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Polymer Degradation and Stability 83 (2004) 71–77

Polymer Degradation and Stability

www.elsevier.com/locate/polydegstab

Structure of a boron-containing bisphenol-F formaldehyde resin and kinetics of its thermal degradation

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Received 29 January 2003; received in revised form 9 May 2003; accepted 16 May 2003

Abstract

The structure and thermal degradation of a boron-containing bisphenol-F formaldehyde resin (BBPFFR) synthesized by the formalin method have been studied. The results showed that a six-membered ring containing boron–oxygen coordinate linkage was formed in the thermosetting process, and the coordinated oxygen atom was provided by the phenolic hydroxyl. The degradation of this resin began with the oxidation and breakage of ether linkages and carbonyl groups. The kinetic parameters of thermal degradation were determined by thermogravimetric analysis.

Keywords: Boron-containing phenol-formaldehyde resin; Bisphenol-F; Boric acid; Thermal analysis

1. Introduction

Phenolic resin modified by boric acid is a thermosetting resin with excellent performance, such as thermal stability, mechanical strength, electric properties and shielding of neutron radiation. Bisphenol-F has a methylene group not a propane group like bisphenol-A, so it has relatively higher freedom of rotation. In contrast with other boron-containing phenol-formaldehydes, the viscosity of this resin is low and the tenacity is perfect. Some reports have appeared on the synthesis and application of boron-containing phenol-formaldehyde resin [1–4], while the synthetic structure and thermal properties of boron-containing bisphenol-F formaldehyde resin have not been investigated until now.

In this work, BBPFFR was synthesized by the formalin method [1,2], the structure change of this resin during synthesis, curing and thermal degradation was monitored by Fourier-transform infrared (FTIR) spectrometry, and the weight changes and degradation kinetics were investigated by thermogravimetry analysis (TGA).

2. Experimental

2.1. Materials

Biphenol-F (BPF) was synthesized according to the literature [5], and the melting point was 158–160 °C. Boric acid, 37% aqueous formalin, acetone and NaOH were all analytically pure grade, which were supplied by Tianjin Chemical Reagent Co. of China.

2.2. Synthesis of boron-containing bisphenol-F formaldehyde resin

BPF, aqueous formalin and NaOH were put into a three-necked flask, equipped with a stirrer, a thermometer and a condenser. The mixture was stirred and heated to 70 °C, then the reaction was maintained at this temperature for 1h. When the water was removed in vacuum, salicyl alcohol of BPF was obtained. In the second step, boric acid was added to this system, heated to 102–110 °C and held for 45 min. The water formed in the reaction was then removed in vacuum. Finally the yellow solid BBPFFR was obtained. By Changing the dosage of boric acid, resins with different boron contents were obtained. Material composition and serial number are listed in Table 1.

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doi:10.1016/S0141-3910(03)00225-8

2.3. Infra-red analysis

A FTIR spectrometer (Bro-Rad FTS-40 USA) was used to investigate the structure changes of the BBPFFR during the curing and thermal degradation. The BBPFFR was dissolved in acetone and then coated as a thin film on a potassium bromide plate. When the solvent in the film was completely evaporated in vacuum, the potassium bromide plate was scanned by the FTIR instrument. Then it was scanned after being cured at different temperatures. The salicyl alcohol of BPF was determined by FTIR with the same method.

The principle absorption bands of BBPFFR are: the benzene ring at 1600 cm^{-1}, the borate B–O at 1350 cm^{-1}, phenol hydroxyl C–O at 1250 cm^{-1}, the $-CH_2-$ group at 1450 cm^{-1}, methylol group at 1020 cm^{-1}, ether linkage C–O at 1100 cm^{-1}, carbonyl group at 1650 cm^{-1}. Quantitative analysis was doing according to the literature [6]. The benzene ring absorption at 1600 cm^{-1} was used as internal standard. According to the Beer–Lambert law $A = lgI/I_0$, the ratios of absorbance A_{1350}/A_{1600} (borate value), A_{1250}/A_{1600} (phenol hydroxyl value), A_{1100}/A_{1600}(ether value), A_{1020}/A_{1600} (methylol value), and A_{1650}/A_{1600}(carbonyl value) were obtained.

