Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 44 (2003) 7353–7359
polymer
www.elsevier.com/locate/polymer

Boron-modified phenolic resins for high performance applications

Mohamed O. Abdalla, Adriane Ludwick*, Temisha Mitchell

Department of Chemistry, Tuskegee University, 102 Armstrong Hall, Tuskegee, AL 36088, USA

Received 17 December 2002; received in revised form 11 August 2003; accepted 5 September 2003

Abstract

A boron-modified phenolic resin (BPR) that flows at usable processing temperatures was prepared from the solvent-less reaction of triphenyl borate (TPB) and paraformaldehyde (PF). The reaction of TPB and PF was performed at three different resinifying temperatures, 130, 120 and 90 °C. The BPR produced at 90 °C melted upon reheating, which indicated promising processing applications for this resin. ^{1}H and ^{13}C NMR spectra of resins from the three resinifying temperatures had the same pattern of absorptions. Substitution of methylol groups occurred at the *ortho* and *para* positions of the ester phenyl rings (4.86–4.75 ppm). Aromatic, methylene and ether linkage protons were assigned at about 7.45–6.74, 4.93–3.36 and 5.30–4.91 ppm, respectively. The synthesis of BPR from the reaction phenolic resins, produced under basic conditions (resoles) and boric acid was not feasible. The reactivity of the resoles species with each other is more favorable than that with boric acid.

Keywords: Phenolic resin; Boron; Flame retardancy

1. Introduction

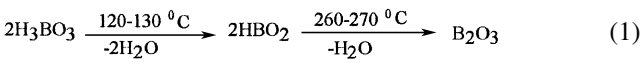
Phenolic resins (PR) are used principally in reinforced thermoset molding materials. Generally, PR are used in combination with organic or inorganic fibers and fillers. The curing of these combined materials at elevated temperatures usually provides dimensionally stable compounds with excellent moldability. Moreover, these compounds possess remarkable thermal stability, flame retardancy and heat resistance properties [1–4]. The rapid growth of PR applications has enhanced extensive research to improve their thermal properties. From their primary usage as binders in wood composites, the use of PR has evolved to composites for critical applications in military and aerospace industries. To improve the flame retardancy and thermo-oxidative resistance of PR, the addition of boron, phosphorus or silicon compounds has been reported [4–7]. At Tuskegee, we have focused on the preparation of a boron-containing phenolic resin (BPR) that can be processed using common techniques such as resin transfer molding (RTM). The prepared BPR is intended for use as the innermost lining in a multilayer composite for tank armor and related future applications.

The usage of borates in enhancing flame retardancy of polymeric materials was reported early in the twentieth century [7–9]. The effectiveness of the borates as flame-retardants in various materials has been explained by their formation of nonpenetrable glass coatings in these materials upon their thermal degradation. The glass coatings exclude oxygen and prevent further propagation of combustion. Boric acid and the hydrated inorganic borates have low melting points and nicely fit this scheme of forming glass coatings. When slowly heated, boric acid (mp 171 °C) loses water and changes first to metaboric acid, HBO_2, and finally to boric oxide, B_2O_3 (Eq. (1)). Above 325 °C, B_2O_3 softens to glass and becomes pourable only at 500 °C. The flame retardant action of the boron-containing compounds on polymeric materials is chemical as well as physical. It was found that these inorganic boron compounds promote char formation in the burning process [7–11]. The mechanism involving the formation of the char is clearly related to the thermal action of boric acid with alcohol moieties [7]. The borate esters formed further dehydrate, probably by carbocation mechanisms. Thus boron is found to exert its flame retardant action on polymeric materials at a temperature well below that of the normal pyrolysis of

* Corresponding author. Tel.: +1-334-727-8220; fax: +1-334-724-4492.
E-mail address: aludwick@tusk.edu (A. Ludwick).

