

New Bismaleimide Resin with Improved Tack and Drapability Properties for Advanced Composites

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ABSTRACT: In order to improve the tack and drapability properties of prepregs based on bismaleimide (BMI) resins, a new allyl compound containing diglycidyl ether of bisphenol A backbone, designated as AE, was prepared by reacting *m*-allylphenol (1 mol) with an equimolar amount of diglycidyl ether of bisphenol A (0.5 mol). The copolymer of BMI/AE was prepared and characterized. The softening point of the copolymer is lower than room temperature. The prepregs based on BMI/AE have very good tack and drapability properties and a long work life (three weeks) at room temperature. Thermogravimetric analysis (TGA) in nitrogen atmosphere revealed that the cured copolymer was stable up to 515°C. The hot/wet resistance properties of the cured copolymer were investigated by aging it in boiling distilled water. After aging for 100 h, the water absorption and heat deflection temperature (HDT) were 3.6% and 248°C, respectively. In addition, the cured copolymer has good mechanical properties at ambient and elevated temperature. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 273–279, 1997

Key words: bismaleimide resin; tack and drapability properties; advanced composites; heat resistance

INTRODUCTION

Bismaleimide (BMI) is a kind of high-performance matrix resin, which has been used in the aerospace industry.^{1–5} But the cured resin, however, is extremely brittle due to its high cross-linking density. There are many methods to modify BMI resins.^{6–10} One of the most desirable methods is the copolymerization of BMIs with allyl resins. Typical allyl resins are *o,o'*-diallylbisphenol A and *o,o'*-diallylbisphenol A ether when they are copolymerized with BMI, respectively. The obtained copolymers have very good properties, but when they are used as impregnating resins, the resultant prepreg has poor tack and drapability properties. So tackifiers were often used, but this usually results in the reduction of thermal and

thermooxidative stability. In this paper, a new allyl compound based on the diglycidyl ether of bisphenol A, designated as AE, was synthesized and characterized, the properties of copolymers with BMI and composites were prepared and characterized.

EXPERIMENTAL

Reagents and Solvents

4,4'-Bismaleimidodiphenyl methane, obtained from Hubei Fengguang Chemicals, China, was recrystallized from ethyl alcohol and chloroform. 3-Chloropropylene and *m*-methyl phenol were supplied by Xi'an Reagents Chemical Plant (Xcrp), China, and used without purification.

Diglycidyl ether of bisphenol A was obtained from Yuegang Epoxies Chemicals, China, and used as supplied.

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Formulation/Processing

Five different formulations were evaluated to see the effect of differing stoichiometries of each component on the processing and performance parameters and also to establish the formulative latitude this system provides.

The systems were as follows.

System	BMI : AE (weight ratio)
I	1 : 2
II	2 : 3
III	1 : 1
IV	3 : 2
V	2 : 1

For each system, appropriate quantity of each component was placed in a three-necked round bottom glass flask equipped with a mechanical stirring device and thermometer. The contents were heated with stirring, and the temperature was maintained between 110–130°C until a clear, homogeneous melt was obtained. The melt was maintained at 130°C for additional 20 min; the resultant liquid is defined as prepolymer.

For the neat resin properties presented in this paper, the prepolymer was degassed while hot at 110°C and then poured into the glass molds and cured per the following cure cycle: 140°C/2h + 160°C/2h + 180°C/2h + 200°C/2 h + 230°C/10h. Ordinary convection ovens were used for curing and postcuring purposes.

Preparation of Composite

A 50 w/o solution of prepolymer **IV** in acetone was used to impregnate E-PW-220 plain woven glass cloth, using brushing impregnation technique. The prepreg was then dried on the rotating drum under a quartz heat lamp to a volatile content of 12–13 wt %. The tapes were removed from the drum and then cut in plies and stacked in a mold for the compression molding process. The conditions used in the fabrication process were as follows: room temperature, 125°C; contact P (2°C/min), at 125°C application of press (1.38 MPa) to STOPS; 125–180°C (2°C/min), hold 180°C/2h (press 7 MPa) + 200°C/2h, press 7 MPa + 230°C/8 h (air circulation oven).

