Influence of T31 content on combustion and thermal degradation behaviors on flame-retardant epoxy composites

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Abstract To study the influence of the T31 content on the combustion properties and thermal degradation behaviors of flame-retardant epoxy composites, a series of flame-retardant epoxy composites were prepared using E-44 epoxy resin as matrix, T31 curing agent as curing agent, and intumescent flame retardant (IFR, based on phosphorus acid, melamine, and pentaerythritol) as flame retardant. The influence of T31 content on combustion behaviors and thermal degradation properties of the flame-retardant epoxy composites were studied using cone calorimeter test (CCT) and thermal-gravimetric analysis (TG), respectively. The cone calorimeter test results indicate that the decrease of T31 can significantly decrease the HRR, THR, SPR, and enhance the char residue of the epoxy composites. EP-4 with 7.0 wt% T31 shows the lowest HRR, SPR and the highest char residue. Furthermore, the TG results indicate that the EP-4 has the highest char residue among all the epoxy composites.

Keywords T31 · Combustion behaviors ·
Flame retardant · Epoxy

Introduction

Epoxy resin based on the diglycidyl ether of bisphenol A (DGEBA) has been widely used in many applications such as construction, coating, electrical work, and reinforced plastics because of their balance of excellent heat, solvent and chemical resistance, good mechanical and electrical properties.

However, their flammability limited their usage in the field of electrical/electronic substrate [1–3]. Halogen flame retardants had been widely used to improve flame retardancy of polymeric materials, but some of them have been prohibited because of environmental issues of halogen flame retardants and toxicity of some synergistic additives [4]. So it is really needed to find eco-friendly flame retardants to replace halogen ones.

Recently, halogen-free intumescent flame retardant (IFR) are attracting more and more attention from both academic and industrial communities for their multifold advantages including low toxic, low smoke, low corrosion, no corrosive gas, and so on [5, 6]. In a fire, the IFR system disintegrates to form the char layer before the matrix decomposes. The char layer itself does not combust, and the swollen char layer can isolate the transfer of mass and heat between materials and flame, protecting the underlying materials [6]. Intumescent systems are highly effective in polymers. A typical and widely studied IFR system is the combination of ammonium polyphosphate, pentaerythritol, and melamine (APP/PER/MEL) [7, 8]. In this system, the water resistance is poor.

What's more, because of epoxy resins' inherently brittle nature, additives and modifiers are generally used to improve their physical and mechanical properties [9]. It is reported that the equivalent ratio of epoxy resin and hardener can change the crosslinking density of epoxy resins, which can affect their physical and mechanical properties [10]. So, the crosslinking density may affect the intumescent flame-retardant properties of epoxy resins.

In this study, a series of epoxy composites were prepared with E-44 epoxy resin as matrix, T31 as curing agent, and single molecule intumescent flame retardant as flame retardant. And, the influence of T31 content on the intumescent flame- retardant properties of epoxy compounds was investigated by cone calorimeter test (CCT) and thermal-gravimetric analysis (TG).

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Experimental

Materials

E-44 epoxy resin used as film-forming material was purchased from the Shijiazhuang Stanley Technology Co. Ltd., China; Pentaerythritol (PER) and melamine (MEL) were purchased from BASF Chemical Co. Ltd., Tianjin, China; Phosphoric acid was from Yantai Sanhe Chemical Reagent Co. Ltd., China; Ethanol was obtained from Laiyang Economic Development Zone, Fine Chemical Plant, China. T31 curing agent from Jinan Wang Boley Chemical Co., Ltd. was used as curing agent. The IFR was synthesized in our laboratory based on phosphorus acid, melamine, and pentaerythritol with the molar ratio of 1:1:2.

