Cumhuriyet Science Journal
CSJ

e-ISSN: 2587-246X
ISSN: 2587-2680

Cumhuriyet Sci. J., Vol.38-4 (2017) 603-610

Effect of Organic Reinforcement Usage on Mica/Polyester Composite Material

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Received: 13.02.2017; Accepted: 07.06.2017 *http://dx.doi.org/10.17776/csj.348276*

Abstract: The problem of environmental pollution has sprung to the fore with today's over-population and packaged product sales have risen due to the changing consumption behaviors pursuant to today's rising living standards, which caused solid waste composition to differentiate. Poly ethylene terephthalate (PET) bottle that is mostly used for the purpose of marketing liquids can be recycled as PET chips after a certain set of procedures. Pine forests have an important place in Turkey. Pine cones that fall seasonally either stay on the ground or are collected and burned. That being said, creating alternative usage areas for a huge amount of PET bottle wastes and pine cone wastes and, in the same scope, production of composite materials with high added value will create both economical opportunities and variety in terms of life cycle, more efficient usage of raw material resources and better sales cost for future needs of people.

Two different materials, which were grinded pine cones (P) and PET bottle chips (B), as polyester matrix composite organic reinforcement samples, where an inorganic material known as mica was used at different ratios as filling, were reinforced separately and their resulting effect on mechanical properties was researched. Wt% (6:0, 9:0, 12:0, 6:6, 9:6 and 12:6) was established between mica as the filling in the composite material and the reinforcements (P/B). The effect induced by reinforcing mica at different ratios on the composite material, which was manufactured separately via both pine cone and PET bottle chip, was determined via tests to possess bending, impact resistance etc..

Keywords: Mica, Organic Reinforcement, Polyester Composite, Pine Cone, PET Bottle

Mika/Polyester Kompozit Malzemeye Organik Takviye Kullanımının Etkisi

Özet: Günümüzde artan nüfusla birlikte çevre kirliliği problemleri ön plana çıkmış ve yükselen hayat standardına bağlı değişen tüketim alışkanlıkları, ambalajlı ürün satışlarının artmasına bu da katı atık kompozisyonun farklılaşmasına yol açmıştır. Çoğunlukla su, meşrubat, sıvı yağ, sirke gibi sıvı gıdaların piyasaya sürülmesi amacıyla kullanılan PET ambalajı, geri dönüşüm tesislerinde kırma, yıkama, kurutma vb. bir dizi işlem kademesi sonrasında PET talaşları olarak geri kazanılabilmektedir. Türkiye'de çam ormanları önemli bir yer tutmaktadır. Mevsimsel olarak dökülen kozalak ya toprak üzerinde kalmakta ya da toplanıp yakılmaktadır. Ancak yaşam döngüsü açısından, hammadde kaynaklarının daha verimli kullanması ve zamanla ortaya çıkan yeni ihtiyaçların uygun maliyetlerle karşılanması için oldukça yüksek miktardaki PET ambalaj atıkları ve kozalak atıkları için alternative kullanım alanlarının yaratılması bu kapsamda katma değeri yüksek kompozit malzeme üretimi hem ekonomik bir fırsat hem de çeşitlilik sağlayacaktır.

Bu çalışmada inorganik bir malzeme olan mikanın farklı oranlarda dolgu olarak kullanıldığı polyester matriksli kompozite organik takviye örneği olarak iki farklı malzemenin; öğütülmüş çam kozalağı (P) ve PET şişe talaşının (B) ayrı ayrı takviye edilmesinin mekanik özelliklere etkisi araştırılmıştır. Kompozit malzemede dolgu maddesi mika ve takviyeler (P/ B) arasında % ağırlıkça (6:0, 9:0, 12:0, 6:6, 9:6 ve 12:6) oranı sağlanmıştır. Farklı oranlarda yapılan mika katkısının hem çam kozalağı hem de PET şişe talaşıyla ayrı ayrı üretilmiş kompozit malzemeye etkisi eğme, darbe direnci, sertlik, yoğunluk gibi testlerle belirlenmiştir.