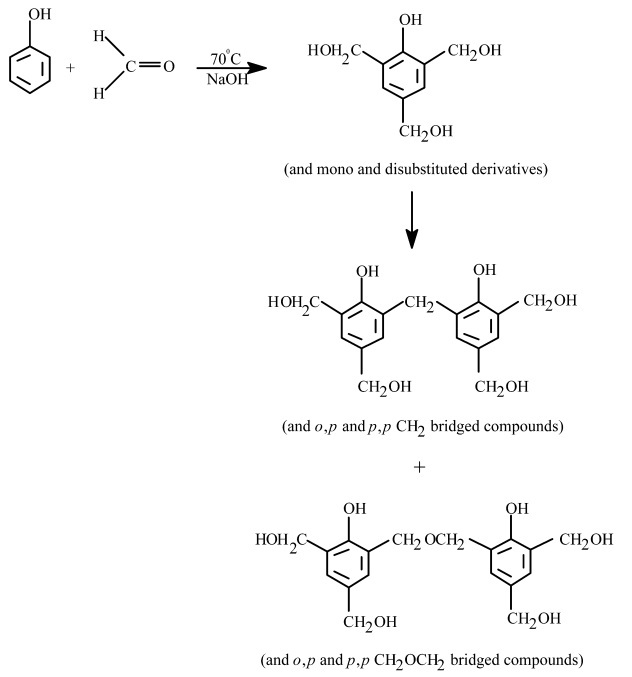
0032-3861/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2003.09.019

these materials:

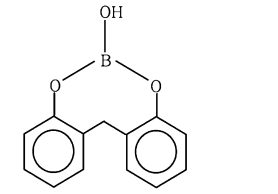


(1)

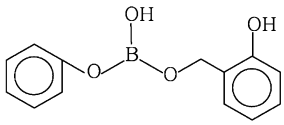
The synthesis of BPR has been reported previously [12–16]. Hirohata and coworkers [12,13] reported a solid-state preparation method for BPR (Eqs. (2) and (3)). They suggested that the phenyl borates prepared were a mixture of mono-, di- and tri-phenyl substituted boric acid depending on the molar ratio of phenol to boric acid used. No structural characterization for the prepared resins was reported in Hirohata's study. However, thermal characterization of the hardened prepared resin showed the BPR to have superior resistance against thermo-oxidative degradation in comparison to the hardened regular and halogenated PR [13]. Jungang [14–16] reported an aqueous preparation method for the BPR in a basic medium. Initially, resoles were synthesized by reacting phenol (or bisphenol-A) with 37% formaldehyde solution in a basic medium at 70 °C for 1 h, resulting in a product of various structures (Scheme 1). Water was removed from the product under vacuum to concentrate the resoles. Boric acid was added to the concentrated resoles and the reaction temperature was maintained at 102–110 °C for 40 min to produce a solid yellowish-green resin. Jungang also studied the reactivity of boric acid with phenolic hydroxyl groups, to give compounds such as **1** versus that of the methylol hydroxyl groups, to give compounds such as **2**. Boric acid was reacted with benzyl alcohol (1:3 molar ratio) as a model compound for the methylol substituted phenol. For comparison, boric acid was reacted with phenol under the same reaction conditions. Jungang calculated the percent conversion for both reactions based on the eliminated water. His results showed that the percent conversion for the reaction of boric acid/benzyl alcohol was 50%, while the percent conversion for the boric acid/phenol reaction was only 4%. For the boric acid/phenol conversion, Jungang observed precipitation of boric acid from the reaction when the stirring was stopped. These results indicated that the reactivity of the methylol hydroxyl groups with boric acid was much higher than the reactivity of phenol hydroxyl groups with boric acid.



Scheme 1. Reaction of phenol and formaldehyde solution in presence of NaOH to produce resoles.

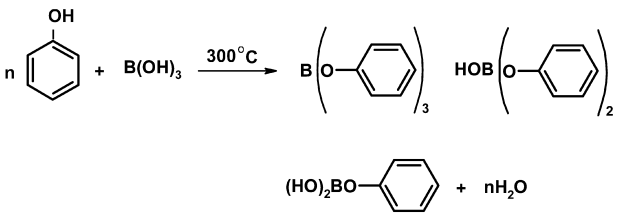


1

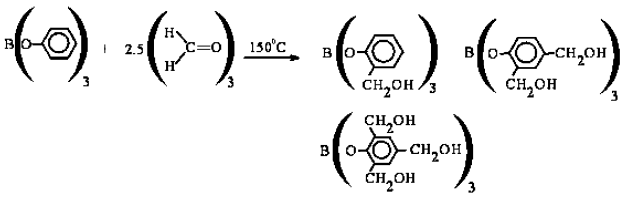


2

In this paper we present a solid-state preparation method and spectroscopic characterization of a processable BPR that can flow at usable processing temperatures. Three resins were prepared at three different temperatures (130, 120, and 90 °C) from the reaction of a commercial triphenyl borate TPB and paraformaldehyde (PF). This paper also presents the results of several trials conducted to prepare BPR by an aqueous solution method.



