

# Bismaleimide Resin Modified with Diallyl Bisphenol A and Diallyl *p*-Phenyl Diamine for Resin Transfer Molding

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**ABSTRACT:** *O,O'*-diallyl bisphenol A (DBA) and *N,N'*-diallyl *p*-phenyl diamine (DPD) were used for the reactive diluents of 4,4'-bismaleimidodiphenol methane (BDM). The objective was to obtain a modified BDM resin system suitable for resin transfer molding (RTM) process to prepare the advanced composites. The processing behavior was determined by time–temperature–viscosity curves, gel characteristics, and differential scanning calorimetry (DSC). The injection temperature of the resin system in RTM could be 80°C, at which its apparent viscosity was only 0.31 Pa/s, and the apparent viscosity was still less than 1.00 Pa/s after the resin was held at 80°C for 16 h. The gel time test result indicated that at low temperatures, the reactivity of the resin system is low, whereas at high temperatures, the resin could cure very fast, which was beneficial to RTM. The postcure of the cured resin at a given temperature was necessary because the resin had a wide and flat cure exothermic peak, observed by DSC curve. The cured resin displayed both high heat and hot/wet resistance and high mechanical properties, especially tensile strength, tensile modulus, and flexural strength at room temperature, which reached 96.2 MPa, 4.8 GPa, and 121.4 MPa, respectively. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2245–2250, 2001

**Key words:** bismaleimidodiphenol methane; diallyl bisphenol A; diallyl *p*-phenyl diamine; resin transfer molding; reactive diluents

## INTRODUCTION

In the process of resin transfer molding (RTM), preformed fiber mats are first placed in the mold cavity, after which resin is injected into the closed mold filled with dry fiber reinforcement. RTM provides the potential to produce high-quality surface finish components of complex shapes with tight tolerance and low void concentration. In addition, RTM has the advantages of low resin injection pressure and fast processing for large composite parts. Hence much attention has been paid

to RTM in many fields, especially the aerospace and automobile industries.<sup>1–5</sup> However, not all resins can be used for RTM. For RTM, they should generally have low viscosity and sufficient pot-life at injection temperature, and cure fast at processing temperature, as well as have no volatile molecules released in the course of curing.<sup>6</sup> The resins suitable for RTM can be unsaturated polyesters, vinyl esters, acrylates, low-viscosity epoxy systems, and the like. But none of these materials can meet the requirements in aerospace applications for strength and module and thermo-oxidative stability.<sup>7</sup>

Bismaleimides (BMIs) are primary candidates as matrix resins for advanced composites based on the fact that their cured resins have high heat resistance, mechanical strength, and hot/wet re-

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sistance. However, neat BMI resins cannot be used for RTM because of their high melting temperature, solid state at room temperature, poor solubility, and brittleness of their cured resins. Therefore, much research work has been focused on the modification of BMI resins through copolymerizing with various reactive diluents or comonomers.<sup>8–11</sup>

In previous studies, a modified BMI resin system for RTM was developed in the presence of diallyl bisphenol A (DBA) and allyl methyl phenol as reactive diluents. The results showed that the processability of the resin system was suitable for RTM, but its resultant mechanical properties and heat resistance were reduced greatly in comparison with properties of the neat BMI resin. This is because allyl methyl phenol contains only one allyl group, which cannot provide sufficient reactive points for crosslinking reaction; subsequently, the crosslinking density is rather low. To overcome the drawback, 1,4-diallyl phenyl ether (DPE) with double-reactive points of allyl methyl phenol was employed to substitute for allyl methyl phenol. It was found that the heat resistance and mechanical properties were increased, but the compatibility between BMI and reactive diluents were poor. When the prepolymer of BMI, DBA, and DPE was kept for 24 h at 25°C, the BMI was crystallized and separated out from the prepolymer. So in future investigation, it is a basic task to keep the heat resistance and mechanical properties, and improve the compatibility between BMI and the reactive diluents.

