ATLANTIS PRESS

Advances in Intelligent Systems Research, volume 154

6th International Conference on Measurement, Instrumentation and Automation (ICMIA 2017)

Synthesis of a Self-intumescent Flame Retardant of Branched Polyphosphoramide and Its Performance for Epoxy Resins

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Keywords: Branched polyphosphoramide; epoxy resins; flame retardant; applications

Abstract. A novel self-intumescent flame retardant of branched polyphosphoramide (BPCDC), was synthesized by the solution polymerization. The chemical structure of BPCDC has been demonstrated by fourier transform infrared spectroscopy (FTIR), and the flame-retardant properties of EP/BPCDC composites was investigated by vertical burning (UL-94), limiting oxygen index (LOI), and the cone calorimeter (CONE) test. The results rereveal that the BPCDC could effectively improve the flame-retardant performance of EP, When the 15 wt % BPCDC loading, the EP composite reached an LOI value of 32.9 % and a V-0 rating in the UL-94 test, and the peak of heat release rate and total heat release value was decreased by 54.8 % and 42.7%, respectively. The flame retardancy properties of EP/BPCDC composites with APP was also investigated, and the test results rereveal that BPCDC have a synergistic effect with APP in flame-retardant epoxy resins.

Introduction

Epoxy resins (EP) have the excellent characteristics of shrinkage, mechanical and electrical properties. Its widely used as a matrix for encapsulating material, electrical and/or electronic parts and so on [1-2]. Despite epoxy resins have these excellent properties, its outstanding application value is restricted by its flammability. Therefore, it is necessary to improve the flame-retardant properties of EP.

As families of polymeric flame retardant, polyphosphoramides are highly desirable by virtue of their good thermal stability and more importantly inherent synergistic effect between phosphorus and nitrogen [3-4]. In comparison with polyphosphate, polyphosphoramides exhibit higher hydrolytic stability than polyphosphates due to the partly hydrolysable P-O-C bond substituted by P-N bond . Moreover, it was reported that phosphoramide structure could be more effective than phosphate structure in promoting the char formation and reducing the pyrolysis gases [5].

In this work, A novel self-intumescent flame retardant of branched polyphosphoramide (BPCDC), was synthesized by the solution polymerization. To demonstrate its flame retardancy for EP, the EP composites with different BPCDC contents have been prepared. The flame-retardant properties of EP composites were studied in detail.

Experimental

Materials

Pentaerythritol , cyanuric chloride, phosphorus oxychloride , 4,4□-diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulfone were supplied by Anhui Jinlong Chemical Industry Co. Ltd. All solvents were supplied by Sinopec Baling Company.

Synthesis of SPDPC

SPDPC was synthesized by the method according to a published procedure [6].

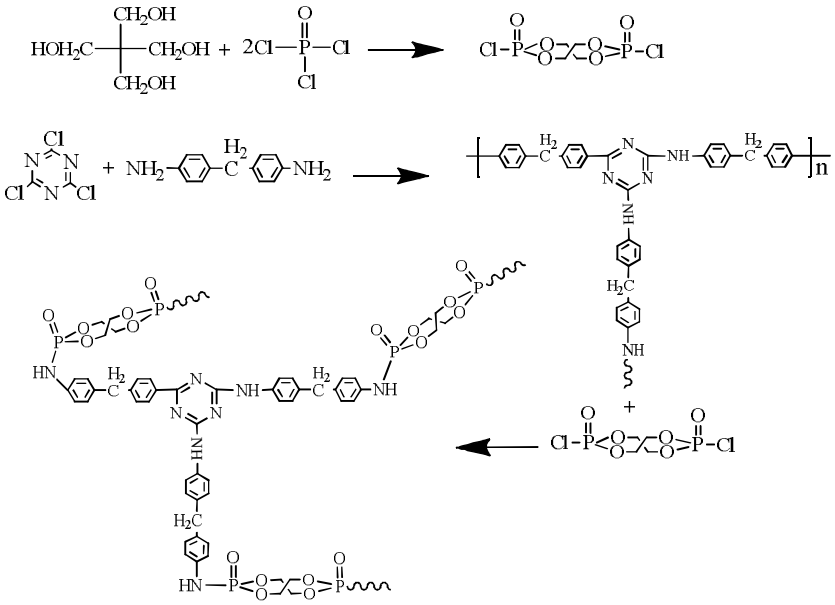

Fig 1. Synthetic route of BPCDC

Synthesis of branched polyphosphoramide (BPCDC)

As shown in Fig 1, cyanuric chloride (18.44g, 0.10mol) , DDM (39.64g, 0.20mol), and 300ml acetonitrile were charged into a 500 mL round-bottom glass flask equipped with an magnetic stirrer and a dropping funnel, the mixture was reaction at 70 °C until no HCl gas was emitted (approximately 4–8 h). Then, the SPDPC (31.60g, 0.10mol) solution was slowly added into the flask via the dropping funnel. After the completion of the addition, the mixture was further reaction for 10h. The product was washed with acetone twice, after the product was dried in a vacuum at 70°C for 6h, a brown solid powder of BPCDC was obtained (60.6 g).

