Investigation of Flame Retardancy and Physical–Mechanical Properties of Zinc Borate/Boric Acid Polyester Composites

Miyaser Demirel, Vecihi Pamuk, Nursel Dilsiz

Department of Chemical Engineering, Gazi University, Maltepe, Ankara 06570, Turkey

Received 15 February 2008; accepted 2 August 2009
DOI 10.1002/app.31210
Published online 15 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The glass fiber reinforced polyester composite materials were prepared with varying contents of boric acid, zinc borate, and magnesium hydroxide as flame retardants to improve the flame retardancy of the composites. Experimental results showed that boric acid exhibited a good flame retardant effect on the polyester composite. When boric acid content is used as 15 wt %, the Limiting Oxygen Index (LOI) value of the composite reached upto 25.3. The increase in boric acid content from 15 to 30 wt %, the LOI values of composite were enhanced from 25.3 to 34.5 by 9.2 units. The LOI values of the composite samples increased with increasing boric acid content. The smoke density results showed that the addition of glass fiber and flame retardants decreased the smoke density of the unreinforced polyester resin. The mechanical properties of the composites have decreased by the addition of flame retardants. The scanning electron micrographs taken from fracture surfaces were examined. The flame retardants, such as boric acid, were well dispersed in the glass fiber reinforced polyester composites and obviously improved the interfacial interaction between glass fibers and polyester composites. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2550–2555, 2010

Key words: polyesters; glass fiber; flame retardant; boric acid; zinc borate

INTRODUCTION

The use of flame retardants to reduce combustibility of the polymers, and smoke or toxic fume production is a pivotal part of the development and application of new materials. Flame retardancy is required for industries dealing with construction, electrical, and electronics components and transportation.[1–4] It is essential that new flame retardant systems are developed to meet the constantly changing demand of new regulations, standards, and test methods.[2]

A flame retardant should inhibit or even suppress the combustion process. Depending on their nature, flame retardants can act chemically and/or physically in the solid, liquid, or gas phase. They interfere with combustion during a particular stage e.g. heating, decomposition, ignition, or flame spread.[3–8] Although, halogens are the most widely applied flame retardant materials for polymers used in composite organic matrices or in electronic equipment, they do have clear disadvantages because of their toxicity during combustion.[2,4,5] A growing demand to avoid the generation of such toxic and corrosive gases during thermal degradation has led to the development of non halogen containing flame retardant polymers.[2,3] An inorganic flame retardant acts simultaneously on the surface of the solid phase by cooling the polymer via endothermic breakdown process and reducing the formation of pyrolysis products. In addition, as in the case of inorganic boron compounds, a glassy protective layer can form on the substrate, thus taking off the effects of oxygen and heat.[3,6] Unlike organic compounds, inorganic flame retardants do not evaporate under the influence of heat; rather they decompose, giving off nonflammable gases like water, carbon dioxide, and sulphur dioxide, mostly in endothermic reactions. They act by diluting the mixture of flammable gases and by shielding the surface of the polymer against oxygen attack.[3,6] In this study, the effect of different flame retardants on the fire, mechanical, and thermal properties of glass fiber reinforced polyester composites were investigated with Limiting Oxygen Index (LOI), smoke density, thermogravimetric analysis (TGA), flexural, and tensile test.

EXPERIMENTAL

Materials

In this study, unsaturated polyester resin (PE) Polipol^{TM} 3872-I was purchased from Poliya Poliester and was used as matrix system. BMC1-3 type

Correspondence to: N. Dilsiz (ndilsiz@gazi.edu.tr).
Contract grant sponsor: State Planning Organization (DPT); contract grant number: 2001K-120590.

