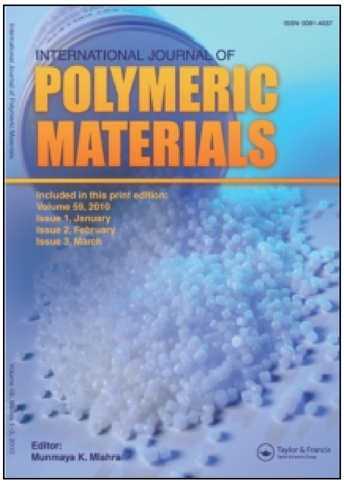

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis and Structure Characterization of Boron-Nitrogen Containing Phenol Formaldehyde Resin

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To cite this Article Gao, Jungang , Su, Xiaohui and Xia, Liya(2005) 'Synthesis and Structure Characterization of Boron-Nitrogen Containing Phenol Formaldehyde Resin', International Journal of Polymeric Materials, 54: 10, 949 — 961

To link to this Article: DOI: 10.1080/009140390504762

URL: http://dx.doi.org/10.1080/009140390504762

International Journal of Polymeric Materials, 54:949–961, 2005
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ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/009140390504762

Synthesis and Structure Characterization of Boron-Nitrogen Containing Phenol Formaldehyde Resin

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A boron-nitrogen modified phenol formaldehyde resin (BNPFR) was prepared from phenol, formalin, ammonia water, n-butyl alcohol, boric acid, and paraformaldehyde. The reaction mechanism and structure of BNPFR during the synthesis and curing process were investigated by FTIR, NMR. The thermal stability was determined by thermogravimetric analysis. The results showed that borate, ether linkage, methylene bridges, and hexatomic ring containing coordinate linkage of boron-nitrogen were formed mostly in the synthesis and thermosetting process. The carbonyl group was formed in the synthesis and curing process at higher temperature. The initial thermal degradation temperature of BNPFR is 100°C higher than common phenol formaldehyde resin (PFR).

Keywords: phenolic resin, boron-nitrogen containing, synthesis

INTRODUCTION

Phenol formaldehyde resins (PFRs) are used principally in the reinforced thermosetting materials. To improve the flame retardancy and thermo-oxidative resistance of PFR, the addition of boron has been reported [1–4]. The effectiveness of the borate as flame-retardants in various materials has been explained by their formation of nonpenetrable glass coating in these materials upon their thermal degradation. The glass coatings exclude oxygen and prevent further

Received 17 June 2004; in final form 26 June 2004.

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combustion propagation. Some reports have appeared on the synthesis, curing, and thermo-degradation process of boron-containing phenol-formaldehyde resin (BPFR) [5–6]. But the general BPFRs are extremely sensitive to moisture. To improve the hydrolytic resistance of BPFR, resins containing B–O and B–N coordination bond have been synthesized [5, 7–9]. The structure and thermo-stability of the resin containing B–O coordination bisphenol-A formaldehyde resin (BBPAFR) has been studied [7]. Although the resin containing B–N coordination was synthesized by the methods of hexamethylenamine and ammonia water [9–10], the reaction mechanism, structure change during synthesis and curing process, and the effect of N content on thermal stability have not been investigated until now.

In this article, BNPFR was synthesized from phenol, boric acid, formalin, ammonia water, and paraformaldehyde. The structure change of this resin during the synthesis and the curing process was investigated by Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectra (NMR). The thermal stability was determined by thermogravimetric analysis (TGA)

EXPERIMENTAL

Materials

Phenol, boric acid, formaldehyde solution (37% w/w), oxalic acid, 25% ammonia water, toluene, n-butyl alcohol, and paraformaldehyde were all analytical pure grade, which were supplied by Tianjin Chemical Reagant Co. of China.

