A Diallyl Bisphenol A Ether and Diallyl Phenyl Ether Modified Bismaleimide Resin System for Resin Transfer Molding

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ABSTRACT: A modified bismaleimide (BMI) resin system for resin transfer molding was prepared by using o,o′-diallyl bisphenol A ether and 1,4-diallyl phenyl ether as reactive diluents for BMI. The processing behavior was studied through time–temperature–viscosity curves, gel characteristics, and differential scanning calorimetry. The results indicate that the injection temperature can be 80°C, at which its apparent viscosity is only 0.30 Pa · s. Moreover, after it had been maintained at 80°C for 15 h, the apparent viscosity was still less than 1.00 Pa · s. The cured resin had remarkable heat resistance, hot/wet resistance, and mechanical properties. The heat stability and mechanical properties of the composite based on this resin system and woven glass cloth are also discussed. For short beam shear strength, in tests at 150 and 180°C, 90 and 65% of the original room temperature strength was retained. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1649–1653, 1999

Key words: bismaleimide resin; resin transfer molding; diallyl bisphenol A ether; diallyl phenyl ether; reactive diluent; processing behavior

INTRODUCTION

The properties of fiber reinforced polymeric composites are decided not only by the resin systems and fiber reinforcements, but also by the processing techniques. Traditional techniques, involving the costly and labor-intensive use of hand lay-up with prepreg, are becoming increasingly undesirable.

Resin transfer molding (RTM), developed for application to the manufacture of high-performance composites in the aerospace and automobile industry, has received much attention because of its comparatively low cost and flexibility in producing complex shapes.[1–5]

In the RTM process, preformed fiber mats are first placed in the mold cavity, and resin is then injected into the closed mold filled with dry fiber reinforcement. RTM has the advantages of producing high-quality surface finish components of complex shapes with tight tolerance and low void concentration. However, not all resins can be used for RTM. For RTM they should have the following characteristics[6]: (i) low apparent viscosity (0.2 ∼ 0.5 Pa · s) at injection temperature, (ii) sufficient pot-life at injection temperature and fast curing at processing temperature, (iii) high adhesive strength between resin matrix and reinforcement, and (iv) no volatile molecules released during curing and low shrinkage in cured resin. According to the literature,[7] resins suitable for RTM can be unsaturated polyesters, vinylesters, acrylates, and low viscosity epoxy systems, etc. However, none of these materials can satisfy the increasing need in aerospace for strength, module and thermo-oxidative stability.

Bismaleimide (BMI) resin has been developed to meet the requirements in aerospace based on the fact that it has high heat resistance, thermal-oxidative stability, and outstanding mechanical properties. It is becoming one of the most important matrix resins for advanced composites.[8–11] However, neat BMI resin cannot be used for RTM because of its high melting point, solid state at room temperature, poor solubility, and brittleness. BMI resins prepared for RTM are currently all modified through introducing various reactive diluents or comonomers.[12,13] The weakness of these resin systems is that they have either a low injection temperature with high viscosity or a low viscosity with high injection temperature.

In recent research,[14] a modified BMI resin system for RTM was developed in the presence of diallyl bisphenol A and allyl methyl phenol as reactive diluents. The results showed that the behavior of the resin system was suitable for processing RTM, but its resultant mechanical properties and heat resistance were reduced greatly in comparison with the neat BMI resin. This is because allyl methyl phenol contains only one allyl, which cannot provide sufficient reactive points for crosslinking reactions, so that the crosslinking density is rather low.

This paper discusses further investigation into modifying BMI resin for RTM. A new BMI resin system was prepared that contains o,o′-diallyl bisphenol A ether (DBAE) and 1,4-diallyl phenyl ether (DPE) as reactive diluents for the object to increase the reactive points in the resin systems. Through time–temperature–viscosity curves, gel characteristics, differential scanning calorimetry (DSC), and mechanical properties tests, the results show that the resin system possesses both low injection temperature and low apparent viscosity at injection temperature, as well as remarkable mechanical properties.

