

Preparation and Properties of Halogen-Free Flame-Retarded Phthalonitrile–Epoxy Blends

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ABSTRACT: Halogen-free flame-retarded blends composed of 2,2-bis[4-(3,4-dicyanophenoxy) phenyl] propane (BAPh) and epoxy resin E-44 (EP) were successfully prepared with 4,4'-diaminodiphenyl sulfone as a curing additive. The structure of the copolymers was characterized by Fourier transform infrared spectroscopy, which showed that epoxy groups, a phthalocyanine ring, and a triazine ring existed. The limiting oxygen index values were over 30, and the UL-94 rating reached V-0 for the 20 : 80 (w/w) BAPh/EP copolymers. Differential scanning calorimetry and dynamic rheological analysis were employed to study the curing reaction behaviors of the phthalonitrile/epoxy

blends. Also, the gelation time was shortened to 3 min when the prepolymerization temperature was 190°C. Thermogravimetric analysis showed that the thermal decomposition of the phthalonitrile/epoxy copolymers significantly improved with increasing BAPh content. The flexible strength of the 20:80 copolymers reached 149.5 MPa, which enhanced by 40 MPa compared to pure EP. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3580–3586, 2012

Key words: blends; flame retardance; polymer blends; thermal properties

INTRODUCTION

Much work has been focused on the development of halogen-type flame-retarded polymeric materials because they give rise to toxic gases and smoke, which do damage to peoples' health and costly equipment.¹ Some halogen-containing flame-retardants that have high flame-resistant efficiency have been forbidden gradually over recent years. Consequently, it is essential to develop new halogen-free flame-retarded (HFFR) materials that have minimum impacts on human health and the environment.^{2–4}

Epoxy resins are widely used as matrices in advanced composites because of their great versatility and favorable mechanical and physicochemical properties.^{5–8} However, the main drawback of epoxy resins is their limitations where high thermal stability and flame retardancy are needed. Two approaches of addition and reaction are used to improve the flame retardancy of polymers. The flame retardancy of epoxy resins can be improved by the physical incorporation of flame-retardant additives into the epoxy resins.^{9,10} However, some of them can generate corrosive and toxic fumes and may be lost in processing during combustion.¹¹ In view of this, the approach of the reaction has been

given much attention recently to reduce the flammability of epoxy resins through the addition of reactive flame retardants that are chemically bound the flame retardant with the polymer.¹² They can produce less toxic gas and smoke compared with halogen-containing flame-retardants.

Phthalonitrile resins have been studied for many years and form a unique class of materials because of their rigidity, outstanding thermal and thermooxidative stabilities, excellent mechanical properties, and fire resistance.^{13–15} They are used as flame retardants because of their excellent flame retardancy and have the potential to replace halogen-containing flame retardants.^{16–19} However, there have been few articles on the flame retardancy of phthalonitrile–epoxy materials.

Thus, in this work, to investigate both the properties of flame retardancy and thermal properties of epoxy resin, a series of HFFR phthalonitrile–epoxy blends were prepared. The effects of 2,2-bis[4-(3,4-dicyanophenoxy) phenyl] propane (BAPh) on the flame-retardancy and thermal and mechanical properties of the epoxy resins were assessed systematically. The flame retardancy of the phthalonitrile–epoxy copolymers were studied by limiting oxygen index (LOI) testing and the vertical burning test (UL-94). The thermal properties of the phthalonitrile–epoxy system were also investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and rheological measurements.