Anahtar Kelimeler: Mika, Organik katkı, Polyester kompozit, Çam kozalak, PET şişe

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1. INTRODUCTION

Many a new studies on recycling have gained speed for copious reasons such as insufficient amount of raw material resources during manufacturing, desire to minimize the damage given to environment during the manufacturing of a product and its application, decrease the detriments that occur during product manufacturing/disposal, and preserving energy and resources that were spent in product manufacturing [1,2]. Because polymers product can survive in the nature intact for a very long time, are pollutant and especially PET bottles among waste polymers have a big hand in this; finding ways to recycle polymer-based products as composite materials are important in waste utilization [3]. In fundamentals, composites are comprised of two main phases; continuous and particulates. The particulate phases we have named as the reinforcing member can be fibrous or in particles, can be organic or inorganic. Currently, there are various studies regarding the use of PET wastes and pine cones in composite materials. Ayrılmış et al., used waste pine cones as the reinforcing member in thermoplastic composite manufacturing. In said study, they determined the mechanical and physical properties of the polypropylene composites, which were reinforced with pine cones. They observed that the properties of water absorption and bending were negatively affected, as the number of cones increased [4]. Gökdai et al., examined the effect of marble powder and pine cone reinforcements on the physical and mechanical properties of the polyester matrix composite material. Pine cone: lost its strength and hardness values, as the amount of marble reinforcement increased [5]. PET is used in many applications because of its excellent mechanical strength, thermal resistance and inertness to many chemical reactions. Composites include high amount of PET have higher mechanical properties and low cost [3,6]. Won et al., researched the usability of PET wastes on cement composites. Freezing and melting test results showed that the recyclable PET fiber-reinforced cement compound had perfect durability properties [7]. The synthesis and characterization of PET-halloysite nanotubes were researched by Gorrasi et al. Mechanical analyses put forth that when the PET matrix was reinforced with halloysite at different ratios, a decrease occurred in elongation at break [8]. Ahrabi et al., manufactured composite material by using PET wastes. In the wake of the conducted experiments, material durability and strength was observed to have decreased due to the admixture reinforcement. It was found that the material hardness underwent serious changes based on the size and proportions of the filling material [9].

An investigation was performed regarding the mechanical and thermal behavior of PP composites containing recycled polyethylene terephthalate fibers (rPET) by Nonato and Bonse. They used maleic anhydride grafted polypropylene as a compatibilizer to provide interfacial adhesion between the matrix and filler materials. Mechanical properties were determined by tensile, flexural, impact and fatigue tests, and thermal properties by HDT (Heat Deflection Temperature). They concluded that addition of compatibilizer increased flexural strength and tensile strength, flexural modulus, fatigue life and HDT. They also obtained tensile modulus, strain at break and impact strength values were decreased [10]. In the study of Javier et al. polyethylene-terephthalate was used as thermoplastic resin while sawdust as fiberfill to investigate optimization of tensile and flexural strength of a wood-plastic composite. Unlike other studies PET was not used as filler in this study. It was used as a matrix phase. The goal of this study was to obtain the operating conditions that ensure the optimum properties of the composites, with minimum changes [11].

Yang and Liu studied the possibility of usage polypyrrole/conductive mica composites in supercapacitor applications. By using in situ chemical oxidative polymerization method polypyrrole/conductive mica (PPy/CM) composites were prepared by coating polypyrrole onto the surfaces of the conductive mica. According to the charge/discharge behavior of the PPy/CM composites, it was found that the composites performed typical electrochemical supercapacitor behavior [12]. Gan et al. investigated the effect of filler content on physical properties of poly/mica composites. Poly ether ketone ketone composites filled with mica were manufactured by using sulfonated poly as an interfacial modifier. They obtained improved mechanical properties for the compatibilized composites. They also observed that the content of mica is effective on friction behavior of the composite materials [13]. Because of their renewable internal and possibility to form added-value in industry biobased composite materials play a significant role for sustainable development of environment [14,15].

As a starting point the overall challenges in waste management of biopolymer materials have been investigated in this study. After this investigation the effect of separate reinforcements of the polyester matrix composite pine cone and the PET bottle chip, in both of which mica was used as filling at different ratios, on the material's mechanical properties was examined in this study.

2. MATERIALS AND METHODS

2.1. Materials

In the experimental studies, the main filling material Mica was acquired from the company - Mikron'S Mikronize Mineral End. Tic. A.S. - in microcrystal muscovite form (sericite) under the trade name 'Mica 20'. The flakes obtained from the PET (polyethylene terephthalate) wastes that were used to determine the effect of organic reinforcement were acquired from a recycling company known as Plaspak Kimya San. Tic. A.S. and the grinded pine cones as the other organic reinforcing member were collected from the Bilecik region (Figure 1).

