Mechanical and Flame Retardancy Properties of Polyester-(pine cone/boron oxide) Composites

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Abstract In recent years researchers focused on solid waste management due to the environmental issues and ecological susceptibility. Renewable resources such as natural fibers are environmentally friendly and low-cost alternatives when compared to other fibers like glass and carbon. Turkey has much potential of pine forests which is 54,000 ha and its total stone pine cone production is annually 3500 tons. Pine cone as a solid waste was used to produce composite materials due to these various advantages. Boron compounds compresses combustion by sealing the surface of the burning material and inhibit mass transfer of combustible vapors by blocking its contact with oxygen. Considering these properties of boron it was used with pine cone as a filler to provide flame retardancy. Boron oxide and waste pine cone fibers were used to manufacture the polyester composites by using casting process. Flame retardancy (limiting oxygen index (LOI)), some mechanical (bending strength, flexural modulus) and physical properties (water absorption, swelling thickness) were investigated at different fiber content. SEM analysis of the final products was performed to observe morphological structure.

Keywords: Polymer matrix composites, boron oxide, waste pine cone, flame retardancy, mechanical properties

1. Introduction

The composite materials have superior properties such as stiffness, corrosion resistance, strength, high temperature performance and hardness. Due to these properties composite materials are more preferable than the individual components (Bagherpour, 2012). Recently researchers are interested in natural based fiber composites due to the environmental issues. Fiber reinforced polyesters have great potential to use in various application areas like packaging, construction, furniture, electronics and automotive industries (Baştürk *et al*., 2015). Not only their good mechanical properties but also their resistance to fire is also an important issue to use these composites in different areas (Bagherpour, 2012). The mechanical properties of composites may show difference depend on the type of matrix and reinforcement. There are several studies on natural fiber composites. Ramanaiah *et al*. have investigated mechanical and fire properties of composites reinforced with sansevieria. The effect of fiber content on mechanical properties was studied. They concluded that tensile strength and impact strength at maximum fiber content were 2.55 and 4.2 times to that of pure resin, respectively. Oxygen consumption cone calorimeter technique was used to determine the fire behavior of composite. The addition of sansevieria fiber has effectively reduced the heat release rate (HRR) and peak heat release rate (PHRR) of the matrix by 10.4%, and 25.7%, respectively (Ramanaiah *et al*., 2013). Mechanical properties of pine cone fiber/clay hybrid composite were investigated by Arrakhiz *et al*. They indicated that the tensile properties results show the Young's modulus has increased for whole systems reaching a gain of 80%, while tensile strength remained stable with the use of both fiber content (Arrakhiz *et al*., 2013). Fire properties of composites were also studied by researchers. Idumah *et al*. determined the influence of exfoliated graphene nanoplatelets on flame retardancy of kenaf flour polypropylene hybrid nanocomposites. Limiting oxygen index test instrument was employed for flammability investigations. They mentioned that the graphane nanoplatelets char structure improved flame retardancy by acting as heat shield and protective layering on surface of the materials (Idumah *et al*., 2017). In this study mechanical and flame reterdancy properties of pine cone/boron oxide composites were investigated at different fiber content.

2. Materials and Method

2.1. Materials

In this study composite materials were produced from 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), waste pine cone obtained from Bilecik Seyh Edebali University garden and boron oxide supplied by Eti Maden in Turkey. Boron oxide (density of 1.84 g/cm^3, particle size 0.315 mm), and waste pine cone were used as a reinforcement. Methyl ethyl ketone peroxide was hardener (MEKP) (Butanox™ M-60, AkzoNobel Products) and Cobalt 1% solution was promoters used in the curing of polyester resins. Polypropylene graft maleic anhydride (Aldrich Chemistry) was used as a coupling agent. In Fig. 1 powder form of reinforcements can be seen.

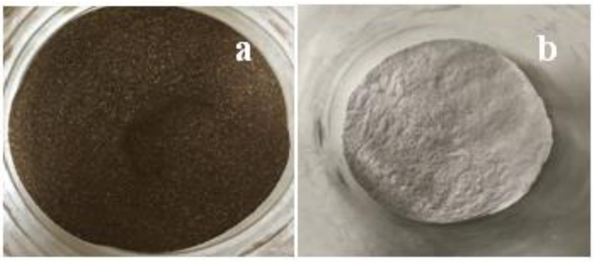

Figure 1. a) Waste pine cone powder and b) boron oxide powder

2.2. Composite preparation

Pine cones which were selected from university garden firstly dried in air. Then the polyester matrix was compounded, respectively, with reinforcement fillings in different ratios by volume. The raw material formulations, which are given per the volume proportion in percentage, used for the composites are presented in Table 1.

