

Flame retardant effect of boron compounds on red phosphorus containing epoxy resins



Mehmet Dogan^{a,*}, S. Murat Unlu^b

^a Department of Textile Engineering, Erciyes University, 38039 Kayseri, Turkey

^b Department of Mechanical Engineering, Erciyes University, 38039 Kayseri, Turkey

ARTICLE INFO

Article history:

Received 1 August 2013

Received in revised form

11 November 2013

Accepted 7 December 2013

Available online 16 December 2013

Keywords:

Red phosphorus

Zinc borate

Boric acid

Boric oxide

Flame retardant

ABSTRACT

The effect of zinc borate (ZnB), boric acid (BA) and boric oxide (B_2O_3) was studied on the flame retardant and thermal stability properties of epoxy resin containing red phosphorus (RP). The flame retardancy of epoxy based composites was investigated using limiting oxygen index (LOI), UL-94 standard, thermogravimetric analysis (TGA), mass loss calorimeter, scanning electron microscopy (SEM) and attenuated total reflectance – fourier-transform infrared spectroscopy (ATR-FTIR). The addition of 15 wt% RP based flame retardant additive increased the LOI value from 19.5 to 32.5 and V0 rating was obtained from UL-94 test. According to flammability properties, the maximum adjuvant effect was observed at ratio of 9:1 (RP:boron compounds) with the addition of ZnB and BA and at a ratio of 7:3 with the addition of B_2O_3 . With the partial substitution of boron compounds for RP, lower heat release rate (HRR) and total heat evolved (THE) was obtained. According to fire performances, ZnB containing composite showed lowest HRR and THE values. The boron compounds showed beneficial effect by increasing char yield in the condensed phase.

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1. Introduction

Epoxy resins are widely used in different industrial sectors due to their good chemical and physical properties. However, their wider application is restricted by their high flammability properties. The flammability properties of epoxy resins can be improved by additive and/or reactive approach [1, 2]. Organic bromine compounds with antimony oxide, ammonium polyphosphate (APP), metal hydroxides and red phosphorus (RP) can be widely used as flame retardant additive with epoxy resins [3–11].

RP, most concentrated source of phosphorus, shows flame retarding effect in variety of polymers including polyamides, polyesters, polyolefins and so forth. It shows its flame retarding effect both in condensed and gaseous phases via different mechanisms depending upon the type of polymer used with [12–14]. It is proposed that RP shows its flame retarding effect in polymers containing oxygen and nitrogen atoms via the formation of thermally stable char in the condensed phase and the formation of phosphorus radicals in the gas phase [15]. Boron compounds considered as environmentally friendly are also used as flame retardant agent either solely [16,17] or with commercial flame

retardants [18–26] for their synergistic effect to improve the flame retardant properties polymers.

The main purpose of present work is to investigate the combustion characteristics and thermal degradation of flame retardant epoxy based composites containing RP with three different kinds of boron containing additives (zinc borate (ZnB), boric acid (BA) and boric oxide (B_2O_3)). The combustion and the thermal degradation characteristics are investigated by using limiting oxygen index (LOI), UL-94 standard, thermogravimetric analysis (TGA) and mass loss calorimeter. Char residues remained after mass loss calorimeter test are investigated by conducting attenuated total reflectance – fourier-transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM) analysis.

2. Experimental

2.1. Materials

The epoxy resin system was purchased from Polikem Kimyevi Maddeler San. Tic. Ltd. Sti. (Istanbul, Turkey). The system was composed of bisphenol A based epoxy resin (Polires 188, 182–192 g/epoxy equivalent) and polyamine based hardener (CeTePox 1393 H, 93 g/eq). RP based flame retardant additive (FR), Exolit RP 6500, a blend of micro encapsulated RP in an epoxy resin carrier, was kindly obtained from Clariant (Frankfurt, Germany). The

* Corresponding author. Tel.: +90 352 207 66 66/32904; fax: +90 352 4375784.
E-mail address: mehmetd@erciyes.edu.tr (M. Dogan).

encapsulation of RP is quite common and crucial to reduce the intrinsic problems with respect to hydrolysis and phosphine formation. FR has the RP and the epoxy resin content of 43–47% and 52–57% by weight, respectively. Zinc borate (ZB 467), $4\text{ZnO} \cdot 6\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$, was purchased from Great Lakes Chemical GmbH. Boric oxide was kindly donated by ETI Mine Works (Ankara, Turkey). Boric acid was purchased from Sigma Aldrich.

