A Novel Intumescent Flame-Retardant Epoxy Resins System

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ABSTRACT: Pentaerythritol diphosphonate melamine–dicyandiamide–formaldehyde resin salt, a novel macromolecular intumescent flame retardants (IFR), was synthesized, and its structure was a caged bicyclic macromolecule containing phosphorus characterized by IR, NMR and element analysis. The flame retardancy and thermal behavior of a new IFR system for epoxy resin were investigated by LOI, UL-94 test, TG, and IR. Activation energy for the decomposition of samples was obtained using Kissinger equation. 25% of weight of IFR were doped into epoxy resin to get 27.5 of LOI and UL 94 V-0. The TG curves and IR spectra show that IFR decreases the initial decomposition temperature and the maximum weight loss rate of epoxy resin, and enhances the thermal stability of epoxy resin at high temperatures and char yield. The activation energy for epoxy resin containing IFR was decreased by 44.8 kJ/mol, which shows that IFR can catalyze decomposition of epoxy resin. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2346–2351, 2010

Key words: epoxy resins; degradation; flame retardant; synthesis; TG

INTRODUCTION

The ecological safety of polymer flame retardant has become a major subject in the modern polymer industry, and there is an international demand for the control of polymer flammability without the use of halogenated additives. Consequently, current research is mainly focused on looking for environmental friendly additives in the form of organophosphorus compounds, which are being thought as the alternatives of the halogen containing flame retardants.[1,2]

Compared to halogen containing flame retardants, the generations of intumescent flame retardants (IFR) have the advantages of low smoke, low toxicity, low corrosion and no molten dropping during a fire.[3–5] 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.[6–8] Among IFR system, the organophosphorus flame retardants, caged bicyclic phosphates such as 1-Oxo-4-methoxy-2,6,7-trioxa-1- phosphabicyclo[2,2,2]octane (PEPA),[9] melamine salt of bis (2,6,7-trioxa-l- phosphabicyclo[2.2.2]octane-4-methanol) phosphate (Melabis),[10–12] phosphate tri(2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane-1-oxo-4-methanol) phosphate (Trimer),[13] have attracted many interests, and many investigations have been done about them. However, these IFRs were synthesized in oganic reagents, using POCl₃, which are expensive, not environment friendly. In our work, a novel cheap macromolecular IFR, environment friendly, 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 dicyandiamide were received from Beijing Chemical Reagents Co.

Instrumentation

The IR spectra were measured on a NEXUS-470 FTIR (Nicolet) spectrophotometer using KBr. The
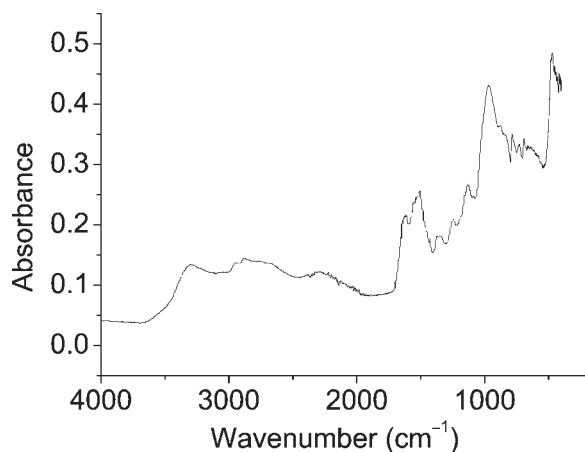

Figure 1 The fourier transform IR spectra of IFR.

^{13}C-NMR spectra were recorded on a DSX—300MHz spectrometer using DMSO-D6 as solvent. The elemental analysis was carried out using a Carlo Eroa 1102 Elemental Analyzer. 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. Thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out on a DTA-2950 thermal analyzer (Dupont, Wilmington, DE) under a dynamic nitrogen (dried) atmosphere at a heating rate of 10°C min^{-1}.

Synthesis of IFR

Formalin (37%) as formaldehyde [F] 1 mol was brought to PH 8–8.5 with NaOH and heated. Then melamine [M] 0.3 mol and dicyandiamide [D] 0.1 mol were added to the above solution, stirred until dissolved and heated under reflux for 50 min. Heat-

ing was stopped and the solution was allowed to cool to get MDF prepolymer A.

