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Combustion behavior and thermal degradation properties of epoxy resins with a curing agent containing a caged bicyclic phosphate

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Abstract

A caged bicyclic phosphate structure was combined into epoxy resin to obtain halogen-free flame retardant polymers. LOI, UL-94 test, Cone calorimeter, TG and FTIR techniques were used to characterize the flammability, combustion behavior, thermal degradation properties and char structure. The results show that the incorporation of caged bicyclic phosphate into the epoxy thermosetting structure can greatly improve both the flame retardancy and thermal stability. The toxic gases and smoke generated during combustion are also decreased. The caged bicyclic phosphate 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo [2.2.2] octane (PEPA) acts not only as a curing agent and intumescent flame retardant but also as a smoke inhibitor for epoxy resin. PEPA is a good environmentally friendly flame retardant suitable for many purposes. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Caged bicyclic phosphate; Intumescent flame retardant; Epoxy resin; Thermal stability; Char formation

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1. Introduction

Epoxy resins are widely used as adhesives, coatings, casting and matrix materials for electronic and aerospace industries, due to their excellent mechanical and chemical properties. However, the thermal and flame resistance of epoxy polymers are still inadequate for some applications. Although halogen-containing fire retardants (FRs) show remarkable efficiency, they lead to environmental problems by generating great quantities of toxic and corrosive fumes during combustion, which restricts the range of their applications [1]. In an exploratory project to find halogen-free flame-retardant systems for epoxy resins, one approach is to explore intumescent systems. The term intumescent refers to foamed char formed during the combustion. This char layer could serve as an insulating layer to shield the organic polymers underneath from the heat of the fire and also serve as a diffusion barrier to slow down the gasification and vaporization of organic polymers [2].

The incorporation of organophosphorus functionality in the structure of polymeric materials, either as a constituent of the backbone or as a group appended to it, has been an area of particular interests for a number of years [3–7]. Organophosphorus fire retardants mainly act as intumescent flame retardants resulting in a char layer in the condensed phase, which can produce less toxic gas and smoke compared with halogen-containing FRs. Besides, P can also act in the gas phase as a catalytic radical scavenger, when degradation produces volatile P containing moieties. Therefore, the incorporation of organophosphorus functionality in the polymeric structure is recognized as one of the most efficient ways to obtain an environmentally friendly flame retardant system.

Among the organophosphorus flame retardants, caged bicyclic phosphates have attracted much interest, and many investigations have been reported [8–13]. It is found that caged bicyclic phosphates and their derivatives can serve as effective intumescent flame retardants in some polymers [14,15]. The purpose of the present study was to combine one of the caged bicyclic phosphates—(1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo [2.2.2] octane PEPA; Fig. 1) into epoxy resins to

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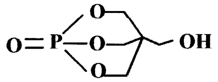


Fig. 1. Chemical formula of PEPA.

obtain halogen-free intumescent flame retardant systems. Many measurements, such as LOI, CONE, TG and FTIR, etc. were used to investigate the action of PEPA as flame retardant to the epoxy resin. The results indicate that the incorporation of caged bicyclic structure into the epoxy thermosetting structure is helpful to improve the flame retardance and thermal stability of the epoxy resin without bringing about serious environmental problems.

2. Experimental

2.1. Materials

Both diglycidyl ether of bisphenol A epoxy resins E44 and E51 were obtained from Shanghai Reagent Factory. The epoxy equivalent weights (EEW) of the resins were 245.12 and 204.19 g/mol for E44 and E51, respectively, which were determined by the HCl/acetone titration method [16].

