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Synthesis of Novel Polyphosphonate Flame Retardants for Epoxy Resins

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Abstract. A novel halogen-free flame retardant of polyphosphonate (PDDP), has been synthesized by the melt polymerization. The structure of PDDP has been characterized by fourier transform infrared spectroscopy and nuclear magnetic resonance spectra. Results of vertical burning (UL-94), limiting oxygen index (LOI), and the cone calorimeter test rereveal that the PDDP could effectively improve the flame-retardant performance of EP, and PDDP also have a synergistic effect with APP. With the 12wt. % PDDP loading, the EP composites reached UL-94 V-0 rating with a LOI value of 35.0%, the peak of heat release rate and total heat release value decreased by 54.8 % and 26.8%, respectively. The comprehensive test results shows that the improvement of flame retardancy of the EP composites is attributed to the synergistic action of the condensed and gas phases.

Introduction

Epoxy resin (EP) have the excellent characteristics of toughness, chemical resistance, and superior electrical properties, it is widely used in coatings, electronic/electrical appliances, and adhesives [1-5]. However, the application value of EP is restricted by its flammability. Therefore, improving the flame-retardant performance of EP is necessary. The incorporation of halogen-containing compounds into EP, has been proven to be an extremely efficient approach [6]. However, the halogen-containing flame-retardant system usually accompanied by the release of toxic during combustion, which is restricted by the current legislation.

In this work, A novel Halogen-free flame retardant of polyphosphonate (PDDP) flame retardant, was synthesized by the melt polymerization. To demonstrate its flame retardancy for EP, different PDDP contents EP composites have been prepared. The flame retardancy and thermal properties of EP composites have been comprehensively evaluated.

Experimental

Materials

PPDC, aniline, and 4,4-Dihydroxybenzophenone (DHBP) were supplied by Sinopharm Chemical Reagent Co. Ltd. DOPO, epoxy resin (E-44), and DDM was supplied by Hefei Jiangfeng Chemical Industry Co. Ltd. All solvents were supplied by Sinopec Baling Company.

2.2. Synthesis of DOPO-PhOH

DOPO-PhOH was synthesized by the method according to a published procedure [2].

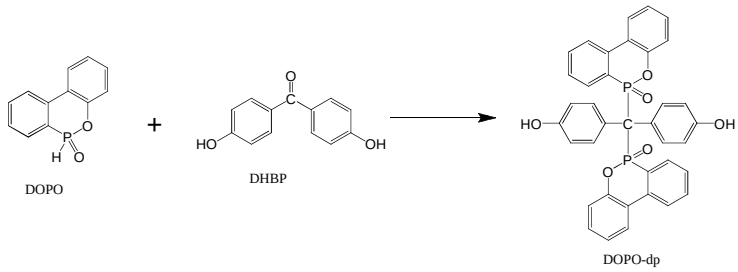

Figure 1. Synthetic route of DOPO-PhOH

Synthesis of polyphosphonate PDDP

As shown in Scheme 1, PDDP was synthesized by melt polymerization of the Cl–P bond of PPDC and H–O bond of DOPO-PhOH. DOPO-PhOH (6.12 g, 0.01 mol), PPDC (9.75 g, 0.05 mol) and were mixed in a 250mL round-bottom glass flask equipped with an magnetic stirrer and a temperature controller. The mixture was heated up to 120 °C and reaction for 6h. Then, 4.68 g aniline was added dropwise into the flask. The product was washed with acetone twice and washed by water twice, after the product was dried in a vacuum at 90°C for 4h, a brown solid powder of PDDP was obtained (10.6 g).

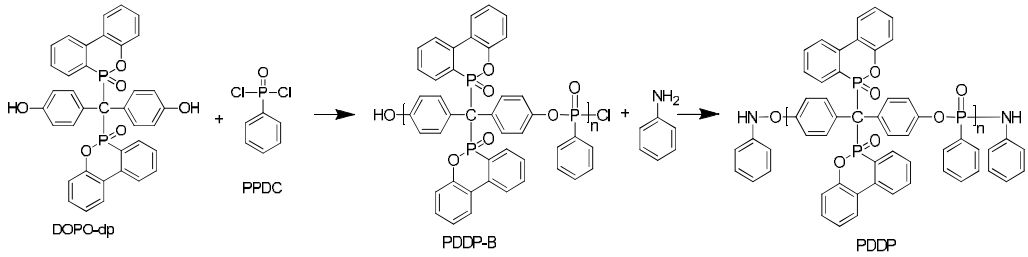

Figure 2. Synthetic route of PDDP

Preparation of EP and EP composites

Typically, EP composites with 4 wt.% PDDP were prepared as follows: epoxy resin (50.0 g) and PDDP (2.5 g) were mixed in a 250 mL beaker equipped with a mechanical stirrer, and stirred until a homogeneous liquid was obtained, the curing agent DDM (10.9 g) was added. The mixture was poured into molds and degassed for 3 min in a vacuum oven. Then, it was cured at 100°C for 3h, and postcured at 160°C for 3h. Thereafter, the thermoset was gradually cooled to room temperature to prevent cracking. EP composites with other contents of PDDP and APP were also prepared by the similar process. The Formulas and flame retardancy of pure EP and flame-retardant EP are listed in Table 1.

