

Flame retardant epoxy resin based on bisphenol A epoxy resin modified by phosphoric acid

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Abstract Flame retardant epoxy resin (FREP) were synthesized from phosphoric acid and bisphenol A epoxy resin (BAEP). The structure of the FREP was characterized using FTIR and ^{31}P NMR. Then, several FREP/BAEP mass ratios were used to obtain materials with different phosphorus contents. The properties of the thermosetting materials were evaluated by limiting oxygen index, UL 94, cone calorimeter test, and thermogravimetric analysis. The results showed that the heat release rates and smoke production rates decreased greatly, and char residue increased with the increasing of FREP. It indicates that good flame retardant properties are related to the formation of a protective phosphorus-rich char layer.

Keywords Epoxy resin · Flame retardant · Phosphoric acid

Introduction

Epoxy resins are high-performance thermosetting resins that have a unique combination of properties including good adhesion to many substrates, chemical and heat resistance, superior electrical and mechanical properties, and good dimensional stability [1, 2]. On account of these characteristics,

epoxy molding compounds are widely used for encapsulating semiconductor devices. The multi-functionality of both the epoxy and curing agent results in highly cross-linking resins for microelectronic protective layers. However, some disadvantages such as poor flame resistance of epoxy resins limit their usage in some fields, such as special adhesives and coatings, advanced composites in aerospace, and electronic industries. Therefore, it demands the development of flame retardant systems to reduce fire hazards.

Classical flame retardants commercially used are inorganic compounds or halogen-based organic compounds, which can, however, give rise to corrosive gases and toxic smoke during combustion. Therefore, the trend is toward using halogen-free flame retardants in polymers [3–5]. Among the halogen-free flame retardants, phosphorus-containing retardants have demonstrated good flame retardancy for epoxy resins and also been found to generate less toxic gas and smoke than halogen-containing retardants [6].

Epoxy polymers could be endowed with flame retardancy by covalent incorporation of phosphorus [7–10]. Series of diglycidyl phosphates, diglycidyl phosphonates, and glycidyl phosphinates have been prepared. A large number of publications discuss the use of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide in the formulation of epoxy resins [7]. Moreover, phosphine oxide structures are often used to impart flame retardancy to epoxy resins, especially through curing agents, because polymers with phosphine oxide moieties have these major advantages, such as good flame retardant properties, high thermal oxidative stability, enhanced solubility in organic solvents, improved miscibility, and good adhesion to other compounds [11–13].

In our previous work, it has been found that phosphoric acid can react with epoxy group [14]. So, phosphoric acid

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could be used to modify bisphenol A epoxy resin. In this study, we reported the synthesis of a flame retardant epoxy resin (FREP) used as a reactive-type flame retardant from bisphenol A epoxy resin (BAEP) and phosphoric acid. The final product was characterized by FTIR and ^{31}P NMR. Then, several FREP/BAEP mass ratios were used to obtain materials with different phosphorus contents. The properties of the thermosetting materials were evaluated by cone calorimeter test and thermogravimetric analysis (TG).

Experimental

Materials

BAEP [SM618, epoxy equivalent mass (EEW) = 196 g eq $^{-1}$] was obtained from Jiangsu Sanmu Group (Yixing, China) and used as received. Phosphoric acid and all other chemicals with analytical pure mentioned in this paper were purchased from Shanghai First Reagent Co., China, and used as received without any purification.

Synthesis of FREP

BAEP (0.30 mol) in 200 ml of acetone was placed in a 500 ml round-bottomed flask in an ice-bath and stirred. Phosphoric acid (0.10 mol) was then added dropwise into the above flask. After the addition of the phosphoric acid, the mixture added with methoxy phenol (1,000 ppm over total amount of the reactants) was stirred at reflux for 3 h. The water and acetone were removed by distillation at reduced pressure. Then, the colorless product (FREP) was obtained (Scheme 1). The epoxy equivalent mass (EEW)

of FREP is 76 g eq $^{-1}$. The IR and ^{31}P NMR are shown in Figs. 1 and 2.