Eighty five percent 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. The reactions are shown in Scheme 1.

Characterization of IFR

The fourier transform IR and ^{13}C-NMR spectra of IFR are shown in Figures 1, 2.

IR (KBr), (cm^{-1}): 3300 (—OH, N—H), 2952, 2890(w, CH$_2$), 1253 (P=O), 1521, 814 (C=N), 1012, 780, 655 (dicyclic P—O—C).

^{13}C-NMR (300 MHz, DMSO-D$_6$, ppm): 38.610 ~ 40.288 (DMSO—D$_6$), 49.915 (CH$_2$ of cycle), 55.368 ~ 55.969 (—NH—CH$_2$—NH—), 64.780 (—NH—CH$_2$OH), 71.415: —N (CH$_2$—) —CH$_2$OH, 159.094 ~ 159.674: —NH—C(NH) —NH—, 90.559 (formaldehyde), 160.089 ~ 160.923 (—N=C in melamine), 162.555 ~ 166.708 (—NH—CO—NH—).

Element analysis (%): ω(P)=14.85, ω(N) = 14.77.

RESULTS AND DISCUSSION

Flame retardancy of epoxy resins

Flame retardant properties of EP containing different IFR were list in Table I. From the Table I, we can see the good flame retardancy of the IFR. With the increases of IFR, the LOI values increase. 25% weight of IFR were doped into EP to get 27.5 of LOI and UL 94 V-0. The epoxy resins obtained qualified for the UL 94 V-0 rating at low phosphorus contents of 3.70 to 4.44% phosphorus with a LOI of up to 28.5%.
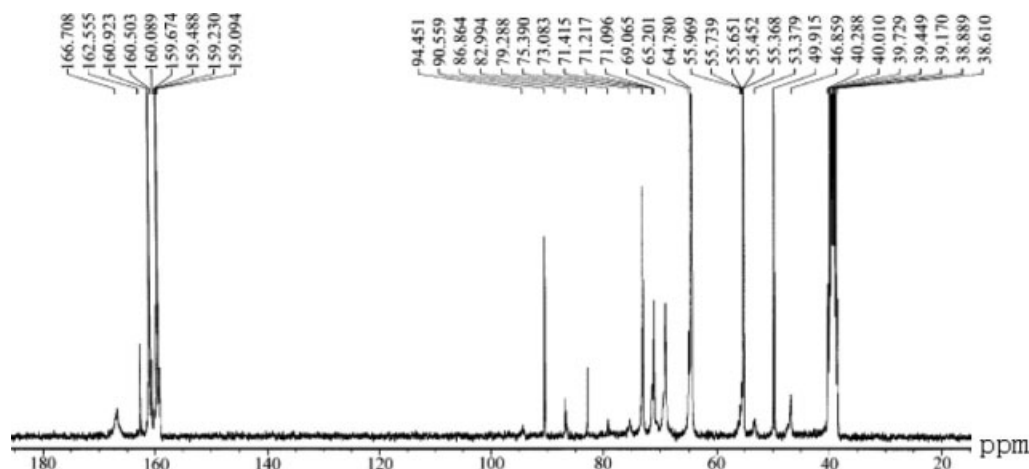

Figure 2 The ^{13}C-NMR spectra of IFR.

TABLE I
Flame Retardant Properties of EP Containing Different Content of IFR

IFR (%)	LOI (%)	UL 94
0	20.0	Not rated
10	24.6	Not rated
15	25.7	Not rated
20	26.5	V-1
25	27.5	V-0
30	28.5	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 Figures 3, 4. The initial decomposition temperature (IDT) is define as the temperature when the weight loss is 5%, integral procedure decomposition temperature (IPDT), char yield at 600°C, temperatures at the maximum weight loss rate (T_m) and the value of the maximum weight loss rate (R_{max}) were measured, list in Table II.