Figure 1. Organic reinforcement for polyester composite; Pine cones and PET bottle chips.

The polyester resin (Polipol383-G) with a density of 1.076±0.05 g/cm^3 in the main matrix that was obtained from the Poliya Composite Resins and Polymers Inc. was used. The metile ethyl ketone peroxide (MEKP, Akzo Nobel Products) polyester resin catalyst was chosen as the hardening agent, and 2% Cobalt solution was used as an accelerator in the curing process of the polyester resin. The grinded pine cone, the waste PET chip and the theoretical densities belonging to the mica filling were calculated by using a Micromeritics brand AccuPyc II 1340 model Helium-gas pycnometer (Table 1).

Table 1. Filling materials theoretical density and volume.

Material	Mean Density (g/cm^3)	Mean Volume (cm^3)
Mica	2.7111± 0.0017	1.7857± 0.0011
Pine cone powder	1.4179± 0.0008	1.9555± 0.0011
Waste PET bottle chips	1.3387±0.0005	2.4295± 0.0009

2.2. Method

Castings at three different mica (M) filling: polyester ratios were made. The organic reinforcements of this study; grinded pine cones (P) and waste PET chips (B) were used to produce composite resin, whose reinforcement-filling and polyester ratios are given in Table 2, and resin-castings were made accordingly. Furthermore, as each receipt possessed different compositions, hardening agents and accelerators at different amounts were added into the mixture.

Table 2. Composition of polyester composites.

Sample Code	Filler *[wt%]			Polyester *[wt%]
	**P	**M	**B	
MC1	0	6	0	94
MC2	0	9	0	91
MC3	0	12	0	88
MPC1	6	6	0	88
MPC2	6	9	0	85
MPC3	6	12	0	82
MBC1	0	6	6	88
MBC2	0	9	6	85
MBC3	0	12	6	82

*[wt%]: Weight Percent
**P: pine cone powder, M: Mica, B: PET bottle chips

Mixtures were stirred in a mechanical stirrer (Stuart scientific stirrer SS3, UK). The mixture preparation and casting processes are given in Figure 2.

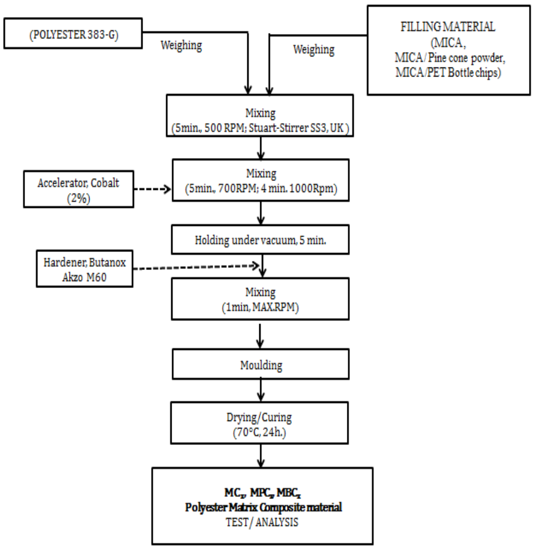

Figure 2. Composite production flowchart.

The cast sizes used in the experimental studies were 10mm x 4 mm x 100 mm. 3-point bending strength was calculated using the device Shimadzu AG IC100 kN, and the izod impact test was conducted with the device DVT CD, Devotrans Quality Control Test Instruments Ltd., Turkey.

The data, which was required for the calculations of the bending strength applied via 3-point load at the velocity of 2 mm per minute, the elastic module and the maximum strength applied on a certain area; was collected. Results were gathered compliant to the equations given below, by calculating the mean of the three samples.

$$\sigma = (3LP)/(2bd^2) \quad (1)$$

$$E_f = (L^3m)/(4bd^3) \quad (2)$$

σ Flexural strength (N/mm^2),
E_f Flexural modulus (MPa),
L the support span (mm),
P the maximum load (N),
b the width of the composite sample (mm),
d the thickness of composite sample (mm),
m the slope of the initial straight line portion of the load–displacement curve.

