



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



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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

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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.

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