2.2. Sample preparation

Epoxy resin was first mixed with flame retardants for 20 min at room temperature using mechanical mixer (Heidolph RZR 2041). After the curing agent had been added into mixture, the mixture was mixed again for 10 min. The resulting mixtures were cured in a teflon mold at room temperature for 24 h and post cured at 70 °C for 2 h. As the producer suggestion, the ratio of epoxy resin and hardener was kept constant at 2:1 by weight in all mixtures. Three different amount of FR containing epoxy resin (5, 10 and 15% by weight) were prepared and the flammability properties were characterized by LOI and UL-94 rating to understand at which concentration was chosen in the studies with boron compounds. At the beginning, the ratio of FR to boron compounds was adjusted as 9:1 and 7:3. According to the LOI values and UL-94 results, the upper (5:5) or lower ratios (12:1) were prepared and characterized. The composition of formulations, LOI values and UL-94 ratings are given in Table 1.

2.3. Characterization methods

LOI values were measured using Fire Testing Technology Limiting Oxygen Index Analyzer instrument on test bars of size $130 \times 6.5 \times 3.2 \text{ mm}^3$, according to the standard oxygen index test ASTM D2863. Vertical burning tests (UL-94) were also conducted to investigate the flammability properties of composites on the test bars of $130 \times 13 \times 3.2 \text{ mm}^3$ according to ASTM D3801. TGA was carried out on Perkin Elmer Diamond TG/DTA at a heating rate of 10 °C/min up to 800 °C under nitrogen flow of 50 ml/min. The mass loss calorimeter test was carried out following the procedures in ISO 13927 using Mass Loss Cone with thermopile attachment (Fire testing Technology, U.K.). Square specimens ($100 \times 100 \times 3 \text{ mm}^3$) were irradiated at a heat flux of 35 kW/m², corresponding to a mild fire scenario. Microstructure of residual chars remained after mass loss calorimeter test were examined with SEM (LEO 440 computer controlled digital, 20 kV). All specimens were sputter-coated with Au/Pd before examination. Attenuated Total Reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) was used to analyze char residues remained after mass loss calorimeter test at an optical resolution of 4 cm⁻¹ with 32 scans.

Table 1
The composition of formulations, LOI values and UL-94 ratings.

Sample	LOI	UL-94
E	19.5	NR
E/5 FR (2.15–2.35) ^a	27.6	NR
E/10 FR (4.3–4.7)	28.2	NR
E/15 FR (6.5–7.1)	32.5	VO
E/12 FR/1 ZnB (5.2–5.6)	28.0	NR
E/9 FR/1 ZnB (3.9–4.2)	29.5	V1
E/7 FR/3 ZnB (3.0–3.3)	27.3	NR
E/12 FR/1 BA (5.2–5.6)	27.0	NR
E/9 FR/1 BA (3.9–4.2)	28.5	V1
E/7 FR/3 BA (3.0–3.3)	26.0	NR
E/9 FR/1 B ₂ O ₃ (3.9–4.2)	27.0	NR
E/7 FR/3 B ₂ O ₃ (3.0–3.3)	29.5	VO
E/5 FR/5 B ₂ O ₃ (2.15–2.35)	26.5	NR

NR: Non rated.

^a Active RP content by weight.