TABLE I
Sample Code and Composition (Weight %) of Composite Samples

Sample	Polyester resin	Glass fiber	Flame retardants		
			Boric acid	Zinc borate	Magnesium hydroxide
PE100	100	–	–	–	–
PE-GF-BA15	80	5	15	–	–
PE-GF-ZB15	80	5	–	15	–
PE-GF-MH15	80	5	–	–	15
PE-GF-BA20	75	5	20	–	–
PE-GF-BA30	65	5	30	–	–

TABLE II
The LOI Values of the Samples

Sample code	LOI (%)
PE100	19.5 ± 0.20
PE-GF-BA15	25.3 ± 0.16
PE-GF-ZB15	20.7 ± 0.16
PE-GF-MH15	22.7 ± 0.18
PE-GF-BA20	27.5 ± 0.27
PE-GF-BA30	34.5 ± 0.21

chopped E glass fiber, which was supplied by Glass Fiber was used as reinforcement system. Magnesium hydroxide (MH) from Acros Organics, boric acid (BA) from J.T. Baker and zinc borate (ZB) from Riedel-de Haen were used as flame retardants. Butanox-M60 MEK-P was used as starter from Akzo Nobel and Cobalt oktoat was used as accelerator from Ege Chemical.

Preparation of composite

The formulation of the composites mainly included polyester, glass fiber, and flame retardants (boric acid, zinc borate, and magnesium hydroxide). Composite sample formulations were prepared by adding different amounts (15%, 20%, and 30%) of flame retardants to PE containing 5% glass fiber. The formulation of the composites prepared was specified in the Table I. PE and cobalt oktoat (0.15 wt %) were initially mixed and then MEK-P (1 wt %) was added. After that, flame retardants and glass fiber were added and mixed about 5 min. Then, the mixture was poured into aluminum molds. The composites were cured for 20 min at 25°C and postcured at 50°C, 80°C, and 110°C for 1hr, respectively.

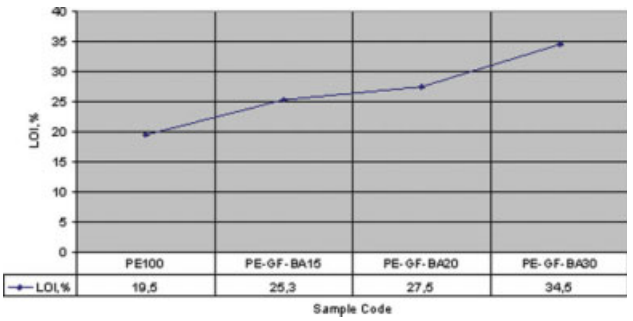

Figure 1 The LOI values of samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Characterization of prepared composites

The LOI and smoke density tests of the composites were carried out by Dynisco Polymer Test–Limiting Oxygen Index Chamber testing machine according to ASTM D 2863-00[9] and ASTM D 2843-99 standards,[10] respectively. To study the mechanical properties of the composites, tensile, and flexural tests were carried out with AG-I 5 kN Shimadzu Autograph testing machine according to ASTM D 638M-91[11]

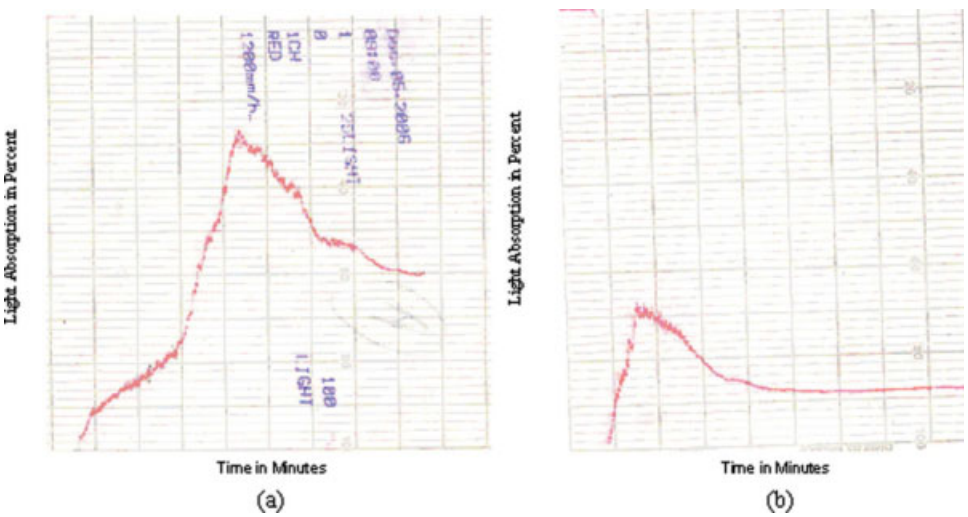

Figure 2 Light Absorption versus Time (a) PE100 and (b) PE-GF-BA15. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

