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ORIGINAL PAPER



Intrinsically modified self-extinguishing fire-retardant epoxy resin using boron-polyol complex

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Abstract

A novel fire-retardant epoxy thermoset, containing boron polyol complex, was prepared and characterised. The fire-retardant additive was a stoichiometric mixture of boric acid and glycerol. Flame retardancy of the epoxy resin was improved by the formation of stable char layer that protected the underlying epoxy from further burning. Phonon transport through the polymer matrix via hydrogen bonding was identified. The hydrogen bonding acted as a thermal bridge for intermolecular phonon transport to gain improved thermal conductivity resulting early char formation. The hydrogen bonding between the complex and the epoxy matrix was demonstrated using Fourier Transform Infrared Spectroscopy. The phonon transport and a high degree of graphitization was confirmed using Raman Spectroscopy. Thermogravimetric analysis was used for polymer decomposition to confirm a char yield of over 20%. Reaction to fire test revealed enhancement in fire retardancy and self-extinguishing properties of the blend compared to the neat epoxy. Cone calorimetry testing confirmed decreased peak heat release rate and total smoke production by the effect of boron compound in the epoxy matrix. Hydrogen bonding, formation of thick stable layer of char at the polymer surface, and a blowing out effect caused by pyrolytic gases escaping to the gaseous phase, were attributed to the improved fire retardancy. This research may find applications in thermal insulation material of electronic circuit boards, coating in aerospace materials, as well as building and construction industries.

Keywords Fire retardancy \cdot Epoxy polymers \cdot Boron complex \cdot Hydrogen bonding \cdot Thermal conductivity \cdot Char formation \cdot Fire hazard

Introduction

Epoxy resins represent a large group of thermoset polymers with unique mechanical, electrical, and chemical properties. Epoxy composites and blends are popularly used in many industries such as aerospace, automotive, defence, electronics, and construction [1]. Being a product derived from petroleum, epoxy resins are inherently flammable, and may represent a fire hazard in high temperature environments. Intrinsic modification of the epoxy resins, blending epoxy resins with fire retardants, and epoxy-composite fabrication are few important methods to improve fire retardancy. In particular, altering polymer properties in the molecular level has been an efficient technique for reducing flammability. In recent years, materials including benzoxazines, ammonium polyphosphate, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, boron nitride nanosheets and bio-based materials such as vanillin, genistein, resveratrol have been successfully utilised for reducing flammability of epoxy resins [2–9].

A typical drawback of many fire-retardant additives is the negative impact when released into the environment. Most fire-resistant materials are not eco-friendly. The popular flame retardant additives on the market are halogenated ones [10] but unfortunately majority of them are harmful chemicals. The use of organohalogen flame retardants are controlled with strict regulations and its replacement products such as organophosphate ester flame retardants are under

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Fig. 1 Synthesis of a boron chelate complex from boric acid and glycerol

scrutiny due to its environmental impact and toxicity [11]. The release of halogenated fire retardants to the landfill will leach compounds that are stable, persistent, bioaccumulated and may enter the human food chain to cause several diseases. The use of compounds such as *tris* (dibromo propyl) phosphate is now forbidden due to recycling requirements and environmental impact [12, 13]. Therefore, it is critical to develop a novel benign flame-retardant combination.

As inert materials, boron compounds are desirable to enhance fire retardancy of epoxy resins. Boron compounds are relatively nontoxic, naturally available, ecofriendly [14] and have proven to enhance the fire retardancy of epoxy polymers, wood, cellulose, cotton, etc. [15–17]. Boron compounds such as ammonium pentaborate, melamine diborate, and zinc borate are currently used as fire retardants in epoxy composites and coatings [18]. Recently, a boron containing triazine derivative 2,4,6-*tris*-(4-boronphenoxy)-(1,3,5)triazine (TNB), was used to generate an epoxy blend which exhibited a V-0 rating in UL-94 vertical burning test, and a limiting oxygen index of 31.2% for combustion [19].