3. Results and discussion

3.1. Thermal decomposition

Thermal properties of composites are investigated by TGA under nitrogen atmosphere. TGA data of all compositions are given in Table 2. The calculated and experimental TGA curves of E/10 FR sample are shown in Fig. 1. The pure epoxy resin degrades through a double step with a maximum rate at 186 °C and 356 °C with 7.9% carbonaceous char. In the first step, epoxy resin loses about 15.5% its weight due to the formation of C–C unsaturations via water elimination [27, 28]. In the second step, epoxy resin loses 76.6% its weight due to the volatilization of small fragments [29]. The weight loss pattern is not changed much and the char yield increases to 9% with the addition of 10 wt% FR. Phosphorus vaporization mainly occurs during thermal degradation of RP containing polymers under nitrogen atmosphere [13]. Accordingly, it is thought that the slight increase in char yield arises from the remaining phosphorus rather than the formation of a stable char. The resulting char contains mainly carbonaceous char (about 90%) and slight amount of phosphorus based inorganic residue. The inclusion of RP into epoxy resin increases $T_{5\%}$, and T_{max} value by 20 °C and 6 °C, respectively. The calculated and experimental TGA curves of E/10 FR are almost similar to each other. This result supports that there is no interaction observed between RP and epoxy resin under nitrogen atmosphere.

TGA curves of selected compositions are given in Fig. 2. It is seen from Fig. 2 that boron compounds has little effect on the shape of curve. The $T_{5\%}$ values decrease with the inclusion of boron compounds regardless of their kinds and no meaningful difference is observed at T_{max} values with respect to E/10 FR sample. The char yield of all composites increases as the amount of boron compounds increases regardless of the type due to thermally stable inorganic decomposition products of boron compounds. According to Fig. 3, ZnB, BA and B₂O₃ retains about 85, 55 and 99% its weight, respectively. The resulting inorganic residue mainly composed of B₂O₃ and additionally ZnO formation occurs in the case of ZnB. Thus, it is thought that the char residues of BA and boric oxide containing composites mainly consist of carbonaceous residue and B₂O₃. The char residues of ZnB containing composites mainly consist of carbonaceous residue, ZnO and B₂O₃.

The calculated and experimental TGA curves of selected boron containing epoxy resins are given in Fig. 4. The experimental char yields are slightly higher than calculated char yield with the addition of boron compounds. It is thought that the increase in experimental char yield results from the limited formation of boron phosphate due to the reaction between RP and boron compounds.

Table 2
TGA data of all composites.

Sample	$T_{5\%}$ (°C) ^a	T_{max} (°C) ^b	Char yield (%) ^c
E	166	356	7.9
E/10 FR	186	362	9.0
E/12 FR/1 ZnB	170	360	9.5
E/9 FR/1 ZnB	180	360	9.7
E/7 FR/3 ZnB	170	365	12.6
E/12 FR/1 BA	164	362	11.7
E/9 FR/1 BA	181	360	12.7
E/7 FR/3 BA	167	362	13.8
E/9 FR/1 B ₂ O ₃	163	362	13.6
E/7 FR/3 B ₂ O ₃	168	360	19.8
E/5 FR/5 B ₂ O ₃	159	365	19.5

^a Temperature at 5% weight loss.

^b The maximum degradation rate temperature.

^c Char Yield at 800 °C.

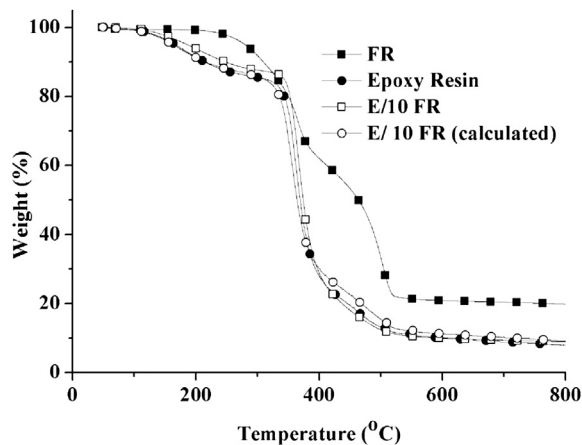


Fig. 1. The calculated and experimental TGA curves of E/10 FR sample.

Thus, some part of RP reacts with B_2O_3 rather than vaporizes and stays in the condensed phase in form of boron phosphate. The detailed analysis made by previous studies supports that boron phosphate formation occurs in the condensed phase via reaction between phosphorus based flame retardants and B_2O_3 [21–24].

