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Effect of Chicken Feather and Boron Compounds as Filler on Mechanical and Flame Retardancy Properties of Polymer Composite Materials

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Abstract Sustainable utilization of solid waste has been influenced by increasing population of the world. Benefits of using solid waste based on natural fiber in polymer material are biodegradability and cost effectiveness. In poultry farms, chicken poultry, one of the slaughterhouse wastes, is confronted as 30 thousand tons of waste per year in Turkey. The evaluation of this waste, which is quite rich in keratin, is extremely important both for the solution of the waste problem and for bringing this valuable material to the economy. These fibers are stable, durable and biodegradable because they have a crystalline structure. However, this valuable waste will have a positive effect when used together with boron minerals which both increase the mechanical properties, flame retardancy and biodegradation of composite material. The aim of this study is to manufacture superior polyester-based composite materials reinforced with three kinds of boron minerals such as; boron oxide, borax pentahydrate, borax decahydrate and fibers recycled from waste chicken feathers. The effect of different filling ratios of filling materials on the mechanical and physical properties of composite materials was examined. Flame retardancy properties of the composites with best mechanical results were investigated. After pouring by means of the pre-casting process, the water absorption and swelling thickness of final products, as well as density, bending strength, flexural modulus, limiting oxygen index (LOI), TGA (Thermogravimetric Analysis) and SEM analysis, was performed. Mixing prescriptions and conditions with the best properties were determined. According to mechanical, physical and flame retardancy analysis it can be concluded that chicken feather and boron compounds have a good synergic effect when used together in composite material instead of using boron compounds /chicken feather alone.

Keywords: Polymer matrix composites, boron, waste chicken feather, flame retardancy, mechanical properties

1. Introduction

Products of various animal sources are generally used for useful purposes. Studies about short fiber composites based on agricultural waste have increased more recently. These fibers are generally more environmentally friendly and relatively easier to obtain at lower densities than inorganic fibers (Barone and Schmidth, 2004). Beside these superior properties flame retardant of composites are also important in order to provide safety necessity of the products. Fire retardants are chemicals that increase the temperature to above normal and literally increase the ignition point of the materials. This limit varies as a function of the retarder, but in any case it tries to reduce the risk of fire (Oliwa *et al*., 2016). Recently, biochar, wool, calcium carbonate with diammonium phospate etc. was used to bring a flame retardant property to the composite material (Das *et al*., 2017; Das *et al*., 2016; Suharty *et al*., 2012). The effect of zinc borate, boric acid and boric oxide on flammability of epoxy resin containing red phosphorus was investigated by Doğan and Unlu. According to the LOI values and thermal gravimetric analysis (TGA) results the boron compounds showed a good effect by increasing char yield in the condensed phase (Doğan and Unlu, 2014). Yhang *et al*. also proved that contribution of boron to epoxy composites was successful to form swollen and glassy char layers with barrier effect on providing free radicals (Yang *et al*., 2016). Beside flame retardancy of composites there are also several studies on mechanical properties of composites reinforced with chicken feather. In the study of Barone and Schmidt mechanical properties of polyethylene reinforced with chicken feathers were obtained. The results show that improvement of a polymer matrix can be provided with keratin feather fiber. According to their mechanical analysis there is an observed increase in flexural modulus when the keratin feather fiber loading increased (Barone and Schmidth, 2005). Cheng *et al*. also concluded in their study chicken feathers had a positive effect on mechanical properties of composites. They used poly lactic acid as a polymer matrix and chicken feather fiber (CFF) as filler. Due to the CFF reinforcement the flexural modulus of CFF/PLA composites were significantly higher than that of pure PLA (Cheng *et al*., 2009).

In literature studies about investigation of the flammability of composites reinforced with chicken feather and boron minerals have not been researched yet. In this study unlike the literature synergic effect of chicken feather and boron minerals on polymer composite materials was investigated.

