Novel Modified Bismaleimide Resins with Improved Ablativity

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ABSTRACT: To improve the ablativity of bismaleimide-type resins, a series of novel allyl compounds containing boron in their molecular structure, designated as ACB, were synthesized and characterized. The copolymers made up of 4,4′-bismaleimidodiphenyl methane (BDM) and each ACB were prepared. The properties of the prepolymers and cured resins were all studied in detail. Results show that the prepolymers of BDM/ACB systems have similar processing characteristics such as solubility in acetone and reactivity to those of ordinary BMI resins made up of BDM and allyl compounds without boron, such as the famous BDM/BA (*O*,*O*′-diallylbisphenol A) system, while the thermal resistance and ablativity of the former are better than those of the latter. Thermogravimetric analysis (TGA) in a nitrogen atmosphere revealed that the BDM/ACB systems were stable up to 480°C and their char yields at 800°C under anaerobic conditions were more than 50%. However, the char yield at 700°C of the BDM/BA system is only about 21%. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1623–1631, 1999

Key words: ablativity; bismaleimide; boron; allyl compound

INTRODUCTION

Bismaleimides (BMIs) are primary candidates as matrix resins for advanced composites. Due to their brittleness and poor processing characteristics, almost all BMIs used are modified. Many modified BMIs overcoming these problems have been developed.[1–15] Those obtained by copolymerizing BMI with allyl compounds have been successful.[11–15] They are widely used as matrices for advanced composites and high-performance adhesives owing to their outstanding properties, such as good processing characteristics, outstanding heat resistance, high strength and modulus, good toughness, and hot/wet resistance. But their ablativity is not good enough to meet the needs of some special fields. Hence, it is of particular interest to develop a new kind of BMI system having improved ablativity while retaining the above-mentioned good inherent properties of BMI/allyl compound systems.

The present article reports on the synthesis and characterization of a series of novel allyl compounds containing boron in their molecular structure, designated as ACB, as well as the preparation and properties of a copolymer of BMI with ACB. As the polymers containing boron usually have outstanding heat resistance, radiation resistance, and ablativity,[16,17] the copolymers of BMI and ACB, therefore, were expected to be a new kind of high-performance improved ablativity material.

EXPERIMENTAL

Reagents and Solvents

4,4′-Bismaleimidodiphenyl methane (BDM) was supplied by Fengguang Chemicals (Wuhan, China).

