Study on Properties of Low Dielectric Loss Resin Matrix

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ABSTRACT: Allyl phenyl compounds, allyl epoxy resins, and epoxy acrylate resins are adapted to copolymerize with bismaleimide (BMI) resins and to modify mechanical properties and processing properties. Reaction activity, physical properties, mechanical properties, dielectric properties, and thermal stability were investigated. Impact strength and flexural strength of modified BMI resin are increased about twice and 42% than that of pure BMI resin, respectively. Fracture elongation is from 1.6 to 2.3%. The fracture surfaces of the broken specimens are examined by scanning electron microscopy (SEM). As a result, modified BMI resins put up typical toughness rupture. The modified BMI resins possess excellent dielectric properties, and dielectric constant and dielectric loss almost hold the line with increasing epoxy concentration. When the test frequency scope is from 1 to 20 GHz, the dielectric constant and dielectric loss of modified BMI resins is 3.05–3.12 and 0.0089–0.012, respectively. The modified BMI resins still possess fine properties after hydrothermal aging. After 100 h in boiling water, the reservation ratios of both the impact strength and flexural strength of modified system exceeded 90%, and the water absorption and heat distortion temperature (HDT) is 2.6% and 235°C, respectively. J Appl Polym Sci 102: 315–319, 2006

Key words: bismaleimide; mechanical properties; dielectric properties; hot-thermal properties

INTRODUCTION

With the development of military technology, the need to increase the performance of materials used for radome of high-speed warfare planes and missiles have become higher. Materials used in advanced radome must possess outstanding insulating properties and transparence electromagnetic wave properties. Moreover, they should also have excellent thermal stability, mechanical properties, and environmental resistance. Presently, high performance polymer matrix composites are adapted to build a radome. Hence, the study on resin matrix is quite important, as the resin has close relationship with high temperature resistance, hot–wet properties, condition resistance, and processing properties, as well as the physical properties of composites.

Bismaleimine (BMI) resin is a high performance matrix of composites, and has become the focus of material science due to its excellent heat-resistance and processing properties.[1] BMI resin, however, possesses good properties of crystallizability and regular structure, which renders it dissolvable only in a high boiling point solvent without proton like *N*,*N*′-dimethylformamide (DMF). In addition, the resin is extremely brittle because of the highly crosslinked structure at high curing temperature. Overcoming these disadvantages has become a considerable problem.[2–5] The present article reports on the modification by copolymerizing the modified agent with BMI and also studies the physical properties, heat-resistance, hot–wet stability, and dielectric properties of the modified BMI resin.

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EXPERIMENTAL

Materials

4,4′-Bismaleimidodiphenyl methane (BDM), industrial grade, was supplied by Northwestern Chemical Institute and recrystallized from chloroform/methanol mixture (volume ratio 1:1). *O*,*O*′-Diallylbisphenol A (BA), epoxy acrylate, and allyl epoxy resins were self-synthesized.

Preparation of modified resin monomer

O,*O*′-diallylbisphenol A (BA), epoxy acrylate, and allyl epoxy were placed into a three-necked flask equipped with a mechanical stirring device and a thermometer. The contents were heated with stirring; BDM was added to the stirring solution at 100°C; then the temperature was maintained between 130 and 150°C until the solution was transparent, while being continuously stirred, the transparent solution was prepolymerized for 30–60 min, stopped, and poured onto

the film with a release agent to obtain the modified resin.

Preparation of molding system

The modified BMI monomer was heated until transparent and symmetrical in oil at 120°C, prepolymerized for 10 min and was poured into a preheated (110°C) mold, which was degassed for 15 min under a vacuum (700 mmHg) while being maintained at 100°C. The following process was used for curing in oven: 150°C for 1 h + 180°C for 2 h + 200°C for 2h. The postcuring procedure was carried out at 220°C/10 h. Finally, the product was cooled to room temperature naturally and cut into samples.

Testing of properties

The flexural strength and modulus of cured resin were both obtained according to GB2570–1981 by material testing machine. The impact strength was obtained according to GB2571–1981 by XCJ-40 impact testing machine. The tensile strength, modulus and elongation were all obtained according to GB2586–1981 by ZD10190 material testing machine.

The fracture surface of cured resin was disposed with gold, and characterized by HITACHI *S*-570 SEM under 20 kV scanning accelerated voltage.