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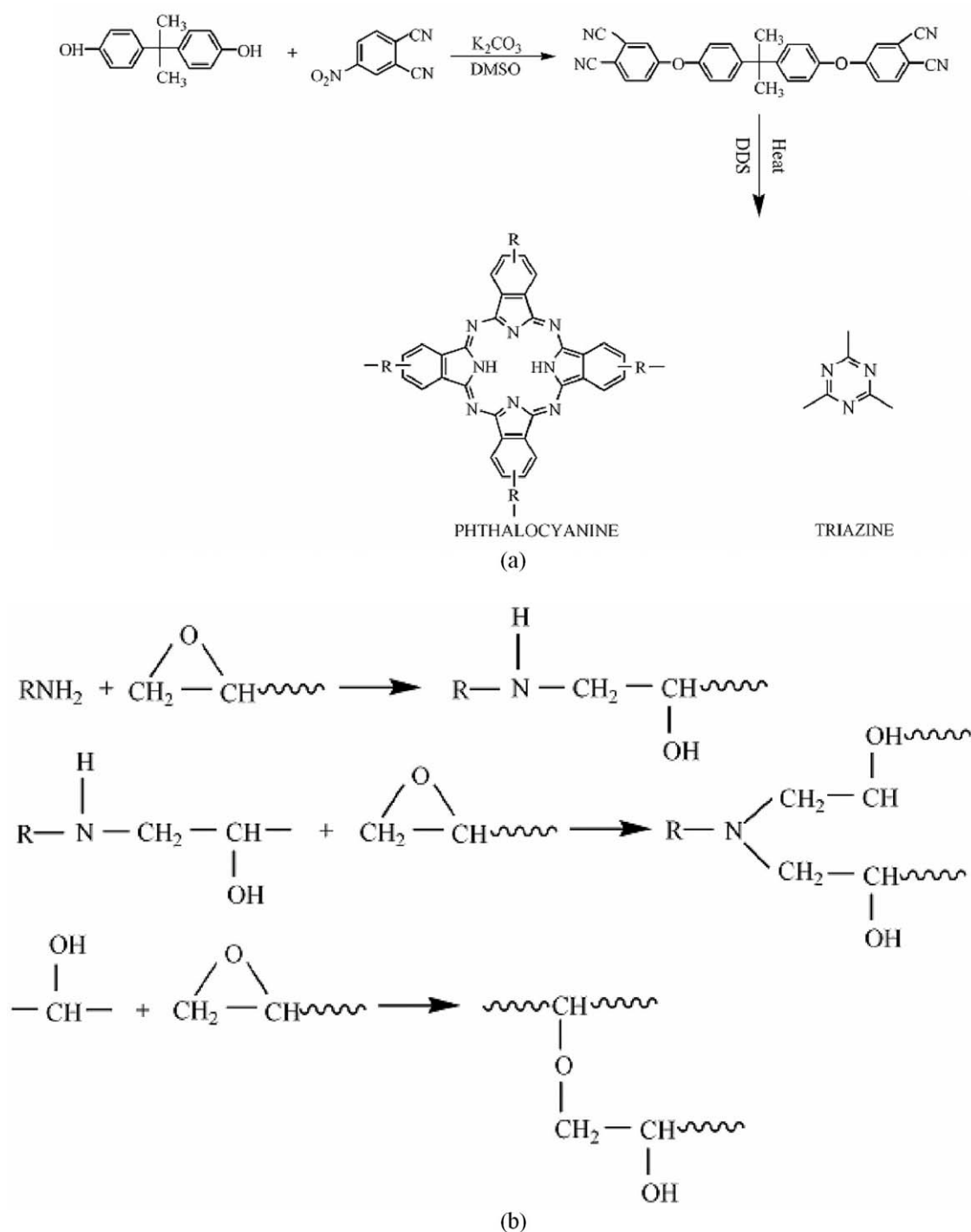


Figure 1 Chemical structures and reactions: (a) synthetic route and curing mechanisms of BAPh and (b) curing mechanisms of epoxy.

EXPERIMENTAL

Materials

Bisphenol A was purchased from Tianjin Guangfu Research Laboratory (China). 4-Nitrothalonitrile (99%) was obtained from Alpha Chemicals (Dezhou) Co., Ltd. Dimethyl sulfoxide (DMSO) and anhydrous potassium carbonate were purchased from Tianjin BODI Chemicals. Diglycidyl ether of biphenol A epoxy

resin E-44 (EP) and 4,4'-diaminodiphenyl sulfone (DDS) were obtained as market purchases. All of the reagents were used without any further purification before use.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu FTIR-8400S (Beijing, China) spectrometer in KBr pellets between 4000 and 400