Boron compounds present in an epoxy matrix promotes the formation of a thermally stable char layer on the surface of the degrading polymer. This char layer inhibits heat feedback from the combustion zone to reduce the pyrolytic formation of volatile fuel fragments that support combustion [20, 21]. Amongst the boron compounds, boric acid is well known for its fire retardancy [22, 23]. As an inorganic reagent, boric acid shows relatively low toxicity [24] and exerts its flame retardant properties at a temperature well below the normal pyrolysis temperature of polymeric materials [25].

To take advantage of low toxicity, and fire-resistant properties of boric acid, together with miscibility in epoxy resin, a stoichiometric mixture of boric acid and glycerol referred to as a boron polyol complex (BPC) was utilized as a flameretardant. Boric acid and glycerol form a boron chelate complex [26] as shown in Fig. 1 that is structurally similar to an ionic liquid [27]. Because of facile proton transfer, this complex is more acidic than boric acid [26, 27] and had been used as an efficient catalyst for regioselective ring-opening of epoxide by an aromatic amine in water (Fig. 2) [27].

The objective of this research was to invent a simple, inexpensive, and ecofriendly fire-retardant additive for epoxy polymer. A novel fire-retardant polymer blend from diglycidyl ether of bisphenol-A (DGEBA) and BPC, cured with 4,4'-diaminodiphenylmethane was prepared and characterised. The BPC mixture was prepared by mixing boric acid and glycerol. The fire-retardant epoxy blend was synthesised by blending BPC with DGEBA binder followed by the addition of DDM hardener. The effectiveness of this complex was reflected in the early thermal degradation to promote the formation of thick layer of char at the surface of the polymer. This process was enhanced by improved thermal conductivity in the epoxy matrix via hydrogen bonding. The fire resistance of the blend was additionally contributed by a blowing-out effect and self-extinguishment caused by pyrolytic gases liberated to the gaseous phase. The BPC complex was chemically bonded to the epoxy matrix via hydrogen bonding to form an intrinsic fire-retardant epoxy resin.

Experimental

Materials

A low molecular weight (340.41 g/mol) DGEBA precursor and 4, 4'-diaminodiphenylmethane curing agent were used for epoxy resin synthesis. Boric acid and glycerol were used for the boron polyol complex synthesis. Boric acid (100%), glycerol (100%), DGEBA and DDM were obtained from



Fig. 2 Ring opening of epoxides with aromatic amines promoted by boric acid and glycerol in water



diglycidylether of bisphenol-A, DGEBA

Fig. 3 Chemical structure of materials used to synthesise fire retardant epoxy blend

Sigma-Aldrich. The chemical structures of these compounds are shown in Fig. 3.

Synthesis of fire-retardant epoxy blend

The fire-retardant epoxy resin blend was synthesised in two steps. A 25% mixture of boric acid in glycerol (BPC) was prepared by mixing 17.5 g boric acid in 52.5 g glycerol at 40 °C under constant stirring in a conical flask until boric acid was completely dissolved. The resultant mixture was highly viscous, saturated with boric acid devoid of any neutralising agents [16]. Boric acid was completely dissolved in glycerol at 40 °C. In the second step, the BPC complex was blended with DGEBA resin under constant stirring at 40 °C until homogenised, followed by the addition of proportionate amount of DDM. The mixture was thoroughly blended and degassed, allowed to settle under room temperature prior to curing at 120 °C for 24 h in an oven and post curing at 180 °C for 1 h. The mixing ratio and compositions were detailed in Table 1.

Characterization

Differential scanning calorimetry (DSC) Phase behavior of the blend was investigated using a NETZSCH-PRO-TEUS-70 DSC. The cured polymer samples were heated

Table 1	DGEBA-BPC	composition
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Mixing ratio			Composition				
Polymer ID	DGEBA (g)	BPC Soln. (g)	Hardener (g)	PHR of BPC Soln.	Boric acid (g)	Boron equivalent (g)	% Boron in cured thermoset
DGEBA-0	5	0	1.5	0	0	0	0
DGEBA-0.5	5	0.5	1.5	10	0.125	0.022	0.31
DGEBA-1	5	1	1.5	20	0.25	0.044	0.58
DGEBA-2	5	2	1.5	40	0.5	0.088	1.03
DGEBA-3	5	3	1.5	60	0.75	0.132	1.39
DGEBA-4	5	4	1.5	80	1	0.175	1.67
DGEBA-5	5	5	1.5	100	1.25	0.219	1.91

up to 100 °C with temperature ramp rate of 20 °C/min and held for 5 min at 100 °C. Then the samples were cooled down to -30 °C and then reheated to 250 °C at 20 °C/min. The glass transition temperature (T_g) was measured at the midpoint of transition.