Testing

Infrared (IR) spectra were recorded on a SPEC-ORD-79. A standard laboratory hot plate equipped with a temperature controller was used

to determine the prepolymers gel time at various temperatures. The time required for the resin to stop stringing and become elastic is called the gel time.

Thermal analysis of samples was carried out on a DuPont 990 thermal analyzer unit equipped with a Perkin–Elmer DSC IV differential scanning calorimetric unit and at a heating rate of 10°C/min.

Tensile, flexural, and impact data of neat resins were obtained according to GB 1451-83, GB 3356-82, and GB 1042-79, respectively. Heat deflection temperature (HDT) was done by ASTM D 648.

Thermogravimetric analysis (TGA) was conducted with a Perkin–Elmer DEL 7A SERIES TGA 7 in a nitrogen atmosphere at a heating rate of 10°C/min.

Out time is considered the “work life” of the prepreg. This is the time over which the prepreg maintains its tack, drape, and handleability. The out time at room temperature was measured as the time over which the prepreg still passes the tack test, which consisted of a 1 × 3 in. prepreg specimen adhering to a clean corrosion-resistant glass plate for 30 min while it is held in the vertical position.

Volatile content was determined by placing a weighed 2 × 2 in. piece of prepreg between perforated FEP in an air circulating oven at 163 ± 4°C for 20 ± 5 min.

The gel time was determined with the use of a Fisher–Johns melting point apparatus, which was preset at 160°C. The prepreg sample was sandwiched between two cover glasses and placed on the heated platform. The gel point was reached when no resin movement was observed through the cover glass when moderate pressure was applied.

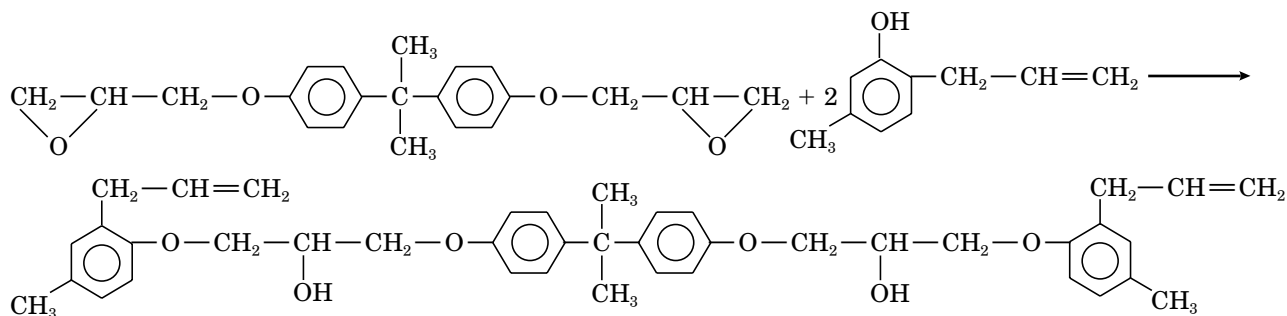
Composite tensile, flexural, and impact properties were measured by GB 1447-83, 1449-83, and 1042-79, respectively. In addition, short beam shear strength was done by GB 3357-82.

Humidity resistance was measured by putting samples into boiling distilled water and determining the water absorption, HDT of neat resin, and SBS strength of composite samples aged for various length of time.

RESULTS AND DISCUSSION

Synthesis and Characterization of AE

The following allyl compound was prepared and characterized.



Scheme 1

The structure of the above compound was selected in such a manner that the copolymer of BMI and AE have good thermal and mechanical properties. The preregs based on the prepolymer of the copolymer of BMI and AE are expected to have good tack and drape properties because of the presence of —OH in the backbone of AE.

AE was synthesized according to the reaction sequence outlined in Scheme 1. From this scheme, it can be seen that the synthesis of AE was based on the reaction of allyl (*m*-methylphenol) with diglycidyl ether of bisphenol A. The allyl (*m*-methylphenol) was prepared by reacting *m*-methylphenol with allyl chloride.

