PROMOTION EFFECT OF MELAMINE ON FLAME RETARDANCY OF EPOXY RESINS CONTAINING CAGED BICYCLIC PHOSPHATE*

Jing-ping Hu, Dao Li, Yan Qin and Xing-yi Wang**
Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science & Technology, Shanghai 200237, China

Abstract Caged bicyclic phosphate (CBP) and its dimelamine salt (PDS) were synthesized and added to epoxy resins to obtain the flame retarded epoxy resin composites. The flammability of the composites was characterized by the limiting oxygen index (LOI) and cone calorimeter tests. The LOI values of flame retarded composites increase consistently with the increase of flame retardant amounts, and they are almost the same when the loading of CBP is the same as that of PDS, although the phosphorus content of PDS is much lower than that of CBP. The total heat release increases in the order of CBP30/ER < PDS30/ER < PDS15/ER < CBP15/ER, whereas that of specific extinction area is CBP15/ER > CBP30/ER > PDS30/ER ≅ PDS15/ER. PDS exhibits more effective inhibition of oxidation of combustible gases. In the tests of thermogravimetric analyses (TG) and Fourier transform infrared spectroscopy (FT-IR), it is found that the degradation of the composites is influenced greatly by the addition of flame retardants. By scanning electron microscopy (SEM), a thick and tight char-layer is observed for PDS30/ER, resulting from the interaction of nitrogen species with phosphorus species. Therefore, the combination of CBP with melamine in the flame retarded system can improve the flame retardancy greatly.

Keywords: Flame retardancy; Thermal degradation; Melamine; Caged bicyclic phosphate; Epoxy resin.

INTRODUCTION

Epoxy resins are used widely as adhesives, sealing compounds, casting resins and as the resin matrix in reinforced composites[1]. However, the poor flame resistance of epoxy resins limits their usage in special adhesives and coatings, advanced composites in aerospace and electronic industries[2]. A practical approach to improve the flame resistance is the incorporation of flame retardant (FR) in epoxy resins. Most flame retardants commercially used are inorganic compounds or halogen-based organic compounds, nevertheless, which can give rise to toxic and corrosive gases and smoke during burning[3]. For this reason, intumescent flame retardants (IFR)[4-9] are playing a significant role. The key of the flame retardancy of IFR is the formation of an expanded char layer, which acts as a thermal insulation shield for reducing heat transfer from fire to polymer and as a physical barrier hindering the diffusion of volatiles toward fire and that of oxygen toward polymer[10-12].

Because phosphorus-containing flame retardants tend to react with OH groups at fire-exposure temperatures, they are particularly effective in epoxy resins which have high concentrations of OH groups. Flame retardancy can be obtained with phosphorus-containing curing agents[13]. Reactive phosphorus-containing epoxy monomers are reported frequently in the technical literature with special attention to the use of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) and its derivatives[14].

1-Oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane (PEPA) and its derivatives are effective intumescent flame retardants in polymers. Li et al.[15] introduced PEPA into epoxy resins and found

---

that PEPA acted not only as a curing agent and intumescent flame retardant but also as a smoke inhibitor. Halpen *et al.*[16] synthesized melabis and revealed that it is efficient in flame retarded polypropylene and has less adverse effect on the physical properties. Allen[17] prepared a series of ester derivatives of PEPA, which were thermally stable at polymer processing temperatures and showed excellent intumescent properties.

In the previous work, the attention has been paid to the amount of phosphorus needed to achieve a certain flame retardant level[14, 18]. However, the effect of the ratio of phosphorus to nitrogen compounds such as melamine, which releases uninflammable gases such as NH_3, H_2O and CO_2 that dilute oxygen and reduce temperature in the flame zone, has not been studied in detail. On the other hand, the effect of melamine on the formation of expanded char-layer in epoxy resins has not been taken into account.

In the present work, two kinds of caged bicycle phosphate of PEPA derivatives as flame retardants were synthesized and combined with epoxy resins. The obtained flame retarded composites were studied using limiting oxygen index (LOI), TG, cone calorimeter (CONE), FT-IR, SEM and energy dispersive spectrometry (EDS), and the effect of melamine in the flame retardant system was discussed.