2.4. Thermal analysis

A Shimadzu TGA-40 thermobalancer was used to determine the weight loss behaviour of BBPFFR during degradation. About 8 mg BBPFFR power cured at 180 °C for 4 h was introduced into the thermobalance, then heated to 900 °C at 10 °C/min in air.

3. Results and discussion

3.1. Structure of boron-containing bisphenol-F formaldehyde resin

The process of synthesizing BBPFFR was divided into two steps. The salicyl alcohol of BPF was formed in the first step, then reacted with boric acid. According to the literature [2], the reactivity of the methylol group with boric acid was higher than that of phenol hydroxyl. So in the second step, the reaction of boric acid with methylol groups precedes that of boric acid with phenol hydroxyl, and a six-membered ring will formed if the resin is set aside to harden at higher temperature. The infrared spectrum analysis proved this hypothesis.

Table 1
Composition and serial number of BBPFFR

Composition		Biphenol-F: formaldehyde: Boric acid (mol ratio)
Serial number	1.6 B	3 : 7.2 : 1.6
	1.0 B	3 : 7.2 : 1.0
	0.6 B	3 : 7.2 : 0.6
	0.0 B	3 : 7.2 : 0.0

Fig. 1 shows the IR absorption variation of BBPFFR during the synthesis and curing reaction. The salicyl alcohol of BPF has strong absorptions from methylol groups at 1020 cm^{-1} and phenol hydroxyl at 1225 cm^{-1}.

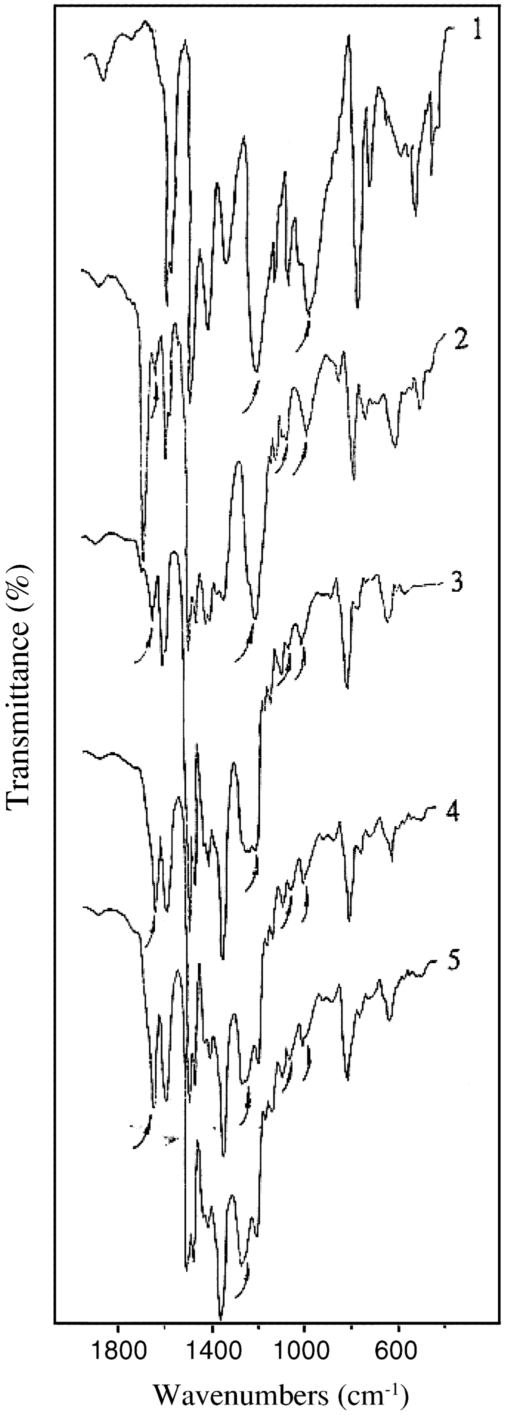
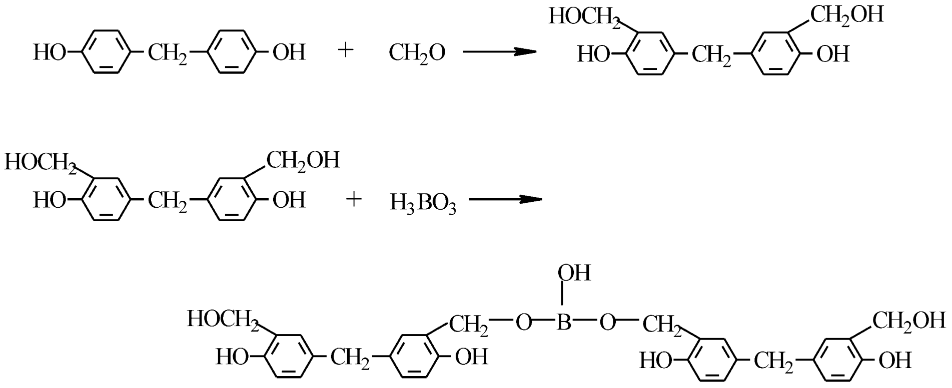