Thermogravimetric analysis (TGA) The thermal stability and char formation of the cured epoxy blend was investigated using Q500 TGA instrument. Samples was heated in a platinum pan up to 800 °C with 10 °C per minute increment under N₂ environment.

Fourier transform infrared (FTIR) spectroscopy KBr method was used to determine the FTIR characteristics of the blend on a Bruker FTIR spectrometer. The cured solid samples were placed on the clean surface of sample holder. The spectra were recorded in the standard wavenumbers range of 400 and 4000 cm⁻¹ at an average 28 scans.

Vertical burning test The specimens were tested for vertical flammability under laboratory conditions at a wind speed of 0.2-0.4 m/s and an ambient temperature of 23 °C.

Cone calorimetry Cone calorimetry test was carried out using the iCone cone calorimeter with the heat flux of 50 kW/m² on a 100 mm \times 100 mm carbon fiber (CF) reinforced epoxy composite system. The rough side of the specimen was the exposed face, and the unexposed face was covered with aluminium foil. The CF composites were prepared by hand layup method.

Raman spectroscopy Raman spectrum of the char layer and the unburned blend was captured by Renishaw inVia Raman instrument. A 514 nm laser wavelength was selected to analyse graphitization.

Optical microscope Structure of the char layer was analyzed under the optical digital microscope Olympus BX61.

Result and discussion

Fourier transform infrared spectroscopy

Infrared spectrum of the polymer exhibited significant changes in the hydroxyl group region of DGEBA-BPC polymer that can be explained in connection with the hydrogen bonding between BPC and DGEBA-DDM as illustrated in Fig. 4. Intermolecular hydrogen bonding in epoxy was beneficial for improved phonon transport through the matrix [28, 29], which in turn accelerated thermal conductivity [28] to promote char formation, that resulted in better flame retardancy. Hydrogen bonding enabled a thermal connection between DGEBA and BPC to form a strong linear network for phonon transport.

Initially, the structure of BPC was analysed using FTIR spectroscopy. Figure 5 represents FTIR spectral comparison of boric acid, glycerol, and BPC complex.

In boric acid spectrum, peaks at 548 and 710 cm⁻¹ linked to boric acid (H_3BO_3). Peak at 631 cm⁻¹ represented deformation vibrations of atoms in B-O [30]. Peak at 1194 cm⁻¹ belonged to -O-B < vibrations in orthoboric acid [31] that disappeared in BPC complex and did not exist in BPC as confirmed from previous report [32]. In glycerol spectrum, the C-H stretching vibrations at 2931 and 2875 cm⁻¹ were replicated in the BPC complex.

In the BPC complex spectrum, peaks at 1037 cm^{-1} and 1417 cm^{-1} were the symmetric and asymmetric stretching vibrations of B-O bond. Boron spiro structure vibration was observed at 658 cm⁻¹ and B-O deformation vibration at 840 cm⁻¹ [32].

Figure 6 represents the hydroxyl stretching region from 3100 cm^{-1} to 3600 cm^{-1} of neat and blend DGEBA in the infrared spectrum. Neat epoxy showed two important bands at 3390 and 3545 cm⁻¹, attributed to self-associated hydroxyl groups and non-associated free hydroxyl groups respectively. The shoulder peak at 3545 cm⁻¹ - as seen in neat DGEBA - was the free hydroxyl groups which



Boron-glycerol complex

Fig. 4 Hydrogen bonding between BPC and DGEBA-DDM at the hydroxyl groups

Fig. 5 FTIR spectrum of Boric acid, glycerol, and BPC complex comparison





Fig. 6 FTIR peaks confirming hydrogen bonding in DGEBA blend with BPC



disappeared with increased addition of BPC. This indicated that the free hydroxyl group of the DGEBA created a hydrogen bonding with hydroxyl group of BPC complex (Fig. 4) [33].

