

In Situ Modification of Cyclohexanone Formaldehyde Resin with Boric Acid for High-Performance Applications

Nilgün Kızılcan, Pelin Dinçer

Department of Chemistry, Faculty of Science, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

Correspondence to: N. Kızılcan (E-mail: kizilcan@itu.edu.tr)

ABSTRACT: A boron-containing cyclohexanone formaldehyde resin (BCFR) was synthesized from cyclohexanone, formaldehyde, and boric acid. The effects of the boric acid concentration, solubility, molecular weight, and thermal properties on the product were investigated. Characterization of the BCFRs was done by NMR spectroscopy, gel permeation chromatography, and Fourier transform infrared-attenuated total reflectance spectroscopy. The thermal properties of the samples were determined with differential scanning calorimetry and thermogravimetric analysis. The study results demonstrate that the resin had higher heat-resistance properties than the commonly modified cyclohexanone formaldehyde resin. The obtained samples were also characterized morphologically by scanning electron microscopy. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2813–2820, 2013

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INTRODUCTION

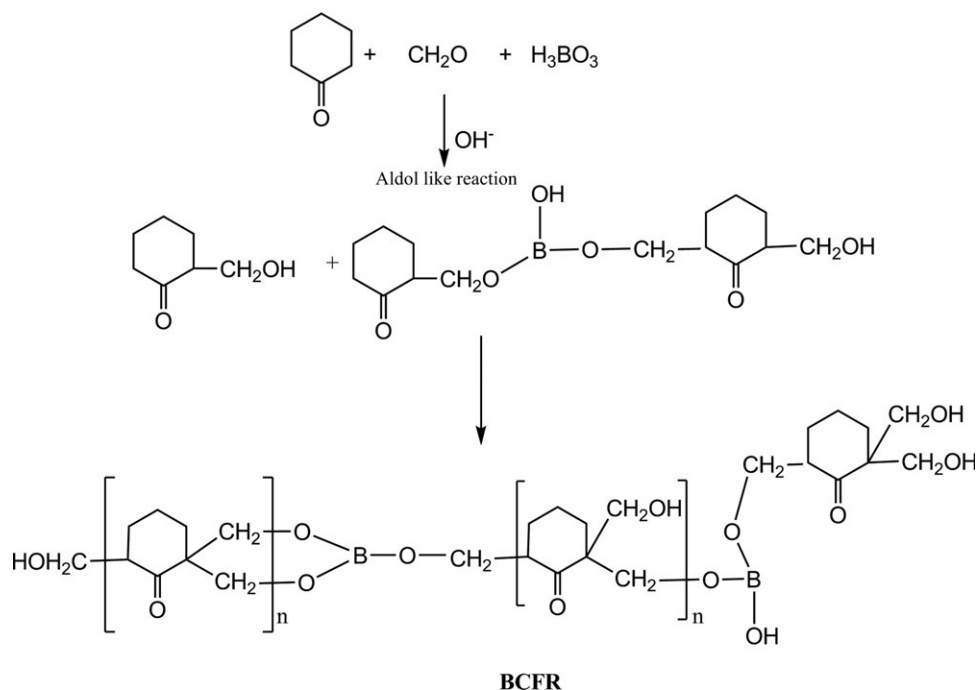
Boric acid and borate salts have been used as flame-retardant additives since the early 1800s, but there have been fewer studies on them than those on phosphorous, halogen, and other compounds. The use of borates for enhancing the flame retardancy of polymeric materials was reported earlier in the 20th century.¹ The flame-retardant effect of boron-containing compounds on polymeric materials is chemical and physical. The influence of boron-containing reactive groups, such as polystyrene and poly(vinyl alcohols), has also been reported.²

Phenolic resin, bisphenol A formaldehyde, and bisphenol F formaldehyde resin that are modified by boric acid are thermosetting resins with excellent performances. They are obtained by the introduction of boron into the main chain of a phenolic resin. The boron-containing phenol-formaldehyde resin has high-performance properties, including good thermostability, mechanical strength, and electrical properties. The synthesis and applications of boron-containing phenol and bisphenol formaldehyde resin have been reported to a degree,^{3–10} whereas the synthesis, structure, and thermal properties of boron-containing cyclohexanone formaldehyde resin (BCFR) have not been investigated until now.

The use of borates for enhancing the flame retardancy of polymeric materials was reported in 20th century.¹¹ The affectivity of borates as flame retardants in various materials has been explained by their formation of nonpenetrable glass coatings, which exclude oxygen and prevent the further propagation of

combustion. Boric acid and hydrated inorganic borates have low melting temperatures (T_m 's) and fit nicely into this scheme of forming glass coatings. When it is slowly heated, boric acid (mp 171°C) loses water and changes first into metaboric acid, then to HBO₂, and finally to boric oxide (B₂O₃). Above 325°C, B₂O₃ softens to into glass and becomes pourable only at 500°C. The flame-retardant action of the boron-containing compounds on polymeric materials is chemical and physical. It was found that these inorganic boron compounds promote char formation in the burning process.¹² The borate esters formed were further dehydrated, probably by carbocation mechanisms.