Heat deflection temperature (HDT) was measured according to GB1634–1988 by a self-made analyzer at the flexural strength of 18.5 kg/cm^3.

Thermogravimetric analysis (TGA) and glass transition temperature (T_g) were conducted on Perkin–Elmer instrument in a nitrogen atmosphere at a heating rate of 10°C/min and at an initial temperature of 50°C.

The dielectric properties of cured resin were tested by wave-guide short method at the frequency of 10 GHz.

The water absorption of cured resin, after being dipped in boiling water until balance, was obtained according to GB1462–1978.

TABLE I
Physical Properties of Modified BMI Resin

Properties	Value
Surface appearance	Light brown transparent solid
Dissolvability	Dissolved in acetone and methylbenzene
Softening point (°C)	45–55
Gel time (150°C) (min)	20–40
Viscosity (120°C) (Pa s)	0.98
Storing time (room temperature) (month)	6

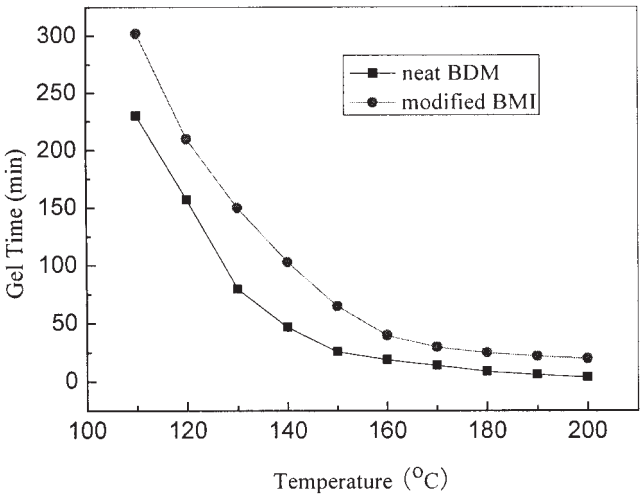


Figure 1 Relationship between temperature and gel time of modified BMI.

RESULTS AND DISCUSSION

Physical properties of modified resin

BDM is a yellow powder at room temperature with a melting point (m.p) of 120°C. *O,O′*-diallylbisphenol A (BA), epoxy acrylate, and allyl epoxy resin are all pale brown transparent, viscous liquids, and they can be easily dissolved in common solvents such as acetone and alcohol. The physical properties of modified BMI resin are shown in Table I. It could be found that modified BMI is a light brown transparent solid and with low softening point of 45–55°C. In addition, modified BMI have excellent dissolvability in common solvents and is able to dissolve in acetone and methylbenzene with any ratio. The viscosity of modified BMI resin at 120°C is 0.98 Pa s and the gel time at 150°C is 20–40 min. That means, modified BMI resin system possesses wide processing windows. After

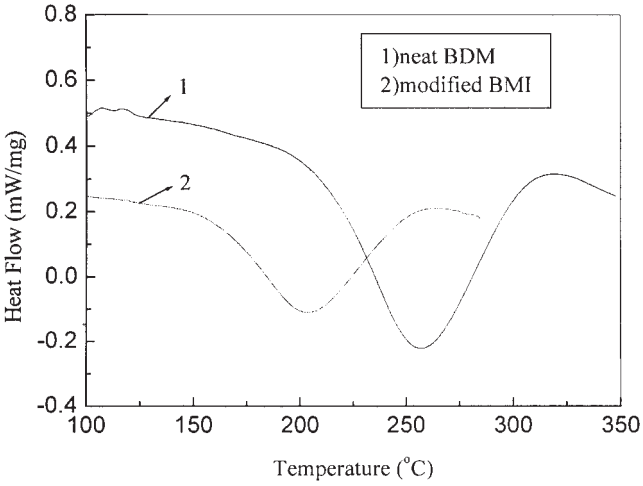


Figure 2 DSC curves of neat BDM and modified BMI.

