Polyamide-Enhanced Flame Retardancy of Ammonium Polyphosphate on Epoxy Resin

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ABSTRACT: An attractive intumescent flame retardant epoxy system was prepared from epoxy resin (diglycidyl ether of bisphenol A), low molecular weight polyamide (cure agent, LWPA), and ammonium polyphosphate (APP). The cured epoxy resin was served as carbonization agent as well as blowing agent itself in the intumescent flame retardant formulation. Flammability and thermal stability of the cured epoxy resins with different contents of APP and LWPA were investigated by limited oxygen index (LOI), UL-94 test, and thermogravimetric analysis (TGA). The results of LOI and UL-94 indicate that APP can improve the flame retardancy of LWPA-cured epoxy resins. Only 5 wt % of APP can increase the LOI value of epoxy resins from 19.6 to 27.1, and improve the UL-94 ratings, reaching V-0 rating from no rating when the mass ratio of epoxy resin to LWPA is 100/40. It is much interesting that LOI values of flame retardant cured epoxy resins (FR-CEP) increase with decreasing LWPA. The results of TGA, FTIR, and X-ray photoelectron spectroscopy (XPS) indicate that the process of thermal degradation of FR-CEP consists of two main stages: the first stage is that a phosphorus rich char is formed on the surface of the material under 500°C, and then a compact char yields over 500°C; the second stage is that the char residue layer can give more effective protection for the materials than the char formed at the first stage do. The flame retardant mechanism also has been discussed according to the results of TGA, FTIR, and XPS for FR-CEP. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2644–2653, 2008

Key words: ammonium polyphosphate; epoxy resin; intumescence; flame retardance

INTRODUCTION

Epoxy resins are widely used in laminating, adhesive, coating, and casting applications because of their many attractive properties such as dimensional stability, satisfactory mechanical properties, suitable weather, chemical and thermal resistance. Diglycidyl ether of bisphenol A (DGEBA) is one of the most important current epoxy resins, whose structure is shown in Scheme 1.[1] However, its lack of flame retardancy is the major problem in applications where high thermal stability and flame retardant are needed. The flame retardancy of epoxy resins can be improved by the introduction of flame retardant elements such as halogen and phosphorus into epoxy resins or curing agents.[2] Halogen-containing compounds are reported to be effective flame retardants for various epoxy resins. For example, diglycidyl ether of tetrabromobisphenol A has been used for imparting flame retardancy to commercial laminates. However, these systems containing halogen generate dense toxic smoke and corrosive products during combustion.[3–5] Therefore, the preparation of halogen-free flame retardants is the subject of extensive investigations. A number of compounds for flame retardant materials are reported including epoxy monomers,[6–8] cure agents,[9–13] and additives,[14–16] which are halogen-free.

Intumescent flame retardant additives have aroused a great deal of attention in the flame retardant for epoxy resins.[4,17–22] Generally, three kinds of components are incorporated into formulations to obtain intumescent flame retardancy: (1) an acid source which is inorganic salt or inorganic acid ester such as ammonium polyphosphate (APP); (2) a carbonization agent which is polyhydric compound currently such as pentaerythritol; (3) a blowing agent which can bring noncombustible gas in air such as melamine. The mechanism of intumescent flame retardant is usually described as follows: first, the acid source breaks down to produce an inorganic acid under heat, then it takes part in the dehydration of the carbonization agent to yield the char, meanwhile the blowing agent decomposes to yield gaseous products which can not flame in air. The gas causes the char to swell and finally an insulating multicellular protective layer yields over the surface of the material. This shield limits the heat transfer from the heat source to the substrate and the mass trans-
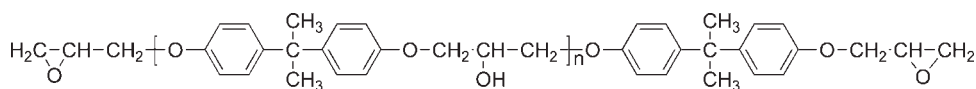
Scheme 1 The structure of diglycidyl ether of bisphenol A.

fer from the substrate to the heat source resulting in a conservation of the underlying material.[4,19,23] However, one of the major problem for intumescent flame retardants is that the loading of intumescent flame retardants are over 30 wt % to reach good effect currently.[19]

Intumescent flame retardants for epoxy resins are widely used as coatings,[20,21] and they can also use as additives for thermoplastics.[18] However, to the best of our knowledge, there is few reports about the content of cure agent effect on flammability of flame retardant cured epoxy resin. In this article, epoxy resins are cured by low molecular weight polyamide (LWPA) which has a larger range of dosage than other amines in applications. In the present work, our research focuses on the correlation between the effects of the content of LWPA and APP in epoxy resins. The thermal stability of the cured epoxy resins has been studied by thermogravimetric. The flame retardant mechanism of flame retardant cured epoxy resins (FR-CEP) also has been studied by thermogravimetric analysis (TGA), FTIR, and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

Diglycidyl ether of biphenol A (E-44) was provided by Wuxi Resin Factory of Xingchen New Chemical Material (Wuxi, China). LWPA was purchased from Haitian Chemical Reagent (Hunan, China). APP was supplied by Changfeng Chemical Corp. (Shifang, China).

Preparation of flame-retardant epoxy samples

The cured epoxy resins were obtained by thermal curing. The reactants (E-44, LWPA) were mixed in a certain (100/30, 100/35, 100/40, 100/45, and 100/50) equivalent ratio with epoxy resin. Then different contents (0, 5, 7.5, 10, 12.5, 15 wt %) of APP were added into the reactants, respectively, to form a series of mixtures with stirring. Finally, the mixtures were cured for 12 h at room temperature and for 5 h at 80°C, and then the solid products were obtained.

Characterization

The limited oxygen index (LOI) values were measured on a HC-2C oxygen index meter (Jiangning, China) with sheet dimensions of $130 \times 6.5 \times 3.2$ mm^3 according to ASTM D2863-97.

