# Thermosetting Resin System Based on Novolak and Bismaleimide for Resin-Transfer Molding

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**ABSTRACT:** A thermosetting resin system for resin-transfer molding based on novolak and bismaleimide (BMI) was developed. The novolak resin was allylated and BMI was used as the curing agent, and allyl phenyl ether, as the diluent. The viscosity–temperature curve and the viscosity–time curve were used to characterize the processing property of the resin system. The resin system had a long pot life at the injection temperature. Based on the DSC data, a regime for the curing and postcuring cycles was established. The cured resin showed outstanding heat resistance and good flexural properties. Composites based on the resin system and woven glass fabric were fabricated using RTM technology. The composites showed very good flexural properties at room temperature and high retention rates at 200 and 300°C. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1651–1657, 2002

**Key words:** novolak; bismaleimide; allyl phenyl ether; resin-transfer molding; processing property; heat resistance; resins; processing properties; thermal properties

## INTRODUCTION

Resin-transfer molding (RTM) for the fabrication of composite materials is receiving more and more attention because of its comparatively low cost and high efficiency.[1,2] It is an environmentally friendly process as the whole operation is carried out under airtight conditions. The products made by RTM have good surfaces, precise dimensions, and a low void content.[3]

The resins for RTM should have the following characteristics[4]: (1) low viscosity (<0.5 Pa s) and a long pot life at the injection temperature; (2) good adhesion between the resin matrix and the reinforcement; (3) fast curing at the processing temperature and no volatile releasing upon curing; and (4) low cure shrinkage. According to the

aforementioned requirements, resins suitable to RTM are unsaturated polyesters, vinyl esters, and acrylates. However, none of these resins can meet the need of high-performance composites for strength, modulus, and thermooxidative stability.

Phenolic resins have a high aromatic content in the structure. They have a high char yield and good strength retention at high temperatures. However, phenolic resins are not suitable for RTM because of their high viscosity and volatile releasing upon curing. Viscosity control of the resin is possible through water content and temperature control. Resole resins containing from 7 to 15% water have been applied to RTM.[5] Water is also the byproduct of curing, this can present significant problems in RTM. Borden Chemical Co. developed a phenolic resin system for RTM,[6] which used a two-component acid catalyst. The catalyst gave rise to more flexibility in compromising the pot life and the reactivity. Menfredi et al.[7] reported the blends of an epoxy (1,4-butane-
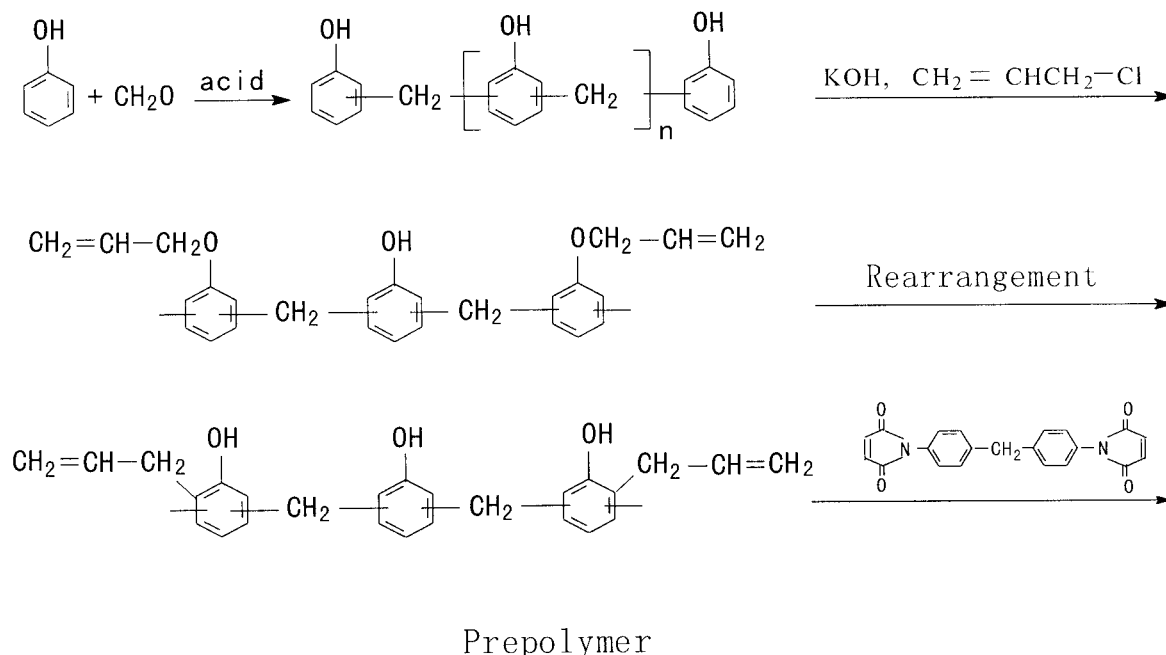
**Figure 1**  Preparation of the BMI-modified novolak resin.