(2)



(3)

2. Experimental

2.1. Reagents

Commercial triphenyl borate (TPB) was obtained from TCI America. Formaldehyde solution (37%, w/w), sodium hydroxide and paraformaldehyde (PF) were obtained from Fisher Scientific.

2.2. Measurements

Solution nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ with 1% TMS (Wilmad Glass Co., 99.8% D min.) on a Fourier transform NMR spectrometer (Bruker 250) with a ^{13}C frequency of 62.89 MHz and ^{1}H frequency of 250.133 MHz. Infrared spectra were obtained (KBr pellet) on a FT-IR spectrometer (Bomem, Michelson Series, model: MB-102). Elemental analysis was performed by Galbraith Laboratories, Inc. for the resin obtained from commercial TPB and PF reaction at 90 °C and the filtrate obtained from the resoles/boric acid reaction.

2.3. Syntheses

Two methods for the synthesis of boron-modified phenolic resins were performed.

2.3.1. Method 1. Reaction of TPB with PF

TPB (3.01 g, 0.01 mol) was placed in a 25 mL three-necked round bottom flask. The ester melted at 60–70 °C and PF (2.33 g, 0.03 mol) was added to the melted ester. The reaction temperature was increased at a rate of 1–2 °C/min to 130 °C. A yellow solid product was obtained at 130 °C. The reaction was repeated at 120 and 90 °C using approximately similar amounts of reactants. Highly viscous yellow products that solidified upon cooling were obtained from these latter reactions. All products were soluble in DMSO with variable solubility in chloroform depending on the preparation temperature. For NMR analysis, a 30.0 mg sample of the resin prepared at 130 °C was left overnight in about 2.0 ml of $CDCl_3$. The resulting mixture was warmed gently for 10 min below the boiling point of $CDCl_3$ until approximately one-third of the solid dissolved. The liquid was separated from the solid by decantation. For preparation of NMR samples for the 120 and 90 °C resins, 30.0 mg samples of the resins were placed in about 2.0 ml of $CDCl_3$. The samples were gently warmed for 10 min until half of the solids were dissolved. The solids were separated by filtration through Pasteur pipettes filled with glass wool.

2.3.2. Method II. Resin from resoles/boric acid

2.3.2.1. Resoles. Aqueous formaldehyde (37%) (87.78 g, 2.92 mol) was placed in a 250 ml three-necked round bottom flask equipped with a magnetic stirrer and phenol (84.87 g, 0.90 mol) was added. Sodium hydroxide (0.35 g, 0.009 mol), as a catalyst, was added to the reaction flask. The reaction flask temperature was monitored by a thermometer inserted into the reaction medium. The temperature of the reaction was maintained at 70 °C for 1 h. The product was allowed to cool to 40–45 °C and water (30 ml) was removed under vacuum.

2.3.2.2. Resoles/boric acid reaction. Approximately half of the resoles obtained (66.04 g) was placed in a 100 ml three-necked round bottom flask equipped with a stirrer. Boric acid (7.23 g, 0.012 mol) was added and the reaction temperature was maintained at 102–110 °C for 40 min. A solid precipitated from the viscous product upon cooling. The mixture of solid and liquid product was separated by suction-filtration using a sintered-glass funnel. The precipitate was analyzed by IR spectroscopy.

3. Results and discussions

3.1. Method I. Synthesis of BPR using commercial triphenyl borate

Despite the thermal stability of the phenyl borates, their extreme sensitivity to moisture makes their synthesis a challenge [10,11]. Thus, in this work we utilized a commercial TPB in the reaction with PF to produce the BPR. In previous work, Hirohata and coworkers [12,13] reacted the TPB with PF at a temperature of 150 °C to resinify, and hardened this resin at 80 °C for 24 h and at 100 °C for 24 h.

