Pine Cone and Boron Compounds Effect as Reinforcement on Mechanical and Flammability Properties of Polyester Composites

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Abstract

In recent years focus on the development of natural fiber composites has been increased due to their superior properties such as light-weight, high strength and stiffness. Natural fibers are known environmentally friendly and they can be used alternatively to glass and carbon fibers because of their low-cost. Pine cone fibers are good preference to use for composite manufacturing because they are mainly consisted with cellulose, hemicelluloses and lignin macromolecules which provide a hydrophilic character. Potential pine cone forest reserve of Turkey is 54,000 ha and its total stone pine cone production is annually 3500 tons. Boron compounds such as borax, boric acid and zinc borate are generally used for their flame reterdant effect. These compounds can inhibit mass transfer of combustible vapors by blocking its contact with oxygen. In this study three kinds of boron compounds such as boron oxide, borax pentahydrate and borax decahydrate were used to provide better mechanical properties and better incombustibility. Synergistic effect of both waste pine cone and boron compounds were sampled to manufacture the polyester composites by using casting process. Some mechanical (bending strength, flexural modulus, izod impact), flame retardancy (limiting oxygen index (LOI)), and physical properties (water absorption, swelling thickness, open porosity, bulk density) were obtained at different fiber content. SEM analysis of the final products was performed to observe morphological structure. According to mechanical test results boron oxide showed better bending strength and flexural modulus compared with the other boron compounds. LOI of composites with boron compound was higher than the composites with only pine cone reinforcement.

Keywords: *Pine cone waste, boron, mechanical properties, flame reterdancy, physical properties*

1. Introduction

Recently natural fibers are more preferable compared with the other conventional fibers due to their various advantages in composite materials (Perez-Fonseca, Robledo-Ortiz, Ramirez-Arreola, Ortega-Gudiño, Rodrigue & González-Núñez, 2014). The fibers in polymer composites have generally high strength and modulus and they bonded to a matrix to provide a discrete interface between matrix and fibers (Boopalan, Niranjanaa & Umapathy, 2013). Natural fibers are renewable and environmentally friendly. Several natural fibers such as henequen, alfa, coir or sugarcane bagasse, banana, chestnut, (Arrakhiz, El Achaby, Benmoussa, Bouhfid, Essassi & Qaiss, 2012) cellulose, wool, hair and chicken feather (Tran , Prosenc, Franko & Benzi, 2016) were used as reinforcement to manufacture polymer composite materials. In literature pine cone waste were rarely used in polymer composites although they have advantages as reinforcement. Pine cones are mainly consisting with lignin, cellulose and hemicelluloses that give hydrophilic character to them. Also they can inhibit the weak coherence between polymer matrix and natural fibers (Arrakhiz, Benmoussa, Bouhfid & Qaiss, 2013). Polymers are known to have high flammability. For this reason, the development of safety and environmental flame retardancy polymers is of great importance. Composite materials composed of polymers are widely used in our daily life (such as housing materials, transport and electrical engineering) and new flame retardants are being studied for polymer composites in order to decrease their high flammability properties (Katancic, Travas-Sejdic & Hrnjak-Murgic, 2011). One of the flame retardant can be used in polymer composites is boron that are known as a halogen-free flame retardant group similar to phosphorus and nitrogen flame retardants. The main elements of the flame retardant preference of boron compounds are their extraordinary nature, low toxicity, low cost and easy availability. For this reason, these properties make boron compounds interesting and they can easily used to provide flame retardant property for various materials such as wood, fiber and cellulose (Intharapat, Nakason & Kongnoo, 2016). Recently there are several studies on this subject. Arrakhiz et al. have investigated the mechanical properties of polypropylene composites reinforced with pine cone fibers. In their study pine cone fibers were alkali washed to remove waxes and non cellulosic surface component. They obtained the effect of alkali treatment on mechanical properties of pine cone composites. The results indicated that a gain of 43% in the Young's modulus was occured because of improved adhesion between fibers and matrix at the interface (Arrakhiz et al., 2012). In the study of Perez-Fonseca et al. effect of hybridization on the physical and mechanical properties of polyethylene-pine/avage composites was investigated. The effect of hybridization was carried out with morphological, mechanical and water immersion tests for two total fiber contents, 20 and 30 wt. %, and different pine-agave fiber ratios (100–0, 80–20, 60–40, 40–60 and 0–100). The results showed that addition of fibers provide better tensile, flexural and impact strength, while pine fibers decreases water absorption (Perez-Fonseca et al., 2014). Other study was the evaluation of mechanical properties of banana and sisal fiber reinforced epoxy composites by Arthanarieswaran et al. Determination of mechanical properties based on influence of glass fiber hybridization. It was obtained that the addition of two and three layer of glass fiber was improved the tensile strength by a factor of 2.34 and 4.13 respectively. The flexural properties of banana–sisal fiber with two layers of glass fibers rather than three layers and the laminate with sisal and three glass ply offers better impact strength (Arthanarieswaran, Kumaravel & Kathirselvam, 2014). Intharapat et al. researched the effect of boric acid on flammability properties of natural rubber. Different boric acid concentrations were used into the rubber molecules. They concluded that the increase of mole% of boron content caused the increase of LOI values over original epoxidized natural rubber (Intharapat et al., 2016).

