Research Article Open Access

Alev Akpinar Borazan*, Duygu Gokdai

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

https://doi.org/10.1515/chem-2018-0054
received January 30, 2018; accepted March 19, 2018.

Abstract: Natural fibers are known to be environmentally friendly, and they can be used as an alternative to glass and carbon fibers because of their low cost. Pine cone fibers are a good choice for use in composite manufacturing because they mainly consist of cellulose, hemicelluloses, and lignin macromolecules which provide a hydrophilic character. The potential pine cone forest reserve of Turkey is 54,000 ha. Boron compounds such as borax, boric acid. and zinc borate are generally used for their flame-retardant effect. In this study, three kinds of boron compounds, boron oxide, borax pentahydrate and borax decahydrate, were used to provide better mechanical properties and better incombustibility. The synergistic effects of both waste pine cone and boron compounds were sampled for the manufacture of polyester composites by using a casting process. The composites produced with different fiber contents were characterized by some mechanical properties (bending strength, flexural modulus, izod impact); physical analyses (water absorption, swelling thickness, open porosity, bulk density); flame retardancy (LOI); and TGA, SEM-EDS, and FT-IR analyses. According to mechanical test results, boron oxide showed better bending strength and flexural modulus compared to the other boron compounds. The LOI of composites with a boron compound was higher than the composites with only pine cone reinforcement.

Keywords: Boron, Characterization; Flame Retardancy; Mechanical Properties; Physical Properties.

1 Introduction

In recent years, natural fibers have been preferred to conventional fibers due to their various advantages for use in composite materials [1]. The fibers in polymer composites generally have high strength and modulus, and they bond in a matrix to provide a discrete interface between matrix and fibers [2]. Natural fibers are renewable and environmentally friendly. Several natural fibers such as henequen, alfa, coir or sugarcane bagasse, banana, chestnut, [3] cellulose, wool, hair, and chicken feathers [4] were used as reinforcement in the manufacture of polymer composite materials. In the literature, pine cone waste was rarely used in polymer composites; although, they have advantages as reinforcement. Pine cones mainly consist of lignin, cellulose, and hemicelluloses that give them a hydrophilic character. Also, they can inhibit the weak coherence between a polymer matrix and natural fibers [5]. Polymers are known to have high flammability. For this reason, the development of safe and environmentally-friendly flame retardancy polymers is of great importance. Composite materials composed of polymers are widely used in our daily life (such as in housing materials, transport, and electrical engineering), and new flame retardants are being studied for their polymer composites in order to decrease their properties of high flammability [6]. One of the flame retardants which can be used in polymer composites is boron; it is part of a halogen-free flame-retardant group similar to phosphorus and nitrogen flame retardants. The main elements of the flame-retardant properties of boron compounds are their extraordinary properties of low toxicity, low cost, and easy availability. These properties make boron compounds interesting, and they can easily be used to provide flame retardant properties to various materials such as wood, fiber, and cellulose [7]. There are several recent 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

---

***Corresponding author: Alev Akpinar Borazan,** Bilecik Seyh Edebali University, Department of Chemical Engineering, Bilecik, Turkey, E-mail: alev.akpinar@bilecik.edu.tr
Duygu Gokdai: Bilecik Seyh Edebali University, Department of Chemical Engineering, Bilecik, Turkey

components; this had the effect of alkali treatment on the mechanical properties of pine cone composites. The results indicated that a gain of 43% in the Young's modulus was achieved because of improved adhesion between fibers and matrix at the interface [3]. In the study by Perez-Fonseca et al., the effect of hybridization on the physical and mechanical properties of polyethylene-pine/agave 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 the addition of fibers provide better tensile, flexural, and impact strength, while the addition of pine fibers decreases water absorption [1]. Another study by Arthanarieswaran et al., evaluated the mechanical properties of banana and sisal fiber reinforced epoxy composites. The mechanical properties were determined based on the influence of glass fiber hybridization on the natural fibers-reinforced epoxy composites. It was observed that the addition of two and three layers of glass fiber improved 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 laminate with sisal and three glass ply offers better impact strength [8]. Intharapat et al. researched the effects of boric acid on the flame-retardant properties of natural rubber. Different boric acid concentrations were added to the rubber molecules. They concluded that the increase of the mole percentage of the boron content caused an increase in LOI values over original epoxidized natural rubber [7]. Madakbaş et al. investigated the flame-retardant properties of polyacrylonitrile/hexagonal boron nitride composites. Flame retardancy of the PAN composite materials improved with the addition of h-BN, and the LOI value reached 27% from 18% [9].

The synergistic effect of an aromatic boronic acid derivative and magnesium hydroxide on the flame retardancy of epoxy resin was investigated by Zhang et al. The two compounds were mixed with epoxy resin to investigate the flame-retardant properties. It was shown that mixing epoxy resin with both boronic acid and magnesium hydroxide results in better thermal stability and flame-retardant properties than mixing with only one of the compounds. As a result of the impact strength test, boronic acid was found to be able to prevent combustion without decreasing the mechanical strength [10]. In the study by Uddin et al., the properties of flammability and thermal stability were studied with respect to adding boric acid. Boric acid, which was used as flame retardant, was mixed in transparent, hybrid films that were manufactured by solvent casting. Chitosan films showed fire retardant properties as the amount of boric acid increased. On the other hand, some mechanical properties such as tensile strength and Young's modulus of films improved with intermediate boric acid addition [11].

