fatigue loading has not been completely understood although some experimental studies exist in literature. Boukharouba et. al. examined the fatigue behavior of CFRP faced and Nomex honeycomb cored sandwich structures. They evaluated the stiffness degredation of samples under fatigue load [6]. Belouettar et. al. studied the fatigue behavior of aluminum faced and nomex/ honeycomb cored sandwich structures. They found the fatigue failure modes and stiffness degredation for their developed structures [1]. Chemami et. al. studied on GFRP faced and PVC foam cored sandwich structures. They characterized the fatigue bahavior of this structure wiht Wöhler curves [7]. Coskun and Turkmen studied about bending fatigue behavior of CFRP faced and aramid honeycomb cored sandwich structures. They investigated the effect of test frequency on the fatigue life and stiffness degredation of structures [8].

In this study, carbon fiber reinforced epoxy faced aluminum honeycomb cored sandwich structures were developed. Static flexural behavior of developed sandwich structures were examined. Load-displacement curves and failure modes of the sandwich structures under flexural loadind were determined. Fatigue behavior of sandwich structures were characterized under different load levels. Low cycle Wöhler(SN) curves and fatigue failure modes of the structures were obtained.

Experimental

In this study, carbon fiber reinforced polymer matrix composites(CFRP) were used as face material in sandwich structures. Unidirectional carbon fabrics and epoxy resin were used as reinforcing and matrix material for faces respectively. Face sheets were manufactured via vacuum infusion method. Carbon fabrics were placed to the mold in the orientation of [0/90]. Each face sheets contain four layer of fabric.
Aluminum honeycombs with hexagonal cell configuration were used as core material in sandwich structures. Thickness of aluminum honeycomb is 21 mm. In order to manufacture sandwich structures, face sheets and honeycomb core were bonded together by an adhesive. Sandwich panels were cured at room temperature for 24 hours, and a post-curing process applied to panels at 40 ^{o}C for 24 hours.
Static three point bending tests were carried out to the sandwich structures according to ASTM C393 standart order to evaluate flexural behavior of sandwich structures. Flexural test set-upis shown in Figure 1. Tests were performed using universal mechanical test machine with the rate of 6 mm/min. Four specimens were tested and flexural load-displacement curves of sandwich panel were determined.

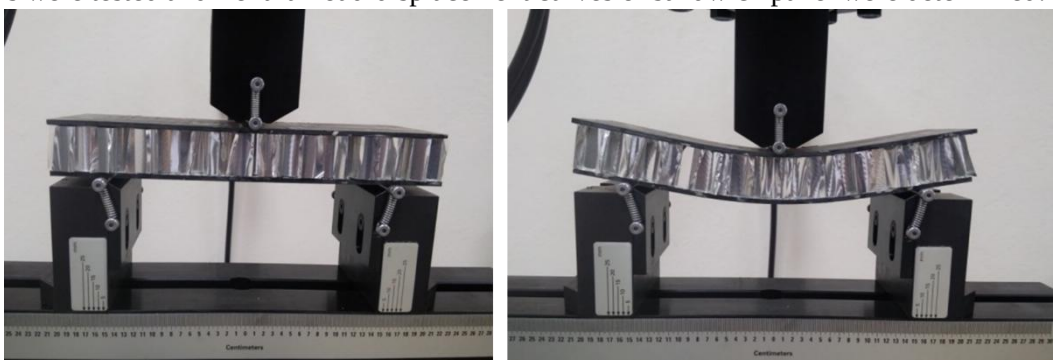


Figure 1: Test set-up for flexural test of sandwich panels

Load controlled fatigue tests were performed using MTS servo-hydraulic test machine with three point bending fixture. Stress ratio (R) and frequency were selected as 0.1 and 2 Hz respectively. Tests were carried out with respect to 80, 70, 60 and 50% of ultimate flexural loads evaluated from static three point bending tests. Low cycle fatigue behavior and fatigue failure modes of sandwich structures were characterized.

Results and Discussion

Static Flexural Test Results

Load-displacement curve of four specimens are given in Figure 2. Three different phenomena was determined in load displacement curves. These phenomena represent the failure modes of sandwich structures. Initial failure was observed in the core area when the linearity of load-displacement curve ends. Therefore, first failure mode is assumed as core failure. Secondary failure was observed as debonding of core material and face sheet in interface area at the edges of sandwich panel. It corresponds the second linear area of load-displacement curve. Last failure occured in the face sheet. CFRP face sheet failed due to compressive stresses on the face skin.

Face failure observed when load decreased dramaticcally at the end of the curve. All failure modes are shown in Figure 3.

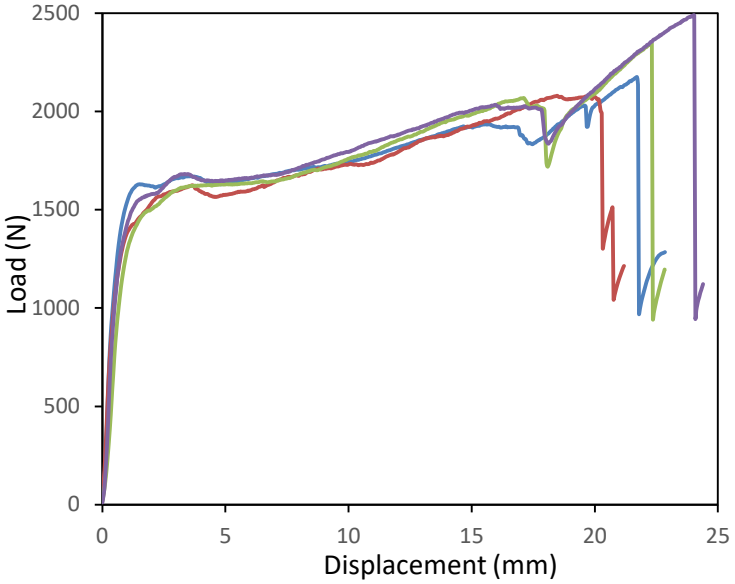


Figure 2: Load-Displacement Curve of Four Sandwich Panels

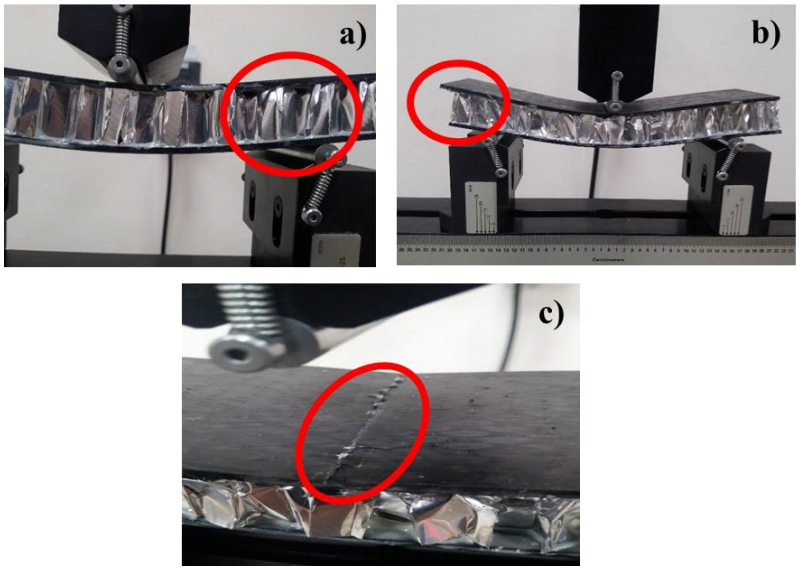


Figure 3: Failure modes of sandwich structure after three point bending test; a) core crush, b) interface failure, c) face failure.

Fatigue tests were performed with respect to load value at first failure mode which was assumed as ultimate flexural load.

Fatigue Tests Results

Fatigue tests were performed in four different load levels (80%, 70%, 60%, 50% of ultimate flexural load) and failure modes were observed for each stress levels. Besides, low cycle SN curve was obtained. Figure 4 shows the fatigue failure modes for 80% stress level.

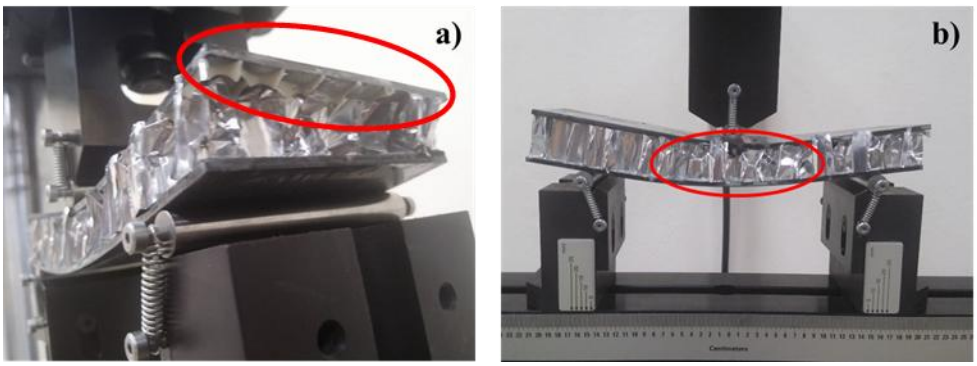


Figure 4: Fatigue failure modes for 80% load level; a)interface failure, b) core crush

Although the first failure mode was core failure under static flexural loads, primary failure was observed at core-face sheet interface region at the edges of specimen at fatigue tests at 1100 cycle. Secondary failure was determined at the core ragion at 1800 cycle.

Figure 5 illustrates the fatigue failure modes for 70% stress level.

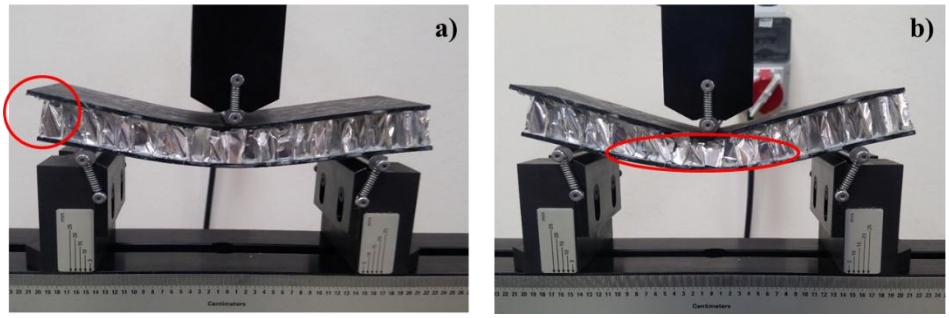


Figure 5: Fatigue failure modes for 70% load level; a)interface failure, b) core crush

Primary fatigue failure occured at the core-face interface region at 70% load level at 1800 cycle. Secondary failure mode was core failure at 2700 cycle as well as 80% load level. Figure 6 shows the fatigue failure modes of 60% load level samples.

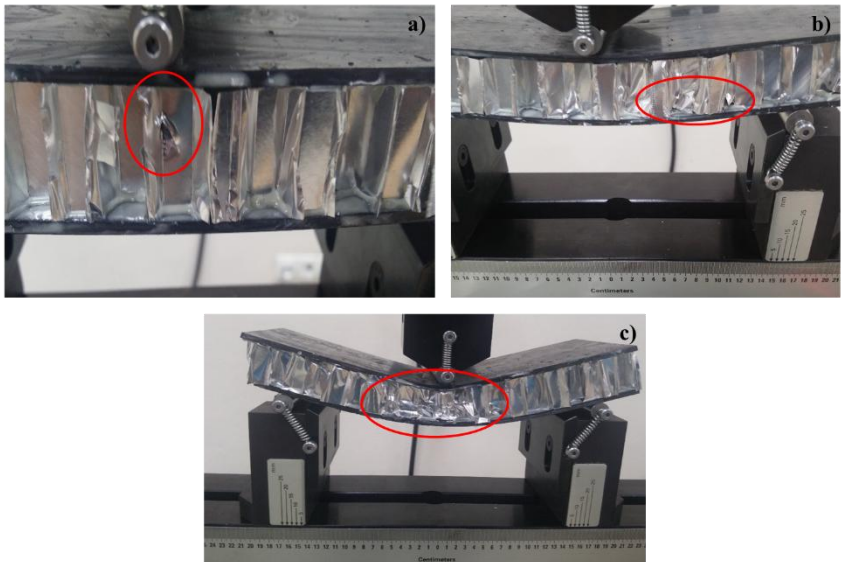


Figure 6: Fatigue failure modes for 60% load level; a)tearing at core, b) interface failure, c) core crush

Tearing at core materials were observed in 2100 cycle at 60% load level. This phenomenon was not assumed as a failure because the structure maintained to bear the load. First failure mode was assumed as interface failure which occured at 6500 cycle in the middle of the specimen. Core failure was the secondary failure mode was observed near after interface failure. Figure 7 shows the fatigue failure modes of 50% load level samples.



Figure 7: Fatigue failure modes for 50% load level

Interface failure and core crush was observed at the same time at 11500 cycle at 50% load level. Low cycle SN curve was obtained with respect to fatigue test results. Figure 8 shows the low cycle SN curve of aluminum honeycomb cored carbon fiber reinforced polymer based sandwich structures.

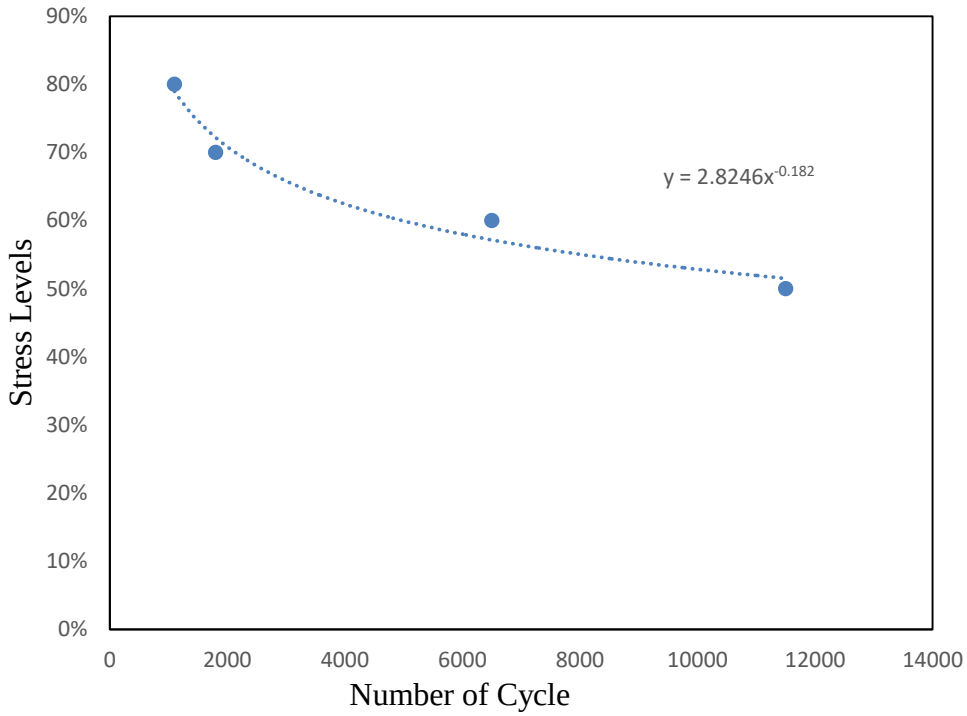


Figure 8: Low cycle SN curve of sandwich structures

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CAM ELYAF TAKVİYELİ POLİMERİK KOMPOZİT MALZEMELERDE LAZERLİ KESME VE DELME PARAMETRELERİNİN BELİRLENMESİ

DETERMINATION OF CUTTING AND DRILLING PARAMETERS OF FIBERGLASS REINFORCED POLYMERIC COMPOSITE MATERIALS USING LASER

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Özet. Cam elyafı silika, kolemanit, alüminyum oksit, soda gibi malzemelerden üretilir. Bu hammaddeler cam fırınlarında yüksek sıcaklıkta harman edilerek basınç altında mikron seviyesinde ki küçük deliklerden akıtılarak cam elyafı üretimi yapılır. Cam elyafı, elyaf takviyeli polimerik kompozit üretiminde en çok kullanılan elyaf çeşididir. Mukavemeti oldukça yüksektir. Isıl dirençleri oldukça düşüktür. Kimyasal malzemelere karşı dirençlidirler. Nem soğurma özelliği yoktur. Elektrik iletkenliği yoktur.

Cam elyaf takviyeli polimerik kompozit malzemeler, takviye malzemesi ve taşıyıcı olarak kullanılan reçinenin (matris) birlikte kalıplanması yöntemiyle elde edilmektedir. Bu kalıplama işlemi birçok farklı şekilde yapılmaktadır. Bu kalıplama işleminde önemli olan cam elyafı ile matriksin uygun şekilde ıslatılabilmesidir. Bu kalıplama işleminde matris; kuvvetin elyafa iletilmesi ve düzgün dağılım sağlanması, liflerin ortamın etkilerinden ve darbelerden korunması, kompozit malzemenin tokluğunun arttırılması ve malzemelerde oluşan çatlak, kırılma vb. engellenmesi görevi üstlenmektedir. Cam elyaf takviyeli polimerik kompozit mazleme mukavemeti yüksek, oldukça hafif olmasından dolayı havacılık, uzay teknolojisi, otomotiv, gıda, inşaat, eğlence, teknoloji vb. birçok sektörde kullanılmaktadır.

Cam elyaf takviyeli polimerik kompozit üretiminde, kalıplama işlemi sonrası fazlalıkların kesilmesi, parçanın üretim prosesi gereği tesviyesi, mekanik olarak yapılmaktadır. Bu durum yüksek maliyet, zaman kaybı oluşturmakta ve hata oranlarını arttırmaktadır. Bu çalışmada lazer kullanarak kesme ve delme işlemleri yapılmıştır. Optimum lazer parametreleri, kesme hızları belirlenmiştir. Farklı renklerde 5 mm kalınlığındaki cam elyaf takviyeli polimerik kompozit plakalar farklı puls genişliğinde ve dalga boyundaki Nd:YAG lazerleri kullanarak kesme ve delme çalışmaları başarıyla gerçekleştirilmiş ve optimum lazer parametreleri belirlenmiştir.

Anahtar kelimeler: Cam elyaf takviyeli polimerik kompozit, Nano/mili saniye lazer, Polimerik kompozit

Abstract. Fiberglass is produced from materials such as silica, colemanite, aluminum oxide, soda. These materials are blended at high temperatures in glass furnaces and then flowed through small holes (micron level) under high pressure to produce fiberglass. Fiberglass is most used in fiber reinforced polymer composite production. Strength of the materials is very high. Moreover, the thermal resistances are very low. It has resists to chemical materials. There is also no absorbs of humidity and no electrical conductivity.

Fiberglass reinforced polymeric composite materials are obtained by molding together the reinforcing material and the resin (matrix) used as the carrier. The molding process is carried out in many ways. The important thing in this molding process is that the matrix can be wetted properly with fiberglass. In this molding process, the matrix is used for transmission and distribution of force to the fibers, protection of the fibers from the environmental effects and

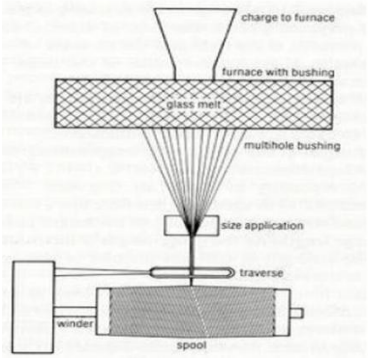
damages, increase of the toughness of the composite material and blocking cracks and broken. Fiberglass reinforced polymeric composites have high abrasion resistance and are very light weight, therefore, it is used in many sectors such as aerospace, space technology, automotive, food, construction, entertainment, technology and so on.

In the production process of glass fiber reinforced polymeric composites, cutting of burrs forms after the molding process and smoothing which is part of production processes are performed mechanically. This creates high cost, time loss and increases error rates. In this work, laser cutting and drilling operations were performed. Optimum laser parameters, cutting speeds are determined. Glass fiber reinforced polymeric composite plates with different colors of 5 mm thicknesses were successfully cut and drilled using Nd: YAG lasers with various pulse duration and wavelength. It was also optimum laser parameters were determined.

Keywords: Fiberglass Reinforced Polymeric Composite, Nano/milli-second Laser, Polymeric Composite

1. Giriş

Cam elyafı silika (SiO_2), kolemanit, alüminyum oksit (Al2O3), soda (NaHCO3) gibi malzemelerden üretilir. Bu hammaddeler cam fırınlarında yüksek sıcaklıkta harman edilerek basınç altında mikron seviyesinde ki küçük deliklerden akıtılarak cam elyafı üretimi yapılır. Cam elyafı, elyaf takviyeli polimerik kompozit (CTP) üretiminde en çok kullanılan elyaf çeşididir. Isıl dirençleri oldukça düşük, kimyasal malzemelere karşı oldukça dirençlidir. Nem absorbe etme özelliği ve elektrik iletkenliği yoktur.



Şekil 1. Cam Elyafı Üretim Şeması [1].

Cam elyaf takviyeli plastik kompozit (CTP) mazleme mukavemeti yüksek, oldukça hafif olmasından dolayı günümüzde farklı alanlarda kullanılarak popüler sanayi malzemesi haline gelmiştir. Bu malzeme ilk zamanlar uzay ve uçak sanayinde kullanılmaktayken günümüzde otomotiv, gıda, inşaat, eğlence, teknoloji vb. birçok farklı sektörde kullanılmaya başlanmasıyla önemini gittikçe arttırmıştır. Bu kullanım ise malzeme üzerinde oldukça farklı ihtiyaçları ön plana çıkarmaktadır.

Cam elyaf takviyeli polimerik kompozit (CTP) malzemeler, takviye malzemesi ve taşıyıcı olarak kullanılan reçinenin (matris) birlikte kalıplanması yöntemiyle elde edilmektedir. Bu kalıplama işlemi birçok farklı şekilde yapılmaktadır. Bu işlemde önemli olan cam elyafı ile matrisin uygun şekilde ıslatılabilmesidir. Matris; kuvvetin elyafa iletilmesi ve düzgün dağılım sağlanması, liflerin ortamın etkilerinden ve darbelerden korunması, kompozit malzemenin tokluğunun arttırılması ve malzemelerde oluşan çatlak, kırılma vb. engellenmesi görevi üstlenmektedir [1].

Polyester reçineler, cam takviyeli plastik kompozit (CTP) üretiminde en çok kullanılan matris malzemeleridir. Liflerle takviye edilmiş kompozitlerde matris malzemesi olarak kullanılan bir diğer termoset malzeme grubu da epoksi reçinelerdir. Epoksi reçineler, nitelikli kompozitlerin üretiminde kullanılan, sertleşme sırasında hiçbir yan ürün meydana getirmeyen malzemelerdir. Sertleşme sonunda meydana gelen madde, çok üstün mekanik, kimyasal ve elektriksel özellikleri olan, her türlü elyafla kullanılabilen bir polimerdir [2].

Reçine Transfer Kalıplama (RTM) Üretim Yöntemi: Deney numunesi olarak kullandığımız malzeme RTM metodu ile üretilen aquapark kaydırak malzemesidir. Jelkotlu olarak üretimi yapılan ürünlerin her iki yüzeyi de aynı parlaklıkta ve pürüzsüz olarak kalıptan çıkmaktadır. Bu yöntemle gözeneksiz ve karmaşık yapılarda CTP malzeme üretmek mümkündür. Bu metodda takviye malzemesi olarak cam elyaf çeşidi olan kuru keçe kullanılmaktadır. Takviye malzeme önceden kalıba yerleştirilir ve kalıp kapatılır. Reçine basınç altında kalıba pompalama işlemi yapılarak ürünün elde edilmesi sağlanır. Bu esnada hem kalıp içerisindeki havanın dışarı çıkarılması hem de reçinenin kalıp içerisinde düzgün ilerlemesi için vakum sistemi kullanılır. RTM metodu ile üretimi yapılan 5 mm kalınlıkta CTP malzemenin mekanik özellikleri Tablo 1'de verilmiştir.

Tablo 1. Deneysel malzemeye (CTP) ait mekanik özellikler.

Mekanik Özellikler	Değer
Çekme Dayanımı (MPa)	90,00
Çekme Modülü (MPa)	7800,00
Eğme Dayanımı (MPa)	160,00
Eğme Modülü (MPa)	7800,00
Basma Dayanımı (MPa)	100,00



Şekil 2. RTM yöntemi ile farklı renkte üretilmiş CTP Aquapark kaydırak malzemesi

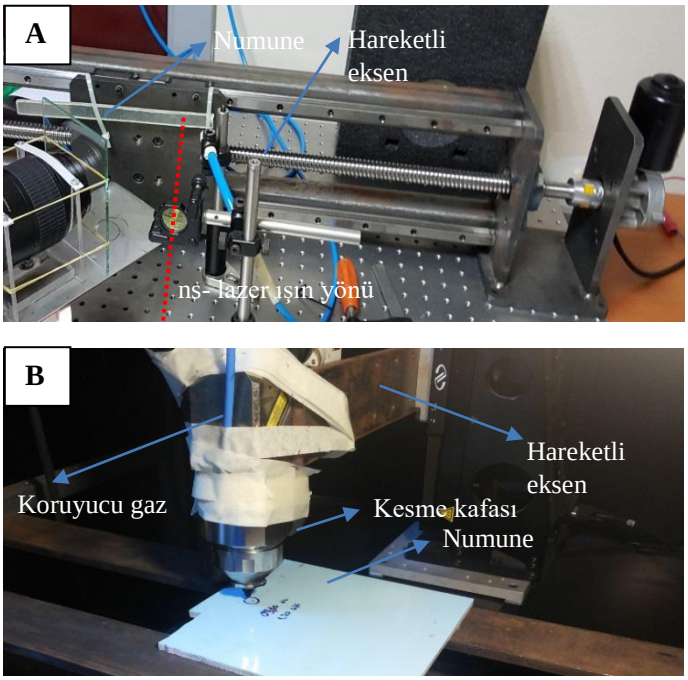
Polimerik kompozit malzemelerin hassas olarak kesilmesi ve mikron mertebesinde delinmesi özellikle medikal uygulamalar açısından oldukça önemlidir[3,4]. Literatürde özellikle polimerlerin lazerle mikro-işleme konusunda son zamanlarda çalışmalar artmıştır[3-6]. Bunun altında yatan sebep polimerlerden yapılan mikro-lensler ve medikal uygulamalar için doku-polimer esaslı membran yapısının oluşturulmasıdır. Çünkü oluşturulacak desen ve gözenek yapısıyla doku etkileşimi farklılık göstermektedir [3]. Yapılan bu çalışmada ise 5 mm kalınlığında cam elyaf katkılı kompozit malzemeler üzerinde farklı dalga boylu lazerler kullanılarak kesme ve delme çalışması gerçekleştirilerek optimum lazer parametreleri tespit edilmiştir.

2. Yöntem

Şekil 1'de cam elyaf üretimi şematik olarak gösterilmiştir [1]. Tablo 1'de ise deney numunesi olarak kullandığımız cam elyaf takviyeli plastik kompozit (CTP) malzemeye ait mekanik özellikler verilmiştir.

Malzemelerde kesme ve delme işlemleri yapabilmek için Şekil 2'de verilen deneysel düzenekler kullanılmışlardır. Mili-saniye(ms) atımlı lazerde ağırlıklı olarak kesme işlemi, Nano-saniye(ns) atımlı

lazerde ise delme işlemleri gerçekleştirilmiştir. Kullanılan lazer parametreleri Tablo 2'de verilmiştir. Tüm kesme ve delme işlemlerinde koruyucu gaz olarak Argon (Ar) kullanılmıştır.



Şekil 3. Deneysel düzenek. (A) ns- atım süreli Nd:YAG lazer ile delme işlemi için kullanılan deneysel düzeneği, (B) ise ms- atım süreli Nd:YAG lazer ile kesme ve delme işlemi için kurulan deneysel düzeneği göstermektedir.

Hazırlanan düzeneklerin tamamı hassas ve kontrollü hareket eden sitemlerden oluşmaktadır. Mikroskobik görüntüler Olympus marka mikroskoptan alınmıştır.

3. Tartışma

3.1. Lazer ile delme

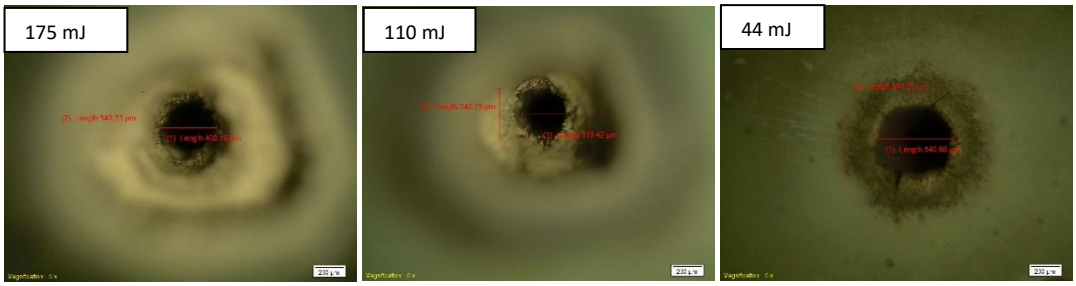
Kocaeli Üniversitesi bünyesinde ki Lazer Teknolojileri Araştırma ve Uygulama Merkezi (LATARUM) var olan ms ve ns atım genişliğindeki lazer kullanılarak cam elyaf katkılı kompozit malzemede delme işlemi gerçekleştirilmiştir. Kullanılan lazer parametreleri ise ayrıntılı olarak Tablo 2'de (ns lazer için) verilmiştir. Benzer olarak yapılan delme işlemlerinin mikroskobik görüntüleri Şekil 4 ve Şekil 5'te farklı lazerler için verilmiştir.

Tablo 2. ns- atım süreli lazer ile yapılan delme işleminde kullanılan lazer parametreleri (Dalga boyu (λ) 532 nm).

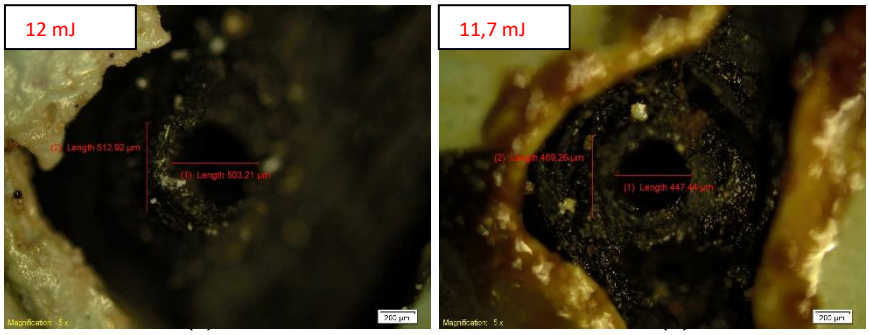
Enerji = 44 mJ, λ= 532 nm								
Deney no	**Enerji**	**İşlem Süresi**	**Atım Süresi**	**Frekans**	**Gaz**		**Odak**	**Delme süresi (s)**
	Mili Joule	**s**	**ns**	**Hz**	**Tipi**	**bar**	**mm**	
1	44	80	6	10	Argon	1	15	**300**
2	44	160	6	10	Argon	1	15	
3	44	240	6	10	Argon	1	15	
4	44	300	6	10	Argon	1	15	

Enerji = 110 mJ, λ= 532 nm								
Deney no	**Enerji**	**İşlem Süresi**	**Atım Süresi**	**Frekans**	**Gaz**		**Odak**	**Delme süresi (s)**
	Mili Joule	**s**	**ns**	**Hz**	**Tipi**	**bar**	**mm**	
1	110	80	6	10	Argon	1	15	**280**
2	110	160	6	10	Argon	1	15	
3	110	240	6	10	Argon	1	15	
4	110	280	6	10	Argon	1	15	

Enerji = 175 mJ, λ= 532 nm								
Deney no	**Enerji**	**İşlem Süresi**	**Atım Süresi**	**Frekans**	**Gaz**		**Odak**	**Delme süresi (s)**
	Mili Joule	**s**	**ns**	**Hz**	**Tipi**	**bar**	**mm**	
1	175	80	6	10	Argon	1	15	**225**
2	175	160	6	10	Argon	1	15	
3	175	225	6	10	Argon	1	15	



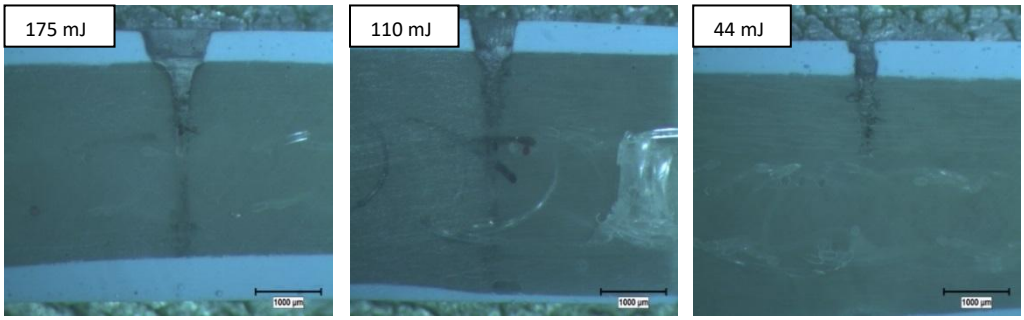
Şekil 4. ns-atım süreli lazer kullanarak 80 s işlem süresi için farklı lazer güçlerindeki delme işlemi. Bu işlem için 532 nm dalga boylu ışınlar kullanılmıştır.



Şekil 5. (a) ms-atım süreli lazer kullanarak 8 s işlem süresi için farklı lazer güçlerindeki 1 bar basınçta delme işlemi. Bu işlem için 1064 nm dalga boylu ışınlar kullanılmıştır.
(b) ms-atım süreli lazer kullanarak 7 s işlem süresi için farklı lazer güçlerindeki 4 bar basınçta delme işlemi. Bu işlem için 1064 nm dalga boylu ışınlar kullanılmıştır.

Şekil 2 ve Şekil 3'ten de anlaşılacağı üzere ns atım süreli lazer kullanılarak yapılan delme işleminde yanma işlemi gerçekleşmeden malzeme üzerinde delme işlemi yapılabilmektedir. Lazer gücü arttıkça delik çapında yaklaşık bir değişiklik olmamakta, fakat jelkot kısmında oluşan HAZ (ısıdan etkilenmiş bölge) bölgesinin çapı artmaktadır. Bu durum Şekil 6'da daha açık görünmektedir. ms atım süreli lazerle yapılan delme işleminde ise yanma işlemi gerçekleşmiştir. Bunun sebebi darbe süresinin uzun olmasından kaynaklanan enerji aktarımının büyüklüğüdür.

Polimerlerin lazerle yapılacak işlemlerinde toksit gaz çıkışı oluşmaktadır. Bu sebepten yapılacak çalışmalar havalandırılmalı ortamlarda yapılmalıdır. Ayrıca birçok polimer kolayca yanabildiğinden atım süresi düşük lazerle çalışmalar gerçekleştirilmelidir.



Şekil 6. ns-atım süreli lazer kullanarak delme işleminin yapıldığı numunelerin kesit görüntüleri.

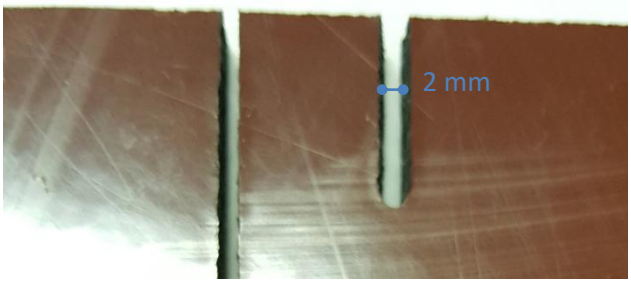
Şekil 6'da ns-atım süreli lazer kullanılarak farklı lazer güçlerinde delme işleminin yapıldığı numunelerin kesit görüntüleri verilmektedir. Şekilden de anlaşılacağı jelkot bölgesinde artan enerji ile oluşan kraterin çapı artmaktadır. Kompozit içinde oluşan delik çapı malzeme içerisine girdikçe azalmaktadır. Malzeme içerisinde yaklaşık 200 µm çaplı düzgün delikler oluşmuştur

3.2. Lazer ile kesme

Şekil 7'de ms-atım süreli lazer kullanarak yapılan kesme işlemini göstermektedir. Tablo 3 ise kesme işleminin yapıldığı lazer parametrelerin belirtmektedir. Şekil 7'den de görüleceği üzere yaklaşık 2 mm kalınlığında keskin kenarları bulunan düzgün bir kesim başarıyla gerçekleştirilmiştir.

Tablo 3. Kesme işleminde kullanılan lazer parametreleri,

Kesme Parametreleri						
Enerji	**Atım Süresi**	**Frekans**	**Gaz**		**Hız**	**Kalınlık**
Joule	**s**	**Hz**	**tipi**	**bar**	**mm/s**	**mm**
12,4	5	20	Argon	5	3	5



Şekil 7. ms-atım süreli lazer kullanarak gerçekleştirilen kesme işlemi.

4. Sonuçlar

Bu çalışmada 5 mm kalınlığında cam elyaf katkılı kompozit malzemeler üzerinde farklı dalga boylu lazerler kullanılarak kesme ve delme çalışması başarıyla gerçekleştirilmiş ve optimum lazer parametreleri belirlenmiştir. Elde edilen sonuçlar aşağıda liste halinde verilmiştir.

1. Her iki lazerde de kompozit malzemenin boyalı jelkot tabakası üzerinde 500 µm çaplı delikler başarıyla oluşturulmuştur. ms-atım süreli lazer kullanılarak yapılan delme işleminde jelkot kısmının yandığı gözlenmiştir.
2. ns-atım süreli lazerler cam elyaf katkılı kompozit malzemelerde yapılacak mikron seviyedeki delme işlemleri için daha uygundur. Kompozit malzeme içerisinde yaklaşık 200 µm çapında düzgün kanallar başarıyla oluşturulmuştur.
3. ms-atım süreli lazerler polimerlerde yapılacak lazerli kesme işlemi için daha elverişlidir.

Teşekkür

Katkılarından dolayı Polin Waterparks şirketine (Kocaeli / TÜRKİYE) teşekkür ederiz.

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OPTIMUM DESIGN OF HYBRID CARBON-GLASS/EPOXY LAMINATED COMPOSITE FOR MINIMUM COST AND MAXIMUM FREQUENCY USING A STOCHASTIC OPTIMIZATION METHOD

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Özet

Ticari ve askeri havacılık araçlarında (örneğin: AV-8B uçak gövdesi, F-22 savaş uçağı) ağarlık azaltılması ve maliyet çok önemli iki parametredir. Fiber katkılı tabakalı kompozit malzemeler özellikle yüksek hızlı ve şiddetli yükleme şartlarına maruz yapılarda tercih edilmektedir. Bu gibi durumlarda kompozit plakaların doğal frekans performansının belirlenmesi, kompozit yapıların tasarımı için çok önemlidir. Özellikle, dinamik mühendislik sistemlerinde, dış etkilerden kaynaklanan rezonansı önlemek için doğal frekans dikkate alınmalıdır. Bu bağlamda birçok araştırmacı, maksimum doğal frekans elde etmek için çalışma yürütmüştür. Mekanik bakış açısına ek olarak, mühendislik problemlerinde maliyet faktörlerini de dikkate almak çok önemlidir. Geleneksel elyaf takviyeli kompozit malzemeler genellikle cam, karbon ve / veya bunların kombinasyonlarından oluşmaktadır. Dayanıklı olmasının ve yüksek rijitliğin yanı sıra, bu malzemeler karıştırıldığında, maliyet ve ağırlık tasarrufu da sağlar. Bu bağlamda, tabakalı hibrit kompozit sistemler, doğal frekanstan ödün vermeden maliyeti düşürmek için kullanılabilir. Bu çalışmada ele alınan malzeme sistemi, yüksek rijitlik ve pahalı karbon takviyeli dış tabakalar; bunun yanında düşük rijitlik ve ucuz cam takviyeli iç tabakalardan oluşan hibrit yapı şeklinde düşünülmüştür. Bu yapının kullanımı, karbon fiberin yüksek frekans sağlaması, cam tabakaların ise maliyeti düşürme etkisi göstermesi amacıyla tercih edilmiştir. Tabakalı hibrit yapıyı analiz etmek için klasik lamine plak teorisi kullanılmıştır. Mevcut çalışmada, optimizasyon problemlerini çözmek için Differential Evolution (DE) optimizasyon algoritması önerilmiştir. Bu çalışmanın amacı, hibrit kompozit yapının fiber açı dizilimlerini belirleyerek, çok yönlü optimizasyon yaklaşımıyla doğal frekansı maksimize etmek ve maliyeti en aza indirmektir. Ayrıca, carbon katmanlarının sayısının, plakanın çeşitli en / boy oranlarında karbon-cam / epoksi hibrit yapısı üzerindeki etkisi, doğal frekans açısından incelenmiştir. Sonuçlar, çözüm için önerilen Differential Evolution algoritmasının literatürde mevcut benzer tasarım problemi için doğal frekans açısından Genetik algoritma (GA) ve benzetimli tavlama algoritması (SA) ile karşılaştırılabilir performans sergilediğini göstermektedir. Ayrıca hibrid yapı kullanılarak rijitlik / ağırlık oranından ödün vermeden, yüksek doğal frekanslı ve düşük maliyetli tabakalı kompozitlerin tasarlanmasının mümkün olduğu görülmüştür.

Abstract

In military and commercial aircraft structures (i.e., the airframe of AV-8B, F-22 fighter aircraft) weight reduction and cost are crucial. Fiber reinforced laminated composites are preferred especially for higher speeds and increased payloads. In these statements, determination of the fundamental frequency performances of laminated composites are main issue. For design of military and aircrafts composite structures, especially in dynamical engineering systems, fundamental frequency have to be taken into account in order to prevent resonance arising from external excitations. In this regard many researchers have conducted studies to obtain maximum fundamental frequency of the structures. In addition to mechanical point of view, it is also crucial to consider the cost factors in engineering problems. Traditional fiber reinforced composite materials generally have consisted of glass, carbon and /or combination of these. In addition to being strong and rigid, when these materials are mixed, they save up cost and weight, simultaneously. For this reason, hybrid laminated composites can be used to decrease

cost without sacrificing from fundamental frequency. Hybrid laminated composite comprising high stiffness and expensive carbon surface and low stiffness and inexpensive glass core layers is considered. In this structure, carbon provide high frequency, glass layers decrease cost. Classical laminated plate theory is utilized to analyze interply hybrid laminated structure. Differential Evolution (DE) optimization method is proposed to solve the problems. The goal of this study is to determine the optimum stacking sequences of carbon-glass/epoxy hybrid composite structures in order to maximize the fundamental frequency and minimize the cost by multi objective optimization approach. Furthermore, the effect of the number of carbon layers on carbon-glass/epoxy hybrid structures with various aspect ratios in terms of fundamental frequency are investigated. The results show that the proposed algorithms DE exhibit comparable performance versus Genetic algorithm (GA) and Simulated Annealing algorithm (SA) in terms of fundamental frequency for the same laminated structure design problem available in the literature. Also by using hybrid structure, it is possible to design laminated composites with high fundamental frequency and low cost without sacrificing in stiffness-to-weight ratios.

Introduction

Laminated composites are fairly utilized in marine, automotive, aerospace, military and other engineering applications because of their high specific modulus (ratio between the young modulus and the density) and high specific strength (ratio between strength and density). In addition to these features, fiber reinforced composites have inherent tailorability such as fiber orientation and stacking sequence and provide great possibilities to designers against isotropic materials. Engineers have considered deflection, buckling load, resonance frequency, impact resistance, fatigue life and dimensionally stability as mechanical design requirement for composite structures. Especially, in dynamical engineering systems, fundamental frequency is an important issue in order to prevent resonance arising from external excitations therefore, many researchers have solved fundamental frequency optimization problems including practical applications of engineering. Maximum fundamental frequency based on single objective approach for laminated plates was investigated by using continuous design variables [1-3]. The same design for cross-ply laminates was studied by Duffy and Adali [4] and for anisotropic laminates by Adali [5]. Fukunaga et al. [6] optimized the composite structures under natural frequency constraints, where only the thickness of each lamina is taken as the design variable. Narita and Leissa [7] handled free vibration problem for cantilever rectangular angle-ply and cross-ply laminated composite plates using Ritz method. Apalak et al. [8] conducted the layer optimization of laminated composite with different edge conditions for maximum fundamental frequency by Genetic Algorithm.

Apart from above mechanical requirements, composite materials should have same features such as low cost, weigh and low density. In this regard, hybridization process is frequently used to design fiber reinforced laminated composite including more than one fiber or matrix material. Interply hybrid laminated construction is one of the designs used this process and involves high-stiffness and expensive material in the surface layers and low-stiffness and cheap one in inner layers. This type of construction provides both suitable structural rigidity and low cost-weight, simultaneously. This attempt can be achieved either by multi objective or single objective optimization approaches. For instance, by single objective approach: Adali and Duffy [9] viewed minimum cost design of antisymmetric, angle-ply hybrid laminates under fundamental frequency constraint. Adali and Verijenko [10] deal with fundamental frequency, frequency separation and cost factor for graphite-glass/epoxy symmetric interply hybrid laminates and determined the optimum discrete stacking sequence design. By multi objective approach: Abachizadeh and Tahani [11] solved multi objective optimization problem of composite graphite-glass/epoxy symmetric interply hybrid laminates for maximum fundamental frequency and minimum cost. Beluch et al. [12] determined optimum stacking sequence and the number of inner and outer layers for graphite-glass/epoxy interply hybrid structure in terms of minimum cost and maximum fundamental frequency and frequency separations. Grosset et al. [13] carried out minimum cost-weight design under frequency constraint.

Design and optimization problems of laminated composites include complicated, highly nonlinear functions, hence stochastic optimization methods become appropriate to solve them. Differential

Evolution method is preferred to find the optimum stacking sequence for symmetric and unsymmetric laminated composite plates with simply supported and clamped boundaries considering maximum natural frequency and constant stiffness [14]. Genetic Algorithm [15], Simulated annealing [16] and Ant colony [11] were also used to maximize fundamental frequency and minimize cost by multi objective approach. Elitist ant system [17] and GA [13] were used to optimize the number and angle of glass/epoxy and carbon/epoxy layers in order to get minimal cost and weight subject to the first natural frequency. Moreover, some researchers [18-20] compared different stochastic optimization methods such as Genetic Algorithm, Generalized Pattern Search, and Simulated Annealing for laminated composite optimization problems.

In the present study, in order to maximize the fundamental frequency and minimize the cost, multi objective optimization of symmetric-balance interply hybrid laminate which consist of carbon-glass/epoxy is considered by utilizing Differential Evolution stochastic optimization method. Fiber orientations, the numbers and the thicknesses of the surface and core layers are selected as design variables.

Mechanical Analysis

In the present study, Classical Lamination Theory is used to analyze thin laminated structures. In this theory, it is assumed that (i) laminate is thin and wide, (ii) perfect bounding exists between laminas, (iii) there exists a linear strain distribution through the thickness, (iv) all laminas are macroscopically homogeneous, and (v) they behave in a linearly elastic manner.

Fundamental Frequency Analysis

Considered laminated plate is simply supported, specially orthotropic and symmetric. Dimensional properties of rectangular plate are length a, width b, total thickness h and fiber orientation angle θ in the x, y, z, 1 directions, respectively (Fig. 1). The material of the composite laminated plate is assumed to be homogeneous and the layers have equal thickness [11]. The governing equation of the free vibration process based on the Classical Laminated Plate Theory for the described symmetric laminate is given as follow [21] :

$$D_{11}\frac{\partial^4 w}{\partial x^4}+4D_{16}\frac{\partial^4 w}{\partial x^3\partial y}+2\left(D_{12}+2D_{66}\right)\frac{\partial^4 w}{\partial x^2\partial y^2}+4D_{26}\frac{\partial^4 w}{\partial x\partial y^3}+D_{22}\frac{\partial^4 w}{\partial y^4}=\rho h\frac{\partial^2 w}{\partial t^2} \qquad (1)$$

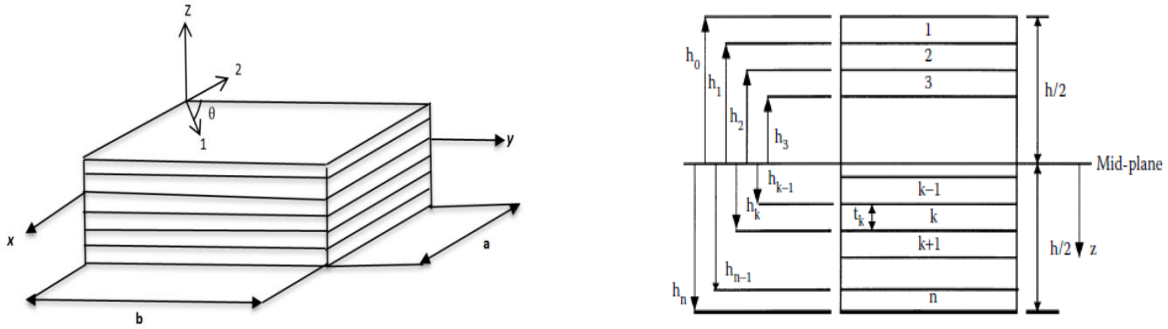


Figure 1. a.) A thin fiber-reinforced laminated composite b.) Coordinate locations of plies [22]

where w is the deflection in the z direction , h is the total thickness of the laminate , t is time and ρ is the mass density as

$$\rho = h^{-1}\int_{-h/2}^{h/2}\rho^{(k)}dz=\frac{1}{N}\sum_{k=1}^{N}\rho^{(k)} \qquad (2)$$

The bending stiffnesses D_{ij} appearing in Eq. (1) are defined as

$$D_{ij} = \sum_{k=1}^{N} \int_{z_k}^{z_{k+1}} \bar{Q}_{ij}^{(k)} z^2 dz \qquad i, j = 1,2,6 \tag{3}$$

where N is the total number of plies, k is the ply number and $\bar{Q}_{ij}^{(k)}$ is the transformed reduced stiffness of the kth layer. The boundary conditions for the simply supported plate are given as

$$w = 0 \ \ at \ x = 0, \ w = 0 \ \ at \ y = 0$$
$$M_x = 0 \ at \ x = 0, \ M_y = 0 \ at \ y = 0 \tag{4}$$

where the moment resultants are defined as:

$$\left(M_x, M_y\right) = \int_{-h/2}^{h/2} \left(\sigma_x, \sigma_y\right) dz \tag{5}$$

where σ_x, σ_y are the normal stress resultants in x and y directions.

If the stacking sequence of laminated composite comprise only 0 and 90 degree , this laminate is called specially orthotropic. For symmetric specially orthotropic laminate, $A_{16}=A_{26}=B=D_{16}=D_{26} = 0$, thus , no coupling occurs between the normal-shear forces, bending - twisting moments and force-moment terms. Nemeth [23] have given the detail about bending–twisting interaction in composite laminates for buckling problems. In case of laminated composite is not specially orthotropic, the effect of bending – twisting terms D_{16} and D_{26} will be neglected if the non-dimensional parameters have the conditions:

$$\gamma \le 0.2, \ \delta \le 0.2 \tag{6}$$

where

$$\gamma = D_{16}(D_{11}{}^3 D_{22})^{-1/4}$$

$$\delta = D_{26}(D_{11} D_{22}{}^3)^{-1/4}$$

Because of the similarity between buckling and free vibration analysis, the same constraints are used to reduce complexity of the problem.

The deflection w for the natural vibration mode (m , n) is obtained by solving the governing equation (Eq.1) with the boundary conditions (Eq.4) as :

$$w(x, y, t) = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} A_{mn} \sin\frac{m\pi x}{a} \sin\frac{n\pi y}{b} e^{i\Omega_{mn} t} \tag{7}$$

where Ω_{mn} is the natural frequency of the vibrating mode (m , n) obtained by solving the eigenvalue problem as

$$\Omega_{mn}{}^2 = \frac{\pi^4}{\rho h}\left[D_{11}\left(\frac{m}{a}\right)^4 + 2\left(D_{12} + 2D_{66}\right)\left(\frac{m}{a}\right)^2\left(\frac{n}{b}\right)^2 + D_{22}\left(\frac{n}{b}\right)^4 \right] \tag{8}$$

Here, different values of m and n give different mode shapes of the laminated plate. Clearly, fundamental frequency can be obtained with the condition m=n=1.

Normalized fundamental frequency is defined as

$$\omega_{mn} = (\Omega_{mn} b^2 / h)(\rho_0 / E_0)^{1/2} \tag{9}$$

where ρ_o = 1,000 kg/m^3 and E_o = 1 GPa are taken as reference values.

Optimization

Single and multi-objective optimizations are the main approaches used in structural design problems. In single objective approach, an optimization problem consists of one objective function,

constraints, and bounds. However, the design of practical composite structures often requires the maximization or minimization of multiple, often conflicting, two or more objectives, simultaneously. In such a case, multi-objective formulation is used and a set of solutions are obtained with different trade-off called Pareto optimal. Moreover, since composite design problems generally have discrete search spaces, the traditional optimization techniques cannot be used. In these cases, the use of stochastic optimization methods such as Genetic Algorithms (GA), Differential Evolution (DE) and Simulated Annealing (SA) are appropriate [24]. In this work, differential evolution algorithm is used to solve the composite optimization problems based on multi and single objective approaches.

Differential Evolution

Differential Evolution (DE) is a stochastic optimization method which permits alternative solutions for some of the complex composite design and optimization problems such as increasing frequency and frequency separation and obtaining lightweight design. Differential Evolution algorithm includes the following main stages: initialization, mutation, crossover and selection as shown in Fig. 2. The optimum results of the algorithm change with the parameters: scaling factor, crossover and population size. DE always considers a population of solutions instead of a single solution at each iteration and is also computationally expensive. It is relatively robust and efficient in finding global optimum of the objective function. However, it is not guaranteed to find the global optima [24]. Detail description of the DE can be found in [25].

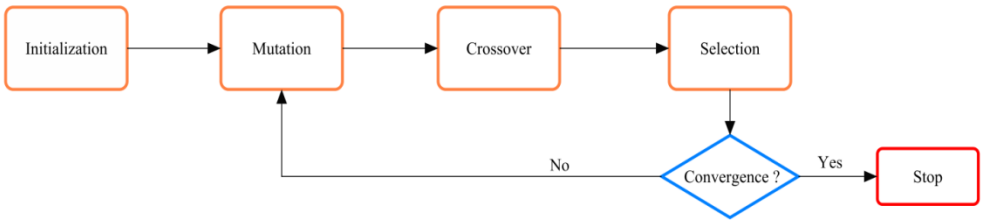


Figure 2. Flowchart of the DE algorithm [26].

Table 1. DE optimization method options

Options Name	DE
CrossOver fractions	0.5
RandomSeed	0
ScalingFactor	0.6
Tolerance	0.001

Problem Definition

In this study, the optimum designs of non-hybrid (carbon/epoxy and glass/epoxy) and interply hybrid (carbon-glass/epoxy) laminated composite plates are considered for various aspect ratios (0.2-2) by using Differential Evolution method (See Fig. 3). The laminates are 64 layered and symmetric-balance. The length of plate is 0.508 m and thickness of each layer is 0.127 mm. The width of plate has been calculated from the plate aspect ratios (a/b). In non-hybrid cases, fundamental frequency is maximized for single objective approach. In hybrid cases, maximum fundamental frequency and minimum cost based on multi objective approach are considered simultaneously. The mechanical properties of glass-epoxy and carbon-epoxy laminated composite materials are also given in Table 2.

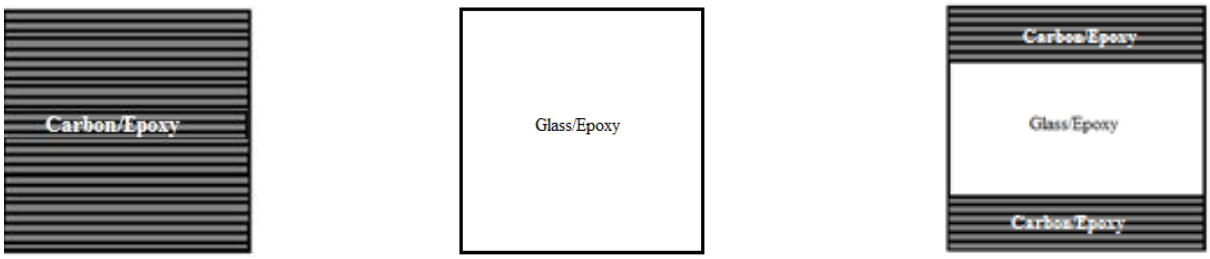


Figure 3. Symmetric arrangement of carbon/epoxy and glass/epoxy layers

Table 2. Glass-epoxy, carbon-epoxy mechanical properties [27]

Parameters	Carbon-Epoxy	Glass-Epoxy
Longitudinal modulus (GPa)	181	38.6
Transverse Modulus (GPa)	10.3	8.27
In-plane shear modulus (GPa)	7.17	4.14
Poisson ratio	0.28	0.26
Material density (kg/m3)	1600	1800

In the following part, detail descriptions of the model problems (problems 1-3) are introduced.

Problem I

The problem given in [27] is selected as benchmark for fundamental frequency maximization with symmetric-balance 64-layered carbon/epoxy (non-hybrid) including various aspect ratios by using Differential Evolution (DE) stochastic optimization method. After that the obtained values are compared to results based on GA and SA [27] methods. Fiber orientation angles of the layers of the plate are considered in the range of -90 and 90 with 45 degree increments in order to take into account the manufacturing constraints.

Problem II

Stacking sequence design and optimization of 64-layered symmetric-balance glass/epoxy (non-hybrid) composite structure is carried out to maximize fundamental frequency including various aspect ratios by using DE method. Stack of layers intervals -90 and 90 with 45 degree increments.

Problem III

Optimum design of symmetric-balance 64-layered interply hybrid carbon-glass/epoxy are considered for various aspect ratios (0.2-2). The optimization problem is to find the number of high stiffness and less expensive laminates maximizing the fundamental frequency and minimizing the cost by multi objective optimization approach. Fiber orientation angles of the layers of the plate are considered in the range of -90 and 90 with 45 degree increments. In this problem, penalty function formulation is used for multi objective optimization. Now, in order to evaluate both of the quantities “frequency” and “cost”, a function F can be introduced as linear combination of the squares of the parameters f_1, f_2, g_1, g_2 as [11]

$$F = k_1 f_1^{\,2} + k_2 f_2^{\,2} + c_1 g_1^{\,2} + c_2 g_2^{\,2} \tag{10}$$

where the parameters f_1 ,f_2 , g_1, g_2, k_1, k_2, c_1, and c_2 can be defined as

$$f_1 = \left(\frac{\omega_{\max} - \omega}{\omega_{\max}} \right) \tag{11}$$

$$f_2 = \left(\frac{\text{cost}}{\text{cost}_{\max}} \right) \tag{12}$$

$$g_1 = \delta - 0.2 \tag{13}$$

$$g_2 = \gamma - 0.2 \tag{14}$$

$$k_1 = k_2 = c_1 = c_2 = 1 \tag{15}$$

The parameters "ω" and "cost" occurs in Eqs. (11) and (12) represent optimum frequency and cost values. The parameters *"*$\omega_{\max}$" and "$\text{cost}_{\max}$" indicate the maximum fundamental frequency and the maximum cost for all layers being consisted of non-hybrid carbon/epoxy layered. Namely, the numerical value of $\omega_{\max}$ is based on the results of problem 1, which can also be utilized for corresponding aspect ratios in problem 3. In Eqs. (13–15), g_1 and g_2 are the penalty terms, the other parameters, k_1, k_2, c_1, and c_2 are sensitivity coefficients depending on weights of the objective functions in the optimization problem. The value of the parameters (k_1, k_2, c_1 and c_2) are selected as "1" due to the fact that objective functions (fundamental frequency and cost) have to be assumed equally important.

$$\text{cost} = ab\frac{h}{N} g(\alpha_0 \rho_0 N_0 + \rho_i N_i) \tag{16}$$

where a and b are the length and width of the plate, respectively; the number of carbon and glass layers are N_0 ,N_i ; the total number of layers is $N=N_0 + N_i$; ρ_0 and ρ_i are the mass densities of the outer (carbon/epoxy) and inner (glass/epoxy) layers, respectively. α_0=8 is comparative cost ratio of the carbon/epoxy layers to glass/epoxy layers and g represents acceleration of gravity.

Results and Discussion

In this part, results of 64-layered laminated composite optimal design studies based on the single and multi-objective approaches are presented for maximum fundamental frequency and minimum cost. In order to validate the optimization code used in this study, the problem given in [27] is solved by using DE method and then compared. It can be seen that DE, GA and SA give same results for the problem and hence, DE shows potential to obtain reliable results for similar design problems.

Table 3. Comparison of fundamental frequencies performance for 64-layered symmetric-balance non-hybrid carbon/epoxy laminates with 45^0 increment (a=0.508 m, t=0.000127 m)

a/b	Stacking sequence	ω		
	DE (Present)	DE (present)	GA [27]	SA [27]
0.2	$[0_{32}]_s$	762.18	762.18	762.18
0.4	$[0_{32}]_s$	192.81	192.81	192.81
0.6	$[0_{32}]_s$	87.56	87.49	87.49
0.8	$[\pm 45_{16}]_s$	56.01	56.01	56.01
1	$[\pm 45_{16}]_s$	44.16	44.16	44.16
1.2	$[\pm 45_{16}]_s$	37.13	37.16	37.16
1.4	$[\pm 45_{16}]_s$	32.63	32.62	32.62
1.6	$[90_{32}]_s$	31.61	31.60	31.60
1.8	$[90_{32}]_s$	31.33	31.32	31.32
2	$[90_{32}]_s$	31.14	31.13	31.13

Table 3 shows that firstly, the optimal configurations are $[0_{32}]_s$ for aspect ratios from 0.2 to 0.6, $[\pm 45_{16}]_s$ from 0.8 to 1.4 and $[90_{32}]_s$ from 1.6 to 2; secondly, frequency decreases 93% for $0.2 \leq a/b \leq 0.6$, 26% for $0.8 \leq a/b \leq 1.4$, 1.5% for $1.6 \leq a/b \leq 2$; thirdly, it can be said that cost varies from 134.2 to 13.4 between 0.2 to 2 aspect ratios.

The optimum stacking sequence designs of 64-layered symmetric-balance glass/epoxy laminated composite for maximum fundamental frequency utilizing the proposed DE algorithm are given in Table 4. It can be seen that with increasing of the aspect ratios from 0.2 to 2, the optimum fiber orientation angles are also increase in the interval [0,90]. Moreover, the value of fundamental frequency varies dramatically (88%) between 0.2 and 0.6 aspect ratios, moderately (42%) between 0.8 and 1.4 and slightly (4%) between 1.6 and 2. Cost varies from 18.9 to 1.9 between 0.2 to 2 aspect ratios. Also, it can be said that if the carbon/epoxy is used as an alternative material instead of glass/epoxy for laminated composite design, although 56% frequency increment are obtained, cost of structure increases 86%. The forms of laminated composites given in Problems 1 and 2 are non hybrid and only frequency is considered as design objective. However, it should be noted that cost is a crucial factor for all the engineering problems and therefore, it has to be taken into account in the design and optimization problems of the laminated composite materials. Carbon/epoxy composite have higher strength value if it is compared to glass/epoxy, however, it is about eight times more expensive. Namely, it can be concluded that the usage of carbon/epoxy together with glass/epoxy in an interply hybrid structural system can take advantage in terms of both frequency and cost simultaneously.

Table 4. Fundamental frequencies performance for 64-layered symmetric-balance non-hybrid glass/epoxy laminates with 45^0 increment based on DE (a=0.508 m, t=0.000127 m)

a/b	Stacking sequence	ω
0.2	$[0_{32}]_s$	335.85
0.4	$[0_{32}]_s$	86.76
0.6	$[0_{32}]_s$	40.81
0.8	$[\pm 45_{16}]_s$	26.36
1	$[\pm 45_{16}]_s$	20.71
1.2	$[\pm 45_{16}]_s$	17.45
1.4	$[\pm 45_{16}]_s$	15.41
1.6	$[90_{32}]_s$	14.81
1.8	$[90_{32}]_s$	14.47
2	$[90_{32}]_s$	14.23

Table 5. Optimum stacking sequences design in terms of fundamental frequencies, cost and index F for 64-layered symmetric-balance hybrid carbon-glass/epoxy laminates with 45^0 increment based on DE (a=0.508 m, t=0.000127 m)

a/b	Stacking sequence	N_o	ω	cost	Frequency reduction (%)	Cost reduction (%)	F
0.2	$[0_{32}]_s$	12	553.43	40.5088	27.39	69.82	0.1660
0.4	$[0_{32}]_s$	12	140.61	20.2544	27.07	69.82	0.1644
0.6	$[0_{32}]_s$	12	64.34	13.5083	26.52	69.82	0.1614
0.8	$[\pm45_{16}]_s$	12	41.24	10.1272	26.37	69.82	0.1606
1	$[\pm45_{16}]_s$	12	32.49	8.1018	26.43	69.82	0.1609
1.2	$[\pm45_{16}]_s$	12	27.34	6.7462	26.37	69.82	0.1606
1.4	$[\pm45_{16}]_s$	12	24.04	5.7893	26.33	69.82	0.1603
1.6	$[90_{32}]_s$	12	23.25	5.0716	26.45	69.82	0.1609
1.8	$[90_{32}]_s$	12	22.97	4.4974	26.68	69.82	0.1622
2	$[90_{32}]_s$	12	22.78	4.0509	26.85	69.82	0.1631

Table 5 shows the optimum stacking sequence designs of 64 layered symmetric-balance interply hybrid carbon-glass/epoxy in terms of frequency, cost and index F. A close look at the results given in Table 5 clearly demonstrate that while the higher frequency value (553.43) of carbon-glass/epoxy is gained for $[0_{32}]_s$, the lowest material cost (4.0509) is obtained for $[90_{32}]_s$. By using interply hybrid carbon-glass/epoxy instead of carbon/epoxy, material cost decreases up to 69% and frequency reduces 27%. In this study, we considered that objective functions (frequency and cost) have to be equally important, thus the usage of interply hybrid carbon-glass/epoxy structure instead of non hybrid carbon/epoxy and glass/epoxy is more advantages. Namely, by using interply hybrid composite structures, it is possible to design laminated composite with high fundamental frequency and low cost without sacrificing in stiffness-to-weight ratios.

Variation of the fundamental frequency and the cost which depend on number of carbon layers and aspect ratios for 64 layered symmetric balance hybrid composite plates are given in Figure 4. When considered the effect of the number of carbon layers on change of fundamental frequency for 64 layered plate, frequency increases dramatically by the number of carbon layers reach to 40.

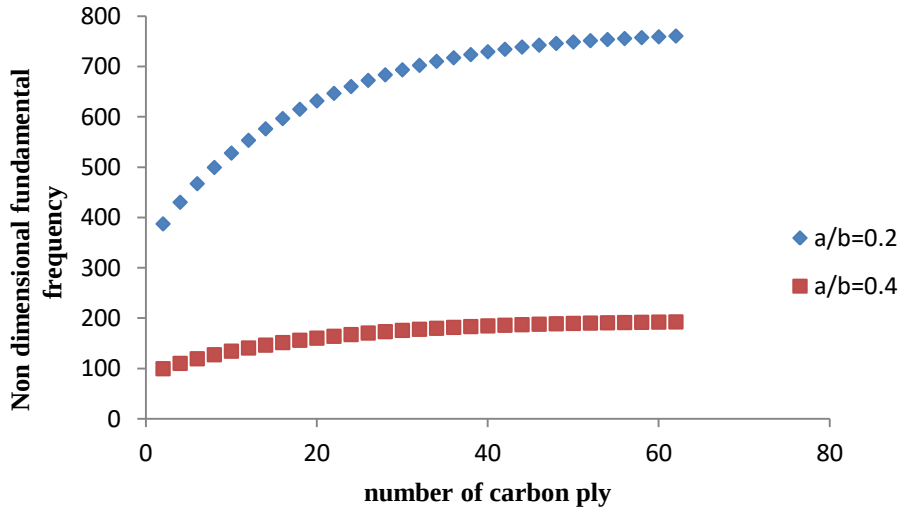


Figure 4. Fundamental frequency of laminated composite for 64 ply depends on aspect ratio and number of carbon ply

Conclusion

In this study, comparison of laminated composite designs for symmetric-balance non hybrid carbon/epoxy, glass/epoxy and interply hybrid carbon-glass/epoxy composite materials have been conducted. Maximum fundamental frequency and minimum cost based on multi objective approach are considered by using Differential Evolution algorithm. The design variables of the optimization problems are selected as fiber angles, the number of outer layers (N_o)having high-stiffness and more expensive (carbon/epoxy) and the number of inner layers (N_i) having low-stiffness and inexpensive (glass/epoxy).
It can be discovered from the results that if fundamental frequency is considered as an objective function, the results regarding carbon/epoxy corresponds to the higher values comparing glass/epoxy and carbon-glass/epoxy. If cost is considered as an objective function, glass/epoxy can be preferred as suitable material. However, when frequency and cost are considered as objective function simultaneously, the usage of interply hybrid structure including carbon/epoxy in outer layers and glass/epoxy in inner layers instead of non hybrid carbon/epoxy and glass/epoxy is appropriate.

