Bio-based polymeric nanocomposites:

An example: Polylactic acid - clay

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Abstract

Bio-based polymers have been considered as important alternatives to the existing commodity polymers especially in packaging industries in which the shelve-lives are quite short. They are produced by renewable resources - in contrary to commodity polymers which are produced from fossil resources- which will not be exist in the future-; biodegradable and their degradation products are safe and environmentally-friendly. On the other hand, they are costly, and both processing and final product properties are not good enough for their widespread uses. Their properties may significantly improved by incorporating nanofillers – producing nanocomposites-. Layered clays are the most widely used nanofillers. However, they may be first modified with organomodifiers to increase their compatibility with the organic polymer phase, and to reach "intercalated" or "exfoliated" structures. PLA has one of the highest potentials among bio-based polymers particularly for packaging due to its reasonable price and availability in the market. Its properties may be improved significantly by incorporating nanofillers (e.g., organoclays). Both organoclay and

organomodifier type, size and content and also production protocol (from solution or melt) should be optimized to reach the desired improvements.

1. Introduction

Polymers have been used in diverse applications because they are produced in large quantities (hundred thousand tons) and are quite in expensive (around 1 USD/kg); they are easily processed in complex shape products; in many applications they do offer desirable properties, and therefore have replaced many products made of other materials. Packaging industry consumes about 30% of the total polymers produced in yearly basis. Because of the hygienic concerns, huge amount of polymers are used especially in food packaging. However, because of their short shelf life, they directly go to waste in a rather short time and get accumulated in the environment which is one of the main concerns in waste management in sustainable development policies.

In recent years, bio-based products have raised great interest due to increasing environmental concerns and also decreasing the fossil resources that are use to produce many polymers today. Different terms are used to describe the materials considered in this category. "Biopolymers" or "natural polymers" are the polymers synthesized by the nature in natural pathways having special purposes to be produced/exist which is a part of normal life cycle. "Biodegradable polymers" are materials that are degraded in biological environment, induced by the vital activity of an organism, and not simply the degradation of a material in a physiological environment. Other terms as "bioresorption", "bioabsorption", "bioerosion", etc. are also used in the literature to describe the overall degradation phenomenon. Natural polymers are biodegradable, nature knows both how to synthesize and how to degrade. Synthetic polymers may be also biodegradable. The term "bio-based polymers" covers not only biopolymers but also polymers produced from natural resources such as polylactic acid, which is produced from a natural material, L-lactic acid. Bio-based polymers are mostly biodegradable. They may also degraded in the environment by only physical means (hydrolysis, oxydation, etc.). The important note is that not only the polymers themselves but also their degradation products should be safe. As conclusion, we should note that developing novel materials labelled as "environmentally-friendly", i.e., materials produced from alternative resources, with lower energy consumption, biodegradable and non-toxic to the environment is an important challenge. Most biopolymers are costly, there are difficulties to process them, their properties may change from one resource to another, and they are sometimes too weak for practical use. Therefore, it is necessary to improve these biopolymers to make them fully competitive with common thermoplastics is another an important challenge.

To extend their applications, these bio-based polymers have been formulated and associated with nano-sized fillers, which could bring a large range of improved properties including stiffness, permeability, crystallinity, and thermal stability. Here, in this short text, important biodegradable polyester, polylactic acid and its clay nanocomposites, are taken as an example and their properties are briefly described.

2. Polylactic acid

Lactic acid (milk acid) is an ɑ-hydroxy acid, a natural substance, exist in two stereo isomers the L (+) and the D (-) (Fig. 1). The L (+) form is the natural one, and is present in animal and human tissues as well as in numerous food products (meat, milk products, pickles, beer, etc.). Lactic acid can be produced by chemical processes, or by fermentation of carbohydrates from lactic bacteria, belonging mainly to the genus *Lactobacillus*, or fungi [1,2]. Today, lactic acid, its salts and esters are extensively used in food, cosmetic and pharmaceutical industries mainly as preservative. Lactic acid and polymers undergo a biodegradation process and leaving only H_2O and CO_2; they are thus re-entering the natural life cycle without leaving behind harmful pollutants.

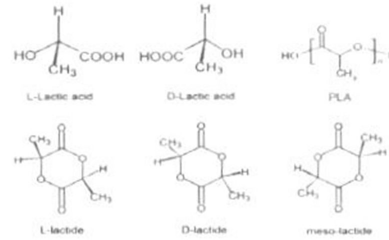

Figure 1. Monomers, dimers and polymers of lactic acid.

As shown in Figure 2, ɑ-hydroxy acids, being bifunctional molecules, are converted into linear polymers by heating with or without using a catalyst by direct polycondensation reactions (or in other terms by intermolecular esterification), which was first described by Filachione and Fisher in 1944 [3]. This technique produces only low-molecular-weight polymers (oligomers). Polycondensation reaction reaches the equilibrium therefore to increase the average molecular weights, water has to be removed during polymerization. However, even by exhaustive azeotropic distillation using an effective agent one might expect to produce polymers with number average molecular weights not more than 10, kDa [4]. In order to produce polyesters with higher molecular weights that lactic acid is first converted to the respective cyclic dimer, i.e. "lactides". These processes are usually based on the transformation of lactic acids into a low molecular weight polymer by heating or also using a catalyst (e.g., antimony trioxide, zinc chloride), and then heating the polymer under reduced pressure to generate the desired cyclic ester. Then, ring-opening polymerization of cyclic dimers using various catalysts (e.g., stannous octoate) are being conducted, usually in bulk or in reactive extruders which is the main approach for the synthesis of polyesters with high molecular weights [5-10].

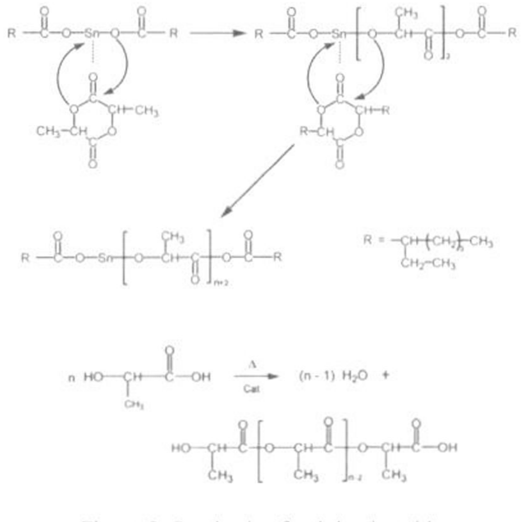

Figure 2. Synthesis of polylactic acids.

Homo and copolymers of lactic acid (or lactide) can be processed into different forms by common polymer processing. Special consideration needs to be given to dry these polyesters before processing and rigorously exclude humidity during processing to prevent hydrolytic degradation especially at elevated temperatures. Monomer formation during processing can act as a plasticizer, changing the material's mechanical properties, and can catalyze the hydrolysis of the material, thus altering degradation kinetics. Therefore, these materials should be processed at the lowest temperatures under dry conditions with a minimum monomer residual. Several plasticizers, including lactic acid oligomers, polyethylene glycols (PEG) with different molecular weights and citrate ester are used, which increases the chain mobility and allows crystallization [11-15].

The biodegradable polyesters, homo and copolymers of lactic acid have ester bonds on their backbone (main) chains which are cleaved by the reaction with water, which is so-called hydrolysis [16,17]. Generally, two step hydrolysis mechanism is assumed, in which first water molecules diffuse in the amorphous regions and start a random hydrolytic scission at the susceptible ester linkages, and then degradation continuous in the crystalline regions. The degradation products (both oligomers and monomers) carrying carboxylic acid end groups in the case of degradation of polyesters are responsible for the autocatalytic bulk degradation of the materials made of these polymers, in which degradation rate is even much faster than ordinary hydrolysis [16]. For a specific application, correct polymer with the required degradation behavior can be selected by considering morphology (crystallinity, orientation, etc.) which is closely related with the chemistry and molecular weight. Several groups have been investigated degradation of homo and copolymers of lactic acid. The methyl groups in lactic acid, polylactic acids contributes the hydrophobicity of the polymer, which reduce water molecule penetration and reduces the degradation rate. Degradation rate is significantly reduced by increasing the molecular weight. Furthermore, including D-lactide in L-lactide as a comonomer reduces the crystallinity of the final stereocopolymer and increases the degradation rate [18]. PLA is mainly degraded by hydrolysis and enzymatic depolymerization in this process remains open to debate [19].

PLA has one of the highest potentials among bio-based polymers particularly for packaging due to its reasonable price (about 2 US Dollars per kg) and availability in the market [20-22]. At present, Cargill is leading in the market (NatureWorks®, Cargill, USA, http://www.natureworksllc.com). The other producers are Dainippon Ink Chemicals, Mitsubishi, Mitsui Chemicals, Shimadzu and Toyota in Japan, Biomer (Germany), Galactic-Total (Belgium), Purac (Netherlands), and Treofan (Netherlands).

2. PLA-Clay Nanocomposites

Polymer nanocomposites are prepared by dispersion of nano-sized materials (nanofillers) into the polymer matrix usually less than 10% [23, 24]. Layered clays and silicates (e.g., montmorillonite, hectorite, saponite, fluoromica, fluorohectorite, vermiculite, kaolinite, magadiite) are the most widely used nanofillers. Layered double hydroxides (e.g., $M_6Al_2(OH)_{16}CO_3nH_2O$; M:Mg, Zn); metal chalcogenides (e.g., $(PbS)_{1.18}$, $(TiS_2)_2$, MoS_2); carbon oxides (e.g., graphite oxide); metal phosphates (e.g., $Zr(HPO_4)$); spherical particles (e.g., silica) and acicular materials (e.g., whiskers, carbon nanotubes) have been also studied. Incorporation of nanofillers, due to huge interfacial surface area (may go up to 750 m^2 for instance with layered clay) improves polymer properties (such as mechanical properties; thermal stability; flame retardance; barrier properties, etc.) drastically.

Layered nanofillers are one of the important reinforcing agents used in hybrid organic-inorganic nanocomposites due to their high aspect ratio. However their preferred face-to-face stacking in agglomerated tactoids prevents their homogeneous dispersion in organic (polymer) phase. Dispersion of the tactoids into discrete monolayers is further hindered by the intrinsic incompatibility of hydrophilic layered silicates and hydrophobic (usually) polymer matrices. Therefore they have to be **"intercalated"** or even converted into a better form, **"exfoliated"** (Fig. 3). Several organo-modifier, usually organic onium ions (e.g., N+(Me)2(C8)(tallow)-C25A-, hexadecylamine-C16-, dodecyltrimethyl ammonium bromide-DTA; *n*-hexadecyl trimethylammonium bromide; bis(4-hydroxy butyl) methyloctadecyl, dimethyl distearyl ammonium) are used to prepare organophilic clays, which are then dispersed in the polymer matrix (both in solution or in melt) to prepare the nanocomposites.

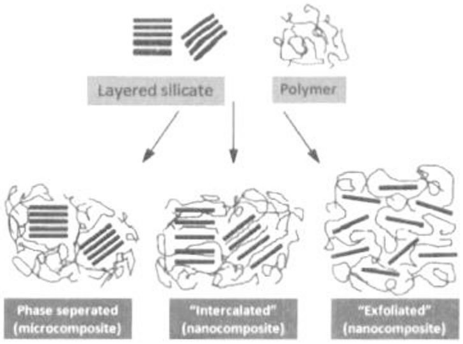

Figure 3. Layered silica nanocomposite structures.

PLA is a very promising material, as also mentioned above, since it is commercially available with reasonable prices, exhibit good thermal plasticity and mechanical properties suitable for many applications including packaging films. However, some of its properties, like flexural properties, gas permeability and heat distortion temperature, are too low for widespread applications. Therefore, PLA have been one of the most widely studies bio-based polymers to prepare nanocomposites in order to improve its properties.

Several parameters affect nanocomposite properties, including both organoclay type, size/shape and clay content, and also organomodifier type and content. Aspect ratio (the ratio of length to diameter of the clay) is one of the most important parameters, material properties usually improved by increasing the aspect ratio. For instance the aspect ratios for hectorite, saponite, montmorillonite and synthetic mica are 46, 165, 218 and 1230, respectively. The relative permeability coefficient can be decreased from 1 (for hectorite) to 0.1 (for synthetic mica).

By creating intercalated structures significant improvements both in mechanical and barrier properties can be reached with only small amount of fillers (about 4-6%) which also depends on the type of organomodifier. Increasing the clay content, first tensile modulus increases, for instance from 3 to 6 GPa by incorporating about 10% nanosilicate. Note that higher clay contents may cause layered silicate agglomeration which gives negative results. Exfoliated materials with randomly distributed clay platelets via solvent intercalation may further improve properties exfoliated materials with randomly distributed clay platelets via solvent intercalation.

The elaboration of PLA/clay nano-biocomposites by melt intercalation is also widely described in the literature [25-40], leading to various materials structures. As a consequence of the nanostructure, despite of the fact that incomplete exfoliation was obtained by melt intercalation, all these nano-biocomposites exhibited dramatic enhancements of various materials properties. These improvements included mechanical and flexural properties, heat distortion temperature, and O_2 gas permeability. However, it has to be noticed that the increments strongly depend on the structure of the nanocomposites. This was attributed to the clay nucleating effect.

Nano-biocomposites from PLLA-based masterbatches which were dispersed into different matrices (PLLA, PDLLA, PBAT) have been also studied. They exhibit enhanced film properties, showing a potential extend to film applications as, e.g., compostable packaging.

Regarding the thermal properties, it was proved that clays acted as nucleating agent since the cold crystallization temperature was decreased by 15°C. Developing plasticized PLA-based nanocomposites to reduce the brittleness and to improve the flowability during the process is another strategically approach. Oligo-PCL or PCL, PEG with different molecular weights, diglycerine tetraacetate-PEG, etc. have been included in the recipes as compatibilizer and plasticizer which induce a flocculated state due to hydroxylated edge–edge Interactions of layered silicates leading to great enhancement of mechanical properties and crystilization [41-47]. In-situ polymerization of lactide from end-hydroxylated PEG in presence of C30B with tin octoate (Sn(Oct)2) as an activator/initiator have been also investigated [48]. This polymerization method, called the "coordination-insertion" method, leads to PLA chains grafted onto the clay surface via the hydroxylated ammonium organomodifier and to PLA-b-PEG-b-PLA triblock copolymer intercalated into the clay gallery. The plasticizing effect is ensured by the PEG sequence of the triblock without phase separation. These nanocomposites exhibit also superior properties.

As conclusion, limitations of bio-based polymers may be significantly reduced by preparation of nanocomposites, which makes them a very important alternative to the existing fossil resources-based synthetic polymers (usually non-degradable), especially for packaging industry, in the frame of a sustanaible-enviromentally-friendly strategically development policy.

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CARBON FIBRE REINFORCED POLYVINYLIDENE FLUORIDE COMPOSITE: TAILORING ADHESION FOR IMPROVING COMPOSITE PERFORMANCE

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Abstract

The application of carbon fibre reinforced polymer composites in oil and gas pipelines and risers will allowed the industry to explore deepwater oil-fields. Carbon fibre composites being relatively lightweight have the potential to overcome limitations encountered with conventional (flexible) steel tubing. The combination of high strength of carbon fibres with the excellent corrosion resistance and wide range of service temperatures of polyvinylidene fluoride (PVDF) can offer a potential for the development of ultra-inert carbon fibre reinforced composites. However due to the inertness and hydrophobic nature of PVDF, the compatibility/adhesion between PVDF and carbon fibre has to be addressed. Here, we show how to tailor the interface between the two constituents by incorporating in-line continuous atmospheric plasma fluorination (APF) of carbon fibres into the manufacturing of unidirectional carbon fibre-reinforced PVDF composite tapes via a powder impregnation process. Initial results show that as high as 3.7 at. % of fluorine was found on the carbon fibre surface upon APF treatment. The produced carbon fibre/PVDF composite tapes, which are 10.5 mm wide and 0.1 mm thick, with fibre volume content between 58 to 62% were compression moulded into test laminates and interface-dominated composite properties were tested. Short-beam shear test results showed an improvement of up to 70% while the flexural strength and modulus of the carbon fibre/PVDF composites increased by 45% and 38%, respectively.

