Novel Thermosetting Resin with a Very High Glass-Transition Temperature Based on Bismaleimide and Allylated Novolac

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ABSTRACT: Thermosetting resin systems with very high glass-transition temperatures were formulated on the basis of bismaleimide and allylated novolac (BMAN). When the allylation degree of the novolac resin was high enough, the bismaleimide (BMI) proportion was not critical to the heat resistance of the cured resin. The BMAN15 resin with a high allylation degree and a low BMI proportion was appropriate for resin-transfer molding. Composites of BMAN15, with quartz woven cloth as reinforcement showed good strength and modulus retention rates at 350°C. The curing of the BMAN15 resin was illustrated by Fourier transform infrared and differential scanning caloriety studies. It turned out that allyl groups participated via ene reaction and the Diels–Alder reaction, as the maleimide groups did, forming a densely crosslinked structure in the cured resin. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 443–448, 2005

Key words: thermosets; resins; glass transition

INTRODUCTION

Composite materials designed to withstand thermal and aerodynamic stress at high temperatures need matrix resins with high glass-transition temperatures (T_g's). Thermosetting resin systems based on bismaleimide (BMI) and allyl compounds, such as bisphenol A diallyl ether,[1,2] allylated novolac,[3,4] and allylated xylok,[5] showed T_g's up to about 300°C. They were of high modulus and good toughness, and some products are commercially available for composite matrices. Special resin systems based on BMI and allylated Novolac have been formulated recently for the resin-transfer molding (RTM) process of composite fabrication,[3,4] where resin systems of low viscosity and long pot life that do not release volatiles on curing are required.

The curing of BMI–allyl compound resin systems was considered to occur mainly through the addition and polymerization of unsaturated groups, as shown in Scheme 1.[6–11] The equimolar consumption of maleimide groups and allyl groups in the curing of 4,4'-(N,N'-bismaleimide)-diphenylmethane/2,2'-diallyl-bisphenol A systems has been found.[10,12,13] Therefore, usually a high proportion of the maleimide group is utilized to give a dense network. In practice, however, a high maleimide proportion is unfavorable for the limited solubility of 4,4-bismaleimidodiphenylmethane in allylated Novolac and is unnecessary in the formulation of a BMI/allylated Novolac thermosetting resin with good heat resistance.

In this article, we report a novel thermosetting resin system with a very high T_g based on BMI and allylated Novolac. Important chemical reactions responsible for the curing are discussed as well.

EXPERIMENTAL

Materials

Phenol (AR) and formaldehyde (37% solution in water, AR) were obtained from Beijing Organic Chemicals Factory and were used as supplied. Allyl chloride was obtained from Qilu Petrochemical Co., Ltd., and was used after distillation. 4,4-Bismaleimidodiphenylmethane was purchased from Fengguang Chemical Co., Ltd., and was used as supplied.

Preparation of the bismaleimide–allylated Novalac (BMAN) resin system

Allylated Novolac resins were prepared according to the procedure described in a previous article.[3] Novolac (100 g) was dissolved in 120 g of *n*-butyl alcohol in a three-necked flask, and then, 47 g of potassium hydroxide was added. After it was stirred at 80°C for 1 h, the solution was cooled to 40°C, and 71 g of 3-chloropropene was dropped in slowly over 1 h. The temperature was raised to 80°C, and the reaction was
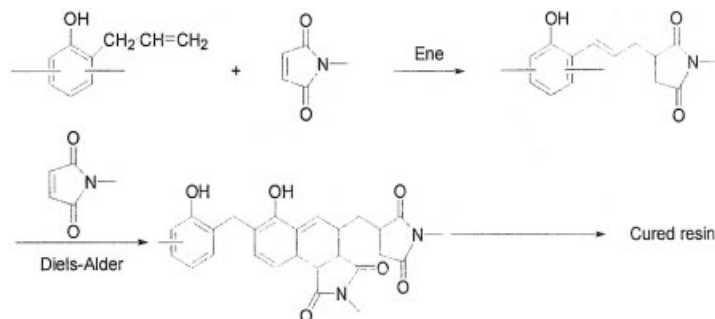
Scheme 1 Curing of the BMI–allyl compound resin system.
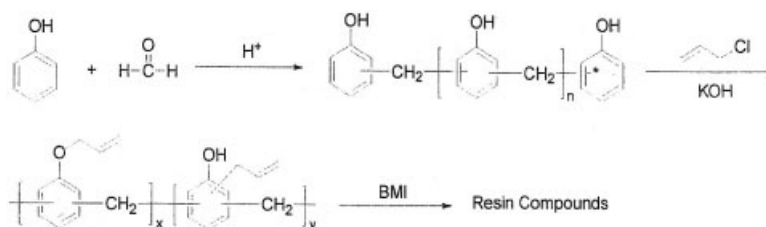
Scheme 2