Pentaerythritol was reagent grade and was purified from diluted HCl solution before use. Phosphorus oxychloride was A.R. Grade. It was distilled under atmospheric pressure and the distillate between 102 and 104 °C was collected for synthesis. Both reagents were obtained from Beijing Tongxian Yucai Fine Chemical Plant. PEPA was prepared from pentaerythritol and phosphorus oxychloride according to reference [9]. The compound melts at 210–212 °C. Elemental analysis for PEPA($C_{15}H_{24}O_{16}P_4$): Calcd.%: C, 33.33; H, 5.00; Found%: C, 30.14; H, 4.98. FTIR spectrum (KBr) shows characteristic peaks at 3396.7, 2912.7, 1301.7, 1029.8 and 884.0 cm^{-1}. The curing agents ethylenediamine (EDA) and phthalandione (PA) were both A.R. Grade and were used without further purification. They were supplied from Beijing Chemical Plant.

2.2. Preparation of the samples

The sample formulations are listed in Table 1. For the EDA series samples, the epoxy resin, EDA and PEPA were mixed well by vigorous agitation at room temperature, and the resulting mixture was poured into aluminum molds and cured at room temperature for 24 h, and then postcured at 80 °C for 2 h. When using PA and PEPA as curing agents, the epoxy resin was first heated to 120–140 °C, and then mixed well with PA and PEPA with mechanical stirring. Then the mixture was poured into the molds and cured at 160 °C for 4 h. The cured epoxy resin was cut and trimmed into the test samples.

Table 1
Sample formulation (all compositions are in parts)

Sample	E_{44}	EDA	PA	PEPA	
EDA-Al	100		6.8		
EDA-A2	100		5.8		10
EDA-A3	100		4.9		20
EDA-A4	100		3.6		30
EDA-B1		100	8.1		
EDA-B2		100	7.2		10
EDA-B3		100	6.3		20
EDA-B4		100	4.9		30
PA-Al	100			48.6	
PA-A2	100			41.9	10
PA-A3	100			35.4	20
PA-B1		100		58.1	
PA-B2		100		51.4	10
PA-B3		100		44.9	20

2.3. Measurement and testing

The limiting oxygen index (LOI) was measured using a Stanton Redcroft FTA instrument (Tarlin Scientific) according to the standard "oxygen index" test (ASTM D2863/77) with sample dimensions of 100 × 6.5 × 3 mm. A UL-94 test was performed on a CZF-2 Flammability Unit according to the procedure of FMVSS 302/ZSO 3975 with specimen dimensions of 127 × 12.7 × 3 mm.

All of the Cone calorimetric measurements were achieved on the Stanton Redcroft Cone Calorimeter at a heat flux of 35 kW/m^2 (ca. 700 °C) according to the ASTM E-1354 standard. The specimen dimension was 100 × 100 × 3 mm. Samples were horizontally arranged and protected by stainless grid to prevent bending and expansion during heating. Professional software combined with EXCEL5.0 was used for data processing.

The TGA measurement was done using a DuPont TGA-2950 themogravimetric analyzer at a heating rate of 10 $°C{\cdot}min^{-1}$, heating from 50 to 600 °C under nitrogen with a flow rate of 40 ml/min.

A MAGNA 560 FTIR spectrophotometer was used, and powder polymers and degradation residues were examined in KBr discs.

3. Results and discussion

3.1. Flame retardance

The LOI value and results of UL-94 test are listed in Table 2. It can be seen that the incorporation of PEPA

Table 2
The LOI value and results of UL-94 test

Sample	PEPA content/%	LOI/%	UL-94
EDA-Al	–	20.3	Burning
EDA-A2	8.6	24.5	V-2
EDA-A3	16.0	25.4	V-2
EDA-A4	22.5	26.6	V-1
PA-A1	–	28.5	Burning
PA-A2	6.6	34.0	V-0
PA-A3	12.9	36.9	V-0
EDA-B1	–	21.1	Burning
EDA-B2	8.5	25.5	V-2
EDA-B3	15.8	26.2	V-1
EDA-B4	22.4	27.8	V-1
PA-B1	–	27.4	Burning
PA-B2	6.2	31.7	V-1
PA-B3	12.1	34.3	V-0

into epoxy resins is beneficial to improve their flame retardance. The LOI value of the epoxy resin increases consistently with the increasing amount of PEPA. UL-94 V-0 rating can be achieved with a PEPA content of 12.9 and 12.1% for PA-A series and PA-B series, respectively. In general, the sequence of flame retardance is PA-A > PA-B > EDA-B > EDA-A, which may be related to many factors, such as the structure of the epoxy resin (aromaticity, chain rigidity, crystallinity and orientation and so on [1], flame retardant properties and the conditions of curing, etc.