BIODEGRADABLE COMPOSITES

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Abstract

The aim of the present study is to give a review of biodegradable composites. An applicability of a starch-based biodegradable polymer composite reinforced by agricultural byproducts was investigated. The plan had been to make a composite which are comparable properties with commodity polymers such as polyethylene. Glycerol and maltitol were used to produce plasticized starch with an extruder, and then 30wt% sugarcane bagasse was put in the compound as reinforcing components. Dumbbell specimens were injected to determine quasi-static and dynamic mechanical properties.

Introduction

The application of biodegradable composites has a historical precedent from A.C. 4000 in Mesopotamia. It was adobe which contains clay as matrix and straw as reinforcement. It was strong enough to keep own weight and stand against nature. Nowadays more and more researchers deal with development of environmental friendly composites. The cause of this the petroleum resources are limited and the blooming use of conventional fiber reinforced composites has caused serious environmental problems [1]. In biodegradable composites the matrix and the reinforcement have to be biodegradable too. Depending on the origin different categories of biodegradable polymers as matrix have been proposed (Fig. 1.) [2]:

1. Agro-polymers such as starch or cellulose from agro-resources.
2. Polymers obtained by microbial production (e.g. polyhydroxyalkanoates).

3. Chemically synthesized polymers from monomers derived from agro-resources (e.g. poly(lactic acid)).

4. Chemically synthesized polymers from monomers obtained conventionally by chemical synthesis.

Out of these, starch is a potentially useful material for biodegradable matrix because of its natural richness and low cost [1, 3]. Starch can be found in plants in a granular form. The granular starch cannot be processed with the conventional technologies so we need to destruct the granular structure with help gelatinization to generate thermoplastic starch (TPS) [4,5]. The TPS has limited long term stability and poor mechanical property. To improve these properties we can use cellulose based fibers (flax, hemp, jute fibers etc.) [2,6] or basalt fiber [7] as reinforcement.

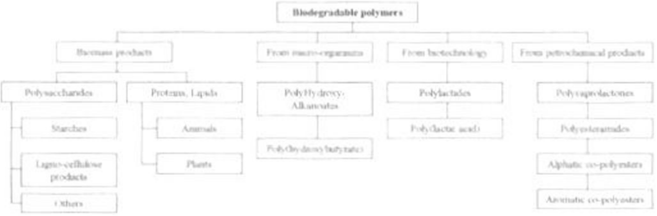

Figure 1. Classification of the biodegradable polymers [12]

The composite have to agree standards (for example ASTM D-6400) which contain definition of biodegradable plastic:

1. *Biodegradable plastic*: "A degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae" [8].

2. *Compostable plastic*: "A plastic that undergoes degradation by biological processes during composting to yield carbon-dioxide, water, inorganic compounds and biomass at a rate consistent with other known compostable materials and leave no visible, distinguishable or toxic residue" [8].

The biodegradable polymers which derived from renewable agricultural resources are reduced environmental charging. The life cycle of biodegradable polymers are shown in Fig. 2.

Experimental

The native maize starch (Amyzet 100) as matrix material were obtained from Hungrana Ltd, Hungary and sugarcane bagasse as reinforcement was supplied from University of Mar del Plata, Argentina was used. The two types of plasticizer, glycerol (49780) and maltitol (63415) were purchased from Sigma-Aldrich Ltd, Hungary. Silica (Aerosil 200) was obtained by Dagussa AG, Germany and glicerolmonostearat (Estol 1473) by Unichemia International, Germany was used as process supporting additions. The referenced material was Eraclene MQ70 HDPE (Polimeri Europa, Italy).

During the experiments 30m% sugarcane bagasse was mixed with glycerol and maltitol plasticized starch (TPS). The mixtures were homogenized in a double-screw extruder (Brabender Plati-Corder Pl2100) with 90, 120, 105, 90°C (from feeding to die zone) and a preproduction with the diameter of 3 mm was drawn and later ground by the chipping machine type Brabender 881203. Dumbbell and rectangular specimens were injection molded from the chips on an injection molding machine type ARBURG Allrounder 370C at 120°C, by pressure of 1200 bar.

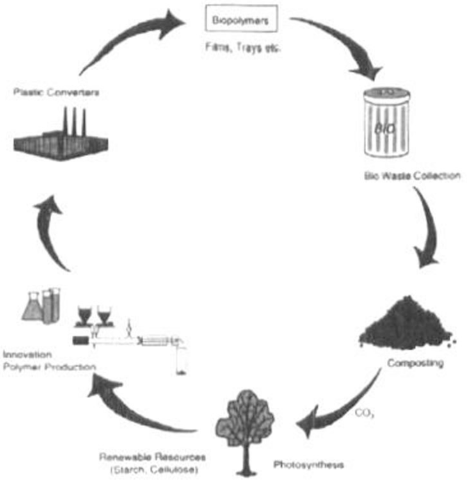

Figure 2. Life cycle of biodegradable polymers [9]

Methods

Five specimens were tested for each composite formulation to obtain a reliable average of studied properties as well as their corresponding standard deviations. Tensile tests were carried out on dumbbell specimens according to ISO 527-1 on a computer controlled universal tensile tester type Zwick Z020 at room temperature at 5 mm/min loading speed. The initial distance between grips was 110 mm. Three-point bending tests were performed by Zwick Z050 equipment according to ISO 178 at room temperature at 5 mm/min loading speed with 64 mm span length. The Charpy notched impact strength were tested on rectangular specimens by a Ceast Resil Impact Junior impact tester with a 15 J hammer, 62 mm span length. The depth of the notch was 2 mm.

Results and Discussion

The results of mechanical tests are shown in Table 1. The reference PE has good resistance against dynamic stress. The TPS-B has same Charpy notched impact strength like PE. The tensile modulus of the TPS is 2,5 times bigger than the used reference PE. The bagasse increased this property of the matrix. The flexural stress at 0,6% deflection of the bagasse filled thermoplastic starch is better than PE as well.

Table 1. Results of mechanical tests

	Flexural stress at 0,6% deflection [MPa]	Tensile strength [MPa]	Tensile modulus [GPa]	Charpy notched impact strength [kJ/m^2]
PE	6,20±0,09	19,91±1,15	1,03±0,06	4,13±0,32
TPS	21,48±1,27	18,94±1,59	2,52±0,15	4,72±0,45

Conclusion

The aim of our work was to develop a biodegradable agricultural byproduct filled starch-based composite which can substitute the commodity polymers such as PE. In the tests it was found that the bagasse filled TPS has good resistance against dynamic and quasi-static stresses as well. We stated the developed material can substitute the commodity polymers in the area of one way products such as pizza spacer. A further task is to improve the process ability of this material.

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POLİMERİK KOMPOZİTLERİN TEMEL YAPI MALZEMELERİ /

MAIN MATERIALS OF POLYMERIC COMPOSITES

PETROKİMYA VE NANOKOMPOZİTLER

PETROCHEMISTRY AND NANOCOMPOSITES

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Özet

Ham petrol ve doğal gazdan başlayan Petrokimya endüstrisi tüm endüstriyel ham maddeler ve son ürünler zincirinin ortalarında yer almaktadır. Dünya ticaretinin %8'ini, tüm kimya ürünlerinin ise %3'unu oluşturan bu sanayinin ticaret potansiyeli yılda yaklaşık 500 milyar civarındadır.

Son yıllarda dünya çapında baş gösteren krize ve petrol fiyatlarındaki dalgalanmalara rağmen petrokimyanın ana sektörlerinden olan plastik endüstrisindeki büyüme, dünyadaki ortalama büyümenin üzerindedir. Yıllık % 4-5'lik büyüme hızı ile başlıca termoplastikler ürünlerinden olan polietilenin küresel talebi 71 milyon tona, polipropilenin talebi ise 47 milyon tona ulaşmıştır.

Türkiye'de petrokimya ürün talebi 2009 yılında 4.4 milyon ton (yaklaşık 5-6 milyar US$) olsa da son 10 yıllık büyüme hızına göre 2015 yılında 7.0 ve 2020 yılında ise 11.2 milyon tona ulaşması beklenmektedir. Termoplastiklerde ise bu talebin 3.3 milyon tondan sırası ile 5.7 ve 9.6 milyon tona ulaşacağı tahmin edilmektedir.

Türkiye'deki en büyük petrokimya üreticisi olan Petkim'in ana hammaddesi nafta olup olefinler, poliolefinler, klor-vinil zinciri, aromatikler ve diğere temel kimyasal ürün gruplarında üretim yapmaktadır. Petkimdeki üretim hacimlerine göre ilk beş petrokimyasal ürün PVC, AYPE, PP, benzen ve ACN'dir. Petkim, yurt içinde 2009 yılı itibarı ile petrokimya ürünlerine göre yaklaşık %26, termoplastiklere göre ise %23 pazar payına sahiptir.

Polimerik kompozit sektörüne baktığımızda, 2009 yılında dünya kompozit pazarının 65 milyar US$'a ulaştığı görülmektedir. Kompozit sektörünün yaklaşık %23'ü otomotiv, %21'i inşaat ve bayındırlık işleri, %17'si havacılık ve %11'i ise sportif malzemeler pazarına hitap etmektedir.

Bilindiği gibi kompozit malzemelerde matris olarak termoset ve termoplastik malzemeler kullanılmaktadır. Ancak, otomasyon sistemlerine daha uygun olması, geri kazanılabilirliği, çözücü-bazlı reçine sistemlerine olan çevresel kaygılar ve maliyetinin düşüklüğü gibi nedenlerle termoplastik malzemelerin kompozitlerde kullanımı gittikçe artmaktadır. Bu nedenle %3'lerde olan termoset kompozitlerdeki büyüme hızı genel kompozit pazar büyüme hızının altında kalmış ve yıllık % 6-15 büyüme hızı ile termoplastikler bunların yerini almıştır.

Son yıllarda çevre ve yüksek taleplere cevap veren ürünler geliştirilmesine imkan vermesi nedeni ile, polimerik kompozit malzemeler alanında yapılan bilimsel çalışmalarda yeni nanokompozitler oluşturulması ön sıraları almağa başlamıştır. Bu nanokompozitler farklı özellikleri ile hem araştırmacıların, hem de sanayicilerin dikkatini çekmektedir. Petkimde bu alanda gerek nanokatkılar, gerekse polimer matriksleri acısından çalışmalara başlanılmış ve başarıyla devam edilmektedir.

Abstract

Petrochemical industry starting from crude oil and natural gas is located on the mid of the chain of whole industrial raw materials and end products. Petrochemical industry with the 8% of world trade and about 30% of the total chemical products has a market value of about 500 billion dollars.

Although the global economic crisis during the last years and price volatility in crude oil, the growth in plastics industry which is the major sector of petrochemicals is over the global growth.

The petrochemical demand of Turkey which was 4.4 million tons (approx. 5.5 billion USD as market value) in 2009 is expected to reach 7 million tons in 2015 and 11.2 million tons in 2010 due to the growth rate in the last 10 years. Thermoplastics demand is forecasted to grow from 3.5 million tons to 5.7 and 9.6 million tons in order.

Owing naphtha as the main feedstock of Petkim, the major petrochemical producer of Turkey, has a production in olefins, polyolefins, chlor-vinyl chain, aromatics and

other basic chemical group. In comparison to production volume, LDPE, PVC, PP, benzene, and ACN are the fist five petrochemicals in the production range. Petkim has a domestic share of petrochemicals and thermoplastics as 26% and 23% in order.

For the composite industry, it is indicated that the volume of the global composite market is reached to 65 billion US $. The biggest growth is shown as 20% in the wind energy sector in the world. The European composite industry serves to the automotive (23%), building and public works (21%), aeronautics (17%) and sports (11%) markets mainly.

As it is known, thermoset and thermoplastic materials are used as matrix in composites. But the usage of thermoplastics in composites gradually increases due to the adaptability in automated systems, easier recycling, environmental concerns on the solvent-based resins and low cost. Thus the growth rate of thermoset composites is 3% which is under the overall growth rate of composite market and thermoplastics with the growth rate of 6-15% per year is replaced with the thermosets.

Due to enabling the development of the new products, scientific studies on nanocomposites are begun to be in the front ranks. These materials are to bring scientists and manufacturers attention because of various and excellent properties. Regarding nanocomposites, several research projects based on the matrix materials and additives are successfully carried in Petkim.

NANOSTRUCTURED POLYMERIC MATERIALS BY TEMPLATING STRATEGIES

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Abstrakt

Bu bildiri gurubumuzun anodize edilmis aluminyim oksit membrane filmler icerisinde olusturulmus nanoyapilarin dizayni, fabrikasyon/sentez ve karekterisyonu uzerine yapmis oldugu calismalari ozetlemektedir. Bu calislamar icerinde ozellikle anodik alumina membrane filmlerin optik waveguide spektroskopi uygulamalarina agirlik verilecektir. Farkli fonksiyonel monomerik gruplar kullanilarak duzenli polimerik nano-cubuk dizileri elde edildi. Bu yapilar alumina membranenin cozulmesinden sonra da isigi yonlendirme ozelliklerini kaybetmediler. Bu gozlem nano yapili malzemelerin entegre-optik platformlar alanina kullanimina yeni bir boyut katti. Kullanilan nano-cubuklar cyanate ester monomerlerinin isil islemle polimerizasyonundan elde edilip, caplari 65 nm ve kalinliklari 600nm dir.

Abstract

This contribution summarizes some of our efforts in designing, assembling/synthesizing, and structurally and functionally characterizing nanostructured materials using anodized aluminum oxide (AAO) as thin film template. A particularly powerful analytical tool is optical waveguide spectroscopy using the nanoporous template as the guiding structure. We demonstrate growth of polymeric nano-rod arrays from different functional monomers which after the dissolution of the template are still able to guide light. This opens up novel concepts for integrated optics platforms with nanostructured materials. The nanorods, with diameter of 65 nm and length of and 600 nm, are formed by thermal polymerization of cyanate ester monomers within porous alumina mold. Polycyanurate nanorod sensor distinguished subtle refractive index changes upon replacement of the surrounding medium with high resolution ($\Delta n < 0.003$). The sensitivity of nanorod array biosensor was tested with binding of a small biological molecule (taurine) on the nanorods surfaces via reacting with the residual cyanate groups. Particular attention is paid to the ability to differentiate, in situ, processes that occur on nanorod surface. OWS and X-ray powder diffraction (XRD) techniques proved a successful surface modification on the nanorods surface. Based on these results, we introduce the applicability of PCN array platform as a novel concept in optical biosensor and other related applications.