Synthesis of BNPFR

105.75 g (1.124 mol) phenol, 33 g (0.407 mol) 37% formalin and 9.25 g (0.066 mol) 25% ammonia water were placed in a three-necked round bottom flask, equipped with a stirrer, a thermometer, and a condenser. The mixture was stirred and heated to 104°C, the reaction was maintained at this temperature for 90 min, then the temperature was decreased to 80°C. In the second step, 22.5 g (0.364 mol) boric acid, 0.625 g (0.007 mol) oxalic acid, 12.5 mL toluene and 29.625 g (0.38 mol) n-butyl alcohol were added to this system, refluxed for 4 h to remove the formed water, then the temperature was decreased to 80°C. In the third step, 38.75 g paraformaldehyde were added, the temperature was increased to 110°C and held for 4 h. Then the residual solvent was removed in vacuum. Finally, a yellow solid BNPFR was obtained. Changing the dosage of ammonia, resins with different nitrogen-boron ratio were obtained. Their material proportion and serial numbers are listed in Table 1

TABLE 1 Materials Proportion and Serial Number of BNPFR

Serial no.	Composition Phenol:Boric acid:Ammonia (mol ratio)
0	17:0.0:0.0
1	17:5.5:1.0
2	17:5.5:1.4
3	17:5.5:2.2

The resin of non-boron containing phenol formaldehyde (PFR) was synthesized in the first step, and the water was removed in vacuum.

FTIR Measurements

A Fourier-transform infrared (FTIR) spectrometer (Bro-Rad FTS-40 USA) was used to investigate the reaction mechanism and the structure changes of the BNPFR during the synthesis and curing process. The BNPFR sample was dissolved in tetrahydrofuran 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 bormide plate was scanned by the FTIR instrument. Then it was scanned after being cured at different temperatures for 30 min or 1 h. The first step production of BNPFR (non-containing boron) was determined by FTIR with the same method.

The principal absorption bands of BNPFR [11] are: the benzene ring is at 1600 cm^{-1}, the borate linkage B–O is at 1350 cm^{-1}, phenol hydroxyl C–O is at 1250 cm^{-1}, the methylol group is at 1020 cm^{-1}, either linkage C–O is at 1100 cm^{-1}, carbonyl group is at 1650 cm^{-1}, and the C–N linkage is at 1580 cm^{-1}. Quantitative analysis was done according to the literature [11]. The benzene ring absorption band at 1600 cm^{-1} was used as internal standard. According to the Beer-lambert law $A = 1gI/I_0$, the ratios of absorbance, A_{1350}/A_{1600} (borate value), A_{1250}/A_{1600} (phenol hydroxyl value) and A_{1650}/A_{1600} (carbonyl value) were obtained.

NMR Analysis

Solution nuclear magnetic resonance (NMR) spectra was obtained in dimethyl sulfoxide (D-DMF) with TMS (Wilmad Co., 99.8% D min.) on a Fourier transform NMR spectrometer (Bruker 400) with ^{1}H frequency at 400 MHz [12]. About 30.0 mg resin each of the first step production and boron-nitrogen containing phenol formaldehyde were placed in about 2.0 ml of DMF-d_6, respectively. The samples were gently warmed for 10 min until the solids were dissolved.

Thermal Analysis

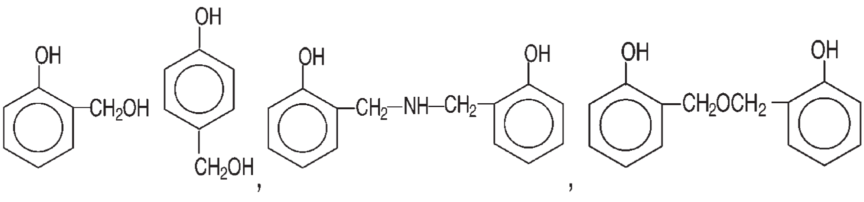
A Shimadzu TGA-40 thermobalance was used to determine the weight loss behavior of BNPFR during degradation [13]. About 8 mg BNPFR power cured at 180°C for 4 h was introduced into the thermobalance, then heated to 800°C at 10°C/min in air.