Xia et al. studied the mechanical properties of hybrid boron nitride-natural fiber composites. Kenaf fiber and different amounts of boron nitride were mixed to form composite material. With the increase of the boron nitride amount, elastic modulus was increased from 4.4 GPa to 13.3 GPa, which was attributed to the property of inorganic filler. As a result of this work, it can be concluded that the boron compounds are in good accord with the natural fibers. [12].

In our previous paper, mechanical properties were slightly better in polyester composites prepared with the addition of pine cone powder as filler [13]; therefore, the objective of this study is to investigate the effect of the incorporation of boron compounds while increasing the amount of pine cone powder on mechanical, morphological, thermal. and physical properties of polyester composites. Various characterization techniques such as FTIR and SEM were also used.

2 Materials and Method

2.1 Raw Materials

Waste pinecones were collected from the university garden. Air dried samples were ground (Brook Crompton Series 2000) and screened to give an average particle size of 0.2575 mm for individual characterization and production of composites. Boron compounds such as boron oxide, borax decahydrate, and borax pentahydrate were supplied from the Eti Mine Company Kırka Boron Works in Eskişehir, Turkey. All boron minerals were ground in a ball mill and sieved before usage. 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), and borax pentahydrate (density of 1.81 g/cm^3, particle size 1.180 mm) were used as reinforcement. Composite materials were produced from polyester resin (Polipol 383-G, Poliya Composite Resins, and Polymers Inc. with density of 1.076±0.05 g/cm^3 as a standard ISO 1675).

2.2 Development of Pine cone/Boron compounds-Reinforced polyester Composites

To produce the composites, the matrix and the fillers were mixed together in predetermined proportions as shown in

Table 1. Compositions of the composite were expressed by volume percentage.

To achieve homogeneous particle distribution of the fillers within the polyester matrix structure of composites, mixing was done by using the mechanical stirrer (Stuart Scientific, UK) with speeds of 700, 1200, and 1700 rpm cycle time for each. The accelerator (cobalt 1% solution), coupling agent (polypropylene graft maleic anhydride, Aldrich Chemistry), and hardener (Butanox™ M-60, AkzoNobel Products) were also added. To remove air from the casting dispersion and help to achieve a non-porous material, the prepared composite mixtures were left under vacuum for five minutes. The composite mixture was added to molds made of aluminum. Afterwards, the filled molds were allowed to air cure for two hours. Composites were extracted from the molds and kept at room temperature for a day, then placed in an oven (Binder, Germany) maintained at 110°C for 2 hours, and, lastly, slowly cooled to room temperature inside the oven.

Table 1: Composition of the Pine cone - Boron compounds reinforced polyester composites.

Composite codes	**% Matrix/Filler (by volume)**				
	P	**PI**	**B1**	**B2**	**B3**
B1P	92	-	8	-	-
B2P	92	-	-	8	-
B3P	92	-	-	-	8
PI1P	95	5			
PI2P	93	7			
PI3P	92	8			
PI1B1P	87	5	8	-	-
PI2B1P	86	7	8	-	-
PI3B1P	84	8	8	-	-
PI1B2P	87	5		8	
PI2B2P	86	7		8	
PI3B2P	84	8		8	
PI1B3P	87	5	-	-	8
PI2B3P	86	7	-	-	8
PI3B3P	84	8	-	-	8

PI: pine cone powder; B1: boron oxide; B2: borax pentahydrate; B3: borax decahydrate; P: Matrix(Polyester)

3 Method

3.1 Evaluation of bending properties

To evaluate the bending properties of composites, a mechanical testing machine (Shimadzu AG IC100 kN) was used. Flexural strength and flexural modulus are the most important mechanical parameters for brittle materials like particle reinforced composites. Flexural strength describes the ability of materials to withstand deformation under load. The flexural properties of the material were determined by a 3-point bending test as specified in ASTM D790. For this test, samples were with a width of 10 mm, a thickness of 4 mm, and a length of 100 mm. The crosshead velocity was assumed to be 2 mm/min, and the support span length was 60 mm. A minimum of five samples were tested for each processing condition. Flexural strength (σ) and flexural modulus (E) were then obtained using the expressions:

$$\sigma = ((3PL) / (2bd^2)) \tag{1}$$

$$E = (L^3 / (4bd^3)) * m \tag{2}$$

where L is the support span, mm; b, the width of the specimen, mm; d, the thickness, mm; P, the maximum load, N; and m, the slope of the initial straight-line portion of the load-displacement curve, N/mm.

3.2 Testing of physical properties

The density of the samples was determined using the Archimedes principle with distilled water. The physical properties examined were bulk density, thickness swelling (TS), open porosity, and water absorption (W_A). These tests were carried out with test sample sizes of 5x5 cm. The following formulas were used to obtain the physical properties of composite materials:

$$W_A, \% = ((W_3 - W_1) / W_1) * 100 \tag{3}$$

$$\text{bulk density} = (W_1 / (W_3 - W_2)) * 100 \tag{4}$$

$$\text{open porosity} = ((W_3 - W_1) / (W_3 - W_2)) * 100 \tag{5}$$

where W_1 *is* dry weight, W_2 is suspended weight, and W_3 is saturated weight.

