ELSEVIER

European Polymer Journal 37 (2001) 207–210

EUROPEAN POLYMER JOURNAL

Structure and properties of boron-containing bisphenol-A formaldehyde resin

Jungang Gao [*], Yanfang Liu, Fengli Wang

Department of Chemistry, Hebei University, Baoding 071002, People's Republic of China

Received 22 April 1997; received in revised form 21 February 2000; accepted 13 March 2000

Abstract

The boron-containing bisphenol-A formaldehyde resin from bisphenol-A, formaldehyde and boric acid was synthesized. The mechanism of synthesis and curing reaction were investigated by infrared spectroscopy and chemical analysis method. The kinetics of thermal degradation and thermal stability were determined by thermal analysis. The results show that the resin has higher heat resistant property and oxidative resistance than common phenol–formaldehyde resin. In addition, the fiberglass-reinforced laminate has good mechanical and electric properties. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Boric acid; Bisphenol-A; Formaldehyde; Thermal analysis; Infrared analysis

1. Introduction

The common phenol–formaldehyde resins (PFRs) formed from phenol and formaldehyde in the presence of alkaline or ammonia water are extensively used as polymer composites and coating materials. The mechanism of synthesis and curing of the resin had been investigated [1,2]. The boron-containing bisphenol-A formaldehyde resin (BBPAFR) formed from bisphenol-A (BPA) has good heat resistance, mechanical properties, electric properties and defence of neutron radiation [3–5]. This resin had been synthesized by the method of formalin [4]; however, the mechanism of synthesis and curing, the thermal stability and the kinetics of thermal degradation were not investigated until now. The structure of this resin was not proved by experiment. In this paper, the structure of boron-containing bisphenol-A formaldehyde was investigated by chemical and infrared spectral analysis. The thermal stability and the kinetics of thermal degradation were investigated. The mechanical and electric properties of its fiberglass-reinforced laminate were determined.

2. Experimental

2.1. Materials

BPA, 37% aqueous formalin, boric acid, NaOH, acetone and ethyl alcohol were all of an analytically pure grade, which were supplied by Beijing Chemical Reagent Co. fiberglass cloth (Tianjin Chemical Co.) was treated at 350–370°C.

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

In the mole ratio, BPA:formaldehyde:boric acid = 1:2.4:0.5, to a four-necked flask, equipped with a stirrer, a thermometer, and a condenser was added to BPA, formaldehyde, and NaOH as catalyst. The mixture was first stirred and heated to 70°C, then the reaction was maintained at this temperature for 1 h; thereafter, the water was removed in vacuum, and finally, the salicylalcohol of BPA was obtained. In the second step, boric acid was added to this system, heated to 102–110°C and then held for 40 min. Thereafter, the reactive water was removed in vacuum, and finally the solid BBPAFR was obtained.

---

[*] Corresponding author.

PII: S0014-3057(00)00095-1

2.3. *Infrared spectrum analysis*

A Hitachi-260 infrared spectrum analyzer was used for infrared (IR) analysis. The resin was dissolved in acetone and coated on a KBr sheet, cured at different temperatures in air and then analyzed by the method of Patts [6]. The IR absorption bands seen were borate linkage B–O at 1350 cm^{-1}, ether linkage C–O at 1050 cm^{-1}, phenol hydroxyl C–O at 1250 cm^{-1} and benzene ring at 1600 cm^{-1}. The benzene ring absorption at 1600 cm^{-1} was used as internal standard. According to the Beer–lambert law, the ratios of absorbance, A_{1350}/A_{1600} (borate value) and A_{1250}/A_{1600} (phenol hydroxyl value) were obtained.

2.4. *Thermal analysis*

The resins were cured at 160°C for 4 h. Thermal analysis was carried out on a Shimadzu DT-40 thermal analyzer. The kinetics of thermal degradation and thermal stability were investigated according to the method found in the literature [7,8].

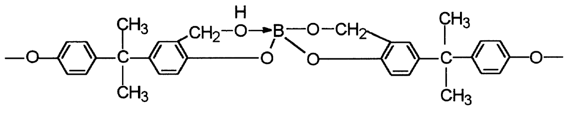
2.5. *Determination of mechanical and electric properties*

Fiberglass-reinforced boron-containing phenolic resin was used in this study. The laminate was prepared from resin alcohol solution impregnated glass sheets that originally consisted of 31 wt.% resin. The mechanical and electric properties were determined according to a method in the literature [5].

