

THERMAL DEGRADATION AND FLAME RETARDANCY OF EPOXY RESINS CONTAINING INTUMESCENT FLAME RETARDANT

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Pentaerythritol diphosphonate melamine-urea-formaldehyde resin salt, a novel cheap macromolecular intumescent flame retardants (IFR), was synthesized, and its structure was a caged bicyclic macromolecule containing phosphorus characterized by IR. Epoxy resins (EP) were modified with IFR to get the flame retardant EP, whose flammability and burning behavior were characterized by UL 94 and limiting oxygen index (LOI). 25 mass% of IFR were doped into EP to get 27.2 of LOI and UL 94 V-0.

The thermal properties of epoxy resins containing IFR were investigated with thermogravimetry (TG) and differential thermogravimetry (DTG). Activation energy for the decomposition of samples was obtained using Kissinger equation. The resultant data show that for EP containing IFR, compared with EP, IFR decreased mass loss, thermal stability and R_{max} , increased the char yield. The activation energy for the decomposition of EP is $230.4 \text{ kJ mol}^{-1}$ while it becomes $193.8 \text{ kJ mol}^{-1}$ for EP containing IFR, decreased by 36.6 kJ mol^{-1} , which shows that IFR can catalyze decomposition and carbonization of EP.

Keywords: degradation, epoxy resins, flame retardant, synthesis, TG

Introduction

Epoxy resins are one of the most versatile classes of polymers. Their long service life and good physical and chemical properties often provide a favorable cost benefit ratio when compared to other thermosets [1, 2]. When listing their advantages, the high flammability of epoxy resins certainly has to be considered a major disadvantage.

The main fields fire retardancy of epoxy resins are required in electronic and electrical applications (printed-circuit boards, encapsulations) and transportation (automobiles, trains and military and civilian aircraft) [3–5]. Therefore, cured epoxy resins containing bromine are particularly useful when flame retardancy is desired. However, major problems encountered with this system include the generation of toxic and corrosive fumes during combustion and waste disposal. This led to the search for alternative flame retardants.

The generations of IFR have the advantages of low smoke, low toxicity, low corrosion and no molten dropping during a fire [6–8]. Generally, IFR contains three main ingredients: acid source, carbon source and gas source. Phosphorus-containing compounds are often used as an acid source in IFR. They degrade to form char layer before the polymer decomposes during a fire. Nitrogen-containing compounds are used as gases source in IFR system, to produce incombustible gases when they degrade. The heat gases can swell the

just formed char. The swollen char can isolate the transfer of mass and heat between the materials and the flame in a fire. That protects the unburned materials [9–11]. However, the three ingredients often come from different compounds in IFR, which all were incorporated into EP through blending. In our work, a novel cheap macromolecular IFR, which contains acid source, gas source and char source at the same time, has been synthesized. The IFR is incorporated into EP, whose flame retardancy and the thermal degradation behaviors are studied here.

Experimental

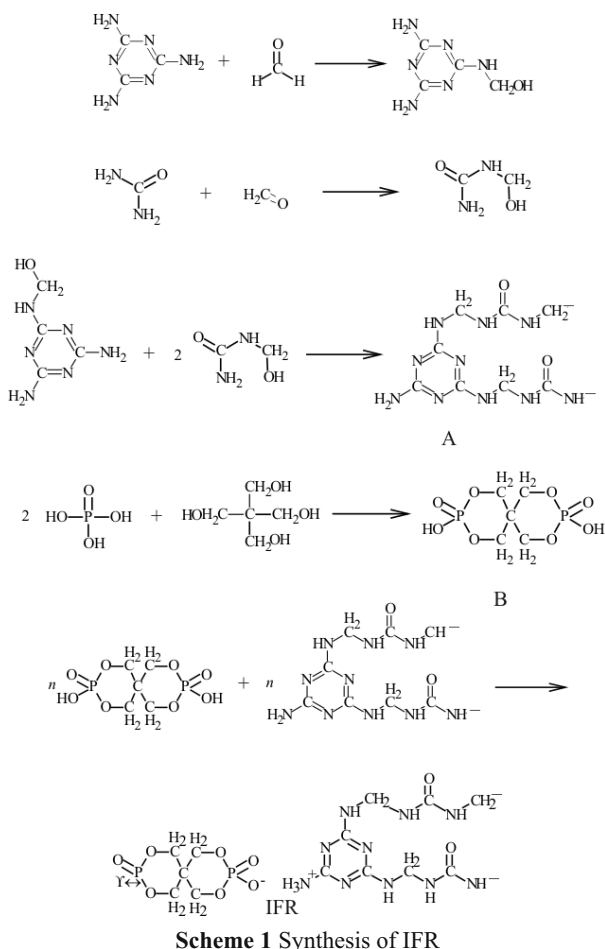
Materials

Pentaerythritol, 85% of phosphoric acid, melamine, 37% formalin as formaldehyde, and urea were received from Beijing Chemical Reagents Co.