In the present study, *N,N'*-diallyl *p*-phenyl diamine (DPD) was used to replace DPE to achieve the above-mentioned goal because the amine group and BMI can interact strongly both physically and chemically. Through time–temperature–viscosity curves, gel characteristics, differential scanning calorimetry (DSC), and mechanical properties tests, the novel BMI resin system for RTM was studied extensively.

## EXPERIMENTAL

### Materials

4,4'-Bismaleimidodiphenyl methane (BDM) is the commercial product of Fengguang Chemical Co. (China). At room temperature it is yellowish crystal powder with a melting temperature of 152°C. *O,O'*-diallyl bisphenol A (DBA) was kindly supplied by Jangyou Chemical Materials Co. (China), and was used without further purification. It is brown liquid with a boiling point of approxi-

mately 260°C, its viscosity at 25°C is 0.05 Pa/s, and its density at room temperature is 1.12 g/cm<sup>3</sup>. *N,N'*-diallyl *p*-phenyl diamine (DPD) was prepared in the authors' laboratory by reacting between *p*-phenyl diamine and chloropropylene. It is a light yellow liquid, whose boiling point is 258°C and viscosity at 25°C is 0.05 Pa/s.

### Preparation of Prepolymer of BDM/DBA/DPD

Appropriate quantities of BDM, DBA, and DPD were placed in a three-necked separable flask with a mechanical stirrer and a thermometer. The mixture was heated gradually to 135°C and polymerized for 20 min. After the reaction, a clean homogenous viscous liquid, a prepolymer, was obtained, which was then cooled to room temperature.

The related cured resin was prepared by pouring the heated (80°C) liquid prepolymer into a preheated rectangular mold after it was degassed *in vacuo* at 80°C for 30 min. The mold consisted of a pair of glass sheets held by upright and metal clips and spaced by a U-shaped silicon rubber stick. The mold was put into an ordinary air-convection oven for curing and postcuring according to the following cure cycle: 150°C/1 h; 180°C/2 h; 200°C/2 h; 230°C/2 h; 250°C/6 h. After curing, the oven temperature was decreased gradually from 250°C to ambient temperature and the time taken was about 6 h. The cured resin plaque was consequently achieved, and then machined into various samples, such as tensile, impact, flexural, and heat distortion coupons.

### Measurement and Characterization

The processing properties of the resin system were determined by apparent viscosity and reactivity measurements.

Time–temperature–viscosity curves were generated by the use of a rotaviscometer with a temperature controller.

Pot-life is the time required to increase the viscosity of the resin system to 1.0 Pa/s when the resin is kept at the selected injection temperature of 80°C. The pot-life measurement procedure was also performed on the rotaviscometer.

The reactivity of the resin system was investigated by gel characteristic and DSC. The gel times, which are the times needed for the resin to become a gel state at the given temperatures, were measured from 120 to 220°C. Thermal analysis of the resin system was carried out on a Perkin–Elmer 7 DSC (Perkin–Elmer, Foster City, CA) at a heating rate of 10°C/min in a nitrogen atmosphere. Tensile and flexural tests were con-

ducted in terms of GB 1040-79 and GB 1042-79, respectively. Each team was composed of five samples and an average value was reported. The heat distortion temperature (HDT) was tested according to GB 1634-79. Fracture toughness, characterized by the impact strength and critical strain energy release ( $G_{1c}$ ) value, was measured by GB 1451-83.