Properties of AE

AE, a red-brown viscous liquid at room temperature, has a room temperature viscosity of 6.85 Pa

s. Its IR spectrum (Fig. 1) showed a peak at around 3500 cm^{-1} due to the hydroxyl group as a result of the etherification reaction between the hydroxyl group and epoxy ring. Other characteristic bands of benzene ring were observed in the ranges of 1590 , 1515 , and 1488 cm^{-1} .

The diglycidyl ether of bisphenol A showed three characteristic absorptions at 1250 , 920 , and 830 cm^{-1} . The first band is overlapped by carbon-oxygen single band stretching of phenyl ether, and the third one appeared as a shoulder band due to the overlapping by out-of-plane vibration of hydrogen in the *p*-substituted ring. However, the second band is very important and is found to be absent in the corresponding allyl compound, indicating that the reaction of hydroxyl group and epoxy ring has taken place.

AE is soluble in ordinary low boiling point sol-

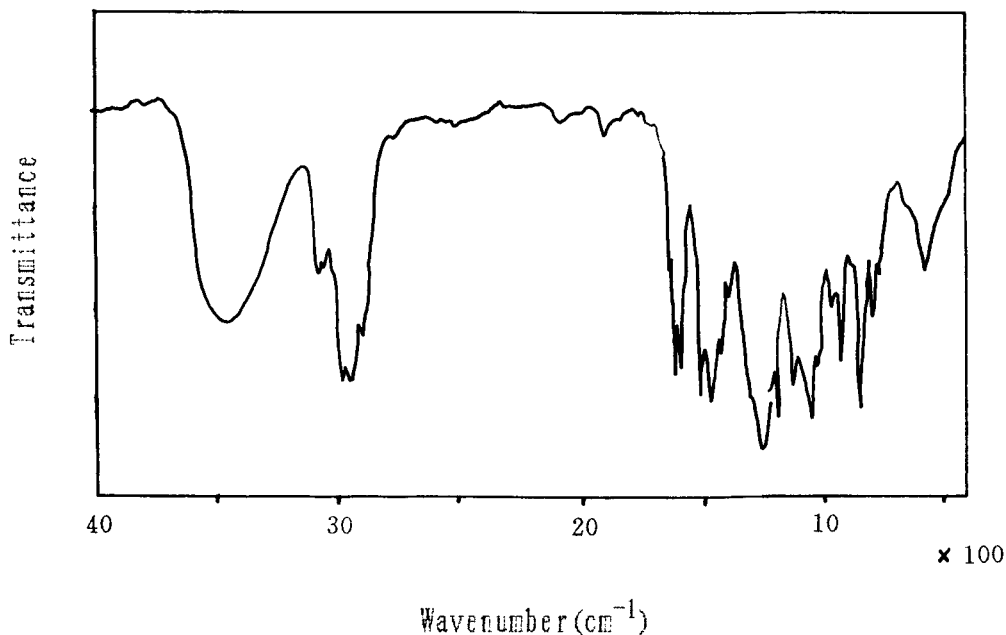


Figure 1 IR spectrum of AE.

Table I Physical Properties of Prepolymers

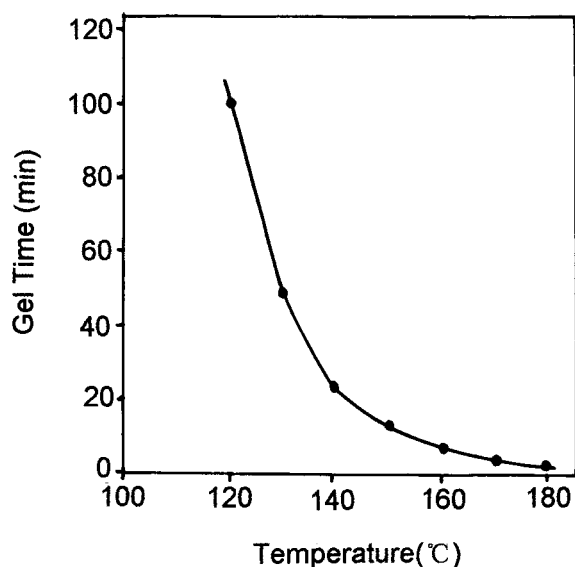
Property	System				
	I	II	III	IV	V
Softening point (°C)	<10	11	17	22	33
Solubility in acetone	good	good	good	good	poor