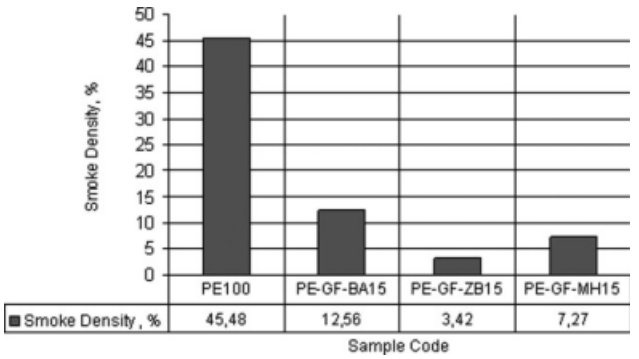

Figure 3 Smoke density values of some samples.

and ASTM D 790M-92,[12] respectively. The topography of fracture surfaces of composites were investigated at various magnification by using JEOL 6400 LV Scanning Electron Microscopy (SEM). The TGA thermograms were taken from 35°C to 900°C with 10°C/min heating rate under nitrogen atmosphere by using SETARAM SETSYS Evolution 1760.

RESULTS AND DISCUSSION

LOI test results

LOI is the minimum concentration of oxygen, determined in a flowing mixture of oxygen and nitrogen that will just support flaming combustion of the material.[11–13] The LOI values of the composite samples were shown in Table II. Boric acid showed the best flame retardant effect in the glass fiber containing polyester composite. Figure 1 shows that the LOI value of pure PE was obtained 19.5, the LOI value of the composite prepared with 15 wt % loading of boric acid and 5 wt % loading of glass fiber has reached up to 25.3. As the concentration of boric acid was doubled the LOI value of the composite increased to 34.5. It is observed that the LOI values of the composite samples increased with the increasing boric acid contents. Sain et al.,[14] examined magnesium hydroxide flame retardant effect with boric acid and zinc borate for natural fibre-PP composites. Zinc borate showed better flame retardant effect than boric acid for natural fibre-PP composites.

Smoke density test results

Each of the tests was carried out as triplicate for 4 min. The total smoke produced was determined by measuring the area under the curve obtained from light absorption versus time plots. The smoke density results of the samples are given in Figures 2 and 3. The test results showed that the addition of glass fiber and flame retardants decreased the smoke density of the unreinforced PE. When 15 wt % of the zinc borate was used, the smoke density value of the composite was 3.42. It is observed that the lowest smoke density value of the composite samples was obtained by the addition of zinc borate as flame retardants.