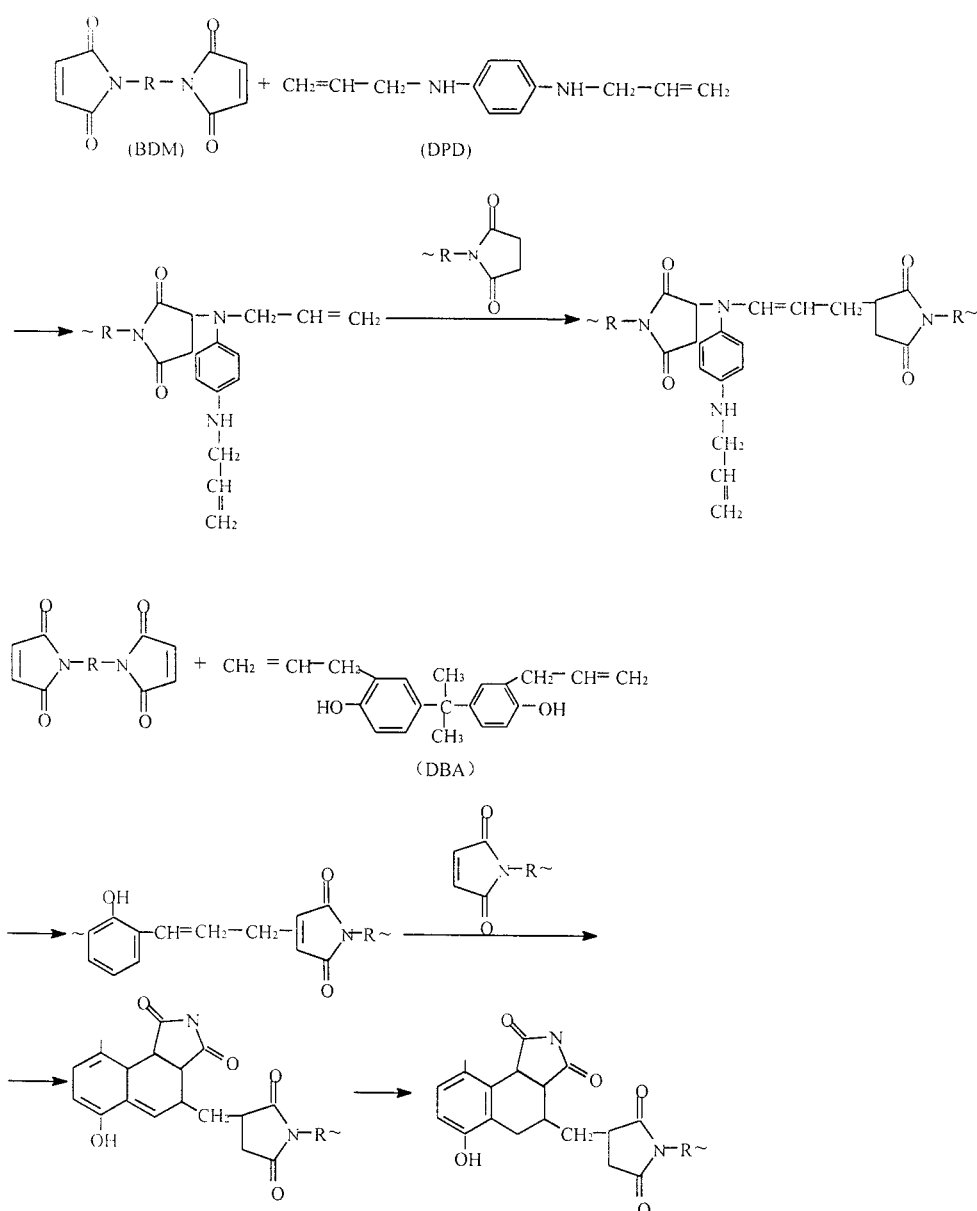
## RESULTS AND DISCUSSION

### Copolymerization Reaction of BDM/DBA/DPD

The reaction mechanism of copolymerizing BMI with allyl group compounds is very complicated. In

this study, BDM can react with both DBA and DPD, where DPD contains amine and allyl groups, which can both interact chemically with BDM according to different reaction routes. In general, the double bonds of the maleimide ring in BDM, and the allyl in DBA and DPD react via the ene-type linear chain extension reaction followed by the Diels–Alder reaction. Moreover, the Michael addition reaction, which can occur between the amine group and BDM, tends to take place easily compared to the “ene” and Diels–Alder reaction. The reaction process is roughly outlined in Scheme 1.