Fig. 1. Infrared spectrum of boron-containing bisphenol-F formaldehyde resin (1) salicyl alcohol of BPF (2) uncured (3) 120 °C (4) 140 °C (5) 170 °C cured 1 h.

In the spectrum of uncured BBPFFR, the absorption of methylol group decreased sharply, but the absorption of phenol hydroxyl is still strong. This means most methylol groups had taken part in the reaction, but only a few phenol hydroxyls were reacted. So the main reactions in this step are as Scheme 1.

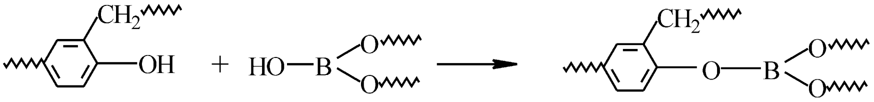
According to the literature [1,2], in the curing resin, when the six-membered ring containing B–O coordination bond is formed, the IR absorption band of B–O borate at 1350 cm^{-1} should disappear. From Fig. 1 and Table 2, it can be seen that the IR spectrum of uncured BBPFFR has an absorption peak at 1350 cm^{-1} and the borate value is 2.4. When this resin was heated at 120 °C, the absorption peak at 1350 cm^{-1} became larger, and the borate value reached 4.7. The results show that the six-membered ring structure had not been formed in the uncured resin, and more phenol borate linkages were formed. Because most methylol groups had reacted, the curing reaction mainly occurred between phenol hydroxyl and unreacted –OH groups in boric acid, and this can be proved by the decrease of phenol hydroxyl value (Table 2). Thus the reaction in this step is as Scheme 2. When this resin was heated to 140–170 °C, the borate value and phenol hydroxyl value decreased. These results show that the six-membered ring structure containing B←O coordination bond was



Scheme 1.

Table 2
The changes of functional group values of BBPFFR during curing

Resin	T(°C)	Borate value	Phenol hydroxyl value	Methylol value	Ether value	Carbonyl value
1.6 B	Uncured	2.4	2.6	0.85	0.93	0.50
	120	4.6	2.9	0.83	1.1	0.63
	130	4.7	2.8	0.86	1.1	0.80
	140	4.0	2.7	0.82	0.99	1.0
	150	3.7	2.6	0.72	0.90	1.0
	170	3.2	2.4	0.70	0.86	1.0
	200	3.8	0.0	–	–	0.98
	220	1.2	0.0	0.50	0.71	0.90
1.0 B	Uncured	1.8	2.2	0.74	0.84	0.58
	120	2.2	2.2	0.69	1.0	0.58
	130	3.2	–	–	1.5	1.4
	140	2.2	2.1	0.78	1.0	0.94
	150	2.0	1.9	0.62	0.88	0.98
	170	1.8	1.7	0.62	0.86	0.92
	200	1.2	0.0	0.50	0.73	0.86
	220	0.0	0.0	0.0	0.67	0.83
0.6 B	Uncured	1.8	2.5	0.57	0.75	0.53
	120	2.2	2.6	0.53	0.93	0.57
	130	2.4	2.6	0.58	1.0	0.58
	140	1.9	2.0	0.60	0.96	0.82
	150	1.6	1.8	0.43	0.80	0.76
	170	1.3	1.5	0.48	0.79	0.77
	200	1.0	0.0	0.32	0.59	0.75
	220	0.0	0.0	0.0	0.47	0.76



