



Effect of Phosphorus-Nitrogen based Flame-Retardant Combined with Zinc Borate on Thermal Stability and Flame Retardancy of Epoxy Clay Nanocomposites

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A phosphorus-nitrogen containing 6,6'-(piperazine-1,4-diyl)bis(6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-oxide) (DOPO-PZ) flame-retardant was synthesized and its effect combined with zinc borate (ZnB) and nanoclay (NC) on thermal stability and flame retardancy of epoxy resin was studied. Various epoxy composites containing DOPO, DOPO-PZ, ZnB and NC using curing agent diaminodiphenylsulfone (DDS) were prepared. The X-ray diffraction (XRD) and transmission electron microscope (TEM) micrographs of the composites showed intercalated nanostructure of epoxy-clay nanocomposites. In thermogravimetric analysis (TGA), pure epoxy gave 3.4% char yield at 700 °C in nitrogen atmosphere, while in case of EP/DOPO-PZ/ZnB/NC sample having 1% phosphorus content, 5 wt.% zinc borate (ZnB) and 3 wt.% nanoclay (NC), the char yield is increased to 24.0%. Differential scanning calorimetry (DSC) study showed decrease in the glass transition temperature (T_g) on the addition of flame-retardant due to plasticization effect and increase in T_g on addition of nanoclay due to formation of nanostructure of epoxy composites. The EP/DOPO-PZ/ZnB/NC nanocomposite sample exhibited a limiting oxygen index (LOI) value of 29.2% and passed the UL-94 test with a V-0 rating and thus achieved a sufficient flame retardancy.

Keywords: Epoxy resin, Nanoclay, Nanocomposite, Flame retardancy, Thermal stability.

INTRODUCTION

In polymer industry, composite materials represent one of the most promising fields. Polymers, in the form of composites, have a lot of applications in numerous areas. Epoxy resin is an extremely versatile and comprehensive high-performing thermoset accessible and used as encapsulating stuff in electrical and electronic instrument production and modern composite matrices for structural overlay owing to their excessive strength, excellent chemical resistance and low-cost [1-5]. Its low thermal conductivity and high degradability at high temperature limits its application in aerospace in which electronic devices produce a huge amount of heat energy [6-8]. There are also some other demerits of epoxy resin, such as brittleness, high coefficient of thermal expansion and high flammability, which limits its application in transportation, composite structural and furnishing elements [9,10]. So, there is scope for the improvement in the thermal stability and flame retardant properties of epoxy material.

Halogen-based compounds are used as flame retardants in epoxy resin. However, due to the excretion of toxic gas and

environmental concerns, these are not commonly favoured [11]. Epoxy matrices doped with an inorganic filler such as boron, antimony trioxide, aluminum hydroxide and silicon exhibit better flame-retardant properties by enhancing the ignition time and decreasing the amount of total heat released. However, these fillers are needed in large amounts producing difficulty in processing and limiting their use. Recently, phosphorus and nitrogen-based compounds have been used as fruitful flame retardants [12-20]. Huo *et al.* [21] synthesized phosphorus-containing imidazole derivative and implied it as a curing agent for epoxy resin and recorded a V-0 rating with an LOI value of 37.20%. Wu *et al.* [22] also prepared a curing agent with nitrogen and phosphorus for epoxy resin and recorded an LOI value of 49 % with a V-0 rating in the UL-94 test. Doping a little amount of phosphorus enhanced the flame retarding effects of epoxy resin by increasing the char yield and LOI value [23]. Recently, nanocomposites of nanoclay mainly montmorillonite (MMT) and fluorohectorite are formed. The literature survey revealed that the mixing of nanoclay improved the thermal properties of epoxy resin by producing char which reduces the

transit of flammable gases from the composite array that works as continuous fuel for the fire. However, it has been generally seen that the addition of clay alone is not sufficient for flame retardancy [24,25]. The present work focuses on enhancing the thermal stability and fire safety of epoxy composites by using 6,6'-(piperazine-1,4-diyl)bis(6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-oxide) (DOPO-PZ) flame retardant and zinc borate (ZnB) and nanoclay (NC) as additives.