Introduction

In biosensing high sensitivity and selectivity are desired. For high sensitivity, it is desirable to maximize the number of binding sites in order to enhance sensing capabilities. The use of the nanoporous AAO matrix to provide an extra internal surface for binding is one step towards that goal. Production of organic nanorod arrays with outer surface covered with polymer brushes to create more binding sites per unit area represents another strategy. The fabrication of one-dimensional nanostructures by replicating shape-defining nanoporous templates has become a well-established synthetic methodology [1,2]. Self-ordered anodic aluminum oxide (AAO) [3] containing arrays of aligned cylindrical nanopores characterized by narrow pore diameter distributions is a template system widely used to this end. Functionalized AAO membranes and other inorganic nanoporous scaffolds were employed as optical waveguide for visible light [4] and various sensing applications [5, 6, 7, 8]. The template-based fabrication of released nanorod arrays stable under real-live conditions is still challenging [9]. Plasmonic gold nanorod metamaterials obtained be electrodeposition into AAO have been employed for biosensing [10]. The integration of optically transparent nanorod arrays into device architectures enabling optical waveguide spectroscopy (OWS) has, up to now, not been accomplished. OWS, which is based on evanescent wave optics and the monitoring of sharp waveguide modes, has been employed to characterize optical properties of thin films [11,12]. A schematic diagram illustrating a OWS set-up shown in Figure 1. Here, we focus on planar OWS based on prism coupling named as Kreteshmann configuration. In this geometry, incident light irradiates the metal layer through a prism. When a beam directed onto the base of a glass prism at an angle greater than a critical angle (θ_c), given by Snell's law, the light is totally internally reflected (TIR) at the interface. The electric field couples with the charge density fluctuations of free electrons in the metal and excites a surface plasmon. At this time, an evanescent wave is produced outside the film whose amplitude decays exponentially away from the metal surface due to the conservation of momentum and energy of the light. The evanescent wave propagates in parallel to the interface. If an additional dielectric layer (with higher refractive index than its surroundings) is incorporated onto the metal film, the incident light excites leaky guided modes in this waveguide structure. The momentum at which the incident light beam is coupled into waveguide modes is depended on the refractive index and the thickness of the substrate, superstrate and waveguide material. Both SPR (only in P-polarization) and waveguides modes excited by both P- and S-polarized light are observed as a sudden drop of reflectivity as shown in Fig. 1. The propagation in these waveguides can be analyzed on the basis of Maxwell's equations and of the boundary conditions, which will be explained in the following section in detail. The electric field distributions and the reflectivity vs. incidence angle (R vs. θ) trace shown in Fig.1 were calculated by solving the Maxwell equations for light incident on a 1-dimensional layer system described by the thickness and refractive indices of the different layers.

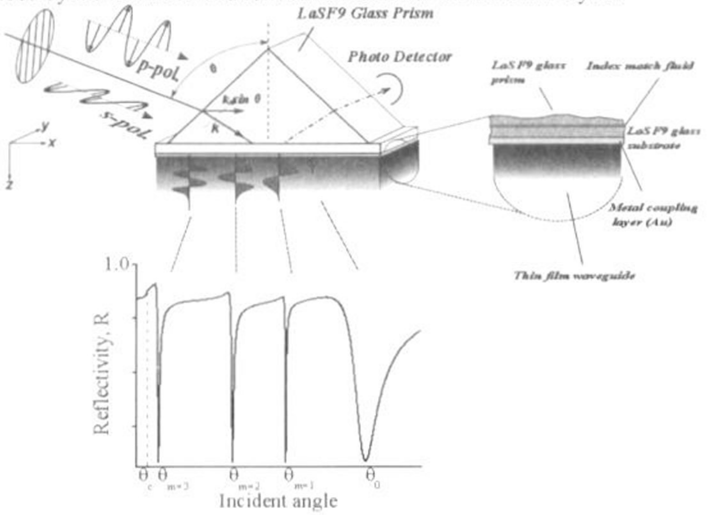

Figure 1. Schematic of prism coupling in the Kretschmann configuration and the waveguide mode detection scheme. θ_c is the critical angle for total internal reflection. Schematics of the waveguide mode electric field distributions (transverse electric (TE) modes) are overlaid on the waveguiding film model. The R vs. θ trace on the lower right shows waveguide modes for a model thin film. The number of waveguide modes excited and their angle positions depend on the exact thickness and n_{eff}. The modes are indexed according to the number of modes of their field distribution in the waveguide structure.

The high surface area of the nanorod array provides increased sensitivity for biosensing by amplifying the amount of material attached to the surface of the dielectric and therefore increases the signal-to-noise ratio. Moreover, OWS modes of both polarizations, i.e. transversal magnetic (TM) and transversal electric (TE) modes can be excited by probing different components of hybrid nanorod arrays. This property is particularly important and helpful for the characterization of optically anisotropic multiple layers used in integrated optics configurations [13], since the different electric field distributions within the waveguding film for different waveguide modes confer the ability to differentiate processes occurring in different directions of the film [14].

Cyanate ester monomers (CEMs)[15] are ideally suited for the synthesis of nanorod waveguides because of their capability to self-cure and their low viscosity (liquid at room temperature). The polycyanurate thermoset nanorods (PCN) obtained in this way have high chemical and mechanical stability as well as a high dielectric constant (ε=3.41-3.75 at 1MHz) related to the polarizable aryl ether linkage. Most importantly, PCNs have –OCN groups on their surfaces that allow for their further functionalization. The PCNs were prepared as follows. A 2 nm Cr film and subsequently a 50 nm thick Au layer was evaporated on high refractive index glass (LaSFN9, Hellma Optik, n=1.845). The gold surface was amino-funtionalized by dipping in 5 mM 2-aminoethanethiol in absolute ethanol (Sigma-Aldrich) solution for 45 min. The CEMs were infiltrated in AAO by spin coating (3000 rpm, 2 min) and kept under vacuum (5-10mbar) at 120 °C for 12 h. After removal of excess monomer from the AAO surface, the CEM-filled AAOs were pressed against the gold deposited glass substrates and thermally cured under N_2 by heating to 120°C for1h, to 180°C for 8h, to 260°C for 3h and to 290°C for 1h. The PCNs thus obtained were covalently bond to the functionalized Au substrate. The AAO was then dissolved with 10% H_3PO_4 aqueous solution at room temperature for 12h, and an array of freestanding PCNs oriented normal to the substrate surface was obtained (Figure 2).

(a) (b)

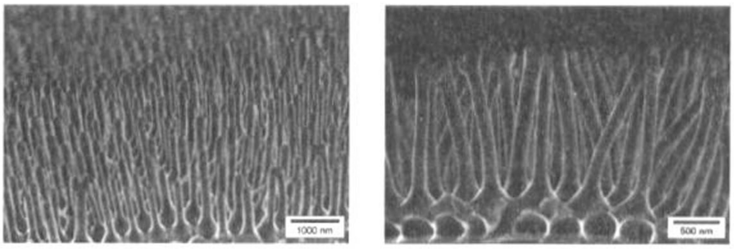

Figure 2. SEM (a) top and (b) side view images for polycyanurate nanorod arrays on Au substrates. Scale bar is 1pm (left) and 500nm (right), respectively.

Guided optical modes were observed as sharp minima in reflectivity vs. incidence angle scans (R vs. t) (Figure 3) when nanorods were subjected to a solvent exchange test. Simple example of solvent exchange around the PCNs was followed, which effectively changes the dielectric constant of the interfaces between nanorod and surrounding medium results in detectable shifts of the waveguide modes. Three solvents were chosen as inter-rod space filling medium: water (n=1.333), ethanol (n= 1.361) and isopropanol (n=1.378). Solvents were chosen in a way that PCNs might keep their chemically stability for extended time duration. They have relatively close refractive indexes, which makes them more attractive for verifying the achievable sensitivity for a biosensor system.The refractive indices of ethanol and isopropanol are higher that water and thus the effective refractive index of the sample is altogether increased. This was detected as a shift of the waveguiding modes to higher angles; $\Delta\theta_{m1}$= 0.79°, $\Delta\theta_{m2}$= 1.67° for TM modes and $\Delta\theta_{m1}$= 0.75°, $\Delta\theta_{m2}$= 1.38° for TE modes (Figure 3)

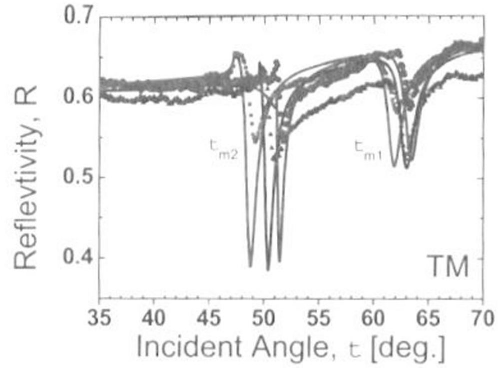

Figure 3. OWS *R* vs. *θ* scans of the PCN arrays in different environments in transverse magnetic mode: Milli-Q water (squares); ethanol (circles); isopropanol (triangles). The spectra are well described by Fresnel calculations.

Changes in the external media produced larger waveguide minimum angle shifts for higher order modes. The highest figure of merit FOM = $(\Delta n/\Delta\theta)\ (1/J)$ (where J is the full-width of the waveguide mode dip at half-minimum and $\Delta\theta$ is the mode shift for Δn refractive index change) was 98 for the TE modes at $m=2$ for ethanol-isopopanol system. This value reached 5 for localized surface plasmon resonance spectroscopy (LSP) [16] and 26 for the sensors based on long-range SPR [17]. The functionality and sensitivity of biosensor platform was further tested during the taurine attachment (data not shown). The successful tethering of taurine at the surface of polycyanurate nanopillars was evident from the XPS analyses before and after surface modification. XPS spectrum of taurine modified polycyanurate nanopillars showed a peak between 170-175 eV, characteristic of S2p, originating from the sulphonate group of the taurine.

Conclusions

We employed highly oriented cyanate ester nanorods as an effective optical waveguiding platform. The waveguiding capability of the sensor has been demonstrated through two examples: First, by exchanging the interrod environment between different solvents. The waveguiding modes were sensitive to the changes of the respective optical properties. Second, by attaching ultrathin film of taurine molecule on the surfaces of nanorods which was characterized with OWS and XPS, independently. High sensitivity is achieved by the large surface area of the nanorod structure, which leads to high response even to minute dielectric changes and amplifies the amount of material adsorbed. Reacting the residual cyanate groups with amine functional groups enables the use of the nanostructure for specific analyte binding, for example for layer-by-layer deposition of electrolytic materials. The future work also includes the potential use of nanorod arrays as scaffolds for optical biosensors with molecularly imprinted polymers (MIPs). What makes this hybrid biosensor platform attractive is the high surface area increases the number of functional sited available for surface specific processes and sharp wave guides modes improves the sensitivity for detection limit.

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KOMPOZİTLERDE TAKVİYE MALZEMESİ OLARAK KULLANILAN CAM ELYAF'IN GELİŞİMİ VE GELECEĞİ

DEVELOPMENT AND FUTURE OF THE GLASS FIBER AS A REINFORCING ELEMENTS IN COMPOSITES

Aref Cevahir

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Özet

Camelyafı mineral bazlı elyaftır ve 1938 yılında Amerika'da üretildi ve yaygın bir şekilde kullanıldı ve asbest'in bazı sağlık sorunları ortaya çıkınca 1950'larda asbest'in yerine doldurmayı başladı. Asbest lifleri ve camelyafı arasındaki şekil benzerliği nedeniyle cam elyafı elektrik, termal ve ses yalıtımı uygulamalarında ve ayrıca malzemelere yapısal takviye ve sıcaklık direnci sağlaması nedeniyle asbestin yerine doldurdu.

1930'larda Cam Elyaf Takviyeli Polimerden imal edilen ilk ürün tekne oldu. Bu ilk proje, 1930'larda tamamlandı ve 1940'larda ABD Hava Kuvvetleri, Deniz Kuvvetleri ve petrol endüstrinin birçok elyaf takviyeli polimer ürünleri yapıldı.

1950 lilerde cam takviyeli plastik (CTP) kompozit ürünler otomotiv sektorunde yaygın olarak kullanılmaya başlandı ve bu malzemeler kopru ve gemi yapımlarında da kullanıldı. 1994 e kadar, yaklaşık 600 milyon ton mimariye uygun cam elyafı yapı sektöründe kullanıldı.

1990'larda uzun elyaf takviyeli termoplastiklerin üretimi başlamıştır (LFT) ve polimer kompozit sektöründe en hızlı büyüyen malzemelerinden biri oldu. Yüksek çekme dayanımı, geri kazanabilirliği, düşük yoğunluk, yüksek modüllü ve darbe dayanımı onların avantajları günlük yaşamın çeşitli alanlarında metaller ve termoset kompozitlerin yerini almıştır.

Bu derlemede, cam elyaf ürünleri ve ilgili kompozit ürünleri tanıtılıp ,küresel talepler doğrultusunda cam elyaf ürünlerinin olası trendi geniş olarak ele alınacaktır.

Abstract

Fiberglass is a man-made mineral fiber that was invented in 1938 is widely used in America and it became a popular substitute for asbestos in the 1950's when some of the deleterious health effects from asbestos were first becoming apparent. Because of the similarity in shape between the fiberglass and the asbestos fibers, fiberglass was able to effectively replace asbestos in many applications such as in electrical, thermal, and acoustic insulation and in adding structural reinforcement and heat resistance to a material.

It's believed that the very first product manufactured from Glass Fiber Reinforced Polymer was a boat hull, which was manufactured using a mold made of foam. This first project was completed during the 1930s, and the 1940s saw the construction of many fiber reinforced polymer products for the U.S. Air Force, the Navy, and the oil industry.

Over the following decades, the automotive industry began using GFRP extensively, and FRP was also used to construct bridges and boats. After the failed House of the Future demolition, the building industry also began to employ fiberglass in a wider variety of construction applications. In fact, by 1994, the building industry had used almost 600 million tons of architectural fiberglass to craft a variety of buildings and elements

In 1990's, production of long fiber termoplastics (LFT) have been started and it became rapidly developed materials in composite industry.

LTF compoistes easily replace metals and thermosets due to their superior properties like high tensile properties, high modulus, high impact resistance, low density and recycling.

In this review, Glass fiber and its related composite products and future trends will be discussed.

THE NEW BUSINESS OF AKSA- CARBON FIBER

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AKSA's first commercial production line for high quality, competitively priced, reliably supplied PAN based carbon fiber for industrial applications started production in the 3rd quarter of 2009. AKSA, having 300.000 tpa acrylic fiber production capacity, which represents 12% worldwide market share, is ranked among Turkey's leading economic enterprises. Out of its 40 years of experience, AKSA has developed new "AKSACA" family of carbon fiber products. A dedicated R&D oriented 34 tpa pilot line established in mid-2008 has become the initial step of today's first commercial line running with a capacity of 1.500 tpa since Q3 2009. As being the new player, AKSA intends to maintain its well known reputation in product, process and after sales quality with its reliable consistency in the carbon fiber sector as well.

Carbon fiber, which is a reinforcement material for composites, is manufactured by oxidation and carbonization of Special Acrylic Fiber (PAN-based). Once formed, the carbon fiber has a surface treatment applied to improve matrix bonding, and chemical sizing, which serves to protect it during handling. The properties of carbon fiber such as high tensile strength, low weight, high thermal conductivity, excellent creep resistance, good chemical resistance and low thermal expansion make it very popular in aerospace, military, several industrial applications, like civil engineering, pressurized vessels, wind mills, marine, and motorsports, along with other competition sports.

PAN-based carbon fibers are supplied as small tows (1K-24K) and large tows (>40K), the tows referring to the number of carbon fiber filaments.

Carbon fibers are supplied in continuous or chopped/milled forms and can be converted by a variety of processes to a range of intermediate and moulded composite components. There are three main processing groups, "intermediate processing", "direct conversion" and "moulding processes". Intermediate processes convert carbon fiber into semi-usable product (e.g. textiles, prepreg). Direct conversion processes convert carbon tow/chopped carbon fiber directly into a finished composite; includes filament winding, pultrusion and carbon-carbon composites (CCCs). Moulding processes are used to convert/combine the carbon and matrix to the final composite.