vents like acetone and ethyl alcohol but also miscible with epoxy resin, unsaturated polyester, etc. Although AE has unsaturated double bond ($c=c$), but it has very long pot life at room temperature. After storing at room temperature for one year, its physical properties (such as color, viscosity at room temperature, solubility in acetone, etc.) and reactivity with BMI almost do not change. In addition, when heating at 200°C for several hours, it doesn't self-polymerize. These experiments indicate that AE has very good storage stability.

On the other hand, AE can easily react with BMI when they are mixed and heated to the temperature up to about 110–130°C; then, the mixture becomes a homogenous transparent liquid.

Prepolymer Characterization

Physical properties of prepolymers I–V are shown in Table I. It can be seen that prepolymers are deep brown solids at room temperature, and their

**Figure 2** A plot of the gel characteristic of prepolymer IV.

softening points are no more than 23°C (except in system V, which are lower than the room temperature); so the low softening point is a variable that assures a good tack and drape properties of prepreps from these prepolymers.

The solubility of prepolymers in acetone are affected by the weight ratio of BMI and AE. The bigger the weight ratio, the poorer the solubility. When the weight ratio of is 2 : 1, prepolymer V isn't fully soluble in acetone. Prepolymers I, II, III, and IV can be soluble in that there is no stratification and are no materials settled out of the solution; therefore, prepregs based on the prepolymer can be prepared by the solvent technique.

Figure 2 is a plot of the gel characteristic of prepolymer IV. It shows that when held at lower temperature, it demonstrates a long pot life. At 120°C, it maintains a working life of about 100 min. When the prepolymer is raised to 160 or 180°C, it will gel in 8 or 2 min, respectively.

A typical DSC thermogram of prepolymer IV present in Figure 3. It shows a wide and flat exotherm peak from 206 to 308°C; it is beneficial for processing of both neat resin and composites. The onset temperature (T_1) for polymerization, the exothermic peak temperature (T_{exo}), and the temperature for completion of polymerization (T_2) were determined. The T_1 and T_2 were obtained by extrapolating the front side and the back side

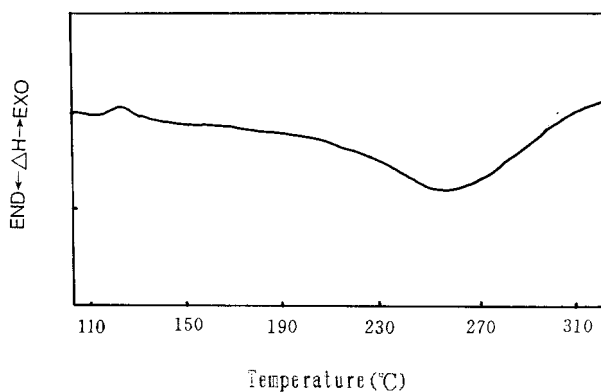
**Figure 3** Typical DSC thermogram of prepolymer IV.

Table II Properties of Neat Resins

Property	System				
	I	II	III	IV	V
Room temperature					
Tensile strength (MPa)	73	75	77	79	74
Modulus (GPa)	3.53	3.54	3.56	3.61	3.52
Elongation (%)	2.4	2.6	2.8	2.7	2.2
Flexural strength (MPa)					
Room temperature	115	107	104	103	97
200°C	—	—	83	87	80
Room temperature impact strength (kJ/m ²)	15.2	13.1	9.4	9.6	
HDT (°C)	138	156	266	280	>300

of the exothermic peak, respectively, to the baseline. Results show that the system has higher T_{exo} and T_2 , so it is necessary to postcure at some lower temperature for a longer time according to the time–temperature equivalence to obtain high crosslinking network.