From the Figures 3, 4 and Table II, it can be seen that there is some difference between EP-1 and EP-2 in the thermal behavior. For EP containing IFR (EP-2), compared with EP-1, IDT are decreased. It is suggested (Scheme 2) that the initial reactions are dephosphorylation of EP-2 and that the released acids then catalyze the dehydration and decomposition of EP to form a carbonaceous char, which changed into heat-resistant intumescent char by gaseous products such as NH_3 to retard the weight loss rate of EP at high temperatures.[14–16] Moreover, R_{max} (0.69%/°C) are decreased, and char yields (23.7%) are increased. The decrease significantly of weight 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.[17] Introduction of flame-retardants
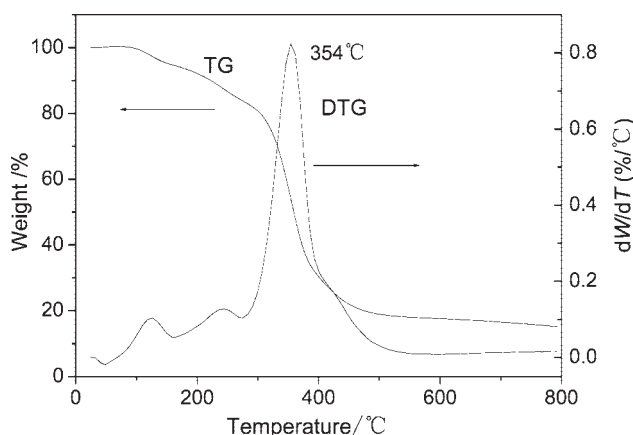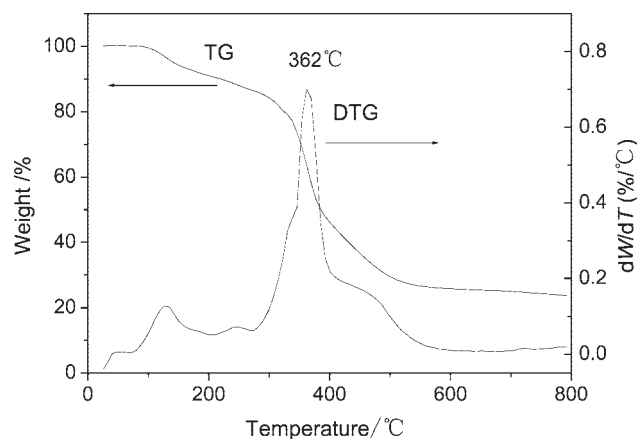

Figure 4 TG and DTG curves of EP containing IFR.