diol diglycidyl ether) and a resol resin for RTM with the aim of improving the processability of resoles and the fire resistance of epoxies. However, the heat resistance of the modified phenolic resins was sacrificed.

It is well known that bismaleimides (BMI) are good matrix resins for high-performance composites because of their high heat resistance, thermooxidation stability, and outstanding mechanical properties. To introduce the BMI component into a structure, allyl groups are introduced into the phenolic backbone to make the resin copolymerize with maleimide.[8–12] Upon curing, the reaction of maleimide groups and allyl phenolic proceeds via the "Ene" reaction and Diels–Alder reactions[13–16] without volatile releasing. Therefore, it is possible to develop a thermosetting resin system for RTM based on phenolic resin and BMI.

The objective of this work was to develop a novel thermosetting system, which keeps the good properties of phenolic resins and is suitable for the RTM process. The network of the thermosetting resin is formed through copolymerization of allylated novolak resin and BMI. Detailed results are described in the present article.

## EXPERIMENTAL

### Starting Materials

Phenol (CP) and formaldehyde (37% in water, CP) were from the Beijing Organic Chemicals Factory (Beijing, China) and were used as supplied. Allyl chloride was obtained from the Qilu Petrochemical Co. (Zibo, China) and used after distillation. 4,4′-Bismaleimidodiphenylmethane (BMI) was purchased from the Fenguang Chemical Co., Ltd. (Honghu, China). It is a crystalline substance with a melting temperature of approximately 172°C and a molecular weight of 286. Allyl phenyl ether was synthesized in our laboratory. It is a transparent liquid with a boiling point of 220°C and a viscosity of 0.01 Pa s at 25°C.

### Synthesis of the BMI-modified Novolak Resin

The BMI-modified novolak resin was prepared by the following steps: (1) synthesis of the novolak resin; (2) allylation of the novolak resin; (3) rearrangement of the allyl groups; and (4) prepolymerization of the allyl novolak resin with BMI (see Fig. 1). The novolak resin was prepared through condensation of formaldehyde and phenol catalyzed by oxalic acid. The molar ratio of phenol to formaldehyde was 1:0.9. The molecular weight of the novolak resin was 454, determined by $^1$H-NMR.[17] For the allylation of the novolak resin, 0.5 mol of allyl chloride was used for 1 mol of the phenol group in the resin. The reaction was carried out at 80°C in a butanol solution for 5 h. The degree of allylation of the phenol groups in the novolak resin was 48%, determined by $^1$H-NMR.
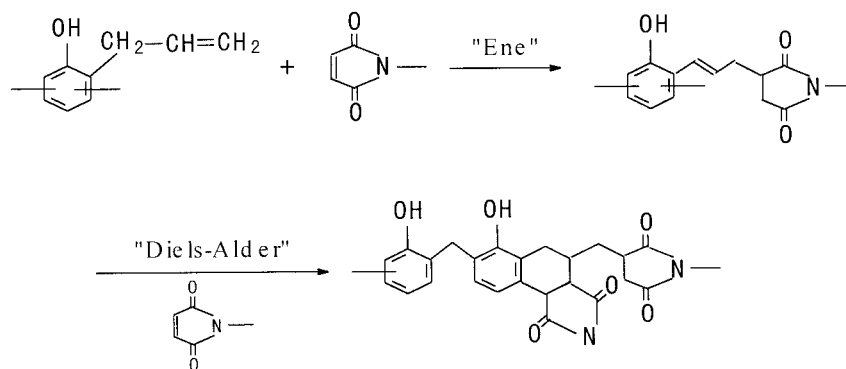
**Figure 2**   Reactions responsible for the network formation.

