# EFFECT OF MARBLE: HOP WASTE RATIOS ON MECHANICAL PROPERTIES OF POLYESTER MATRIX COMPOSITES

**ANDOGLU E.M.[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

Natural fibers include agricultural wastes (wheat straw, hemp fiber, shells of various dry fruits, etc.) have so many advantages like low cost, high physical and mechanical properties and thus they are used reinforcement phase in polymer matrix. In this study, polymer matrix composites were manufactured using hop 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 hop: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 hop:marble waste ratio.

**Keywords**: Polymer matrix composites, marble wastes, hop wastes, polyester, mechanical properties

## 1. Introduction

In developing countries, the methods used to recycle and re-use waste materials should be investigated in order to benefit from natural resources effectively. In our country, there are a lot of waste materials which have economic value. One of them is waste marble (Uygunoğlu *et al.*, 2014). As a result of its geological location, Turkey possesses very rich, natural stone reserves in various colours and patterns (Çelik and Sabah, 2008). Marble wastes are generated by quarries and processing plants in different forms. The large amount of marble wastes is a serious problem for the industry and the environment (Tozsin *et al., 2014).*The by-product generated from marble processing is a powdered dust and may represent an environmental problem (Ghazy and Gad, 2014). Many researchers recently were interested in studying the possibility of recycle and re-use of such wastes in useful industries (Aliabdo *et al*., 2014). Natural stone powder is generally used as a raw material or reinforcement material in various areas such as building materials, bricks, ceramics, cement additives, desulphurization processes and infiltration. In addition, natural stone powder can be used in the production of polymer based composite material (Bilgin *et al.*, 2012).

The composite manufacturing has been a wide area of research and it is the preferred choice due to its superior properties like low density, stiffness, light weight and possesses better mechanical properties. This has found its wide applications in aerospace, automotive, marine and sporting industries (Gopinath *et al*., 2014). A composite material is a non uniform solid consisting of two or more different materials that are mechanically bonded together. Each of the various components retains its identity in the composite and maintains its characteristic structure and properties. Generally, the structure of a composite consists of two phases, matrix and reinforcement. Composite materials may be selected to give unusual combinations of stiffness, strength, weight, high-temperature performance, corrosion resistance, hardness, or conductivity (Askeland *et al*., 2010).

Continuous fiber reinforced composites are a new kind of material with such properties as low density, high strength, high modulus, damage tolerance and safety. Today, man-made

lignocellulosic composites are becoming attractive in both commercial and non-commercial applications (Ndazi *et al*., 2006; Wang *et al*., 2011). Various natural fibers such as banana, sunflower stalk, corn stalk, bagasse, coir, sisal, jute, wheat straw, maize, oat, barley and rye have been tested as new reinforcement agents in polymer-based composite materials (Pothan *et al*., 2003; Ashori and Nourbakhsh, 2010; Santafé Júnior *et al*., 2010; Ramesh *et al*., 2013; Gopinath *et al*., 2014; Mamun *et al*., 2015; Panthapulakkal and Sain, 2015).

In this study polymer matrix composites were manufactured using hops 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.

## 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$^3$ as a standard ISO 1675) was used as the matrix in all tests. Methyl ethyl ketone peroxide (MEKP)(Butanox™ M-60, Akzo Nobel Products) was a catalyst used for polyester resins. It reacted with the resin to turn it from a liquid to a solid (cure it). MEKP is organic peroxide. Cobalt 1% solution was promoters used in the curing of polyester resins with MEKP type catalysts. Hop fibers and marble wastes were used as reinforcement. Fig. 1 shows the plant and other waste. The hops were air-dried before further use. Finally hops and marble wastes were grinded respectively in the hammer mill (Brook Crompton Series 2000, England) and in a precision grinder (Fritsch-Pulverisette9, GmbH) equipped with sieve (Fritsch, Analysette 3).