In the study of Madakbaş et al. flammability properties of polyacrylonitrile/hexagonal boron nitride composites were investigated. It was aimed to prepare polyacrylonitrile (PAN)/hexagonal boron nitride (h-BN) composites with improved flame retardancy properties. In the result of study flame retardancy of the PAN composite materials improved with the addition of h-BN and the LOI value reached to 27% from 18% (Madakbaş, Çakmakçı & Kahraman, 2013).

In this study it is aimed to observe mechanical and flame retardancy properties of pine cone/boron compounds polymer matrix composites at different filler ratios with a casting method.

2. Materials and Method

2.1. Materials

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 compounds such as boron oxide, borax decahydrate and borax pentahydrate were supplied by Eti Maden in Turkey. Boron oxide (density of 1.84 g/cm^3, particle size 0.315 mm), borax decahydrate (density of 1.71 g/cm^3, particle size 1.180 mm), borax pentahydrate (density of 1.81 g/cm^3, particle size 1.180 mm) and waste pine cone were used as 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 images belong to powder form of reinforcements can be seen.

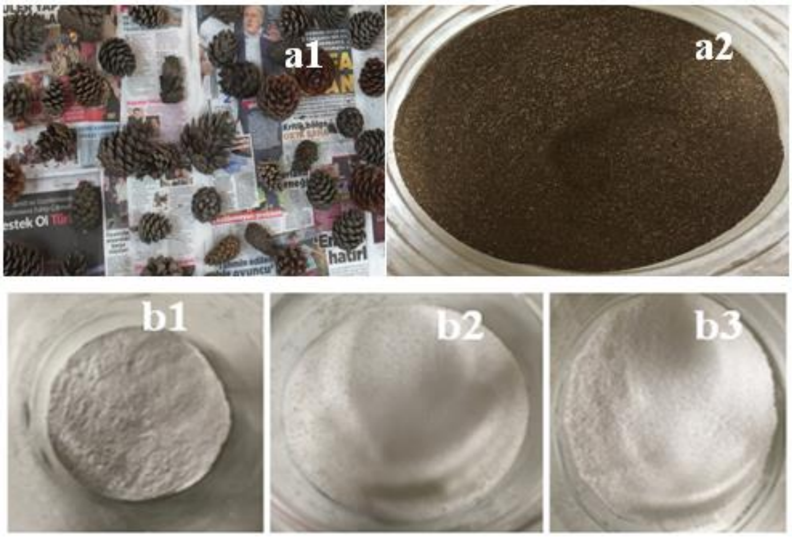

Figure 1: *a1) Waste pine cone a2) waste pine cone powder b1) boron oxide, b2) borax decahydrate, b3) borax pentahydrate*

2.2. Composite preparation

Pine cones which were collected from university garden firstly dried in air atmosphere. 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 composite production are indicated in Table 1.