The peak at 3390 cm⁻¹ represented the stretching vibration of self-associated hydroxyl group in neat DGEBA, which shifted towards lower wave number region with the addition of BPC complex, confirming hydrogen bonding [34, 35] and increased bond length as a result. It has been proven in previous studies that a hydrogen bond could increase the bond length of C-O bond in an epoxide [36, 37] and a similar increase in bond length is observed in C-O bond linked to the hydroxyl group here. DGEBA contained an ether group (-O-) which is an acceptor, and a hydroxyl group (-OH) which is both an acceptor and a donor of hydrogen bonds with the hydroxyl group of BPC [38]. A hydrogen bond formed at the hydroxyl group of DGEBA contributed to the peak shift at 3390 cm^{-1} (Fig. 6). This reconfirmed the formation of hydrogen bonding between free hydroxyl group and BPC.

In addition to that, the spectral region between 3200 and 3300 cm⁻¹ showed an increasing bulge that exhibited the presence of O-H bonds [39] originated from hydrogen bonding between the hydroxyl groups of cured DGEBA and BPC.

Figure 7 compared the FTIR spectrums of BPC complex, neat DGEBA and 20phr DGEBA-BPC blend. The bimodal peak around 2900 cm⁻¹ represented the C-H symmetric and asymmetric stretching vibrations. The corresponding peaks at 2930 cm⁻¹ and 2880 cm⁻¹ of glycerol was present in BPC complex [40] with higher intensity indicating increased amount of C-H bonds in the blend contributed from the BPC additive. In addition to that, a broadening of the hydroxyl group is attributed to the cross-linking reaction and formation of hydrogen bonds.

Differential scanning calorimetry

Transition from solid crystalline state to amorphous rubbery state was evaluated by DSC to characterise the physical properties and phase behaviour of the polymer blends (Fig. 8).

The steady decrease in T_g is attributed to the increased free volume of DGEBA with the addition of BPC. T_g of polymers is a factor of the mobility of polymer chain where an increased free volume in a polymer structure will reduce its T_g [41, 42]. Plasticization effect is a direct result of increased free volume. Low melting point of glycerol boosts the plasticization effect of DGEBA resulting in decreased T_g . Secondly, T_g of a polymer network is related to reactive hydrogen bonding [43]. Decrease in T_g is also explained by lower degree of solidification due to steric hindrance in the curing ring opening reaction to reduce the cross-linking density [44, 45].

Thermogravimetric analysis

Figure 9 illustrated the thermal degradation diagrams of neat DGEBA and the blends. The results showed that neat DGEBA and blends had similar one-stage degradation. This is due to the decomposition of macromolecular chains of epoxy involving the degradation of C-O-C and C-C bonds from the epoxy resin [46]. Neat DGEBA lost 8% of its total weight at 800 °C whereas DGEBA-0.5 and DGEBA-1 lost only 7% and 7% respectively preserving 2% and 2% of their original weight. This implied the increased amount of char formation and presence of non-combustible materials. DGEBA-2 onwards showed a reverse trend in weight loss due to unreacted combustible BPC complex in epoxy matrix. First derivative of weight loss percentage against temperature curve (DTG) indicated increase in degradation temperature with the increased addition of BPC complex



Fig. 7 FTIR spectrum of BPC complex, neat epoxy and 20 phr blend



Fig. 8 DSC curves for DGEBA and its blends



Fig. 9 a comparison of TGA curves of neat DGEBA with its blends and b First derivative of weight loss percentage against temperature curve (DTG) indicates the increase in degradation temperature with the increased addition of BPC complex

as shown in Fig. 9b. High char yield may have influenced lower flammability as confirmed in the vertical burning test. Increased char formation can limit the production of combustible carbon-containing gases, decrease the exothermicity due to pyrolysis reactions, and decrease the thermal conductivity of the surface of a burning material [47].