IR (KBr): 1,296 cm $^{-1}$, stretching vibration of P=O; 1246, 1083 and 940 cm $^{-1}$, stretching vibration of P–O–C (aromatic); 3367 cm $^{-1}$, stretching vibration of C–OH.

Curing procedure for epoxy resins

BAEP, flame retardant epoxy resin (FREP), and their blends in the ratios of 75/25, 50/50, and 25/75 were used as epoxy resins. T31 was mixed separately with above complexes at room temperature. Ph $_3$ P (total amount of epoxy resins) of 0.2 wt% was added to each formulation as a curing accelerator. The mixtures were poured into hot

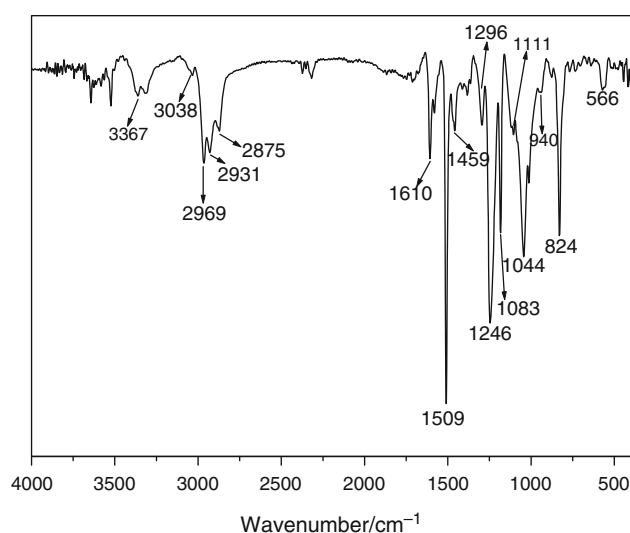
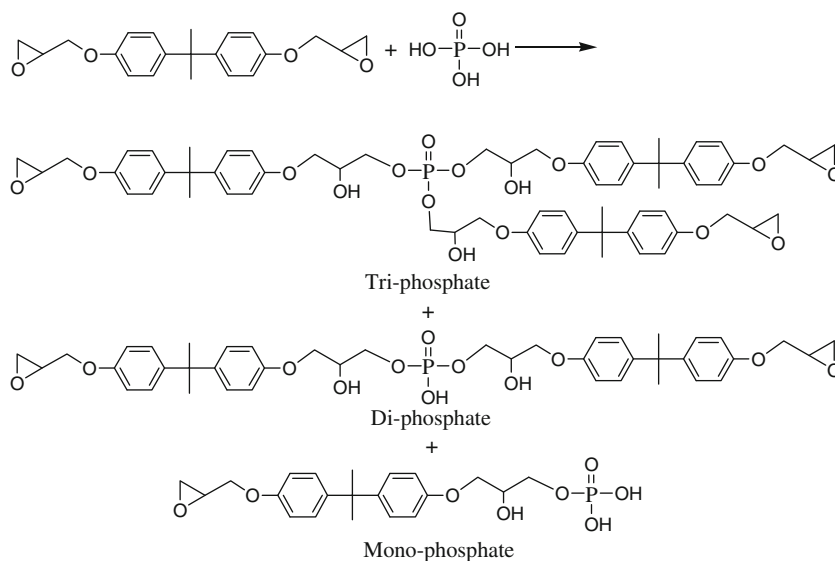