cm^{-1} in air. The thermal curing behaviors of the copolymers were measured by a TA Instruments modulated DSC-Q100 instrument at a heating rate of $10^\circ\text{C}/\text{min}$ and a nitrogen flow rate of $50 \text{ mL}/\text{min}$. The thermal decomposition of the copolymers were determined by a TA Instruments TGA-Q50 thermogravimetric analyzer at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen and air. The rheological behavior of the curing process was examined with a TA Instruments AR-G2 rheometer at a low strain value (0.5%) and at a frequency of 1 Hz in an air (20% oxygen) environment. The mechanical properties of the blends were measured with a SANS CMT6104 series desktop electromechanical universal testing machine (SUNS Technology Stock Co, Ltd., Shenzhen) and were gained as average values for every sample. LOI measurement was performed with an XYZ-75 oxygen index apparatus with a magnetodynamic oxygen analyzer. UL-94 results were measured by a CZF-3 horizontal and vertical burning tester. Five samples, hung vertically over some surgical cotton, were ignited by the butane burner with the same flow. Samples would achieve a UL-94 V-0 flammability rating if the combustion of each sample did not last for 10 s and the cotton below the tested sample could not be ignited by the sparks. The morphology of the phthalonitrile-epoxy blends were observed on a SEM instrument (JSM-5900 LV, Tokyo, Japan) operating at 20 kV after gold sputtering.

Synthesis

Synthesis of the BAPh monomers

To a 250-mL, three-necked flask equipped with a mechanical stirrer, bisphenol A and 4-nitrophthalonitrile with a molar ratio of 1 : 2 were dissolved in DMSO. Then, anhydrous potassium carbonate was added to the flask, and the mixture was stirred at room temperature for 48 h.²⁰ The reaction mixture was poured into 1000 mL of water. The precipitate was collected by decompression filtration and dried at 80°C *in vacuo*. The crude product was purified with ethanol and dried *in vacuo*. Thus, pure product was obtained. The synthetic route and structure of BAPh are shown in Figure 1(a).

FTIR (cm^{-1}): 2233 (stretch, $-\text{CN}$); 1250 (stretch, $\text{Ar}-\text{O}-\text{Ar}$); 889 (bend, 1,2,4-substituted benzene); 835 (bend, 1,4-substituted benzene); 777, 717 (bend, benzene). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 1.691 ($-\text{CH}_3$); 7.136, 7.353, 7.787, 8.082, 8.109 ($\text{Ar}-\text{H}$).

Preparation of the phthalonitrile-epoxy blends and copolymers

Rectangular solid copolymer samples were prepared by the addition of the epoxy resins and the aromatic diamine curing additive (DDS) into the melting

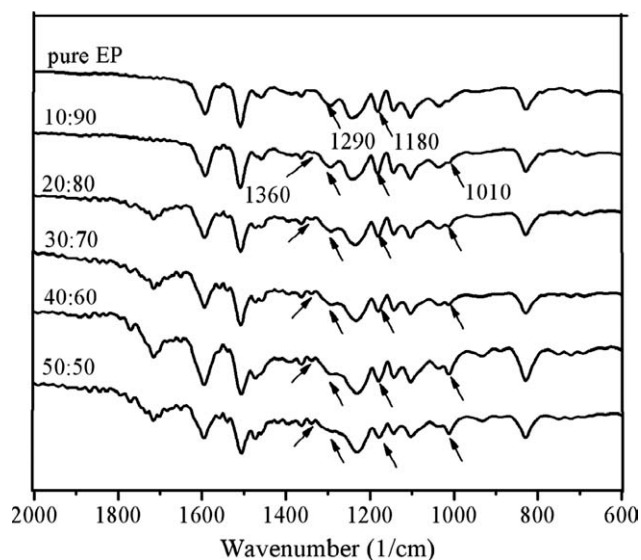


Figure 2 FTIR spectra of the BAPh/EP copolymers.

phthalonitrile monomer under ambient conditions to form a homogeneous mixture. All blends were poured into preheated molds. With the weight ratio of the BAPh/EP blends increased from 10 : 90 to 50 : 50, the mixture was cured in air by the following procedure: 190°C for 4 h, 210°C for 2 h, 230°C for 2 h, 250°C for 2 h, and 270°C for 2 h, respectively. The copolymers were cooled gradually to room temperature and then removed from the molds. The samples were broken into small pieces for TGA. The related curing mechanisms are presented in Figure 1(a,b).