EXPERIMENTAL

Synthesis of Flame Retardants

Pentaerythritol, purchased from Hunan Hengyang Chemical Plant, was purified from diluted HCl solutions before use. Phosphorus oxychloride, obtained from Shanghai Lingfeng Chemical Limited Company, was distilled under atmospheric pressure and the distillate between 102°C and 104°C was collected for synthesis. Acetonitrile was dried by $CaCl_2$, and ethylenediamine (EDA) was used directly without any purification.

PEPA was prepared from pentaerythritol and phosphorus oxychloride according to the reported literature[16]. (1-Oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane) phosphate dimelamine salt (PDS) was synthesized as follows: to a three-necked round-bottom flask equipped with a mechanical stirrer, reflux condenser and addition funnel, 5 mL (0.05 mol) of phosphorus oxychloride and 60 mL of acetonitrile were added. 9 g (0.05 mol) of PEPA was added in batches. The resulting slurry was stirred and heated to 50°C for 3 h under nitrogen and then refluxed for 4 h. Solvent and by-product (HCl) were removed by distillation to leave a sticky yellow fluid. After cooling, 50 mL deionized water, 12.6 g melamine and 13 mL pyridine were added and heated to reflux for 16 h. The reaction mixture was allowed to cool to room temperature, whereupon solid was precipitated and filtered. The white solid was washed with water until no chloride ion was detected and dried to a constant weight. The yield was 56% (12.5 g), M.P. > 300°C. IR analysis: The strong peaks between 3400 cm^{-1} and 3100 cm^{-1} denote the existence of amine salts and $-NH_2$, the vibration absorption peaks at 1531 and 1380 cm^{-1} reveal the presence of triazine rings and NH^+, respectively. The absorption peak at 1690 cm^{-1} belongs to the stretch vibration of C=N, the bands at 1323 cm^{-1} (P=O), 1029 cm^{-1} (P−O−C) and 821 cm^{-1} (−CH_2) are due to the bicyclic structures.

PEPA

CBP

PDS
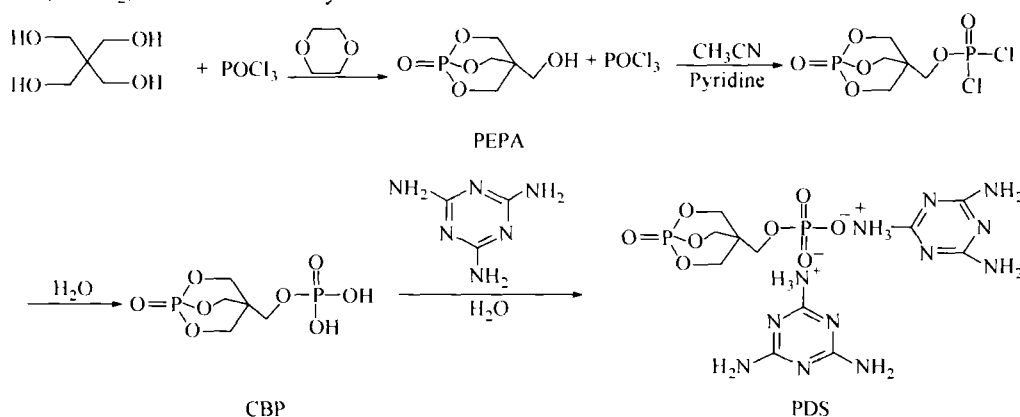
Scheme 1 PDS synthesis route

To obtain (1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo [2,2,2]octane) phosphoric acid (CBP), (1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane) phosphorus oxychloride was hydrolyzed directly (Scheme 1).

Preparation of Flame-Retardant Epoxy Resins

Epoxy resin E-51 (equivalent weight: 0.49 mol/100 g) was obtained from Shanghai Reagent Factory and the curing agent ethylenediamine (EDA) was A.R. Grade. The flame-retardant composites were manufactured by mixing the flame retardant and EDA with the epoxy resin (ER) at room temperature. After vigorous agitation, the mixtures were poured into aluminum molds, cured at room temperature for 24 h and then at 80°C for 2 h. The unfilled epoxy resin was prepared as reference. The formulations are given in Table 1.