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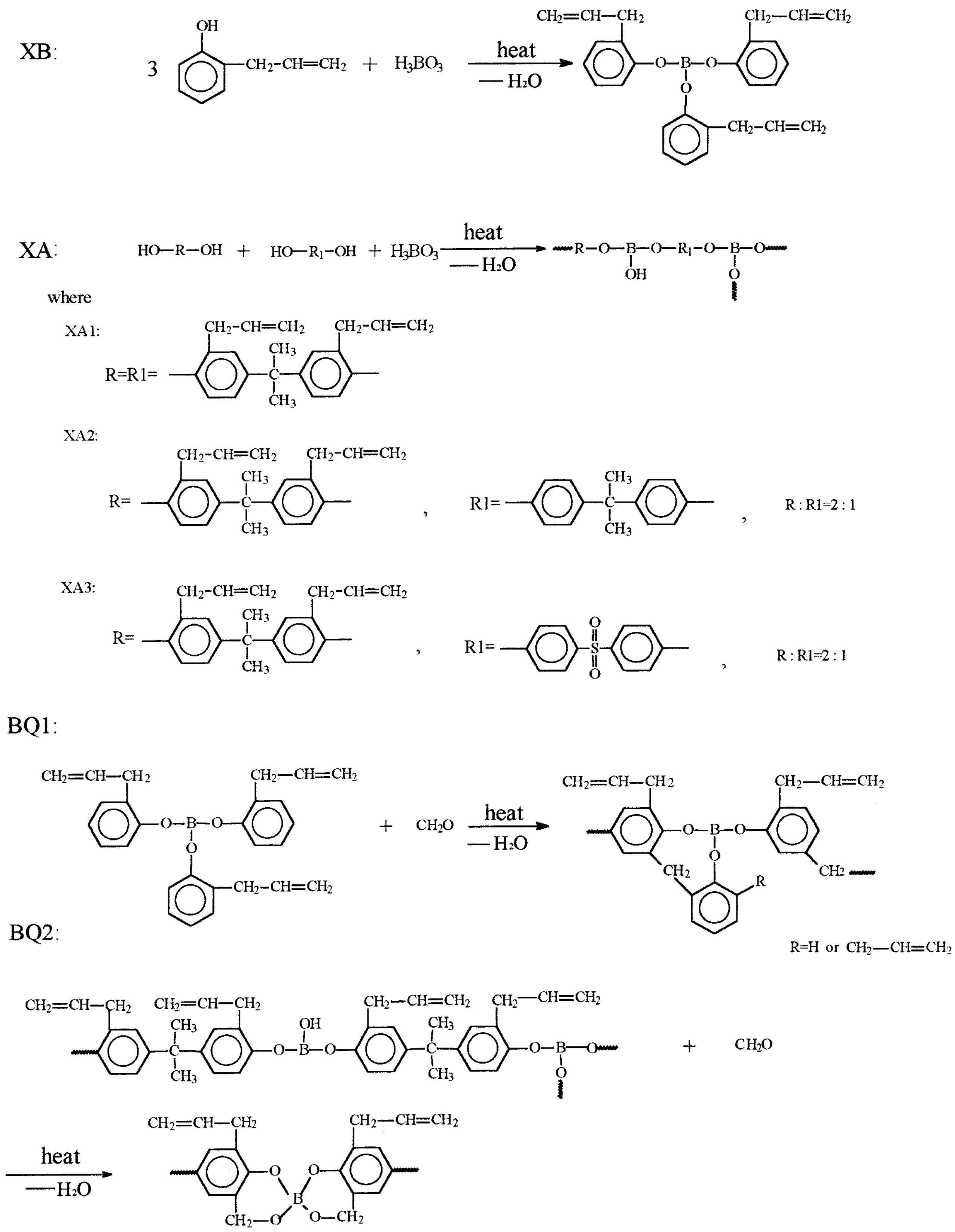
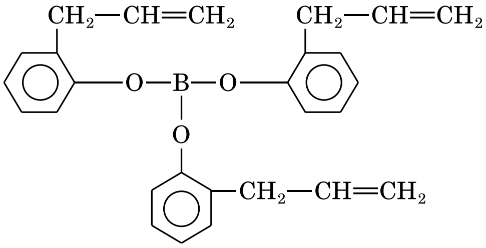

XB:
3
heat
— H₂O
XA:
HO—R—OH + HO—R₁—OH + H₃BO₃
where
XA1:
R=R1=
XA2:
R=
R1=
R : R1=2 : 1
XA3:
R=
R1=
R : R1=2 : 1
BQ1:
CH₂O
heat
— H₂O
R=H or CH₂—CH=CH₂
BQ2:
CH₂O
heat
—H₂O