2. Materials and Method

2.1. Materials

In this study composite materials were produced from polyester resin (Polipol 383-G, Poliya Composite Resins and Polymers Inc., density of 1.076±0.05 g/cm^3 as a standard ISO 1675), waste chicken feather obtained from a poultry in Turkey and three kinds of boron minerals 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 chicken feather 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 of reinforcements can be seen.

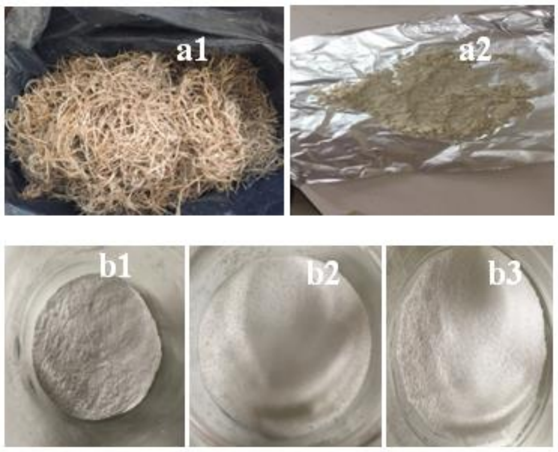


Figure 1. Images of reinforcements, a1) Waste chicken feathers a2) waste chicken feather powder b1) boron oxide b2) borax decahydrate, b3) borax pentahydrate

2.2. Pretreatment of chicken feathers

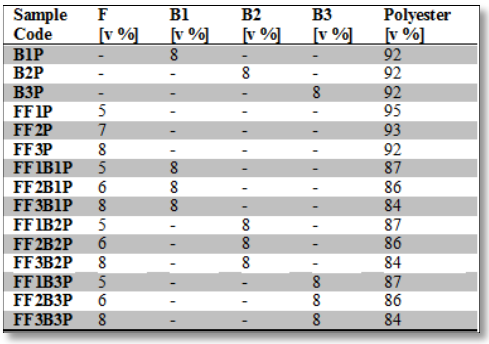
A pre-treatment was required to stabilize and transform chicken feathers into a stable technical material. Firstly chicken feathers were washed with water. Afterward, quill was separated from barbs and cut into small pieces. Finally last drying was again in oven at 105˚C, for 2 hours. Moisture of clean feather fibers was decreased to 10%.

The boron minerals which have more than 10% moisture were dried in a drying oven at 40˚C to provide moisture less than 10%. Finally waste chicken feathers were ground respectively in a precision grinder (Fritsch- Pulverisette9, GmbH) equipped with sieve (Fritsch, Analysette 3).

2.3. Composite preparation

The polyester matrix was compounded, respectively, with reinforcement fillings in different ratios by volume. The raw material formulations, which are given per the volume proportion in percentage, used for the composites are presented in Table 1.

Table 1. Ratio of materials used for composite manufacture



Sample Code	F [v %]	B1 [v %]	B2 [v %]	B3 [v %]	Polyester [v %]
B1P	-	8	-	-	92
B2P	-	-	8	-	92
B3P	-	-	-	8	92
FF1P	5	-	-	-	95
FF2P	7	-	-	-	93
FF3P	8	-	-	-	92
FF1B1P	5	8	-	-	87
FF2B1P	6	8	-	-	86
FF3B1P	8	8	-	-	84
FF1B2P	5	-	8	-	87
FF2B2P	6	-	8	-	86
FF3B2P	8	-	8	-	84
FF1B3P	5	-	-	8	87
FF2B3P	6	-	-	8	86
FF3B3P	8	-	-	8	84

[V %]: Volume percent

F: Chicken feather

B1: boron oxide

B2: borax pentahydrate

B3: borax decahydrate

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

2.4. Experimental Method

Three point bending tests were carried out at a bending speed of 2 mm/min in Shimadzu AG-IC Test Machine to determine the mechanical properties of composites. Following formulas were used for calculations of the three point bending tests. 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).