At a temperature of 130 °C, the reaction of the commercial TPB with PF yielded a yellow solid. Since our focus was the synthesis of a liquid BPR, the limiting reaction temperature of the TPB and PF was lowered to 120 and 90 °C and the products were characterized by solution NMR to determine if their chemical structures matched those from the 130 °C reaction. The physical state of the resins obtained varied with the limiting reaction temperatures. At 120 °C, a very viscous product was obtained that solidified at room temperature. The resin obtained at 90 °C was the least viscous; it solidified at room temperature upon standing for a few hours. Both the 120 and 90 °C resins melted upon reheating, which indicates promise for the processing application of these resins. They could be processed immediately after their preparation or could be warmed if they were to be used after their solidification.

3.1.1. Method I. Characterization of resins obtained from reaction of commercial TPB with PF

3.1.1.1. Spectroscopic characterization. In the syntheses of non-boron containing phenol-formaldehyde resins, the formation of numerous chemical species has been established (see Scheme 1) [1–4]. As a result, the ^{1}H and ^{13}C NMR spectra for these resins are always complicated to analyze [17–20]. In general, the ^{1}H NMR spectra of the resins (Fig. 1(a)–(c)) obtained from commercial TPB/PF reactions resembles those of non-boron containing phenolic resins [18,19], reflecting the complexity of the boron containing system too. Compared to the ^{1}H NMR spectrum of TPB in $CDCl_3$ (Fig. 1(d)), the spectra of the resins prepared at 130, 120 and 90 °C show that substitution of methylol groups occurred, presumably at the *ortho* and *para* positions on the ester phenyl rings (4.86–4.57 ppm) [19]. Absorptions for different characteristic chemical linkages

that usually appear in non-boron containing phenolic resins spectra were also observed in the spectra of boron containing resins prepared. The wide resonance line at about 7.45–6.74 ppm is assigned to the aromatic hydrogens. The resonances at the regions from about 4.93 to 3.36 and 5.29 to 4.91 ppm are assigned to the methylene bridges and ether linkages, respectively. The two resonances at about 10 and 11 ppm are interpreted to result from reactions involving the methylol groups, forming aldehyde and carboxylic acid groups (Eq. (4)) [6]. At elevated temperatures, substitution reactions revert to starting materials (formaldehyde and phenol); the carboxylic acid group results from oxidation of the methylol group to aldehyde and carboxylic acid. The intensities of the two resonances at about 10 and 11 ppm were higher in the spectrum of the resin obtained at 130 °C in comparison to the resins obtained at 120 and 90 °C. This finding was rationalized as due to the effect of the higher resinifying temperature favoring the formation of aldehyde and carboxylic groups from the methylol groups. Generally, the pattern of absorptions was comparable in the 130, 120 and 90 °C resins. This result confirmed that the reaction of the TPB with paraformaldehyde to form the BPR prepolymer could occur at temperatures lower than the 150 °C of the previous work on this system [13]. Further information about the complexity of the BPR system was obtained from the ^{13}C NMR spectra of the resins prepared (Fig. 2(a)–(c)). Although the intensity of the carbons chemical shifts varied among the three products, the pattern