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EFFECT OF TOTAL FILLER CONTENT AND MICRON PARTICLE SIZE ON BIOMECHANICAL PERFORMANCE OF NANOHYBRID COMPOSITES DEVELOPED FOR POTENTIAL DENTAL APPLICATIONS

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Abstract

Composites are preferred materials in dental area due to their high mechanical strength, superior aesthetic appearance, reasonable cost compared to ceramics and the tendency to adhere to the tooth and denture. The recent studies in dental area have focused on materials that can respond to the mechanical needs as well as repairing of losses that occur due to decay and other various reasons in dental tissues. The amount of filler material and particle-matrix interaction have been improved using different size of particles in composites, and consequently, increased mechanical strength and improved aesthetic properties have been obtained without compromising the processability of the composite. The aim of this study was to determine optimal total particle content and to determine the most important properties -such as three point bending strength, water sorption and solubility characteristics –of nanohybrid composites that were prepared by using different micron particle sizes.

Keywords: Dental composite, Nanohybrid composite, Biomechanical property

1. Introduction

Today, apart from being an engineering branch, material science has been making progress that forms the basis of technological developments. The material science is divided into classes such as metal, nonmetal, organic, inorganic, polymer and composites. Because of readily available components, low cost, easiness to manufacture, compatibility with other materials, and capability of responding to the desired physical / chemical properties, composite materials have found a wide application area in relation to the increasing demand [1]. Major industry branches such as aerospace, automotive, textile and health have adopted composite materials' criticality and have taken share from their continuous development. According to matrix content, the polymer matrix from composites that are classified as metal, ceramic, and polymer matrix is widely used in the development of dental biomaterials that are involved in the displacement and/or restoration of transplanted or degenerated of organs or tissues [2]. These dental polymer based composites used in dentistry are composed of three main components: organic matrix, inorganic particles and a binding -coupling- agent that holds them together. These materials which are obtained by embedding one or more inorganic discontinuous phases into the continuous organic phase have passed on to dentistry history as "resin composites" [3]. Although each component of the composite has a critical importance for the final product's success, the most important part of the development and the change in today's commercial composites have been the result of used inorganic particle sizes' change [4]. Organic matrix that is the component of composite based on dental resin comprises of prepolymer and comonomer as main monomers. Prepolymers are high molecular weight aromatic resins used to provide strength and stiffness. Difunctional organic monomers can be exemplified such as urethanedimethacrylate (UDMA), 2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]-propane (BISGMA). The organic matrix that is developed by using prepolymers constitutes the chemically active part of the composite. Just like

triethyleneglycoldimethacrylate (TEGDMA), Glycol methacrylates are preferred to decrease prepolymer viscosity as diluent/crosslinking monomer [5]. In the inorganic phase of the composites, various particles that contain silicon dioxide, lithium, barium, strontium having a size range from 20 nm-0.05 μm to 0.5 μm-60 μm are used. In addition, composites based on dental resin involve a coupling agent to hold organic matrix and inorganic particles together [1]. The most commonly used coupling agents are organofunctional trialkoxysilane compounds. Particle surface modification takes place through two reactive groups on the coupling agent. This process makes it easier to wet and processes the surface-modified inorganic particles in the organic matrix.

Mechanical properties, indicative of material strength, determine the performance of dental composite materials and play an important role in determining clinical success. The strength properties of composite materials are determined by mechanical testing methods. In the test methods used to determine the properties, samples are subjected to controlled force until failure. Variables in each test method (content, particle size, shape, stor conditions, thermal cycle) have significant effects on composite strength. By using bending strenght test, one of these methods used in specifying mechanical properties, repeatable and reliable results can be obtained. Three-point, four-point and biaxial methods are used in the bending strength test in which the pressing, pulling and shearing forces have been formed at the same time. The three point flexural strength test is based on the measurement of the reached maximum force until the specimen fracture during vertical load application and nonhomogeneous central stress field is ensued.

In terminology, absorption, one of the physical properties of dental resin based composites, is the diffusion of a solid to liquid molecules. Water sorption of dental composites has mechanical properties [6]. Composites must be resistant to degradation in aqueous media in order to be clinically long-term. The amount of water absorbed in composites depends on the amount of hydrophilic monomer forming the organic matrix [7]. Hydrophilic monomers are migrated to the oral environment by undergoing hydrolytic degradation with effect of water sorption. Undesirable reactions can occur in the pulp or in the surrounding tissues as a result of substitution of unpolymerized monomer with water in matrix [8]. Furthermore, mechanical properties of composites are deteriorated because of the breaking of the bonds between particle and matrix [9]. The water solubility, which is defined as the separation of the constituent components and their dispersion in water, causes the deterioration of the composite and its mechanical properties. The dissolution of dental composites depends on the type and proportion of monomer forming the matrix. The shortening of the polymerization time of the composite materials is clinically important because it negatively affects the solubility and restoration life [10].

Composites that contain nanoparticles have recently been presented as the most interesting materials. In the developed composite, the increase of ratio of filler and particle-matrix surface contact have been provided by using nanosize particles. Consequently, an increase in mechanical strength and an improvement in aesthetic properties without sacrificing the machinability of the composite have been provided [11]. Clinical applications of nanohybride composites show that these materials have less abrasion than microhybrid materials. Nanosized particles improve the abrasion properties of the composite as well as its transparency and polishability. For this reason, "Nanohybrid composites" attract the attention of dental clinicians [12]. Various investigations have been made on the effect of particle size and particle loading on mechanical properties, which are the most important selection parameters of dental composites. However, these studies are mostly in the form of a comparison of the behavior of existing commercial products. The aim of this study was to determine optimal total inorganic particle content and to specify the most important properties -such as three point bending strength, water sorption and solubility characteristics- of nanohybrid composites that were prepared by using different micron particle size.

2. Materials and Methods

Urethanedimethacrylate (UDMA), 2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]-propane (BISGMA) and tri-ethyleneglycoldimethacrylate (TEGDMA) were all provided by Esschem Europe Ltd. and directly used as monomers without any purification. Surface modified fumed silica Aerosil R709 was purchased Evonik Industries and M8000, M6000, M4000, M3500, and M3000 silica micron particles were received from Sibelco. 3-methacryloxypropyltrimetoxysilane (MPTS) and benzoil peroxide (BOP) were supplied by Abcr and Merck, respectively.

2.1 Preparation of Nanohybrid Composites

As a continous phase, The organic matrix is comprised of a mixture of urethanedimethacrylate (UDMA), 2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]-propane (BISGMA) and tri-ethyleneglycoldimethacrylate (TEGDMA) monomer in a ratio of (40:40:20 wt%). In the development of composite materials, nano and micron sized inorganic particles were used as a discontinous phase. The nano sized Aerosil R709, microsized M8000 (1,8 μm), M6000 (4 μm), M4000 (6 μm), M3500 (11 μm), M3000 (17 μm) silica particles which were modified with 3-methacryloxypropyltrimetoxysilane (MPTS) were added in the matrix. After the mixture was injected into molds, it was polymerized at a certain temperature and time using hydraulic press. And then the mold was transferred to the cold press to end the polymerization.

2.2 Characterization of Nanohybrid Composites

For three point bending test, five plate specimens (2 mm x 2 mm x 25 mm), were prepared for each composite and immersed in distilled water at 37±1 °C for 24 hours, and then tested at 0,75 mm/min (Shimadzu, AGS-X) according to the method described in ISO 4049. Flexural strength, in megapascal, was calculated from Equation 1:

$$\sigma = \frac{F \times l}{2 \times b \times h^2} \quad (1)$$

where F is the maximum force, in Newton; l is the distance between the supports, 20 mm; b and h are the width and thickness of specimen, millimeter, respectively.

For water sorption and solubility tests, cylindrical discs (diameter:15 mm and thickness:1 mm) were prepared by using stainless steel mold and the test was carried out according to the method described in ISO 4049. The prepared specimens were stored in a desiccator with silica gel at 37 °C until a constant mass (m_1) was obtained. The disc-shaped specimens' volumes (in mm^3) were calculated using diameter and thickness. Then, specimens were placed in distilled water at 37±1 °C for seven days. And then they were weighed to an accuracy of 0.1 mg (m_2) and conditioned to constant mass (m_3). Water sorption (ws) was obtained using the Equation 2:

$$w = \frac{m_2 - m_3}{v} \quad (2)$$

Solubility (s) was calculated from the following equation:

$$s = \frac{m_1 - m_3}{v} \quad (3)$$

The morphology and surface analysis were characterized by using scanning electron microscopy, SEM (Gemini SUPRA 35VP).

3. Results and Discussion

The organic matrix forming the backbone of the composite is the most important component. Therefore, the first study was associated with verification of the influence of organic matrix composition on flexural strength of BISGMA, UDMA and glycol dimethacrylates containing resin matrix.

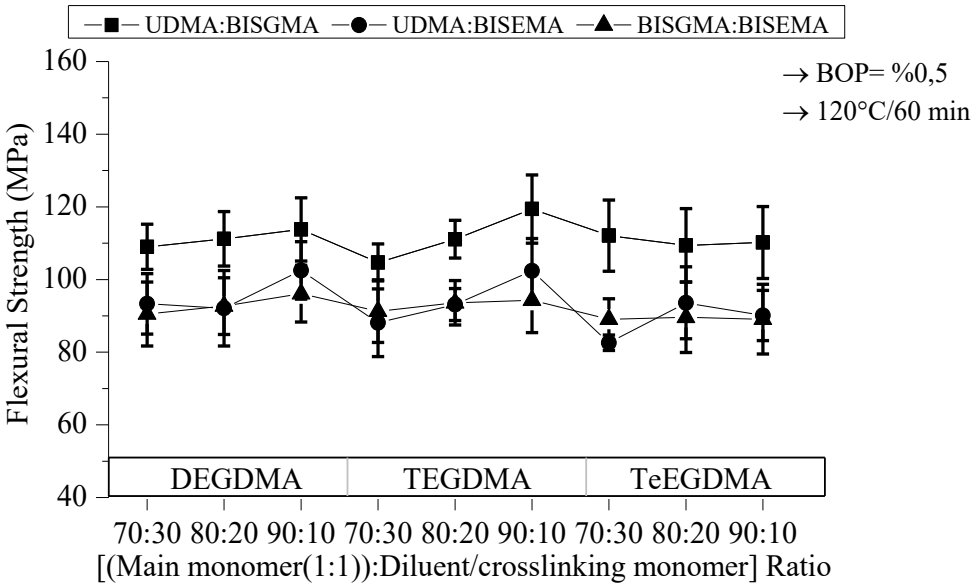


Figure 1. Flexural strength graph of organic matrix systems containing triple [(main monomer (1: 1): diluent / crosslinking monomer] at different ratio.

The flexural strength values of organic matrix systems prepared by using [UDMA:BISGMA], [UDMA:BISEMA] and [BISGMA:BISEMA] main monomer twins and DEGDMA and TEGDMA increased with the increasing amount of main monomer while the strength values of the triples prepared by using TeEGDMA increased in the direction of increasing / decreasing and remained same.
The increase in the flexural strength values of the monomer triples prepared by using DEGDMA is less. It can be said that this change is caused by the lower reactivity of DEGDMA compared to other diluent / crosslinking monomers. When TEGDMA is used as diluent / crosslinking monomer, the increase in flexural strength values is more pronounced. TEGDMA has given high strength by the homogeneous polymeric network which is formed by providing the cross-link density and easy workability. Change in the flexural strength values of monomer triple prepared using TeEGDMA monomer was less pronounced and standard deviations are high. This case is associated with low number of double bonds per unit weight of TeEGDMA monomer and BISGMA's low carbon double bond conversion degree. The average flexural strength values of the monomer triple of [(35:35): 30], [(40:40):20] and [45:45]:10] ratios were 109 MPa, 110 MPa and 114 MPa, respectively, when [UDMA:BISGMA] monomer pair was used as the main monomer; 88 MPa, 93 MPa and 98Mpa, respectively, when [UDMA:BISEMA] monomer pair was used; and 90 MPa, 92 MPa and 93 MPa, respectively, when [BISGMA:BISEMA] monomer pair was used. The viscosities of UDMA and BISEMA monomers were lower than those of BISGMA main monomer. Therefore it is expected that a homogeneous polymeric network will be obtained by making it easier to process with these diluent / crosslinking monomers [1]. The accuracy of this result was supported by the fact that the increase trend in flexural strength values was similar when the main monomer pair was used with all other ethylene glycol dimethacrylates and that the standard deviation was low.

The highest flexural strength values in all of monomer triples prepared by using DEGDMA, TEGDMA and TeEGDMA were obtained using [UDMA:BISGMA] main monomer pair. Flexural strengths of three

different monomer triples prepared using DEGDMA and TEGDMA were as follows: [UDMA:BISGMA] > [UDMA:BISEMA] ≥ [BISGMA:BISEMA], when values of monomer triples prepared using TeEGDMA were: [UDMA:BISGMA] > [BISGMA:BISEMA] ≥ [UDMA:BISEMA]. Average bending strength values at three ratio of monomer pair prepared with all diluent / crosslinking monomers were as follows in descending order: [UDMA:BISGMA]> [UDMA:BISEMA]≥ [BISGMA:BISEMA], 111 MPa, 93 MPa and 92 Mpa, respectively. As a result of the evaluation, water sorption test and water solubility test were applied to matrix systems with flexural strength values equal to or higher than 100 MPa (≥100 MPa), and the results are presented in Figure 2.

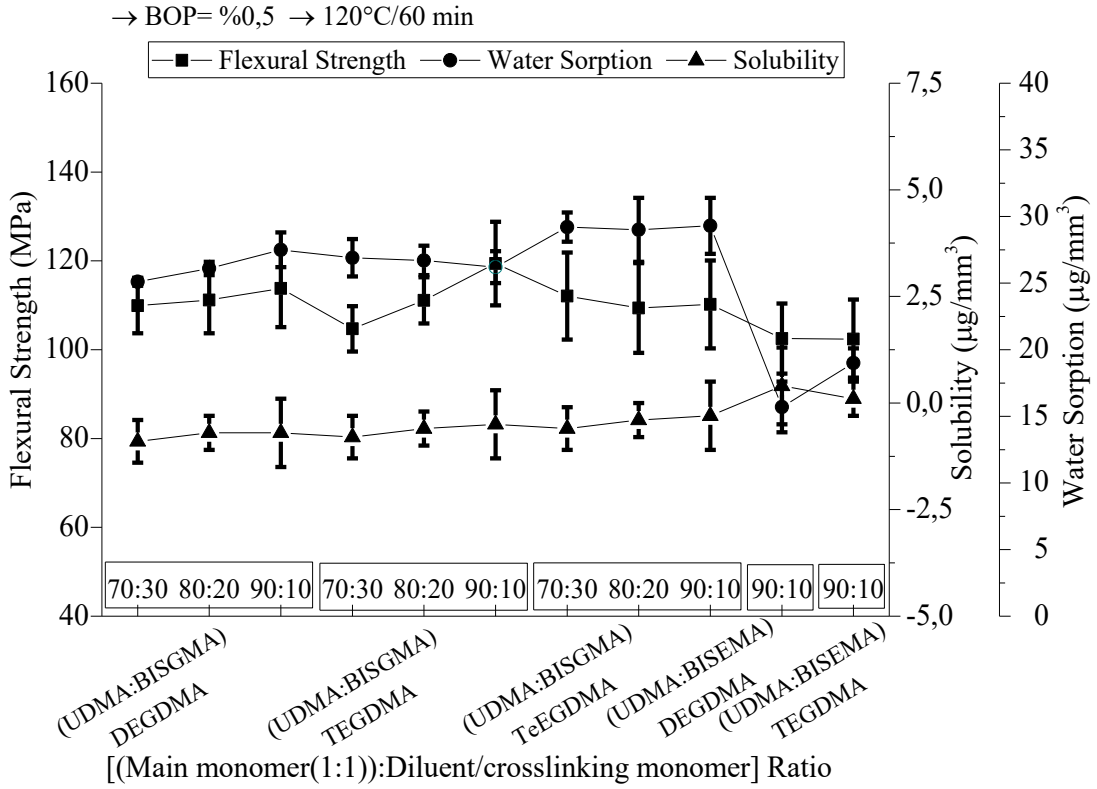


Figure 2. Flexural strength, water sorption and solubility graphs of organic matrix systems with flexural strength values equal to or higher than 100 MPa (≥100 MPa)

In selected systems, general trend of water sorption values of monomer triples prepared using (UDMA:BISGMA) main monomer pair and DEGDMA, TEGDMA and TeEGDMA ascented with the increasing amount of main monomer. This result is related to the increase in the content of the ether linkage having capable hydrogen bonding in DEGDMA, TEGDMA and TeEGDMA. The water absorption of the organic matrix prepared using (UDMA:BISEMA) monomer pair with DEGDMA and TEGDMA was less. This result is related to the fact that BISEMA, unlike UDMA and BISGMA, has no functional group that is capable of forming hydrogen bonds. The water solubility values are higher because of the small number of groups having the ability to hold water.

This monomer triple is more suitable because of the simplicity to manufacture according to the standard and high mechanical and low water sorption values having low standard deviation. Compared to other monomers, BISGMA imparted more rigidity to the polymeric matrix after polymerization. Polymerization of UDMA monomer in the matrix gave a more flexible material. [(40:40):20] ratio has shown high

flexural strength and low standard deviation because of the suitable reactivity and viscosity of TEGDMA and the processibiliy that it imparted to the (UDMA:BISGMA(1:1)) main momoner pair [13].

The flexural strength distributions of composites prepared by increasing the total amount of particles to 50%, 60% and 65%, and decreasing the organic matrix or PMMA ratios, are shown in Figure 3.

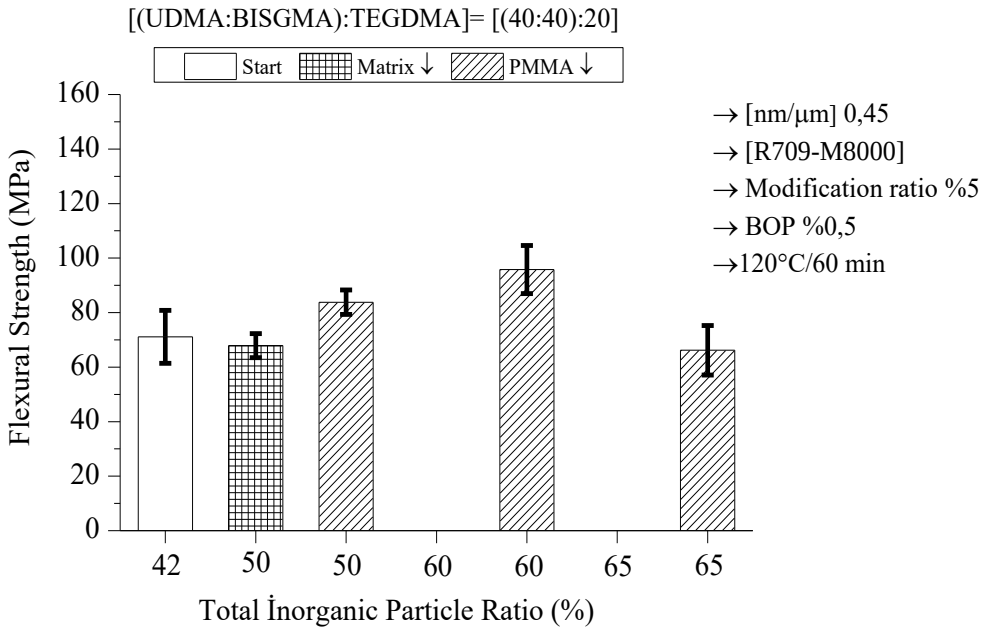


Figure 3. Flexural strength graph of composites prepared by increasing the total amount of particles and decreasing the organic matrix or PMMA ratios

There has been no change in flexural strength of the composite prepared by decreasing the amount of matrix and increasing the total content to 50%. When matrix amount decreased and the total particle content increased to 60% and 65%, the composites could not be prepared. The organic matrix forming the backbone of the composite is the most important component that holds the particles together, provides stress transfer between the particles and protects the particles from physical and chemical external effect [1]. Because the amount of matrix falls below the value that is enough to cover all particles' surfaces, composites containing a total particle content of 60% and 65% could not be prepared. There was an increase in the flexural strength of the composite prepared by decreasing the amount of PMMA and increasing the total content to 50% and 60%, respectively. It is expected that the mechanical properties of composites increase by using harder inorganic particles as filler instead of organic based PMMA alone. When matrix amount decreased and the total content increased to 65%, the flexural strength values of the composites decreased. As mentioned earlier, if the organic matrix ratio is below a certain value, this situation affects the system negatively. When the flexural strength of the composites prepared by increasing the total particle content was evaluated, it was decided that the total solid ratio should be 60% by decreasing the amount of PMMA.

Figure 4 shows the flexural strength values of the composites prepared by increasing from 42% to 60% of the total particle content by using micron size particles instead of M8000.

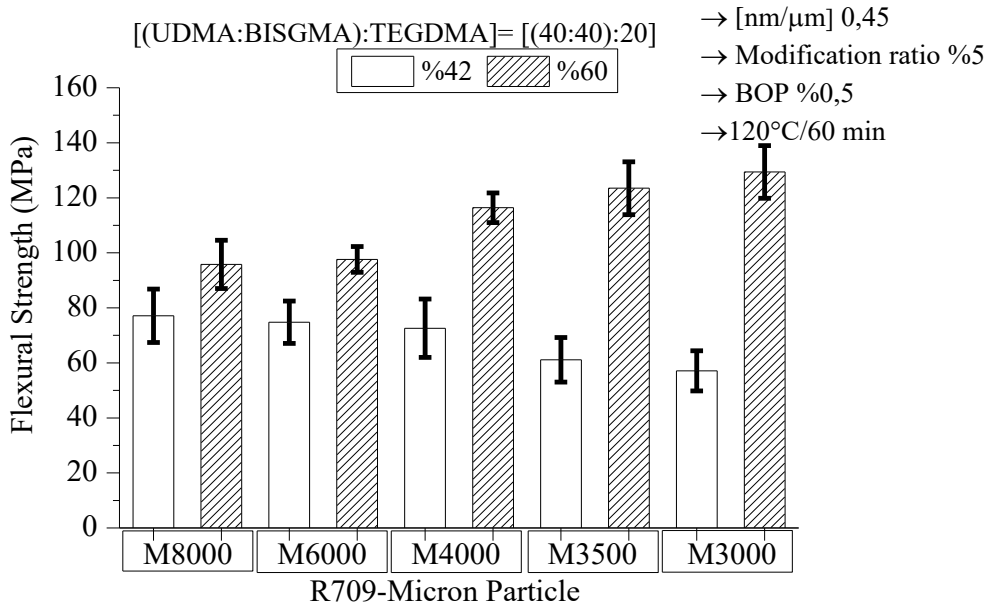


Figure 4. Flexural strength graph of composites containing 42% and 60% nano-micron sized inorganic particles

The flexural strength of the composites increased when the total particle content increased from 42% to 60% by using nano-micron sized particles. The particles that act as a roof in composite provide the mechanical strength of the composite structure. Thus, the flexural strength of composites increased with increasing amount of particles [14]. On the other hand, changing particle type from M8000 to M3000, an increase in flexural strength became more pronounced. With increasing amount of particles having a high surface area/volume ratio, the volume ratio covered by unit area of matrix reduced. When M3000 was used as micron sized particle, this decrease became more evident and increase in flexural strength of composite became more pronounced. As a result of the work done, it was determined that the composite contained 60% [R709-M3000] particle pair has the highest flexural strength.

Figure 5 shows the flexural strength values of the composites prepared using [R709-M3000] particle pair and other micron size particles with an increase from 42% to 60% in the total particle content.

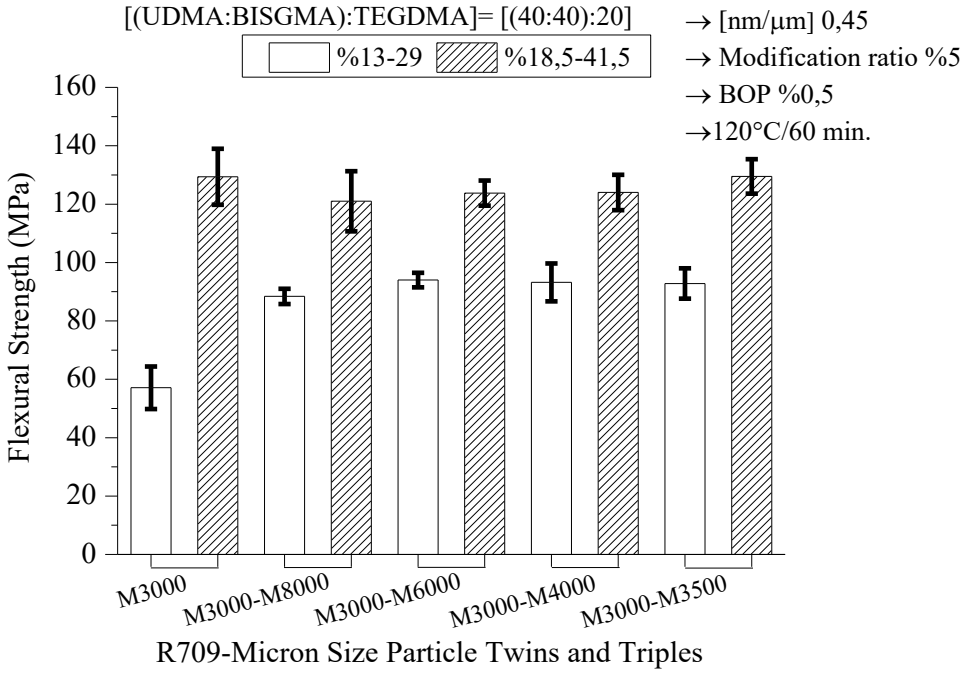


Figure 5. Flexural strength graph of composite prepared using M3000 with particle pair and triples as fillers

The flexural strength of the composites whose total particle content increased from 42% to 60% by using nano-micron sized particles increased. When the composites having the total particle content of 60% were compared within themselves, no significant differences were observed in the flexural strength values. When all of the prepared composites were evaluated, composites that contained [R709-M3500], [R709-M3000] and [R709-M3000-M3500] had the highest flexural strength values. When the water absorption and solubility behaviors were evaluated, the values were found to be 19,2±0,3 and -1,7±0,6; 20,5±0,6 and -0,8±0,6; 20,6±0,6 and -0,9±0,6; respectively.

SEM images of particle distribution in the matrix of some selected [R709-M3000-M3500] triple as filler material are given in Figure 6.

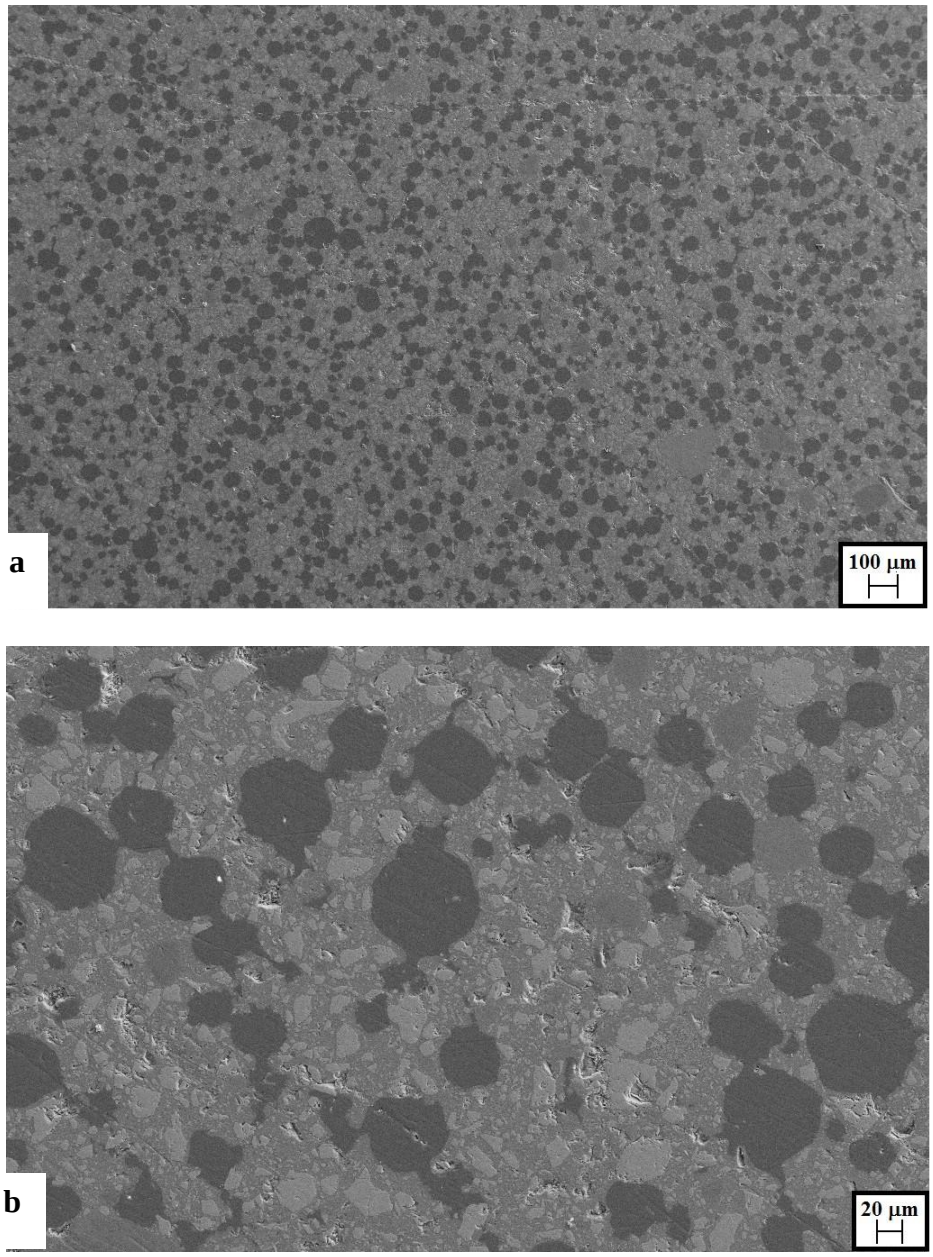


Figure 6. Scanning electron micrographs of the distribution of the particles in the matrix of [R709-M3000-M3500] as filler material a) 100X magnification, b) 500X magnification

When the SEM images of the composite dental material are examined, it is seen that the particles are homogeneously distributed in the matrix. Furthermore, it was understood that the modification process was performed as desired due to the absence of agglomeration between the particles.

4. Conclusion

The weight ratio [(UDMA:BISGMA):TEGDMA] [(40:40):20] was selected after examining the effects of main monomer, diluent/crosslinking monomer type and ratios on the flexural strength of organic matrix. The optimum total content of particles was determined as 60% by reducing the amount of organic matrix or PMMA. It has been shown that composites could be prepared using this determined amount of different

sizes of micron particles and according to the results of tests performed on the systems, the developed nanohybrid composites were found to be suitable for potential dental applications. Because the amount of matrix falls below the value that is enough to cover all particles surfaces, composites containing a total particle content of 60% and 65% could not be prepared. When the content of total particle was 42% in composite, their flexural strength values can be increased by reducing particle size. Otherwise, while the content of the total particle was 60% in composite by reducing the amount of PMMA, their flexural strength values can be reduced by reducing particle size.

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INTERFACE ENHANCEMENT OF CELLULOSE AND LDPE BASED POLYMERIC COMPOSITES FOR BIODEGRADABLE PACKAGING

BİYOBOZUNUR AMBALAJ UYGULAMALARI İÇİN SELÜLOZ VE AYPE ESASLI POLİMERİK KOMPOZİTLERDE ARA YÜZEY GELİŞTİRİLMESİ

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ÖZET

Bu çalışma iki temel amacı kapsamaktadır. İlki, doğada bol miktarda bulunan biyopolimerlerden biri olan karboksimetil selülozdan (CMC), sürdürülebilir ve çevre dostu gıda ambalajı malzemesi geliştirmektir. CMC zayıf mekanik özellikleri nedeniyle ambalaj malzemesi olarak tek başına yetersizdir. CMC'nin özelliklerini iyileştirmek amacı ile plastikleştirici olarak polietilen glikol (PEG, PG), gliserol monooleat (G), oleik asit (O) ve inorganik katkı maddesi olarak kil (C) kullanılmıştır. İkinci amaç ise biyobozunur olmayan alçak yoğunluk polietilene (AYPE, L) istenilen özelliklere bağlı kalarak biyobozunurluk kazandırmaktır. Bunu gerçekleştirmek için birçok malzeme ile uyumlu ve biyobozunur olan polikaprolakton kullanılmıştır. AYPE/PCL kompozitlerinde iki farklı plastiğin birlikte uyumunu geliştirmek için aynı plastikleştiriciler ve katkı maddesi olarak maleik anhidrit (M), dikümil peroksit (D) ve kil (C) kullanılmıştır. Hazırlanan AYPE/PCL kompozit filmlerinin simüle toprak altında biyobozunurluk davranışları incelenmektedir.

Filmlerin yüzey morfolojileri ve kristal yapıları optik mikroskop görüntüleri ile incelenmiştir. Kristal yapılarının filmler için katkı maddeleri ve soğutma sürecine bağlı olarak değiştiği gözlemlenmiştir. Hazırlanan tüm filmlerin fonksiyonel gruplarındaki değişim FTIR analizleri ile takip edilmiştir. CMC filmlerinde değişen plastikleştirici tipi ve miktarına göre FTIR profillerindeki değişim dikkat çekicidir. Mekanik özellikler çekme-kopma testleri sonuçlarına göre karşılaştırılmıştır. LDPE/PCL kompozit filmlerinde PCL miktarı arttıkça elastikiyette artma beklenmektedir, fakat iki farklı polimerin uyumsuzluğu nedeniyle, filmler daha kırılgan hale gelmiştir. CMC filmlerinde ise plastikleştirici tipinin mekanik özelliklere etkisi daha belirgin olarak görülmektedir ve PEG (Merck) ile en iyi sonuçlar alınmıştır. Filmlerin termal özellikleri incelendiğinde CMC'nin 250 °C'ye kadar %20'sinin bozunduğu ve 450 °C sıcaklığına ulaşıldığında kalan kül miktarının yaklaşık %45 olduğu görülmektedir. AYPE filmleri ise yüksek sıcaklıklara kadar dayanmış, neredeyse 400 °C sıcaklığa kadar hiç bozunmamış ve 500 °C sıcaklıkta geri kalan kül miktarı neredeyse yoktur. Biyobozunurluğu takip edilen film gruplarında ise en fazla bozunurluğa %16 ile L_P30_010 ve %21,54 ile L_P30_G10 filmleri ulaşmıştır. katkısız LDPE'in 14 aydaki bozunurluğu %12,5 iken, katkısız polikaprolakton film %100 bozunmuştur.

Anahtar kelimeler: *CMC, biyopolimer, AYPE, PCL, biyobozunur, ambalaj*

ABSTRACT

There are two main objectives in this study. The first one is to develop sustainable and environmentally friendly food packaging materials with desired properties from carboxymethyl cellulose (CMC) which is one of the most abundant biopolymers. CMC is insufficient alone to be

used as a packaging material because of weak mechanical properties. To enhance the properties of CMC, polyethylene glycol (PEG, PG), glycerol monooleate (G) and oleic acid (O) as plasticizers and clay (C) as an inorganic additive were used. The second objective is to give biodegradability to non-biodegradable low density polyethylene (LDPE, L) without changing desired properties. Polycaprolactone (PCL, P), biodegradable and compatible with many materials, was used for this purpose. For LDPE/PCL composites, same plasticizers and maleic anhydride (M), dicumyl peroxide (D) and clay were used to enhance the compability between these two different polymers.Biodegradation behaviour of LDPE/PCL composite films prepared in simulated soil is under investigation.

To examine the surface morphologies and crystal structures of the films, optical microscope images were taken. Crystal structures are varied, depending on the additives and the cooling process. FTIR analyses were performed to follow the functional groups of all prepared films. In CMC films, FTIR profiles vary greatly depending on the type and amount of plasticizer. Strain-stress tests have been carried out to determine the mechanical properties. As the amount of PCL in LDPE/PCL films increases, elasticity is expected to increase, but films become more fragile because of the incompatibility of the two polymers. In CMC films, the effect of the plasticizer type on mechanical properties is very obvious. The CMC film prepared with PEG (Merck) has better mechanical properties than others. When thermal properties were investigated, it can be seen that, CMC films started to degrade at 250 °C and 20% of the film lost. At 500 °C, almost 45% remained as ash. In contrast, LDPE films have withstand as high temperatures as 400 °C and the amount of ash at 500 °C is almost zero. For the film groups followed by biodegradation, L_P30_010 and L_P30_G10 films reached 16% and 21.5% weight loss, respectively. For the total 14 months under simulated soil, neat LDPE film has 12.5% and neat PCL film has 100% degradation.

Key words: *CMC, biopolymer, LDPE, PCL, biodegradable, packaging*

1. INTRODUCTION

The extensive production of conventional plastics and their use in different commercial applications poses a significant threat to both the fossil fuels sources and the environment. Alternatives called bioplastics evolved during development of renewable resources. Utilizing renewable resources like agricultural wastes (instead of petroleum sources) and their biodegradability in different environments enabled these polymers to be more easily acceptable than the conventional plastics [1]. Although bioplastics are considered to be environmental friendly materials, they also have some limitations such as high production cost and poor mechanical properties. High production cost drawback can be managed by utilizing the low cost of renewable resources such as agricultural wastes [2]. Nowadays, packaging plays an increasingly important role in the whole food chain “from the field to table”. In recent years, active packaging systems for food have gained much attention mainly due to increased demands on product safety, shelf life extension, cost efficiency, environmental issues, and consumer convenience [3]. The primary purpose of food packaging is to protect and preserve foods from oxygen, water vapour, ultraviolet light, and both chemical and microbiological contamination.

Carboxymethyl cellulose (CMC) is an alternative polymer due to its excellent viscosity, biocompatibility, and availability. Cellulose is the most abundant and renewable biopolymer in the world [4, 5, 6]. Carboxymethyl cellulose (CMC), a derivative from cellulose, shows suitable

film forming properties and leads to transparent films with good oxygen and lipids barrier [7, 8, 9]. Despite several advantages such as biodegradability, no toxicity, relatively good barrier properties to gases, and abundance in nature, polysaccharide based films show low water barrier properties due to their hydrophilic character, which in turn affects their mechanical, gas permeability and thermal properties [10, 11].

The objectives of this study, first, to obtain CMC films with desired food packaging properties. The second objective is to give LDPE biodegradable property as keeping desired film properties by adding of PCL which is biodegradable polymer with different weight percentages. Using different types of plasticizer and additives, the effect of these parameters are investigated. Previously, biodegradation of PCL composite films with organic (glycerol monooleate and oleic acid) and inorganic additives was investigated for understanding which additive and the amount of additive was more effective on biodegradation [12].

2. MATERIALS AND METHODS

The biopolymer CMC was obtained from Sate Chemistry. LDPE, wasfrom PETKIM (H2-8) and Polycaprolactone was from Aldrich (Mn: 70000-90000). Different solvents were used for different polymers as Xylene (Merck) for LDPE, dicholoromethane (Merck) for PCL and distilled water for CMC. As plasticizers, polyethylene glycol-400 was supplied from three different producers (Sigma, Merck, Tekkim, PG), oleic acid (Riedel, O). The other plasticizer, glycerol monooleate (Kimpeks, G) were used. Modified organoclay (Nanoclay, nanomer I.34TCN ®, 25-30 wt% of hydrogenated tallow methyl dihydroxyethyl ammonium bromide containing side-modified montmorillonite clay, Aldrich, C), maleic anhydride (Aldrich, M) and dicumylperoxide (Aldrich, D) were used as additives for the preparation of the polymeric composite films.

2.3 Preparation of Polymeric Composite Films

All films were prepared by solvent casting method. To prepare biofilms, 4.2 g of CMC was weighed; then, 70 ml of distilled water was added and mixed by a magnetic stirrer heater at 40°C. After CMC fully dissolved, one of the three types of plasticizers was added as 1% or 3 wt% and clay as 0.1% or 0.4 wt% and further mixed until homogeneous solution is obtained. Finally, CMC solution was casted on a preheated Teflon pan and left for evaporation of water at room temperature (**Figure 1**).

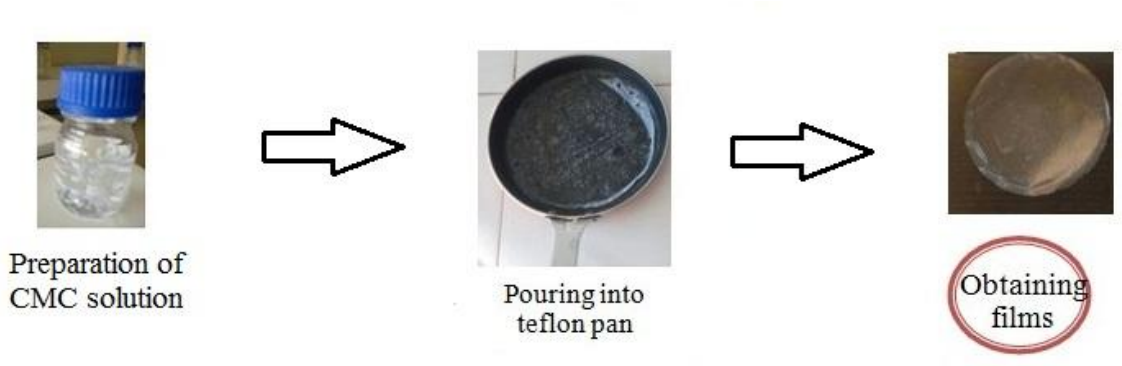


Figure 1. Preparation steps of CMC films

To produce LDPE/PCL composite films, 1.4 g of LDPE granules were weighed, then, 20 ml of xylene and one of the plasticizers selected were added, and mixed for an hour in the ultrasonic

bath which was set to 70°C for the perfect dissolution. Dicumyl peroxide (D), clay (C) and maleic anhydride (M) were added with different weight percentages. To prepare the PCL solution, 10wt% or 50wt% of PCL was weighed; 10 ml dichloromethane was added into another bottle and mixed by the magnetic stirrer at the ambient temperature approximately 20°C. After dissolution of both LDPE and PCL, two solutions were combined slowly at 70°C. Finally homogeneous solution was casted on the Teflon pan which was heated up before, to vaporize the solvent. Then the film left for cooling for an hour by decreasing the temperature of the heater as 1°C/min (**Figure 2.**).

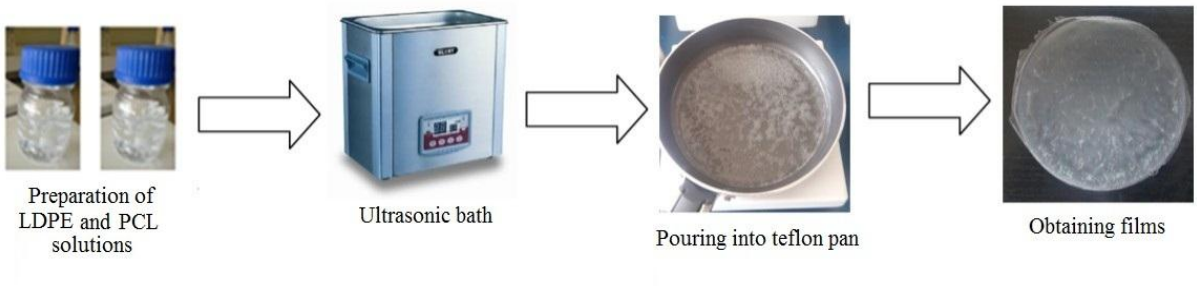


Figure 2. Preparation steps of LDPE/PCL composite films

2.4 Tests Performed

Properties of films have been investigated by using special tests to check the films suitability for packaging area. Therefore, optical microscopy (Leica DFC 295) was used to observe the crystallinity and surface structure. FTIR (Perkin Elmer, Spectrum 100) was used to characterize the functional groups. Mechanical tensile tests were done according to ASTM-D882 with the strain rate of 100 mm/min by tensile test analyser (SHIMADZU AG-15). They were cut as dogbone. The prepared sample as 2.5 cm of the top and 2.5 cm of the bottom was attached to the chins of the test device. Thermal degradation behaviour of films was followed by TGA. Biodegradation was examined under simulated soil and prepared according to literature (23% loamy silt, 23% organic matter (50wt % mature and 50wt % fresh cow manure), 23% sand and 31% distilled water). All films are cut as 2×2 cm^2 and weights and thicknesses are measured. Cut LDPE/PCL composite films are buried in small beakers filled with simulated soil and kept in a desiccator which is kept in a dark corner. Biodegradation was followed almost every month by measuring the weight losses and thickness changes. The buried specimens were recovered from the soil, washed with distilled water, and dried at room temperature until there is no further variation in weight, after weighed, optic microscope images are taken, and then thicknesses of films were measured. Following, the specimens were buried again in their respective beakers. The weight loss% and thickness change% of LDPE/PCL composite films are calculated by the following equations:

$$\boldsymbol{weight\ loss}\% = \frac{\boldsymbol{the\ weight\ of\ film\ before\ buried - the\ weight\ of\ film\ after\ buried}}{\boldsymbol{the\ weight\ of\ film\ before\ buried}} \times \mathbf{100}$$

3. RESULTS AND DISCUSSION

Optical microscope images were taken to investigate the surface morphology and crystal structure of the films. In **Figure 3**, the effect of plasticizer on CMC can be observed. It can be seen that the crystal structure of LDPE films changes with the addition of plasticizer (**Figure 4**) The films have porous structure because of the solvent casting method.

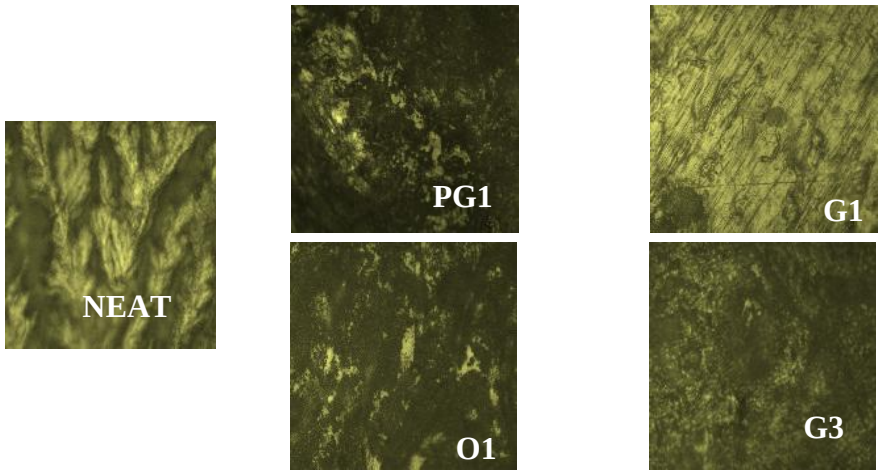


Figure 3. Effect of plasticizers on CMC polymeric films

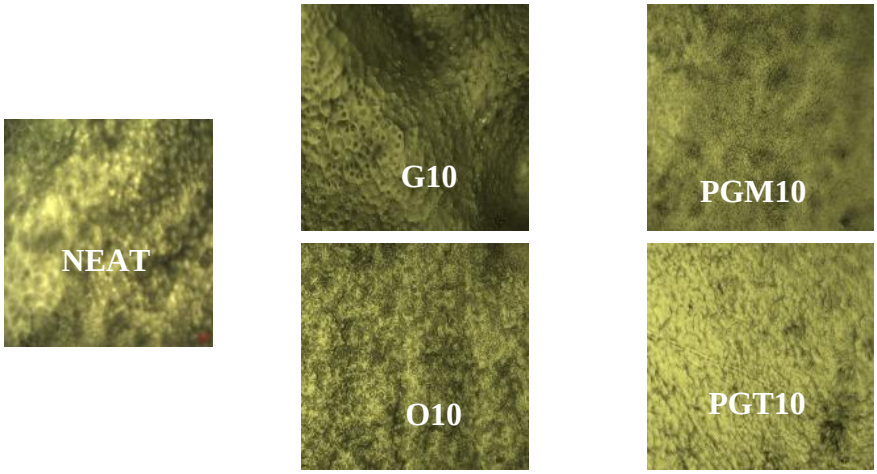


Figure 4. Effect of plasticizer on LDPE

FTIR analysis was used to determine the composite films functional groups.The effect of type and amount of plasticizer and the effect of clay addition on CMC films is shown in **Figure 5.**

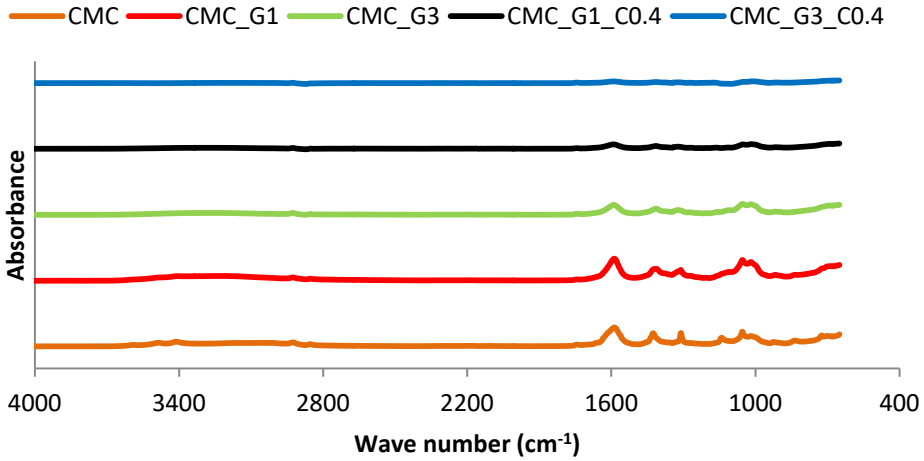


Figure 5. Effect of amount of plasticizer and clay addition on CMC by FTIR

The plasticizer is one of the important parameters that affect the mechanical properties of CMC films. Neat CMC has poor mechanical properties. With addition of PEG (Merck) plasticizer, the mechanical property of the film was enhanced (**Figure 6**).

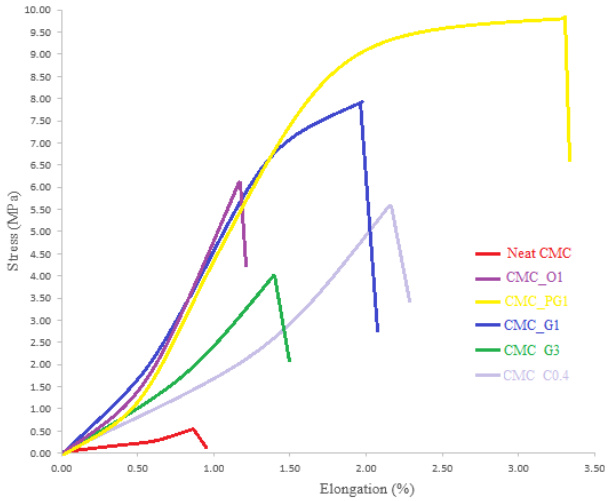


Figure 6. Effect of plasticizer and clay addition on CMC polymeric films

When neat CMC film is compared with other films, it can be easily understand that neat CMC is brittle and weak. Different plasticizers give strength and elasticity to CMC. The mechanical properties of LDPE/PCL composite films can be seen in **Figure 7**. In LDPE/PCL composites, it was expected that as increasing PCL amount, the mechanical properties of LDPE would be improved. However, 50% of PCL addition films were sensitive and they broke very quickly and they have less elongation. LDPE with PEG films have better mechanical properties. Especially, Turkish PEG (Tekkim) performance is satisfactory which has the lowest price.

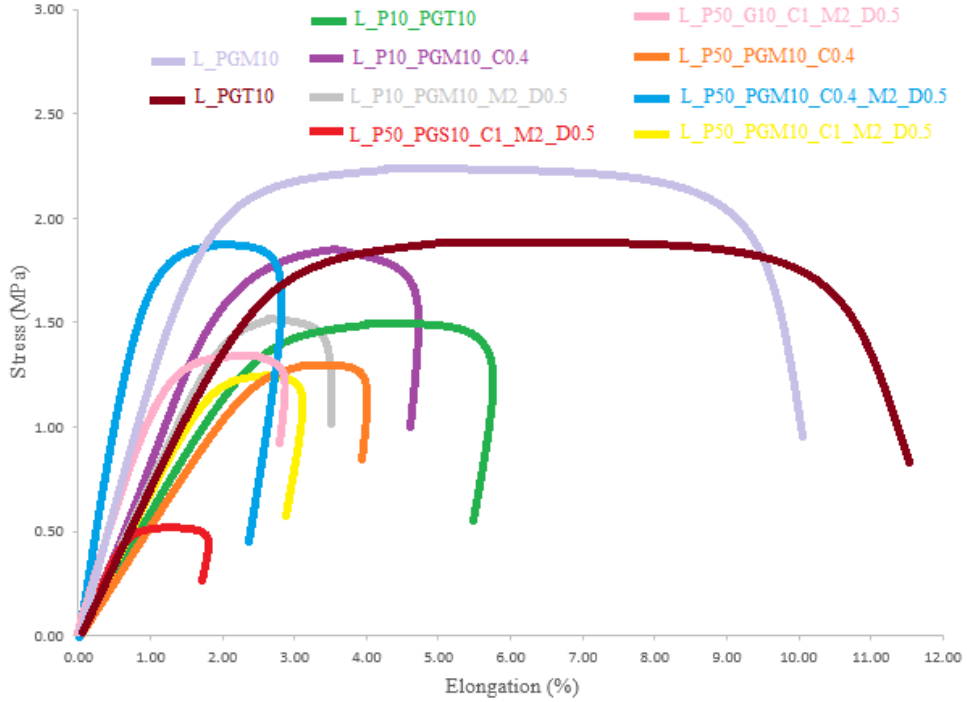


Figure 7. Effect of plasticizer and clay addition on LDPE/PCL composite films

Thermal degradation behavior of CMC and LDPE/PCL composite films was analyzed by TGA and the results were given in **Figure 8** and **Figure 9**, respectively. The thermal decomposition was carried out under nitrogen atmosphere from 30°C to 600°C at a heating rate of 10°C/min.

The first stage of mass loss for CMC films is about the removal of water from the sample. The higher values of mass loss are related with the degradation of cellulose chains and the loss of CO_2 from the structure. At the end of the test, almost 50% of CMC was remained as ash.

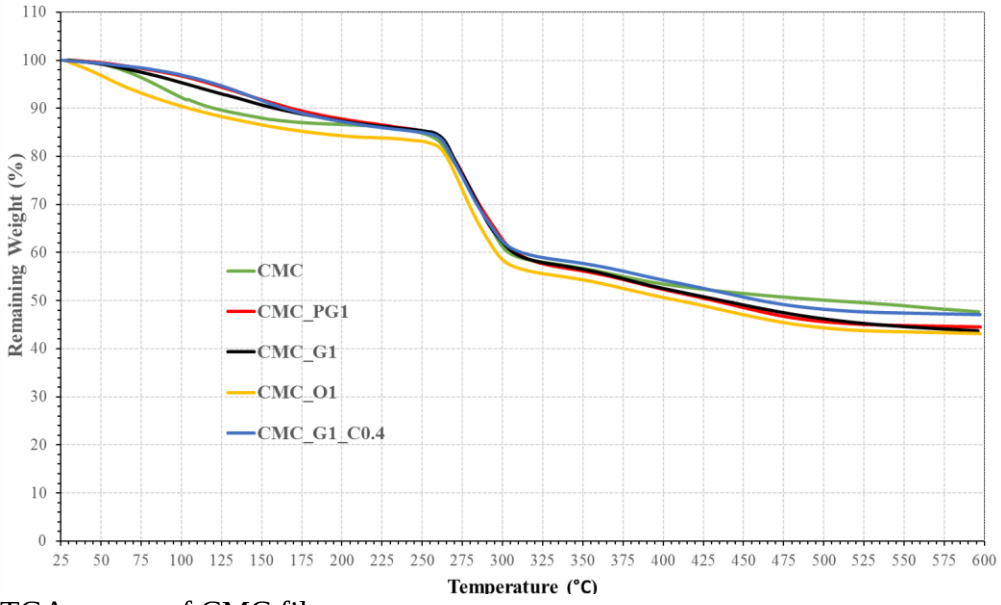


Figure 8. TGA curves of CMC films

LDPE has a remarkable resistance to heat. Up to 400 °C, there is a slight weight loss. Then, the weight is sharply decreased. The degradation is completed at 500 °C with no ash remain.

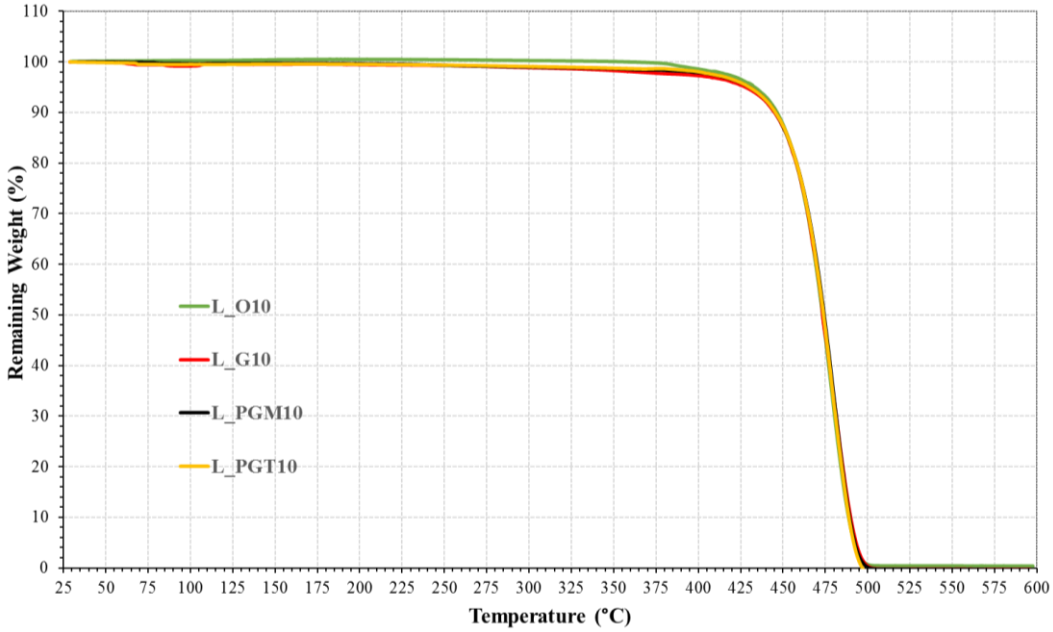


Figure 9. TGA curves of LDPE films

For the biodegradation process of LDPE/PCL composites, for each month, optical microscope images and the weight and film thickness changes are given in Table 1, Table 2, Table 3 and Table 4 for GMO and oleic acid addition. The structure changes with time can be seen.

Table 1. OM images of LDPE/PCL composite films with glycerol monooleate

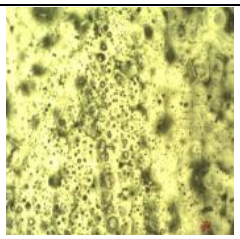
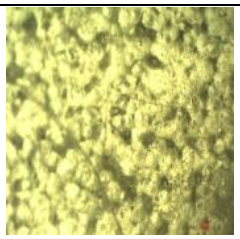
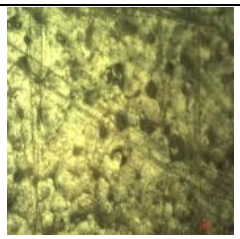
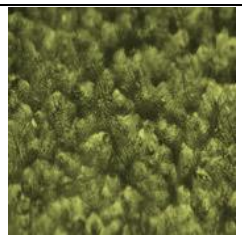
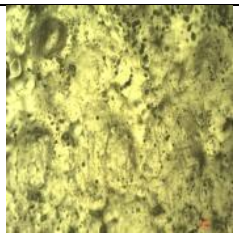
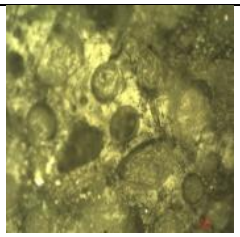
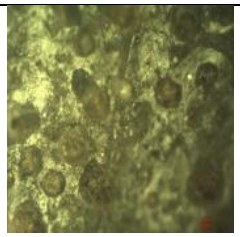
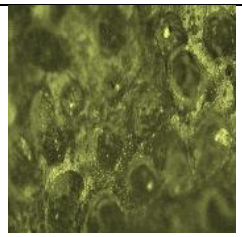
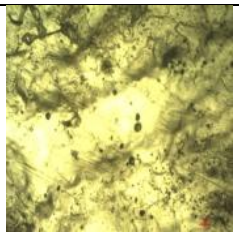
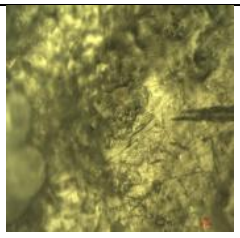
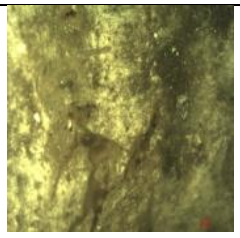
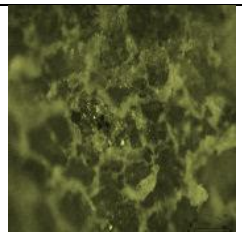
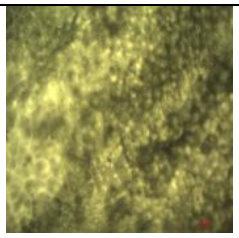
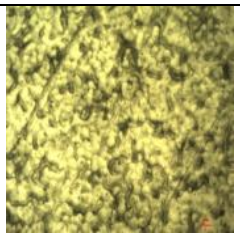
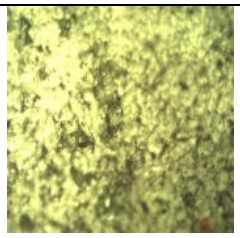
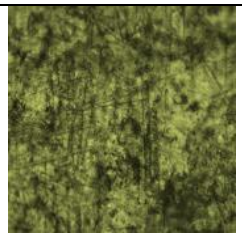
FILM	Optical microscope images			
	Time passed (month)			
	0	4	10	14
L_P5_G10				
L_P20-G10				
L_P30-G10				
NEAT LDPE				

Table 2. Biodegradation results of LDPE/PCL with GMO

FILM	Film thickness (µm)/ Weight (g)/Weight loss (%)			
	Time passed (month)			
	0	5	10	14
L_P5_G10	135/0.045/0	152/0.043/4.4	131/0.04/11.1	128/0.041/8.9
L_P10_G10	154/0.052/0	168/0.049/5.8	153/0.046/11.5	162/0.044/15.4
L_P20_G10	136/0.045/0	151/0.042/6.7	127/0.039/13.3	143/0.038/15.6
L_P30_G10	173/0.065/0	197/0.062/4.6	166/0.053/18.5	176/0.051/21.5
NEAT LDPE	93/0.032/0	112/0.031/3.1	78/0.03/6.3	87/0.028/12.5

Table 3. OM images of LDPE/PCL composite films with oleic acid

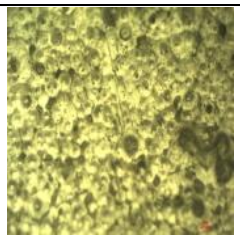
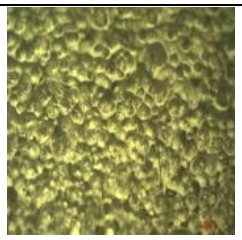
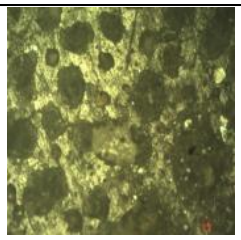
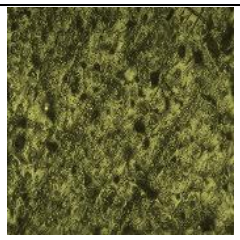
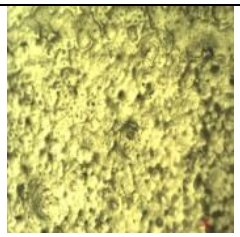
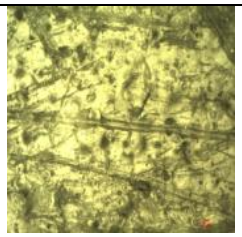
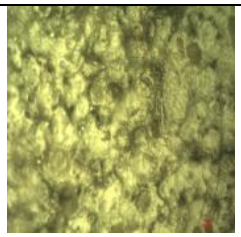
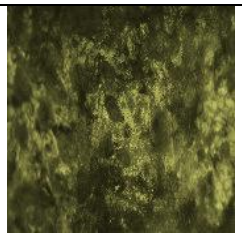
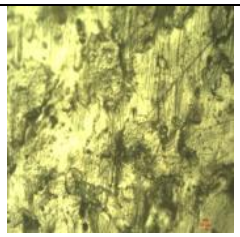
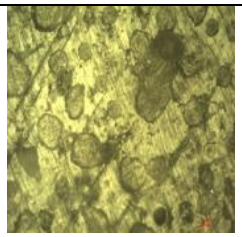
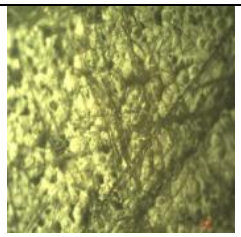
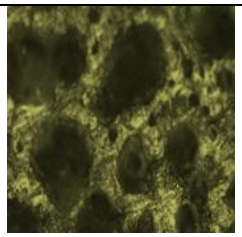
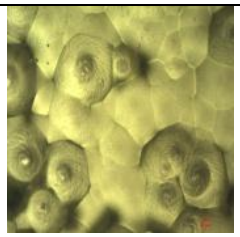
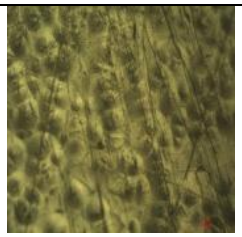
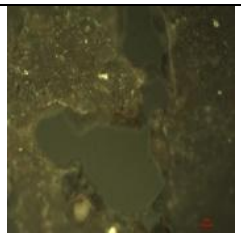
FILM	Optical microscope images			
	Time passed (month)			
	0	4	10	14
L_P5_O10				
L_P20-O10				
L_P30-O10				
NEAT PCL				Degraded

Table 5. Biodegradation results of LDPE/PCL with OA

FILM	Film thickness (µm)/ Weight (g)/Weight loss (%)			
	Time passed (month)			
	0	5	10	14
L_P5_O10	125/0.037/0	137/0.035/5.4	120/0.034/8.1	134/0.033/ 10.8
L_P10_O10	188/0.059/0	197/0.055/6.7	193/0.051/13.5	184/0.050/15.2
L_P20_O10	158/0.066/0	182/0.061/7.5	167/0.058/12.1	181/0.057/13.6
L_P30_O10	130/0.05/0	160/0.047/3.75	121/0.043/14.0	131/0.042/16.0
NEAT PCL	117/0.05/0	120/0.051/-0.02	101/0.044/12.0	- /0/100

L_P30_G10 film has the highest weight loss with 21.5% at the end of 14 months and neat PCL is fully degraded.

4.0 CONCLUSION

The production rate of petroleum based plastics and their use in different commercial applications poses a danger for the environment. Biopolymers can be the answer because of their renewable and abundant nature. CMC is one of the biopolymer derived from cellulose. CMC has advantages due to its biodegradability but it has poor mechanical properties. In this study, CMC films were prepared by using different plasticizers and additives. CMC is very weak behaviour. Using different types of plasticizer, the structure was gained strength and elasticity. CMC with PG (Merck) 1% is much stronger and elastic than others.

The other aim was to enhance LDPE biodegradation property by addition of PCL. Three different plasticizers (polyethylene glycol, glycerol monooleate, oleic acid) have been used for the incompatibility between two different plastics and additives in different amounts (organo nanoclay, maleic anhydride, dicumyl peroxide) to improve film properties. Biodegradation behaviour of LDPE/PCL composites was investigated. The amounts of PCL addition were 0, 5, 10, 20 and 30%. There were two main groups with GMO and with OA. In biodegradation results, PCL was completely degraded. L_P30_010 and L_P30_G10 films reached 16% and 21.5% weight loss, respectively in 14 months.

Acknowledgements: This study is supported by TÜBİTAK 2209/A and BAP 16-MÜH-127.

