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BMI Based Composites With Low Dielectric Loss

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Summary

O,O'-diallylbisphenol A (BA), allyl epoxy resins and epoxy acrylate resins are adopted to copolymerize with 4,4'-bismaleimidodiphenyl methane (BDM) resins and modify mechanical properties and processing charicteristics. The new modified BMI resin systems have more than two times improved impact strength without a great decrease in excellent dielectric properties or thermal and hot–wet resistance of neat BDM resin. Composites based on modified BMI resins and reinforced by glass fibre and quartz fibre possess excellent mechanical properties. The fracture surfaces of the composites are examined by scanning electron microscopy (SEM). It is indicted that modified BMI resin matrix composites put up typical toughness rupture and the adhesion efficiency in interface of composites is fine. When the test frequency scope is from 1GHz to 20GHz, the dielectric constant and dielectric loss of composites almost hold the line. After 100h in boil water, mechanical and dielectric properties of composites are higher than 85% retention of their original values.

Introduction

In recent years, significant advances have been made in the development and manufacturing of advanced composite materials. Fibre-reinforced polymeric matrix composites, in particular, are unparalleled in terms of specific strength, weight savings and corrosion resistance. These characteristics of composite materials make them suitable for structural applications such as aircraft, automobiles, and space and marine vehicles, in which a high degree of performance is required.
As a protected part of the radar antenna of aircrafts, the radome has to exhibit excellent dielectric properties, heat-resistant properties, mechanical properties, environment-resistant properties and feasible processing characteristics. Presently, the composite matrix to prepare advanced radome is mainly polyimide (PI) and high-performance epoxy resin (EP). Because of bad hot-wet properties and high dielectric loss, EP could not meet the need of advanced radome. Although possess outstanding humidity-resistant properties and low dielectric loss, it has high viscosity, high temperature of molding and complicated processing [1]. Over the past two decade, bismaleimide resin (BMI) has become established as a new and unique class of high-

performance thermosetting resin for use as prepregs and matrices, in both the electronic and aerospace industries, because of their excellent elevated temperature and dielectric properties, low moisture absorption, and good flammability characteristics [2-7].
In this paper, allyl phenyl compounds and epoxy acrylate resins are adopted to co-cure with BMI resins to improve the toughness and dissolvability of BMI resin in order to prepare a kind of resin matrix composite which possesses low dielectric loss and integrated mechanical properties to be used for radome. Mechanical, dielectric properties and hot-wet stability of modified BMI resin matrix composites are also studied.

Experimental

Materials

4,4'-bismaleimidodiphenyl methane (BDM) was supplied by Northwestern Chemical Institute and recrystallized from the chloroform/methanol mixture (volume ratio 1:1). Acetone was obtained from the Chemical Plant of Xi'an Reagents. Both reagents above were of industrial grade. O,O'-diallylbisphenol A (BA), epoxy acrylate and allyl epoxy resins were self-synthesized. Plain glass fabric, Ew210, silane treated E-glass fabric with a thickness of 2mm, (Glass Fiber Academe of Nanjing, China), was used without any surface treatments.

Preparation of Modified Resin Monomer

O,O'-diallylbisphenol A (BA), epoxyacrylat and allyl epoxy resin 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 120°C, then the temperature was maintained between 130 and 150°C until the solution was transparent. While being continuous stirred, the transparent solution was prepolymerized for 30-60min, stopped and poured onto film with release agent to obtain the modified resin.

Preparation of Laminate Composite

Glass fabric reinforced laminate composites (12 plies, 16×9 cm^2) of modified BMI resin were prepared by acetone solution (resin: acetone=1:1) dipping of the glass fabrics followed by drying for 18hr at room temperature. The plies were cut and stacked between two metallic sheets and dried in a vacuum for 5min at 50°C to remove any entrapped solvent. A thin layer of release fabric was kept between the metal and prepreg to prevent adhesion of the resin to the metal. Prior to heating, a pressure of 0.7MPa was applied for initial compaction of the plies. After this compaction the pressure was released and the platens were heated with the prepreg under contact pressure. At the point of gel of the resin, a pressure of 0.7MPa was applied and this pressure was maintained throughout the process. The time-temperature schedule for the cure process of the composites is as follows: 130°C/1hr + 150°C/1hr +180°C/2hr + 200°C/2hr, then slowly cooled to room temperature. The cured glass-laminate composite was demolded, and post cured at 230°C for 10hr in an oven.