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

$$\text{impact strength} = (\text{fracture energy, Joule}) / \\ /(\text{cross sectional area, m}^2) \tag{6}$$

3.3 Flammability properties of composites

The flame retardancy properties of composite materials were tested according to the ASTM D 2863 standard with the LOI test. The LOI test method was one of the best test methods for observing the flammability and combustion characteristics of materials. LOI value means the amount of oxygen needed to keep a material burning in the air. The high LOI value indicated that the material was more difficult to burn in standard atmospheres. Composite samples were placed vertically in the center of the glass column using a sample holder. After placement, composite samples were burned in a controlled atmosphere of oxygen and nitrogen [14].

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

3.4 Thermogravimetric analysis

The thermal stability of the composite samples was studied using a TGA device (Seteram LabSys Evo analyzer). TGA analysis was carried out in an alumina crucible. The crucibles were placed in the sample holder and heated in the presence of a continuous stream of gas with a controlled heating program. In the application, the sample was heated with a constant heating rate (20ºC/min) from room temperature to a desired ultimate temperature of 820º C, and their weight loss was recorded.

3.5 Characterization of composites

Fourier transform infrared spectroscopy (FTIR spectroscopy) is a useful way to identify the different functional groups present and to characterize the changes in the chemical structure of composite samples in the infrared region 4000–400 cm^{-1}. A Fourier transform infrared spectrometer (Perkin Elmer Spectrum 100, FTIR Spectrometer) was used to investigate the chemical structure of the composite.

The surface and cross-sectional morphology of the composite samples were examined using a scanning electron microscope (SEM., Zeiss Supra 40VP). Energy-dispersive X-ray (EDS) analysis was also carried out with the same microscope. Microstructural images of the composite samples were taken from the cracked surface of composites.

Ethical approval: The conducted research is not related to either human or animals use.

4 Results and discussions

4.1 Some mechanical and physical properties of composites

The mechanical test results of composite samples showed that the bending properties of the composite containing boron oxide (B1P) were better than the composite containing other boron compounds (B2P and B3P). Boron oxide (B_2O_3), known as anhydrous borax; borax penta; and decahydrate compounds consisted of five and ten molecules H_2O, respectively. B1P composite sample had the highest flexural strength and flexural modulus value compared with the composites containing borax penta and decahydrate compounds. It was thought that the water in the borax compounds negatively affected the bending properties of the composites.

Water molecules led to microvoids at the interface between the polymer and fibers; these voids caused a decrease in mechanical properties [5].

The effect of using boron compounds and adding increasing amounts of pine cone on the flexural properties of polyester composites are shown in Figure 2. Results indicated that the increase in the amount of pine cone decreased the flexural strength and increased the flexural modulus. The flexural strength decreased with the increase in loading up to eight percent by volume of pine cone to polyester composites as presented in Figure 2. This showed that addition of pine cone enhanced the rigidity of the composite and led to poor interfacial bonding between the fiber and the matrix.

At similar filler content, adding boron oxide (B1) to composites exhibits higher flexural strength and flexural modulus compared to polyester composites including either boron pentahydrate (B2) or boron decahydrate (B3). From the bending properties, it can be concluded that boron oxide was better aligned with the pine cone filler. This was caused by the enhancement of interfacial adhesion between the pinecone-boron oxide filler and the polyester matrix.

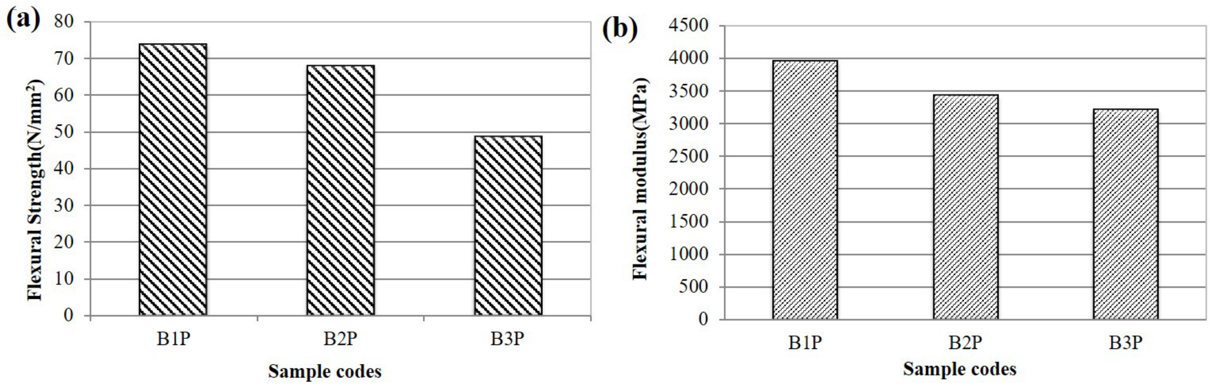

Figure 1: Bending properties of boron/polyester composites a) flexural strength, b) flexural modulus.