Table 1. The composition and LOI values of flame retarded composites

Samples	Epoxy	EDA	CBP (wt%)	PDS (wt%)	P content (wt%)	LOI (%)	UL-94
ER (epoxy resin)	100	10	0	0	0	20	–
CBP15/ER	100	10	15	0	3.69	26	V-1
CBP20/ER	100	10	20	0	4.92	32	V-0
CBP25/ER	100	10	25	0	6.15	32	V-0
CBP30/ER	100	10	30	0	7.38	35	V-0
PDS15/ER	100	10	0	15	1.84	28	–
PDS20/ER	100	10	0	20	2.46	30	V-0
PDS25/ER	100	10	0	25	3.08	33	V-0
PDS30/ER	100	10	0	30	3.69	36	V-0

Characterization

Limiting oxygen index (LOI) analyses were carried out in a Stanton Redcroft instrument with samples measuring 100 mm × 6.5 mm × 3 mm, following the procedure described in the ISO 4589-2 standard.

Thermogravimetric analyses (TG) were performed by a TGA-2050 thermogravimetric analyzer at a heating rate of 10 K/min under nitrogen atmosphere. The mass of each sample was 5–10 mg, and the TG curves were recorded in the course of heating from room temperature to 750°C and were used to determine the percentage weight loss.

Cone calorimeter (CONE) tests were performed according to the ASTM 1356-90 standard. Each specimen of 100 mm × 100 mm × 3 mm dimensions was wrapped in aluminum foil and exposed horizontally to an external heat flux of 50 kW/m^2.

Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet NEXUS 470 spectrophotometer. Powder resins and combustion residues were studied in KBr discs.

The char residues of epoxy resins after the complete combustion were observed with a JSM-6360LV scanning electron microscope (SEM), using 15 kV and 60 mA electric current. The energy dispersive spectrometry (EDS) was conducted by scanning electron microscope acting on samples to get character X-ray energy, which confirms the sample's micro-region component.

RESULTS AND DISCUSSION

Flame Retardancy

Table 1 lists the compositions of the flame retarded material and their LOI values and UL-94 levels. The LOI of pure epoxy resin is only 20% and increased greatly with the addition of CBP and PDS, consistently with the increase of flame retardant loadings. When the content of CBP is the same as that of PDS, the LOI values of the corresponding samples are almost the same. With a 20% loading of flame retardant, LOI values of the composites can reach 30%, whereas they are as high as 35% or 36% with 30% loading of flame retardants. The epoxy resins added with 20% or more loading of flame retardants meet UL-94 V-0. It must be pointed out that the phosphorus content for PDS20/ER is 2.46 wt%, much lower than that of CBP20/ER, 4.92 wt%. Epoxy resins

containing DOPO with phosphorus contents of 3%[19] achieve the same flame retardant level as PDS20/ER. On the other hand, the flame retarded composites with CBP can't reach the same flame retardancy as those with PDS having the same phosphorus content (such as CBP15/ER and PDS30/ER).