Cyclohexanone formaldehyde resin (CFR) has a low molecular weight and shows unique compatibility with a great number of polymers. It is soluble in most organic solvents, including aromatic hydrocarbons, ketones, esters, and alcohols. Because of its good compatibility, it is usually used as a coating additive. Common *in situ* modified CFRs have been formed from cyclohexanone, formaldehyde, and modifier compounds in the presence of sodium hydroxide.^{13–21} The effects of the type of modifier compound and concentration, solubility, molecular weight, and thermal properties of modified CFRs have been investigated. The modifier compounds included phenols, bisphenols, melamine, *p*-toluenesulfonamide,^{13,14} salicylic acid, *o*-cresol, *p*-cresol, citric acid,¹⁵ polydimethylsiloxane,¹⁶ aniline, 4-amino-diphenylamine and *N,N'*-diphenyl-1,4-phenylenediamine,¹⁷ carbazole-9-carbonyl chloride,¹⁸ carbazole,¹⁹ lignosulfonate,²⁰ and 4-vinyl aniline.²¹ Ketonic resin has a methylene group and hydroxymethyl groups, so it has a relatively higher free rotation



Scheme 1. Formation of BCFR.

and mobility. The synthesis structure and thermal properties of BCFR have not been investigated until now.

In this study, BCFR was synthesized by an *in situ* method and was characterized by the physical, thermal, and spectroscopic properties of the resin samples by thermal analysis, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, B-NMR, and Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Cyclohexanone, boric acid, and cyclohexane were obtained from Fluka Chemical Co. (Buchs, St. Gallen, Switzerland), and a 37% formaline solution was received from J. T. Baker (Avantor), Griesheim, Germany. All chemicals were used without further purification.

Analysis

FTIR spectra was measured with a PerkinElmer Spectrum One FTIR spectrophotometer (Cambridge, UK) [with a attenuated total reflectance (ATR) sampling accessory] directly from the sample without the help of the KBr discs.

All $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and $^{11}\text{B-NMR}$ data were obtained from a Varian spectrometer (AC 500 MHz, Darmstadt, Germany) with CD_2Cl_2 and CDCl_3 as solvents and tetramethyl silane (TMS) as an internal reference. $^{11}\text{B-NMR}$ was obtained with special tubes that were made of borosilicate glass.

The morphologies of the products were examined with a scanning electron microscope (ESEM XL30 ESEM-FEG, Philips), and the samples for SEM measurement were prepared by gold coating.

Table I. Molar Ratio of the Reactants and Solubilities of BCFR

Resin	Molar ratio Cyclohexanone/ H_3BO_3 /formaldehyde	Solubility					
		Tetrahydrofuran	Dimethyl sulfoxide	CHCl_3	CH_3OH	$(\text{CH}_3)_2\text{CO}$	Dimethylformamide
CFR	1:0:2	sl	s	s	sl	sl	sl
BCFR1	1:0.5:2	s	s	s	sl	sl	s
BCFR2	1:0.75:2	s	s	s	sl	s	s
BCFR3	1:1:2	s	s	s	sl	s	s
BCFR4	1:1.5:2	s	s	s	sl	s	s
BCFR5	1:3:2	s	s	s	sl	s	s
BCFR5.1	Water layer of BCFR5	i	i	i	i	i	i