Properties Tests

The hot–wet resistance of glass laminate composites was determined by placing samples into boiling distilled water for various lengths of time, removing and wiping off the sample with a dry fabric, and weighing the sample to the nearest 0.001g immediately. Then, the value of water absorption was calculated according to ASTM D 570-81, and the value of properties was tested.

Tensile strength and modulus of laminate composites was obtained according to ASTM D 638 using ZD10/90 material experimental instrument. Flexural strength and inter-laminate shear strength (ILSS) of laminate composites were performed according to ASTM D 790 and ASTM D 2344, respectively, using FDL-1000B electronic pull instrument. The impact strength was obtained according to ASTM STP 410 using XCJ-40 impact testing machine. The compress strength was obtained according to ASTM D 3410. The dielectric properties were measured according to GB1409-78 using wave-guide short circuit method, and the frequency was 10GHz.

The composite specimens after impact, flexural and ILSS test were fractured in liquid nitrogen, and subsequently examined in a scanning electron microscope (SEM, JEOL JSM model 820). The fractured surfaces were coated with a thin layer of gold prior to SEM examination. The scanning accelerated voltage is 20kV.

Results and discussion

Properties of the Cured Modified Resin Matrix

Both processing characteristics and ultimate properties of a resin are very important for developing a new system. The former gives information on whether the resin can be processed via conventional industrial methods, and the latter determines whether the resin has the potential to be used widely. These investigations prove that the addition of modified agent in BDM can greatly enhance the processing properties, so it is necessary to study the ultimate properties of modified BMI resin and the effect of the addition of modified agent on the properties of neat BDM resin. The properties of BDM resin and modified BMI systems are listed in Table 1.

Table 1 Physical properties of modified BMI resin curing

Properties		Modified BMI resin	Neat BDM 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 moudulus, GPa		3.7	3.9
Impact strength, kJ/m^2		15.2	5.83
HDT	Dry	265	283
	Wet (aged 100h in boiling water)	231	234
T_g (DSC), °C		274	293
T_d, °C		424	438
Water absorption		2.3	2.0
tanδ(10 GHz)		0.012	0.013
ε(10 GHz)		3.14	3.09

The modified BMI resin systems have good mechanical properties. In particular, the impact strengths of modified BMI resin system is 2.6 times of that of neat BDM resin, which may be due to the existence of many soft linkages in the networks. This improvement may be also reflected by the increase of the tensile elongation with the addition of modified agent.

The thermal stability is defined by heat deflection temperature (HDT), glass transition temperature (Tg), and thermogravimetric analysis (TGA). Cured neat BDM resin has the best thermal stability, which may be attributed to its thermally resistant crosslinked structure. The thermal stability of the modified BMI resin systems decreases slightly because the addition of modified agent reduces the crosslinking density of BDM resin. However, the reduced range of thermal stability of modified BMI resin is very limited, and the modified BMI resins still possess excellent thermal resistance.

A resin with poor hot–wet resistance usually has high moisture absorption, causing a lowering of thermal stability and associated reliability problems. Therefore, hot–wet resistance is very important for developing a new resin. After aging for 100 h in boiling distilled water, modified BMI systems and neat BDM resin have water absorptions of 2.0 and 2.3%, respectively, their HDT values decrease from 265 to 231°C and 283 to 244°C, respectively. Both of these changes are higher than 85% retention of their original values, indicating that modified BMI resin systems have good hot–wet resistance.

From the results in Table 1, it can be seen that the dielectric properties of the modified BMI resin system is almost as good as that of neat BDM resin, which are generally considered to be good dielectric materials.