EXPERIMENTAL

Diglycidyl ether of bisphenol A (DGEBA), 4,4'-diamino diphenyl sulfone (DDS) and Nanomer[®] 1.31PS nanoclay (NC) were obtained from Sigma-Aldrich, India. TCI Chemicals, India supplied 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). Piperazine and zinc borate was bought from Himedia Laboratories Pvt. Ltd., India. A DOPO derivative (DOPO-PZ) was prepared in the laboratory. The Gurgaon Giant Sales Corporation supplied the mould-releasing medium.

Synthesis of DOPO-PZ: 6,6'-(Piperazine-1,4-diyl)bis(6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-oxide) (DOPO-PZ) compound as flame-retardant was synthesized according to the Atherton-Todd reaction [26] by dissolving DOPO (56.16 g, 0.26 mol), piperazine (11.19 g, 0.13 mol) and triethylamine (39.02 mL, 0.28 mol) in dichloromethane and followed by a dropwise addition of carbon tetrachloride (27.08 mL, 0.28 mol) at 0 °C with continued stirring overnight. The white precipitates of DOPO-PZ was filtered and then washed with water and acetone. After that the DOPO-PZ was dried in a vacuum oven (**Scheme-I**).

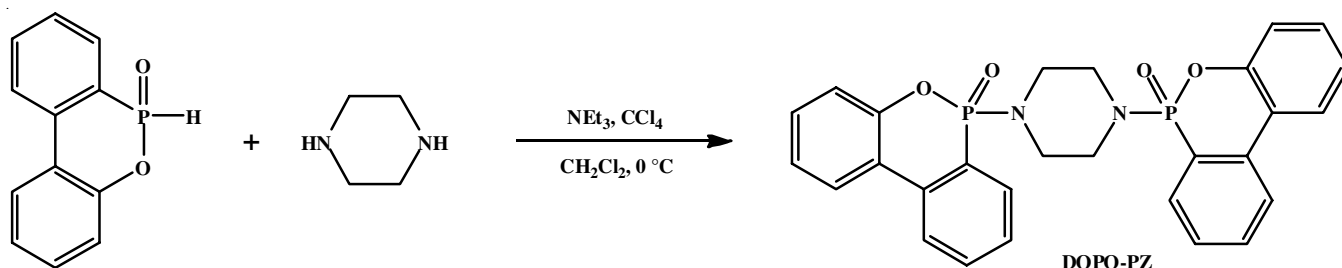
Preparation of epoxy-clay composites. The nanoclay was dried thoroughly in a vacuum oven. The various epoxy composites were prepared by adding a suitable quantity of DOPO/DOPO-PZ/ZnB/NC substances in epoxy resin using curing agent. The composition of the prepared samples is given in Table-1. The mixture was heated at 120 °C with constant stirring until it became homogenous. Then curing agent DDS

was mixed and stirred till it turned uniform. At last, the blend was poured into a mould which was pre-heated at 100 °C. Air bubbles were removed using a vacuum oven a 120 °C for 0.5 h. The samples were pre-cured for 12 h in a vacuum oven at 130 °C and then post-cured at 150 °C and 180 °C for 2 h each in a hot air oven.

Characterization: FTIR spectrophotometer (Perkin-Elmer Spectrum, BX II) was used to record the spectra of samples fused with KBr powder ranging between 4000-400 cm⁻¹. Bruker AVANCE III instrument was operated on frequencies of 400 MHz and 101 MHz to record ¹H and ¹³C NMR of DOPO-PZ in deuterated chloroform (CDCl₃). The XRD analysis (Philips Powder XRD-SXRD) operating on CuKα radiation (1.54 Å) ranging between 3 to 30° to determine the extent of clay dispersion and d-spacing between clay layers in epoxy nanocomposites was performed. The nanoclay dispersion (intercalation or exfoliation) in epoxy matrix was determined by using a high-resolution transmission electron microscope (JEOL JEM 2100 plus) operating at 200 kV. The surface micrographs of composites and char residues left after limiting oxygen index (LOI) tests after coating with gold were obtained using a high resolution field emission scanning electron microscope (7610F Plus/JEOL).