Özet

AKSA, 308.000 ton/yıl üretim kapasitesi ve 12% Pazar payı ile "dünyanın tek çatı altındaki en büyük entegre akrilik elyaf üreticisidir". Ürün portföyünü genişletmek ve katma değerli ürünlerini artırmak amacı ile AKSA, kendi karbon elyaf üretim teknolojisini geliştirmeye 34 ton/yıl kapasiteli pilot tesisi ile 2008 yılında başlamıştır. 2009 3.çeyreğinde 1500 ton/yıl kapasiteli üretim tesisi ve "AKSACA" markası ile pazarda yerini almıştır.

Kompozit endüstrisinin hammaddesi olan karbon elyaf, uygun reçineler ile birleştirildiğinde olağanüstü dayanım ve sağlamlık özellikleri gösterir. Yüksek dayanım, düşük yoğunluk, düşük korozyon ve düşük ağırlık özelliklerinin üstün kombinasyonu ile havacılık, savunma sanayi, spor gereçleri ve endüstriyel kullanım alanlarında yerini almaktadır.

Fig. 1 A spool of AKSACA

POLİMERİK KOMPOZİT YAPILAR VE UYGULAMA ALANLARI /

POLYMERIC COMPOSITE STRUCTURES AND APPLICATION AREAS

BIOLOGICALLY INSPIRED ANTIMICROBIAL TEXTILES FOR HEALTH-CARE APPLICATIONS

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Textile industry continuously searches for new technologies in order to accomplish new applications. Especially in recent years, new developments allowed the production of functional and smart textiles which are capable of sensing changes in environmental conditions or body functions and responding to these changes. Likewise, consumers' attitude towards hygiene and active lifestyle has created a rapidly increasing market for a wide range of textile materials with bioactive properties, which in turn has stimulated intensive research and development. As a consequence, the number of biofunctional textiles with a bioactive activity has increased considerably over the last few years. Application is nowadays extended to underwear, sportswear, home furnishing and protective clothing in areas with high risk of infection by pathogens (hospitals, schools and hotels); and because they are able to absorb substances from the skin and can release therapeutic compounds to the skin, they find applications for prevention, as surgical lab coats, or therapy, as wound dressings.

However, there is a need to overcome the risks, disadvantages and side effects associated with the use of synthetic bioactive agents along with the mild activity and durability. Consequently, novel strategies based on biologically inspired systems that are found in several living organism have focused the attention of several authors. Accordingly, there is a measureless resource of natural antimicrobial agents which can be exploited for imparting antimicrobial properties to textile substrates being promising candidates for future therapeutic and an innovative approach which may open new avenues for the biomimetic design of biologically inspired bioactive textiles for health-care applications.

Thus, this presentation reports an overview on biologically inspired processes and products for potential use in medical, geriatric and pediatric fields.

Key Words: Antimicrobial Textiles, Wound-dressings, L-Cysteine, Antimicrobial Peptides, Transdermal Drug Delivery

Introduction

1. Microorganisms and textiles

Textiles are an excellent substrate for bacterial growth and microbial proliferation under appropriate moisture, nutrients and temperature conditions [1-3]. In a clinical setting, they can be an important source of bacteria that may contaminate the patients and clinician personnel [1]. Bacteria and fungus, either pathogenic or not, are normally found on human skin, nasal cavities, and other areas, such as in the genital area.

Microbial shedding from our body contributes to microorganism spreading into a textile material either directly in clothes or on surrounding textiles. Recent studies strongly support that contamination of textiles in clinical settings may contribute to the dispersal of pathogens to the air which then settle down and infect the immediate and non-immediate environment. It is one of the most probably causes of hospital infections [1]. Typically, pathogenic microorganisms like *Klebsiella pnuemoniae*, *Pseudomonas aeuroginosa, Staphylococcus epidermidis, Staphylococcus aureus* and *Candida albicans* have been found on textiles.

In addition, microorganism proliferation can cause malodours, stains and damage of mechanical properties of the component fibres that could cause a product to be less effective in its intended use. Additionally, may promote skin contamination, inflammation and in sensitive people, atopic dermatitis [4]. Fortunately, the use of antimicrobial textiles may significantly reduce the risk of infections especially when they are used in close contact with the patients or in the immediate and non-immediate surroundings.

2. Biological Inspiration: Present perspectives and major challenges

To overcome the risks, disadvantages and side effects associated with the use of synthetic antimicrobial agents along with the mild activity and durability associated with the above described natural compounds, new solutions are expected. In this way, an innovative strategy could be the utilisation of natural defensive amino acids and peptides that are found in every living organism as new biocides for material´ functionalisation.

New Strategies

1. Antimicrobial amino acids and peptides

Due to the widespread resistance of bacteria to the available drugs, naturally occurring antimicrobial peptides (AMPs) are considered promising candidates for future therapeutic use [5-10]. Virtually, all life forms express cationic AMPs as an important component of their innate immune defenses. AMPs isolated from bacteria, fungi, plants, invertebrates and vertebrates are very heterogeneous in length, sequence and structure, but most of them are small, cationic and amphipathic.

AMPs fall into 4 principal categories based on their size, conformational structure, or predominant amino acid structure [11]. These comprise group I: linear, α-helical peptides without cysteine (e.g., Cecropin, a family of 3-4 kDa linear amphipatic peptides); group II: cysteine-rich open-ended peptides containing single or several disulfide bridges (e.g., β-defensins a highly complex group of 4-kDa); group III: linear peptides rich in 1 or more amino acids (The smallest is represented by thanatin and brevinin); and group IV: peptides with sphere structures (e.g., bactenecin and ranalexin).

The cationic peptides represent the majority of antimicrobial peptides already registered, and there are more than a thousand peptides with antimicrobial activity characterized [12,13].These peptides belong predominately to the three main classes above described: Group I, II and III.

Anionic peptides are a group of much smaller dimensions, only recently identified mainly in mammals. These peptides are small, hydrophilic and contain specific regions that confer a negative charge. Zinc can be used as a cofactor in anionic peptides to enable them to overcome the negative charge on the surface of microorganisms, thus obtaining a maximum bactericidal activity [11]. Subfamilies of these peptides can quote: neuropeptide derived molecules, aspartic acid-rich molecules, aromatic dipeptides and proteins derived from hemocyanin [10,11,12].

These cationic and anionic peptides exhibit broad-spectrum activity against Gram-positive and Gram-negative bacteria, yeasts, fungi and enveloped viruses [16,17,19]. Consequently, considerable efforts have been expended to exploit the therapeutic potential of AMPs, especially regarding the pharmaceutical industry [9-13]. Moreover, because of the membrane-disturbing mode of action of most AMPs, there is a reduced likelihood of the acquisition of resistance by bacteria [11,13].

1.2 The potential for material functionalisation

Our earlier studies revealed the success of biofunctionalisation of wool and polyamide fibres with L-Cysteine (L-Cys) (National Patent . A durable antimicrobial effect over *Staphylococcus aureus* and *Klebsiella pneumoniae* was obtained without cytotoxicity. Apparently, the effect results from the interaction of free sulphydryl groups of L-Cys with the sulphydryl groups from the proteins and enzymes that are essential to the survival of microorganisms, as discussed by Kyung and Lee in studies with tiosulfinates from garlic [14].

In addition, due to the widespread resistance of bacteria to the available drugs, naturally occurring antimicrobial peptides (AMPs) are considered promising candidates for future therapeutic use. Furthermore, the peptides should have a broad spectrum against Gram-positive bacteria, Gram-negative bacteria and fungi.

Few studies have exploited the immobilization of AMPs in several films through a covalent attachment and by oppositely charged polypeptide to make 10-bilayer polyelectrolyte films by electrostatic layer-by-layer self-assembly (LbL), with success. In both cases, several advantages are related including long-term stability and lower toxicity of the AMPs when compared to the incorporation into release-based systems [15,16]. Bagheri et al. concluded that among the various methods of immobilization of AMPs, covalent attachment of two highly active α-helical peptides (that rendered the different substrates (resins) antimicrobial properties) offers several advantages, including long-term stability and lower toxicity of the AMPs compared to incorporation into release-based systems [15]. In another work, Zhong et al. used oppositely charged polypeptide to make 10-bilayer polyelectrolyte multilayer films by electrostatic layer-by-layer self-assembly (LbL), with success. Cysteine was included in the peptides to promote disulfide bond formation and film stability [16].

In general, cationic AMPs with best antimicrobial activity are molecules that have the charged and hydrophilic portions separated from the hydrophobic areas. This means that either amphipathic or cationic double-wing structures with a hydrophobic core separating two charged segments are preferred [14]. In accordance to this, Cathelicidin peptides range in length from 12 to 80 residues, and may have α-helical, β-sheet or other types of tertiary structures [13,15]. In contrast, defensins are more uniform in their appearance. They are small cysteine-rich AMPs that mainly form β-sheet structures stabilized by three or (rarely) four conserved intramolecular cystine disulphide bridges [12,13,15].

AMPs which can both be attached to polymers or form films are expected to bind several polymer-based textiles by exhaustion or LbL assembly. Likewise, our previous results with L-Cys give a guarantee of success for these new antimicrobial textiles because peptides can be attached to textiles in a similar way.

Conclusions

New strategies are considered for material functionalisation with antimicrobial properties. In particular, it was discussed the potential of L-Cys and AMPs as natural antimicrobial agents for textiles. This could not only find a sphere of influence in the wellness sector but the ambition is to use them as prophylaxis and therapy tools. Consequently, biofunctionalisation of textile-based materials with defensive amino acids and peptides at nanoscale is an innovative approach and may open new avenues for the design of medical and healthcare composite textiles.

This is a new strategy and approach aiming to mimetize nature through biologically inspired tools to give "protective skin" to textiles.

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BİYOMİMETİK KİTOSAN/ÇİFT FAZLI KALSİYUM FOSFAT KOMPOZİTLERİNİN KEMİK DOKU MÜHENDİSLİĞİ İSKELESİ OLARAK KULLANIMI

BIOMIMETIC CHITOSAN/BIPHASIC CALCIUM PHOSPHATE COMPOSITE SCAFFOLDS FOR BONE TISSUE ENGINEERING

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Özet

Kitosan FDA ve CE tarafından yara iyileşmesinde kullanılmak üzere onaylanmış, pek çok kontrollü ilaç salımı ve doku mühendisliği uygulaması için denenen doğal bir biyobozunur polimerdir. Ancak kemik hücrelerinin tutunması ve üremesi için gerekli olan osteokonduktiviteyi göstermemektedir. Kalsiyum fosfatlar ise kemik onarımında sıkça kullanılan, kimyasal yapıları kemik mineraline benzeyen minerallerdir. Bu çalışmada BCP parçacıkları kitosanla karıştırılarak kültür ortamında biyomineralizasyonu mimik eden kompozitler üretilmiş ve bu kompozitlerin *in vitro* osteokonduktiviteleri ile kemik matris organizasyonu üzerine etkileri incelenmiştir. Dondurup kurutma (freeze drying) yöntemi ile ortalama 100 mm çaplı, istenen birbiriyle bağlantılı gözenek yapısı elde edilmiştir. Kültür besiyeri içinde üç gün içinde kompozit iskelelerde biyomimetik, kemik minerali benzeri bir kalsiyum fosfat (CaP) çökeltisi gözlenmiştir. Hücreler iki hafta içinde tip1 kolajen ekstraselüler matris üretimine başlamışlardır. Dört hafta sonunda ise hücrelerin ürettiği kolajen fibriller üzerinde doğal mineralizasyon gözlenmiştir. Bu mineraller besiyerinden yüzeye biriken CaP çökeltilerinden farklı morfoloji göstermekte ve doğal kemik oluşumunda olduğu gibi kolajen liflerin üzerinde küçük çubuklar halinde olmaktadır. Dört haftalık kültüvasyon dönemi sonunda kompozit iskeleler içindeki hücre ve matris dağılımı homojen olurken kitosan iskelelerde hücreler iskele yüzeylerinde yoğunlaşmıştır. Ayrıca kompozit iskeleler içinde osteoblastik tanımlayıcı proteinlerin daha yüksek oranda eksprese edilmesi sağlanmıştır. Bu sonuçlar, ekstraselüler kalsiyumun kemik hücrelerinde var olan Ca^{2+} reseptörlerini tetikleyerek hücreler üzerinde kemotaksi yaratmasına ve iskele yüzeylerinde oluşan çökeltinin hücre morfolojilerini osteoblastik olgunlaşmayı destekleyici yönde değiştirmesine bağlıdır. Bu sonuçlar, BCP'nin polimer iskelelere eklenmesinin iskele osteokonduktivitesini arttırdığını ve kitosan/BCP kompozit iskelelerinin kemik doku mühendisliği uygulamalarında iskele malzemesi olarak başarıyla kullanılabileceğini göstermektedir.

Abstract

Several biodegradable polymers including polylactides, polyglycolides, polyanhydrides and collagen are being investigated as bone tissue engineering scaffolds [1,2]. Chitosan has several potential advantages over other biodegradable polymers in these applications. It is hydrophilic and has a net (+) charge that enables electrostatic interactions with cells and proteins. Its principal degradation product, glucosamine, is a naturally occurring sugar [3]. It is also approved by FDA and received CE mark for wound healing applications. But chitosan lacks the osteoconductivity that is required for attachment and proliferation of bone cells. Calcium phosphates are commonly used for bone repair and regeneration because their chemical composition resembles the inorganic component of bone [7-8]. Biphasic calcium phosphate (BCP) is a mixture of hydroxyapatite, and tricalcium phosphate with a degradation rate that is intermediate between the two phases and more compatible with new bone formation rates [9]. In this study, BCP particles were added to chitosan to produce a composite structure that mimics bio-mineralization after they are cultured in cell growth media, and the composites were evaluated for their osteoconductivity and effects on bone matrix organization.

Cylindrical scaffolds measuring 5 mm diameter and 4 mm height were fabricated using a freeze-drying technique. 2% chitosan solutions in 0.2M acetic acid were frozen in molds to induce solid – liquid phase separation and lyophilized. Composite scaffolds were fabricated by mixing 25 %wt BCP particles into the solutions before freezing. Porosity and the pore size were measured by mercury porosimetry. Scaffold microstructure was evaluated using scanning electron microscopy (SEM), and elemental analysis was performed by EDX. Scaffolds were sterilized by 70% EtOH prior to cell seeding. Mouse mesenchymal stem cells were suspended in expansion media and seeded onto chitosan and composite scaffolds at a density of $8x10^4$ cells/scaffold. After one day of culture, the media were replaced with bone differentiation media. Cell – scaffold constructs were cultured for up to 4 weeks. At specified time points, samples were fixed with 2.5% gluteraldehyde for SEM and transmission electron microscopy (TEM), 4% paraformaldehyde for histology, or

homogenized with TritonX-100 buffer for spectrophotometric measurements. Histology sections were stained with hematoxylin and eosin (H&E). Alkaline phosphatase (ALP) enzyme activity and osteocalcin production were measured by spectrophotometric assays.
All constructs supported cell growth and proliferation. Precipitation of a biomimetic bone mineral-like calcium phosphate (CaP) phase onto composite scaffolds was observed as early as the third day of culture. No such precipitation was observed on chitosan scaffolds. Extracellular matrix production by cells was visible by 2 weeks. By 4 weeks, composite scaffolds showed a more uniform cell distribution and matrix production throughout the scaffolds while the cells were located preferentially on the surface of chitosan scaffolds without BCP. This can be explained by the chemotaxis effect of Ca^{2+} within the biomimetic precipitations. Composite scaffolds showed higher values for both ALP and osteocalcin. ALP is expressed after the proliferative stage and it is commonly used as a marker of osteoblastic maturation. Osteocalcin is a bone specific protein expressed highest at the onset of mineralization. Higher values of ALP and osteocalcin on composite scaffolds suggest increased maturation and phenotype expression of cells with the presence of extracellular Ca^{2+}, and the organization of cell morphology on the CaP precipitates in a way to support osteoblastic maturation.