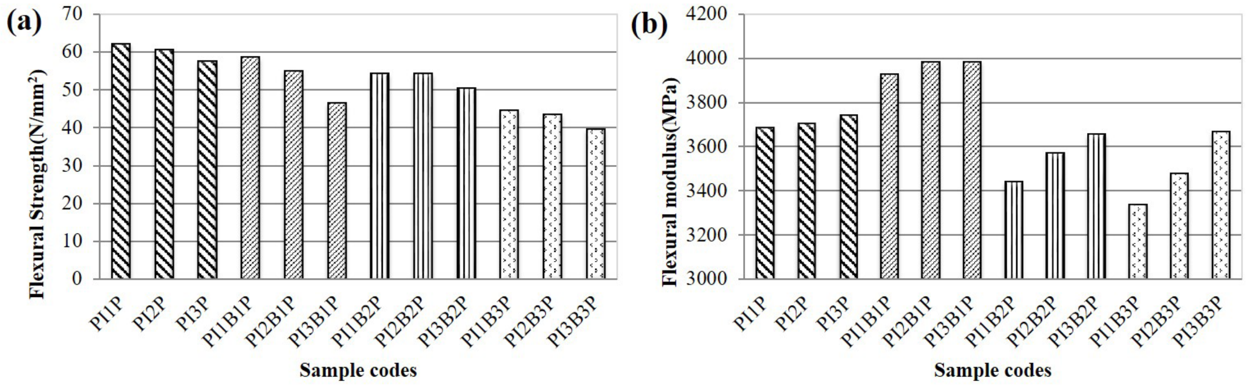

Figure 2: Bending properties of pine cone/boron polyester composite materials, a) flexural strength, b) flexural modulus.

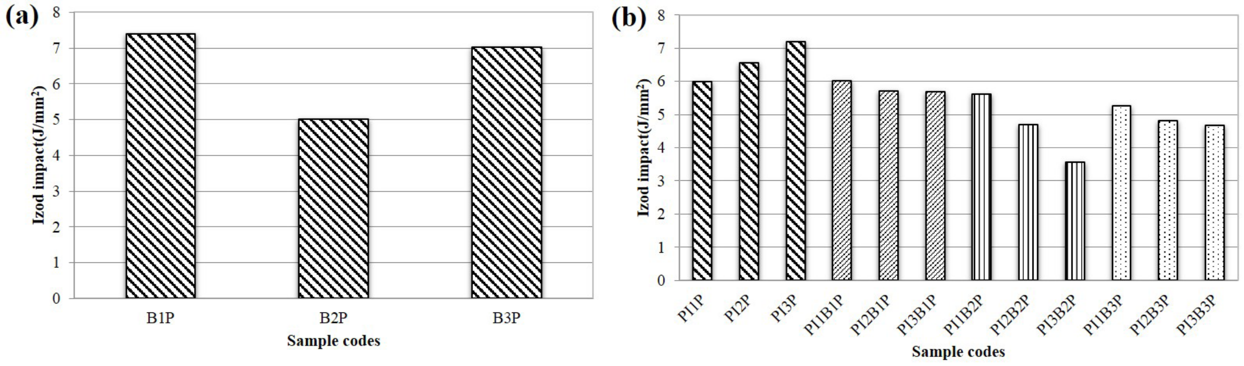

Figure 3: Izod impact values of composite materials a) boron/polyester composites, b) pine cone/boron polyester composites.

The impact strength of the composites is given in Figure 3. Boron oxide polyester composite has the highest izod impact value when compared to other boron composites. All polyester composites with pine cones in an increased amount and any boron compounds in the constant ratio were shown to reduce impact strength. Incorporation of boron compounds into pine cone/polymer matrix reduced the capability of composites to absorb energy.

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

Table 2: Physical properties of composite materials.

Sample Code	Bulk Density (g/cm^3)	Open Porosity (%)	Water Absorption (%)	Thickness Swelling (%)
B1P	1.241	0.664	0.535	3.510
B2P	1.190	1.911	1.607	1.466
B3P	1.164	3.683	3.278	1.690
PI1P	1.156	1.959	1.696	1.701
PI2P	1.151	1.993	1.743	1.705
PI3P	1.141	2.192	1.921	1.707
PI1B1P	1.191	2.296	2.244	2.362
PI2B1P	1.150	2.849	2.724	3.100
PI3B1P	1.212	3.278	2.756	3.360
PI1B2P	1.171	3.122	2.685	0.888
PI2B2P	1.206	3.272	2.785	1.212
PI3B2P	1.162	3.739	3.223	2.965
PI1B3P	1.172	1.211	1.039	1.100
PI2B3P	1.169	1.307	1.101	1.242
PI3B3P	1.162	1.367	1.175	1.315

fiber absorbs water due to the presence of hydroxyl groups which absorb water through the formation of hydrogen bonding [15]. The results showed that the bulk density of composites decreased linearly with an increase of the pine cone ratios.

4.2 Flammability properties of composite materials

The flammability properties of the best mechanical properties composites were determined according to the ASTM D 2863 standard. LOI values of the three samples with better mechanical properties (B1P, PI1P, and PI1B1P) are given in Table 3 and images of burned samples are given in Figure 4.

When both mechanical and physical properties were evaluated, boron oxide had better properties than other boron minerals as filler. Because of this approach, a flammability test was applied to these three samples. If the composite sample has a higher LOI value, it means it has a more stable behavior when exposed to fire, and it takes longer to burn it completely. As is known, polymer is a flammable material when compared to others, and research is ongoing to increase the flame-retardant properties of all polymers [16]. We can see from the results that pure boron oxide and pure pine cone samples have lower LOI values compared to the pine cone polyester composite reinforced with boron oxide.

Table 3: Flammability properties of composite materials.