Synthesis of single molecule intumescent flame retardant [11]

98.3 g pentaerythritol and 115.1 g phosphoric acid were added to a three-necked round bottom flask equipped with a mechanical stirrer, condenser, and thermometer. The mixture was heated at 90 °C in oil bath with a stirring rate of 380 r min^{-1} for 2.5 h, then stopped heating with a stirring rate of 200 r min^{-1} until there was condensed liquid on the wall. Then, 500 ml ethanol and 94.7 g melamine were added to the above three-necked round bottom flask. After completion of the ethanol and melamine addition, the reaction mixture was maintained at the temperature of 80 °C in oil bath with a stirring rate of 360 r min^{-1} for one hour. At last, the intumescent flame retardant was obtained after the suspension was filtrated and dried.

Preparation of epoxy composites

A certain amount of epoxy resins and IFR were weighted separately by electronic balance. Then, they were mixed with high speed dispersion machine at 2,000 r min^{-1} for 20 min. A corresponding amount of T31 curing agent was added into the above mixture, and stirred into uniform. And, the mixture containing T31 was poured into aluminum foil boxes with the size of $100 \times 100 \times 10$ mm, which can be used for cone calorimeter test. The mixture was cured in room temperature for 5 days. The formulations of flame-retardant epoxy resins are listed in Table 1.

Characterization

Cone calorimeter test

The cone calorimeter (Stanton Redcroft, UK) tests were irradiated at a radiation heat flux of 50 kW m^{-2} according to ISO 5660 standard procedures. Specimens for cone

Table 1 The formulations of the cured epoxy resins

Sample code	Epoxy/wt%	T31/wt%	IFR/wt%
EP-0	80.0	20.0	–
EP-1	49.0	21.0	30.0
EP-2	56.0	14.0	30.0
EP-3	59.5	10.5	30.0
EP-4	63.0	7.0	30.0

calorimeter test were $100 \times 100 \times 3$ mm^3. And, three samples has been carried out in the cone calorimeter test.

Thermogravimetric analysis (TG)

Thermogravimetric analysis was examined under nitrogen flow on a DT-50 (Setaram, France) instrument. About 10.0 mg of sample was put in an alumina crucible and heated from 25 to 900 °C. And, the heating rate was set as 10 K min^{-1}.

Results and discussion

Cone calorimeter test

Cone calorimeter is one of the most effective bench-scale methods that attempts to simulate real-world fire conditions, showing great important significance in the research and development of new flame-retardant materials [11–13].

Heat release rate (HRR)

Among many fire reaction properties, HRR is generally recognized as the most important in controlling fire hazards [14]. Figure 1 gives the HRR curves of the epoxy resin composites as a function of time. The HRR curve of EP-0 shows a very rapid increase after ignition and reaches the maximum (910 kW m^{-2}) at 140 s, with a total burning time of 225 s. The presence of IFR in cured epoxy samples significantly decreases the HRR values. With the decrease of T31, the HRR decreased, the combustion time increased, and the HRR curves gradually tend to be smoother. In the case of EP-4 with 7.0 wt% T31, it shows a slower combustion rate giving a bimodal HRR curve with a peak reduced to 237 kW m^{-2}, which is 75 % lower than that of EP-0. The above phenomenon can be explained by the crosslinking density of the epoxy composites, and it can be included that EP-4 has the least crosslinking density. In the cone calorimeter test, when the mass ratio of T31 and epoxy resin is high than 1:4, there was some small fragments flee from the sample surface, which is unfavorable for the formation of intumescent char residue. In the case of EP-3 and EP-4, there was no phenomena of small
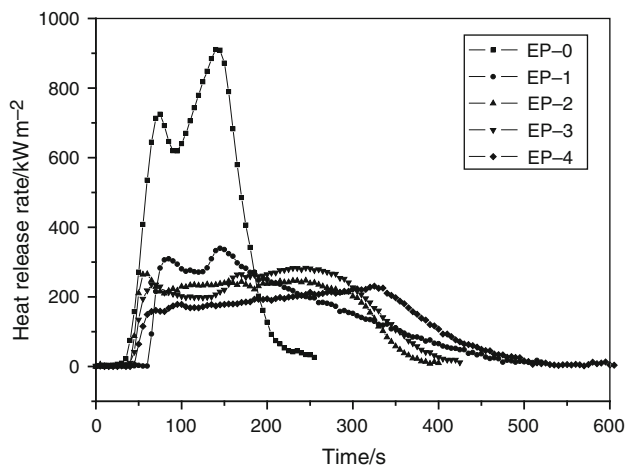
Fig. 1 The heat release rates of the epoxy composites at a flux of 50/kW m^{-2}

