High-Performance Bismaleimide Resin Film for Resin Film Infusion

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ABSTRACT: A novel high-performance resin film, coded 4508B, suitable for the resin film infusion (RFI) process, was developed. It was prepared from 4,4′-bismaleimidodiphenylmethane (BDM), *o,o′*-diallylbisphenol A (BA), polyethersulfone (PES), and polyimide (PI). The resin and its composite, reinforced by glass fiber cloth, were prepared and characterized in detail. The results showed that the resin film was stable at room temperature, its infusion temperature was 120°C, and the pot life was more than 60 min. In addition, the cured resin and the composite prepared by the RFI process had good thermal and mechanical properties and hot-wet resistance. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2918–2922, 2001

Key words: resin film infusion; bismaleimide; thermoplastics; composites

INTRODUCTION

Resin infusion techniques are new techniques for manufacturing advanced composites.[1–4] They allow us to produce higher-performance and higher-quality composites with a high fiber-to-resin ratio, super low void contents,[2,5,6] and good mechanical properties as well as good process repeatability. In addition, because the laminate physicals are higher, almost doubled in some cases, and more consistent, more efficient, and profitable, parts can be designed.[7] A representative group of infusion systems include the Seeman composite resin infusion-molding process (SCRIMP), Paddle Lite, ultrawave vacuum-assisted resin transfer molding (UV–VARTM), the resin injection recirculation method (RIRM), and Prestovac.[5] All of them do not need prepared prepregs and can dramatically reduce the emissions of volatile organic compounds (VOCs) and supply a cleaner and safer workplace with low worker VOC exposures.[3,6] The resin film infusion (RFI) technique,[1,7] as a new technique, does not need a large complex resin computation facility since resins are put into common molds in the solid state. In addition, the resin films can be stored and transported with little care, and the manufacture of composites via the RFI process needs relatively low skilled labor.

4501C resin film, a 4,4′-bismaleimidodiphenylmethane (BDM)/*o,o′*-diallylbisphenol A system developed by our research group, has good mechanical properties, high-temperature performance, and hot/wet resistance. However, the 4501C film has a relatively low tack temperature, which limits its application. The authors modified the 4501C resin film by adding different thermoplastics (TPs) and developed a new BMI resin film, coded 4508B, with good process characteristics for the RFI technique.

EXPERIMENTAL

Materials

4,4′-Bismaleimidodiphenylmethane (BDM) was obtained from Hubei FengGuang Chemicals

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(Honghu, China) and recrystallized from the chloroform/methanol mixture (volume ratio 1:1). *o,o′*-Diallylbisphenyl A (BA) was supplied by the Sichuan Jiangyou Insulation Plant (Jiangyou, China); polyethersufone (PES) was obtained from the Xuzhou Engineering Plastics Factory (Xuzhou, China); and polyimide (PI) was purchased from the Shanghai Synthesized Resins Institute (Shanghai, China). E-PW-210, a kind of isotropic plain-woven glass cloth surface-treated with a 1–2 wt % water solution of a compound, made up of silane and a methyl acrylic chromic oxide complex compound, was supplied by the Nanjing Fibers Institute (Nanjing, China).

Preparation of Prepolymer

Appropriate quantities of PES, PI, and BA were placed into a three-necked flask equipped with a mechanical stirring device and a thermometer. The contents were heated with stirring, and the temperature was maintained between 130 and 140°C until PES and PI were completely dissolved; then, BDM was added to the stirring solution at 120°C. After continuous stirring, and maintaining at 120°C for 3–5 min, a viscous, homogeneous, and transparent solution was obtained, which was denoted as the 4508B prepolymer.

Properties of Resin Film

The 4508B prepolymer solution (120°C) was coated on a polyester film using the flow-casting method. After cooling to room temperature, a transparent resin film was obtained. Another polyester film was covered on the surface of the resin film for protection.

Preparation of Cured Resin

The above-prepared prepolymer was degassed under a vacuum, while being maintained at 110°C, and poured into a preheated (110°C) glass mold and cured. The following cycle was used for curing: 120°C/2 h + 150°C/3 h + 180°C/2 h + 200°C/2 h. The postcure procedure was 220°C/10 h.

Preparation of Composites

Composites based on the 4508B film and glass cloth were prepared by using a vacuum-bag infusion technique. The reinforcement consisted of 13 layers of the plain-weave glass fabric. The weight ratio of the resin to the reinforcement was 2 to 3.