3.2. Mass loss calorimeter study

Mass loss calorimeter is used to monitor heat release rate (HRR) during combustion. Low values of peak heat release rate (pHRR) and total heat release (THE) normally indicate improved flame retardancy. Fig. 5 and Table 3 show the HRR curves and mass loss calorimeter data of selected compositions at a heat flux of 35 kW m^{-2} .

According to Fig. 5, epoxy resin burns very fast after ignition and one sharp HRR peak appears with a heat release peak of 459 kW m^{-2} with a char yield of 9.9%. The char yield of epoxy resin at mass loss calorimeter studies is higher than that of TGA due to the some thermo oxidative decomposition [29]. When FR is added to epoxy resin, the pHRR, average HRR and THE decrease at about 15.6, 24.6 and 15.4% with extended burning time, respectively. Time to ignition (TTI) value does not change with the addition of RP. The char yield of FR containing composite (19.4%) at mass loss calorimeter studies is also much higher than that of TGA due to the thermo-oxidative degradation products of RP which are further reacting with epoxy resin [30, 31]. Despite the high amount of char,

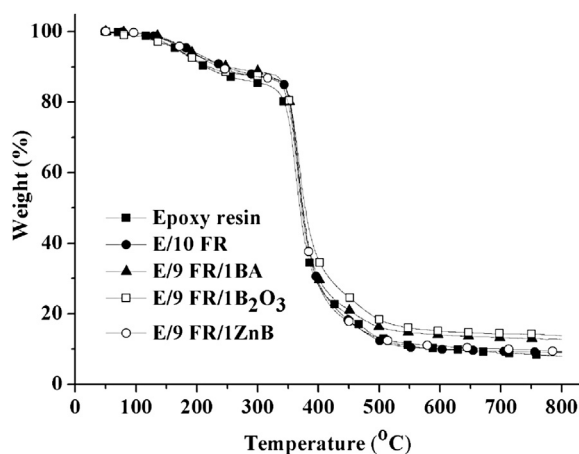


Fig. 2. TGA curves of selected compositions.

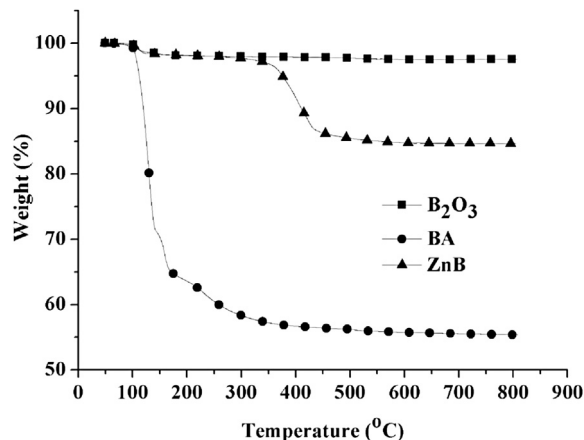


Fig. 3. TGA curves of boron compounds.

the shape HRR curve does not resemble that of flame retardant systems forming the efficient protective char which stays relatively constant and slowly decreases toward the end of combustion [32]. Total heat evolved to total mass loss ratio (THE/TML) is a measure for the effective heat of combustion and a reduction of this value indicates that the flame retardant additive shows its effect in the gas phase by flame inhibition [33]. The reduction at THE/TML value by 18.4% with the addition of 10 wt% FR shows that RP is also effective in the gas phase due to the formation of PO radicals whose several hundred ppm in the flaming zone is enough to trap active radicals in the gas phase [15, 31]. With the reduction at THE/TML value and the increase at the char yield, it can be clearly seen that RP shows its flame retardant effect both in the condensed and gas phases.

Both the addition of BA and ZnB increases TTI values due to the dilution of fuel in the gas phase by water release [34, 35]. The addition of boron compounds further reduces the pHRR, average HRR and THE values with respect to 10 wt% FR containing sample. The reduction at pHRR and THE values arises from the improvement of the barrier effect of formed char. ATR-FTIR studies (Fig. 6) clearly show that the addition of boron compounds increases the barrier effect of char. The changes of C–H absorption of aliphatic groups can be used for evaluating the thermal stability of composites during thermal decomposition. Wu et al. showed that the characteristic peaks seen at 2920 and 2860 cm^{-1} arising from asymmetric and symmetric vibrations $-CH_2$ and $-CH_3$ gradually decrease as the thermo-oxidative degradation of epoxy resin increases [36]. According to Fig. 6, the intensities of the bands at 2980 , 2895 and 1410 cm^{-1} increases with addition of boron compounds in order of BA, B_2O_3 and ZnB. The intensity of the peak seen at 1580 cm^{-1} arising from the formation of polyaromatic species [37] reduces with the addition of boron compounds.