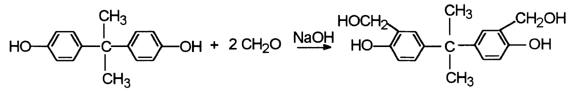
3. Results and discussion

3.1. *Structure of boron-containing bisphenol-A formaldehyde resin*

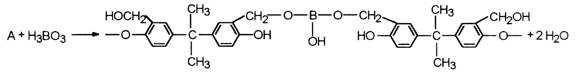
According to the literature [4,5], the structure of the condensation product of salicylalcohol of BPA with boric acid is as follows:



However, for the mole ratio of boric acid:benzyl alcohol = 1:3, the conversion rate of the reaction was determined at 90–120°C, and the reaction water should be taken into account. The results show that the conversion rate of the reaction of benzyl alcohol with boric acid was over 50% in 50 min, while it was only 4% in 150 min in the reaction of phenol with boric acid. It was shown that the reactivity of benzyl alcohol with boric acid was higher than that of phenol. So, the reaction and A stage resin have the following main form:



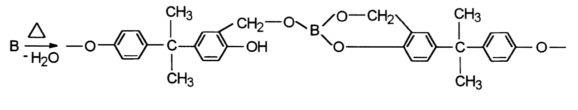
(A)



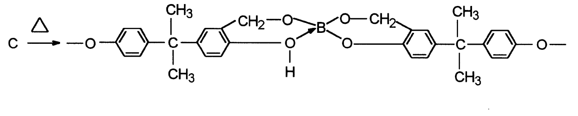
(B)

According to the literature [4,5], in the curing resin, when the six membered ring containing B ← O coordinate bond was formed, the IR absorption band of B–O borate at 1350 cm^{-1} would disappear, but from Fig. 1, curve 1, it can be seen that the IR spectrum of uncuring BBPAFR has an absorption peak at 1350 cm^{-1}, and when this resin was heated at 120°C, the absorption peak at 1350 cm^{-1} became larger (Fig. 1, curve 2). The results show that the six membered ring structure had not been formed in the uncuring resin. The borate value and phenol hydroxy value during the curing process were listed in Table 1.

As seen from Table 1 and Fig. 1, curve 1, the borate value of the uncuring resin was 0.30, but after being cured at 120°C for 1 h, the borate value of the resin reached 0.91. When this resin was heated to 140–180°C, the borate value and phenol hydroxy value were decreased (Fig. 1, curves 3–5). These results show that the six membered ring structure of borate and B ← O coordinate bond was formed at higher temperatures. But the coordinate structure was different from (1) [4,5], and it had the following form:



(C)



(D)

Fig. 1. Infrared spectrum of boron-containing bisphenol-A formaldehyde resin (1) uncuring, (2) 120°C, (3) 140°C, (4) 160°C, and (5) 180°C curing 1.5 h.

Table 1
The changes of borate values and phenol hydroxy values of BBPAFR during curing process

T (°C)	Uncuring	120	140	160	180
Borate value	0.30	0.91	0.73	0.32	0.12
Phenol hydroxy value	1.00	0.74	0.62	0.16	0.10

3.2. Thermal degradation and stability

In order to prepare TGA samples, the BBPAFR and common PFRs were cured at 160°C for 4 h. A 3 mg powder sample was subjected to TGA analyzer. Thermal degradation was carried out at a linear heating rate of 10°C min^{-1} in a static air atmosphere to the maximum temperature of 800°C. The weight loss fractions of resin were calculated, and the weight loss rates were shown as a function of temperatures in Fig. 2 and Table 2.

As seen from Fig. 2 and Table 2, the common phenol–formaldehyde resins had higher weight loss rates than BBPAFR. The weight loss for common PFR was over 96% at 650°C, while the BBPAFR was only 47.42% at the same temperature and the weight remained at 800°C was 34.00%. The temperature of semi-weight loss is about 150°C higher than that of common phenol–formaldehyde resin.

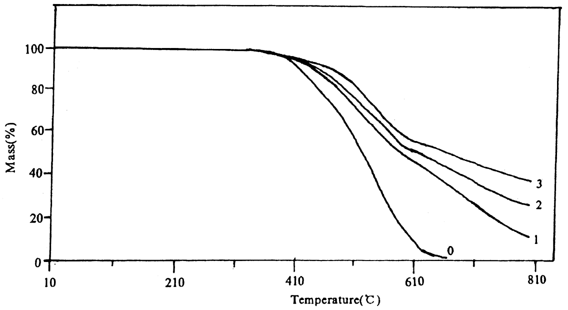


Fig. 2. Thermogravimetric analysis of PFR and BBPAFR heating rate – 0: PFR, 10°C min^{-1}; 1–3: BBPAFR, 1: 5°C min^{-1}; 2: 10°C min^{-1}; 3: 15°C min^{-1}.