Combustion Behavior

Cone calorimetry is one of the most effective bench-scale methods for studying the flammability properties of materials. Heat release rate (HRR) and total heat release (THR) are the most important parameters to evaluate fire safety[20]. Figure 1 presents the HRR and THR curves of the pure and flame retarded epoxy resins, respectively. The data from cone calorimeter tests are summarized in Table 2. From Fig. 1(a), it can be seen that the pure epoxy resin burns very fast after ignition at a heat flux of 50 kW/m². A sharp HRR peak appears at the maximum heat release rate of 1381 kW/m², and THR reaches 114 kJ/m² within 250 s (shown in Fig. 1b). For the four flame retarded composites, the peak HRR values decrease greatly, depending on the amount and composition of FR. They are 786 and 421 kW/m² for composites with 15% and 30% of CBP, respectively, and are 587 kW/m² and 592 kW/m² for composites with 15% and 30% of PDS respectively. Two or three HRR peaks appear in these composites due to the collapse of charred structure leading to the liberation of trapped volatiles, as reported previously[21]. The THR shown in Fig. 1(b) increases in the order of CBP30/ER < PDS30/ER < PDS15/ER < CBP15/ER < ER, and the value of ER is much higher. The heat released resulted from combustion of ER is decreased to a large extent by the combination with CBP or PDS. CBP30/ER produces the lowest heat due to its highest phosphorus content.
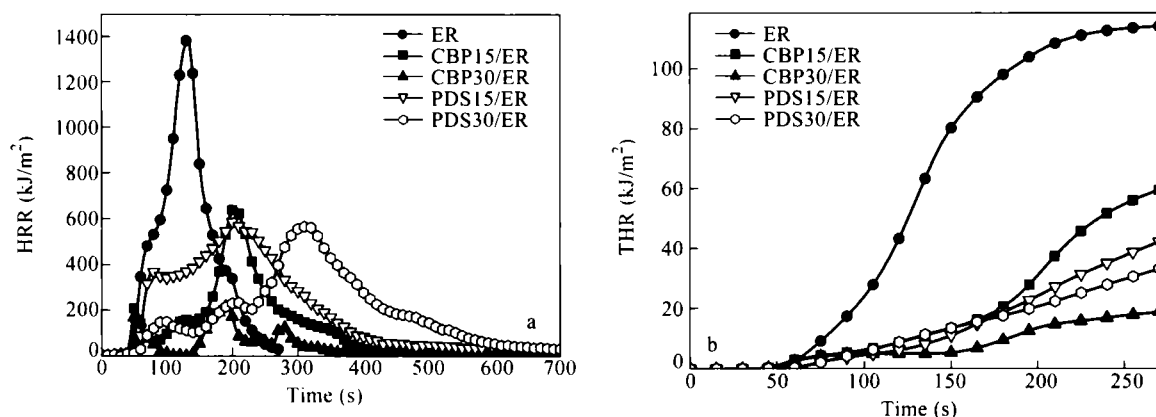

Fig. 1 HRR (a) and THR (b) curves of ER, CBP15/ER, CBP30/ER, PDS15/ER and PDS30/ER

Table 2. The cone calorimeter data of the pure and flame retarded epoxy resins

Samples	Peak HRR (kW/m²)	Average EHC (MJ/kg)	Average SEA (m²/kg)	Peak-SPR (m²/s)	Flameout (s)
ER	1381	31.7	656	0.41	289
CBP15/ER	786	35.3	521	0.33	345
CBP30/ER	421	33.8	403	0.25	553
PDS15/ER	587	31.60	390	0.21	581
PDS30/ER	592	30.74	358	0.21	761

On the other hand, the average specific extinction area (SEA) results indicate that the value for pure epoxy resin is 656 m²/kg, 25%, 60%, 68% and 84% larger than that of CBP15/ER, CBP30/ER, PDS15/ER and PDS30/ER, respectively, in line with the results of smoke production rate (SPR). This effect of melamine on the SEA of flame retarded epoxy resins with caged bicyclic phosphate has not been reported previously in literature. Levchik *et al.*[22] showed that the fire retardant effectiveness of phosphorus-containing compounds went through

a maximum with increasing phosphorus concentration, and it was attributed to the competition between the char-forming fire retardant action and evolution of combustible gases because of the catalysis of the degradation of epoxy. Here, during heating, melamine-containing PDS decomposes and then releases incombustible gas such as NH_3 to barrier or dilute oxygen, retarding combustion. PDS exhibits more effective inhibition of oxidation of combustible gases. So, it takes a longer time for PDS flame retarded epoxy resins to reach the flameout. PDS of low phosphorus content has a high flame retardancy through this synergistic effect between phosphorus species and melamine.

The average effective heat of combustion (EHC) values of pure epoxy resin almost are not affected by the addition of the two flame retardants. By combining these results with the HRR values, it can be deduced that CBP promotes the formation of charred layers in the condensed phase, and melamine can inhibit the oxidation of combustible gases.