Fig. 2 Mass curves of the epoxy composites at a flux of 50/kW m^{-2}

fragments fleeing. There was good char layer rapidly formed on the samples of EP-3 and EP-4, which had low crosslinking density. Furthermore, the phenomenon also can be clearly illustrated by the char residue formed on the surface of the sample in the cone calorimeter test (Fig. 3).

Mass

Figure 2 shows the mass of the char residues of the epoxy composites. The addition of IFR can increase the char residues and prolong the combustion time. It can be seen that when EP-0 is completely burnt at 200 s, the epoxy composites containing the IFR are still not burnt for 40–50 % of their original masses. And, EP-4 has the highest char residue among all samples. The above results are correlated well with HRR results. That is, the greater the amount of char residue, the more is the decrease in HRR. There is compact char residue formed on the surface (Fig. 3) of the samples with IFR between 50 and 350 s in the cone calorimeter test [15–17]. The physical process of the char residue would act as a protective barrier, which can thus limit the oxygen diffusion to the substrate or low the volatilization rate [16, 18].

Digital photos of residues

Figure 3 gives the digital photos of residues of the series of epoxy composites. It can be found that EP-0 is almost complete combustion, and a more coherent and dense char formed with the addition of IFR. What's more, the char residues show different degrees of expansion. Expansion becomes higher with the T31 content decreasing. And, EP-4 shows the highest expansion, which indicates that the property of EP-4 is the best. Thus, it can explain why it has low HRR, high mass and low SPR.
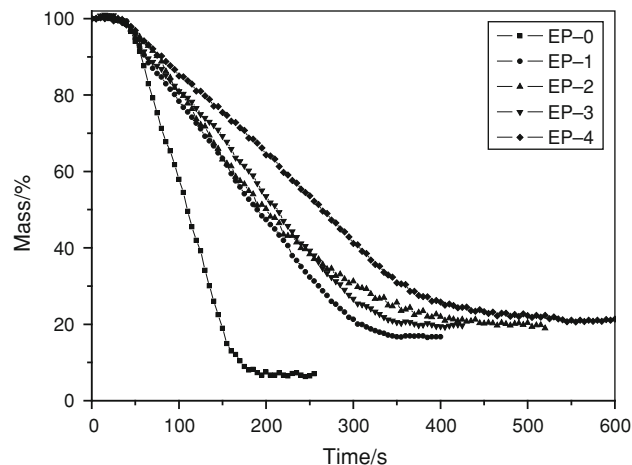
Total heat release (THR)

THR is almost independent of the external heat radiation, ventilation rate and the extent of damage of samples. It is a measurement of the internal energy of the material, to a certain extent, independent of the environmental factors [13, 19].

The THR curves of the epoxy composites are shown in Fig. 4. As can be seen from Fig. 4, the THR of epoxy composites with IFR have different degrees of reduction than EP-0 without any flame additives under the same conditions, which may be the fact that there is much char residue formed in the case of the sample with IFR. And, with T31 curing agent decreasing, THR of composites decrease. The slope of THR curve can be assumed as representative of fire spread [20, 21]. From Fig. 4, we can see that EP-4 has the lowest fire spread, which due to the char residue formed during combustion.

Smoke production rate (SPR)

The smoke consists of suspension of solid particles, liquid particles, and gaseous substances generated in the process of pyrolysis or combustion by the material, inseparable from the material combustion pyrolysis and other. Therefore, smoke production rate is also an important parameter to evaluate the flame retardancy. The bigger the SPR is, the worse the flame retardancy of the materials is [23–26].

