Bitlis Eren Üniversitesi Fen Bilimleri Dergisi
BİTLİS EREN UNIVERSITY JOURNAL OF SCIENCE
ISSN: 2147-3129/e-ISSN: 2147-3188
VOLUME: 12 NO: 1 PAGE: 97-103 YEAR: 2023
DOI:10.17798/bitlisfen.1195035

Effect of UV Aging on the Physical Properties of Polypropylene/Zinc Borate Polymer Composites

Elif ULUTAŞ[1*], Münir TAŞDEMİR[1]

1Marmara University, Technology Faculty,
Department of Metallurgical and Materials Engineering, İSTANBUL
(ORCID: 0000-0001-7753-8878) (ORCID: 0000-0001-8635-7251)

Keywords: Polypropylene, polymer composites, zinc borate, physical properties, UV aging.

Abstract
Plastics, which have a wide range in terms of production methods, have replaced traditional materials because their chemical and physical properties can be changed in the desired direction. The structural changes that occur when functional filler additives are used during production cause improvements in many physical properties of the new plastic. Using boron and boron compounds as additives positively affects the mechanical, thermal, electrical, optical, and physical properties of polymer composites. As it is known, plastics, which are flammable by nature, have a low oxygen index and therefore pose a danger to human life and the environment due to the threat of fire. In this study, the effects of zinc borate, which has flame-retardant properties, on the physical and morphological properties of polypropylene were investigated. In addition, the effects of aging were investigated by UV aging at 70°C for 15 and 30 days on the polymer composites produced in the study. PP/ZnB polymer composites with different concentrations (5, 10, 15, and 20%) were produced in a twin screw extruder to provide a more homogeneous mixture. Test samples of polymer composites, which were granulated with the help of a grinder, were successfully molded in the injection machine. Limit oxygen index (LOI) to examine the flaming behavior of the samples, heat deflection temperature (HDT), Vicat softening point, melt flow index (MFI) test to examine the thermal behavior, moisture content, and density test to examine the physical properties of the samples were performed. The microstructure examination of polymer composites was made with a scanning electron microscope (SEM).

1. Introduction

Polymers have a wide usage area in daily life and industry due to their easy processing, low cost, high corrosion resistance, lightweight, and many other advantages [1]. Despite these positive features, when used in the industry, they often do not give the desired feature and do not meet expectations. In such cases, fillers and additives of various sizes are added to alleviate the limitations in their mechanical and physical properties and to expand the application area [2]. Nowadays, inorganic particle reinforcement of organic polymers has become an area of great interest to improve the properties of polymers [3], [4], [5].

Although it has many application areas around the world, polypropylene is easily flammable due to its chemical composition, namely the C, H, and O elements it contains [6], [7]. However, they pose a serious threat to both the human body and the environment due to dripping and burning [8].

Polymers such as polypropylene emit toxic gases and smoke during their combustion, which causes a serious problem for the production and use of polymers. It is also known that aromatic polymers are less flammable than aliphatic polymers. Flame retardants are added during polymerization or processing to improve the burning behavior of polymers. Due to their low cost and ease of use,

* Corresponding author: elif.ulutas@marmara.edu.tr

Received: 26.10.2022 , Accepted: 03.02.2023

additive-type flame retardants are preferred more in industrial applications [9], [10], [11], [12], [13]. Especially zinc borate is among the boron components in the studies carried out for flame prevention and flame retardant in polymers. Zinc borate, which has smoke and afterglow suppressant properties, is used for both halogenated and non-halogenated polymers since they have a flame-retardant mechanism [14], [15], [16]. It is used to improve fire performance in paints, cables, fabrics, carpets, interior parts of automobiles and airplanes, textiles, paper, and polymeric materials [17], [18], [19], [20]. As a flame retardant and smoke suppressant, zinc borate is widely used in the plastics and electrical industries. Feng et al. [8] study investigated the flame retardancy effect of zinc borate on polypropylene composites. When 1% zinc borate was added to polymer composites, the LOI value increased from 27.1 to 30.7%, and in this case, zinc borate had a positive effect on the flame retardant properties and combustion performance of the composites. Similarly, Qin et al. [20] added zinc borate to the blend obtained by melting LLDPE/EVA mixtures and investigated the flammability and thermal stability behavior of the new mixture. Zinc borate, used as a flame retardant, increased the LOI value of the composites and also improved the UL-94 rating.

