EFFECT OF MARBLE: PINE CONE WASTE RATIOS ON MECHANICAL PROPERTIES OF POLYESTER MATRIX COMPOSITES

GOKDAİ D.[1], AKPINAR BORAZAN A.[1]and ACIKBAS G. [2]

[1] Bilecik Seyh Edebali University Chemical and Process Engineering Department, 11210, Bilecik, [2] Vocational School of the Bilecik Seyh Edebali University, Metallurgy Program
E-mail: alev.akpinar@bilecik.edu.tr

ABSTRACT

There is still a going research interest to find out alternative source of materials for composite manufacturing. Therefore, alternative non-wood based materials may play an important role in the forest product industry. Pine cone, a renewable resource, has not been used effectively. It is collected, dried to facilitate seed release, and generally discarded or burned in stoves in winter. Also, cone collection does not require extra costs. In this study, polymer matrix composites were manufactured using pine cone and marble wastes as filler and polyester as polymer matrix with casting method. Methyl ethyl ketone peroxide as hardener and cobalt naphthenate as accelerator were used to produce polyester matrix composites. Polyester: filler ratio was kept in constant and pine cone: marble waste ratios were changed. Mechanical properties of composite materials were investigated and the final product tested to determine their flexural strength, elastic modulus, hardness as well as some physical features such as density and water absorption. The experimental results showed that strength and hardness of the composite materials decreased with the increase in pine cone: marble waste ratio.

Keywords: Polymer matrix composites, marble wastes, pine cone wastes, polyester, mechanical properties

1. Introduction

Composites, the wonder material with light-weight, high strength-to-weight ratio and stiffness properties have come a long way in replacing the conventional materials like metals, woods etc (Gopinath *et al.*, 2014). Polymers used in composite materials cannot provide the desired features singly. Therefore fibers are reinforced with polymer composites. Natural fibers reinforced polymer composites have received a wide interest as innovative material in such industrial applications (Arrakhiz *et al.*, 2013). Usage of polymer based composite materials increasing because of their light weight, good mechanical and tribological responses (Gopinath *et al.*, 2014). Instead of expensive glass fibers natural fibers are preferred to be used as reinforcement (Dieter and Kaobjilowski, 2003, Ku *et al.*, 2011). The advantage of using this type of bio-resources to be multifunctional, flexibility and can be supplied extensively in worldwide without damaging the environment. Recently conducted several studies on this subject are available. Bending properties of Macadamia nut shell/polyester composites have been investigated by Dong, C. *et al.*(2012). Mechanical and chemical properties of kenaf pulp derived by addition of polylactic acid composites were studied by Syafinaz *et.al*. The breaking point in the composite is average of less than 9%. 36% flexural strength and modulus, respectively, increased to 54% (2012). Guru, M. and colleagues (2007) have studied fly ash and marble powder addition on production of the composite polymer matrix. Mechanical properties of composite materials were examined. Optimal three-point bending strength and stiffness values were respectively 30.42 N / mm^2 and 98 Shore D. In the study of F.Z., Arrakhiz *et al*. a various amount of pine cone and clay were melt mixed with the polymer (Arrakhiz*e et al.*, 2012). Physical and mechanical properties of medium density fiberboards (MDF) made from various mixtures of wood fibers and stone pine (*Pinus*pinea L.) cones were evaluated using European standards in the study of Ayrilmis, N. *et al.* (2009). Sahin and Arslan (2011) combined red pine cone and barks with red pine wood particles in various

proportions were used as the raw materials for one and three layered experimental particleboard manufacturing. In this study polymer matrix composites were manufactured using pine cone and marble wastes as filler and polyester as polymer matrix with casting method. Butanox as hardener and cobalt naphthenate as accelerator were used to produce polyester matrix composites.

2. Materials and methods

2.1. Materials

Polyester resin (Polipol 383-G, Poliya Composite Resins and Polymers Inc., density of 1.076±0.05 g/cm^3) was used as the matrix in all tests. Methyl ethyl ketone peroxide (MEKP,Butanox™ M-60, AkzoNobel Products) was a catalyst used for polyester resins. It reacted with the resin to turn it from a liquid to a solid. MEKP is organic peroxide. Cobalt 1% solution was promoters used in the curing of polyester resins. Pine cone fibers and marble wastes were used as reinforcement. Fig. 1 shows the plant and other waste. The pine cones were air-dried before further use. Finally pine cones and marble wastes were grinded respectively in the hammer mill (Brook Crompton Series 2000) and in a precision grinder (Fritsch-Pulverisette9) equipped with sieve (Fritsch, Analysette 3).