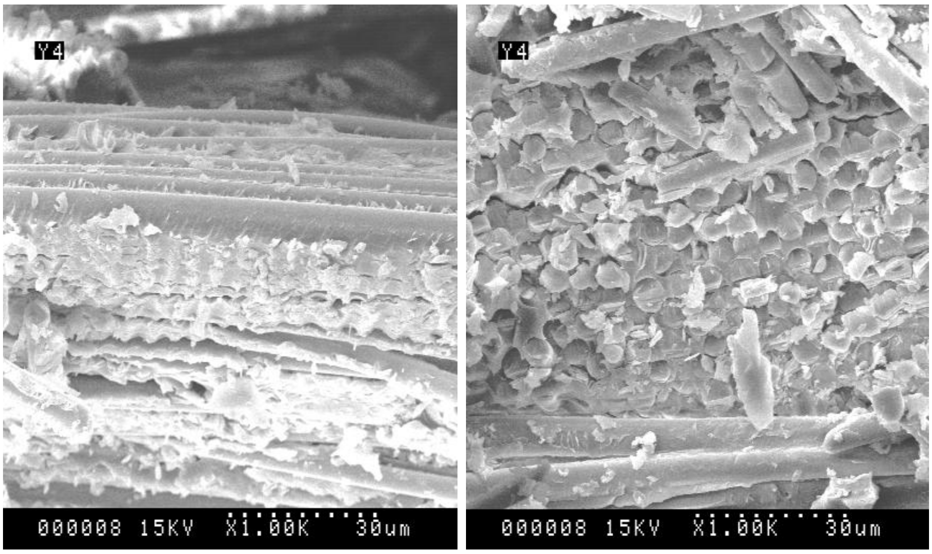
Mechanical Properties of the glass fibric reinforced BMI composites

The mechanical properties of modified BMI/glass fabric composites and modified BMI/quartz fabric composites are shown in Table 2. It presents that the modified BMI resin matrix composites possess excellent mechanical properties. When the fiber contents of two kinds of composites are similar, both of composites possess high fracture toughness, and the impact strengths of the composites are 173kJ/m2 and 157 kJ/m2, respectively. The values of interlaminate shear strength (ILSS) of two kinds of composites are more than 40MPa, indicating that modified BMI resin matrix composites have good toughness and interface adhesive strength. In addition, the flexural strengths are both between 490Mpa and 520Mpa. Considering the properties of ILSS, tensile strength and impact strength, the mechanical properties of composites reinforced by glass fabric are better than the one of composites reinforced by quartz fabric. However, considering the tensile modulus and flexural strength, the composites reinforced by quartz fabric are better than the one of composites reinforced by glass fabric.

The flexural and ILSS rupture SEM photos of modified BMI resin matrix composites reinforced by glass fabric are shown in Figure 1 (a) and (b), respectively. From the rupture surface in Figure 1, lots of resin matrix is found adhering on surface of glass fiber. Resin matrix and glass fiber adheres to each other tightly, and there is not obvious interstice and crack between resin matrix and glass fiber, and the fracture is mainly in the resin matrix and reinforced fabric, indicating that composite has excellent interface strength.

Table 2 Mechanical properties of Modified BMI Matrix Composites

Property	BMI/glass fabric	BMI/quartz fabric
Fiber content，wt%	36.4	35.8
Interlaminar shear strength, MPa	45	43
Impact strength, KJ/m^2	173	157
Tensile strength, MPa	356	350
Tensile modulus, GPa	25	28
Flexural strength, MPa	490	512
Compress strength, MPa	410	405



(a) Shearing surface (b) Flexural surface

Figure 1 SEM images of the surface of BMI/glass fabric composites

Dielectric Properties of the glass fibric reinforced BMI composites

To be good dielectric functional materials, the dielectric constant (ε) and dielectric loss (tanδ) should be as low as possible. The dielectric constant and dielectric loss of modified BMI resin matrix composites reinforced by glass fabric and quartz fabric under different frequency are shown in Figures 2 and 3. It could be found that both of two kinds of composites possessed outstanding dielectric properties. In the range of frequency between 0 and 20Hz, they also have low change of dielectric constant and dielectric loss. The dielectric constants of two kinds of composites are 3.24~3.28 and 2.92~2.98, respectively, and the dielectric loss are 0.012~0.014 and 0.0083~0.0096, respectively. Therefore, both of modified BMI matrix composites possess excellent dielectric properties in a wide frequency range.