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.

$$\text{Bulk density} = (W_1/(W_3-W_2))*\rho_{water} \qquad (2.1)$$

$$\%\ \text{Open porosity} = ((W_3-W_1)/(W_3-W_2))*100 \qquad (2.2)$$

$$\%\ \text{WA} = (W_3 - W_1)\ /\ W_1 * 100 \qquad (2.3)$$

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

The flame retardancy properties of composite materials were carried out according to ASTM D 2863 standard.

(Dynisco Polymer Test LOI Limiting Oxygen Index Chamber) This standard covers the methods used to determine the minimum oxygen concentration required to be present in nitrogen-oxygen mixtures for the continuation of the flushes of the test specimens in the upright position under certain test conditions. In principle, a small test sample is placed vertically into a transparent chimney passing through a mixture of oxygen and nitrogen up through it. The top of the test sample is ignited, followed by the burning behavior of the test sample, and the duration of the burn or the duration of the burning test sample is compared to predetermined threshold values for such combustion. Experiments using a series of test samples at different oxygen concentrations predict the smallest oxygen concentration value required for continuation of the burn (Ayar *et al*., 2014). The results are given in terms of the oxygen index value (ASTM D2863-13).

Thermal properties of the composite samples were carried out by using Seteram LabSys Evo analyzer. 5–9 mg of measured composite was kept in alumina crucible under nitrogen atmosphere with a flow rate of 20 ml/min by raising its temperature from 20° C to 800° C in steps of 20° C/min.

3. Results and Discussions

3.1. Mechanical Properties of Composites

Figure 2 shows the flexural strength value of boron/ polyester composites. If we compare three kinds of boron minerals it can be indicated that boron oxide has higher strength.

This is because of the anhydrous structure of boron oxide while the other compounds consist water molecules in their formulas (B2; borax pentahydrate, $Na_2B_4O_7$. $5H_2O$, B3; borax decahydrate, $Na_2B_4O_7$. $10H_2O$). 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 3 shows the effect of chicken feather filler on mechanical properties of composites. Bending properties of each chicken feather/boron compounds were investigated. When graphs were evaluated it can be clearly seen that chicken feather filler only improved the boron oxide strength. The other boron compounds (B2 and B3) with chicken feather composites have not strength values as much as FFB1 composite series. The highest value of flexural modulus belongs to chicken feather/polyester composites is nearly 3600 MPa. We can exactly see from figure 3 all kind of boron doped chicken feather composites have higher flexural modulus values. It can be concluded that especially boron oxide improved the composite resistance to being deformed elastically.

3.2. Physical Properties of Composites

Table 2 shows the physical properties of composite materials such as bulk density, open porosity, thickness swelling and water absorption.