Data in Table 2 illustrate percentage weight loss at some important temperature points. It leads to an interesting fact that at 100 °C, the percentage weight loss of all blends and neat DGEBA are relatively equivalent. The decomposition temperature of neat DGEBA was higher than that of blends up to 390 °C. But from 400 °C onwards, the decomposition temperature of blends increased with minimised polymer mass loss. Percentage weight of DGEBA-0 (6%) was lower than DGEBA-0.5 (7%) and DGEBA-1 (7%) meaning the blend has better weight stability compared to the neat DGEBA above 400 °C. Neat epoxy lost 31.95% of its original weight at 400 °C due to the presence of volatile components. Slower degradation of blends over 400 °C is attributed to the formation of dense and stable char layer that protected the underlying epoxy resin from further degradation. Increased addition of BPC complex in polymer promoted degradation of epoxide in the 100 to 400 °C region promoting early formation of thick stable layer of char that enhanced the thermal stability over 400 °C by participating in charring. This is further confirmed by the images from optical microscope (Fig. 16). The amount of char formed at 800 °C indicated the presence of non-combustible inorganic boron compound in the blend [48]. Neat DGEBA left a residue of 5% whereas DGEBA-0.5 and DGEBA-1 produced over 0% char residue. TGA graphs of neat DGEBA and its blends are shown in Fig. 9a.

A useful result obtained from TGA analysis is the statistic heat resistance index (*Ts*) and is calculated with the temperature of degradation at 5% and 30% using Eq. (1). *Ts* of neat DGEBA is 193 °C and *Ts* decreased gradually with increased amount of additive up to 40 phr and then increased as shown in Table 3. Decrease in *Ts* of blends compared to neat DGEBA is attributed to lower thermal stability of the blend under 400 °C which is re-confirmed by TGA data analysis [7].

$$Ts = 0.49[T_{-5\%} + 0.6(T_{-30\%} - T_{-5\%})]$$
(1)

Table 2 Percentage mass of neat DGEBA and blends at various temperatures

Blend	% Wt. at 100 °C	% Wt. at 390 °C	% Wt. at 400 °C	% Wt. at 410 °C	% Wt. at 420 °C	% Wt. at 430 °C	% Wt. at 475 °C	Char @ 795 °C
DGEBA-0	99.9	91.7	68.1	50.3	40.3	34.7	24.0	15.2
DGEBA-0.5	99.7	88.0	73.0	58.3	49.0	43.0	33.6	22.0
DGEBA-1	99.4	84.4	72.0	58.5	50.0	44.1	34.0	23.0
DGEBA-2	99.9	83.1	70.0	56.0	47.4	41.7	31.4	21.4
DGEBA-3	99.0	88.5	80.4	66.6	55.0	47.0	33.0	21.0
DGEBA-5	99.6	84.4	75.0	61.5	51.0	43.0	29.0	19.3

Blend	Temp at T-5%	Temp at T-30%	Ts (°C)
Dielia	Temp at 1 5 %	Temp ut 1 50%	15 (0)
DGEBA-0	386	399	193
DGEBA-0.5	329	402	183
DGEBA-1	261	401	169
DGEBA-2	194	400	156
DGEBA-3	271	408	173
DGEBA-5	305	404	179

 Table 3
 tatistic heat resistance index (Ts) of neat DGEBA and blends

Flammability tests

Vertical burning test of samples revealed that the epoxy blends with BPC fire retardant showed improved flame retardancy with self-extinguishing properties compared to the neat epoxy. A comparison of flammability test between neat epoxy and DGEBA-1 in 10 s interval is shown in Fig. 10a. DGEBA-1 was chosen for comparison due to the deterioration of mechanical properties in the higher blend compositions. Both samples were ignited within 10 s of exposure to flame. Neat DGEBA was completely burned within 50 s. DGEBA-1 self-extinguished within 15 s. A blowing out effect of DGEBA-1 is obvious to cause quenching at 20 s. Second ignition self-extinguished in 55 s. Third and fourth ignition self-extinguished quickly within 10 and 20 s. DGEBA was introduced to flame after every selfignition to test its ability to retard fire after initial ignition. The total burning event lasted for 80 s and retained its shape and size after complete ignition as seen at 60 s. A polymer with high aromatic ring content in the chain backbone usually has high heat and flame resistance [47].