3.2. Combustion behavior

The Cone calorimeter is one of the most effective bench-scale methods for studying the flammability of materials [16]. The Cone calorimeter gives many parameters such as time to ignition (TTI), heat release rate (HRR), total heat released (THR), effective heat of combustion (EHC), specific extinction area (SEA), mass loss rate (MLR), total smoke production (TSP), carbon monoxide and carbon dioxide yield and so on. The results derived from the Cone calorimeter turn out to be closely related to the large-scale results.

We have characterized the flammability properties of some samples under fire-like conditions using the cone calorimeter. The thermal data taken from the cone calorimeter are included in Table 3, Table 4 and Fig. 1, respectively. Table 3 reveals that both the peak and average HRR are reduced significantly for PEPA-containing epoxy resins. The pk-HRR of PA-A3 is reduced by 62.1% relative to pure epoxy resin PA-Al. A quite similar reduction of 61.0% can be seen for EDA-B4 with regard to EDA-B1. It also takes longer time for the phosphorus containing samples to reach the pk-HRR (see Fig. 1). Meanwhile, the EHC and MLR are also reduced. Furthermore, as listed in Table 4, the SEA and TSP have similar reduction, and there is corresponding change in the amount of carbon monoxide and carbon dioxide liberated during the combustion. In general, nearly all of the systems, show essentially similar behavior when evaluated in the cone, except for EDA-B3 which shows different HRR and MLR after 1 min burning; this needs further experiments to explain.

These phenomena indicate that there is some relation between the mechanism of PEPA flame-retarded epoxy resin systems studied. In all trials, intumescent char formation is observed, and the char yield increases with the PEPA content (see Table 4). For PA series samples, the char production is less, but the char surface is more compact and the apertures in the char are smaller and more homogeneous compared with the EDA series.

In general, HRR and MLR of the intumescent flame retardant system decreased measurably, and TTI also decreased [17]. However, for the PEPA flame retarded series, the TTI of the flame-retarded samples increase as the PEPA content increases, which means that the

Table 3
Results of cone calorimeter

Sample	TTI /s	pk-HRR /kW m^{-2}	av-HRR /kW m^{-2}	THR /MJ	av-EHC /MJ kg^{-1}	pk-MLR /g s^{-1}
EDA-Al	52	1309.2	308.4	63.8	97.0	0.64
EDA-A3	78	1197.7	279.8	58.1	32.5	0.59
EDA-B1	42	1519.8	418.3	83,9	50.8	0.75
EDA-B2	47	1449.0	347.5	72.3	22.9	0.72
EDA-B3	53	897.5	264.7	56.8	17.5	0.63
EDA-B4	64	591.7	227.0	39.5	16.7	0.41
PA-Al	40	1165.7	270.1	56.0	43.2	0.66
PA-A3	102	442.1	187.0	37.6	9.4	0.40
PA-B1	79	866.5	338.5	59.0	20.9	0.62
PA-B3	119	441.6	129.5	33.7	9.0	0.36

Table 4
Results of cone calorimeter

Sample	av-SEA /m^2 kg^{-1}	av-Smoke Ratio /m	TSP /m^2 kg	av-Yield of CO /kg kg^{-1}	av-Yield of CO$_2$ /kg kg^{-1}	Char yield /%	FPI
EDA-Al	6245	4.0	769.4	0.87	11.55	8.98	0.040
EDA-A3	2383	3.8	718.4	0.26	9.83	22.31	0.065
EDA-B1	1411	4.8	973.2	0.29	13.73	5.9	0.028
EDA-B2	1090	4.3	871.2	0.14	8.48	11.62	0.032
EDA-B3	964	3.7	719.3	0.12	4.39	24.46	0.059
EDA-B4	706	3.2	541.7	0.074	1.06	35.05	0.108
PA-Al	3220	6.3	1237.5	0.13	2.41	1.47	0.034
PA-A3	1477	*5.2*	1056.9	0.063	0.67	17.80	0.231
PA-B1	1735	7.9	1394.7	0.042	1.71	1.08	0.091
PA-B3	1068	5.7	1095.2	0.012	0.32	12.14	0.269