The allylated novolak resin was diluted with about 5% wt of allyl phenol ether. BMI was introduced at the molar ratio of the allyl group to the maleimide group of 1:1. After the prepolymerization at 115°C for 40 min, a clear homogeneous BMI-modified novolak resin was obtained. Other BMI-modified novolak resin systems were obtained by the same process as mentioned above.

**Preparation of the Cured Resin**

The resin mixture was degassed in a vacuum oven at 100°C for 4 h, then poured into a rectangular mold. The cure cycle was 170°C/2 h + 200°C/6 h, and the postcure procedure was 250°C/6 h.

**Fabrication of Composites via RTM**

Composites were fabricated in a home-made RTM setup. The rectangular mold with a woven glass reinforcement was preheated to 100°C. The resin was heated to 100°C and injected into the mold using a vacuum. The cure cycle was 170°C/2 h + 200°C/6 h, and the postcure was effected at 250°C/6 h. The composites were machined into specimens for flexural testing.

**Characterization and Measurements**

The viscosity was determined on an NDJ-79 viscometer. The gel time was measured in a controlled-temperature instrument. Thermal analysis of the resin system was performed on a Perkin–Elmer 7 DSC at a heating rate of 10°C/min in a nitrogen atmosphere.

The glass transition temperature ($T_g$) of the cured resin was obtained from the DSC curves, and the scans were carried out at a heating rate of 20°C/min in a nitrogen atmosphere. The thermal stability of the cured resin was studied with a Perkin–Elmer 7 thermogravimetric analyzer, at a heating rate of 20°C/min in a nitrogen atmosphere.

Measurements of the heat-distortion temperature (HDT), water absorption, and flexure strength were conducted according to the standards GB1634-79, GB1034-86, and GB1042-79, respectively. The flexure tests for the composites were carried out according to the standard GB1449-83.

**RESULTS AND DISCUSSION**

**Molecular Design of the Thermosetting Resin System**

To avoid volatile releasing during curing of the novolak resin and to introduce the BMI component into the structure, the novolak resin was allylated. Upon curing of the resin, the network was formed through an Ene reaction and the Diels–Alder reaction (Fig. 2).[18]

The major parameters controlling the network structure and the properties of the cured resin were

- The molecular weight of the novolak resin;
- The degree of the allylation;
- The molar ratio of the allyl group and the maleimide group.

To keep a balance between the processing properties and the performance of the cured resin, a compromise was made in the design of the resin.

A high molecular weight of the novolak resin was advantageous for the mechanical properties of the cured resin, but was unfavorable for the

**Table I    Effects of Molecular Weight of the Novolac Resin, Degree of Allylation, and Diluent Concentration on the Viscosity of the Modified Resin and the Glass Transition Temperature**

| Code | $M_n$ | Allyl (%) | Diluent Concentration (wt %) | $\eta$ at 100°C (Pa s) | $T_g$ by DSC (°C) |
|------|-------|-----------|------------------------------|------------------------|-------------------|
| 1 | 334 | 48.9 | 0 | 0.15 | 181 |
| 2 | 454 | 48.3 | 0 | 0.42 | 295 |
| 3 | 551 | 48.6 | 0 | 0.67 | 297 |
| 4 | 618 | 47.1 | 0 | >1.0 | 316 |
| 5 | 454 | 38.7 | 0 | 0.18 | 243 |
| 6 | 454 | 57.0 | 0 | 0.71 | 314 |
| 7 | 454 | 48.3 | 5 | 0.21 | 288 |
| 8 | 454 | 48.3 | 10 | 0.13 | 271 |
| 9 | 454 | 57.0 | 10 | 0.30 | 279 |
| 10 | 551 | 48.9 | 5 | 0.40 | 289 |
| 11 | 618 | 47.1 | 10 | 0.66 | 292 |

injection molding. A high degree of allylation for the novolak resin allowed incorporation of more of the BMI component into the resin. This resulted in a high degree of crosslinking, but also in a high viscosity. A high molar ratio of the allyl group to the maleimide group resulted in a low viscosity, which was desirable for the molding. However, the deficiency of BMI also resulted in an inferior heat resistance of the cured resin.