Table 4 Vertical burning testratings of neat and blend epoxy	Sample	UL-94
resins	DGEBA-0	NR
	DGEBA-1	V-1
	DGEBA-2	V-0
	DGEBA-3	V-0
	DGEBA-5	V-0
	-	

A complete combustion was observed for DGEBA-0.5, but DGEBA-3 self-extinguished in 2 s. DGEBA-5 selfextinguished in multiple occasions within first 50 s and failed to ignite from normal flame after the char formation. High temperature torch was utilised to ignite thereafter. Blends from DGEBA-1 onwards demonstrated better fire retardancy and self-extinguishing properties. The improved UL-94 rating of the epoxy blend is attributed to the presence of boron compound in the epoxy matrix [49]. The vertical burning test ratings for the neat epoxy and the blends are shown in Table 4.

Random shaped blends were ignited to identify the combustion time as shown in Fig. 10b. The results prove self-extinguishing properties and non-flammability with the increased addition of BPC fire retardant to the polymer matrix. The neat epoxy and DGEBA-1 were exposed to fire in an aluminium foil to observe the char formation. It was identified that neat epoxy undergone complete combustion and DGEBA-1 formed a layer of char on the surface of the specimen as shown in Fig. 11. The vertical burning photographs of DGEBA-1 at 25 and 80 s were shown in Fig. 12.



Fig. 10 a Flammability of neat DGEBA and 20phr blend, b Flammability of neat DGEBA and blends in randomly shaped samples

Fig. 11 a Complete combustion of neat epoxy and **b** char formation on DGEBA-1 surface



Cone calorimetry

Three sets of carbon fibre reinforced epoxy composites were prepared by hand layup method using room temperature curing resin, kinetix R118 and H120 hardener. Three layers of carbon



Fig. 12 Vertical burning event photos of DGEBA-1 at **a** 25 s and **b** 80 s to compare the surface char formation

fibre woven sheets were used for each set. Each layer was wetted out with resin by hand using a brush. The first set was wetted out with neat epoxy (CFR-EP), the second set was wetted out with 8 wt% BPC epoxy blend (CFR-FREP-1) and the third set was wetted out with 16 wt% BPC-epoxy blend (CFR-FREP-2). Every layer in each set was separately coated, and a final coat of epoxy was applied on the surface of the third layer. The mixing ratio and other details of the carbon fibre reinforced composites are described in Table 5 and an illustration is presented in Fig. 13. The composites were cured at room temperature for 24 h and tested for reaction to fire performance under a cone calorimeter.

As described in Table 6, the time to ignition of the FREP composites were shorter than the neat EP. This is caused by the weakened resistance to ignition by the presence of BPC. This result is similar to the findings from TGA analysis where early decomposition of EP-BPC blends were detected as described in Table 2 [50]. The peak heat release rate (peak HRR) of the modified epoxy system was reduced with increased addition of BPC complex. The neat EP composite burned rapidly with the peak HRR of 1234.4 kW/m² but the addition of 8 wt% of BPC to the EP composite system reduced the peak HRR to 1129 kW/m² and 16 wt% of BPC decreased the Peak HRR to 876.4 kW/m². Moreover, the total smoke release (TSR) was decreased with increased addition of BPC



Fig. 13 Preparation of carbon fibre reinforced epoxy composite.

Table 5 Mixing ratio of carbonfibre reinforced epoxy polymers

Table 6Cone calorimetrytest results of neat and fire-retardant carbon fibre reinforced

composite

Samples	R118 resin	(g) H120 h (g)	hardener BPC (g)	Number of CF layers	Final wt. (g)
CFR-EP	24	6	0	3	11.41
CFR-FREP-1	24	6	2	3	11.44
CFR-FREP-2	24	6	4	3	11.42
Samples	TTI (s)	Peak HRR (kW/m ²)	THR (MJ/m ²)	TSR (m ² /m ²)	TSP (m ²)
CFR-EP	21	1234.4	14.95	436.0	3.9
CFR-FREP-1	16	1129.0	17.99	341.2	3.6