Table 5
Data of TG and DTG

Sample	$T_{5\%}$[a] /°C	$T_{10\%}$ /°C	$T_{\max}$ /°C	$T_{\max}$[b] /% min^{-1}	Char residue at 600 °C /%
EDA-Al	319.7	333.2	360.1	1.262	9.0
EDA-A3	235.6	277.6	350.0	1.160	16.0
EDA-B1	318.0	334.9	363.5	1.500	11.4
EDA-B2	289.4	304.6	350.0	1.133	19.4
EDA-B3	250.7	281.0	333.2	0.966	18.9
EDA-B4	242.3	274.3	331.5	0.949	21.9
PA-Al	232.2	257.5	413.9	0.989	4.6
PA-A2	192.3	307.9	398.0	1.000	8.6
PA-A3	313.0	333.2	380.3	1.271	12.0
PA-B1	168.3	210.3	419.0	1.200	3.4
PA-B2	191.8	301.2	360.1	1.153	7.4

[a] $T_{10\%}$, is the temperature when 10% weight loss occurs, which is usually thought as initial decomposition temperature.

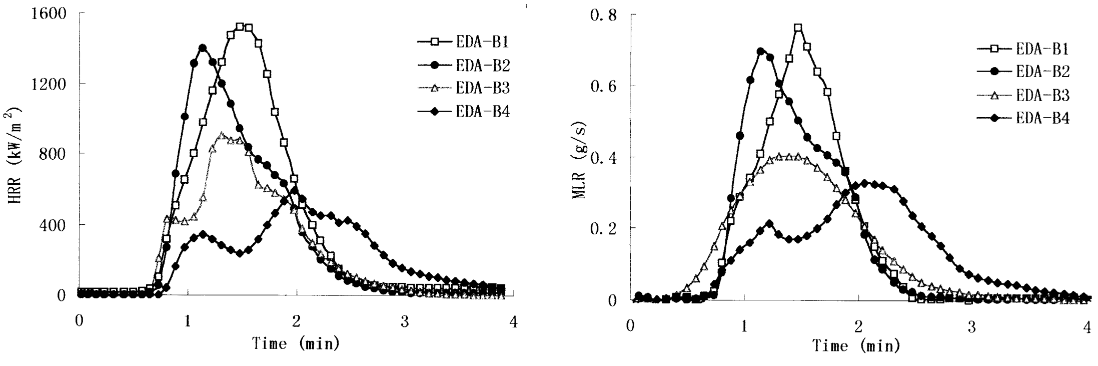
[b] $R_{\max}$ is the peak of weight loss rate

flame-retarded samples become more difficult to ignite. For example, the TTI of PA-A3 is 62 s longer than the pure epoxy resin, which is 1.55 times that of the pure epoxy resin. The prolongation of the TTI is important for people to evacuate safely in a fire.

Sometimes FPI (Fire Performance Index) (TTI/pk-HRR) is used to predict whether a material can easily develop drastic combustion after ignition. The FPI is independent of the test piece thickness, and may be thought of as an intrinsic characteristic of the material and be used to evaluate the combustion performance of the material [18]. In the above series, the PA-B series have the highest FPI, but the PA-A series have the maximal increment. The FPI of PA-A3 is 6.7 times that of the pure resin, and the other series spans from 1.6 to 3.9 times. It is shown that PEPA can contribute much to prevent fire from developing.