Table 1: *Ratio of materials used for composite manufacture*

Sample Code	P (v, %)	B1 (v %)	B2 (v %)	B3 (v %)	Polyester (v %)
B1P	-	8	-	-	92
B2P	-	-	8	-	92
B3P	-	-	-	8	92
PI1P	5	-	-	-	95
PI2P	7	-	-	-	93
PI3P	8	-	-	-	92
PI1B1P	5	8	-	-	87
PI2B1P	6	8	-	-	86
PI3B1P	8	8	-	-	84
PI1B2P	5	-	8	-	87
PI2B2P	6	-	8	-	86
PI3B2P	8	-	8	-	84
PI1B3P	5	-	-	8	87
PI2B3P	6	-	-	8	86
PI3B3P	8	-	-	8	84

[v %]: Volume percent
P: pine cone powder
B1: boron oxide
B2: borax pentahydrate
B3: borax decahydrate

Stuart scientific mechanical stirrer was used to mix the polyester and powders to obtaine a homogenous particle distribution with a speed of 700, 1200 and 1700 rpm cycle time for each. To eliminate the gas bubble formation, the prepared composite mixtures were left under vacuum 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). Figure 2 shows experimental procedure of composite manufacturing.

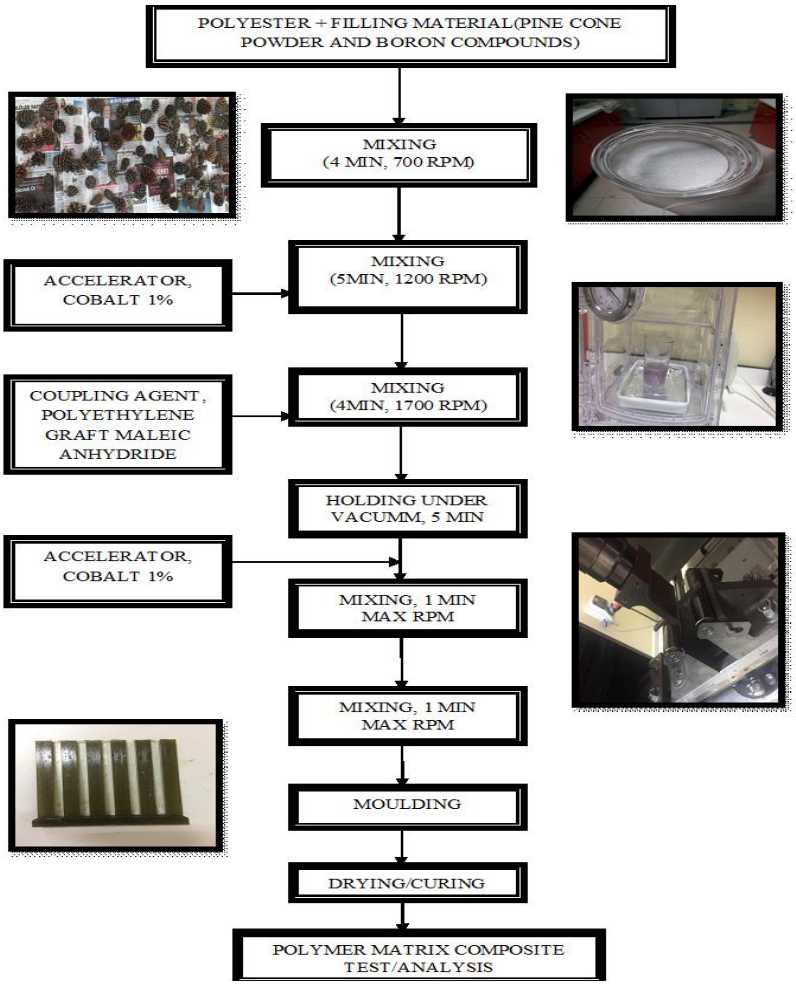

Figure 2: *Experimental procedure of composite manufacturing*

2.3. Experimental Method

The tests were conducted in an SCHIMADZU™ mechanical testing machine at a cross-head displacement rate of 2 mm/min. Following formulas were used for calculations of the three point bending tests. 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 1 and 2.