Scheme 1

Table I Molecular Structure of ACB

Code	Molecular Structure
XB	
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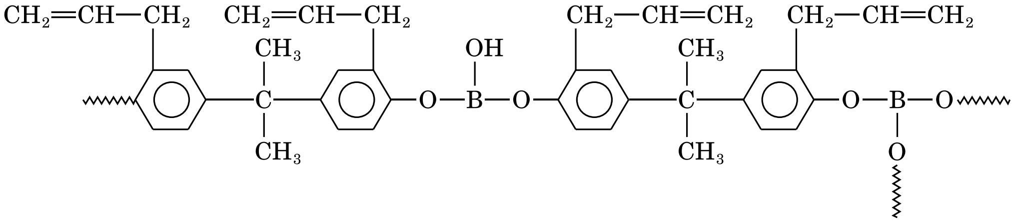
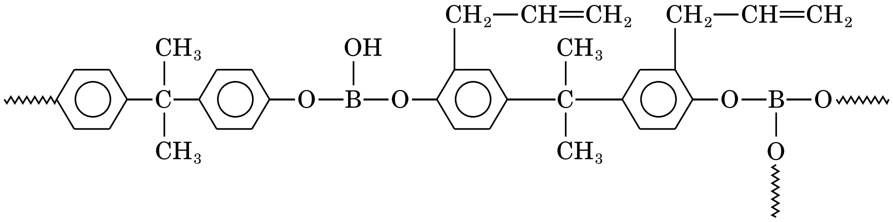
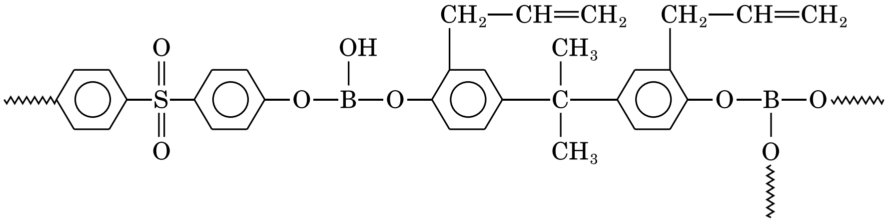
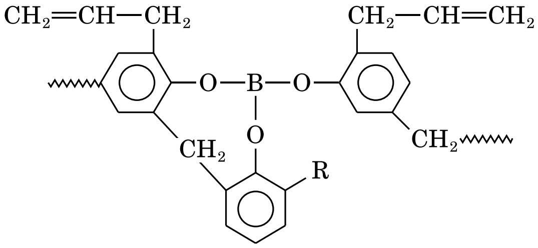
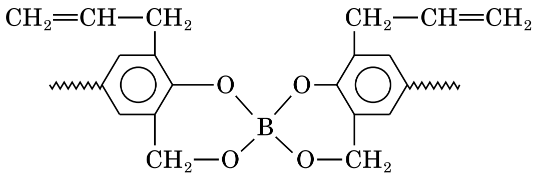
XA1	
XA2	
XA3	
BQ	
BQ1	
BQ2	

Table II Characterization of XB

Molecular Weight	^{13}C-NMR (ppm)	IR Absorptions (cm^{-1})	Elemental Analysis (%) Found (Calcd) C	H
410	117.2 (CH2 = in allyl) 132.6 (CH = in allyl) 52.3 (CH2 = in allyl) 109.1, 114.3, 127.0, 129.3, 131.6, 132.7, 133.7, 159.1, 162.8 (Ar′c, Ar″c)	1610, 1500, 1110 (Benzene ring) 100, 920, 830, 760 (allyl) 1332 (B—O)	78.99 (79.02)	6.61 (5.56)

Boracic acid, formaldehyde, and toluene were obtained from the Xi'an Reagents Chemical Plant (Xi'an, China). *O*,*O*′-diallylbisphenol A (BA) and allyl phenol were from the Sichuan Jiangyou Insulation Factory (Jiangyou, China). 4,4′-Dihydroxydiphenyl propane (bisphenol A) and 4,4′-dihydroxydiphenyl sulfone (bisphenol S) were from the No. 1 Chemical Plant of Shanghai Reagents (Shanghai, China). All the above reagents were used as supplied and were of reagent grade.

Preparation of ACB

Boracic acid (0.1 mol) was added gradually to a stirred solution of allyl phenol (0.6 mol) in 70 mL toluene under a nitrogen atmosphere at ambient temperature. The mixture was refluxed at 100°C for 1 h, 130°C for 3 h, and 160°C for 5 h, successively. During reflux, water (by-product) must be segregated continually. Then, the reaction was continued under a vacuum at 130°C until no water was produced to yield XB as a dark brown viscous liquid.

Formaldehyde, 0.1 mol, was then added dropwise to the above XB at room temperature. The mixture was gradually heated and the reaction was allowed to proceed at 60–65°C for 1 h and at 120–125°C for 1 h, successively. The reaction mixture was dehydrated under reduced pressure until no more water was evident to obtain a brown viscous liquid, designated as BQ1.