The SEM images of char residues remained after mass loss calorimeter test are shown in Fig. 7. According to Fig. 7, there is no morphological difference observed among the char residues. It is concluded that the improvement in the barrier effect of char arises from increase in char thickness due to the higher char yield and the formation of boron phosphate in the condensed phase. According to Fig. 6, a sharp peak seen at 1080 cm^{-1} and a shoulder around 910 cm^{-1} correspond to asymmetric stretching of phosphate vibrations in boron phosphates [38, 39].

On contrary to char yields in TGA experiments under nitrogen atmosphere in descending order of B_2O_3 , BA, ZnB, the char yields in mass calorimeter studies are in descending order of ZnB, BA and B_2O_3 containing composites. It is thought that this trend arises from the thermo oxidative degradation in mass calorimeter studies. As is

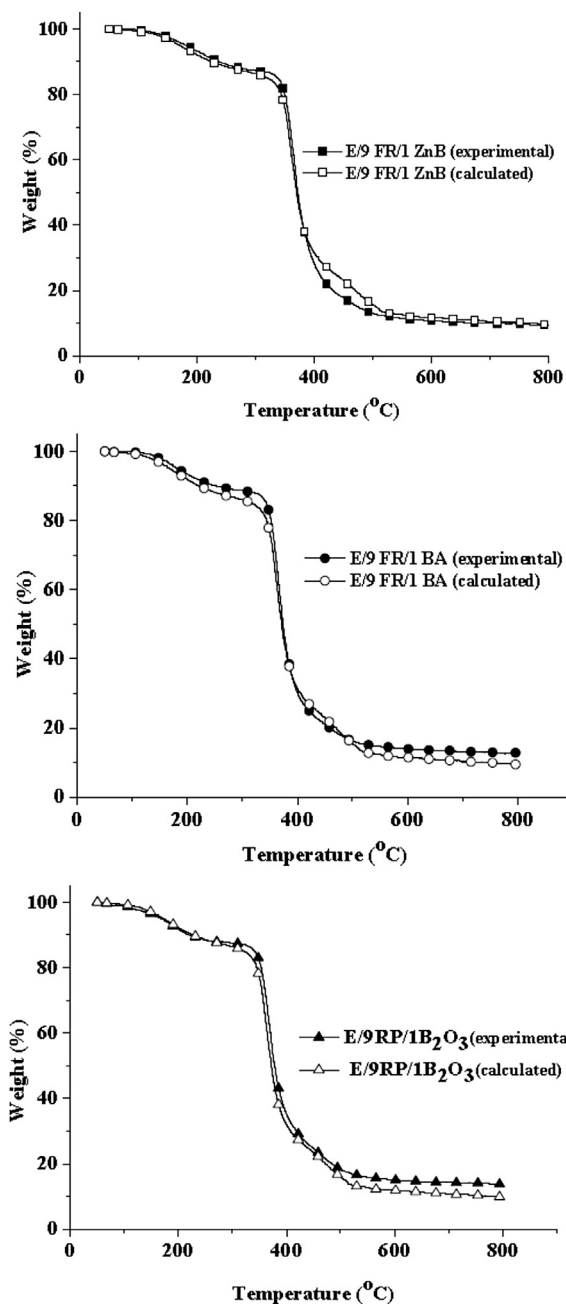


Fig. 4. The calculated and experimental TGA curves of selected boron containing epoxy resins.

known that dominantly anaerobic decomposition and some thermo oxidative degradation occur during mass loss calorimeter test. The detailed analysis made by Braun et al. [13] and Fichera et al. [14] clearly show that when RP is combinedly used with water releasing source, the oxidation of phosphorus in the condensed phase increases. BA and ZnB releasing water during decomposition favors the oxidation of RP and increases char yield as stated in the previous studies. The studies made by Laoutid et al. and Levchik et al. show that the metal oxides in the presence of RP favors the char formation in poly (ethylene terephthalate) and polyamide 6 [40, 41]. It is thought that ZnO, the decomposition product of ZnB, stabilizes RP and further increases the char yield. Thus ZnB containing sample which has highest char yield (31.4%) shows the lowest pHRR and THE values.