After the bending test, each sample was divided into two pieces. These separated samples were dried in a drying oven (110°C) until they reached a constant weight. After reaching room temperature, they were measured with an assay balance and their dry weights (W_K) were calculated. They were then waited in boiling water for two hours, subsequently at room temperature for 24 hours. The suspended weights of the samples were measured in water in a mechanism prepared by using the Archimedes density determination kit (W_A). The samples were taken out of the water and their surfaces were dried with a towel. They were then measured by a balance, thus the aerial weight of the water-absorbed sample (W_D) was recorded. By using the equations given below (3-5); water absorption, bulk density and % open porosity values were calculated.

$$A, \% = (W_D - W_K) / W_K * 100 \quad (4)$$

$$B = [W_K / (W_D - W_A)] * \rho_{su} \quad (5)$$

$$P, \% = [(W_D - W_K)/(W_D - W_A)]*100 \quad (6)$$

A : Water Absorption,
B : Bulk Density,
P : Apparent Porosity

3. RESULTS AND DISCUSSION

The obtained results from the bending test; i.e. the maximum force value that the mica-filled polyester composites that was reinforced with organic (P) and (B) put forth in the bending test are given in Table 3.

Table 3. Bending properties of composite samples.

Sample Code	Max. Force (N)	Flexural Strength (N/mm^2)	Elastic Modulus (MPa)
MC1	140.65	63.19	4.244,46
MC2	143.75	68.60	4.521,86
MC3	146.88	73.59	4.833,96
MPC1	140.63	66.28	4.636,70
MPC2	153.13	64.48	4.567,78
MPC3	137.51	61.15	4.459,85
MBC1	90.63	42.27	4.265,78
MBC2	125.00	56.37	4.415,31
MBC3	137.50	59.96	4.500,32

The mica-filling that was added in increasing ratios caused the bending strength and the elastic module to increase as well. According to the Hashin analytical model Young modulus should increase with the increase of mica. Experimental results of Martias et al. show that addition of mica (between 5 and 15 w%) did not improve the mechanical properties of the composite [16]. But when compared with the values obtained even the increasing of mica from 6% to 12% improved the mechanical properties of composites. Here it can be indicated mica provides different interactions with various filler materials. In result of bending test the other two organic reinforcements used in the study were observed to have affected the composite material differently.

3-point bending test results showed that recyclable grinded PET wastes decreased the bending strength by 18% on average [10]. It was also mentioned in study of Ahrabi et al. They concluded that pure PET had a 65 MPa of flexural strength. After mixing PET with the marble dust and increasing amount of marble had led to decreasing of flexural strength [9]. It was also observed in the sample of MBC series. Due to the increasing mica filling the PET reinforcement at constant ratio lost some of its strength-reducing effect. Thus the overall strength value increased. By adding PET wastes into composite material a negative effect was observed in the Elastic module test results. This situation can be evaluated by examining the SEM images.

Addition of the grinded pine cones caused bending strengths to occur that was less powerful than the values of mica/polyester composite. However as different from the result obtained from the other organic admixture (B); the fact that the bending strength lessened due to the increasing mica powder and the constant pine cones has proved that pine cone reinforcement can actually affect the composite in a positive way and that a mixture between filling-reinforcement and matrix was enabled. Arrakhiz et al. also showed that in their study pine cone fillers have positive effects on mechanical properties of polymer composites [17]. Also, the fibrous grinded pine cone reinforced samples were observed to have snapped at higher strengths as opposed to the other samples. By adding pine cone powder into composite material, the elasticity of the fibrous structure increased and another relative increase was observed in the elastic module results. In the study of Baştürk et al. it was determined that the elastic modulus of the composite filler with pine cone was about 1.3 GPa [18]. According to Table 3 it can be clearly said pine cone interaction with the mica has increased this value near to 4.5 GPa. In order to determine the reinforcement-filling materials' and the polyester matrix interface properties in the manufactured composite samples Scanning Electron Microscope(SEM., Zeiss Supra 40VP, Germany) was used to obtain images and utilized to distinguish transformations in pore formation. SEM images of the PET waste and grinded pine cone reinforced composites taken from a cracked surface are given in Figure 3.

When looked at SEM images, it can be seen that the porosity amount of the P reinforced samples are higher due to the (fibrous-structured) fibrils. PET chips, on the other hand have sharp formations and displayed a non-compliant interlayer structure. Izod impact resistance of the composite samples and the Shore D hardness results showed parallelism with the bending test results (Table 4).