s, soluble; sl, slightly soluble; i, insoluble

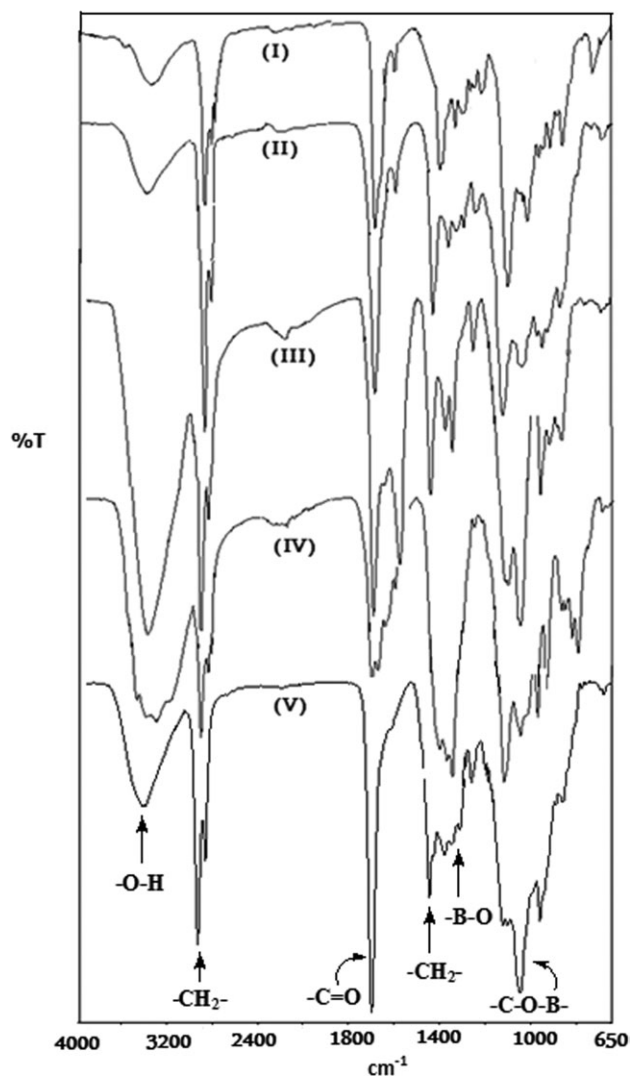


Figure 1. FTIR spectra of (I) BCFR1, (II) BCFR2, (III) BCFR3, (IV) BCFR4, and (V) BCFR5.

Differential scanning calorimetry (DSC) thermograms were obtained with a PerkinElmer DSC-6 instrument; the heating rate was 10°C/min under a nitrogen atmosphere.

Thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere at a heating rate of 10°C/min up to 900°C

Table II. FTIR Peaks of the BCFRs (cm⁻¹)

Resin	-O-H	-CH ₂ -	-C=O	-CH ₂ -	-B-O-, -CH ₂ -O	-C-O-	-C-O-C	-C-OH
CFR	3430	2933, 2860	1704	1449	1378	1261	1140	1060
BCFR1	3422	2928	1715	1446	1375	1259	1140	1047
BCFR2	3419	2927	1708	1447	1377	1255	1138	1052
BCFR3	3387	2927	1698	1448	1351	1260	1135	1053
BCFR4	3320	2928	1713	1475	1382	1265	1139	1042
BCFR5	3408	2928	1696	1447	1380	1261	1130	1049
BCFR5.1	3360, 3327	2989	1640	1407	1351	1251	1090	944

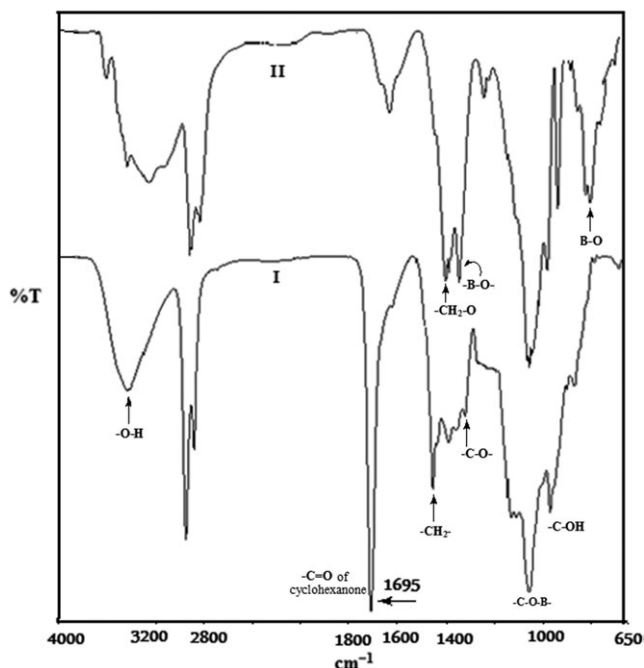


Figure 2. FTIR spectra of (I) BCFR5 and (II) BCFR5.1.

by a PerkinElmer Pyris 1 instrument. The percentage weight loss of the samples was calculated within the temperature range 20–900°C.

Synthesis of BCFR

Into a three-necked flask equipped with a stirrer and a condenser, 104 g of cyclohexanone, 20 mL of cyclohexane, 30 mL of 37% formalin, and 31.5 g of boric acid were added. When the temperature of the mixture was raised to 65–70°C, refluxing was started. Subsequently, 100 mL of 37% formalin was added. The reaction was further continued under pH values of 11–12 for 5 h. After the reaction time was completed, two layers were formed. The modified resin was separated and purified by the decanting of the water layer (the water layer was later over the condensation reaction, and BCFR5.1 was produced). The modified ketonic resin was washed several times with warm water until it was free from formaldehyde odor, and it was dried at 60°C *in vacuo*. In the second step, the water layers of BCFR5 were stirred and heated to 90°C. Then, the reaction temperature was maintained under pH values of 11–12 for 2 h; thereafter, the