Scheme 2.

formed at higher temperatures and the coordinated oxygen was supplied by the phenolic hydroxyl. The final molecular structure may be described as in Scheme 3.

According to Table 2, with the decrease of boron content in BBPFFR, the disappearrance temperature of the phenol borate linkage also decreased. The borate value of 1.6 B resin at 220 °C is 1.2, while 1.0 B resins borate linkage disappeared at 220 °C. This is because with the increase of boron content, the opportunity of boron being coordinated is reduced and it is more difficult to form the integrated six-membered ring. Moreover, it can be speculated that if excess boric acid was used in the resin, the hydrolysis resistance would be reduced.

In contrast with BBPAFR, the disappearance temperature of the phenol borate linkage of BBPFFR is higher than that of BBPFAR [4]. The phenol borate absorption peak of 0.8 BBPAFR is entirely disappeared at 200 °C, but the BBPFFR with the same boron content has a large phenol borate absorption peak at 220 °C. This means it is more difficult to form the six membered ring for BBPFFR than BBPAFR.

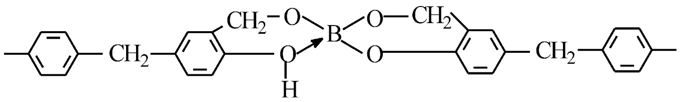
3.2. Structure changes of BBPFFR during thermal degradation

As can be seen from Fig. 1, absorptions of ether linkage and carbonyl group were obviously appeared in the spectra of cured and uncured resin. It is generally true that the condensation reaction among methylol groups forms ether linkages [7,8]. But the stability of ether linkage is poor, and it is liable to be oxidized to a carbonyl group at 140 °C. This could be proved by the decreases of ether value and the increases of carbonyl value (Table 2). Some ether linkages were oxidized at the second step of synthesis, so a small carbonyl group absorption appeared in the spectrum of uncured resin. This is one factor that influences the stability of BBPFFR. The reaction is as Scheme 4.

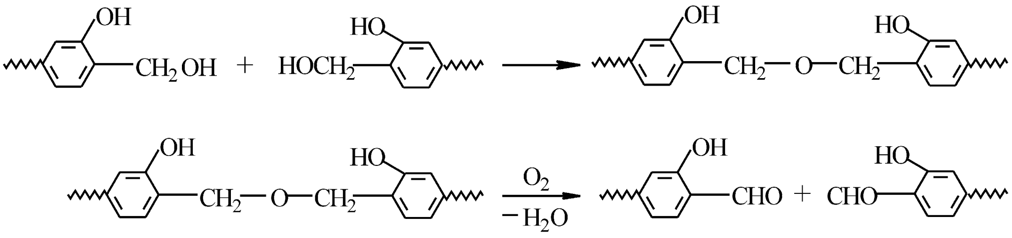
Fig. 2 shows the IR absorption variation of BBPFFR during thermal degradation. As can be seen from Fig. 2, with the increasing temperature, the absorption peak of carbonyl group at 1650 cm^{-1} decreases first, then the absorption of borate B–O linkage decreases gradually. At 300 °C about 1 h, the absorption of carbonyl group has disappeared. After 400 °C, the absorption of $–CH_2–$ at 1430 cm^{-1} is also very strong. This means that the stability of $–CH_2–$ is much higher than that of ether linkage and carbonyl group. So ether linkage and carbonyl group in the resin intensely affect the thermal stability of BBPFFR.