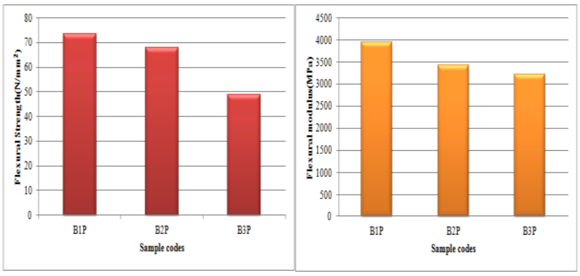


Figure 2. Bending properties of boron/polyester composites

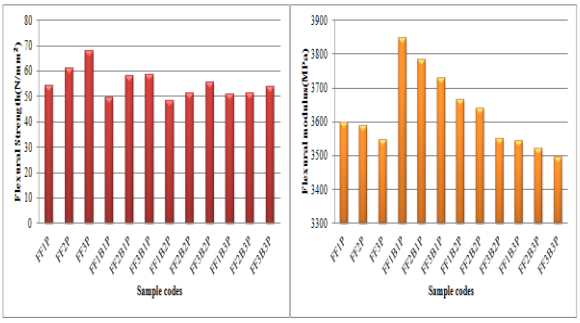


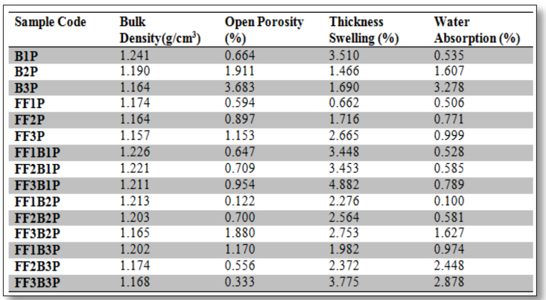
Figure 3. Bending properties of waste chicken feather powder/boron compounds polyester composites

Among the composites B3P has the highest water absorption value. It was thought because of the high amount of water molecules in borax decahydrate. We can conclude that water absorption values show compliance with swelling thickness and open porosity values. While the composites swelling and open porosities in composite structure increased their capability of water absorption increased. For all composites bulk density values decreased with the increasing amount of fillers.

3.3 Flame Retardancy Properties of Composites

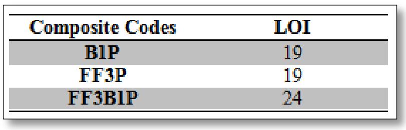
Flame retardancy properties of composites which give the best mechanical properties were obtained according to ASTM D 2863 standard. LOI values of three samples with better mechanical and physical properties (B1P, FF3P and FF3B1P) were given in Table 3 and images of burned samples were given in Figure 4. It is known that 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. From Table 3 and Figure 4 it can be observed that polyester composites reinforced with boron oxide and chicken feather have higher LOI values than the others.

Table 2. Physical properties of composite materials



Sample Code	Bulk Density(g/cm^3)	Open Porosity (%)	Thickness Swelling (%)	Water Absorption (%)
B1P	1.241	0.664	3.510	0.535
B2P	1.190	1.911	1.466	1.607
B3P	1.164	3.683	1.690	3.278
FF1P	1.174	0.594	0.662	0.506
FF2P	1.164	0.897	1.716	0.771
FF3P	1.157	1.153	2.665	0.999
FF1B1P	1.226	0.647	3.448	0.528
FF2B1P	1.221	0.709	3.453	0.585
FF3B1P	1.211	0.954	4.882	0.789
FF1B2P	1.213	0.122	2.276	0.100
FF2B2P	1.203	0.700	2.564	0.581
FF3B2P	1.165	1.880	2.753	1.627
FF1B3P	1.202	1.170	1.982	0.974
FF2B3P	1.174	0.556	2.372	2.448
FF3B3P	1.168	0.333	3.775	2.878

Table 3. Flame retardancy properties of composite materials



Composite Codes	LOI
B1P	19
FF3P	19
FF3B1P	24

Boron oxide can be used as a flame retardant in many manufacturing process. From these results it can be concluded that boron oxide improved the flame retardancy of polyester composites with a gain of approximately 26%.

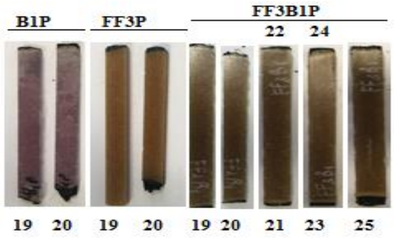


Figure 4. Composite samples measured for LOI test

3.4. 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 5. 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 chicken feather the residual mass value increased to 20.67 % from 8.74 %. It is also compatible with the LOI test results as boron oxide gives a flame reterdancy to composites. B_2O_3 is known as hard glass and the crystal structure begin to deteriorate at 300˚C, and a series of suboxides are produced by partial melting until full fusion is reached at 700˚C. As boron oxide is anhydrous it can behave as blowing agent which provide a “glue” to keep the combustion char and provide structural unity to the char (Jimenez *et al*., 2006).