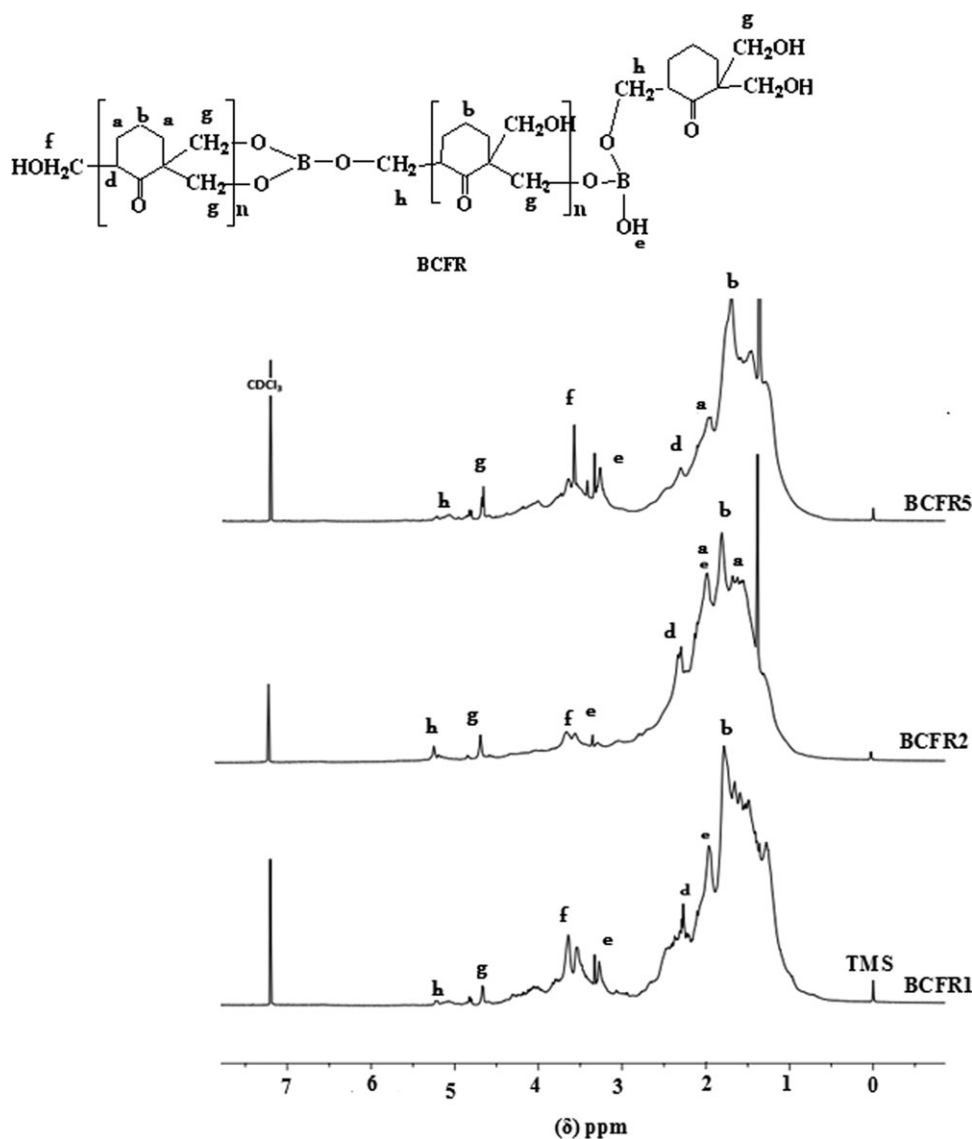


Figure 3. ¹H-NMR spectra of BCFRs.

reaction time was completed, and two layers were formed. The resin phase (BCFR5.1) was separated and purified by the decanting of the reactive water layer. BCFR5.1 was washed several times with warm water until it was free from formaldehyde odor and dried at 60°C *in vacuo*. Finally, solid BCFR5.1 was obtained.

Commercial CFR was modified with boric acid at three molar ratios (ketone/formaldehyde/boric acid = 1:2:0.5, 1:2:0.75, and 1:2:1) and two ratios of the cyclohexanone to formaldehyde to boric acid (1:2:1.5 and 1:2:3) to give BCFR1, BCFR2, BCFR3, BCFR4, and BCFR5, respectively.

RESULTS AND DISCUSSION

We prepared five BCFR samples by the esterification of boric acid with hydroxymethyl groups of CFR in one step by an *in situ* method.

The formation of BCFR starts with an aldollike reaction after a base-catalyzed elimination reaction of water from hydroxy-

methyl derivatives of cyclohexanone.^{13–21} The reaction of boric acid with hydroxymethyl groups precedes that of boric acid with the hydroxy methyl of cyclohexanone.⁷ Boric acid probably combines with resin molecules from its hydroxymethyl by the effect of the base-catalyzed condensation reaction (Scheme 1). In this study, the BCFRs were synthesized in basic media with cyclohexanone/formaldehyde/boric acid molar ratios of 1:2:0.5 (BCFR1), 1:2:0.75 (BCFR2), 1:2:1 (BCFR3), 1:2:1.5 (BCFR4), 1:2:3 (BCFR5). These resins, which acted as boron reagents, were very soluble in organic solvents such as acetone, chloroform, alcohol, and dimethyl formamide, and that made the reaction with hydroxyl groups easier (Table I).