RESULTS AND DISCUSSION

Mechanism and Structure of BNPFR

The synthesis process of BNPFR was divided into three steps. In the first step, salicyl alcohol was produced by phenol and formalin, according to the literature [6, 8]. Because the reactivity of methylol group was higher than that of phenol hydroxyl [14], it reacted with ammonia to produce the first meso-production (see Scheme 1).

It can be seen from IR spectra (Figure 1, curve 1) that the absorption band of ether linkage appears at 1100 cm^{-1}, and the absorption band of C–N linkage appears at 1580 cm^{-1}, but there is no absorption of methylol group at 1020 cm^{-1}. Hence, most of the methylol groups have reacted to form ether and ammoniate. There is a strong absorption band of phenol hydroxyl at 1250 cm^{-1}, which indicates that the phenol hydroxyl group had not reacted in the first step. Figure 1, curve 2 is the IR spectrum of uncured BNPFR, the absorption band of phenol hydroxyl group at 1250 cm^{-1} had decreased sharply, and the absorptions of carbonyl and borate at 1650 cm^{-1} and 1350 cm^{-1} appeared, respectively. It shows that phenol hydroxyl group has reacted with butyoxyl borate through ester exchange, and some methylol groups have been oxidized during the synthesis process. The formation of numerous chemical species has been established (Scheme 2).



SCHEME 1 Products of first meso-reaction.

