Study on the thermal decomposition kinetics and flammability performance of epoxy resins containing solid polyphosphate

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Abstract: Solid polyphosphate(PBDP) was synthesized with respect to its use as additive flame retardant for epoxy resins. The influence of PBDP on the flame retardancy of epoxy resins was studied by UL-94 vertical burning test and pyrolysis combustion flow calorimetry (PCFC). With the addition of 20 wt% PBDP, the flame retardant epoxy resins pass a UL-94 V-0 level. The heat release rate, total heat release was reduced with the increased loading of PBDP. The thermal degradation kinetics results of EP and EP/PBDP composites by the Kissinger method showed that the apparent activation energy (E_a) reduced with incorporation of PBDP.

1. Introduction

Epoxy resins (EP), one of the most important thermosetting resins, are widely used in adhesives, automobiles, buildings and engineering, owing to the low density, good mechanical properties and relatively low cost.[1-2] However, the high flammability of EP limits its applications which required specific flame retardant standards.[3] Halogen flame retardants, such as tetrabromobisphenol A, polybrominateddiphenyl ethers, are used in preparations of flame retardant EP in the past decades. With the development of technologies and regulations, the flame retardant EP were required to produce less toxic gases during combustion. In recent years, several halogen-free flame retardants, such as phosphorus-, nitrogen-, silicon-, sulfur-containing compounds, have been developed and used in EP.[4-6]

Among them, polymeric flame retardants (PFRs) are preferred to be used as flame retardant for EP. Polymeric flame retardants are regarded as durable, high flame retardancy, high compatibility with matrix.[7,8] Tauber et al. synthesized an efficient polyphosphate with hyperbranched structure (hbPPE).[9] The synthesized hbPPE showed good performance in enhancing the charring formation in the condensed mode and flame inhibition effect in the gas mode. Tang et al. developed a phosphorus-containing POSS.[10] The prepared EP/POSS composites showed high flame retardancy and flexural modulus than pure EP.

In our previous research, we synthesized several PFRs containing phosphorus, nitrogen, sulfur.[11] The PFRs showed good flame retardancy and have slightly influence on the glass transition temperature and mechanical properties of the matrix. But, its flammability performance and flame retardant mechanism on EP need further evaluation and exploration. In this work, to better understand the flame retardant properties of solid polyphosphate (PBDP) applied to EP, pyrolysis combustion flow calorimetry and Kissinger method was employed to study the thermal decomposition kinetics of PBDP on EP.

2. Experimental

2.1 Materials

Phosphorus oxychloride, phenol, aluminium chloride ($AlCl_3$), bisphenol A and *m*-Phenylenediamine (*m*-PDA), were purchased from Sinopharm Chemnical Reagent Co. Ltd (Beijing, China) and used as received. Bisphenol A diglycidyl ether (DGEBA) were provides by Sinopec Baling Company (Yueyang, China). Solid polyphosphate(PBDP) were prepared through melt polymerization according to the reported literature.[12]
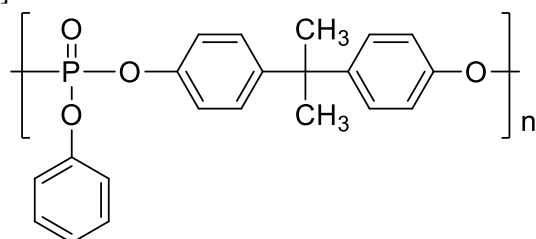
Figure1 Chemical Structure of PBDP

2.2 Preparation of EP/PBDP composites

PBDP was blended with DGEBA by mechanical stirring for 10 min at 80 °C. Then, *m*-PDA was added and mixed with the mixture for 5 min. EP/PBDP was cured at 80 °C and 120 °C for 2 h, respectiely. The formulations of EP/PBDP composites were listed in Table 1.

Table 1 Formulations, flame retardancy of EP composites.

Sample	EP	PBDP	UL-94 rating
EP	100	--	Fail
EP-1	95	5	Fail
EP-2	90	10	V-1
EP-3	85	15	V-1
EP-4	80	20	V-0

2.3 Characterization

The flammability of EP composites were operated according to the UL-94 standard with a sample size of 125 ×12.5 ×3 mm^3.