3.3. Thermal stability and degradation kinetics

As can be seen from Fig. 3, the common bisphenol-F formaldehyde resin (BPFFR) has higher weight loss rates than BBPFFR. The weight loss for common BPFFR is over 99% at 580 °C, while the BBPFFR (1.6 B) it is only 44.8% at 700 °C. The temperature of half-weight loss is about 240 °C, higher than that of common BPFFR, and the start temperature of weight loss is about 50 °C higher then that of the BPFFR. The thermal stability of BBPFFR is as excellent as that of boron-containing bisphenol-A formaldehyde resin (BBPFAR) [4]. It is because of the formation of phenol borate linkage, decreased the formation of ether linkage, that the heat resistance of BBPFFR has increased extremely.



Scheme 3.



Scheme 4.

From 230 to 340 °C,as can be seen from Fig. 3, the three resins with different boron content have the same weight loss, which is about 2%. We believe that it is caused by the evaporation of water and small molecules and it is not considered in the degradation kinetics. According to the TGA curves (Fig. 3), the degradation can be divided into three stages. In the first stage (about 340–550 °C), the total weight loss for 1.6 B resin at the 10 °C/min heating rate is about 12%, which is less than 1.0 B resin and 0.6 B resin at this stage. In the second

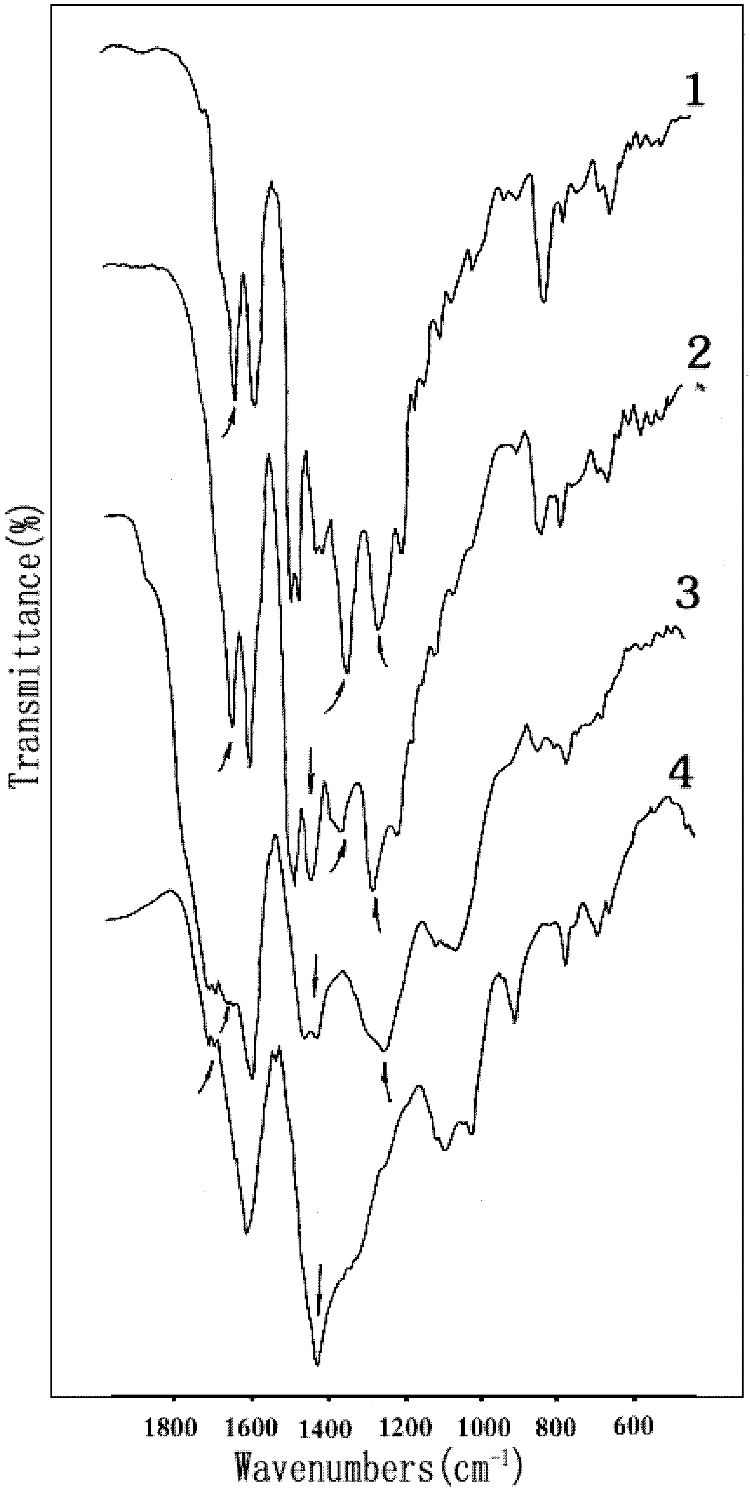


Fig. 2. Infrared spectrum of boron-containing bisphenol-F formaldehyde resin (1) 200 °C, (2) 220 °C, (3) 300 °C, (4) 400 °C decomposed 1 h.

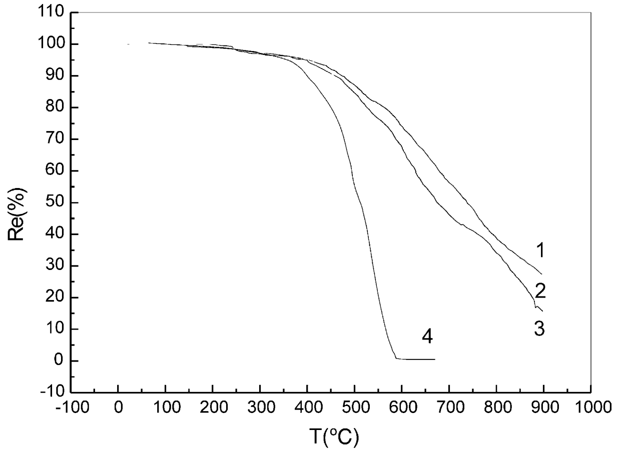


Fig. 3. Thermogravimetric analysis of BBPFFR (1) 1.6 B, (2) 1.0 B, (3) 0.6 B, (4) 0.0 B at heating rate of 10 °C/min in air.