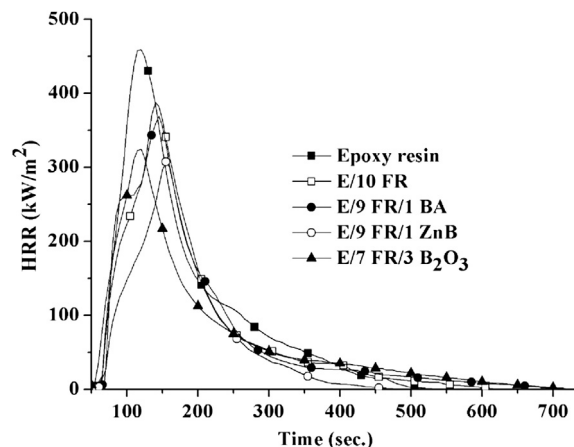


Fig. 5. HRR curves of selected compositions.

3.3. Flammability properties

The flammability characteristics of composites are determined by LOI and UL-94 rating. The relevant data are given in Table 1. From the LOI data, epoxy resin has a LOI value of 19.5% and increases sharply with the increasing amount of RP. The epoxy resin has V0 rating and LOI value of 32.5% at low RP contents of 6.45–7.05% which correspond to 15 wt% FR.

With the addition of ZnB, LOI value of 29.5% and V1 rating are achieved at a ratio of 9:1. However, with further loading of ZnB (7:3), LOI value decreases to 27.3% and classifies as non-rated (NR) according to UL-94 test. The largest beneficial effect in LOI (28.5) and UL-94 (V1) rating is obtained with the inclusion of BA at a ratio

Table 3
Mass loss calorimeter data of selected compositions.

Samples	TTI (sec.)	pHRR (Kw m ⁻²)	Av. HRR (Kw m ⁻²)	THE (MJ m ⁻²)	THE/TML (MJ m ⁻² g ⁻¹)	Residue (%)
Epoxy resin	57	459	114	55.3	1.74	9.9
E/10 FR	57	387	86	46.8	1.42	19.4
E/9 FR/1 BA	66	369	77	39.8	1.45	29.1
E/9 FR/1 ZnB	61	307	80	35.8	1.41	31.4
E/7 FR/3 B ₂ O ₃	55	324	67	37.6	1.45	28.6

TTI: Time to ignition, pHRR: Peak Heat Release Rate, Av. HRR: Average HRR, THE: Total Heat Evolved, TML: Total Mass Loss.

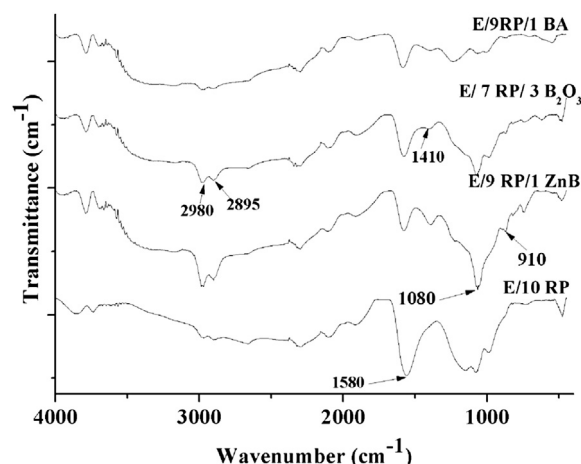


Fig. 6. The FTIR spectra of char residues remained after mass calorimeter test.