Composite Codes	LOI
B1P	19
PI1P	20
PI1B1P	22

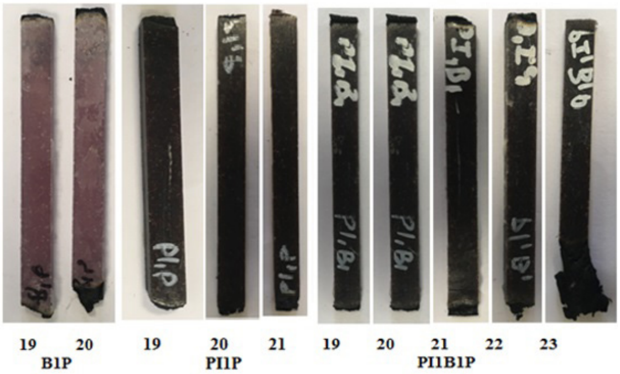

Figure 4: Composite samples taken from LOI test.

It is clear from Table 3 that boron oxide gave a flame-retardant property to pine cone/polyester composites. In the study by Polat and Kaynak, they also indicated that boron oxide improved the flame-retardant properties of glass fiber reinforced composites [17]. In the study by Ayar et al., it was also indicated that the boron compound improved the flame-retardant properties of woven cotton. The LOI value of original woven cotton was determined to be 19.39%. This value increased to 42.43% oxygen content after the treatment of cotton wool with zinc borate [18]. In polymer composites, boron oxide increased the LOI values of composites approximately 10%. It can be concluded that when boron oxide and pine cone fillers are used together, there is a positive effect on the flame-retardant properties of composites.

4.3 TGA analysis of composites

The thermal stability results of composite samples which were exposed to the LOI test are given by TG, DTG and DTA analysis in Figure 5. The top curve refers to TG, the bottom curve refers to DTA, and the middle curve refers to the DTG curve of the composite samples.

According to our results, it can be concluded that when boron oxide filler was used with pine cone fillers, the residual mass value increased to 25.19% from 8.50%. This is also compatible with the LOI test results since boron oxide gives flame retardancy to composites. In Figure 5, a boron oxide, pine cone filler, and polyester composite (PI1B1P) is compared to a PI1P and B1P composite; the results show a slight increase in the thermal degradation temperature of PI1B1P composite with a boron oxide loading of 8% vol. It is probable that boron-pine cone fillers and polyester are fully cross-linked with boron, forming an amorphous structure. It is consistent with the literature that the degradation peak was broadened and decreased to 590ºC for the boron cross-linked composite sample [16]. The first stage is related to a small weight loss because of the dehydration that occurs at a temperature range between 150ºC and 250ºC. The second stage refers to the main evaporation reactions where most of the sample weight is lost as volatile matter. From a temperature of 460ºC to 790ºC, it was determined that weight loss would not significantly affect the results. The thermal degradation of pine cone fibers that occurs between 220 and 300°C is associated to the degradation of hemicellulose and lignin. The results showed that the addition of boron increased the stability of the fiber and gave the PI1B1P composites higher thermal stability compared to composites to which boron oxide was not added [3, 20].

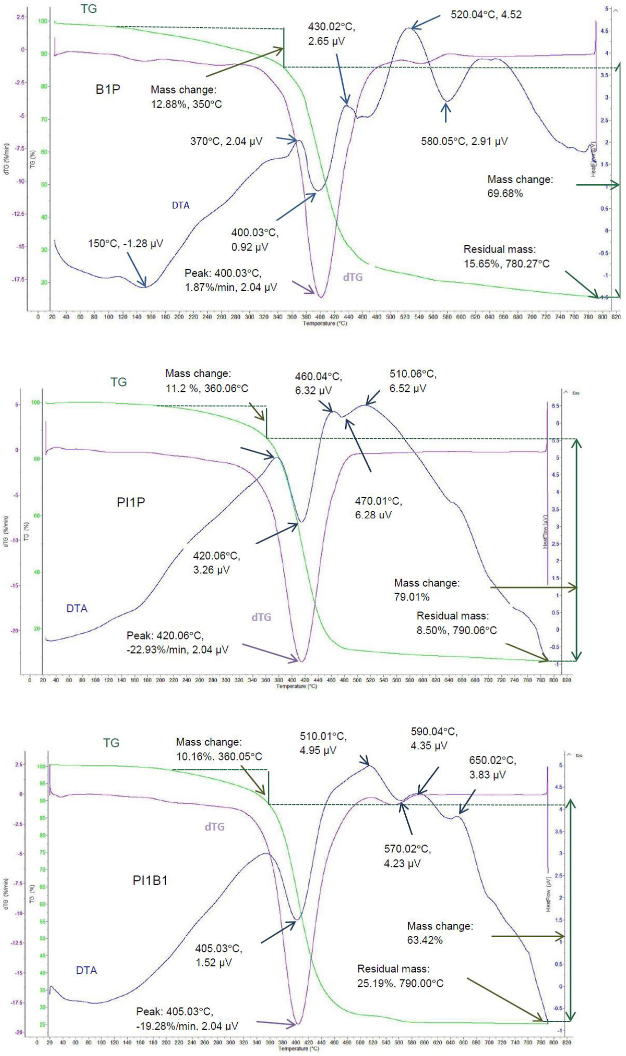

Figure 5: TG, DTG, and DTA curves of polyester composite samples.