For the prepolymer, the components only underwent linear chain extension reaction. The



**Scheme 1** The reaction process of the resin system.

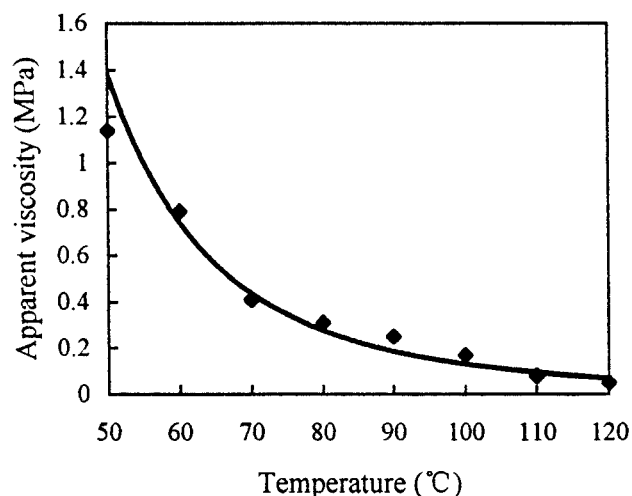
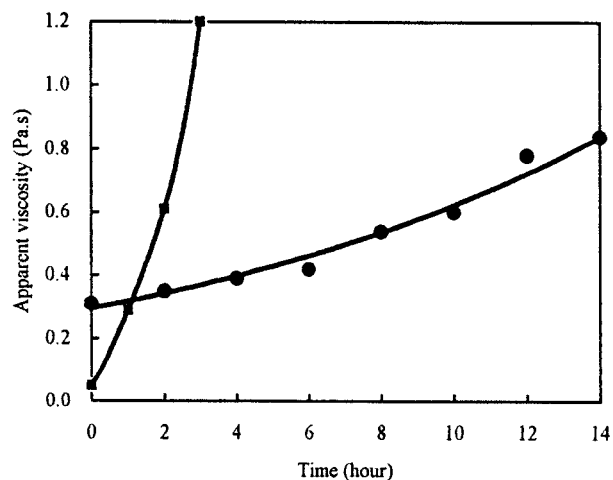
**Table I** Some Physical Properties of the Prepolymer

Color	Brown
Viscosity at 25°C (Pa/s)	2.5
Solubility in diluents at 25°C	Good solubility in acetone, ethanol, etc.
Miscibility with other resins	Good miscibility with epoxy resin, unsaturated Polyester, etc.
Density (g/cm <sup>3</sup> )	1.12
Stability	Homogenous and stable after being held for 30 days

crosslinking reaction took place in the curing process of the prepolymer. Some typical physical properties of the BDM/BDA/DPD prepolymer are presented in Table I. It can be found that the compatibility of the DBM/BDA/DPD prepolymer components is significantly improved in comparison with that of the DBM/DBA/DPE resin system (reported above).

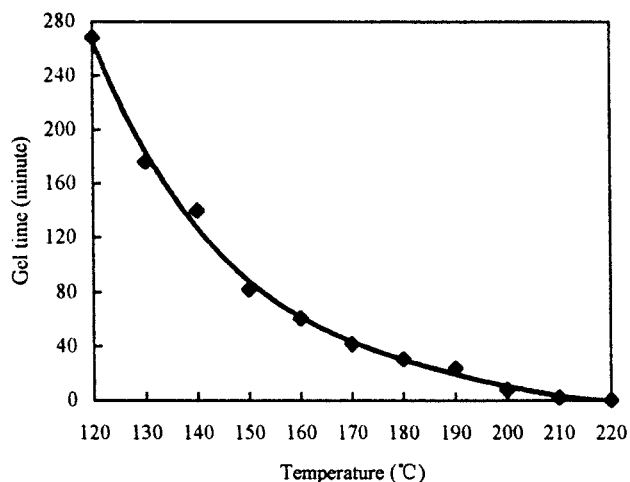
#### Processing Characteristics of BDM/DBA/DPD Prepolymer