Thermal Analysis

Figure 2 shows the thermal decomposition of the flame retarded composites by TG. From Fig. 2(a) it is found that the initial decomposition temperature (the temperature where the weight loss exhibits 5 wt%[23]) of CBP is about 205°C, and the major thermal degradation occurs in the temperature range of 205–280°C. No weight loss is observed after 400°C, and the yield of residue is about 9.0 wt%. The pure epoxy resin begins to degrade at 320°C. The decomposition of epoxy resin is promoted greatly by the addition of CBP. With the increase of CBP content the thermostability of materials decreases, and the 10 wt% weight loss temperature of CBP30/ER is 50 K lower than that of CBP10/ER, indicating that CBP speeds up the degradation of epoxy resin, and the high loading level causes the contribution to remarkably affect the thermal behavior. Shau and Wang[24] found that phosphorus-containing epoxy resins showed higher LOI than non-phosphorus-containing resins, however the decomposition temperature of phosphorus-containing polymers was somewhat lower. Phosphoric acid species were formed upon thermal decomposition, which may catalyze dehydration of the resins at lower temperature. On the other hand, the char residues of flame retarded composites are increased to some extent.
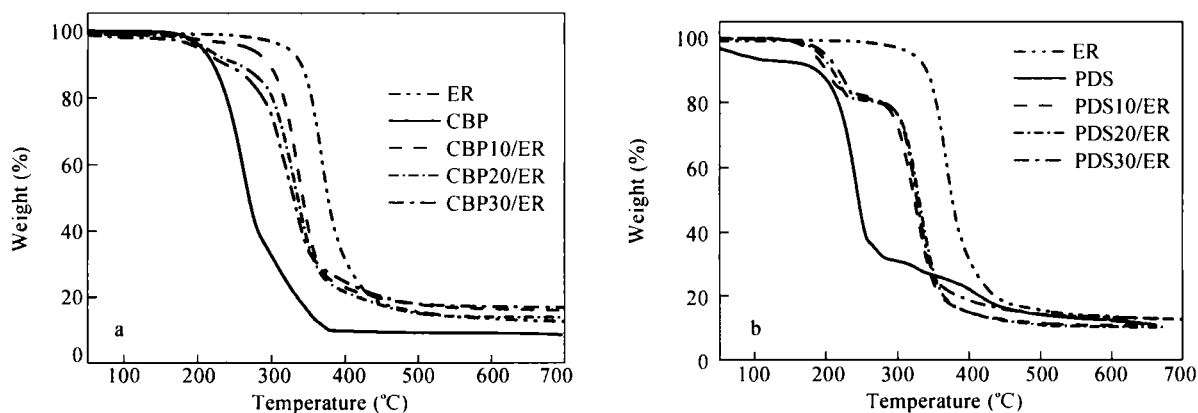

Fig. 2 TG curves of flame retarded materials with CBP (a) and PDS (b)

As can be seen in Fig. 2(b), PDS has two degradation stages, and its initial decomposition temperature is around 182°C, approximately 20 K lower than that of CBP, indicating that the presence of melamine induces difference in decomposition behavior. The main weight loss in PDS degradation takes place in the first stage of temperature range in 182–260°C, corresponding a weight loss of 61.8 wt% due to the removal of most of nitrogen species and water. The second stage of PDS degradation is between 300°C and 600°C. It should be noted that the existence of melamine delays the further decomposition of the remaining to higher temperatures and increases the yield of char residue at 700°C from 9 wt% to 11 wt%. This may be attributed to the formation of viscous semi-solid P, N-containing substance. When PDS is added to epoxy resin, the thermal stability of the

material is strongly modified, and two degradation stages are also presented, which would be related with the overlapping of the decomposition process of PDS and the degradation of ER. The first degradation stage starts at 180°C, in accordance with the decomposition temperature of PDS, and is assigned to the decomposition of melamine. The latter weight loss is attributed to the degradation of hydrocarbon chains[25] between 300°C and 400°C. The TG curves are similar among these three materials with PDS, which may be caused by the preferential degradation of melamine of PDS. However, the yields of char residue for epoxy resins with PDS are lower than those with CBP, which is not consistent with the conclusions of LOI. Therefore, it is concluded that the quantity of char is not the major element in flame retardancy.