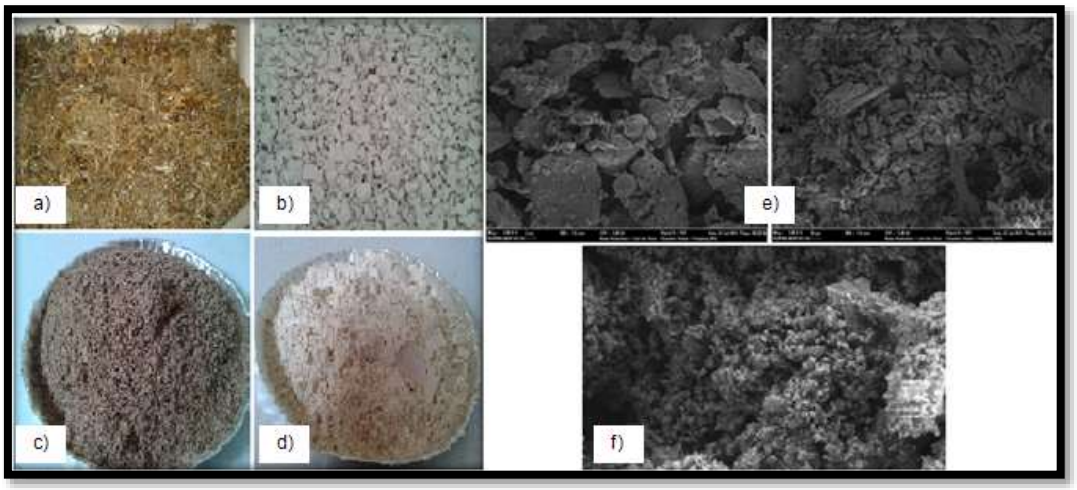



**Figure 1:** Photographs a) the Hops plants, b) marble wastes, c) powder of Hops, d) powder of marble wastes; SEM images of grinded e) hops and f) marble waste

Polyester matrix was combined with marble wastes and hops at different particle size content. In this work the average particle size was calculated ≤90 μm for both fillers. Fig. 1 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 hops 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.

**Table 1:** Mass ratio % of composites

| | H1* (%) | H2 * (%) | H3* (%) |
|---|---|---|---|
| Polyester | 41.81 | 45.98 | 51.06 |
| Hops 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

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.

### 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(2.1) 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 Eq.(2.2).

$$\sigma = \frac{3FL}{2WD^2} \tag{2.1}$$

$$E = \frac{L^3}{4WD^3} m \tag{2.2}$$

In Equations (2.1) and (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.

$$BulkDensity = \frac{W_1}{W_3 - W_2} x\rho_{water} \tag{2.3}$$

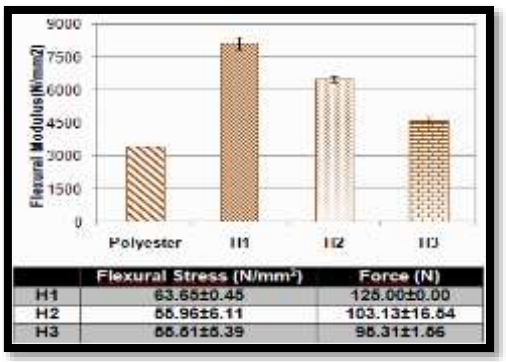
$$\%\ Open\ Porosity = \frac{W_3 - W_1}{W_3 - W_2} x100 \tag{2.4}$$

In Equations (2.3) and (2.4); $W_1$ is the weight of clean, dry sample (g); $W_2$ is the weight of saturated sample, immersed in water (g); $W_3$ is the 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 hops 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 4000-400$cm^{-1}$ at 25°C.