Higher proliferation, more uniform distribution and matrix production of osteoblastic cells in the presence of BCP, as well as enhanced expression of marker proteins for the osteoblastic phenotype are possibly due to a chemotactic effect of Ca^{2+} and the modification of composite scaffold surfaces due to precipitation of CaP crystals during culture. These effects support the use of BCP as a means for increasing osteoconductivity in polymeric scaffolds and suggest that chitosan/BCP composites are attractive candidates for bone tissue engineering applications.

Giriş ve Amaç

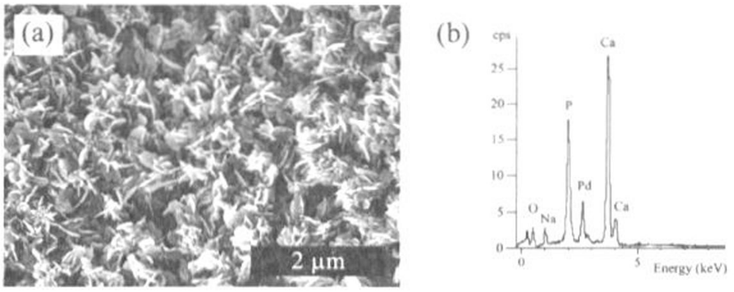
Polilaktitler, poliglikolitler, polianhidritler ve kolajen gibi pek çok biyobozunur polimer kemik doku mühendisliği iskelesi olarak kullanılmak amaçlı araştırılmaktadır [1,2]. Bu tip uygulamalarda kitosanın diğer biyobozunur polimerlere kıyasla pek çok avantajı bulunmaktadır. Örneğin kitosan hidrofiliktir ve üzerindeki net (+) yük hücreler ve proteinlerle elektrostatik olarak etkileşmesini sağlamaktadır. Bozunma sonucu açığa çıkardığı glukozamin doğal bir şekerdir [3]. Ayrıca kitosan FDA ve CE tarafından yara iyileşmesinde kullanılmak üzere onaylanmıştır. Bu sebeplerden ötürü kitosan pek çok kontrollü ilaç salımı ve doku mühendisliği uygulaması için denenmektedir [4-6]. Ancak kitosan kemik hücrelerinin tutunması ve üremesi için gerekli olan osteokonduktiviteyi göstermemektedir. Kalsiyum fosfatlar ise kemik onarımında sıkça kullanılan, kimyasal yapıları kemik mineraline benzeyen minerallerdir [7-8]. Çift fazlı kalsiyum fosfat (BCP), hidroksiapatit ve trikalsiyum fosfatın bir karışımı olup bozunma süresi her iki fazın arasında bulunan ve yeni kemik oluşumuna daha uyumlu bir mineraldir [9]. Bu çalışmada BCP parçacıkları kitosanla karıştırılarak kültür ortamında biyomineralizasyonu mimik eden kompozitler üretilmiş ve bu kompozitlerin *in vitro* osteokonduktiviteleri ile kemik matris organizasyonu üzerine etkileri incelenmiştir.

Materyal ve Metodlar

5 mm çap ve 4 mm yüksekliğindeki silindirik doku iskeleleri dondurup kurutma (freze drying) yöntemi ile üretilmiştir. 0.2 M asetik asit içinde %2'lik kitosan çözeltisi hazırlanmış ve kalıplar içinde katı-sıvı faz ayrışması için dondurulan çözeltiler liyofilize edilmiştir. Kompozit iskelelerde BCP parçacıkları çözeltilere dondurma öncesinde eklenmiştir. Gözeneklilik oranı ve gözenek büyüklükleri cıva porozimetresiyle ölçülmüştür. İskele mikroyapısı taramalı electron mikroskobu (SEM) ile görüntülenmiş ve elemental analiz EDX yöntemiyle yapılmıştır. Hücre ekimi öncesi doku iskeleleri %70'lik etanol ile sterilize edilmiştir. Fare kemik iliği kökenli mezenşimal kök hücreler süspanse halde iskelelere $8x10^4$ hücre/iskele yoğunluğunda ekilmiştir. İskele içinde hücreler çoğaltma besiyerinde bir gün tutulduktan sonra askorbik asit ve beta glisero-fosfat içeren kemik farklılaştırma besiyerine geçilerek dört haftaya kadar kültüve edilmiştir. Belirlenen zamanlarda iskeleler SEM ve transmisyon elektron mikroskop (TEM) analizi için %2,5'lik gluteraldehitle, histoloji için %4'lük paraformaldehitle sabitlenmiş, ya da spektrofotometrik ölçümler için TritonX-100 tampon çözeltisi ile homojenize edilmiştir. Histoloji kesitleri hematoksilin ve eozin (H&E) ile boyanmıştır. Spektrofotometrik olarak da alkalin fosfataz (ALP) enzim aktivitesine ve osteokalsin üretimine bakılmıştır.

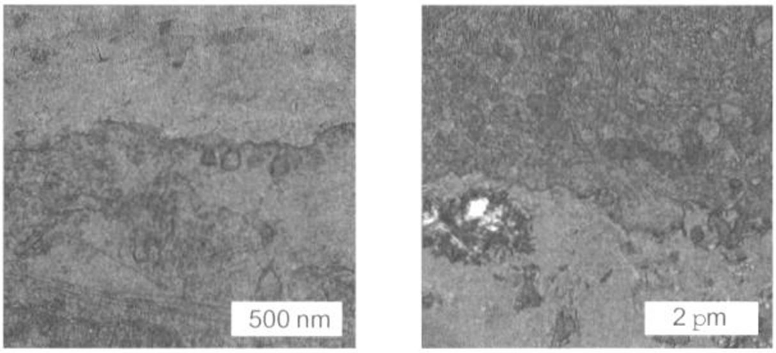
Bulgular

Dondurup kurutma yöntemi ile ortalama 100 mm çaplı, istenen birbiriyle bağlantılı gözenek yapısı elde edilmiştir. Bütün iskeleler hücre büyüme ve çoğalmasını desteklemiştir. Kültür besiyeri içinde üç gün içinde kompozit iskelelerde biyomimetik, kemik minerali benzeri bir kalsiyum fosfat (CaP) çökeltisi gözlenmiştir. Kitosan iskeleler üzerinde benzer bir çökelti gözlenmemiştir (Şekil.1).



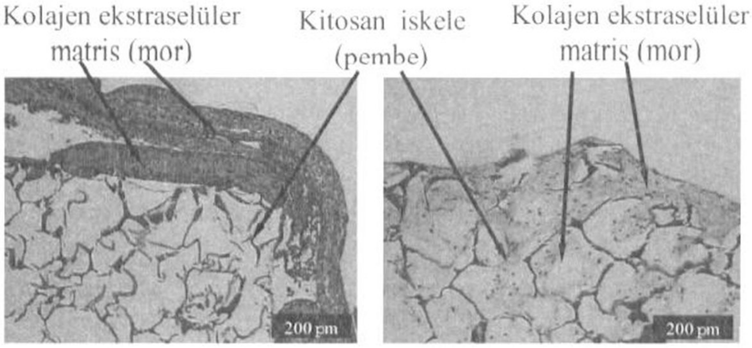
Şekil.1: *(a) Kitosan/BCP iskeleler üzerinde gözlenen biyomimetik CaP çökeltileri (SEM). (b) EDX analizi oluşan çökeltilerin kemik mineralini ile benzer Ca/P oranına (1.67) sahip olduklarını göstermiştir.*

Hücrelerde iki hafta içinde tip1 kolajen ekstraselüler matris üretimi gözlenmiştir. Dört hafta sonunda ise hücrelerin ürettiği kolajen fibriller üzerinde doğal mineralizasyon gözlenmiştir. Bu mineraller besiyerinden yüzeye biriken CaP çökeltilerinden farklı morfoloji göstermekte ve doğal kemik oluşumunda olduğu gibi kolajen liflerin üzerinde küçük çubuklar halinde oluşmaktadır (Şekil.2).



Şekil.2: *Elektron mikroskobu (TEM) görüntüleri hücrelerin kompozit iskeleler üzerinde tip 1 kolajen üretip dört hafta içinde bu kolajenin mineralizasyonunu sağladıklarını göstermiştir.*

Dört haftalık kültüvasyon dönemi sonunda kompozit iskeleler içindeki hücre ve matris dağılımı homojen olurken kitosan iskelelerde hücreler iskele yüzeylerinde yoğunlaşmıştır (Şekil.3).



Şekil.3: *Histoloji sonucu dört hafta sonunda hücrelerin ve ürettikleri kolajen ekstraselüler matrisin kitosan iskelelerin yüzeyinde biriktiği gözlenirken kompozit iskeleler içince homojen bir dağılım gözlenmektedir.*

Bu gözlemin sebebi kemik hücrelerinin bütün iskele içine dağılmış biyomimetik CaP'ın kemik hücrelerinde var olan Ca^{2+} reseptörlerini tetikleyerek hücrelerde kemotaksi oluşturmasıdır [10]. Kompozit iskeleler üzerinde ALP ve osteokalsin değerleri de daha yüksek bulunmuştur. ALP hücrelerin osteoblastik olgunlaşmasının göstergesi olarak kullanılan bir enzimdir. Osteokalsin de kemik hücrelerinde mineralizasyonun başlaması ile salgılanır. Bu iki değerin kompozit iskeleler üzerinde daha yüksek olması ortamdaki ekstraselüler kalsiyumun hücreleri uyarması ve CaP çökeltileri üzerinde hücre morfolojisinin osteoblastik farklılaşmayı destekleyici yönde gelişmesinden kaynaklanmaktadır.

Tartışma ve Sonuç

Kompozit iskelelerde BCP'nin varlığı biyomimetik CaP çökeltileri oluşturmuş ve bu çökeltiler sayesinde hücrelerin ve ekstraselüler matrislerinin iskele içinde daha homojen dağılımı ve osteoblastik tanımlayıcı proteinlerin daha yüksek oranda eksprese edilmesi sağlanmıştır. Bu sonuçlar, ekstraselüler kalsiyumun hücreler üzerinde kemotaksi yaratmasına ve iskele yüzeylerinde oluşan çökeltinin hücre morfolojilerini osteoblastik olgunlaşmayı destekleyici yönde değiştirmesine bağlıdır. Bu sonuçlar, BCP'nin polimer iskelelere eklenmesinin iskele osteokonduktivitesini arttırdığını ve kitosan/BCP kompozit iskelelerinin kemik doku mühendisliği uygulamalarında iskele malzemesi olarak başarıyla kullanılabileceğini göstermektedir.

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GIDA AMBALAJI UYGULAMALARINA YÖNELİK MISIR PROTEİNİ NANOKOMPOZİTLERİ KAPLI POLİPROPİLEN FİLMLERİN HAZIRLANMASI

CORN ZEIN NANOCOMPOSITE COATED POLYPROPYLENE FILMS FOR FOOD PACKAGING APPLICATIONS

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ÖZET

Petrol bazlı sentetik polimerler sundukları çeşitli çözümler nedeniyle gıda ambalajı uygulmalarında çok yoğun bir biçimde kullanılmaktadırlar. Ancak günümüzde sentetik polimerlerin çevre üzerine olan etkileri sorgulanmaktadır. Biyopolimerler doğada çok yavaş bozunan sentetik bazlı polimerlere alternatif olarak dikkat çekmektedirler. Yıllık bitkisel yenilenebilir kaynakları ve biyobozunurluk özellikleri nedeni ile protein bazlı polimerler pek çok gıda ambalaj uygulaması çalışmasına konu olmuşlardır. Mısır proteinin de dahil olduğu pek çok protein polimeri ekstrüzyon ile film haline getirilebilmekte; güçlü oksijen bariyeri ve ortalama su buharı bariyeri ile potansiyel birer gıda ambalaj malzemesi olarak görülmektedirler. [1] Mısır proteininin gıda ambalajı uygulamaları açısından pek çok ilgi çekici özelliği olsa da, özellikle zayıf mekanik özellikleri nedeni ile halihazırda tek başına kullanımı imkansızdır. Protein bazlı biyobozunur filmlerin özelliklerini iyileştirmek amacı ile pekçok çalışma yapılmakta, ve bu çalışmalar arasında nanokompozit uygulamaları özellikle gelecek vaadetmektedirler. Tabakalı silikatlar ile hazırlanan nanokompozitler; nano-dolguların verimli bir biçimde matris içerisinde başarılı bir şekilde dağıtılmaları sonucu oluşturdukları güçlü bağlar nedeni ile polimer özelliklerinde benzersiz iyileştirme olanakları sunmaktadırlar. Pek çok çalışmada

nanokompozit uygulamaları ile polimerlerin bariyer, mekanik ve termal özelliklerinde kayda değer iyileşmeler olduğu bildirilmiştir. [2,3,4]

Bu çalışmada, mısır proteininin yüksek oksijen bariyerinden faydalanarak mevcut bariyer filmlere alternatif olabilecek gıda ambalaj uygulamalarına yönelik mısır proteini nanokompozitleri ile kaplanmış (MPNK) polipropilen (PP) filmleri hazırlanmıştır. Mısır proteini nanokompozit tabakasının hazırlanmasında kullanılan nano kil miktarının, tipinin ve nanokompozit hazırlama metodunun MPNK kaplı PP filmlerin (MPNK-PP) bariyer, optik ve yüzey özellikleri üzerine olan etkileri incelenmiştir. Sıvı yaklaşımı metodu ile polimer yapıya dahil edilen organomodifiye tabakalı silikat nanokillerinin (OMTS) MPNK-PP filmlerin bariyer özelliklerini belirgin biçimde iyileştirdiği gözlemlenmiştir. 5.9 mikrometre kalınlığındaki, kütlece %5 OMTS içeren MPNK katmanı ile kaplanan filmler baz PP filmler ile karşılaştırıldığında, oksijen geçirgenliği değerlerinin 4 kat, su buharı geçirgenliklerinin ise %30 oranında azaldığı görülmüştür. MPNK tabakalarının tek başına özellikleri de bu çalışmada incelenmiştir. Oksijen ve su buharı bariyer özelliklerinde elde edilen iyileşmelerin nanoboyutlu silikat tabakalarının etkili biçimde açılması sonucu artan dolambaçlı difüzyon yoluna bağlı olarak gerçekleştiği belirlenmiştir. Ağırlıkça %5 nanodolgu içeren tek başına mısır proteini tabakasının oksijen geçirgenliği %65 oranında, su buharı geçirgenliği ise %60 oranında düşürülmüştür. Su buharı bariyeri ile uyumlu olarak, MPNK kaplı yüzeylerin hidrofobik özellikleri OMTS ilavesi ile artmıştır. Bunun yanında, modifiye olmayan doğal kil ve sonikasyon yerine karıştırma ile hazırlanan filmlerde gözlemlenen iyileşmelerin daha az belirgin olduğu gözlemlenmiştir. Bariyer iyileştirmelerine ek olarak, organomodifiyeli nanokiller ile hazırlanan filmlerin renginde çıplak göz ile ayırt edilebilecek herhangi bir değişiklik gözlemlenmezken, doğal kil ile hazırlanan filmlerde kil dağılımının iyi olmamasından kaynaklı belirgin renk değişimlerine rastlanılmıştır.

Sonuç olarak biyobozunur bir polimer olan mısır proteininin yüksek oksijen bariyeri ile mekanik olarak dayanıklı olan PP filmlerinin özellikleri mevcut bariyer filmlerine çevreci bir alternatif oluşturabilecek şekilde başarılı bir biçimde birleştirilmiştir. Mısır proteini tabakasına dahil edilen organomodifiyeli tabakalı silikatlar ile oksijen ve su buharı bariyer özellikleri başarılı bir şekilde arttırılmıştır. Bunun yanında polimer matrise dolgu eklenmesi ile kompozit sistemler için bilinen bir sorun olan renk kayıpları ise minimumda tutulmuştur.