RESULTS AND DISCUSSION

FTIR spectra

The structure of phthalonitrile-epoxy copolymers shown in Figure 2 were verified by FTIR spectroscopy. The evolution of the selected bands of the $2000\text{--}600\text{-cm}^{-1}$ interval are shown in Figure 2. The absorption peaks at 1180 and 1290 cm^{-1} contributed to the epoxy groups. On the other hand, new absorption peaks at 1010 and 1360 cm^{-1} were observed; this indicated the formation of a phthalocyanine ring²¹ and a triazine ring²¹ during the polymerization of the cyano groups. The peaks at 1180, 1290, 1010, and 1360 cm^{-1} all changed with increasing BAPh content. The absorption of epoxy groups at 1180 and 1290 cm^{-1} decreased with increasing BAPh content, and those at 1010 and 1360 cm^{-1} increased; this was attributed to the reaction between the epoxy and cyano groups.

DSC and rheological behaviors

The curing and rheological behaviors of the phthalonitrile-epoxy blends were investigated by DSC and

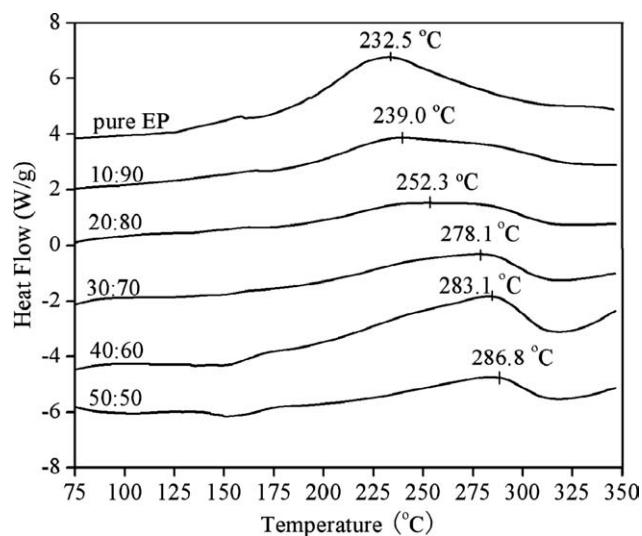


Figure 3 DSC curves of the BAPh/EP blends.

rheological measurement, as shown in Figures 3–6. As shown by the DSC results of Figure 3, the DSC curves were generated by the heating of the blends with 27 wt % DDS as a curing additive. In the thermograms of the blends, the phthalonitrile–epoxy blends for the pure EP, 10 : 90, 20 : 80, 30 : 70, 40 : 60, and 50 : 50, all had one exothermic transition, and the peak shifted slowly to a higher temperature with increasing BAPh content. The exothermic transition was due to the DDS-catalyzed copolymerization reaction between phthalonitrile and the epoxy resins. As shown in Figure 4, the glass-transition temperature (T_g) of the phthalonitrile–epoxy copolymers increased with increasing BAPh content; this further confirmed the reaction of the phthalonitrile and epoxy resins. T_g of the 50 : 50 phthalonitrile–epoxy

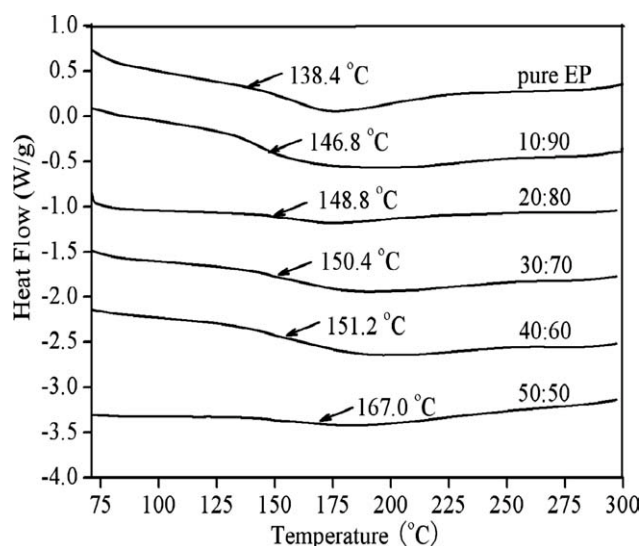


Figure 4 Influence of the BAPh contents on the T_g of copolymers.