Properties of Neat Resin

Table II shows the properties of neat resins. It can be seen that no significant change has occurred in the system's flexural strength. But the properties, especially the HDT and impact strength, vary dramatically according to the weight ratio of BMI and AE. The bigger the weight ratio is, the higher the HDT is, and the lower the impact strength is; so

there is an optimum weight ratio range of systems described here. Formulations **III** and **IV** have better integrated properties than other formulations (compare **III** and **IV**). Formulation **IV** utilizes the higher ratio of BMI, so it has higher values for HDT, and lower values for toughness. System **IV** also shows better strength, and at elevated temperature testing.

Neat resin was also thermally characterized by dynamic TGA. The temperature of initial weight loss (T_{d2}), the maximum polymer decomposition temperature (PDT_{max}) in N_2 atmosphere, as well as the temperature of complete pyrolysis (TCP) and the char yield (Y_c) at 800°C under anaerobic condition were determined from the TGA traces and are listed in Table III. It indicates that the copolymer

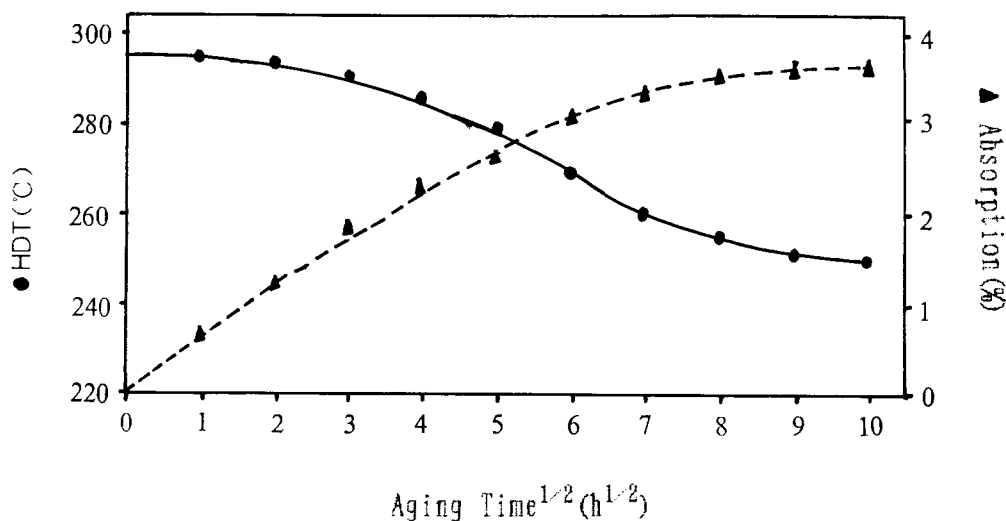
**Figure 4** Water absorption–HDT–time correlation of cured resin **IV**.

Table III TGA Data of Neat Resins

	System		
	III	IV	V
T_{di} (°C)	515	520	522
PDT_{max} (°C)	564	568	569
TCP (°C)	672	676	675
Y_c (800) (%)	33.9	34.1	34.9

has excellent thermal stability; up to a temperature of $\sim 515^\circ\text{C}$, the PDT_{max} is $\sim 564^\circ\text{C}$ and a char yield about 33% at 800°C . These data suggest that the copolymer has excellent thermal stability.

Humidity properties were determined by measuring the moisture absorption and HDT after the cured neat resin specimens were immersed in boiling distilled water for different length of time. As shown in Figure 4. It can be seen that system **IV** has good hot/wet resistance. After aging 100 h in boiling water, it absorbed 3.6 wt %, HDT was reduced from 292 to 248°C .

Properties of Prepregs and Composites

The prepreg physical properties are listed in Table IV. It can be seen that the prepreg has good tack, drape, and handleability. The prepreg has an out time in excess of three weeks, which exceeds the generally accepted out time requirements of 10–14 days minimum.

Table V presents glass fiber cloth reinforcement composite properties. The overall composite properties are excellent; and, particularly upon elevated temperature testing, good strength retention of the original room temperature values were observed. In the case of SBS strength, when tested at 200 and 230°C , and 75 and 60% of the original room temperature, strength is retained.