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Abstract

Synthetic polymers are dominating the food packaging industry today, since they offer versatile solutions for requirements of food packaging. For over decades, environmental impact of polymers are being questioned because of their very slow degradation in nature. Biopolymers offer a noticeable potential of replacing conventional petroleum based polymers in food packaging materials. Protein based biopolymers are attracting many research because of their annually renewable sources and high biodegradability. Protein based biopolymers including corn zein can be shaped into films and have excellent barrier to gases and moderate barrier to water vapor [1]. Corn zein can not be used in stand-alone film applications due to current status, since it has characteristic disadvantages of biopolymers such as poor mechanical properties. Many research has been done on protein based biopolymers in order to improve their properties. Among these efforts, nanocomposites, that draw attention in many fields of materials science offer significant potential. Layered silicate nanocomposites offer unique improvements in polymer properties because of stronger interactions due to high aspect ratio of nanofillers when they are efficiently dispersed in the polymer matrix. Significant improvements in mechanical, barrier and thermal properties of polymers were reported in many studies [2,3,4].

In this study, feasibility of prepared novel corn zein nanocomposite (CZNC) coated polypropylene (PP) film (CZNC-PP) structures as an alternative for traditional synthetic barrier films for food packaging applications were investigated. The effect of nano-sized layered silicate amount, type and processing of CZNC layer on the barrier, optical and surface properties of the CZNC-PP films were investigated. Incorporation of organomodified montmorillonite (OMMT) by solution intercalation into zein coating matrix improved barrier of PP films significantly. Prepared CZNC-PP films achieved nearly 4 times reduced oxygen permeability while WVP of the films were reduced by 30% with 5 wt% OMMT content in 5.9 μm corn zein coating. The properties of single CZNC layers were also investigated. Fine delamination of

OMMT in zein coating was found to be responsible for the improvements in oxygen and water vapor barrier of single corn zein layers due to more tortuous path formed for permeation of oxygen and water vapor. 5 wt % nanofiller content delaminated in the zein layer reduced the oxygen permeability of single corn zein layers by 65% and reduced water vapor permeability by 60% as well. Hydrophobicity of CZNC surface increased with increasing OMMT loading in accordance with WVP results. Meanwhile, improvements were less significant for unmodified nanoclay loadings due to the incompatibility between unmodified MMT and corn zein and also for samples prepared by stirring only instead of sonication. Besides barrier improvements in CZNC layers, no detectable color difference by naked eye was observed in CZNC coatings for samples prepared by using organomodified nanoclays. On the contrary, samples prepared by using natural montmorillonite exhibited significant color deteriorations due to inefficient dispersion of nanoclays in the coating matrix.

Finally, excellent barrier properties of corn zein nanocomposites were successfully combined with mechanically strong PP as an eco-friendly promising alternative to conventional barrier packaging systems. Organomodified layered silicates incorporated to corn zein matrix successfully improved oxygen and water vapor barrier properties. Additionally, color deteriorations, being a known problem for conventional composite systems kept at minimum by the application of nanocomposites.

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GIDA AMBALAJLARI İÇİN OKSİJEN BARİYER ÖZELLİĞİ SAĞLAYAN DAYPE/ORGANOKİL NANOKOMPOZİTLERİN GELİŞTİRİLMESİ

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Polimerler içerisinde nanotaneciklerin dağılımı, polimere geleneksel mikro boyutlu katkıların kullanılmasından çok daha üstün özellikler kazandırmaktadır. Sinerjik reaksiyonlardan kaynaklanan yeni özellikler, nanokompozitleri çok geniş bir kullanım alanı için cazip hale getirmektedir. Bu olağandışı özellikler, katmanlı silikatların dağılımı ve nanometre seviyelerinde polimer matris ile sarmalanması ile ilişkilendirilmektedir. Nanotanecikler vasıtasıyla mekanik dayanım, yanmazlık ve bariyer özelliklerinin geliştirilmesi özellikle gıda paketleme endüstrisinin ilgisini çekmektedir.

Gıdaların raf ömrünü uzatabilecek polimer nanokompozit ambalajların elde edilmesine yönelik bu çalışmada, tarafımızdan geliştirilmiş masterbatch katkıların ambalaj malzemelerine kazandırdığı özellikler incelenmiştir.

Bu amaçla çalışmanın ilk aşamasında doğrusal alçak yoğunluklu polietilen (DAYPE, MFI:20 g/10 dk.), maleik anhidrit aşılanmış polietilen (PE-g-MA, MFI:23 g/10 dk.) ve organik olarak modifiye edilmiş nano tanecikler, çift vidalı ekstrüderde karıştırılarak ağırlıkça %20 nanokil içeren bir masterbatch hazırlanmıştır. Çalışmanın ikinci aşamasında doğrusal yoğunluklu polietilen (DAYPE, MFI:2 g/10 dk.) içerisine hazırlanan bu masterbatchten çeşitli oranlarda katılarak "cast film" hattında 100 mikron kalınlığında filmler çekilmiştir.

Bu üretilen filmlerin fiziksel ve kimyasal özellikleri X-Işınları Kırınımı (XRD), Fourier Dönüşümlü İnfrared Spektroskopisi (FTIR), Taramalı Elektron Mikroskop

(SEM), Diferansiyel Taramalı Kalorimetri (DSC), çekme testi ve oksijen geçirgenlik ölçümü ile belirlenerek filmlerin performansları değerlendirilmiştir. Ürünlerin raf ömrü analizlerini yapmak amacı ile de DAYPE ve DAYPE nanokompozit filmlerden 260mm x 370 mm ebatlarında ambalajlar üretilmiş ve bu ambalajlar içerisinde taze meyveler +4°C' de muhafaza edilerek görsel raf ömrü analizleri gerçekleştirilmiştir. Bu esnada; ürünlerde meydana gelen fizyolojik bozunmalar üzerindeki O_2 ve CO_2 gazlarının etkileri görebilmek amacıyla da, ambalaj içi atmosferde meydana gelen değişimler (O_2/CO_2) günlük olarak kaydedilmiştir.

Bu deneysel değerlendirmeler neticesinde, filmlerde "exfoliated/intercaleted" karışımı bir yapının elde edildiği, filmin saydamlığı, tokluğu ve toklukla bağıntılı mekanik özelliklerinde önemli bir azalma olmaksızın oksijen geçirgenliğinin %42 oranında azaltıldığı tespit edilmiştir. Bu filmler kullanılarak elde edilen ambalajlarda muhafaza edilen gıdaların raf ömrünün ise, ambalaj içi atmosferdeki oksijen seviyesinin %10'lara kadar düşürülmesi sayesinde, 2 kata kadar uzatılabildiği ispatlanmıştır.

Anahtar Kelimeler: Polimer Nanokompozit, Bariyer Film, Masterbatch, Gaz Geçirgenlik, Gıda Ambalajlama

1. Introduction

Research showed that, 25% of the total annual fruit and vegetable production are discarded in our country, without consuming them. Millions of people cannot reach to staple food because of global warming, economical crisis and rising population. Therefore the shelf-life and preservation of these food products are more important than before.

Understanding the degradation mechanisms in the foods is important for preserving them properly and for increasing their shelf-lives. Although preservation techniques such as "controlled atmosphere storage" and "active packing system" developed on the basis of the degradation mechanisms are effectively used at the present time. The most important reason for these techniques cannot fulfill the effective/economical/ergonomic preservation conditions fully. Nowadays, in order to provide better preservation conditions, a lot of studies about polymer nanocomposites are conducted.

Nanoclays offer several advantages over conventional micro-sized clays in polymer composites, and provide better thermal stability, better conductivity properties, and better mechanical and gas barrier properties, without any significant reduction in other relevant properties, including toughness [1-4]. Another advantage is that the material keeps its transparency, if clay loading level is not higher than 5%. Food packaging using nanocomposites extends the shelf life of food by preventing diffusion of humidity, oxygen, ethylene, aroma etc. Furthermore, natural silicates are approved by institutions such as Food and Drug Administration (FDA) for use as additives in plastic materials and articles intended to come into contact with foodstuffs [5].

The present study includes optimization of experimental variables involved in the production of LLDPE nanocomposite films. Some properties of these films were determined by XRD, FTIR, SEM, DSC and tensile tests. The shelf life analysis and oxygen permeability tests were done on fruits which were stored in LLDPE based nanocomposite films. The significant results of the study are that the transparencies of the films are not changed appreciably; oxygen permeability decreased by 42% and the shelf-lives of foods preserved using these films extended up to 2 fold.

2. Experimental

2.1. Materials

In this study, the used nanoadditive was onium ion modified montmorillonite (MMT) (CEC=125 meq/100 g) supplied from Nanocor Inc. Two different LLDPE's were used. For preparing of masterbatch, LLDPE (SABIC-LLDPE M200024) (MFI=20 g/10 min.), for preparing of nanocomposite film, LLDPE (SABIC-LLDPE 218N) (MFI=2 g/10 min.). The used compatibilizer is 1% maleic anhydride containing PE grafted maleic anhydride (PE-g-MA) which was supplied from CLARIANT PE-g-MA 435 (MFI=23 g/10 min).

2.2. Sample Preparation

Masterbatch and nanocomposite samples were prepared by melt blending in a Werner&Pfleider GmbH. Z SK 25 (Diameter=25 mm, L/D=48), co-rotating screw extruder. Firstly, a masterbatch was formed by mixing 20% LLDPE with 60%wt PE-g-MA and 20%wt nanoclays in the twin screw. Then, nanocomposite was prepared by mixing of 25% prepared masterbatch with 75%wt LLDPE. The temperature zones and screw speeds of extruder were set in suitable conditions. Final nanocomposite composition was designated 80%wt LLDPE, 15%wt PE-g-MA, and 5%wt organoclay. Finally, nanocomposite films were produced by using cast film line with the screw speed of 50 rpm and drawing ratio of 2.5 m/min.

2.3. Sample Characterization

Sample characterization was done with XRD, FTIR, SEM and DSC. Mechanical test, oxygen permeability and shelf life analysis were also applied to films.

3. Results and Discussions

3.1. X-Ray Diffraction (XRD)

X-Ray Diffraction was used to characterize to clay dispersion in the LLDPE nanocomposites and made by using Shimadzu XRD 6000 Model Diffractometer CuKα radiation (λ=1.5405 Å). XRD spectrums samples are showed in Figure 1.

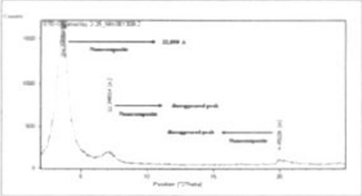

Figure 1. XRD Spectrums of Nanoclay and LLDPE Nanocomposite Sample

As it can be seen in Figure 1, distance between interlayer of nanoclay of 24 Å increased to 32.95 Å in nanocomposite where the other two peaks were disappeared. As a result of these evaluations, it is determined that nanocomposite sample has a mixture of intercalated/exfoliated morphology.

3.2. Fourier Transform Infrared Spectrometer (FTIR)

The FTIR spectra of LLDPE and LLDPE nanocomposite samples were recorded with a Digilab spectrometer, Excalibur-FTS 3000 MX model (Digilab, USA) in the region of 400-6500 cm^{-1} with a 2 cm^{-1} resolution. Characteristic absorption bands that do not exist in FTIR spectrum of LLDPE films but are observed in FTIR spectrum of nanocomposite films give information about the evidence of the presence of nanoparticles in structure and composition of nanoparticles. This is explicitly seen in Figure 2.a and 2.b. Identification of FTIR spectrum peaks is given in Table 1.

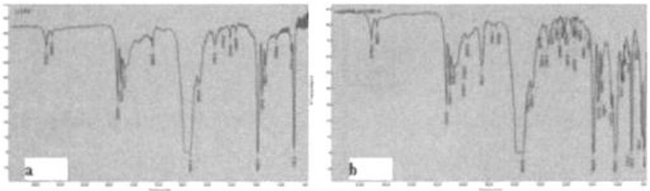

Figure 2. FTIR spektrum of **a)** LLDPE film **b)** LLDPE-nanocomposite film

Table 1. Identification of FTIR Spectrum Peaks

Peaks (cm^{-1})	Identification
64, 521	Si-O-Si and Si-O-Al bending peaks
847, 889, 918	AlMgOH, AlFeOH, AlAlOH

950-1150	Vibration bands of Si-O bonds
1043	Absorption band of the silicate group
3632	OH bond

3.3. Scanning Electron Microscopy (SEM)

SEM Jeol JSM 7000F microscope was operated for SEM analysis at 5 kV. Film samples cross sections were prepared by cryo-microtomy.

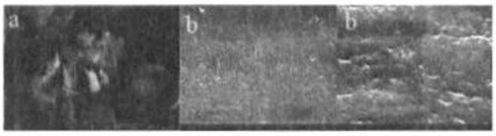

Figure 3. SEM Micrograph of **a)** Presence of a Nanoclay Agglomerated in LLDPE **b)** Nanocomposite Films Dispersed Homogenous

SEM micrographies of the nanoclays that have been agglomerated in polymer matrix are given Figure 3.a. It can be seen in Figure 3.b that there is no agglomeration in nanocomposite films obtained and nanoclays have homogeneous dispersion in polymer matrix.

3.4. Differential Scanning Calorimeter (DSC)

The melting temperature and the dynamic crystallization temperature (Tc) of samples were determined using a TA Instruments DSC Q400 (in helium atmosphere). The crystal content was determined according to the following equation:

$$X = \Delta Hm \ / \ f \ . \ \Delta Ho \qquad (1)$$

where ΔHm is entalphy melting, *f* is effective weight fraction of PE in mixture; and ΔHo is enthalpy of melting for 100% crystalline PE (293.6 J/g).

Table 2. DSC Results of the Nanocomposite Film

Sample	Heating			Cooling			X (%)
	Tm(°C)	Tmp(°C)	ΔHm(J/g)	Tc(°C)	Tcp(°C)	ΔHc(J/g)	
LLDPE	116.84	123.93	40.10	109.15	105.84	89.61	13.66
Nanocomposite	116.73	120.14	28.97	108.98	106.65	79.38	10.39

where Tm is melting temperature, Tmp is the peak point of melting temperature, Tc is crystallization temperature, Tcp is is the peak point of crystallization temperature, and ΔHc is enthalpy of crystallization.

The melting point decreases by the addition of clay to the polymer. Moreover, addition of clay decreases the percent crystallinity.

3.5. Tensile Tests

Tensile tests were performed on an Instron 3345 testing machine at room temperature. Tensile strength test results are shown in Table 3. 20% better tensile strength can be obtained by addition of nanoclays in polymer matrix. Moreover, increase in tensile strength of LLDPE nanocomposite film samples compared to LLDPE samples is the indicator of a high interaction between polymer molecules and clay layers and homogeneous dispersion of clay layers.

Table 3. Mechanical Test Results

Sample	Strength at max (MPa)	Strain at max (%)	Strength at break (MPa)	Strain at break (%)	50 % Secant modulus (MPa)
LLDPE	11.42 (±2.5)	794 (±2.2)	11.33 (±2.6)	801 (±2.0)	16.77 (±2.0)
Nanocomposites	14.35 (±5.5)	667 (±5.2)	14.19 (±4.6)	669 (±5.6)	15.00 (±3.1)

3.6. Oxygen Permeability Measurement

Oxygen permittance rates of film samples were obtained by using Brugger Feinmechanik GDP-C Gas Permeability Tester at 35°C and 1 atm. Oxygen permeability values are listed in Table 4. Oxygen permeability of nanocomposite films can be decreased by about 42% compared to LLDPE control sample while transparency is saved.