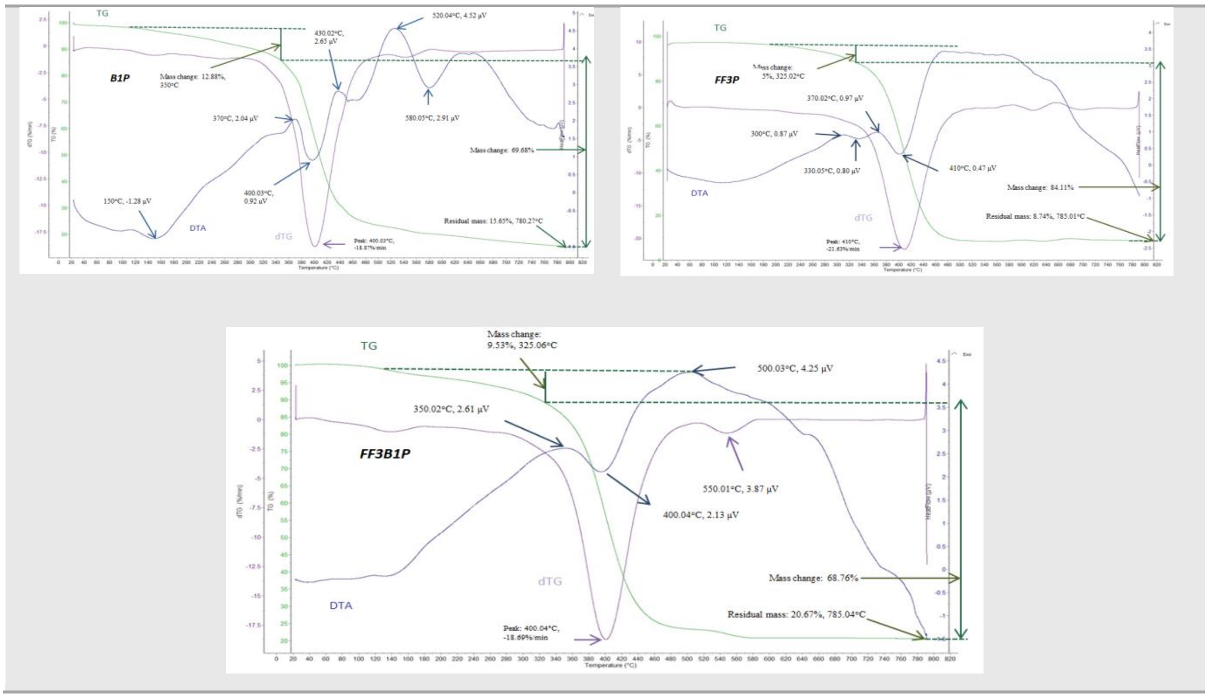


Figure 5. TG, DTG and DTA curves of composite samples

3.5. Morphological Analysis of Composites

Figure 6 shows the SEM images of these 3 composite samples where it can be seen that feather barbs were located in the voids so that they can easily have a good adhesion between the polymer and fibers in the composite structure.

Barbs have the length, strength and flexibility that make them convenient as natural protein fibers (Reddy and Yang, 2007). Moreover, as it seen from figure these chicken barbs have a unique cross-section that cannot be observed in any other protein fibers. The rachis and barbs are soft and readily can absorb water (Akpinar Borazan and Gokdai, 2017). Addition of boron oxide improved the connection of waste chicken feather with polyester and it filled the voids in the structure and made the composite with high strength.

4. Conclusions

According to the some mechanical and physical properties of the composites it can be concluded that boron oxide had better contribution to bending properties of composites. Especially flexural modulus of the FF3B1P series was higher than the FF3P series. When three kinds of boron minerals were compared it can be indicated that boron oxide is more compatible with waste chicken feather in polymer composites. In results of LOI test and TGA analysis it was clearly obtained boron oxide improved the flame retardancy properties of polyester with a gain of 26%.