Synthesis of IFR

37% formalin as formaldehyde [F] 1 mol was brought to pH 8–8.5 with NaOH and heated. Then melamine [M] 0.2 mol and urea [U] 0.5 mol were added to the above solution, stirred until dissolved and heated under reflux for 50 min. Heating was stopped and the solution was allowed to cool to get MUF prepolymer A.

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85% phosphoric acid 1 mol and pentaerythritol 0.5 mol were mixed, heated to 120°C, stirred for 4 h until without water distilled to get caged bicyclic pentaerythritol diphosphonate B. B was added slowly into A under stirring to obtain IFR (Scheme 1).

Characterization of IFR

IR (KBr), (cm^{-1}): 2938, 2890 (w, CH_2), 1240~1280 (P=O), 1521, 814 (C=N), 1278.8 (P=O), 1020, 880, 780, 655 (dicyclic P-O-C) (Fig. 1).

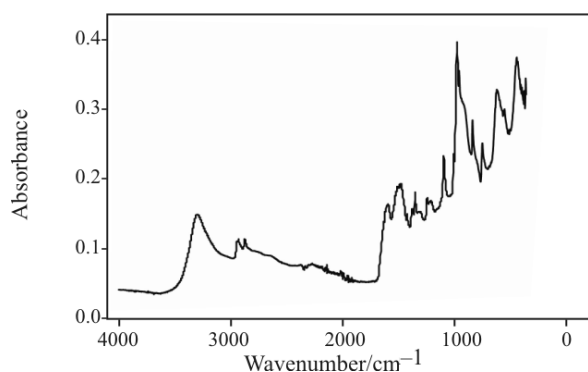


Fig. 1 The FTIR spectra of IFR

Instrumental methods

The IR spectra were measured on a NEXUS-470 FTIR (Nicolet) spectrophotometer using KBr. LOI values were determined in accordance with ASTM D2863-70 by means of a General Model HC-1 LOI apparatus. The UL 94 vertical burning classification was obtained using an ATLAS HVUL 2 burning chamber according to FMVSS 302/ZSO3975. The sample was 127×12.7×3 mm. TG and DTG were carried out on a DTA-2950 thermal analyzer (Dupont Co., USA) under a dynamic nitrogen (dried) atmosphere at a heating rate of 10°C min⁻¹.

Results and discussion

Flame retardancy of epoxy resins

Flame retardant properties of EP containing different IFR were list in Table 1. From the Table 1, we can see the good flame retardancy of the IFR. With the increases of IFR, the LOI values increase. 25 mass% of IFR were doped into EP to get 27.2 of LOI and UL 94 V-0. The epoxy resins obtained qualified for the UL 94 V-0 rating at low phosphorus contents of 3.60 to 4.32% phosphorus with a LOI of up to 28.4%.

Table 1 Flame retardant properties of EP containing different content of IFR

IFR/%	P/mass%	N/mass%	LOI/%	UL 94
0	—	—	20.0	not rated
10	1.44	1.43	23.8	not rated
15	2.16	2.15	25.0	not rated
20	2.88	2.86	26.0	V-1
25	3.60	3.58	27.2	V-0
30	4.32	4.29	28.4	V-0

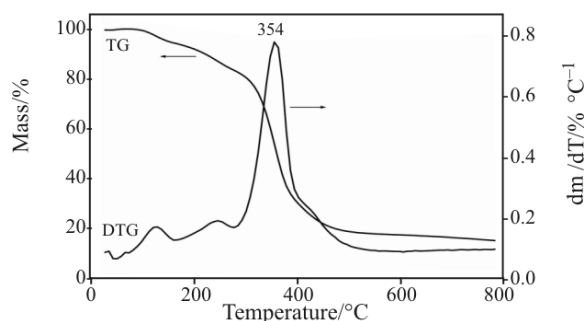
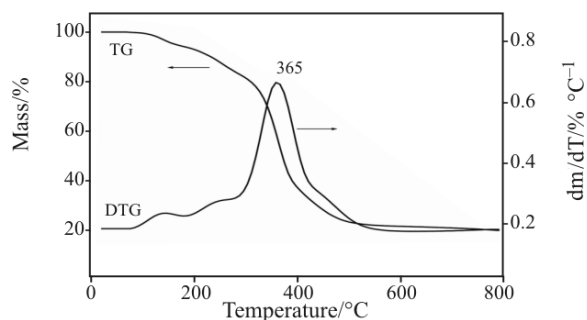
Degradation of epoxy resins

The simultaneous DTG and TG curves of EP-1 and EP-2 were carried out in dynamic nitrogen from ambient temperature to 800°C and are shown in Figs 2 and 3. The initial decomposition temperature (IDT), integral procedure decomposition temperature (IPDT), the mass loss at IDT, char yield at 600°C, temperatures at the maximum mass loss rate (T_m) and the value of the maximum mass loss rate (R_{max}) were measured, list in Table 2.