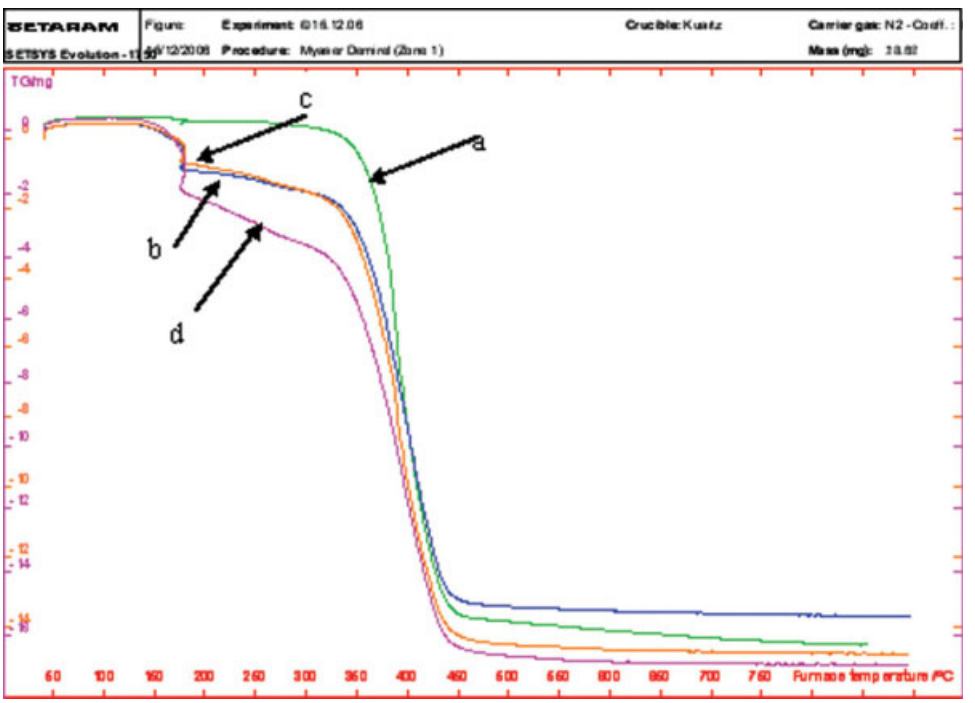

Figure 4 TGA thermograms of (a) PE100, (b) PE-GF-BA15, (c) PE-GF-BA20, (d) PE-GF-BA30. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

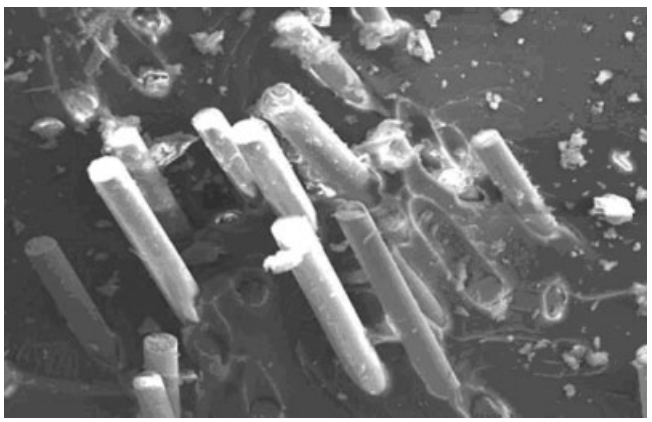

Figure 5 SEM micrograph of the sample code PE-GF-BA15 (×500).

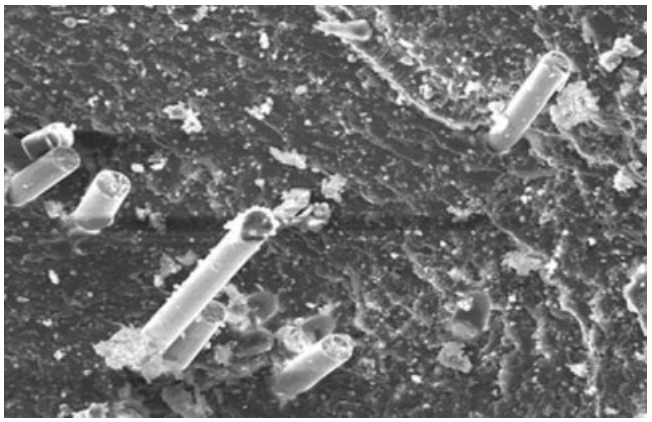

Figure 6 SEM micrograph of the sample code PE-GF-ZB15 (×500).

Thermal analysis

The thermal degradation behaviors of pure PE (PE100) and 15, 20, and 30 wt % boric acid flame retardant containing glass fiber reinforced polyester composites (PE-GF-BA15, PE-GF-BA20, and PE-GF-BA30) were investigated by TGA. Figure 4. shows the thermograms of samples PE100, PE-GF-BA15, PE-GF-BA20, and PE-GF-BA30.