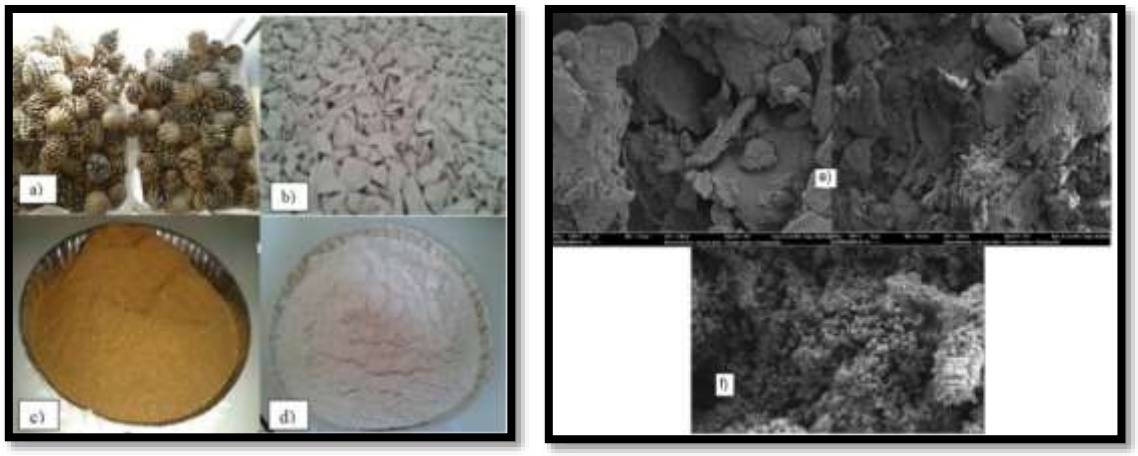


Figure 1: Photographs a) the Pine cone plants, b) marble wastes, c) powder of cones, d) powder of marble wastes; SEM images of grinded e) pine cone and f) marble wastes

Polyester matrix was combined with powder of marble wastes and pine cone at different particle size content. In this work the average particle size was calculated ≤90 μm for both fillers. Fig. 1-e and f illustrates the fiber board range of 1-100 μm.

2.2. Composite preparation

The polyester matrix was compounded, respectively, with reinforcement fillings in different ratios by weight. The raw material formulations, which are given per the mass proportion in percentage, used for the composites are presented in Table 1. Absolute volume measurement and true density calculation of pine cone was obtained with gas pycnometer, Micromeritics the AccuPyc II 1340 model (respectively 4.1120±0.0029 cm^3 - 1.4493±0.0010 g/cm^3).Matrix: reinforcement in 2:3 ratios was preserved and other supplements waste marble powder: ATH 4:1 ratio is provided.

The reinforcement material and polyester resin was first mixed in the indicated ratios. After Compounding was performed using a speed of 500, 1000 and 1500 rpm (Stuart scientific mechanical stirrer), cycle time for each 5 minutes, mixture was hold on under the vacuum in 5 min. Then accelerator and hardener were added to mixture and the last mixture was poured into a mold. Curing condition for composites were 60°C, 2 hours in an oven (Binder,Germany), 1 hour at ambient temperature.

Table 1: Mass ratio % of composites

	P1* (%)	P2 * (%)	P3* (%)
Polyester	41.81	45.98	51.06
Pine Cone Powder	0.70	2.30	4.26
Marble Wastes	45.99	41.38	35.74
ATH**	11.50	10.34	8.94

* Code for composite recipes, ** abbreviation of Alumina tri hydrate

2.3 Experimental Method

Three point bending tests were carried out at a bending speed of 2 mm/min in Shimadzu AG-IC Test Machine. The maximum fracture loads of the three-point bending test were obtained. Calculations of the three point bending tests were carried out by the following formula according to EN ISO 178 TS 985. The 3 samples of each group were tested and average values were reported. The flexural test specimens were also cut from the composite panels with dimensions of 100 mm × 10 mm × 4 mm (thickness). The bending measurements were also performed at the ambient conditions of 23±2°C. The flexural modulus of the elasticity in the bending tests is calculated within the linear limit by using the equation 2.2.