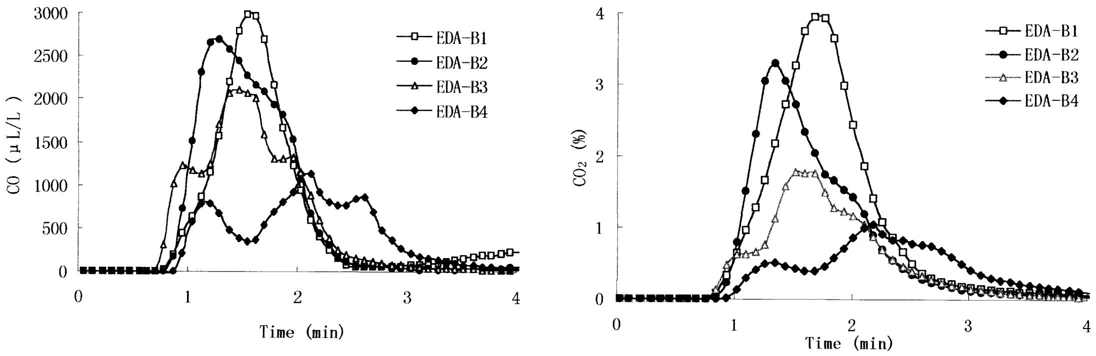
3.3. Thermal analysis

The thermal degradation behaviors of the samples were monitored via thermogravimetric analysis in nitrogen atmosphere. Table 5 shows the results of TG and DTG. It can be seen that the yield of char residue at 600 °C increases with the PEPA content, and for all sets of samples the char yield increases in the order: PA-B < PA-A < EDA-A < EDA-B, in agreement with the results from the Cone calorimeter, but different from the LOI results. This behavior suggests that the amount of the char yield is important but not the exclusive factor affecting the flame retardancy of polymers. Several properties of char have been mentioned in the literature as desirable from the point of view of flame retardant performance: mechanical strength and integrity, coherence and adherence, openness of cells,



(a) HRR curves of EDA-B series

(b) MLR curves of EDA-B series



(c) CO yields of EDA-B series

(d) CO_2 yields of EDA-B series

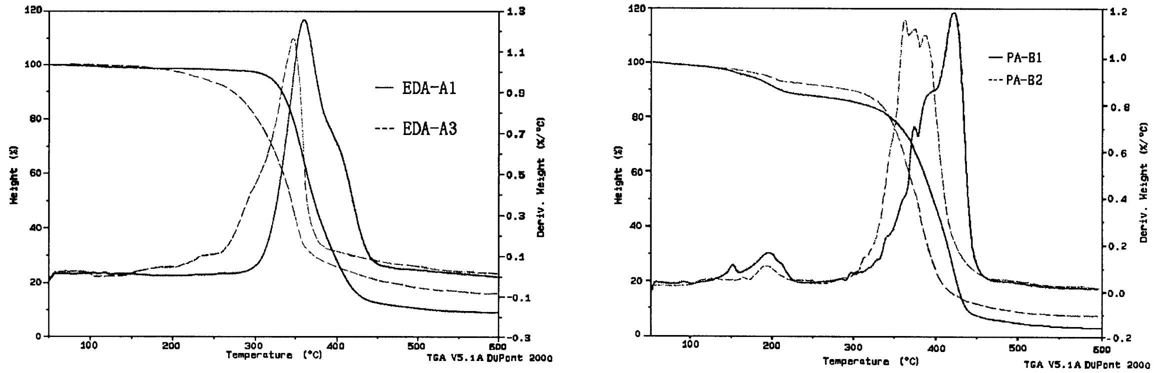
Fig. 2. Cone calorimeter data of EDA-B series samples.

impenetrability of gases and liquids [1,7]. It seems that in the case of intumescence the quality and structure of the char are more significant to influence the pyrolysis and combustion process. Many investigations have indicated that the char formed via cross-linking reactions does enhance thermal stability [1,4,19]. Therefore, it can be proposed that the incorporation of phosphorus in the epoxy resin can facilitate cross-linking reactions with the consequence of an increased production of intumescent char, to which the enhanced thermal stability must be attributed.