When boric acid is slowly heated, boric acid (m.p 171°C) loses water and changes first to metaboric, HBO_2, and finally to boric oxide, B_2O_3. Above 325°C, B_2O_3 softens to glass and becomes pourable only at 500°C.[15] Thus, boric acid is found to exert its flame retardant action on polymeric materials at a temperature well below that of the normal pyrolysis of these materials;

$$2H_3BO_3 \xrightarrow[-2H_2O]{120-130^\circ C} 2HBO_2 \xrightarrow[-H_2O]{260-270^\circ C} B_2O_3$$

The composite samples for PE100 have only one step degradation peak, which is around 390°C. Pure polyester (PE100) starts to decompose at 386°C and subsequently experiences a violent degradation till 800°C almost any residue left. The thermal degradation of PE-GF-BA15, PE-GF-BA20, and PE-GF-BA30 samples is divided into three steps. The first degradation step, in the range of 100–200°C, can be assigned to the loss of water of boric acid. The second degradation step, in the range of 200–250°C, can be assigned to the loss of water of metaboric acid,

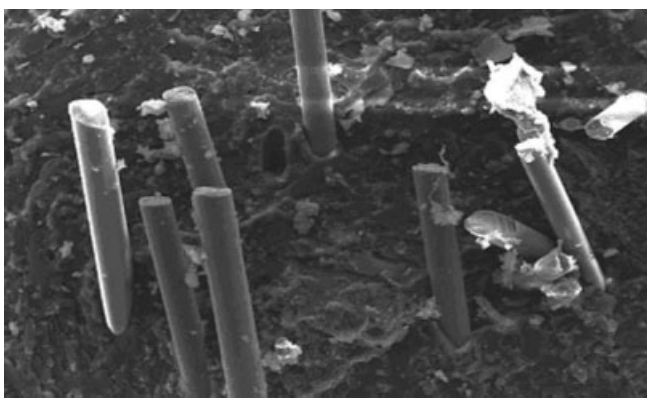

Figure 7 SEM micrograph of the sample code PE-GF-MH15 (×500).

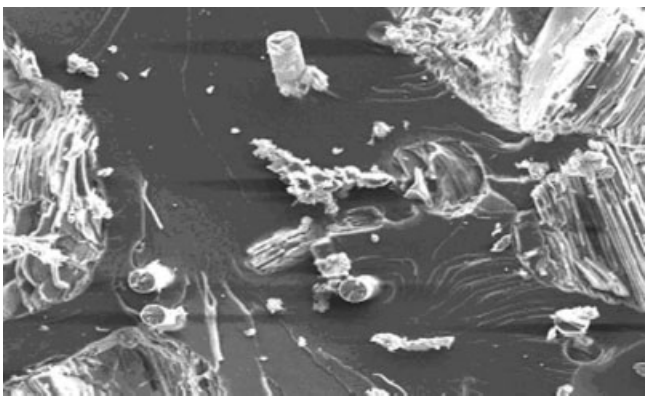

Figure 8 SEM micrograph of the sample code PE-GF-BA20 (×500).

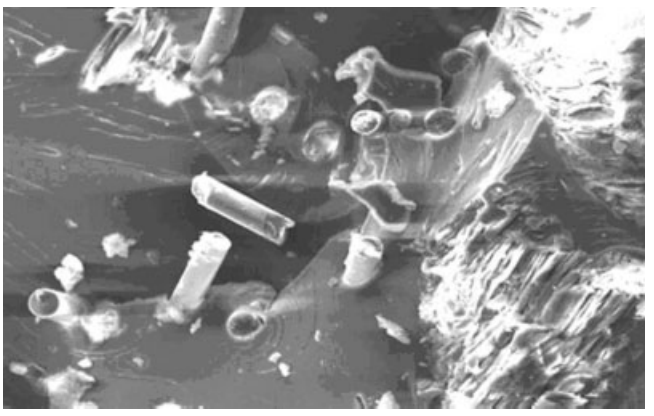

Figure 9 SEM micrograph of the sample code PE-GF-BA30 (×500).