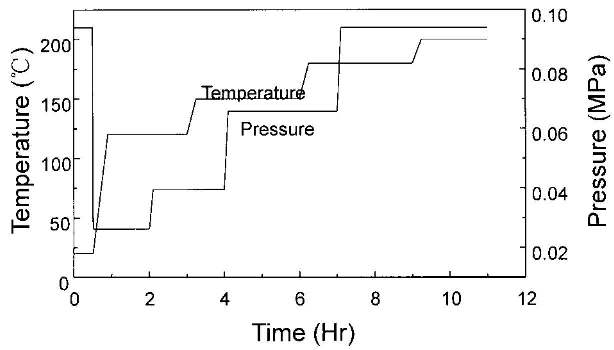

Figure 1 Temperature/pressure cycle for manufacturing composites via RFI.

The infusion and curing procedure was as follows: The sample was kept at 0.09 MPa at room temperature for 30 min; then, the pressure was reduced to 0.026 MPa and the temperature was increased to 120°C at a heating rate of 4°C/min. After maintaining that temperature for 2 h, the laminate was cured via a curing cycle of 150°C/3 h + 180°C/2 h + 200°C/2 h at a heating rate of 2°C/min and a ladder procedure on the pressure was used. Postcuring of the laminate was performed in an air-circulation oven at 220°C for 10 h. Figure 1 shows the temperature/pressure cycle for preparing the composites.

Tests

The gel time at various temperatures was determined using a standard laboratory hot plate with a temperature controller. The time required for the sample to stop stirring and become elastic was considered the gel time. The viscosity of the resin film was measured using an NBJ-79 viscometer with a temperature controller.

Tensile, flexural, and impact data of the cured resins were obtained according to GB1451-83, GB3356-82, and GB1042-79, respectively. The heat-deflection temperature (HDT) was determined by ASTM D-648. Composite tensile, flexural, and impact properties were measured by GB1447-83, GB1449-83, and GB1042-79, respectively. In addition, the short-beam shear strength (SBS) was obtained by GB3357-82.

The hot/wet resistance of the cured resins was determined by putting samples into distilled water at 38°C for 100 h, then testing the water absorption and the HDT of the samples. The hot/wet resistance of the composites was determined by putting the samples into distilled water at 50°C for 2 weeks, then testing the water absorption and the SBS of the samples.

Table I Effects of Thermoplastics on Film Properties

Properties	4501C	4501C/PI
Film formation (23–25°C)	Desirable	Desirable
Sticking point (°C)	36	45
Viscosity at 120°C (Pa s)	0.34	0.54

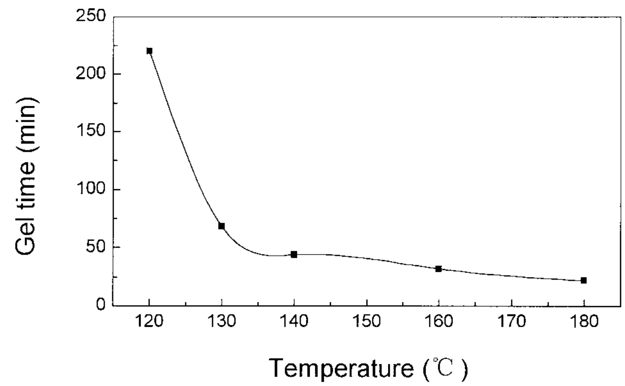

Figure 3 Curve of gel time versus temperature of 4508B film.

RESULTS AND DISCUSSION

Resin Formulation

The 4501C (BDM/BA) resin film, developed by our research group, has good mechanical properties, high-temperature performance, and hot/wet resistance. However, it has a relatively low tack temperature (about 35°C), which limits its application. To overcome this problem, TPs were considered to be employed. However, TPs often have a relatively high viscosity, which is unsatisfactory for a resin used for RFI, so low molecular weight TPs are desirable. Because of this, to avoid a decrease of the thermal properties due to the addition of TPs, TPs having outstanding thermal properties should be chosen. Consequently, PES and PI with low molecular weights were selected as the modifiers for developing a new BMI resin used for RFI. Table I lists the film-formation feature, tack temperature, and melting viscosity of the 4501C and 4501C/PI systems. It can be seen that the tack temperature of the system increased from 36 to 45°C by adding PI in 4501C, while its melting viscosity also increased to 0.54 Pa s. Figure 2 describes the relationship of the mol ratio of PES/PI in the BMI/BA system with the tack temperature and melting viscosity of the resin films. The tack temperature was linear with the mol ratio of PES/PI: When the mol ratio of PES/PI increased, the tack temperature increased linearly. The viscosity of the system decreased with increase of the mol ratio of PES/PI.