Thermal analysis: Thermogravimetry analysis (TGA) of epoxy composite samples was carried out by operating a simultaneous TGA-DSC (TA Instruments Q-600SDT) under 100 mL/min flow of N₂ from room temperature to 700 °C at 10 °C/min heating rate. The glass transition temperature (T_g) of epoxy composite samples was determined using a DSC (DSC2-00347) device from room temperature to 250 °C in an N₂ environment at heating rate of 10 °C/min.

Flammability tests: UL-94 vertical test as per ASTM D-3801 standard (sample dimension 130.0 mm × 13.0 mm × 3.0 mm) was used to study the burning behaviour of samples and rating of samples was done as V-0, V-1, V-2 and NR (no rating). LOI test as per ASTM D 2863 standard (sample size 130.0 mm × 65.0 mm × 3.0 mm) was used to determine the LOI value.



Scheme-I: Synthesis of DOPO-PZ

TABLE-1
COMPOSITIONS OF EP COMPOSITES

Sample	DGEBA (g)	DDS (g)	DOPO (g)	DOPO-PZ (g)	NC (g)	ZnB (g)
EP	36.87	13.12	0.00	0.00	0.00	0.00
EP/DOPO	33.08	11.70	5.22	0.00	0.00	0.00
EP/DOPO-PZ	33.81	12.03	0.00	4.15	0.00	0.00
EP/DOPO-PZ/NC	32.70	11.64	0.00	4.15	1.50	0.00
EP/DOPO-PZ/ZnB/NC	30.86	10.98	0.00	4.15	1.50	2.50

RESULTS AND DISCUSSION

NMR studies: ^1H NMR spectrum of DOPO-PZ (Fig. 1a) was observed in CDCl_3 using tetramethylsilane as an internal standard. The peak at δ 3.26 ppm (8H) is of aliphatic protons. The peak due to aromatic protons was observed in the region 7.26-8.05 ppm. The ^{13}C NMR spectrum of DOPO-PZ (Fig. 1b) was carried in CDCl_3 using tetramethylsilane as an internal standard. This compound gives a peak at δ 44.02 ppm due to aliphatic C and a peak at 149.06 ppm is due to C attached to oxygen. The remaining aromatic carbon gives peaks in region 120.45 to 137.73 ppm.

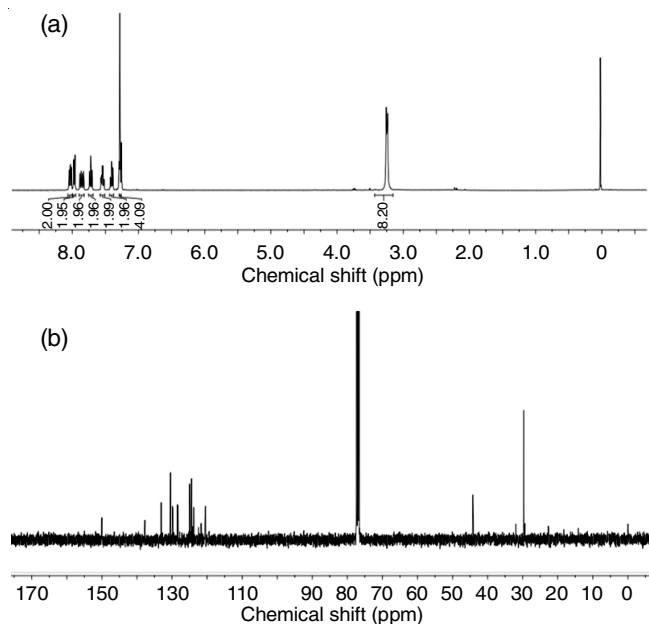


Fig. 1. ^1H NMR (a) and ^{13}C NMR (b) spectra of DOPO-PZ

FTIR studies: The FTIR spectrum of DOPO-PZ was recorded using KBr pellets in the range of 4000-400 cm^{-1} . The absorption band due to P-N stretching vibration is observed at 1108 cm^{-1} , which indicated the formation of compound. Absorption bands due to P-Ph (1594, 1475), P=O (1221 cm^{-1}) and P-O-Ph (925, 755 cm^{-1}) were also observed.