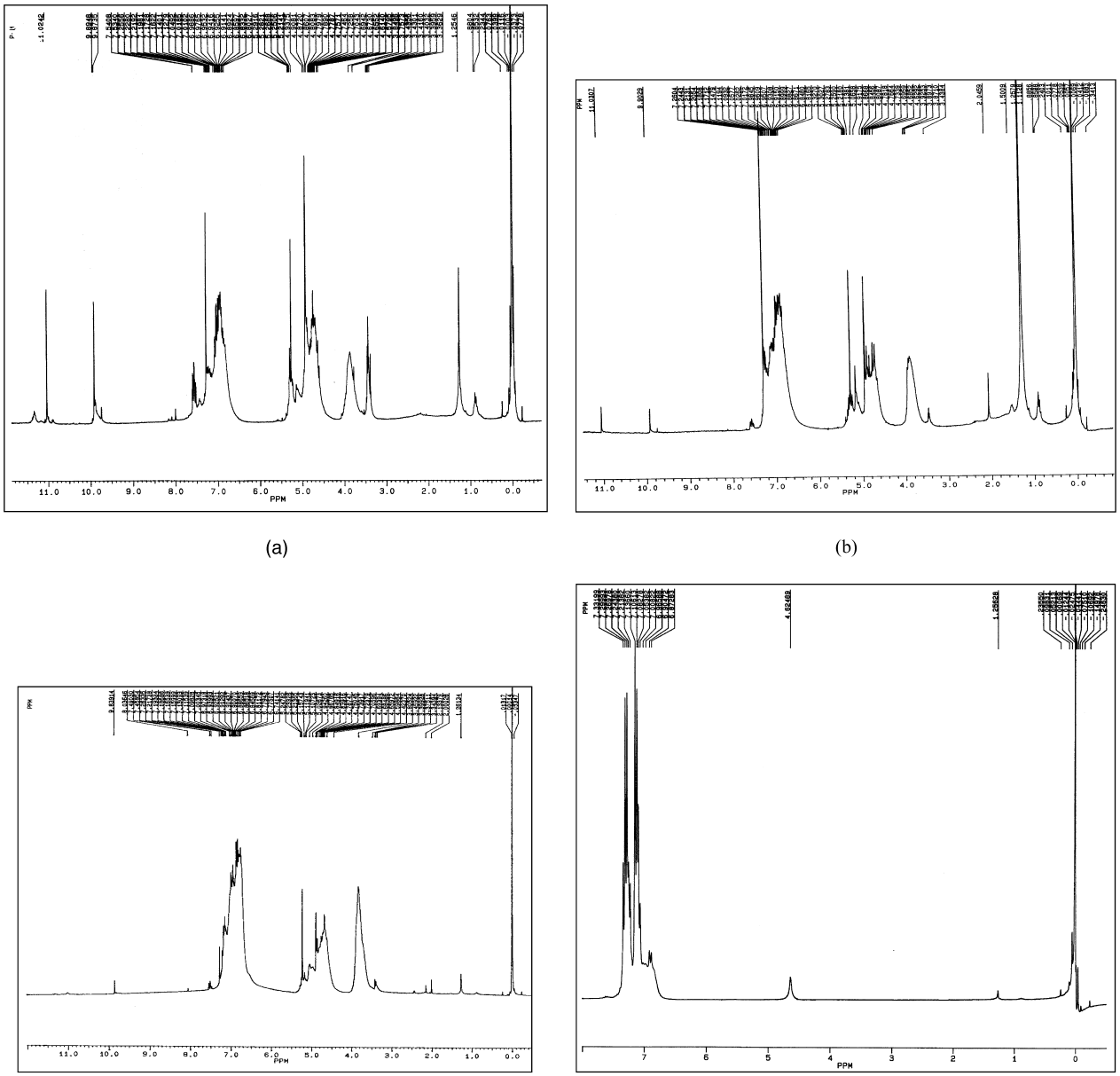
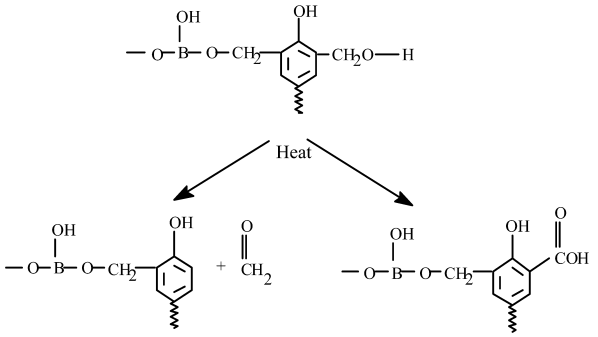


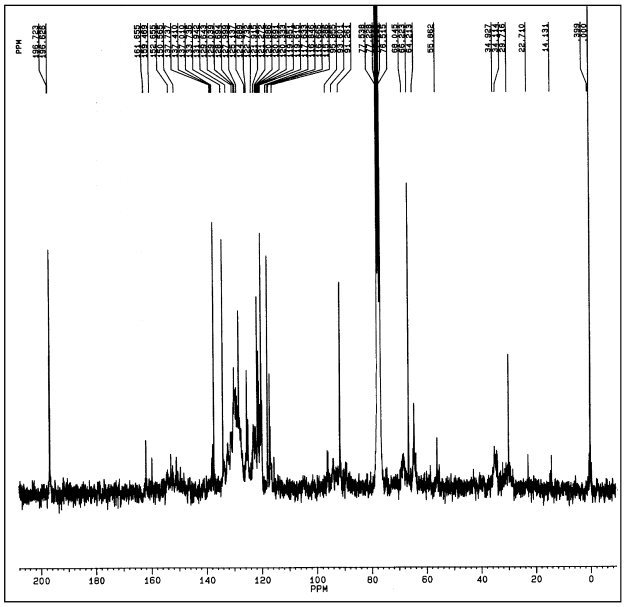
Fig. 1. ^{1}H NMR spectra of resins from commercial TPB/PF reaction in $CDCl_3$ at (a) 130 °C; (b) 120 °C; and (c) 90 °C, (d) pure TPB.