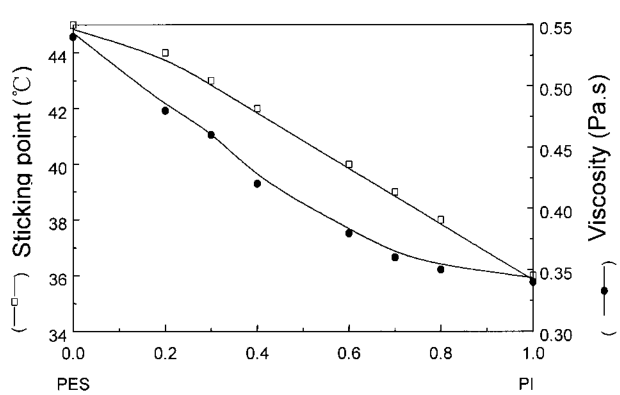

Figure 2 Dependence of tack temperature and viscosity of resin on the mol ratio of PES/PI in BDM/BA system.

Properties of Resin Film

The 4508B film was a yellow transparent solid at room temperature; it was flexible and could be bent freely without breaking. It had proper tack and drape characteristics. After storage at room temperature for 1 month, its physical properties, such as color, tack, and drape features and flexibility, did not change.

Figure 3 shows the relationship of the gel time and temperature of the 4508B film. For a temperature lower than 120°, the gel time of the 4508B film was more than 220 min, which was desirable for infusing the resin at 120°. In the range of 120–140°, the gel time was greatly dependent on the temperature, which suggested that the reaction speed of the 4508B film was sensitive to temperature. With increasing temperature, the gel time decreased, and at a temperature of 180°, it was only 20 min. These data suggested that the 4508B film was stable at relatively lower temperatures ($<120°$) and reactive at relatively higher temperatures ($>120°$).

From the plot of the viscosity versus the aging time at 120° of the 4508B film (Fig. 4) and the viscosity–temperature correlation curve of the 4508B film (Fig. 5), it can be seen that 4508B had a viscosity of 0.36 Pa s at 120°, and after aging 60 min, it had a viscosity of 0.64 Pa s, indicating that the pot life and the viscosity at the infusion tem-

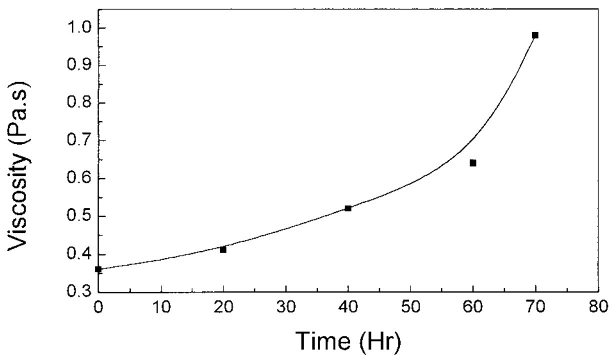

Figure 4 Dependence of viscosity on time at 120° of 4508B film.

perature of the 4508B film met the needs of the RFI technique.

Properties of Cured 4508B Resin

Table II gives the properties of the cured 4508B and 4501C resins, and it also lists the properties of a typical commercial BMI-type resin system 5405 resin for comparison.[8] It can be seen that the cured 4508B resin had good mechanical performance. Each property value of the cured 4508B listed in Table II was higher than that of the cured 4501C resin, due to the existence of PES/PI, and only the impact strength of the cured 4508B was lower than that of the 5405 resin. However, the RFI technique uses mainly tridimensional woven or stitching fabrics, which can dramatically increase the impact strength of the composites.

Figure 6 shows the curve of the water absorption of the cured samples versus the aging time in 38°C distilled water. It can be seen that the water absorption of the samples increased quickly with an increasing aging time. After aging for 22 h, water absorption of the samples nearly reached saturation: Its value was 2.67%. Meanwhile, the value of the HDT of the samples decreased quickly during the first 30 h aging time, then decreased slowly. After aging for 100 h, the HDT decreased from 256 to 222°C. It can be seen that 4508B has good hot/wet resistance.