$$\sigma = \frac{3FL}{2WD^2} \quad (1) \qquad E = \frac{L^3}{4WD^3} m \quad (2)$$

- 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

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= $(W_1/(W_3-W_2))*\rho_{water}$ (3)

% Open porosity= $((W_3-W_1)/(W_3-W_2))*100$ (4)

%, WA= $(W_3 - W_1) / W_1 * 100$ (5)

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

The energy values absorbed by the composite materials were recorded by Izod impact test device, brand of DVT CD, Devotrans Quality Control Test Instruments Ltd. The load applied to the composite specimens was 6 joules; impact test was carried out with hammer energy. The impact strength was obtained by the following formula.

$$Impact\ resistance = \frac{Fracture\ energy, Joule}{Cross\ sectional\ area, m2} \tag{6}$$

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. Composite samples were placed vertically in the center of the glass column (figure 3) using a sample holder. After placement composite samples were burned in a controlled atmosphere of oxygen and nitrogen (Tomak & Cavdar, 2013).

Figure 3: *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 2 test samples at different oxygen and nitrogen concentrations (adjusted according to the LOI values given in standard) 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. Some Mechanical and Physical Properties of Composites

The mechanical test results show that bending properties of boron oxide (B1) are better than the other boron compounds (B2 and B3). Boron oxide has higher flexural strength and flexural modulus value compared with borax penta and decahydrate. It was thought due to the water consist of B2 and B3. Boron oxide (B_2O_3) known as anhydrous borax and borax penta and decahydrate consist 5 and 10 H_2O respectively. The boron compound containing the most water showed the lowest strength as expected (Figure 4). Water molecules led to microvoids at the interface between the polymer and fibers these voids cause a decrease in mechanical properties. (Arrakhiz et al., 2013).

