Flame retardancy and thermal degradation mechanism of epoxy resins composites based on a PEPA-substituted polyphosphoramide

Wei Zhao[1, a], Jiping Liu[1, b*]

[1]School of Material Science and Engineering, Beijing Institute of Technology, Beijing, 100081, P. R. China

[a]tozw87@163.com, [b]liujp@bit.edu.cn

Keywords: polyphosphoramide, epoxy resins, flame retardant, thermal stability.

Abstract. A series of flame retardant epoxy resin composites with different content of PEPA-substituted polyphosphoramide (PSA) were prepared. The flame retardancy of EP/PSA composites was evaluated by UL-94 vertical burning test and the pyrolysis combustion flow calorimetry (PCFC). With the incorporation of 20 wt% PSA, the EP/PSA composites could reach the UL-94 V-0 rating and remarkable reduction of heat release rate could be observed. The thermal degradation mechanisms of the EP/PSA composites were investigated by Fourier transform infrared spectra (FTIR). FTIR analysis indicated that PSA could catalysis the decomposition of EP at lower temperature. The thermal degradation kinetics results of EP and EP/PSA composites by the Kissinger method showed that the apparent activation energy (E_a) reduced with incorporation of PSA, which indicated PSA could efficiently catalysis and promote the char forming process of EP.

Introduction

Epoxy resins (EP) play an important role in our daily life, because of its low cost, excellent mechanical properties[1, 2]. However, its highly inherent flammability always limits the application in electronic fields. Therefore, improving the flame retardancy of EP is very important and necessary. In the past decades, halogenated flame retardants were regarded as the most efficient additive to improving the flame retardancy of EP[3]. Nevertheless, with the in-depth research, halogen-containing systems generated large amount of toxic and corrosive gases during combustion. Nowadays, most researchers have focus on the development of halogen-free flame retardants for epoxy resins[4-6].

Among these halogen-free systems, polymeric flame retardants are promising choice to enhance the flame retardancy of EP due to its highly thermal stability, low flammability, and more importantly nearly negligible negative effects on the mechanical properties or glass transition temperature[7, 8]. For instance, Hu synthesized a DOPO substituted polyphosphates which could impart both good flame retardancy and better failure strain on epoxy resins[9].

In previous work, we have prepared a novel PEPA-substituted polyphosphoramide (PSA), which could impact epoxy resins both high flame retardancy and glass transition temperature[10]. In a continuing effort to develop flame retardant epoxy resins for practical application, we study the flame retardancy and thermal degradation process of EP/PSA composites through PCFC, dynamic FTIR in the condensed phase activity, and kinetics of thermal degradation in non-isothermal conditions.

Experimental

Materials

Epoxy resin (DGEBA, commercial name: E-44, epoxy equivalent = 0.44 mol/100 g) was purchased from Sinopec Baling Company (Yueyang, China). Phosphorus oxychloride, triethylamine, dioxane, acetonitrile purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China) were dried with 4Å molecular sieve and freshly distilled before use. Pentaerythritol (PER), 4,4'-diaminodiphenylsulfone (DDS), m-Phenylenediamine (m-PDA) obtained from Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China), were all reagent grade and used as received.

PEPA-substituted polyphosphoramide (PSA) (Fig. 1) were prepared through solution polycondensation, according to the procedure in reported literature [10].

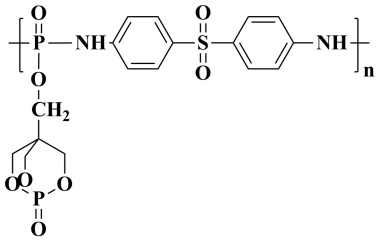

Fig. 1 Structure of PSA.

Preparation of EP/PSA composites

The EP/PSA composites were prepared by mixing EP with PSA for 10 min under mechanical stirring at 65 °C. Then, the curing agent m-PDA was added. The mixture was poured into polytetrafluoroethylene molds, cured at 80 °C for 2 h, and then post-cured at 120 °C for 2 h. After curing, all samples were slowly cooled to room temperature to avoid stress cracking. The fomulation of the EP/PSA composites were listed in Table 1.

Table 1 Formulations, flame retardancy of EP and EP/PSA composites.

Sample	E-44 (wt. %)	m-PDA (wt. %)	PSA (wt. %)	UL-94 rating
EP-0	89	11	0	Fail
EP-1	84.5	10.5	5	Fail
EP-2	81	10	10	V-1
EP-3	75.6	9.4	15	V-1
EP-4	71.2	8.8	20	V-0

Measurements and characterization

The flammability of EP and EP/PSA composites were determined on a CZF-3 instrument (Jiangning Analysis Instrument Factory) according to the UL-94 standard (ASTM D3801, 2010), with a sample size of 125 ×12.5 ×3 mm^3.