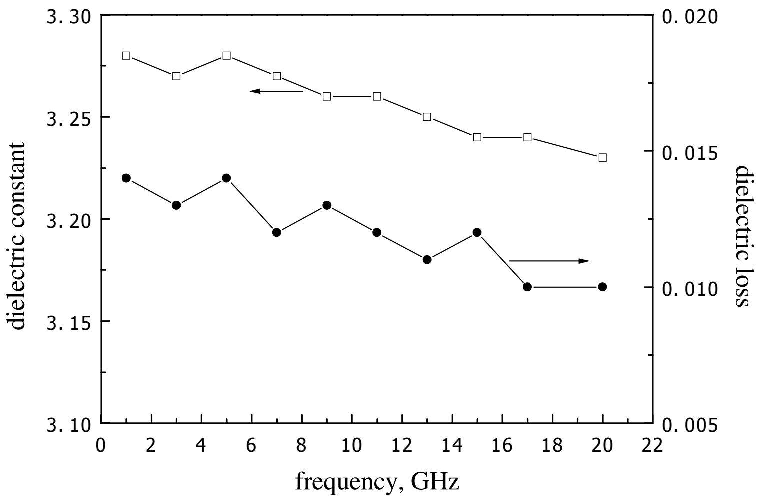


Figure 2 Dielectric properties of BMI/glass fabric

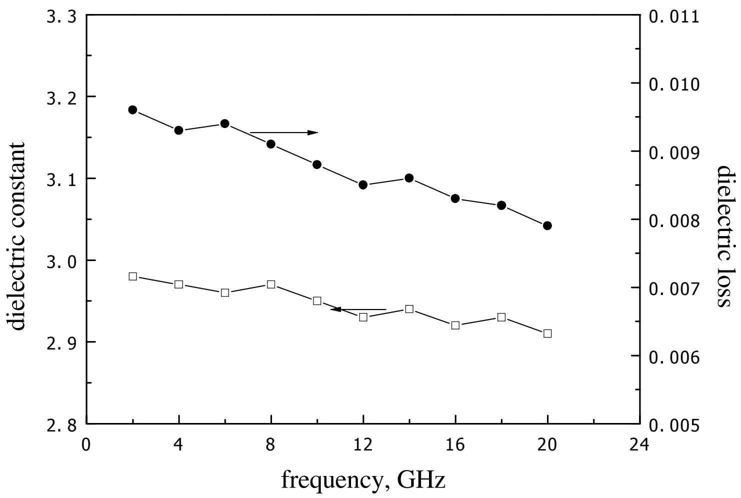


Figure 3 Dielectric properties of BMI/quartz fabric

Hot-wet Properties of the glass fibric reinforced BMI composites

Being adapted to some structure and functional component in aerospace field such as radome, the composites will be corroded by high temperature pneumatic pyrogenation and impact of raindrop because of conversion of environment temperature and humidity. The corrosion could cause aging of composites. Therefore, the good hot-wet resistance is very necessary to the composites.

The relationship of water absorption of modified BMI matrix composites reinforced by glass fabric and quartz fabric versus hot-wet aging time is shown in Figure 4. It could be found that the water absorption of both of composites increase with

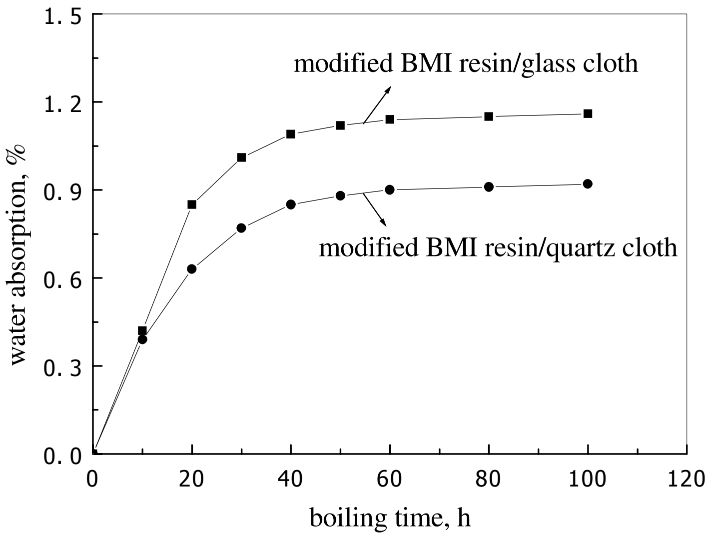


Figure 4 Water absorptions of BMI/glass fabric and BMI/quartz fabric

prolonging of aging time. After aging for 100h in boiling distilled water, the water absorptions of two kinds of composites are less than 1.1%. Especially the modified BMI matrix composites reinforced by quartz fabric have lower water absorption and the maximum is even less getting to 0.84%.