Preparation of EP and EP composites

EP, BPCDC, and APP were dried under vacuum at 100°C for 8h. EP and BPCDC/APP were mixed with a mechanical stirrer, until a homogeneous liquid was obtained. Then the curing agent DDS was added and rapid mixing in a minute. After that the mixture was poured into the preheated stainless steel mold, it was cured at 120°C for 2h, and postcured at 160°C for 4h. 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.%)	BPCDC(wt%)	APP(wt%	LOI(%)	UL-94	Drippi
EP-0	100	—	—	25.7	N.R.	Y
EP-1	95	5	—	29.0	V-2	Y
EP-2	90	10	—	31.3	V-1	N
EP-3	85	15	—	32.9	V-0	N
EP-4	90	5	5	33.6	V-0	N

Characterization

The chemical structure of BPCDC was characterization by the fourier transform infrared (FTIR) spectra. 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 BPCDC

The chemical structure of BPCDC was characterized by FTIR. Fig. 1 shows FTIR of the BPCDC. The characteristic bands at 3430, 3260 cm^{-1} ($-NH_2$), 2933, 2860 cm^{-1} (C-H), 1616, 1530 cm^{-1} (benzene ring), 1230 cm^{-1} (P=O), 1105 cm^{-1} (P-O-C), 995 cm^{-1} (P-N) [7]. Therefore, the chemical structure of BPCDC was verified.

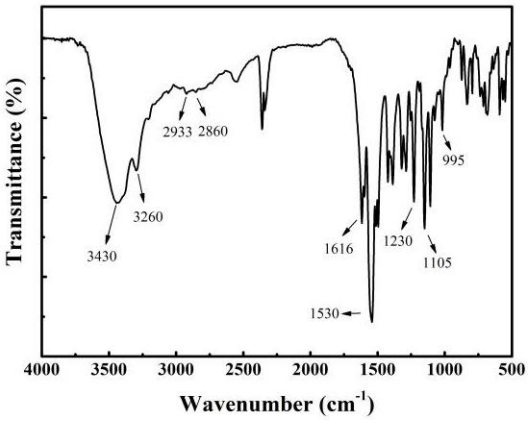

Fig 2. FTIR spectra of BPCDC

Flame-retardant properties of EP composites

LOI and UL-94 tests

The flame retardancy properties of EP/BPCDC composites were evaluated initially using LOI and UL-94 tests. The relevant data are listed in Table 1 and the digital photographs of EP and the EP composites after the LOI tests are shown in Fig 3. As presented in Table 1, the EP-0 is flammable, give an LOI value of 25.7 % and a no rating in the UL-94 test. When the 15 wt % BPCDC loading, the EP-3 composite reached an LOI value of 32.9 % and a V-0 rating in the UL-94 test. Moreover, the flame retardancy properties of EP/BPCDC composites with APP was also investigated. When 5 wt % BPCDC and 5 wt % APP were loading, the composite of EP-4 reached an LOI value of 33.6 % 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 BPCDC and APP.

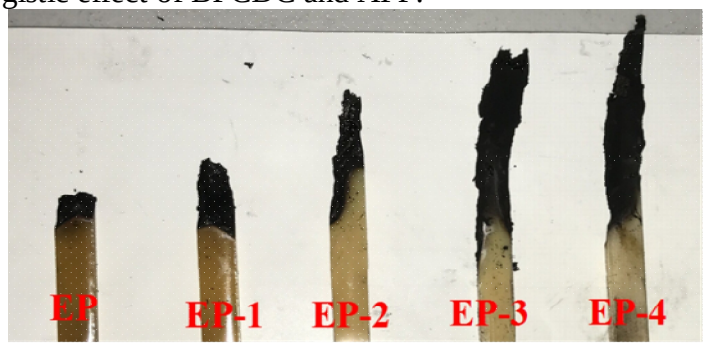

Fig 3. Digital photographs of EP and the EP/PDPA composites after the LOI tests.

Cone calorimetry test

Cone calorimetry is a useful tool to evaluate the flammability of materials under real fire condition. The important parameters of peak of heat release rate (P-HRR) and total heat release (THR) were obtained from cone calorimetry test. The HRR and THR curves as a function of time are presented in Fig 4 and Fig 5, respectively.