FT-IR Study of the Degradation Process

The thermal degradation of CBP30/ER and PDS30/ER were investigated by FT-IR at different temperatures (see Fig. 3). At 25°C FT-IR spectra confirm the integrated CBP structure in ER: the absorptions at 2963 cm^{-1} and 858 cm^{-1} are attributed to the stretching vibration of C−H. The bands at 1305 cm^{-1} and 1253 cm^{-1} are assigned to the stretching vibration of P=O in bicyclic and ester, respectively. The presence of the 1033 cm^{-1} peak is attributed to P−O−C. At temperatures up to 260°C, the peak at 1305 cm^{-1} (P=O in bicyclic) disappears, while the band at 1607 cm^{-1} (P−O−H) increases, and new bands at 1716 cm^{-1} (POH of O=P−OH dimmer) and 1080 cm^{-1} (P − O − P) appear, which indicate the breakage of bicyclic structure and the formation of phosphorous acid and polyphosphoric acid. Since the decomposition of epoxy resin could be promoted by the acid catalysis, the thermal degradation of the composites shifts to a lower temperature (see Fig. 2a). With the further increase in degradation temperature, the relative intensity of the absorption peaks continues to decrease. The bands at 3439 cm^{-1} and 1629 cm^{-1} corresponding to the adsorbed moisture on char layer surface occur at 400°C, and the bands at 1253 cm^{-1} (P=O in ester) and 1080 cm^{-1}(P−O−P) remain with weak strength, suggesting phosphorus species such as phosphorate ester and polyphosphoric acid exist in the structure of residue.
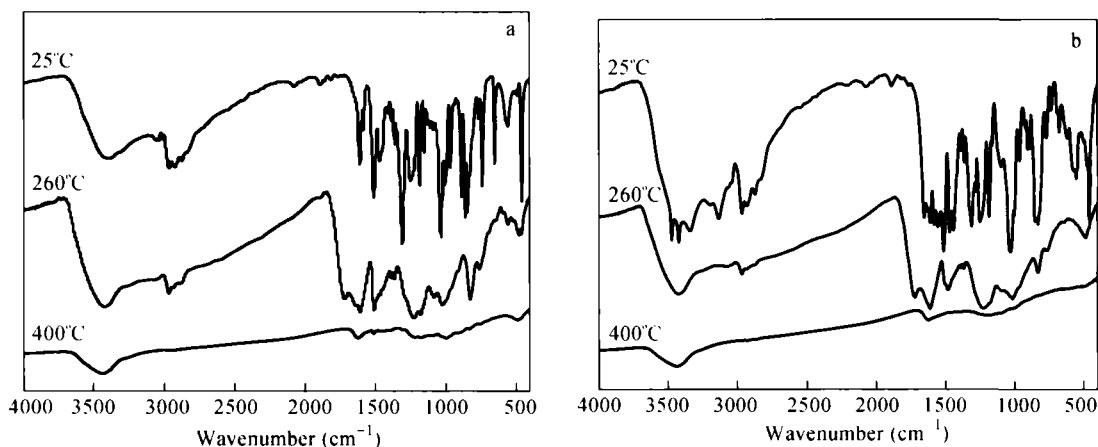

Fig. 3 FT-IR spectra of CBP30/ER (a) and PDS30/ER (b) treated at different temperatures

According to the FT-IR spectra shown in Fig. 3(b), the bands at 3134 cm^{-1} (N−H), 1654 cm^{-1} (C=N), 1608 cm^{-1} (P−O−H), 1554 cm^{-1} (triazine ring), 1392 cm^{-1} (NH$^+$), 1304 cm^{-1} (P=O), 1248 cm^{-1} (P=O) and 1023 cm^{-1} (P − O − C) are observed, which proves that PDS is combined in ER. The disappearances of 3134 cm^{-1} and 1554 cm^{-1} bands at 260°C are believed to be caused by the decomposition of melamine and verify that the first degradation stage of PDS and flame retarded composites with PDS is caused by the breakdown of melamine. At 400°C the spectra of PDS30/ER are the same as those of CBP30/ER, which shows that the structures of residues of the two flame retarded composites are similar to each other.