Table 4. O_2 Permeability Test Results of LLDPE and LLDPE Nanocomposite

Sample	O_2 Permeability (cc.100 μm/m^2.day.atm)	Changing Percent
LLDPE	1521	-
Nanocomposite	878	42.20

The decrease in oxygen permeability occurs because the nanoparticles act as a physical obstacle retarding movement of oxygen through the film, slowing down its speed of flow and increasing the distance that oxygen must cover to cross the film. In the LLDPE sample, oxygen does not find any obstacle to prevent its movement through the film. The resulting increase in the shelf life should make the product attractive to diverse markets as the nutritive and organoleptic properties of the food are protected for longer.

3.7. Shelf Life Analysis

Packaging samples of LLDPE and LLDPE nanocomposites films (260 mm x 370 mm) were prepared. Visual shelf-life analysis was accomplished using 300 g fresh fruits wrapped by these packaging materials and kept at +4°C. On the other hand, the variations in the atmosphere within the packaging (O_2 /CO_2) were recorded in order to observe the influence of O_2 and CO_2 on the physiological degradations of the products due to ISO 22000 standard using Oxybaby M O_2/CO_2 analyzer (WITT-GASETECHNICK TYPE).

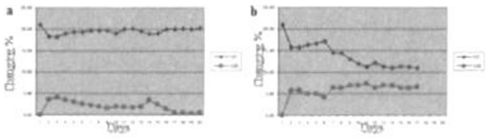

Figure 4. Changes of O_2/CO_2 of Pears Depending on Time in **a)** LLDPE Package **b)**LLDPE Nanocomposite Package

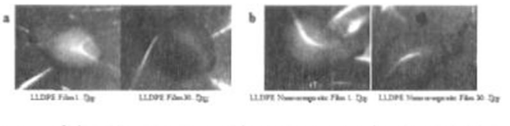

Figure 5. Photos of the Pears Kept **a)** in LLDPE **b)** in LLDPE Nanocomposite Package

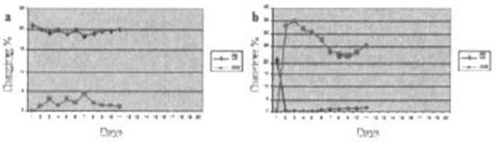

Figure 6. Changes of O_2/CO_2 of Bananas Depending on Time in **a)** LLDPE Package **b)**LLDPE Nanocomposite Package

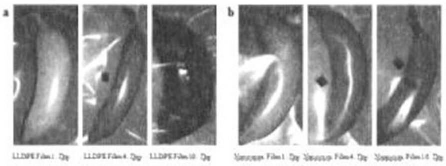

Figure 7. Photos of the Bananas Kept **a)** in LLDPE **b)** in LLDPE Nanocomposite Package

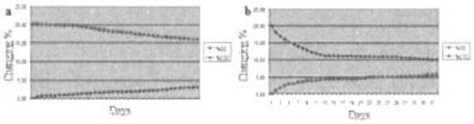

Figure 8. Changes of O_2/CO_2 of Apricots Depending on Time in **a)** LLDPE Package **b)** LLDPE Nanocomposite Package

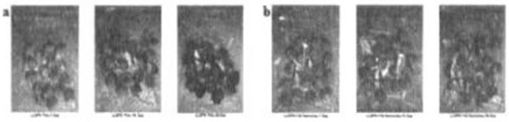

Figure 9. Photos of the Apricots Kept **a)** in LLDPE **b)** in LLDPE Nanocomposite Package

Photos of pears, bananas and apricots and atmospheric gas (O_2/CO_2) analyses are seen at figures. It is thought that fruits continued the respiration activities in the packages. According to the analyses, concentration of O_2 and CO_2 do not change significantly in LLDPE packages which have low oxygene barrier property but concentration of O_2 decreases to 0-10% in LLDPE nanocomposite packages that have high oxygene barrier property. It is clearly seen that shelf lives of the products are increased up to two fold by means of this barrier property.

4. Conclusions

In this study, LLDPE nanocomposite films are prepared and used for packaging in order to increase the shelf-lives of the pears, bananas, and apricots. 100 microns thickness LLDPE nanocomposite films are characterized by physically and chemically. SEM, XRD, FTIR, mechanical tests, O_2 permeability and shelf life analyses of the films are also evaluated. As a result of these evaluations, it is proved that the intercalated nanocomposite films, decrease the oxygen permeability by 42% and increase the shelf-lives of foods up to 2 fold.

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ÜRETİM TEKNOLOJİLERİ I /

PRODUCTION TECHNOLOGIES I

POLİMERİK KARMA(KOMPOZİT) ÜRETİMİNDE SAĞLIK VE GÜVENLİK RİSKLERİ

HEALTH AND SAFETY RISKS IN POLYMERIC COMPOSITES PRODUCTION

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Özet

Polimerik karma(kompozit) işletmelerinde iş sağlığı ve iş güvenliği günümüz en güncel ve önemli konularından biridir. Çünkü, çalışanların sağlık ve güvenliğini korumak şirketler için yasal ve etik bir zorunluluktur. Bu çalışmada, karma süreçlerinde temel sağlık ve güvenlik incelenmiştir. Reçine sistemi ve çözücülerin sağlık riskleri öncelikle ele alınmalıdır. Doğru mühendislik yaklaşımları, yönetimsel kontrollar uygulandığı taktirde işyerleri daha sağlıklı ve güvenli olacaktır.

Abstract

Occupational health and safety in composites businesses today is one of the most current and important issues. To protect employees' health and safety is a must for companies due to the legal requirements and ethical reasons. In this study, substantial health and safety risks in composites processes were discussed. Health risks of resin system used as matrix and solvents should be addressed first. If proven engineering approaches, and administrative controls are applied, the workplaces can be more safe and healthy.

1. Giriş

Herhangi bir işkolunda çalışanların sağlık ve güvenliklerinin korunması ancak sağlık ve güvenliği tehdit eden etkenlerin belirlenmesi, tanınması ve bu etkenlere karşı önlemlerin alınması ile olanaklıdır.

Temel Kavramlar:

Konunun daha iyi anlaşılabilmesi için bazı temel kavramlar üzerinde görüş birliğine varılması gerekmektedir. Pratikte çoğu kez tehlike (hazard), zarar (harm) ve risk kavramları birbiri yerine kullanılmaktadır. Oysa tehlike ve risk farklı kavramlardır. Tehlike "***Büyük zarar veya yok olmaya (yaralanma ve ölümlere) yol açabilecek durum"*** olarak tanımlanmaktadır. Risk ise "***Algılanmakta olan özel bir tehlikenin gerçekleşme olasılığı ve tehlikenin sonuçlarını kapsayan bir kavram"*** dır. OHSAS 18001 standardında da benzer şekilde ***"belirlenmiş tehlikeli bir olayın oluşma olasılığı ve sonuçlarının bileşimi"*** olarak tanımlanmaktadır.

Risk kavramı, içinde hem belirsizlik, hem de riskin algılanmasını kapsamaktadır. Riskteki bilinmezlik ve algılamanın düzeyi karar vericilerin ve çalışanların tutumları üzerinde belirleyici olmaktadır. Sigaranın tehlikeleri çok iyi bilindiği halde, sağlık riskleri bireyler tarafından farklı düzeyde algılanmaktadır. Temel kavramların iyi anlaşılabilmesi için başvurulması gereken iki Türk standardı *"TS ISO/IEC GUIDE 73- Risk Yönetimi- Terim ve Tarifler Standard (Nisan 2005)"* ve *"TS EN 31010-Risk Yönetimi-Değerlendirme Teknikleri (Haziran 2010)"* dur.

Risk değerlendirmesi, ise ***"herhangi bir tehlikeye (örneğin bir tehlikeli kimyasala) maruz kalındığında olabilecek olumsuz etkilerin belirlenmesi sürecidir"*** (Şekil 1). Kimyasal tehlikelerin bulunduğu tipik bir risk değerlendirmesi süreci:

- Tehlikenin belirlenmesi,

- Doz-tepki değerlendirmesi,

- Etkilenim(Maruziyet) değerlendirmesi,

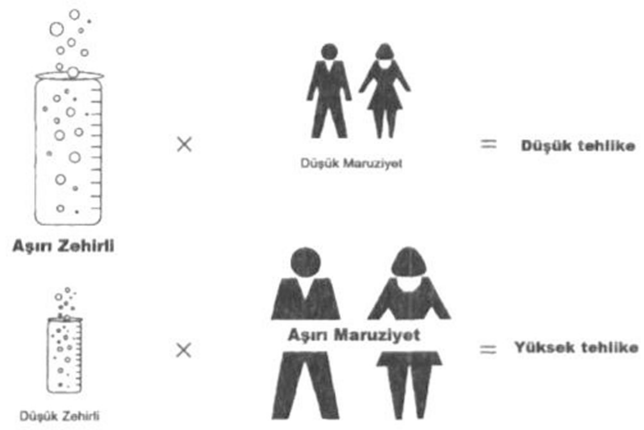
- Risklerin tanımlanması,

adımlarını kapsar.

Risklerin tanımlanması için ilk 3 aşamadaki bilgilere gereksinim vardır. Riskler değerlendirildikten sonra bu risklere maruz kalanlara etkilenenlere iletilmesi, risklerin

anlaşılıp kabullenilmesi ve azaltılması için politika ve stratejilerin belirlenmesi ise "risk yönetimi" olarak bilinir. Görüldüğü gibi bu süreç, tehlikelerin neler olduğunun belirlenmesini, zararın olasılığının ve etkisinin nicel olarak hesaplanmasını, riskli durum gerçekleşirse ne sonuçlar doğuracağının anlaşılmasını, bu sonuçlara katlanılıp katlanılamayacağına karar verilmesini ve zarar azaltma çalışmalarını kapsamaktadır.

Polimerik karma üretiminde de, kimya sanayisinin diğer kollarında olduğu gibi öncelikle "hangi maddeler kullanılmakta?", "bu maddeler nasıl elleçlenmekte (handling)?", "bu maddeler hakkında hangi bilgilere sahibiz?" ve "bu maddelerle ilgili risklerden kaynaklanan zarar nasıl azaltılabilir?" sorularının yanıtlarını aramakla işe başlanır.



Şekil 1: Risk Değerlendirme Eşitliği

2. Polimerik Karma Üretiminde Riskler

Polimerik karma endüstrisinde kullanılan malzemelerin zehirlilik(toksikolojik) etkileri hakkında literatürde pek çok yayın mevcuttur[1]. Bu yayınlar arasında en önemlisi, İleri Kompozit Malzeme Tedarikçileri Derneği (The Suppliers of Advanced Composite Materials Associations, SACMA)'nin İş sağlığı ve Güvenliği(İSG) alt komitesinin yayınladığı "Safe Handling of Composite Materials, 3rd Ed. April 1996)'dır. Bu çalışma polimerik karma üretimi yapanlar için temel bir başvuru kaynağıdır. Bu çalışmada belirtilen polimerik karma endüstrisindeki temel sağlık ve güvenlik tehlikeleri Tablo 1.'de verilmektedir.

Polimerik karma üretiminde mühendislik önlemleri ve yönetimsel kontroller ile önlenebilecek tehlikelerin başında ısıveren(ekzotermik) tepkimelerin kontroldan çıkması gelmektedir. Bu durum genellikle reçine veya prepeg üretimi esnasında tepkimenin ısıl etki ile kontroldan çıkması (runaway) şeklinde kendini gösterir. Kontrolsuz ısıl süreçlerin aşağıdaki durumlarda meydana geldiği bilinmektedir[3]:

... Bir reçinenin uzun süre karıştırılması veya ısıtılması
... Reçinenin çok hızlı ısıtılması
... Reçine aşırı ısındığında müdahale etmemek
... Kirlenme veya yanlış kimyasal kullanımı

Tablo 1: Karma üretim süreçlerinindeki potansiyel sağlık ve güvenlik maruziyetleri

	KARMA(KOMPOZİT) ÜRETİM SÜREÇLERİ										
POTANSİYEL SAĞLIK TEHLİKELERİ	Reçine formulasyonu	Film hazırlama ve prepreg üretimi	Islak elyaf çekme	Elle yatırma	Otomatik bant yerleştirme	Reçine transfer kalıplama	Çekmeli sıkma(pulturusion)	Enjeksiyon kalıplama	Vakum torbalama ve otoklav	Talaşlı üretim ve son işlem	Tamir
1. Deriyle temas, Dermatit/Kızarıklık	X	X	X	X	X	X	X		X	X	X
2. Toz ve/veya çözücü soluma	X	X	X	X	X	X	X	X	X	X	X
3. Sistemik etkiler	X	X	X	X		X	X		X		X
4. Göze sıçrama/Gözle temas	X	X	X	X							X
5. Duman soluma (Ekzotermik)	X	X	X			X	X		X		X
6. Havalandırma/oksijen yetersizliği											X
7. Gürültü										X	X
POTANSİYEL GÜVENLİK TEHLİKELERİ											
8. Mekanik	X	X	X	X	X	X	X	X	X		
9. Elektriksel, Statik elektrik	X	X	X	X		X	X		X	X	
10. Temizlik, tertip, düzen yetersizliği	X	X	X	X		X	X		X		X
11. Isı çıkışları (exoterms)	X	X	X			X	X		X		X
12. Tutuşma, parlama/Patlama	X	X	X	X		X	X	X	X	X	X
13. Kesilme		X	X	X	X				X		X
14. Yanma	X	X				X		X	X		
15. Lazer kesik ve yanıkları										X	
16. Yüksek basınçlı su										X	

Aşağıdaki etkenlerin yine kontrolsuz ısıl süreçleri başlattığı veya büyüttüğü bilinmektedir:

... Reçinenin kütlesinin artması ve ekipmanın yeterli soğutma yapamaması
... İşletme talimatlarına uymama
... Makine koruma cihazlarının devre dışı bırakılması
... Sıcak reçineyi çok derin kalıba dökmek
... Süreç(proses) ekipmanlarının doğru çalışmaması
... Ham madde değişkenlikleri
... Birbiri ile karışmayan kimyasal ve pişiricilerin kullanılması
... Kimyasalların kirlenmesi ve yetersiz çevre temizliği
... Reçineyi fırında veya otoklavda pişirmeye çal

Karma üretimindeki malzemelerin sağlık etkileri bakımından en önemlileri reçine sistemi ve çözücülerdir. Güçlendirme(takviye) malzemeleri ise ikinci planda kalır. Bilindiği gibi reçine sisteminde ana reçinenin dışında, pişiriciler, seyrelticiler, hızlandırıcılar, pigment ve çözücüler de bulunur.

Epoksi Reçineler:

Epoksi reçineler glisidil(glycidyl) temelli bileşiklerdir. Karma üretiminde yaygın olarak kullanılmaktadır. En çok tanınanı ve kullanılanı Bisfenol A esaslı epoksi reçineleridir. Bunlardan başka glisidil eter, glisidil ester, glisidil amin ve epoksi novalaklar da mevcuttur. Epoksilerin en önemli etkisi deri yoluyla olur. Doğrudan temas sonuca deride kızarıklar, alerji ve dermatitlere neden olduğu bilinmektedir. Tablo 2.'de epoksi reçinelerinin etkileri verilmektedir.

Tablo 2: Epoksi reçinelerin sağlık etkileri

Epoksi tipi	CAS No	Bilinen sağlık etkileri	Notlar
Bisfenol A esaslı	1675-54-3 25036-25-3 25068-38-6 25098-99-8	Deri hassaslaştırıcısı, düşük akut zehirleyici, orta düzeyde tahriş edici	Son yıllarda kanserojen olduğunu gösteren birçok yeni çalışma mevcuttur.
Glisidil aminler	28768-32-3	Deri hassaslaştırıcısı, düşük akut zehirleyici,	Mutajenik testlerin bazıları pozitif, bazıları negatif çıkmıştır.
Siklo alifatikler	2336-87-0 30583-72-3	Deri ve mukoz membranları tahriş edici	Mutajen veya kanserojen değildir.
Glisidil eterler	2210-79-9 2426-08-6 3101-60-8 17557-23-2 26447-14-3	Deri hassaslaştırıcısı, düşük akut zehirleyici, Deri ve mukoz membranları tahriş edici	Nepentilglikol diglisidil eterin farelerde deri kanserine neden olduğu biliniyor.