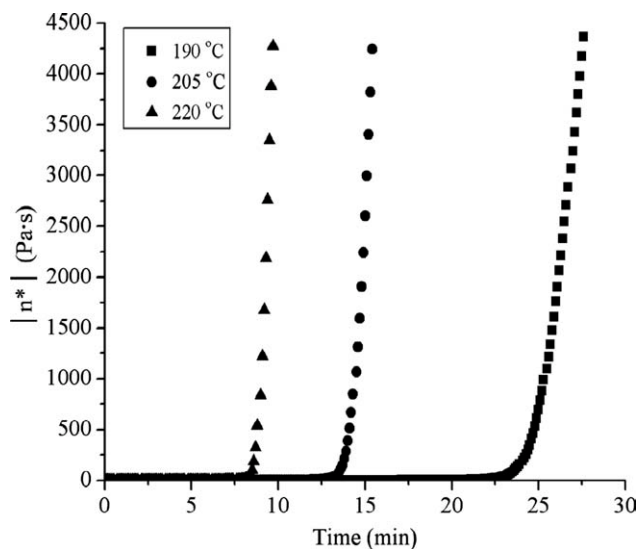


Figure 5 Time-sweep viscosity curves of the BAPh/EP prepolymers under different temperatures with no prepolymerization.

oxy copolymers increased by 28.7 °C in comparison with that of pure EP.

The rheological behavior of a material is a key factor in determining its processability. The curing behavior of the 20 : 80 phthalonitrile–epoxy blends was also investigated by rheological analysis. We carried out the study by heating the phthalonitrile–epoxy blends between parallel plates in a rheometer. From Figures 5 and 6, it can be observed that the viscosity of the phthalonitrile–epoxy blends was low before the curing reaction and increased sharply after the curing reaction started until gelation occurred. The viscosity of the phthalonitrile–epoxy blends increased sharply with the increase of the prepolymerization temperature when the same prepolymerization time remained

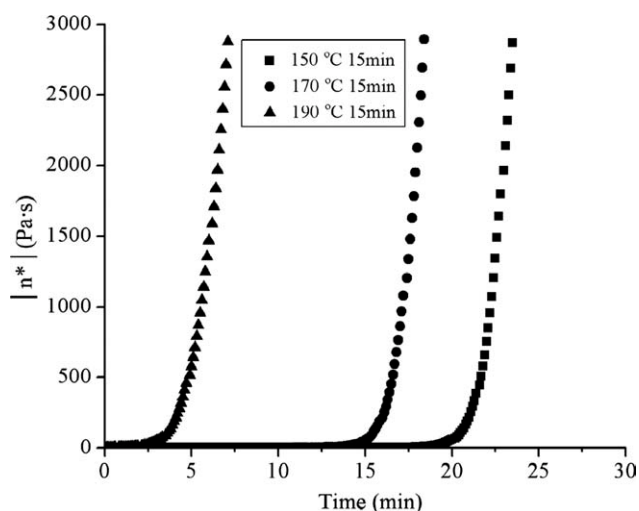


Figure 6 Time-sweep viscosity curves of the BAPh/EP prepolymers under 190 °C with different prepolymerization conditions.