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 molding. On the other hand, IPDT exhibits the resins' inherent thermal stability, i.e., the decomposition characteristics of the resins' volatile composition. From Table II, 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 weight loss rate of the polymers at high temperatures. The high IPDT implies the epoxy resins' potential application in highly antithermal coatings and thermal insulating materials. The temperatures at the maximum weight loss rate (T_m) are also increased.
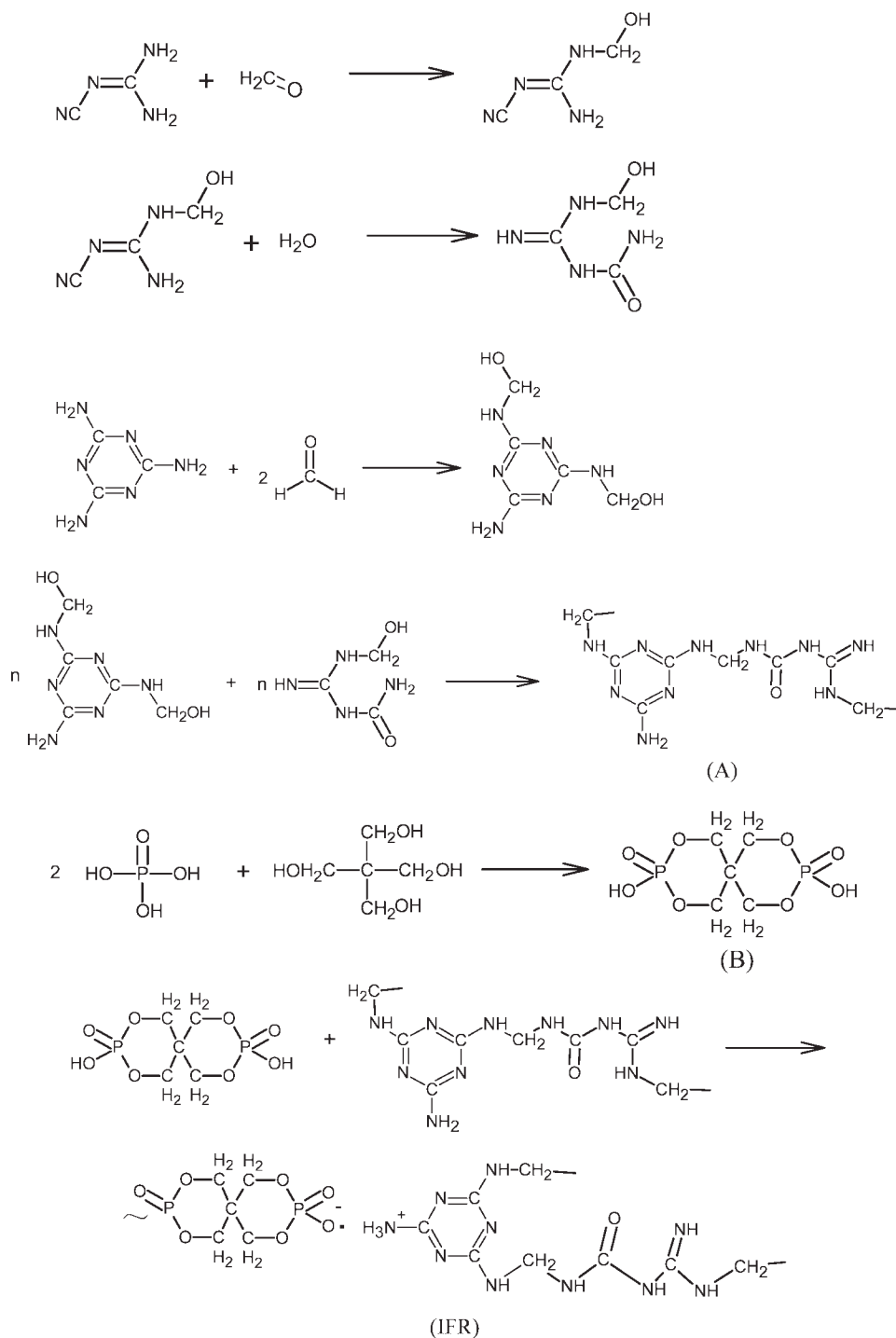
The decomposition activity energies

The decomposition activity energies of EP-1 and EP-2 were studied by the equation of Kissinger.[18] The equation is as follows:

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

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

Figure 3 TG and DTG curves of EP.

TABLE II
Thermal Data of the Epoxy Resins from Thermogravimetrtic Analysis

No.	IFR (%)	IDT (°C)	IPDT (°C)	Char yield (%)	T_m (°C)	R_{max} (%/°C)	Ea/(kJ/mol)
EP-1	–	160	422	15.2	354	0.82	230.4
EP-2	25	142	492	23.7	362	0.69	185.6

Scheme 1 Synthesis of IFR.
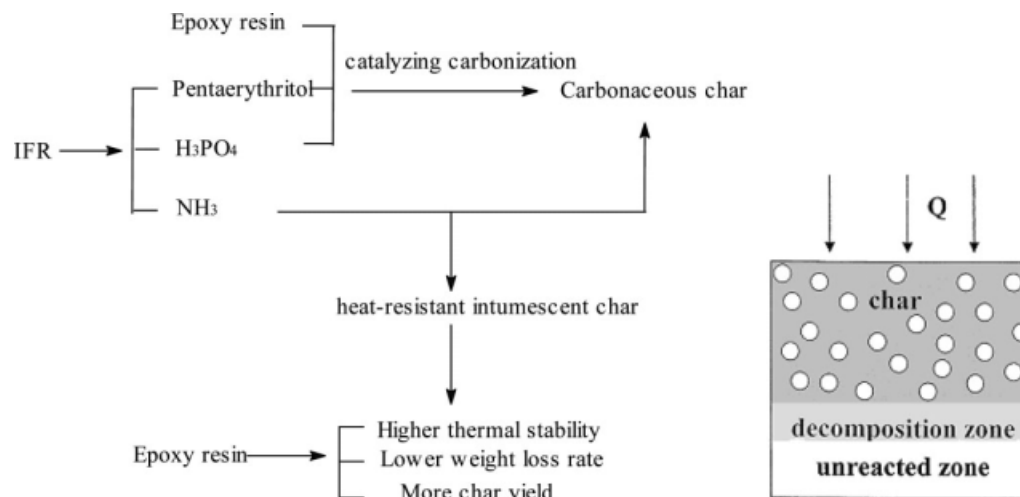
Scheme 2 Thermal degradation mechanism of epoxy resin containing IFR.