4.4 Characterization of composites

The chemical and morphological structures of the composites with the best mechanical, physical, and flame-retardant properties (B1P, PI1P, and PI1B1P) were determined by using FTIR spectroscopy and SEM/EDX. The FTIR spectra of pine cone powder/polyester, boron oxide/ polyester, and pine cone powder-boron oxide/ polyester composites are shown in Figure 6.

The FTIR spectrum of PI1B1P composite showed a broad band at 3354.34 cm^{-1} due to OH stretching vibrations. The peaks at 2918.47 cm^{-1}, 1432.87 cm^{-1}, and 1235.64 cm^{-1} were due to the aliphatic C-H stretching and bending vibrations, respectively. A strong absorption peak at a wave number of 1718.23 cm^{-1} was due to the carbonyl stretching band of the PI1B1P composite. The peak at 1143.43 cm^{-1} was due to the stretching of –C-O- vibrations and CH skeletons. The bands at 699.38 and 729.33 cm^{-1} indicate the presence of B in the composite. The bands in region 700 cm^{-1} were due to the bending of B-O-B linkage in BO_3 [3, 19]. The

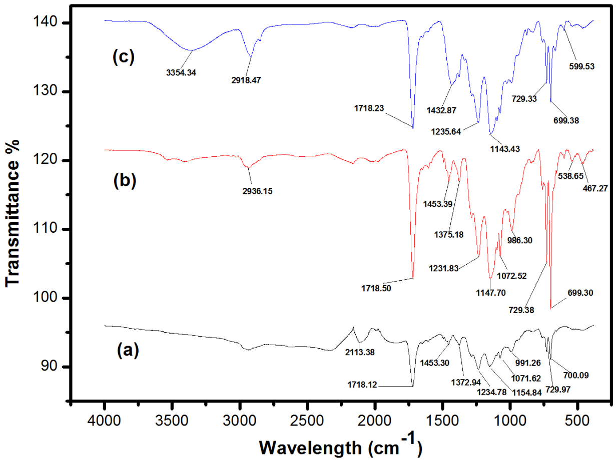

Figure 6: IR spectrum of polyester composite materials a) B1P b) PI1P c) PI1B1P.

FT-IR spectrum of PI1P composite is shown in Figure 6b. The peak at 1072.52 cm^{-1} was due to –C-O- vibrations. The peaks around 1147.70 and 699.30 cm^{-1} were attributed to stretching vibrations of intermolecular ester bonding and C-OH out of plane bending mode from the glyosidic units. The peak at 1718.5 cm^{-1} was due to the carbonyl stretching band. Peaks at 1453.39 and 1375.18 cm^{-1} were due to the OH bending in the carboxylic group and CH deformation. The FT-IR spectrum of B1P composite is shown in Figure 6a. The spectrum shows evidence for the presence of boron atoms. The bands in the region of 700–1400 cm^{-1} are indicative and correspond to the B–O stretching and vibrational modes of BO_3 units. The bands at about 700 cm^{-1} indicate the presence of B in the compound. The strong absorption bands near 1372.94 and 1234.78 cm^{-1}