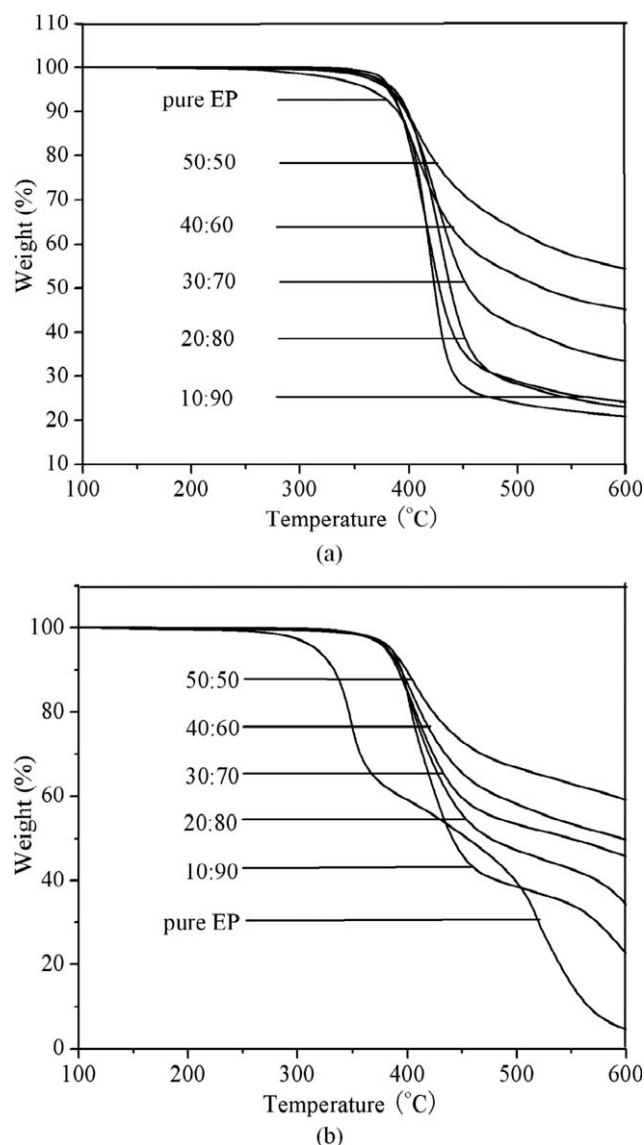


Figure 7 TGA curves of the BAPh/EP copolymers: (a) nitrogen and (b) air.

the same. This indicated that a higher prepolymerization temperature could accelerate the crosslinking reaction between the phthalonitrile and epoxy. On the basis of the principle of rheological theory, the gelation time (determined from the storage modulus and the loss modulus crossover point)¹⁴ was shortened to 3 min when the prepolymerization temperature was 190°C. The storage modulus and loss modulus become stable for an extended period of time; this indicated that the copolymers could be cured completely. These characteristics of the phthalonitrile-epoxy exhibited good processability and thermally activated polymerization.

TGA

TGA curves of the phthalonitrile-epoxy copolymers are shown in Figure 7(a,b). According to these

results, the copolymers' thermal decomposition properties improved with increasing BAPh content. The initial decomposition temperatures of pure EP increased by 29.2 and 74.3°C in nitrogen and air, respectively, when the ratio was 50 : 50. The thermal properties were enhanced after different heat-treatment conditions, and the initial decomposition temperature of the 20 : 80 copolymers was 406.5°C when the curing temperature was 350°C. These results show that the phthalonitrile-epoxy copolymers exhibited good thermal and thermooxidative stabilities when they were blended with BAPh. Also, the char yield at 600°C was enhanced with increasing BAPh content in nitrogen and air.

Flame retardancy of the phthalonitrile-epoxy copolymers

To investigate the effects of different phthalonitrile contents on the flame retardancy of the epoxy resins, the copolymers were tested by LOI testing and UL-94. The equipment used for the LOI test was a Bunsen-burner-type flame, which was applied from the top. LOI was determined by the minimum oxygen concentration for which no self-extinction within 30 s occurred after the flame was removed, so the higher the LOI was, the better the flame retardancy was. UL-94 classifies materials as V-0, V-1, V-2, and NR according to the time period needed before self-extinction and the occurrence of dripping after removal of the flame. NR means no rank, and V-0 is the most desired classification.