BA, 0.2 mol, boracic acid, 0.2 mol, and some toluene were charged in a three-necked flask. The mixture was stirred and gradually heated to 100°C and kept at that temperature for 1 h, then refluxed at 130°C for 2 h and at 160°C for 7 h, successively, until no by-product (water) was produced to obtain a brown viscous liquid, designated as XA1.

XA2 and XA3 were also prepared employing the above procedure for preparing XA1, except the amounts of toluene used were increased to 70 mL because bisphenol A and bisphenol S are solids and difficult participants in the reaction. In addition, XA3 is relatively easy to gel; its viscosity is high and difficult to pour from the flask. Hence, the reflux time at 160°C was reduced from 7 h (for XA1 and XA2) to 4 h.

BQ2 was prepared using the procedure of BQ1, except the reactants employed were XA1 and formaldehyde. The molecular structures of ACBs are listed in Table I.

Preparation of Copolymers of BDM/ACB

Six different formulations were evaluated to see the effect of the differing molecular structure of each allyl compound containing boron on the processing and performance parameters and also to establish the formulational latitude for the ACB-modified BDM systems. For each system, appropriate quantities (the weight ratio of BDM : ACB is 6 : 4) of each component were placed in a flask. The contents were heated with stirring and prepolymerized at 140°C for 30 min, then cooled to room temperature. The resultant solid was defined as a prepolymer.

Neat resin was prepared by pouring the corresponding preheated (100–110°C) prepolymer into preheated (100–110°C) glass sheet molds, then by degassing under a vacuum (0.9 MPa) at 130°C for 30 min. After that, the molds were put into ordinary convection ovens for curing and postcuring

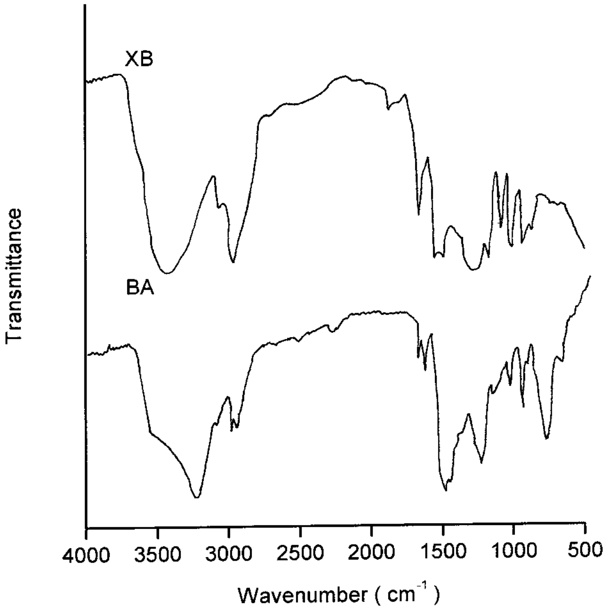


Figure 1 IR spectra of BA and XB.

per the following cure cycle: 160°C /1 h + 180°C/1 h + 200°C/2 h + 230°C /2 h + 250°C/5 h.

Measurement and Characterization

Infrared (IR) spectra were recorded on a SPECORD-79. A standard laboratory hot plate equipped with a temperature controller was used to determine the gel times of the prepolymers at various temperatures. The time required for the resin to stop stringing and become elastic is called the gel time.

Thermal analysis of the samples was carried out on a DuPont 990 thermal analyzer unit equipped with a Perkin–Elmer DSC differential scanning calorimetric unit and at a heating rate of 10°C/min. Tensile, flexural, and impact data of the neat resins were obtained according to GB1451-83, 3356-82, and 1042-79, respectively. The heat deflection temperature (HDT) was determined according ASTM D-648. The thermogravimetric analysis (TGA) was conducted using a Perkin–Elmer DEL 7A SERIESTGA 7 in a nitrogen atmosphere at a heating rate of 10°C/min. Viscosity determinations were done at 23°C using a Brookfield rotating spindle viscometer, Model LVT, according to the ASTM D-2293 test method. ^{13}C-NMR spectra were recorded at 25.2 MHz on a Bruker spectrometer (WP80) using DMF as a solvent (ref. CDCl3, 77.0 ppm). The elemental analysis was done with a CHN-O-Rapid Elemental Analyzer. Molecular weights were obtained by using a Knauer VPO molecular weight instrument with DMF as a solvent.