Pyrolysis combustion flow calorimetry (PCFC) was conducted with a Govmark MCC-2 pyrolysis combustion flow calorimeter according to ASTM D 7309. About 5.0 mg of each sample was placed in a sample cup and heated at 1 K s^{-1} to 900 °C. All experiments were performed three times, and heat release rate (HRR) values are reproducible to ±5%.

Fourier transform infrared (FTIR) spectra were obtained on a Bruker Tensor 27 Fourier transform infrared spectrophotometer from samples in KBr pellets over the range 4000-400 cm^{-1}. To investigate the non-volatile pyrolysis products of EP and EP/PSA composites, residues at different temperature were obtainded by heating the samples under nitrogen in tube furnace.

Thermogravimetric analysis (TGA) was carried out on a Metter-Toledo TGA/DSC-1 thermogravimetric analyzer in nitrogen, at different heating rates: 2.5 °C min^{-1}, 5 °C min^{-1}, 10 °C min^{-1}, and 20 °C min^{-1}, using samples of 5.0 mg in alumina crucibles.

Results and discussion

Flammability of EP and EP/PSA composites

To evalute the flame retardancy of EP and EP/PSA composites, UL-94 vertical buring test were used to determine the flame retardancy of these samples, and the results were listed in Table 1. Pure EP burned quickly once the specimens were ingnitied, and can not reach any rating in UL-94 vertical buring test. With the incorperation of PSA, the flame retardancy of EP significantly increased, and in the UL-94 verical buring tests EP-2 and EP-4 passed the V-1 and V-0 rating, respectively, indicating that PSA imparts excellent flame retardancy to epoxy resin.

The flammability of EP and EP/PSA composites were measured by PCFC, which is a novel and rapid method to evalucate the flammability of polymeric materials. Many important data such as heat release rate (HRR), heat release rate capacity (HRC), obtainded by dividing the PHRR by the heating rating, and the total heat release (THR) can be obtainded. The heat release rate of EP and EP/PSA

composites are presented in Fig. 2, and Table 2 summarizes the PCFC results for these samples. As shown in Fig. 2 and Table 2, EP give the highest PHRR value of 645.2 and the highest maximume PHRR temperautre of 430.6 °C. The addition of PSA significantly decreased the PHRR and THR of the composites. When 20 wt. % PSA was added to EP, EP-4 showed the lowest PHRR and THR compared to that of EP. Meanwhile, it can be drawn that the maximum PHRR temperature of EP-4 was lower than that of EP and EP-2, which could be attribute the catalysis effect of PSA on EP. Meanwhile, both EP-2 and EP-4 exhibit much lower HRC values of 273 and 213 J g^{-1} K, compared with pure EP. Above all, a conclusion can be drawn that PSA is an effective flame retardant for EP because it could significantly reduce the heat release for EP during combustion.

Table 2 PCFC results of EP and EP/PSA composites

	HRC (J g^{-1} K)	THR(kJ g^{-1})	PHRR (J g^{-1} K)	Max PHRR Temperature (°C)
EP	399	25.4	645.2	430.6
EP-2	273	21.3	432.8	386.1
EP-4	213	19.1	343.3	374.4

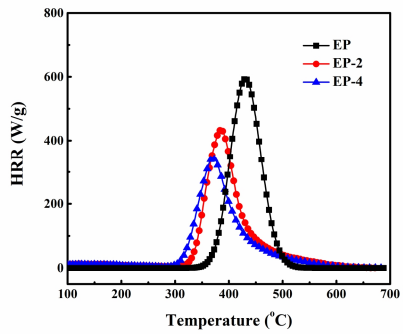

Fig. 2 HRR curves of EP and EP/PSA composites.

Thermal degradation of EP and EP/PSA composites

Dynamic FTIR was employed to analysis the solid pyrolysis products of EP and EP-4. The FTIR spectra of EP and EP-4 at different temperatures are shown in Fig. 3. As for pure EP, characteristic absorptions can be found at room temperature. The bands at 3380 cm^{-1} nearly disappeared at 250 °C, which could be assigned to release of water. When the temperature higher than 380 °C, the main peaks of EP disappear, indicating the main decomposition happened at this stage.

As for EP-4, the characteristic absorptions of EP-4 were similar to EP. In comparison to EP, the main characteristic peaks of EP-4 disappeared at 300 °C, which were lower than that of EP. This could be explained that the incorperation of PSA catalyzed the decomposition process of EP. Meanwhile, at high temperature, new peaks at 1610, 1508 cm^{-1}(polyaromatic compounds), 960 cm^{-1}(P-O-P) were observed, which means that the incorperation of PSA also catalyzed the char formation process[11].