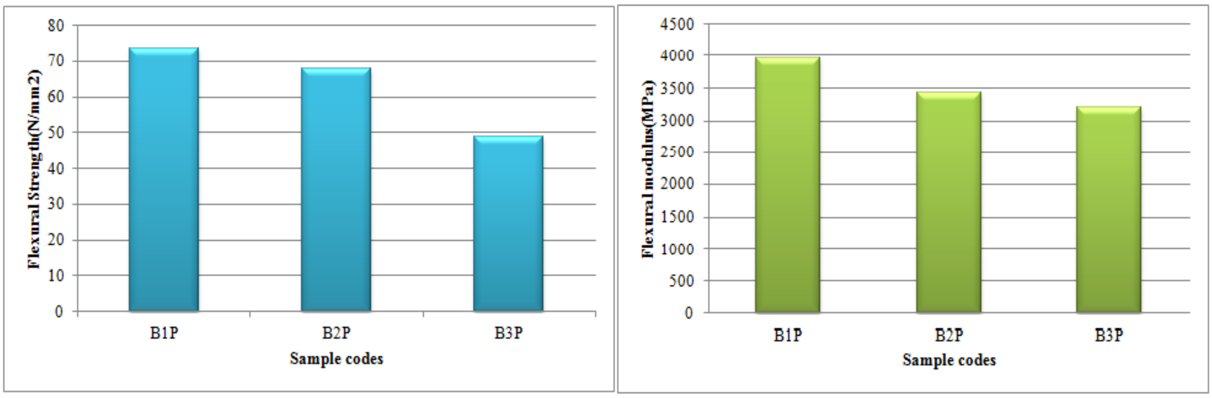

Figure 4: *Bending properties of boron/polyester composites*

Figure 5 includes the bending properties of pine cone/boron polyester composites. When the graphics were evaluated, the increase in the amount of pine cone decreased the bending strength and increased the flexural modulus. In the graph of flexural modulus of composites it can be clearly seen that boron oxide has higher flexural modulus than pine/polyester composites. While the other boron compounds (B2 and B3) have lower flexural modulus than PI series, flexural modulus of boron oxide series increased sharply. According to the bending properties it can be concluded that boron oxide was better aligned with the pine cone filler. And in general, a decrease in the mechanical strength for different boron compounds in increasing amounts of pine cone.

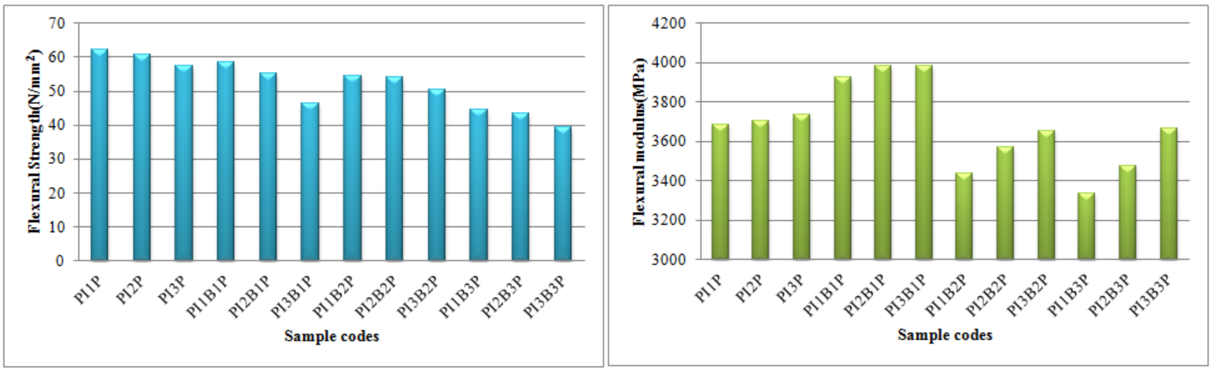

Figure 5: *Bending properties of pine cone/boron composite materials*

Impact values of composites were given in Table 2. Boron oxide polyester composite has the highest izod impact value when compared with other composites. Boron oxide polyester composite showed also better mechanical properties.

From Table 2 it can be clearly seen that when the filler amount increased izod impact values were not changed significantly.

Table 2: *Physical and mechanical properties of composite materials*

Sample code	Bulk Density (g/cm^3)	Open Porosity (%)	Water Absorption (%)	Thickness swelling, (%)	Izod Impact (J/mm^2)	Flexural Strength (N/mm^2)	Flexural Modulus (MPa)
B1P	1.241	0.664	0.535	3.510	7.397	73.61	3954.22
B2P	1.190	1.911	1.607	1.466	5.021	67.85	3427.05
B3P	1.164	3.683	3.278	1.690	7.013	48.73	3203.26
PI1P	1.156	1.959	1.696	1.701	6.001	62.06	3682.16
PI2P	1.151	1.993	1.743	1.705	6.562	60.56	3702.72
PI3P	1.141	2.192	1.921	1.707	7.193	57.41	3737.73
PI1B1P	1.191	3.278	2.756	2.362	6.010	58.57	3926.75
PI2B1P	1.150	0.849	0.724	3.100	5.699	55.00	3980.46
PI3B1P	1.212	0.296	0.244	3.360	5.685	46.44	3983.64
PI1B2P	1.171	3.122	2.685	0.888	3.560	54.25	3439.14
PI2B2P	1.206	0.272	2.785	1.212	4.693	54.16	3571.45
PI3B2P	1.162	3.739	3.223	2.965	5.605	50.30	3655.06
PI1B3P	1.172	1.211	1.039	1.315	5.251	44.57	3336.09
PI2B3P	1.169	1.307	1.101	1.242	4.810	43.51	3476.59
PI3B3P	1.162	1.367	1.175	1.100	4.674	39.50	3667.90

In Table 2 when some physical properties of samples were evaluated it can be indicated that open porosity and water absorption values are compatible with each other. As the number of voids in composite materials increases, the demand for water to fill these voids increases and it means more water absorption values. Also higher water absorption values led to higher thickness swelling in general.