The structure of the BCFR was identified by FTIR-ATR spectroscopy. The spectra of BCFR1, BCFR2, BCFR3, and BCFR5 are illustrated in Figure 1. The infrared spectra of all of the resins showed strong bands of absorption at 3430–3320 cm⁻¹, including both stretching vibrations of —OH groups of hydroxymethyl and —B—OH groups. Strong bands of

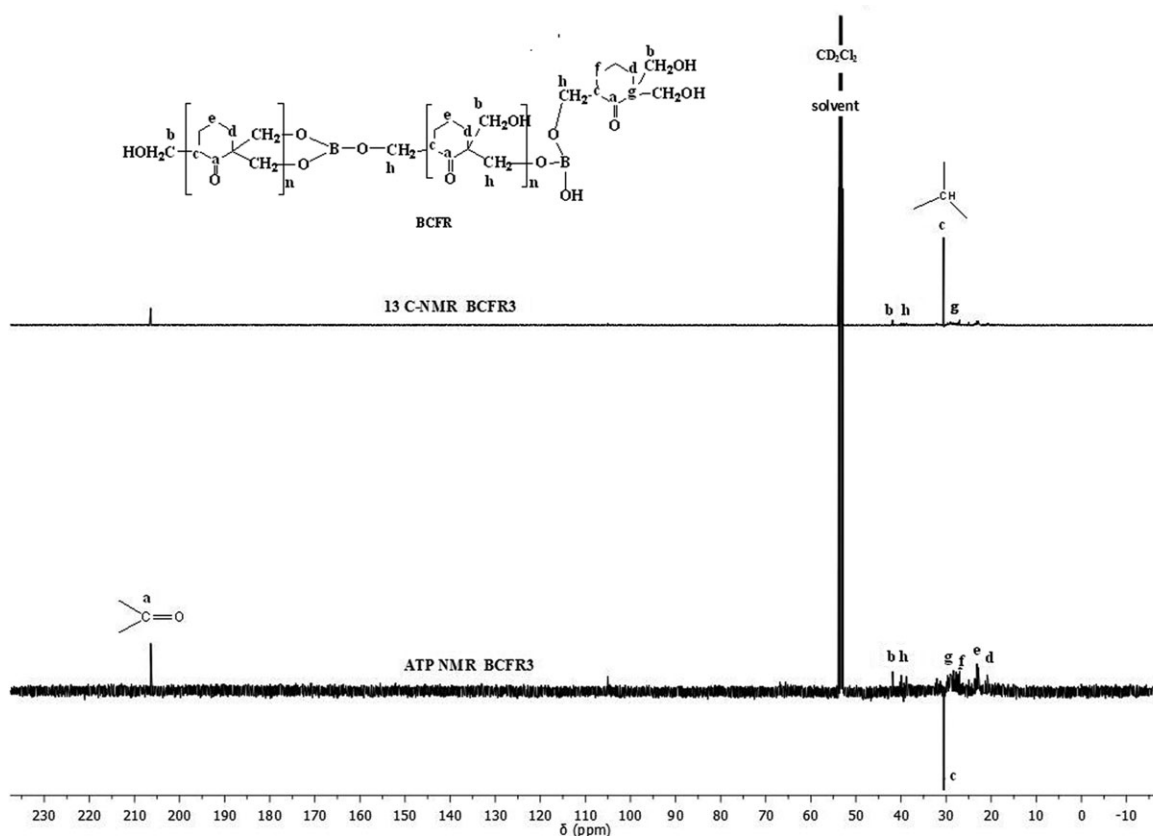


Figure 4. ^{13}C -NMR and attached proton test spectrum of BCFR3.