Combustion Residues of Flame-Retardant Epoxy Resins

Figure 4 presents the SEM pictures obtained on the residues of ER, CBP30/ER and PDS30/ER. The residue surface of ER consists of shaggy pellets, and swollen char layers are generated on the char-layer surfaces of CBP30/ER and PDS30/ER, which insulate the underlying polymer matrix from the oxygen source and slow down the heat release as a physical barrier. The pores in char layer exhibit the impact of released volatiles and heat on the protective layer during the degradation of the composite, in accordance with the HRR curves. It is worth noting that residue char of CBP30/ER is layers of folium, whereas that of PDS30/ER is thick and tight. Since the most important factors of the foamed char are thickness and density[26], the char of PDS30/ER could insulate the heat transfer and volatile diffusion more effectively, which result in its high flame retardancy with low phosphorus content.
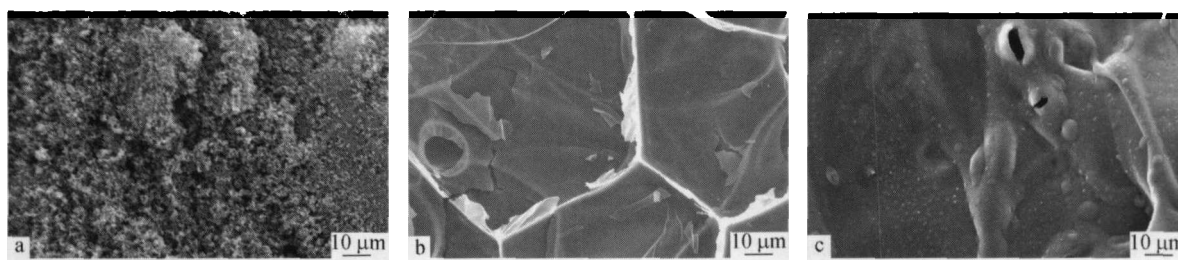

Fig. 4 SEM of charred residues of ER (a), CBP30/ER (b) and PDS30/ER (c)

EDS was carried out to analyze the components of the char of CBP30/ER and PDS30/ER, and the results are shown Table 3. There remains a considerable amount of oxygen and phosphorus in the residue of both CBP30/ER and PDS30/ER samples, which is comprised of phosphorus species such as polyphosphoric acid seen in Fig. 3. The low phosphorus content in char layer of CBP30/ER suggests that a great deal of volatile phosphorus is produced during degradation and acts as catalytic radical scavenger. In the char layer of PDS30/ER, there exists nitrogen element besides phosphorus, of which the amount is almost the same as that of CBP30/ER char. This indicates that the interaction between melamine and phosphoric acid results in the formation of viscous semi-solid P, N-containing substance, leading to the thick and tight char-layer. Therefore, it is due to the existence of melamine, better flame-retarding bulwark appears, and higher LOI is shown when phosphorus content is greatly reduced in the flame retarded composites containing PDS.

Table 3. Residue components of CBP30/ER and PDS30/ER

Element	CBP30/ER residue component		PDS30/ER residue component	
	(wt%)	(atom%)	(wt%)	(atom%)
C	74.46	82.96	69.76	78.71
N	0	0	3.46	3.35
O	12.38	10.35	15.19	12.87
P	10.83	4.68	11.59	5.07

CONCLUSIONS

The addition of caged bicyclic phosphate derivatives to epoxy resin could increase the flammability resistance of epoxy resin. The LOI values of the composites containing CBP are all close to that of the composites containing PDS at the same additive level of flame retardants. The LOI value of the epoxy composites increases consistently with increasing the loading of CBP. At 20% flame retardant content the LOI value reaches 32%. The maximum HRR peaks of flame retarded composites are dramatically delayed and lowered, which shows the high flame retardant effectiveness for CBP. And the composites with 20% PDS, containing 2.46% phosphorus,

has a similar flame retardancy. The average SEA of the PDS containing epoxy resin is much lower than that of the CBP containing epoxy resin. From TG data it can be seen that CBP and PDS speed up the degradation of epoxy resin. The decomposition of melamine induces the release of uninflammable gases that enhance the flammability resistance. The flame retardancy of CBP30/ER is attributed not only to the insulation effect of char, but also the volatile phosphorus produced during degradation acting as a catalytic radical scavenger. The superior performance of PDS30/ER is ascribed to its thick and tight char-layer formed by the interaction between melamine and phosphoric acid. Therefore, the addition of melamine in the flame retarded system could improve the flame retardancy greatly.