The results are given in Table I. The LOI value (oxygen index) of the 50 : 50 phthalonitrile-epoxy copolymers was 34.5%, which was an increase of 5.0% compared with that of pure EP and demonstrated that phthalonitrile had a good flame-retardancy effect on the epoxy systems. Furthermore, the flame retardancy of the phthalonitrile-epoxy copolymers was also verified by UL-94 measurement, and the burning grade improved from no grade to V-0 grade. The phthalonitrile-epoxy copolymers possessed good properties in flame retardancy; this was due to the network structure formed by crosslinking reactions between the epoxy and phthalonitrile resins.^{22,23} These results from LOI and UL-94

TABLE I
Flame-Retardancy Data from LOI and UL-94
Measurements of the Phthalonitrile-Epoxy Copolymers

Sample	BAPh/EP (w/w)	LOI (%)	UL-94
1	Pure EP	29.5	NR
2	10 : 90	30.5	V-1
3	20 : 80	31.5	V-0
4	30 : 70	32.5	V-0
5	40 : 60	33.5	V-0
6	50 : 50	34.5	V-0

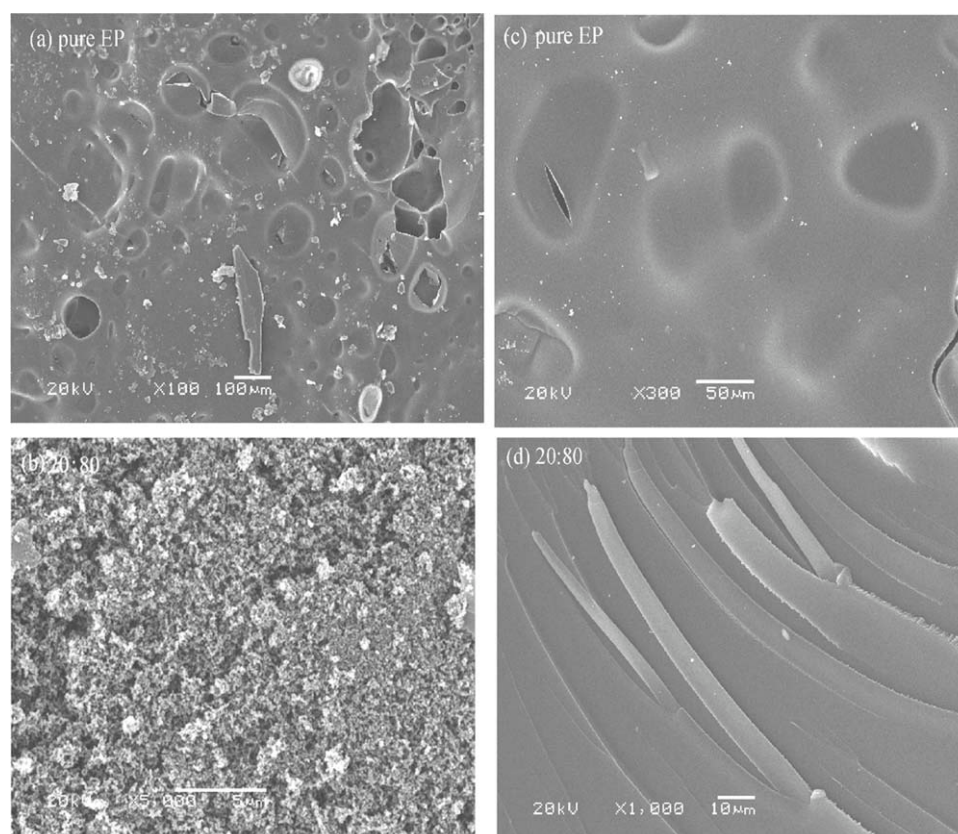


Figure 8 SEM images of carbon layer of the pure EP and 20 : 80 BAPh/EP copolymers: (a,b) external surface and (c,d) fracture surface.

measurements indicated that the flame retardancy of the epoxy resins was improved greatly by the blending with the phthalonitrile resins. In agreement with the results of rheological measurement, the excellent flame-retardant properties of the phthalonitrile-epoxy copolymers were attributed to the reaction between the epoxy groups and cyano groups.