Figure 5 shows the SPR curves of the epoxy composites at the heat flux intensity of 50 kW m^{-2}. It can be seen that IFR can significantly suppress the SPR of the epoxy composites. The SPR peak of EP-0 (0.22/m^2 s^{-1}) is the largest one of all the samples. And, the SPR reduces with the T31 curing agent content reducing. The EP-1 and EP-2 curves reach a peak rapidly then tend to be flat, yet there

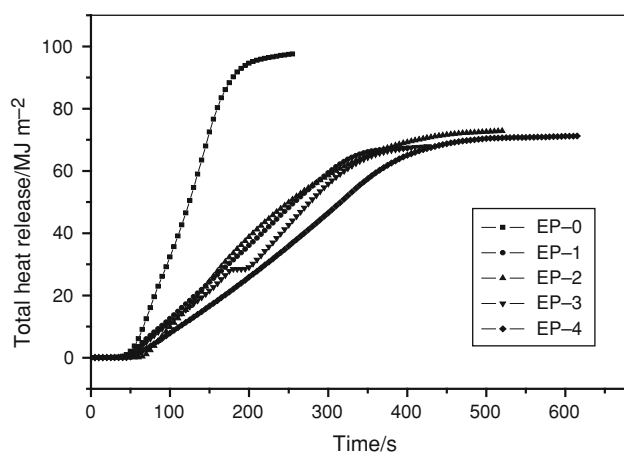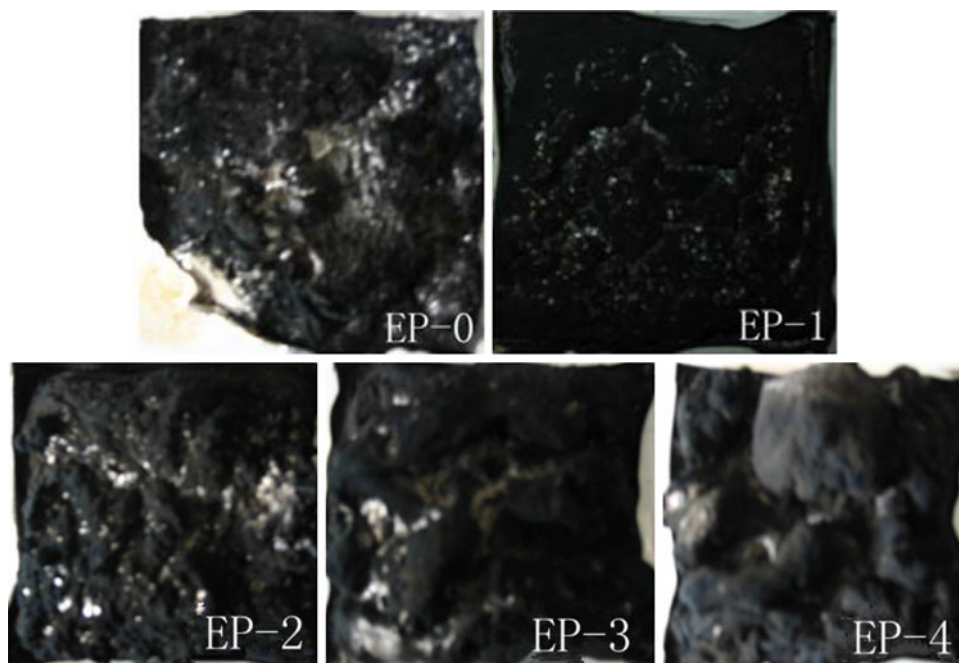Fig. 3 Char residue of the
epoxy composites

Fig. 4 The total heat release of the epoxy composites at a flux
50/kW m^{-2}

Fig. 5 The smoke production rate of the epoxy composites at a flux
of 50/kW m^{-2}

are no prominent peaks in SPR curves of EP-3 and EP-4, and the curves are serrated with small change, which due to the high quality dense carbon layer on the surface. Also, the phenomenon can be explained by the char residue.