The vertical burning test (UL-94) of samples was conducted on a CZF-2 instrument (Jiangning, China) according to ASTM D 3801 testing procedure. The samples were made to a size of $125 \times 12.7 \times 3.2$ mm^3.

TGA was conducted on Q500 V6.4 Build 193 thermal analyzer at heating rate of 10°C/min. Samples were heated in the temperature range from room temperature to 700°C under air at a flow rate of 60 mL/min.

The FTIR spectra of residues of cured epoxy resins with or without APP at a series of temperatures in muffle were recorded with KBr powder by using a Nicolet FTIR 170SX infrared spectrophotometer.

XPS was recorded by a XSAM80, using Al Kα excitation radiation (hv = 1486.6 eV). Binding energies were referenced to the carbonaceous carbon at 284.6 eV.

Scanning electronic microscopy (SEM) observed on a JEOL JSM-5900LV was used to investigate the surface of residues of cured epoxy resin with or without APP. The residues of samples for SEM were obtained after combustion in their limiting oxygen

TABLE I
Flammability Tests of PCEP and FR-CEP with Different Contents of Cure Agent

Samples	E-44/LWPA (mass ratio)	Content of LWPA (wt %)	Content of APP (wt %)	LOI values (%)[a]	UL-94 rating	Drip
Sam 1	100/30	19.6	0	19.6	N.R.	Yes
Sam 2	100/40	24.3	0	19.6	N.R.	Yes
Sam 3	100/50	28.3	0	19.5	N.R.	Yes
Sam 4	100/30	19.6	15	32.0	V-0	No
Sam 5	100/35	22.0	15	31.2	V-0	No
Sam 6	100/40	24.3	15	30.2	V-0	No
Sam 7	100/45	26.4	15	29.7	V-0	No
Sam 8	100/50	28.3	15	29.6	V-0	No

[a] The uncertainty of measurement for LOIs is ±0.5.

Samples	Content of APP (wt %)	LOI Values (%)[a]	UL-94 rating	Drip
Sam 2	0	19.6	N.R.	Yes
Sam 9	5	27.1	V-0	No
Sam 10	7.5	27.7	V-0	No
Sam 11	12.5	28.9	V-0	No
Sam 6	15	30.2	V-0	No

[a] The uncertainty of measurement for LOIs is ±0.5.

concentration. SEM graphs of the samples were recorded after gold coating surface treatment.

RESULTS AND DISCUSSION

Flammability

The LOI values describe a procedure for measuring the minimum concentration of oxygen that will just support flaming combustion in a flowing mixture of oxygen and nitrogen. The UL-94 test is commonly used to determine the ignition resistance of materials. In this study, LWPA is chosen as a cure agent, which is environment friendly. Furthermore, it can be used in a larger range of dosage for epoxy resins than other cure agents. Table I presents the LOI values and UL-94 testing results which show the effect of the content of LWPA on flame retardancy of cured epoxy resins. We can observe that the LOI values of pure cured epoxy resins (PCEP) with different content of cure agent are very similar even the same, which indicates that the content of LWPA has no effect on the flame retardancy of pure cured epoxy resin in applications. However, the LOI values of FR-CEP containing 15 wt % APP increase from 29.6 to 32.0 with reducing the content of LWPA from 28.3 to 19.6 wt %, which shows that there is an optimal ratio between APP and LWPA. The LOI values rise by adding APP into the cured epoxy resins, about from 19.6 to 32.0. The UL-94 test results of FR-CEP systems are V-0 rating, while PCEP systems have no rating, and all the samples of FR-CEP generate no drip compared with the dripped PCEP samples.

Table II presents the LOI values and UL-94 testing results, which show the relationship between the flame retardancy and the content of APP for epoxy resin cured by 24.3 wt % LWPA. From Table II, when the content of LWPA was kept at the same value (24.3 wt %), it can be seen the LOI values of FR-CEP increase from 27.1 to 30.2 while the amount of APP increase from 5 to 15 wt %. It is very interesting that even when the content of APP is as low as 5 wt %, the samples of FR-CEP also could achieve V-0 rating during UL-94 test and all the samples of FR-CEP do not generate drip. The results of Table I and Table II indicate that the flame retardancy of cured epoxy resin could be improved by reducing the content of LWPA and adding APP.

Figure 1 shows the effect of APP on cured epoxy resin clearly. The residues of pure cured epoxy resin are only a few after combustion [Fig. 1(a)], And the flame retardant cured epoxy resin with 15 wt % APP remaining much more residues which are compact and intumescent char [Fig. 1(b)]. It suggests that a protective intumescent carbonaceous char was formed on the surface of the material as encountering fire.