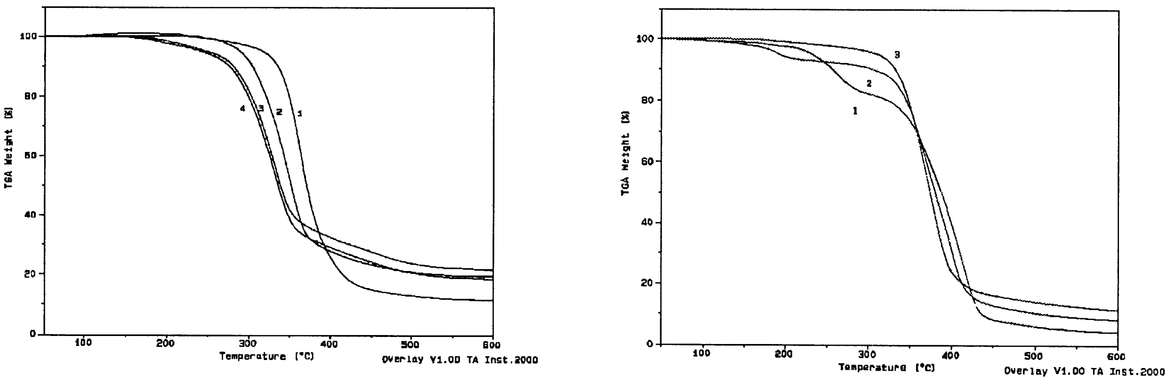
Fig. 2 gives some of the TG and DTG curves of the samples. These figures combined with the data of Table 5 indicate that nearly all the samples, except for PA-A series, begin to decompose at lower temperatures when the PEPA content is increased, and the $R_{\max}$ is also reduced at the same time. Compared with the DTG curves of Fig. 2, it is obvious that the $R_{\max}$ shifts to an earlier time and lower temperature as the PEPA content increases. Moreover, the pyrolysis process of the EDA series and PA-A series is different from each other. The thermal degradation of EDA series mainly occurs at 280–430 °C, and the weight loss is rapid and acute in this temperature range (see Fig. 3a and e). But for PA series, the process usually divides into two main stages: the first stage is within the range of 150–220 °C, and the decomposition is minor, and the second stage at 340–460 °C corresponding to the cross-linking reaction region is broad and shows two or more minute peaks (see Fig. 3b and f). Most of the mass loss occurred in the second stage. For most of the samples tested, the more the add-on flame retardant, the earlier the char formation, and the higher the char yield. Obviously, this can impart better fire retardancy to the material. In addition, the combination of PEPA into epoxy resin can promote the cross-linking reaction occurring at earlier time and lower temperature, which will reduce the production of volatile fuel and thus will also increase the char yield.

3.4. FTIR investigation on thermal decomposition

Samples EDA-B3 and PA-A3 were chosen for further study of the thermal degradation investigated by FTIR. Figs. 4 and 5 show the FTIR spectra of EDA-B3 and PA-A3 at different temperatures. Both P=O (1250 cm^{-1}) and P–O–C (1181 cm^{-1}) absorption were observed in Figs. 4 and 5, which indicate that the caged bicyclic phosphate moiety is combined into the epoxy resin structure. As the temperature was raised to 200 °C, there was no distinct change in the intensity of these two absorptions. This result, which agrees with the fact that there is no notable weight loss in the TGA investigation before 200 °C, reveals that these two samples are thermally stable below 200 °C. When the treatment temperature increased to 300 °C, changes of the absorption intensity appeared. As for EDA-B3, the decrease and alteration is more evident than that of PA-A3. It is clear for this case that PA-A3 has a higher thermal stability than EDA-B3, which is consistent with the conclusions of LOI and UL-94 test. Similar results have been observed for the aromatic group