XRD studies: The dispersion of nanoclay in epoxy composites was studied by X-ray diffraction method. The XRD spectra of epoxy composite and nanoclay are depicted in Fig. 2. The Bragg's law ($d = n\lambda/2\sin\theta$) was used to determine the interlayer

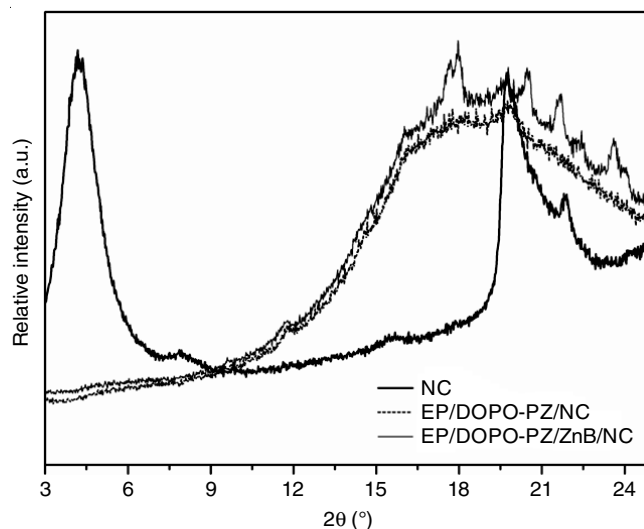


Fig. 2. XRD spectra of nanoclay (NC), EP/DOPO-PZ/NC and EP/DOPO-PZ/ZnB/NC

distance of nanoclay in the 2θ range of 3-30°. The characteristic nanoclay diffraction peak was obtained at $2\theta = 4.20^\circ$ ($d_{001} = 2.10$ nm). This characteristic peak disappeared in EP/DOPO-PZ/NC and EP/DOPO-PZ/ZnB/NC samples. This indicates that the characteristic peak was shifted below $2\theta = 3^\circ$, indicating the intercalation or exfoliation of nanoclay in composites, which was on the far side of the operated XRD instrument. Hence, the dispersion of nanoclay in the epoxy (EP) composites matrix was determined with the help of TEM.

TEM studies: Dispersion of nanoclay in EP/DOPO-PZ/NC and EP/DOPO-PZ/ZnB/NC composites was investigated by conducting an accelerated voltage of 200 kV. NC layers were represented by dark lines as obtained in Fig. 3. Stacks of silicate layers can be seen in the TEM micrograph of nanoclay as shown in Fig. 3a, while the TEM micrograph (Fig. 3b-c) of EP/DOPO-PZ/NC and EP/DOPO-PZ/ZnB/NC showed the intercalation indicating dispersion of nanoclay in the epoxy matrix.

Thermal studies: To study the thermal degradation and stability of epoxy samples, TGA was conducted in an N_2 environment. The TGA and DTG curves are illustrated in Fig. 4. The temperature of 10% mass loss (TGA curves, $T_{10\%}$) defined as onset temperature, the temperature at which degradation took place with the maximum weight loss rate (DTG peak, T_{max}), the char yields at 700 $^\circ\text{C}$ and the glass transition temperatures (T_g) of samples (DSC curves, Fig. 5) are listed in Table-2. It

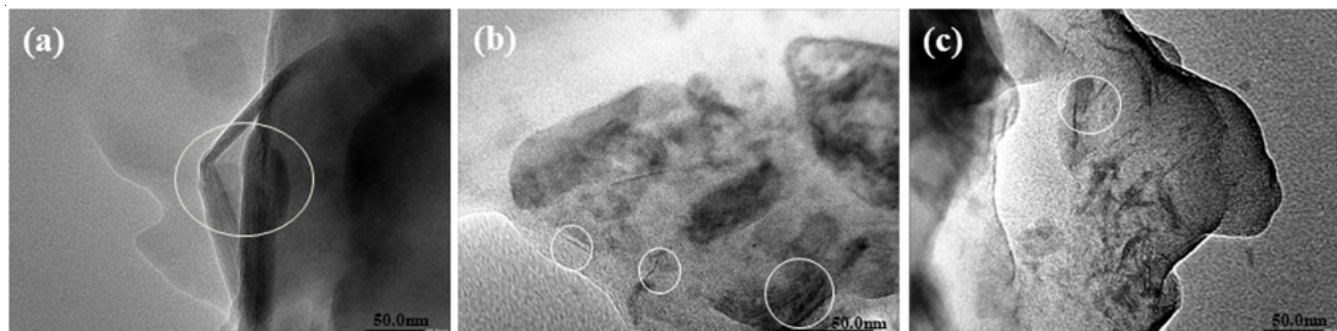


Fig. 3. TEM micrographs of (a) NC, (b) EP/DOPO-PZ/NC and (c) EP/DOPO-PZ/ZnB/NC samples