Pyrolysis combustion flow calorimetry (PCFC) was employed to study flame retardancy of EP and its composites according to ASTM D 7309.

X ray photoelectron spectroscopy (XPS) tests were measured on an PHI Quantera II SXMat 25 Wunder avacuum lower than 10^{-6} Pa.

Thermogravimetry analysis (TGA) was performed on a Metter-Toledo TGA/DSC-1thermogravimetric analyzer from 50 to 700 °C in nitrogen at different heating rates: 2.5 °C min^{-1}, 5 °C min^{-1}, 10 °C min^{-1}, and 20 °C min^{-1}. About 5.0 mg of samples were used for each test.

3. Results and discussion

3.1 Flammability of EP composites

UL-94 vertical burning tests are widely carried out to determine the flamability of the flame retardant materials. The results of UL-94 vertical buring tests were given in Table 1. Pure EP is a highly inflammable polymeric material and no rating in the UL-94 vertical buring test. When the addition of 10 wt% of PBDP into EP, EP-2 could achieve a UL-94 V-1 rating, indicating 10 wt% of PBDP could not enough to form a protective char layer to prevent the spread of the fire. After adding 20 wt%

PBDP into EP, EP-4 passed the UL-94 test with a V-0 rating.

The flammability of EP composites were measured by PCFC, which is a rapid method to evacuate the flammability of polymeric materials. The results, 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), were listed in Table 2. It can be observed from Fig. 2, the HRR value of pure EP increases very fast after decomposition, and a sharp peak of HRR (PHRR) (645.2 J g^{-1} K) appears. Compared with pure EP, the PHRR is decreased by adding PBDP. With the addition of 20 wt% of PBDP, the PHRR and THR of EP-4 is decreased, indicating that the fire spreading is decreased. Moreover, both EP-2 and EP-4 exhibit slightly lower HRC values of 381 and 378 J g^{-1} K compared with pure EP, which maybe associate with the flame inhibition effect of PBDP in the gas phase. From the data above, it can be demonstrated that the flammability of EP are reduced greatly by adding PBDP into EP.

Table 2 PCFC results of EP and EP/PSA composites

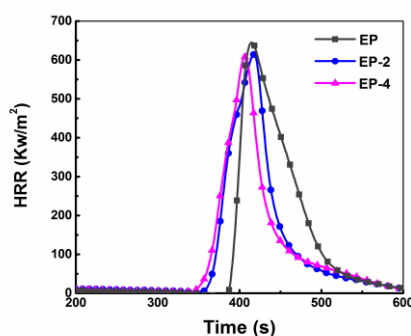|	HRC (J g^{-1} K)	THR(kJ g^{-1})	PHRR (J g^{-1} K)	Max PHRR Temperature (°C)
EP	399	25.4	645.2	430.6
EP-2	381	24.6	614.2	411.9
EP-4	378	23.4	608.3	405.0

Figure 2 HRR curves of EP composites.

3.2 Chemical components of the residual char of EP and EP/PBDP

XPS analysis were employed to investigate the chemical components of the residual char for EP and EP-4 after UL-94 vertical burning tests. The results are listed in Fig. 3 and Table 3. Three bands are observed from C_{1s} spectra: the peaks at around 284.6, 285.9 and 288.2 eV, assigned to the carbon atoms in C–H, C–C, C–O, and C=O, respectively. The O_{1s} spectrum has two peaks at around 532.1 and 531.2 eV, attributable to P=O in phosphate and –O– in the C–O–P or P–O–P structure. The peaks at around 399.1 and 400.5 eV, as seen for EP and EP, can be assigned to the N_{1s} of oxidized nitrogen compounds in the residual char. The single peak at around 134 eV in P_{2p} spectrum can be assigned to pyrophosphate and/or polyphosphate.[12]

From Table 3, it can be seen that the addition of PBDP changed the decomposition route. The atom percent of oxygen in the char residues of EP-4 is higher than that of EP. That can be explained by the formation of protective char layers and improved thermal oxidative resistance of matrix.