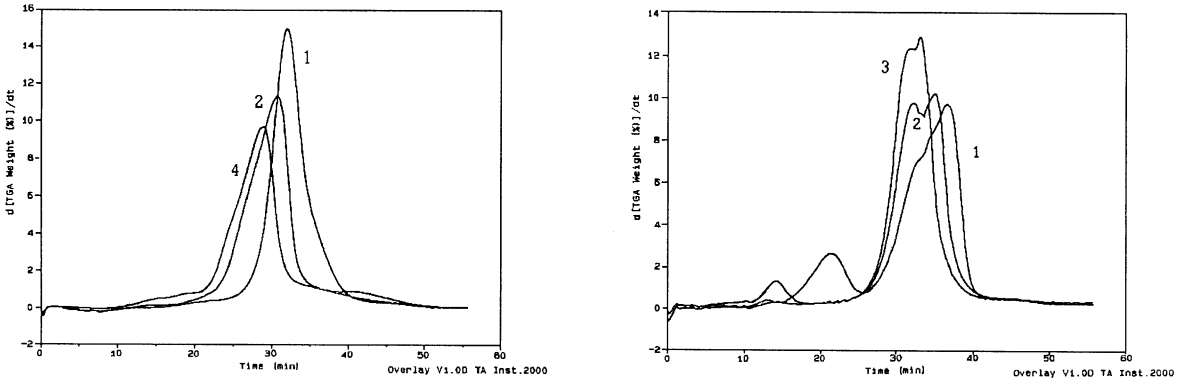


(a) TG and DTG curves of EDA-A1 and EDA-A3 (b) TG and DTG curves of PA-B1 and PA-B2



(c) TG curves of EDA-B series
1: EDA-B1, 2: EDA-B2
3: EDA-B3, 4: EDA-B4

(d) TG curves of PA-A series
1: PA-A1, 2: PA-A2
3: PA-A3



(e) DTG curves of EDA-B series
1: EDA-B1, 2: EDA-B2, 4: EDA-B4

(f) DTG curves of PA-A series
1: PA-A1, 2: PA-A2, 3: PA-A3

Fig. 3. TG and DTG curves.

absorptions (1605, 1575, 1503 and 1461 cm^{-1}). At 400 °C, the intensity of the P–O–C group absorption decreased, which implies that P–O–C chain scission occurred. Meanwhile, broad peaks at around 1605 cm^{-1} and 1225 cm^{-1} appeared, the former implying the formation of C=C bonds and the latter maybe the absorption of a poly-phosphonate structure. This formation of C=C bonds probably resulted from the cross-linking reaction stage in the char residue as a poly-aromatic structure [20,21].