RESULTS AND DISCUSSION

Preparation and Properties of ACB

Each novel ACB was prepared according to the reaction sequence outlined in Scheme 1. From this scheme, it can be seen that the synthesis of XB and XA was based on the esterification of boracic acid and phenolic hydrogen. The reaction usually proceeds easily, but the phenolic hydrogen in the molecular structure of allyl phenol and BA is difficult to react with boracic acid in normal reaction conditions due to the electron effect and steric hindrane of allyl groups. In addition, esterification is reversible and the esterification product is easy to hydrolyze. Hence, the by-product (water) must be continually segregated and the reaction conditions must be carefully chosen to allow the esterification to proceed with a high yield. The role of toluene is to segregate water from the reaction mixture by azeotropic distillation.

The synthesized XB in this article was characterized by molecular weight, IR, ^{13}C-NMR spectrum, and elemental analyses. All data are listed in Table II. Figure 1 presents the typical IR spectra of XB and BA. By comparing the two IR spectra, it can be seen that both have the characteristic absorptions of the benzene ring and the allyl group. On the other hand, the spectrum of BA

Table III Typical Physical Properties of ACB

	XB	XA1	XA2	XA3	BQ1	BQ2
Surface appearance (25°C)	Red–brown transparent liquid	Dark brown to yellow–brown viscous liquid				
Viscosity (25°C), Pa s	0.1	0.3	0.5	0.9	0.7	0.75
Solubility (25°C)	Have good solubility in acetone and ethanol and are also miscible with expoxy resin and unsaturate polyester, etc.					

Table IV Typical Physical Properties of Prepolymers

Property	BDM/BX	BDM/XA1	BDM/XA2	BDM/XA3	BDM/BQ1	BDM/BQ2
Softening point (°C)	60	65	55	70	65	60
Solubility in acetone (25°C)	Good					

shows the absence of the bands characteristic of the B—O structure, while the spectrum of XB has obvious absorption at 1350 cm^{-1}, demonstrating the existence of B—O bonds in its molecular structure. XA and BQ were also characterized by the above methods employed for XB.

The typical physical properties of ACB are listed in Table III. It can be seen that all the ACBs are viscous liquids with different viscosities at room temperature. XB has the lowest viscosity because it has the shortest molecular chain and exists as a monomer; BQ has the highest viscosity due to its partial netted structure. All the ACBs prepared are soluble in ordinary low boiling-point solvents such as ethanol and acetone and are also miscible with epoxy resin, unsaturated polyester, and phenolic resins.

Properties of Prepolymers of BDM/ACB

The physical properties and reactivity of prepolymers are closely related to the prepolymerization procedure. The procedure can be adjusted according to the last usage of the copolymers and the processing method chosen, that is, if the copolymer will be used as a matrix resin for composites and prepregs, it will be made by the solvent technique (as reported in this article). Then, the prepolymerization procedure must guarantee that the resultant prepolymer is soluble in the chosen solvent and the obtained prepolymer solution is stable. Hence, the prepolymerization procedure in this article depends on the solubility of the resultant prepolymer in acetone and the stability of the prepolymer solution.

Table IV lists the physical properties of the prepolymers. It can be seen that the prepolymers are brown transparent solids at room temperature; their melting points are 60–70°C and they can be stored at room temperature for at least 1 year. In addition, all are soluble in acetone to form transparent stable prepolymer solutions (for 1 month).