Table 1. Formulas and flame retardancy of pure EP and flame-retardant EP

Samples	EP(wt.%)	PDDP(wt%)	APP(wt%	LOI(%)	UL-94	Drippi
EP-0	100	—	—	26.1	N.R.	Y
EP-4	96	4	—	29.3	V-2	Y
EP-8	92	8	—	33.3	V-1	N
EP-12	88	12	—	35.0	V-0	N
EP-4+4	92	4	4	34.6	V-0	N

Characterization

The chemical structure of PDDP was characterization by the Fourier transform infrared (FTIR) spectra and Nuclear magnetic resonance (NMR) spectra. The thermal properties of EP and EP/PDDP composites were characterization by theThermogravimetric analysis (TGA), and the flame-retardant performance was evaluation by Vertical burning test (UL-94), Limiting oxygen index (LOI), and the Cone calorimeter (CONE) test.

Results and discussion

Structural characterizations of PDDP

The chemical structure of PDDP was characterized by FTIR and 1H NMR. Fig. 1 and Fig. 2 shows FTIR and 1H NMR spectra of the PDDP, respectively. The characteristic bands at 3437 cm-1 (-NH2), 3059, 2924 cm-1 (C-H), 1595,1490 cm-1 (benzene ring), 1209 cm-1 (P=O), 1084 cm-1 (P-O-C), 752 cm-1 (P-N) are observed [3]. The 1H NMR spectra of PDDP further confirm the structure of PDDP, In the 1H NMR spectra of PDDP, the peak at approximately 8.20 ppm correspond to N-H(labeled a), and those between 6.30-7.85ppm correspond to the protons of phenyl ring. Therefore, the chemical structure of PDDP was verified.

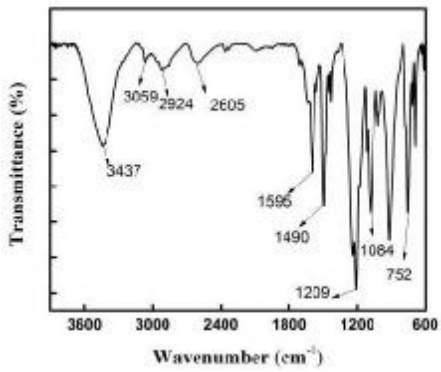

Figure 3. FTIR spectra of PDDP

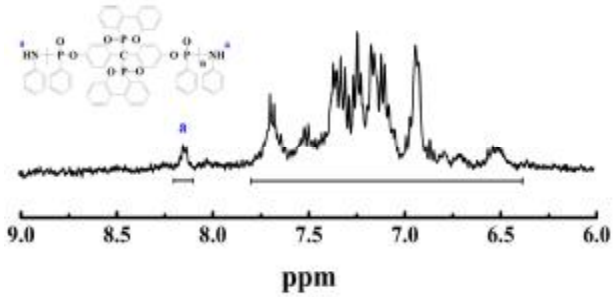

Figure 4. 1H NMR spectra of PDDP

Flame-retardant properties of EP composites

LOI and UL-94 tests

The flame-retardant properties of epoxy thermosets were evaluated by LOI and UL-94 tests. The corresponding data are listed in Table 1.As shown in Table 1, the pure epoxy of EP-0 is highly flammable, with an LOI value of 26.1 % and a no rating in the UL-94 test. Compared with the pure EP, the LOI values were highly enhanced by addition of PDDP. With 12 wt % loading, the EP-12 composite reached an LOI value of 35.0 % and a V-0 rating in the UL-94 test. Meanwhile, the flame-retardant properties of EP/PDDP composites with APP was also investigated. When 4 wt % PDDP and 4 wt % APP were loading, the composite of EP-4+4 reached an LOI value of 34.6 % and a V-0 rating in the UL-94 test. Thus, the flame-retardant efficiency of EP composites were improved by the synergistic effect of PDDP and APP.

Cone calorimetry test

To further investigate the flame-retardancy of EP composites, the Cone calorimetry was used to investigate the flame-retardancy performance of EP composites in real fire conditions. Many important date including peak of heat release rate (P-HRR), total heat release (THR), total heat release per total mass loss (THR/TML), and char yield (CY) are summarized in Table 2.