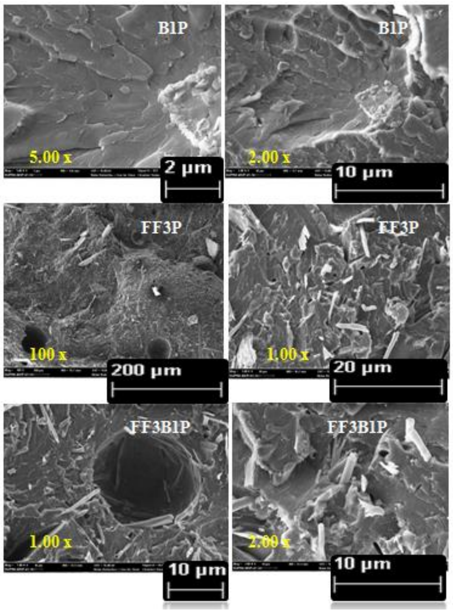


Figure 6. SEM images of composite materials at different magnifications

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References

Akpinar Borazan A. and Gokdai D. (2017), Polymer Composites Reinforced With Waste Marble Dust and Fibers From Chicken Feathers as an Alternative Material, *Fresenius Environmental Bulletin*, **26,** 2093-2101.

Arrakhiz F.Z., Benmoussa K., Bouhfid R. and Qaiss A. (2013), Pine cone fiber/clay hybrid composite: Mechanical and thermal properties, *Materials and Design*, **50**, 376-381.

ASTM D2863-13, Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index), ASTM International, West Conshohocken, PA, 2013, www.astm.org.

Ayar B., Gürü M. and Çakanyıldırım Ç. (2014), Solid Phase Synthesis of Anhydrous Zinc Borate from Zinc and Boron Oxide and Utilization as a Flame Retardant in Dye and Textile, *Gazi University Journal of Science*, **27,** 987-991.

Barone J.R. and Schmidth W.F. (2005), Polyethylene reinforced with keratin fibers obtained from chicken feathers, *Composite Science and Technology*, **65**, 173-181.

Cheng S., Lau K., Liu T., Zhao Y., Lam P. and Yin Y. (2009), Mechanical and thermal properties of chicken feather fiber/PLA green composites, *Composites Part B*, **40**, 650-654.

Das O., Bhattacharyya D., Hui D. and Lau K. (2016), Mechanical and flammability characterisations of biochar/polypropylene biocomposites, *Composites Part B*, **106**, 120-128.

Das O., Kim N.K., Sarmah A.K. and Bhattacharyya D. (2017), Development of waste based biochar/wool hybrid biocomposites: Flammability characteristics and mechanical properties, *Journal of Cleaner Production*, **144**, 79-89.

Doğan M. and Unlu S.M. (2014), Flame retardant effect of boron compounds on red phosphorus containing epoxy resins, *Polymer Degradation and Stability*, **99**, 12-17.

Jimenez M., Duquesne S. and Bourbigot S. (2006), Intumescent fire protective coating: Toward a better understanding of their mechanism of action, *Thermochimica Acta*, **449,** 16-26.

Oliwa R., Heneczkowski M., Oleksy M. and Galina H. (2016), Epoxy composites of reduced flammability, *Composites Part B*, **95**, 1-8.

Reddy N. and Yang Y. (2007), Structure and Properties of Chicken Feather Barbs as Natural Protein Fibers, *Journal of Polymers and the Environment*, **15**, 81-87.

Shuarty N.S., Almanar I.P., Sudirman, Dihardjo K. and Astasari N. (2012), Flammability, Biodegradability and Mechanical Properties of Bio-Composites Waste Polypropylene/Kenaf Fiber, *Procedia Chemistry*, **4,** 282-287.

Yang S., Zhang Q. and Hu Y. (2016), Synthesis of a novel flame retardant containing phosphorus, nitrogen and boron and its application in flame-retardant epoxy resin, *Polymer Degradation and Stability*,**133**, 358-366.