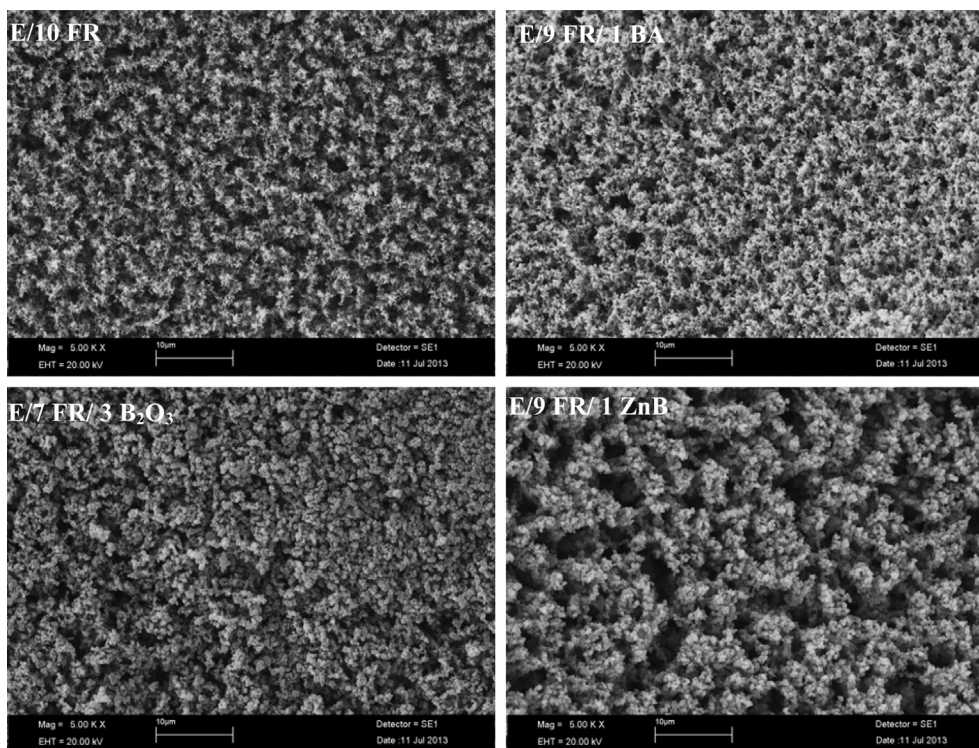


Fig. 7. The SEM images of char residues remained after mass calorimeter test.

of 9:1, as well. On contrary to ZnB and BA, the maximum beneficial effect is observed with the addition of B_2O_3 at a ratio of 7:3 with a LOI value of 29.5 and highest UL-94 (V0).

4. Conclusions

This study deals with the effect of three different boron compounds on flame retardant and thermal stability of RP containing epoxy resins. The results of current study show that the addition of 6.45–7.05 wt% RP is enough to achieve highest UL-94 rating (V0) with a LOI value of 32.5. RP shows its flame retardant effect through the formation of thermally stable char in the condensed phase and flame inhibition effect in the gases phase.

According to LOI and UL-94 tests, the maximum beneficial effect is seen at ratio of 9:1 with the addition of BA and ZnB. The highest UL-94 rating (V0) is achieved with the inclusion of boric oxide at a ratio of 7:3. According to mass calorimeter studies, the addition of RP does not change the ignition time and reduces pHRR and THE of epoxy resin. The addition of boron compounds regardless of their types further reduces the pHRR and THE values with respect to 10 wt% FR containing composite. The boron compounds show adjuvant effect by favoring char yield and the formation of boron phosphate in the condensed phase. The increase in char yield arises from the different mechanisms via the formation of boron phosphate and the favoring the thermo oxidative degradation of RP depending upon the boron compound used. There boron compounds used favor the char formation via the formation of boron phosphate in the condensed phase. The inclusion of BA and ZnB also increase the char formation by water releasing which favors the oxidation RP. ZnB further increases the char formation by the stabilizing effect of ZnO. The main result of this study is that boric oxide shows maximum beneficial effect in terms of flammability properties and ZnB exhibits highest fire performances.

Acknowledgments

This study was supported by the Boron Institute of Turkey, project no: BOREN 2012 C 0354.

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