Thermal stability

TGA measurements made in air reveal more real information relevant to the behavior of combustion,
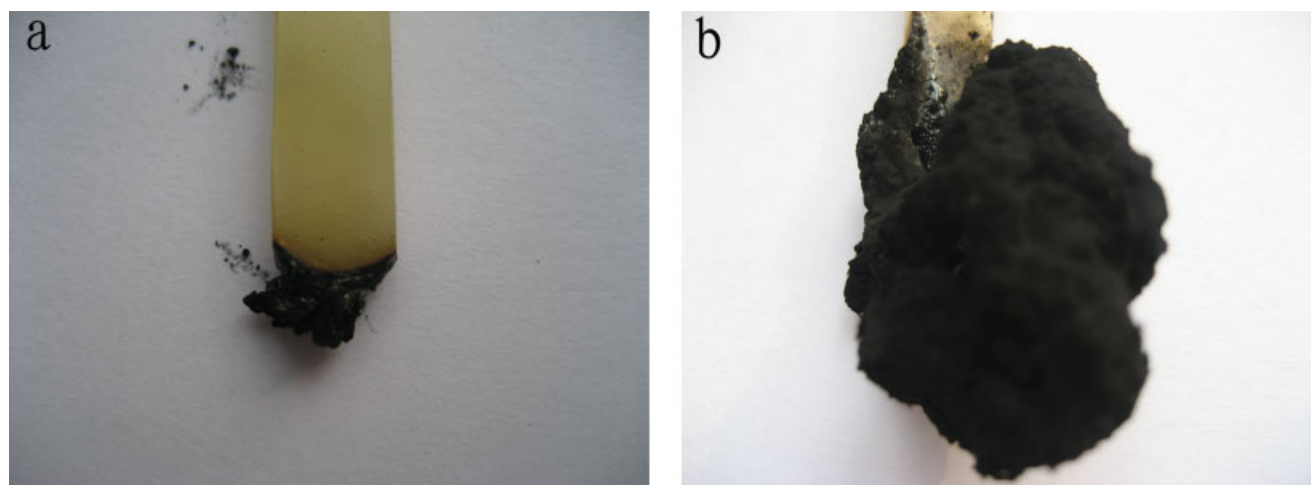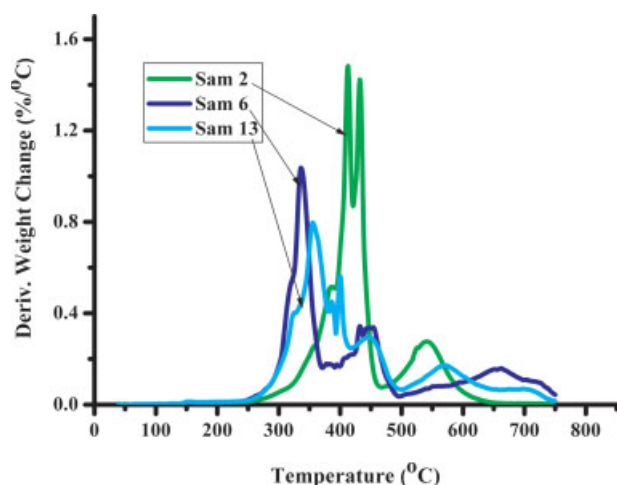

Figure 1 Pictures of residues of samples after LOI test PCEP (a), FR-CEP containing 15 wt % APP (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
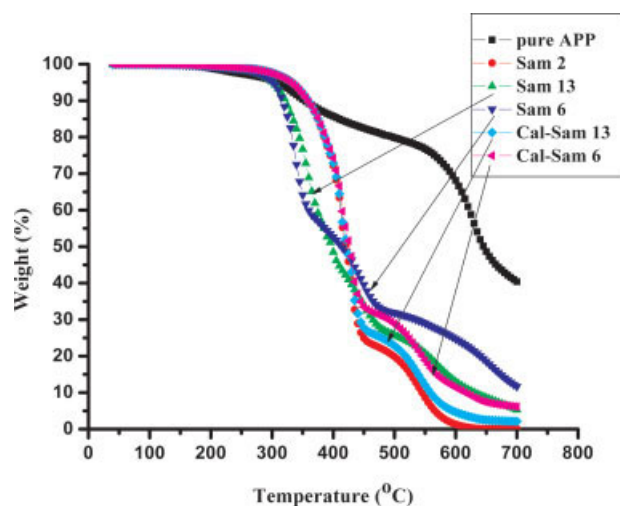
Figure 2 TGA thermographs of APP, PCEP, and FR-CEP containing different contents of APP. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

TABLE III
TGA Data for APP, PCEP, and FR-CEP

Samples	Content of LWPA (wt %)	Content of APP (wt %)	T_{onset}[a] (°C)	T^1_{max} (°C)	T^2_{max} (°C)	Char at 700°C (%)
APP	–	–	309	627	–	40.4
Sam 2	24.3	0	334	413	541	0.1
Sam 4	19.6	15	299	335	654	14.6
Sam 6	24.3	15	301	336	662	11.7
Sam 13	24.3	5	301	355	570	5.3
Cal-Sam 6	24.3	15	330	–	–	6.2
Cal-Sam 13	24.3	5	332	–	–	2.1

[a] T_{onset} is the temperature of 5% weight loss.

and serve as useful indicators of polymer flammability. Figures 2 and 3 show the TGA and DTG thermograms of pure cured epoxy resin and flame retardant epoxy resins. The calculated TGA curves for FR-CEP (Sam 6 and Sam 13) are given in the Figure 2. We get the mass weight of FR-CEP for calculated TGA curves as follows: mass weight of pure APP × content of APP + mass weight of cured epoxy resin × content of cured epoxy resin. The comparison between real curves and the calculated curves of Sam 6 shows a significantly decrease in thermal stability at the temperature range from 300 to 420°C, but a clear increase in thermal stability over 500°C. It suggests that there were reactions between APP and cured epoxy resin (CEP) and there might be two important thermal degradation stages. From Figure 3
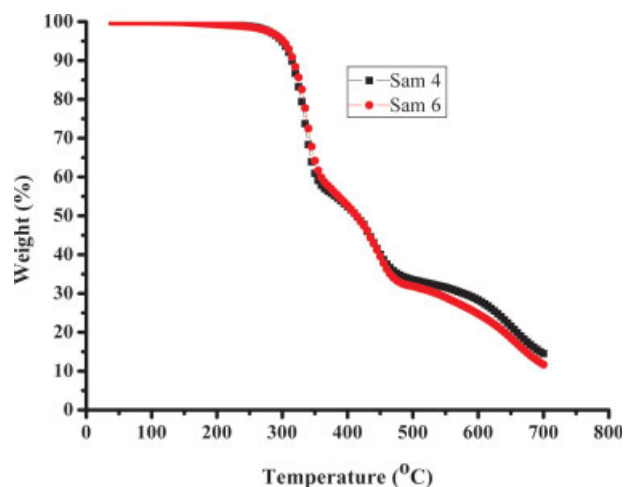
we can observe a stronger peak at temperature ranging from 250 to 500°C (the first stage of thermal degradation) and the other stronger peak at the temperature from 500 to 700°C (the second stage of thermal degradation), which are considered as T^1_{max} and T^2_{max}. From Figure 3 and Table III we can get the information that T^1_{max} of FR-CEP are 335, 336, and 355°C, which are lower than that of PCEP (413°C), and T^1_{max} of FR-CEP decrease with increasing APP. However, T^2_{max} of FR-CEP are higher than that of PCEP (541°C), and increase from 570 to 662°C with decreasing APP. It indicates that the addition of APP in cured epoxy resin decreases the thermal stability of FR-CEP at the first stage and increases the thermal stability at the second stage. Therefore, the thermal degradation of FR-CEP may take place as follows: at the first stage APP interacts with CEP leading to produce volatile compounds and form a phosphorus rich layer, which could protect the polymer matrix under heat, and then the protective layer would decompose to yield a compact char on the