REFERENCES

1   Potter, W.G., "Uses of Epoxy Resins", Newnes-Buterworths, London, 1975, p.1

2   Deng, J. and Shi, W.F., J. Eur. Polym., 2004, 40: 1137

3   Zhu, S.W. and Shi, W.F., Polym. Int., 2004, 53: 266

4   Reshetnikov, I., Antonov, A., Rudakova, T., Aleksjuk, G. and Khalturinskij, N., Polym. Degrad. & Stab., 1996, 54: 137

5   Lewin, M., Polym. Degrad. & Stab., 2005, 88: 13

6   Chiu, S.H. and Wang, W.K., Polymer, 1998, 39: 1951

7   Bourbigot, S., Le Bras, M. and Delobel, R., Carbon, 1995, 33: 283

8   Kahraman, M.V., Kayaman-Apohan, N., Arsu, N. and Gungor, A., Progress in Organic Coatings, 2004, 51: 213

9   Wu, Q. and Qu, B.J., Chinese Journal of Polymer Science, 2002, 20(4): 377

10 Liu, W.C., Varley, R.J. and Simon, G.P., J. Appl. Polym. Sci., 2004, 92: 2003

11 Christophe, D., Sophie, D., Le Bras, M., Jérôme, L., René, D., Andrea, C., Carole, M. and Moïse, V., J. Appl. Polym. Sci., 2004, 94: 717

12 Xie, R.C., Qu, B.J. and Hu, K.L., Polym. Degrad. & Stab., 2001, 72: 313

13 Wang, Q.F. and Shi, W.F., Polym. Degrad. & Stab., 2006, 91: 1747

14 Levchik, S., Piotrowski, A., Weil, E. and Yao, Q., Polym. Degrad. & Stab., 2005, 88: 57

15 Li, X., Ou, Y.X. and Shi, Y.S., Polym. Degrad. & Stab., 2002, 77: 383

16 Halpern, Y., Mott, M. and Niswander, R.H., Ind. Eng. Chem. Prod. Res. Dev.,1984, 23: 233

17 Allen, D.W., Anderton, E.C. and Christopher, B., Polym. Degrad. & Stab., 1995, 47: 67

18 Toldy, A., Tóth, N., Anna, P. and Marosi, G., Polym. Degrad. & Stab., 2006, 91: 585

19 Lengsfld, H., Altstadt, V., Sprenger, S. and Utz, R., Kunststoffe, 2001, 91: 37

20 Tang, Y., Hu, Y., Wang, S.F., Gui, Z. and Chen, Z.Y., Polym. Int., 2003, 52: 1396

21 Lv, P., Wang, Z.Z., Hu, K.L. and Fan, W.C., Polym. Degrad. & Stab., 2005, 90: 523

22 Levchik, S.V., Camino, G., Luda, M.P., Costa, L., Muller, G., Costes, B. and Henry, Y., Polym. Adv. Tech.1996, 7: 823

23 Liu, Y.L. and Chou, C.I., Polym. Degrad. & Stab., 2005, 90: 515

24 Shau, M.D. and Wang, T.S., J. Polym. Sci. Part A: Polym. Chem., 1996, 34: 387

25 Chuang, T., Wenjeng, G., Cheng, K.C., Chen, S.W., Wang, H.T. and Yen, Y., J. Mater. Res., 2004, 11: 169

26 Bertelli, G., Camino, G., Marchetti, E., Costa, L., Casorati, E. and Locatelli, R., Polym. Degrad. & Stab., 1989, 25: 277