In this research article, the effect of zinc borate, which is used as a flame retardant in polymers, on the mechanical, thermal, and morphological properties of polypropylene was investigated. In addition, the effect of UV aging on polymer composites was investigated at 70°C for 0, 15, and 30-day periods. For the production of polymer composites containing zinc borate in different ratios, the melt mixing method in the extruder and the injection forming technique for the production of test samples were successfully applied. LOI was used to examine the flaming behavior of the samples; MFI, HDT, and Vicat softening point tests were used to examine the thermal behavior; and density, moisture content, and density tests were performed to examine the physical behavior of the samples. In addition, the microstructure examination of polymer composites was made with SEM. Then, the properties of the UV applied samples and the untreated samples were compared.

2. Material and Method

The values of PP (Moplen EP 3307) used in the study and supplied by Lyondell Basell are given as density 0.900 g/cm^3, MFI value 15 g/10 min (230°C, 2.16 kg), and thermal distortion temperature (0.45 MPa, unannealed) 95°C. Zinc borate ($ZnHBO_3$), containing B_2O_3 45.0-48.0% and ZnO 37.5-39.0% in its structure, was supplied by Jinan ShiChao Chemical Co., Ltd. (China) and had a specific gravity of 2.72 g/cm^3, particle diameter ≤ 5.0µ.

Table 1. Composition of the PP/ZnB polymer composites formulations.

Groups	Polypropylene (wt%)	ZnB (wt%)
1	100	-
2	95	5
3	90	10
4	85	15
5	80	20

Before polymer composite production, polypropylene, and zinc borate were dried in a vacuum oven at 105°C for 24 hours. Initial mixing of the solid compositions was done in an LB-5601 liquid-solid mixer (The Patterson-Kelley Co., Inc. USA) for 20 minutes. The mixture, which was prepared according to the ratios in Table 1, was mixed at a temperature of 180-220°C at a pressure of 15 bar and a rotation speed of 20 rpm using a Mikrosan brand twin screw extruder (Mikrosan Instrument Inc. Türkiye). As a result of this process of obtaining a homogeneous mixture, PP/ZnB polymer composites were produced. To remove the water from the structure of the composites exposed to water during cooling in extrusion, the drying process was carried out again in the vacuum oven. Then, the injection molding technique was successfully applied between 180-220°C temperatures, 90-100 bar pressure and 20 rpm speed. Moisture, HDT, Vicat softening point, density, MFI and LOI tests were performed on the produced test samples. SEM was used to examine the microstructure of polymer composites. The Devotrans brand test device was used to examine the thermal properties of polymers and for HDT and Vicat softening point tests performed by ISO 75 and ISO 307 standards, respectively. Density determination according to the ISO 2781 standard was made by taking the average of three samples. The MFI test, which allows commenting on the fluidity of the materials, was performed on the Zwick 4100 brand test device by the ISO 1133 standard. Moisture content testing of all mixtures was performed with Kern DBS 60-3 equipment according to the ASTM D6980 standard. LOI testing of all blends was performed with Devotrans LOI equipment according to the ISO 4589 standard. In the Devotrans brand preheated UV test cabinet was used for the UV aging process, the light distance was set to 50mm and Osram 300W ultra-vitalux lamp type was used.

Figure 1. UV aging of PP/ZnB polymer composites

The fractured surfaces of the PP/ZnB polymer composites were coated to a thickness of 20Å gold-palladium mixture to avoid electrical charging by Polaron SC7640 (high-resolution spray coater) (UK). Microstructure investigation of polymer composites was carried out with a FEI Sirion XL30 FEG brand (Netherlands) SEM device at 20kV acceleration voltage.