Table 2. Cone calorimetry test data of EP and EP composites

Sample	TTI（s）	P-HRR (kW/m^2)	THR	THR/TML(MJ/m^{2}g)
EP-0	58	1236	72.5	2.60
EP-4	32	993	67.3	2.56
EP-8	39	796	61.6	2.43
EP-12	43	558	53.1	2.31
EP-4+4	32	460	46.5	2.15

The experimental data of HRR and THR curves are presented in Figure 3. As illustrated in Figure 3, the pure EP burned was violent, with a P-HRR value of 1236 kW/m2 and a THR value of 72.5 MJ/m2. With an increase in PDDP loading, the P-HRR and THR values of the EP composites decreased obviously. When 12 wt% PDDP was added to EP, the P-HRR and THR value decreased by 54.8 % and 26.8%, respectively. Moreover, when PDDP and APP were simultaneously added to EP, the EP-4+4 give a lowest P-HRR value of 460 kW/m2 and a lowest THR value of 46.5 MJ/m2, which were lower than the EP-12.The THR/TML values of the EP composites decrease obviously with an increase in PDDP content, which indicates that the gas-phase flame-retardant effect of PDDP and APP was strengthened in EP.

Thermal properties of EP and EP composites

As shown in Figure 4, the initial degradation temperature of the EP composites decrease compare with pure EP, The depressed initial degradation temperature values may be attributed to the fact that the O=P−O bond is less stable than the C−C bond [4,5]. The char yield of the EP composites at high temperatures (beyond 430°C) are higher than that for EP , these results reveal that the PDDP and APP could promote enhance the thermal stability of EP at higher temperatures. When the DTG HRR curves are further observed, we can found that the decomposition rate of EP composites

decrease compare with pure EP, and the drop-out values increase when more PDDP and APP is added. It can be concluded that the PDDP cloud improve the thermal stability of EP at the high temperatures and reduce the decomposition rate of EP.

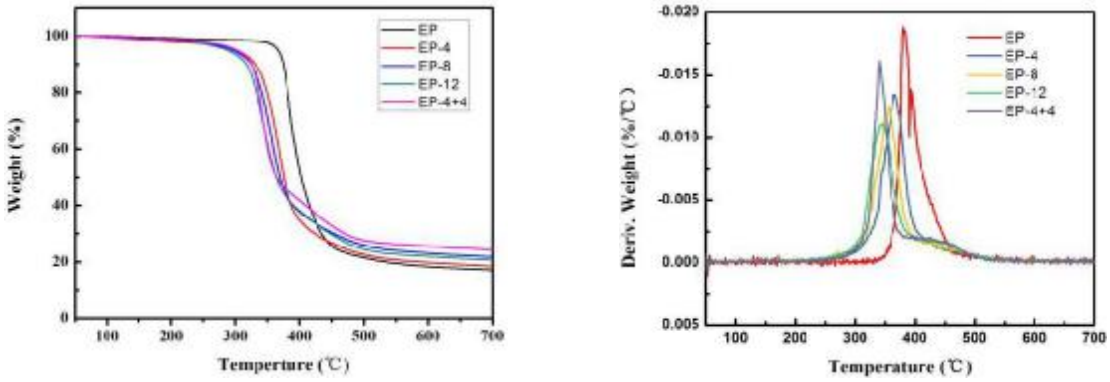

Figure 4. (a) TGA and (b) DTG curves of epoxy thermosets in nitrogen

Macroscopic morphologies of residual char after CONE test

A digital camera was used to investigate the morphology of residual char. Digital photographs of the residual char of EP, EP-12, and EP-4+4 after CONE test are shown in Figure 5. It is found that the residual char of EP was low and crisp. However, the EP-12 and EP-4+4 had a rich and intumescent char layer after CONE test. Those char layer could delay the transfer of flammable gases, heat, and oxygen, thus, the flame-retardant property of EP composites were improved.Thermal properties of EP and EP composites.

Figure 5. Digital photographs of residual char of EP, EP-12，and EP-4+4 after CONE test.

Conclusions

A novel flame retardant polyphosphonate (PDDP) was synthesized through the melt polymerization and has been applied into EP. The test results of the UL-94, LOI and CONE tests reveal that the PDDP could effectively enhanced flame-retardant properties of EP, and PDDP also have a synergistic effect with APP. When 4 wt % PDDP and 4 wt % APP were incorporated, UL-94 V-0 rating was achieved with a LOI value of 34.6%, and the values of P-HRR and THR decreased 62.7% and 35.9%, respectively. The comprehensive test results shows that the improvement of flame retardancy of the EP composites is attributed to the synergistic action of the condensed and gas phases.

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