14.19



876.4

Fig. 14 Heat release rate and smoke production rate of carbon fibre composites of neat epoxy, 8 wt % FR and 16 Wt% FR composite

in the composite. The neat EP composite released 436 m²/m² smoke, whilst the 8 wt% and 16 wt% BPC composites showed significant reduction in total smoke production with 341.2 m²/m² and 404.0 m²/m² respectively. A gradual minor decrease in the total smoke production (TSP) was observed in the FREP composites compared to the neat EP composite. The reduced smoke production is attributed to the presence of boron compound in the epoxy matrix [51]. The boron containing BPC was bonded to the epoxy matrix to prevent further ignition. The bonding was confirmed with FTIR analysis and char formation was confirmed with Raman spectroscopy. The heat release rate and smoke production rate of the composites are shown in Fig. 14.

CFR-FREP-2

11

Raman spectroscopy

Raman spectroscopy is generally adopted to investigate the order degree of carbonasious materials. Raman spectrum of burned and unburned DGEBA-1 was captured using a 514 nm edge laser beam. There were two distinctive peaks



404.0

3.0

Fig. 15 Raman spectrum of DGEBA-1 showing significant D and G band peaks

Fig. 16 Optical microscope images of **a** burned surface of neat DGEBA and **b** DGEBA-1 showing thick layer of char



at 1360 cm⁻¹ and 1595 cm⁻¹ from char section that linked to D and G bands as shown in (Fig. 15). The unburned DGEBA-1 did not have a peak. The D and G bands were attributed to the breathing and scattering of phonon [52, 53]. D band corresponds to breathing mode of k-point phonons A_{1g} symmetry and G band is the first order scattering of E_{2g} phonons [54]. Degree of graphitization is calculated from the ratio of integrated intensities of D and G band (ID/IG). The ratio of the relative peak intensity of the D band and G band is a measure of disorder degree and average size of the sp^2 domains in graphite materials [55]. A lower ID/IG value indicated higher degree of graphitization. The ID/IG value of DGEBA-1 exhibited a lower value of 0.96 from Raman spectral data whereas neat DGEBA value was higher (4.2, according to the literature) [56, 57]. This indicated higher degree of graphitization for DGEBA-1. This was attributed to the early thermal degradation and char formation on the epoxy surface due to the enhanced thermal conductivity. More char was formed with graphitisation structure triggered by boron compounds.

Optical microscope

Figure 16a, b were the optical microscope images of char layer from the neat DGEBA and DGEBA-1. The surface of the char layer was unstable and uneven and porous for neat DGEBA, whereas images of DGEBA-1 confirmed nonporous, continuous thick layer of char.

Conclusion

An intrinsically modified fire retardant epoxy system was synthesized using boron polyol complex (BPC), blended with DGEBA epoxy resin. Intermolecular hydrogen bonding between BPC complex and DGEBA was confirmed by FTIR spectrum analysis. The thermal conductivity of the epoxy resin was improved by enhanced phonon transport through hydrogen bonding. D and G bands of Raman spectrum confirmed breathing and scattering of phonons in the char of the epoxy BPC blend with high degree of graphitization. Thermogravimetric analysis results confirmed an increase of over 20% char formation in condensed phase. Formation of char in early stage of combustion below 400 °C was confirmed by 5 wt% decomposition temperature data analysis. Improved thermal stability of the blend was attributed to the higher char yield and presence of noncombustible inorganic boron compounds. The char protected underlying DGEBA epoxy from further burning. Improved thermal conductivity and presence of boron in DGEBA promoted early thermal degradation and char formation. A blowing out effect and self-extinguishing property during ignition was caused by the formation and quick emission of pyrolytic gases in condensed phase. This was also attributed to the thick layer of char beneath which the gases accumulate and was verified by optical microscope images. Cone calorimetry testing proved reduced peak heat release rate and smoke production with the increased addition of BPC complex. The UL-94 vertical burning tests confirmed that a 20 phr blend of BPC with the epoxy achieve V-1 rating and 40 phr blend achieve V-0 rating. Ultimately, the fire-retardant thermoset preserved its size and shape after 80 s of complete combustion that involved multiple self-extinguishing events.

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Data availability The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

Declarations

Conflicts of interest There are no Conflicts of interests/Competing interests to declare.

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