3. Results and Discussion

The relationship between the LOI and the percentage of zinc borate in polypropylene polymer composites is shown in Figure 2-A. The inclusion of ZnB in the PP matrix increases the LOI value of the composites. For example, the LOI of the four different samples (5, 10, 15, and 20% wt ZnB, without UV) are measured as 21, 23, 24.3 and 25% respectively. The LOI of pure PP is 17%. In comparison with the LOI of pure PP, the LOI increases by 47% for the composites with a 20% wt ZnB concentration. Similar results are found in the other groups. On the other hand, UV holding time affects the LOI as well. For example, the LOI of PP/ZnB (80/20, without UV), PP/ZnB (80/20, 15 days UV), and PP/ZnB (80/20, 30 days UV), polymer composites are 25, 25.7 and 27% respectively. As the UV holding time increases, the LOI of the composites increases. The relationship between the HDT and the percentage of zinc borate in polypropylene polymer composites is shown in Figure 2-B. The inclusion of ZnB in the PP matrix increases HDT of the composite. For example, the HDT of the four different samples (5, 10, 15 and 20% wt ZnB, without UV) are measured as 101, 103, 105 and 108ºC respectively. The HDT of pure PP is 96ºC. In comparison with the HDT of pure PP, the HDT increases by 13% for the composites with a 20% wt ZnB concentration. Similar results are found in the other groups. On the other hand, UV holding time affects the HDT as well. For example, the HDT of PP/ZnB (80/20, without UV), PP/ZnB (80/20, 15 days UV), and PP/ZnB (80/20, 30 days UV), polymer composites are 108, 124 and 125ºC respectively. As the UV holding time increases, the HDT of the composites also increases. Ersoy and Tasdemir [21] investigated the effects of 5, 10, 15 and 20% zinc borate on the properties of HDPE. According to the results of the HDT test applied to the composites obtained by using a twin screw extruder it was observed that the addition of zinc borate decreased this value.

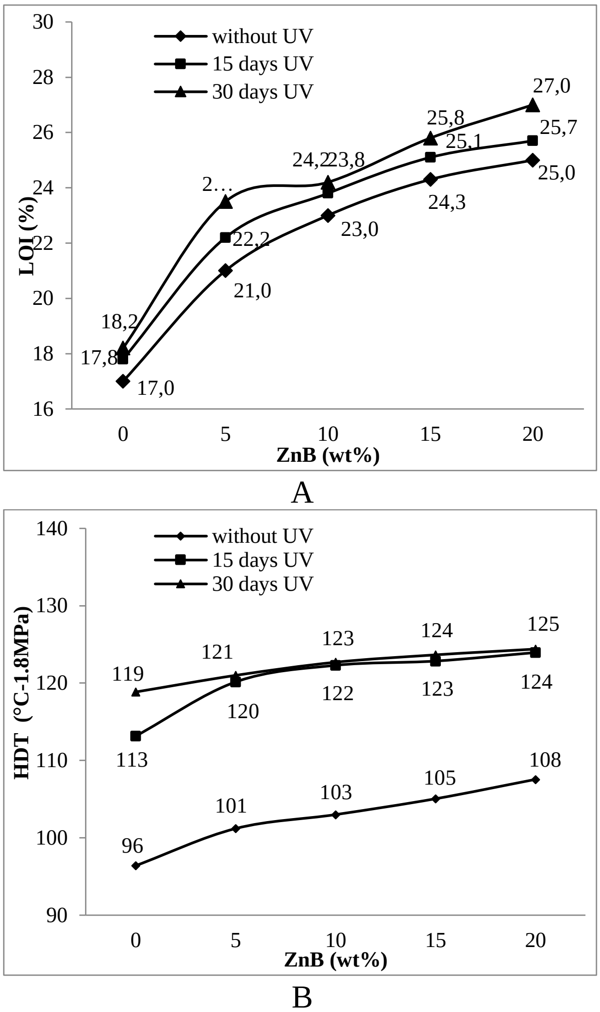


Figure 2. LOI and HDT values of the PP/ZnB polymer composites.

The relationship between the Vicat softening point and the percentage of zinc borate in polypropylene polymer composites is shown in Figure 3-A. With the inclusion of ZnB in the PP matrix, the Vicat softening point of the composite is found to be increasing. For example, the Vicat softening points of the four different samples (5, 10, 15 and 20% wt ZnB, without UV) are measured as 139, 140, 141 and 141ºC respectively. The Vicat softening point of pure PP is 138ºC. In comparison with the Vicat softening point of pure PP, the Vicat softening point increases by 2% for the composites with a 20% wt ZnB concentration. Similar results are found in the other groups. On the other hand, the UV holding time affects the Vicat softening point as well. For example, the Vicat softening point of PP/ZnB (80/20, without UV), PP/ZnB (80/20, 15 days UV), and PP/ZnB (80/20, 30 days UV), polymer composites are 141, 145 and 154ºC respectively. The Vicat softening point of the composites increases by about 9% when the UV holding time is increased. Yerlesen and Tasdemir [22] investigated some properties of the composites obtained by adding zinc borate and zinc oxide at different rates to HDPE. The HDT and Vicat softening point tests have obtained similar results in their study. Depending on the increase in zinc oxide or zinc borate ratio, the HDT and Vicat softening point values of the composites increased.