Fig. 1 IR spectrum of FREP

Scheme 1 Synthesis routes of FREP



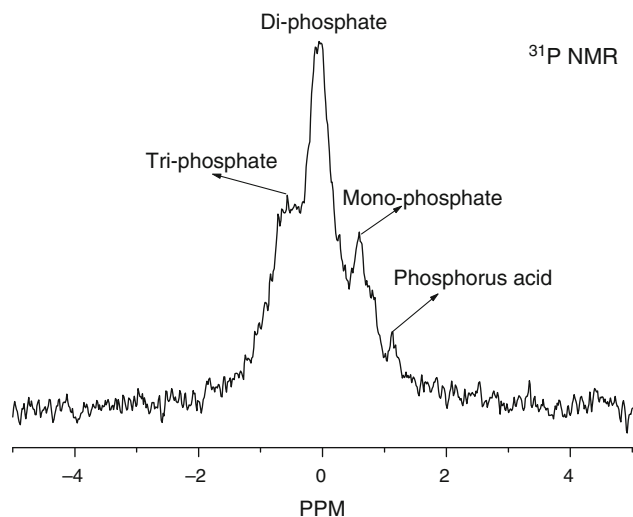


Fig. 2 ^{31}P NMR spectrum of FREP

aluminum molds, and then thermally cured at 140 °C for 3 h to obtain cured specimens. The cured specimens were denoted as EP-0, EP-1, EP-2, EP-3, and EP-4.

Measurements

FTIR Spectra

FTIR spectrum was recorded with an IR Prestige-21 spectrometer from Shimadzu Corporation, Japan.

NMR

^{31}P NMR spectra were obtained with a Bruker Avance 300 spectrometer operating at 300 and 121.5 MHz, respectively, using dimethyl sulfoxide- d_6 (DMSO- d_6) as a solvent.

Limiting oxygen index (LOI)

LOI was measured according to ASTM D2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions $100 \times 6.5 \times 3 \text{ mm}^3$. And five samples were carried out in the LOI test.

UL 94 testing

The vertical test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL 94 test standard. The specimens used were of dimensions $100 \times 13 \times 3 \text{ mm}^3$, and three samples were carried out in the UL 94 test.

Cone calorimeter test

The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen of dimensions $100 \times 100 \times 3 \text{ mm}^3$ was wrapped in aluminum foil and exposed horizontally to an external heat flux of 50 kW m^{-2} . And, three samples were carried out in the cone calorimeter test.

Thermogravimetric (TG) analysis

TG analysis of the cured sample was performed using a DT-50 (Setaram, France) instrument. About 10.0 mg of sample was put in an alumina crucible and heated from 25 to 700 °C. The heating rate was set as 10 K min^{-1} (nitrogen atmosphere, flow rate of 20 mL min^{-1}).

Results and discussion

Characterization of FREP

In this study, the specific conditions for the polycondensation of BAEP and phosphoric acid were determined according to the literature [14]. The initial molar ratio of BAEP to phosphoric acid was set to be 3:1.

The outcomes obtained from ^{31}P NMR spectra demonstrated the reaction mechanism. Figure 2 displays the ^{31}P NMR spectrum of a typical FREP prepared with a 3:1 molar ratio of BAEP to phosphoric acid. Three signals at -0.59 , -0.04 , 0.59 , and 1.12 ppm are assigned to tri-phosphate, di-phosphate, mono-phosphate, and phosphoric acid, respectively, on the basis of a comparison with previous works [14, 15]. Comparing the peak area ratio of four characteristic signals, the di-phosphate structure is the mainly produced compound. And, there is some minor phosphoric acid left in the flame retardant epoxy resin.

LOI and UL 94 rating

LOI is defined as the minimum fraction of oxygen in an oxygen–nitrogen mixture that is just sufficient to sustain combustion of the specimen after ignition. Thus, the flame retardant properties of these cured epoxy resins were further examined by measuring the LOI, and the results are also listed in Fig. 3. It is demonstrated that a higher LOI value is obtained with higher FREP content. It increases drastically from 19.1 to 34.2 by replacing BAEP with FREP. The increase of LOI is linear with the content of FREP, which can be explained that FREP is able to form char residue as a protective layer on the polymer surface during degradation.