Table 1. Ratio of materials used for composite manufacture

Sample Code	P [v %]	B1 [v %]	Polyester [v %]
B1P	-	8	92
PI1P	5	-	95
PI2P	7	-	93
PI3P	8	-	92
PI1B1P	5	8	87
PI2B1P	6	8	86
PI3B1P	8	8	84

[v%]: Volume percent

P: pine cone powder

B1: boron oxide

Polyester resin and reinforcement materials were first mixed in the indicated ratios using a speed of 700, 1200 and 1700 rpm (Stuart scientific mechanical stirrer), 5 minutes cycle time for each. Mixture was hold on under the vacuum in 5 min. After the accelerator and hardener were added to mixture last mixture was poured into a mold (Figure 2). Composites which were in the mold for 2 hours were kept at room temperature for 1 day and then kept at 110˚C for 2 hours in an oven (Binder, Germany).

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 to determine the mechanical properties of composites. Following formulas were used for calculations of the three point bending tests (2.1 and 2.2). The 5 samples of each group were tested and average values were reported. The bending measurements were performed at the ambient conditions (23±2°C). The bending strength and flexural modulus of the elasticity in the bending tests were calculated by using the equation 2.1 and 2.2.

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

- σ is the bending stress of the specimens, N/mm^2
- E is the flexural modulus of elasticity of the specimens, 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

Izod impact values were recorded by Izod impact test device, brand of DVT CD, Devotrans Quality Control Test Instruments Ltd. Shore hardness is a measure of the resistance of a composite sample.

Density measurements of the composite specimens were done according to the Archimedes' Principle. The physical properties examined were bulk density, thickness swelling (TS), open porosity and water absorption (WA). These tests were carried out with test sample sizes of 5x5 cm. Following formulas were used to obtain physical properties of composite materials.

Bulk density= $(W_1/(W_3-W_2))*\rho_{water}$ (2.3)

% Open porosity= $((W_3-W_1)/(W_3-W_2))*100$ (2.4)

%, WA= $(W_3 - W_1) / W_1 * 100$ (2.5)

- W_1; dry weight
- W_2 ;suspended weight
- W_3; wet weight

The flame retardancy properties of composite materials were carried out according to ASTM D 2863 standard with LOI test. The LOI test method is one of the best test methods for seeing the flammability and combustion characteristics of materials. The LOI value means the amount of oxygen needed to keep a material burning in the air. The high LOI value indicates that the material is more difficult to burn in standard atmospheres. In principle, a small test sample is placed vertically into a transparent chimney passing through a mixture of oxygen and nitrogen up through it (figure 2).

Figure 2. LOI Test Machine

The top of the test sample is ignited, followed by the burning behavior of the test sample, and the duration of the burn or the duration of the burning test sample is compared to predetermined threshold values for such combustion. Experiments using a series of test samples at different oxygen concentrations predict the smallest oxygen concentration value required for continuation of the burn. The results are given in terms of the oxygen index value.

3. Results and Discussions

3.1. Mechanical Test Results

From figure 3 it can be seen the flexural strength values of pine cone/polyester composites are lower than boron oxide/polyester composites. When flexural strength and flexural modulus were both evaluated boron oxide has better mechanical properties compared with pine cone/polyester composites. Increasing ratio of pine cone had led to decrease of bending strength and increase of flexural modulus.

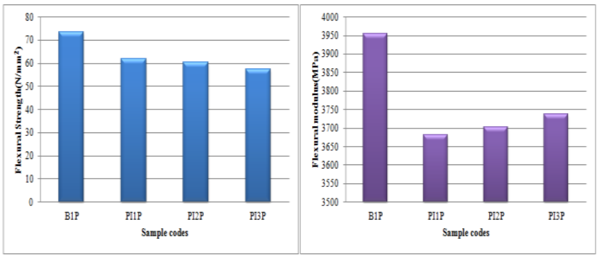

Figure 3. Bending properties of boron oxide/polyester and waste pine cone/polyester composites

Figure 4 shows us the bending properties of boron oxide/pine cone composites. When both filler was used together it can be indicated that while flexural strength decreased with the increasing ratio of pine cone, flexural modulus increased from 3950 MPa to 3980 MPa. It can be concluded that boron oxide had led to partial improvement on mechanical properties of pine cone/polyester composites.

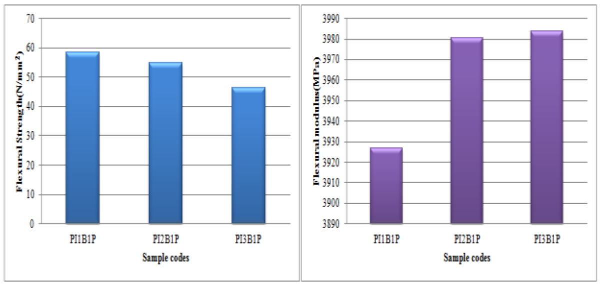

Figure 4. Bending properties of waste pine cone/boron oxide composites

3.2. Physical Test Results

Table 2 includes the physical properties of boron oxide and waste pine cone/polyester composites like bulk density, open porosity, thickness swelling and water absorption.