Figure 3 DTG curves of PCEP and FR-CEP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]


Figure 4 TGA thermographs of flame retardant cured epoxy resin with 19.6 wt % LWPA and 24.3 wt % LWPA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
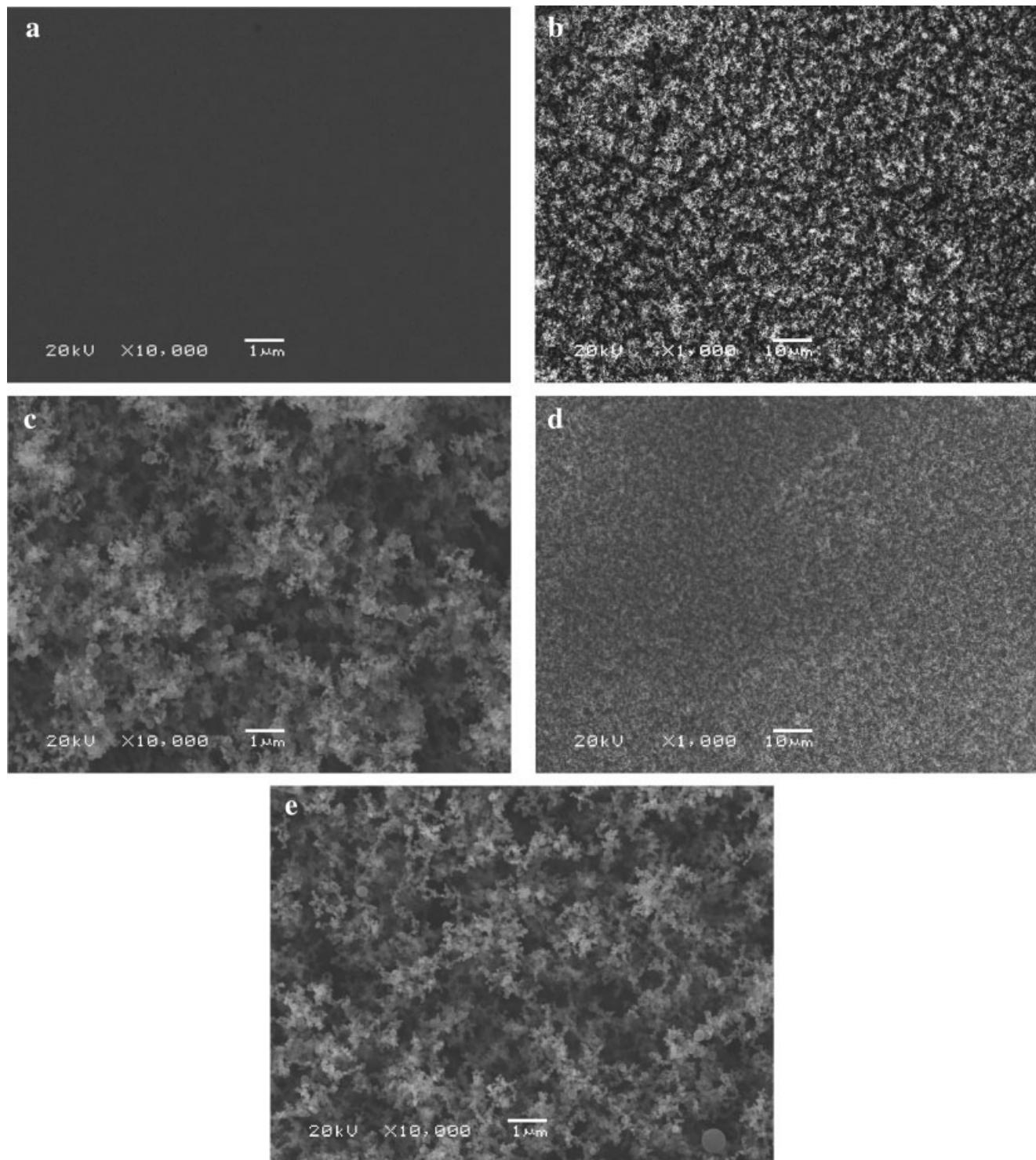
Figure 5 SEM for residues of samples, PCEP (a), outer surface (b, c), and inner surface (d, e) of residue of FR-CEP containing 15 wt % APP.

surface of the material to protect the polymer matrix effectively at the second stage. TGA thermograms of FR-CEP with different content of cure agent are illustrated in Figure 4. The curves of two samples is extra similar; however, the weight loss of Sam 6 is a little larger than that of Sam 4 from 500°C to 700°C.

The brief information of TGA results are given in Table III. The onset degradation temperature (T_{onset}) of FR-CEP are around 300°C, which are lower than that of PCEP and pure APP, and the difference of T_{onset} of FR-CEP (299 and 301°C) is very small, which is due to the addition of APP. In other words, the
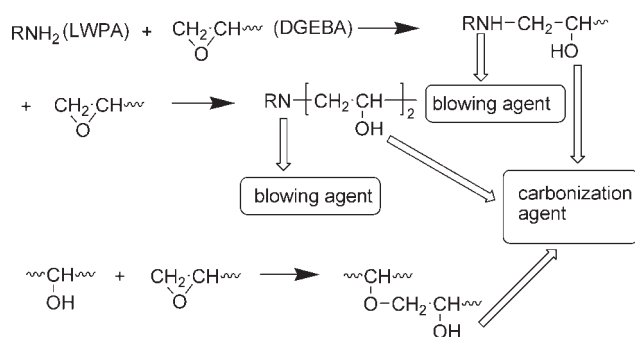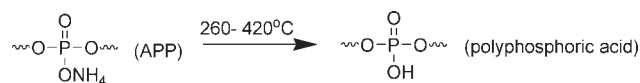
Scheme 2   The reactions of epoxy resins cured by LWPA.