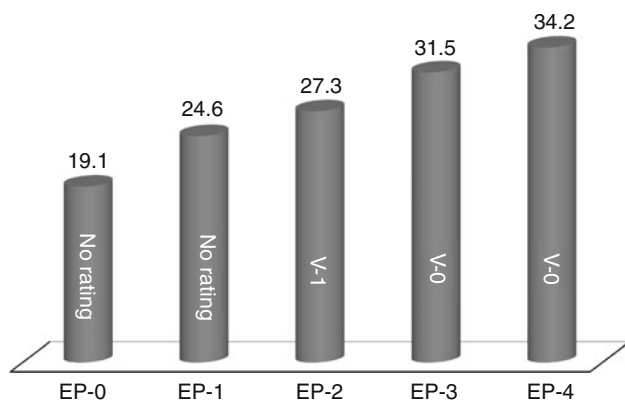


Fig. 3 LOI and UL 94 results of cured epoxy resins

The results obtained from the UL-94 tests showed that 50.0 wt% FREP could raise the UL 94 rating of EP-2 to V-1. And, EP-3 with 75.0 wt% FREP and EP-4 with 100.0 wt% FREP can pass the UL 94 test. These results indicated that FREP can raise the UL 94 test rating of flame retardant epoxy resin.

Cone calorimeter test

Heat release rate (HRR)

Cone calorimeter test is an effective approach to compare the combustion behavior of flame retardant polymers. HRR results are shown in Fig. 4. The presence of FREP in cured epoxy samples decreases the HRR values significantly compared with cured epoxy sample by only BAEP (the HRR peak value of the latter is 1208 kW m^{-2}). In the case of the cured epoxy samples with FREP, their peak HRR value is behind that of the sample EP-0, and their peak values are much lower compared with EP-0. The peak values of the samples with FREP are 650 and 590 kW m^{-2} ,

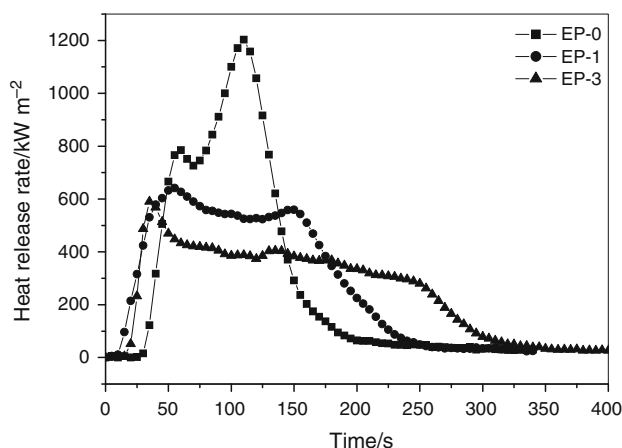


Fig. 4 HRR of EP-0, EP-1, and EP-3

respectively. The above phenomenon can be explained by the compact char residue formed on the surface of the sample in the cone calorimeter test. However, it is noted that the ignition time of the cured epoxy samples with FREP is less than that of EP-0. The reason is due to the fact that phosphate ester decomposes at low temperature after the cone heater irradiated the surface of the composite, and some small volatile molecules are produced from the decomposition of FREP [16]. It can be seen in Fig. 4 that the HRR curves of the cured samples with FREP are very flat and the values of HRR decrease further with the addition of FREP. Moreover, the addition of FREP strongly prolongs the combustion process compared with EP-0. From the above results, it can be concluded that the addition of FREP can remarkably enhance the flame retardant properties of cured epoxy materials.

Mass

Figure 5 shows the mass of the char residues. It can be seen from Fig. 5, the char residue mass of samples containing FREP is higher than that of EP-0 without FREP. In case of the samples with FREP, a compact char residue will be formed during combustion. It has been reported that phosphate ester can decompose at low temperature to form char residue [16]. There is compact char residue formed on the surface of the samples with FREP between 10 and 75 s in the cone calorimeter test. The physical process of the char residue would act as a protective barrier and can thus limit the oxygen diffusion to the substrate or give a less disturbing low volatilization rate.