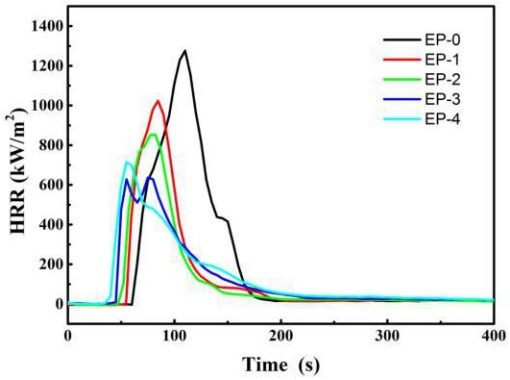

Fig 4. HRR curves of EP and EP composites.

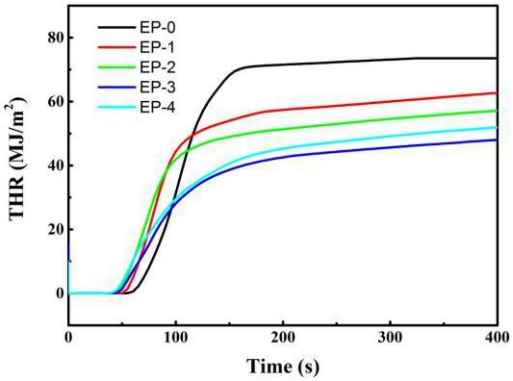

Fig 5. THR curves of EP and EP composites.

As illustrated in Fig 4 and Fig 5, the pure EP burned was flammable, with the P-HRR value of 1324 kW/m^2 and a THR value of 73.1 MJ/m^2. When the BPCDC was incorporated, the

flame-retardant properties of the EP/BPCDC composites increased obviously. With the 15 wt% BPCDC loading, the P-HRR and THR value of EP-3 decreased by 54.8 % and 42.7%, respectively. Moreover, when 5 wt % BPCDC and 5 wt % APP were added to EP simultaneously , the EP-4 give a P-HRR value of 700 kW/m^2 and a THR value of 43.6 MJ/m^2, which have the similar value to the EP-3. Thus, BPCDC and APP shown the synergistic flame-retardant effect in flame-ratardant EP.

3.4. Macroscopic morphologies of residual char after CONE test

A camera was adopted to study the morphology of residual char. The photographs of the residual char of EP-0, EP-3, and EP-4 after CONE test are shown in Fig 6. It is found that the residual char of EP-0 was little. And the EP-3 and EP-4 had a rich and intumescent char layer after CONE test. This type of residual char can provide protection for the EP matrix effectively. thus, the flame-retardant property of EP composites were improved.

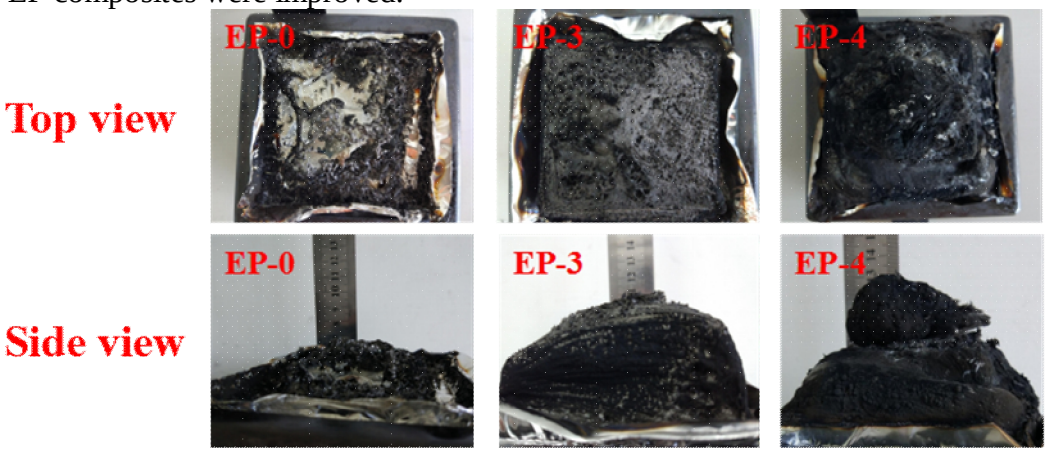

Fig 6. Digital photographs of residual char of EP-0, EP-3 ，and EP-4 after CONE test.

Conclusions

In this work, A novel self-intumescent flame retardant of branched polyphosphoramide (BPCDC), was synthesized by the solution polymerization. A series of flame-retardant EP composites has been prepared from BPCDC and APP. The test results of the UL-94, LOI and CONE tests reveal that the BPCDC could effectively enhanced flame-retardant properties of EP, When the 15 wt % BPCDC loading, the EP composite reached an LOI value of 32.9 % and a V-0 rating in the UL-94 test, and the peak of heat release rate and total heat release value was decreased by 54.8 % and 42.7%, respectively. An integration of all the tests shows that the BPCDC have a synergistic effect with APP.

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