E = R × slope. Table II presents the activation energies (Ea) for EP-1 and EP-2.

The activation energy for the decomposition of EP is 230.4 kJ/mol while it becomes 185.6 kJ/mol when IFR is doped into, decreased by 44.8 kJ/mol, which shows that IFR can catalyze decomposition and carbonization of EP. It is supported by the lower IDT (142°C).

Spectral studies of chars

The IR spectra of the chars of EP-1 and EP-2 obtained at different temperatures (200°C, 300°C, 400°C, and 500°C) were recorded as shown in Figures 5–8.

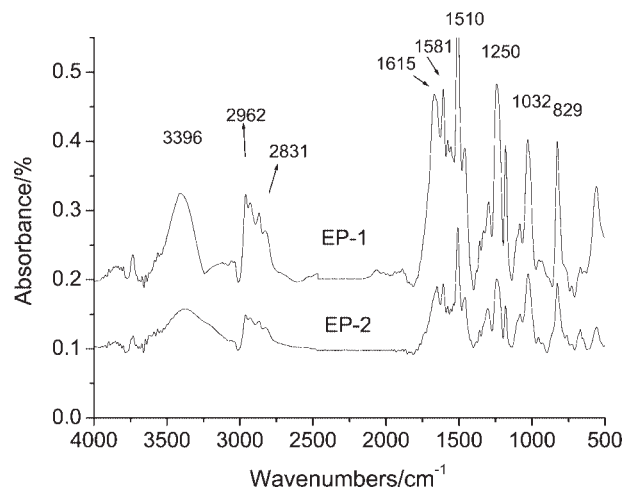From Figure 5, we can see the similar IR spectra of EP-1 and EP-2 charred at 200°C: 3396 cm^{-1} (O—H, N—H), 2962 cm^{-1}–2831 cm^{-1} (CH$_2$—), 1615 cm^{-1} (C=C), 1581 cm^{-1}, 1510 cm^{-1} (C=C in Ar), 1250 cm^{-1} (Ar-O-R), 1032 cm^{-1} (C—O), 829 cm^{-1} (C—H in Ar). However, the intensities of these absorption bands for the EP-2 are all much lower than those for EP-1, which shows that the decomposition occurs more for EP-2 than EP-1 at 200°C. This may be accounted for the dephosphorylation of EP-2 then the catalyzing decomposition of the released acids.

Figure 6 presents the similar IR spectra of EP-1 and EP-2 charred at 300°C. The characteristic absorption bands of EP such as 3396 cm^{-1} (O—H, N—H), 2962 cm^{-1}–2831 cm^{-1} (CH$_2$—), 1615 cm^{-1} (C=C), 1581 cm^{-1}, 1510 cm^{-1} (C=C in Ar), 1250 cm^{-1} (Ar-O-R), 1032 cm^{-1} (C—O) and 829 cm^{-1} (C—H in Ar) still exist though their intensities are decreased, which shows that the skeleton of EP is not broken.
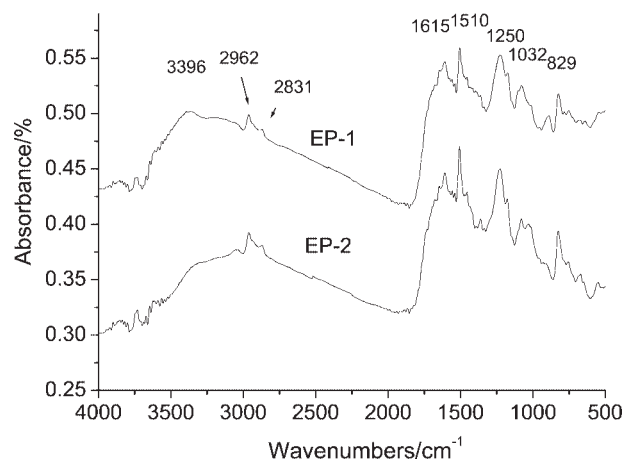