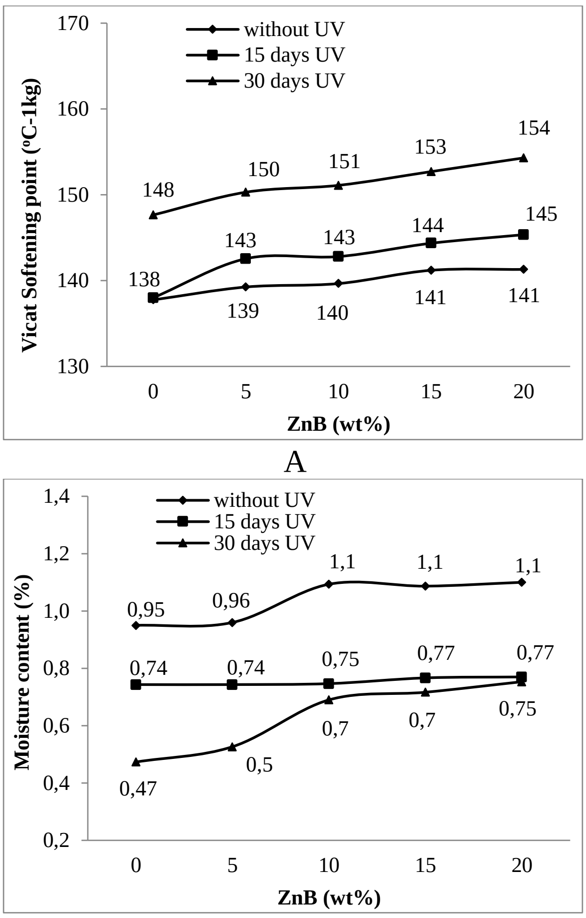


Figure 3. Vicat softening point and moisture content values of the PP/ZnB polymer composites.

The relationship between the moisture content and the percentage of zinc borate in polypropylene polymer composites is shown in Figure 3-B. With the inclusion of ZnB in the PP matrix, the moisture content of the composite is found to be increasing. For example, the moisture contents of the four different samples (5, 10, 15 and 20% wt ZnB, without UV) are measured as 0.96, 1.1, 1.1 and 1.1% respectively. The moisture content of pure PP is 0.95%. In comparison with the moisture content of pure PP, the moisture content increases by 16% for the composites with a 20% wt ZnB concentration. Similar results are found in the other groups. On the other hand, the UV holding time affects the moisture content as well. For example, the moisture contents of PP/ZnB (80/20, without UV), PP/ZnB (80/20, 15 days UV), and PP/ZnB (80/20, 30 days UV), polymer composites are 1.1, 0.77, and 0.75% respectively. As the UV holding time increases, the moisture content of the composites decreases by about 32%.