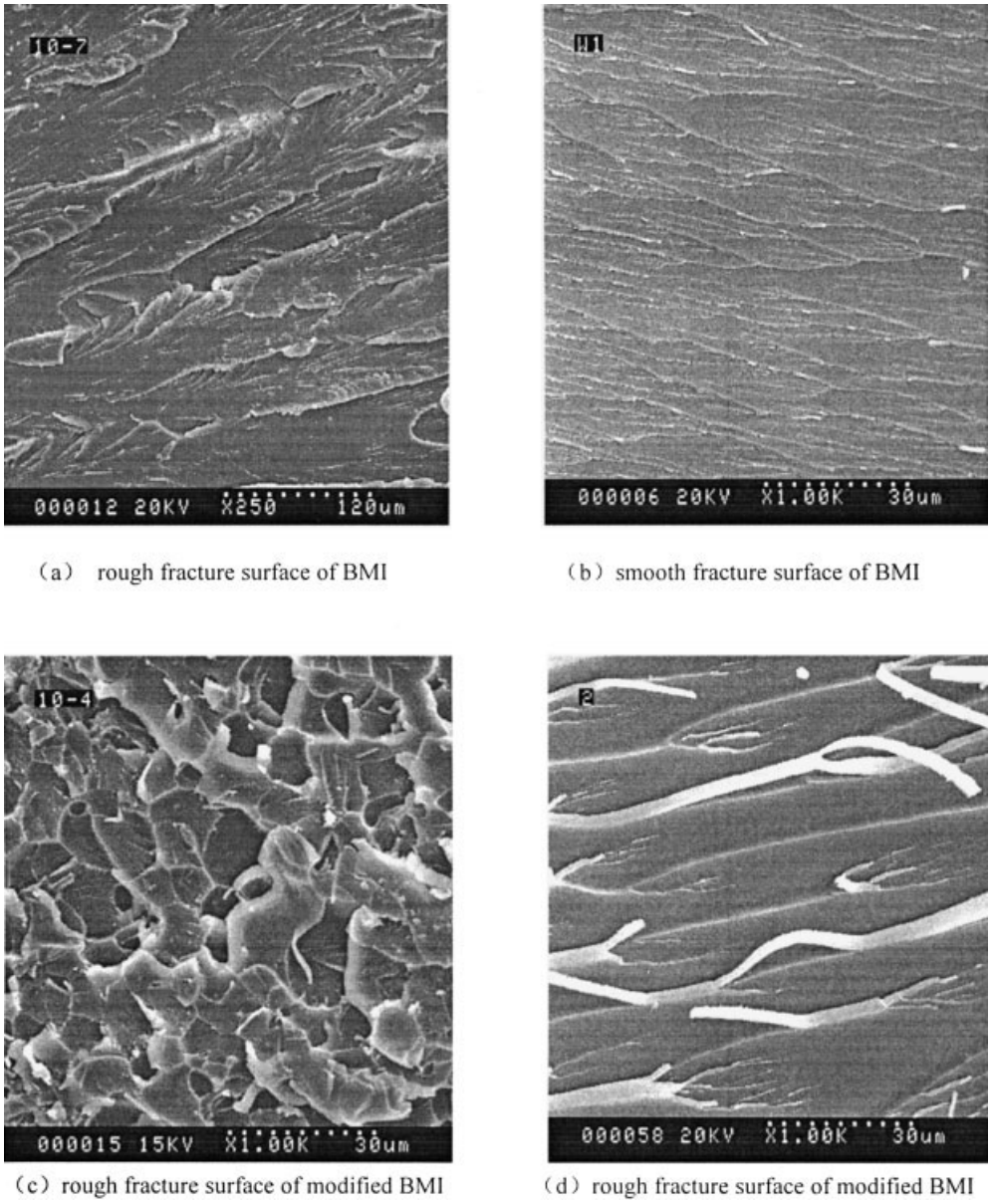
TABLE II
Physical Properties of Modified BMI Resin Curing

Properties	Modified BMI resin	Neat BMI resin
Tensile strength (MPa)	78	55
Tensile modulus (GPa)	3.6	3.8
Tensile elongation (%)	2.3	1.6
Flexural strength (MPa)	108	100
Flexural modulus (GPa)	3.7	3.9
Impact strength (kJ/m^2)	15.2	5.83

storing at room temperature for 6 months, their color and solubility had no change, indicating that modified BMI resin systems have good storage stability.