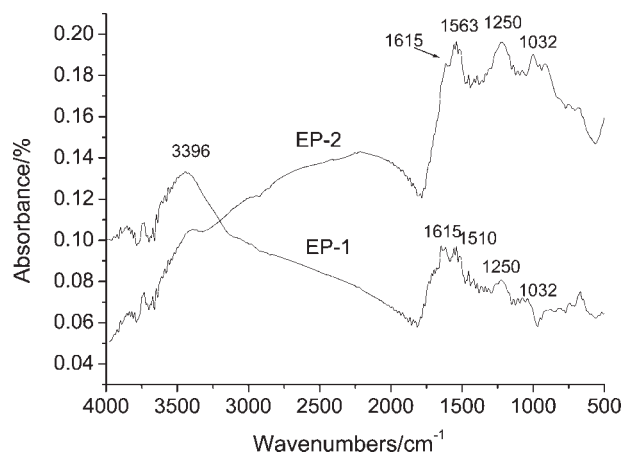Figure 5 The fourier transform IR spectra of EP-1 and EP-2 charred at 200°C.

Figure 6 The fourier transform IR spectra of EP-1 and EP-2 charred at 300°C.

Figure 7 The fourier transform IR spectra of EP-1 and EP-2 charred at 400°C.

Figure 8 The fourier transform IR spectra of EP-1 and EP-2 charred at 500°C.

Figure 7 presents that the bands at 2962 cm^{-1}–2831 cm^{-1} (CH$_2$—), 829 cm^{-1} (C—H in Ar) disappear, and other characteristic absorption bands are much decreased, which shows that the skeleton of EP is broken. The intensities of main absorption bands are more than those of EP-1, which shows that decomposition occurs less for EP-2 than EP-1 at 400°C. This is due that the existence of IFR (EP-2) enhances the thermal stability of EP at high temperatures, which is consistent to the result in TG. However, intensity of 3396 cm^{-1} (O—H, N—H) of EP-1 is much more than that of EP-2, which is due that the acids produced in dephosphorylation of EP-2 catalyze the dehydration of EP, consuming the bands (O—H, N—H). The similar results can be seen in Figure 7 where the absorption bands at 3396 cm^{-1} (O—H, N—H) for EP-1 exist.

From Figure 8, the broad absorption bands at 1622 cm^{-1} indicates formation of conjugated aromatic compounds containing C=C and C=O, which shows that the resultant product is a highly condensed and crosslinked aromatic components.

CONCLUSIONS

We succeed in synthesizing a novel cheap macromolecular IFR with a structure of a caged bicyclic pentaerythritol diphosphonate. 25% weight of the IFR are doped into EP to get 27.5 of LOI and UL 94 V-0. For EP containing IFR, compared with EP, incorporating IFR into epoxy resins alters degradation characteristics, which decreases weight loss, R_{max}, IDT
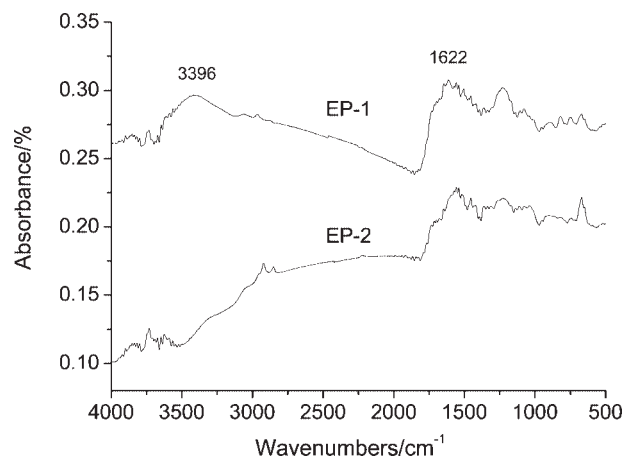
and activation energy, increases the char yield. In the thermal degradation of EP containing IFR, phosphorus groups decompose at relatively low temperature, then catalyzing dehydration, decomposition and carbonization of EP to form a heat-resistant char, retarding the weight loss rate of the EP at high temperatures. IR spectra results agree with TG, indicating a highly condensed and crosslinked aromatic components of char.

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