Diğer reçinelerin de önemli sağlık etkileri olduğu bilinmektedir. Örneğin, poliüretan üretiminde kullanılan izosiyanatlardan Touen diizosiyanat,TDI (CAS : 584-84-9) ve 1,6 Hekzametilen diizosiyanat,HDI (CAS:822-06-0) kanserojen maddelerdir(NTP Group 2, IARC 2B). Fenolik ve amino reçine grubunun üretiminde kullanılan Formaldehit'in(CAS:50-00-0) kanserojen olduğu bilinmektedir(NTP Group 2, IARC 2A,ACGIH A2, EPA B1). Termoplastik reçine üretiminde ise en büyük tehlike stiren monomerinden kaynaklanmaktadır. Stiren(CAS:100-42-5), kanserojendir(IARC Group 2A). Reçine sisteminde kullanılan sertleştirici ve pişiricilerin sağlık riskleri Tablo 3.de verilmiştir.

Tablo 3: Sertleştirici ve pişiricilerin sağlık etkileri

Sertleştirici ve Pişiriciler	**CAS No**	**Bilinen sağlık etkileri**	**Notlar**
Aromatik Aminler		Deri ve mukoz membranları orta düzeyde tahriş edici, karaciğerleri etkiliyor, kanın hücrelere taşınmasını azaltıyor	Bazı aminlerin kanserojen olduğundan kuşkulanılmaktadır.
4,4'-Methylenedianiline (MDA)	101-77-9	Akciğere zehirli, troid,dalak, böbrek, kan ve göze etkili, deri hassaslaştırıcısı	Kanserojen(NTP Group 2, IARC 2B)
4-Aminophenyl sulfone, 4,4'-Diamindiphenyl Sulfone(44DDS)	80-08-0	Kronik maruziyette kan bozucu	Mutajen veya kanserojen olarak sınıflandırılmamıştır.
Meta Phenylene Diamine (MPDA)	108-45-8	Deri ve mukoz membranları tahriş edici, Deri hassaslaştırıcısı, karaciğere etkili	TWA= 0.1 mg/m3

Toluenediamin izomerler	25376-45-8	Deri ve mukoz membranları tahriş edici, Deri hassaslaştırıcısı, karaciğer ve böbreğe etkili, kanın hücrelere taşınmasını azaltıyor	Bazı izomerleri kanserojen
Alifatik ve siklo alifatik aminler	111-40-0 112-24-3 140-31-8 694-83-7	Kuvvetli baz, deriye etkili, göz ve korneayı tahriş edici	Diethyl tri amin için TWA= 1 ppm
Poliamino amidler	68410-23-1	Potansiyel göz ve deri tahriş edici	
Poliamidler	68082-29-0	Potansiyel göz ve deri tahriş edici	
Anhidrid tipi pişiriciler	85-43-8 85-42-7 26590-20-5 552-30-7 89-32-7	Kuvvetli göz ve deri tahriş edici, mukoza tabakasına etkili	

Çözücülerin sağlık etkileri sektörde genellikle bilinmektedir. Ketonlar ve klorlu çözücülerin olumsuz sağlık etkileri nedeniyle mutlaka işyeri hava kalitesi kontrol edilmelidir. İşyeri havalandırması eşik değerleri sağlayacak biçimde tasarlanmalıdır. Yine sektörde yaygın olarak kullanılan Dimetil formamid, DMF kanserojen bir çözücüdür (IARC Group 2B).

3. İsg Mevzuatına Genel Bakış

Polimerik karma doğrudan ilgilendiren 4857 sayılı iş yasası kapsamında yayınlanan yönetmelikler ve dayandığı AB mevzuatı Tablo 4'de , standartlar ise Tablo 5.'de verilmiştir. Bu tablo sadece polimerik karma üretimi için değil, tüm plastik ve kauçuk işletmeleri için de geçerli mevzuatı göstermektedir[4].

Tablo 4: Polimerik karma endüstrisine uygulanabilir ulusal ve AB mevzuatı

AB MEVZUATI	**AMAÇ**	**ULUSAL MEVZUAT**	
General frame work directive on Health and Safety at Work (Dir89/ 391/EC)	işyerlerinde sağlık ve güvenlik şartlarının iyileştirilmesi için alınacak önlemleri belirler. Bu amaçla; a) Mesleki risklerin önlenmesi, sağlık ve güvenliğin korunması, risk ve kaza faktörlerinin ortadan kaldırılması, b) İş sağlığı ve güvenliği konusunda işçi ve temsilcilerinin eğitimi, bilgilendirilmesi, görüşlerinin alınması ve dengeli katılımlarının sağlanması, c) Yaş, cinsiyet ve özel durumları sebebi ile özel olarak korunması gereken kişilerin çalışma şartları ile ilgili genel prensipler ve diğer hususları belirler	İş Sağlığı ve Güvenliği Yönetmeliği (**Not:** Danıştay tarafından yürütme durdurulduğu için askıdadır. Aynı yönetmeliğin tüzük olarak çıkması beklenmektedir	26/12/2003 RG: 25328
Chemical Agents (Dir 98/24/EC) Exposure limits Values (*) (Dir 2000/39/EC) (Dir 2006/15/EC)	işyerinde bulunan, kullanılan veya herhangi bir şekilde işlem gören kimyasal maddelerin tehlikelerinden ve zararlı etkilerinden işçilerin sağlığını korumak ve güvenli bir çalışma ortamı sağlamak için asgari şartları belirlemektir.	Kimyasal Maddelerle Çalışmalarda Sağlık ve Güvenlik Önlemleri Hk. Yön.	26/12/2003 RG: 25328
Carcinogens (Dir 90/394/EC)	işçilerin, kanserojen ve mutajen maddelere maruziyetinden kaynaklanan risklerden korunması	Kanserojen ve Mutajen	

(Dir 97/42/EC) (Dir 99/38/EC)	için bu maddelere maruziyetin önlenmesi de dahil olmak üzere gerekli sağlık ve güvenlik önlemlerini belirlemektir.	Maddelerle Çalışmalarda Sağlık ve Güvenlik Önlemleri Hk.Yön.	26/12/2003 RG: 25328
Physical Agents- noise (Dir 2003/10/EC)	işçilerin gürültüye maruz kalmaları sonucu sağlık ve güvenlik yönünden oluşabilecek risklerden, özellikle işitme ile ilgili risklerden korunmaları için alınması gerekli önlemleri belirlemektir.	Gürültü Yönetmeliği	23/12/2003 RG : 25325
Work places (Dir 89/654/EEC)	işyeri bina ve eklentilerinde bulunması gereken asgari sağlık ve güvenlik şartlarını belirlemektir.	İşyeri Bina ve Ek-lentilerinde Sağ. ve Güv. Önl. İliş Yön.	10/02/2004 RG : 25369
Use Of Work Equipment (Dir 89/655/EEC) (Dir 95/63/EC) (Dir 2001/45/EC)	işyerinde iş araç ve gereçlerinin kullanımı ile ilgili sağlık ve güvenlik yönünden uyulması gerekli asgari şartları belirlemektir.	İş Ekipmanlarının Kullanımında Sağlık ve Güvenlik Şartları Yön. Y	11/02/2004 RG : 25370
Use of Personal Equipment (Dir 89/656/EEC)	işyerindeki risklerin önlenmesinin veya yeterli derecede azaltılmasının, teknik tedbirlere dayalı toplu koruma ya da iş organizasyonu veya çalışma yöntemleri ile sağlanamadığı durumlarda, kullanılacak kişisel koruyucuların özellikleri, temini, kullanımı ve diğer hususlarla ilgili usul ve esasları belirlemektir.	Kişisel Koruyucu Donanımlarınİşyer- lerinde Kullanıl-ması Hakkında Yönetmelik	11/02/2004 RG : 25370
Safety signs (Dir 92/58/EC)	işyerlerinde kullanılacak güvenlik ve sağlık işaretlerinin uygulanması ile ilgili kuralları belirlemektir.	Güvenlik ve Sağlık İşaretleri Yön.	23/12/2003 RG : 25325

Work with screen displays (Dir 90/270/EEC) (offices only)	ekranlı araçlarla çalışmalarda alınacak asgari sağlık ve güvenlik önlemlerini belirlemektir.	Ekranlı Araçlarla Çalışmalarda Sağlık ve Güvenlik Önlemleri Hk.Yön.	23/12/2003 RG : 25325
Manual Handling (Dir 90/269/EC)	elle yapılan taşıma işlerinde iş sağlığı ve güvenliği yönünden ortaya çıkabilecek risklerden, özellikle sırt ve bel incinmelerinden işçilerin korunmasını sağlamak için, alınması gerekli önlemleri belirlemektir.	Elle Taşıma İşleri Yönetmeliği	11/02/2004 RG : 25370
Pregnant Workers (Dir 92/85/EC)	işyerlerindeki gebe, yeni doğum yapmış veya emziren işçilerin işteki güvenlik ve sağlığının sağlanması ve geliştirilmesini destekleyecek önlemler uygulamak ve bu işçilerin hangi dönemlerde ne gibi işlerde çalıştırılmalarının yasak olduğunu, çalıştırılabileceği işlerde hangi şart ve usullere uyulacağını, emzirme odalarının veya çocuk bakım yurtlarının (kreş) nasıl kurulacağını ve hangi şartları taşıyacağını belirlemektir.	Gebe ve Emziren Kadınların Çalış-tırılma Şartlarıyla Emzirme Odaları ve Çocuk Bakım Yurtlarına Dair Y.	14/07/2004 RG : 25522 (**)
	on sekiz yaşını doldurmuş kadın işçilerin gece postalarında çalıştırılmasına ilişkin usul ve esasları düzenlemektir.	Kadın İşçilerin Gece Postalarında Çalıştırılma koş.hk Yönetmelik	09/08/2004 RG : 25548 (**)
Temporary Workers (Dir 91/383/EC)	geçici veya belirli süreli iş sözleşmesi ile çalıştırılan işçilerin sağlık ve güvenlikleri bakımından işyerinde çalışan diğer işçilerle aynı düzeyde korunmalarını sağlamaktır.	Geçici veya Belirli Süreli İşlerde İş Sağlığı ve Güv. Hk. Yönetmelik	15/05/2004 RG : 25463

(*) Dir 2006/15/EC henüz ulusal mevzuatımıza uyarlanmamıştır.

(**) Her iki yönetmelikte de 92/85/EC direktifine atıf yapılmamıştır. Ancak benzer konuları kapsamaktadır.

Tablo 5: Polimerik karma üretiminde İSG ile ilgili standartlar[3].

	Standart No	**Konusu**	**Yayın Tarihi**
1	**TS EN 31010**	Risk yönetimi - Risk değerlendirme teknikleri	Temmuz 2010
2	**TS EN ISO 14121-1**	Makinalarda güvenlik- Risk değerlendirmesi - Bölüm 1: Prensipler	Haziran 2010
3	**EN 1005-5:**	Makinaların Güvenliği-İnsanın Fiziksel Performansı-Bölüm 5:Yüksek sıklıkta tekrarlayan elleçme için risk değerlendirmesi	Şubat 2007
4	**TS EN 15198**	Potansiyel patlayıcı ortamlarda kullanılması amaçlanan elektrikli olmayan donanım ve bileşenlerin risk değerlendirme metodolojisi	Ağustos 2007
5	**TS EN ISO 15265**	Isıl ortamın ergonomisi - Isıl çalışma ortamlarında gerilme veya huzursuzluğun önlenmesi için risk değerlendirme stratejisi	Aralık 2004
6	**TS EN ISO 15743**	Isıl ortam ergonomisi - Soğuk çalışma alanları - Risk değerlendirme ve yönetim	Temmuz 2008
7	TS 12442	İşçi Sağlığı ve İş Güvenliği-İş Kazası Raporu	Nisan1998
8	**TS 12463**	İşçi Sağlığı ve İş Güvenliği-Aerosollere Karşı Alınacak Tedbirler	Nisan 1998
9	**TS 12811**	Çevre Sağlığı- İşçi Sağlığı ve İş Güvenliği- Ketonlara Maruz Kalınan İş Yerlerinde Alınması Gerekli Tedbirler	Mart.2002

10	**TS 12851**	Çevre Sağlığı- İş Sağlığı ve İş Güvenliği- Nitril Kullanılan İş Yerlerinde Alınması Gerekli Tedbirler	Nisan 2002

4. Sonuç

Tüm endüstriyel faaliyetlerde olduğu gibi polimerik karma üretimi süreçlerinde de çeşitli sağlık ve güvenlik tehlikeleri mevcuttur. Karma(kompozit) endüstrisinin nispeten yeni bir teknoloji olması, her geçen gün yeni malzeme ve teknolojilerin kullanılmaya başlaması nedeniyle yeni sağlık ve güvenlik sorunları ortaya çıkabilir.

Bu nedenle, diğer endüstriyel aktivitelerde olduğu gibi polimerik karma sektöründe de en azından ulusal mevzuatların öngördüğü risk belirleme, eğitim ve tehlikelerin kontrol edilerek risklerin yönetilmesi için çaba harcanmalıdır. İş sağlığı ve güvenliği bir "değer" olarak benimsenmeli ve kabul edilmelidir.

Reçineleriçindeki katkı maddelerinin büyük bir kısmı, düşük molekül ağırlıklı ve uçucu olmaları nedeniyle, bulunduğu plastikten besinlere, ortam havasına, ya da doğrudan vücut içi sıvılara geçebilme riskini taşımaktadır. Hayvanlar üzerinde yapılan testler ile, söz konusu kimyasalların başta genetik etkin(mutojenik) ve kanser yapıcı etkiler olmak üzere çeşitli sağlık risklerine sahip olduğu tespit edilmistir. Bu kimyasal maddelerin tamamının henüz sınıflandırılamamıs olmasından kaynaklanan bosluktan yararlanarak, birçok tıbbi bulgu aksini göstermesine rağmen, en basta meslek kuruluşlarının ve onlara yakın kuruluşların güvenlik telkin eden açıklamalarda bulunmaları da etik olarak doğru değildir. Bu konuda doğru yaklaşım, ***"tehlikesiz oldukları kesinlikle kanıtlanıncaya kadar"*** dikkatli olunmasını öğütlemektir. Sağlık etkileri bulunan kimyasalların alternatifleriyle değiştirilmesi gündemdedir. Çalışmalar devam etmektedir. Katkı maddelerinin tartışılmakta olan sağlık riskleri her şeyden önce çalışanları tehdit etmektedir. Ülkemizde genellikle risk küçümsenmekte, hatta yokmuş gibi gösterilmeye çalışılmaktadır. Yukarıda belirttiğimiz gibi "tehlikeli olduğu, öldürücü olduğu henüz kanıtlanmamıştır" denilmektedir. Önerimiz, maruz kalınan riskin değerlendirilmesi yönünde atılacak ilk adım, *"masum oldukları kanıtlanana dek bu kimyasallara karsı dikkatli olunması"* olacaktır. Bugün zehirli (toksik) etkileri nedeniyle kullanımda olmayan katkı maddelerinin de yıllar önce masum olarak nitelendirilerek, yıllarca kullanıldığı unutulmamalıdır. Bu nedenle, reçine sistemi ve çözücülerin sağlık riskleri öncelikle ele alınmalıdır. Mühendislik yaklaşımları, organizasyonel kontrollarla riskler yönetildiği taktirde işyerleri daha sağlıklı ve güvenli hale gelecektir.

Kaynaklar

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