Scheme 3   The thermal degradation of APP under 420°C.

addition of APP in cured epoxy resin decreases the thermal stability of FR-CEP.

It is known that the flame retardant properties of materials can be forecasted from the char yields at high temperature.[24–26] From Table III we can see that the char of FR-CEP at 700°C are 14.6%, 11.7%, and 5.3%, which are higher than that of PCEP (0.1%) at 700°C, and the order of the char of FR-CEP are as follows: Sam 4 > Sam 6 > Sam 13, which agrees with the order of the results of LOI values for these samples. We also can get the information that the char of Sam 6 is much more than that of Cal-Sam 6 at 700°C and the similar current appears in comparison between the Sam 13 and Cal-Sam 13, which suggests that there are chemical reactions between APP and cured epoxy resin.

Morphologies of the residues

The morphologies of the residues of pure cured epoxy resin and flame retardant cured epoxy resin containing 15 wt % APP after LOI testing were examined by SEM to investigate the microstructure of the char; the results are presented in Figure 5. It can be observed that nearly nothing remains on the surface of the residues from Figure 5(a). However lacunaris and compact charred layers can be found from Fig-

ure 5(c,e), which can form protective shields on the surface of materials to protect matrix effectively by limiting the heat transfer from the heat source to the substrate and flammable compounds transfer from the substrate. Compact char can be seen in Figure 5(b) and multicellular-like char would be seen after further blowup in Figure 5(c), the same phenomena could be seen in Figure 5(d,e). There are few differences between the outer surface and inner surface as shown in Figure 5(b–e). However, lacunaris and compact char-like crumb can be seen in Figure 5(c,e), which indicates that an effective char yielded either outer surface or inner surface of the residues. Therefore, FR-CEP exhibit good flame retardancy after adding APP, which agrees with the results of TGA, LOI, and UL-94 testing.

Flame retardant mechanism of APP in cured epoxy resins

As we all know, an integrated intumescent flame retardant system must contain three parts: acid source, carbonization agent, and blowing agent. Epoxy resin cured by LWPA has a high concentration of hydroxyl (OH) groups and nitrogenous groups, which can be considered as both carbonization agent and blowing agent (as shown in Scheme 2). Therefore, an intumescent flame retardant system will be formed once it is used with acid source. It is known that APP is mostly used as an acid source, which is a very important part in intumescent flame retardant system. Camino et al. investigated the mechanism of interactions between APP and pentaerythritol and reported that APP could produce polyphosphoric acid at the temperature ranging from 260 to 420°C in air
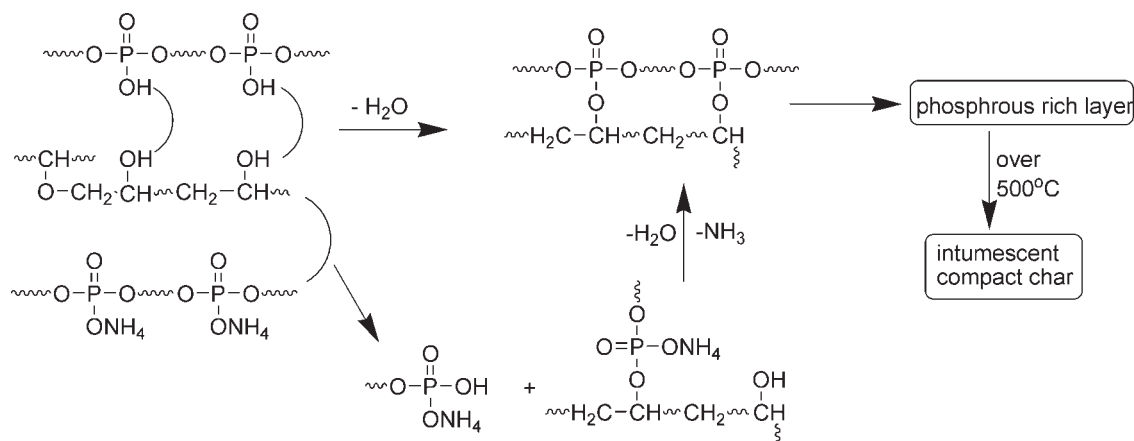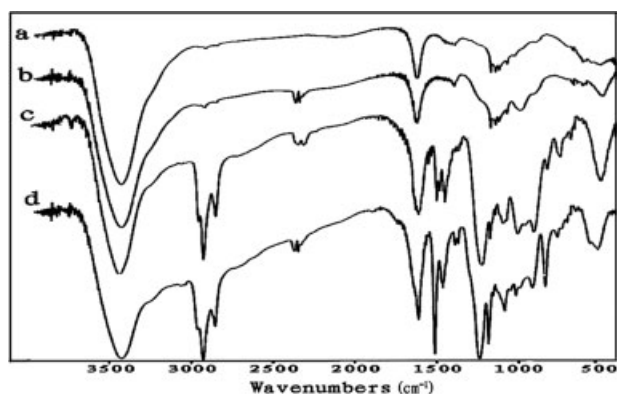

Scheme 4   The mechanism of interactions between APP and cured epoxy resin.
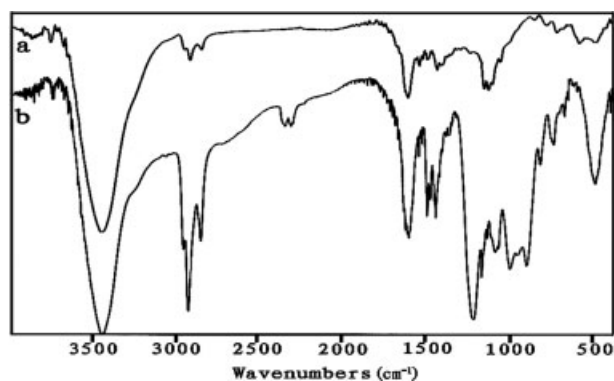
Figure 6 FTIR of residues of PCEP (a) and FR-CEP (b) at 500°C in a muffle for 3 min.