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YÜKSEK YOĞUNLUKLU POLİETİLEN-HİDROKSİAPATİT (YYPE-HA) NANOKOMPOZİT SİSTEMLERİNİN HAZIRLANMASI VE KARAKTERİZASYONU

PREPARATION AND CHARACTERIZATION OF HIGH DENSITY POLYETHYLENE – HYDROXYAPATITE (HDPE- HA) NANOCOMPOSITE SYSTEMS

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Özet

İnsanların daha iyi bir yaşam sürebilmesi için yüzyıllardır implant malzeme geliştirilmeye önem verilmiştir. İmplant malzeme olarak metal, seramik, polimer ve kompozit malzemeler yaygın olarak kullanılmaktadır. Polimerler hazırlama, kullanım ve işleme kolaylığı, malzeme çeşitliliği vb. nedenleri ile sıklıkla tercih edilmektedir. Polimerlerin bu gibi avantajlarına rağmen implant malzemelerin doğasıyla uyumlu hale getirilebilmesi için geliştirilmesine ihtiyaç duyulmaktadır. Bu yüzden organik kısmı polimerler ve inorganik kısmı hidroksiapatitden oluşan kompozit karışımların hazırlanması son yıllarda önem kazanmıştır. Hidroksiapatit kemiğin ana bileşiminde olması ve yüzeyin gözenekliliğinin kemik büyümesine ortam sağlaması nedeni ile önemli avantajlar sağlamaktadır. Kompozitlerdeki dolgu malzemelerinin kompozit ara yüzeyine uyumluluğunu geliştirmek için uyumlaştırıcılar kullanılmaktadır. Bunların yanında nano katkıların kullanılması da diğer katkılara göre daha geniş yüzey alanı ve daha iyi dağılım sağladığı için polimerlerin mekanik özelliklerinin iyileştirilmesinde daha etkin olmaktadır. Bu malzemelerin fiziksel olarak da uyumlu olabilmesi için dayanıklılığının ve yapısal özelliklerinin geliştirilmesi gerekmektedir. Malzemenin bulunduğu çevre ile benzer gözeneklilikte ve yapısal özelliklerde olması da hedeflenmektedir. Ayrıca implant malzemelerin aşınması nedeniyle vücutta oluşacak toksikolojik etki gösterebilen atıklar da önemli bir sorundur. Bu atıkların zararlı etkilerinin kontrol edilmesi gerekmektedir. Bundan dolayı dayanıklı, biyo-uyumlu, bulunduğu çevreye benzer ve zararsız yeni implant malzemelerin geliştirilmesi büyük önem taşımaktadır.

Bu çalışmada çene ve kafatası cerrahisinde ticari olarak kullanılan Ultra Yüksek Molekül Ağırlığına sahip (UHMWPE) yerine kullanılabilecek yeni bir implant malzemenin hazırlanmasına çalışılmıştır. Ticari implant malzemelerin kimyasal yapısı ve eriyik akış değerleri incelenerek yüksek yoğunluklu polietilenle (YYPE) çalışılmasına karar verilmiştir. Kompozit malzeme elde etmek için hidroksipatitin (HA) ve yüksek yoğunluklu polietilenin (YYPE) farklı formülasyonlarda karıştırılması ile hazırlanan karışımlar kimyasal ve mekanik yöntemle karakterize edilmiştir. Karışımın uyumluluğunu ve mekanik dayanımını arttırmak için maleik anhidrit aşılanmış yüksek yoğunluklu polietilen hidroksiapatit kompozit sistemler hazırlanmıştır. Yüksek yoğunluklu polietilen ve hidroksiapatit kompozit sistemine poli(hedral oligomerik silseskioksan) (POSS) eklenerek kompozit sistemin hem mekanik dayanımının hem de organik-inorganik bileşenler arasındaki uyumluluğunun arttırılması hedeflenmiştir. Yapılan deneysel çalışmalar sonunda maleik andihrit aşılanmış YYPE ve HA kullanılarak hazırlanan kompozit sistemlerin mekanik özelliklerinin ticari UHMWPE esaslı implantların özelliklerine yakın olduğu görülmüştür. Hazırlanan malzemelerin vücutta uyumluluğu sitotoksite deneyleriyle incelenmiştir. Sonuç olarak mikro ve nanoboyuta sahip HA kullanılarak hazırlanan YYPE-g-MA+HA kompozitlerinin toksik özelliliğinin olmadığı tespit edilmiştir. Hazırlanan kompozit sistemlerin gelecekte kemik doku mühendisliğinde kullanım alanı bulabilecek potansiyel malzemeler olduğu sonucuna varılmıştır.

Abstract

For centuries, importance has been given to the development of implant materials so that people can live a better life. Metal, ceramic, polymer and composite materials are widely used as implant materials. The use of polymers is often preferred due to some important advantages. As a polimeric biomaterials, total of 69 high-density porous polyethylene implants (Medpor® Biomaterial; Porex Surgical, Newman, GA) were used in forty patients (22 males, 18 females) by Angela Ridwan et al. [1]. Some of these advantages of polymers are useful, processable and variety of materials and etc.. Despite these advantages of polymers, there is a need to develop such materials in order to be compatible with the nature of the implant material. For this reason, it is important to prepare composite mixtures containing polymer as an organic part and hydroxyapatite as an inorganic part. Hydroxyapatite has significant advantages, that is in the basic composition of the bone and also ensures environmental compatibility in bone growth due to the surface porosity [2]. Hydroxyapatite materials are fragile and have low stiffness because they are in the class of ceramic materials. As a solution to this problem, the composite material can be prepared. There are studies in the literature where hydroxyapatite, which is an inorganic component in implant material designs, and polymer materials which are organic components are used. One of these is the article on the preparation of high-density polyethylene and hydroxyapatite in screw systems [3].

Compatibilizers are additives used in most reinforced filler composites, particularly those used to improve the compatibility at the composite interfaces, which are usually incompatible due to the non-polarity of polar matrix and the polar character of the filler. In the past decade, many chemicals have been evaluated and used as compatibilizers in polyethylene (PE)-based composites, including silanes, itaconic acid and graft copolymers of maleic anhydride and polyolefin. Among the above mentioned compatibilizers, polyethylene grafted maleic anhydride (PE-g-MAH) is the most widely used in various polymer composites, as well as polymer blends [4]. Moreover, the use of nano additives is more effective in improving the mechanical properties of polymers, because it provides a wider surface area and better distribution than other additives. Interest in studies of nanocomposite materials made with polyhedral oligomeric silsesquioxane has started to increase day by day. In order for these materials to be physically compatible, it is necessary to improve their mechanical and structural properties. The structure of materials are also aimed to have similar porosity and structural characteristics with the environment in which the material is. It is also required to have similar porosity and structural characteristics to the environment in which the material is located. However, the toxic waste that form on the body causes serious problems due to wear of the implant material. The side effects of these wastes should be controlled. For this reason, the development of new implant materials that are mechanically durable, biocompatible, environmentally similar to the material and harmless is of great importance.

In this study, the chemical structure and melt flow values of commercially implants in jaw and skull surgeons were examined and then it was decided to study with high density polyethylene. Hydroxypatite and high density polyethylene were mixed in different formulations and the prepared mixtures were characterized by chemical and mechanical methods to prepare composite material. In order to increase the compatibility and mechanical strength of the mixture, high density polyethylene grafted with maleic anhydride-hydroxyapatite composite systems were prepared. It is aimed to increase both the mechanical strength and the compatibility between the organic-inorganic composite systems by adding poly (hedral oligomeric silsesquioxane) to high density polyethylene and hydroxyapatite composite systems. At the end of the experimental studies, it was found that the mechanical properties of the composite systems prepared using high density polyethylene grafted maleic anhydride-hydroxyapatite are close to those of commercial Ultra High Molecular Weight Polyethylene (UHMWPE) used implants.

The body compatibility of these prepared materials was examined by cytotoxicity tests. As a result, it was determined that the toxic effects of high density polyethylene grafted with maleic anhydride composites by adding micro and nanosize hydroxyapatite have not been observed. It has been concluded that these prepared composite systems are potentially useful materials in bone tissue engineering for the future.

Giriş

İmplant hasarlı veya iş göremez durumda olan doku veya organın fonksiyon ve görünüşünü kazandırmak için kullanılabilecek olan malzemelerdir. İmplant malzeme tasarımında kullanılacak ürünlerde istenilen bazı temel özellikler bulunmaktadır. İdeal implant malzeme biyo-uyumlu, kolay şekillendirilebilir ve dayanıklı olmalıdır. Gelişen teknoloji ile birlikte implant malzemelerin her türlü ihtiyaca cevap verebilmesi için litaratürde çok sayıda çalışma yapılmıştır ve polietilen malzemeler yüksek mekanik özelliklerinden dolayı implant malzemelerde kullanımı tercih edilmektedir. Angela Ridwan-Pramana ve arkadaşları yaptığı çalışma ile gözenekli polietilenin implant malzeme olarak kullanımını incelemiştir [1]. Hidroksiapatit ve trikalsiyum fosfat, kemik ve dişin yapısında bulunan bir bileşendir ve hücre tutunmasını (adhezyon) teşvik etmektedir [2]. Hidroksiapatit malzemeler seramik malzemeler sınıfında olduğu için kırılgandır ve düşük dayanıma sahiptir. Bu da malzemenin diğer malzemelerle kompozit yapılma ihtiyacını doğurmaktadır. Literatürde implant malzeme tasarımlarında inorganik bileşen olan hidroksiapatit ve organik bileşen olan polimer malzemelerin kullanıldığı çalışmalar vardır. Bunlardan biri yüksek yoğunluklu polietilen ve hidroksiapatit ile vida sistemlerinin hazırlanması konusunda yapılan çalışmadır[3]. Polar bileşenlerin polar olmayan doldurucu malzemeler ile kullanımında kompozit arayüzeyine uyumluluğunu geliştirmek için polar karakteristiklere sahip uyumlaştırıcı malzemelerin kullanılması gerekmektedir. Uyumlaştırıcı olarak kullanılan kimyasallardan bazıları polietilen ile yapılan ve silanlarıda kapsayan kompozitler, itakonik asit, maleik anhidrit ve poliolefin aşılanmış kopolimerlerdir [4]. Bahsedilen uyumlaştırıcılar arasında en yaygın kullanılanı polietilen-aşılanmış maleik anhidrit'tir. Maleik anhidrit-aşılanmış polietilen mekanik özellikleri geliştirirken, maleik anhidrit HA gibi seramik doldurucuların polar doğasıyla uyumlaştırılır. Polimer matrisi nano ya da mikro seviyede polimerik nanokompozitlerle de kuvvetlendirilebilmektedir. Polihedral oligomerik silseskioksan ile yapılan nanokompozit malzemelerle yapılan çalışmalara ilgi gün geçtikçe artmaya başlamıştır. POSS molekülünde Si moleküllerine farklı fonksiyonel ya da fonksiyonel olmayan organik gruplar eklemek mümkündür. Böylece POSS molekülü, kopolimerizasyon, yapışma (adhezyon), ışık duyarlılığı, bağlama katalizörü türleri ve organik çözücülerde geliştirilmiş çözünürlük için sentetik olarak modifiye edilebilir. POSS kafeslerinin polimerik malzemelerle kullanılması; kullanım sıcaklığında artış gibi termal kararlılık, oksidatif dayanım ve yüzey sertleşmesi gibi geliştirilmiş mekanik özelliklerin yanı sıra yanıcılık ve ısı değişiminde azalma gibi polimer özelliklerde önemli gelişmelere neden olabilmektedir [5]. Araştırmacılar malzemenin kullanım yerine uygun özellikleri taşıyan ve ticari olarak kullanılanlara alternatif yenilikçi malzemelerin geliştirilmesine çalışmaktadır. Aynı zamanda bu malzemelerin fiziksel olarak da uyumlu olabilmesi için dayanıklılığının ve yapısal özelliklerinin geliştirilmesi gerekmektedir. Malzemenin bulunduğu çevre ile benzer gözeneklilikte ve yapısal karakteristikte (mekanik dayanım vs.) olması da hedeflenmektedir. Bunların yanında implant malzemelerin aşınması nedeniyle vücutta oluşacak toksikolojik atıklar da önemli bir sorundur. Bu atıkların zararlı etkilerinin çeşitli biyolojik testler ile kontrol edilmesi gerekmektedir. Bundan dolayı dayanıklı, biyo-uyumlu, bulunduğu çevreye benzer ve zararsız yeni implant malzemelerin geliştirilmesi büyük önem taşımaktadır. Yapılacak araştırmalar sayesinde elde edilecek olan yeni malzemelerin, implantların kullanım alanlarını genişleteceği ve yeni ticari uygulama alanları ortaya çıkaracağı düşünülmektedir.

Deneysel Teknikler

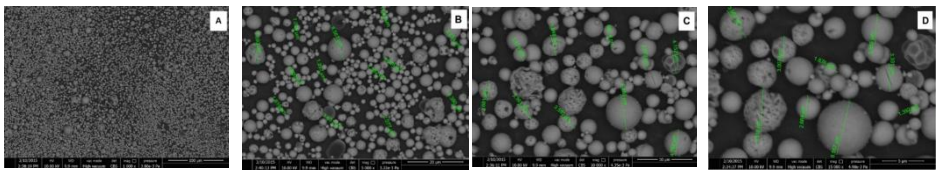
Çalışmada farklı yoğunluklara sahip polietilenler arasından YYPE kullanılmıştır. YYPE, PETKİM firmasından temin edilmiş olup, 0,25-0,45 (g/10 dak.) eriyik akış hızına (ASTM D1238, 2160 g, 190ºC), ve 0,959-0,963 g/cm^3 yoğunluğa (ASTM D1505, 23ºC) sahiptir. Kompozit hazırlamada kullanılan poli(hedral oligomerik silseskioksan)'lar (Aminopropil İzobütil POSS, Metakril POSS, İzooktil POSS) Hybrid Plastics firmasından ve maleik anhidrit Merck firmasından temin edilmiştir. Deneylerde iki farklı

hidroksiapatit kullanılmış olup, HA1 kalsiyum hidroksiapatit, polidisperse medikal grade olup HKPB Biomaterials Ltd T/A Premier Biomaterials firmasından temin edilmiştir, ikinci hidroksiapatit (HA2) araştırma laboratuvarlarında kimyasal çöktürme metoduyla sentezlenmiştir [6].

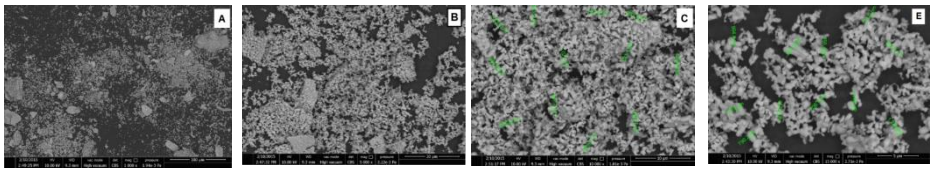
YYPE granülleri kullanarak polimer/HA ikili karışımları kütlece farklı oranlarda tork reometre cihazı ile hazırlanmıştır. (Thermo Scientific Measuring Mixer and Extruder System, Haake Polylab OS). Her örnek 190 ^{o}C sıcaklıkta, 50 rpm hızında, 15 dakika karıştırılarak hazırlanmıştır. Örnekler Brabender marka, polystat 200 T model ısıtıcı tablanın iki plakası arasında 2 dakika süre ile 190 °C'de 150 bar basınç uygulanarak film haline getirilmiştir. Film haline getirilen örnekler ASTM D638 standardına göre uygun olarak kemik şeklinde kesilerek çekme-uzama testleri için kullanılmıştır. Mekanik testler 500 mm/dak. çekme hızıyla Zwick Z010 Evrensel test cihazı kullanılarak gerçekleştirilmiştir. Çalışma kapsamında üretilen malzemelerin sitotoksitite analizi L929 fare fibroblast hücreleri ile (NCTC clone 929, ATTC) gerçekleştirilmiştir.

Sonuçlar ve Tartışma

Kompozit sistemlerin hazırlanmasında kullanılan hidroksiapatitlerin özellikleri incelendiğinde HA1 olarak isimlendirilen hidroksiapatitin tanecik boyutunun 2-5 µm (**Şekil 1**) aralığında çoğunlukla homojen görünümde küresel parçacıklardan, HA2 tanecikleri incelendiğinde tanecik boyutunun 600-700 nm (**Şekil 2**) aralığında çoğunlukla homojen görünümde kümelenmiş ince taneli çubuk benzeri parçacıklardan oluştuğu gözlenmiştir. HA1 ve HA2'in atomik yüzdesi incelendiğinde Ca/P oranlarının birbirine yakın olduğu, hem atomik hem de ağırlıkça yüzde Ca/P değerlerinin teorik HA değerine (1,67) yakın olduğu görülmüştür. Kafatası ve çene kemiği restorasyonunda kullanılan ticari implant malzemeler geri mühendislik çalışması ile incelenmiş temel polimerik yapının UHMWPE olduğu tespit edilmiştir.



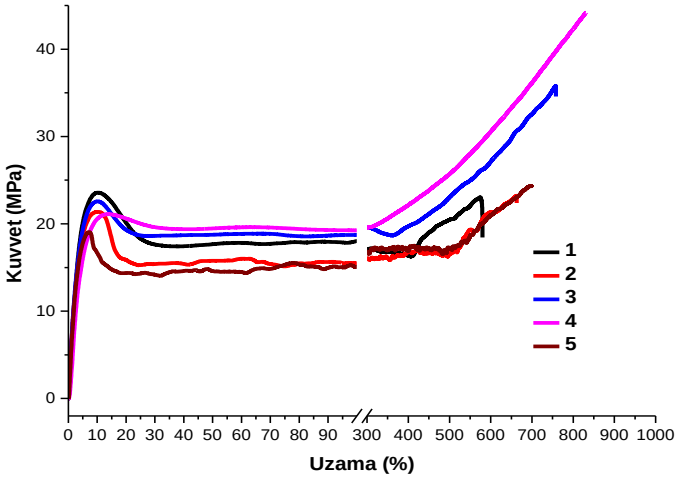
Şekil 1. HA1 örneklerinin 1 kX (A) , 5 kX (B) , 10 kX (C) ve 15 kX (D) farklı büyütmelerdeki SEM görüntüleri



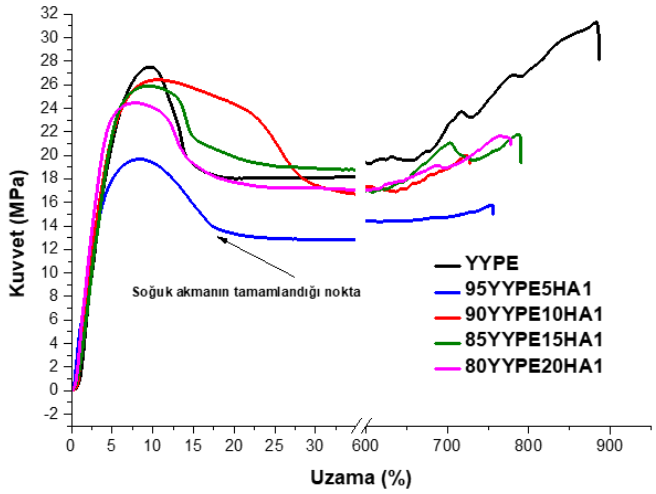
Şekil 2. HA2 örneklerinin 1 kX(A), 5 kX(B), 10 kX(C) ve 15 kX(D,E) farklı büyütmelerdeki SEM görüntüleri

Ticari implantların eriyik akış indeks ve mekanik test sonuçları değerlendirilerek, UHMWPE yerine YYPE kullanılarak bu ürünlerin yerine geçilebilecek sistemler hazırlanmaya çalışılmıştır. Ticari implant malzemelerin mekanik özellikleri incelendiğinde, elastik modülüs 6 MPa civarında kopmadaki kuvvet 22 MPa civarında, kopmadaki % uzama 700 civarında olduğu bulunmuştur **(Şekil 3)**. Kompozit sistemlerin hazırlanması için karıştırma süresi Thermo Haake Tork Reometre ile belirlenmiştir. Homojen karışımın HA eklendikten sonra yaklaşık 10 dak. içinde gerçekleştiği gözlemlenmiştir. YYPE+HA kompozit sistemlerinde nano boyuta sahip hidroksiapatit(HA2) için mekanik özelikler incelendiğinde HA2'nin PE'nin kırılganlığını arttırdığı görülmüştür. % uzama değerlerinde ise azalma görülmüştür. Mikro yapıya sahip HA1 ile hazırlanan karışımlarda termoplastik karakter korunurken (**Şekil 4**), nano boyuta sahip HA2 ile hazırlanan karışımlar termoplastik karakterini yitirmiştir (**Şekil 5**). YYPE+HA kompozitlerinde eriyik akış indeksleri incelendiğinde mikro boyuta sahip HA1 oranının artmasıyla yoğunluğun arttığı ve eriyik

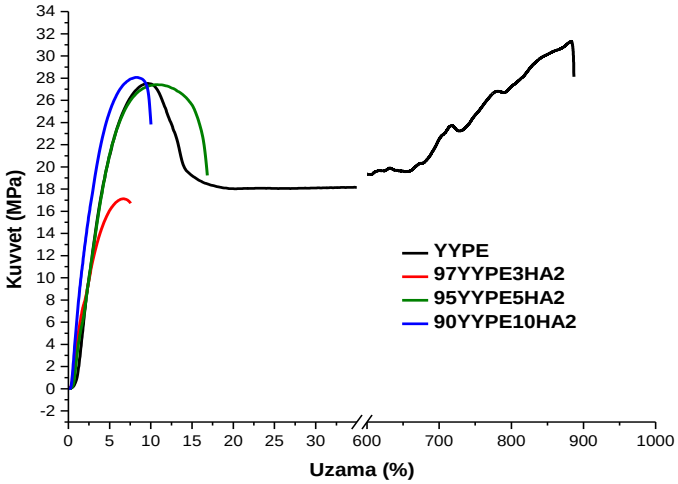
akış indeksinin azalması gözlenirken, nano boyuta sahip HA2 ile hazırlanan karışımlarda hiçbir akış gözlenmemiştir. YYPE'e aşılanmanın etkisi incelendiğinde YYPE-g-MA ile hazırlanan kompozit karışımlarda kopmadaki kuvvet, akmanın başladığı ve akmanın tamamlandığı kuvvet değerlerinde artış gözlenmiştir (**Şekil 6**). YYPE-g-MA+HA1 kompozitlerde akma noktasındaki kuvvet değeri ve kopma mukavemet değerlerinde aşılanmamış haline göre daha yüksek değerler elde edilmiştir. Aynı zamanda YYPE-g-MA+HA1 kopmadaki uzama değerleri, kopmadaki kuvvet ve modülüs değeri ticari implantlardan hala yüksek olduğu görülmüştür (**Şekil 6**). YYPE-g-MA+HA2 ile hazırlanan karışımlarda malzeme HA katılmamış haline göre daha fazla kırılgan özellik göstermiş, % uzama değerlerinde düşüş gözlenmiştir (**Şekil 7**).



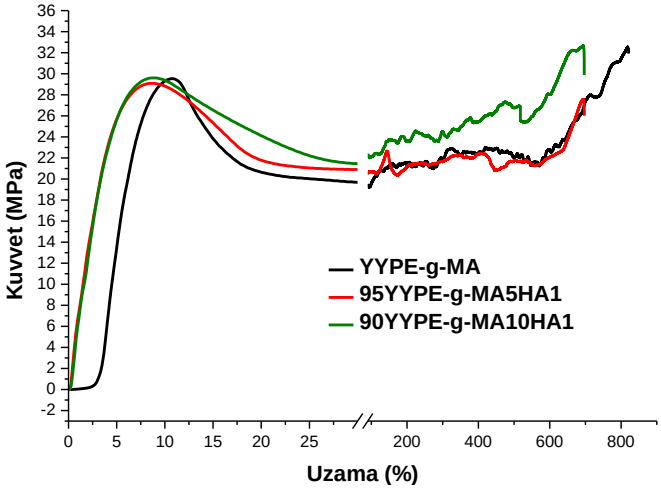
Şekil 3. Kafatası ve çene kemiği restorasyonunda kullanılan ticari implant malzemelerin kuvvet-uzama grafikleri



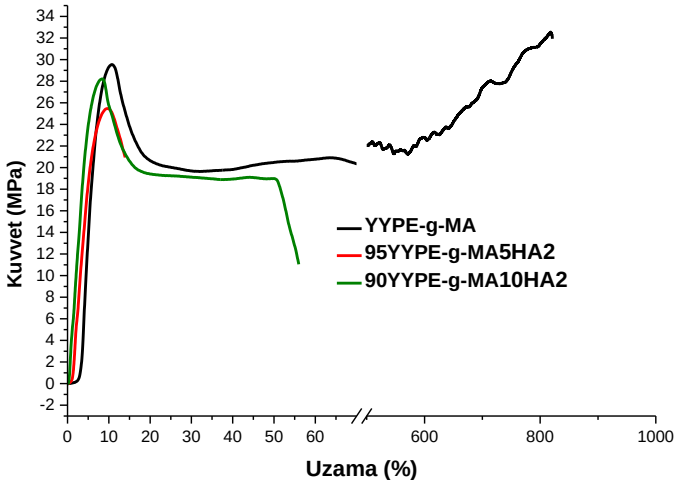
Şekil 4. YYPE ve YYPE+HA1 karışımlarının kuvvet uzama eğrileri



Şekil 5. YYPE ve YYPE+HA2 karışımlarının kuvvet uzama eğrileri



Şekil 6. YYPE-g-MA ve değişik oranlarda HA1 kullanılarak hazırlanan kompozitlerin kuvvet uzama eğrileri



Şekil 7. YYPE-g-MA ve değişik oranlarda HA2 kullanılarak hazırlanan kompozitlerin kuvvet uzama eğrileri

Hazırlanan tüm karışımlar için kopmadaki uzama, kopma dayanımı ve modülüs değerleri **Tablo 1**'de verilmiştir. POSS'un kompozit yapı üzerinde etkisinin incelenmesi amacıyla YYPE-POSS ve YYPE-POSS-HA karışımları hazırlamıştır.

Tablo 1. YYPE ve YYPE-g-MA kompozitlerinin mekanik test sonuçları

Örnek Adı	Elastik Modülüs(MPa)	Kopmadaki Kuvvet (MPa)	Kopmadaki % Uzama
YYPE	6,41	27,5	889
95YYPE5HA1	4,09	19,8	758
90YYPE10HA1	5,44	26,4	729
85YYPE15HA1	5,86	25,9	792
80YYPE20HA1	6,22	24,4	778
97YYPE3HA2	3,51	17,2	16,7
95YYPE5HA2	6,41	27,5	19,1
90YYPE10HA2	7,72	28,8	23,6
YYPE-g-MA	6,21	29,4	821
95YYPE-g-MA5HA1	8,59	28,9	696,4
95YYPE-g-MA10HA1	8,57	29,6	696,8
95YYPE-g-MA5HA2	6,25	25,3	14,3
90YYPE-g-MA10HA2	6,81	28,2	56,1

YYPE-POSS karışımları incelendiğinde, iPOSS daha hidrofobik yapıya sahip olduğu ve PE ile daha fazla yapısal benzerlik gösterdiği için termoplastik özellik korunmakta iken APOSS ve MPOSS'da amin grubu ve metakril grubu gibi polar grupların olması uyumluluğu azaltarak YYPE'nin mekanik dayanıklılığının (toughness) azalmasına neden olmaktadır. Maksimum kuvvet değeri çok değişmemesine ve modülüs değeri bir miktar artmasına rağmen kopmadaki uzama değerinin % 10'lar civarına düşmesi mekanik dayanımın düşmesinin asıl nedenidir. YYPE-POSS+HA karışımları incelendiğinde, dolgu maddelerinin YYPE'nin elastik modülüs değerini arttırdığı maksimum kuvvet değerini ve kopmadaki uzama değerini

azalttığı için mekanik dayanımını kötüleştirdiği tespit edilmiştir. Bunun en önemli nedeni kimyasal yapı itibariyle YYPE ile hem POSS hem de HA'in uyumlu olmamasından kaynaklanmaktadır. Bu katkılarla YYPE'nin uyumlu hale getirilmesi amacıyla çalışmanın son aşamasında MA ile aşılanmış YYPE ve HA+ POSS kullanılarak YYPE-g-MA+HA+POSS karışımları hazırlanmıştır. YYPE-g-MA+HA karışımlarına POSS sisteminin eklenmesinin sistemin uyumluğunu arttırmadığı aksine biraz daha bozduğu görülmüştür. YYPE-g-MA+HA+POSS karışımları ile kafatası ve çene cerrahisinde kullanılan ticari malzemelerin mekanik özelliklerine ulaşılamamıştır. Kompozit yapıda POSS kullanılmasının bir avantaj olmadığı tespit edilmiştir. Bu aşamaya kadar yapılan çalışmalar sonunda yurt dışı kaynaklı ticari implant malzemelerin mekanik özelliklerinden daha yüksek özelliklere YYPE-g-MA+HA sistemleri ile yakalandığı için bu malzemenin implant olarak kullanılması durumunda herhangi bir toksik etkisinin olup olmadığı sitotoksitite çalışmaları ile araştırılmıştır. İki malzeme türü için de malzeme konsantrasyonunun azalmasına bağlı olarak artan hücre canlılığı dikkat çekicidir. Her iki grup malzeme için canlılığın %70'in üzerinde bulunması malzemenin sitotoksik olmadığını ifade etse de malzeme üretiminden gelen safsızlıkların hücre canlılığını etkilediği kanaatine varılmıştır. Sonuç olarak 90YYPE-g-MA10HA1 ve 90YYPE-g-MA10HA2 karışımının toksik olmadığı tespit edilmiştir. Malzemeler sitotoksik olmadığı için kemik doku mühendisliğine yönelik in- vitro çalışmalara uygun olduğu anlaşılmıştır.
İmplant malzemelerde sıklıkla kullanılan UHMWPE yerine, ticari olarak daha kolay temin edilebilen YYPE-g-MA'den ekonomik, dayanıklı ve sağlığa nispeten zararsız bir kompozit malzeme elde edilmiştir. İleride yapılacak çalışmalarla bu kompozit karışımları fare pre-osteoblast hücreleri ile kullanılarak kemik doku mühendisliğinde kullanım potansiyeli de araştırılacaktır.

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KOLEMANİT/POLİPROPİLEN KOMPOZİTLERİN TERMAL DEKOMPOZİSYON KİNETİĞİNİN İNCELENMESİ: TERMOGRAVİMETRİK ANALİZ İLE AKTİVASYON ENERJİSİNİN HESAPLANMASI

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Özet

Cam, seramik ve kimya endüstrilerinde uygulama alanı olan bor bileşiği kolemanit ($2CaO.3B_2O_3.5H_2O$) bileşimindeki 5 mol kimyasal su ile polimer kompozit uygulamalarında termal dayanım arttırıcı katkı malzemesi olarak kullanılmaktadır. Yapılan çalışmada, (ağırlıkça) %10, 20 ve 30 olmak üzere kolemanit/polipropilen kompozitler üç farklı katkı oranıyla üretilmiştir. Üretilen kompozitlerin termo-gravimetrik analizleri 5, 10 ve 15 °C/dk ısıtma hızlarında gerçekleştirilmiştir. Termo-gravimetrik veriler kolemanit/PP kompozitlerin termal degredasyon davranışlarının belirlenmesi amacıyla Kissinger (diferansiyel) ve Horowitz-Metzger (integral) metotlarından yararlanılarak aktivasyon enerjileri hesaplanmıştır. Kolemanit minerali, saf PP, %10 Kolemanit/PP, %20 Kolemanit/PP ve %30 Kolemanit/PP'nin Kissinger metoduyla elde edilen aktivasyon enerjileri sırasıyla 32,918 kJ/mol, 272,215 kJ/mol, 88,796 kJ/mol, 70,558 kJ/mol ve 57,916 kJ/mol ve Horowitz-Metzger Metoduyla ise 53,390 kJ/mol, 338,892 kJ/mol, 116,360 kJ/mol, 107,463 kJ/mol ve 83,841 kJ/mol olarak hesaplanmıştır. Sonuçlar genel olarak değerlendirildiğinde diferansiyel ve integral metodlardan elde edilen aktivasyon enerjisi değerleri arasında farklılıklar gözlemlenmektedir.
Anahtar kelimeler: kolemanit, polipropilen,termal degredasyon, aktivasyon enerjisi

Abstract

The boron compound, which is applied in glass, ceramics and chemical industries, is used as thermal strengthening additive material in polymer composite applications with 5 moles of chemical water in colemanite ($2CaO.3B_2O_3.5H_2O$) composition. In the present study, colemanite/polypropylene composites were produced with three different filler ratios 10%, 20% and 30% (weight). Thermo-gravimetric analyzes of the composites produced were carried out different heating rates of 5, 10 and 15 °C/min. Activation energies were calculated using the Kissinger differential method and the Horowitz-Metzger integral method. TGA curves were used in these calculations in order to determine thermal degradation behaviors of materials. The activation energies of ulexite mineral, neat polypropylene (PP), 10% colemanite/PP, 20% colemanite/PP and 30% colemanite/PP by Kissinger method were 32.918 kJ/mol, 272.215 kJ/mol, 88.796 kJ / mol, 70.558 kJ/mol and 57.916 kJ/mol, respectively, and based on Horowitz-Metzger Method, 53.390 kJ/mol, 338.892 kJ/mol, 116.360 kJ/mol, 107.463 kJ/mol and 83.841 kJ/mol, respectively. When the results are evaluated in general, there exist some differences between activation energy values obtained from differential and integral methods.
Keywords: colemanite, polypropylene, thermal degradation behavior, activation energy

Giriş

Polimer kompozitler evsel ve endüstriyel alanlarda uzun zamandır yaygın olarak kullanılmaktadır. Yapısal uygulamalar ve termal koruma gibi kullanım alanları için polimerlere birçok farklı katkı malzemesi eklenerek kompozit malzemeler geniş bir yelpaze de çevreci ve ekonomik şekilde üretilmektedir [1]. Polimer kompozitlerin termo-fiziksel ve termo-mekanik özellikleri hizmet ömrü boyunca kullanıldığı çevreden büyük ölçüde etkilenmektedir. Yapısının bozulmasında iki temel unsur ısı ve nemdir ve literatürde bu etkileri inceleyen çalışmalar mevcuttur. [2].
Malzemelere iletim, taşınım veya ışınımla önemli miktarda termal enerji depolandığında, termo-kimyasal ve/veya termo-mekanik yüzey aşınmaları oluşmaktadır ve bu aşınma mekanizmalarında malzeme kaybı artan sıcaklıkla gerçekleşmektedir. Malzemelerin maruz kaldığı bu enerjiler sonrasında yapısal performansının değerlendirilmesi oldukça önemlidir. Bununla birlikte, kompozit malzemeler yeteri kadar ısıya maruz kaldığında termal degredasyon davranışı sergilese de yüzey resesyonları oluşmayabilir. Özellikle termal uygulamalarda katkılanan bu malzemelerin ısı akısı karşısında davranışlarının ortaya konulması oldukça önemlidir ve bu gibi durumlarda termal degredasyon özelliklerini ortaya koyan matematiksel modellerden faydalanılmaktadır [2-4].
Polimer kompozitlerin ısıl davranışı iyileştirmek amacıyla birçok farklı inorganik malzeme katkı maddesi olarak kullanılmaktadır. Özellikle bu inorganiklerin bileşimindeki fiziksel ve kimyasal su içerikleri kompozitin termal davranışını değiştirmede önemli etkiye sahiptir. Kimyasal su içeriği yüksek kolemanit, üleksit ve tinkal gibi ülkemizin yeraltı zenginliklerinden olan bor bileşiklerinin polimer [5, 6], seramik [7, 8], cam [9, 10] ve kimya [11] endüstrilerinde çok önemli kullanım alanları bulunmaktadır. Polimer kompozit üretiminde ise polimer matrise özellikle alev geciktirme davranışının kazandırılması amacıyla bor bileşikleri kullanılmaktadır [12, 13]. Bu alanlarda 5 mol kristal su içeriğiyle kolemanit minerali ($2CaO.3B_2O_3.5H_2O$) kullanılan önemli kalsiyum-bor ticari minerali olarak dikkat çekmektedir.
Bu çalışmanın amacı, kolemanit ile katkılanmış PP kompozitlerin termal degredasyon davranışlarını termo-gravimetrik analiz ve kinetik modeller kullanarak araştırmaktır.

Teorik Yaklaşım ve Metotlar

Literatürde malzemelerin termal davranışlarını incelemek için diferansiyel ve integral olmak üzere iki farklı matematiksel metot ortaya konmuştur. Kinetik çalışmalar için kullanılan temel denklem (Denklem 1'de) verilmiştir.

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

Burada, k oran sabitini, f (α) reaksiyon modelini simgelemektedir. Denklem 1, oran sabitinin bir fonksiyonu olarak sabit sıcaklıkta dα/dt dönüşüm oranını ve t, zamanı ifade etmektedir. Ağırlık dönüşüm oranı α, malzeme kütlesi cinsinden Denklem 2 kullanılarak hesaplanabilmektedir.

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \tag{2}$$

Burada, w_0 başlangıç kütlesini, w_t anlık kütleyi ve w_f ise son kütleyi simgelemektedir. Oran sabiti k genellikle Arrhenius eşitliği (Denklem 3) ile birlikte verilmektedir.

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

Denklem 3'de yer alan A frekans faktörünü, E_a aktivasyon enerjisini (kJ/mol), R (8,314 J/ mol K) gaz sabitini ve T mutlak sıcaklığı simgelemektedir. Denklem 1 ve 3'ün kombinasyonu denklem 4'ü vermektedir:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (4)$$

Zaman skalasından sıcaklık skalasına geçiş yapmak için zincir kuralı kullanılarak lineer ısıtma oranları (β) ile birlikte Denklem 5'teki ifade yazılabilir. β ısıtma oranı zamana bağlı değişen sıcaklığı simgelemektedir.

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} = \beta\frac{d\alpha}{dT} \quad (5)$$

Denklem 4 ve 5'in kombinasyonundan Denklem 6 elde edilmektedir.

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (6)$$

Denklem 5 ve 6, analitik yöntemler için termogravimetrik verilere dayalı kinetik parametrelerin hesaplanmasında kullanılmaktadır. Kissinger diferansiyel metodu [14], kolay kullanıma sahip bir metot olması nedeniyle sıklıkla tercih edilmektedir ve genellikle farklı ısıtma oranlarında (β) aktivasyon enerjisinin tanımlanması için kullanılmaktadır. Horowitz-Metzger metodu [15] ise integral metodun bir türüdür. Bu metotta her bir β değeri için tek bir aktivasyon enerjisi hesaplanmaktadır. Her iki metodun temel denklemleri ve çıktıları Tablo 1'de verilmektedir.

Tablo 1 Aktivasyon enerjisinin değerlendirilmesinde kullanılan kinetik metotlar

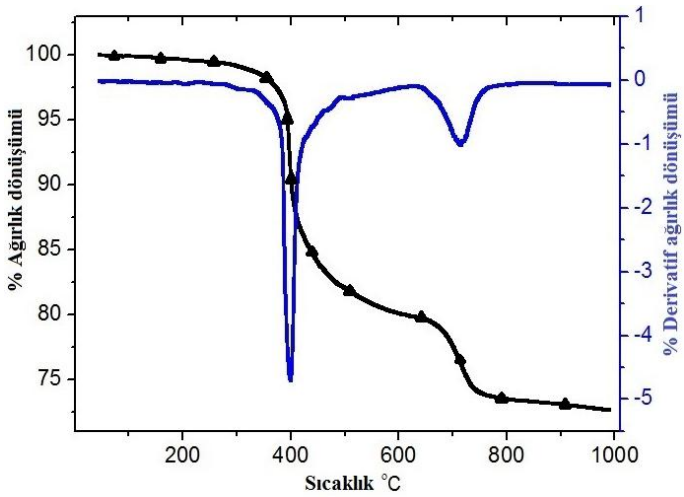
Methodlar	**Denklemler**	**Çıktılar**
Kissinger [14]	$ln\left(\frac{\beta}{T_m^2}\right) = ln\left(-\frac{AR}{E_a}f'(\alpha_m)\right) - \left(\frac{E_a}{RT_m}\right)$	$\ln(\beta/T^2)$-1/T
Horowitz-Metzger [15]	$ln\left(\frac{1-(1-\alpha)^{1-n}}{1-n}\right) = ln\left(\frac{ART_s^2}{\beta E_a}\right) - \frac{E_a}{RT_s} + \frac{E_a\theta}{RT_s^2}$	$\ln(\ln(1/1-\alpha))$-θ

Malzemeler-Metotlar

Yapılan çalışmada matris malzemesi olarak tarafından erime akış hızı 4,5 g /10 dk, erime noktası 163 °C ve yoğunluğu 0,905 g/cm^3 (23 °C'de) olan granül formundaki polipropilen PETKIM Petrol Endüstrisi (İzmir, Türkiye)'den tedarik edilmiştir. Dolgu malzemesi olarak kullanılan 45µm altı parçacık boyutuna sahip kolemanit minerali Eti Madenleri (Batı Anadolu Bölgesi, Türkiye)'den tedarik edilmiştir. Kompozit karışımları ağırlıkça %0-30 oranında kolemanit dolgu maddesi ile herhangi bir uyumlaştırıcı ajan kullanılmadan hazırlanmıştır. Kompozit numunelerin üretimi yüksek hızlı termo-kinetik karıştırıcı ve kalıplama sistemleri kullanılarak gerçekleştirilmiştir. Kolemanit/PP kompozitlerin termo-gravimetrik analizleri üç farklı ısıtma oranı (5, 10 ve 15 °C/dk) için gerçekleştirilmiştir.

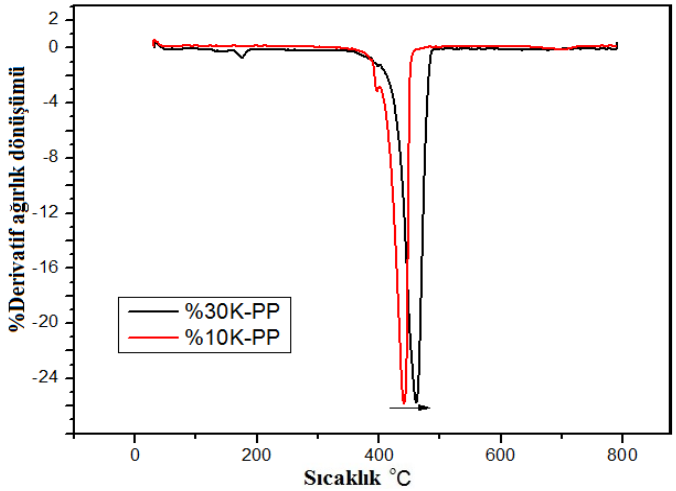
Sonuçlar ve Yorumlar

Çalışma kapsamında, farklı ısıtma oranlarında termogravimetrik analizler yapılmış ve kinetik modellere yer verilerek kolemanit ve kolemanit/PP kompozitlerin aktivasyon enerji değerleri ortaya konmuştur.
Kolemanit mineraline ait termogravimetrik analiz sonucu, 10 °C/dk ısıtma oranında yüzde ağırlık dönüşümü ve derivatif ağırlık dönüşümü eğrileri Şekil 1'de sunulmuştur.



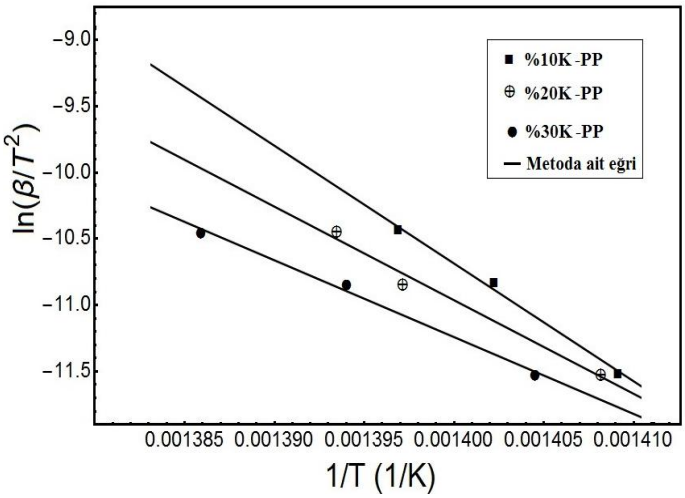
Şekil 1 Kolemanit mineraline ait % ağırlık dönüşümü-derivatif ağırlık dönüşümü eğrisi

Kolemanit minerali için degredasyonun gerçekleştiği ilk aşama 336,8-493,7 °C aralığında gerçekleşirken, ikinci aşamada ise daha geniş dağılımlı 639,40-763,748 °C aralığında gerçekleştiği görülmektedir. Kompozitlere ait termo-gravimetrik değişim, Şekil 2'de sıcaklık-% derivatif ağırlık dönüşümü yardımıyla gösterilmiştir. Artan katkı oranlarının, kompozitlerin termal degredasyon sıcaklıklarına etki ettiği gözlemlenmektedir.



Şekil 2 Kolemanit katkılı PP kompozitlerin sıcaklık-% derivatif ağırlık dönüşümü (K:Kolemanit)

Kolomanit/PP kompozitlerin termogravimetrik analiz eğrilerinden yararlanılarak Şekil 3'te verilen kinetik parametreler Kissinger metodu kullanılarak hesaplanmıştır.



Şekil 3 Kolemanit/PP kompozitlere ait Kissinger metot sonuçları (K: Kolemanit)

Kissinger diferansiyel metoduyla elde edilen ortalama aktivasyon enerji değerleri her malzeme için Tablo 2'de gösterilmektedir. Şekil 3'de gözlemlendiği üzere, korelasyon katsayılarının her kompozit için -1'e çok yakın olduğu görüldüğünden hesaplanan aktivasyon enerji değerlerinin anlamlı olduğu düşünülmektedir. Her üç katkı oranı için elde edilen deneysel verilerin Kissinger metot tahminleriyle yüksek derecede (R^2>96) uyum gösterdiği gözlemlenmiştir. Aktivasyon enerji değerlerinin şiddetli bir biçimde sapma göstermediği hem Şekil 3'deki grafiğe ait eğimlerden hem de Tablo 2 de hesaplanan değerlerden gözlemlenebilmektedir.

Tablo 2 Kissinger metoduyla hesaplanmış aktivasyon enerjisi değerleri

Malzeme	**E_a (kJ/mol)**
Kolemanit	32,918
%10Kolemanit-PP	88,796
%20Kolemanit-PP	70,558
%30Kolemanit-PP	57,916
Saf PP	272,215

Horowitz-Metzger'in integral metodu kinetik parametrelerin belirlenmesi için uygulanmıştır. Tüm ısıtma oranları için elde edilen aktivasyon enerjilerini hesaplamak mümkündür. Tablo 3'de farklı ısıtma oranlarından elde edilen aktivasyon enerjilerinin ortalama değerleri özetlenmiştir.

Tablo 3 Horowitz-Metzger metoduyla hesaplanmış ortalama aktivasyon enerji değerleri

Malzeme	**Ortalama E_a (kJ/mol)**
Kolemanit	53,390
%10Kolemanit-PP	116,360
%20Kolemanit-PP	107,463
%30Kolemanit-PP	83,841
Saf PP	338,892

Çalışma kapsamında, PP matris içerisine katkılanan kolemanitin termal degredasyon üzerine etkisi analiz edilmiştir. Sıcaklık değişimine bağlı olarak kompozitlerde tek pikte degredasyon süreci olduğu kabul edilmiştir. Deneysel bulgulara dayanarak, degredasyon süreçleri iki farklı kinetik model kullanılarak ağırlık dönüşüm oranına bağlı olarak aktivasyon enerji değerleri elde edilmiştir.
Sonuçlar genel olarak incelendiğinde diferansiyel ve integral metodlardan elde edilen aktivasyon enerjisi değerleri arasında farklılıklar gözlemlenmektedir. Kissinger diferansiyel metodu ise yalnızca T_m sıcaklık

noktasını kullanarak çözümleme gerçekleştirirken Horowitz-Metzger integral metodu ağırlık dönüşüm oranından yararlanmaktadır. Literatürdeki benzer çalışmalarda da görüleceği üzere aktivasyon enerjilerinin hesaplanması sonucu elde edilen değerler büyük farklılıklar içermektedir. Mevcut malzeme (kolemanit-PP kompozit) için de bu çalışma kapsamında gerçekleştirilen model tahminleri benzer farklılıkları sergilemektedir.

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INVESTIGATION OF THERMAL DECOMPOSITION KINETICS OF ULEXITE/POLYPROPYLENE COMPOSITES: ACTIVATION ENERGIES WITH THERMOGRAVIMETRIC ANALYSIS

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Abstract

Ulexite mineral, which has many application fields such as glass, ceramics and chemical industry, generally is used as thermal resistance filler material in polymer composite applications. In the present study, ulexite/polypropylene composites were produced with three different filler ratios 10%, 20% and 30% (weight). Thermo-gravimetric analyzes of the composites produced were carried out different heating rates of 5, 10 and 15 °C/min. Activation energies were calculated using the Kissinger differential method and the Horowitz-Metzger integral method. TGA curves were used in these calculations in order to determine thermal degradation behaviors of materials.
The activation energies of ulexite mineral, neat polypropylene (PP), 10% ulexite/PP, 20% ulexite/PP and 30% ulexite/PP by Kissinger method were 118.249 kJ/mol, 272.215 kJ/mol, 219.745 kJ / mol, 194.829 kJ/mol and 175.906 kJ/mol, respectively, and based on Horowitz-Metzger Method, 279.114 kJ/mol, 53.390 kJ/mol, 128.844 kJ/mol, 93.895 kJ/mol and 87.912 kJ/mol, respectively. When the results are evaluated in general, there exist some differences between activation energy values obtained from differential and integral methods.

Keywords: ulexite, polypropylene, thermal degradation, activation energy

Özet

Cam, seramik ve kimya endüstrisi gibi birçok uygulama alanına sahip olan üleksit minerali genellikle polimer kompozit uygulamalarda termal dayanım sağlamak için katkı malzemesi olarak kullanılır. Yapılan çalışmada, (ağırlıkça) %10, 20 ve 30 olmak üzere üleksit/polipropilen kompozitler üç farklı katkı oranıyla üretilmiştir. Üretilen kompozitlerin termo-gravimetrik analizleri 5, 10 ve 15 °C/dk ısıtma hızlarında gerçekleştirilmiştir. Termo-gravimetrik veriler üleksit/PP kompozitlerin termal degredasyon davranışlarının belirlenmesi amacıyla Kissinger (diferansiyel) ve Horowitz-Metzger (integral) metotlarından yararlanılarak aktivasyon enerjileri hesaplanmıştır. Üleksit minerali, saf PP, %10 üleksit/PP, %20 üleksit/PP ve %30 üleksit/PP'nin Kissinger metoduyla elde edilen aktivasyon enerjileri sırasıyla 118,249 kJ/mol, 272,215 kJ/mol, 219,745 kJ / mol, 194,829 kJ/mol and 175,906 kJ/mol ve Horowitz-Metzger Metoduyla 53,390 kJ/mol, 279,114 kJ/mol, 128,844 kJ/mol, 93,895 kJ/mol and 87,912 kJ/mol olarak hesaplanmıştır. Sonuçlar genel olarak değerlendirildiğinde diferansiyel ve integral metodlardan elde edilen aktivasyon enerjisi değerleri arasında farklılıklar gözlemlenmektedir.

Anahtar kelimeler: üleksit, polipropilen, termal degredasyon, aktivasyon enerjisi

Introduction

Polymer materials have shown significant developments in recent years and have become materials used in daily life and in almost every branch of industry. The basic approach to polymer composite production is to be environmentally and economically viable [1]. Polymers have many different filler materials for their application areas such as structural applications and thermal protection [2]. The thermo-physical and mechanical properties of polymer composites are greatly influenced by their use over the service life. An important factor in the decomposition of the structure is the heat and there are many studies in the literature that examine these effects. Thermo-chemical and/or thermo-mechanical surface wear occurs when significant quantities of thermal energy are stored in the materials through conduction, convection, or radiation and material loss in these mechanisms occurs with increasing temperature. It is very important to assess the structural performance of these materials after these materials are exposed and especially for these materials, which are added in thermal applications, to exhibit their behavior against heat flow. In addition degradation in the material cannot always reflect to the surface of the material. In such cases, mathematical models that exhibit thermal degradation properties are utilized [3, 4].
Many different inorganic materials are used as fillers to improve the thermal behavior of polymer composites [2, 5]. In particular, the physical and chemical water content of these inorganic compounds has a significant effect on the thermal behavior of the composite [4]. In the scope of the study, ulexite mineral, which is one of the underground riches of our country, has been added to improve the thermal properties of PP. In the production of composites (weight) 10, 20 and 30% of three different filler ratios are used. Thermo-gravimetric analyzes were carried out at different heating rates and then the obtained TG curves were used to find the activation energy in the Kissinger and Horowitz-Metzger methods.

Kinetic Analysis of Thermal Degradation

For thermo-gravimetric analysis, conversion rate (α) is generally determined as the rate of actual weight loss to total weight loss related to the degradation process.
Weight loss to total weight loss related to the degradation process can be expressed as:

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \quad (1)$$

where w represents weight and the subscripts 0, t and f denotes initial, actual and final weight of the specimen, respectively. The conversion rate ($\frac{d\alpha}{dt}$) is based on weight and temperature of the specimen. It can be defined mathematically as:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

where k is the rate of conversion constant and $f(\alpha)$ is the functional reaction model and it depends on the reaction mechanism.
The rate of conversion constant k is generally expressed by the Arrhenius equation:

$$k = A \exp(\frac{-E}{RT}) \quad (3)$$

where A is the frequency factor to temperature in min^{-1}, E is the activation energy in kJ mol^{-1}, R is universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature in K.
The following equation combines Eqns. (2) and (3); one has given all rate of loss of material.

$$\frac{d\alpha}{dt} = A\exp(\frac{-E}{RT})f(\alpha) \quad (4)$$

For a linear heating rate of β can be expressed as:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} = \beta\frac{d\alpha}{dT} \quad (5)$$

The combination of Eqns. (4) and (5) gives the following expression:

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \quad (6)$$

with Eqns. (5) and (6) are used to calculate kinetic parameters based on thermo-gravimetric data for the analytical methods.

The Kissinger method [6] is one of the most popular approaches used in the determination of kinetic parameters by thermal analysis. The Kissinger peak displacement approach is easy to implement, is suited to very small sample sizes, and achieves kinetic parameters (E and A) quickly and easily. The Kissinger method is based on recording the exothermic reaction peak when material is analyzed at different heating rates. During thermal analysis, the exothermic peak temperature (T_m) is measured for each heating rate. [7]. The Horowitz-Metzger method [8] is a type of integral method. In this method single activation energy is calculated for each β value. The basic equations and outputs of both methods are given in Table 1.

Table1 Kinetic methods used in the evaluation of activation energy

Methods	**Equations**	**Plots**
Kissinger [6]	$ln\left(\frac{\beta}{T_m^2}\right) = ln\left(-\frac{AR}{E}f'(\alpha_m)\right) - \left(\frac{E}{RT_m}\right)$	$\ln(\beta/T^2)$-1/T
Horowitz-Metzger [8]	$ln\left(\frac{1-(1-\alpha)^{1-n}}{1-n}\right) = ln\left(\frac{ART_s^2}{\beta E}\right) - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2}$	$\ln(\ln(1/1-\alpha))$-θ

Material-Method

PP, as the matrix materials, is supplied by PETKIM Petroleum Industry (Izmir, Turkey) in granule form with a melt flow index 4.5 g/10 min, melting point 163 °C and density 0.905 g/cm^3 (at 23 °C). Ulexite mineral, as the filler materials, has under 45μm particle size and supplied by Eti Mines Inc's located in West Anatolia Region of Turkey. Preparation of the composite samples have been conducted with a high-speed thermo-kinetic mixer and molding process. PP matrix compounds are prepared with 0-30 wt % ulexite fillers and no coupling agent or additives were used in these products. The thermal characterization and kinetic analysis of decomposition process of ulexite/PP composites were investigated by using thermo gravimetric data.

Results and Discussion

Thermo-gravimetric analysis (TGA) shows the decomposition process of materials with increasing temperature and the TGA curve shows the relationship between the mass change of the sample and the temperature. The DTG curve shows the correlation between the mass loss rate (t) and the temperature (T) over the course of the TGA test. Fig. 1 is presented the TGA curves and DTG curves of the ulexite mineral.

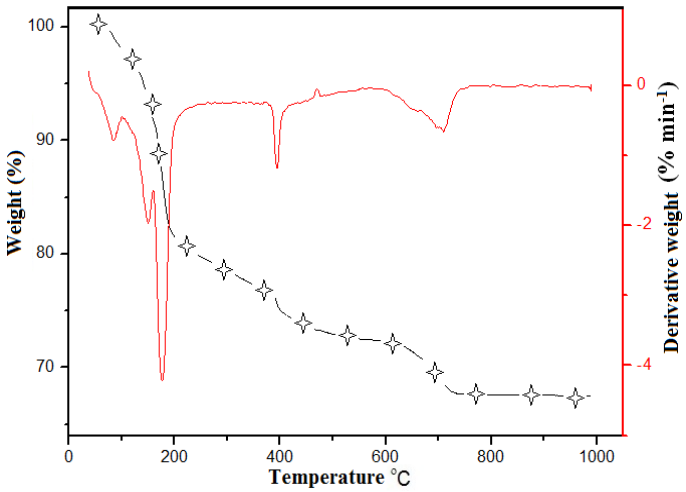


Fig. 1. TG-DTG curves of ulexite mineral

The thermo-gravimetric analysis of the composites is shown in Fig. 2. It is observed that the increased filler ratios affect the thermal degradation temperatures of the composites.

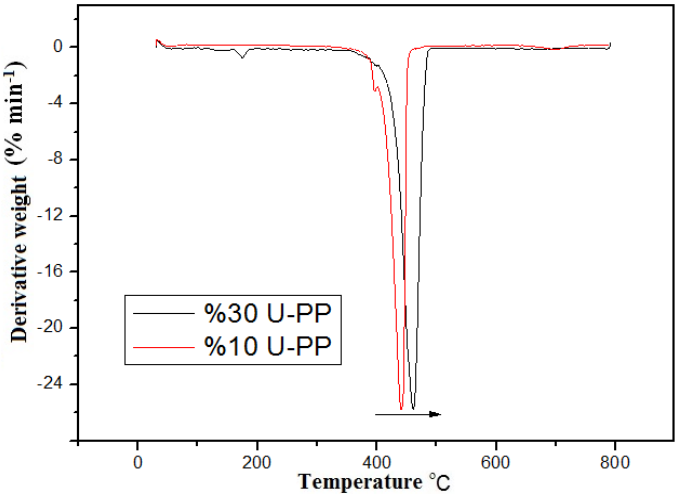


Fig. 2. DTG curves of %10 and %30 ulexite filled PP composites (U: Ulexite)

The kinetic parameters given in Fig. 3 were calculated by using the Kissinger method due to thermo-gravimetric analysis curves of ulexite/PP composites.

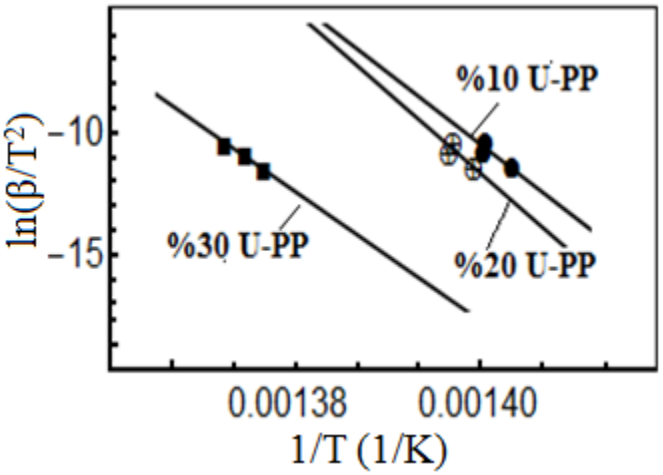


Fig. 3. Kissinger method results of U/PP composites

The average activation energy values are shown in Table 2. As observed in Figure 3, it is considered that the activation energy values calculated because the correlation coefficients are found to be very close to -1 for each composite. It has been observed that the experimental data obtained for all three additive ratios agree well with the Kissinger method estimates (R^2>0.97).

Table 2 Activation energy values calculated by Kissinger method

Material	**E (kJ/mol)**
Ulexite	118.249
%10 Ulexite-PP	219.745
%20 Ulexite-PP	194.829
%30 Ulexite-PP	175.906
Neat PP	272.215

Horowitz-Metzger's integral method was applied to determine kinetic parameters. It is possible to calculate the activation energies obtained for all heating rates. Table 3 summarizes the average values of activation energies obtained from different heating rates.

Table 3 Average activation energy values calculated by the Horowitz-Metzger method

Material	**Average E (kJ/mol)**
Ulexite	53.390
%10 Ulexite-PP	128.844
%20 Ulexite-PP	93.895
%30 Ulexite-PP	87.912
Neat PP	279.114

In the present study, the effect on the thermal degradation of PP matrix filled with ulexite was analyzed. Depending on the temperature change, it was considered that the process of single-peak decomposition in composites. The Kissinger differential method uses only the T_m point and the Horowitz-Metzger integral method uses the weight transformation ratio. When the results are examined, differences between the activation energy values obtained from the differential and integral methods are observed.

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PLA/PBAT/OCTAISOBUTYL-POSS TERNARY BLENDS: "EFFECT OF OCTAISOBUTYL-POSS LOADING RATIO ON THE MORPHOLOGICAL, MECHANICAL AND RHEOLOGICAL PROPERTIES"

PLA/PBAT/OKTAİZOBÜTİL-POSS ÜÇLÜ KARIŞIMLARI : "OKTAİZOBÜTİL-POSS YÜKLEME ORANININ MORFOLOJİK, MEKANİK VE REOLOJİK ÖZELLİKLERE ETKİSİ"

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Aim

After the usage of plastic based materials, wastes are extinguished by incineration process. Greenhouse gases that occur after incineration negatively affects global warming. For this reason, there has been great attention about usage of biodegredable polymers. Poly(lactic acid) (PLA), is one of the featured biodegredable polymers, which has high tensile strength and elastic modulus. On the other hand, PLA has low impact strength and its brittleness restricts its application. In order to improve the properties of PLA blending with a tough and a flexible polymer is a practical and economical method. For this purpose, poly(butylene adipate-co-terephtalate) (PBAT), is one of the biodegradeble polymers can be used to toughen the PLA. Polymer blends show generally immiscible and partially-miscible behaviour as in PLA/PBAT blends. Nano-filler addition to the polymer matrices is an efficient way to improve the properties by enhancing compatibility. Polyhedral oligomeric silsesquioxanes (POSS) are alternative nano-fillers to conventional fillers because of having relatively lower price and flexible chemical, physical properties. Moreover, POSSs improve the properties both polymer and polymer blends.

In this study, the effect of OPOSS loading ratio on the PLA/PBAT/OPOSS ternary blends were investigated in terms of morphological, mechanical and rheological properties fort he first time in the literature.

Materials and Method

PLA was supplied from NaturePlast, France, PBAT was supplied from SaSa Polyester, Turkey and OPOSS was puchased from HybridPlastics, USA. Blends were prepared in a Xplore microcompunder in Argon atmosphere at 190 ºC , with 100 rpm rotor speed and 3 min retention time. Standard test bars were obtained via XPlore microinjection moulding machine. Morphological results were determined from a scanning electron microscopy (SEM), mechanical

properties were determined by means of tensile and impact tests and rheological analysis were examined by an oscillatory rheometer.

Discussion and Recommendations

According to SEM results, dispersed phase particle size slightly decreased in higher OPOSS ratios in PLA/PBAT/OPOSS blends. Tensile strength was not affected by OPOSS loading ratio while elongation at break and impact strength were increased. Therefore, toughness was improved with higher content of OPOSS. Rheological results revealed that in the presence of OPOSS, the physical/chemical interactions were enhanced between PLA and PBAT components. As a result, high OPOSS loading ratios enhanced the properties of PLA/PBAT/OPOSS ternary blends.

Keywords: Poly (lactic acid), poly(butylene adipate-co-terephtalate), POSS

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Amaç

Plastik temelli malzemelerin kullanımı sonrasında oluşan atıklar genellikle yakılarak bertaraf edilmektedir. Yakma işlemi sonucunda oluşan sera gazlarının küresel ısınmayı olumsuz bir şekilde etkilemesi ise biyobozunur polimerlere olan ilgiyi oldukça arttırmıştır. Biyobozunur polimerler içerisinde yüksek çekme dayanımı ve elastisite modülüne sahip poli(laktik asit) (PLA) öne çıkan polimerlerden biridir fakat PLA' nın darbe dayanımı oldukça düşüktür ve PLA kırılgan bir yapıya sahiptir. PLA' nın özelliklerini iyileştirmek amacı ile daha esnek ve tok bir polimer ile karışım hazırlamak en etkili yollardan biridir. Bu amaçla kullanılabilecek biyobozunur polimerlerden biri poli(bütilen adipat-ko-teraftalat) (PBAT)' dır. Polimer karışımları çoğunlukla karışamaz veya kısmen karışabilir karakterdedir. PLA/PBAT karışımları karışamaz niteliktedir bu sebeple özelliklerinin iyileştirilmesi gerekmektedir. Özelliklerin iyileştirilmesi amacı ile nanokatkı ilavesi hem ekonomik hem de pratik yollardan biridir. Geleneksel nano katkı maddelerine alternatif olarak, görece daha düşük fiyatları ve esnek kimyasal ve fiziksel özellikleri nedeni ile poli(hedraloligomeriksilseskuioksan) (POSS) ilave edildiği polimerin/polimer karışımlarının özelliklerini geliştirmektedir ve bu nedenle son yıllarda oldukça önem kazanmıştır. Bu çalışmada, PLA/PBAT/Oktaizobütil-POSS (OPOSS) üçlü karışımlarında OPOSS yükleme oranının etkisinin morfolojik, mekanik, reolojik özelliklere etkileri incelenmiştir.

Materyal ve Metot

PLA, NaturePlast , Fransa, PBAT, SaSa Polyester A.Ş., Türkiye,' den temin edilmiş olup OPOSS, Hybrid Plastics, ABD' den satın alınmıştır. Eriyik harmanlar Xplore marka mikroharmanlayıcıda 190ºC, 100 rpm koşulları altında elde edilmiş olup alıkonma süresi 3 dakikadır. Ayrıca harmanların hazırlanması esnasında termo-oksidatif bozunmayı engellemek amacı ile sürekli bir şekilde sisteme Argon gazı beslenmiştir. Standart test örnekleri ise XPlore marka mikroenjeksiyon kalıplama cihazı ile elde edilmiştir. Morfoloji analizleri taramalı elektron

mikroskobu (SEM) ile, mekanik özellikler çekme ve darbe testleri ile ve reoloji analizleri ise reometre ile gerçekleştirilmiştir.

Tartışma ve Öneriler

SEM sonuçlarına göre PLA/PBAT/OPOSS karışımlarında OPOSS yükleme oranının artışı ile dağılan faz parçacık boyutunda kısmi bir azalma gözlemiştir. Çekme dayanımı OPOSS yükleme oranının artışı ile net bir şekilde değişim göstermez iken kopmada uzama ve darbe dayanımı artış göstermiştir. Dolayısı ile OPOSS yükleme oranının artışı karışımların tokluğunda artışa neden olmuştur. Reolojik analizler neticesinde OPOSS miktarının fazla olması ile PLA ile PBAT bileşenleri arasındaki fiziksel/kimyasal etkileşimlerin arttığı gözlenmiştir. Dolayısı ile OPOSS yükleme oranının artışının PLA/PBAT/OPOSS karışımlarının özelliklerini iyileştirdiği sonucuna varılabilir.

Anahtar Kelimeler: poli(laktik asit), poli(bütilenadipat-ko-teraftalat), POSS

Teşekkür: Bu çalışma 115M576 proje numarası ile TÜBİTAK tarafından desteklenmiştir.

EFFECTS OF NONAROMATİC OİL AS A FİLLER ON TO MECHANİCAL AND RHEOLOGİCAL PROPERTİES OF THREE DİFFERENT TİRE-TREAD RECİPES

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Abstract

In the tire industry, petrol and natural based oils are used as a filler and process aids components for different types of tire parts compound recipes. Petrol based oils have polycyclic aromatic hydrocarbon (PAH) contents which is a carcinogenic and contaminating chemicals for human being. With some kinds distillation methods, these PAH groups are extracted and nonaromatic different types of oils are obtained. In this study, three tire-tread compound recipes were prepared with aromatic oil and nonaromatic oil with 1.2 lt. laboratory type banbury mixer to investigate the effects of PAH's on the compounds. The rheological behaviors of the compounds were analyzed according to ASTM D5289 by the moving disk rheometer (MDR). Viscosities of the compounds were measured by the Mooney disk viscometer (MDV) according to ASTM D1646. Mechanical properties of the compounds were tested with universal mechanical test machine as it was in ASTM D412. Tanδ of the compounds reduced. While t5 and t35 scorch times of the compounds increased, viscosity decreased. Elastic moduli of the nonaromatic oily compounds nearly decreased to 10% and elongation of the compounds increased up to 20%. It may be concluded that nonaromatic oil usage might not be appropriate enough for recipes prepared with aromatic oil.

Key words: PAH, tire, rheology, nonaromatic oil, compound.

Introduction

Rubber processing equipment manufacturing and chemicals are secured by tire companies. Tire parts recipes are business secrecy and as a know-how for commercial tire manufacturer. Lots of chemicals are used for production of tire.[1] Rubbers, fillers, process aids, oils, resins, antioxidants, accelerators, etc. are used in the rubber compounds.[2]

Oils are very important ingredients of compounding. It helps to process the compound and uses as filler.[3] Aromatic oils are common ones in tire industry. After the 2012 at all European Union (EU) PAH free oils were started to use in tire compounds for according to environmental law of EU.[4] PAHs are known as cancerogenic cycle-aromatic chemicals.[5] Nonaromatic oils are defined as PAH free oils. Totally PAH free oils are named as totally distillated aromatic oils (TDA). After the some distillation process all PAHs cannot remove from oil, these types of oils are called distillated aromatic extract (DAE) oils. These oils PAH content are lower than 1% of total oil mass.