Table 3 XPS results of the residual char of EP and EP-4

Element	Binding Energy (eV)	Atomic Percentage (%)
EP		
C_{1s}	284.6, 285.9, 288.2	85.37
O_{1s}	532.1, 531.2	11.10
N_{1s}	399.1, 400.5	3.48
P_{2p}	134.7	0.05

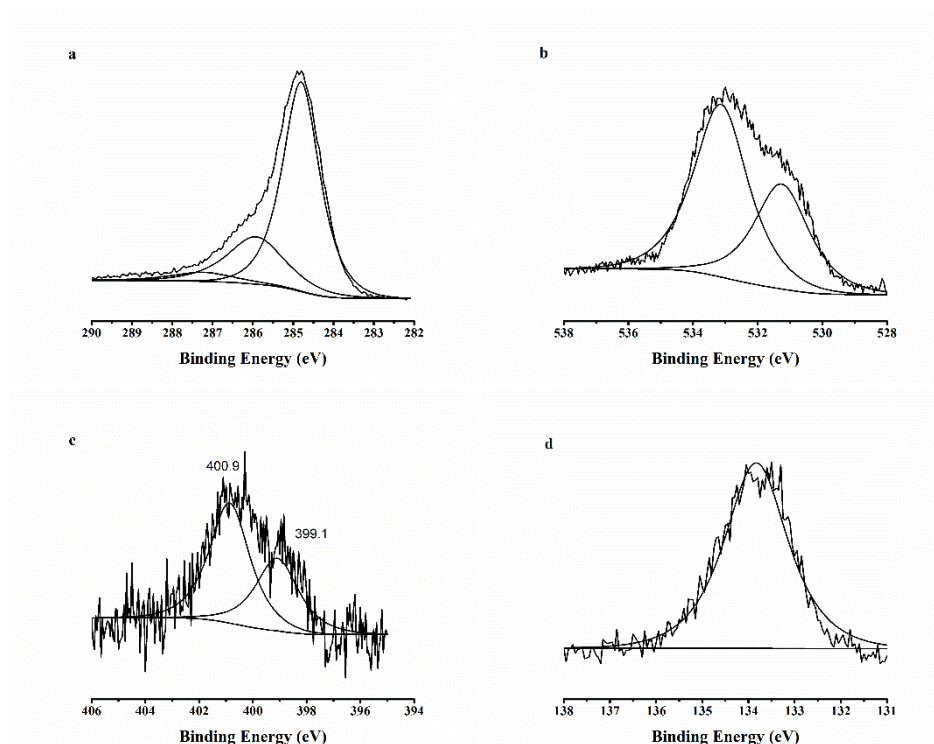| EP-4		
C_{1s}	284.8, 285.9, 287.2	79.51
O_{1s}	531.3, 533.2	14.40
N_{1s}	399.0, 400.8	4.03
P_{2p}	134.0	1.96

Figure 3 (a) C_{1s}, (b) O_{1s}, (c) N_{1s}, (d) P_{2p} XPS spectra of the char residue of EP-4.

3.3 Kinetics analysis of EP composites using the Kissinger Method
Kissinger method have been widely used to calculate the activation energy (E) and pre-exponential factor of the degradation reaction, which is obtained from plots of the logarithm of the heating rate *vs* the inverse of temperature at the maximum reaction rate (T_p) as constant heating rate. The equation of Kissinger method can be used:

$$\ln(\beta/T_p^2)=\ln(AR/E)-E/RT_{p.} \tag{1}$$

The TGA and DTG curves of EP and EP-4 at different heating rate are shown in Figs. 4 and 5, respectively.Accoring to equal 1, plots of $\ln(\beta/T_p^2)$ agaist $1/T_{max}$ produce the fitted straight lines (Fig. 6). As for EP and EP-4, the relativity of the various fitted straight lines is very good, indicating the feasibility of the Kissinger method. Table 3 presents 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-4 decrease to 142.10 kJ mol^{-1}, indicating the addition of PBDP promote the decomposition process and the formation of protective char layer.