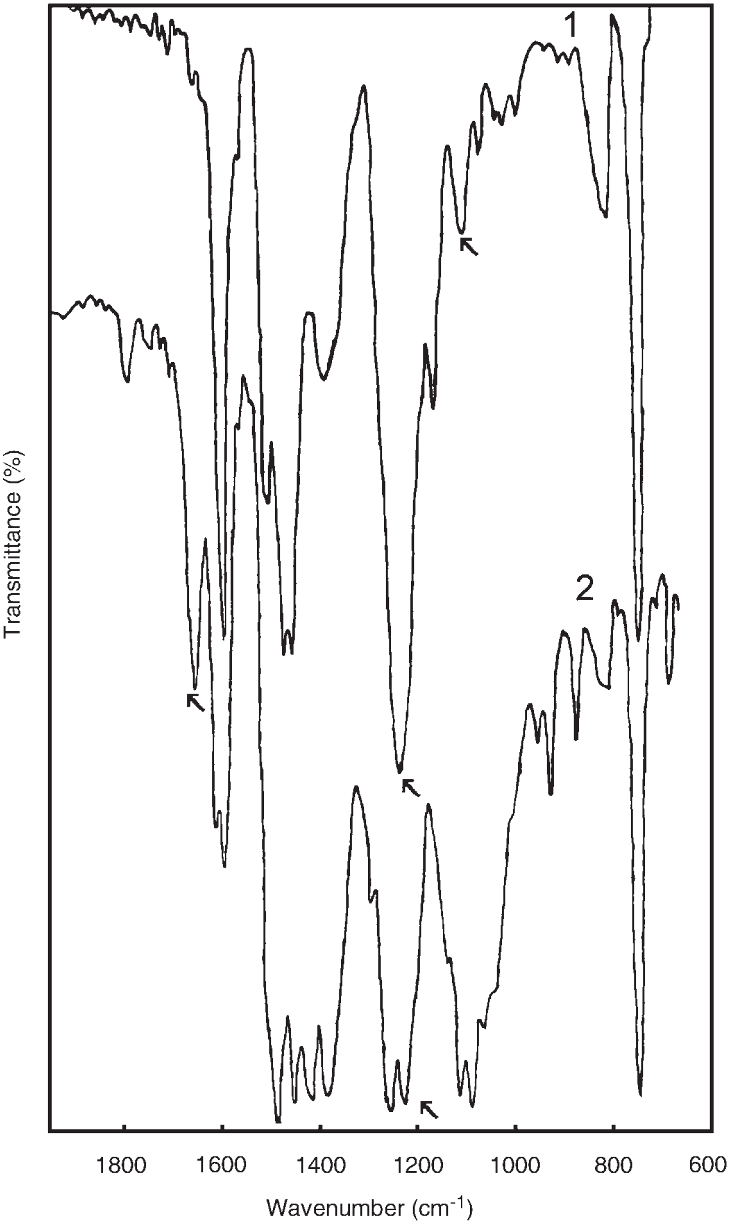
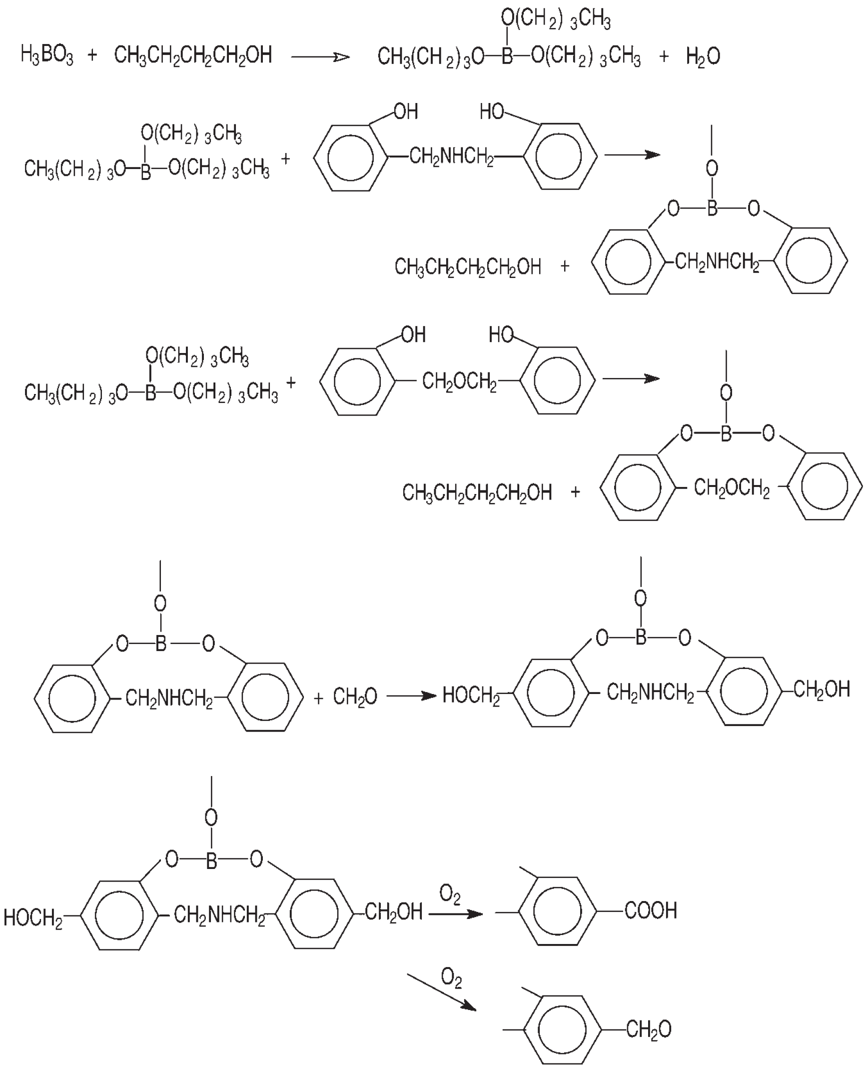