and third stages, the weight losses of 1.6 B resin are also less than that of 1.0 B resin and 0.6 B resin (shown by Fig. 3 and Table 3). Related with structure changes shown in Fig. 2, the weight loss in the first stage may be caused by the oxidation and breakage of some ether linkages and carbonyl groups. In the second stage, most ether linkage, carbonyl group and some –CH_2– group, borate B–O linkage, benzene ring may be oxidized and broken. The breakage of benzene ring is the main reaction in the third stage.

To determine the kinetic parameters of the decomposition from the thermogravimetric data, the first step is to evaluate the conversion of the reaction. In dynamic TGA experiments, the weight change of the sample is regarded as a function of temperature and the conversion can be expressed as

$$a = \frac{w_i - w_T}{w_i} \qquad (1)$$

where w_i is the sample weight in i stage, w_T is the residual weight of w_i at temperature T. Therefore, with the TGA curves and using Eq. (1), the conversions are calculated for different degradation stages.

In this work, considering the multi-stage degradation process of BBPFFR, the TGA data were analysed on the basis of the Madhusdanan–Krishnan–Ninan method [9,10], which can be expressed by the following equation:

$$\ln\left(G(a)/T^{1.92}\right) = \ln\frac{AE}{\phi R} + 3.77 - 1.92\ln E - \frac{E}{RT} \qquad (2)$$

where A is the pre-exponential factor in the Arrhenius equation, E is the apparent activation energy, R is the universal gas constant, ϕ is the heating rate, T is absolute temperature, and $G(a)$ is the integral form of the conversion dependence function. The correct form of $G(a)$ depends on the proper mechanism of the decomposition reaction [10]. Different expressions of $G(a)$ for some solid-state reaction mechanisms can be described as following: in first order, $G(a)$ is $-\ln(1-a)$; in second order, $G(a)$ is $1/(1-a)$; in third order, $G(a)$ is $1(1-a)^2$.