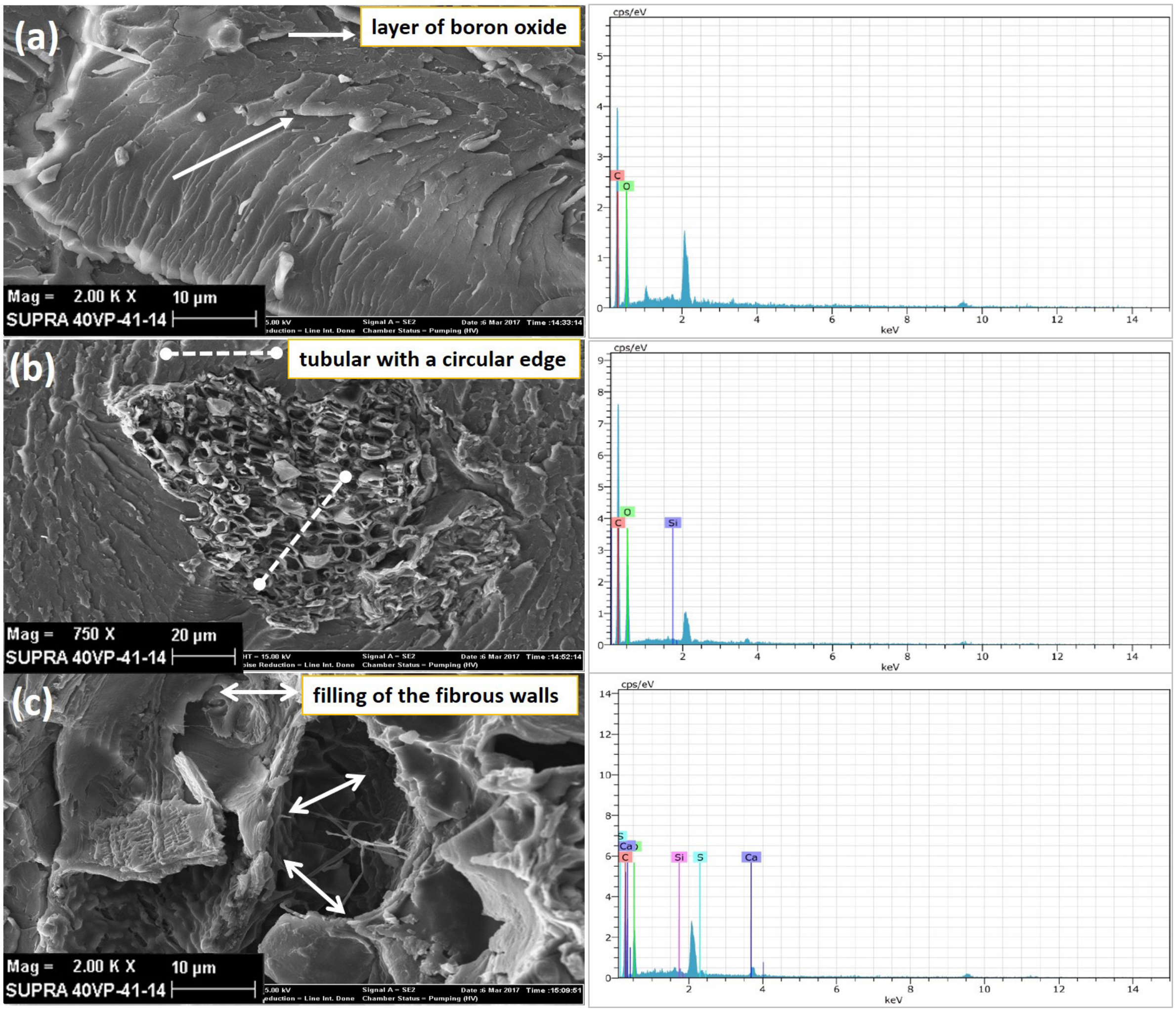

Figure 7: SEM images and EDX results of composite materials a) B1P b) PI1P c) PI1B1P.

correspond to the symmetric stretching vibration of BO_3 units [21-23].

Figure 7 shows the SEM images and EDS results of these three composite samples where it can be observed that pine cone fiber has a tubular shape with a circular edge. Cellulose in the pine cone structure was located in the fibrous walls (PI1P). The image of the composite reinforced with boron oxide and pine cone fillers (PI1B1P) indicated that boron oxide filled the fibrous walls in the pine cone structure providing good adhesion with pine cone fillers. The adhesion between boron oxide and pine cone can clearly be seen from the SEM image of the PI1B1P composites. It was also thought that the coupling agent (polypropylene graft maleic anhydride) provided good adhesion between polymer and fibers. It is known that the addition of coupling agents to natural fiber composites leads to a decrease in the voids between the polymer and the fibers [1]. As visible in the SEM image of PI1B1P, the contraction between the fillers and the polymer is better than in the PI1P composite. From the EDS results, it can be seen that composites include mostly oxygen and carbon elements in their structures; this is clearly due to the organic groups in the polyester as well as the cellulosic character of pine cone powder [24]. It is thought that the silicon and sulfur in the composites containing pine cone comes from the soil. Because the amount of boron in the composite is low, the boron phase could not have been obtained in the EDS analysis. On the other hand, the analysis with EDS is based on the fact that elements with low atomic number do not give exact results. When analyzed along with an element having a higher atomic number than the boron element, these elements are able to cover the peak of the boron element after the coincidence while giving the higher-spectrum peak. This high absorption in the detector can lead to false analysis, since elements with low atomic weight cause high absorption in the sample and the detector. Even if the volume occupied by low atomic weight elements is higher than in the volume occupied by high atomic weight elements, the formation of Auger electrons in applied voltage can be produce less X radiation. For this reason, they can be absorbed before reaching the sample surface [25].

5 Conclusions

The effect of boron compounds with increasing amount of pine cone powder on mechanical, morphological, thermal, and physical properties of polyester composites were investigated in this study. From the obtained results, the following conclusions are derived.

- When both mechanical and physical properties were evaluated, boron oxide (B1P) had better properties than other boron minerals (B2P and B3P) as filler.
- The increase in the amount of pine cone decreased the flexural strength and increased the flexural modulus.
- According to the bending properties, it can be concluded that the boron oxide was better aligned with the pine cone filler.
- Boron oxide polyester composite has the highest izod impact value when compared with other boron composites.
- In polymer composites, boron oxide increased the LOI values of composites approximately 10%. It can be concluded when boron oxide and pine cone fillers are used together, they showed a positive effect on the flame-resistant properties of composites.

Composites can be further improved by increasing the amount of boron filler.

Acknowledgement: We would like to thank Bilecik Seyh Edebali University Scientific Research Project (No: 2016-02.BSEÜ.03-05) for their support.

Conflict of interest: Authors state no conflict of interest

References

[1] Perez-Fonseca A.A., Robledo-Ortiz J.R., Ramirez-Arreola D.E., Ortega-Gudiño P, Rodrigue D, González-Núñez R., Effect of hybridization on the physical and mechanical properties of high density polyethylene–(pine/agave) composites, Mater. Design., 2014, 64, 35-43.

[2] Boopalan M., Niranjanaa M., Umapathy M.J., Study on the mechanical properties and thermal properties of jute and banana fiber reinforced epoxy hybrid composites, Compos. Part B-Eng., 2013, 51, 54-57.

[3] Arrakhiz F.Z., El Achaby M., Benmoussa K., Bouhfid R., Essassi E.M., Qaiss A., Evaluation of mechanical and thermal properties of Pine cone fibers reinforced compatibilized polypropylene, Mater. Design, 2012, 40, 528-535.