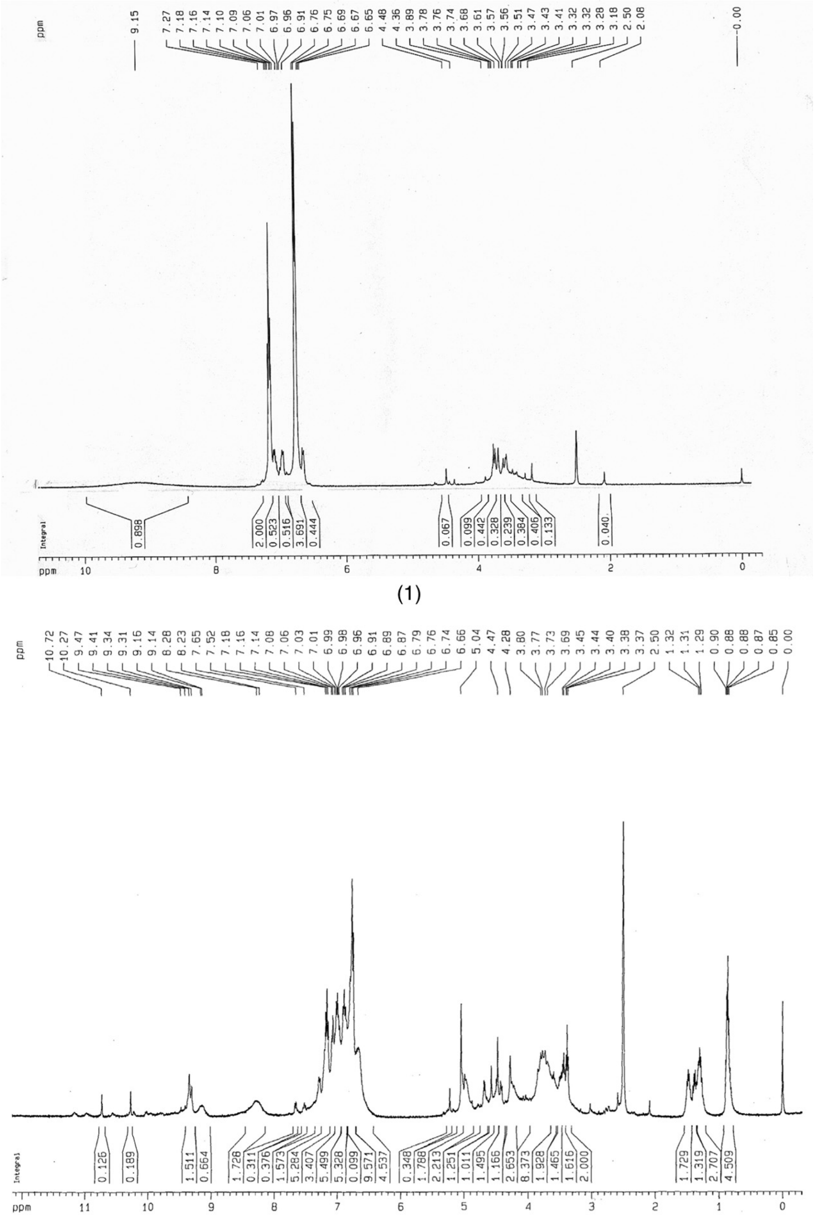