of absorptions was comparable:

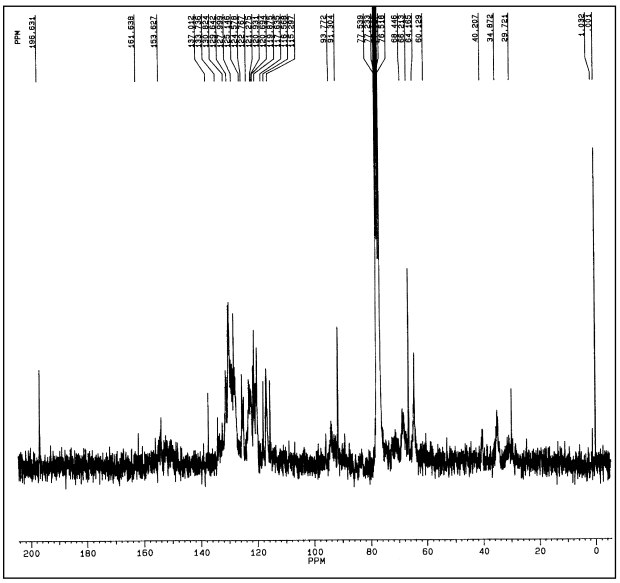


(4)

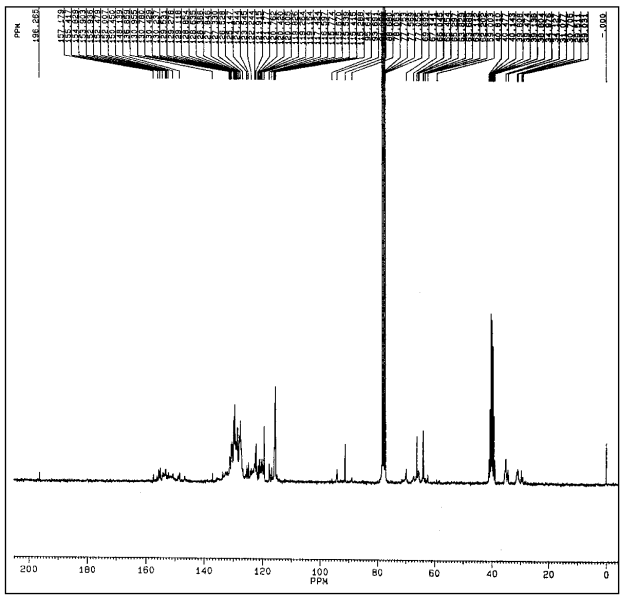
3.1.1.2. Elemental analysis. The BPR produced at 90 °C appeared to be the best resin for potential processability. Thus, the focus of our further analysis was on this resin. Elemental analysis of this resin showed that the elements present were 63.02% carbon, 5.78% hydrogen, and 2.71% boron. A mass balance calculation (Eq. (3)) of percent boron was done for the cases of mono-, or di- or tri-substituted TPB molecule as the sole product of the reaction. In this calculation, we assumed that the product of TPB with PF at 90 °C would not contain significant percentage of crosslinks (methylene and ether



(a)



(b)



(c)

Fig. 2. ^{13}C NMR spectra of resins from commercial TPB/PF reaction in $CDCl_3$ at (a) 130 °C; (b) 120 °C; and (c) 90 °C.