The common phenol resin and cured boron-containing bisphenol-A resin were subjected to TGA analyzer, the measurement was performed at linear heating rates of 5°C min^{-1}, 10°C min^{-1}, 15°C min^{-1} in air atmosphere. The TG curves for the thermal degradation of the samples were shown in Fig. 2. As shown in Fig. 2, the common phenol resin was degradated in one stage, while the boron-containing bisphenol-A resin occurred in two stages. In the first stage, weight loss started at 350°C and continued till 600°C with 40.15% weight loss. In the second stage it started from 600°C to 800°C, the weight loss was 25.85%. The following kinetic equation was assumed to hold for the reaction [8]

$$\ln\left[C/T^{1.92}\right] = \ln\left(\frac{AE}{\Phi R}\right) + 3.77 - 1.92\ln E - \frac{E}{RT},$$

where $C = W/W_0$, W is the remained weight, W_0, the total weight loss in this stage, E, the activation energy, A, the frequency factor, Φ, the heating rate, and R, the ideal gas constant, respectively. The reaction activation energies and frequency factors can be obtained from TG curves and the above equation, and the results were listed in Table 3.

From Table 3, it can be seen that the thermal degradation activation energy in the second stage is higher than that in the first stage. It is illustrated that the B–O linkage cleavage is principal in the second stage, and it has higher heat oxidative resistance.

3.3. Mechanical and electric properties

Fiberglass-reinforced resins were used to study the mechanical and electric properties of the resins. The laminate was prepared from resin-impregnated glass sheets. The sheets, which originally consisted of 31%

Table 2
Thermal weight loss (%) of resins at different temperatures

T (°C)	350	400	450	500	550	600	650	700	750	800
BBPAFR	1.65	6.25	12.53	21.91	34.40	40.15	47.42	56.79	61.22	66.00
PFR	1.87	8.75	20.62	38.11	64.35	86.22	96.22	96.84	100	

Table 3
Activation energies and frequency factors of degradation of BBPAFR in air atmosphere

Heating rate (°C min^{-1})	First stage		Second stage	
	ΔE (kJ mol^{-1})	ln A	ΔE (kJ mol^{-1})	ln A
5	103.6	20.60	269.6	39.66
10	111.3	22.19	206.4	31.05
15	106.0	21.42	225.5	34.46

Table 4
Mechanical properties of different laminates

Resin	Impact strength (kg cm^{-2})	Tensile strength (kg cm^{-2})	Flexural strength (kg cm^{-2})	Compressive strength (kg cm^{-2})
BBPAFR	92	975	1590	2480
PFR	82	736	1000	1410

Table 5
Electric properties of different laminates

Resin	Dielectric constant ε (10^6 Hz)	Dissipation factor tan δ (10^6 Hz)	Volume resistivity ρ_v (Ω cm)	Surface resistivity ρ_s (Ω)
BBPAFR	5.06	2.24×10^{-2}	5.89×10^{14}	2.71×10^{12}
PFR	5.40	1.66×10^{-2}	1.70×10^{12}	5.70×10^{11}

wt.% resin, were B staged in a 160°C oven for 1 h. Then, they were thermoset at 160–200°C and pressed at 70 kg cm^{-2} for 30–45 min. The cured laminate was allowed to cool to room temperature in the press, and then post-cured at 120°C for 10 h. The mechanical and electric properties are shown in Tables 4 and 5, respectively.

As seen from Tables 4 and 5, fiberglass-reinforced boron-containing bisphenolic resins have better mechanical and dielectric properties than common fiberglass reinforced phenolic resin. The volume resistivity and surface resistivity of it were 10^1–10^2 higher than that of common phenolic resin laminate, and the dissipation factor, tan δ, was also in approximation with PFR.

4. Conclusions

In the BBPAFRs formed from the formalin method, the benzyl borate linkage was mainly formed during the synthesis process, and the phenol borate linkage and six membered ring were formed in the curing process at high temperature. This resin has better heat oxidative resistance and thermal stability than common phenol resin. In addition, this resin has good mechanical and electric properties. It can be used as fiberglass reinforced laminate, heat-resistant adhesive and coating material.

References

[1] Elias HG. Macromolecules. New York: Plenum Publishing Corporation; 1977. p. 952–8.
[2] Wu Y, Huang Z. Lett Polym 1981;6:403.
[3] Heefel HB, Kiessling HY, Lamper F, Schoenrogge B. Ger.offen 2,436.359, 1975.
[4] America Patash Chem Corp Br Pat 957611, 1964.
[5] Tu W, Wei S. Plastics Ind 1981;4:16.
[6] Patts Jr WJ. Chemical infrared spectroscopy, vol. I. New York: Wiley; 1963. p. 191–200.
[7] Liu Z. Introduction of thermal analysis. Beijing: Chemical Industry Publishing Co; 1991. p. 100–10.
[8] Madhusudanan PM, Krishnan K, Ninan KN. Thermochim Acta 1986;97:189.