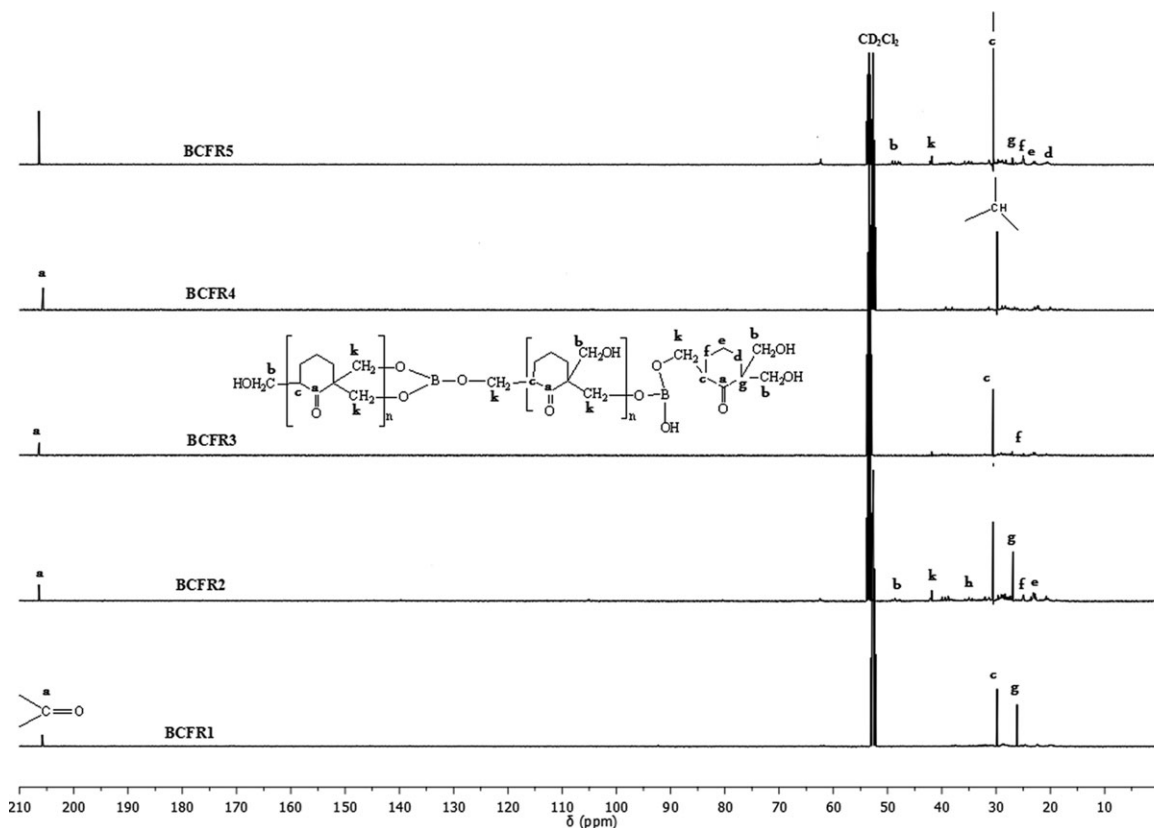


Figure 5. ^{13}C -NMR spectra of BCFRs.

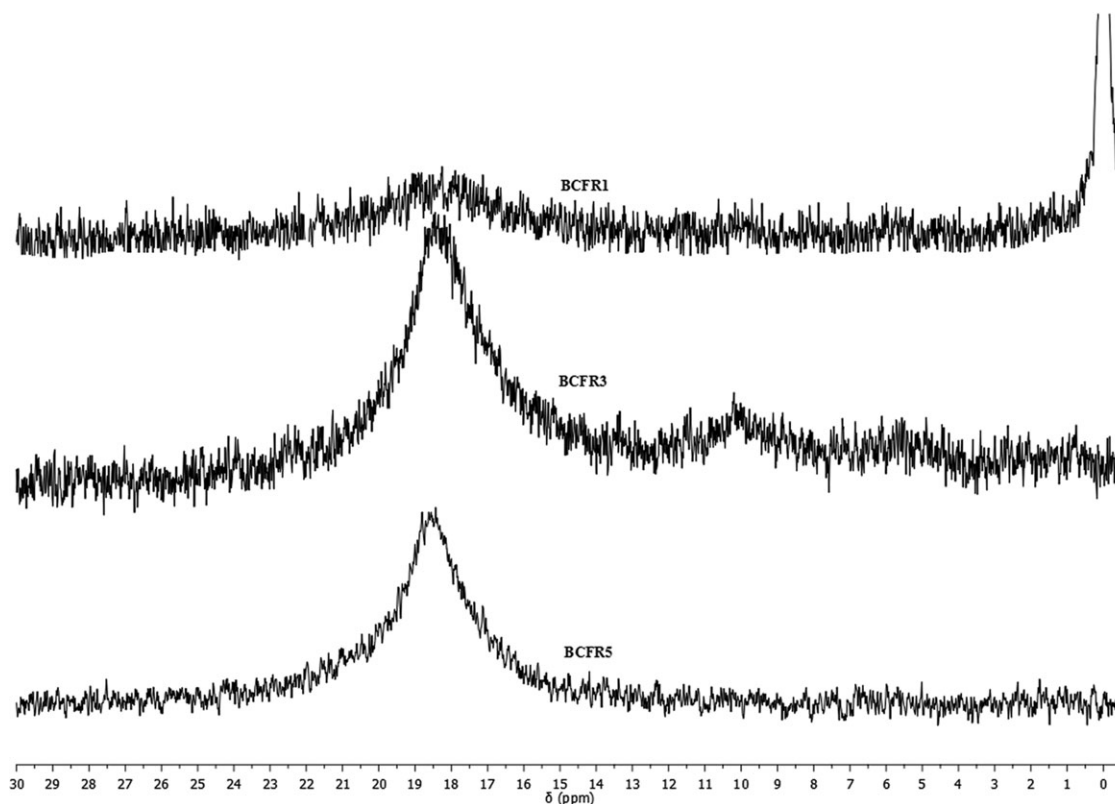


Figure 6. ^{11}B -NMR spectra of BCFRs.