EXPERIMENTAL

Materials

4,4′-Bismaleimidodiphenol methane (BMI) was obtained from Fenguang Chemical Co., Ltd. (China). At room temperature it is crystal state with a melting temperature of approximately 172°C and molecular weight is 286. DBAE is the commercial product of Jiangyou Chemical Material Co. (China). The boiling point is 260°C, its viscosity at 25°C is 0.05 Pa · s, and its density at room tem-

perature is 1.12g/cm^3. 1,4-diallyl phenyl ether (DPE) was synthesized in our laboratory. It is a transparent yellow liquid, whose boiling point is 252°C and viscosity at 25°C is 0.02 Pa · s.

BMI Resin System Preparation (Prepolymer)

BMI, DBAE, and DPE, used in a weight ratio of 100:80:20, were added in a three-necked separable flask equipped with a mechanical stirrer and a thermometer. After continuous stirring at a constant heat of 135°C for 15 min, a clear homogenous solution, the BMI resin system, was obtained. The reaction mixture was then stirred while allowing it to cool to room temperature.

Preparation for Related Cured Resin

The resulting reaction mixture was degassed *in vacuo* at 80°C, then poured into a rectangular mold that had been preheated to 80°C. The mold consisted of a pair of glass plates held by upright and metal clips and spaced by a U-shaped silicon rubber stick. The curing cycle was 120°C/2 h + 150°C/1 h + 180°C/1 h + 200°C/1 h and the post ure procedure was 220°C/12 h. Both were performed in a controlled temperature oven.

Preparation for Composite

The resin system was injected into a mold containing a rectangular plaque of woven glass cloth reinforcement.

The curing and postcuring cycles were identical to those of the cured resin preparation mentioned above. The rectangular plague was machined into various samples, including tensile, impact, flexural,and heat distortion samples.

Measurement and Characterization

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

Time–temperature–viscosity curves were generated using 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 held at the selected injection temperature of 80°C. A rotaviscometer was utilized for measuring the pot-life of the resin system.

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
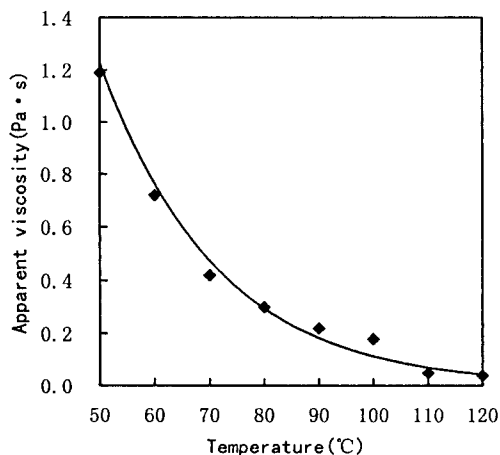
Figure 1 Viscosity–temperature correlation for the resin system.

reach the gel state at the given temperatures, were measured at 120, 140, 160, 180, 200°C, and so on. Thermal analysis of the resin system was carried out on a Perkin-Elmer 7 DSC at a heating rate of 10°C/min in a nitrogen atmosphere.

Mechanical Measurement of the Cured Resin

Tensile and flexural data were obtained according to GB 1040-79 and GB1042-79, respectively. Heat Distortion Temperature (HDT) was conducted according to GB1634-79. Fracture toughness, in terms of the impact strength and critical stain energy release rate (G_{1c}) value, was measured by GB 1451-83 and density by GB1033-86.

Measurement of Composite Properties

GB1447-87, GB1451-87, GB1451-83, and GB1449-83 were used for flexural, short beam shear (SBS) strength, and tensile testing, respectively.

RESULTS AND DISCUSSION

Processing Characteristics of the BMI Resin System

Viscosity is one of the primary variables that affects all aspects of RTM. The apparent viscosity–temperature correlation of the resin system is presented in Figure 1. It shows that the viscosity decreases with temperature. At temperatures lower than 45°C, the viscosity exceeds 1.0 Pa · s, which is too high for the RTM process since high viscosity needs very high pressure to cast resin system into a mold. On the other hand, when the

temperature is higher than 100°C, the viscosity becomes too low, less than 0.1 Pa · s. Such viscosity can lead to form turbulence during the RTM processing, which may result in the washing out of the preformed parison and therefore have influence on the size precision of the product. Moreover, the pot-life becomes shorter at high temperatures. For the present experiment, 80°C was selected as the injection temperature. The viscosity–time curves of the resin system at 80 and 120 °C are shown in Figure 2. It can be seen that the apparent viscosity at 80°C is only 0.30 Pa · s and after being maintained at the same temperature for a period of 15 h, its viscosity is still less than 1.0 Pa · s. While for the resin tested at 120°C, its viscosity rises quite fast with time, and reaches a gel state after 5 h, which makes it impossible to inject the resin into a mold. So pot-life at 80°C is sufficient for RTM.