FIGURE 1 Infrared spectrum of boron-nitrogen containing formaldehyde resin: (1) the first step meso-production and (2) uncured BNPFR.



SCHEME 2 Some reaction products of the synthesis.

Figure 2 is the ^{1}HNMR spectrum of PFR and uncured BNPFR. As a result, the ^{1}H spectra for these resins are always complicated to analyze [15–16]. The wide resonance line at about 7.65 to 6.66 ppm is assigned to the aromatic hydrogen. The resonances at the regions from about 3.80 to 3.37 and 5.04 to 4.28 ppm are assigned to the methylene bridges, ether linkages, and ammoniate, respectively. The two



(1)

(2)

FIGURE 2 NMR spectrum of boron-nitrogen containing formaldehyde resin: (1) the first step production and (2) uncured BNPFR.

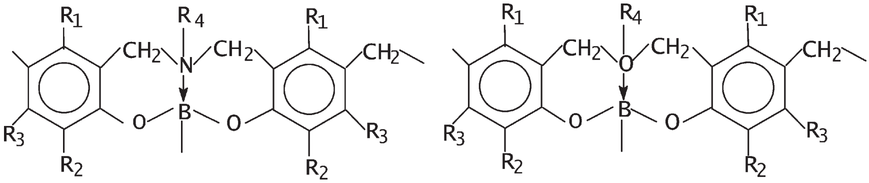
resonances at about 10.27 and 10.72 ppm (Figure 2, 2) are interpreted to result from reactions of forming aldehyde and carboxylic acid group [12]. At elevated temperature, the oxidation of the methylol group and ether linkage produces an aldehyde group and a carboxylic acid group.

Curing Process of BNPFR

According to the literature [8–17], when the hexatomic ring formed, the IR absorption band of B–O borate at 1350 cm^{-1} decreased. From Figure 1 and Table 2, it can be seen that the IR spectrum of uncured BNPFR has an absorption peak at 1350 cm^{-1}, and the borate value is 1.992. When this resin was heated to 120°C, the absorption peak at 1350 cm^{-1} became larger, and the borate value reached 2.896. The

TABLE 2 Changes of Functional Group Values of BNPFR During the Curing Process

Resin	T(°C)	Borate value	Phenol hydroxyl value	Carbonyl value
No.1	Uncured	1.992	2.280	0.670
	120°C (30 min)	2.896	2.614	0.644
	130°C (30 min)	3.528	2.513	0.685
	140°C (30 min)	3.191	2.523	0.697
	150°C (1 h)	3.354	2.500	0.766
	170°C (1 h)	3.383	2.399	0.766
	200°C (1 h)	2.983	1.991	0.667
	220°C (1 h)	2.004	1.616	0.694
	250°C (1 h)	1.756	0	0.714
No.2	Uncured	1.642	1.921	0.589
	120°C (30 min)	2.328	2.143	0.525
	130°C (30 min)	2.799	2.167	0.517
	140°C (30 min)	2.424	2.096	0.511
	150°C (1 h)	2.506	2.085	0.528
	170°C (1 h)	2.498	1.953	0.489
	200°C (1 h)	2.649	1.939	0.388
	220°C (1 h)	2.004	1.668	0.46
	250°C (1 h)	1.628	0	0.612
No.3	Uncured	1.795	2.228	0.545
	120°C (30 min)	2.584	2.326	0.501
	130°C (30 min)	3.145	2.320	0.548
	140°C (30 min)	2.710	2.284	0.561
	150°C (1 h)	2.914	2.232	0.605
	170°C (1 h)	2.791	2.118	0.649
	200°C (1 h)	2.767	1.928	0.552
	220°C (1 h)	1.969	1.630	0.573
	250°C (1 h)	1.463	0	0.667



SCHEME 3 Structures containing B–N and B–O coordinated bonds.

result is different from references [5, 8–10]. It shows that the hexatomic ring structure had not been formed in the uncured resin, while more phenol borate linkages were formed, which can be proved by the decrease of phenol hydroxyl value (Table 2).

When this resin was heated to 150–220°C, the absorption band of ether linkages at 1100 cm^{-1}, C–N linkage at 1580 cm^{-1}, and borate value (Table 2) have all decreased. These results show that the hexatomic ring structures containing B–N and B–O coordination bond were formed at higher temperature. Because the probability of B–N coordinate linkage formation is higher than that of B–O, the higher the content of N, the more B–N and the less B–O coordinate linkage are formed. The resin structure can be described as Scheme 3.