According to the above equation, the activation energy can be obtained at different heating rates from fitting the $\ln[G(a)/T]$ versus $1/T$ plots. For different degradation stages, the apparent activation energies and pre-exponential factors were all tested for different mechanism functions. Some results are listed in Table 4.

Table 3
The weight loss of BBPFFR in three degradation stages

Weight loss (%)	First stage (340–550 °C)	Second stage (550–720 °C)	Third stage (720–900 °C)
1.6 B	12	32	22
1.0 B	18	34	27
0.6 B	20	36	34

Table 4
The kinetic parameters of thermal degradation of 1.6 B resin for different mechanism functions at 10 °C/min heating rate

1.6 B Resin	Reaction order	Correlation coefficient	ΔE (kJ/mol)	$\ln A$ (s^{-1})	Standard deviation
First stage	1	0.9939	108.4	15.5	0.0574
	2	0.8406	60.8	13.0	0.1790
	3	0.8631	133.3	21.8	0.3594
Second stage	1	0.9932	112.1	12.3	0.0585
	2	0.9467	94.6	10.8	0.1290
	3	0.9327	117.9	22.5	0.3164
Third stage	1	0.9929	193.4	19.4	0.0679
	2	0.8626	202.2	21.7	0.3357
	3	0.8721	421.9	47.5	0.6723

Table 5
Kinetic parameters of thermal degradation of BBPPR for 10 °C/min heating rate

	Resin	Reaction order	Correlation coefficient	ΔE (kJ/mol)	ln$A$ (s^{-1})	Standard deviation
First stage	1.6 B	1	0.9939	108.4	15.5	0.0574
	1.0 B	1	0.9914	90.0	12.4	0.0926
	0.6 B	1	0.9858	89.8	12.5	0.1154
Second stage	1.6 B	1	0.9932	112.1	12.3	0.0585
	1.0 B	1	0.9926	123.7	14.5	0.0674
	0.6 B	1	0.9987	144.1	17.9	0.0450
Third stage	1.6 B	1	0.9929	193.4	19.4	0.0679
	1.0 B	1	0.9986	178.4	17.6	0.0407
	0.6 B	1	0.9808	157.5	16.7	0.1253

As shown in Table 4, for the same degradation stage at a given heating rate, the correlation values for different mechanisms are different. According to the principle that the probable mechanism has high correlation coefficient value and low standard deviation value, the probable mechanism functions are deduced from the calculated results: the three degradation stages are all following first order mechanism. The kinetic parameters in every stage are listed in Table 5. As shown in Table 5, the ΔE values of a certain BBPFFR in the three degradation stages are increased step by step and the resin with higher boron-containing has bigger ΔE value in every stage. This evidence that the resin with more boron has better thermal stability and the degradation of BBPFFR was more difficult in the later stages.

4. Conclusions

During the progress of synthesis and curing of BBPFFR by formalin method, ether linkages and borate B–O linkages were formed and ether linkages can be oxidized to carbonyl groups. This indicated that the condensation reaction among methylols and ester reaction of boric acid co-existed. The cured BBPFFR has a six-membered ring structure with coordination linkage of boron–oxygen at high temperature, and the coordinated oxygen was supplied by the phenolic hydroxyl because the reactivity of benzyl hydroxyl group with boric acid was higher than that of phenol hydroxyl.

Thermal degradation of this resin begins with the oxidation and breakage of ether linkage and carbonyl group. The thermal stability of $-CH_2-$ is higher than that of ether linkage. The thermostability of BBPFFR is better than BPFFR and it can be improved by increasing the boron content.

The TGA results show that the decomposition reaction of this resin can be divided into three stages, and in every stage the decomposition reaction follows first order kinetics. The activation energies of thermal degradation of BBPFFR in the three degradation stages increased step by step, and the resin with higher boron content has larger ΔE value at every stage. This is evidence that the resin with more boron has better thermal stability.

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