Table III. DSC and TGA results for the BCFRs

Sample	T_g ($^{\circ}\text{C}$) ^a	T_m ($^{\circ}\text{C}$) ^a	$T_{50\%}$ ($^{\circ}\text{C}$) ^b	Residue at 900 $^{\circ}\text{C}$ (wt %) ^b
CFR ²²	30	115	350	2.60
BCFR1	83	258	352	6.23
BCFR2	110	234	395	6.89
BCFR3	—	228	402	7.66
BCFR4	106	180	408	18.23
BCFR5	—	136	431	29.64
BCFR5.1	60	146	—	54.54

^aDetected by DSC.

^bDetected by TGA.

T50%: The temperature at which it loses its weight by 50%.

absorption characteristic for the carbonyl linkage and the borate appeared at 1715–1640 cm^{-1} and were assigned to C=O stretching vibrations, and the borate B—O appeared at 1350 cm^{-1} . Aliphatic hydrogens of methylene bridges between boron and carbon were observed as peaks at 2930 and 1450 cm^{-1} . Hydroxymethyl groups were observed at 1040–1060 cm^{-1} and ether linkages (C—O) appeared at 1130–1140 cm^{-1} ; these were similar to the methylene bridges of BCFR (Figure 1, lines I–V). The FTIR spectra details are shown in Table II.

BCFR5.1 was synthesized by a one-step condensation reaction at 90 $^{\circ}\text{C}$ for 2 h. BCFR5.1 was formed by the reaction of unreacted cyclohexanone, boric acid, and formaldehyde. The

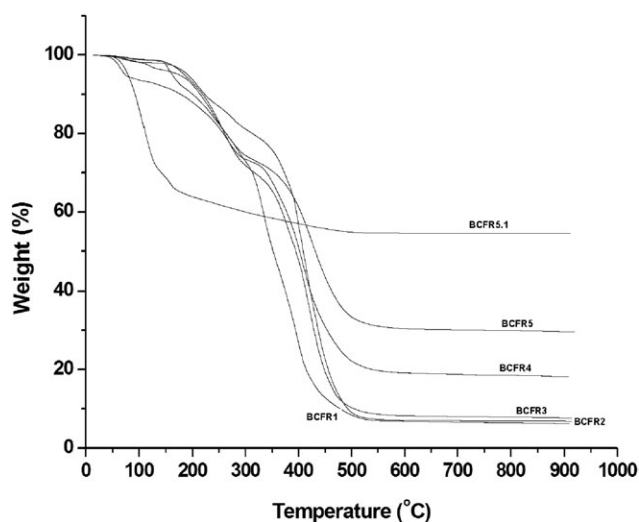


Figure 7. TGA thermograms of BCFRs.

structure of the BCFR5.1 was identified by FTIR-ATR spectroscopy. The FTIR spectra of BCFR5 and BCFR5.1 (lines I and II) are given in Figure 2. Although typical peaks of cyclohexanone groups disappeared at 1695 cm^{-1} , the absorption peak of borate B—O linkages at 1350 cm^{-1} increased (Figure 2, Line II). BCFR5.1 did not have any solubility properties (Table I).

^1H -NMR, ^{13}C -NMR, and ^{11}B -NMR spectra of the BCFRs also confirmed the estimated structural formulas, as shown in Figures