The reactivity of the prepolymers may be measured by their gel characteristics and DSC traces. Figure 2 shows the relationships of gel time and temperature of the BDM/ACB systems. It can be seen that (1) their gel times are longer than 60 min when the temperature is lower than 160°C, suggesting that they all have a long potlife at room temperature (with increase of the tem-

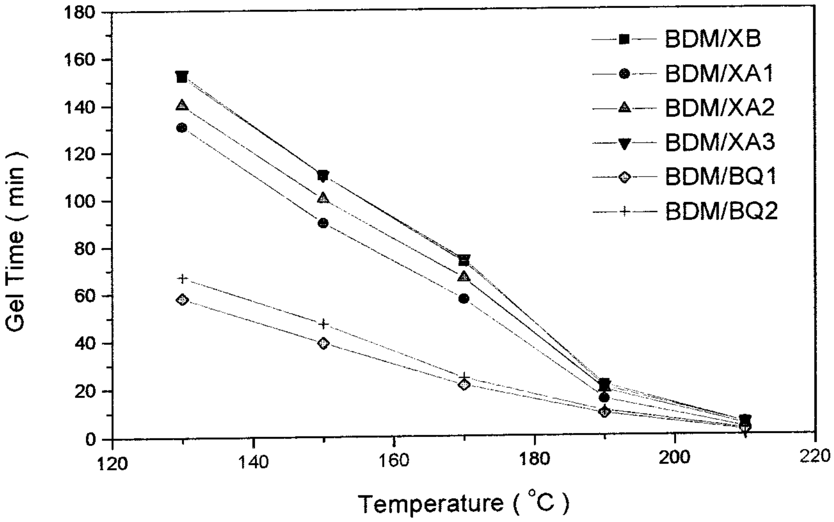


Figure 2 Gel time–temperature cure of prepolymers.

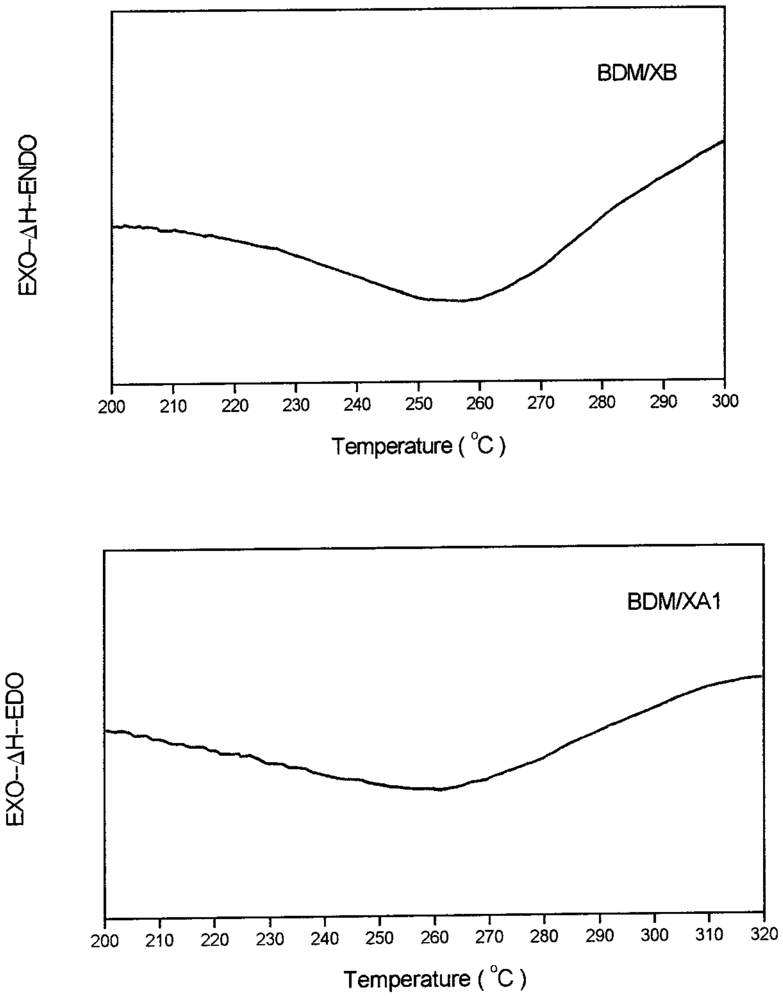


Figure 3 Typical DSC thermograms of prepolymers.

perature, the gel time is about 5 min at 200°C) and (2) the relative order of the gel time at the same temperature was BDM/XA3 > BDM/XA2 > BDM/XB > BDM/XA1.