The gel times of the resin system at different temperatures indicate the reactivity of the resin. The desirable gel time can be observed by the gel time–temperature curve shown in Figure 3. When the resin system is held at lower temperatures, it has a long pot-life. At 120°C, it maintains a gel time of about 300 min. When the resin is kept at 150 and 210°C, it will gel within 30 and 1 min, respectively, which suggests that the resin system has a long pot-life at lower temperatures and increases in reactivity with temperature.

The DSC curve of the resin system, shown in Figure 4, indicates that the system has a wide and flat exothermic peak (from 105 to 265°C). This is beneficial to the processing of both neat resins and composites based on the resin system, because a small fluctuation in temperature during curing has little influence on the cure reaction
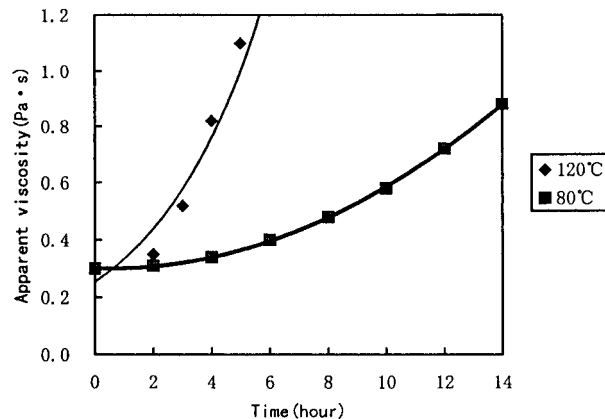

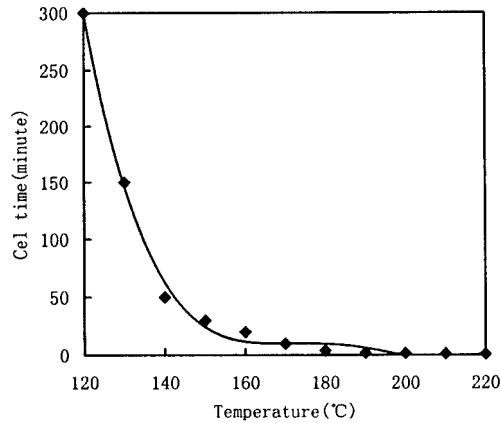**Figure 2** Viscosity–time curve of the resin system.

Figure 3 Gel time–temperature plot of the resin system.

Table I Properties of the Neat Cured Resin

Properties	Value
Tensile strength (MPa)	90.0
Tensile modulus (GPa)	0.41
Elongation at break (%)	4.5
Flexural strength (MPa)	112.0
Impact strength (KJ/m^2)	15.0
HDT (°C)	245
T_g (DSC) (°C)	272
Initial decomposition temperature (°C)	445
Density (g/cm^3)	1.25
G_{1c} value (J/m^2)	235.0

and there is a wide exerting pressure zone for processing composites. On the other hand, the system has a high onset temperature (141°C) and a higher temperature (265°C) for the completed cure, which shows it is necessary to postcure at a given temperature for rather a long time in order to obtain low residual stress and high crosslinking networks. The postcure cycle of 220°C/12 h was adopted in this study.