3.2. Flammability Properties of Composite Materials

Flammability properties of composites given the best mechanical properties were determined according to ASTM D 2863 standard. LOI values of three samples with better mechanical properties (B1P, PI1P and PI1B1P) were given in Table 3 and images of burned samples were given in Figure 6.

Table 3: *Flammability properties of composite materials*

Composite Codes	LOI
B1P	19
PI1P	20
PI1B1P	22

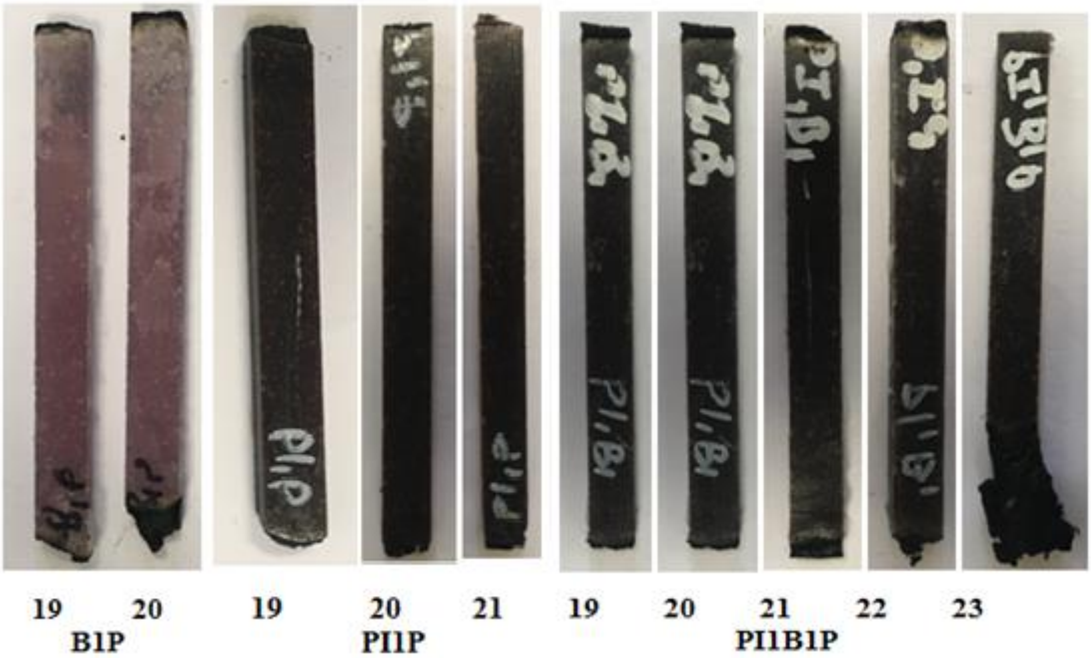

Figure 6. *Composite samples taken from LOI test machine*

When both mechanical and physical properties were evaluated boron oxide had better properties than other boron minerals as filler. Because of this approach flammability test were applied for these 3 samples. If the composite sample has higher LOI value it means it has more stable behavior in flame and duration to burn it completely is longer. Polymer is a flammable material as known when compared with the others and researches are still going on to increase flammability properties of all polymers (Gilman, Jackson, Morgan &Harris, 2000). We can see from the results that pure boron oxide and pure pine cone samples have lower LOI values compared with the pine cone polyester composite reinforced with boron oxide. It is clear from the table 3 boron oxide gave a flame retardant property to pine cone/polyester composites. In the study of Polat and Kaynak it was also indicated that boron oxide was improved the flammability properties of glass fiber reinforced composites (Polat & Kaynak, 2014). Boron oxide increased the LOI values of composites approximately 10%. It can be concluded when boron oxide and pine cone fillers used together they showed a positive effect on the flammability properties of composites.

