A High-Performance Bismaleimide Resin with Good Processing Characteristics

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SYNOPSIS

A new bismaleimide (BMI) resin system, designated 4504, with excellent heat resistance and good mechanical properties for advanced composites was developed. The 4504 resin was made up of 4,4'-bismaleimidodiphenyl methane, diallyl bisphenol A, and desirable catalysts. The reactivity of 4504 was investigated by gel characteristics and differential scanning calorimetry (DSC). Data showed that 4504 had a long work life under 100°C, but would gel within 7 min or 40 s at 140 or 160°C, respectively. The glass transition temperature (T_g) and heat-deflection temperature (HDT) of the cured 4504 resin were 315 and 290°C, respectively, which were much higher than the postcure temperature (200°C). In addition, the cured resin is also tough. Thermogravimetric analysis (TGA) in a nitrogen atmosphere revealed that the neat resin was stable up to 450°C; its char yield at 700°C under anaerobic conditions was 29.4%. Carbon fiber T300 laminates based on 4504 were prepared and characterized. In the case of short-beam (SBS) strength, when tested at 230°C, 51% of the original room temperature strength was retained. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The modern aerospace and aeronautic industry urgently needs matrix resin with excellent thermal and mechanical properties and good processing characteristics for advanced composites. Bismaleimide (BMI) is one of the most important resins today owing to its outstanding thermal properties. The disadvantages of it are poor solubility in ordinary solvent (i.e., acetone), high processing temperature, and brittleness of the cured resin. From the 1970s on, modification of BMI has been an active field, and much research has been successful,[1-5] but such modifications need to be postcured at high temperatures (such as 220–250°C) to obtain satisfactory properties. So, it remains a goal of the art to provide a new BMI resin system of high performance while exhibiting low processing temperature.

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EXPERIMENTAL

Materials

4,4'-Bismaleimidodiphenyl methane, mp 156–158°C, was obtained from Hu Bei Feng Guang Chemicals, China. Diallyl bisphenol A was supplied by the Sichuan Jiangyou Insulation Plant, China. Imidazole and diisopropylbenzyl peroxide were obtained from the Xi'an Reagent Co., China. Carbon fiber T300 was kindly supplied by Torayca Co., Japan. All other chemicals used were of laboratory grade.

Preparation of Prepolymer and Neat Resin

To 80 g diallyl bisphenol A was added 100 g of 4,4'-bismaleidodiphenyl methane. The reaction mixture was stirred at 140–160°C for 30–50 min to form a homogeneous solution. After the solution had cooled to 60–70°C, 0.25 g of imidazol and 0.65 g of diisopropylbenzyl peroxide were incorporated. The resultant homogeneous liquid was prepolymer 4504.

The prepolymer 4504 was degassed under vacuum (0.09 MPa) while being maintained at 100–110°C and poured into preheated (110–120°C) glass sheet molds (18 × 18 cm^2) and cured. For the neat resin properties presented here, the following cure cycle was used: 130°C/2 h + 150°C/2 h + 180°C/2 h, then postcured at 200°C for 10 h.

Preparation of Composites

For the composite properties presented here, the directional prepreg was prepared by using a drum winding technique. Carbon fiber T300 was used as a reinforcement. The impregnating bath used contained a 50% by weight solution of the prepolymer 4504. The prepreg was dried on the mandrel to strip off the acetone solvent. After removal from the drum, the resultant prepreg had good tack and drape and needed no further staging prior to molding. The prepreg ply stack, laid directionally, was placed in a mold with Teflon-coated peel plies at the top and bottom. The mold was placed in a hydraulic press under contact pressure and the temperature was increased from room temperature (RT) to 120°C at a 2°C/min heat-up rate. The prepreg was held at 120°C for 20–30 min under contact pressure. At the end of this period, 0.7 MPa pressure was applied and held for 2 h at 130, 150, and 180°C, successively, at these conditions. After that, the mold was cooled slowly to RT under pressure. The laminate was demolded and postcured in an air-circulating oven at 200°C for 10 h.

Measurements

The gel time of the prepolymer was determined using a hot-plate technique. The prepolymer was spread

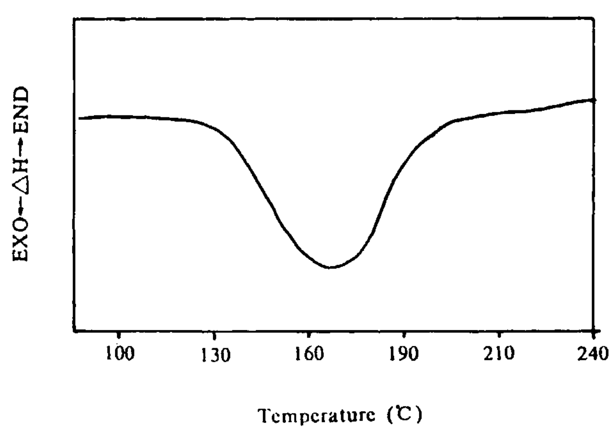

Figure 1 DSC plot of prepolymer 4504.