Total heat release (THR)

Figure 6 presents the THR for all samples. The slope of THR curve can be assumed as representative of fire spread

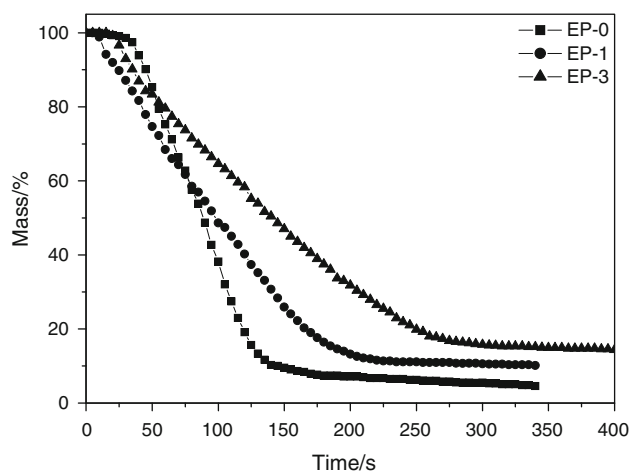


Fig. 5 Mass curves of EP-0, EP-1, and EP-3

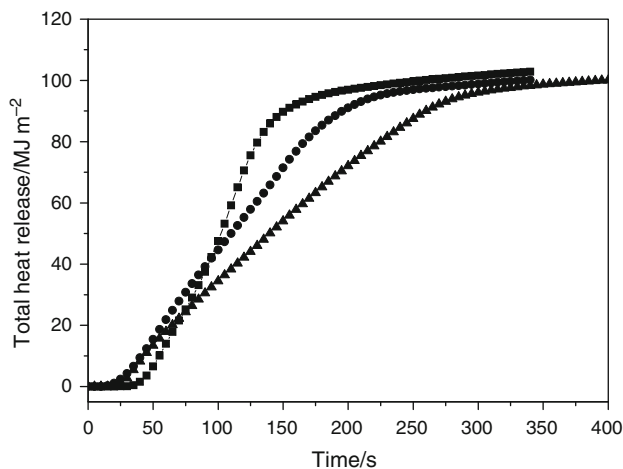


Fig. 6 THR curves of EP-0, EP-1, and EP-3

[17]. From Fig. 6, the THR of the sample containing FREP is lower than that of the sample without FREP, which may be the fact that there is much char residue formed in the case of the sample with FREP. With the addition of FREP, the THR decreases. It also can be seen that the THR of EP-3 is the lowest one among all the samples in the time between 60 and 400 s. That is, the flame spread of EP-3 is the lowest among all the samples. In the combustion process, there is condensed and compact char residue formed, which can isolate heat from the outside and combustible gases from the inside. For the EP-3, the structure of char is good enough to stop flame spread. It is also suggested FREP shows good flame retardance.

Smoke production rate (SPR)

SPR values of cured epoxy resins are illustrated in Fig. 7. The peak SPR value of EP-0 was the highest one ($0.31 \text{ m}^2 \text{ s}^{-1}$) among all the samples. The peak SPR value decreased greatly with the addition of FREP. When the loading of FREP is 20 wt% of all epoxy resins, the peak SPR value of EP-1 is $0.21 \text{ m}^2 \text{ s}^{-1}$. And, the time to the peak SPR value of EP-1 is 145 s, which is longer than that of EP-0 (100 s). When the loading of FREP is raised to 60 wt% of all the epoxy resins, the peak SPR value is $0.22 \text{ m}^2 \text{ s}^{-1}$, which is higher than that of EP-1. Also, it should be figured out that the time to the peak SPR value of EP-3 is decreased to 30 s. The results imply that moderate content of FREP produces obvious smoke suppression in the flame retardant epoxy system by decreasing the peak SPR value, and delays time to the peak SPR value. Smoke suppression by FREP can be explained as follows: moderate content of FREP can promote charring and enhance the quality of char, which can protect the inner matrix and reduce the amount of combustible gas and smoke-forming materials in the gas phase during combustion. In the case of