All recipes have two level for mixing. First one is main level that is mixing of polymer (rubber), carbon black (CB), ZnO, oil and Stearic acid. Second one is adding special chemicals, accelerators and Sulphur which is important for curing of rubber. Some different steps can added

between these two levels for decreasing viscosity of compound or adding different type of carbon black (CB).[6]

Three different tire tread recipes were chosen for analyzing mechanical and rheological properties of compounds. Rubber composition and filler ratios were different but usage area of tires was same that was off-road tire treads.

Material and Methods

All compounds were mixed in 1,2 Lt laboratory type mixer. Recipes of compounds are given Table 1. Aromatic tread compound one is given by TA1 code and nonaromatic oily tread compound one is named TN1, also the other codes were given compound two and three like first one. Ingredients mixture rate was evaluated by part per rubber weight. All components of first stage of recipes were added directly to banbury and mixed until production temperature. At second stage the other chemicals and Sulphur were added and mixed. Compounds were milled by laboratory type mill. Before curing step, five samples were taken to each compound mixture and were analyzed by Moony disc rheometer and MDR. Curing process of compounds were made by the hot press at 180 C°, 6 bar pressure and for ten minutes and compounds sheets were prepared for tensile tests.

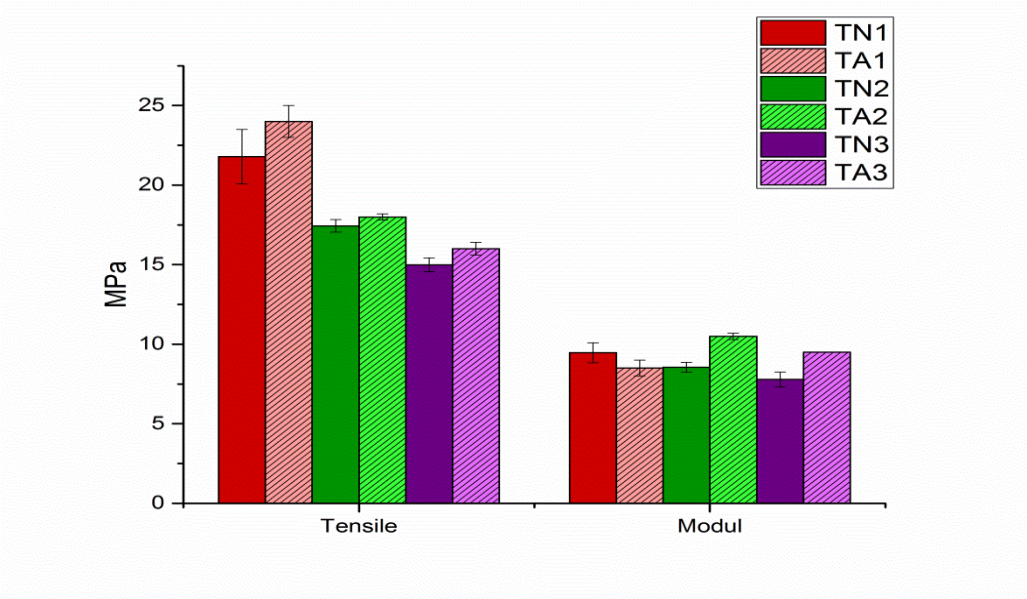
Table 1. Chemical composition of tire-tread recipes of compounds.

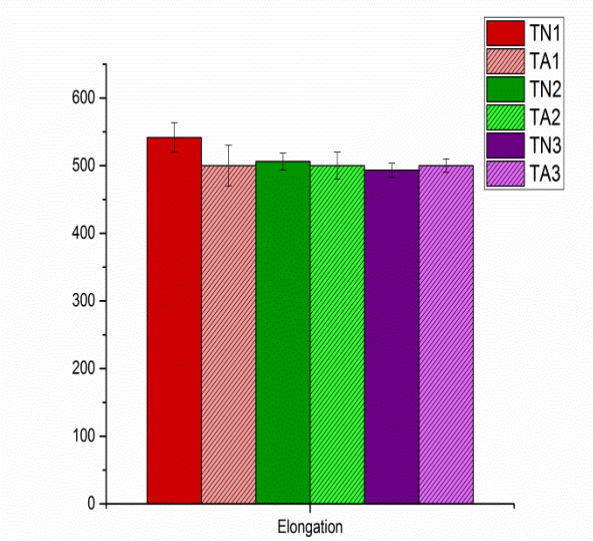
Ingredients for first stage	**TA1 (Phr)**	**TN1 (Phr)**	**TA2 (Phr)**	**TN2 (Phr)**	**TA3 (Phr)**	**TN3 (Phr)**
Naturel Rubber	20,00	20,00	20,00	20,00	20,00	20,00
Styrene Butadiene Rubber	80,00	80,00	80,00	80,00	80,00	80,00
CB (N-375)	75,00	75,00	56,00	56,00	57,00	57,00
Aromatic Oil	31,00	-	10,00	-	15,00	-
Nonaromatic Oil	-	31,00	-	10,00	-	15,00
Stearic Acid	2,00	2,00	2,00	2,00	2,00	2,00
ZnO	1,25	1,25	1,25	1,25	2,25	2,25
Micro crystalline wax	2,00	2,00	1,25	1,25	2,00	2,00
Paraffin wax	2,00	2,00	1,25	1,25	2,00	2,00
Antioxidant 1	4,00	4,00	3,50	3,50	3,50	3,50
Antioxidant 2	1,00	1,00	1,00	1,00	1,00	1,00
Ingredients for second stage						
Sulphur	1,80	1,80	1,60	1,60	1,80	1,80
DPG	0,45	0,45	0,30	0,30	0,20	0,20
MBTS	0,56	0,56	0,40	0,40	0,70	0,70
TBBS	1,00	1,00	0,75	0,75	1,80	1,80
PVI	0,40	0,40	0,25	0,25	0,40	0,40

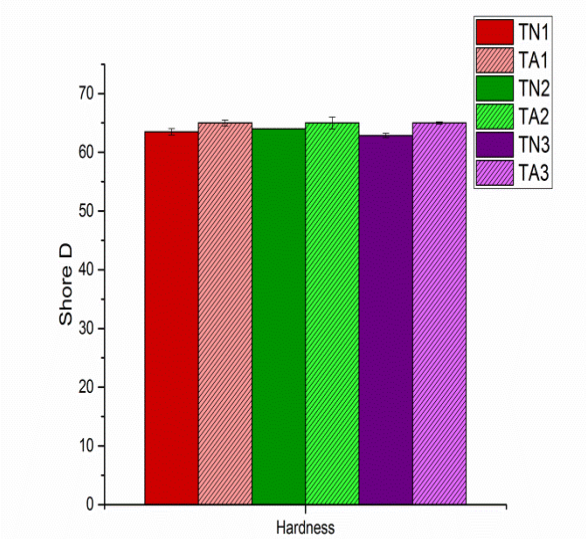
Tensile Test

All cured sample sheets were cut as dumbbell shape according to ASTM D638 for tensile test Shimadzu AGS-X 5KN universal test machine was used. Test method was adopted from ASTM which was D412 at room temperature. Analysis results were given **Figure 1**.

Figure 1. Mechanical analysis results of tire tread compounds.



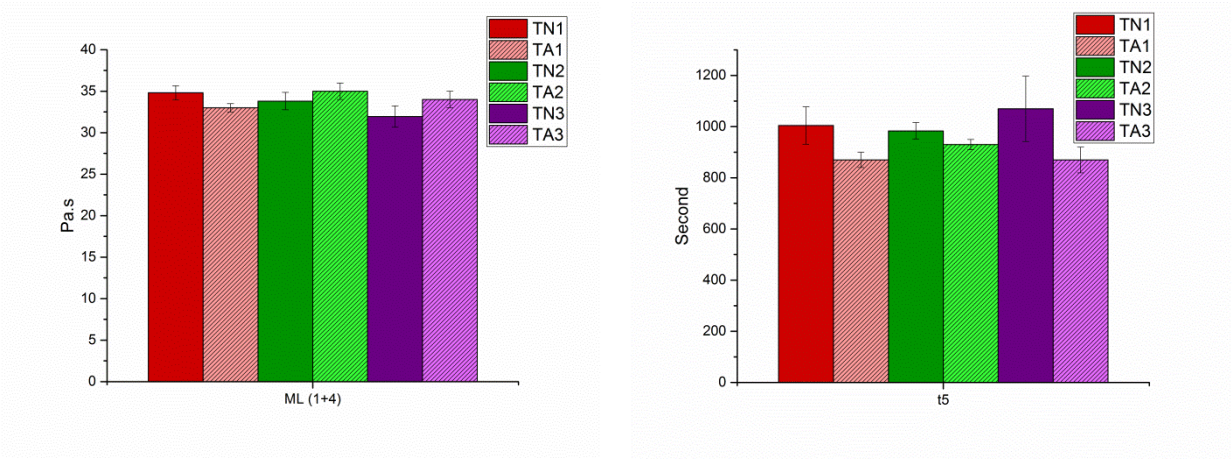




Mooney Disc Rheometer Analyses

Model of Moony disc rheometer was Alpha Technologies Mooney MV 2000. Mooney disc rheometer samples were waited for 1 minute under experiment conditions and after than 4 minutes measured the viscosity (ML 1+4) of samples and 5% curing temperature which is t5. The test was made according to ASTM D1646. Analysis results were given figure 2.

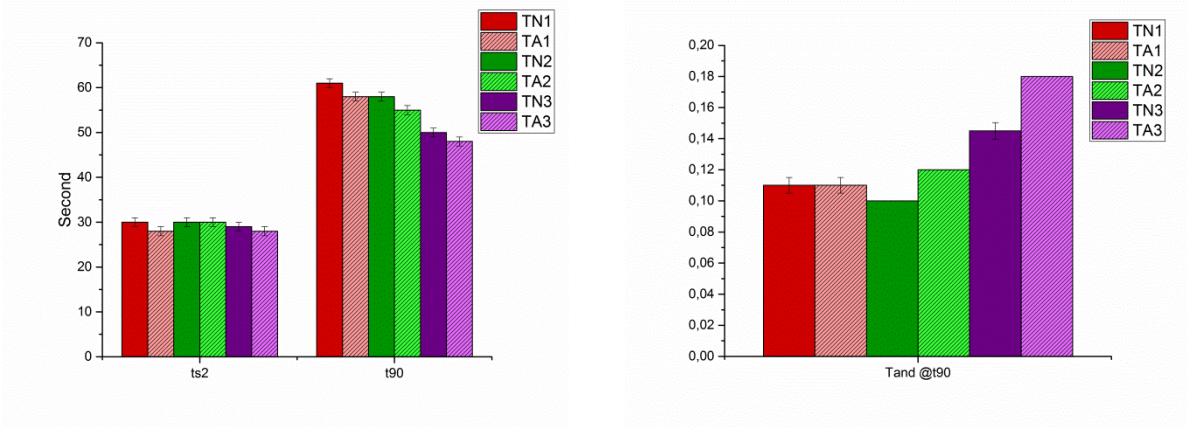
Figure 2. Mooney disc rheometer analysis results of tire tread compounds.



MDR Analysis

MDR model was Alpha Technologies Moving Die Rheometer. MDR analyses were made to according to ASTM D5289. Analysis results were given figure 3.

Figure 3. MDR analysis results of tire tread compounds.



Results and Discussion

According to Figure 1 tensile properties of compounds reduced with nonaromatic oil addition to compound recipes. Moduli of tread compounds TA2 and TA3 were better than TN2 and TN3 but TA1 moduli was lower than TN1. First recipe CB content was higher than the other recipes, although it could be worked with nonaromatic oil better than aromatic oil and increase dispersion of CB homogenously.[7] Aromatic oil viscosity was higher than nonaromatic oil that effected distribution of CB. Mechanical tests showed that, nonaromatic oil plasticizers properties were high for low CB added rubber compounds.[8]

Mooney Disk Rheometer analysis was shown that viscosity of compounds was upper than aromatic compounds.[9] But for first tire tread recipe aromatic oily recipe viscosity was nearly 5% above than nonaromatic one. Viscosity of TA1 was affected by CB portion in to recipe as differences of mechanical properties. t5 is very important parameter for extrusion process of compounds. t5 values of

compounds decreased with nonaromatic oily recipes. Reducing of curing time of compounds affects total production line and it decreased storage time of compounds for tire production.

MDR results were shown that lots of differences between aromatic and nonaromatic oily compounds.[10] All recipes are designed in rubber industry for their mechanic and visco-elastic properties. Tanδ value is an important parameter for getting to understand compounds visco-mechanic behaviors. TA1 and TN1 compounds Tanδ values were nearly same, but the other recipes, Tanδ values were increased by changing oil type. Tanδ increased with the nonaromatic oil. Nonaromatic oils were much plasticized rubber than aromatic oil. ts2 can define as scorch time of the 2% compound and t90 is 90% of compound scorch time.[11] These times are characteristic values of compounds in to press. Nonaromatic oil was accelerated curing process of rubber and it decreases curing time. All results were showed that recipes of aromatic oily compounds are not suitable for nonaromatic oily compound production.

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INVESTIGATION OF THERMAL CONDUCTIVITY AND MECHANICAL PROPERTIES OF THREE DIFFERENT PARTICLES SIZED 50% SILICON CARBIDE (SiC) LOADED POLYPROPYLENE (PP) MATRIX BASED COMPOSITES

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Abstract

Thermal conductivity of materials are essential for cooling of microprocessors and battery systems of small electronic devices at electronic industry. Electrically insulating and cooling of electronic devices are an important for working of electronic system's properly. Polypropylene (PP) is electrically and thermally insulating material. SiC has high thermal conductive but low electrical conductive ceramic based material. These two material composites are used as thermal conductive and electrically insulating material. In this study, thermal conductivity and mechanical properties of three different particle sized of SiC's PP composites were investigated. For all the samples 50% (w%) of SiC was added to PP matrix. All composites were mixed in the high speed thermos-kinetic mixer. Thermal conductivity of composites was measured by C-Therm thermal conductivity measurement system. Mechanic analysis was tested with Shimadzu AGX-5KN universal test machine. According to the results, mechanical properties of composites increased as SiC particles size reduced. Thermal conductivity of composites increased with SiC particle size decrease.

Key words: Thermal conductivity, composite, polypropylene (PP), Silicon carbide (SiC).

Introduction

PP is an important thermoplastic raw material for lots of industrial manufacturer. It has good mechanical properties and impact resistivity. The PP is one of the most miscellaneous polymers available with a wide range of packaging applications. [1]Although PP is used to produce fiber, slit tape, cast and biaxially oriented films, containers and automotive interior trim, appliance housings and components.[2] PP is a polyolefin group polymer that has general characteristics like thermally and electrically insulating behaviors.[3] Low thermal conductivity of PP restricts to application area of electronic packing industry. However its electrical conductivity, low density and antistatic nature support to use in microchips and processors interphase material.

Ceramic based materials show different feature in their specific lattice orientations. Lattice of crystallic structure gives new kind of usage area to material.[4] Silicon carbide (SiC) has got different lattice forms and it effects basic properties of material like electrically, thermally or appearance. Pure electrical conductivity of SiC leads to use electrical insulating parts manufacturing. Two types commercial SiC is available in to the market. Black SiC thermal conductivity is higher than green SiC thermal conductivity.[5] However economic values of two type of SiC are different. Green SiC is cheaper and commercially available with different particle size.

Thermal conductive enhancement of thermoplastics started to be very important for electronic industry.[6] It leads to use polymers for cooling of microchips in their low weight and low manufacturing costs. In this study three different particle size SiC loaded to polyolefin group thermoplastic which was PP matrix composites mechanical and thermal conductivities was compared and suitable particle size PP/SiC composite is investigated.[7] Increasing of filler content was not affected composites thermal conductivity linearly.[8] However, thermal conductive particles concentration was started show its effect in to composite after 40% (w/w) loading of filler. For planning prototype compounds production was made by high speed thermokinetic mixer, however some limitation of mixing facilities defensed upper loading capacity of thermal conductive particles in to polymeric matrix at this process. 50wt% SiC loading to PP matrix occupied better dispersion results and became upper mixing ratio for components.

Materials and Methods

PP is supplied from Petkim A.Ş. which is the MH 418 with UV protector has been added pellets. Its melting temperature is 168 C° and melt flow index according to ASTM D1238 is between 4,0 to 6,0. This PP is suitable for melting into high speed thermokinetic mixer. Three different size SiC particles were used which are F120 (106 micron), F320 (29 micron) and F800 (6 micron). Before mixing PP and SiC were dried under 80C° 1 hour into drier oven. Equal weight PP and SiC were added to mixer chamber and mixed at almost 1 minute. Composite dough was pressed under 120 Psi 3 minute at heating side of press and cooled at same pressure for 1 minute cooling side of press. Shaped plates were cut and mechanically analyzed according to ASTM D638 and ASTM D790 by Shimadzu AGX-5KN universal test machine. Thermal conductivity of plaques was measured by C-Therm Thermal conductivity measurement system.

Result and Discussion

Figures 1 and 3 show the variations of the tensile and flexural strength as a function of powder size of SiC for composites, respectively. Tensile strength values of PP, F120, F320, and F800 composites were obtained to be,35.22, 23.19, 24.01 and 25.46 MPa, respectively. As shown in Fig. 3, the flexural strength values for PP, F120, F320 and F800 were determined to be, and 50.30, 38.15, 41.07, and 40.37 MPa, respectively.

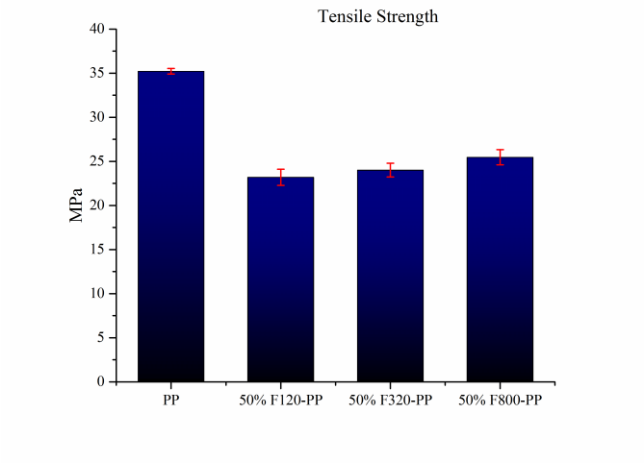


Figure 1. Tensile strength of PP and SiC reinforced PP composites

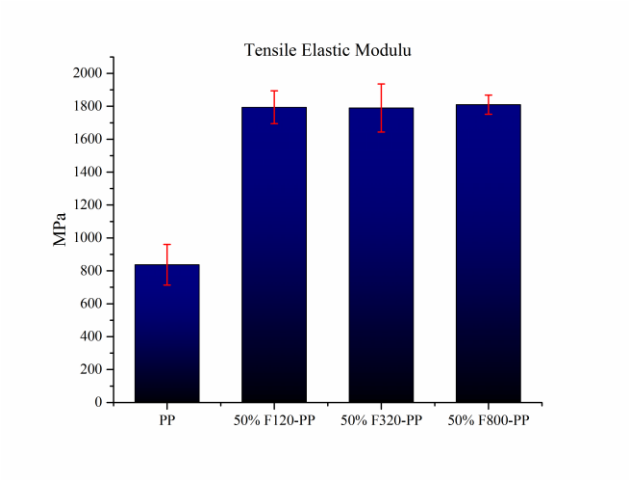


Figure 2. Tensile elastic modulu of PP and SiC reinforced PP composites

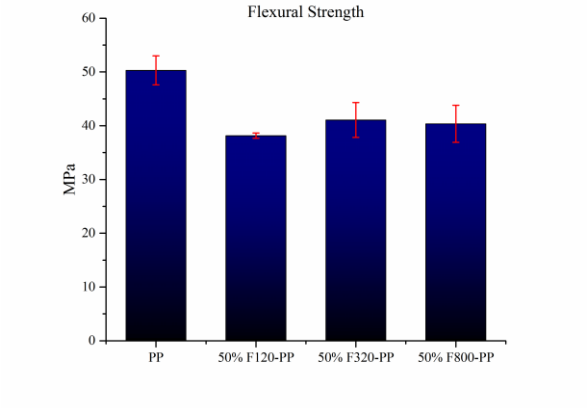


Figure 3. Flextural strength of PP and SiC reinforced PP composites

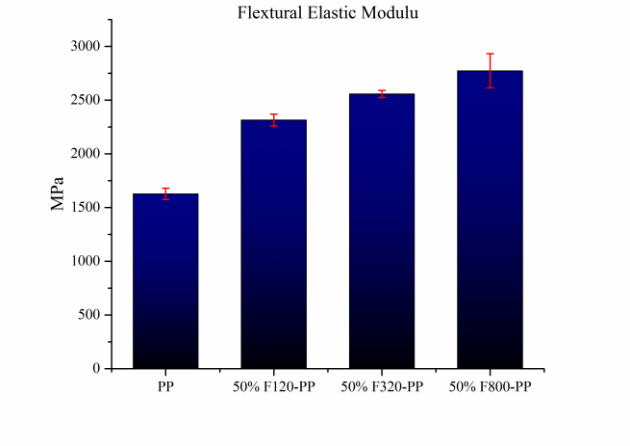


Figure 4. Flextural elastic modulu of PP and SiC reinforced PP composites

The effects of powder size on the tensile and flexural elastic modulu of SiC reinforced PP composites are given in figure 2 and 4, respectively. It can be seen that the tensile and flexural modulu of the PP increase with the addition of SiC in the studied powder size (F120, F320 and F800).[9] When SiC powder was added into PP, the tensile and flexural elastic modulu were increased by about 120%, respectively. This is due to the addition of SiC powder into PP where the SiC powders acts as a load carrier in the composite.[10] Thus, the stiffness of PP increases with SiC powders incorporation.

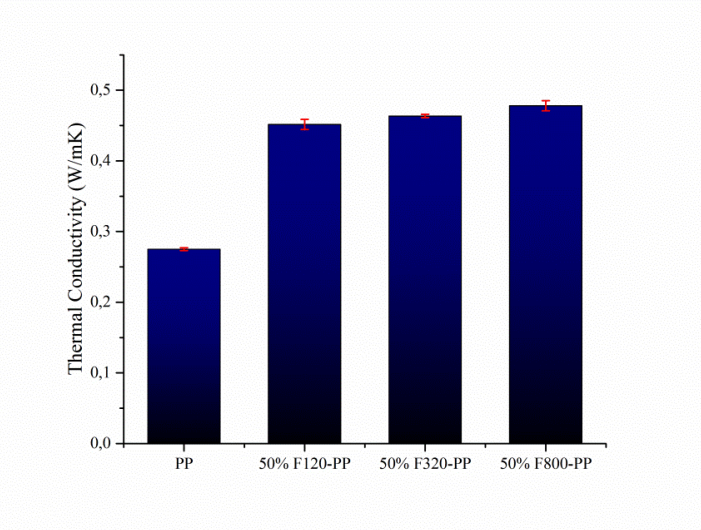


Figure 5. 50% different particle sized SiC loaded PP matrix thermal conductivities.

Thermal conductivity of SiC/PP matrix composites were shown at figure 5. Neat PP thermal conductivity was almost 0,27 W.m/K. After addition of F120 type of SiC to PP matrix, thermal conductivity value increased 67%. SiC particle size decreasing, thermal conductivity of SiC/PP composites get a little bit better values. F320 SiC loaded PP matrix thermal conductivity increase 69% than neat PP. F800 loaded PP matrix thermal conductivity increase 72% better than neat PP.

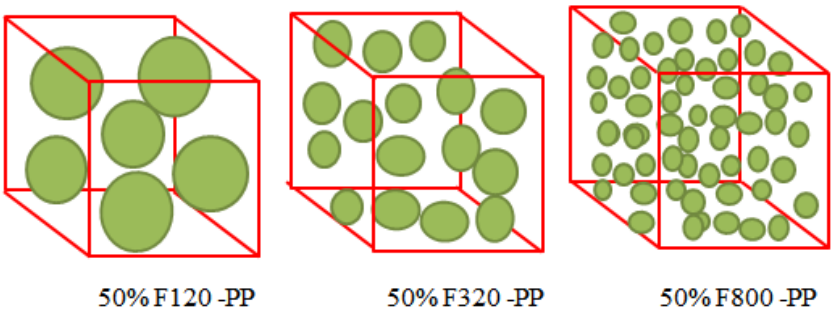


Figure 6. Theoretical distribution of SiC particles is into PP matrix.

All values of thermal conductivity taken at 21C° room temperature and all composites heat capacity at constant pressure evaluated same for all composites and diffusivity values of composites calculated form thermocouple of measurement system. Figure 6 shows that theoretical SiC particles distributions and orientations in to PP matrix composites in x,y and z directions. SiC and PP matrix surface inter action increases by decreasing particle size and theoretically heat transfer could have been better.

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KIVRIMSIZ ELYAF TAKVİYELİ KOMPOZİT PLAKALARDA CIVATA BAĞLANTILARININ KADEMELİ HASAR MODELLEMESİ

PROGRESSIVE DAMAGE MODELLING OF BOLTED JOINTS IN NON-CRIMP FABRIC (NCF) COMPOSITE PLATES

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ÖZET

Prepregler ve dokuma kumaşlar gibi alışılagelmiş takviye malzemelerine ek olarak tekstil teknolojileri yeni takviye sistemleri geliştirmektedir. Yeni bir tip takviye sistemi olan kıvrımsız elyaf (KE) kumaşlar uygulamada popülerlik kazanmaktadır. KE kumaşlar vakum esaslı yöntemlerle kolaylıkla ve düşük maliyetlerle üretilebilmektedir. Birçok KE kumaş çeşidi yat/tekne, otomotiv ve rüzgâr türbin kanatlarında kullanılmaktadır. Bu sebeple, bu malzemelerdeki hasar davranışı ve mukavemet kestirimi önem kazanmıştır. Bu öneme binaen, bu çalışmada yarı tek-yönlü KE kumaş esaslı kompozit malzeme sistemlerinde cıvata bağlantıları incelenmiştir. Farklı elyaf sıralamalarına sahip kompozit plakaların hasar modellemesi ve mukavemet kestirimi kademeli hasar modellemesi (KHM) yöntemiyle incelenmiştir. Sonlu eleman modeli, malzeme sisteminin eşdeğer elastik ortotropik malzeme özellikleri atanan 8-düğüm noktalı elemanlarla oluşturulmuştur. Hasar başlangıcı için Hashin ve maksimum gerilme kriterleri karşılaştırılmıştır. Hasar ilerlemesini simüle etmek için elastik malzeme özellikleri indirgeme yaklaşımı kullanılmıştır. KHM sonuçlarının deneysel sonuçlarla uyumlu olduğu görülmüştür. Ayrıca hasar ilerlemesi de doğru şekilde simüle edilerek bütün numunelerde hasar modları deneylerle tutarlı olacak şekilde bulunmuştur.

ABSTRACT

Introduction

Beyond the classical composite material systems, the textile technologies offer new reinforcement systems for composite structures. A new type of reinforcement, the non-crimp fabrics (NCF) are gaining popularity in practical applications. The NCF dry preforms were suited the vacuum based technologies which are easier and cheaper for manufacturing. Several types of NCF based composites were employed in marine, automotive and wind energy applications.

Regardless of the material system, the joining of the sub-structures plays an important role on the reliability of the main structure. Therefore, the mechanical behaviour of joining alternatives for a specific material system is very important. The most popular joining methods in the composite structures are bonding, mechanically fastening and their combinations. Bonding method comprises a sufficient load transfer but the joint cannot disassemble for maintenance and repair options. On the other hand, mechanical fasteners are easy to assemble/ disassemble but they create stress concentrations due to fastener holes. Thus, that is really important to estimate the behaviour of joint for the design purposes. This study is dealing with the bolted joint configurations of quasi-unidirectional NCF based composites.

The progressive damage modelling (PDM) method is widely used to estimate the behaviour of mechanical joints. In this method, two important inputs are required; the damage initiation criteria and the material property degradation rules. When an element satisfies the criteria, the elastic material properties of the element degrade according to degradation rules. The solution continues with the updated elastic properties and this loop continues until the solution converges. In this study, two damage initiation criteria

were used for comparison of their efficiency: Hashin and maximum stress. Hashin criteria was originally designed to predict the failure initiation in the unidirectional composite laminates. However, the criteria are widely used for simulating the failure in various types of composite structure. The other criterion, maximum stress criterion, is also used in many studies due to its simplicity. Hashin criteria were failed to estimate the strength values due to the contribution of the shear stress in the matrix tension, matrix compression and fiber tension damage modes. The analyses were completed with maximum stress criterion. The degradation rules were taken from a previous study due to their determination including the physical material behaviour of different damage mechanisms. The PDM results were compared with the experimental results and a good correlation was found except two cases. The reason behind the high error of those two cases was explained with the shear stress distribution. The damage propagation was also simulated very correctly. The damage propagation with the increasing load and also some particular damage events were shown. The damage mode of all specimens was successfully predicted either.

Giriş

Kıvrımsız elyaf (KE) kumaş takviyeli kompozitler uzay-havacılık, yat-tekne, otomotiv ve rüzgar enerjisi uygulamalarında düşük maliyetleri, üretim kolaylıkları ve iyi mekanik özellikleri sebebiyle popülerlik kazanmaktadırlar. Vakum esaslı üretim yöntemleriyle kolayca üretilebilen bu malzemeler, bir araya gelerek fiber demetlerini oluşturan kıvrımsız fiberler sebebiyle yeterli mekanik özelliklere sahiptir [2-4]. Geçmişteki çalışmaların çoğu KE kompozitlerin mikro yapısını incelemektedir [5-10]. KE kompozitle üretilen en bilinen iki ürün Airbus A-380 uçağının arka basınç kapağı [11] ve İsveç Deniz Kuvvetleri'ne ait Visby Korvetidir.

Malzeme sisteminden bağımsız olarak ana yapıyı oluşturan bileşenlerinin birbirleriyle birleştirilme yöntemi ana yapının bütünlüğü üzerinde büyük bir öneme sahiptir. Bu nedenle her bir malzeme sistemi için birleşim seçeneklerinin mekanik davranışı önemlidir. En çok kullanılan birleştirme yöntemleri yapıştırma, mekanik bağlama ve bu ikisinin kombinasyonlarıdır. Yapıştırma yöntemi iyi yük aktarımı sağlasa da, tamir, bakım gibi işlemler için birleşimin sökülebilmesine olanak sağlamamaktadır. Diğer yandan mekanik bağlama ucuz ve kolay olmasına ve tamir, bakım gibi ihtiyaçlar için sökülebilmesine rağmen bağlantı elemanlarının geçmesi için açılan delikler (süreksizlikler) gerilme yığılmalarına yol açarak yapıyı zayıflatmaktadır. Bu sebeplerle bağlantının mekanik davranışının önceden kestirilebilmesi çok önemlidir.

Önceki çalışmalara bakıldığında KE takviyeli kompozit malzemelerde mekanik bağlantılar üzerine bir çalışma yapılmadığı görülmüş ve bu çalışmada Kademeli Hasar Modellemesi (KHM) yöntemi kullanılarak hasar ilerlemesi ve mukavemet kestirimi yapılmaya çalışılmıştır. KHM mekanik bağlantıların hasar ve mukavemet durumlarını tahmin edebilmek için yaygın kullanılan bir yöntemdir. Bu yöntemde iki tane önemli girdi gereklidir. Bunlar; hasar başlangıç kriteri ve elastik malzeme özelliklerini indirgeme katsayılarıdır. Eğer sonlu eleman modelindeki herhangi bir eleman kriterin şartlarını sağlarsa, o elemanın elastik özellikleri kurallara göre düşürülür. Bu işlem bir döngü olarak çözüm bitene kadar tekrarlanır. Bu çalışmada iki farklı hasar kriteri verimliliklerini karşılaştırmak amacıyla seçilmiştir. Bu kriterler Hashin kriteri [12] ve maksimum gerilme kriteridir. Hashin kriteri her ne kadar tek-yönlü kompozit plakalarda hasar kestirimi yapmak için geliştirilmiş olsa da, birçok araştırmacı tarafından çeşitli kompozit malzeme sistemlerinde hasar ve mukavemet kestirimi için kullanılmaktadır [13-16]. Maksimum gerilme kriteri ise sadeliği sebebiyle tercih edilmiştir. Malzeme özelliklerinin indirgeme kuralları, farklı hasar mekanizmalarının fiziksel davranışlıları göz önüne alınarak oluşturulması sebebiyle, önceki bir çalışmadan alınmıştır [14].

Oluşturulan sonlu eleman modelinde KHM uygulanmış ve sonuçlar deneylerle karşılaştırılmıştır. Deneyler ve simülasyon arasındaki farklar açıklanmıştır.

Deneysel Çalışma

Malzeme sisteminde takviye fazı 300 g/m^2 alan ağırlıklı yarı tek-yönlü kıvrımsız E-cam elyaf ve matris fazı ise oda sıcaklığında kürleşebilen bir epoksi reçinedir. Düzlemsel kompozit plakalar vakum destekli reçine transfer yöntemiyle üretilmiş ve karbür takımlar kullanılarak kesilmiştir. Malzeme sistemine ait eşdeğer elastik ortotropik malzeme özellikleri ve mukavemet değerleri sırasıyla Tablo 1 ve Tablo 2'de verilmiştir. Cıvata bağlantılı numuneler ASTM D-5961'e göre [17] hazırlanmıştır. Üretilen numunelerin elyaf sıralamaları Tablo 3'te görülmektedir. Bütün numunelerde serbest kenar uzaklığı/delik çapı ve genişlik/delik çapı oranları 3 ve 6 olarak sabittir. Yine bütün numunelerde cıvata sıkma torku 3 Nm olarak belirlenmiştir. Deneyler Zwick-Roell test cihazında 2 mm/dk deplasman kontrollü olarak gerçekleştirilmiş ve Tablo 4'te görülen mukavemet değerleri kaydedilmiştir. Deneysel çalışma ile ilgili detaylar [18, 19] numaralı referanslarda verilmiştir.

Tablo 3: KE/epoksi malzeme sistemine ait eşdeğer elastik ortotropik malzeme özellikleri [18, 19].

E_{11} (GPa)	$E_{22}=E_{33}$ (GPa)	$G_{12}=G_{13}$ (GPa)	G_{23} (GPa)	$\nu_{12}=\nu_{13}$	ν_{23}
28	13.2	3.9	4.85	0.22	0.36

Tablo 4: KE/epoksi malzeme sisteminin mukavemet değerleri [18, 19].

X_T (MPa)	X_C (MPa)	$Y_T=Z_T$ (MPa)	$Y_C=Z_C$ (MPa)	$S_{XY}=S_{XZ}=S_{YZ}$ (MPa)
641	421	85	178	35

Tablo 5: Çalışmada kullanılan numunelerin elyaf sıralamaları ve numune kodları.

Çapraz-katlı numuneler	**Yarı-izotropik numuneler**
C-1 $[90°/0°]_s$	Q-1 $[+45°/0°/-45°/90°]_s$
C-2 $[90°_2/0°_2]_s$	Q-2 $[90°/+45°/-45°/0°]_s$
C-3 $[90°/0°]_{2s}$	Q-3 $[0°/90°/+45°/-45°]_s$

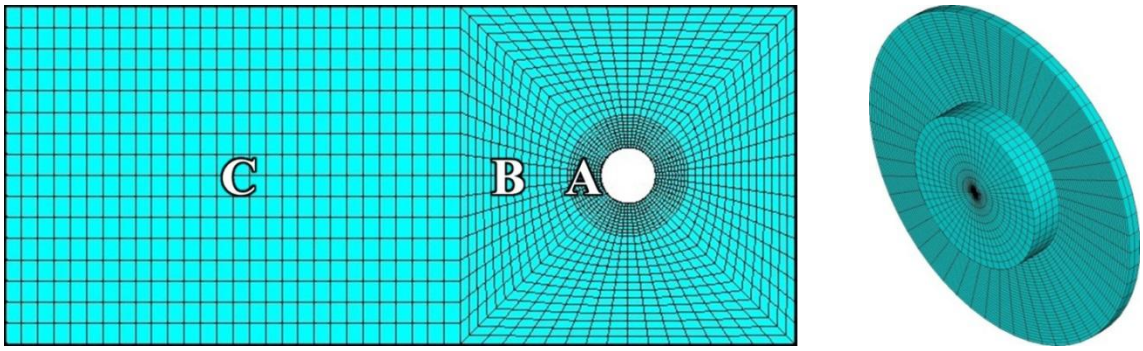
Tablo 6: Test edilen numunelerin yatak mukavemetleri ve hasar modları [18, 19].

Elyaf Sıralaması	**Hasar Modu**	**Hasar Yükü (N)**		**Yatak Mukavemeti (MPa)**		**Varyasyon Katsayısı**
		Ortalama	Sapma	Ortalama	Sapma	
		x	s	x	s	v
C-1	B+S	2887	142.6	343	17.09	4.94 %
C-2	B+S	6231	98.6	415	6.57	1.58 %
C-3	B+S	6523	373.7	434	24.91	5.72 %
Q-1	B	6091	402.1	406	26.80	6.60 %
Q-2	B	7319	217.1	487	14.47	2.96 %
Q-3	B	6926	267.4	461	17.83	3.86 %

Kademeli Hasar Modellemesi (KHM)

Cıvata bağlantılı numunelerin sonlu eleman modelleri Ansys R14.5 sonlu elemanlar programında oluşturulmuştur. 8 düğüm noktalı SOLID185 eleman kullanılarak yapılan modellemede kompozit malzeme için indirgenmiş integrasyon, cıvata-pul için tam integrasyon formülasyonları uygulanmıştır. Kalınlık yönünde her tabaka için bir eleman (one element per layer) stratejisi kullanılmıştır. Boyut oranı (sonlu eleman uzunluğu/tabaka kalınlığı) A bölgesinde 1, B bölgesinde 3 ve C bölgesinde 8 olacak şekilde ağ yapısı (mesh) oluşturulmuştur. Sonlu eleman modeli Şekil 1'de görülmektedir. KE/epoksi malzemenin

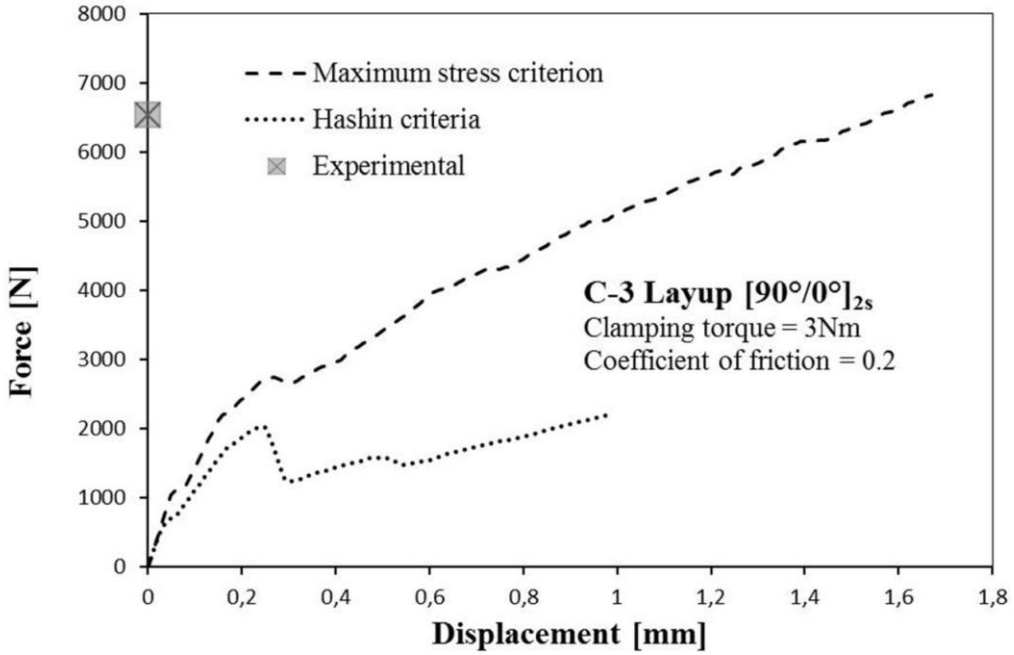
mekanik özellikleri (bkz: Tablo 1-2) programa girildikten sonra cıvata/pul çiftinin elastik özellikleri de E=210 GPa ve ν=0.3 olarak girilmiştir. Bütün temas yüzeylerinde sürtünme katsayısı 0.2 olarak atanmıştır [20]. 3Nm sıkma torku cıvata/pul çiftine eksenel yönde deplasman vermek suretiyle uygulanmıştır.



i) **ii)**

Şekil 2: Sonlu elemanlar modeli. i) kompozit plakanın sonlu eleman modelinin mesh yapısı, ii) cıvata/pul çiftinin mesh yapısı.

Sonlu eleman modeli oluşturulduktan sonra Hashin ve maksimum gerilme kriterleri uygunluklarını tespit etmek amacıyla karşılaştırılmıştır. C-3 plakası deneylerde görülen bütün hasar modlarına sahip olduğu için referans numune olarak seçilmiş ve bütün doğrulama adımları bu plakanın üzerinde gerçekleştirilmiştir. Şekil-2'de görüldüğü gibi maksimum gerilme kriteri Hashin kriterinden daha iyi sonuç vermiştir.



Şekil 3: Hashin kriteri [12] ve maksimum gerilme kriterinin referans numune üzerinde yapılan karşılaştırılması.

Uygun hasar kriteri seçildikten sonra, malzeme elastik özellikleri indirgeme kuralları uygulanmıştır ve KHM geliştirme aşaması tamamlanmıştır. Camanho ve Matthews'in [14] yaptığı çalışmadan alınan indirgeme kuralları Tablo 5'te gösterilmiştir.

Tablo 7: Elastik malzeme özellikleri indirgeme katsayıları [16].

Hasar türü	**İndirgenen malzeme özelliği**		
Fiber çekme ($\sigma_{11}\geq 0$)	$E_{11}^{d} = 0.07E_{11}$		
Fiber basma ($\sigma_{11}<0$)	$E_{11}^{d} = 0.14E_{11}$		
Matris çekme veya kayma ($\sigma_{22}+\sigma_{33}\geq 0$)	$E_{22}^{d} = 0.2E_{22}$	$G_{12}^{d} = 0.2G_{12}$	$G_{23}^{d} = 0.2G_{23}$
Matris basma veya kayma ($\sigma_{22}+\sigma_{33}<0$)	$E_{22}^{d} = 0.4E_{22}$	$G_{12}^{d} = 0.4G_{12}$	$G_{23}^{d} = 0.4G_{23}$

Not: *d* indirgenmiş malzeme özelliğini belirtmektedir.

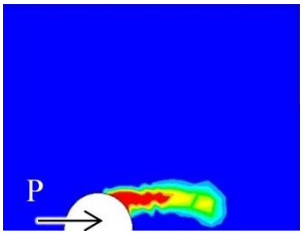
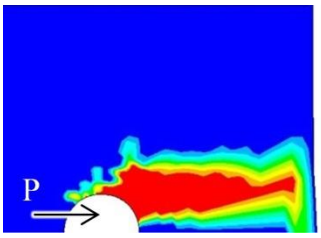
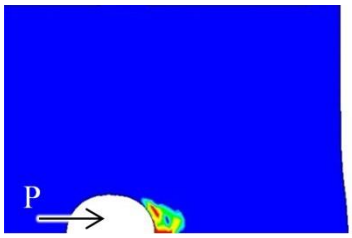
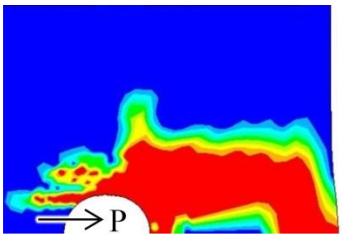
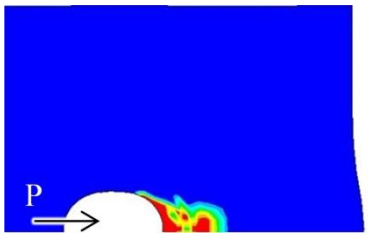
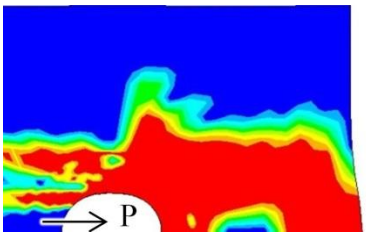
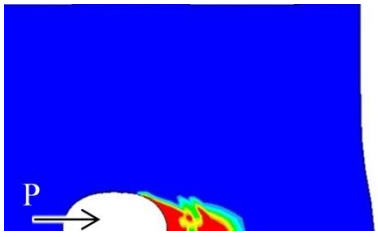
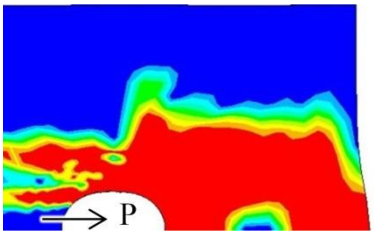
Sonuçlar

KHM'den elde edilen sonuçlarla deneysel veriler Tablo 6'da karşılaştırılmıştır. Çapraz-katlı numunelerin cıvata bağlantısı mukavemeti %5.1 maksimum sapmayla bulunmuştur. Yarı-izotropik numunelerde ise sapma Q-1 ve Q-3 elyaf sıralamalarında artmıştır. Q-1 ve Q-3 elyaf sıralamalarında sapmanın artmasının nedeni ±45° tabakalarda oluşan kayma gerilmelerinin erken hasar tetikleyici şekilde ortaya çıkmasıdır [13].

Şekil-3'te hasarın artan yükle birlikte yayılışı C-3 plakasının orta düzlemindeki 0° tabaka örneğiyle gösterilmiştir. Kırmızı renk tamamen hasar almış bölgeleri, mavi renk ise hasarsız bölgeleri temsil etmektedir.

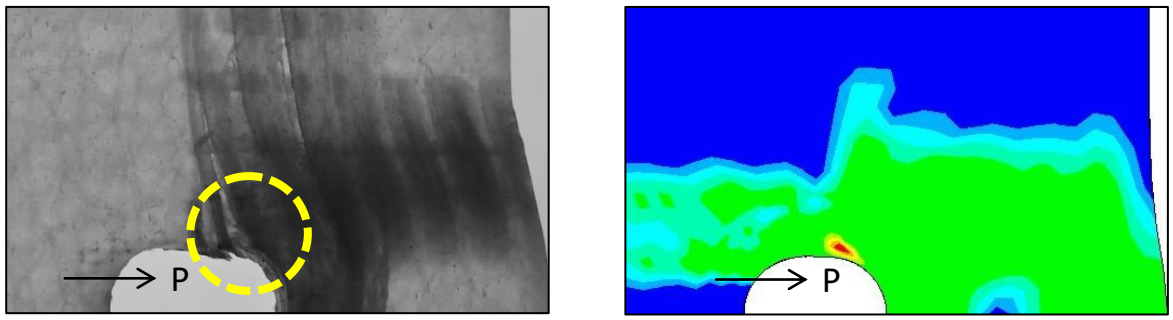
Tablo 8: KHM sonuçları ile deney sonuçlarının karşılaştırılması (B: yataklama hasar modu, S: dışa-kayma hasar modu).

Elyaf sıralaması	**Hasar Modu**		**Hasar yükü**		**Sapma (%)**
	Deney	KHM	Deney	KHM	
C-1 $[90°/0°]_s$	B+S	B+S	2887 N	2738 N	-5.1
C-2 $[90°_2/0°_2]_s$	B+S	B+S	6231 N	5962 N	-4.3
C-3 $[90°/0°]_{2s}$	B+S	B+S	6523 N	6818 N	4.5
Q-1 $[+45°/0°/-45°/90°]_s$	B	B	6091 N	7294 N	16.5
Q-2 $[90°/+45°/-45°/0°]_s$	B	B	7319 N	7527 N	2.8
Q-3 $[0°/90°/+45°/-45°]_s$	B	B	6926 N	6001 N	-13.4

	Fiber Hasarı	**Matris Hasarı**
25. alt-adım (2681 N) (U_x=0.25 mm)	Hasar yok.	
50. alt-adım (3369 N) (U_x=0.5 mm)	Hasar yok.	
100. alt-adım (5065 N) (U_x=1 mm)		
150. alt-adım (6313 N) (U_x=1.5 mm)		
167. alt-adım (6818 N) (U_x=1.67 mm) (Bitiş)		

Şekil 4: C-3 plakasının orta düzlemdeki 0° tabakası örneğiyle fiber ve matris hasarlarının yayılması.

Sonlu elemanlar modeli Şekil-4'te görüldüğü gibi deliğin kenarında oluşan belirgin bir hasarı da tespit edebilmiştir. Sarı çemberin içerisinde yüzeydeki hasar net görülebilmektedir. Bu da KHM'de bulunan hasarlı bölgeye tekabül etmektedir.



i) **ii)**

Şekil 5: Delik kenarında oluşan yüzey hasarı. i) C-3 numunesine ait bir fotoğraf. ii) KHM'de tespit edilen hasarlı bölge.

Q-1 ve Q-3 elyaf sıralamalarının mukavemet kestirimindeki yüksek hata oranlarından dolayı ağ yapısı düzenlenerek sonlu elemanlar analizi tekrarlanmıştır. B bölgesindeki elemanların boyut oranı 4 yerine 3 olarak güncellenmiş ve çözüm yapılmıştır. Q-1 ve Q-3 elyaf sıralamaları için hatanın büyük oranda azaldığı görülürken, C-3 ve Q-2 elyaf sıralamaları için ise Tablo 7'de listelendiği gibi artmıştır.

Tablo 9: KHM ve deney sonuçlarının yenilenmiş ağ yapısı için karşılaştırılması.

Elyaf sıralaması	**Hasar yükü (Deney)**	**İlk ağ yapısı**		**Düzenlenmiş ağ yapısı**	
		Hasar yükü	Hata (%)	Hasar yükü	Hata (%)
C-3 $[90°/0°]_{2s}$	6523 N	6818 N	4.5	5806 N	-11
Q-1 $[+45°/0°/-45°/90°]_s$	6091 N	7294 N	16.5	6285 N	3.2
Q-2 $[90°/+45°/-45°/0°]_s$	7319 N	7527 N	2.8	6469 N	-11
Q-3 $[0°/90°/+45°/-45°]_s$	6926 N	6001 N	-13.4	6699 N	3.2

Değerlendirme ve Öneriler

Bu çalışmada Kademeli Hasar Modellemesi (KHM), yarı tek-yönlü kıvrımsız E-cam elyaf takviyeli kompozit plakaların cıvata bağlantılarındaki hasar ve mukavemet kestirimi için kullanılmıştır. Cıvata bağlantılarının mukavemeti kestirimleri başarıyla gerçekleştirilmiştir. Ayrıca, hasarın ilerleyişi de deneylerle yüksek tutarlılık göstermiştir. Kompozit malzemelerin homojen olmamasına rağmen sonlu eleman modelleri homojen olarak kabul edilse de sonuçlar tatmin edici seviyededir. Buradan klasik modelleme yaklaşımının kıvrımsız elyafların modellemesinde de kullanılabileceği çıkarımı yapılabilir. Kritik-altı hasar mekanizmaları, delaminasyon başlangıç ve ilerleyişi, malzemenin homojen olmaması gibi parametrelerin de ilave edilmesiyle çözümün doğruluğu ve verimliliği artırılabilir.

Teşekkür

Bu çalışma Balıkesir Üniversitesi Bilimsel Araştırma Projeleri Birimi tarafından BAP.2017.005 numaralı proje kapsamında desteklenmiştir.

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FATIGUE, TENSILE AND IMPACT BEHAVIOUR OF SHORT GLASS/CARBON FIBER REINFORCED HYBRID POLYAMIDE COMPOSITES

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Abstract

Short fiber reinforced polymer composites (SFRPCs) have been widely used in many applications. These materials can be subjected to impact and fluctuating loading, therefore their impact and fatigue behavior are important for usage of these composites. This study investigates the effect of the short glass fiber (SGF) and short carbon fiber (SCF) reinforcement on the tensile, impact and fatigue behavior of polyamide-6 (PA6) based composites. 30 wt. % SGF, 30 wt. % SCF and hybrid (15 wt. % SGF and 15 wt. % SCF) reinforced PA6 composites and master-batches were prepared by using twin-screw extruder and injection molding technique, respectively. The composite specimens were tested under tensile, impact and fatigue loading. Results showed that under impact and fatigue loading, short fiber addition decreased the impact energy and fatigue life of PA6 significantly. On the other hand, tensile strength and modulus values of the PA6 were significantly improved due to the addition of SCF and SGF, under static loading. The fracture surfaces of composites after tensile and impact tests were examined by scanning electron microscopy (SEM) to reveal the changes on failure modes.

Introduction and Objective

PA6 is widely used matrix material for composites due to their light weight, capability of manufacturing in complex geometries, heat distortion, electrical properties, fatigue strength, chemical stability and low cost. In order to improve the performance of thermoplastics, several types of reinforcing materials or fillers have been commonly used in industrial applications. Short fibers are generally preferred for their availability and cost, increasing the strength and stiffness of unreinforced thermoplastics [1].

Short carbon and short glass fibers are the most popular reinforcing materials for thermoplastic composites. To manufacture hybrid composites, a mixture SCFs and SGFs can be used in a single matrix system. In hybrid system carbon fiber provides a strength, stiffness and low density while glass fiber provides low cost [2]. In order to prepare the short fiber reinforced polymers (SFRPs), extrusion compounding and injection molding techniques are the most commonly used methods.

Some studies are reported in the literature about the effect of short fiber content on the mechanical properties of PA6 composites. Unal and Mimaroglu investigated the effect of SGF and mica fillers on the mechanical properties of polyamide 6. The content of reinforcement materials are 10 to 30% by weight. The results showed that increasing the SGF and mica content increased the tensile strength and modulus of PA6 composites. Moreover, addition of SGF and mica reinforcement decrease the impact strength of neat PA6 [3]. Karsli et.al. studied the effect of short carbon fiber content and length on the mechanical, thermal and morphological properties of SCF reinforced PA6 composites. According to test results, increasing SCF content increased the tensile strength, modulus and hardness values, however decreased the strain at failure values. Also it was shown that initial fiber length have no significant effect on the properties of composites due to the fiber breakage during processing [4]. Fu et.al. studied the tensile

properties of SGF and SCF reinforced polypropylene composites by considering the hybridization effect of these two type short fibers. They reported that tensile strength and modulus of the hybrid composites increased with increasing carbon fiber volume fraction however strain at failure values increased with decreasing carbon fiber volume fraction [2].

Another important property for composites is fatigue behavior of those systems since in many applications, cyclic loading over the period of service life of material is a critical concern. Therefore, it is also quite critical to investigate the fatigue behaviour of composites. Zhou and Mallick, examined the effect of cyclic frequency of the 33 wt. % short E-glass fiber reinforced PA6. At frequencies lower than 2 Hz, the fatigue life increased with increasing frequency. However at frequencies higher than 2 Hz, the fatigue life decreased with increasing frequencies due to the thermal failure [5]. Pegoretti et. al. investigated the effect of fiber weight fraction and the test frequencies to the fatigue crack propagation of the SGF reinforced polypropylene composites. During the fatigue tests, loading ratio (R) was selected as 0.4 and the frequencies were; 0.1, 1 and 10 Hz. Resistance to fatigue crack propagation increased with increasing fiber weight content. However, resistance to fatigue crack propagation decreases with increasing test frequency [6].

There is very limited number of study in the literature on the hybridization of SGF and SCF on the impact behaviour, fatigue life and mechanical properties of injection molded PA6 composites. Also, to our knowledge, there is no study about the impact behaviour and fatigue life of SGF and SCF reinforced hybrid PA6 composites. The aim of this work is to investigate the effect of SGF and SCF hybridization on the impact behaviour, fatigue life and mechanical properties of PA6 composites. The SGF and SCF were blended together with PA6 matrix by extrusion compounding and injection molding techniques by 30 wt. % SGF, 30 wt. % SCF and hybrid (15 wt. % SGF and 15 wt. % SCF).

Experimental

In this study, PA6 was used as a matrix material and SGF (short glass fibers) and SCF (short carbon fibers) were used as reinforcement materials. Since PA6 absorbs the water and this strongly affects the mechanical behaviour of PA6, SGFs and SCFs dried at 80^{o}C for 24 hours before preparing the composite pellets. Composites containing 30 wt. of % SGFs, 30 wt. % of SCFs and hybrid (15 wt.% SGFs and 15 wt.% SCFs) were prepared using a bench-top modular twin-screw extruder (Prism Eurolab 16XL). The barrel temperature and screw speed set as 240^{o}C and 70 rpm, respectively. The prepared composite pellets were dried at 80^{o}C for 3 hours. Composite specimens for fatigue, tensile and Charpy impact tests were prepared using an injection molding machine (Permak Inc., Turkey) at 240^{o}C and the injection pressure of 25 bars.

Tensile tests were carried out according to ISO 527 using a Shimadzu AGS-X Universal test machine with a crosshead speed of 5 mm/min. The tension tests were performed using at least five specimens and tensile strength, modulus of elasticity and strain at break values were determined. In order to determine the impact strength of composites, standard Charpy notched impact test specimens were used. The tests were done using falling-hammer-type Ceast™ impact tester and at least eight specimens were used. The dimensions of specimens were 3x13x60 mm.

Fatigue test were performed using MTS™ Landmark servo-hydraulic test machine with MTS 647 hydraulic wedge grips. The frequency was 2 Hz and the load factor was R=0.1. Low frequency was selected in order to prevent thermal failure. The load controlled fatigue test were performed under tension to tension loading with a stress levels of 90, 80, 70% (with respect to ultimate stress level) for each compounds and at least three specimens were tested.

The fractured surfaces were investigated by scanning electron microscopy (SEM) after tensile tests in detail. Surfaces of all tensile test specimens were coated with gold prior to SEM examination.

Results and Discussion

The representative stress-strain curves of neat PA6 and SGF and SCF reinforced composites under tensile loads are given in Figure 1. Tensile strength of neat PA6 increased significantly by the addition of short fiber reinforcements. The tensile strength of neat PA6 was measured as 66 MPa. It was observed that tensile strength and modulus of elasticity values of PA6 increases, on the other hand strain at failure values decreases with the addition of SGF and SCF reinforcement in to PA6 matrix. Due to the addition of SCF, the strength of PA6 based composites improved up to 165 MPa (about 150 % higher than those for neat PA6). The modulus of elasticity of neat PA6 was measured as 3.2 GPa. Due to the addition of SGF, this value increased up to 6.1 GPa (about 90 % higher than those for neat PA6). The tensile test results also showed that the strain at failure values decreased from 0.23 to up to 0.04 due to SGF and SCF reinforcements. This reduction in strain values associates with the restrictions for the mobility of polymer molecules due to the presence of the fibers. Moreover, the results showed that hybrid composites have similar mechanical properties with 30 % SCF composites. This imply that usage of hybrid fibers offers a potential to reduce cost due to carbon fiber.

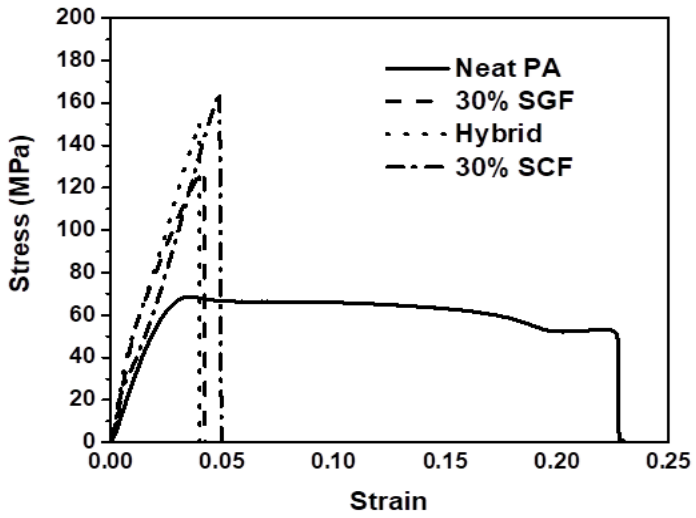


Figure 1. Stress- strain curves of SGF (short glass fiber) and SCF (short carbon fibers) reinforced PA6 based composites.

The Charpy impact energy values of the neat PA6 and SGF and SCF reinforced composites are shown in Figure 2. The average impact energy for neat PA6 was measured as 31 kJ/m^2. However, the results imply that SGF and SCF reinforcement decreased the impact energy significantly. This energy values associated well with the area under tensile-stress graphs. The SGF/SCF reinforced PA6 composites exhibited relatively brittle fracture, all samples failed into two separate pieces and no substantial plastic deformation observed. However, neat PA6 exhibited extreme plastic deformation during impact loading.

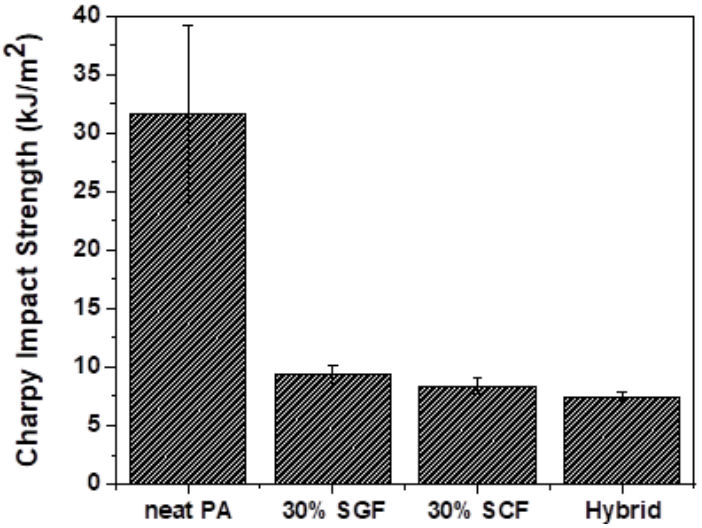


Figure 2. Chapry impact energy of SGF and SCF reinforced PA6 composites.

Figure 3 and 4 shows the S-N curves for neat PA6 and SGF/SCF reinforced PA6 composites respectively. Fatigue behavior of neat and SGF/SCF reinforced PA6 composites was investigated at stress levels of 70, 80 and 90 %. These applied stress levels for fatigue test were determined based on the tensile strength of the specimens measured based on tensile test. As it can be seen from Figure 4, fatigue life of the neat PA6 is decreased due to the incorporation of SGF and SCF s into the PA6 matrix. However, in figure 5, SGF reinforced composites have better fatigue life as compared to SCF and hybrid reinforced composites. Also fatigue test results imply that hybridization has negative effect on the fatigue properties of composites. Also stress level has significant effect on the fatigue properties of composites. When the stress level decreased, fatigue life of composites increased.

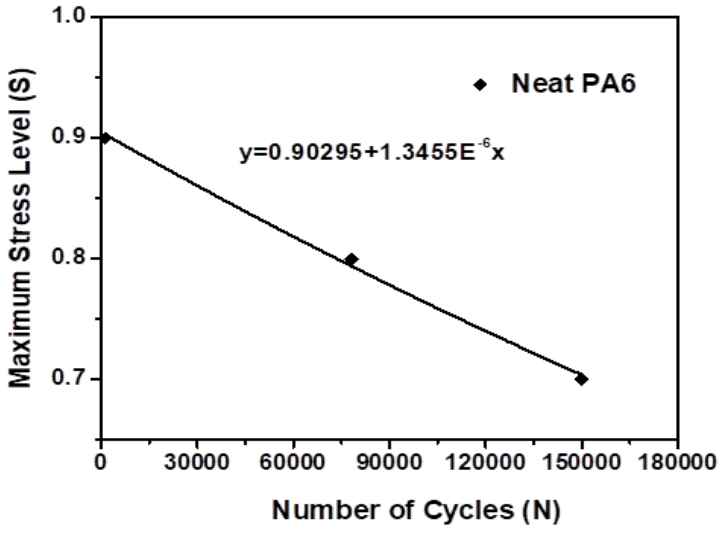


Figure 3. S-N curves of Neat PA6

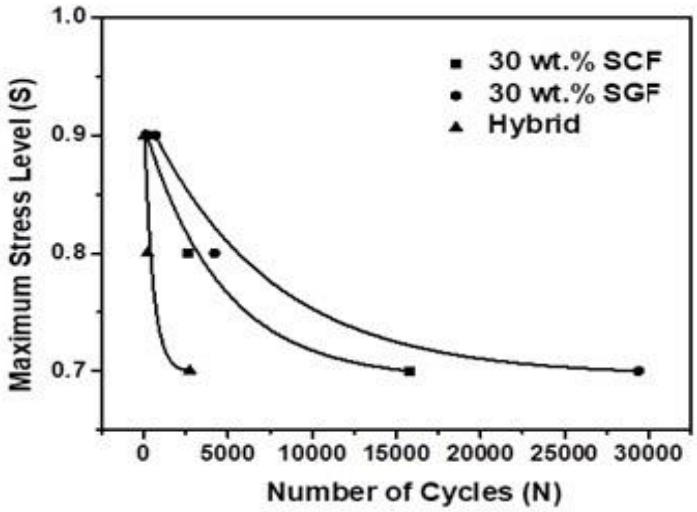


Figure 4. S-N curves of SCF and SGF reinforced composites

Figure 5 shows the fractured surface SEM images of SGF and SGF reinforced PA6 after tensile testing. Due to high stress concentration at the end of the fibers, crack firstly occurred at the end of the fibers. Consequently it resulted with the pull-out of the fibers from the matrix. Also debondings at fiber matrix interface were observed after tensile loading.

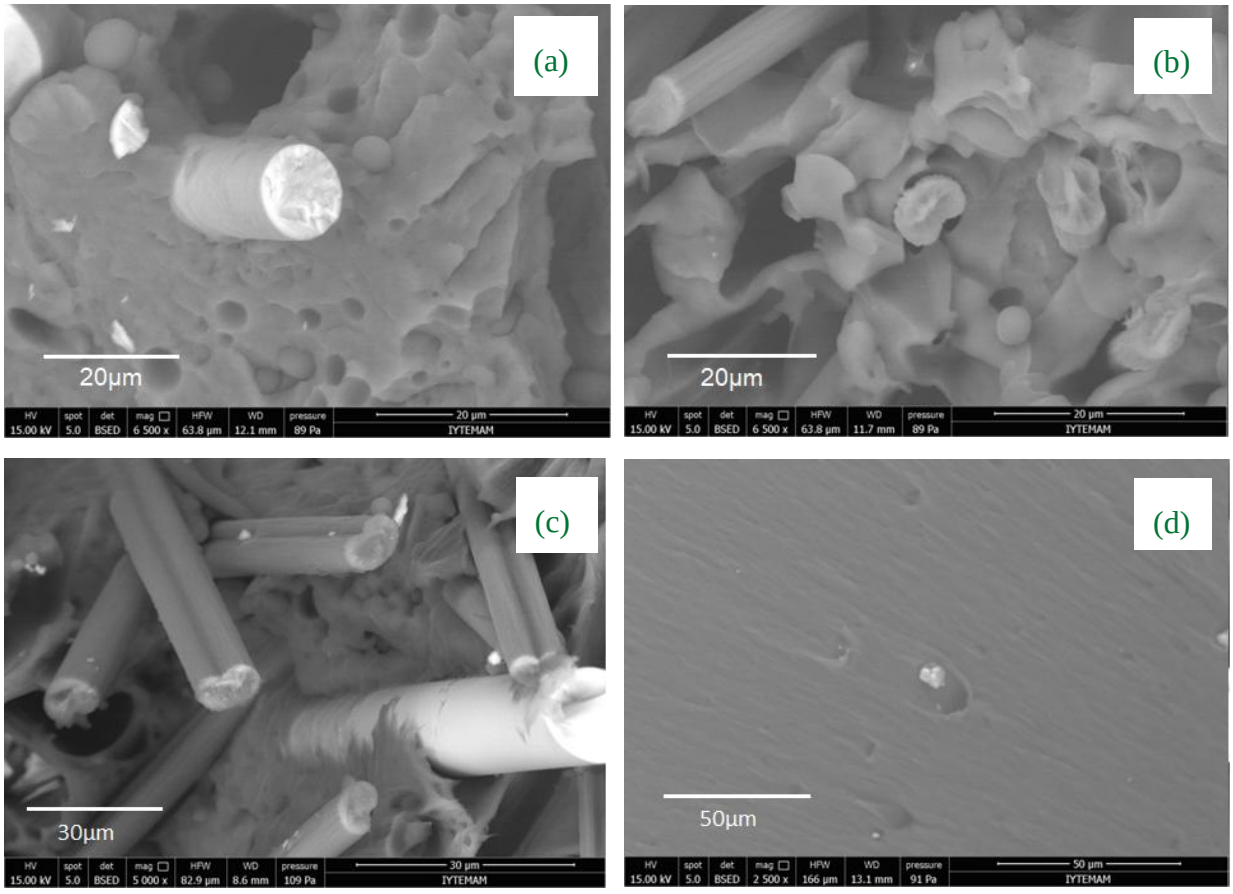


Figure 5. SEM micrographs of tensile fracture surfaces of (a) 30% SGF added PA6, (b) 30% SCF added PA6, (c) hybrid reinforced PA6, (d) neat PA6

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DEVELOPMENT OF FLAME RETARDANT GLASS FIBER REINFORCED POLYESTER COMPOSITES

ALEV GECİKTİRİCİ CAM ELYAF TAKVİYELİ POLYESTER KOMPOZİTLERİN GELİŞTİRİLMESİ

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Amaç

Cam elyaf takviye edilmiş polyester kompozitler taşımacılık, otomotiv, inşaat, denizcilik ve elektirik-elektronik gibi birçok sektörde yaygın olarak kullanılmaktadır. Özellikle insan faktörünün ön planda olduğu toplu taşıma araçları, yapı malzemeleri gibi uygulamalarda mekanik özelliklerin yanında alev geciktiriciliğin de yüksek olması gerekmektedir. Bu çalışmanın amacı Fibrosan Cam Takviyeli Polyester Sanayi ve Ticaret A.Ş. tarafından üretilen cam elyaf takviyeli polyester kompozit ürünlerin alev geciktiricilik özelliğinin arttırılmasıdır. Hedef eklenen yeni katkılarla firmanın amaçladığı 40 ve üstü LOI değerini karşılamaktır.