The relationship of mechanical properties of modified BMI resin matrix composites reinforced by glass fabric and quartz fabric versus hot-wet aging time is shown in Figure 5 and 6. After aging in boiling water for 100h, the retentions of the flexural strength and interlaminate shear strength of both of composites are more than 89%

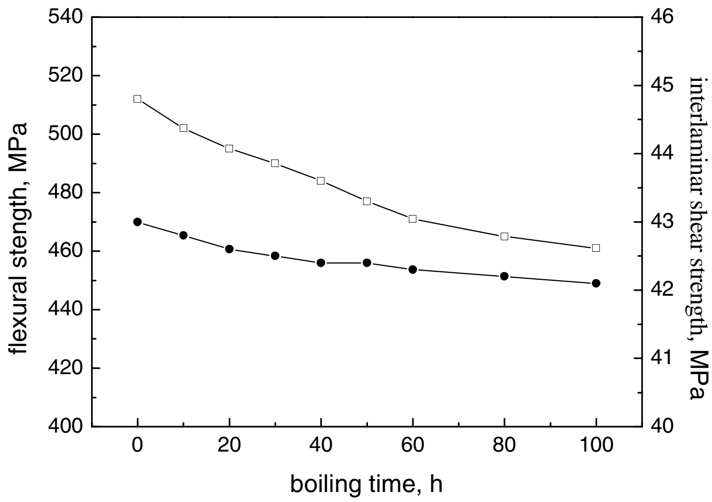


Figure 5 Mechanical properties of BMI/quartz fabric after boiling

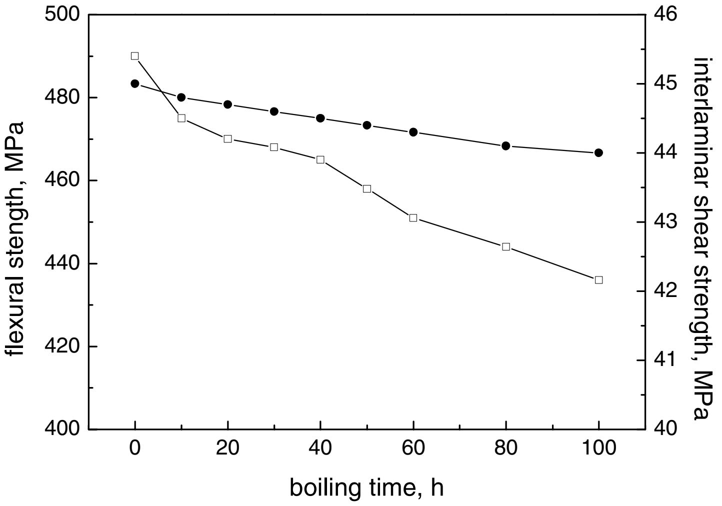


Figure 6 Mechanical properties of BMI/glass fabric after boiling

and 98%, respectively. Those could indicate that both of modified BMI resin matrix composites has excellent hot-wet resistance and to achieve requests for aerospace application.

Conclusions

Modified BMI resin matrix composites reinforced by glass fabric and quartz fabric are prepared and the properties of resin matrix and mechanical, dielectric and hot-wet properties of composites was investigated. Both of the modified BMI matrix composites reinforced by glass fabric and quartz fabric possess excellent mechanical properties. The impact strengths, flexural strengths and ILSS of two kinds of composites are more than 150kJ/m^2, 490MPa and 43Mpa, respectively. SEM photos of fracture surface indicate that the interface of composites bonds compactly. Moreover, both of composites have outstanding dielectric properties within wide frequency between 2-20GHz. After 100h in boil water, water absorption of both of composites are less than 1.1%, and the retention of flexural strengths and shear strengths is more than 85% and 90%, respectively.

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