The effects of the molecular weight of the novolak resin, the degree of allylation, and the diluent concentration on the viscosity of the modified resins and the glass transition temperature of the cured resins are shown in Table I. After a comprehensive study, an optimum thermosetting resin system was obtained. In the BMI-modified novolak resin system developed for RTM, the molecular weight of the novolak resin was about 450, the degree of allylation was about 50%, and the concentration of allyl phenol ether in the allyl novolak resin was 5% wt. The molar ratio of the allyl group to the maleimide group was 1:1.

## Processing Properties of the BMI-modified Novolak Resin

The viscosity of the resin system is the basic processing parameter for RTM. The Ashland Chemical Co.[19] studied the influence of the resin viscosity. A resin viscosity of 0.2–0.3 Pa s was believed to give the best overall processability for RTM.

The viscosity–temperature curve for the BMI-modified novolak resin system is given in Figure 3. It is seen that the viscosity decreases rapidly as the temperature increases. At temperatures below 70°C, the viscosity of the resin exceeds 1.0 Pa s. It is generally believed that if the viscosity is

higher than 0.5 Pa s a high injection pressure and heavier and expensive molds will be required. In addition, a high injection pressure can lead to fiber displacement in the mold cavity. When the temperature is between 100 and 130°C, the viscosity of the resin is in the range of 0.15–0.3 Pa s. In this temperature zone, the resin system is suitable for the RTM process. At a temperature higher than 140°C, the viscosity will be lower than 0.1 Pa s. In this case, a turbulent flow may be formed upon injection, which leads to air entrapment, washing out of the preformed parison and formation of pinholes.

The injection temperature of the resin system was chosen to be 100°C. The viscosity–time curve
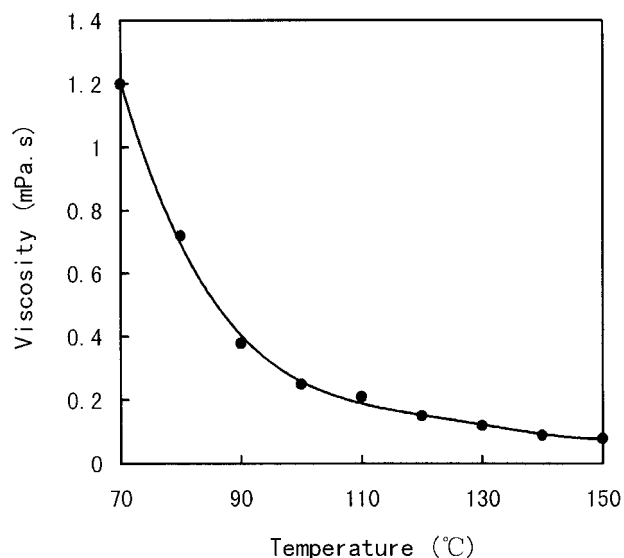


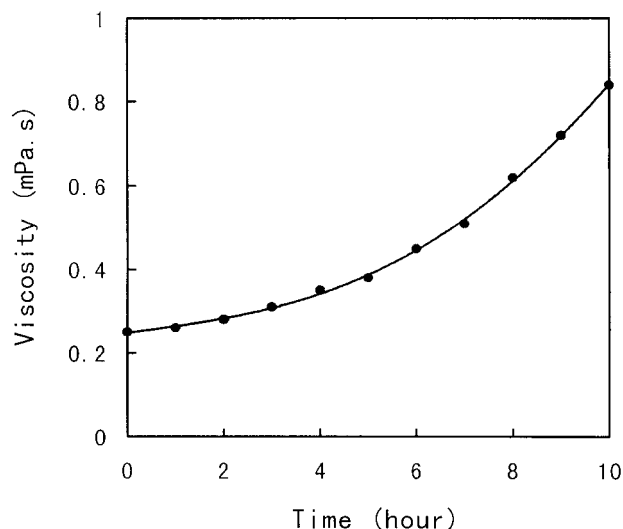**Figure 3**  Viscosity–temperature cruve of the resin system.