In addition, it can be seen from Table 2 and Figure 3 that with rising temperature, the absorption peak of the carbonyl group at 1650 cm^{-1} increased first, then gradually decreased. This is because the condensation reaction among methylol groups forms ether linkages, but the stability of ether linkages is poor, and they are liable to be oxidized to carbonyl or carboxylic acid at higher temperature. Because the carbonyl group can be decomposed gradually at higher temperature, it decreased again before 220°C. These reactions can be described as follows (Scheme 4).

At the same time, it can be seen from Table 2, that with increasing content of nitrogen in BNPFR, the maximum of boron value decreased. The borate value of No. 1 resin at 170°C is 3.383, whereas the borate value of the No. 3 resin is 2.791 at the same temperature. This is due to the fact that is the content of nitrogen increases, the probability of B–N coordination increases. But the existence of borate value above 250°C indicates that B–N and B–O coordination are not EXCLUSIVE because the structure of BNPFR is very complex.

Thermal Stability of BNPFR

Figure 4 shows the thermal weight loss of the resins of different proportions at 10°C/min heating rate. It can be seen that below 320°C,

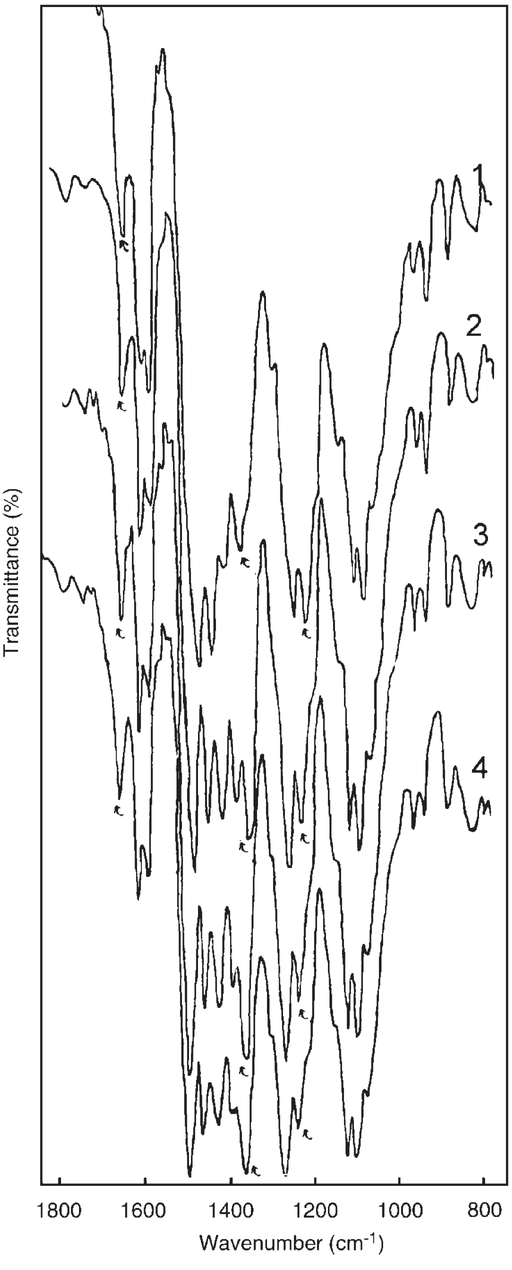
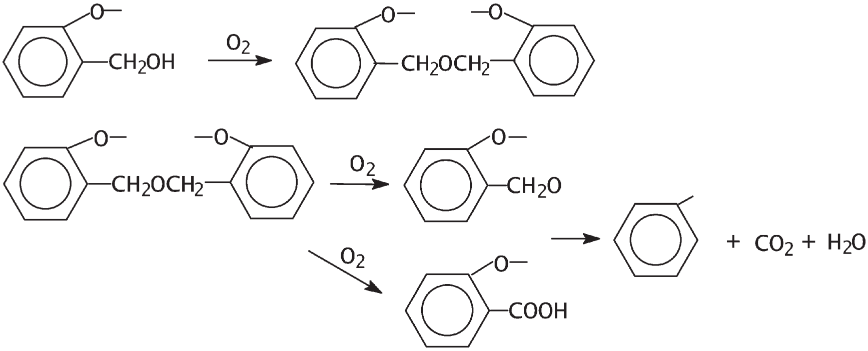