Properties of the Related Cured Resin

The properties of the neat cured resin are listed in Table I. The data show that the cured resin has outstanding tensile strength (90.0 MPa), tensile modulus (0.41GPa), flexural strength (112.0 MPa), and impact strength (15.0 KJ/m^2). The heat resistance is significant in comparision with other common resin systems. This is due to its
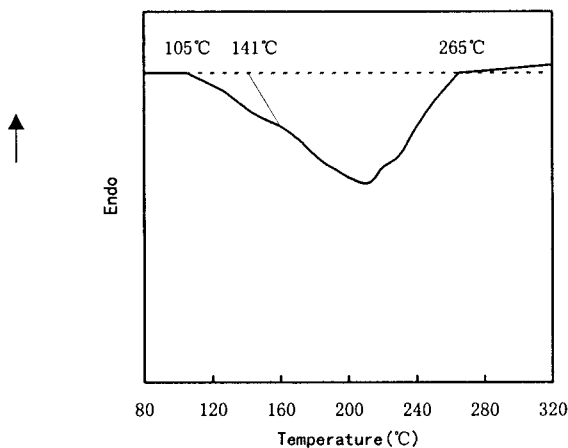
HDT (245°C), glass transition temperature (T_g) (272°C) by DSC curve, and initial decomposition temperature (IDT) (445°C). The resin system, based on BMI resin in the presence of diallyl phenyl ether and diallyl bisphenol A ether as reactive diluents, releases no low molecules during curing. In addition, there is a high aromatic backbone content to its structure and high crosslinking density in the cured resin, indicating the cured resin has little void content and possesses excellent heat resistance and mechanical properties.

The high hot/wet resistance of the cured resin is seen in Figures 5 and 6. After aging 120 h in boiling water, it nears equilibrium. It shows that water absorption is 2.5% by weight and that HDT decreases from 245 to 218°C. The low water intake is presumably the result of fewer water absorption radicals in the resin, higher crosslinking density, and low void in the cured networks.
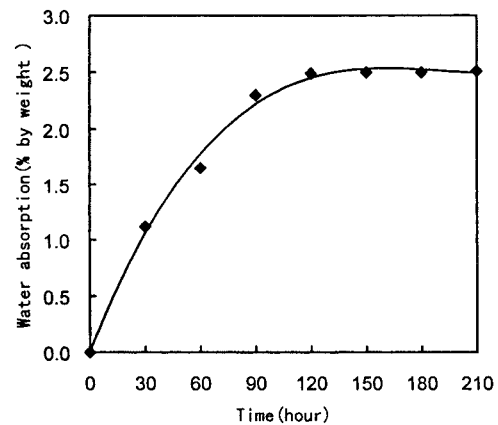

Figure 4 DSC pattern of the resin system.

Figure 5 Water absorption–HDT–time correlation for the composites.

Properties of Composite

Composite properties are shown in Table II. The composite therefore appears to have desirable properties owing to the low viscosity, lack of volatiles, good resin impregnation and high performance of the matrix resin. For SBS strength, in tests at 150 and 180°C, 90 and 65% of the original room temperature strength is retained, respectively. These properties suggest that the BMI resin modified by DBAE and DPE can be used as a matrix resin for advanced composites.

CONCLUSIONS

A diallyl bisphenol A ether and 1,4-diallyl phenol ether modified BMI resin system has been developed. It has outstanding processing and performance characteristics suitable for RTM, such as low apparent viscosity and long pot-life at injection temperature 80°C, desirable reactivity at high temperature, and good resin impregration. The cured resin displays high heat, and mechanical and hot/wet resistances. The properties of the composite based on the resin system and woven glass cloth reinforcement are remarkable. These results further confirm that the resin system can
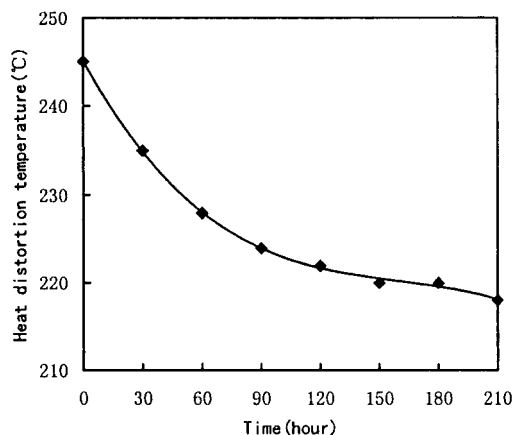
Table II Properties of Glass Cloth Composite Based on the BMI Resin System

Tensile strength (MPa)	720.0
Tensile modulus (GPa)	3.50
Elongation at break (%)	3.5
SBS strength (room temperature) (MPa)	61.5
SBS strength (150°C) (MPa)	55.4
SBS strength (180°C) (MPa)	40
Impact strength (KJ/m^2)	16.5
Flexural strength (MPa)	750

be used not only as a desirable matrix resin for high performance composites, but also for high heat-resistant paint with no solvents.

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Figure 6 HDT–water absorption time correlation for the composites.