(Scheme 3).[19,27] The weight loss of APP (15.7%) at 420°C (in Fig. 2) is very similar as the weight of the ammonium group (15.0%) of APP, which proves the mechanism is exact. From the Table III, it can be seen that the onset degradation temperature of pure cured epoxy resin (Sam 2) is 334°C that is much higher than 260°C, at which APP begins to yield polyphosphoric acid. Therefore, the polyphosphoric acid from APP may react with the OH groups of cured epoxy resin leading to produce crosslinked phosphate ester. The process beginning with alcoholysis of APP by polyhydric compounds takes place, which could also yield crosslinked phosphate ester with elimination of ammonia and water. Then the crosslinked phosphate ester forms a phosphorus-rich layer under heat, which could increase the thermal stability of the rockbottom material. Meanwhile, the gases produced from above reactions cause the char to swell. Finally, the layer turns to an intumescent compact char at high temperature, which protects the material more effective than the layer does (as in Scheme 4). It indicates that there are two main stages of thermal degradation, which accords with the analysis for TG curves.

To investigate the flame retardant mechanism of flame retardant cured epoxy resin, we got FTIR spectra of residues of FR-CEP and PCEP at series of temperatures, and we also got XPS spectra of FR-CEP at room temperatures, 500 and 700°C. Figure 6 shows the changes of the FTIR spectra of PCEP and FR-CEP with 15 wt % APP at 500°C in a muffle for 3 min. As can be seen, new peaks appear in the spectrum b, the peaks at 1235 cm^{-1} (P=O) and 910 cm^{-1} (P—O—P) are due to the addition of APP, and another peak at 1015 cm^{-1} is assigned to P—O—C, which is due to crosslinked phosphate ester yielded by the interactions between APP and cured epoxy resin.[28] When Figure 6(a,b) are compared, the intensities of peaks at 2926, 2855, and 1460 cm^{-1} assigned
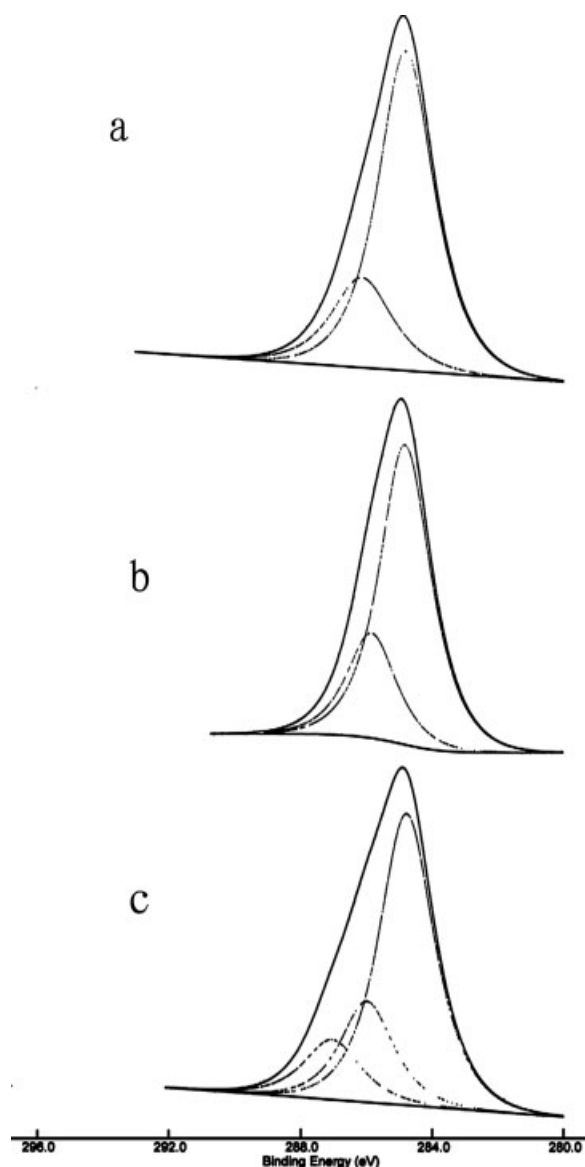
Figure 8 C_{1S} spectra of FR-CEP containing 15 wt % APP at 700°C (a), 500°C (b), and room temperature (c) in a muffle for 3 min.