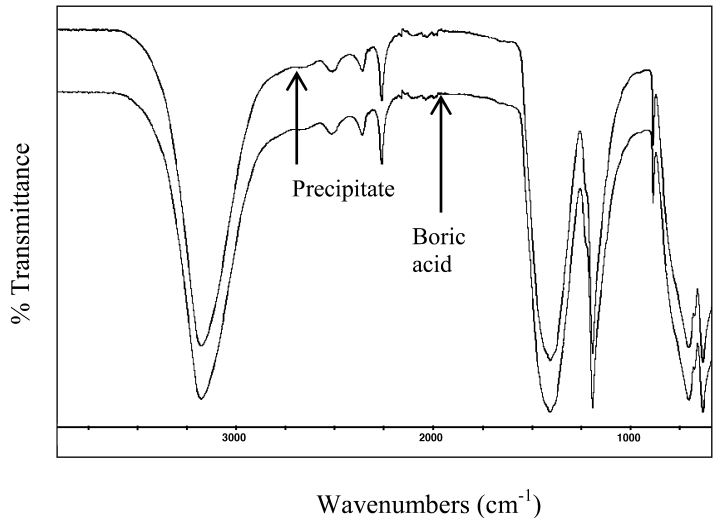
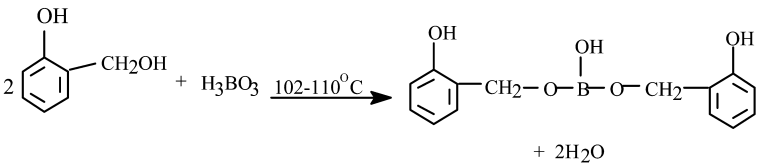


Fig. 3. FT-IR spectrum of precipitate from resoles/boric acid reaction and boric acid.

linkages) among the substituted TPB molecules. The calculation yielded values of 2.85, 2.30, and 1.95% boron for the mono-, di- and tri-substituted TPB, respectively. Comparison of the calculated boron percent value to the experimental value (2.71%) suggested that the mono-substituted TPB (2.85%) is the predominant structure in the resinified product.



(5)

3.2. Method II. Preparation of BPR from resoles/boric acid

A significant amount of yellowish precipitate (8.25 g) was observed to form immediately after completion of the reaction of the resoles with boric acid. The yellowish precipitate was separated by suction-filtration and characterized by infrared spectroscopy.

3.2.1. Infra-red analysis

A comparison of the IR spectra of the precipitate and of boric acid (Fig. 3) indicates that the yellowish solid is essentially boric acid. It is likely that the boric acid (solubility: 6.35^{30} and 27.6^{100} g/cm^3) [21] added to the resoles system dissolves in the hot solution to form a homogenous system. When the temperature of the system is lowered, the boric acid precipitates from the solution. Hence, the reactivity of boric acid with methylol groups of resoles appears to be much less than the reactivity of methylol groups with each other. The methylol groups condense with each other forming methylene and ether linkages (Scheme 1). This trend is supported by the IR results reported by Jungang [14] for the resoles/boric acid system. According to Jungang, an apparent decrease was observed in the peak at 1020 cm^{-1} assigned to the methylol hydroxyl group after the addition of boric acid to resoles. Jungang explained that it was due to the reaction of the methylol hydroxyl group with those of boric acid to form the boric acid benzyl ester (Eq. (5)). However, it is apparent that the decrease in the peak of the methylol hydroxyl group was due to their condensation with each other forming the methylene and ether linkages rather than their reaction with boric acid.

Weight analysis of solids obtained from the resoles/boric acid reactions supports the results obtained from the IR analysis of the precipitate. The initial weight of the precipitate (8.25 g) is higher than the weight of the starting boric acid (7.23 g). This increased weight was attributed to adherence of the highly viscous resoles to boric acid causing an increase in the weight of the precipitate. When the precipitate is washed with acetone, the weight of the recovered boric acid is found to be 6.95 g, which is equivalent to 96.13% of the initial boric acid weight. The high percentage of the recovered boric acid indicates that the reactivity of hydroxyls of the boric acid is very low with either methylol and/or phenolic groups.

3.2.2. Elemental analysis

The elemental analysis of the filtrate showed 68.66% carbon, 6.45% hydrogen, and 0.37% boron. Calculation of the percent value of boron that can be present in a prepolymer obtained from the resoles/boric acid reaction gave a value of about 4%. The calculation was done on the diester product obtained from the hypothesized reaction of boric acid with two molecules of mono-substituted phenol

molecules (Eq. (5)). It is also possible that the small percentage of boron in the filtrate is due to boric acid trapped in the resole molecules.