Reaction activity of modified BMI resin system

The relationship between temperature and gel time of modified BMI resin system and pure BDM resin are shown in Figure 1. The gel time of modified BMI decreases with increase in temperature. The reaction rate is accelerated obviously when the temperature is above 150°C. Furthermore, the gel time is shortened to 4 min at 200°C. Compared with that of neat BDM, the gel time of modified BMI resin system is much shorter. At 150°C, the gel time of modified BMI resin system is only 26 min, however the gel time of neat BDM resin is more than 1 h, indicating that the thermal curing reaction of modified BMI resin system is faster than the thermal curing reaction of neat BDM.



(a) rough fracture surface of BMI

(b) smooth fracture surface of BMI

(c) rough fracture surface of modified BMI

(d) rough fracture surface of modified BMI

Figure 3 Fracture surface of neat and modified BMI.

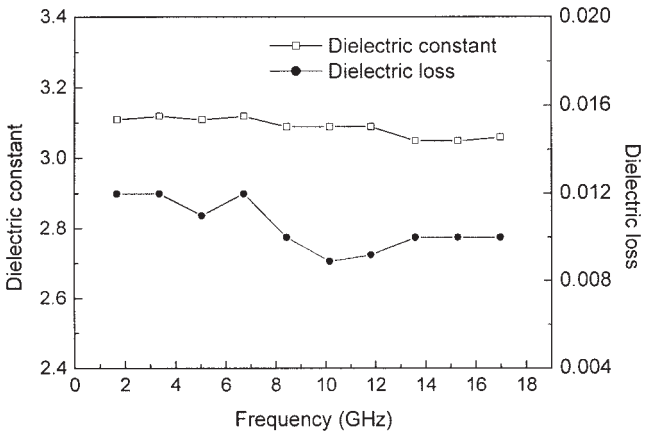


Figure 4 Dielectric properties and frequency curve of modified BMI cured resin.

The DSC analysis of the thermal polymerization behavior of modified BMI resin system and neat BDM resin at a scan rate of 10°C/min was investigated, and the results are depicted in Figure 2. Neat BDM resin has an onset of exothermic polymerization reaction temperature at ~256°C, with a processing window of 211–301°C. The DSC scans of curing process of modified BMI resin system exhibit the temperature of inception of reaction (T_i) and that of completion (T_f) is 164 and 247°C, respectively, with each exothermic peak maximum shifting from ~256 to 201°C.

Hence, the reaction activity of modified BMI resin system was much higher than reaction activity of neat BMI resin. The temperatures of cocuring reaction between allylbisphenol A (BA) resin, VE resin, and BDM resin are both lower than the curing reaction temperature of neat BDM resin. Therefore, the co-curing could increase the reaction activity of modified BMI resin system.

Mechanical properties of modified BMI resin

The BMI resin is extremely brittle because of good crystal ability, regular structure, and highly crosslinked structure at high curing temperature. Since it is used as a structure-function material in aerospace and aeronautic field, such as the radome, they must exhibit excellent physical strength. Allyl phenyl compounds and VE resins are adopted to copolymerize with BMI resins, which can reduce the crosslinked density, modify the toughness and rigidity. Consequently, modified BMI can meet the needs of aerocraft with excellent physical properties.

The mechanical properties of modified BMI were measured and are presented in Table II. It can be seen that with the modified agent, the impact strength of modified BMI resin enhanced nearly double (42%) from 55 to 78 MPa. Meanwhile, the tensile elongation increased from 1.6% to 2.3%, and the flexural strength also had a little increase. Therefore, the modified BMI keeps good integrated physical performances with highly increased toughness.

Figure 3 shows the fracture surface of neat and modified BMI. Figures 3(a) and 3(b) show the tough whorl and the river-fracture surface of BMI molding system near microcracks prolongation after impact. Neat BMI permits prolonging distortion at a certain content owing to its toughness. There exists tearing and curling edge, low ratio of length and diameter, and brittle fracture with smooth surface. Reversely, Figures 3(c) and 3(d) show tough whorl and river-fabric drawn fracture surface. At the initial prolongation of microcracks of modified BMI, there exists more complex tough whorl surface than neat BMI and round tough whorl above the surface. At the end of prolongation, there are some thermoplastic drawn figures with high ratio of length and diameter above the river surface. All the above observations indicate that the toughness of BMI improved a lot with compound modified agent, and the fracture of modified BMI are typical toughness fracture.