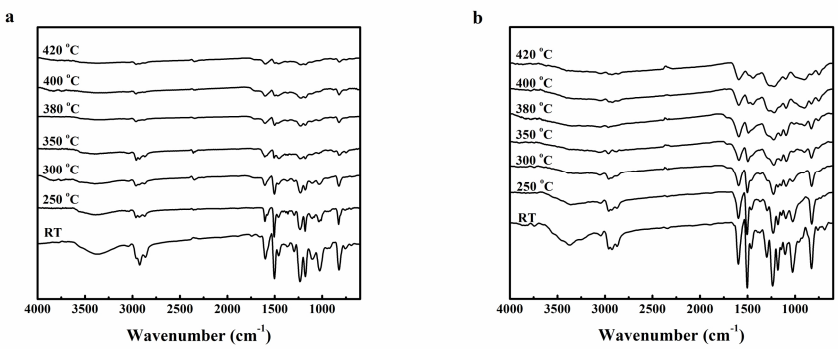

Fig. 3 The FTIR spectra of EP (a) and EP-4 (b) at different pyrolysis temperatures.

Kinetics analysis of EP and EP/PSA composites

As we known, the flame retardancy of polymeric materials not only depends on the thermal stability but also the degradation rate, char forming process and char yields[12]. TGA has been widely used to

estimate the kinetic parameters of degradation process, such as activation energies (E) and pre-exponential factor (A) through Kissinger methods.

$$\ln(\beta/T_p^2)=\ln(AR/E) - E/RT_p. \quad (1)$$

The TG and DTG curves at different heating rate are shown in Fig. 4, respectively. Accoring to equal 1, plots of $\ln(\beta/T_p^2)$ agaist $1/T_{max}$ present the fitted straight lines as shown in Fig. 5. From the slopes of the straight lines, the apparent activation energies of EP and EP-4 can be calculated. As for EP and EP-4, the relativity of the fitted straight lines is very good, indicating that the feasibility of the Kissinger method. Table 3 lists the calculated apparent activation energies using the Kissinger method for EP and EP-4. The apparent activation energy of pure EP is 168.22 kJ mol^{-1}, meanwhile that of EP decrease to 150.48 kJ mol^{-1} after the incorporation of 20 wt. % PSA, suggesting that the addition of PSA accelerate the decomposition process and promote the char forming process, hence contributes to the improvement of the flame retardancy of EP. This behavior is well agreed with the results of UL-94 and PCFC test.

Table 3 The calculated apparent activation energies using the Kissinger method for EP and EP-4