The processing behaviors of the resin system for RTM are usually characterized by viscosity–temperature, viscosity–time, and gel time–temperature correlations. Figure 1 shows the apparent viscosity–temperature correlation of the BDM/DBA/DPD prepolymer. It can be seen from the figure that the viscosity decreased rapidly with

**Figure 1** Apparent viscosity of the resin system as a function of temperature.**Figure 2** Correlation between apparent viscosity and time at selected temperatures.

increasing the temperature from 50 to 120°C. When the temperatures were lower than 50°C, the viscosity was much higher than 1.0 Pa/s, which is too high to suit RTM processing, because high viscosity needs very high pressure to inject the resin system into a mold. At temperatures above 100°C, the viscosity greatly decreased, to less than 0.2 Pa/s. Such viscosity tends to form turbulence in the RTM process, which may cause washing out of the preformed parison and consequently influences the size precision of the products. In addition, high temperature makes the pot-life short because increasing temperature facilitates the reaction. In this work, 80°C was selected as the injection temperature. The viscosity–time curves of the resin system at both 80 and 120°C, respectively, are shown in Figure 2, which indicates that the apparent viscosity at 80°C is only 0.31 Pa/s and, after being maintained at the same temperature for a period of 15 h, its viscosity was still less than 1.0 Pa/s, which is sufficient for RTM. However, for the resin tested at 120°C, its viscosity rapidly increased with time, and became a gel after 4.5 h, which prevented its being cast into a mold.

The gel times tested at different temperatures can show the reaction ability of the prepolymer. For RTM, the resin system must have low reactivity at the injection temperature, whereas during curing, a high reactivity is essential. The test result of the gel time of the prepolymer is shown in Figure 3, in which a desirable gel time characteristic is displayed. When the resin system was held at lower temperatures it had a long pot-life, and at higher temperatures the resin changed quickly into a gel state. For example, the gel time



**Figure 3** Influence of temperature on gel time of the resin system.

tested at 120°C was 270 min, although it was approximately 20 s at 220°C.

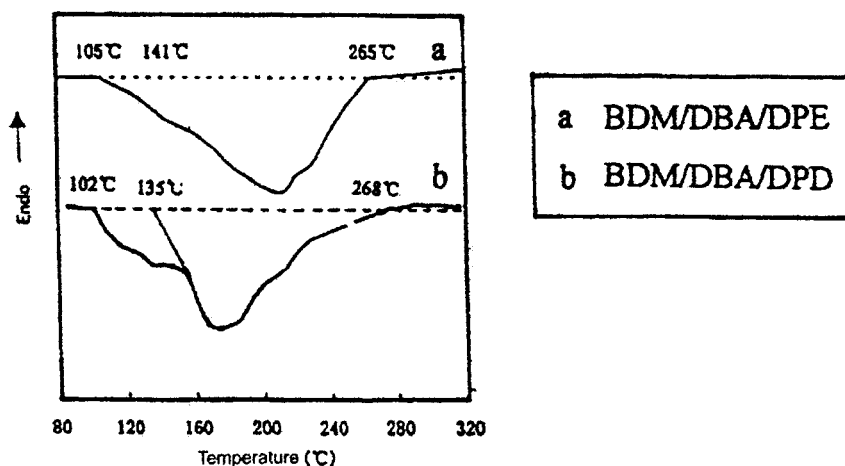
The processing properties of the resin can also be measured by DSC traces. The DSC thermograms of the prepolymer are shown in Figure 4, where for comparison, the DSC curve of BDM/DBA/DPE prepolymer mentioned earlier is also shown. It can be seen that the onset temperature, the exothermic peak temperature, and the temperature for the completion of the BDM/DBA/DPD polymerization were 102, 135, and 268°C, respectively, and that the resin system had a wide and flat exothermic peak (from 102 to 268°C). These data are close to those of the DBM/DBA/DPE prepolymer, except that the maximum exothermic peak approached the lower temperature

zone compared with that of the BDM/DBA/DPD prepolymer.