continued for 6 h. Salt generated in the reaction was filtered, and the filtrate was washed with distilled water. The volatiles were removed by reduced-pressure distillation to obtain the allylated Novolac resin.

For the preparation of the BMAN resin, the allylated Novolac resin was heated to 130°C in a three-necked flask with an oil bath. 4,4-Bismaleimidodiphenylmethane was added under stirring. After the system turned transparent, heating was continued at this temperature for 30 min.

Preparation of the specimens for mechanical testing.

The BMAN resin was cast into a steel mold. Volatiles were removed by treatment at 130°C for 3 h in a vacuum oven. Curing was carried out by heating at 170°C for 2 h, 200°C for 6 h, and 250°C for 6 h.

Measurements

The functional group content of allylated Novolac was calculated on the basis of the integral signal of the

^{1}H-NMR spectra, which were taken on a DMX-300 NMR instrument (Bruker, Germany) with deutero dimethylsulfoxide as the solvent.

To obtain Fourier transform infrared spectra, resin samples were coated on KBr platelets and treated at given temperatures in a vacuum oven: spectra were recorded with a PerkinElmer FT-IR 2000 instrument.

T_g values of the cured BMAN resins were characterized according to the tan δ curves in dynamic mechanical spectra. DSC analysis was carried out on Mettler-Toledo DSC822e instrument at a heating rate of 5°C/min.

Thermogravimetric analysis was carried out on a PerkinElmer 7 series instrument at a heating rate of 20°C/min.

Flexural tests, for the composite materials at different temperatures were carried out with a Thermocraft MTS Alliance RF/100 instrument. The tests were conducted according to ASTM D 790-02. The dimensions of the specimens were 50 × 15 × 2 mm. All specimens were tested after preconditioning for 15 min at the test temperature.

TABLE I
T_g and Modulus Retention at 350°C for the BMAN Resins

Code	Molar ratio of allyl to maleimide groups	T_g by DMA (°C)	Modulus at room temperature (GPa)	Modulus retention at 350°C (%)
BMAN15	100:15	419	2.43	87.6
BMAN20	100:20	407	2.47	77.7
BMAN25	100:25	409	2.06	76.7
BMAN30	100:30	417	2.20	79.7

Curing schedule: 170°C for 2 h, 200°C for 6 h, and 250°C for 6 h. DMA = dynamic mechanical analysis.
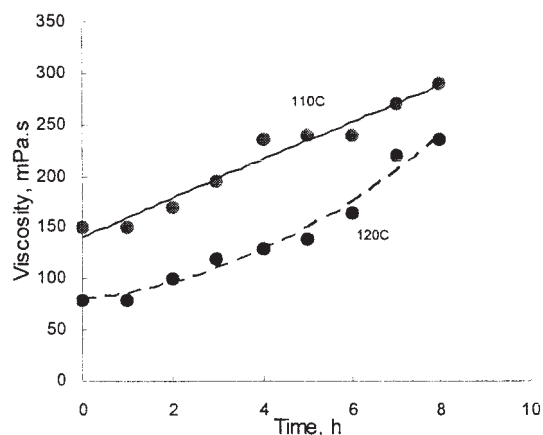
Figure 1 Viscosity versus time for the BMAN15 resin at 110 and 120°C.