$$\sigma = \frac{3FL}{2WD^2} \qquad \textbf{(2.1)} \qquad\qquad E = \frac{L^3}{4WD^3} m \qquad \textbf{(2.2)}$$

σ is the stress in the outer layer at mid-length point of the specimens, N/mm^2
E is the flexural modulus of elasticity of the specimens in bending tests, N/mm^2
F is the load at the loading point (mid-length), N
L is the supporting span of the specimen, mm;
W is the width of the specimens in perpendicular to the loading direction, mm
D is the depth of specimens tested in parallel to the loading direction, mm;
m is the slope of the initial linear portion of the load deflection curve, N/mm
Durometer Hardness is used to determine the relative hardness of composite samples. 8cm in diameter of the composite specimens were first placed on a hard flat surface. The indentor for the instrument was then pressed into the specimens making sure that it was parallel to the surface. The Shore D hardness was read within one second of firm contact with the specimen. Five replicates of each composite formulation were tested to determined averaged hardness. Density measurements of the composite specimens were done according to the Archimedes' Principle. To determination of the porosity into the composite specimens were measured the bulk volume which is the sum of the grain and pore volumes. In Equation 2.3 bulk density, in equation 2.4 open porosity calculations are shown.

$$\text{Bulk Density} = \frac{W_1}{W_3 - W_2} x\rho_{water} \qquad \textbf{(2.3)} \qquad\qquad \%\ \text{Open Porosity} = \frac{W_3 - W_1}{W_3 - W_2} x100 \qquad \textbf{(2.4)}$$

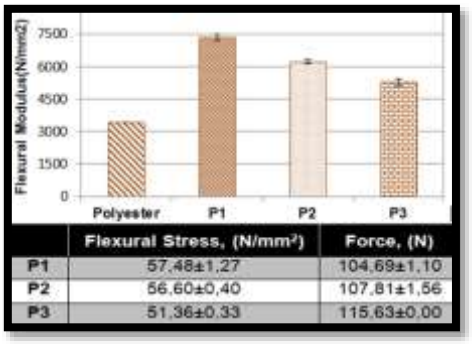
W_1 = Weight of clean, dry sample (g); W_2 = Weight of saturated sample, immersed in water (g); W_3 = Weight of saturated sample in air(g)

The fracture surfaces of the flexural test specimens were characterized with high resolution field emission scanning electron microscopy (SEM, Zeiss Supra 40VP (Germany). The SEM was operated to determine their fracture surface, microstructure, and fiber orientation characteristics. Samples of image analysis and SEM study were prepared from the edges of the three point bending test specimens.

Fourier Transform-Infrared spectra of Pine cone composite series were recorded using an Perkin Elmer, Spectrum 100 (Japan) spectrometer equipped with a single reflectance Attenuated Total Reflectance accessory. The spectra were obtained between wave number 4000-400cm^{-1} at 25°C.

3. Results and discussion

Pine cone fibers are a cellulosic material readily available and can be used as reinforcement in a thermoplastic-based composite.The experimental results showed that strength of the composite materials decreased with the increase in pine cone/ marble waste ratio. The values of tensile properties are summarized in Fig.2.



	Flexural Stress, (N/mm²)	Force, (N)
P1	57,48±1,27	104,69±1,10
P2	56,60±0,40	107,81±1,56
P3	51,36±0,33	115,63±0,00

Figure 2: Some properties of pine cone composite material's ability to resist deformation