DSC results indicate that the reaction characteristics are beneficial to the processing of both neat resins and composites based on the resin system, because a small fluctuation in temperature during curing has no influence on the cure reaction and, for processing composites, there is a wide zone of exerted pressure, that is, the pressure is exerted on the composite a little early or late, either condition of which does not cause waste products. On the other hand, the system has a high temperature for cure completion, which shows that it is necessary to postcure at a given temperature (250°C) for a rather long time (6 h) for the objective to obtain low residual stress and high crosslinking network density.

### Properties of the Related Resin

The cured reaction of BDM, DBA, and DPD involves the addition of allyl groups and the maleimide ring, and amine groups and also the maleimide ring, so not only are there no volatile molecules generated in the process of curing but also the resultant network structure is compact and has few defects such as voids. Moreover, the cured resin contains rigid groups, such as the benzene ring and the imide ring; hence, it has high mechanical properties as well as heat resistance. The properties of the neat cured resin are listed in Table II. The data show that the cured resin has outstanding mechanical properties, especially tensile strength, tensile modulus, and flexural strength at room temperature, which reached 96.2 MPa, 4.8 GPa, and 121.4 MPa, respectively.



**Figure 4** DSC curves of the BDM/DBA/DPD prepolymer and the BDM/DBA/DPE prepolymer.



**Table II** Properties of the Neat Cured Resin

Room temperature	
Tensile strength (MPa)	96.2
Tensile modulus (GPa)	4.8
Elongation at break (%)	2.5
Flexural strength (MPa)	121.4
Impact strength (kJ/m <sup>2</sup> )	10.9
Critical strain energy release ( $G_{1c}$ , J/m <sup>2</sup> )	198
100°C flexural strength (MPa)	92.5
200°C flexural strength (MPa)	76.3
Glass-transition temperature by DSC	
( $T_g$ , °C)	285
Heat-distortion temperature (HDT, °C)	456
Maximum decomposition temperature	
( $I_{max}$ , °C)	515
Char yield at 800°C ( $Y_c$ , %)	43
Water absorption in boiling water for 120 h (%)	
	2.6
HDT after water absorption in boiling water for 120 h (°C)	
	236

The heat resistance is also significant because the retained strength at high temperatures decreased a little, and  $T_g$ , HDT,  $I_d$ ,  $I_{max}$ , and  $Y_c$  values are also comparatively very high, particularly  $T_g$  and HDT, which reached 285 and 268°C, respectively. The high hot/wet resistance of the cured resin is also seen in Table II. After aging 120 h in boiling water, it neared equilibrium for water absorption, which is 2.6%, a low value compared to that of other resin systems (such as unsaturated polyester) and BDM modified by some reactive comonomers. The low water intake is presumably the result of low-absorbing water groups, high crosslinking network density, and low-void content in the cured resin.

## CONCLUSIONS

To improve the compatibility with BDM, a novel reactive diluent, *N,N'*-diallyl *p*-phenyl diamine (DPD) was prepared to copolymerize with BDM and DBA, to develop a resin system for RTM process. The processing characteristics of the resin system show that the resin can satisfactorily meet the requirements of RTM, such as low apparent viscosity and long pot-life at a selected

injection temperature, 80°C, and desirable reactivity at high temperature. The cured resin displays high mechanical properties and heat/wet resistance. These results suggest that the resin system can be used not only as a desirable matrix resin for advanced composites but also for high heat resistance paint with no solvents released.

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