RESULTS AND DISCUSSION

Effect of the BMI proportion

Variables in the BMAN resin system were mainly the molecular weight of the novolac resin, the degree of allylation, and the molar ratio of maleimide to allyl groups. A general discussion on the influences of these variables on the performance of the resin was given in a previous article.[3] To formulate a resin of superior heat resistance, a Novolac resin of reasonably high molecular weight (number average molecular weight = 488) was used as the starting prepolymer. It was allylated by a reaction with allyl chloride (Scheme 2). The degree of allylation was very high; that is, all phenolic hydroxyl groups were converted to allyl ether, and moreover, on average, each phenol ring carried 0.18 allyl groups as the result of Claisen rearrangement.

In the formulation of the BMAN resins, the molar ratio of allyl to maleimide groups was changed in the
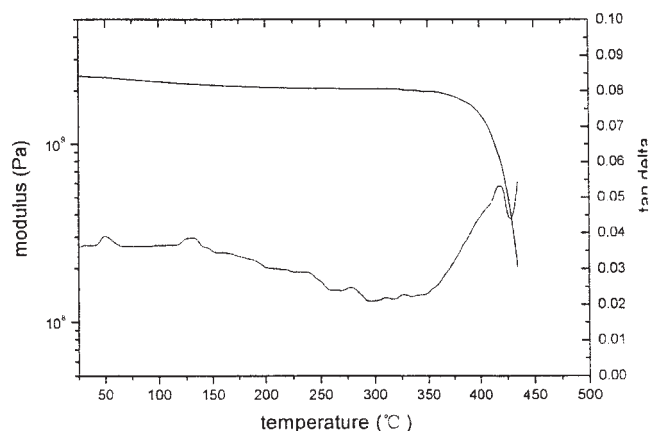
Figure 2 Dynamic mechanical properties of the BMAN15 resin: curing schedule 170°C for 2 h, 200°C for 6 h, and 250°C for 6h.

TABLE II
T_g Values of some BMI and Polyimide Resins

	Resin system				
	Narmco 5270	Narmco 5250-4	PMR-15	QY-8911-II	BMAN15
T_g (°C)	287	295	365	286	418

range of 100:30 to 100:15. Higher BMI proportions were unfavorable because of the limited solubility of 4,4-bismaleimidodiphenylmethane in the allylated Novolac. The T_g and modulus retention at 350°C data are summarized in Table I. The proportion of BMI, over the range of investigation did not have any major influence on the heat resistance of the cured resin. Very high T_g values were achieved with formulations of quite low BMI proportions.

Properties of the BMAN15 resin

Resins of low BMI proportion favored RTM processing due to their low viscosity and good stability against precipitation. In the BMAN15 resin, the molar ratio of allyl to maleimide groups was 100:15. The change in viscosity with time at 110 and 120°C, is shown in Figure 1: the resin was appropriate for RTM at these temperatures by a normal procedure.

The cured BMAN15 resin showed a very high T_g at 418°C, and the modulus retention was over 90% up to 350°C (see Fig. 2). These figures are remarkable compared with commercial resin systems. Some T_g values of BMIs and polyimides are given in Table II.

The flexural properties of the composite of BMAN15 reinforced with quartz woven cloth were tested at room temperature and 300 and 350°C. The data for the flexural strength and flexural modulus are summarized in Table III. By virtue of the high T_g of the matrix resin, the composite exhibited a modulus retention

TABLE III
Properties of the Composite of the BMAN15 and Quartz Cloth

Property	Value	Retention rate (%)
Resin content (wt %)	33.1	
Flexural strength (MPa)		
25°C	392	100
300°C	235	60.0
350°C	182	46.4
Flexural modulus (GPa)		
25°C	18.7	100
300°C	17.8	95.2
350°C	16.7	89.3