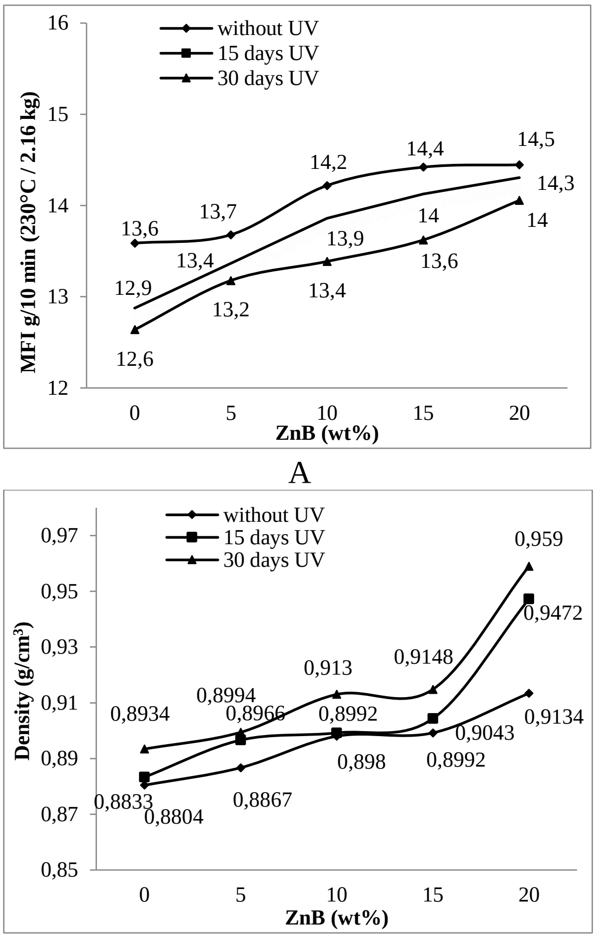
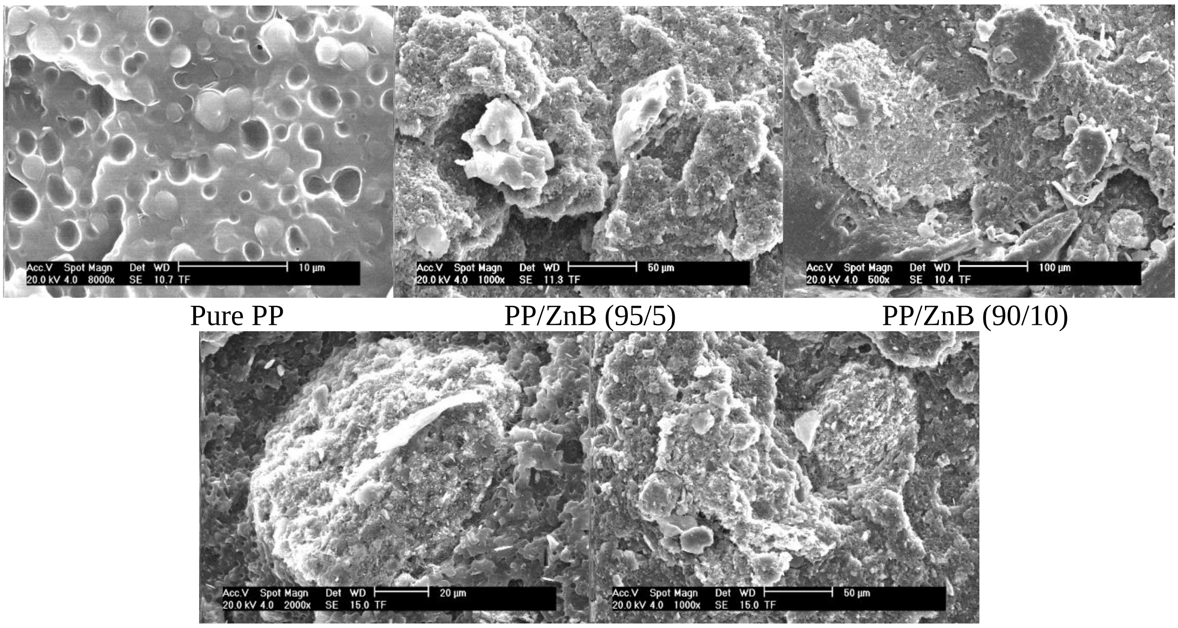


Figure 4. MFI and density values of the PP/ZnB polymer composites.

The relationship between the MFI and the percentage of zinc borate in polypropylene polymer composites is shown in Figure 4. With the inclusion of ZnB in the PP matrix, the MFI of the composite is found to be increasing. For example, the MFI of the four different samples (5, 10, 15 and 20% wt ZnB, without UV) are measured as 13.7, 14.2, 14.4 and 14.5 (g/10 min) respectively. The MFI of pure PP is 13.6 (g/10 min). In comparison with the MFI of pure PP, the MFI increases by 7% for the composites with a 20% wt ZnB concentration. Similar results are found in the other groups. On the other hand, the UV holding time affects the MFI as well. For example, the MFI of PP/ZnB (80/20, without UV), PP/ZnB (80/20, 15 days UV), and PP/ZnB (80/20, 30 days UV), polymer composites are 14.5, 14.3 and 14 (g/10 min) respectively. When the UV holding time increases the MFI of the composites decreases. Guldas et al. [23] investigated the MFI values of the materials by adding different ratios of zinc borate to the powdered PP material. In the tests performed, it was determined that the MFI value increased due to the increase in temperature and pressure, while the MFI value decreased with the addition of zinc borate. The relationship between the density and the percentage of zinc borate in polypropylene polymer composites is shown in the Figure 4-B. With the inclusion of ZnB in the PP matrix, the density of the composite is found to be increasing. For example, the densities of the four different samples (5, 10, 15 and 20% wt ZnB, without UV) are measured as 0.8867, 0.8980, 0.8992 and 0.9134 g/cm^3 respectively. The density of pure PP is 0.8804 g/cm^3. In comparison with the density of pure PP, the density increases by 4% for the composites with a 20% wt ZnB concentration. Similar results are found in the other groups. On the other hand, the UV holding time affects the density as well. For example, the densities of PP/ZnB (80/20, without UV), PP/ZnB (80/20, 15 days UV), and PP/ZnB (80/20, 30 days UV), polymer composites are 0.9134, 0.9472 and 0.9590 g/cm^3 respectively. When the UV holding time increases, the density of the composites increases. The visuals of the microstructure analysis performed to examine the dispersion of the reinforcement/filling phase in the matrix, given in Figure 6, clearly show the contrast and boundaries between pp and zinc borate. Micrographs show that the zinc borate particles are homogeneously dispersed in the polymer matrix.