Table 2. Physical properties of composites

Sample Code	Bulk Density(g/cm³)	Open Porosity (%)	Thickness Swelling (%)	Water Absorption (%)
B1P	1.241	0.664	3.510	0.535
PI1P	1.156	1.959	1.701	1.696
PI2P	1.151	1.993	1.704	1.743
PI3P	1.141	2.192	1.707	1.921
PI1B1P	1.191	3.278	2.362	2.756
PI2B1P	1.150	0.849	2.341	0.724
PI3B1P	1.142	0.296	2.152	0.244

According to results it can be indicated that bulk density of composites decreased when the pine cone filler added in increasing amounts. Boron oxide doped composite has the highest thickness swelling and the water absorption value of B1P is 0.535. Generally lower water absorption values are better for the composite samples to provide better strength (Alomayri *et al.*, 2014). Water molecules can diffuse into the material and become trapped there, especially if the material contains voids that hydrogen bond can the water in place and this cause to decrease in mechanical properties. According to this approach open porosity values are in parallel with water absorption values of composites (Table 2).

3.3. LOI Measurement

LOI measurement was carried out for the composite samples which give the best mechanical and physical properties (B1P, PI1P, and PI1B1P). In Table 3 LOI values for these composites were given.

Table 3. LOI values of composites

Composite Codes	LOI
B1P	19
PI1P	20
PI1B1P	22

From the results it can be indicated that boron oxide/polyester composite has the lowest LOI value. Pine cone/polyester value is higher than B1P sample. When pine cone and boron oxide use together as filler it was observed that boron oxide improved the flammability property of polyester composite with a gain of 10%.

3.4. Morphology of Composite Samples

Morphological analysis of polyester composites can be seen from the SEM images in Figure 5. According to the SEM images it can be clearly seen B1P composite has smoother structure than the composites filled with pine cone as pine cone has a hydrophilic character that made it more porous to enclose water in its structure (Gokdai and Akpinar Borazan, 2016).

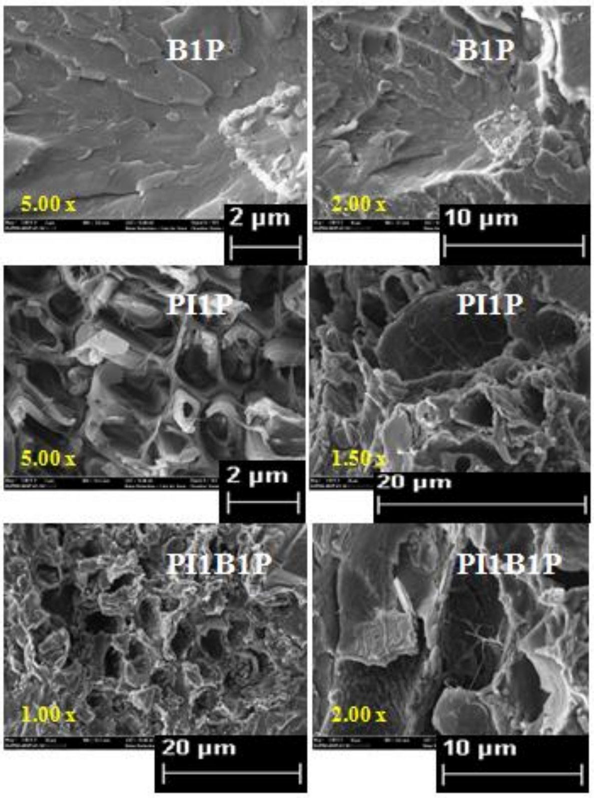

Figure 5. SEM images of composite samples

Addition of coupling agents to natural fiber composites led to decrease the pores between the polymer and reinforcements (Perez-Fonseca *et al.*, 2014). It was observed in the SEM image of PI1B1P that the contraction between the fillers and polymer is better than the PI1P composite.

4. Conclusions

According to the mechanical test results boron oxide has better mechanical properties compared with pine cone/polyester composites. Increasing ratio of pine cone caused to decrease of bending strength and increase of flexural modulus. And in general, increasing amounts of pine cone filler led to a decrease in the mechanical strength for boron oxide filler. In LOI test results pure boron oxide and pure pine cone samples have lower LOI values when compared with the reinforced with boron oxide. It can be finally concluded that boron oxide gave a flame retardant property to pine cone/polyester composites with a gain of 10%.

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