Typical DSC thermograms of the prepolymers BDM/XA1 and BDM/XB are presented in Figure 3. The onset temperature (T_1) for the polymerization reaction, the exothemic peak temperature (T_{exo}), and the temperature for the completion of polymerization (T_2) were determined and are listed in Table V. It can be seen that the three temperatures of the two systems and BDM/BA are similar.

The above results show that the reactivity of BDM/ACB is similar to ordinary systems made up of BDM and allyl compounds without boron, so the newly developed BDM/ACB systems can use the processing equipment and techniques for those presently used for ordinary modified BDM resins obtained by copolymerizing with allyl compounds.

Properties of Cured Copolymers of BDM/ACB

The cured reaction of BDM and ACB is the addition of allyl groups and the maleimide ring, so there are no volatile materials generated during curing and the obtained network structure is com-

Table V DSC Results of Prepolymers

Temperature	BDM/XB	BDM/XA1	BDM/BA (w/w = 100/80)
T_1 (°C)	208.4	206.1	197.1
T_{exo} (°C)	217.2	219.2	245.9
T_2 (°C)	292.4	309.0	294.1

Table VI Properties of Cured Resins

Property	BDM/XB	BDM/XA1	BDM/XA2	BDM/XA3	BDM/BQ1	BDM/BQ2	BDM/BA[a]
RT tensile strength (MPa)	83.6	83.3	80.7	79.5	77.8	74.4	73
Modulus (GPa)	3.72	3.77	3.70	3.78	3.78	3.79	3.67
Elongation (%)	2.3	2.32	2.45	2.25	2.25	2.17	2.2
Flexural strength (MPa)							
25°C	124	139	129	122	116	98	112
150°C	88.3	94.6	90.2	89.3	84.2	83.6	87.3
200°C	78.9	82.4	83.6	82.3	76.7	73.2	75.5
Impact strength (kJ/m^2)	12.6	10.9	9.6	17.7	11.8	8.9	13
T_g (by DSC) (°C)	277	282	278	283	285	330	274
HDT (°C)	262	270	262	274	270	319	268
T_{id} (°C)	489	490	487	495	495	499	426
$T_{\max}$ (°C)	520	533	527	532	531	534	447
Y_c (at 800°C) (%)	57	56	54	60	58	61	21[b]

[a] [18].
[b] Char yield at 700°C.

pact and has few defects. In addition, the cured resin system contains rigid groups, such as the benzene ring and the imide ring, so they have high strength and modulus as well as good heat resistance. On the other hand, they also have good toughness owing to the flexible segment B—O—C in their molecular structure. Table VI lists the properties of cured BDM/ACB resins and BDM/BA.

The ablativity may be characterized by the initial decomposition temperature (T_{id}), the maximum polymer decomposition temperature ($T_{\max}$), and the char yield (Y_c) at different temperatures from the TGA curve (Table VI). In the networks of the BDM/ACB systems, the introduced boron form "C—O—B" bonds. The bond energy of B—O is 185 kcal/mol, which is far larger than that of C—O (80 kcal/mol), so the T_{id} and $T_{\max}$ of the BDM/ACB systems are higher than those of the resin made up of BDM/BA. In addition, the surfaces of the cured BDM/ACB systems tend to form rigid honeycomb thermal protective coatings—boron carbide, which has a high melting point, can prevent heat from continuing to diffuse and to conduct inside, so these systems have better ablativity and thermal resistance than do those having no boron.

CONCLUSIONS

To improve the ablativity of the BMI resin, a novel series allyl compounds containing boron (ACB) have been synthesized and used as the copolymerization monomers of BDM. The results show that the processing characteristics of the prepolymers and the mechanical properties of the cured resins are similar to that of the BDM resin modified by BA (BDM/BA), but the ablativity and thermal properties of BDM/ACB are better than those of BDM/BA, suggesting that the newly developed BDM systems containing boron may be used in fields needing outstanding ablativity and heat resistance as well as good mechanical properties.

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