Curing schedule: 170°C for 2 h, 200°C for 6 h, and 250°C for 6 h.
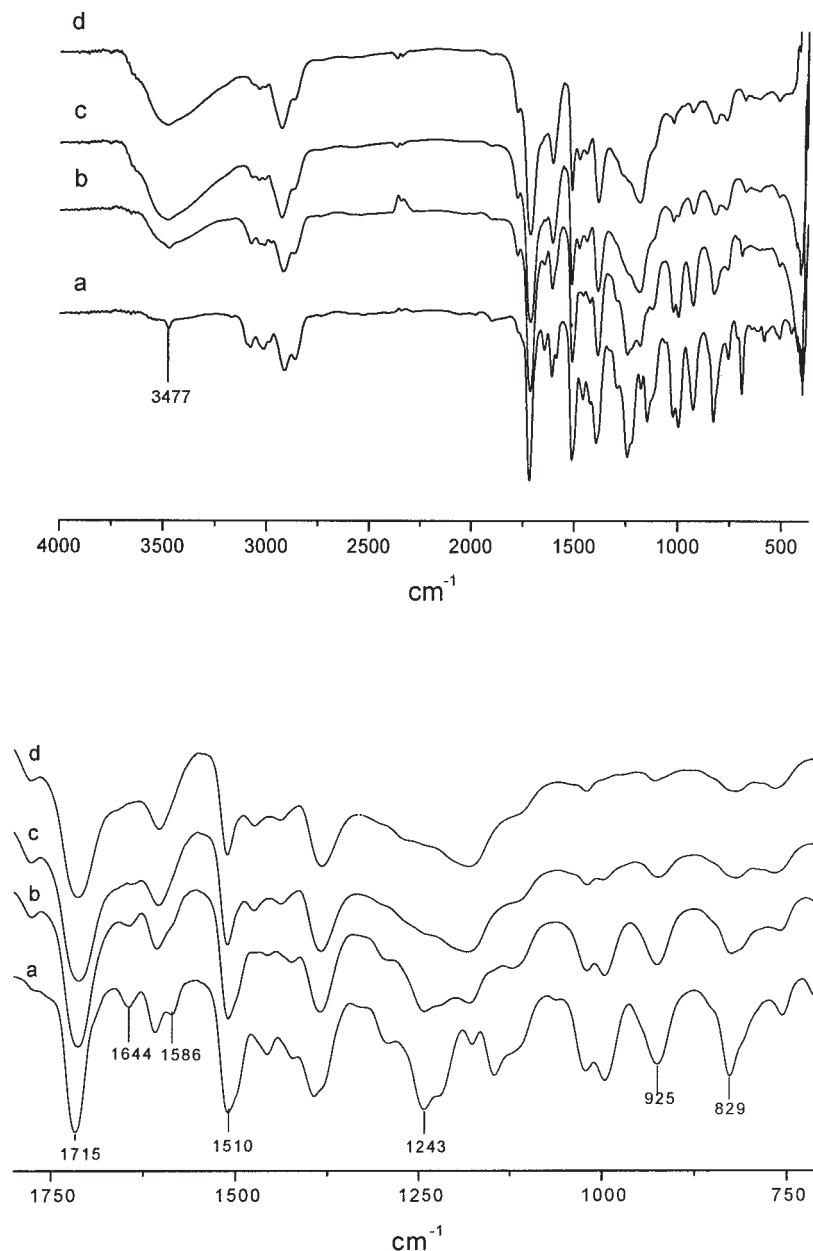
Figure 3 IR spectra for the BMAN15 resin at different curing stages: (a) the starting resin, (b) after 2 h at 170°C, (c) after 2 h at 170°C and 6 h at 200°C, and (d) after 2 h at 170°C, 6 h at 200°C, and 6 h at 250°C.

rate of 89.3% and a strength retention rate of 46.4% at 350°C.

Reactions in the curing of the BMAN resin

To illustrate the chemical reactions responsible for the curing of the BMAN15 resin, IR spectra at different stages were taken. In Figure 3, the spectra for the original resin, the resin after 2 h at 170°C, the resin after 2 h at 170°C and 6 h at 200°C, and the fully cured resin after 2 h at 170°C, 6 h at 200°C, and 6 h at 250°C are shown.