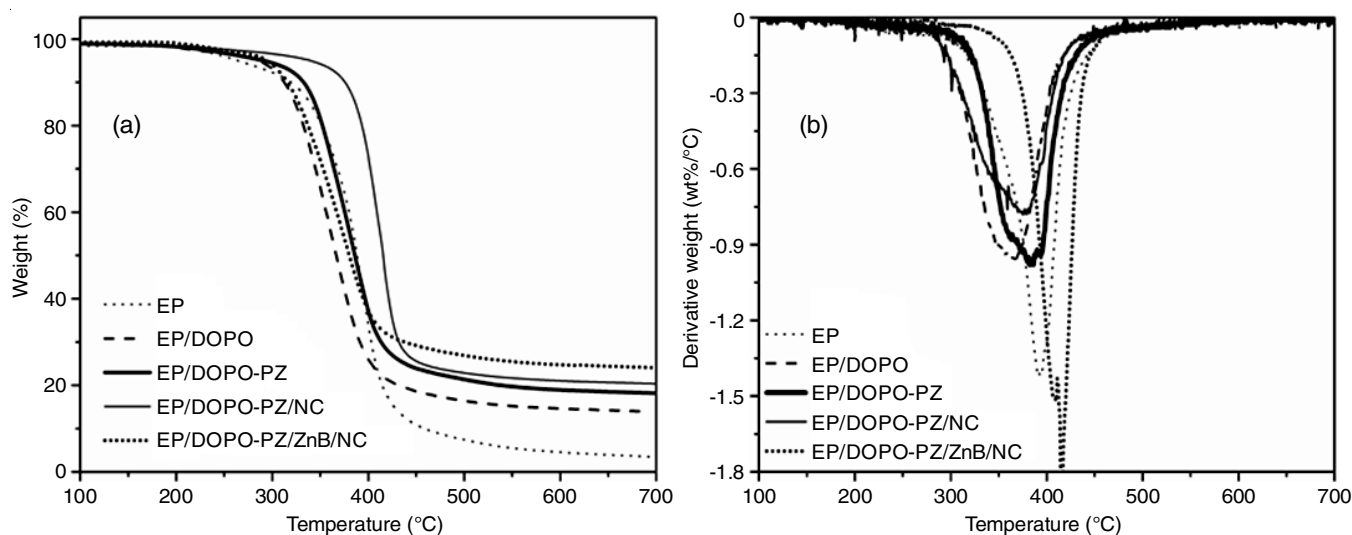


Fig. 4. TGA (a) and DTG (b) curves of EP composites in N₂ atmosphere

was observed that the epoxy composites showed single-stage thermal degradation behaviour. The epoxy undergoes a slow weight loss (10%) up to 319 °C. This weight loss is due to some dehydration and removal of low molecular weight pendant epoxy chains. About 83% weight loss of epoxy in the temperature range of 300 °C to 500 °C occurred due to chain cleavage and fracturing of epoxy resin. The single stage of thermal degradation is also observed in epoxy composites containing flame retardant and additives. However, epoxy composites containing zinc borate (ZnB) and nanoclay start to degrade slightly earlier due to the catalytic effect of ZnB and nanoclay [27] except the EP/DOPO-PZ/NC nanocomposite. The EP/DOPO-PZ/NC nanocomposite shows high thermal stability with 43 °C increase in onset temperature of degradation (Table-2) compared to EP/DOPO-PZ due to formation of good intercalated nanostructure of composite as seen in TEM study (Fig. 3b). Thus, the flame retardant DOPO-PZ and nanoclay showed a strong synergistic effect to increase thermal stability. The addition of flame retardants alone reduced T_{max} as seen from DTG curves. Fig. 4b shows that the addition of nanoclay and ZnB increased the thermal stability of the epoxy composites compared to pure epoxy. In thermogravimetric analysis (TGA), pure epoxy gave 3.4% char yield at 700 °C in N₂ atmosphere, while in case of EP/DOPO-PZ/ZnB/NC sample having 1% P content, 5 wt.% zinc borate (ZnB) and 3 wt.% nanoclay (NC) the char yield is increased to 24%. The presence of ZnB increased the char yield due to formation of glassy layer of on the substrate and making the condensed phase process prominent by stopping the escape