3.3. TGA Analysis of Composites

Thermal stability results of composite samples which were exposed to LOI test were given by TG, DTG and DTA analysis in Figure 7. The top curve refers TG, the bottom curve refers DTA and the middle one mentions the DTG curve of composite samples.

According to results it can be indicated when boron oxide filler was used with pine cone the residual mass value increased to 25.19 % from 8.50 %. It is also compatible with the LOI test results as boron oxide gives flame retardancy to composites. The first stage is related with a few weight losses because of the dehydration of moisture and realize at a temperature range between 150ºC and 250ºC. The second stage refers the main evaporation reactions, where most of the sample weight is lost as volatile matter. From 460ºC to the temperature of 790ºC, a slow weight loss is determined (Blazquez et al., 2012).

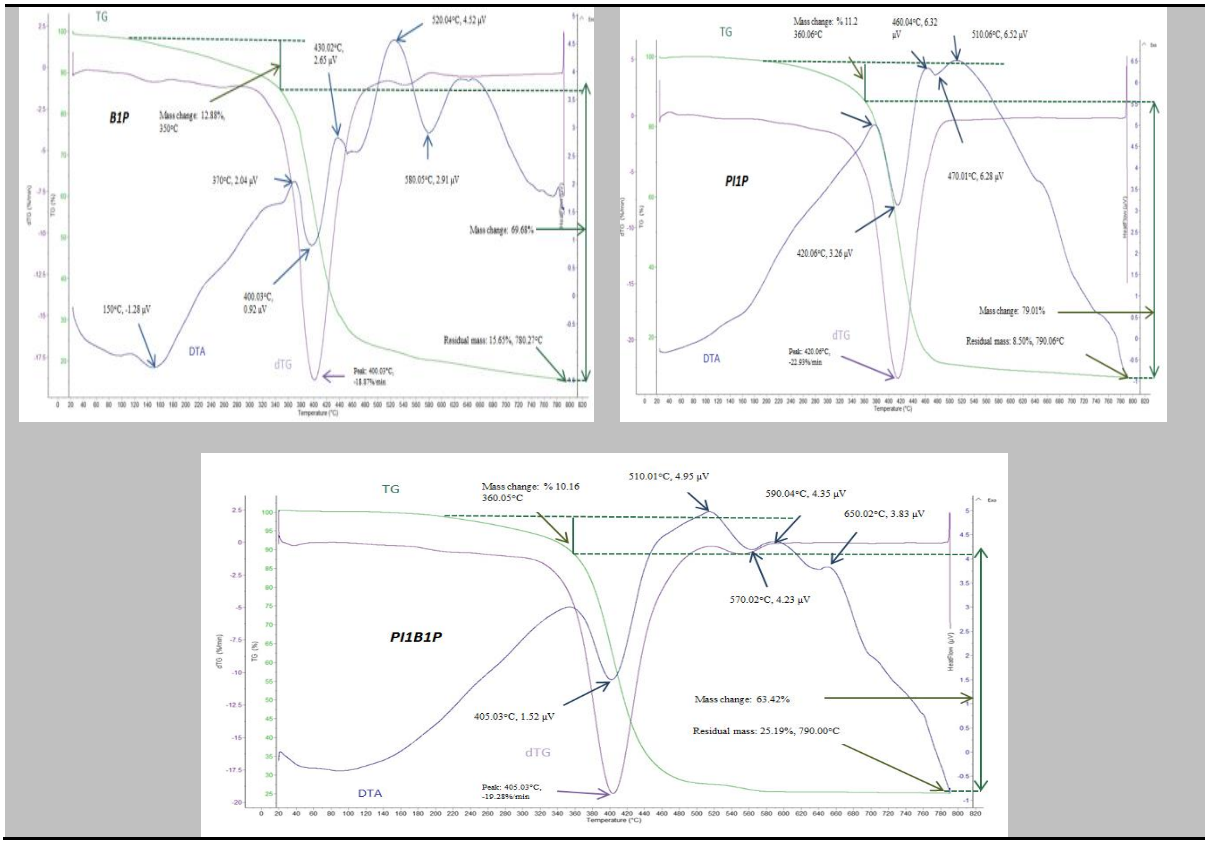

Figure 7. *TG, DTG and DTA curves of composite samples*

3.4. Morphological Characterization of Composite Materials

Morphological characterization of composites (B1P, PI1P, and PI1B1P) which were given the best mechanical, physical and flammability properties were obtained.

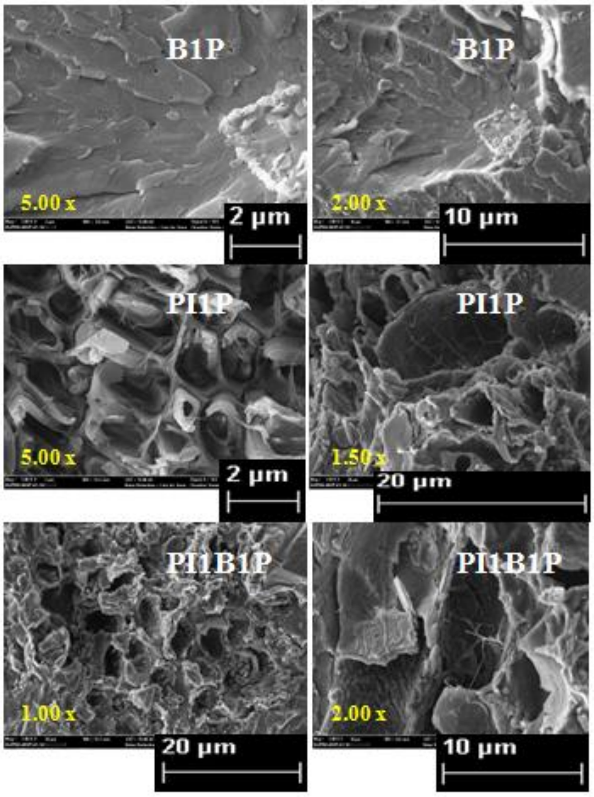

Figure 8. *SEM images of composite materials at different magnifications*