Anahtar Kelimeler

Cam elyaf takviye edilmiş polyester kompozit, alev geciktiricilik, ATH, EG, APP

Materyal-Yöntem

Bu çalışmada, kompozitlerin üretiminde polimer matrisi olarak doymamış polyester reçine ve takviye elemanı olarak da E-cam fiber örgüsüz kumaşlar seçilmiştir. Alüminyum hidroksit (ATH), şişen grafit (EG) ve alüminyum polifosfat (APP) alev geciktirici dolgu malzemeleri olarak kullanılmıştır.

Kompozitler el yatırma yöntemi ile üretilmişlerdir. Kumaşlara farklı kompozisyonlarda alev geciktirici dolgu malzemesi içeren polimer matris emdirilmiş ve kompozitler 60 °C'de 24 saat boyunca kürlenmeye bırakılmıştır.

Kompozitlerin alev geciktiricilik özellikleri LOI ve UL-94 testleri ile incelenmiştir. Malzemelerin kimyasal karakterizasyonu Fourier Dönüşümlü Infrared Spektrofotometresi (FTIR) ile yapılmıştır. Mekanik özellikler çekme testi ile, yüzey morfolojisi ise stereo mikroskop ve taramalı elektron mikroskobu (SEM) ile analiz edilmiştir. Ayrıca, kompozitlerin termal özellikleri Thermogravimetrik/Diferensiyel Termal Analiz cihazı ile karakterize edilmiştir.

Ön Değerlendirmeler

Alev geciktirici dolgu malzemesi olarak sadece ATH içeren kompozitin 33 LOI değerine sahip olduğu bulunmuştur. Daha yüksek LOI değerlerinin elde edilmesi için malzemeye daha yüksek

konsantrasyonlarda ilave edilmesi gereken ATH, malzemenin mekanik özelliklerinde düşüşe neden olmaktadır. Bu sebeple, ATH ile birlikte EG ve/veya APP alev geciktirici dolgu malzemeleri, bileşim polimer matrisine göre sabit tutularak kullanılmıştır. Yapılan testler sonucunda, tüm ikili-alev geciktirici kompozitlerin LOI değerlerinin sadece ATH içeren tekli alev geciktirici kompozitten daha yüksek olduğu bulunmuştur. APP ve EG'nin ATH ile kombinasyonunu içeren üçlü-alev geciktirici kompozitlerin, aynı LOI değerlerine sahip oldukları ve bu formülasyonlarda APP ve EG'nin etkisinin benzer olduğu sonucuna varılmıştır. Ayrıca, şişen alev geciktiricilerin oranı ATH'ye göre arttığında, en yüksek LOI değeri 43 olarak elde edilmiştir.

Çekme testi sonuçlarında ATH-APP kombinasyonu mekanik özellikleri önemli ölçüde etkilemez iken, EG ve ATH'ın birlikte kullanıldığı kompozitlerin mukavemetinde hafif bir düşüş olduğu sonucuna varılmıştır.

Sonuçlar

Sonuç olarak, ATH-APP (1:1) ve ATH-APP-EG (5:3:2) örnekleri ile en yüksek 43 LOI değeri elde edilmiştir. Ayrıca, alev geciktirici dolgu malzemelerinin birlikte kullanılması ile de mekanik özelliklerde herhangi bir olumsuz bir etki gözlenmemiştir.

Abstract

Glass fiber reinforced polyester composites are widely used in many sectors such as transportation, automotive, construction, marine and electric and electronic. Especially in the public transportation vehicles where human factor is at the forefront, and in construction materials applications, it is also necessary to have good flame retardant properties beside good mechanical properties. The aim of this study is to enhance the flame retardant property of glass fiber reinforced polyester composite products which are produced by Fibrosan Cam Takviyeli Polyester Sanayi ve Ticaret A.Ş. Our goal is to achieve the company's target of 40 and more LOI value with the contribution of new additives.

Introduction and objective

In recent years, glass fiber reinforced polymer composites (GFRP) have gained great attention and have been widely used in many fields such as automotive, aerospace, construction and transportation due to the their high strength and stiffness with their low density and highly flexible shaping properties [1]. However, the flammability of polymer matrix induces poor flame retardancy of these composites and it limits their use in further applications. Therefore, it is highly demanded to improve the flame retardancy of the glass fiber reinforced polymer composites [2]. Flame retardants are incorporated into polymer matrix and used to inhibit or to stop the polymer combustion process by physically (fuel dilution, cooling or charring) or chemically (reaction in the solid or gas phase) [3, 4]

Aluminium tri-hydroxide (ATH) is the commonly used mineral flame retardant due to its relatively low cost. It decomposes between 190 °C and 300 °C through an endothermic reaction which leads to release of water and formation of alümina.The reaction absorbs high amount of heat and delays the ignition as well as alumina forms a thermally insulating protective layer. Moreover, water vapor dilutes combustible gasses and forms a protective gas layer [5]. However, in order to increase the flame retardancy high loadings of ATH, generally ≥ 50 wt%, are necessary but it results in a dense and brittle material [6].

Intumescent flame retardants known as the new generation flame retardants are quite popular due to their high performance, low smoke emission, low toxic gas emission and anti-dripping properties. Expandable graphite (EG) and ammonium polyphosphate (APP) have been investigated as intrumescent systems [7]. EG essentially consists of crystalline carbon layers and these layers includes agents such as sulfuric acid molecules or potassium permanganate. When EG exposed to heat, it starts to decompose at

200 °C. The formed gases cause the separation of the carbon layers and char layer which protects the matrix material from flame and heat is formed [8-10].

APP degradation starts at 190 °C with the elimination of ammonia and water and ends up with yielding a cross linked ultra phosphate and highly cross crosslinked phosphoric acid. Polyphosphoric acid esterifies and dehydrates the polymer with formation of a carbonaceous protective char layer [11, 12].

In this study, utilization of ammonium polyphosphate (APP) and/or expandable graphite (EG) with aluminium trihydroxide (ATH) was investigated for the purpose of enhancing a flame retardant property of GFRP composites. Flame, thermal, and mechanical properties of the produced composites were determined and compared.

Experimental

In this study, for the production of composites unsaturated polyester resin and E-glass fiber non-woven fabrics were selected as a polymer matrix and reinforcement, respectively. Aluminum hydroxide (ATH), expandable graphite (EG) and ammonium polyphosphate (APP) were used as flame retardant fillers.

Composites were prepared by hand-lay up method. E-glass fiber non-woven fabrics were impregnated with the polymer matrix containing different flame retardant filler composition. Then, the composites were cured at 60 °C for 24h.

Flame-retardant properties of the composites were tested by LOI and UL-94 tests. Chemical characterization of the materials was done using Fourier transform infrared spectroscopy (FTIR). Mechanical properties were evaluated by tensile test and surface morphology analysis was performed by using scanning electron microscope (SEM).

Results and Discussion

To evaluate flame-retardant properties of the composites, LOI and UL-94 tests were conducted. Table 1 shows composition and flame retardancy of the composites.10A including ATH as the only flame-retardant filler had the LOI value of 33. In order to achieve higher flame retardancy, higher loadings of ATH (generally ≥ 50 wt%) are necessary however it is detrimental to the mechanical properties [6]. Therefore, EG and/or APP were used in combination with ATH while keeping the flame-retardant filler composition fixed with respect to polymer matrix. It was found that LOI values of all dual-flame retardant composites were greater than single-flame retardant composite (10A). When the effect of EG and APP were compared in combination with ATH, LOI values of 5A5E and 5A5P were found as 36 and 43, respectively meaning that ATH-APP combination could improve more the flame retardancy of the composite with a significant change in the LOI value than ATH-EG combination. We also prepared composites with triple-flame retardant system including APP and EG in combination with ATH. The same LOI values of 37 obtained for 7A1P2E and 7A2P1E indicated that in these formulations the effect of APP and EG was similar. On the other hand, when the ratio of the intumescent flame retardants increased with respect to ATH, the highest LOI value was obtained as 43.

UL-94 tests were performed on the composites had the highest flame retardant properties obtained from LOI test. The flame was applied for 10 s and removed. The afterflame time for all samples is zero. They self-extinguished and no droplet formation occured. Therefore, all the samples provide V-0 rating.

Table 1. Composition and flame retardancy of the composites.

Sample code	Flame retardant compositon (wt.%)		filler	Flame retardancy	
	ATH (A)	APP (P)	EG (E)	LOI	UL-94
10A	100	-	-	33	V0
9A1E	90	-	10	34	-
8A2E	80	-	20	35	-
5A5E	50	-	50	36	V0
8A2P	80	20	-	35	-
5A5P	50	50	-	43	V0
7A1P2E	70	10	20	37	-
7A2P1E	70	20	10	37	-
5A3P2E	50	30	20	43	V0

ATR-FTIR spectra are given in Figure 1. C-H and C=O stretching vibrations of polyester matrix appeared at 2978 and 1729 cm^{-1}, respectively. C=C stretching band that belongs to aromatic ring were at 1603 and 1450 cm^{-1}. C-O aromatic ester band was at 1258 cm^{-1}. C-O aliphatic ester stretching bands appeared at 1153 and 1070 cm^{-1} besides =CH aromatic ring bending bands appeared at 760 cm^{-1} and 700 cm^{-1} [13]. In the spectra of 5A5E and 5A5P, S=O stretching band (~1150 cm^{-1}) of the sulfuric acid that is included in the graphite, and P=O (~1250 cm^{-1}) and P-O (1100-1000 cm^{-1}) bands that belong to polyphosphate could not be identified as they overlapped with the polyester absorption bands [7, 14]. The absorbance at 3357 cm^{-1} due to O-H and N-H groups that belong to APP increased in both 5A5P and 5A3P2E. Besides, two new bands appeared in these samples at 1628 cm^{-1} and 794 cm^{-1} which may be due to the interaction of the APP with the polyester.

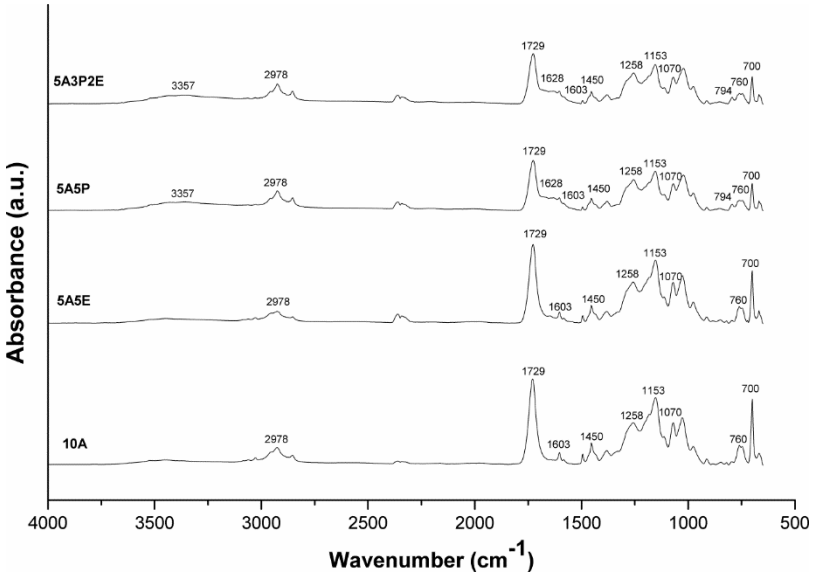


Figure 1. The ATIR–FTIR spectra of the composites.

SEM micrographs of the composites are shown in Figure 2. In 10A and 5A5E, ATH and EG are rather well dispersed in the polyester matrix. In contrast, SEM micrographs of the 5A5P and 5A3P2E show the presence of large particles that can be ascribed to aggregation of APP.

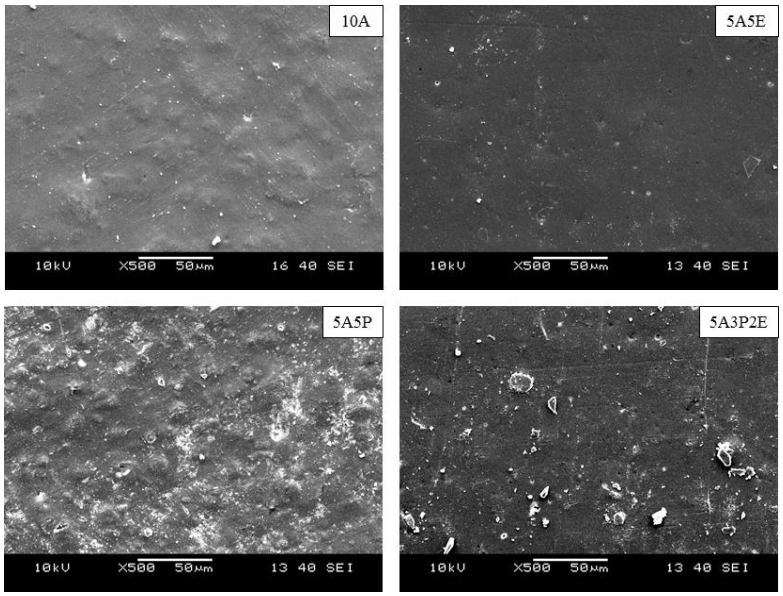


Figure 2. SEM images of the composites.

Table 2 shows the tensile test results of the composites. On the basis of the results, no negative effects of the flame retardants on the mechanical properties of the composites were observed. However EG together with ATH resulted in a slight decrease in the strength of the composites. Kuzdzal et. al. also prepared unsaturated polyester based flame retardant composites and they showed that the composites containing either ATH or APP had similar mechanical properties [15].

Table 2. Tensile test results of the composites.

Sample code	**Tensile strength (MPa)**	**Strain (%)**	**Young modulus (GPa)**
10A	73,2± 5,2	1,24± 0,20	7,38±1,4
5A5E	65,1±6,3	1,08±0,30	7,46±1,5
5A5P	73,1± 7,4	1,44± 0,17	6,87±0,37
8A2P	72,1±5,0	1,50±0,20	5,77±2,2
7A1P2E	70,6±4,3	1,29±0,43	9,40±1,8
7A2P1E	69,0±5,4	1,08±0,38	6,57±1,3
5A3P2E	72,1±6,6	0,97±0,18	9,56±3,3

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FAILURE ANALYSIS AND OPTIMIZATION OF THE CYLINDRICAL PART OF TYPE-III HYDROGEN STORAGE TANKS

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Özet

Günümüzde artan yüksek enerji talebi ile gaz tesisleri, enerji santralleri, havacılık, kimya ve otomotiv endüstrisi gibi çeşitli alanlarda kullanılan yüksek basınçlı hidrojen gazı depolayan ekonomik ve verimli bir basınçlı kap üretebilmek önemlidir. Bu bağlamda, birçok araştırmacı, yüksek basınçlı kaplar için tasarım ve optimizasyon süreçleri geliştirmişlerdir. Mevcut çalışmada, ana hedef, yüksek iç basınç altında silindirik tabakalı kompozit hidrojen depolama tankı geliştirmektir. Çalışmanın ilk bölümü şu adımları içermektedir: (i) Klasik Laminasyon Teorisi'ni kullanarak gerilme dağılımını elde etmek, (ii) tankın patlama basıncını üç farklı ilk tabaka kırılma kriterine göre hesaplamak, (iii) literatürdeki deneysel-nümerik sonuçlar ile karşılaştırmaktır. Çalışmanın son bölümünde ise, mümkün olan en düşük stres konsantrasyonunu sağlayan, sarım açısı, tabaka kalınlıkları ve açı dizilimi kombinasyonu stokastik optimizasyon yöntemleriyle belirlenecektir. Bu çalışmada, yüksek iç basınç altında Al-karbon elyaf / epoksi silindirik tabakalı kompozitin, stres-kırılma analizi ve optimizasyonu üzerine yoğunlaşılmıştır. Hidrojen depolama tankı, iç alüminyum astar ve karbon elyaf / epoksi kompozit tabakalardan oluşur. Astar izotropik ve homojen, karbon elyaf / epoksi kompozitler ise enine izotropik olarak kabul edilmiştir. Başlangıçta, kompozit tabakaların gerilme analizi, Klasik Laminasyon Teorisi kullanılarak yapılmıştır. Tankın hasar gelişimini ve patlama basıncını tahmin etmek için Hashin-Rotem, Maksimum Gerilme ve Tsai-Wu ilk tabaka kırılma kriterleri kullanılmıştır. Kırılma indeksleri elde edildikten sonra, teorik tahminler deneysel ve nümerik (ABAQUS) sonuçlarla karşılaştırılmıştır. Çalışmanın son kısmında, optimum sarım açı dizilimine sahip, yüksek basınçlı Tip-III hidrojen depolama tankı tasarımı öngörülmüştür. Kompozit yapıların optimizasyon problemini çözmek için, yüksek dereceli non-lineer terimler, karmaşık fonksiyonlar ve ayrık çözüm uzayları içeren problemlerin varlığı nedeniyle geleneksel optimizasyon teknikleri yerine, stokastik optimizasyon yöntemleri (DE ve SA) tercih edilmiştir.

Mevcut çalışmanın sonuçlarını aşağıdaki iki başlık altında özetlemek mümkündür.

1-Klasik Laminasyon Teorisi baz alınarak hesaplanan gerilme bileşenleri ve Hashin-Rotem, Maximum Gerilme, von Mises ve Tsai-Wu ilk tabaka kırılma kriterlerine göre hesaplanan patlama basınçları, literatürdeki mevcut deneysel ve nümerik (ABAQUS) sonuçlarla örtüşmüştür.

2-Yüksek basınçlı Tip-III hidrojen depolama tankı tasarım ve optimizasyon problemleri DE ve SA yöntemleriyle çözülmüş ve sonuçlar birbiriyle karşılaştırılmıştır. Bu stokastik yöntemlerle çözülen problemlerin sonucunda, üretilebilir tank tasarımları önerilmiştir.

Abstract

Nowadays, it is crucial to produce economical and efficient pressure vessels that store high pressure hydrogen gas used in various fields such as gas plants, power plants, aerospace, chemical and automotive industry with increasing high energy demand. In these regards, many researchers have developed design

and optimization procedures for high pressure vessels. In the present study, the main objective is to minimize the damage evolution of a cylindrical laminated composite hydrogen storage tank under high internal pressure. The first step is to obtain the distrubition of stress components based on Classical Laminated Plate Theory (CLPT). The second is to evaluate the burst pressure of the tank according to three different first ply failure criteria and then to compare the results with the experimental and numerical ones from literature. In the final part of the study, the best possible combination of winding angles, stacking sequences and thicknesses of laminates satisfying minimum possible stress concentration will be obtained by stochastic optimization methods. This paper concentrates on the stress-failure analysis and optimization of the Al-carbon fiber/epoxy cylindrical laminated composite under high internal pressure. The hydrogen storage tank consists of an inner aluminum liner and laminated carbon fiber/epoxy composite. The liner is assumed to be isotropic and homogeneous; the carbon fiber/epoxy composite are considered as transversely isotropic. Initially, the stress analysis of the composite laminates is performed by using the CLPT. In order to predict the damage evolution and burst pressure of the tank, Hashin-Rotem, Maximum Stress and Tsai-Wu first-ply failure criteria have been used. After obtaining failure indexes, the theoretical predictions have been compared with the experimental and numerical (ABAQUS) results. The last part of the study is to design high pressure Type-III hydrogen storage tank with optimum winding angle orientation. Because there are highly nonlinear, complicated functions and discreate search spaces problems in composite design, stochastic optimization methods, Differential Evolution (DE) and Simulated Annealing (SA), have been performed to solve optimization problem of the composite structures rather than traditional optimization tecniques.
The results of the present study can be summarized as

1- The stress components based on CLPT and, the burst pressures reached according to Hashin-Rotem, Maximum Stress, von Mises and Tsai-Wu first-ply failure criteria, have been complied with experimental and numerical (ABAQUS) results in the literature.
2- Design and optimization problems of high pressure Type-III hydrogen storage tank have been solved by DE and SA methods and then the results compared with each other. As a result of the problems solved by these stochastic methods, manufacturable Type-III tank designs have been proposed.

Introduction

Recently, high pressure hydrogen storage tanks have been used in various fields such as gas plants, power plants, aerospace and automotive industry with increasing high energy demand. In this regard, many researchers have developed design and optimization methods for high pressure composite storage tanks. Many studies have been carried out the optimal design of composite tanks by simplifying problem as cylindrical structures [1]. Due to inherent complicated nature of the structures, optimal design of filament wound composite tanks has not been widely reported. At this point, some researchers [2], [3], [4] have developed generalized optimization formulations using analytical methods and experimental design constraints. These contributions of optimization problem definitions are very significant. However, to improve well-organized optimal design algorithms is necessary for general composite filament wound tanks.

In optimization process, there are two main issues as traditional and non-traditional methods. Traditional optimization methods are analytic and operate well for only continuous and differentiable functions. Optimization and design problems of composites are very complex including lengthy non-linear expressions. Therefore, derivative calculations of objective functions are generally costly. For this reason, to solve the problems by stochastic optimization methods such as Differential Evolution (DE), Simulated Annealing (SA), Genetic Algorithms (GA) and Generalized Pattern Search Algorithm (GPSA) become more efficient.

There are some minimum weight, maximum stiffness, maximum failure loads design and optimization problems in the literature. Generally, in the fiber reinforced composite pressure vessel optimization studies, the main design variables are fiber orientation angles and thickness [5]. In this

respect, Kim et al. have optimized Type III tank subjected to internal pressure by using a Modified Genetic Algorithms and, they have used weight and failure criteria as objective function and constraint, respectively [6]. In order to reach minimum weight and maximum stiffness design for cryotanks, Tomasetti et al. have used an approach associated with optimization and Finite Element Method (FEM) [7]. Liu et al. [8] have studied a method as Artificial Immune System (AIS) to obtain a minimum weight design of a Type III hydrogen storage tank. Xu et al. [9] have proposed an Adaptive Genetic Algorithm to minimize the weight of a high pressurized composite hydrogen tank and also compared the results based on a Simple Genetic Algorithm and a Monte Carlo optimization method. In ref. [10], two developed methods have been applied as (i) Classical Laminated Plate Theory (CLPT) with gradual damage and enumerative optimization and (ii) sophisticated FEM with Reddy's Progressive Damage Law and GA optimization have been compared to optimize design methods Type III hydrogen storage tanks in terms of advantages and limitation. Roh et al. [11] have carried out a design-optimization problem related with Type IV vessels operating at 70 Mpa. Alcantar et al. [12] have also studied weight minimization problem of Type IV high pressure hydrogen tank based on Genetic Algorithms and Simulated Annealing methods. CLPT and Tsai-Wu failure criterion have also been used for 70 Mpa vessels with a safety factor of 2.25. It is shown that the proposed methodology produces more efficient designs by reducing the weight by up to 9.8% and 11.2%. Additionally, there are some comparison studies on theoretical-simulation-experimental burst pressure in the literature.

Zheng et al. [14] have concentrated on the elastic–plastic stress and failure analysis of the Al-carbon fiber/epoxy composite cylindrical laminates under internal pressure and thermal residual stress. Burst strength calculated by using CLPT have been also compared with experimental results. And there are in good agreement between these results with the maximum error of 10%. Liu et al. [15] have investigated on aluminum–carbon fiber/epoxy composite cylindrical laminate structures to predict burst strength using explicit finite element method. The results have also been compared with experiments. As a results of comparison, the explicit finite element analysis have showed consistent burst pressure with implicit analysis and experiments.

In the present paper, the main objective is to minimize the first ply failure index of a cylindrical laminated composite hydrogen storage tank under high internal pressure. The first step is to obtain the distribution of stress components based on Classical Lamination Plate Theory (CLPT). The second is to evaluate the burst pressure of the tank according to three different first ply failure criteria and then to compare the results with the experimental and numerical ones from literature. In the final part of the study, the best possible combination of winding angles and stacking sequences have been proposed satisfying minimum failure indexes for Tsai-Wu, Hashin-Rotem, Maximum Stress first ply failure criteria for each layers. Two different stochastic optimization algorithms, Differential Evolution (DE) and Simulated Annealing (SA), have been used to solve the optimization problem. The results have also been compared each other in order to see capability of the algorithms on design optimization of hydrogen storage tank under high internal pressure.

Stress Analysis of Cylindrical Part of the Tank

Cylindrical part of the Type III tank are considered composed of isotropic aluminum liner and orthotropic carbon fiber/epoxy composite layers. The laminated composite pressure vessel having radius of "r_0" is subjected to the internal pressure "p". The force resultants, calculated via considerations of static equilibrium[13], are

$$N_x = \frac{1}{2}pr_0 \qquad N_y = pr_0 \qquad N_{xy} = 0 \tag{1}$$

In the Eq. (2) given below, *A*, *B* and *D* matrices represent extensional stiffness, coupling stiffness and bending stiffness of the laminate, respectively. Also, M_x, M_y, and M_{xy}, are moment resultants.

$$\begin{bmatrix} N_x \\ N_y \\ N_{xy} \\ M_x \\ M_y \\ M_{xy} \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{16} & B_{11} & B_{12} & B_{16} \\ A_{12} & A_{22} & A_{26} & B_{12} & B_{22} & B_{26} \\ A_{16} & A_{26} & A_{66} & B_{16} & B_{26} & B_{66} \\ B_{11} & B_{12} & B_{16} & D_{11} & D_{12} & D_{16} \\ B_{12} & B_{22} & B_{26} & D_{12} & D_{22} & D_{26} \\ B_{16} & B_{26} & B_{66} & D_{16} & D_{26} & D_{66} \end{bmatrix} \begin{bmatrix} {\varepsilon_{xx}}^0 \\ {\varepsilon_{yy}}^0 \\ {\gamma_{xy}}^0 \\ \kappa_{xx} \\ \kappa_{yy} \\ \kappa_{xy} \end{bmatrix} \quad (2)$$

where, ${\varepsilon_{xx}}^0, {\varepsilon_{yy}}^0$ show mid-plane normal strains, ${\gamma_{xy}}^0$ is mid-plane shear strain , κ_{xx}, κ_{yy} and κ_{xy} are curvatures.

The elements of [A], [B] and [D] matrices are given in Eq. (3 a-c)

$$A_{ij} = \sum_{k=1}^{N} [\bar{Q}_{ij}]_k \, (h_k - h_{k-1}) \quad (3.a)$$

$$B_{ij} = \frac{1}{2} \sum_{k=1}^{N} [\bar{Q}_{ij}]_k \, (h_k^2 - h_{k-1}^2) \quad (3.b)$$

$$D_{ij} = \frac{1}{3} \sum_{k=1}^{N} [\bar{Q}_{ij}]_k \left(h_k^3 - h_{k-1}^3\right) \quad (3.c)$$

where (i,j=1,2,6), $\left[\bar{Q}_{ij}\right]_k$ are the elements of the transformed reduced stiffness matrix and it can be defined as Eq. (4 a-f)

$$\bar{Q}_{11} = Q_{11}cos^4\theta + 2(Q_{12} + 2Q_{66})sin^2\theta cos^2\theta + Q_{22}sin^4\theta$$

$$\bar{Q}_{12} = (Q_{11} + Q_{22} - 4Q_{66})sin^2\theta cos^2\theta + Q_{12}(sin^4\theta + cos^2\theta)$$

$$\bar{Q}_{22} = Q_{11}sin^4\theta + 2(Q_{12} + 2Q_{66})sin^2\theta cos^2\theta + Q_{22}cos^4\theta$$

$$\bar{Q}_{16} = (Q_{11} - Q_{12} - 2Q_{66})sin\theta cos^3\theta + (Q_{12} - Q_{22} - 2Q_{66})sin^3\theta cos\theta$$

$$\bar{Q}_{26} = (Q_{11} - Q_{12} - 2Q_{66})sin^3\theta cos\theta + (Q_{12} - Q_{22} + 2Q_{66})sin\,\theta cos^3\theta$$

$$\bar{Q}_{66} = (Q_{11} + Q_{22} - 2Q_{12} - 2Q_{66})sin^2\theta cos^2\theta + Q_{66}(sin^4\theta + cos^2\theta) \quad (4 \text{ a-f})$$

Q_{ij} is the stiffness coefficients and given as follows

$$Q_{11} = \frac{E_1}{1-v_{21}v_{12}} \quad Q_{12} = \frac{v_{12}E_2}{1-v_{21}v_{12}} \quad Q_{22} = \frac{E_2}{1-v_{21}v_{12}} \quad Q_{66} = G_{12} \quad (5 \text{ a-d})$$

Failure Analysis

Failure is inability of the structure against to the applied loads. The main reasons can be listed as follows: (i) insufficient of the design procedure, (ii) wrong material choice, (iii) inadequate production facilities and (iv) diversity of service conditions. Many researchers have proposed the formulations for failure predictions. The number of the approaches and important progress clearly demonstrated that there is not any criterion universally accepted by designers as enough under various load conditions. In present study, three failure criteria chosen from interactive, partial interactive and non-interactive failure approaches have been used for composite material design. Maximum Shear Strain Energy (Von- Mises) theory have been used for isotropic liner.

Relationships between the stress components and Von-Mises, Tsai-Wu, Hashin-Rotem and Maximum Stress failure theories is defined below:

Maximum Shear Strain Energy (Von-Mises):

The theory considers the principle stresses $\sigma_1 \geq \sigma_2 \geq \sigma_3$ and point out that failure when the following equality is valid.

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 2\sigma_{yield}^2 \quad (6)$$

where σ_{yield} is the yield stress in simple tension,

Tsai-Wu Tensor Failure Criterion

Failure occurs if the following expression is valid according to the theory,

$$\frac{\sigma_L^2}{X^2} - 2F_{12}\sigma_L\sigma_T + \frac{\sigma_T^2}{Y^2} + \frac{\tau_{LT}^2}{S^2} = 1 \quad (7\ a)$$

where F_{12} can be expressed as in ref. [16]

$$F_{12} = -\frac{1}{2}\sqrt{\frac{1}{X_t X_c Y_t Y_c}} \quad (7\ b)$$

Maximum Stress Criterion

In this criterion, the composite is considered to be fails when the stress exceeds the respective allowable. There are three different conditions of failure in this criterion:

- Fibre : $-\left(\sigma_1^C\right)_{ult} < \sigma_1 < (\sigma_1^T)_{ult}$ or (8 a)

-Matrix : $-\left(\sigma_2^C\right)_{ult} < \sigma_2 < (\sigma_2^T)_{ult}$ or (8 b)

-Shear : $-(\tau_{12})_{ult} < \tau_{12} < (\tau_{12})_{ult}$ (8 c)

Hashin-Rotem Criterion

This criterion involves two failure mechanisms as fibre failure and matrix failure, distinguishing between tension and compression [17].

Fibre failure in tension $(\sigma_1 > 0)$

$$\sigma_1 = (\sigma_1^T)_{ult} \quad (9\ a)$$

Fibre failure in compression: $(\sigma_1 < 0)$

$$-\sigma_1 = \left(\sigma_1^C\right)_{ult} \quad (9\ b)$$

Matrix failure in tension: $(\sigma_2 > 0)$

$$\left(\frac{\sigma_1}{(\sigma_2^T)_{ult}}\right)^2 + \left(\frac{\tau_{12}}{(\tau_{12})_{ult}}\right)^2 = 1 \quad (9\ c)$$

Matrix failure in tension: $(\sigma_2 < 0)$

$$\left(\frac{\sigma_2}{(\sigma_2^C)_{ult}}\right)^2 + \left(\frac{\tau_{12}}{(\tau_{12})_{ult}}\right)^2 = 1 \quad (9\ d)$$

Optimization Algorithms

Differential Evolution Method

As a stochastic optimization method, Differential Evolution (DE) enable to find alternative solution for composite design. In DE, there are four main stages: initialization, mutation, crossover, and selection. Scaling factor, crossover, and population size are three parameters checked by the algorithm, also. A

population of solutions instead of a single solution at each of iteration is considered in Differential Evolution method. DE is effective in attaining global optimum avoiding local minimum of the objective function. However, it is computationally expensive. In the literature, DE has been investigated to design of fiber composite structures from simple rectangular plates to complex geometries [5].

Simulated Annealing Method

Simulated Annealing (SA) is a search technique based on thermal annealing of heated solids to achieve the minimum function value in an optimization problem. SA can solve continuous, mixed integer-continuous, or discrete optimization problems. At each iteriation, SA algorithm generates a new point, and stops when any of the defined stopping criteria are satisfied. This algorithms can be find global optima on composite design problems. Boltzmann's probability distribution can be expressed as the distance of the new point from the current point or the extent of the search. For a system in thermal equilibrium at temperature T, Boltzman probability distribution of energy can be defined as in the following form :

$$P(E) = e^{-E/kT}$$

where k symbolizes the Boltzmann's constant, T is temperature and $P(E)$ expresses the probability of reaching the energy level E.

SA algorithms can be summarized with these steps

1.Firstly, begin with an primary vector x_1 and appoint a temperature value to the function.
2. A new design point is created randomly. And the difference in function values is found.
3. It is defined that whether the new point is better or worse than the current point.
4. If the value of a randomly generated value is greater than $e^{-\Delta E/kT}$ accept the point x_{i+1}.
5. If the point x_{i+1} not admitted, then the algorithm assign a new design point x_{i+1} randomly.

Problem Definition

To be able to storage high pressure hydrogen gas in the tanks, there are some important issues as structural stability and airtightness. Thus this thype of tanks is generally made up with a load-sharing aluminum or polimer liner and composite wound layers.

In the present study, due to the significance of the structural stability and airtightness under the internal high pressure, three different design of Type III tank have been used with metallic liner (see Fig 1). Two design possibilities can usually be considered for Type III tanks design: (i) with a liner yield, (ii) without yielding of liner. In present study, yielding of liner have been assumed as constraint under the internal working pressure of 70 Mpa. In addition of this, it hasn't been taken as a constraint over 70 Mpa.

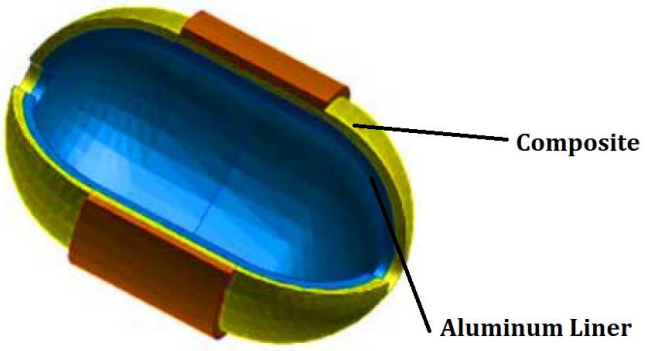


Figure 1. Configuration of the Type III tank [2]

In the verification step of the present study, stress components and failure index values based on Tsai-Wu only (which is related with burst pressure of the tank) have been calculated and then compared to

experimental and Finite Element Analysis results from the literature [14,15] (see Table 1). 6061 Aluminum and T700/epoxy carbon reinforced composite materials are used for the tank. Mechanical properties and strength parameters of these materials are given in Table 1 and 2, respectively.

Table 1
Mechanical properties of 6061 Al and T700/epoxy composite materials

	E_1(Mpa)	E_2(Mpa)	G_{12}(Mpa)	ν_{12}	ν_{23}	$\boldsymbol{\sigma_{yield}}$ (Mpa)
6061Al [15]	70	70	26.92	0.3	0.3	246
T700/epoxy[14]	181	10.3	5.17	0.28	0.49	-
T700/epoxy[15]	154.1	10.3	5.17	0.28	0.49	-

Table 2
Strength parameters of T700/epoxy composite materials (Mpa) [15]

$(\boldsymbol{\sigma_1^T})_{ult}$	$(\boldsymbol{\sigma_1^C})_{ult}$	$(\boldsymbol{\sigma_2^T})_{ult}$	$(\boldsymbol{\sigma_2^C})_{ult}$	$(\boldsymbol{\tau_{12}})_{ult}$
2500	1250	60	186	85

The second step is design and optimization part: overall procedures for different optimizaton cases have been summarized briefly.

- Close-end cylindrical section of the Type III tanks have been only considered subjected to high internal pressure " P ".
- It is considered to be constant over the length of the cylinder for inner radius (R_0= 44 mm), thicknesses of the composite layers (t_c= 0.42 mm or t_c= 0.21 mm) and aluminum liner (t_{liner} = 1.8 mm).
- For the optimization problems 1 and 2, three different failure criteria to be interactive, partial-interactive and non-interactive : Tsai-Wu , Hashin Rotem and Maximum Stress have been used as constraints. In optimization problem 3, Tsai-Wu failure criterion is considered only.
- All optimization cases of composite cylindrical tanks have been asuumed to be single objective optimization problem.
- Fiber orientation angles $\theta_1, \theta_2, \theta_3, \ldots, \theta_n$ and number of layers are selected as the design variables.

Problem 1

In design problem 1, there are two main purposes: (i) to compare the results based on Simulated Annealing and Differential Evolution algorithms and (ii) to propose safety designs of symetric-balanced stacking sequences over 170 Mpa. The yield of the liner is prohibited at working pressure 70 Mpa. Additionally, Tsai-Wu , Hashin Rotem and Maximum Stress failure indexes F_i of all the layers have been proposed to be less than 1. Thicknesses of the composite layers are 0.42 mm.

Problem 1 can be defined as mathematically:

Minimize: $F_{T[1]}$ (Tsai-Wu Failure Index at first layer)

Constraints: $\{F_{\text{Tsai-Wu}}, F_{\text{Hashin-Rotem}}, F_{\text{Maximum Stress}}\} \leq 1, \sigma_{\text{von-Misses}} < \sigma_{yield}$,

$-90^0 \leq \theta \leq 90^0$, $\theta \in$ Integers,

P_{burst}>170 Mpa, Symetric & Balance stacking sequences,

t_c= 0.42 mm, t_{liner}= 1.8 mm

Problem 2

As different from Problem 1, in design Problem 2, minumum burst pressure constraint is given as 157.5 Mpa. Symetric and balance stacking sequences design have also been considered. SA and DE are used as optimization method. It is also supposed to be less than 1 for Tsai-Wu, Hashin Rotem and Maximum Stress failure indexes of the all layers. Each thickness of the composite plies are 0.42 mm.

The mathematical repsentaiton of Problem 2 is defined as

Minimize: $F_{T[1]}$ (Tsai-Wu Failure Index at first layer)

Constraints: $\{F_{\text{Tsai-Wu}}, F_{\text{Hashin-Rotem}}, F_{\text{Maximum Stress}}\} \leq 1$, $\sigma_{\text{von-Misses}} < \sigma_{yield}$,

$-90^0 \leq \theta \leq 90^0$, $\theta \in$ Integers,

$P_{burst} > 157.5$ Mpa, Symetric & Balance stacking sequences,

$t_c = 0.42$ mm, $t_{liner} = 1.8$ mm

Problem 3

The main objective of the optimization problem 3 is to see significance of reduction in thickness of the ply, eventhough the total thickness of the composite part remain unchanged. For this reason, there are two different thicknesses to be 0.42 mm and 0.21 mm. DE have been used for two different design cases.

Minimize: $F_{T[1]}$ (Tsai-Wu Failure Index at first layer)

Constraints: $F_{\text{Tsai-Wu}} \leq 1$,

$-90^0 \leq \theta \leq 90^0$,

$P_{burst} > 110$ Mpa

$t_{liner} = 1.8$ mm

Design Results

The initial options for the Differential Evolution and Simulated Annealing Algorithm were generated as in Table 3 and design problems were performed. Table 4 shows comparison results of the predicted burst pressure values based on Tsai-Wu failure criterion with the experimental and Finite Element analysis results. It can be seen that good agreement is reached between them with the maximum error of 10%.

After the solution of the optimization problem 1, two different stacking sequences designs of composites having burst strength over the 170 Mpa have been proposed (See Table 5). As DE have reached solution at 24 layers, SA managed to solve at 28 layers. There are two design results satisfying 70 Mpa working pressure and 2.25 safety factor in Problem 2. DE and SA results have also been compared with each other in the view of finding global optimum. As an optimum stacking sequences, DE have proposed design of fiber orientation configuration at 20 layers, whereas SA have suggested a 24 layered solution. It should be noted that, designs 1 and 2 proposed by using DE and SA have symetric, balanced and integer fiber orientation angles, therefore, it provides easy manufacturable productions. According to results of composite design problems 1 and 2, DE is more effective than SA and.

Table 3
Options of the DE and SA solvers on Wolfram Mathematica v.11

Options	DE	SA
CrossProbability	0.5	-
RandomSeed	0	0
ScalingFactor	0.6	-
Search Points	-	1000
Tolerance	0.001	0.001
Contract Ratio	-	-
ExpandRatio	-	-
ReflectRatio	-	-
ShrinkRatio	-	-
LevelIteration	-	50
PerturbationScale	-	0.1

Table 4
Comparison of the burst pressure (MPa)

	Analytical [Present]	Finite Element [15]	Experimental [15]
Burst Pressure	95.5	99.8	106

In design problem 3, two design results with 10 and 20 layers capable of the strength over 110 Mpa have been proposed by using DE. Difference between 10 and 20 layers the design is %0.018 in terms of the burst pressure. First design in case 3 has 20 layers with 0.21 mm and 112 Mpa burst pressure. The second has also 10 layers with 0.42 mm and 110 Mpa. Stacking sequences and burst strength results have given for all of the cases in Table 6.

Table 5
Results of optimization

Prob. No	Obj. Func.	Constraints	Optim. Alg.	Ply Thicknes (mm)	Stacking Sequences	Ply No	Burst Press. (Mpa)
1	$F_{T[1]}$	$F_{Tsai\text{-}Wu} \leq 1$ $F_{Hashin\text{-}Rotem} \leq 1$, $F_{Maximum\ Stress} \leq 1$ $\theta \in$ Integers Symetric-Balanced P_{burst}>170 Mpa	DE	0.42	$[90_2/\mp46/\pm45/\mp61/\pm46/\pm50]_s$	24	172
			SA	0.42	$[90_2/\mp27/\pm59/\mp54/\pm85/\mp48/\mp32]_s$	28	176
2	$F_{T[1]}$	$F_{Tsai\text{-}Wu} \leq 1$ $F_{Hashin\text{-}Rotem} \leq 1$, $F_{Maximum\ Stress} \leq 1$ $\theta \in$ Integers Symetric-Balanced Safety Factor= 2.25 $P_{working}$=70 Mpa P_{burst}>157.5Mpa	DE	0.42	$[\mp54/\pm54/\pm54/\ \mp54/\pm66]_s$	20	157.5
			SA	0.42	$[\pm87/\ \pm45/\ \pm68/\ \mp65/\ \mp42/\pm29]_s$	24	157.5
3	$F_{T[1]}$	$F_{Tsai\text{-}Wu} \leq 1$ $\theta \in \{-90,90\}$ P_{burst}>110 Mpa	DE	0.42	[85.2/47.5/53/47.5$_2$/-53$_3$/47.5/-53]	10	110
				0.21	[90/-52$_2$/51.9$_2$/-52/51.9$_2$/-52$_2$/51.9$_2$/-52$_2$/ 51.9$_3$/ -52$_3$]	20	112

Conclusion

In present study, optimal design of cylindrical part of Type III tanks subjected to three different internal pressures have been performed by using DE and SA methods. Optimal design algorithms have composed of stress analysis, failure analysis and DE and SA methods. Two optimization method DE and SA have been compared. Different designs for hydrogen storage tanks have been reached. Due to be symetric balanced and integer features of the composites, manufacturable stacking sequences design have been achieved. From the present study, conclusions can be sortable as:

- For problem 3, despite of the same total thickness, doubling of the number of layers haven't made an advantage in terms of burst pressure.
- By using DE and SA, two designs with 24 and 28 layers have been suggested as manufacturable design. Both designs are capable of the burst strength over the 170 Mpa.
- Two different stacking sequences of fiber orientation angles composed of 20 and 24 layers have been caried at 157.5 Mpa burst pressure.
- According to comparison of the optimization results, DA is better than SA to find global optimum of design problems for composite pressure vessel.

Acknowledgements

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INVESTIGATIONS OF ANTIBACTERIAL PROPERTIES OF CHITOSAN/ZnO NANOPARTICLES REINFORCED EPOXY COMPOSITE COATINGS

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Abstract

Antibacterial materials are becoming important not only in the hospital and healthcare environments, but also for laboratory, home, marine and some industrial applications. Chitosan can be called as environment purification functional materials as it can effectively control the growth, reproduction of hazardous bacteria and control toxic pollutants. Zinc Oxide (ZnO) nanoparticles are known about their excellent stability and long shelf life with organic antimicrobial agents. In this study, an epoxy dye was converted to an antibacterial composite coating by using chitosan/ZnO nanoparticles. Firstly ZnO NPs were prepared by the sol-gel (citrate route) method using Zinc Nitrate, $Zn(NO_3)_2 \bullet 6H_2O$ as the starting materials. Different proportions of chitosan colloids and ZnO nanoparticles (%0.5 ZnO-Epoxy, %10 Chitosan-Epoxy, %10 Chitosan-%0.5 ZnO-Epoxy and %10 Chitosan-%1 ZnO- Epoxy) were inserted to the polymer matrix. Glass substrates were coated with obtained polymeric composites. FTIR (Fourier Transform Infrared) and XRD (X-ray Diffraction) tests were conducted to determine the structural and morphological properties of the test samples. In order to investigate chitosan colloids and ZnO nanoparticles, Scanning electron microscopy-Energy dispersive spectroscopy (SEM-EDS), analysis were evaluated. Antibacterial activity against Staphylococcus Aureus (S. Aureus) of the samples were measured as a main objective of this research. Chitosan/ZnO nanoparticles reinforced composite samples were subjected to type of the antibacterial test called “percent decreasing test”. Percent decreasing test: 50 microliters of Staphylocoocus aureus liquid culture (7,9x107 CFU / ml) was added to the samples and incubated for 1 hour in room conditions. At the end of the period, the number of area S. aureus on the sample surface was determined by dilution plate technique. The difference between the number of the bacteria obtained at zeroth hour and the one obtained after 1 h will show the antibacterial performance. The difference between the number of the bacteria obtained at zeroth hour and the one obtained after 1 hour and percent decreasing were calculated. ZnO nano particles and chitosan were found to provide antibacterial properties 99.6%, 99.22%, 99.8% and 99.65%, respectively. It was concluded that ZnO nano particles and chitosan colloids were effective to get antibacterial property.

Keywords: Composites, Chitosan, Zinc Oxide, Antibacterial materials, S. Aureus, Percent decreasing test.

1. Introduction

Antibacterial and antimicrobial materials and systems are either becoming increasingly important in the hospital and healthcare environments,or for home, laboratory, marine and some industrial applications. Materials and systems are being improved to avoid the set up, spread and transfer of detrimental bacteria and viruses, as well as actively disabling them. Antibacterial and antimicrobial factors are becoming important each day. They have been studied for use in a range of the healthcare applications, industries, house, environments and laboratories. The most important usage is to adjust medical environments and equipment for the sterilization in order to prevent deaths caused from hospital-associated infections [1].

Chitosan has become a promising polymer in many fields, as a result of increased work on chitosan and consequently very important properties of chitosan such as renewability, non-toxicity, biodegradability, biocompatibility, antibacterial, antimicrobial and antitumor effect. Chitosan has displayed high antimicrobial activity against a wide variety of pathogenic and spoilage microorganisms, containing fungi, and Gram-positive and Gram-negative bacteria. One of the reasons for the antimicrobial character of chitosan is its positively charged amino group which interacts with negatively charged microbial cell membranes, primarily to the leakage of proteinaceous and other intracellular constituents of the microorganisms [2].

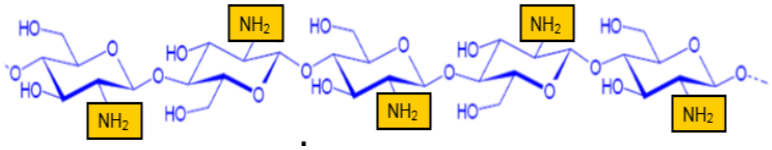


Fig. 1. Chemical structure of chitosan.

The synthesis of nano-sized ZnO has caused to the investigation of its use as new antibacterial agent. In addition to its distinctive antibacterial and antifungal properties, ZnO- NPs have high catalytic and high photochemical activities [3]. ZnO exhibits significant antimicrobial activities when particle size is reduced to the nanometer range, then nano- sized ZnO can interact with bacterial surface and/or with the bacterial core where it enters inside the cell, and afterwards exhibits distinct bactericidal mechanisms [4].

In an ideal photocatalytic process, organic pollutants are mineralized into carbon dioxide (CO_2), water (H_2O) and mineral acids in the presence of ZnO particle and reactive oxidizing species,like oxygen or air. The photocatalytic reactions were begun when ZnO particle absorbs photons with energies greater than that of its band gap energy from the illumination. Thus, photo-induced electron is promoted from the valence band (VB) to the conduction band (CB), forming positively hole (h^+_{VB}) and electron (e^-_{CB}) on the surface of ZnO particle. The general photo-catalysis mechanism processes are shown in Fig. 1 [5].

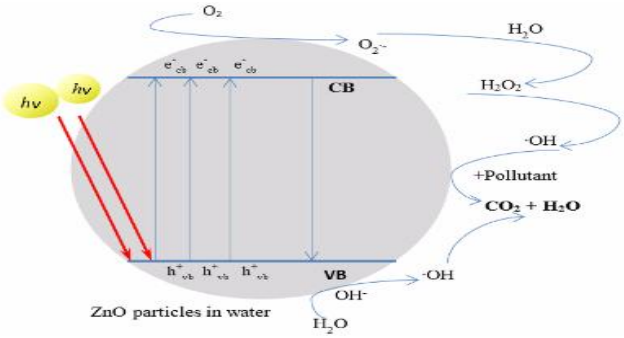


Fig. 2. General mechanism of the photocatalysis.

2. Materials and Methods

2.1. Production of ZnO Nano Powder by Sol-Gel Method

Nanoparticles of Zinc oxide were prepared by the sol-gel (citrate route) method using Zinc Nitrate, $Zn(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar) as the starting materials. Citric acid $C_6H_8O_7 \cdot H_2O$ (Sigma-Aldrich) was used as a complexing agent. A stoichiometric weight of metallic cation was homogeneously mixed in deionized water using magnetic stirring at 70 °C. Then, Citric acid was also dissolved in deionized water for 30 minutes. The Citrate/Nitrate ratio used was 1. The solution of Citric acid was added to slowly in the solution of Zinc Nitrate. The reaction mixture was heated at 70 °C with continuous stirring until gel formation. The product obtained was dried at 130 °C for 12 hours and pulverized for 30 minutes.

The precursor materials were calcined at the calcination temperature (Tc) of 550 °C for 21 hours. The oven temperature was increased by 0.5 °C in 1 minute to 330 °C. It was fixed at 330 °C for 30 minutes. Then increased by 0.5 degrees Celsius in 1 minute to 550 °C. It was fixed at 550 °C for 180 minutes. These samples were denominated in ZnO form. The reaction of zinc oxide formation can be written as described in equation (1):

$$Zn(NO_3)_2 \cdot 6H_2O + C_6H_8O_7 \cdot H_2O + 4O_2 \rightarrow ZnO + NO_2 + 6CO_2 + 11H_2O \quad (1)$$

Infrared spectra were carried out in a Fourier transform spectrophotometer Thermo Scientific Nicolet iS50 FT-IR in the range of wavenumber 4000-600 cm-1. X-ray diffraction (XRD) measurements were performed on a diffractometer Empyrean in 2θ range of 10-80, with speed of 5.0 deg/min using CuKα1 (K=1.54) source, maintaining applied voltage of 45 kV and current at 40 mA. Scanning electron microscope-Energy dispersive spectroscopy (SEM-EDS) analysis was performed in order to examine ZnO powder structures.

2.2. Preparation of Chitosan colloids

Chitosan was used in colloid form. Chitosan colloids were prepared as presented in Fig. 3. For obtaining the chitosan colloids, Chitosan(Poly-(D) glucosamine, Sigma) was dissolved in the acid solution. 1 g of chitosan dissolved in 100 mL of 1 vol% aqueous acetic acid solution. After a complete mixture by using magnetic stirrer at 25 °C for 20 min, homogeneous chitosan colloids were obtained.

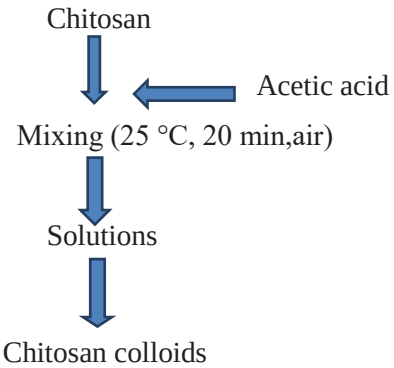


Fig. 3. Preparing method of chitosan colloids [58].

2.3. Preparation of Chitosan/ZnO Powder Epoxy Dye Coatings

For the manufacture of the composites, epoxy dye was used as a polymeric matrix supplied from DYO, Turkey. The obtained chitosan colloids were added to epoxy dye as a polymer matrix with different loading levels to determine the concentration depence of material's antibacterial activity. ZnO powder was used as filler, to improve the antibacterial properties of the coating. Epoxy dye was diluted by adding thinner and stirred at about 500 rpm for 5 minutes. ZnO powder with different loading levels was directly added to the resin thinner solution and stirred at a speed of 500 rpm for at 20 minutes, using magnetic stirrer.

Glass substrates were coated with those chitosan/ZnO nano powder reinforced epoxy dye composites. After obtained composite coatings were afterwards dried for 24 h at the room temperature in the air. The sample codes and descriptions coatings are represent in Table 1.

Table 1. Description and sample codes of composite coatings.

Sample codes	Chitosan percentage in the composite (%)	Zinc oxide Percentage in the composites(%)
E/Z-05	None	0.5
E/C-10	10	0
E/C-10/Z-0.5	10	0.5
E/C-10/Z-1	10	1

Infrared spectra were carried out in a Fourier transform spectrophotometer (Thermo Scientific Nicolet iS50 FT-IR) in the range of wavenumber 4000-400 cm^{-1}. Scanning electron microscope (SEM) analysis was performed in order to examine structures of chitosan/ZnO powder reinforced epoxy dye composites. In addition, antimicrobial properties of the samples against Staphylocoocus aureus were determined. Antibacterial properties of the samples were measured by percent decreasing test explained below:

Percent Decreasing Test: 50 microliters of Staphylocoocus Aureus liquid culture (7,9x107 CFU / ml) was added to the samples and incubated for 1 hour in room conditions. At the end of the period, the number of area S. aureus on the sample surface was determined by dilution plate technique. The difference between the number of the bacteria obtained at zeroth hour and the one obtained after 1 h will show the antibacterial performance described in equation (2):

$$\% \text{ decrease} = \left[\frac{A-B}{A}\right] \text{x } 100 \qquad (2)$$

in which, A: Bacteria number at zeroth hour and B: Bacteria number after 1 h.

3. Results and Discussions

The effect of crystallization of zinc oxide nanoparticles was investigated by X-ray analysis method. X-ray diffraction patterns of zinc oxide powder is shown in Figure 4.

Fig. 4 shows a typical XRD pattern of as-prepared ZnO nanoparticles. It can be observed that all diffraction peaks can be indexed to the wurtzite ZnO structure (JCPDS 036-1451) [6]. There can be said no characteristic peaks of impurity phases were observed, which indicates that the powders obtained in the present work were single- phase hexagonal ZnO.

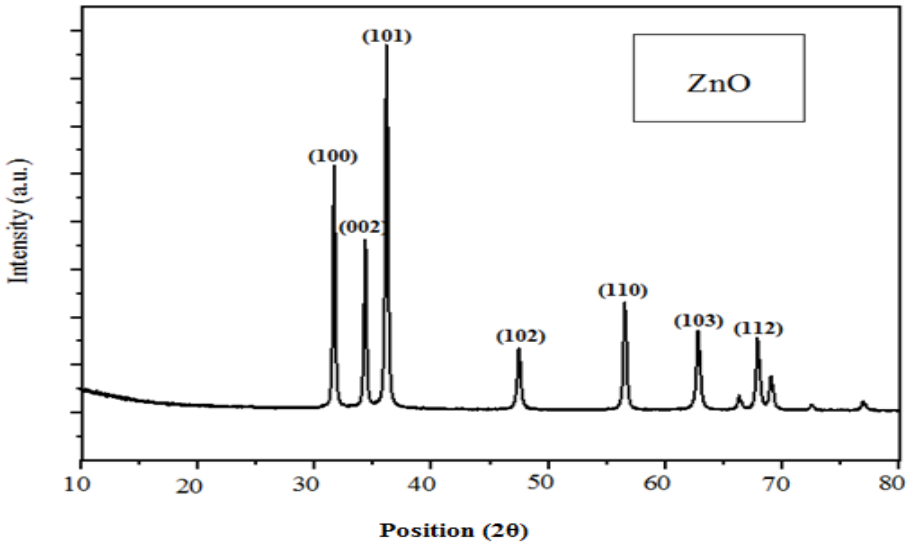


Fig. 4. X-ray diffraction patterns of zinc oxide powder produced by Sol-Gel method using zinc nitrate as the starting materials.

FTIR analysis was used to examine the chemical composition and structure of material. The structural and characteristic groups of material were determined. FTIR spectra were recorded in the absorbance mode. Fig. 5 demonstrates FTIR analysis results of the ZnO powder and coated samples. In FTIR spectra, absorbance is characteristic of Zn–O vibrations and generally depends on the particle's morphology. In ZnO NPs sample, the FTIR spectrum shows the Zn-O peak at 589 cm^{-1} suggesting formation of ZnO. Series the hydroxyl probably results from hydroscopic nature of ZnO and carboxylate results from reactive carbon containing plasma groups during preparation of ZnO nanoparticles. Presence of peaks between 2897 and 3000 cm^{-1} are due to C–H stretching vibration of the various alkane groups. Peaks observed at 1310 cm^{-1} are due to symmetrical and asymmetrical stretching of the zinc carboxylate groups. The peaks absorption at 1333 and 1415 cm^{-1} correspond to the stretching vibration of the C–H group. The peaks at 1065 cm^{-1} were the stretching vibration mode of C–O groups [7,8]. Broadband at around 3500 cm^{-1} is assigned to O–H stretching mode of the hydroxyl group.

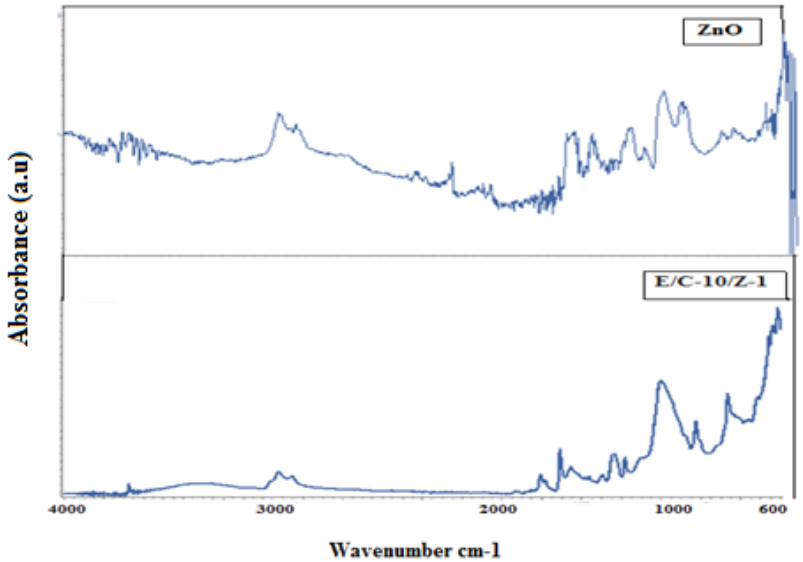
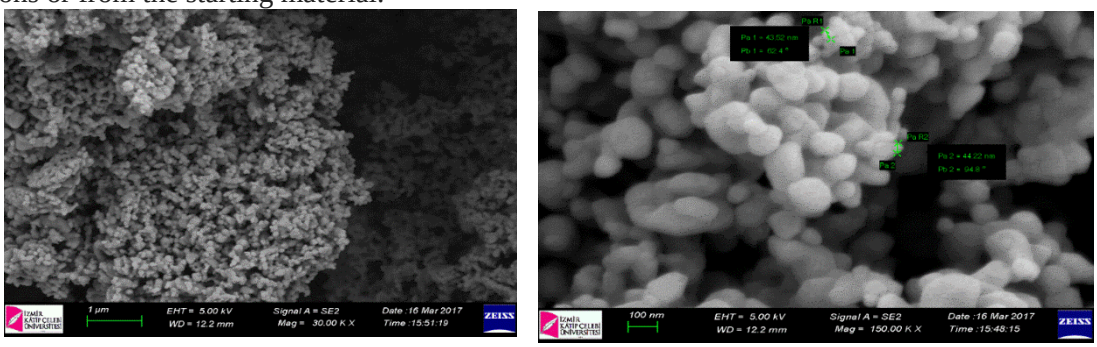


Fig. 5. FTIR analysis of ZnO NPs and ZnO/Chitosan reinforced composite

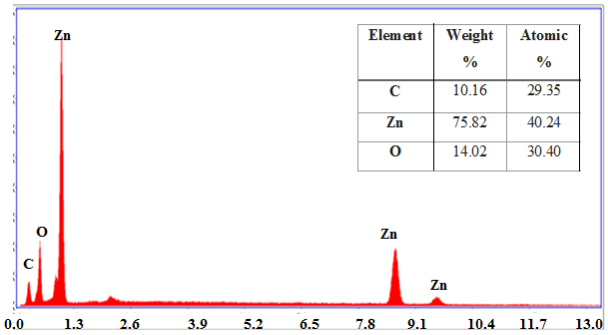
It can be seen from the figure that the chitosan exhibits main characteristic bands of carbonyl (C-O-NHR) and amine group (–NH_2) at 1455 cm^{-1}. Nevertheless, this band can correspond to C–H bending from epoxy matrix. Zinc oxide powders are not organic minerals and they cannot be indicated for FTIR. In the same way, CH_3COH group band can be observed at 748 cm^{-1} related with the chitosan but this may come from the epoxy, because the characteristic peaks of epoxy indicate the formation of Si–O, Si–O–Si, and Si–C at 668, 1012, 1240 cm^{-1}, respectively [9].

SEM analysis was performed on Zeiss Sigma 300 VP-FESEM. Figure 6 (a) and (b) show low (X30.000) and high (X150.000) magnification SEM micrographs of the ZnO particles. SEM image of ZnO powder Fig.6 (b) shows that most ZnO powders spherical and short rod shape when compared to the studies of Wei Bai et al. (2009) [10]. The microstructure of crystalline ZnO can be interpreted as a skeletal form resulting from the process of calcination Fig.6 (a) according to the studies of Barbara Hutera et al. (2013) [11]. As a result of measurement, grain size was determined at nano size.
According to the EDS result showed Fig.7, some amount of carbon was detected in three zones. Although it is not known as the cause of this, it can be interpreted that the carbon remains from the environmental conditions or from the starting material.



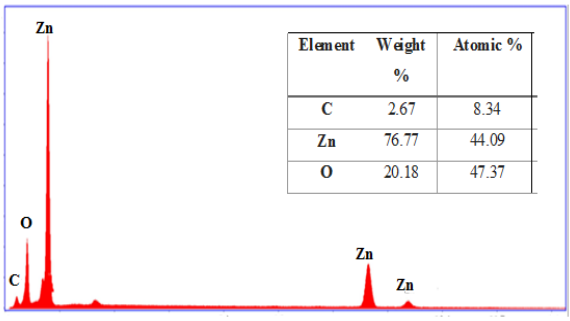
(a) (b)

Fig. 6. SEM micrographs of (a) ZnO particles at X30.000 magnification; (b) at X150.000 magnification.



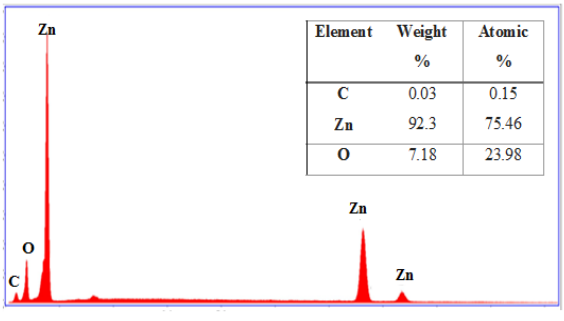
Element	Weight %	Atomic %
C	10.16	29.35
Zn	75.82	40.24
O	14.02	30.40

(a)



Element	Weight %	Atomic %
C	2.67	8.34
Zn	76.77	44.09
O	20.18	47.37

(b)



Element	Weight %	Atomic %
C	0.03	0.15
Zn	92.3	75.46
O	7.18	23.98

(c)

Fig. 7. EDS analysis of (a) ZnO powder at selected area 1; (b) at selected area 2 and (c) at selected area 3.

Fig. 8 depicts SEM micrographs of pure chitosan which is not indicated any crystalline structure. It shows the smooth areas which could be visualized of naturally polymeric material of chitosan. SEM images of composite coatings were given in Fig. 8. It can be seen that chitosan particles look like sphere, not flake, and they were well blended with dye homogeneously. Smooth and rough areas could be seen in chitosan incorporated into the coatings. As characteristic property of chitosan, large crystals were appeared [12].

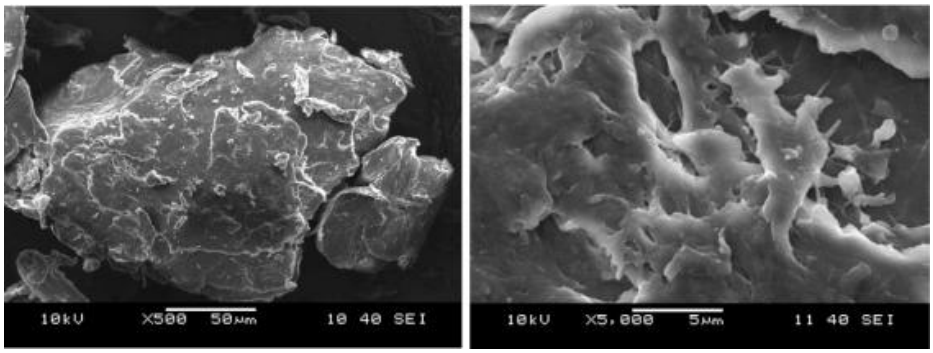
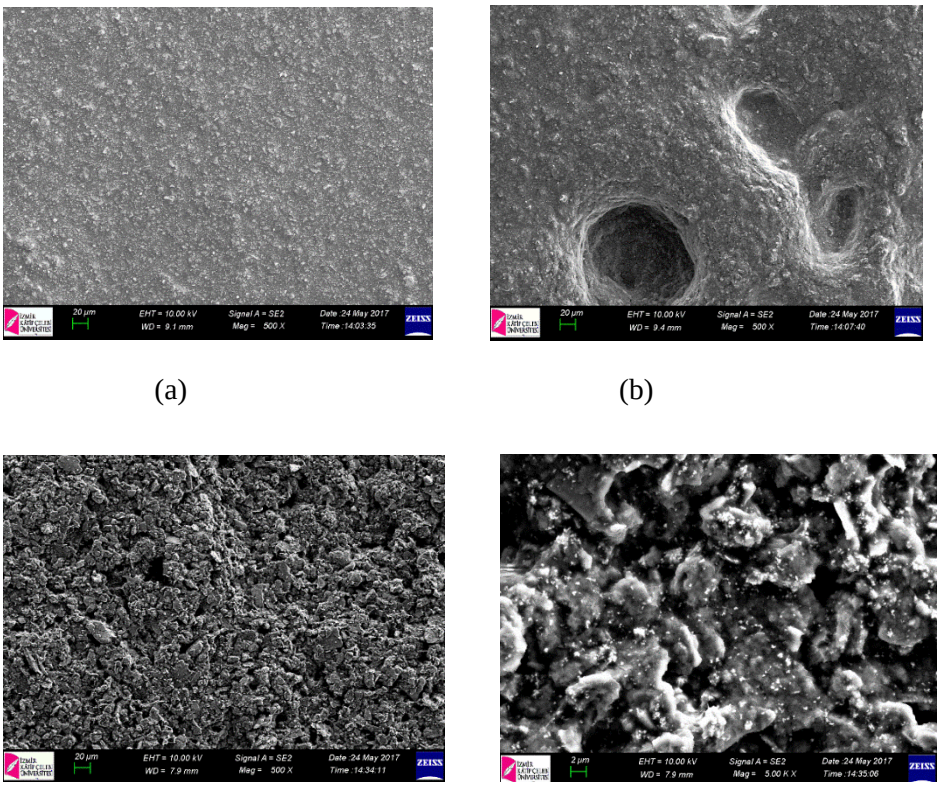


Fig. 8. SEM micrographs of pure chitosan material.