**Figure 4**  Change of the viscosity of the resin system with time at 100°C.

at 100°C is presented in Figure 4. It is seen that the viscosity is only 0.25 Pa s at the beginning and still less than 0.5 Pa s after 6 h. Therefore, the pot life at 100°C is long enough for RTM.

The gel time, the time needed for the resin to reach the gel state at a given temperature, reflects the reactivity of the resin system. The gel time ($t_{gel}$) of the BMI-modified novolak resin system at different temperatures ($T$) is shown in Figure 5. The curing is thermally activated, and the relation between the gel time and the temper-
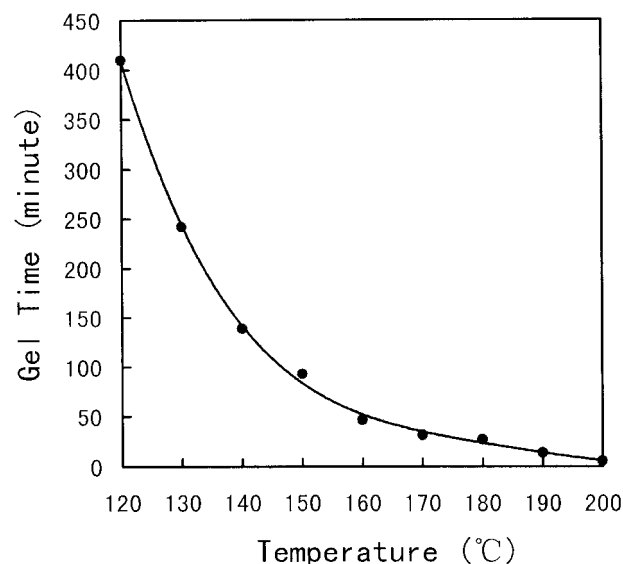


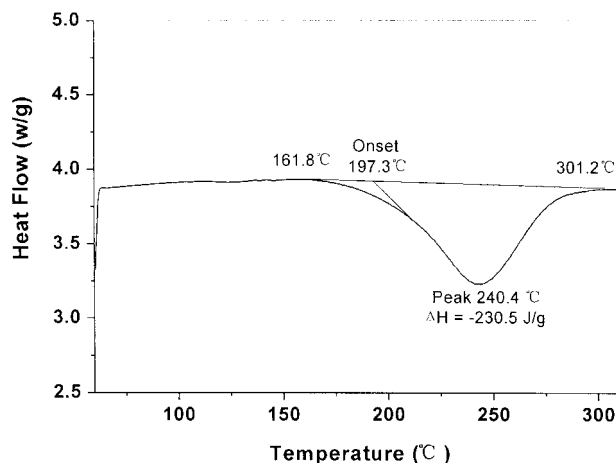**Figure 5**  Gel time–temperature correlations of the resin system.



**Figure 6**  DSC curve of the resin system at a rate of 10°C/min.

ature can be described in terms of an Arrhenius type equation:

$$\ln t_{gel} = \ln A - \frac{E}{RT}$$

The apparent activation energy for the curing was obtained by the linear regression of the ln $t_{gel}$ versus $1/T$ diagram. The value was 65.21 kJ/mol.

## Establishment of the Cure and Postcure Cycles

To establish a reasonable curing cycle for the resin system, DSC studies were carried out. A typical DSC thermogram at a heating rate 20°C/min is given in Figure 6. It is seen that the exothermic process of the curing begins at 161.8°C and ends at 301.2°C with a total enthalpy of 230.5 J/g.

DSC scans at a series of heating rates $\beta$ (2.5, 5, 10, and 20°C/min) were conducted, and the initial temperature ($T_i$), the peak temperature ($T_p$), and the finish temperature ($T_f$) were plotted against the heating rate. By extending the $T$–$\beta$ curves to $\beta = 0$, the reference temperatures $T_i^0$ (157°C), $T_p^0$ (233°C), and $T_f^0$ (289°C) were obtained. It is reasonable to choose a curing temperature between $T_i^0$ and $T_p^0$ and a postcuring temperature between $T_p^0$ and $T_f^0$. We used a curing cycle for the resin system of 170°C/2 h + 200°C/6 h and a postcure procedure of 250°C/6 h.