Sample	E_a (kJ mol^{-1})	Correln coeff (r)
EP	168.22	0.9920
EP-4	150.48	0.9963

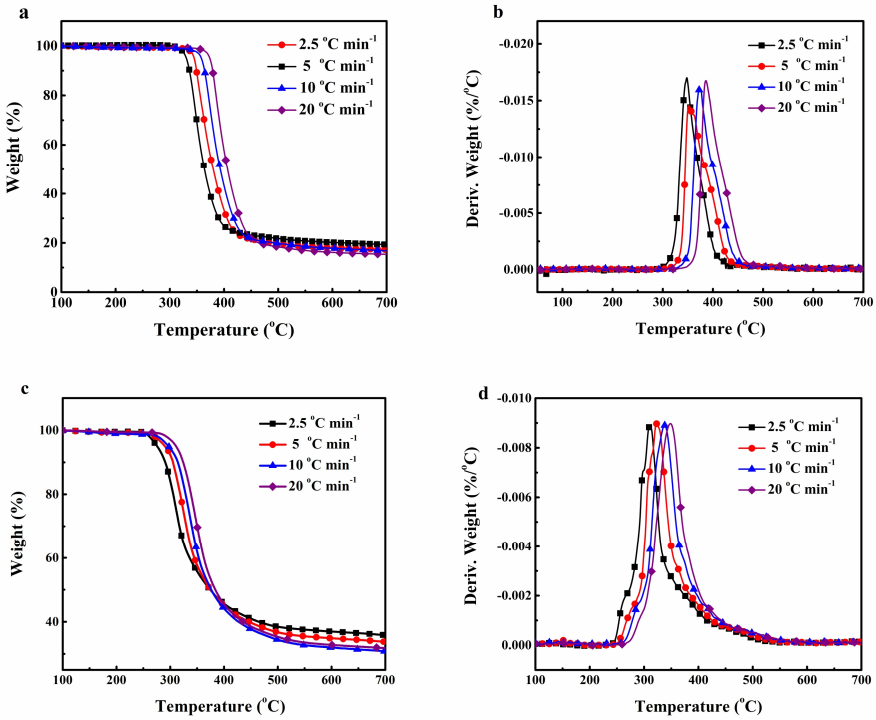

Fig. 4 TG and DTG curves of EP (a, b) and EP-4 (c, d) under nitrogen

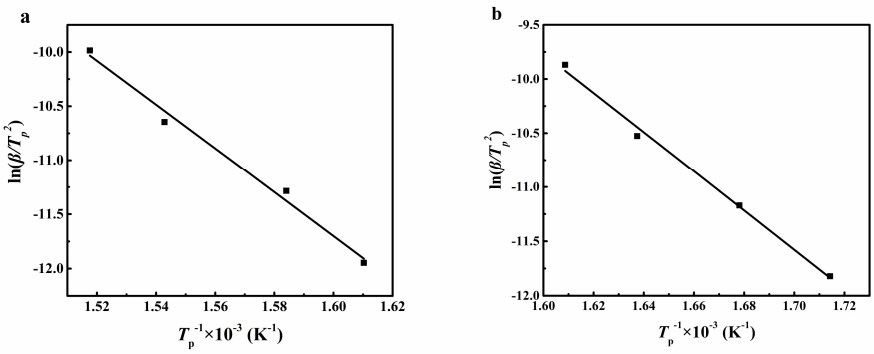

Fig. 5 Plots of $\ln(\beta/T_p^2)$-$1/T_p$ by Kissinger method(a: EP, b: EP-4)

Conclusions

A series of epoxy resin/PSA composites containing different content of PSA were prepared. With 20 wt.% PSA was added, the EP/PSA composites pass the UL-94 V-0 rating. The incorporation of PSA can improve the flame retardancy of EP and obviously reduce the heat release of the composites. The flame retardancy of PSA on epoxy resins mainly act in the condensed-phase and promote the decomposition process and char forming process.

References

[1] M. W. Szyndler, J. C. Timmons, Z. H. Yang, A. J. Lesser, T. Emrick, Multifunctional deoxybenzoin-based epoxies: synthesis, mechanical properties, and thermal evaluation, Polymer. 55 (2014) 4441-4446.

[2] T. Mariappan, C. A. Wilkie, Flame retardant epoxy resin for electrical and electronic applications, Fire Mater. 38 (2014) 588-598.

[3] Y. Zhou, J. Feng, H. Peng, H. Q. Qu, J. W. Hao, Catalytic pyrolysis and flame retardancy of epoxy resins with solid acid boron phosphate, Polym. Degrad. Stab. 110 (2014) 395-404.

[4] M. Rakotomalala, S. Wagner, M. Doring, Recent developments in halogen free flame retardants for epoxy resins for electrical and electronic applications, Materials. 3 (2010) 4300-4327.

[5] U. Braun, A. I. Balabanovich, B. Schartel, U. Knoll, J. Artner, M. Ciesielski, M. Döring, R. Perez, J. K. W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech, Influence of the oxidation state of phosphorus on the decomposition and fire behaviour of flame-retarded epoxy resin composites, Polymer. 47 (2006) 8495-509.

[6] B. Perret, B. Schartel, K. Stöß, M. Ciesielski, J. Diederichs, M. Döring, J. Krämer, V. Altstädt, A new halogen-free flame retardant based on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide for epoxy resins and their carbon fiber composites for the automotive and aviation industries, Macromol. Mater. Eng. 296 (2011) 14-30.

[7] Z. Li, P. Wei, Y. Yang, Y. G. Yan, D. A. Shi, Synthesis of a hyperbranched poly(phosphamide ester) oligomer and its high-effective flame retardancy and accelerated nucleation effect in polylactide composites, Polym. Degrad. Stab. 110 (2014) 104-112.

[8] K. Täuber, F. Marsico, F. R. Wurm, B. Schartel, Hyperbranched poly(phosphoester)s as flame retardants for technical and high performance polymers, Polym. Chem-UK. 5 (2014) 7042-7053.

[9] X. Wang, Y. Hu, L. Song, W. Y. Xing, H. D. Lu, P. Lv, G. X. Jie, Flame retardancy and thermal degradation mechanism of epoxy resin composites based on a DOPO substituted organophosphorus oligomer, Polymer. 51 (2010) 2435-2445.

[10] W. Zhao, J. P. Liu, H. Peng, J. Y. Liao, X. J. Wang, Synthesis of a novel PEPA-substituted polyphosphoramide with high char residues and its performance as an intumescent flame retardant for epoxy resins, Polym. Degrad. Stab. 118 (2015) 120-129.

[11] N. N. Tian, J. Gong, X. Wen, K. Yao, T. Tang, Synthesis and characterization of a novel organophosphorus oligomer and its application in improving flame retardancy of epoxy resin, RSC adv. 4 (2014) 17607-17614.

[12] N. N. Tian, X. Wen, Z. W. Jiang, J. Gong, Y. H. Wang, J. Xue, T. Tang, Synergistic effect between a novel char forming agent and ammonium polyphosphate on flame retardancy and thermal properties of polypropylene, Ind. Eng. Chem. Res. 52 (2013) 10905-10915.