(a) (b)

(c) (d)

Fig. 9. SEM micrographs of (a) chitosan reinforced epoxy dye coating at X500 magnification; (b) Chitosan reinforced epoxy dye coating at X5000 magnification; (c) Chitosan/ZnO powder reinforced epoxy dye coating at X500 magnification; and (d) Chitosan/ZnO powder reinforced epoxy dye coating at X5000 magnification.

Chitosan/ZnO NPs reinforced composite samples were subjected to type of the antibacterial test called "percent decreasing test". The difference between the number of the bacteria obtained at zeroth hour and the one obtained after 1 hour and percent decreasing were calculated shown in Table 2 below:

Table 2. *Percent Decreasing Test Results.*

Sample	**% Decreasing**
E/Z-0.5	99,6
E/C-10	99,22
E/C-10/Z-0.5	99.8
E/C-10/Z-1	99,65



Fig. 10. An example of antibacterial test results.

It can be expressed that all samples showed antibacterial property. When the antibacterial activity of the samples is compared, there is little difference between them. Regarding the samples including chitosan and ZnO, antimicrobial effects are seen on the surface of the coated region.

4. Conclusion

The production of antibacterial composite coating was investigated. An epoxy dye was converted to material which shows antibacterial activity. Two different types of materials were incorporated into polymer matrix for antibacterial property, Chitosan and ZnO NPs.

ZnO powders were obtained by sol-gel processing. Chitosan was used as a homogeneous colloid by using an acid solution. Then, the obtained additives were added to epoxy dye with different loading levels and the glass substrates were coated with those polymer composites. ZnO Nanoparticles were prepared by the sol-gel (citrate route) method using Zinc Nitrate, $Zn(NO_3)_2 \bullet 6H_2O$ as the starting materials. FTIR (Fourier Transform Infrared) and XRD (X-ray Diffraction) and Scanning electron microscopy-Energy dispersive spectroscopy (SEM-EDS) analysis were conducted and evaluated. The formation of wurtzite-type structure of zinc oxide was observed. It was seen that ZnO particles is spherical and nano size from SEM analysis images. According to EDS analysis that is made in 3 different regions, no impurities were found in the structure.

Chitosan/ZnO Powder Reinforced Epoxy Dye Coating was also investigated. FTIR (Fourier Transform Infrared), Scanning electron microscopy (SEM) and *Percent decreasing test were performed. In detail, regarding the antibacterial property, E/Z-0.5, E/C-10, E/C-10/Z-0.5 and E/C-10/Z-1 showed antibacterial value 99,6%, 99,22%, %99,8, %99,65, respectively.* The results are very close to each other. For more

detailed and comparable results to measure the individual effect of each additive material, different antibacterial tests can be performed such as agar disc diffusion method that shows the presence or absence of growth in a halo around the samples.

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NANOPARTICLE REINFORCED CHITOSAN/NA-CARBOXYMETHYL CELLULOSE POLYELECTROLYTE SCAFFOLDS FOR BONE TISSUE REGENERATION

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Abstract

In recent studies, the composites consisting biopolymers and silica particles show potential in biomedical applications and silica-based nanoparticles came into prominence to induce bone tissue regeneration as an alternative to hydroxyapatite (HAP) crystals. Among synthetic silica sources, polyhedral oligomeric silsesquioxanes (POSS) are the smallest synthetic silica particles which are hybrid structures composed of inorganic part (silicon/oxygen cage) and organic part (hydrocarbon functional groups) which allows stronger interfaces with polymer matrix. Therefore, the main objective of this study is to develop POSS incorporated chitosan/Na-carboxymethyl cellulose porous scaffolds for bone tissue engineering applications and to determine the effect of POSS on the physical, mechanical and biological characteristics of the polymer. In addition, it is also aimed to compare the effect of POSS nanoparticles with the most widely used synthetic HAP nanoparticles as reinforcement agents. The microstructure of CS/Na-CMC scaffolds showed large pores with thick pore wall structure inducing high surface area for cell attachment. The porosity of the scaffolds was found as 61-70% which was found to be appropriate for cell migration and nutrient supply in the trabecular bone. Synthetic POSS particles increased the mechanical strength by reinforcing the structure and enhanced the water uptake capacity of CS/Na-CMC scaffold due to its hydrophilic nature. The weight loss % of silica incorporated scaffolds slightly increased at the 21day of incubation due to the possible dissolution of silica particles from the scaffold surface. *In vitro* cytotoxicity results indicated that POSS reinforced scaffolds did not show any cytotoxic effect on MG-63 cell line. ALP activity on POSS composite scaffolds was found to be higher than HAP incorporated scaffolds. Besides, POSS incorporation enhanced the biomineralization on scaffold surface which is an important step for bone regeneration.

1.Introduction

Biopolymer-based composites for tissue engineering applications are named to be the new generation of high-performance materials by combining the advantages of inorganic materials and organic polymers such as flexibility, ductility, and processability [1]. Nano-hydroxyapatite (HAP) is generally incorporated into biodegradable polymers because it is the main component of bone tissue as an inorganic phase. The hydroxyapatite crystals provide calcium and phosphate ion source on the material surface which is substantial for cell differentiation and osteogenic cell proliferation [2].

Recently, silica-based nanoparticles came into prominence to induce bone tissue regeneration as an alternative to HAP crystals. Silica, hydrated silicon dioxide, is the second most abundant biogenic mineral produced by various plants and animals [3].

Usage of silica in bone tissue engineering is getting attendance to support cell adhesion by increasing the bioactivity and osteoinductivity by enhancing the bone ingrowth as a calcifying agent. Silica particles stimulate osteogenic proliferation and activate bone-related gene expression. Besides, silica particles can improve mechanical properties of polymers by providing an enhancement in the structure. In literature, studies showed that silica incorporation induced the CaO accumulation and nucleation of the apatite layer

on the surface which are essential steps in the formation and mineralization of hard tissues [4,5,6].Among synthetic silica sources, polyhedral oligomeric silsesquioxanes (POSS) are the smallest synthetic silica particles which have inorganic part composed of silicon/oxygen cage and organic portion consists hydrocarbon functional groups attached to corner Si molecules [7,8]. POSS nanocages provide a larger surface area when it is compared with the microscale ceramic particles by means of its nanosized structure. Thus, stronger interfaces can be obtained with POSS incorporation in a polymer matrix [9]. Besides, POSS nanocages can be used as nanofiller in biomedical applications as drug delivery systems [10]; cardiovascular [11,12] and dental nanocomposites [13,14].

Chitosan (CS) is a natural cationic polysaccharide that has been used as a scaffold material promoting cell adhesion and functional expressions of osteoblasts with its structural similarity to glycosaminoglycan groups in the extracellular matrix. Therefore, it can be widely preferred in biomedical applications such as drug delivery, wound healing, tissue engineering, cancer diagnosis [15]. However, its lower stability and faster degradation profile needs to be used with crosslinkers, reinforcement materials or polymer blends. Na-Carboxymethyl cellulose (Na-CMC) is the only water-soluble derivative of cellulose. The remarkable point is its opposite charge and structural similarity to chitosan. which enables the formation of polyelectrolyte complex due to the electrostatic interactions between CS and Na-CMC. CS/Na-CMC based scaffolds are promising biomaterials for possible medical applications with their good biocompatibility, biodegradability and hydrophilic surface [16,17].

2.Objective

The aim of this study is to reinforce CS/Na-CMC polyelectrolyte complex scaffolds with POSS nanoparticles and determine their physical, mechanical and biological characteristics for bone tissue engineering applications. In addition, the results were compared with the most used synthetic HAP nanoparticles as reinforcement agents.

3. Materials & Methods

3.1 Materials

Commercial low molecular chitosan (MW=50-190 kDa, DDA%= 75-85) and Na-CMC (50-200 cP, 4 % in H_2O at 25 °C) were purchased from Sigma-Aldrich and used for the preparation of scaffolds. HAP (Sigma-Aldrich) and POSS Octa TMA® (Hybrid Plastics TM) were used as reinforcements. MG-63 cell line was supplied from Dr. Berivan Erik Cecen. Minimum essential medium (MEM, Sigma-Aldrich), fetal bovine serum (FBS) penicillin-streptomycin solution and L-glutamine (Lonza) were used for cell culture studies. WST-1 ready to use cell proliferation reagent (BioVision Inc.), Resazurin Cell Viability Kit (Cell Signaling Technology Inc.) and ALP-Enzyline PAL optimise kit (Biomerieux Inc.) were used for *in vitro* assays.

3.2. Preparation of Nanoparticle Incorporated Polyelectrolyte Complex Scaffolds

The scaffolds were prepared with freeze-drying technique to obtain a microporous structure required for vascularization. HAP and POSS nanoparticles were dried at 80°C for 24h in to remove the moisture and prevent the agglomeration. Equal amounts of CS and Na-CMC aqueous solutions were prepared separately. Polymer solutions and inorganic aqueous dispersions were mixed under vigorous stirring. Finally, 1% v/v acetic acid was added dropwise to the solution. The homogeneous mixtures were moulded and prefreezed at -20°C for 24h. Finally, mixtures were lyophilized at -46°C.

3.3. Characterization of Scaffolds

Composite scaffolds were analyzed with SEM to observe the surface morphology and average pore size. The open porosity of the composite scaffolds was determined with the liquid displacement method. The mechanical strength of dry scaffolds was measured by compression test according to the ASTM-D 5024-95a. Swelling test was performed to obtain water uptake capacity of scaffolds for 24h. Degradation study was performed in enzymatic solution to mimic the body environment.

3.4. *In vitro* Studies

MG-63 osteosarcoma cell line was used as osteoblast model. *In vitro* cytotoxicity assay was performed with the indirect extraction method (ISO-10993). Cell proliferation on scaffolds was determined by using Resazurin Cell Viability kit. ALP activity was determined to observe the effect of POSS nanoparticles on osteoblast differentiation at the early stage of bone regeneration. von Kossa and Alizarin Red S staining protocols were performed to observe the calcium-phosphate depositions indicating bone mineralization.

4.Results& Discussion

SEM images showed that highly interconnected, porous CS/Na-CMC polyelectrolyte scaffolds were fabricated by freeze-drying method (Figure 1). In this study, prepared CS/Na-CMC scaffolds have convenient pore size required for vascularization and cell attachment which is found as 100µm, critical for the diffusion of nutrients and oxygen for cell survival the required minimum pore size of (Hulbert et al., 1970). Maximum pore sizes were observed on HAP incorporated scaffolds as 307±30µm and incorporation of POSS nanocages decreased the pore size. The microstructure of CS/Na-CMC scaffolds were observed as having large pores with thick pore wall structure inducing high surface area for cell attachment.

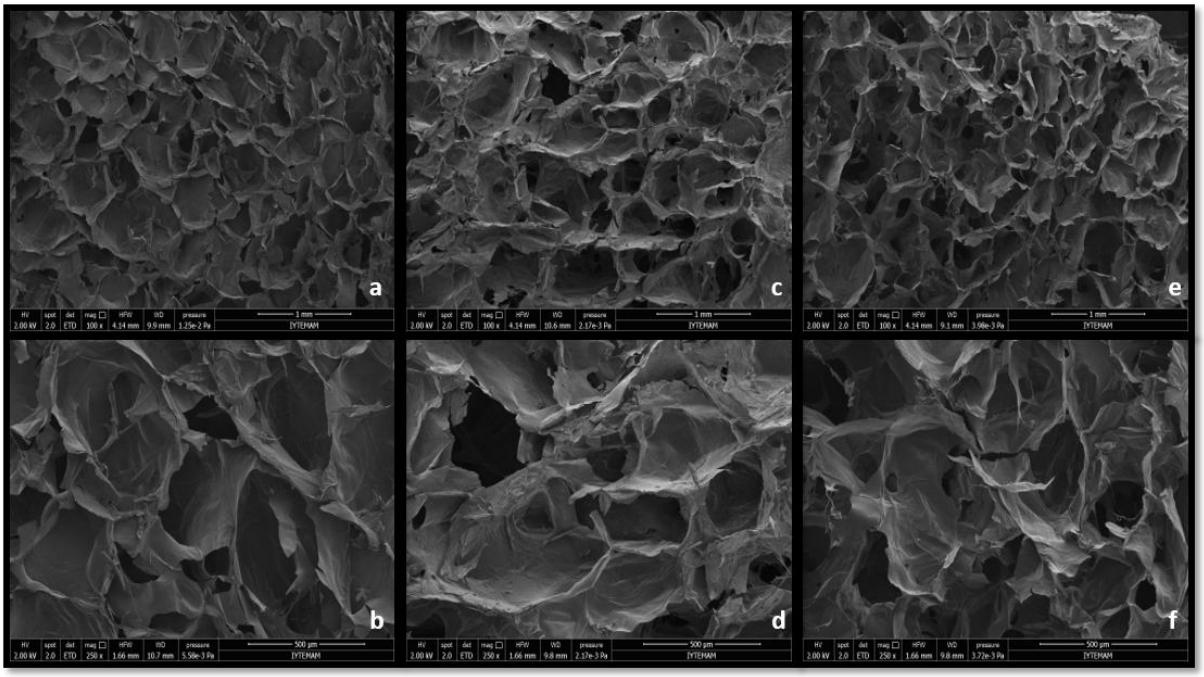


Figure 1. SEM images of CS/Na-CMC (a,b), HAP (c,d) and POSS (e,f) reinforced CS/Na-CMC scaffolds with 100 and 250X magnifications, respectively.

The porosity of the scaffolds was found as 61-70% which was found to be appropriate for cell migration and nutrient supply in the trabecular bone having a porosity range between 50-90% (Costa-Pinto, Reis, & Neves, 2011).

Generally inorganic reinforcements are preferred to overcome the mechanical disadvantage of natural polymeric scaffolds. Therefore, in this study, HAP and POSS nanoparticles were used to reinforce the CS/Na-CMC blends. Compression test results of dry scaffolds were depicted in Figure 2. Synthetic POSS particles increased the mechanical strength by reinforcing the structure of CS/Na-CMC scaffold. HAP reinforced CS/Na-CMC scaffolds were used to compare the effect of POSS nanoparticles with the HAP crystals mainly found in the bone structure. POSS nanoparticles increased the mechanical strength of

CS/Na-CMC polyelectrolyte blend from 179.3 kPa to 228 kPa. Maximum mechanical strength was obtained for HAP incorporated scaffolds (254.3 kPa).

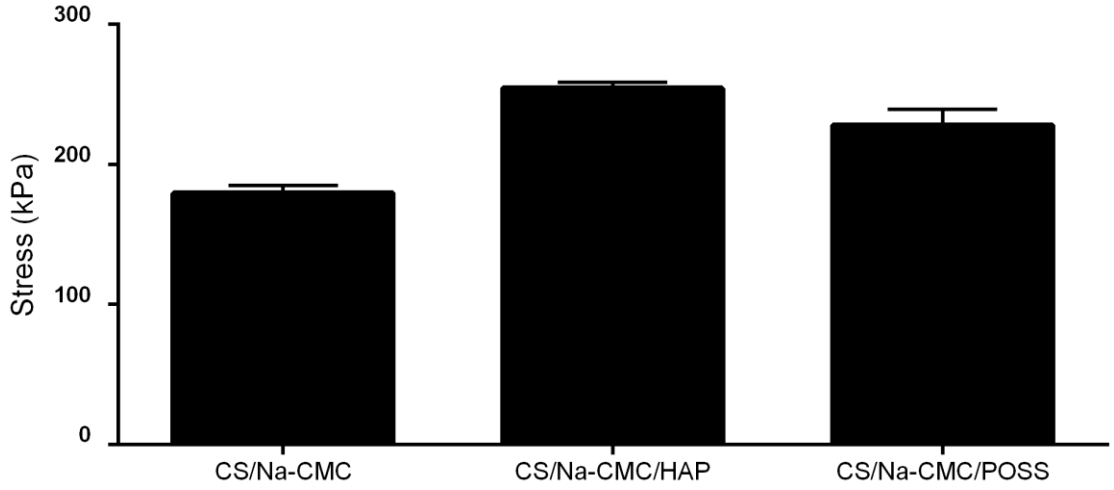


Figure 2. Mechanical strength of HAP and POSS reinforced CS/Na-CMC scaffolds

POSS incorporation increased the swelling ratio of the composite scaffolds due to its hydrophilic nature (Figure 3). In addition, high porosity % affected the water uptake capacity groups.

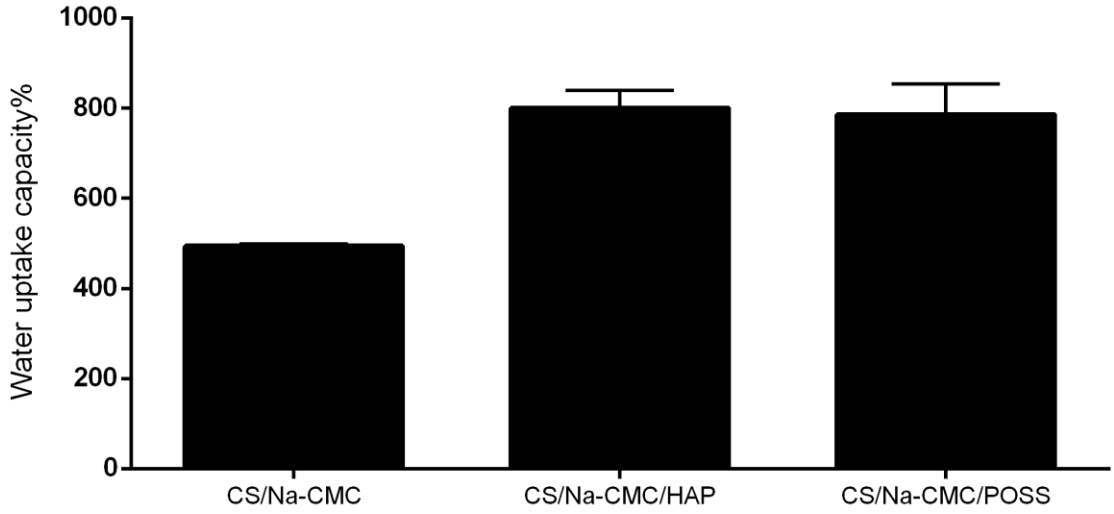


Figure 3. Water Uptake Capacity of CS/Na-CMC scaffolds for 24hour incubation.

Enzymatic degradation was observed with scaffold weight loss % determination occurred enzymatically in the presence of lysozyme for 7 and 21 days of incubation (Figure 4). Nanoparticle reinforced groups performed higher degradation rate compared to control group. The weight loss % of silica incorporated scaffolds slightly increased at the 21day of incubation due to the possible dissolution of silica particles from the scaffold surface. POSS composite scaffolds degraded slowly compared to the HAP composite scaffolds.

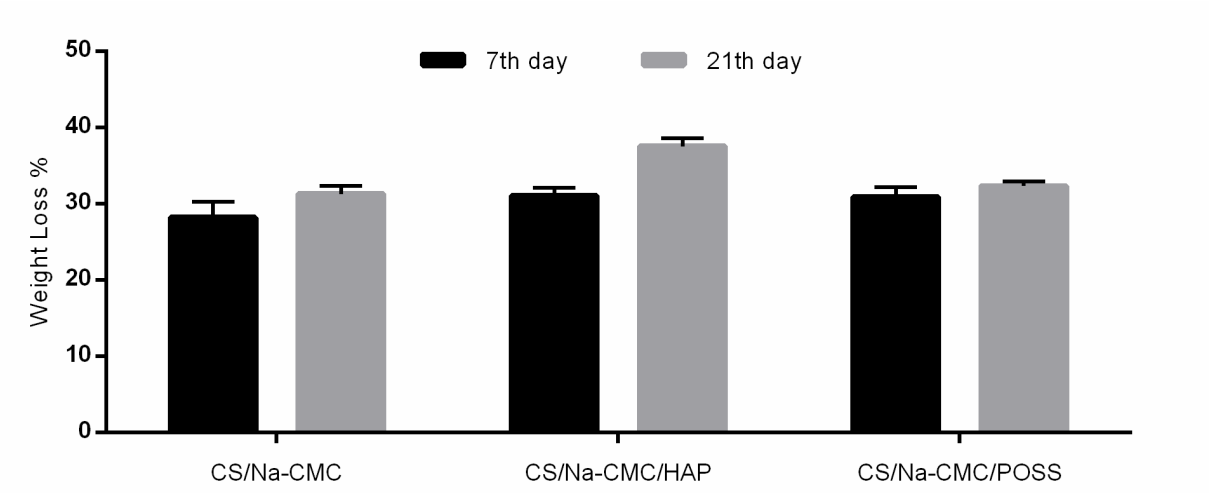


Figure 4. Enzymatic degradation of HAP and POSS reinforced CS/Na-CMC scaffolds for 7 and 21 days.

In vitro cytotoxicity of scaffolds on MG-63 cells was evaluated by 24h extraction of scaffolds in 24, 48 and 72h of incubation periods and depicted in Figure 5. Cell viability results indicated that POSS reinforced scaffolds did not show any cytotoxic effect on MG-63 cell line.

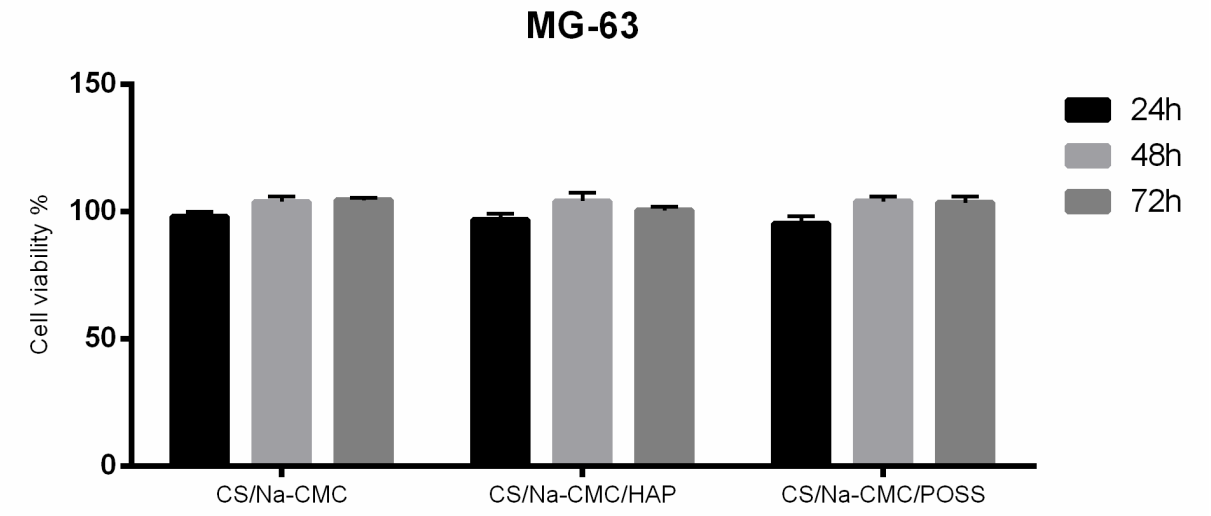


Figure 5. *In vitro* cytotoxicity of CS/Na-CMC scaffolds reinforced with HAP and POSS nanoparticles.

ALP is known as an early marker for osteoblast differentiation in bone regeneration and postulated to increase inorganic phosphate concentration locally (Golub, & Boesze-Battaglia, 2007; Rutkovskiy, Stensløkken, & Vaage, 2016). Therefore, ALP activity determination was performed at 7 and 14 days to observe the effect of POSS nanoparticles on osteoblast differentiation at the early stage of bone regeneration (Figure 6). ALP activity on POSS reinforced CS/Na-CMC scaffolds was found to be higher than HAP incorporated scaffolds.

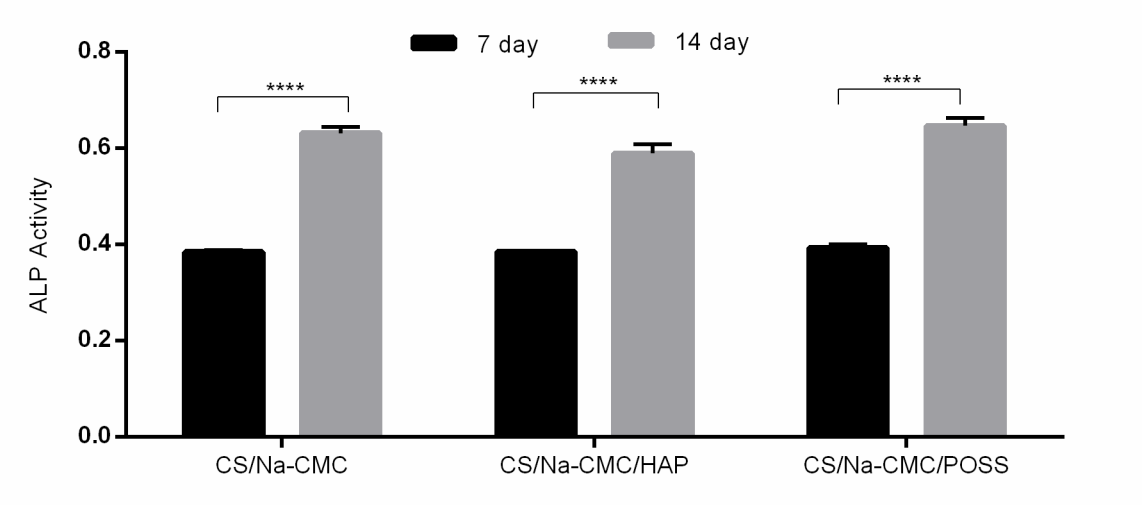


Figure 6 ALP activity of MG-63 cells on CS/Na-CMC scaffolds for 7 and 14 days of incubation

Calcium and phosphate depositions are very important constituents of bone mineralization during HAP crystal formation. Therefore, von Kossa and Alizarin Red S stainings were performed to observe these depositions on scaffold surface (Figure 7). Stereomicroscopy images showed enhanced mineralization on POSS reinforced scaffold surfaces compared to HAP reinforced groups concerning the von Kossa images. As a result, POSS nanoparticles enhanced the biomineralization step on scaffold surface which is an important step for bone regeneration.

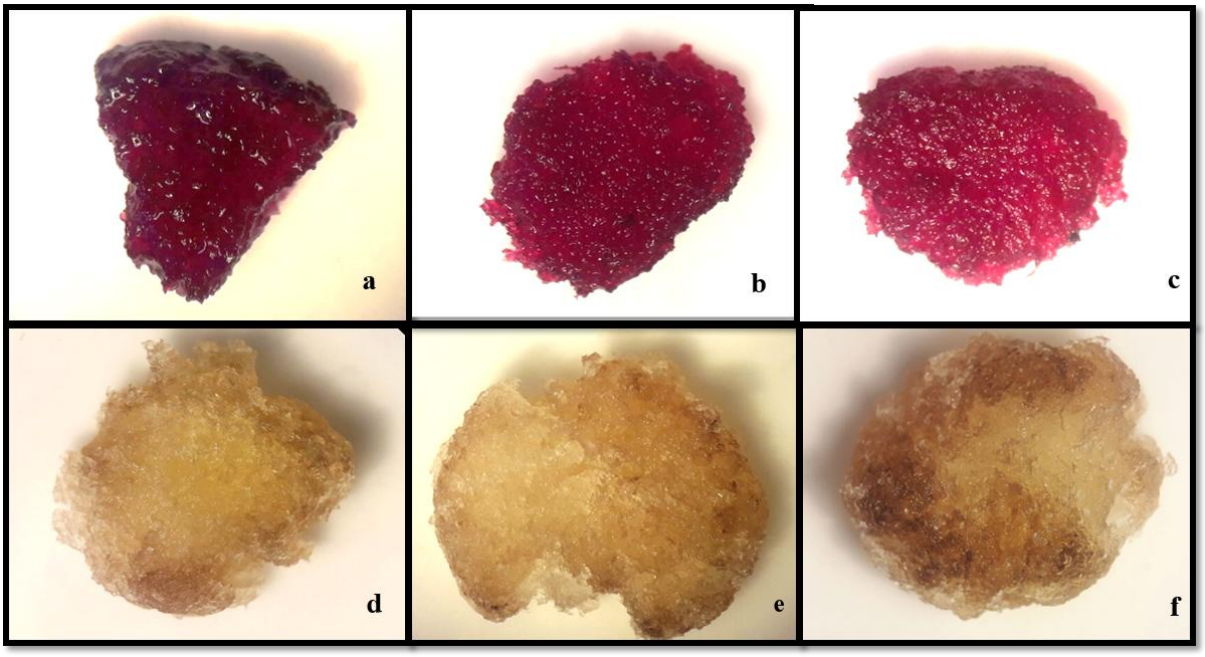


Figure 7. Stereomicroscopy images of Alizarin red and von Kossa staining on control (a, b) and HAP (c, d); POSS (e, f) at 14 days, respectively.

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DEVELOPMENT OF FLAMMABILITY AND MECHANICAL PROPERTIES OF NEW EPOXY COMPOSITES USING RED MUD WASTE WITH FLAME RETARDANT COMPOUNDS

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Abstract

In this study, red mud waste (RM) and aluminum hydroxide (AH)-ammonium tetrafluoroborate (AFB) were used as filler and flame retardants for the first time together to prepare epoxy composite materials with enhanced flammability properties. The wt% of RM, AFB and AH in composites varied in the range of 15-20%, 5-20% and 5-10%, respectively. The combustion properties of the neat epoxy as well as the mechanical properties have been improved significantly. The appropriate ratio of RM:AFB:AH both in terms of combustion and mechanical properties was found to be 15 wt% : 10 wt% : 5 wt%. The tensile strength of composite in this ratio was obtained as 112 MPa while neat epoxy show 46 MPa. The composite burnout decreased in the first 10 seconds, and extinguished in 32 seconds. Moreover, the burned area of this composite at the first 10 seconds is smallest among the others. According to flame spread classification, materials with flame spread rating of 25-50 are considered as fire retardant, 50-75 are slow-burning, 75-200 are combustible and over 200 are highly combustible [1]. The burning test results show that AH-AFB blend is effective free halogen flame retardant for epoxy-based materials, which can be successfully evaluated with the advantages mentioned in many industrial fields such as construction, coating, flooring etc.

1. Introduction

Epoxy resins, which are a representative of advanced resin matrices, are widely used in laminates, coatings, adhesives and many other areas because of their superior physical and mechanical properties, good chemical and corrosion resistance, high adhesion and remarkable electrical insulation properties To extend the applications of epoxy resins in the electrical industry, it is important to improve their flame resistance [2]

Most of polymers are flammable due to large quantities of combustible elements such as hydrogen. Hence, with or without bisphenol-A, epoxy resins were found to be combustible and that they burn out completely on application of a flame [3].

Halogen compounds are used intensively to prepare flame retardant polymer materials. However, halogen flame retardant systems produce toxic fumes and corrosive substances that are released during combustion which is harmful to the environment and human health. For this reason, non-halogen flame retardants containing phosphorus, nitrogen, silicon and boron were applied to the polymeric materials [4].

2. Experimental

2.1. Materials

Commercially available diluted epoxy resin NPEK 114 called as ER, (Konuray Chemical Co.) was the bisphenol A-type epoxy resin and used as matrix. The epoxy embedding medium accelerator is a 2,4,6-tris(dimethylaminomethyl)phenol (Sigma-Aldrich). Polypox hardener 043 (Sigma-Aldrich) was used as a

hardener. Aluminum hydroxide (AH) and red mud waste (RM) are supplied by the Eti Mine Enterprises. Alfa Aesar brand ammonium tetrafluoroborate (AFB) was used as flame retardant. Red mud is a waste material produced during the production of bauxite alumina by Bayer process. It is used for aluminum production. The characteristic fine grains of red mud are used as additives in concrete and mortar. In this study, red mud with a pH value of 13.5 was used. The contents of red mud are given in Table 1.

Table 1. Red mud content according to XRD analysis (Eti Mine Enterprises)

Compound	**%**
Bohmite AlO(OH)	1,10
Diaspore AlO(OH)	3,93
Gibbsite $Al(OH)_3$	3,75
Sodium Titanat $Na_2Ti_6O_3$	1,05
Tridymite SiO_2	0,74
Cancrinite $3NaSiO_4$-NaOH	6,92
Sodalit	2,66
Hemalite Fe_2O_3	33,07
Goethite Fe+3O(OH)	4,60
Rutile,syn TiO_2	1,65
Anatase, syn TiO_2	1,96
Calcite,syn $CaCO_3$	1,59
Sodium aluminum Silicate Hydrate	32,48
Katoite,syn	0,19
Perovskite,syn $CaTiO_3$	0,92
Portlandite,syn	0,5
Amorf	2,89
H/G	7,20

2.2. Methods

The filler (AFB/RM/AH) (particle size<53 μm) in various wt% and epoxy matrix were mixed with mechanical stirring (stirring rate of 2000 rpm) for 3 h and ultrasounded for 1 h at 60 ºC in order to obtain a good dispersion. Afterwards, the curing agent at 30 wt% and epoxy accelerator (1 wt%) were added, and the mixture was degassed for 60 min at room temperature and then transferred into the mold. Samples were prepared in stainless-steel molds according to ASTM D 638 standard (Fig. 1). The molds were allowed to stand at room temperature until the air bubbles on the samples had completely disappeared, then cured for 1 day at 40 °C and 2 days at 80 °C. The molds were expected to cool and the composites were removed from the molds.



Fig. 1. Preparation of mold composites according to ASTM D 638 standards

3. Results and Discussion

3.1. Characterization of composites

3.1.1. Mechanical properties

In order to investigate mechanical properties such as tensile strength, elongation at break, and hardness of the composites, mechanical testing was performed. The results are summarized in Table 2.

Table 2. Mechanical properties of composites containing RM, AFB and AH

RM (wt%)	AFB (wt%)	AH (wt%)	Elongation at break (%)	Tensile strength (MPa)	E-modulus (GPa)	Hardness (Shore D)
neat ER			0.8	46	3.3	83
15	5	5	1.5	110	5.6	86
15	10	5	1.5	112	4.5	83
15	15	5	1.3	96	4.7	71

The wt% of RM, AFB and AH in composites varied in the range of 15-20%, 5-20% and 5-10%, respectively. The combustion properties of the neat epoxy as well as the mechanical properties have been improved significantly. The appropriate ratio of RM:AFB:AH both in terms of combustion and mechanical properties was found to be 15 wt% : 10 wt% : 5 wt%. The tensile strength of composite in this ratio was obtained as 112 MPa while neat epoxy show 46 MPa. The hardness values decrease as the addition ratio increases.

3.1.2. SEM

Fig. 2. illustrates SEM images of neat ER. Surface morphologies of composite materials containing AFB, AH and RM were investigated also by SEM (Fig.3). SEM images of AFB:AH:RM reinforced composites showed good distribution of fillers in epoxy matrix. However, random distribution and occasional clustering of AFB:AH:RM particles in the polymer matrix are also observed, but these particles are well bonded to each other and to the polymer matrix. It is believed that such aggregations are due to the interaction between the matrix and the structure and amount of the filler material. Compared to neat ER in general terms, it was noted that AFB:AH:RM has a good distribution in composites, which is also seen in mechanical tests, especially in tensile strength and hardness. In addition, the SEM images of the composites in which the three different additives are used are quite similar. The fact that the mechanical properties of these materials are close to each other supports this situation.

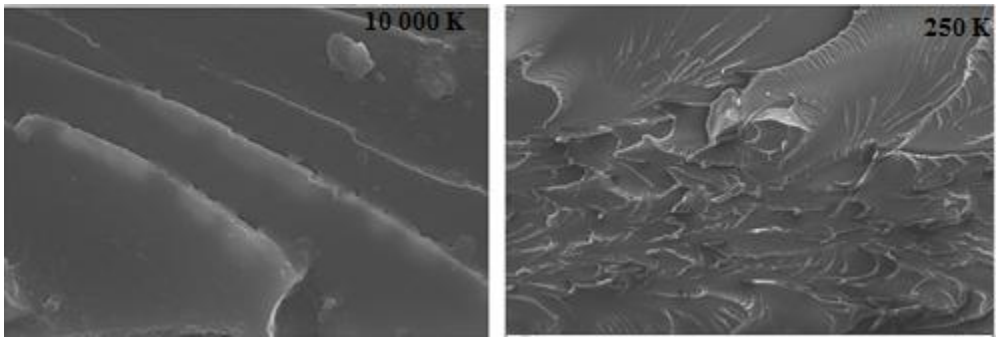


Fig.2. SEM images of neat ER

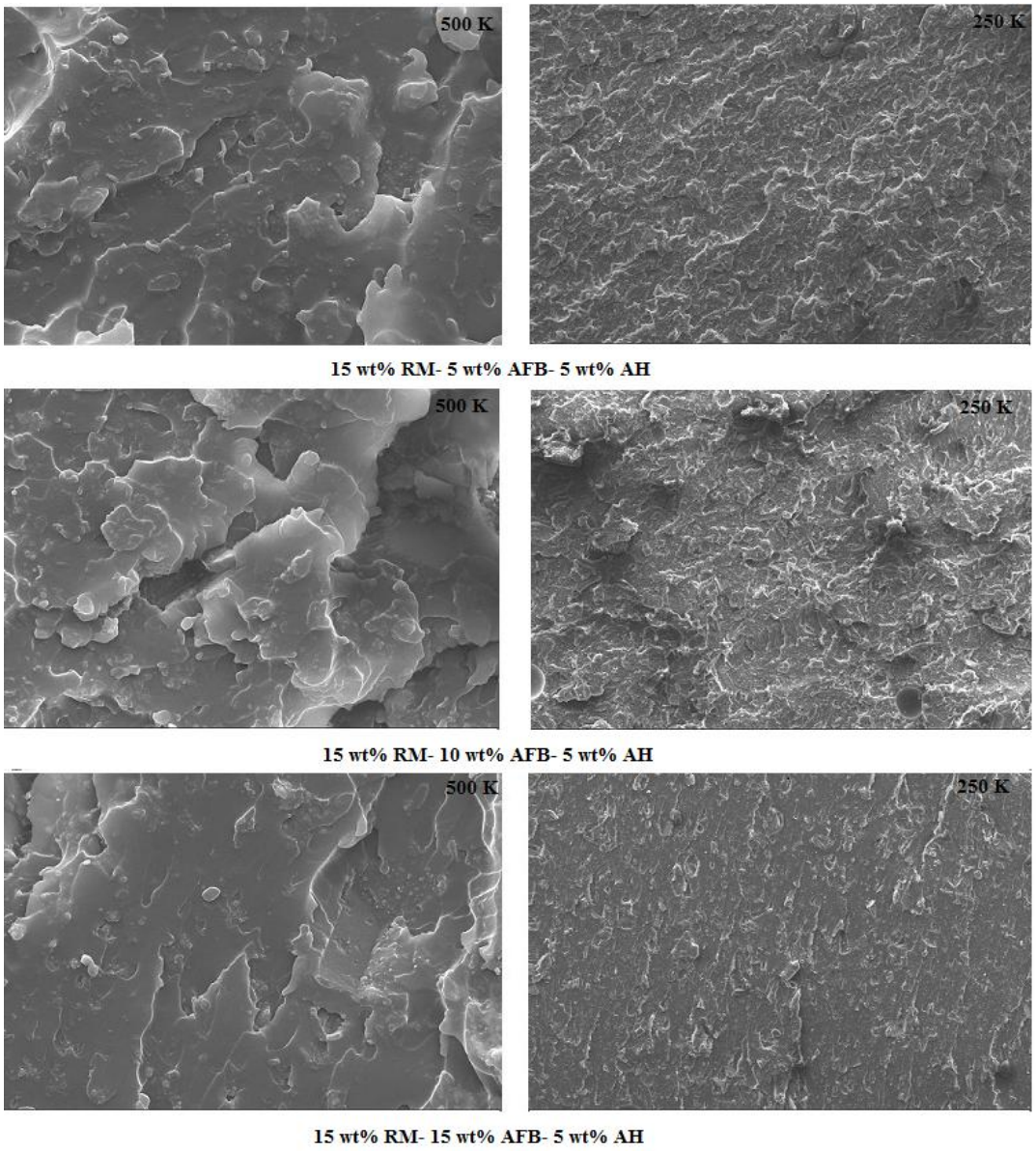


Fig. 3. SEM images of RM:AFB:AH reinforced composite materials

3.1.3. Flammability

Fig. 4 shows the composite material containing 15 wt% RM, 10 wt% AFB and 5 wt% AH during the burning process.

The minimum ignition rate was found in this composite material including three additives. The composite burnout decreased in the first 10 seconds, and extinguished in 32 seconds. Moreover, the burned area of this composite at the first 10 seconds is smallest among the others.

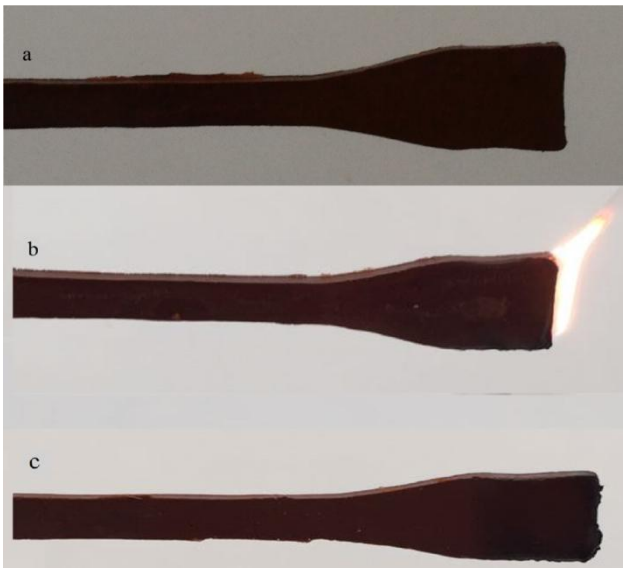


Fig. 4. Burning test photographs of composites with 10 wt% RM:10 wt% AFB:5 wt% AH. a) before burning, b) at the 10th minute, c) after burning

According to flame spread classification, materials with flame spread rating of 25-50 are considered as fire retardant, 50-75 are slow-burning, 75-200 are combustible and over 200 are highly combustible. The burning test results show that AH-AFB blend is effective free halogen flame retardant for epoxy-based materials, which can be successfully evaluated with the advantages mentioned in many industrial fields such as construction, coating, flooring etc.

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POLİANİLİN-KARBON NANOTÜP KOMPOZİTLERİNİN AMONYAK BUHARINI ALGILAMA ÖZELLİKLERİ

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Özet

Bu çalışmanın amacı, oksitlenmiş çok duvarlı karbon nanotüpler içeren polianilin kompozitlerinin amonyak buharını algılama özelliklerini incelemektir. PANI ve %1 ve %2 derişimlerinde oksitlenmiş karbon nanotüpleri (KNT'leri) içeren PANI-KNT kompozitleri, asidik ortamda amonyum persülfat kullanılarak anilinin kimyasal oksidatif polimerizasyonu ile hazırlandı. PANI ve PANI kompozitleri FTIR ve AFM ölçümleriyle karakterize edildi. Bu malzemelerin örnek şeritlerinin amonyak buharına tutulmasıyla elektriksel dirençlerinde meydana gelen değişim, iki nokta tekniği ile ölçülerek izlendi. PANI ve kompozitlerinin farklı derişimlerindeki amonyak çözeltilerine karşı direnç ölçümleri, desorpsiyon modunda saf gliserin, saf su ve gliserin-su karışımı kullanılarak ayarlanan çeşitli bağıl nem (BN) seviyelerinde gerçekleştirildi. PANI ve PANI-KNT kompozitlerin sensör yanıtlarının NH_3 derişimi artışı ile azaldığı gözlenirken, PANI-KNT kompozitlerinde KNT yüzdesi arttıkça, adsorpsiyon-desorpsiyon döngülerinde sensör yanıtı kararlılığının PANI'ye göre arttığı görüldü. PANI-KNT kompozitlerinin amonyak buharı için sensör yanıtları zamanla BN seviyesi arttıkça azaldı.

Anahtar Sözcükler: Polianilin, karbon nanotüp, kimyasal oksidatif polimerizasyon, amonyak, sensör

Abstract

The aim of this study is to examine sensing properties of polyaniline (PANI) composites with oxidized multiwall carbon nanotubes to ammonia vapor. PANI and PANI composites containing the carbon nanotubes (CNTs) at concentrations of 1% and 2% were synthesized by chemical oxidative polymerization of aniline using ammonium persulfate in acidic medium. PANI and PANI-CNT composites were characterized by FTIR and AFM measurements. The change in electrical resistances of sample strips of these materials when exposed to ammonia solution vapor was monitored along the stripe length by the two-point technique. The resistance measurements of them to ammonia solutions of different concentrations were carried out at various relative humidity (RH) levels adjusted by using pure glycerin, water and glycerin–water mixture. While the sensor responses of the PANI and the composites to ammonia vapor decreased with increasing NH_3 concentration, PANI-CNT composites showed higher stability in the sensor response than PANI as the percentage of CNT increased. The sensor responses of PANI-CNT composites to ammonia vapor decreased as the RH level increased.

Keywords: Polyaniline, carbon nanotubes, chemical oxidative polymerization, ammonia, sensor

1. Giriş

İletken polimerler arasında polianilin (PANI) elektriksel ve optik özelliklerinden dolayı en çok çalışılan polimerlerden biridir. Ayrıca kimyasal ve elektrokimyasal olarak kolaylıkla sentezlenebilir, protik asitlerle kolaylıkla katkılanabilir ve ayrıca oda sıcaklığında kimyasal olarak kararlıdır. Günümüzde

genel olarak kullanılan "polianilin" terimi, farklı benzenoid/kinoid halkaları oranı içeren, 1000 veya daha fazla tekrar eden halka birimlerinden oluşan bir polimer sınıfını kapsamaktadır [1].

PANI proton alıcı ve verici reaktiflerle etkileşebilir, bu da onun iletkenliğini azaltır. Ayrıca PANI film hazırladıktan sonra bir süre sonra iletkenlik kaybı gösterebilir. Bu soruna olası çözümlerden biri, bu filmlerde yük transferini artırmak için karbon nanotüpleri (KNT) kullanmaktır. Böylece yüksek iletkenliğe ve kararlılığa sahip KNT'lerle, reaktivitesi yüksek PANI filmlerin kombinasyonu gaz sensör uygulamaları için daha iyi sonuçlar elde etmede gelecek vaat eden bir çözüm olabilir [2]. PANI, amonyak ile etkileşime maruz bırakıldığında elektriksel iletkenliği ve absorpsiyonunda meydana gelen değişim nedeni ile amonyak sensörü için mükemmel bir adaydır. Özellikleri polimerin oksidasyonu ve protonlaşması ile değiştirilebilmektedir [3]. PANI, ve bazı PANI kompozitlerinin amonyak [4, 5] kloroform [6], toluen [7] gibi başka buhar veya gazları algılama özellikleri incelenmiştir. Bu çalışmanın amacı, oksitlenmiş çok duvarlı karbon nanotüpler içeren polianilin kompozitlerinin amonyak buharını algılama özelliklerini incelemektir.

2. Yöntem

2.1 Materyal ve Yöntem

Çalışmada kullanılan çok duvarlı karbon nanotüpler Sun Nano firmasında temin edilmiştir. Diğer kimyasallar ise analitik saflıktadır. Karbon nanotüpler, nanotüp yüzeyine kovalent bağlı karboksil grupları üretmek için HNO_3 ve H_2SO_4 (1: 3 v/v) karışımı ile muamele edildi. PANI ve %1 ve %2 derişimlerinde modifiye edilmiş KNT'leri içeren PANI-KNT kompozitleri, asidik ortamda amonyum persülfat kullanılarak anilinin kimyasal oksidatif polimerizasyonu ile hazırlandı. Elde edilen dispersiyon cam elyaf filtresi üzerinde vakum filtrasyonu ile biriktirilerek Şekil 1'deki disk elde edildi. Bu diskler FTIR ve AFM analizleriyle karakterize edildi. Disklerden aynı boyutlarda kesilerek hazırlanan PANI ve PANI-KNT kompozit örnek şeritlerinin elektriksel direnci, şerit uzunluğu boyunca Fluke 289 endüstriyel multimetre kullanılarak iki nokta tekniği ile ölçüldü. PANI ve PANI-KNT kompozit şeritlerinin farklı derişimlerindeki amonyak çözeltilerine (% 5, % 10, % 15, % 20) karşı direnç ölçümleri, desorpsiyon modunda saf gliserin, saf su, gliserin-su karışımları kullanılarak ayarlanan çeşitli bağıl nem (BN) seviyelerinde (~% 0, % 30, % 100) gerçekleştirildi.



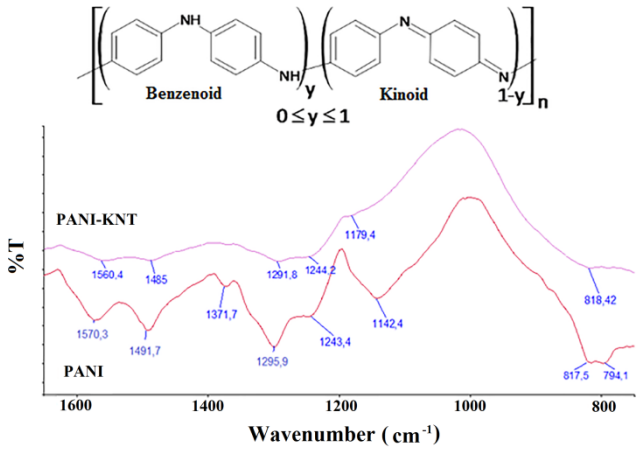
Şekil 1:Vakum filtrasyonu ile elde edilen PANI-KNT%1 kompozit disk örneği

3. Bulgular ve tartışma

3.1 FTIR spektrumları

PANI ve PANI-KNT kompozit örneklerinin FTIR spektrumları Şekil 2'de gösterilmiştir. Şekil 2 incelendiğinde PANI'nin FTIR spektrumunda 1570 ve 1492 cm^{-1}'deki sırasıyla kinoid ve benzenoid piklerinin, PANI-KNT kompozitinde 1560 ve 1485 cm^{-1}'e kaydığı görülmektedir. Elde edilen PANI'de kinoid pikinin şiddetinin benzoidinkinden daha fazla olması PANI'ın yapısında kinoid gruplarının benzoide göre daha fazla olduğunu gösterir. 1243 ve 1296 cm^{-1}'deki pikler sırasıyla benzenoid birimindeki C-N ve kinoid grubundaki C=N gruplarının titreşim modlarına aittir [8]. KNT ilavesiyle C=N titreşimi daha yüksek dalga boyuna kaymıştır. PANI'nin FTIR spektrumundaki 1142 cm^{-1}'deki pik elektronların delokalizasyon derecesinin ölçüsü olarak düşünülmektedir [9]. Bu pikin kompozitte 1179 cm^{-1}'e kaydığı görülmektedir. Gözlenen bu kayma, KNT ilavesinin kinoid grupları ve KNT'ler arasındaki π-π etkileşimi nedeniyle, PANI'nin delokolalizasyon derecesini yani iletkenliğini değiştirdiğini gösterebilir. Ayrıca

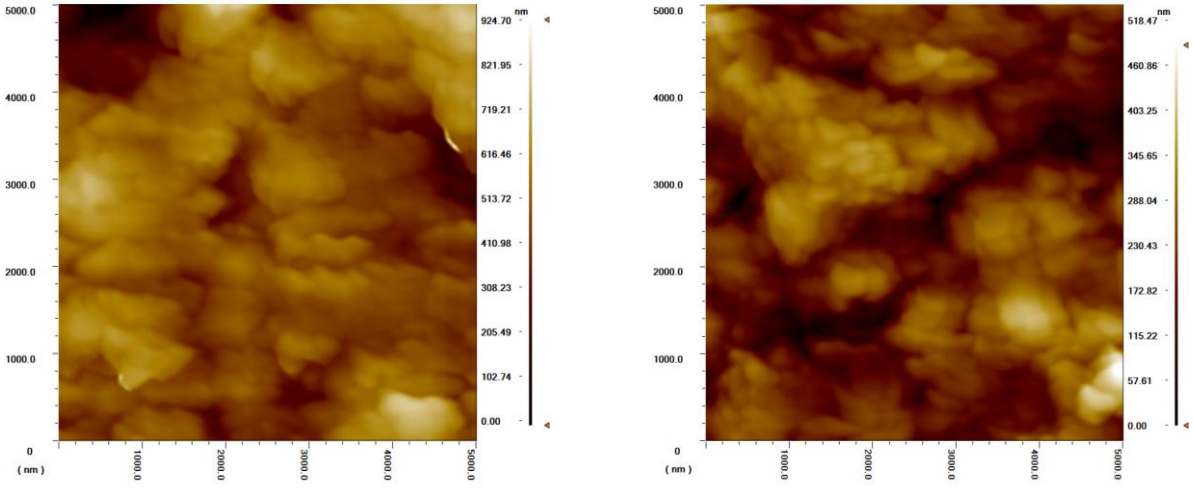
PANI yapısına KNT katılmasıyla PANI piklerinin şiddetinde görülen azalmanın nedeni, KNT yüzeyine anilin monomerlerinin adsorplanması ve daha sonra da polimerizasyonunun polimerin titreşim modlarını sınırlaması olabilir.



Şekil 2: PANI ve PANI-KNT kompozit örneklerinin FTIR spektrumları

3.2 AFM analizleri

PANI ve PANI-KNT%1 kompozitinin AFM görüntüleri Şekil 3a-b'de verilmiştir. PANI filminin granüler bir morfolojiye [10] sahip olduğu, KNT eklenmesiyle bu granüllerin küçüldüğü görülmektedir. Hesaplanan *RMS* yüzey pürüzlülüğü *değeri PANI için 110 nm iken,* PANI-KNT%1 kompoziti için *71 nm'dir. Kompozitte PANI granüllerindeki küçülmenin nedeni PANI ve KNT'ler arasındaki etkileşme olabilir.*



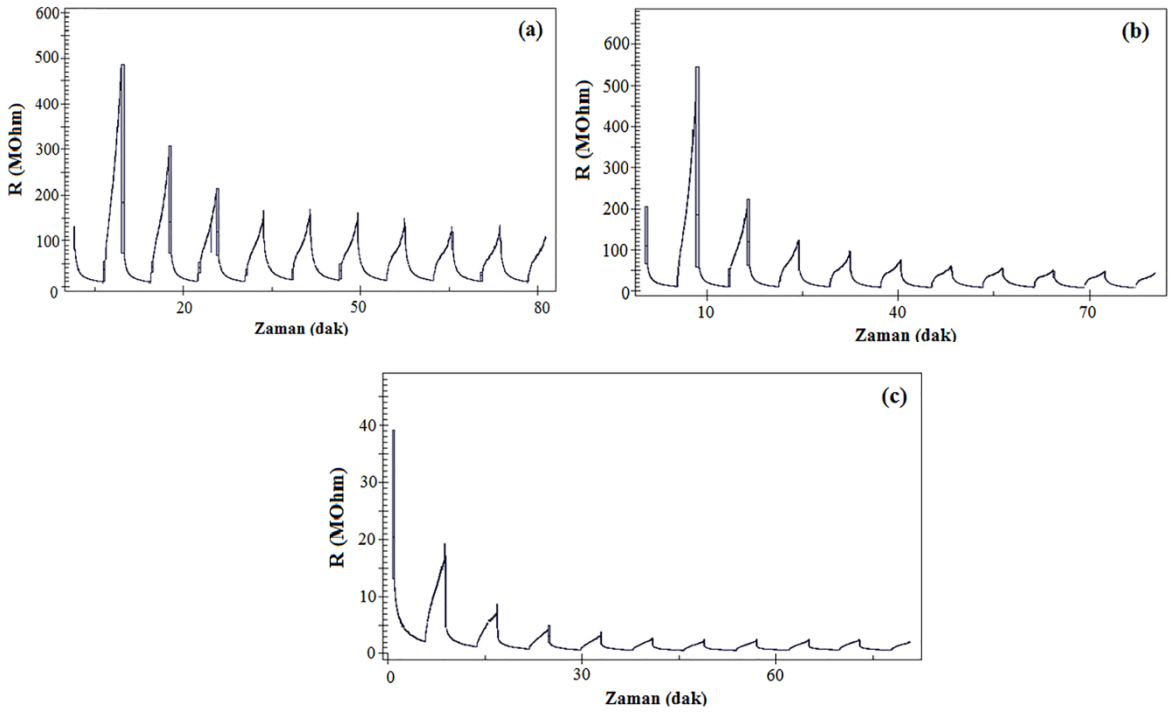
(a) **(b)**

Şekil 3: AFM görüntüleri: PANI (a) ve PANI-KNT%1 (b)

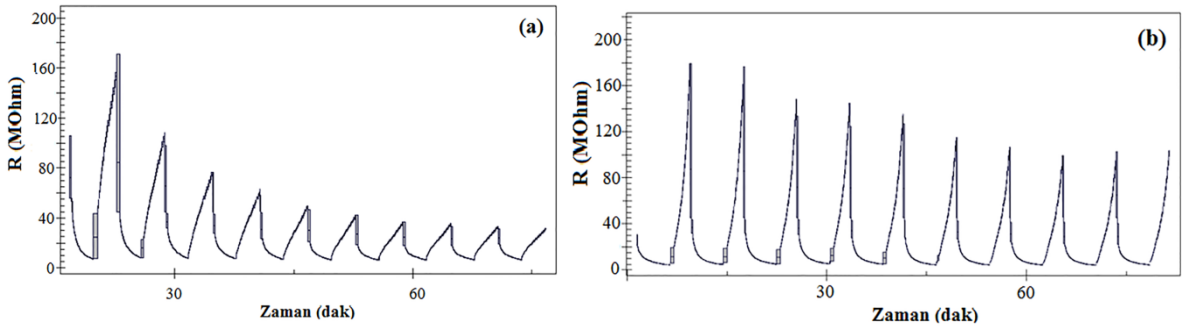
3.3 Direnç ölçümleri

PANI'nin çeşitli yüzde derişimlerdeki NH_3 çözeltilerine maruz bırakılmasıyla direncinde zamanla meydana gelen değişimler Şekil 4a-c'de gösterilmiştir. NH_3 adsorpsiyonu ile direncin azalması, desorpsiyonu ile direncin artması n-tipi polianilinin oluştuğunu göstermektedir. FTIR sonuçlarında görülen kinoid gruplarının fazlalığı bu durumu açıklayabilir. Ayrıca yapıda uzaklaşmadan kalan suyunda katkısı olabilir. Her üç derişimde de PANI'nin NH_3'e karşı sensör yanıtının zamanla azaldığı görülmektedir. Şekil 4a-c incelendiğinde PANI'nin direncindeki değişimin NH_3 derişimi artışı ile azaldığı da gözlenmektedir.

Şekil 5a-b'de PANI-KNT%1 ve PANI-KNT%2'nin dirençlerinde %10'luk NH_3 çözeltisi için zamanla gözlenen değişim incelendiğinde, KNT eklenmesiyle PANI'nin zamanla direnç değişimi azalırken, adsorpsiyon-desorpsiyon döngülerinde direnç değişimi kararlılığının PANI'ye göre arttığı görülmektedir. NH_3 çözeltisi buharına tutulan PANI'nin direncinde kompozitlerine oranla daha fazla değişme meydana gelmesinin nedeni, PANI'nin kompozitlere oranla NH_3 için daha fazla adsorpsiyon noktasının olması olabilir. Bu da başlangıç direncini yükseltir. PANI-KNT kompozitlerinin sensör yanıtlarının PANI'den daha düşük olmasının nedeni yüzeyinde karboksil grubu içeren KNT'lerin p-tipi yarı iletkenlik göstermesi olabilir [11].

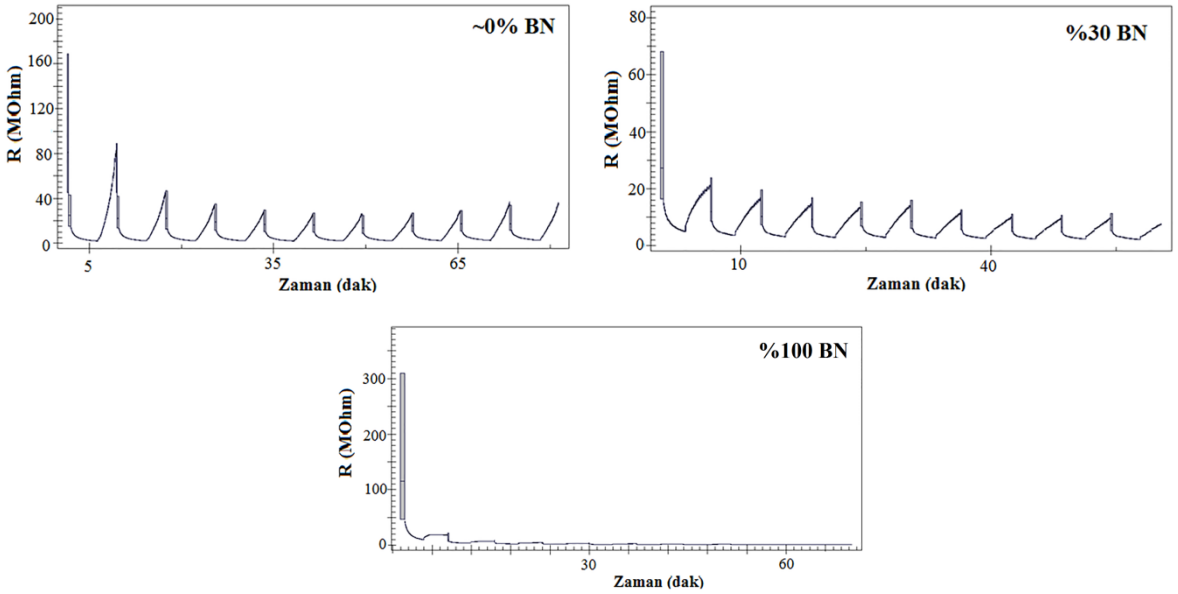


Şekil 4: PANI'nin NH_3 çözelti buharlarına karşı direncindeki değişim: %5 (a), %10 (b), %20 (c)



Şekil 5: Kompozitlerin %10'luk NH_3 çözeltisi için direnç-zaman değişimleri: PANI-KNT%1 (a), PANI-KNT%2 (b)

Farklı nem düzeylerinde PANI-KNT için direnç-zaman değişimi Şekil 6'da gösterilmektedir. Farklı nem düzeylerinde PANI-KNT%2'ün direnç değişimi (sensör yanıtı) incelendiğinde, nem düzeyi azaldıkça değişim artmıştır. PANI'nin iletkenliği su buharı varlığında proton etkisi nedeniyle artar. PANI emeraldin tuzunda birçok yüklü kısım (-NH-, -N, $-NH^+$, $-NH_2^-$, vb) bulunmaktadır. Bu yükler suyun ayrışma dengesini hidrojen bağı ve yük etkileşimleri aracılığıyla proton oluşumu yönüne değiştirir. Sonuç olarak, PANI tarafından absorplanan su molekülleri proton kaynağı olarak davranır ve polimerin doplama düzeyini değiştirir ve/veya absorplanan su moleküllerinin networku aracılığıyla yük iletilir [12]. Ayrıca su moleküllerinin aşırı miktarda olması amonyak moleküllerinin adsorpsiyonunu engeller ve iletim protonlar aracılığıyla yürütülür. Bu süreç amonyak için yarışmalı adsorpsiyonunu azaltır ve PANI ve PANI kompozitlerinin amonyak için zamanla direnç değişimini azaltır.



Şekil 6: PANI-KNT%2'nin %5'lik NH_3 çözeltisi için çeşitli bağıl nem (BN) düzeylerindeki direnç-zaman değişimleri

4. Sonuçlar

Bu çalışmada PANI-KNT kompozitlerinin amonyak buharını algılama özellikleri incelendi. NH_3 adsorpsiyonu ile direncin azalması, desorpsiyonu ile direncin artması n-tipi PANI ve PANI-KNT kompozitlerinin oluştuğunu gösterdi. AFM ve FTIR ölçümlerinde gözlenen farklılıklar PANI ve KNT'ler arasında bir etkileşim olduğunu doğruladı. PANI ve PANI-KNT kompozitlerin sensör yanıtlarının NH_3 derişimi artışı ile azaldığı gözlenirken, PANI-KNT kompozitlerinde KNT yüzdesi arttıkça adsorpsiyon-desorpsiyon döngülerinde sensör yanıtı kararlılığının PANI'ye göre arttığı görüldü. PANI-KNT kompozitlerinin sensör yanıtının desorpsiyon modunda nem düzeyi arttıkça azaldığı gözlendi.

Teşekkür
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DEVELOPMENT of COMPOSITE ARMOR PLATES by PULTRUSION TECHNIQUE

KOMPOZİT ZIRH LEVHALARIN PULTRÜZYON TEKNİĞİ KULLANILARAK GELİŞTİRİLMESİ

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ÖZET

Günümüzde giderek artan güvenlik tehditlerine karşı savunma sistemlerinin ve dolayısı ile kompozit zırh sistemlerinin geliştirilmesi önem kazanmıştır. Bu amaçla son yıllarda yapılan çalışmalarda, kompozit ve kompozit/seramik esaslı sistemlerin ağırlık azaltımı, düşük maliyet v.b. unsurlarından dolayı savunma sanayisinin duyduğu ihtiyaçları karşılamada geleneksel zırh sistemlerine göre daha etkili olduğu görülmektedir. Bu çalışmanın amacı da, kompozit sistemlerin bahsedilen özelliklerinin gerek askeri gerek sivil savunma sanayii kullanımları için etkin bir şekilde geliştirilmesi ve yerli üretim ile öncelikli olarak Türk Savunma Sanayisi'nin hizmetine sunulmasıdır.

Bu sebeple yürüttüğümüz çalışmada, seri olarak kompozit malzeme üretimi gerçekleştirmekte etkinliğinden dolayı pultrüzyon prosesi kullanılmıştır. 10-15-20 mm kalınlıklarda üretilmiş, multiaksiyel cam kumaş, Poliüretan (PUR) ve doymamış polyester (DP) sistemlerinden oluşan kompozit paneller pultrüzyon prosesi ile imal edilmiştir. V_{50} (FSP, fragment simulating projectile) ve National Institute of Justice (NIJ) standardına göre balistik testler gerçekleştirilmiş, levha kalınlığının kompozitlerin balistik performansına etkileri incelenmiştir. İlave olarak, multiaksiyel E-cam kumaş /Alumina seramik hibrit kompozit sistemleri üretilmiş ve balistik dayanımı ölçülmüştür. Ayrıca, 10 mm kalınlıktaki doymamış polyester ve poliüretan içerikli levhaların eğilme mukavemet analizleri ile enerji sönümleme değerleri Izod yöntemi ile belirlenmiştir.

Elde edilen sonuçlara göre, cal elyaf/ polyester içerikli 10-15-20 mm levhaların FSP tehdidi karşısında V_{50} test sonuçları; 564.6, 971.8 ve >1009 m/s olarak ölçülmüştür. Poliüretan ile üretilen levhanın FSP tehdidi karşısında ise 566.8 m/s limitinde V_{50} değeri göstermiştir. Yinecam elyaf/ polyester içerikli levhaların NIJ II-NIJ IIIA seviyesinde balistik dayanıma sahip olduğu, panellerde kısmi penetrasyon gerçekleştiği ölçülmüştür. Alumina seramik içeren hibrit kompozit sisteminin ise NIJ III seviyesinde koruma sağladığı gözlemlenmiştir. 10 mm kalınlıktaki kompozit levhaların eğilme mukavemeti, eğilme modülü ve basma mukavemeti cam/ polyester kompozit levha için sırasıyla 326.9 MPa, 18.27 GPa, 251.65 MPa, poliüretan levha için ise 517.30 MPa, 17.50 GPa, 316.40 MPa olarak belirlenmiştir. Polyester ve PUR esaslı kompozitlerin Izod enerji absorblama değerleri ise yine sırasıyla 202.76 kj/m^2 ve 337.56 kj/m^2 olarak ölçülmüştür.

ABSTRACT

Nowadays development of the defense systems have become more prominent due to the public security requirements and increasing security threats. At this point, innovative approaches are needed to significantly reduce the weight of the armor systems and thus improve the mobility and transportability of these systems while obtaining efficient strength, reasonable cost and ease of mass production. The recent studies which were conducted for this purpose reveal that composite and composite/ceramic based systems seem to be more effective compared to the conventional armor systems due to the parameters like weight reduction, lower cost etc.. Because of their promise of meeting these requirements, the eyes of the defense world have begun to focus on the development of composite material systems.

The aim of this study is to develop the aforementioned features of the composite systems for both military and civil defense industrial uses and to present it primarily to the service of Turkish Defense Industry with domestic production. Developed materials can be used in militray and civilian area armored vehicles like military personnel carriers, money transportation for banks, armored civilian vehicles, tanks, helicopters, war ships..etc. They also can be evaluated in the production of human life protection systems like, personnel protection (armored vests and barriers) and military and civilian facilities (guard cabins, police stations, airport platforms, etc.) to reduce the casualties.

For these reasons, the pultrusion process has been used in our study because of its efficiency in producing composite materials as a mass. Pultrusion is a continuous process which allows the production of constant cross sectional structures having tailored material properties and therefore enables the high quality mass production.