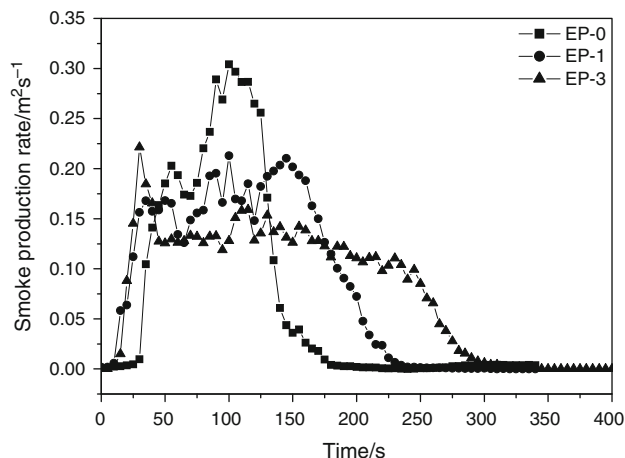


Fig. 7 Smoke production rate curves of EP-0, EP-1, and EP-3

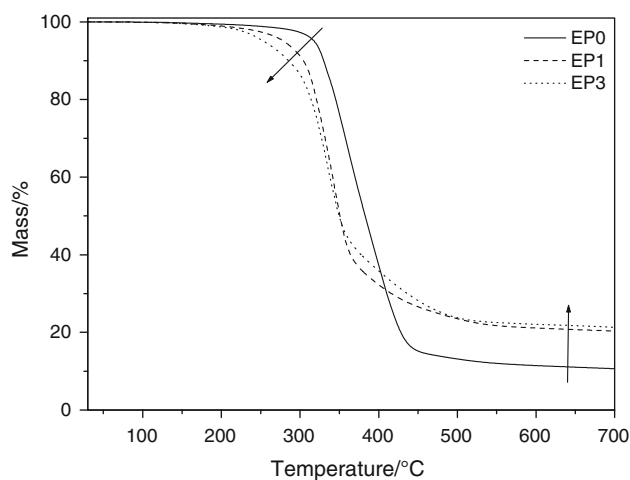


Fig. 8 TG curves of EP-0, EP-1, and EP-3

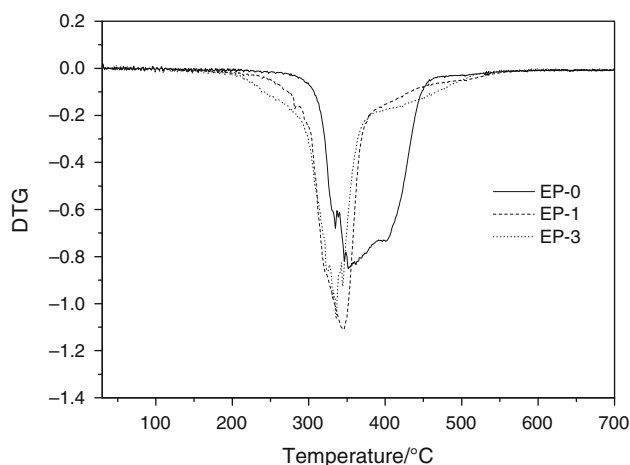


Fig. 9 DTG curves of EP-0, EP-1, and EP-3

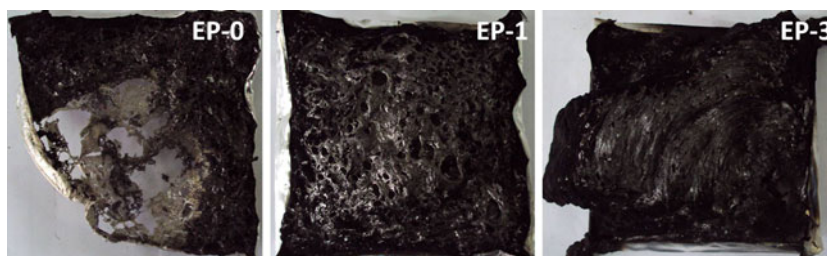


Fig. 10 Photographs of char residues of EP-0, EP-1, and EP-3 after cone calorimeter test

EP-3, phosphate ester at high loading decompose at low temperature producing much smoke at the beginning of the cone calorimeter test.

TG analysis

The thermal stability of a polymeric material is very important when used as a flame retardant, which mainly concerns the release of decomposition products and the formation of a char. Figures 8 and 9 show the TG and DTG curves of cured epoxy samples. EP-0 has one broad main decomposition process. It begins to decompose at about 317 °C (5.0 wt% mass loss). The temperature of maximum mass loss rate (T_{\max}) is 352 °C, as shown in Fig. 8. The residue of EP-0 at 700 °C is about 10.8 wt%.

For EP-1 and EP-3, their initial decomposition temperatures are 288 and 253 °C, respectively, which are lower than that of EP-0. In the degradation process, EP-1 and EP-3 decompose faster than EP-0 owing to the less thermal stability of phosphate structure in synthesized FREP. The reduction of initial decomposition temperature is attributed to the fact that P–O–C is less stable than common C–C bond [14, 18–20]. The degraded phosphate group makes a big contribution to the formation of the compact char residue, which protects the sample from further degradation. Beyond the temperature of 408 °C, EP-1 and EP-3 are more stable than EP-0. From Fig. 9, it can be seen that the degradation of EP-1 and EP-3 is composed of one step like EP-0. The T_{\max} for the two samples are 347 and 336 °C, respectively. Moreover, EP-1 and EP-3 after decomposition at 700 °C left about 20.2 and 21.5 wt% residue, respectively. The flame retardant epoxy with FREP has more char residue than the sample without FREP.

Digital photos of residues