FIGURE 3 Infrared spectrum of boron-nitrogen containing formaldehyde resin (2.2 N): (1) uncured, (2) 120°C, (3) 150°C, and (4) 170°C cured 1 h.



SCHEME 4 Oxidative bond formation and cleavage.

the resins with different B–N proportion have the same thermal weight loss, which is about 3%. It is believed that it is caused by the evaporation of water and other small molecules and should not be considered in the degradation kinetics. According to the TGA curves (Figure 4), the degradation process can be divided into two principal stages. In the first stage (about 420–600°C), the weight loss may be caused by the oxidation and breakage of some ether linkages, methylene bridges and other weak linkages. In the second stage (about 600–800°C), some B–O linkages, B–N linkages, and benzene rings will be

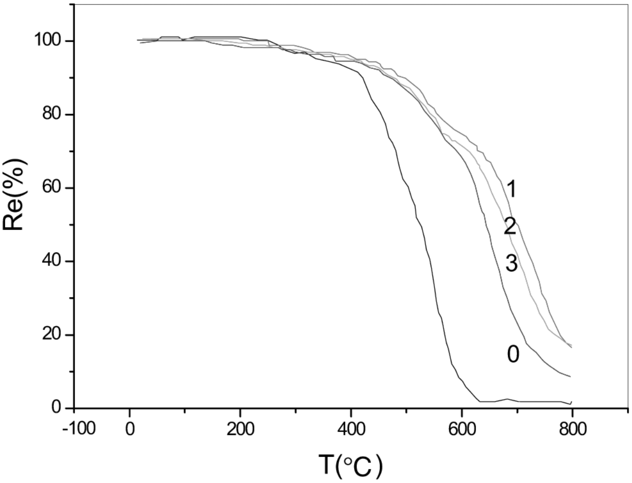


FIGURE 4 Thermogravimetric analysis of PFR (0) common resin, (1) 1.0 N, (2) 1.4 N, (3) 2.2 N, at heating rate of 10°C/min in air.

TABLE 3 The Degradation of Different Resins

Number	0	1	2	3
T_i (°C)	320	420	420	420
$T_{1/2}$ (°C)	520.39	697.76	680.79	642.71
Re (%)	1.83	40.68	30.43	15.73

oxidized and broken. The initial decomposition temperature (T_i), the temperature of half-weight loss ($T_{1/2}$), and the remainder ratio (Re) at 720°C are listed in Table 3.

From Figure 4 and Table 3, it can be concluded that the common PFR has higher weight loss rate than that of BNPFR. The weight loss for the common PFR is about 98% at 720°C, whereas the BNPFR (No. 1) is only 59.3% at the same temperature. Its temperature of half weight loss of about 150°C higher than that of common PFR, and the starting weight loss temperature is about 100°C higher than that of PFR. This indicates that the resin with nitrogen has better thermal stability.

CONCLUSIONS

The borate linkage, B–N linkage, ether linkage, and methylene bridges were formed during the synthesis and curing process of BNPFR. The reactivity of methylol group was higher than that of phenol hydroxyl, so ammonia reacted with methylol group first, then ester exchange between butyoxyl borate and phenol hydroxyl group took place. The hexatomic rings containing coordinate linkage of boron-nitrogen and boron-oxygen were formed mostly in the thermosetting process. BNPFR has better heat-oxidative resistance and hydrolytic resistance [9–10] than common PFR. In addition, its initial thermal degradation is 100°C higher than that of common phenol resin.

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