Composite panels consisting of multiaxial glass fabric, Polyurethane (PUR) or Unsaturated Polyester (UP) systems produced in 10-15-20 mm thicknesses are obtained by pultrusion process. Ballistic tests were carried out according to V_{50} (FSP, fragment simulating projectile) and National Institute of Justice (NIJ) standards and the effects of plate thickness on ballistic performance of composites were investigated. Additionally, Ballistic protective level of multiaxial E-Glass fabric/Alumina (Al_2O_3) ceramic hybrid composite system were measured. Also, the flexural bending strength analysis and energy damping values of the 10 mm thick Unsaturated Polyester and Polyurethane based panels by Izod method were determined.

According to the obtained measurements, V_{50} test results of glass fiber/ polyester based panels having 10-15-20 mm thicknesses against FSP threats were measured as 564.6, 971.8 and >1009 m/s. V_{50} value of Polyurethane based panel were detected as 566.8 m/s against FSP threat. It has also been determined that unsaturated polyester based panels have NIJ II-NIJ IIIA levels of ballistic protection with a partial penetration. Hybrid composite system containing Alumina ceramics was observed to provide protection at NIJ III level. The flexural bending strengths, flexural modulus and compression strengths of 10 mm UP and PUR panels were measured as 326.9 MPa, 18.27 GPa, 251.65 MPa and 517.30 MPa, 17.50 GPa, 316.40 MPa; respectively. Also, their energy absorbing values were measured for these UP and PUR systems as 202.76 kj/m^2 and 337.56 kj/m^2. Polyurethane based system has superior mechanical properties than polyester ones owing to the more stiff nature of the resin.

1. Introduction

Today, the security issues are gradually increasing throughout the world and they became a main concern of defense industry either in military or civilian applications due to the trauma and losses. Conventional armors are the systems which are expensive, bulky, heavy and therefore restrict the mobility and portability. They compose of metallic systems of strengthened steel, aluminum and their foam type

sandwich structures. Recent studies focus on development of polymer composites and polymer composite/ceramic armor systems to reduce these drawbacks [1-5].

In a composite armor system fiber reinforced polymeric part is used as backing material and ceramic part placed on to the strike face. Ceramic parts are responsible for blinding bullets or other objects that hit the surface at high speed during ballistic impact due to their high hardness, compressive strength and abrasion resistance and creating a deforming/destructive shock wave on them also mitigating the local pressure. The polymer composite in the back layer provides structural integrity to the system by glass / polyester the frontal layer because ceramic layers are weak under tensile stresses. Fiber reinforced polymer matrix composites prevent penetration by catching fragments that are damaged and decelerated during impact with a certain sustained speed, due to high energy absorption characteristics by elastic/plastic deformation. Main damage types in a composite material are matrix cracking, delamination and fiber breakage. They can play an important role in energy absorption capability and failure modes during the impact of the projectile to the polymer composite backing layer [4-7]. The schematic illustration of a common polymer composite/ceramic armor system given in Figure 1.
Composites can be produced with numerous techniques either simple or complex like hand lay glass / polyester, Vacuum infusion, Resin Transfer Molding (RTM), Reaction Injection Molding (RIM), filament winding pultrusion etc. Among them, pultrusion provides a continuous production process that enables to obtain constant cross sectional composite structures with low-labor and high quality. In this process resin soaked fiber rovings or fabrics partially shaped by preforming guides and then converted in heated dies to its finished parts [8-10].

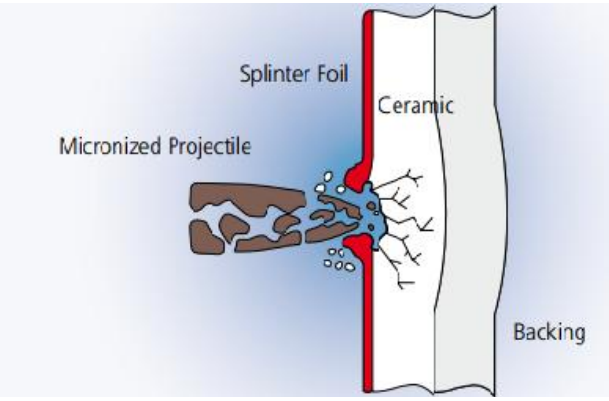


Figure 1. General sequence of a polymer-fiber/ceramic composite armor system [7].

Polymeric composite systems that are used for defence applications are generally prepared on thermoset resins like polyester, vinylester, phenolic, epoxy and polyurethane due to their rigidity, higher strength and thermal resistance. However, more critical parameter for a backing material is the type of the fiber used as reinforcement, its weight/volume ratio and orientation. E-Glass, carbon and aramid fibers are the most preferred types depending on their lower cost, superior tensile strength and higher energy absorption capabilities; respectively [11-16]. General ceramic types which are used for armor-grade applications are Alumina (Al_2O_3), Silicon carbide (SiC) and Boron carbide (B_4C). If they are compared with Alumina, SiC and B_4C have higher hardness however higher cost while alumina has lower hardness but less expensive and ensure ease of production [17-19]. The mechanical and chemical bonding properties of the adhesive layer between polymer composite and ceramic surfaces also affect the response of the composite system. For example, structural adhesives can transfer the impact load through the layers of the armor system. Therefore, high-compliant elastomeric adhesives such as polyurethane, polyurea and acrylates should be used to avoid this problem [18].
The main objective of this study is to develop multiaxial E-glass fabric reinforced polyester and polyurethane matrix polymer composites and combination of them with Alumina ceramic tiles to obtain a hybrid structure which can be used armor for military and civil defence applications. For this reason, the

designed glass / polyester panels were produced by pultrusion method in varying thicknesses to observe the effect of glass fabric layers and the types of the resin. The manufactured composite panels were subjected to FSP testing to observe their V_{50} limits. Also, a certain thickness of PUR based composite panel was investigated in terms of FSP testing. In addition, the striking faces of the polyester matrix composites were covered by ceramic tiles to evaluate their NIJ ballistic level.

2. Experimental

2.1. Materials

Production of composite panels were performed with commercially available thermoset unsaturated polyester and polyurethane resins with the combination of multiaxial glass fabrics having the total areal density of 1200 g/m^2. The multiaxial glass fabrics have the orientation of 0/90/+45/-45^0 composed of 300 g/m^2 E-glass fibers in each direction. Polyurethane resin were obtained by the reaction of polyol and isocyanate components while polyester resin composed of one component.
The high performance Alumina (Al_2O_3) ceramics have the dimensions of 50x50x10 mm. The bonding of the ceramic pieces to the composite backing material surface was conducted by using two component PUR based adhesive due to the flexibility.

2.2. Fabrication of Armor-Grade Composite Panels

Multiaxial glass fabric reinforced unsaturated polyester and polyurethane matrix composites were manufactured in 500 mm width by pultrusion technique. In this technique, glass fabrics were immersed in a resin bath and pushed through the line by hydrolic puller to ensure the continuity of the process. Following the resin bath the fabrics pass through the guides to remove the excessive amount of resin and went into the hot die to give the final form to the panels (Figure 2).
On the other hand, polyurethane matrix panels were produced with the same pultrusion principle but using an injection die instead of resin bath. Polyol and isocyanate components were injected on top of the injection die and went into the hot die again. Polyol and isocyanate reacts with each other exothermically to give polyurethane resin. The increasing temperature around the injection die reduced by cold water coils to prevent the non-homogenous hardening of the resin.
Glass-polyester/Alumina ceramic/ glass-polyester composites were prepared by gluing ceramic pieces with two component PUR based adhesive on to the glass / polyester composite panel to provide strong bonding. 15 mm glass / polyester based composite panel was used as backing material and 50x50x10 mm alumina ceramic pieces were placed front surface of that panel. Figure 3 shows the combination of these two layers. In addition to this, a 5 mm of glass / polyester based composite panel was also placed on to the ceramic tiles to cover the surface.



Figure 2. Image of the pultrusion process line used to produce resin based composite panels.



Figure 3. Alumina ceramic / glass-polyester composite panels for ballistic testing.

3. Results and Discussion

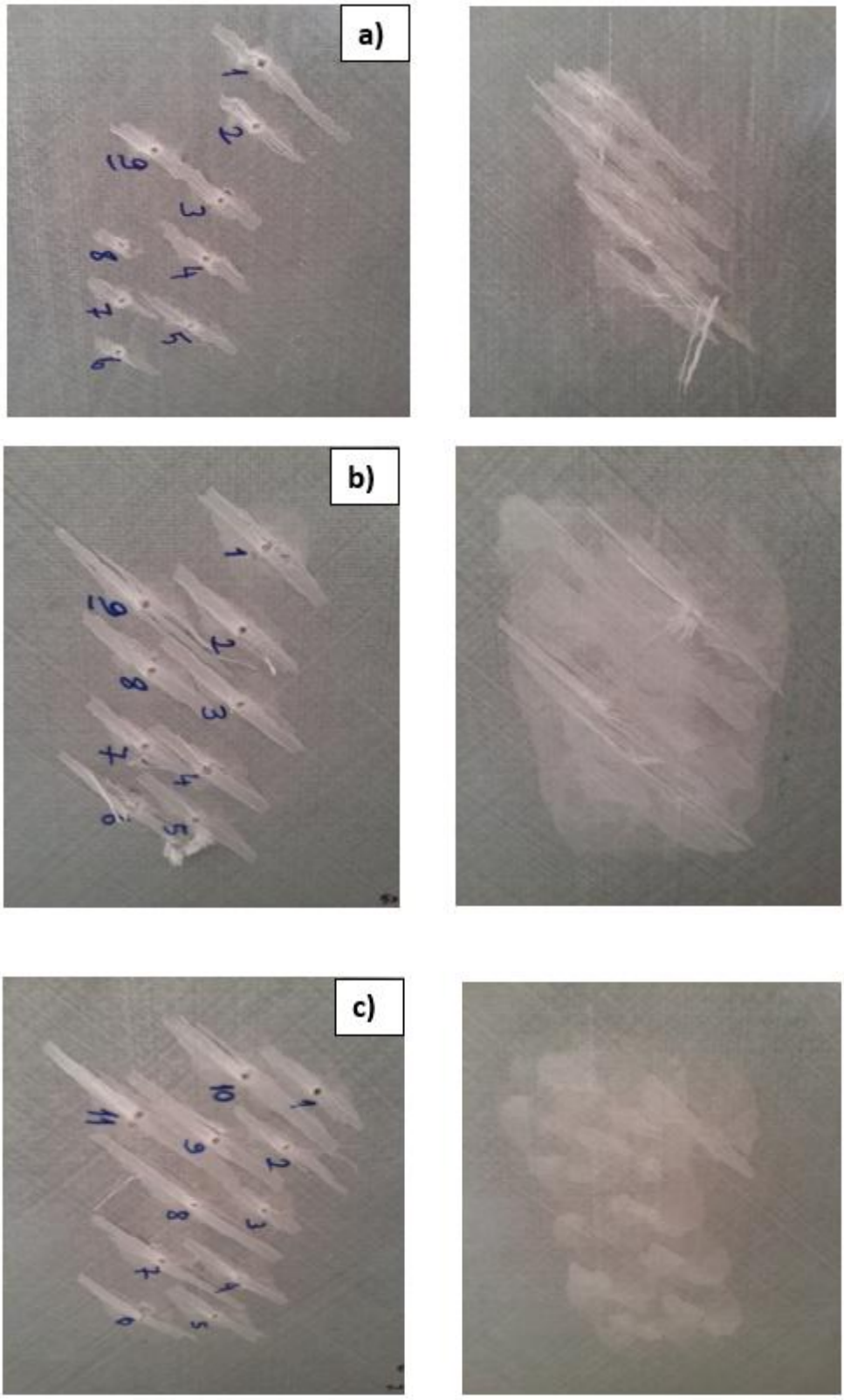
Three different polymer composite material systems were manufactured to determine the protection limits of the panels against 1.1 g fragment simulating projectile (FSP) and 7.62 mm NATO FMJ high velocity projectiles. One of them is multiaxial E-glass fabric / polyester matrix composites which were produced in 10-15 and 20 mm thickness. The second type is multiaxial E-glass fabric- PUR matrix composite. 5 mm glass-polyester / 10 mm ceramic / 15 mm glass-polyester hybrid system were also subjected to bullet testing. Table 1 summarizes the number of glass fabric layers altered due to the varying thickness of the panels and other important properties such as panel areal density, glass ratio..etc and Table 2 shows the ballistic protection levels of the systems.

Table 1. Tailored features of the composite panels.

Matrix type	Thickness (mm)	# of Layers	Glass weight ratio (%)	Glass volume ratio (%)
Glass / polyester	10	13	75.4	56.2
Glass / polyester	15	20	74.3	54.75
Glass / polyester	20	25	74	54.4
Glass / PUR	10	12	74.7	56.9

3.1. Ballistic Testing (Fragment simulating projectile (FSP) and 7.62 mm NATO FMJ high velocity projectiles) of Composite Panels

High velocity impact tests of the samples were performed in terms of both V_{50} (FSP) and 7.62 mm bullets. Figure 4 illustrates that all of the samples resulted with a partial penetration with FSP projectiles. Ballistic limits of 564.71, 971.8 and beyond 1009 m/s were obtained for glass / polyester based composite samples in 10,15 and 20 mm thicknesses; respectively. PUR matrix composite samples exhibited the ballistic limit of 566.8 m/s. Also the images clearly show that the matrix cracks and fiber fractures progresses in the direction of projectile penetration.


a)
b)
c)

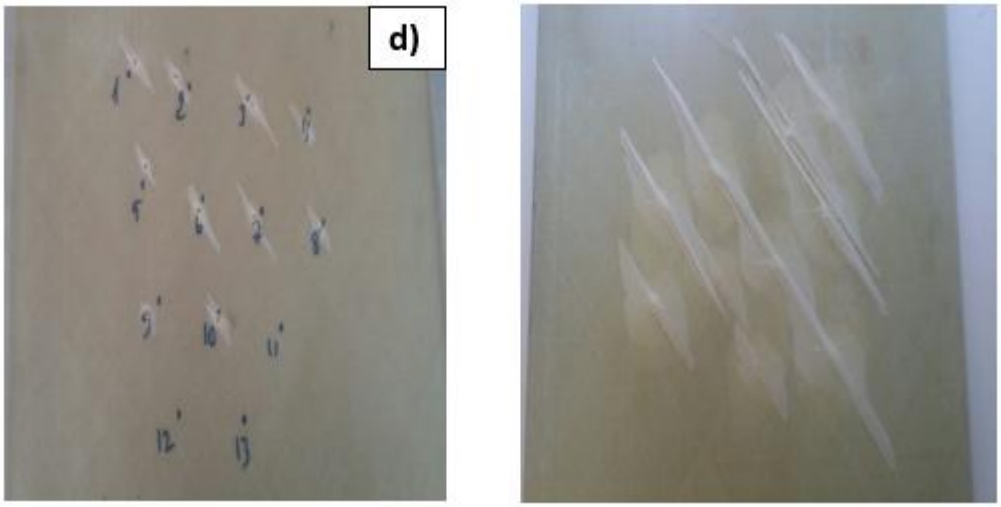
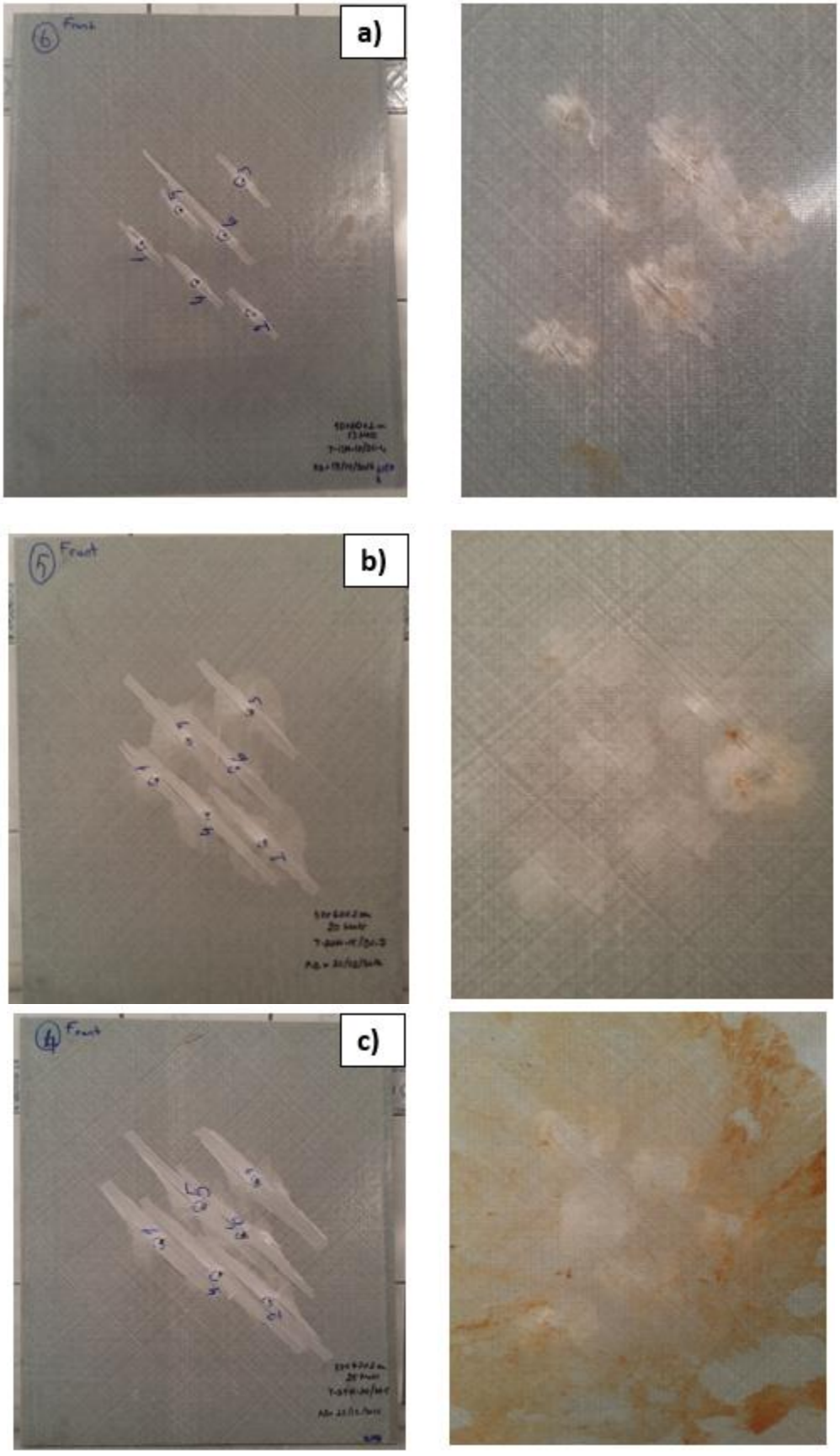


Figure 4. Front and back images of the 500x500 mm a) 10 mm glass / polyester b) 15 mm glass / polyester c) 20 mm glass / polyester and d) 10 mm PUR composite sample after subjected to V_{50} test.

Ballistic protection levels of the 10-15 and 20 mm of the glass / polyester matrix composite panels were obtained as Level II and Level III A according to the NIJ standard. The results revealed that the thickness of the panel affects the ballistic level. On the other hand, 5 mm glass-polyester covering plate / 10 mm Alumina ceramic / 15 mm glass-polyester backing plate system increases the ballistic protection level to the Level III as expected (Table 2). All of the samples in ballistic tests show partial penetration as given in Figure 5.

Table 2. Ballistic performances of the composite panels and ceramic containing system.

Structure	**# of Layers**	**Ballistic Performance (V_{50}) (m/s)**	**Ballistic Performance (Bullet Test)**
10 mm glass / polyester backing plate	13	564.71	Level II
15 mm glass / polyester backing plate	20	971,8	Level III A
20 mm glass / polyester backing plate	25	>1009	Level III A
10 mm PUR backing plate	12	566.8	-
5 mm glass-polyester covering plate / 10 mm Alumina ceramic /15 mm glass-polyester backing plate			Level III


a)
b)
c)

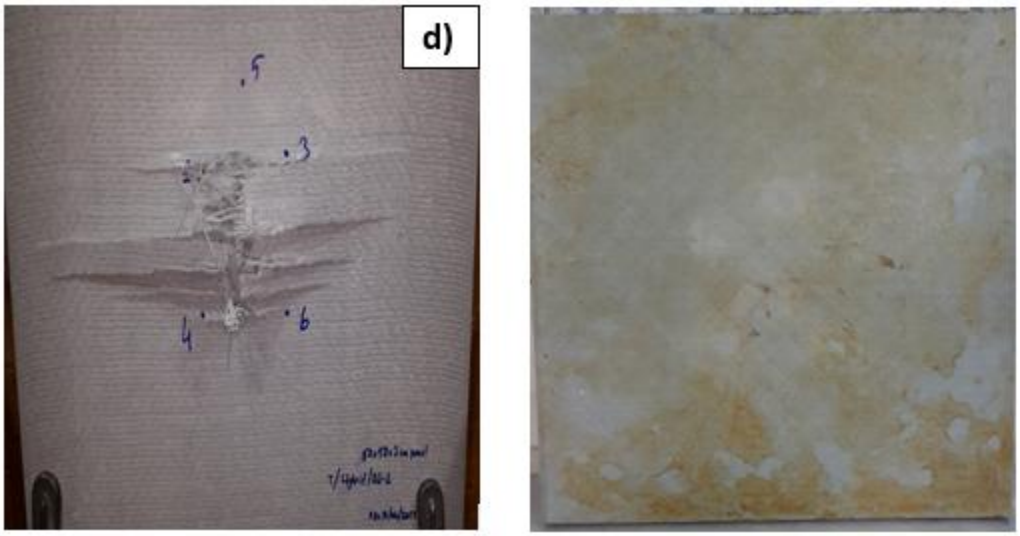


Figure 5. Front and back images of the 500x500 mm a) 10 mm glass / polyester b) 15 mm glass / polyester c) 20 mm glass / polyester and d) 5 mm glass fabric-polyester covering plate / 10 mm alumina ceramic layer / 15 mm glass-polyester composite sample after subjected to ballistic test.

3.2. Mechanical Analysis of Composite Panels

Evaluation of mechanical properties was performed by conducting flexural (3-Point bending), compression and Izod impact tests. At least five specimens were tested for each sample and average results including strength, modulus and energy absorbing values are reported and given in Table 3. According to the results, PUR matrix composites exhibit higher flexural and compression strength values as compared to the glass / polyester matrix composites. The measured results for flexural and compression strength of PUR and glass / polyester based samples are 517.30, 316.40 MPa and 326.9, 251.65 MPa; respectively. On the other hand, obtained flexural modulus of elasticity of PUR matrix composite sample is slightly lower than that of glass / polyester based system with the values of 18.27 and 17.50 GPa. This can be attributed to the more stiff nature of the PUR thermoset resin.
The low velocity energy absorption capabilities of the 10 mm glass / polyester composite is 202.76 kj/m^2 and lower than that of 10 mm glass fabric/PUR composite. This implies that the PUR absorb much higher energy by means of damage mechanisms such as crack formation, fiber, and matrix breakage and delamination.

Table 3. Mechanical properties of fabricated composite structures.

Sample	Flexural Strength (MPa)	Flexural Modulus (GPa)	Compression Strength (MPa)	Izod value (kj/m^2)
10 mm glass / polyester (13 layers of fabric)	326.9	18.27	251.65	202.76
10 mm PUR (12 layers of fabric)	517.30	17.50	316.40	337.56

ACKNOWLEDGEMENT

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CAM ELYAF TAKVİYELİ POLYESTER (CTP) ATIKLARININ GERİ KAZANIMI

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Özet

CTP esaslı kompozit üretiminde temel olarak, kenar kesimi, şekillendirme, montaj deliği açılması gibi aşamalarda çeşitli boyutlarda son ürün atıkları ortaya çıkmaktadır. Türkiye'de yılda yaklaşık 2500 ton, dünyada ise 166000 ton civarında CTP atık çıkmaktadır. Söz konusu atıklar genellikle boyutu küçültüldükten sonra yakılarak, ardından özel sahalara gömülerek ya da yaygın olmamakla birlikte çimento ve inşaat gibi sektörlerde dolgu maddesi olarak kullanılmak amacıyla, ek bir maliyet karşılığında bertaraf edilmektedir. Bu çalışmada, atığın öğütülerek yeni üretilen CTP esaslı ürün içinde kullanıldığı durumda, tane boyutu ve atık miktarı gibi parametreler, malzeme özellikleri üzerindeki etkileri açısından sistematik olarak incelenmiştir.

Anahtar Kelimerler: Cam elyaf takviyeli plastik (CTP), Doymamış polyester, Geri dönüşüm, Geri kazanım, Yapay sinir ağları

Abstract

By the production process of glass fiber reinforced polymers (GFRP), final product waste arises at different stages such as edge trimming, shaping and opening mounting hole. GFRP producers in Turkey declare 2 500 tons composite waste per year and this number increases up to 166 000 tons for overall GFRP production in the world. Although there are many waste disposal methods available for waste GFRP; the most common ones are landfilling after grinding and/or burning process and using in cement/construction sectors as a filler material. These common waste disposal methods create also an additional cost for the waste producers whether the waste consumer company makes an additional profit with using the waste or not.

Carcinogenic waste such as micro-sized carbon particles, polycyclic aromatic hydrocarbons and poisonous CO and CO_2 gas which causes global warming are released during incineration of GFRP waste. Moreover, landfilling process causes soil pollution. In Polin, 350 tons of glass fiber reinforced polyester waste was released in 2016. Polin WP aims to recycle of its own and other companies' wastes which are high value-added. In this study, ground composite waste was used as filler in the production of new GFRP based products and the effects of parameters such as grain size and amount of waste on thermal, mechanical and other properties were observed.

Commercial code of gelcoat was GIN424 and polyester was IR100TP were purchased from İlkalem, Turkey. Glass fiber (MAT8) was kindly obtained from Cam Elyaf as chopped strand mat with 450 g/m^2. Methyl ethyl ketone peroxide (MEK-P), which was used as initiator for gelcoat and polyester, was purchased from Akzo Nobel.

According to results of the study, reduction in mechanical strength was observed with increase both the ratio of the waste and the grain size used in the composite samples, as expected. This was attributed to no chemical interaction and so poor interface between physically recovered waste and fresh resin. For 3 mm waste dimension, the average decrease in tensile and flexural strength was 30%; it was recorded as 20% for impact strength. The other important effect of waste addition was higher resin viscosity, which caused more resin requirement for wetting equivalent amount of fiberglass.

The future stages of this study includes mathematical modelling by using artificial neural network. Aim of the model is to identifty the recovery parameters for the highest waste ratio in GFRP, which result with the most tolerable physical and mechanical properties for a wide range of product spectrum.

Key Words: Glass fiber reinforced plastics (GFRP), Unsaturated polyester, Recycle, Recovery, Artificial neural networks

1. GİRİŞ

Polimerik kompozitler; termoset veya termoplastik yapıda, tek ya da çok yönde takviye özelliği sağlayacak şekilde, cam elyafı ve/veya diğer takviye malzemelerinden yeterli miktarda (uzunluk ve ağırlıkça) katılmış polimerik matrislerdir. Cam elyaf takviyeli plastik (CTP), cam elyaf ile takviye edilmiş doymamış polyester reçineden üretilen, yüksek dayanımlı bir kompozit malzemedir. Havacılık/uzay/savunma ve spor/eğlence alanlarındaki uygulamalar, CTP'lerin en yüksek katma değeri sağlayan uygulamalar olarak gösterilebilir [1].

CTP esaslı kompozit üretiminde kenar kesimi, şekillendirme gibi aşamalarda çeşitli boyutlarda son ürün atıkları ortaya çıkmaktadır. Polin Su Parkları A.Ş. bünyesinde yılda yaklaşık 200, Türkiye'de 2500, dünyada ise 166.000 ton atık çıkmaktadır. Söz konusu atıklar genellikle boyutu küçültüldükten sonra yakılarak ardından özel sahalara gömülerek bertaraf edilmekte ya da yaygın olmamakla birlikte çimento ve inşaat gibi sektörlerde dolgu maddesi olarak kullanılmak amacıyla, ek bir maliyet karşılığında bertaraf edilmektedir. Hem ulusal, hem de uluslararası alanda atığın bertarafı ve değerlendirilmesi için uygulanan prosedürler mevcut durumda benzerlik göstermektedir. Yakılarak bertaraf esnasında mikronize karbon partikülleri, polisiklik aromatik hidrokarbonlar (PAH), karbon monoksit gibi kanserojen olabilen atıklar ve küresel ısınmaya yol açan CO_2 gazı açığa çıkmaktadır. Gömme işlemi ise toprağın kirlenmesine sebep olmaktadır [2].

Literatürde CTP esaslı atıkların yeniden kullanımına yönelik çalışmalar temel olarak ikiye ayrılmaktadır. Bunlar; atığın öğütülerek doğrudan kullanımına yönelik çalışmalar ve atığın içerdiği elyafı geri kazanmak üzere yapılan çalışmalardır. Correria ve Almeida'nın çalışmalarında, ince öğütülmüş (<100 μm) atık CTP tozunun doğrudan hacimce %0, 5, 10, 15, 20 oranlarında beton karışımında kum yerine kullanımını denemiştir. %5'e kadar olan kullanımında CTP tozunun betonun elastikiyetini iyileştirdiği, böylece çatlama eğilimini azalttığı görülmüştür [3]. Cunliffe ve Williams'ın yaptıkları çalışmada CTP'ye 450 °C'de sabit yataklı reaktörde piroliz uygulanmıştır. DMC'lerde (dough moulding compound) katı atıktan kurtarılan cam elyafın %20 oranına kadar yeni cam elyaf yerine kullanılabileceğini göstermiştir [4]. Iwaya ve arkadaşları CTP içindeki polyester reçineyi etkin bir şekilde depolimerize edebilecek ve elyafı dolgu ve reçineden ayırabilecek superkritik solvent ile çalışılmışlardır. Polyesterin dönüşümü, katalizör varlığında katalizör/solvent molar oranı arttıkça hızlanmıştır [5]. Kao ve arkadaşlarının yaptıkları çalışmada solvoliz (hidroliz) teknolojisi ile geri kazanılan cam elyafların mekanik performansa etkisi incelenmiştir. Polyester reçineyi çözmek ve cam elyafı geri kazanmak için yapılan kimyasal reaksiyonda altkritik (subcritical) su kullanılmıştır [6]. Kennerley ve arkadaşlarının yaptıkları çalışmada cam elyaf, 450°C'de akışkan yataklı reaktör kullanılarak SMC atığından ayrılmıştır. %50 oranında kullanıma kadar ise fiziksel ve mekanik özelliklerde önemli bir değişim gözlenmemiştir [7]. CTP'nin tamamen ya da kısmen geri kazanıldığı çok sayıda çalışma olmakla birlikte, çalışmaların çok büyük bir kısmı ana hatlarıyla, yukarıda özetlenen çerçevede gerçekleştirilmiştir. Literatürde hem elyaf hem de reçinenin birlikte yeni karışımlarda değerlendirildiği sistematik bir çalışmaya rastlanmamıştır.

Polin Su Parkları ve Havuz Sistemleri A.Ş.'de 2016 yılında 350 ton cam elyaf takviyeli polyester malzeme (polyester:cam elyafı; 70:30) atığı çıkmıştır. Polin, hem kendi ürünlerini hem de sektörde üretilen yüksek katma değerli kompozitleri geri dönüştürmeyi hedeflemektedir. Bu çalışmada, atığın öğütülerek yeni üretilen CTP esaslı ürün içinde kullanıldığı durumda, tane boyutu ve atık miktarı gibi parametreler, malzeme özellikleri üzerindeki etkileri açısından sistematik olarak incelenmiştir. Malzeme

değeri oldukça yüksek olan bu atıkların, yeni üretilen CTP ürün içinde, uygun tane büyüklüğünde ve/veya uyumluluğunun geliştirilmesi yoluyla matris-atık etkileşimi arttırılıp kullanımının, atıkların katma değerinin arttırılabilmesi ve olumsuz çevresel etkilerinin giderilmesi anlamında önemli bir katkı olabileceği düşünülmektedir.

2. MALZEME VE YÖNTEM

2.1. Malzemeler

GIN 424 kodlu tabanca tipi jelkot ve IR 100 TP kodlu el yatırması reçinesi İlkalem A.Ş.'den temin edilmiştir. 450 g/m^2 ağırlıklı ve MAT8 kodlu keçe elyaf Cam Elyaf firmasından temin edilmiştir. Reçine ve jelkotlar için başlatıcı olarak kullanılan ve %36 peroksit konsantrasyonlu metil etil keton peroksit (MEK-P) Akzo Nobel firmasından temin edilmiştir.

2.2. Yöntem

Atık malzeme, üretim hurdalarının doğrudan öğütülmesi ile hazırlanmıştır. 300 µm, 1 mm ve 3 mm boyutlarındaki öğütülmüş atık, taze polyester reçine içerisine %5, 10, 15 ve 20 oranlarında eklenmiştir. Kompozit örnekler, keçe elyafın atık içeren reçine ile işlenmesiyle, el yatırması yöntemiyle hazırlanmıştır. Öğütülmüş atık içeren numunelerin karakterizasyonu için çekme, üç nokta eğme, darbe, kısa kiriş dayanımı ve kül fırınında yakma testleri yapılmıştır. Bununla birlikte, atık ilavesinin reçine kür profiline etkisini incelemek için jel ve kür süreleri ile pik kür sıcaklığı ölçümü yapılmıştır. Hazırlanan kompozit örneklerinin bileşimleri ve kodları Tablo 2.1'de verilmiştir.

Tablo 2.1.Hazırlanan kompozit örneklerinin bileşimleri ve kodları

	Atık İçeriği (%)	**Atık Boyutu**
100/0-REF	0	-
95/5-B1	5	300 µm
95/5-B2	5	1 mm
95/5-B3	5	3 mm
90/10-B1	10	300 µm
90/10-B2	10	1 mm
90/10-B3	10	3 mm
85/15-B1	15	300 µm
85/15-B2	15	1 mm
85/15-B3	15	3 mm
80/20-B1	20	300 µm
80/20-B2	20	1 mm
80/20-B3	20	3 mm

3. BULGULAR VE TARTIŞMA

3.1. Mekanik Özellikler

Hazırlanan kompozit örneklerinin mekanik özellikleri Tablo 3.1.'de verilmiştir.

Tablo 3.1 Mekanik özellikler

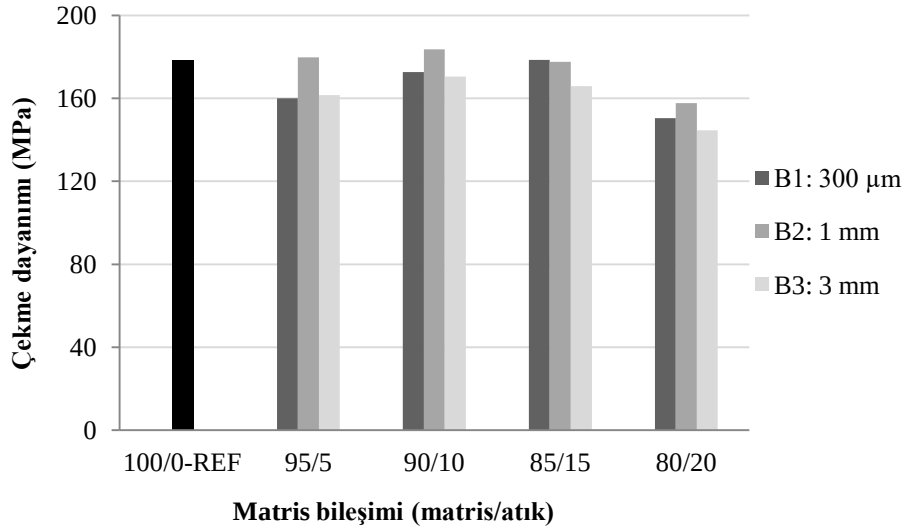
	100/0-REF	**95/5-B1**	**95/5-B2**	**95/5-B3**	**90/10-B1**	**90/10-B2**	**90/10-B3**	**85/15-B1**	**85/15-B2**	**85/15-B3**	**80/20-B1**	**80/20-B2**	**80/20-B3**
Çekme Dayanımı (MPa)	178,6	145,9	137,5	117,1	144,2	135,6	105,5	141,8	128,1	90,4	118,0	108,7	77,5
Çekme Modülü (MPa)	11508	10986	9478	9789	9654	10251	9850	9288	10789	7989	8940	9292	7919
Kopmada Uzama (%)	1,79	1,05	1,89	1,43	1,31	1,76	2	1,26	1,60	1,455	1,87	1,53	1,78
Eğme Dayanımı (MPa)	285,5	222,1	201,6	167,6	157,2	178,2	138,5	172,8	170,4	144,6	166,2	141,8	134,8
Eğme Modülü (MPa)	12612	9736	7431	8293	6726	7446	7616	7540	7290	7591	7876	8257	6246
Eğmede Uzama (%)	9,31	7,49	7,91	5,19	6,74	7,30	4,18	6,71	5,90	4,45	5,83	4,18	3,70
Darbe Dayanımı (kJ/m^2)	120,2	81,7	73,2	75,1	62,7	59,6	77,7	56,6	59,6	57,9	51,4	69,7	54,5
Kısa Kiriş Dayanımı (MPa)	228,3	225,5	163,1	150,6	145,1	193,8	124,3	218,1	159,1	105,8	134,0	175,5	115,5

Artan atık miktarı ile, malzeme mekanik dayanımında beklendiği şekilde kısmi düşüşler gözlenmiştir. Bu durum, CTP atığının sadece fiziksel olarak geri kazanımı sonucunda, taze polyester reçine ile kimyasal olarak ilgisi bulunmadığından dolayı atık-matris arayüzeyinin zayıf olması ile açıklanabilir. %20 oranında 3 mm atık kullanımında çekme ve eğme dayanımlarında ortalama %50, darbe dayanımında ise ortalama %45'lik bir düşüş gözlenmiştir. Bununla birlikte, kullanılan atık boyutunun artışıyla genel olarak mekanik özelliklerde kayıp meydana gelmiştir. Mekanik dayanımlardaki düşüş tane boyutunun küçültülmesi ile azaltılabilmektedir.

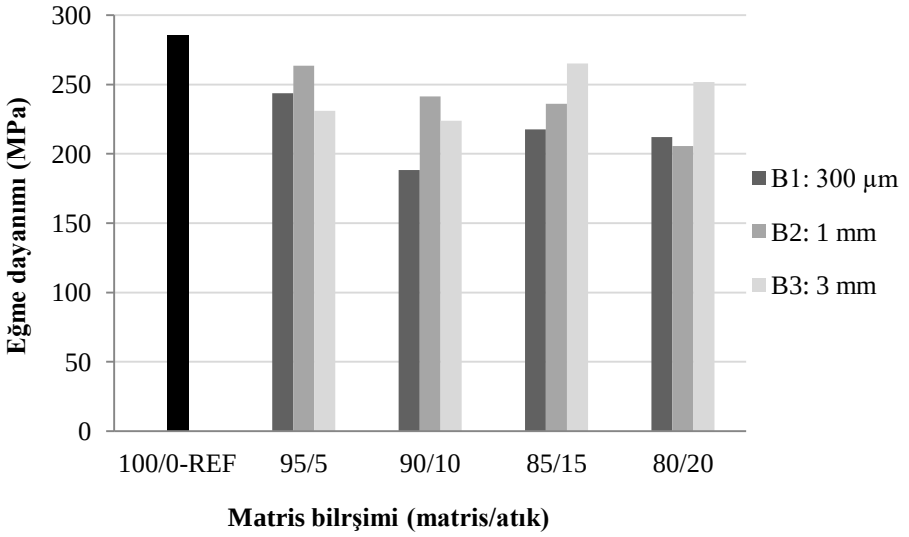
Atık ilavesinin bir başka önemli etkisi de matris viskozitesinin artması sonucu aynı orandaki elyafın ıslantılabilmesinde daha yüksek miktarda reçine gereksinimidir. Hazırlanan kompozit örneklere 650 ^{o}C'de kül fırın testi yapılarak içeriklerindeki elyaf miktarları belirlenmiştir. Atık kullanılmadığı durumda kompozit içerisindeki elyaf içeriği %45,3 iken bu değer atık kullanımının ve tane boyutunun artışı ile birlikte azalmaktadır. Kompozit malzeme içerisine 3 mm tane boyutunda %20 oranında atık girildiğinde elyaf miktarı %24,3 olarak ölçülmüştür. Bu durum, CTP atığının ortalama %25 oranında elyaf içermesine ve reçine içerisindeki atık oranı artışı ile viskozitenin artması sonucu elyafların ıslanması için daha fazla reçineye ihtiyaç duyulması ile açıklanabilir.

Atık kullanımı ile birlikte kompozit içerisindeki elyaf oranları azaldığı için sabit bir elyaf oranında taze atık ve polimerik matris oranının mekanik özellikler üzerindeki etkisini değerlendirebilmek için test sonuçları sabit elyaf oranına göre normalize edilmiş, çekme, eğme ve darbe dayanımları tekrar değerlendirilmiştir (Şekil 3.1, Şekil 3.2, Şekil 3.3). Normalize edilen grafikler incelendiğinde, gerçekte sadece atıktan faydalanılması sonucu malzeme özelliklerindeki kayıpların, Tablo 2'de raporlanan değişimlere kıyasla daha makul seviyelerde olduğu anlaşılmaktadır. Bu etki, icelenen örneklerin darbe dayanımı üzerinde de benzer olmakla birlikte, atığın tane boyutunun artmasıyla birlikte darbe

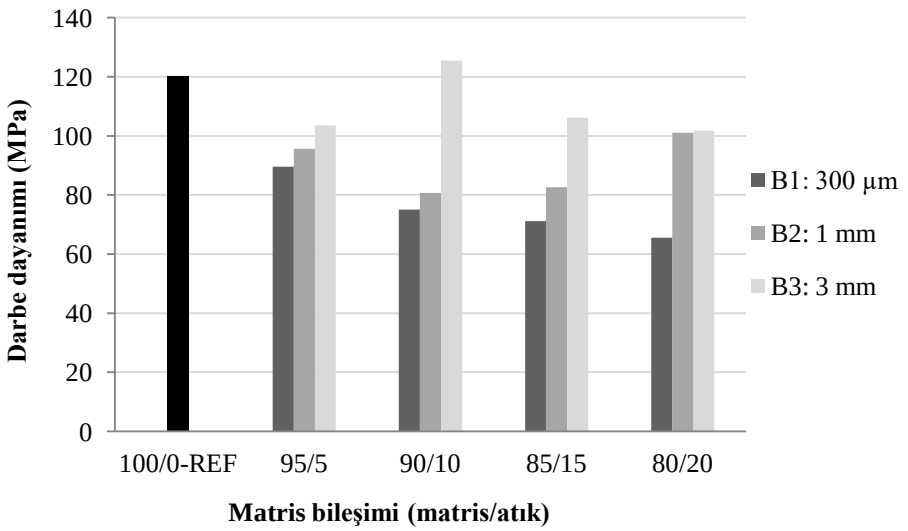
dayanımındaki kayıp oranının düşmesi dikkat çekici bir bulgudur. Darbe sırasındaki kırılma mekanizmasının aydınlatılması için kırılma yüzeylerinin morfolojik incelemeleri devam etmektedir.



Şekil 3.1 Çekme dayanımı



Şekil 3.2 Eğme dayanımı



Şekil 3.3 Darbe dayanımı

3.2. Fiziksel Özellikler

Atık kullanımının reçinenin kür profiline ve fiziksel özelliklerine etkisini incelemek amacı ile referans ve atık içeren reçinelerin jel süresi, pik kür sıcaklığı, pik kür süresi, vizkozitesi, lineer büzülmeleri ve sertlikleri ölçülmüştür. Test sonuçlarına göre atık ilavesi ile jel ve kür süresinin azaldığı görülmüştür. Bu durum, atık içerisinde de çapraz bağlayıcı bulunmasına bağlanabilir. Pik kür sıcaklığının azalması ise, atık oranı artışı ile yığın polyester miktarının azalmasından kaynaklanmaktadır. Atık kullanımının artışı ile viskozite ve sertlik değerleri artmıştır. Post-kür uygulanmadan önceki ve sonraki lineer büzülme değerleri incelendiğinde ise atık ilavesinin karma içerisinde dolgu gibi davranarak polyesterin lineer çekme değerini azalttığı görülmüştür. Kompozit örneklerin hazırlanmasında kullanılan atık içeren ve içermeyen reçinelerin fiziksel özellikleri Tablo 3.3'te verilmiştir.

Tablo 3.3. Fiziksel özellikler

	0	**5**	**10**	**15**	**20**
Jel süresi (dk) %1 Butanox M60 (Akzo Nobel), ISO 2535	18	13,5	13	12,5	12,3
Pik kür sıcaklığı (ºC) %1 Butanox M60 (Akzo Nobel), ISO 2535	176,5	171,1	162,6	162,2	154,2
Pik kür süresi (dk) %1 Butanox M60 (Akzo Nobel), ISO 2535	47	37,6	39,6	36,3	36,4
Viskozite (cP) 20°C, Brookfield RVT, 20rpm #2, ISO 2555	220	328	550	830	1898
Lineer büzülme (%) ASTM D2566	1,41	0,45	0,70	0,70	0,70
Post-kür sonrası lineer büzülme (%) (150 C, 75dk) ASTM D3045	1,41	1,17	0,93	0,70	1,17
Sertlik (barcol) 934-1, ASTM D2583	40	40	41	42	43

Başlatıcı (MEK-P) miktarı, reçinenin kür profilinde etkin rol oynamaktadır. Başlatıcı madde miktarı artışı ile reçine jel ve kür süreleri kısalır. Atığın içerisinde de başlatıcı bulunduğu düşünülerek, atık içeren reçinede başlatıcı miktarı saf reçinenin %1'i kadar alınarak tekrar kür profili çıkarılmıştır. Atık kullanımı ile kısalan jel ve kür süreleri, başlatıcı oranının azaltılması ile birlikte atık kullanılmadığı durumdaki değerlere yaklaşmaktadır. Başlatıcı miktarının kür profiline etkisi Tablo 3.4'te verilmiştir.

Tablo 3.4 Başlatıcı miktarının kür profiline etkisi

	100/0 %1 MEK-P	**70/30 %1 MEK-P**	**70/30 %0,7 MEK-P**
Jel süresi (dk) %1 Butanox M60 (Akzo Nobel), ISO 2535	17	14-15	17
Pik kür sıcaklığı (ºC) %1 Butanox M60 (Akzo Nobel), ISO 2535	176,5	116	107,7
Pik kür süresi (dk) %1 Butanox M60 (Akzo Nobel), ISO 2535	47	53	68

4. SONUÇLAR

Bu çalışmada, atığın öğütülerek yeni üretilen CTP esaslı ürün içinde kullanıldığı durumda, tane boyutu ve atık miktarı gibi parametreler, malzeme özellikleri üzerindeki etkileri açısından sistematik olarak incelenmiştir. Kompozit örneklerde kullanılan atığın hem oranının hem de tane boyutunun artışı ile mekanik dayanımda azalma gözlenmiştir. CTP atığı sadece fiziksel işlemden geçerek toz haline getirildiği için kimyasal bağlanmaya katılmayarak karma içerisindeki çağrazbağ derişimini düşürmektedir. Bu da mekanik dayanımda düşüşe sebep olmaktadır. CTP atığının ortalama %25 oranında elyaf içermesine ve reçine içerisindeki atık oranı artışı ile viskozitenin artması ile birlikte elyafların ıslanması için daha fazla reçineye ihtiyaç duyulması, atık kullanımının ve tane boyutunun artışı ile birlikte elyaf miktarında azalmaya yol açmaktadır. Bu sebeple mekanik değerler elyaf oranı sabit tutularak normalize edilmiş ve elyaf içeriği atık kullanılmadığı durum ile aynı olduğunda çekme ve eğme dayanımlarında referans kompozit değerlerine yakın değerler elde edilmiştir.

Çalışmanın devamında yapay sinir ağları ile modelleme yapılarak tolere edilebilir fiziksel ve mekanik özelliklere sahip, en yüksek atık içerecek CTP bileşimi belirlenecektir. Atık içeren ürünlere ait geniş bir kullanım alanı aralığı hazırlanacak, alternatif ürün spektleri tanımlanacaktır.

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ELEKTRO-EĞRİLMİŞ BNNS/PMMA NANOLİF KATKILI VİNİLESTER REÇİNENİN ÜRETİMİ VE KARAKTERİZASYONU

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1. Özet

Elektro-eğirme (electrospin) tekniği, son zamanlarda nano-boyutta lif üretimi için sıkça kullanılmaktadır. Polimer esaslı nanofiberlerin üretimi için en etkin yöntem electrospinning (elektroeğirme) yöntemidir. Elektrospin yöntemine etki eden 3 temel parametre vardır; çözelti özellikleri (Kullanılan polimerin cinsi, molekül ağırlığı, çözeltinin viskozitesi, konsantrasyonu,), proses değişkenleri (voltaj, akış hızı, toplayıcı ile besleme ünitesi arasındaki mesafe), çevre koşulları (sıcaklık, nem, basınç, atmosfer cinsi). Bu çalışmanın temel amacı elektrospinning parametrelerinin fiberlerin morfolojik yapısına ve camsı geçiş sıcaklığına etkisini görebilmek ve seçilen en iyi parametrelerle elektrospinning yöntemiyle üretilen PMMA ve BNNS/Silan dan oluşmuş fiberlerin vinilester reçine üzerindeki olumlu termal etkilerini gözlemlemektir. Üretimi yapılan nanoliflerin yapısı taramalı elektron mikroskobu (SEM) kullanılarak incelenmiştir. Üretilen fiberlerin ve kompozit plakaların camsı geçiş sıcakları Dinamik mekanik analiz (DMA) ile analiz edilmiştir.

2. Abstract

Polymethylmethacrylate/Boron nitride nanosheets (PMMA/BNNSs) nanofibers were produced by conducting electrospinning.

Electrospinning is a straightforward and cost-effective method to produce novel fibers with diameters in the range of from less than 3 nm to over 1 mm, which overlaps contemporary textile fiber technology [1]. Electrospinning is a technique that utilizes electric force alone to drive the spinning process and to produce polymer fibres from solutions or melts [2-3].

In the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field. Charge is induced on the liquid surface by an electric field. Mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone [4]. When the electric field reaches a critical value at which the repulsiv electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. Since this jet is charged, its trajectory can be controlled by an electric field. As the jet travels in air, the solvent evaporates, leaving behind a charged polymer fiber which lays itself randomly on a collecting metal screen. Thus, continuous fibers are laid to form a non-woven fabric [5]. The number of publicatons on electrospinning has increased dramatically during the past decade, focusing on the morphologies of nanofibers. The morphology of electrospun nanofibers is affected by many factors, such as; applied voltage, flow rate, molecular weight and concentration of polymer, distance between collector and syringe, additives.

To promote the wettability of the fibers with the matrix resin, the surface of the fibers were chemically functionalized using silane coupling agent, (Vinyltrimethoxysilane (VTS)). Of all the produced nano-fibers, the most promising one was selected, considering thermal properties and the surface morphology of each fiber produced. The best processing parameters were then accordingly selected to follow when producing the nanofibers to be added to vinyl ester resin. The incorporation of BNNS modified electrospun PMMA fibers into the vinyl ester resin is expected to improve thermal properties of the resin at no expense of mechanical integrity. Final thermal properties of the resin were further investigated using DMA. The results obtained were then discussed in a conscience manner.

The optimum values determined for the acetone solution as a result of the experiments made are given below;

• Concentration: 4% PMMA + 0.01% BNNS + Silane

• Voltage rating: 25 kV

• Range: 19 cm

• Flow rate: 6 ml \ h

And also ıt is observed that Tg of PMMA increases with increasing Silane and BNNS addition. The increase in the Tg of composites, in comparison with the pure fiber PMMA,is attributed to enhancement of the the adhesion between the polymer and particle surfaces

3. Giriş

Fiber takviyeli tabakalı kompozit malzemeler (FTTKM), otomobil, uzay ve havacılık endüstrilerindeki yapısal tasarımlarda giderek artan oranlarda kullanım alanı bulmaktadır. Hafif olmaları, yüksek özgül dayanımları, yüksek elastik modül katsayıları, korozyon ve mekanik yorulmaya karşı dirençleri ve düşük termal genleşme sabiti gibi özellikleri ile geleneksel mühendislik malzemelerine göre daha avantajlıdırlar. Üretim yöntemlerinin birçoğunun seri üretim ve otomasyona uygun olmaması; ilk yatırım, süreç ve bileşen malzemeleri (fiber ve matris) giderlerinin de yüksek olması üretim maliyetlerini oldukça artırır. Literatürde FTTKM lerden oluşan son ürünlerin maliyetlerini aşağıya çekmek için, alternatif fiber üretim yöntemleri, farklı matris ve takviye malzemesi araştırma ve geliştirme faaliyetleri, mevcut üretim yöntemlerinin eniyilemesi, olası yeni üretim yöntemlerinin kurgulanması gibi çalışmalar büyük ivme kazanmıştır. Bu sayede geçmişe göre FTTKM üretim maliyetleri hatırı sayılır derecede düşmüş olsa da, metaller ve seramikler gibi geleneksel mühendislik malzemelerine kıyasla FTTKM ler halen yüksek maliyetli malzemeler kategorisi altında sınıflandırılmaktadır. FTTKM çeşitli özellikler bakımından farklılıklar gösteren katmanların bir araya gelmesiyle meydana gelmektedir. Bu farklılık, mukavemet, ısı iletimi, ağırlık, yüzey sertliği, su geçirgenliği gibi çeşitli öğeleri içerebilmektedir [6,7]. Bu çalışmada matris malzeme olarak nanoboyutlu bor nitrürü nanatabakalı (BNNS) modifiyeli vinil-ester reçine kullanılmıştır. BNNS parçacıklarının vinil-ester reçine içerisinde homojen dağılımı sağlamak ağırlıkça farklı oranlarda için Polimetil metakrilat (PMMA) esaslı nanofiberler elekto-eğirme (electrospin) tekniği ile üretilmiştir. Elektro-eğirme tekniği, son zamanlarda nano-boyutta lif üretimi için sıkça kullanılmaktadır [8]. Polimer esaslı nanofiberlerin üretimi için en etkin yöntem electrospinning (elektroeğirme) yöntemidir. Nanoliflerin morfolojilerine ve termal özelliklerine odaklanan elektrospinning üzerine yapılan yayın sayısı, son on yılda önemli ölçüde artmıştır. Nanoliflerin özelliklerini etkileyen elektrospin yöntemine etki eden 3 temel parametre vardır; çözelti özellikleri (Kullanılan polimerin cinsi, molekül ağırlığı, çözeltinin viskozitesi, konsantrasyonu,), proses değişkenleri (voltaj, akış hızı, toplayıcı ile besleme ünitesi arasındaki mesafe), çevre koşulları (sıcaklık, nem, basınç, atmosfer cinsi) [9]. Yapılacak olan çalışmalarla ilk olarak elektro-eğirme yöntemine etki eden parametrelerin optimizasyonu amaçlanmaktadır daha sonra üretilen PMMA esaslı nanofiberlerden oluşan matlar daha sonra belli oranlarda vinil-ester reçine içerisine katılarak hem BNNS lerin homojen dağılmasını sağlayacak hem de vinil-esterin mekanik tokluk değerleri ve kürlenme sonrasında oluşan büzülme oranı kontrol edilebilmiştir. Bu matris reçine modifikasyon

literatürde bir ilki temsil etmektedir. BNNS lerin seçilme nedeni; Bor nitrür (BN) eşit sayıda bor ve azot atomlarından oluşan bir bileşiktir. Hekzagonal (hBN) ısıl olarak en kararlı ve en yumuşaktır. hBN grafite benzer tabakalı yapıdan oluşur, sert ortamlar için katı yağlayıcı, UV ışın emici veya kompozitlerde ısıl iletkenlik artırıcı ajan olarak kullanılabilir. Bu kapsamda ekibimizce daha evvelden başarı ile üretilen ve halen üretilmekte olan BNNSs lerin kullanımı ile hem mekanik mukavamet hem de ısıl kararlığın kullanılacak olan matriks reçinede arttırdığı görülmektedir. Bu çalışmada silan bağlayıcı ajanlar elekroeğirme ile elde edilmiş PMMA ve BNNSs lerin yüzeyini iyileştirmek için ve BNNS lerin PMMA ya daha iyi tutunmasını sağlamak için kullanılmıştır. Silan ajanı olarak vinil trimetoksi (VTS) seçilmiştir. Burada amaç VTS sinin PMMA ile bağ yapması ve daha sonra kullanılacak olan vinilester ile ise 3 boyutlu bir arayüzey (interphase) oluşturulmasına olanak sağlamaktır.

4. Materyal – Metot

4.1. Materyal

Elektro spin yöntemiyle nanofiber üretimi için farklı molekül ağırlıklı (81.000 g/mol,350.000 g/mol) PMMA, BNNS ve Silan tayin edildi. Nanolif oluşturmak için NS-24,Inovenso marka elektrospin cihazı kullanıldı. Konsantrasyonu %2,%4 ve %6 olarak hazırlanan PMMA nın 100 ml lik aseton, kloroform, toluen ve DMF/THF çözücülerinde çözünmesi sağlandı. Bu çalışmada POLİYA Polives 701 bisfenol epoksi esaslı vinil-ester termoset reçine kullanıldı. 100 gr vinilester reçine %0.2 oranda Co ve %2 oranda Bütanox M60 ile karıştırıldı. Karışıma daha sonra %5 oranında PMMA ve %1 oranında BNNS/Silan içeren nanofiber katkısı yapıldı.

4.2. Metot

Elektrospinning parametrelerinin fiberlerin morfolojik yapısına ve camsı geçiş sıcaklığına etkisini görebilmek için proses parametrelerinde değişiklik yapılarak fiber üretimleri gerçekleştirildi. İlk olarak nanolif üretiminde çözücü etkisini gözlemlemek için kütlece % 2,4,6 oranındaki averaj molekül ağırlığı 81.000 g/mol olan PMMA ve %1 BNNS içeren karışım 100 er ml olmak üzere aseton, kloroform,toluen, dimetilformamid/tetrahidrofuran (DMF/THF 2:1) içerisinde manyetik karıştırıcıda karıştırılarak farklı çözeltiler hazırlandı.Elektrospinning parametrelerinin üretilen nanoliflerin özelliklerine etkisini gözlemlemek için yapılacak çalışmalarda en iyi çözücünün aseton olduğu belirlendi. Öncelikle konsantrasyon ve moleküler ağırlık etkisini görebilmek için kütlece % 2,4,6 oranındaki averaj molekül ağırlığı 81.000 g/mol ve 350.000 g/mol PMMA , %1 oranda BNNS ile manyetik karıştırıcıda karıştırılarak çözelti hazırlandı. BNNS/SİLAN miktarının oluşan fiberin özelliklerine etkisini gözlemlemek için 4 gr PMMA %0.5,1 ve 1.5 oranlarında silan katkılı ve katkısız BNNS le birleştirildi ve 100 ml aseton içerisinde manyetik karıştırıcıda karıştırılarak çözünmesi sağlandı.. Proses normal çevre koşulları altında (yaklaşık 23°C sıcaklık ve % 60 nem) yürütüldü. Akış hızının fiberin özelliklerine etkisini görmek için 4,6,9 ml/saat akış hızlarıyla elektroda besleme yapıldı. Elektriksel potansiyel farktan yararlanarak toplayıcı ve enjektör tipi uç arasında gerilimin fiberin özelliklerine etkisini görmek için 22,25,28 kV gerilim sağlandı. Toplayıcı ve enjektör tipi uç arasındaki mesafenin fiberin özelliklerine etkisini gözlemlemek için mesafe 13,15, 19 cm olarak belirlendi.Silindir toplayıcı üzerine sarılan 50x30 mm boyutlarındaki dikdörtgen alüminyum folyo toplayıcı olarak kullanıldı. Yapılan deneyler sonucu en iyi fiber oluşumunun gerçekleştiği paramatreler ; PMMA konsantrasyonu %4, BNNS/Silan konsantrasyonu %1, voltaj 25Kv, akış hızı 6ml/sa aralık 19 cm ve en iyi çözücünün aseton olduğu belirlendi. Belirlenen parametreler uygulanarak üretilen fiberler(PMMA/BNNS/Silane) ve vinil ester reçineden oluşan kompozit yapının üretim aşamasına geçildi. PMMA/BNNS/Silane katkısının vinilester reçinenin termal ve mekanik özelliklerine etkisini gözlemlemek amacıyla ilk olarak katkısız 100 gr vinil-ester reçine(Poliver 701) %0.2 oranda Co ve %2 oranda Bütonox M60 ile karıştırıldı. Karışım kalıba dökülüp 120°C de 2 saat süreli kürlenmeye bırakıldı. Daha sonra PMMA dan üretilen fiberlerin granül halde ki PMMA dan farkını ve reçinenin özelliklerine etkisini gözlemlemek için 100 gr vinilester reçine kalıba dökülüp kürlenmeye bırakıldı. Aynı prosedür elektro eğirme yöntemi ile oluşan fiberlerle de tekrarlandı. Üretilen BNNS+Silan

katkılı 81.000 g/mol ve 350000 g/mol molekül ağırlıklı PMMA dan oluşan nanofiberler vinilester reçine içerisine atıldı ve çözünmesi sağladı ve kalıba dökülüp kürlenmeye bırakıldı.

ÇÖZÜCÜ	Konsantrasyon (wt %)	Uygulanan Voltaj (Kv)	Akış Hızı (ml/h)	Aralık (cm)	Molekül Ağırlığı (PMMA) (g/mol)
ASETON KLOROFORM TOLUEN DMF/THF	2 **4** 6	25	6	19	81.000 350.000
	4	22 **25** 28	6	19	81.000 350.000
	4	25	4 **6** 9	19	81.000 350.000
	4	25	6	13 15 **19**	81.000 350.000
	4	25	6	19	81.000 350.000

Tablo 1. İşlem değişkenlerinin fiber morfolojisine etkisini gözlemlemek için seçilen elektro eğirme parametreleri ve en uygun parametreler.

5. Bulgular Ve Tartışma

5.1. Taramalı elektron mikroskobu (SEM)

Taramalı elektron mikroskopu kullanılarak elektro eğirme yöntemine etki eden çözücü cinsi, polimer konsantrasyonu, akış hızı, uygulanan voltaj, toplayıcı ve enjektör tipi uç arasındaki mesafe, polimerin molekül ağırlığı, çözeltide ki BNNS ve silan yüzdeleri gibi çözelti değişkenlerinin ve işlem değişkenlerinin fiber morfolojisine etkisini gösteren değişkenler incelenmiştir.

5.2. Elektro eğirme yöntemiyle oluşan fiberlerin morfolojisine BNNS miktarı etkisi

Elektro eğirme yöntemiyle oluşan fiberlerin morfolojisine BNNS miktarı etkisinin gözlemlenebilmesi için aşağıdaki parametreler seçilmiştir.

Çözücü: Aseton

Konsantrasyon: 100 gr Aseton + 4 gr PMMA+ 0.02 gr BNNS

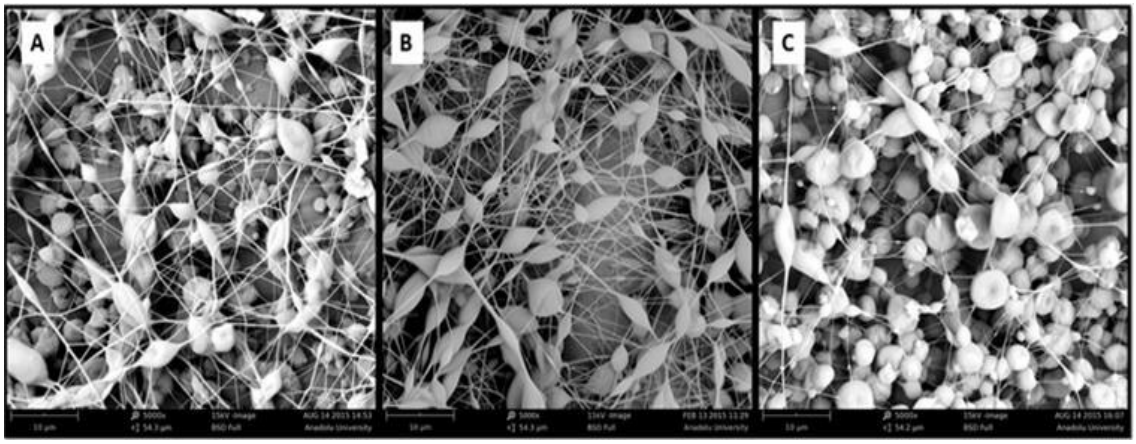
100 gr Aseton + 4 gr PMMA+ 0.04 gr BNNS

100 gr Aseton + 4 gr PMMA+ 0.06 gr BNNS

Voltaj (kv) : 25

Akış hızı (ml/h): 6

Aralık (cm) : 19



Görsel 1. Farklı BNNS miktarlarıyla ile elde edilen elektro eğirme yöntemiyle oluşmuş fiberlerin SEM görüntüleri (A) %0.5 BNNS (B) %1 BNNS (C) %1.5 BNNS

BNNS parçacıklarının vinil-ester reçine içerisinde homojen dağılımını sağlamak için ağırlıkça farklı oranlarda Polimetil metakrilat (PMMA) esaslı nano fiberlerin elektro-lif eğirme tekniği ile akış hızı 6 ml/h, voltaj 25 kv, aralık 19 cm, PMMA konsantrasyonu %4 olmak üzere sabit tutularak, farklı BNNS miktarları ile üretilmesinin ardından sem görüntüleri alınmıştır. Elde edilen sonuçlara göre BNNS miktarının artışı ilk olarak fiber oluşumunu arttırmış ve boncuk oluşumunu azaltmıştır. Fakat %1 in üzerine çıktığımızda tam ters etki gösterip fiber oluşumunu azaltmış ve boncuk oluşumunu arttırmıştır.

5.3. . Elektro eğirme yöntemiyle oluşan fiberlerin morfolojisine silan katkısı etkisi

Elektro eğirme yöntemiyle oluşan fiberlerin morfolojisine silan katkısı etkisinin gözlemlenebilmesi için aşağıdaki parametreler seçilmiştir.

Çözücü: Aseton

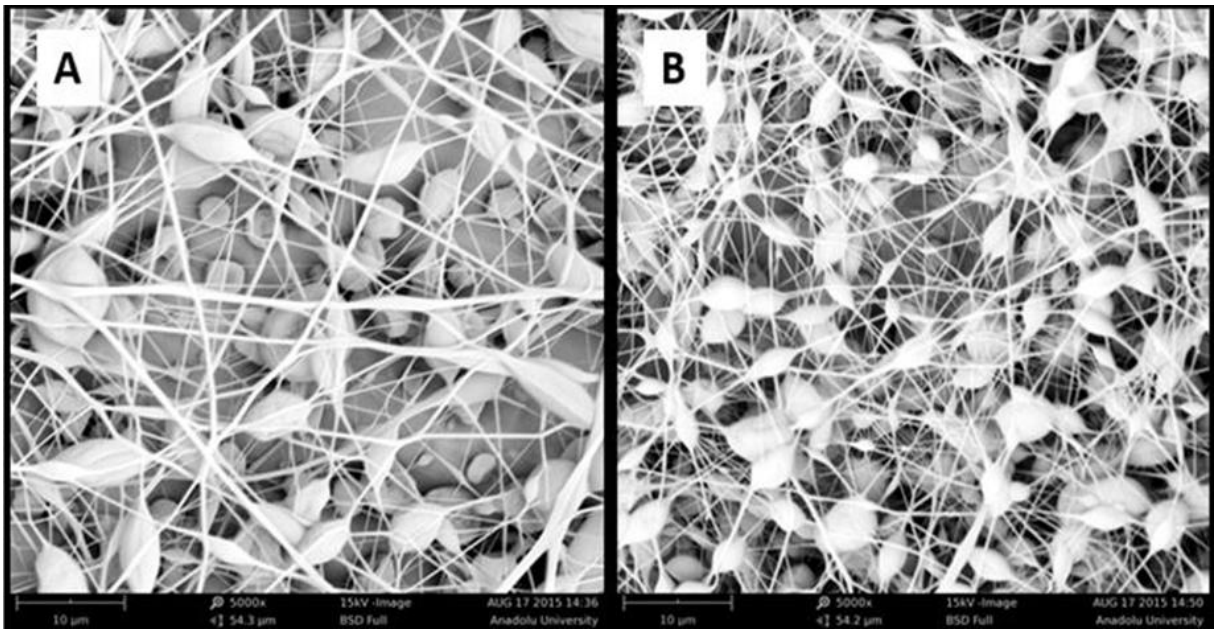
Konsantrasyon: 100 gr Aseton + 4 gr PMMA+ 0.04 gr BNNS

100 gr Aseton + 4 gr PMMA+ 0.04 gr BNNS/Silan katkılı

Voltaj (kv) : 25

Akış hızı (ml/h): 6

Aralık (cm) : 19



Görsel 2. Silan katkılı ve Silan katkısız elde edilen elektro eğirme yöntemiyle oluşmuş fiberlerin SEM görüntüleri (A) Silan katkısız (B) Silan katkılı

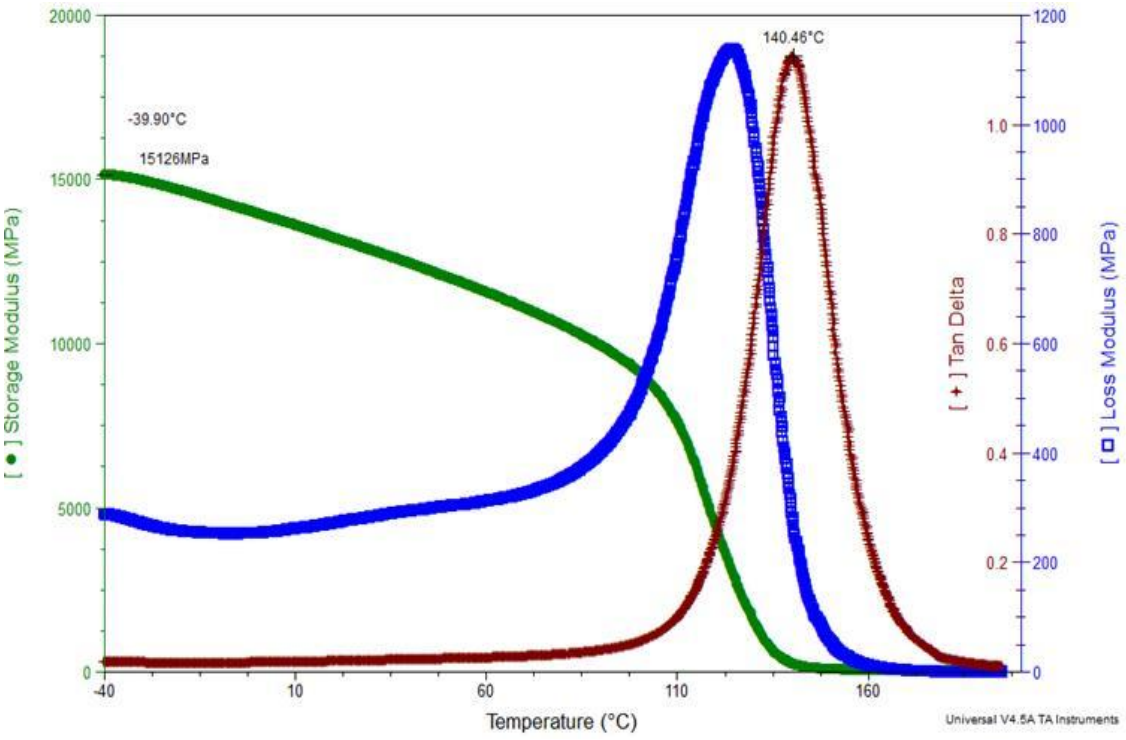
Silan katkısının fiberlerin morfolojisine etkisinin gözlenmesi için fiberlerin ile akış hızı 6 ml/h, voltaj 25 kV, aralık 19 cm, PMMA konsantrasyonu %4 olup sabit tutularak, silan katkılı ve katkısız olmak üzere elektro-lif eğirme tekniği ile üretilmesinin ardından sem görüntüleri alınmıştır. Görüntülerde görüldüğü gibi silan katkısının oluşan fiber miktarında olumlu etkisinin olduğu, boncuksu yapıları azalttığı, fiber yarıçapını arttırdığı görülmüştür.