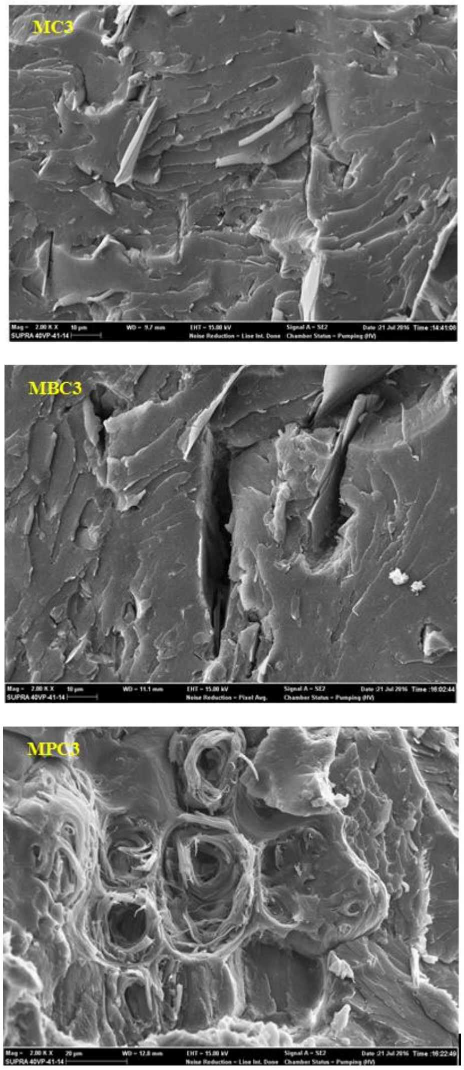

Figure 3. 2.00kx magnified SEM images of the composite samples where mica filling was used the most.

Table 4. Impact strength and Hardness of composite samples.

Sample codes	Hardness Shore D	Izod impact Strength (J/mm²)
MC1	92	4.7
MC2	95	5.18
MC3	96	5.81
MPC1	94	5.36
MPC2	94	5.16
MPC3	93	5.03
MBC1	92	4.98
MBC2	93	5.31
MBC3	94	5.47

The energy required to break the composite material increased because of the fact that the amount of PET wastes decreased due to the increasing mica ratio, thereby the impact resistance of the composite material increased. Reinforcement via waste PET chips caused sharp layers in the micro-structure of the composite to occur their sharp and pointy edges that can be observed in the SEM images, which in turn affected the izod impact resistance. Normally the izod impact value of pure PET is 0.266 J/mm^2 [19] but adding mica has clearly improved the impact values of composites as seen from Table 4. Izod impact resistance was affected positively in the grinded pine cone reinforcement and in the increasing mica-filled polyester composites. This can be linked to the fibrous structure of the pine cone which is clearly observable in the SEM images. The connection between the composite layers that was achieved by the fibrous structure is seen to have increased composite's strength. However increasing mica ratio caused the effect of fiber to diminish, hence the decrement in the izod impact resistance. The pine cone reinforcement influenced the amount of energy the composite material absorbed. Fibrous structure acted as a negative factor point causing the amount of open porosity to increase and consecutively the bending resistance of the composites to decrease.

According to the results presented in Table 5 the highest open porosity was seen in the composite samples reinforced with pine cone (1.78-2.14).

Table 5. Density and the dimensional stability properties of composite samples.

Sample codes	Bulk Density (gr/cm^3)	Water Absorption (%)	Apparent Porosity (%)
MC1	1.24	0.83	1.02
MC2	1.26	0.75	0.94
MC3	1.28	1.20	1.53
MPC1	1.23	1.45	1.78
MPC2	1.26	1.41	1.78
MPC3	1.28	1.67	2.14
MBC1	1.24	1.05	1.29
MBC2	1.26	1.12	1.41
MBC3	1.28	0.86	1.10

PET waste reinforced composites were observed to possess a higher amount of open porosity than the composites with mica filling. Sharp edges of the PET waste and the lamellar structure of mica particles (Figure 3) made it more difficult for the composite materials to form a homogenous mixture. Water absorption in the composite samples showed changes generally based on % apparent porosity. If MPC is compared with MBC series MPC shows higher water absorption. This is expected due to the hydrophilic nature of pine cone in the composites. Another potential reason is that the pine cone consists of lignin and cellulose and the cellulose has a hydrophilic structure which includes hydroxyl groups. This hydroxyl group reacts with hydrogen bond of water molecules that cause high moisture in the composite [20, 21].

All in all organic wastes influenced the Mica/Polyester composites at different ratios based on the amount of reinforcement and the structural properties. Grinded pine cone affected mechanical properties partially positively, increased water absorption but showed no important effects on density whereas; waste PET bottle chips presented no positive effects on any property.

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