After the bending strength test elastic modulus of the sample was calculated using equation 2.1. When the results are evaluated in the composite filled pine, elastic modulus decreased with the increasing of open porosity amount. Also the elastic modulus decreased with the increase of particle size of the filler elements. The highest elastic modulus was obtained in the sample of P1 which has low porosity amount. The size of the amount of porosity as well as porosity size, the distance between each other's affect mechanical properties. A maximum tensile strength of composites is reached at 3% pine cone content after which any more added fiber decrease the tensile strength. These results are parallel with (Arrakhiz *et al.*, 2012) research about pine cone fibers reinforced compatibilized polypropylene. Figure 3 is illustrated that the hardness of the composite materials does not have a critical change with the increase in pine cone/ marble waste ratio but same figure also shows water absorption% is really increased with pine cone fillings. Polyester matrix material has lowest percentage of WA. Reinforcement fillers pine cone and marble wastes have opposite ratio in composite formula. Bulk density of composite is decreased by cone fillers with increasing ratios in formula (Fig. 4.). Visible porosity % is shown Fig. 4., that plant fillers are grown up the percentage void. According to the electron microscope images (Fig. 5.) structure of the varying size from 1 to 150 micron particle size appears to be a non-homogeneous distribution. Closer examination of the large grains shows that most of the grain occurs by agglomeration of small particles and cannot be fully distributed within the structure of the grain.

4. Conclusions

Sample of P1 has a higher elastic modulus due to the content of high inorganic ceramics (ATH& marble) phase. Elastic modulus decreases with the content of increasing cones and decreasing the ceramic phase. Hardness results show similar values for each of three samples. Strength values decrease with the content of increasing cones and decreasing the ceramic phase. This is because, as seen from the SEM-SE images there are a weak matrix-reinforcement interface interaction and the water absorption and as seen in the bulk density values high porosity amount present in a structure. Unfortunately, pine cone/ marble waste reinforced did not produce any improvement on mechanical properties of polyester matrix composite probably because of the low interfacial adhesion between the matrix and reinforcement filler particles. They finally concluded that the addition of any coupling agent or may be any chemical treatments on natural materials will be getting improvement in composite mechanic properties and better yield results.

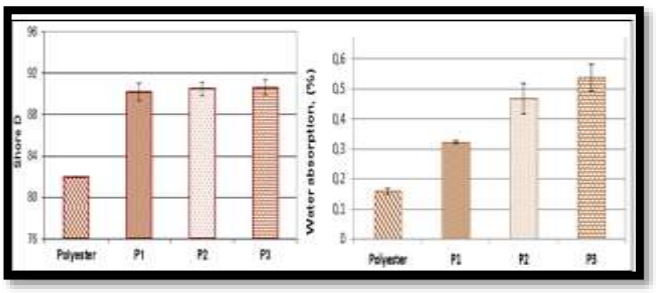


Figure 3: Physical testing results of pine cone/marble waste polyester matrix

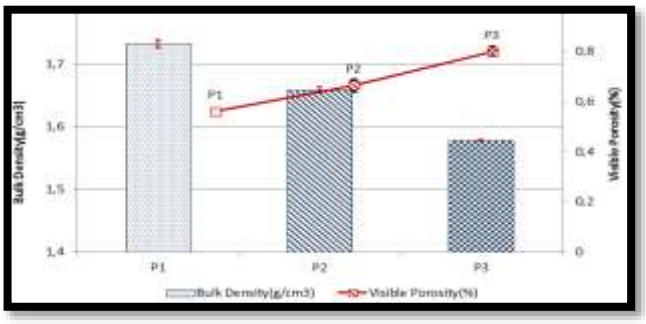


Figure 4: Pine cone/ marble waste reinforcement polyester composite porosity related properties

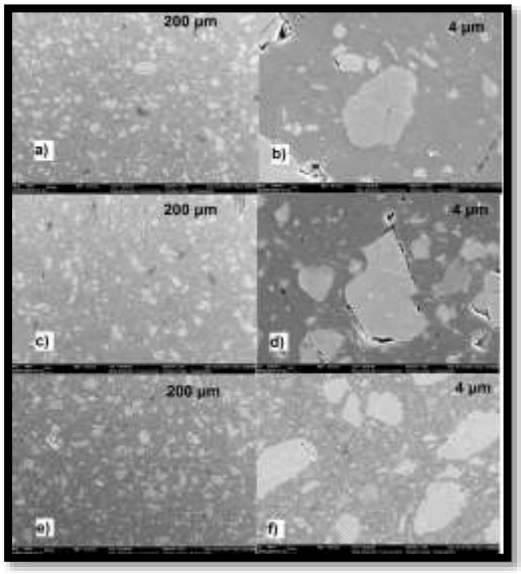


Figure 5: SEM images of the fracture surface of different polyester composites. Figures (a and b), (c and d) and (e and f) are pairs in different magnitudes of P1; P2; P3

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