Yapılan deneyler sonucunda aseton çözeltisi için saptanan optimum değerler aşağıda verilmiştir;

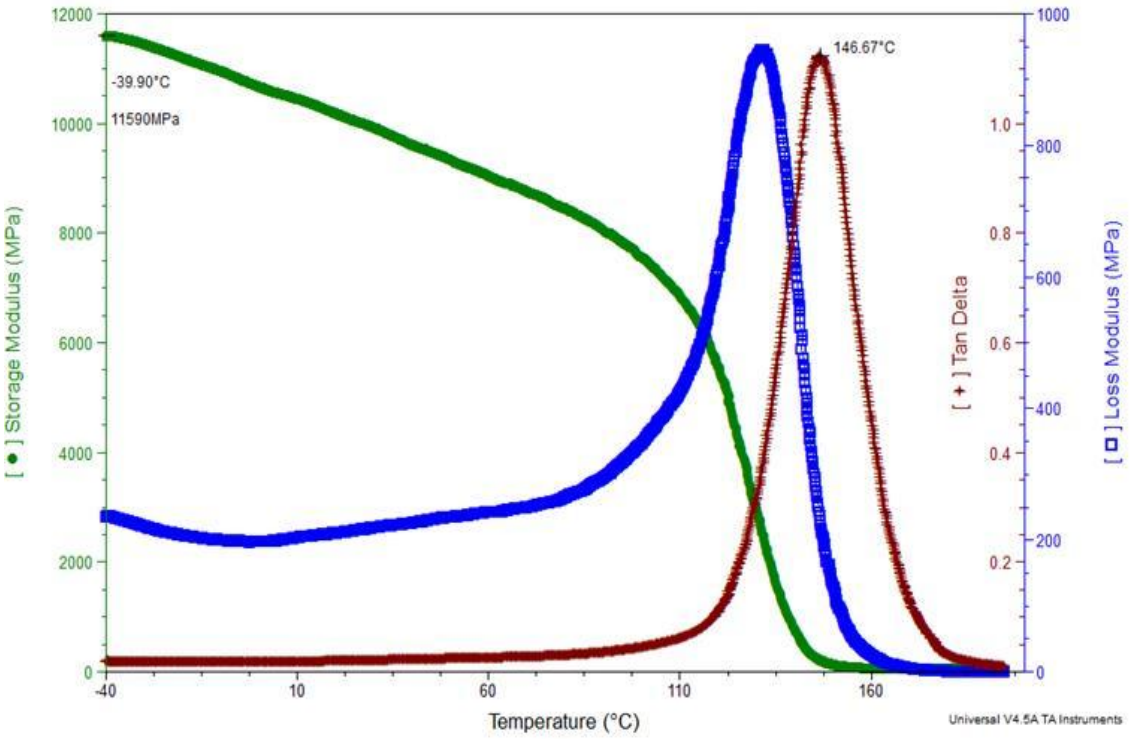
- Konsantrasyon: %4 PMMA + %0.01 BNNS+Silan
- Voltaj değeri: 25 kV
- Aralık : 19 cm
- Akış hızı : 6 ml\h

5.4. Dinamik mekanik analiz (DMA)

Dinamik mekanik analiz (DMA), değişen sıcaklıklarda numune üzerine çevrimsel olarak küçük deformasyonlar uygulayan bir tekniktir. Malzemenin mekanik özelliklerinin, uygulanan gerilme, sıcaklık ve frekansa göre değişimi incelenir. Viskoelastik polimer esaslı malzemenin elastik karakterini bir göstergesi olan depolama modülü (storage modülü), viskoz karakterinin bir göstergesi olan kayıp modülü (loss modülü) ve darbe faktörü olarak adlandırılan, malzemenin sıcaklık değişimi sırasında harcanan enerjinin bir göstergesi olan tanδ özellikleri ölçülür. Sıcaklığa bağlı olarak malzeme içerisinde meydana gelen dönüşümlerle modül değerleri değişkenlik gösterir. Bu da malzemenin sıcaklık değişimine bağlı olarak geçirdiği dönüşümlerin belirlenmesine olanak sağlar. Camsı geçiş sıcaklığı kayıp modülünün pik verdiği maksimum değer noktası olarak kabul edilir, camsı geçişin bir sıcaklık noktası olarak değil, aralık olarak düşünüldüğünde, depolama modülünün düşmeye başladığı sıcaklık ve tanδ eğrisinin pik verdiği maksimum değer noktası arasında kalan sıcaklık bölgesinde camsı geçiş gerçekleşmektedir. Yapılan testler sonucunda Tanδ eğrisinin pik verdiği sıcaklıklar karşılaştırıldığında, camsı geçiş sıcaklığının PMMA miktarıyla ve PMMA'nın molekül ağırlığının artışıyla birlikte artmıştır. Kürlenmiş, katkısız, neat vinilesterin Tg değeri 140 C° iken 350.000 g/mol molekül ağırlıklı PMMA içeren kürlemiş vinil ester reçinenin Tg değeri 147 C° dir. Depolama modül değerleri de artan molekül ağırlığıyla birlikte arttığı gözlenmiştir..



Şekil 1. Kürlenmiş, katkısız, neat vinilesterin DMA grafiği



Şekil 2. 350.000 g/mol molekül ağırlıklı PMMA ve BNNS+Silan ile üretilen fiber ile karıştırılan vinilester kompozitin DMA grafiği

NUMUNE ADI	**Tanδ Pik Sıcaklığı (%C)**
Katkısız Vinil Ester	141
Vinil Ester Kompozit	147

Tablo 2. 350.000 g/mol molekül ağırlıklı PMMA BNNS+Silan ile üretilen fiber ile karıştırılan vinilester kompozitlerin ve katkısız vinilesterin Tanδ değerleri

Yapılan deneyler sonucunda SEM kullanılarak morfolojisi incelenen fiberlerle yapılan çalışma sonuçlarına göre, en iyi nanofiber üretimi %4 PMMA ile hazırlanan aseton çözeltisiyle, 25 kv voltajda, 6 ml/sa akış hızıyla ve 19 cm aralıkla elde edilmiştir. BNNS ve silan katkısının etkisinin en fazla gözlendiği oran %1 dir. Daha sonra en iyi parametrelerle üretilen nanofiberler %5 kütle oranıyla 100 gr vinil ester reçineye katılmıştır ve kürlenmesi sağlanmıştır. Dinamik mekanik analiz(DMA) cihazları kullanılarak oluşan kompozit plakanın Tg değerleri tayin edilmiştir ve katkısız vinilester reçine plaka ile karşılaştırma yapılmıştır. Yapılan karşılaştırmalarda PMMA/BNNS/Silan katkısının vinilester reçinenin Tg değerinde artışa sebep olduğu görülmüştür..

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ELECTRICAL AND MECHANICAL PROPERTIES OF POLYPROPYLENE FIBER REINFORCED MORTARS

POLİPROPİLEN LİF KATKILI HARÇLARIN ELEKTRİKSEL VE MEKANİK ÖZELİKLERİ

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Özet: Beton, tüm dünyada inşaat malzemesi olarak yaygın bir kullanıma sahiptir. Ancak beton yüksek olan basınç dayanımını karşın, oldukça düşük bir çekme dayanımına sahiptir. Betona katılan liflerle betonun bu zayıf yönü iyileştirilmeye çalışılmaktadır. Lifler beton içerisinde uzun bir süredir birçok köprü ve bina uygulamalarında başarıyla kullanılmıştır. Bu çalışmada, dört farklı görünüm oranındaki polimer esaslı polipropilen lifin harç özeliklerine etkileri araştırılmıştır. Öncelikle lif katkısız kontrol numunesi üretilmiştir. Lifler harç içine hacimce %0.0, %0.5, %1.0, %1.5, %2.0 oranlarında katılmıştır. Harçlar üzerinde taze haldeyken işlenebilirlik, sertleşmiş haldeyken de basınç dayanımı, eğilme dayanımı ve elektriksel özdirenç ölçümleri yapılarak kontrol numuneleri ile karşılaştırılmıştır. Deney sonuçlarına göre, polipropilen lif katkısının harçlar üzerinde basınç dayanımını bir miktar düşürdüğü, eğilme dayanımını ve elektriksel iletkenliği bir miktar arttırdığı görülmüştür.

Anahtar Kelimeler: Polipropilen lif; harç; mekanik özelik; elektriksel özdirenç.

Abstract: Concrete is widely used as construction material all over the world. However, the concrete has a very low tensile strength in spite of it has high compressive strength. It is being tried to improve this weakness of the concrete with the adding of fibers into concrete mix. Fibers has been used successfully into the concrete in many bridges and buildings applications for long time. In this study, the effects of polymer based polypropylene fibers with four aspect ratios type on mortar properties have been investigated. Firstly, control samples were produced without fibers. The fibers were added to mortar mixtures in ratio of %0.0, %0.5, %1.0, %1.5, %2.0 by volume. On the mortars, workability in fresh state, compressive strength, flexural strength and electrical resistivity measurements at hardened state were defined and compared with control samples. According to experimental results, it was seen that when workability and compressive strength was decreased by addition of fibers to mortar, bending strength and electrical conductivity was slightly increased.

Keywords: Polyprolylene fiber; mortar; mechanical properties; electrical resistivity.

1. Giriş

Bağlayıcı içeren yapı malzemelerinin özelikle çekme özeliklerini iyileştirmek için bu malzemelere farklı karakteristik özeliğe sahip lifler katılmıştır. Kullanılan lifler önceleri bitkisel kökenliler olurken günümüz teknolojisi ile çelik, cam ve polimer esaslı liflerin de kullanım olanakları ortaya çıkmıştır. Cam liflerinin özellikle alkali ortamlarda durabilite açısından sorun oluşturması nedeniyle günümüzde beton veya harç içerisine çelik ve polimer esaslı lifler ilave edilmektedir. Günümüzde en çok kullanılan yapı malzemelerinden çimento esaslı harç veya beton, aşınma, çekme, kayma, çatlama sonrası yük taşıma, tokluk, yangına karşı dayanıklılığı ve enerji emme kapasitesi zayıf olan bir malzemedir [1-3]. Zayıf olan bu özeliklerini iyileştirmek için birçok çalışma yapılmıştır. Örneğin, ani kırılmayı önleyebilmek ve sünekliliği artırabilmek için matris içerisinde farklı mekanik ve fiziksel özeliğe sahip lifler ilave edilmektedir. Fiziksel ve mekanik özelikleri farklı olan bu lifler, matris içerisinde karma olarak da

kullanılarak, çok gevrek davranış gösteren yüksek dayanımlı çimento esaslı kompozitlere süneklik kazandırma da ve zayıf yönleri daha da iyileştirmede katkı sağlamaktadır [4,5]. Lif grubunda çelik lifler genellikle sünme, ilk çatlak gelişimi, enerji yutma kapasitesi gibi mekanik yükler altındaki davranışlarını iyileştirirken, polimerik olan lifler ise genel olarak rötreden dolayı oluşacak çatlakların önlenmesinde tercih edilmektedir. İnşaat sektöründe en çok kullanılan malzeme grubunda betondan sonraki sırayı harçlar oluşturmaktadır. Sıvalarda, onarım gerektiren yerlerde, tesviye işlemlerinde, seramik yapıştırma, derz dolgu, farklı amaçlı levhaların yapı üzerine yapıştırılması gibi bir çok farklı uygulamalarda harçlar yaygın bir şekilde kullanılmaktadır (Şekil 1).



Şekil 1. Çimento esaslı harcın bazı kullanım alanları

Sıvalar yapıyı çevre şartlarından korumak ve dik yüzeyleri düzgün hale getirme amacıyla kullanılmaktadır. Tesviye harçları da yatay yüzeyleri düzeltmede tercih edilmektedir. Benzer şekilde, onarım harçları da değişik etkenler altında hasar görmüş yapı ve yapı elemanlarının özelliklerinin hasar öncesi duruma getirilmesi ya da özelliklerinin daha da iyileştirilmesi amacı ile kullanılmaktadır [6-8]. Bu tip harçlarda en çok görülen hasar nedenlerini; i) harcın uygulanan zemine aderansının düşük olması, ii) harç yüzeyinde oluşan kılcal çatlaklar şeklinde gruplandırmak mümkündür. Yapışma veya aderans yetersizliğinin önlenmesinde zeminde alınacak önlem yanında harç karışımına giren maddelerin yapışmayı artıracak özellikte olmasına özen göstermek gerekli olmaktadır. İkinci tür hasar nedeni olan kılcal çatlaklar çimento hamurunda, gerek taze durumdayken oluşan büzülme (plastik büzülme) gerekse de sertleşmiş durumdayken oluşan büzülmeler (bünyesel büzülme, karbonatlaşma büzülmesi) sonucunda oluşurlar. Harçlar betona göre daha fazla ince malzeme içerdiklerinden dolayı büzülmeye daha fazla eğilimlidirler. Bu nedenle de harçlarda genellikle büzülme çatlaklarını önleyecek nitelikte polimerik liflerden polipropilenler tercih edilmektedir [8]

Polipropilenlerin en önemli özeliklerinden birisi harçlarda oluşacak plastik rötre çatlaklarını sınırlamasıdır. Özellikle harcın içindeki boşlukları doldurmak, rötre ve büzülme çatlaklarını azaltmak, harcın darbeye karşı dayanımını artırmak gibi önemli faydalar sağladığı için son yıllarda ülkemizde polipropilenli harç üretimi artmıştır [9-10].

Bu çalışmada, polipropilen lifler harç karışımı içerisinde farklı oranlarda kullanılması durumunda başta harçların işlenebilirlikleri olmak üzere mekanik özelikleri ve elektriksel özelikleri de araştırılarak etkileri ortaya konmuştur.

2. DENEYSEL ÇALIŞMA

2.1.Kullanılan Malzemeler

Numunelerin hazırlanmasında hidrolik bağlayıcı olarak TS EN 197-1 [11] standardına uygun olarak üretilmiş olan CEM I-42.5/R tipi Portland Çimentosu kullanılmıştır. Çimentonun Blaine incelik değeri 3312 cm^2/g ve özgül ağırlığı da 3.1'dir. Çimentoya ait kimyasal oksit değerleri Çizelge 1'de sunulmuştur. Agrega olarak 0/4 mm kırma-kumun kullanıldığı harçlarda dört farklı oranlarda polipropilen lif kullanılmıştır. Lifin karakteristik özelikleri Çizelge 2'de verilmiştir.

Çizelge 1. Çimentonun kimyasal bileşenleri

Bileşen, %	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**Na_2O**	**K_2O**	**SO_3**	**KK**
CEM I 42.5	63.6	19.6	4.72	3.27	1.91	0.34	1.06	4.72	2.69

Çizelge 2. Polipropilen liflerin teknik özelikleri

Çap (mm)	**Boy (mm)**	**Narinlik (Boy/Çap)**	**Çekme Dayanımı (MPa)**	**Birim Ağırlığı (gr/cm^3)**	**Erime Noktası (°C)**	**E-Modülü (MPa)**
0.30	12	40	552	0.91	160	3500

2.2. Karışımların Hazırlanması ve deneyler

Harç bileşeni olarak 350 g çimento, 175 g su, 2650 g kum ve farklı oranlarda (%0, %0.5, %1.0, %1.5 ve %2.0) polipropilen lif kullanılmıştır. Harçlar, üretimlerini takiben yayılma tablasında 15 kez darbe sonrasında yayılma çapları ölçülmüştür. Daha sonra 40x40x160 mm boyutlu prizmatik kalıplara yerleştirilen harçlar 24 sa sonra kalıptan alınıp 20±2 ^oC kirece doygun su içerisinde her bir deney gününe kadar kür edilmişlerdir (Şekil 2). Bir gün laboratuar ortamında bekletilen harçlar üzerinde basınç, eğilme, ulrtases geçiş hızı ve elektriksel özdirenç gibi deneyler gerçekleştirilmiştir.



Şekil 2. Polimerik liflerden ve harçlardan görünüm

Deneylere fiziksel özeliklerden başlanılmıştır. Numuneler etüv kurusu hale getirilip ağırlıkları alındıktan sonra, 24 sa su içerisinde doygun hale getirilmiş ve su emme değerleri belirlenmiştir. Mekanik özeliklerin belirlenmesinde otomatik basınç ve eğilme presi kullanıldı. Basınç presinin kapasitesi 200 kN olup, eğilme presinin kapasitesi de 50 kN'dur. Eğilme deneyi ortadan yükleme tipiyle 120 mm mesnet

açıklığında TS EN 12390-5 [12] standardına göre gerçekleştirildi. Eğilme testi sırasında ikiye ayrılan numuneler yine TS EN 12390-5 [12] standardına göre basınç testi için kullanılmıştır. Numunelerin alt ve üstüne aynı düşey eksen çizgisindeki mesafeye gelecek şekilde 40x40 mm plakalar yerleştirilmiştir. Bu halde basınç presi tablaları arasına yerleştirilen numunelere basınç yükü uygulanarak TS EN 12390-3 [13] standardına göre dayanım değerleri belirlenmiştir. Nem koşullarının etkisinden bağımsız halde ölçüm yapabilmek için etüv kurusu duruma getirilmiş harç numuneler üzerinde ASTM C 1760 [14] standardına uygun olarak direnç ölçer (ohm-metre) ile iki plaka yöntemine göre elektriksel direnç değeri (R) ölçülmüştür.

Direnç değerleri (R) ölçülen harçların elektriksel özdirenç değerleri de aşağıda verilen denklem (1) ile belirlenmiştir.

$$\delta = R\frac{A}{L} \quad (1)$$

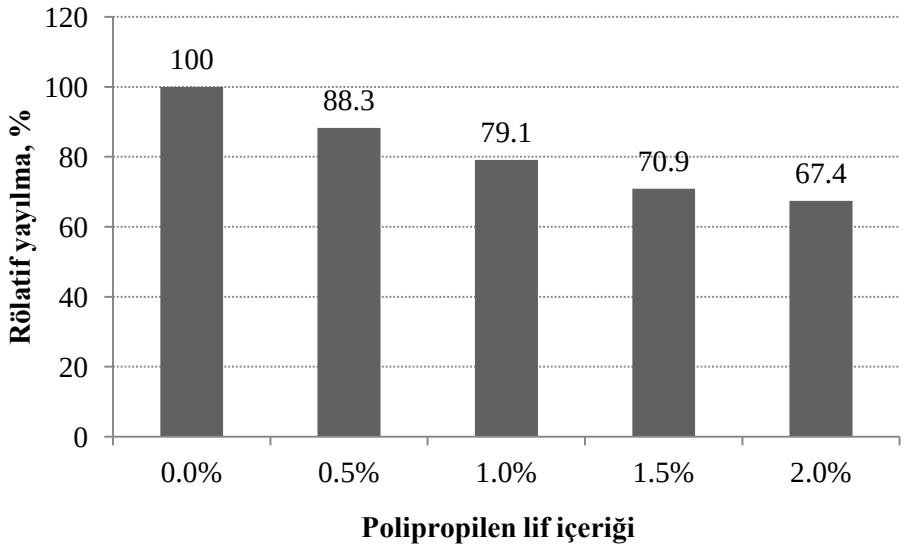
Denklemde, δ, elektriksel özdirenç (kohm.m); R,direnç (kohm); A, numune yüzey alanı (m^2) ve L, plakalar arası mesafeyi (m) simgelemektedir.

Polipropilen lif içeren ve kontrol numuneleri üzerinde mikroyapı incelemeleri Afyon Kocatepe Üniversitesi, Teknolojik Uygulama ve Araştırma Merkezi (TUAM)'nde bulunan LEO 1430 VP model W (Tungsten) filament ile çalışan taramalı elektron mikroskobu (SEM) cihazında yapılmıştır. Bütün lif tipleri yapı olarak polipropilen olduğundan sadece bir seri üzerinde (M19) SEM görüntüleri alınmıştır. Numuneler kırık yüzeyli hazırlanmış olup, yüzeyleri karbon ile kaplanmıştır.

3. DENEY SONUÇLARI VE DEĞERLENDİRME

3.1. İşlenebilirlik sonuçları

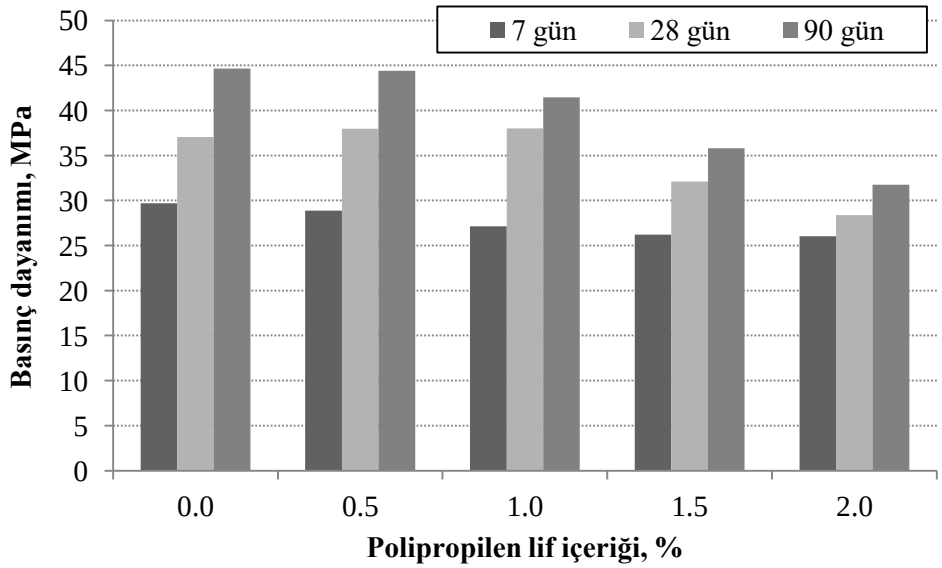
Polimerik lif katkılı harçların işlenebilirlikleri yayılma tablası deneyi ile belirlenmiş ve deney sonuçları rölatif olarak Şekil 3'te karşılaştırılmıştır. Bulgulara göre, polimerik lif ilavesiyle harçların yayılma değerleri azalmaya başlamıştır. Örneğin, kontrol harcına %1 lif ilavesiyle %21 oranında azalan yayılma değerleri %2 lif ilavesi sonucunda %32,6 oranında işlenebilirlik kaybına uğramıştır. İşlenebilirliğin azalması durumunda özellikle liflerin matris işerisinde homojen dağılmaları güçleşmekte, taze haldeki harç nispeten daha zor kalıba yerleştirilebilmektedir.



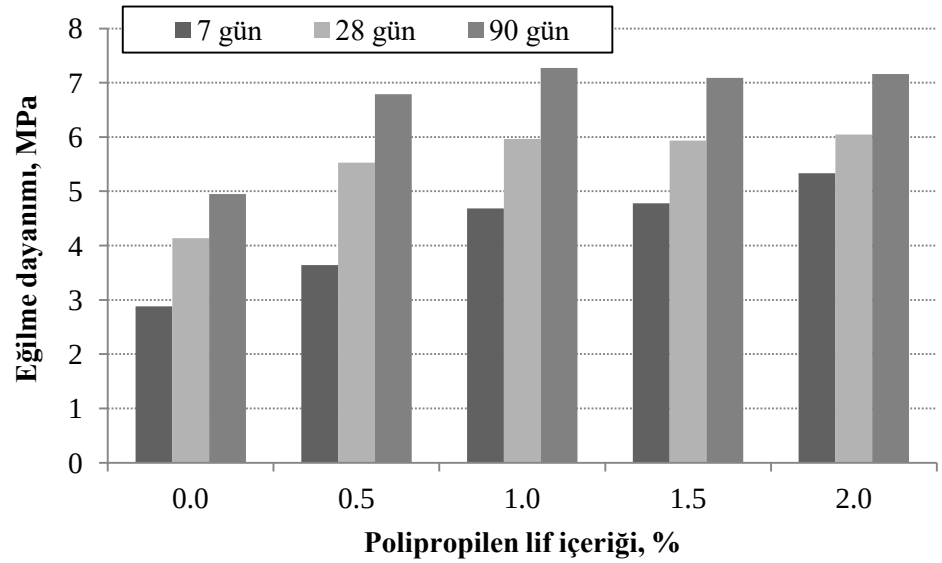
Şekil 3. Polipropilenli harçların rölatif yayılma oranları

3.2. Mekanik Özelikler

Harç içerisine ilave edilen liflerin basınç dayanımı değerleri üzerindeki etkisi incelendiğinde (Şekil 4), lif miktarının basınç dayanımına hem olumlu hem de olumsuz yönde etkisi olmuştur. Bunun sebebi, harca ilave edilen liflerin harcın işlenebilmesini azalttığından veya harç içerisindeki dağılımının ve yöneliminin etkisi sonucu oluşmuş olabileceği belirtilebilir. Yapılan çalışmalarda da lif içeriğinin betonun basınç dayanımı üzerinde önemli bir etkisinin olmadığı ve hatta ±%25 oranında olumlu veya olumsuz yönde etkileyebileceği belirtilmiştir [15-18]. Sonuçlar incelendiğinde; 7-90 günlük kontrol numunelerinin basınç dayanımı değerleri 29-44 MPa arasında değerler alır iken, %2 polipropilen lifli 7-90 günlük kompozitlerin basınç dayanımı değerleri ise 26-32 MPa arasında değişerek %10.3-%27 oranında azaldığı görülmüştür. Buna göre; basınç dayanımı değerlerinin lif katkısı ile birlikte tüm karışımlarda düştüğü görülmüştür. Lif ilavesinin arttırılmasıyla birlikte harçların işlenebilirliklerindeki azalmalar yapılan çalışmalardan bilinmektedir [3]. Lif boylarının ve miktarının artmasıyla birlikte harç içerisindeki topaklanma daha fazla olduğundan harç içerisindeki boşluk oranının artışına neden olarak dayanım değerlerinin azalmasına neden olmuştur.



Şekil 4. Polipropilen lif ilavesiyle harçların basınç dayanımları



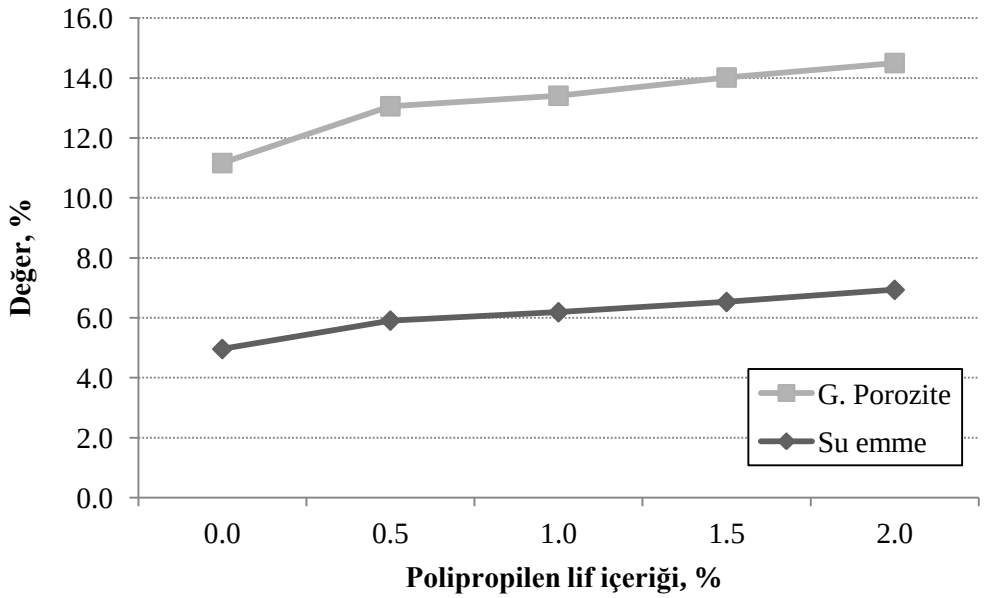
Şekil 5. Polipropilen katkılı harçların eğilme dayanımları

Harç içerisine ilave edilen liflerin eğilme dayanımları üzerindeki etkileri incelendiğinde (Şekil 5), lif miktarının artmasıyla eğilme dayanımlarının da belirgin bir biçimde arttığı görülmektedir. Eğilme dayanımının harç içerisine ilave edilen lif miktarıyla doğrudan ilişkili olduğu açıkça görülmektedir. Liflerin harç içerisinde dağılarak eğilme testi sırasında harcın alt bölgelerinde çekme gerilmelerinden dolayı oluşan mikro çatlakları durdurmada daha etkili olduğu ve buna bağlı olarak da lif miktarının da arttırılmasıyla birlikte eğilme dayanımının da arttığı görülmüştür.

3.3. Fiziksel özelikler

Harç içerisine ilave edilen polipropilen lifler harçların görünen porozite değerlerinin artmasına neden olmuştur (Şekil 6). Harç veya beton içerisine ilave edilen polipropilen liflerin işlenebilirlik değerlerini

azalttığı literatürden bilinmektedir [3]. İşlenebilirlikteki azalmanın en büyük nedeni, artan lif miktarıyla topaklaşmanın ortaya çıkması ve bunun sonucunda bileşenlerin hareket kabiliyetlerinin azalarak harcın kıvamını azaltmasıdır. İşlenebilirlikteki azalma harcın kalıba yerleştirilmesini de etkilemekte ve kısmen de olsa kontrol (lifsiz) harca göre daha boşluklu kalmasına neden olmaktadır. Lif miktarının artmasıyla birlikte kalıba daha boşluklu yerleşmiş olan harçların görünen boşluk oranı değerleri de kontrol harcına göre daha yüksek değerler almıştır.



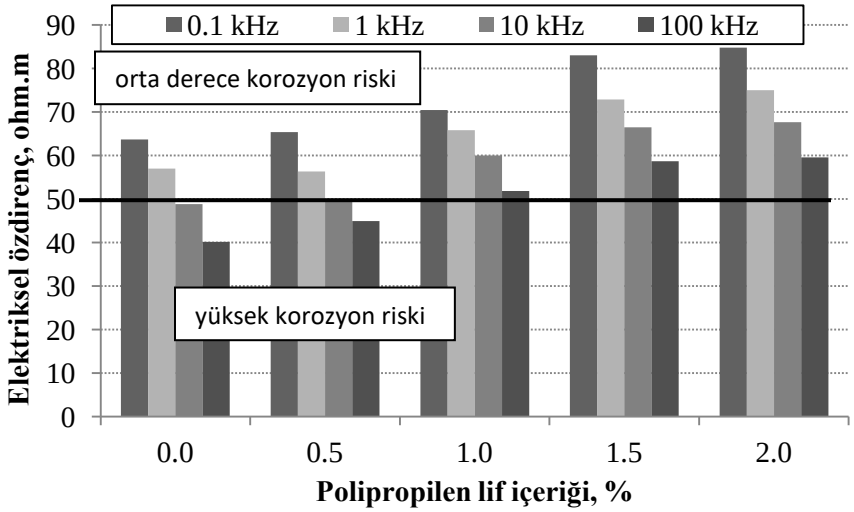
Şekil 6. Polipropilen içeriğine bağlı olarak harçların boşluk oranı ve su emme yüzdeleri

Farklı oranlarda poliporpilen lif içeren harçların ağırlıkça su emme değerleri de belirlenmiştir (Şekil 6). Kullanılan lif miktarının artmasıyla harç içerisinde az da olsa boşlukların arttığı sonucuna varılmıştır. Ancak genel olarak incelendiğinde, polipropilen liflerin su emmeyen yapıda olmaları nedeniyle harçlardaki su emme oranlarındaki artışlar oldukça düşük miktardadır [19,20]. Su emme oranlarındaki artışın nedeni topaklanmaları nedeniyle betonda oluşan boşluklardan dolayıdır. Bu boşluklar aynı zamanda basınç dayanımlarının da kontrol serilerine göre daha düşük değerler almasına da neden olmuştur.

3.4. Elektriksel özelikler

Elektrik iletkenliği çimento bazlı sistemlerde iyonların boşluk solüsyonlarında hareket etmeleriyle meydana gelir. İletkenlik hem poroziteye hem de boşluk solüsyonu iletkenliğine bağlıdır. Birçok özelikle ilişkilendirilebilen betonun veya harcın elektriksel özdirenci beton bileşenlerinin değişkenliği ile de farklı değerler alacaktır. Farklı oranlarda polimerik lifin kullanımıyla üretilmiş harçların elektriksel özdirenç değerleri frekansa bağlı olarak Şekil 7'de verilmiştir. Bilindiği gibi frekans, bir AC sinyalin saniyedeki periyot sayısıdır. Çimento esaslı sistemlerde elektrik iletkenliği boşluk solüsyonlarındaki iyon transferi sebebiyle meydana gelmekte ve frekansın artışıyla birlikte iyon transferi hızlanmaktadır. Dolayısıyla direnç azalmaktadır. Harçlara uygulanan frekans değerinin arttırılmasıyla harç içerisindeki iyonların transfer hızının artması sonucu daha düşük elektriksel özdirenç değerleri elde edilmiştir. Polimerik harçlarda farklı frekanslarda elektriksel özdirencin belirlenmesinin amacı, ölçüm frekansına bağlı olarak elde edilebilecek özdirenç değerinin belirlenmesidir. Diğer bir ifadeyle, malzemelerin özdirenç değerlerinin belirlenmesi sırasında seçilen frekans değeri sonuçları doğrudan etkilemektedir. Yüksek

frekanslı gerilim altında harçlar düşük frekans gerilim altında bulunma durumuna göre daha az dirence sahip olacaklardır.

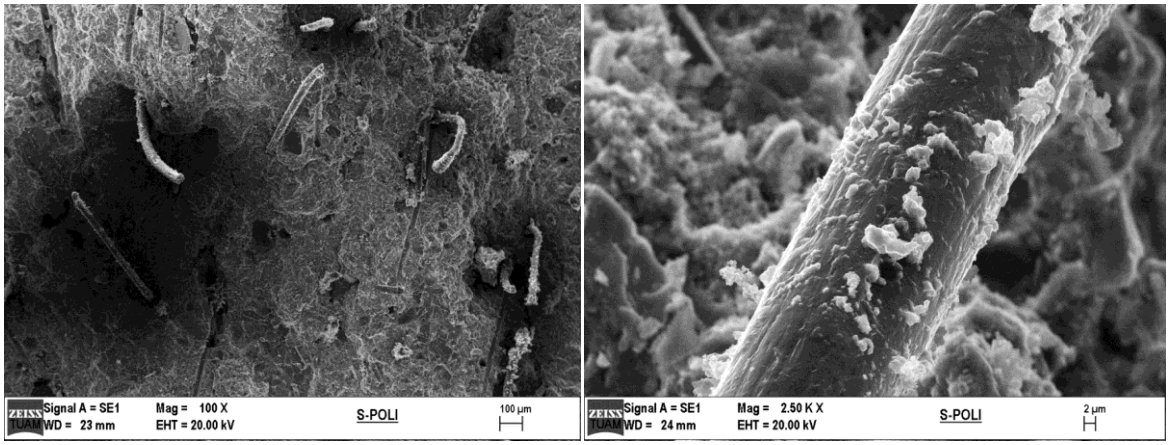


Şekil 7. Harçların elektriksel özdirenç değerleri

Çimentolu sistemlerde elektrik iletkenliği hidroksil (OH^-) iyonları tarafından sağlanır ve bu iyonların artması ortamın pH değerinin azalmasına neden olmaktadır. Ortamda Ca^{++} iyonlarının artması ise pH seviyesini yükselterek elektriksel iletkenliği azaltmakta ve donatılı betonlarda pasivasyon tabakasının korunduğunu göstermektedir [21-24]. Dolayısıyla korozyon riski oldukça azalmış olacaktır. Elektriksel özdirenç değerinin 50 ohm.m değerinden düşük olması ortamda yüksek korozyon riskini gösterirken, elektriksel özdirenç değerinin daha fazla değerler alması da orta derecede donatı korozyonuna yol açacağının göstergesidir [25]. Bu açıdan incelendiğinde, polipropilen lif katkısıyla harçların direnç değerleri arttırılarak özellikle %1 lif içeriğinden sonrası harçların korozyona uğrama riskini de azalmış olmaktadırlar.

3.5. Mikroyapı İncemesi

Çimento esaslı harç içerisindeki hidrate ürünlerin dağılımları ile polipropilen liflerin harç arasındaki aderanslarının gözlenmesi amacıyla mikroyapı incelemeleri gerçekleştirilmiştir (Şekil 8). Harcın matris kısmında yapılan mikroyapı gözleminde, oldukça yoğun çimento hidratasyon ürünleri görülmüştür.



Şekil 8. Polipropilen liflerin harç içerisindeki görünümleri

Lif katkılı harçlarda yapılan mikroyapı gözlemi sonucunda polipropilen lif etrafında oldukça yoğun hidratasyon ürünleri olmasına rağmen aderansın tam olarak sağlanamadığı gözlenmiştir. Bunun muhtemel nedenleri, i) çimento esaslı bağlayıcıyla polimer esaslı lif malzemesinin iki farklı yapıya sahip olması; ii) aderans bölgesinde gözlenen mikro düzeydeki zayıf bölgenin olmasıdır. Buna rağmen polipropilen lif üzerinde hidratasyon ürünlerine de rastlanmıştır.

4. Sonuçlar

Polipropilen lifli harçlar günümüzde gelişim göstermekte olup inşaat sektöründe birçok alanda kullanılmaktadır. Bu çalışmada farklı oranda polipropilen katkılı çimento esaslı harçların mekanik, fiziksel ve elektriksel özelikleri incelenmiş ve aşağıdaki sonuçlar elde edilmiştir:

- Polipropilen lif katkılı taze harçlar üzerinde yapılan yayılma deneylerinden genellikle polipropilen miktarı arttıkça numunelerin işlenebilirlik değerlerinin düştüğü görülmüştür,
- Polipropilen katkılı 7-90 günlük harçlar üzerinde yapılan basınç deneyi sonucunda, polipropilen liflerin dağılım ve yöneliminden dolayı basınç dayanımının %10-27 oranları arasında azaldığı gözlenmiştir.
- Polipropilen lif katkılı harçlar üzerinde eğilme dayanımı deneyi yapıldığında, lif katkısının harçlarda eğilme dayanımını yani çekme dayanımını arttırdığı görülmüştür.
- Polipropilen lif katkılı harçlar üzerinde yapılan görünen boşluk oranı ve su emme deneyleri sonuçlarına göre, lif miktarının değişmesiyle, diğer bir ifadeyle lif miktarının artmasıyla hem boşluk miktarı hem de su emme değerleri artmıştır.
- Farklı frekans değerlerinde yapılan ölçümler sonucunda elde edilen elektriksel özdirenç değerlerinin harç içerisindeki lif miktarının artışıyla birlikte daha yüksek değerler aldığı görülmüştür. Dolayısıyla polimerik lif katkısı harçların elektriksel özdirençlerini arttırmıştır. Durabilite açısından daha dayanıklı harç üretimini sağlamışlardır.

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ENERJİ VERİMLİLİĞİ İÇİN SAYDAM (IŞIK GEÇİREN) BETONLAR

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Şeffaf beton veya ışık ileten beton olarak da bilinen saydam beton, agregaların saydam alternatif malzemelerle değiştirilmesi ile elde edilir. Saydam beton üretiminde ışık geçiren malzeme olarak polimer esaslı optik elyaflar kullanılır. Şeffaf beton, fiber optik ve ince beton kombinasyonu kullanılarak üretilmektedir. Bu lifler diğer agregalar gibi betona karışırlar. Bu optik fiberler, doğal ve yapay kaynaklardan alınan ışığı saydam beton paneller tarafından çevrelenen alanlara iletebilir. Saydam betonun en önemli avantajı, ışığı iletebilmesidir. Bu özeliği ile yeşil binalar yapmak için kullanılabilir. Doğal ve yapay kaynaklardan alınan ışığı iletebildiğinden binanın aydınlatma talebini karşılamak için daha az ışığa ihtiyaç duyulur. Böylece büyük enerji maliyetinden tasarruf sağlanır. Saydam beton, güneş ışığını elektrik enerjisi yerine ışık kaynağı olarak kullanır ve güç tüketimini azaltır. Bu beton tipi aynı zamanda güneş ışığından elde edilecek ısıyı iletmek için soğuk ülkelerde de kullanılabilir. Bu çalışmada, saydam betonun tasarımı, mekanik özelikleri, içeriğindeki optik fiberlerin ışığı geçirme özellikleri ve kullanım alanları tartışılmıştır. Saydam betonun ışığı emme, iletme, iletimdeki mekanizma ve kayıplar üzerindeki araştırmalar üzerinde durulup, gösterdiği dayanım, kullanılan malzemeler ve oranları hakkında bilgi verilmiştir. Sonuç olarak, saydam betonların yapılarda kullanımıyla, ışık kaynağı olarak güneşten yararlanmak suretiyle yapılardaki aydınlatma güç tüketimini azaltacağı, ayrıca yapıya mimari açıdan da estetik katacağı görülmüştür.

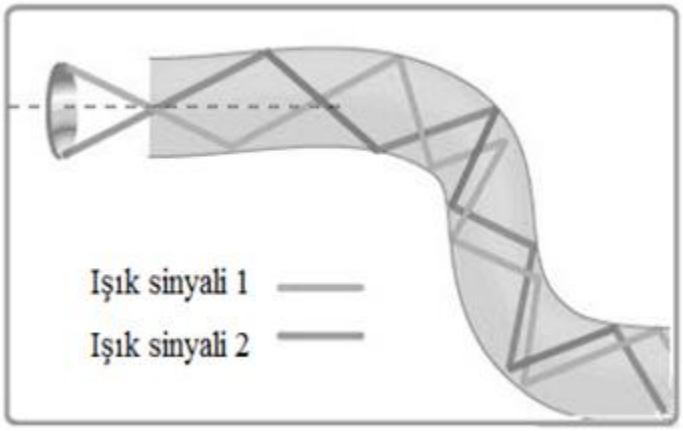
Anahtar Kelimeler: saydam beton, optik fiber, yapısal özelik.

Transparent concrete also called as translucent concrete or light transmitting concrete is achieved by replacing aggregates with transparent alternate materials. In the production of transparent concrete polymer based optical fibers are used as light transmitting. Transparent concrete is manufactured by using combination of fiber optics and fine concrete. These fibers blend into the concrete like any other aggregates. These optical fibers can transmit light from natural and artificial sources into spaces enclosed by the translucent concrete panels. The main advantage of transparent concrete is that it can transmit light. There, it can be used to make green buildings. Since it can transmit light from natural as well as artificial sources, the building can have fewer lights to meet its demand for lighting. Thus saving huge energy cost. Transparent concrete uses sunlight as source of light instead of electrical energy and reduces power consumption. This concrete can also be used cold countries to transmit heat with sunlight. In these study properties of translucent concrete, application fields, light transmission properties of optical fibers are discussed. Absorption, transmission, mechanism of transmission, losses in transmission on translucent concrete focused on this research. Also shown strength, and the materials used rates are given information. As a result, by use of the transparent concrete in structures, to take advantage of the sun as a light source in the structures, lighting power consumption will be reduced, and also it was observed that it adds aesthetic to structure in terms of architecture.

Keywords: Transparent concrete, optical fiber, structural properties.

1. Giriş

Ekonomik büyüme ve bilim teknolojisi gelişimi ile birlikte, artan binalar, yer altı binaları ve yüksek katlı binalar gibi daha büyük ölçekli inşaat mühendisliği yapıları dünya genelinde inşa edilmektedir. Bu binalar insanların optik faaliyetlerini sürdürmek için yalnızca insan yapımı ışıklara dayalı izole edilmiş biyosferdir. Aynı zamanda, büyük binaların çoğu birbirine yakın, hepsi de aynı alanlarda, gökyüzü kazıyıcılar gibi inşa edilir. Birçok bina birbirine istiflenirken, çok fazla doğal güneş ışığı geçmiyor ve doğal güneş ışığının eksikliği farkediliyor. Saydam beton daha kolay günlük aydınlatma için bir çözüm olarak keşfedildi. İlk kez Macar mimar Aron Losonczi, 2001 yılında ışık geçiren beton fikrini piyasaya sürdü ve 2003 yılında LiTraCon adını taşıyan ilk saydam beton blok üretimini başarıyla gerçekleştirdi [1]. Saydam Beton, obtik fiberler ile ince ağregalı betonun birleşimidir. Beton içerisine koyulan obtik fiberler, silika veya plastikten yapılmış, insan saçından biraz daha kalın esnek, şeffaf ve polimerik bir malzemedir. Obtik fiberler iki ucu arasında ışığı iletmek için bir dalga kılavuzu veya ışık borusu olarak işlev görürler. Fiberler, aydınlatma ve görüntüleri taşımak için kullanılır. Özel olarak tasarlanmış bu fiberler, sensörler ve fiber lazerler de dahil olmak üzere çeşitli diğer uygulamalar için kullanılır. Optik elyaflar tipik olarak, Şekil 1'de gösterildiği gibi daha düşük bir kırılma indeksine sahip şeffaf bir kaplama malzemesi ile kuşatılmış şeffaf bir iç kısım içerir. Işık, iç yansıma ile çekirdekte tutulur. Bu, lifin bir dalga kılavuzu olarak hareket etmesine neden olur [2].



Şekil 1. Optik fiber içerisinde ışığın iletimi

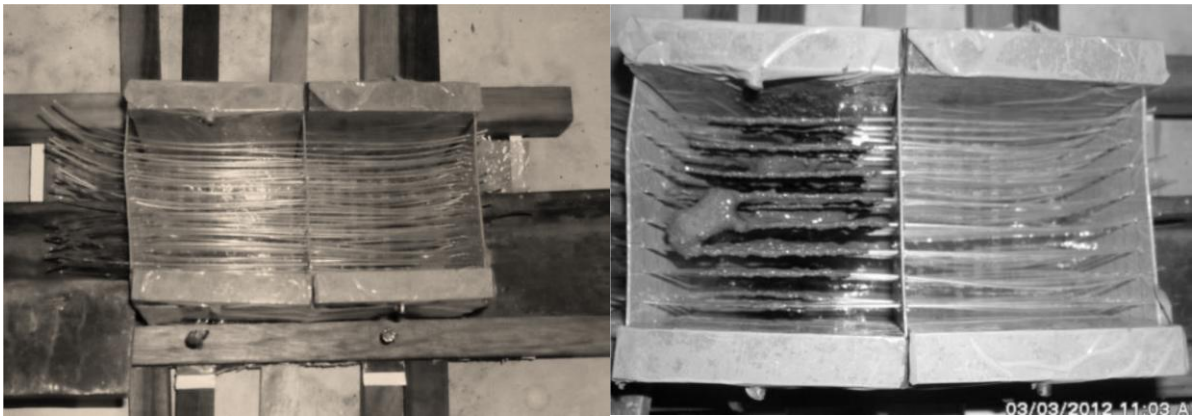
Gaurao vd. [3] Saydam beton üzerine çeşitli ışık testlerine donma çözünme ve klor geçirgenliği gibi dayanıklılık testlerine tabi tutmusturlardır. Deneyler sonucunda saydam betonun ışık geçirme özelliğinin yok denecek kadar az kayıpla olduğunu ve dayanıklılık açısından normal betodan daha iyi sonuçlar verdiğini saptamışlardır. Losonczi [4] yoğunluğu 2100-2400 kg/m^3 ve basınç dayanımı 50 MPa olan beton içine hacimce % 4 oranında kattığı, 2 mikrometre çapındaki optik liflerle ışığın bir taraftan diğerine geçmesini sağlamıştır. Kamdi vd. [5] saydam betonun nasıl üretildiğini ve parlak geleceğini incelemişlerdir, saydam betonun tarihsel olarak sağlam yapı malzemesi üzerinde en ilginç yeni adımlardan biri olduğuna karar vermişlerdir. Omar vd. [6] saydam beton karışımı için en uygun malzeme oranları belirlemeye çalışmışlar ve konuyla ilgili patent almışlardır. Elde edilen saydam betonun basınç dayanımı 150-250, E-modülü ise 2750-3450 MPa arasında değişmektedir. Kashiyani vd. [7] saydam betonun ana amacının aydınlatmanın güç tüketimini azaltmak için güneş ışığını bir ışık kaynağı olarak kullanıp yapının enerji tasarrufuna katkıda bulunduğunu ve aynı zamada estetik açıdan da kullanılabileceğini saptamışlardır.



Şekil 2. Saydam betonun ışığı iletmesi

2. Optik Fiberli Yarı Saydam Betoların Üretim Çalışmaları

Optik fiber, silika veya plastikten yapılmış, insan saçından biraz daha kalın esnek, şeffaf bir elyaftır. Optik fiberler beton içerisinde birbirine paralel olarak uzanırlar ve gömülü oldukları beton elemanın iki yüzeyi arasında ışık iletirler. Düzgün yerleştirilmesi halinde betonda ışık kaybına müsaade etmezler ve ışığı net bir şekilde yansıtırlar [8]. Optik fiberlerin yüksek esneme ve sünme özelliği sayesinde saydam betonun yüksek dayanımlı beton sınıfına girmesini sağlar. Kullanılan optik fiberin kalınlığı ışığı düzgün yansıtabilmesi için 2µm ve 2mm arasında olmalıdır[9]. Saydam betonun üretiminin ilk başlangıcında optik fiberler tek tek kalıplar içerisine yerleştirilip beton dökümü yapılırdı bu da üretimi zaman alıcı ve maliyetli hale getirirdi. Yeni üretim şeklinde ise tekli yerine dokuma optik kumaşlar kullanılır. Kumaş kalıba aralıklarla yerleştirilir genellikle 2mm ile 5mm arasındadır [10]. Üretilen saydam betonlar istenilen boyutlarda üretildiği gibi büyük paneller halinde üretilip kesme işlemiyle istenilen boyuta getirilebilir. Saydam beton kalıptan alındıktan sonra yüzeyler cilalanır.



Şekil 3. Optik fiberlerin kalıplara yerleştirilmesi

3.Saydam Betonların Karakteristik Özellikleri

3.1.Işık Geçirgenlik Özelliği

Saydam betonun esas amacı ışığı iletmektir. Bu nedenle karanlık ortamda yapılan saydam beton üzerine kırmızı, sarı ve yeşil ışıklar gönderilmiştir. Gönderilen ışıkların saydam betonun diğer tarafından aynı renkle yansıdığı görülmüştür[11]. Saydam betonun gönderilen ışığı diğer yüzeyine iletme performansını ortaya koymak amacıyla kırılma indeksi, geçirgenlik oranı, çift kırılma ve yayılma gibi özellikleri ölçülmekte veya hesaplanmaktadır. Bunlar içerisinde en yaygın olarak kullanılanı geçirgenlik oranıdır. Geçirgenlik oranı (1) nolu formül yardımıyla doğrudan belirlenebilmektedir.

$$\%P=Ɛ\ J0/J1*100 \quad (1)$$

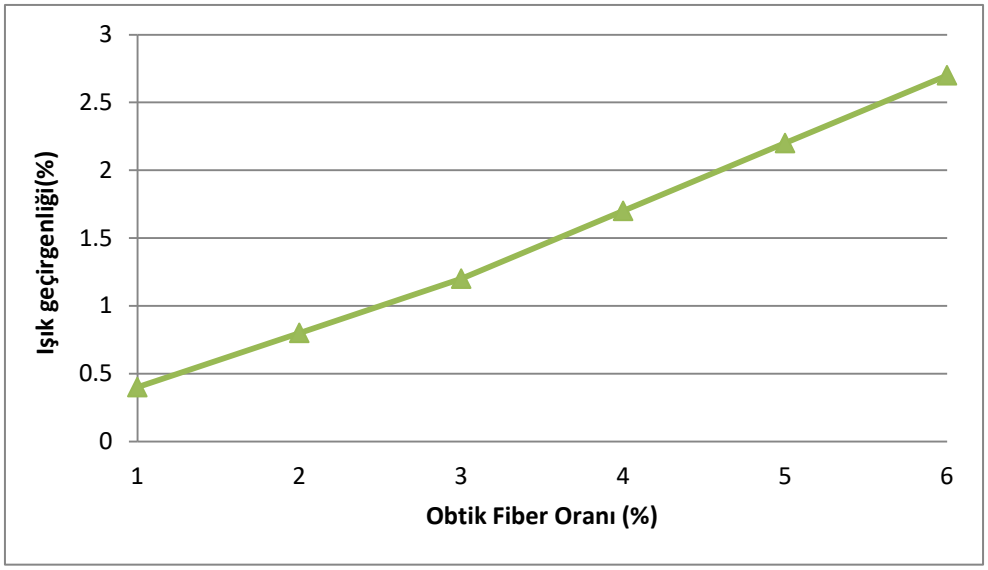
P: Işık geçirgenlik oranı

Ɛ: Cihaz sabiti

J0:ışık kaynağından çıkan enerji

J1: Saydam betonun diğer yüzeyinden alınan enerji

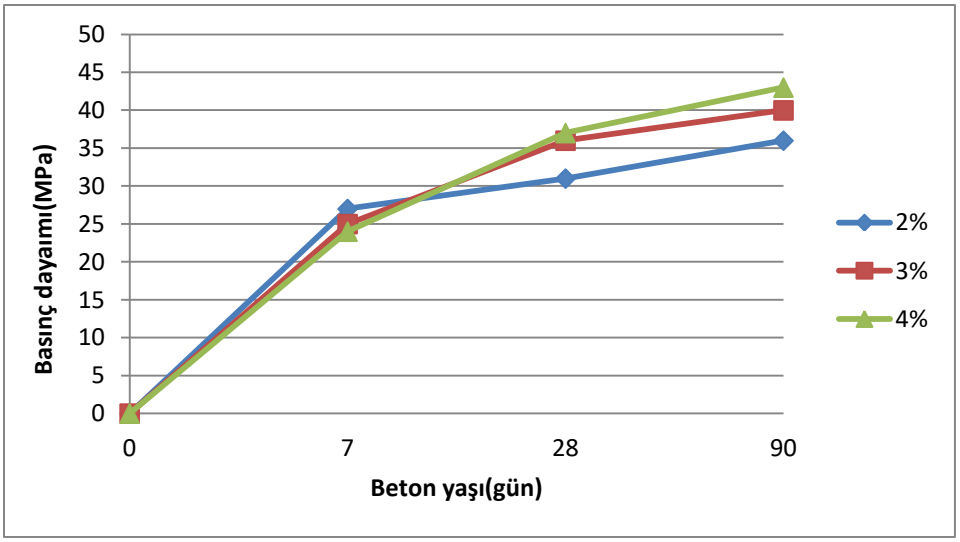
Paul vd. [12] optik fiber oranı % 1,% 2,% 3,% 4,% 5 ve% 6 olan saydam betonları ışık geçirgenlik oranlarını hesaplamışlardır. Şekil 4'te görüldüğü gibi optik fiber oranının artmasıyla birlikte ışık geçirgenliğide artmaktadır.



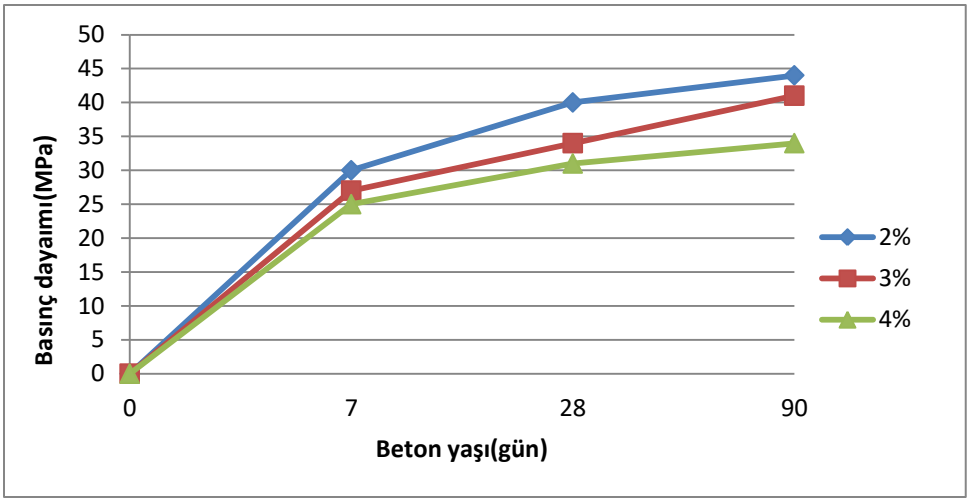
Şekil 4.Optik fiber oranına bağlı olarak betonun ışık geçirgenlik degeri

3.2.Basınç Dayanımı

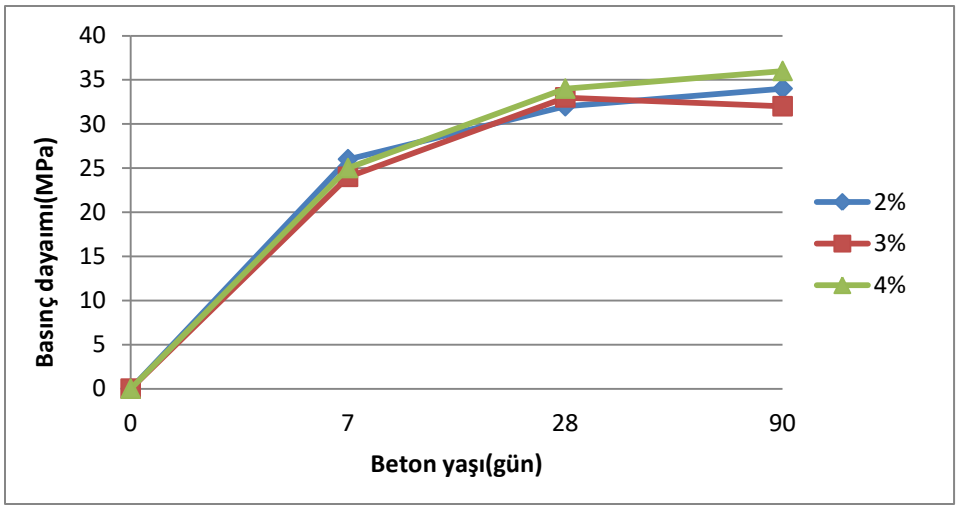
Geleneksel betondan beklenen en önemli özellik basınç dayanımıdır. Saydam betonun geleneksel beton yerine kullanılabilmesi için saydam betonunda basınç dayanımı önemlidir. Kadam [13] boyutları 10*10*10 cm olan küp şeklindeki kalıplara çapları 1,5mm, 2mm ve 3mm olan optik fiberleri kullanarak saydam beton dökmüşlerdir ve 28. gündeki basınç dayanımlarını test etmişlerdir. Sonuçları şekil 5-6-7'de verilmiştir.



Şekil 5. Beton yaşı ile basınç dayanımı değişimi (Optik fiber çapı:1,5 mm)

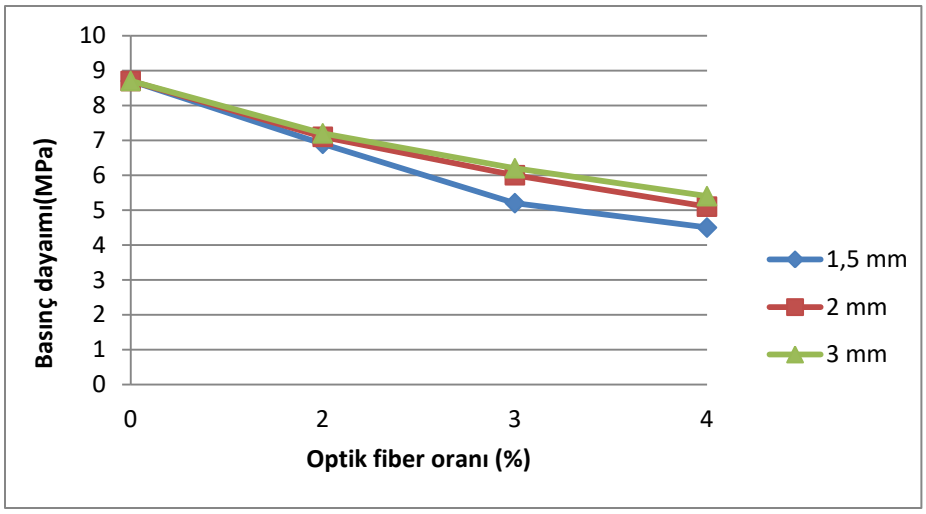


Şekil 6. Beton yaşı ile basınç dayanımı değişimi (Optik fiber çapı:2 mm)



Şekil 7. Beton yaşı ile basınç dayanımı değişimi (Optik fiber çapı:3 mm)

Şekil 5-6-7'de görüldüğü gibi farklı çaplarda optik fiber oranının artmasıyla dayanım kaybı meydana gelmiştir. Optik fiber oranı arttıkça hacim içerisinde ki fiber sayısının artması ve bu nedenle betonun hacim içerisinde hem daha az yer işgal etmesi hem de yerleşme sorunları nedeniyle basınç dayanımı düşmektedir. Örneğin %4 fiber oranında çıkan basınç dayanımı %2 fiber oranında çıkan basınç dayanımına göre yaklaşık olarak %19 oranında düşük çıkmıştır.

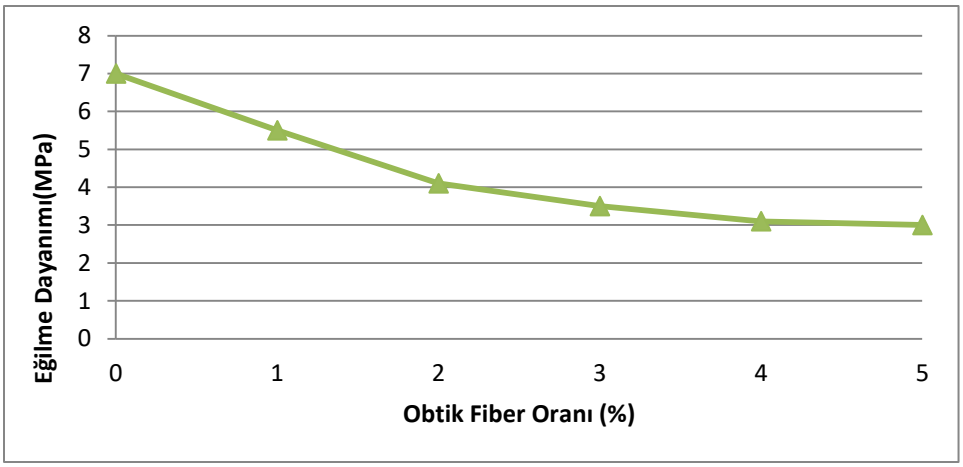


Şekil 8. Optik fiber oranı ile basınç dayanımı değişimi

Şekil 8' de farklı fiber oranlarına göre farklı kalınlıklarda fiberlerden üretilen saydam betonların 7 günlük basınç dayanımları verilmiştir. Aynı hacim içerisinde fiber çapı artarak fiber sayısının azaldığından betonun fiber arasına dökülmesi ve yerleşmesi daha iyi bir şekilde yapılmıştır. Sonuçta daha az boşluklu saydam betonlar küçük çaplı daha fazla fiberli betonlara göre daha yüksek dayanımlara ulaşmıştır.

3.3. Eğilme Dayanımı

Optik fiberler beton içerisinde boyuna uzandığı için eğilme dayanımını arttırdığı düşünülür. Bashbash vd. [14] optik fiber yerleştirilmiş saydam betonların eğilme dayanımlarını tayin etmek için prizmatik 4*4*16 cm boyutlarındaki numuneleri 28. günde eğilme deneyine tabi tutmuşlardır. Deney sonuçları şekil 9'da verilmiştir.



Şekil 9. Optik fiber oranı ile eğilme dayanımı değişimi

Şekil 9'da saydam beton içerisindeki optik fiber oranının artması ile eğilme dayanımının azaldığı görülmüştür. Bunun nedeni optik fiber oranı arttıkça betonun yerleştirme güçlüğü ve düz yüzeyli optik optik fiber ile beton arasındaki aderansın azalmasıdır[15]. Optik fiberlerin tipi ve karışım dizaynının farklı olması durumunda saydam betonun özellikleri de farklılaşacaktır.

4. Avantaj Ve Dezavantajları

Güneş ışığı bedava ve doğal olan en iyi ışık kaynağıdır. Saydam beton kullanılan bir yapıda güneş ışığı ile parlak bir şekil de iç mekanlar aydınlatılabilir buda yapı içerisinde yaz saatlerinde evde daha az ışık kullanılacağı anlamına gelir. Saydam beton içerisine koyulan optik fiberler ışığı yansıtmasının yanında ısı yalıtkanı olarakta işlev görür bu nedenle soğuk ülkelerde daha kullanışlı olurlar [16]. Kış aylarında ısı yalıtımına katkıda bulunduğu için ısıtma işlemine harcanan enerjiyi azaltırlar. Binalara estetik görünüş verdikleri için iyi bir bir mimari özellikleri vardır. Tüm bu olumlu özellikleri yanın saydam beton içerisinde kullanılan optik fiberlerin maliyeti oldukça fazladır [17]. Saydam betonun dökümü oldukça emek ve ciddi bir zaman gerektirmektedir buda işçilik maliyetini arttırmaktadır.

5.Sonuç

Yapılan bu literatür araştırmasında, saydam beton tasarımı, bileşenleri, üretim yöntemi, ışık geçirme özelikleri ile eğilme ve basınç dayanımları incelenmiş ve elde edilen diğer bulgulara göre, beton içerisindeki fiber optik miktarının artmasının betonun dayanımının düşmesine neden olduğu görülmüştür. Fiber optiklerin yerleştirilirken dik olarak yerleştirilmesinin betonun saydamlığına olan etkisi çok yüksektir. Ayrıca, saydam beton harcının en fazla 2 mm ince agrega içermesi ve kıvamının akıcı olması da önerilmektedir. Fiber içeren saydam beton üretiminde küçük çaplı çok sayıda optik fiber yerine, aynı alanı sağlayan daha büyük çaplı ve daha az sayıda optik fiber seçilmesi ile daha dolu bir hacim oluşturulabilir. Geleneksel betonla karşılaştırıldığında saydam betonun normal beton sınıfında üretilebildiği görülmüştür. Bu özellik sayesinde ışık geçirebilme özelliklerine bağlı olarak enerji verimliliği sağlayacak beton duvar panelleri üretimine olanak sağlamaktadır. Günümüzde yaygınlaşan akıllı konut tasarımlarında saydam betonun son derece büyük önemi olacaktır. Elektrik, ısı ve enerji verimliliğinde yarattığı etki ile akıllı binaların daha popüler olması saydam betonun kullanımıyla mümkün hale gelecektir.

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