Pure PP PP/ZnB (95/5) PP/ZnB (90/10)

PP/ZnB (85/15) PP/ZnB (80/20)

Figure 5. SEM photographs of PP/ZnB polymer composites.

4. Conclusion and Suggestions

The effects of zinc borate and UV holding time on some properties, such as LOI, HDT, Vicat softening point, moisture content, MFI, density, and morphology of PP/ZnB composites, were investigated. Zinc borate and UV holding time have marginal effects on some physical properties such as HDT, and moisture content of the composites. The following results were obtained: The inclusion of ZnB into the PP matrix has a positive effect on the LOI values of the composites. The LOI values of the composite obtained by adding 20% ZnB to pure PP increased by 47%. At the same time, the increase in UV holding time has a similar effect on LOI. With the inclusion of ZnB in the PP matrix, the LOI of the composite is found to be increasing. By adding 20% by weight of ZnB to pure PP, HDT and Vicat softening point values increase by 13% and 2%, respectively. Similarly, the increase in UV holding time also increases the HDT and Vicat softening points of composites. The inclusion of ZnB in the PP matrix causes an increase in the moisture content and MFI value. The inclusion of 20% ZnB in the polymer matrix increases the MFI of the composite by 7%. In addition, moisture test results show that composites containing 20% ZnB have 16% more moisture absorption capacity compared to pure PP. On the other hand, the UV holding time increases the moisture content, and the MFI of the composites decreases. The micrographs indicate that the zinc borate particulates are homogeneously dispersed on the fractured surfaces of the PP matrix.

References

[1] Guo Y, Ruan K, Shi X, Yang X, Gu J, "Factors affecting thermal conductivities of the polymers and polymer composites: A review," *Composites Science and Technology*, vol. 193, pp. 108134, 2020.

[2] Fu S, Sun Z, Huang P, Li Y, Hu N, "Some basic aspects of polymer nanocomposites: A critical review," *Nano Materials Science*, vol. 1, pp. 2-30, 2019.

[3] Mamunya YP, Davydenko VV, Pissis P, Lebedev EV, "Electrical and thermal conductivity of polymers filled with metal powders," *European Polymer Journal*, vol. 38, no. 9, pp. 1887-1897, 2002.

[4] Mamunya YP, Zois H, Apekis L, Lebedev E V, "Influence of pressure on the electrical conductivity of metal powders used as fillers in polymer composites," *Powder Technology*, vol. 140, no. 1-2, pp. 49-55, 2004.

[5] Zhu K, Schmauder S, "Prediction of the failure properties of short fiber reinforced composites with metal and polymer matrix," *Computational Materials Science,* vol. 28, no. 3-4, pp. 743-748, 2003.

[6] Fontaine G, Bourbigot S, Duquesne S, "Neutralized flame retardant phosphorus agent: Facile synthesis, reaction to fire in PP and synergy with zinc borate," *Polymer Degradation and Stability*, vol. 93, pp. 68-76, 2008.

[7] Younis AA, "Evaluation flammability, mechanical and electrical properties of polypropylene after using zinc borates and montmorillonite," *Journal of Thermoplastic Composite Materials*, vol. 35, no. 2, pp. 1-15, 2019.