When the flame retardant elements are incorporated into polymeric materials, the mass loss pattern of the polymers is altered. Phosphorus groups decompose at relatively low temperature to form a heat-resistant char, to retard the mass loss rate of the

Table 2 Thermal data of the epoxy resins from TG analysis in nitrogen

No.	IFR/%	IDT/°C	IPDT/°C	Mass loss at IDT/%	Char yield/%	$T_m/°C$	$R_{max}/\% \text{ } ^\circ\text{C}^{-1}$	$E_a/\text{kJ mol}^{-1}$
EP-1	–	310	422	21.1	15.2	354	0.78	230.4
EP-2	25	306	432	22.1	19.1	365	0.65	193.8

**Fig. 2** TG and DTG curves of EP**Fig. 3** TG and DTG curves of EP containing IFR

polymers at high temperatures [12–14]. Nitrogen-containing compounds produce incombustible gases when they degrade. The heat gases can swell the just formed char. The swollen char can isolate the transfer of mass and heat between the materials and the flame in a fire. That protects the unburned materials. The actions play some critical roles in flame retarding polymeric materials through condensed-phase mechanisms as well as gas-phase mechanism.

From the Figs 2 and 3, it can be seen that there is a main and quick decomposition stage, and the mass loss behavior of EP containing IFR is found to follow the patterns discussed above. From Table 2, for EP containing IFR (EP-2), compared with EP-1, R_{max} ($0.65\% \text{ } ^\circ\text{C}^{-1}$) are decreased, and char yields (19.1%) are increased. The decrease significantly of mass loss rates lowers the amount and rate of release of combustible products from the epoxy resins' decomposition, consequently depressing the resins' flammability. The increase of char yields agrees with mechanism of flame retardant [15]. Introduction of flame-retardants leads to more char formed at the expense of flammable volatile products of thermal

degradation, thus suppressing combustion and increasing the LOI.

Thermal stability of epoxy resins

The thermal stability of the epoxy resins is assessed with two parameters: IDT and IPDT. IDT indicates the apparent thermal stability of the epoxy resins, i.e., the failure temperatures of the resins in processing and moulding. On the other hand, IPDT exhibits the resins' inherent thermal stability, i.e. the decomposition characteristics of the resins' volatile composition. From Table 2, phosphorus-containing epoxy resins (EP-2) show relatively lower IDT than do the phosphorus-free resin (EP-1), since phosphorus-groups decompose at low temperatures. On the other hand, the existence of IFR (EP-2) exhibits higher IPDT than the EP-1, retarding the mass loss rate of the polymers at high temperatures. The high IPDT implies the epoxy resins' potential application in highly anti-thermal coatings and thermal insulating materials.

The decomposition activity energies

The decomposition activity energies of EP-1 and EP-2 were studied by the equation of Kissinger [16]. The equation is as follows:

$$\frac{d \ln(\Phi/T_m^2)}{d(1/T_m)} = \frac{-E_a}{R}$$

where Φ is the rate of temperature increase in K min^{-1} ($\Phi=2, 5, 10, 20$), T_m the maximum temperature at the peak position in K , E_a the decomposition activity energy, and R the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). From the slope of the plot of $\ln(\Phi/T_m^2)$ vs. $1/T_m$, the activation energy can be calculated, i.e. $E=R \times \text{slope}$. Table 2 presents the activation energies (E_a) for EP-1 and EP-2.

The activation energy for the decomposition of EP is $230.4 \text{ kJ mol}^{-1}$ while it becomes $193.8 \text{ kJ mol}^{-1}$ when IFR is doped into, decreased by 36.6 kJ mol^{-1} , which shows that IFR can catalyze decomposition and carbonization of EP. It is supported by the lower IDT (306°C) and higher mass loss (22.1%) at IDT.

Conclusions

We succeed in synthesizing a novel cheap macromolecular IFR with a structure of a caged bicyclic pentaerythritol diphosphonate. 25 mass% of the IFR are doped into EP to get 27.2 of LOI and UL 94 V-0. For EP containing IFR, compared with EP, incorporating IFR into epoxy resins alters degradation characteristics, which decreases mass loss and R_{\max} , increases the char yield. However, for EP containing IFR, the IDT and activation energy are decreased, and higher mass loss at IDT are increased, which shows the stability was decreased. In the thermal degradation of EP containing IFR, phosphorus groups decompose at relatively low temperature, then catalyzing decomposition and carbonization of EP to form a heat-resistant char, retarding the mass loss rate of the EP at high temperatures. Nitrogen serving as blowing agents and char-reinforcing components, leads to the production of intumescent chars which protects the underlying combustible substrate to get good flame retardancy.

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