of volatile products. The 18.10% char residue at 700 °C of EP/DOPO-PZ without containing ZnB and nanoclay is observed, which is also significantly higher than that of epoxy. Thus an increase in char residue indicating flame retardant action is due to the char-forming action of phosphorus-based flame retardant (DOPO-PZ) and thermally stable nanoclay and ZnB.

Glass transition temperature (T_g): The glass transition temperature (T_g) of samples was measured from DSC thermograms, which are shown in Table-2. Pure epoxy revealed T_g at 189 °C, which is decreased to 147 °C on addition of reactive flame retardant DOPO for EP/DOPO composite having 1% P content (Fig. 5). This decrease is due to plasticization effect of DOPO [28] by decreasing cross-link density. In case of EP/DOPO-PZ sample, the T_g value is decreased to 168 °C due to bulky DOPO units present in DOPO-PZ. The EP/DOPO-PZ/NC nanocomposite showed a slight decrease in T_g at 180 °C compared to epoxy (189 °C) because nanocomposite structure formation has compensated the plasticization effect of DOPO-PZ flame-retardant.

SEM studies: Fig. 6a indicates that the surfaces of epoxy composites is smooth. This means the composition of epoxy

Sample	$T_{10\%}$ (°C)	T_{max} (°C)	T_g (°C)	Char at 700 °C (wt%)
EP	319	392	189	3.4
EP/DOPO	312	363	147	13.8
EP/DOPO-PZ	332	381	168	18.1
EP/DOPO-PZ/NC	375	397	180	20.3
EP/DOPO-PZ/ZnB/NC	315	415	174	24.0