SEM images of the carbon layer of the copolymers

Figure 8 shows the SEM images of the carbon layers of the pure EP and 20 : 80 copolymers. It can be seen from Figure 8(a,b) that there were lots of expanding bubbles with different diameters on the external surface of pure EP, whereas the 20 : 80 copolymers exhibited intumescent behavior and produced a foamed protective char on the surface at elevated temperatures.^{24,25} The images in Figure 8(c,d) display the fracture surface of the burned copolymers and indicate that the flame was not burned into the 20 : 80 copolymers in comparison with pure EP. It was evident that the flame retardancy of the copolymers was significantly improved by the blending with the phthalonitrile resins.

Mechanical properties of the phthalonitrile-epoxy copolymers

Figure 9 displays the close relationship between the flexible strength and BAPh content. The results indicate that the flexible strength increased up to a copolymer ratio of 20 : 80 and then decreased with

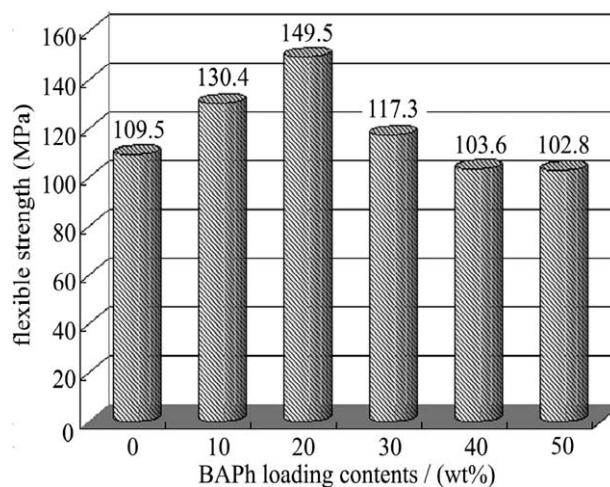


Figure 9 Influence of the BAPh content on the mechanical properties of the copolymers.

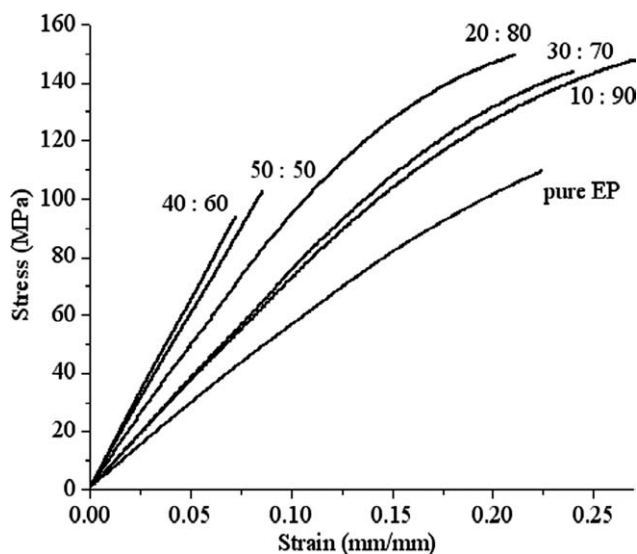


Figure 10 Stress–strain curves of the BAPh/EP copolymers.

further addition of BAPh. The flexible strength reached 149.5 MPa and was enhanced by 40 MPa in comparison with pure EP. The rigid frame might have been due to a higher interpenetrating degree of molecular chains in the two phases and the increase in the extent of polymerization in the polymers. However, more phthalocyanine would have weakened the intermolecular interactions and resulted in a decrease in the mechanical properties. Stress–strain curves of the BAPh/EP copolymers are shown in Figure 10 and indicate that the flexible modulus increased with increasing BAPh content.

CONCLUSIONS

A series of HFFR phthalonitrile–epoxy copolymers were prepared from BAPh and epoxy resins with DDS as a curing additive. The structure and thermal properties of the copolymers were monitored by FTIR spectroscopy, DSC, rheology, and TGA. The studies revealed that phthalonitrile–epoxy copolymers exhibited high flame-retardant properties and thermal properties compared to pure EP. The

mechanical properties of the copolymers were also evaluated, and we found that the flexible strength was enhanced with increasing BAPh content. These performances are the basis of future processes and applications for the development of heat-resistant and flame-retardant materials.

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