Figure 8 shows the SEM images of these 3 composite samples where it can be observed that pine cone has a tubular with a circular edge. Cellulose in the structure of pine cone was located in the fibrous walls (PI1P). From the image of composite reinforced with boron oxide and pine cone fillers (PI1B1P) it can be indicated that boron oxide filled the fibrous walls in pine cone structure providing a good adhesion with pine cone fillers. The adhesion between boron oxide and pine cone can be clearly seen from the SEM image of PI1B1P composites. It was also thought that coupling agent (polypropylene graft maleic anhydride) provided a good adhesion between polymer and fibers. It is known that the addition of coupling agents to natural fiber composites leds to decrease the voids between the polymer and fibers (Perez-Fonseca et al., 2014). It is visible in the SEM image of PI1B1P that the contraction between the fillers and polymer is better than the PI1P composite.

4. Conclusions

It can be concluded according to the mechanical analysis boron oxide (B1) showed better strength with the pine cone filler. And in general, increasing amounts of pine cone filler led to a decrease in the mechanical strength for different boron compounds. Addition of increasing amounts of boron compounds unfortunately did not improve the flexural strength of composites while boron oxide could successfully improved the flexural modulus of composites. We can see from the 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 indicated that boron oxide gave a flame retardant property to pine cone/polyester composites with a gain of 10%. It can be more improved by increasing the amount of boron filler in composites.

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