Thermal properties of the cured epoxy resins

TG is a commonly employed approach to evaluate the thermal stability and thermal decomposition behavior at various temperatures by measuring the onset degradation temperature ($T_{5.0\%}$) at which 5.0 % mass loss occurs, the temperature for the maximum degradation rate (T_{max}), and char residue [18, 19, 22–28]. Figure 6 showed the TG curves of the cured epoxy composites, respectively. It can
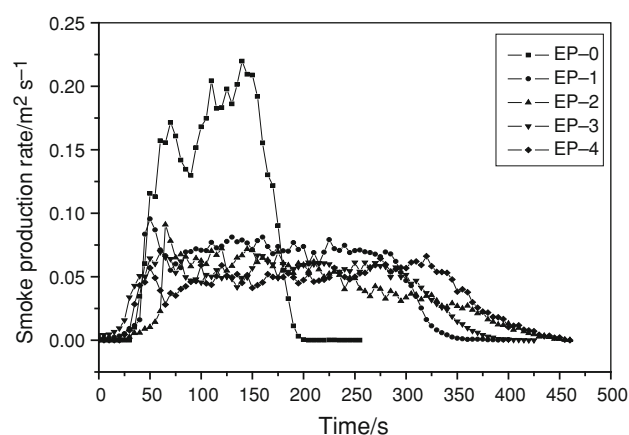
be seen that EP-0 has one broad main decomposition process. It begins to decompose at about 312 °C (5.0 wt% mass loss). The temperature of maximum mass loss rate (T_{max}) is 370 °C, as shown in Fig. 6. The char residue of EP-0 at 700 °C is about 10.8 wt%. The initial decomposition temperatures of the epoxy composites with IFR, from EP-1 to EP-4, are 271, 261, 253, and 253 °C, respectively, which are all lower than EP-0. In the degradation process, epoxy composites with IFR decompose faster than EP-0 owing to the less thermal stability of P–O–C structure in intumescent flame retardant, which can degrade into polyphosphoric acid, catalyzing epoxy resin degradation. It can be seen from Fig. 6 that the char residues (Yc, wt%) at 900 °C of the epoxy composites are, from EP-0 to EP-4,
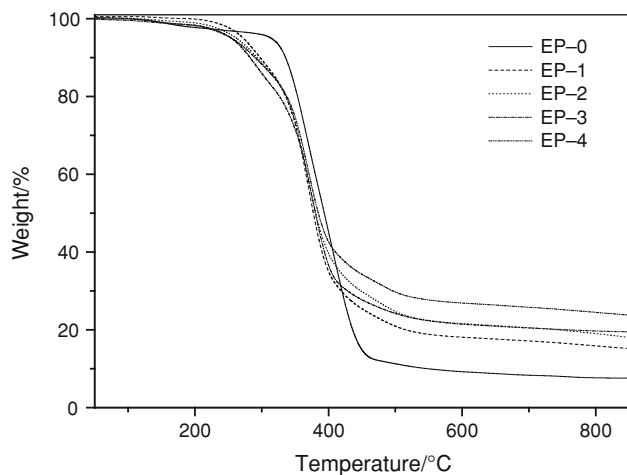
Fig. 6 TG curves of the epoxy resin composites

7.59, 14.85, 17.52, 19.41, and 23.52 wt%, respectively. The above results indicate that the flame-retardant epoxy composites with IFR have more char residue than the sample without IFR. Furthermore, the char residue increased with the decrease of T31.

Conclusions

In this study, the epoxy composites were synthesized based on E-44 epoxy resin, T31 curing agent, and IFR. The results from the cone calorimeter test indicate that the addition of IFR can significantly decrease the HRR, THR, SPR, and enhance the char residue of the epoxy composites. EP-4 shows the lowest HRR, SPR, and the highest char residue, which indicates that EP-4 with the lowest content of T31 has the best flame retardancy comparatively. The TG results show IFR decreases the initial decomposition temperatures of cured epoxy samples, and enhances the residue amount at high temperature. EP-4 with 7.0 wt% T31 content shows the highest char residue among all samples.

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