Dielectric properties of modified resin

The radar antenna cover is a structure-function part to protect the radar. Hence, the material of the radar cover requires good physical strength as well as excellent penetrable properties of electromagnetic wave without distortion. That is to say, the dielectric constant (ε) and dielectric loss (tan δ) should be as low as possible. The dielectric properties of composites have prime dependency on that of resin matrix and enhanced materials. To the enhanced materials appointed, the dielectric properties of wave-penetrated composites, especially the frequency of penetrability, are mostly dependent on that of the resin matrix.

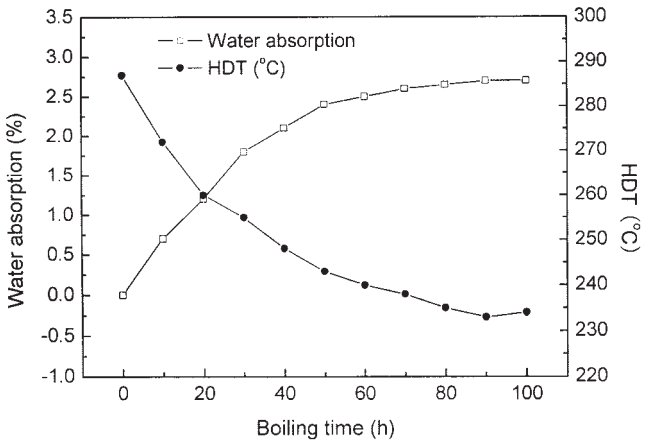


Figure 5 Hot–wet resistance of modified BMI cured resin.

TABLE III
Mechanical Properties of Modified BMI Resin Aging in Hot–Wet Condition

Properties	Dry state	Boiling for 50 h	Maintenance (%)	Boiling for 100 h	Maintenance (%)
Tensile strength (MPa)	78	72	92.4	69	88.5
Tensile modulus (GPa)	3.6	3.3	91.7	3.1	86.1
Flexural strength (MPa)	108	101	93.5	92	85.2
Flexural modulus (GPa)	3.7	3.4	91.9	3.2	86.5
Impact strength (kJ/m^2)	15.2	13.7	90.3	12.8	84.2

Therefore, modified BMI must possess good dielectric properties and toughness.

The data of dielectric constant and dielectric loss under different frequency are given in Figure 4. It can be seen that in the range of frequency between 0 and 20 Hz, both values of dielectric constant and dielectric loss changes little. Furthermore, the values of the dielectric constant are 3.05–3.12 and the values of the dielectric loss are 0.0089–0.012. Hence, modified BMI resin possesses excellent dielectric properties in a wide frequency.

Hot–wet properties of modified resin

As the structure-function part of the radar antenna cover used in aerospace and aeronautic industry, composites will erode and produce hot–wet aging in the condition of pneumatic heating and washing by raindrop. Therefore, the material must exhibit outstanding hot–wet properties. Figure 5 shows the dependency of heat deflection temperature (HDT) and water absorption on boiling time about the two of modified BMI cured resin. It can be seen that the water absorption of modified BMI has increased with the increase in boiling time. Compared with other materials like epoxy, however, modified BMI possesses low water absorption and less than 2.6% after boiling for 100 h. Meanwhile, after boiling for 100 h, the HDT of modified BMI reduces from 287 to 235°C at the dry state, which is higher than other thermoplastic resin matrix and becomes a high performance resin matrix with excellent hot–wet resistance.

Table III shows the physical properties of modified BMI cured system after aging 50 and 100 h in hot/wet condition. From these data in Table III, the maintenance of strength and modulus is more than 90% after boiling for 50 h. The flexural strength is more than 100 MPa and the impact strength is also double of neat BMI. In addition, boiling for 100 h, the maintenance of strength and modulus is 85% and the impact strength is also double of neat BMI.

CONCLUSIONS

Compound modified agent is adopted to copolymerize with bismaleimide (BMI) resins to modify the toughness. The impact strength of modified BMI is twice the value of neat BMI, the tensile strength increases 42% and the tensile elongation enhances from 1.6 to 2.3%. From the SEM figures of neat and modified resin, we can see that modified BMI with compound modified agent exhibits typical toughness fracture. Modified BMI resin possesses excellent dielectric properties in a wide frequency and excellent hot–wet resistance, and its mechanical properties can maintain high ratio of 90 and 84%, respectively, after boiling for 50 and 100 h. Especially, after boiling for 100 h, water absorption is 2.6% and HDT is as high as 235°C.

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