Table II **Properties of Cured Resins**

Properties	4508B	4501C	5405
Tensile strength (MPa)	90.2	73	76.9
Tensile modulus (GPa)	4.31	3.67	3.45
Flexural strength (MPa)	180	112	176
Flexural modulus (GPa)	4.1	—	—
Impact strength (kJ/m^2)	16.7	14.5	25.4
Density (g/cm^3)	1.29	1.21	—

Properties of the Composites

The properties of the composites under dry and wet conditions, based on the 4508B film and the glass cloth, were measured and are presented in Table III. It can be seen that the composites, based on the 4508B film and the glass cloth via the RFI process, have good mechanical performance because of their lower void contents and defects, etc. The tensile strength, which is dependent mainly on fiber properties, changes little after wetting; the interlaminar shear strength (ILS), which is dependent mainly on matrix properties, decreased dramatically after wetting, but regained its values after drying; and the impact strength, which is dependent on fiber and matrix properties, decreased after wetting, but also regained its value after drying.

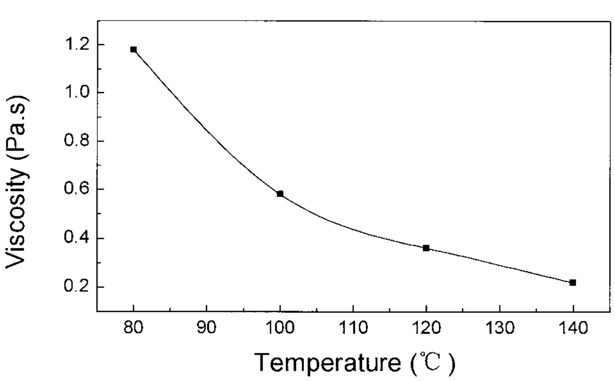

Figure 5 Relationship of viscosity and temperature of 4508B film.

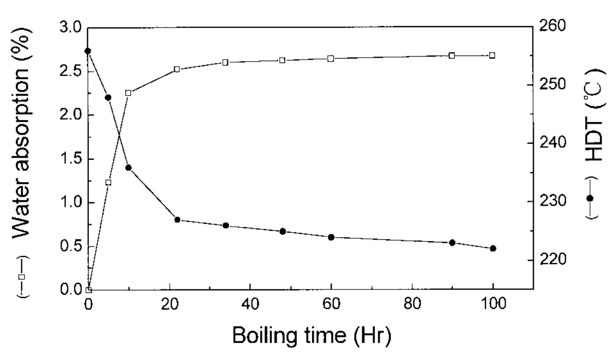

Figure 6 Water absorption and HDT versus aging time of cured 4508B resin.

Table III Hot–Wet Resistance of 4508B Glass Fiber Cloth Composite[a]

Properties	Dry	W_t[b] (Wet Absorption 0.06%)	Dried (Wet Absorption <0.01%)
Tensile strength (MPa)	554	507 (91.5%)	546 (98.6%)
Tensile modulus (GPa)	40.9	37.2 (91.0%)	39.8 (97.3%)
Flexible strength (MPa)	550	489 (88.9%)	546 (98.6%)
Flexible modulus (GPa)	29.6	26.1 (88.2%)	28.7 (97.0%)
ILS (MPa)	57.2	50.8 (88.8%)	56.9 (99.4%)
Impact strength (kJ/m^2)	241	222 (92.1%)	237 (98.3%)

[a] Fiber volume (V_f) is 65%; void volume is less than 1%.
[b] In 50°C, 100% humid environment for 2 weeks.

CONCLUSIONS

A new modified BMI resin, coded 4508B, suitable for the RFI process was successfully developed. It has a good film-forming character and high tack temperature and flexibility and was capable of thoroughly wetting out the fiber perform while maintaining desirable viscosity characteristics, pot life, and gel and cure time. In addition, the cured 4508B resin has high strength, toughness, and outstanding thermal and hot/wet properties. In addition, composites based on 4508B and the glass cloth via the RFI process exhibit good mechanical and hot/wet properties. Mechanical properties, such as tensile strength, flexible strength, and impact strength, in wet conditions could be regained after drying.

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