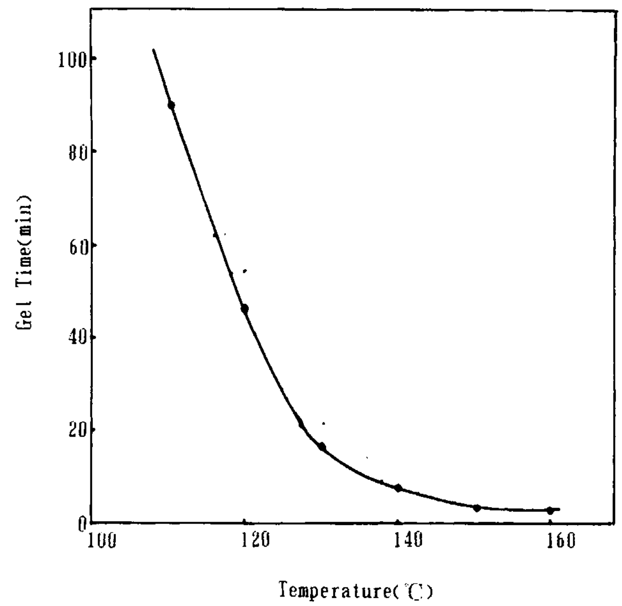

Figure 2 Gel time–temperature curve of prepolymer 4504.

over hot plates heated to 120, 150, 180, and 200°C, respectively. The time required for the resin to stop stringing and become elastic was called the gel time.

Thermal analysis of the prepolymer 4504 and glass transition temperature (T_g) were carried out on a DuPont 990 thermal analyzer unit equipped with a Perkin-Elmer DSC-7 differential scanning calorimetric unit. DSC scans were run at a 10°C/min heat-up rate.

Neat resin flexural and tensile data were obtained according to GB1042-79 and GB1040-79, respectively. The heat-deflection temperature (HDT) and density were done according to GB1634-79 and GB1033-86, respectively. Toughness, manifested by the impact strength was measured according to GB1451-83.

Thermogravimetric analysis (TGA) of the cured resin system was conducted with a Perkin-Elmer DEL 7A SERIS TGA 7 in a nitrogen atmosphere at a heating rate of 10°C/min. GB1447-87, GB1451-83, and GB1449-83 procedures were used for composite flexural, short-beam shear (SBS) strength, and tensile properties, respectively.

RESULTS AND DISCUSSION

Resin Formulation

There are many ways to modify BMI: One of the most desirable methods is the copolymerization of

Table I Cured 4504 Resin Properties

Property	System	
	4504	MBMI/B-A (100/80 w/w)
RT tensile		
Strength (MPa)	72	73
Modulus (GPa)	3.82	3.67
Elongation (%)	1.93	2.2
RT flexural strength (MPa)	110	112
Impact strength (kJ/m^2)	9	13
GIc (J/m^2)	182	210
HDT (°C)	290	268
T_g (by DSC) (°C)	317	274
Initial decomposition temperature (°C)	456	426
Maximum decomposition temperature (°C)	510	447
Char yield (at 700°C) (%)	29.4	21.1
Density (g/cm^3)	1.23	1.23

allyl phenyl compounds with BMI. Here, 4,4′-bismaleimidodiphenyl methane (MBMI) and diallyl bisphenol A (B-A) were employed as the base materials. The main advantages of the MBMI/B-A system are good solubility in an ordinary solvent such as acetone, outstanding toughness, as well as good thermal properties.[6] However, its curing temperature (including postcuring temperature) is more than 220°C and so cannot meet the needs of modern industry. So, selecting desirable latent catalysts became the key problem of this study.

As we know, the copolymerization of MBMI and B-A can be divided into two steps: The first is the addition of the maleimide to the allyl group through a so-called ene addition reaction, and the second is a combination of the Diels–Alder process and an anionic imide oligomerization which needs higher temperature such as 220°C or higher. Imidazole can effectively catalyze the imide oligomerization, but cannot catalyze the copolymerization of MBMI and B-A. On the other hand, diisopropylbenzyl peroxide can obviously speed up the reaction between MBMI and B-A,[7] so a combination of the above two catalysts is expected to reduce effectively the curing and postcuring temperature of the MBMI/B-A system.

Table II Physical Properties of 4504/T300 Prepreg

Property	Value
Fiber areal weight (g/cm^2)	140 ± 5
Resin content (% wt)	40 ± 3
Volatile content (% wt)	⩽ 2
Gel time at 120°C (min)	50–52
Out-time at 23°C	⩾ 2 weeks
Tack (self-adhesion)	Pass/good

Physical Properties of 4504 Resin

Figure 1 is a typical DSC thermogram of 4504 in a nitrogen atmosphere. It is a single exothermal curve with low polymerization energy ($\Delta H = -166.8$ J/g). This indicates that reactions among reaction groups are at the same rate, and as the process is moderate, it is good for controlling the curing reaction and preparing the composite. On the other hand, the peak exotherm temperatures are from 130 to 203.3°C; the exothermic peak temperature is