[4] Tran C.D., Prosenc F., Franko M., Benzi G., Synthesis, structure and antimicrobial property of green composites from cellulose, wool, hair and chicken feather, Carbohyd. Polym., 2016, 151, 1269-1271.

[5] Arrakhiz F.Z., Benmoussa K., Bouhfid R., Qaiss A., Pine cone fiber/clay hybrid composite: Mechanical and thermal properties, Mater. Design, 2013, 50, 376-381.

[6] Katancic Z., Travas-Sejdic J., Hrnjak-Murgic Z., Study of flammability and thermal properties of high-impact polystyrene nanocomposites, Polym. Degrad. Stabil., 2011, 96, 2104-2111.

[7] Intharapat P., Nakason C., Kongnoo A., Preparation of boric acid supported natural rubber as a reactive flame retardant and its properties, Polym. Degrad. Stabil., 2016, 128, 217-227.

[8] Arthanarieswaran V.P., Kumaravel A., Kathirselvam M., Evaluation of mechanical properties of banana and sisal fiber reinforced epoxy composites: Influence of glass fiber hybridization, Mater. Design, 2014, 64, 194-202.
[9] Madakbaş S., Çakmakçı E., Kahraman M.V., Preparation and thermal properties of polyacrylonitrile/hexagonal boron nitride composites, Thermochim. Acta, 2013, 552, 1-4.
[10] Zhang T., Liu W., Wang M., Liu P., Pan Y., Liu D., Synergistic effect of an aromatic boronic acid derivative and magnesium hydroxide on the flame retardancy of epoxy resin, Polym. Degrad. Stabil., 2016, 130, 257-263.
[11] Uddin K.M.A., Ago M., Rojas O.J., Hybrid films of chitosan, cellulose nanofibrils and boric acid: flame retardancy, optical and thermo-mechanical properties, Carbohyd. Polym., 2017, 177, 13-21.
[12] Xia C., Garcia A.C., Shi S.Q., Qiu Y., Warner N., Wu Y., Cai L., Rizvi H.R., D’Souza N.A., Nie X., Hybrid boron nitride-natural fiber composites for enhanced thermal conductivity, Sci. Rep., 2016, 6, 34726, doi: 10.1038/srep34726.
[13] Akpinar Borazan A., Gokdai D., Acikgoz C., Alp Adiguzel G., The Influence of Chemically Pre-treated Chestnut Waste and Pinecone Filler Content on the Properties of Polyester Composites, Environment and Ecology Research, 2017, 5, 235-243.
[14] Tomak E.D., Cavdar A.D., Limited oxygen index levels of impregnated Scots pine wood, Thermochim. Acta, 2013, 573, 181-185.
[15] Chern Chiet E., Nor Azowa I., Norhazlin Z., Hidayah A., Wan M.d. ZinWan Y., Impact strength and flexural properties enhancement of methacrylate silane treated oil palm mesocarp fiber reinforced biodegradable hybrid composites. Sci. World J., 2014, http://dx.doi.org/10.1155/2014/213180
[16] Gilman J.W., Jackson C.L., Morgan A.B., Harris R., Flammability Properties of Polymer-Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites, Chem. Mater., 2000, 12, 1866-1873.
[17] Polat O., Kaynak C., Use of boron oxide and boric acid to improve flame retardancy of an organaphosphorus compound in neat and fiber reinforced polyamide-6, J. Vinyl Addit. Techn., 2014, 22, 300-310.
[18] Ayar B., Gürü M., Çakanyıldırım Ç., Solid Phase Synthesis of Anhydrous Zinc Borate from Zinc and Boron Oxide and Utilization as a Flame Retardant in Dye and Textile, GU. J. Sci. 2014, 27, 987-991.
[19] Uslu I., Daştan H., Altaş A., Yayli A., Atakol O., Aksu M.L., Preparation and characterization of PVA/Boron polymer produced by an electrospinning technique, e-Polymers, 2007, 133, 1-6.
[20] Blazquez G., Martin-Lara M.A., Dionisio-Ruiz E., Tenorio G., Calero M., Copper biosorption by pine cone shell and thermal decomposition study of the exhausted biosorbent, J. Ind. Eng. Chem., 2012, 18, 1741-1750.
[21] Buc D., Bello I., Caplovicova M., Mikula M., Kovac J., Hotovy I., et al., Analysis of magnetron sputtered boron oxide films, Thin Solid Films, 2007, 515, 8723–8727.
[22] Shin W.G., Calder S., Ugurlu O., Girshick S.L., Production and characterization of boron nanoparticles synthesized with a thermal plasma system, J. Nanopart. Res., 2011, 13, 7187–7191.
[23] Zhu X., Mai C., Li M., Effects of B_2O_3 content variation on the Bi ions in Bi_2O_3–B_2O_3–SiO_2 glass structure, J. Non-Cryst. Solids, 2014, 388, 55-61.
[24] Rao K.M.M., Rao K.M., Prasad A.V.R., Fabrication and testing of natural fibre composites: Vakka, sisal, bamboo and banana, Mater Design, 2010, 31, 508-513.
[25] Berlin J., Analysis of Boron with energy dispersive X-Ray Spectrometry, Imaging Microscopy & Research, Development, Production, 2011, 13, 19-21.