[8] Feng C, Zhanga Y, Liang D, Liua S, Chi Z, Xua J, "Influence of zinc borate on the flame retardancy and thermal stability of intumescent flame retardant polypropylene composites," *Journal of Analytical and Applied Pyrolysis*, vol. 115, pp. 224-232, 2015.

[9] Baltaci B, Çakal GO, Bayram G, Eroglu I, Özkar S, "Surfactant modified zinc borate synthesis and its effect on the properties of PET," *Powder Technology*, vol. 244, pp. 38-44, 2013.

[10] Shi X, Xiao Y, Yuan L, Sun J, "Hydrothermal synthesis and characterization of 2D and 3D $4ZnO \cdot B_2O_3 \cdot H_2O$ nano/microstructures with different morphologies," *Powder Technology*, vol. 189, pp. 462-465, 2009.

[11] Ahmad Ramazani SA, Rahimi A, Frounchi M, Radman S, "Investigation of flame retardancy and physical–mechanical properties of zinc borate and aluminum hydroxide propylene composites," *Materials and Design*, vol. 29, pp. 1051-1056, 2008.

[12] Jiang M, Zhang Y, Yu Y,2 Zhang Q, Huang B, Chen Z, Chen T, Jiang J, "Flame retardancy of unsaturated polyester composites with modified ammonium polyphosphate, montmorillonite, and zinc borate," *Journal of Applied Polymer Science*, vol. 136, no. 11, 2019, doi: 47180.

[13] Wang Y, Zhang S, Wu1 X, Lu C, Cai Y, Ma L, Shi G, Yang L, "Effect of montmorillonite on the flame-resistant and mechanical properties of intumescent flame-retardant poly(butylene succinate) composites," *Journal of Thermal Analysis and Calorimetry*, vol. 128, no. 3, pp. 1417-1427, 2017.

[14] Li S, Long B, Wang Z, Tian Y, Zheng Y, Zhang Q, "Synthesis of hydrophobic zinc borate nanoflakes and its effect on flame retardant properties of polyethylene," *Journal of Solid State Chemistry*, vol. 183, pp. 957-962, 2010.

[15] Cui Y, Liu X, Tian Y, Ding N, Wang Z, "Controllable synthesis of three kinds of zinc borates and flame retardant properties in polyurethane foam," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 214, pp. 274-280, 2012.

[16] Makhlouf G, Hassan M, Nour M, Abdel-Monem YK, Abdelkhalik A, "Evaluation of fire performance of linear low-density polyethylene containing novel intumescent flame retardant," *Journal of Thermal Analysis and Calorimetry*, vol. 130, pp. 1031-1041, 2017.

[17] Ozkaraca AC, "Flame retardancy effects of zinc borate and nanoclay in abs, and boron compounds in PET," *Middle East Technical University. The Graduate School Of Natural And Applied Sciences*. The degree of master, 2011.

[18] Bölek H, "Production and characterization of zinc borate-polymer nano composites," *Marmara University Institute For Graduate Studies In Pure And Applied Sciences.* The degree of master, 2011.

[19] Ureyen ME, Kaynak E, "Effect of zinc borate on flammability of pet woven fabrics," *Advances in Polymer Technology,* 2019, doi: 7150736.

[20] Qin J, Liu N, Wang N, Li L, He W, Guo J, Chen X, Zhang K, Yu J, "Synergistic effect of modified expanded graphite and zinc borate on the flammability, thermal stability and crystallization behavior of lldpe/eva composites with $Mg(OH)_2/Al(OH)_3$," *Polymer Composites*, vol. 40, no. S1, pp. 687-694, 2019.

[21] Ersoy S, Tasdemir M, "Zinc oxide (ZnO), magnesium hydroxide [$Mg(OH)_2$] and calcium carbonate ($CaCO_3$) filled HDPE polymer composites: Mechanical, thermal and morphological properties," *Marmara University Journal of the Graduate School of Natural and Applied Sciences*, vol. 24, no. 4, pp. 93-104, 2012.

[22] Yerlesen U, Tasdemir M, "Effect of zinc oxide and zinc borate on mechanical properties of high density polyethylene," *Romanian Journal Of Materials*, vol. 45, no. 4, pp. 364-369, 2015.

[23] Guldas A, Cankaya A, Gullu A, Guru A, "Determinat on of rheological properties of zinc borate reinforced polypropylene," *Journal of the Faculty of Engineering and Architecture of Gazi University*, vol. 29, no. 2, pp. 227-234, 2014.