Table III Composite Mechanical Properties

Property	Value
0° tensile (RT)	
Strength (MPa)	1538
Modulus (GPa)	138
0° flexural (RT)	
Strength (MPa)	1778
0° SBS strength (MPa)	
RT	103
230°C	53 (51%)
0° impact strength (RT) (kJ/m^2)	87

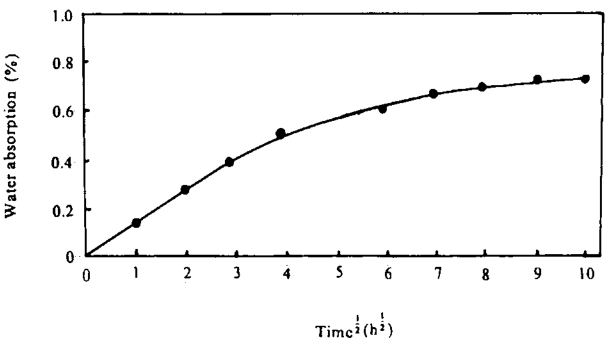

Figure 3 Water absorption dependence on aging time in boiling water for the composite.

171.9°C, so a highly crosslinking cured resin will be obtained after being postcured at a temperature which is no more than 200°C.

Figure 2 is a plot of gel time vs. temperature of the prepolymer 4504 described here. When held at a temperature lower than 110°C, it demonstrates a long pot life, but when held at a temperature higher than 120°C, the gel time will sharply decrease. At 140°C, the gel time is 7 min, which is only 14% of the gel time at 120°C. This means that the polymerizing rate at temperatures from 120 to 140°C is sensitive to the temperature.

From all the data above, the following curing procedures are selected: 130°C/2 h + 150°C/2 h + 180°C/2 h, and the postcuring is at 200°C for 10 h.

Properties of Neat Resin

Excellent thermal and mechanical properties are key features for an advanced composite. Table I lists the properties of the cured resin. It can be seen that its excellent property is heat resistance which is manifested in the high HDT and T_g (i.e., 290 and 317°C, respectively) and both of them are much higher than the postcure temperature (200°C). This is primarily due to the many aromatic and hybrid rings in the neat resin structure as well as the special polymerization mechanism by catalysts.

Prepreg Physical Property

The 4504/T300 prepreg has good tack, drape, and handleability. "Out-time," as measured in Table II, is considered the "work life" of the prepreg. This is the time over which the prepreg maintains its tack, drape, and handleability; the 4504/T300 prepreg has an out-time in excess of 2 weeks, which exceeds the generally accepted out-time requirements of 10–14 days minimum. A gel time of 50–55 min at 120°C is long enough to allow for good fiber wet-out and compaction of the prepreg.

Composite Properties

Composite properties of 4504/T300 are presented in Table III. Since properties fall off dramatically at high temperature, it is a good screening test to assess high-temperature properties. In the case of SBS strength, when tested at 230°C, 51% of the original RT strength is retained. A similar type strength retention is noted in the 0° flexural properties.

Besides outstanding thermal and mechanical properties of the composite, hot/wet resistance is another important property, especially of composites used in aerospace and aeronautic industries. Hot/wet resistance was determined by placing SBS specimens in distilled water for 100 h, with weight measurements taken and tested. Figures 3 and 4 show aging time versus water absorption and strength, respectively. After aging 100 h, equilibrium is almost obtained, with water absorption of only 0.8% by weight and SBS strength of 83 MPa, with an 80% retention of RT properties. All data indicate that the 4504/T300 composite has excellent hot/wet resistance.

CONCLUSIONS

Modified BMI resin, 4504, has desirable processing features, improved toughness, high strength, and excellent thermal properties. It may be suitable as a matrix resin for advanced composites.

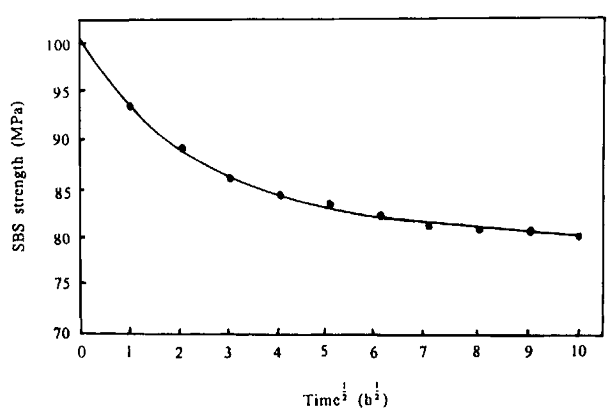

Figure 4 SBS strength dependence on aging time in boiling water for the composite.

4504/T300 prepreg has good tack, drape, and handleability. Its work life is at least 2 weeks at room temperature. 4504/T300 laminates (their curing and postcuring temperatures are no more than 180 and 200°C, respectively) have good thermal and mechanical properties. In the case of SBS strength, when tested at 230°C, 51% of the RT strength retention is retained. In addition, they also have excellent hot/wet properties.

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