Figure 10 is digital photos of residues of the series of samples after cone calorimeter test. It can be seen that a more coherent and dense char can be formed with the addition of FREP. There is almost no char residue left for the EP-0 sample without any FREP. In the case of EP-1

with 25.0 wt% FREP, there is more char residue formed in the combustion process compared with EP-0. And, there are some holes in the surface of the EP-1 char residue, which is unfavorable for good flame retardancy. When the content of FREP is raised to 75.0 wt%, there is the most tightest, densest, highest char residue formed from EP-3 among all samples.

From the char structure, we can explain the combustion phenomenon of the flame retardant epoxy resin. The formation of the efficient char can prevent the heat transfer between the flame zone and the burning substrate, and thus protect the underlying materials from further burning and retard the pyrolysis of polymers. As a result, HRR values are strongly reduced as shown in Fig. 3. The intumescent residue of EP-3 was tighter, denser, and higher than any other residue. The results are in accordance with the order in Fig. 4. This can be explained that the FREP can catalyze carbonization to form compact char residue which will protect the material throughout combustion. The different char residues also contribute to the flame retardancy performance. For the above reasons, the HRR of the samples with FREP is lower than that of EP-0.

Conclusions

In this study, a new flame retardant epoxy resin (FREP) based on bisphenol A epoxy resin and phosphoric acid has been successfully synthesized and studied. The flame retardance of cured epoxy materials increases with increasing FREP content. The results of the cone calorimeter tests indicated that with the increasing FREP, the HRR, THR, and SPR decreased greatly, whereas the char residue amount increased with the increasing FREP content. The TG results showed FREP decreased the initial decomposition temperatures of cured epoxy samples and enhanced the residue amount at high temperature.

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