TABLE III
The Mechanical Properties of the Samples

Sample code	Flexural strength (MPa)	Flexural modulus (MPa)	Tensile strength (MPa)	Tensile modulus (MPa)
PE100	99.73 ± 2.55	27.50 ± 3.91	30.51 ± 5.99	3.77 ± 0.62
PE-GF-BA15	74.40 ± 3.32	41.93 ± 10.78	28.14 ± 7.29	3.58 ± 0.37
PE-GF-ZB15	87.46 ± 1.58	45.35 ± 1.15	35.54 ± 6.14	4.76 ± 0.48
PE-GF-MH15	78.78 ± 10.37	45.19 ± 3.70	32.90 ± 1.97	4.62 ± 0.50
PE-GF-BA20	71.41 ± 4.99	55.94 ± 6.03	27.08 ± 4.31	5.18 ± 0.78
PE-GF-BA30	72.48 ± 8.49	54.56 ± 7.09	26.88 ± 2.34	4.69 ± 0.23

HBO_2. And the last degradation peak of the composite is around 400°C. The degradation temperature of pure polyester was altered by the addition of boric acid from 386 to 399°C.

SEM analysis

The morphologies of the composite samples were observed by SEM, shown in Figures 5–9. The microstructure micrographs are obtained from fractured surfaces of the composites. Figures 5–7 show the images of the glass fiber reinforced polyester composites with 15 wt % loading of flame retardants. From Figures 5–7, it is seen that the surface of glass fiber was smooth and glass fibers were easily pulled out from polyester matrix with 15 wt % loading of flame retardants. This fact indicated that the flame retardants were not well dispersed in the composites, and the interfacial interaction between polyester composites and glass fiber was not good. The interfacial adhesion between polyester and glass fiber was very weak due to weak physical interaction based on fiber break and pullout. In Figures 8 and 9, 20 and 30 wt % loading of flame retardant (boric acid) were well dispersed in the glass fiber reinforced polyester composites and obviously improved the interfacial interaction between glass fibers and polyester composites.

Mechanical test results

The influence of flame retardant content on the mechanical properties of flame retardant reinforced polyester composites at 5 wt % glass fiber loading was summarized in Table III. Three point bending test and tensile test were performed to determine the mechanical properties of the glass fiber reinforced polyester composite. The flexural strength and the tensile strength values of the composites prepared with varying amount of boric acid were given in Figures 10 and 11, respectively. As can be seen, with the addition of the flame retardants, the mechanical properties of the composites present a decreasing trend except for the flexural modulus and tensile modulus. When the addition of boric acid was 15 wt %, mechanical properties of the composites with the boric acid presented the best values. With increasing boric acid loading from 15 to 30 wt %, the tensile strength and flexural strength decrease from 32.90 to 26.88 MPa and 78.78 to 72.48 MPa, respectively. At the higher loading of the boric acid, the mechanical properties of the composites presented the decreasing tendency. Huang et al.[16] have found similar result that at the higher loading, the flame retardant mechanical properties of the composites presented the decreasing tendency.

It was shown that zinc borate gave the maximum strength results among the flame retardants used.

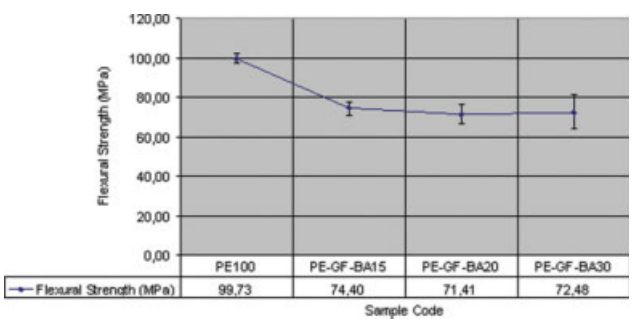

Figure 10 Flexural strength values of the composite samples (MPa). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

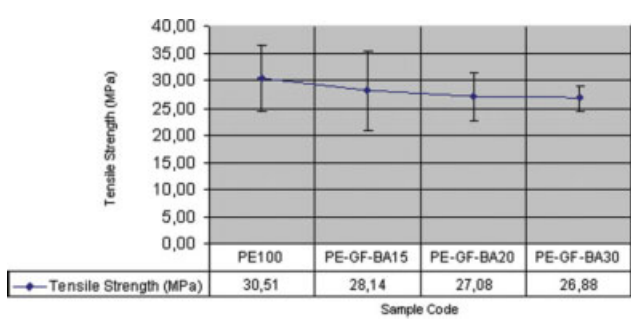

Figure 11 Tensile strength values of the composite samples (MPa). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The flexural strength and modulus of the composites modified with flame retardants, generally tends to decrease with increasing flame retardant contents. Jang et al.[17–20] have found similar result that the flexural properties of the composites decreased with the addition of the flame retardants.