The development of the band for ν_{O-H} at about 3477 cm^{-1} was remarkable. Because phenol groups in the Novolac resin were converted to allyl ether, this band was very weak in the starting BMAN15 resin. Obviously, hydroxyl groups were formed as a result of Claisen rearrangement of the allyl ether. This reaction resulted in a reduction in the 1243-cm^{-1} band as well. The reaction should have been active at 170°C, and completed, overall, in the stage of 200°C for 6 h according to the change in the spectra.

As the curing went on, the bands at 829, 925, 1586, and 1644 cm^{-1}, for unsaturation reduced progres-
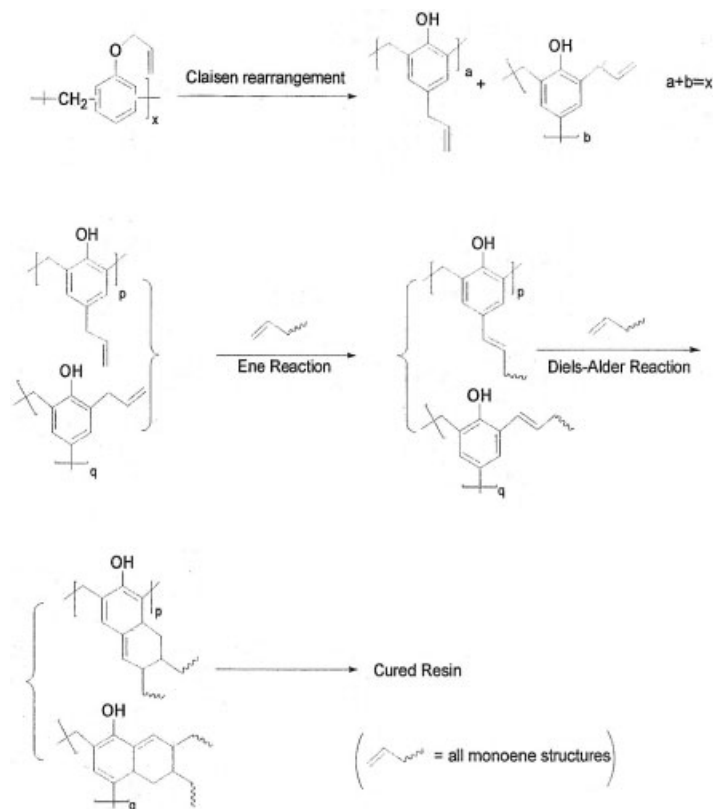
Scheme 3 Possible reactions in the curing of the BMAN15 resin.

sively. Reactions between maleimide groups and allyl groups, as shown in Scheme 1, are known. Because the allyl group was in great excess, these groups should have played an important part in the crosslinking of the resin. Possible reactions were the ene reaction, 4 + 2 cyclo addition, and polymerization, as shown in Scheme 3.

Participation of a benzene ring in the Diels–Alder type 4 + 2 cycloaddition was proposed by Zahir et al.[1] It should have made a considerable contribution to the crosslinked structure. For the BMAN15 resin, the consumption of the benzene ring at different stages of curing was evaluated according to the changes in the IR spectra. The area of the band at 1510 cm^{-1} was used as a measurement of aromatic group concentration, and the peak at 1715 cm^{-1} as the internal standard. The results are summarized in Table IV. At the 200°C for was used 6 h stage, the reduction in the 1510-cm^{-1} band was significant.

Compared to the resin system of high BMI proportion,[3] the BMAN15 resin needed a higher temperature to complete curing. A comparison of DSC thermograms is given in Figure 4.