4. Conclusions

A boron-modified phenolic resin, which flows at usable processing temperatures, was prepared from the reaction of TPB and PF. The physical properties of the resins prepared depended on the limiting resinifying temperatures, 130, 120 and 90 °C. The 130 °C resin solidified at the limiting reaction temperature while the viscous 120 and 90 °C resins solidified upon standing at room temperature. The solidified resins (120 and 90 °C) melted upon reheating, which indicates promising processing applications for these resins. The ^{1}H and ^{13}C NMR spectra of resins from the three resinifying temperatures had similar absorption patterns. Substitution of methylol groups presumably occurred at the *ortho* and *para* positions of the ester phenyl rings (4.86–4.75 ppm). Aromatic, methylene and ether linkage protons were assigned at the absorptions at 7.45–6.74, 4.93–3.36 and 5.30–4.91 ppm, respectively.

The synthesis of BPR from the reaction of resoles (PR prepared on a basic aqueous medium) with boric acid is not feasible. In the resoles/boric acid system, quantitative amounts of boric acid (96%) were isolated at the end of the reaction duration. IR spectra of the isolated material and that of boric acid were identical. The reactivity of the resoles species with each other is more favorable than that with boric acid. Hence, the boric acid reactant dissolves in the heated aqueous medium and precipitates upon cooling this medium.

Acknowledgements

The financial support provided by the Army Research Office under contract DAAH04-95-1-0396 was greatly appreciated. The authors acknowledge Mr Zhenyi Zhang, a technician at Tuskegee-Center for Advanced Materials, for his translation of the article by Jungang [14] to the English language. The authors also acknowledge the Department of Chemistry at Auburn University for their assistance in obtaining NMR spectra.

References

[1] Martin R. The chemistry of phenolic resins. New York: Wiley; 1956. Chapters 1, 2 and 4.
[2] Whitehouse A, Pritchett E, Barnett G. In: Ritchie PD, editor. Phenolic resins, 2nd ed. London: Iliffe Books; 1967. Chapter 1.
[3] Knop A, Scheib W. Chemistry and application of phenolic resins. Berlin: Springer; 1979. Chapters 1 and 8.
[4] Knop A, Pilato LA. Phenolic resins: chemistry, applications, performance and future direction. Berlin: Springer; 1985. Chapters 1 and 9.
[5] Sunshine NB. In: Kuryla WC, Papa AJ, editors. Flame retardancy of polymeric materials, vol. 2. New York: Marcel Dekker; 1973. Chapter 4.
[6] Conley RT, Quinn DF. In: Lewin M, Atlas SM, Pearce EM, editors. Flame-retardant polymeric materials. New York: Plenum Press; 1965. Chapter 8.
[7] Pitts A. In: Kuryla WC, Papa AJ, editors. Flame retardancy of polymeric materials, vol. 1. New York: Marcel Dekker; 1973. Chapter 2.
[8] Hilado JC. Flammability handbook for plastics, 2nd ed. Wesport, Conn.: Technomic; 1974. p. 142.
[9] Shen K, Griffin T. Fire and polymers. ACS Symposium Series, vol. 245. Washington, DC: ACS; 1990. Chapter 12.
[10] Ross VF, Edwards JO. In: Muretterties EL, editor. The chemistry of boron and its compounds. New York: Wiley; 1956. Chapter 3.
[11] Gerrard W. The organic chemistry of boron. London: Academic Press; 1961. Chapter 1.
[12] Hirohata T, Misaki T, Yoshii M. J Soc Mater Sci Jpn, (Engl Transl) 1987;36(401):185–8.
[13] Hirohata T, Misaki T, Komodo S, Yoshii M. J Soc Mater Sci Jpn, (Japanese) 1989;38(432):1098–101.
[14] Jungang G. Acta Chim Sin (Engl Transl) 1990;48:411–4.
[15] Jungang G, Liu Y, Yang L. Polym Degrad Stab 1999;63:19–22.
[16] Jungang G, Liu Y, Wang F. Eur Polym J 2001;37:207–10.
[17] Colclough T, Gerrard W, Lappert MF. J Chem Soc 1955;4:907–11.
[18] Woodbrey JC, Higginbottom HP, Culberston HM. J Polym Sci 1965; 3:1079–106.
[19] King PW, Mitchell RH, Westwood AR. J Appl Polym Sci 1974;18: 1117–30.
[20] Kim GM, Amos LW, Barnes EE. Ind Engng Chem Res 1990;29: 2032–7.
[21] Weast RC, Astle MJ, editors. CRC handbook of chemistry and physics, 62nd ed. Boca Raton, FL: CRC Press; 1981–2.