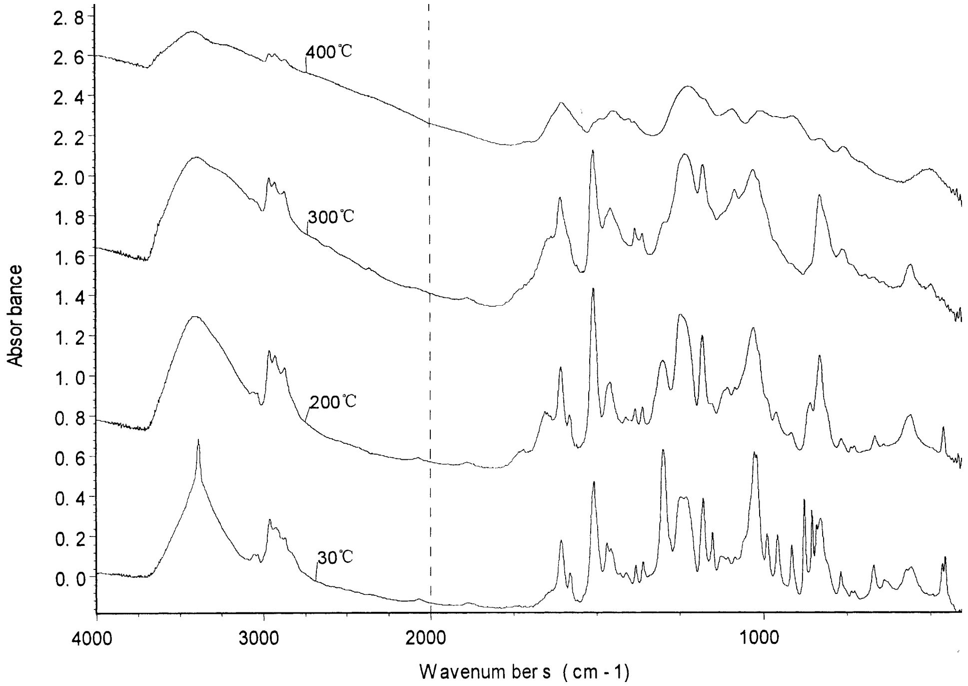


Fig. 4. FTIR spectra of EDA-B3 at different temperatures (Pellets in KBr).

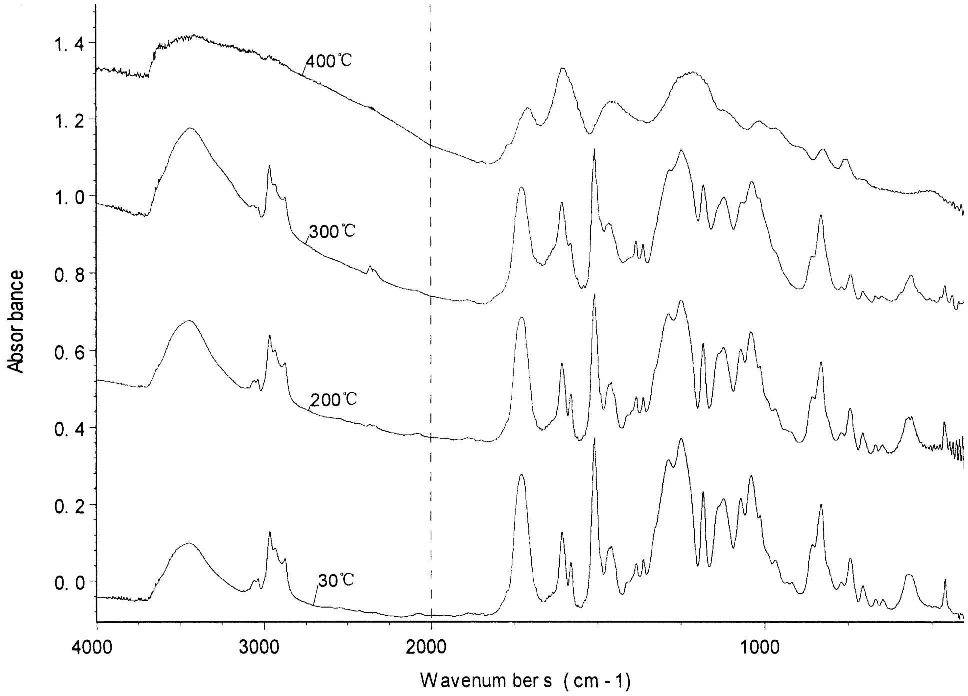


Fig. 5. FTIR spectra of PA-A3 at different temperatures (Pellets in KBr).

4. Conclusions

The combination of a caged bicyclic structure into the diglycidyl ether of bisphenol A epoxy resin molecule can give halogen-free flame retardant epoxy resins. The flammability of the resulting system decreased and the order of enhanced flame retardance is PA-A > PA-B > EDA-B > EDA-A. It seems that many factors work together to influence the flame retardance of the whole system. For all flame retarded epoxy resins, the ignition time increased and the HRR, EHC, MLR, etc. parameters reduced with the PEPA content. In addition, the toxic gases and smoke evolved are obviously lowered. During combustion, the presence of intumescent char was observed, and the char yield increased along with the PEPA content increase. TG and FTIR results demonstrate that the thermal stability of the system is also improved as a result of cross-linking in the process of thermo-oxidative degradation.

Based upon all these results, we can conclude that the incorporation of caged bicyclic structure into the epoxy thermosetting structure is advantageous to improve the flame retardance and thermal stability of the epoxy resins without bring about serious environmental problems.

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