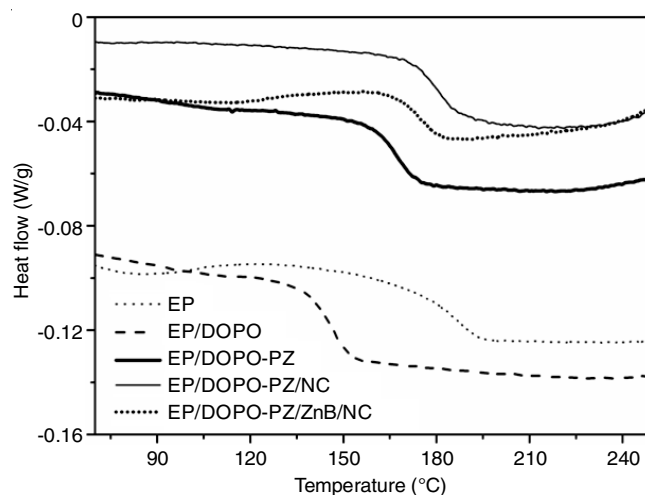


Fig. 5. DSC curves of EP composites in N₂ atmosphere

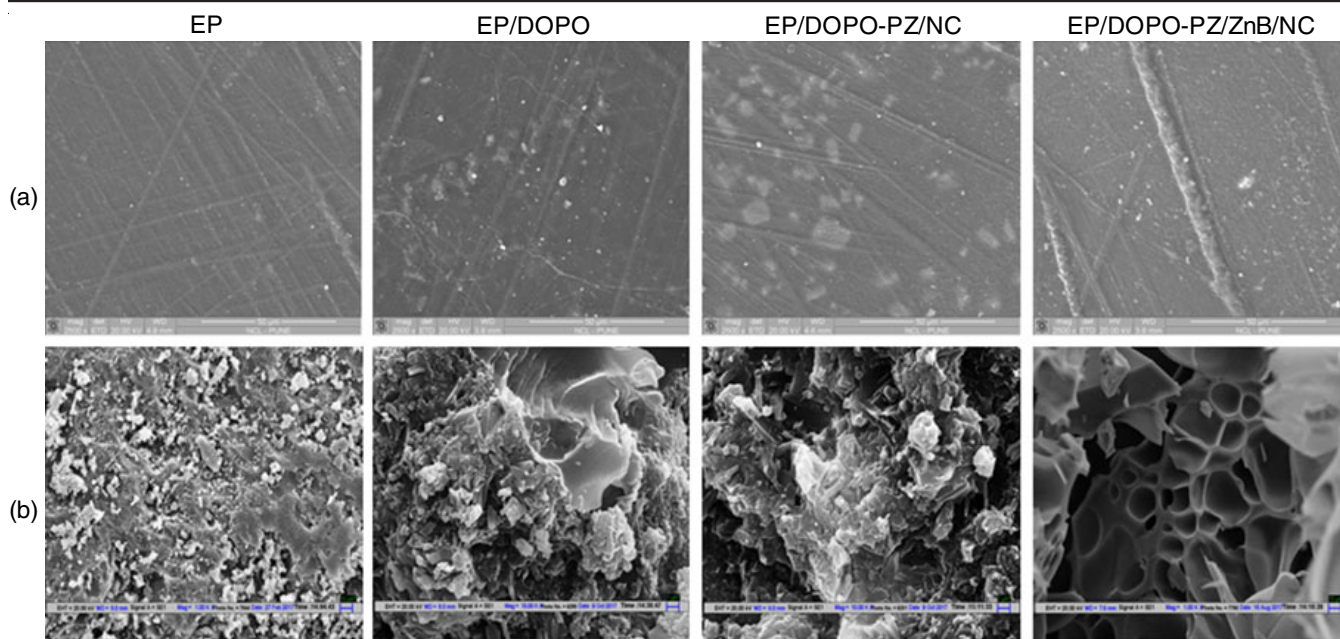


Fig. 6. SEM images of (a) surface of EP composites and (b) inner surface chars of EP composites

composites was uniform. Fig. 6b shows the interior of char of epoxy composites, which showed a honeycomb-like structure due to trapping of volatile products formed on heating. The honeycomb-like structure and glassy layer of char helps to prevent the transfer of heat and flame to the underlying material, thereby enhancing the flame-retardant properties.

Flammability studies: The flame-retardant nature of epoxy composites was assessed by UL-94 vertical combustion and LOI tests. The resulting data is listed in Table-3. Neat epoxy is extremely flammable with an LOI value of 18.2%; and also no rating in the UL-94 test is observed. The LOI value and UL-94 rating of EP/DOPO were observed as 21.6% and V-1, respectively. The LOI value was increased to 25.4% for the EP/DOPO-PZ sample with a V-1 rating in the UL-94 test. With the addition of nanoclay, the LOI value for EP/DOPO-PZ/NC nanocomposite was further increased up to 27.5% along with a V-0 rating due to formation of nanostructure of composite. The addition of ZnB further upgraded the LOI value (Table-3) of EP/DOPO-PZ/ZnB/NC nanocomposite sample to 29.2%.

TABLE-3
LOI AND UL-94 DATA OF EP COMPOSITES

Sample	LOI (%)	UL-94 rating	Dripping
EP	18.2	NR	Yes
EP/DOPO	21.6	V-1	No
EP/DOPO-PZ	25.4	V-1	No
EP/DOPO-PZ/NC	27.5	V-0	No
EP/DOPO-PZ/ZnB/NC	29.2	V-0	No

Conclusion

By reacting phosphaphenanthrene and piperazine, 6,6'-(piperazine-1,4-diyl)bis(6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-oxide) (DOPO-PZ) flame-retardant was prepared and further studied its effect in combination with zinc borate (ZnB) and nanoclay (NC) on thermal and flame retardancy behaviour of

epoxy matrix by forming epoxy-clay nanocomposites. The differential scanning calorimetry study showed a decrease in the glass transition temperature (T_g) on the addition of flame-retardant due to plasticization effect and increase in T_g on addition of nanoclay due to formation of nanostructure of epoxy composites. The LOI and UL-94 flame retardancy tests established that the epoxy-clay nanocomposite (EP/DOPO-PZ/ZnB/NC) having DOPO-PZ with 1% phosphorus, 5 wt.% ZnB and 3 wt.% nanoclay in epoxy matrix giving the 29.2% LOI value and V-0 rating in the UL-94 tests is a sufficient flame-retarded epoxy material.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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