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

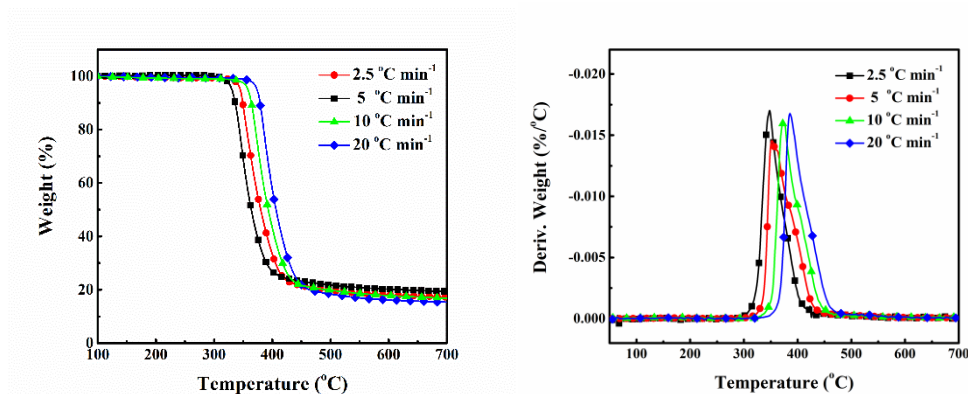| Sample	E_a (kJ mol^{-1})	Correln coeff (r)
EP	168.22	0.9920
EP-4	142.10	0.9999

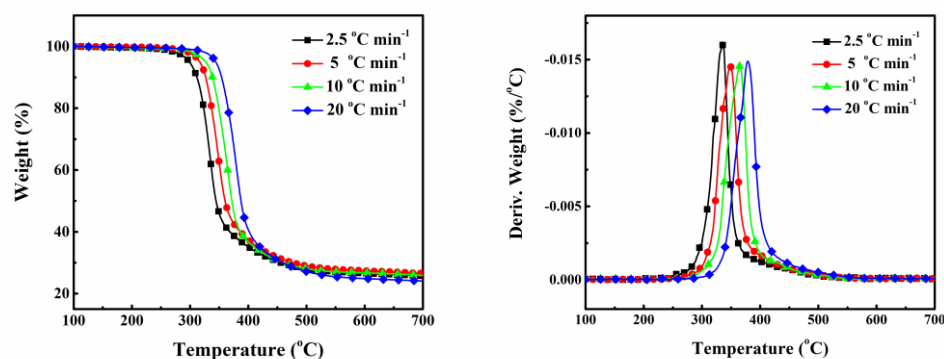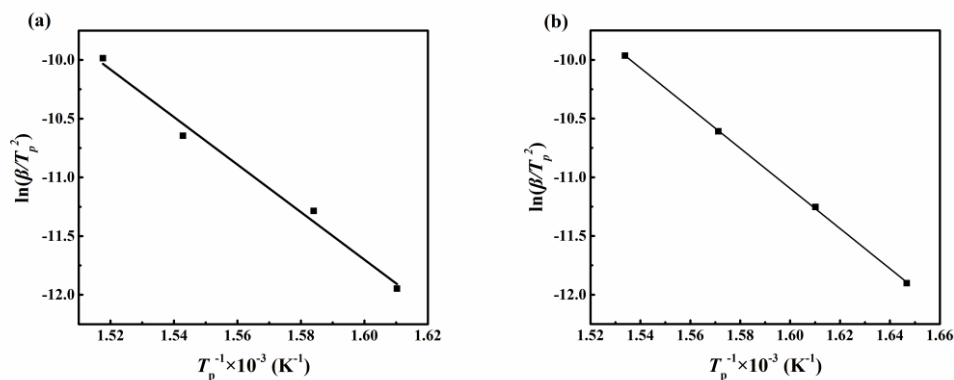Figure 4 TGA and DTG curves of EP under nitrogen

Figure 5 TGA and DTG curves of EP-4 under nitrogen

Figure 6 Plots of $\ln(\beta/T_p^2)$-1/T_p by Kissinger method(a: EP, b: EP-4)

4. Conclusions

Solid polyphosphate as additive flame retardant showed high flame retardancy for EP. With 20 wt% PBDP into EP, UL-94 V-0 rating were achieved. The results of PCFC and XPS analysis indicated EP/PBDP composites have lower heat release rate and improved thermal oxidative stability. The kinetic results showed PBDP could promote the decomposition of EP and char forming process.

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