Table IV Physical Properties of Prepreg

Property	Value
Fiber areal weight (g/cm ²)	143 ± 3
Resin content (wt %)	31
Volatile content (wt %)	1
Flow (wt %)	9.1
Gel time at 160°C (min)	8
Out time at 23°C	>3 weeks
Tack (self-adhesion)	good/pass

Table V Properties of Composites Based on System IV

Property	Value
Resin content (%)	34.2
Room temperature	
Tensile strength (MPa)	496
Modulus (GPa)	23.9
Elongation (%)	2.1
Flexural strength (MPa)	
Room temperature	602
200°C	463
230°C	381
Impact strength (kJ/m ²)	203
SBS strength (MPa)	
Room temperature	49.5
200°C	37.1
230°C	29.7

A similar type of strength retention (76.9 and 63.3%) is noted in flexural strength. These properties suggest that BMI resin modified by AE can be used as matrix resin for advanced composites.

Short beam shear specimens made from system **IV** were boiled in distilled water for 100 h, with weight measurements taken after aging for different lengths of time. No attempt was made to dry the control specimens; they were tested after being exposed to ambient conditions for several hours. Figure 5 gives plots of SBS strength versus boiling time and water absorption versus boiling time. With the increase in boiling time, the water absorption increases and the SBS strength reduces. After aging 100 h, the water absorption is 2.0% by weight, and the SBS strength is 35 MPa, which is 70.7% of the dry strength value. It indicates that the temperature based on the system **IV** has excellent hot/wet properties.

CONCLUSIONS

A new allyl compound containing diglycidyl ether of bisphenol A in its backbone has been synthesized and used to modify and improve the tack and drape properties of prepregs based on bismaleimide resins. The new modified bismaleimide resin provides handling and processing properties comparable with epoxies. Neat resins show excellent thermal and mechanical properties and hot/wet resistance, which translate into glass-fiber-

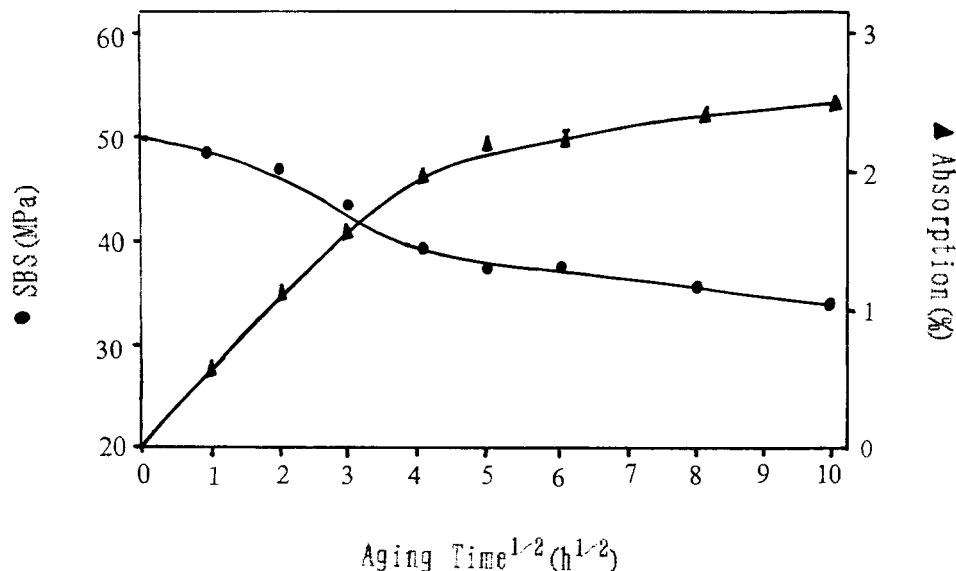


Figure 5 Water absorption–SBS–time correlation of composite based on system IV.

cloth-reinforced composites as indicated by high ambient mechanical properties as well as good strength retentions at evaluated temperatures and hot/wet conditions.

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