In the DSC diagram for the BMAN15 resin, two peaks at 223 and 294°C were present, whereas only one exothermic peak at 240°C was seen in the dia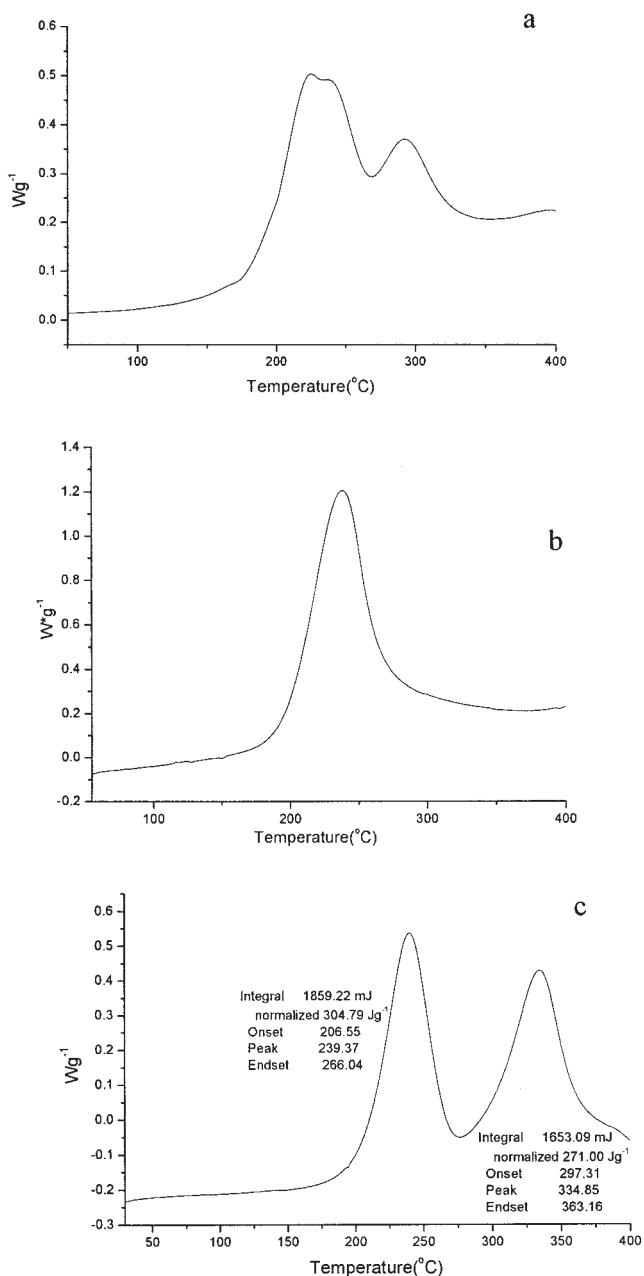gram for the resin with BMI/allyl molar ratio of 0.5. The former diagram was close to that for the neat allylated novolac resin, in which the first peak was located at 239°C and the second was located at 334°C. The second exothermic peak was likely contributed by the addition and polymerization of allyl groups. It is understandable that allyl groups, without electron-withdrawing substitutes, are less reactive than maleimide groups as "ene-phile" in the ene reaction and "dieno-phile" in the 4 + 2 cycloaddition. Therefore, higher reaction temperatures were required.

CONCLUSIONS

Thermosetting BMAN resin systems with very high T_g values were formulated from BMI and allylated no-

TABLE IV
Consumption of Aromatic Groups in the Curing of the BMAN15 Resin

Stage of curing	Relative intensity of the 1510-cm^{-1} band (%)
Starting resin	100
170°C for 2 h	74.2
170°C for 2 h and 200°C for 6 h	39.5
170°C for 2 h, 200°C for 6 h, and 250°C for 6 h	35.3

volac. When the allylation degree of the novolac resin was high enough, the BMI proportion was not critical to heat resistance of the cured resin. The BMAN15 resin with a high allylation degree and low BMI proportion was appropriate for RTM. Composites of the BMAN15 resin with quartz woven cloth as reinforcement had good strength and modulus retention rates at 350°C. Because allyl groups were in much higher molar proportions over maleimide groups in the BMAN15 resin, the ene reaction and the 4 + 2 cycloaddition of allyl groups played significant roles in the curing of the resin.

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Figure 4　DSC thermograms for the (a) BMAN15 resin, (b) BMI/allylated Novolac resin (BMI/allyl = 0.5), and (c) neat allylated novolac.