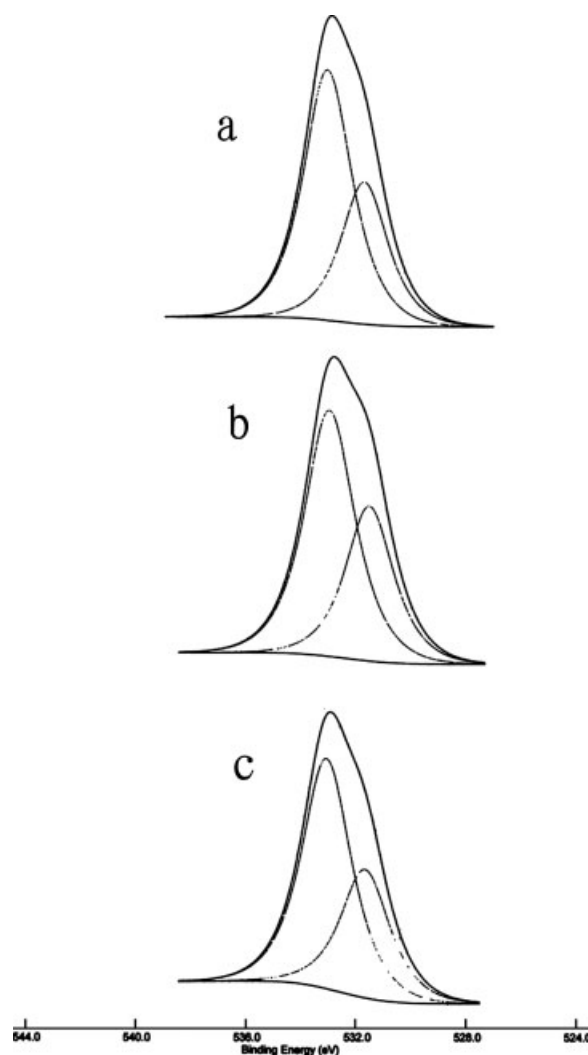**Figure 7** FTIR of residues of FR-CEP containing 15 wt % APP at 700°C (a), 600°C (b), 500°C (c), and 400°C (d) in a muffle for 3 min.
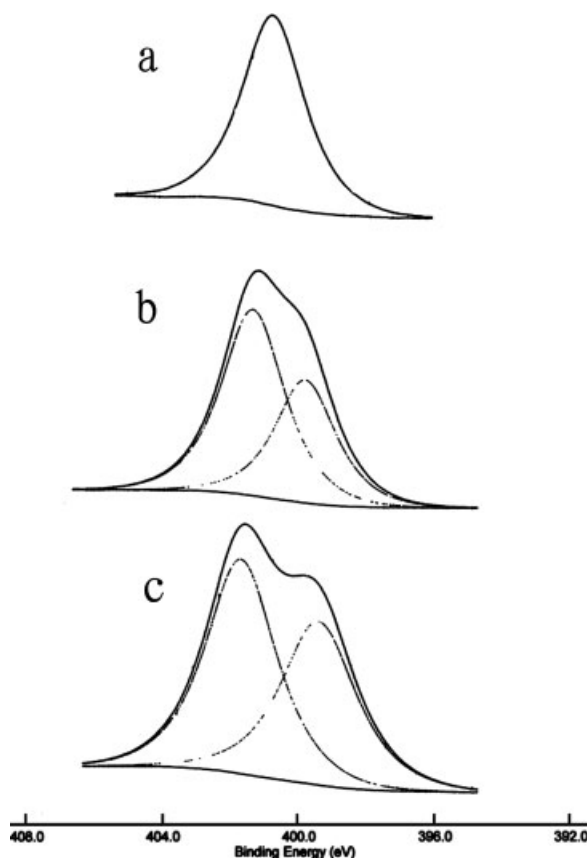
Figure 9 N_{1S} spectra of FR-CEP containing 15 wt % APP at 700°C (a), 500°C (b), and room temperature (c) in a muffle for 3 min.

trum c and d. The results suggest that there are two main stages of the thermal degradation of FR-CEP containing APP, the degradation at 400 and 500°C belong to the first stage and at 600, 700°C remain with the second stage. As shown in Figure 7, at the first stage the residues containing phosphorus, —CH₃, —CH₂— and aromatic compounds save some structure of cured epoxy resin with the interactions between cured epoxy resin and APP, and then the residues decompose further (at the second stage) leading to form a compact char with the absorption of cured epoxy resin decreasing, leaving the absorption of polyarmotic and phosphorous compounds that are the main composing of the char at 600, 700°C. These results agree with the analysis of TGA and DTG curves.

Figures 8–11 show the C_{1s}, N_{1s}, O_{1s}, and P_{2p} XPS spectra of FR-CEP containing 15 wt % APP at room

to vibration of —CH₃ and —CH₂— decrease obviously, and the peaks at 3020, 1510, and 830 cm^{-1} which are the absorption of the structure of bisphenol A in the chain of cured epoxy resin decrease even can not be observed. These results indicate that the residues of FR-CEP under 500°C could protect the material effectively under heat. Figure 7 presents the FTIR spectra of residues of FR-CEP at 400, 500, 600, and 700°C. As can be seen, the characterical absorptions of cured epoxy resin at peaks 2855 to 2930 cm^{-1} and 1270 to 1460 cm^{-1} which are due to —CH₃ and —CH₂—, 1180 cm^{-1} (C—N) and 3020, 1510, and 830 cm^{-1} which are assigned to the structure of the aromatic groups decrease, even cannot be observed. Compared with the spectra in Figure 7, there are some similar peaks at 1610 cm^{-1} (polyaromatic compounds), 910 to 1170 cm^{-1} (compounds containing phosphorus) which are absorption of the char. Furthermore, it can be observed that Figure 7(a,b) are very similar and the same phenomenon can be found between Figure 7(c,d), the peaks 2926, 2855, 1460 cm^{-1} (—CH₃, —CH₂—), 3020, 1510, 830 cm^{-1} (aromatic compounds) and 1180 cm^{-1} (C—N) that prove epoxy resin existing in the residues, which decrease or disappear gradually in spec-