## 3. Results and discussion

The flexural strength decreases with increasing void content. It is shown that the hops fiber does not reinforce polyester. The reason is possibly hydrophilic hops fiber is incompatible with hydrophobic polyester. This will result in poor interfacial adhesionThe strength of the composite materials decreased with the increase in hops/ marble waste ratio. The values of tensile properties are summarized in Fig.2.




| | Flexural Stress (N/mm²) | Force (N) |
|---|---|---|
| H1 | 63.65±0.45 | 125.00±0.00 |
| H2 | 55.96±6.11 | 103.13±16.54 |
| H3 | 56.61±6.39 | 96.31±1.66 |

**Figure 2:** Some properties of hops composite material's ability to resist deformation

Equation 2.1 was used to calculate the bending strength test elastic modulus of the sample. When the results are evaluated in the composite filled hops, elastic modulus decreased with the increasing of open porosity amount. Also the elastic modulus decreased with the increase of the filler elements. The highest elastic modulus was obtained in the sample of H1 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% hops powder content after which any more added fiber decrease the tensile strength.

Figure 4 is illustrated that the hardness of the composite materials does not have a critical change with the increase in hops/ marble waste ratio but same figure also shows water absorption% is really increased with hops fillings. Polyester matrix material have lowest percentage of WA.

## 4. Conclusions

Sample of H1 has a higher elastic modulus due to the content of high inorganic ceramics (ATH&marble) phase. Elastic modulus decreases with the content of increasing hops powder and decreasing the ceramic phase. Hardness results show opposite values for each of three samples. Strength values decrease with the content of increasing hops ratio and decreasing the ceramic phase. This is obtained 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, hops/ 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.

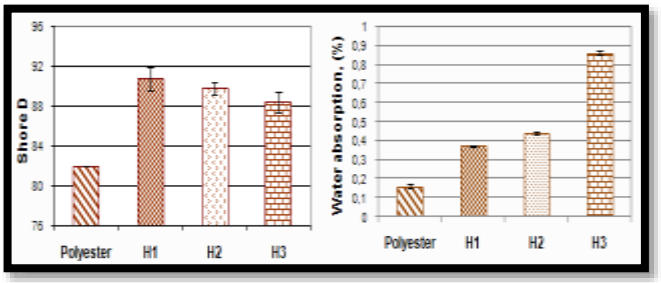



**Figure 3.** Physical testing results of hops/marble waste polyester matrix

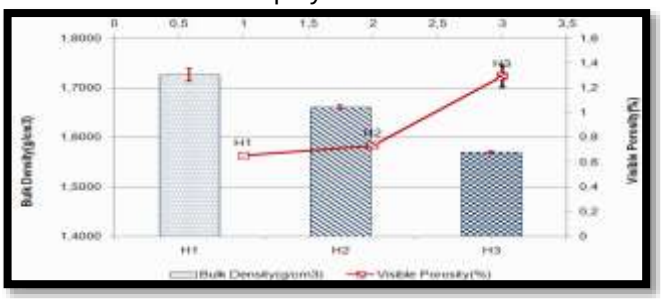



**Figure 4.** Hops/ marble waste reinforcement polyester composite porosity related properties

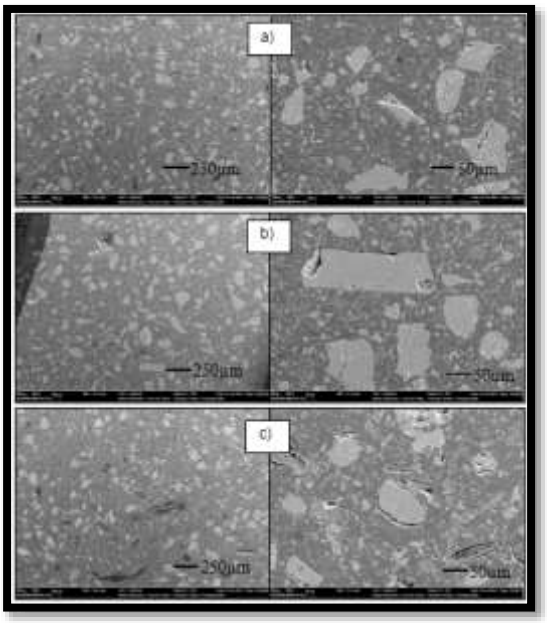



**Figure 5:** SEM images of the fracture surface of different polyester composites. Figures a, b and c are pairs in different magnitudes of H1; H2; H3

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