CONCLUSION

As a result of LOI test, loading of flame retardants increased inflammability of the glass fiber reinforced polyester composite. Boric acid has the most flame retardant effect for the glass fiber reinforced polyester composite. While the LOI value of the unreinforced polyester was resin 19.5, when 5 wt % glass fiber and 30 wt % boric acid were used the LOI value enhanced to 34.5. The test results showed that glass fiber and boric acid decreased the smoke density of the unreinforced PE. When the zinc borate content increased upto 15 wt %, the smoke density value of the composite decreased from 45.5 to 3.4. Zinc borate has the lowest smoke density effect for the polyester composites. The TGA thermogram showed that the degradation temperature of composites was altered by the addition of boric acid from 386 to 399°C. Generally, the mechanical properties of the composites decreased with the loading of flame retardants.

References

1. Innes, J. D. Flame Retardants and Their Market Applications. Flame Retardants-101:Basic Dynamics, Past Efforts Create Future Opportunities; Fire Retardant Chemicals Associations: Baltimore, 1996; pp 61–69.
2. Lu, S.-Y.; Hamerton, I. Prog Polym Sci 2002, 27, 1661.
3. Troitzsch, J. H. Chim Oggi/Chem Today 1998, 16, 1.
4. Nelson, G. L. The Future of Fire Retarded Materials: Applications and Regulations; FRCA: Williamsburg, Virginia, 1994; 135.
5. Ellis, B. In Chemistry and Technology of Epoxy Resin; Ellis, B., Ed.; Blackie Academic and Professional: London, 1993; 72–116.
6. Grand, A. F. In Fire Retardancy of Polymeric Materials; Wilkie, C. A., Ed.; Marcel Dekker Inc.: New York, 2000; p 70.
7. Kisakürek, D. "Flame Retardant Polymers", XVII National Chemistry Conference, Istanbul, Turkey, Ç-20, 2003.
8. Troitzsch, J. H. New Trends in the Use of Halogenated Flame Retardants in Germany; Handbook of Flame Retardant Chemicals and Fire Testing Services; Kidder, R. C., Ed.; Technomic Publishing Company, Inc.: Pennsylvania, USA, 1988; 6–12.
9. American Society for Testing and Materials. "D 2863–00 Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-like Combustion of Plastics (oxygen Index)"; ASTM International: West Conshohocken, PA, 2000; pp 452–464.
10. American Society for Testing and Materials. "D 2843–99 Standard Test Method for Density of Smoke from the Burning or Decomposition of Plastics"; ASTM International: West Conshohocken, PA, 2004; pp 440–448.
11. American Society for Testing and Materials. "D638M-91a Standard Test Method for Tensile Properties of Plastics", 1993 Annual Book of ASTM Stand arts Plastics (1); ASTM International: Philadelphia, 1993; pp 174–182.
12. American Society for Testing and Materials. "D790M-92 Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials", 1993 Annual Book of ASTM Standards Plastics (1); ASTM International: Philadelphia, 1993; pp 284–292.
13. La Rosa, A. D.; Recca, A.; Carter, J. T.; McGrail, P. T. Polymer 1999, 40, 4093.
14. Sain, M.; Park, S. H.; Suhara, F.; Law, S. Polym Degrad Stab 2004, 83, 363.
15. Abdalla, M. O.; Ludwick, A.; Mitchell, T. Polymer 2003, 44, 7353.
16. Huang, X.; Bin, L.; Baoli, S.; Liping, L. Polymer 2008, 49, 1.
17. Kandola, B. K.; Horrocks, A. R.; Myler, P.; Blair, D. Compos Part A: Appl Sci Manuf 2002, 33, 805.
18. Chen, Y.; Wang, Q. Polym Degrad Stab 2006, 91, 2003.
19. Jang, J.; Chung, H.; Kim, M.; Sung, H. Polym Test 2000, 19, 269.
20. Jang, J.; Lee, E. Polym Test 2001, 20, 7.