Figure 10 O_{1S} spectra of FR-CEP containing 15 wt % APP at 700°C (a), 500°C (b), and room temperature (c) in a muffle for 3 min.
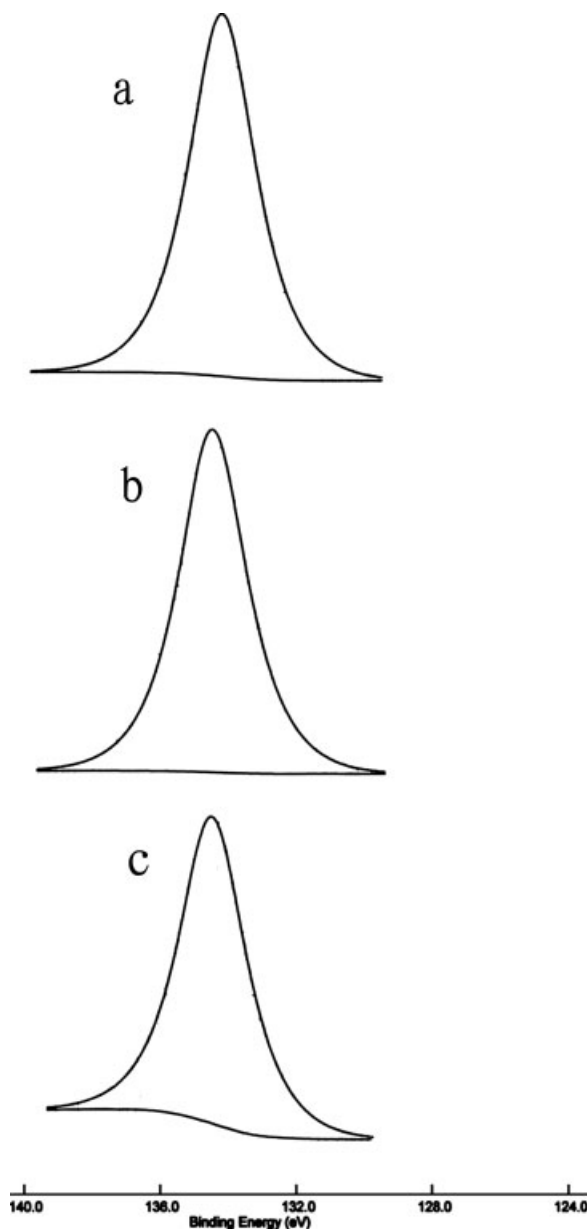
Figure 11 P_{2P} spectra of FR-CEP containing 15 wt % APP at room temperature (a), 500°C (b), 700°C, and (c) in a muffle for 3 min.

temperature and 500, 700°C in a muffle for 3 min. Table IV shows the atomic concentrations of FR-CEP from XPS. The C_{1s} spectra of FR-CEP are shown in

Figure 8. The bands at around 284.8 eV are the contributions of C—H and C—C in aliphatic and aromatic species in the material.[29,30] The peaks around 286.0 eV might be assigned to C—O—C, C—OH, C—O—P, and C—N.[31–33] The peak around 287.0 eV is characteristics of carbonyl which disappears at 500°C.[33] Figure 9 shows the N_{1s} spectra of FR-CEP. There exist two peaks in Figure 9(b,c), one around 399.5 eV is the contribution of C—N of LWPA and the other around 401.4 eV is assigned to NH_4^+.[31,32,34] But there is only one peak that can be assigned to pyidyl in Figure 9(a).[35] It indicates that the C—N of LWPA is transformed into pyidyl at 700°C, which is one component of char. The O_{1s} spectra of FR-CEP are presented in Figure 10. There are two bands in Figure10(a–c), one around 531.6 eV can be assigned to double binding =O in phosphate and carbonyl groups, the other peak around 533.0 eV can be assigned to —O— in C—O—C, C—O—P, P—O—P, and/or C—OH groups.[31,32] The P_{2P} spectra of FR-CEP are shown in Figure 11. The peaks between 134 and 135 eV can be assigned to P—O—C and/or PO_3^- group in phosphate and/or P_2O_5.[31,32] The P_{2P} binding energy in Figure 11(a) is lower than that in Figure 11(b,c), which is the result of further crosslink of polyphosphoric acid. From Table IV, it can be seen that the atomic concentrations of nitrogen of FR-CEP decrease while the atomic concentrations of phosphorus increase from room temperature to 700°C, because of the volatile products of nitrogen compounds such as NH_3, NO, and the crosslinking of phosphate and phosphate ester at high temperature. The crosslinking of phosphorus compounds leads to leave the majority of phosphorus in condensed phase, so the P/C, P/N, and P/O ratios can be used to measure the atomic concentrations change of P, N, C. We can see that the P/C ratio at 700°C is much lower than that at room temperature and 500°C, which indicates the main degradation of carbon takes place over 500°C. The P/O ratios at 500 and 700°C are no large difference, which are much larger than that at room temperature; it shows the crosslinking of phosphorus compounds takes place less than 500°C. So the results of XPS indicate that the degradation of FR-CEP contains two steps, which agrees with the results of FTIR and TGA.

TABLE IV
Atomic Concentrations of FR-CEP from XPS

Temperature	C (wt %)	N (wt %)	P (wt %)	O (wt %)	P/C (%)	P/N (%)	P/O (%)
R.T.[a]	75.51	5.31	4.78	14.40	6.33	90.02	33.19
500°C	76.16	3.65	6.85	13.35	8.99	187.67	51.31
700°C	60.35	1.64	12.76	25.25	21.14	778.05	50.53

[a] Room temperature.

CONCLUSIONS

The flame retardancy of cured epoxy resin can be improved with decreasing the content of cure agent; at the same time, it can be improved by increasing the content of APP. In the present work, LOI value of the FR-CEP containing 15 wt % APP and 19.6 wt % cure agent is the highest (32.0), and all the FR-CEP can reach V-0 rating of UL-94 and non-dripping with the content of APP over 5 wt %. The results of TGA indicate that the char yield of FR-CEP is much more than that of PCEP. The results of TGA, FTIR, and XPS indicate that there are two main stages of the thermal degradation. At the first stage, interactions between APP (polyphosphoric acid) and cured epoxy resin lead to form a phosphorus rich layer under 500°C. At the second stage, the layer decomposes further to yield a lacunaris and compact char coating surface of the material, which can protect the polymer matrix effectively by limiting the heat transfer from the heat source to the substrate and the combustible compounds transfer from the substrate to the heat source. It is very clear that epoxy resin cured by LWPA form an interesting intumescent flame retardant system together with APP, APP is an acid source and cured epoxy resin can be considered as a combination with carbonization agent and blowing agent. The observations of SEM for residues of FR-CEP containing 15 wt % APP confirmed the formation of the compact char.

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