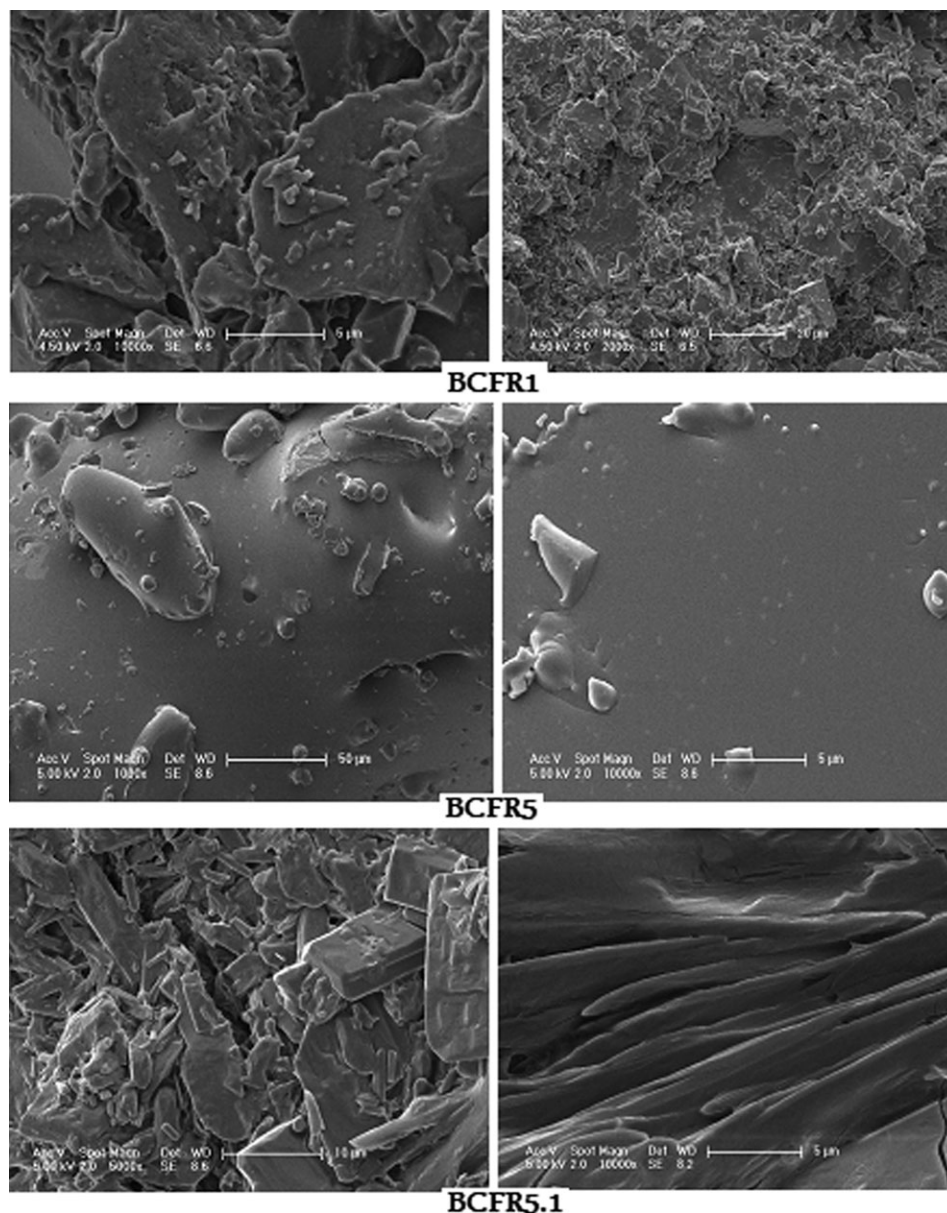


Figure 8. SEM micrographs of BCFR1, BCFR5, and BCFR5.1.

3–6. In the $^1\text{H-NMR}$ spectra of BCFR1, BCFR2, and BCFR5, the signals between 3 and 4.5 ppm were linked to the methylene protons of hydroxymethyl groups and ether linkage protons, and those between 1 and 3 ppm were due to the aliphatic hydrogens of cyclohexanone. The $^{13}\text{C-NMR}$ and attached proton test spectra of BCFR3 (Figure 4) and the $^{13}\text{C-NMR}$ spectra of the BCFRs (Figure 5) showed no peaks of quaternary carbon atoms between 20 and 30 ppm and no peaks of methyl carbon atoms below 20 ppm. The small peaks at 42 and 40 ppm were due to hydroxymethyl bond carbons, with each possessing two hydrogens. The peak at 206 ppm was due to carbonyl carbon, and the peak at 30 ppm was due to the CH of cyclohexanone rings, with each possessing one hydrogen. As shown in Figure 6, the $^{11}\text{B-NMR}$ spectra of the BCFRs that showed signals between 18 and 19 ppm were linked with $\text{B}-(\text{OR})_3$ or $(\text{OH})-\text{B}-(\text{OR})_2$.

The thermal behavior of the resins was examined by DSC in the temperature range 20–300°C. The softening points were higher compared with CFR by about 26–143°C (Table III). To prepare TGA samples, the BCFRs were dried at 100°C for 3 h. A 5-mg powder sample of the cured resin was subjected to TGA and heated at linear heating rate of 10°C/min (Table III). Degradation was carried out in a static air atmosphere up to a maximum temperature of 900°C. The weight loss of the resin was calculated, and the weight loss rates are shown as a function of temperature in Figure 7 and Table III. As shown in Figure 7 and Table III, the weight loss rates of the common CFRs were higher compared to those of BCFR. This was evidence that the resin containing more boron had better thermal stability.

The SEM pictures of the BCFRs obtained by chemical polymerization demonstrated the differences in the roughnesses of the

BCFR1, BCFR5, and BCFR5.1 surfaces, as shown in Figure 8. This might have been due to the differently bounded borons. The SEM micrograph for the BCFRs showed a continuous homogeneous phase of the resin, which makes it suitable for use as a coating material.

CONCLUSIONS

In this study, a new BCFR was synthesized. For the BCFRs formed with the *in situ* modification method, the methylene borate linkage was mainly formed during the synthesis process. The borate linkage had better heat resistance than the ether linkage; therefore, the boron-containing ketonic resin had good thermal stability. These resins had higher glass-transition temperature (T_g) and T_m values than the CFR alone, and they also had enhanced thermal properties. The resulting BCFRs may provide an opportunity for a new breakthrough in the area of polymeric materials for advanced technologies. They could be used as reinforced laminates, heat-resistant adhesives, and coating materials.

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