## Properties of the Cured Resin

As shown by the data in Table II, the cured resin had good flexural strength (122.4 MPa), a high
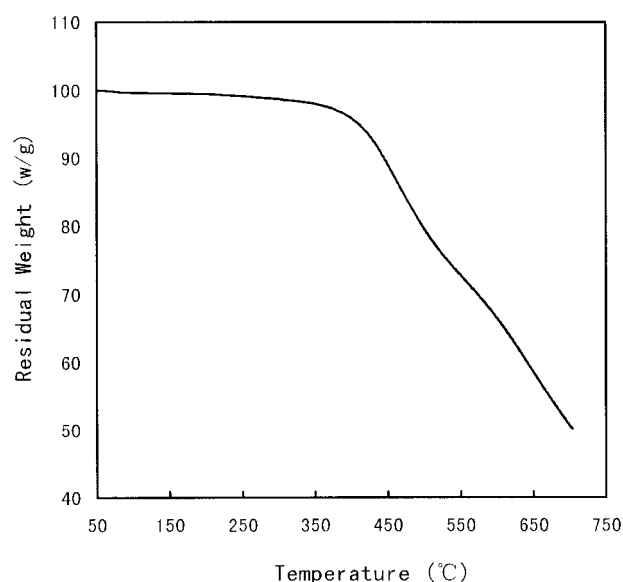
**Table II   Properties of the Cured Resin**

| Properties | Value |
|---|---|
| Flexural strength (MPa) | 122.4 |
| Flexural modulus (GPa) | 3.53 |
| Water absorption (%) | 4.5 |
| HDT (°C) | 273 |
| $T_g$ (°C) | 288 |
| Density (g/cm$^3$) | 1.31 |

**Table III   Properties of the Composite Based on the BMI-modified Novolak and Woven Glass Cloth Fabricated by RTM Process**

| Property | Value | Retention Rate |
|---|---|---|
| Resin content (wt) | 33 | |
| Flexural strength (MPa) | | |
| 23°C | 413 | |
| 200°C | 371 | 90% |
| 300°C | 267 | 65% |
| Flexural modulus (GPa) | | |
| 23°C | 27.7 | |
| 200°C | 25.3 | 91% |
| 300°C | 21.5 | 78% |

modulus (3.53 GPa), and low water absorption (4.5%). The heat resistance was remarkable for its high HDT (273°C) and glass transition temperature (288°C).

The thermal stability of the cured resin was studied by thermogravimetric analysis (TGA). As shown in Figure 7, the inflection temperature in the TGA curve was 402°C, and the temperatures for weight losses of 5 and 10% were 410 and 445°C, respectively. The residual weight at 500°C was 80 wt %, and the char yield at 700°C was 51%. The data indicate that the thermosetting resin based on novolak and BMI had very good thermal stability.

### Properties of the Composite

By virtue of the low viscosity, good adhesion to the glass cloth, and no volatile releasing upon curing, the BMI-modified novolak resin was suitable for composite fabrication by the RTM pro-

cess. The composites of the resin with woven glass cloth were dense and void free. The mechanical properties of the composite are given in Table III. It is seen that the flexural strength and the modulus were good for structural applications. More remarkable is that the retention rates of the strength and the modulus at 200 and 300°C were high. This is very important for the materials to be used at high temperatures.

## CONCLUSIONS

A thermosetting resin system was developed, in which the novolak resin was partially allylated and BMI was used as the curing agent. The resin system showed excellent processing properties for RTM, such as low viscosity and long pot life at the injection temperature and no volatile releasing upon curing. The cured resin displayed good mechanical properties, high heat resistance, and low water absorption. The composite prepared by the RTM process, based on the resin system and woven glass cloth, not only had very good flexural properties at room temperature but also had high retention rates at 200 and 300°C. These confirmed that the thermosetting resin system was ideal for the fabrication of high-temperature-resistant composites by the RTM technology.



**Figure 7**   TGA curve of the cured resin.

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