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Influence of novel additive on BMI resin and BMI resin matrix composite

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Abstract In order to achieve high performance BMI matrix composite manufactured by vacuum bag cure only technique, a novel additive WD-01 was selected to modify BMI-B resin based on modified polyetherketone (PEK-C) toughened 4,4′-bismaleimidodiphenyl methane (MBMI)/O,O′-diallybisphenol A (DABPA) system, and the properties of WD-01 modified BMI resin (BMI-WD) and resin matrix composite were investigated here. Results indicated that the cure shrinkage rate of BMI-B resin was reduced from original 4.0% to 1.8% and the surface morphology of neat resin casting were changed significantly by incorporating 1 wt.% WD-01, no change of chemical cure behavior of BMI resin was observed. Vacuum consolidated BMI-WD/T700 laminates had autoclave cure quality with excellent mechanical properties. A high performance of vacuum-bag curable prepreg with promising characteristics is being developed and expected to find use in advanced composite structures.

Introduction

Bismaleimide resins with their excellent processability and good balance between thermal and mechanical properties, are an important class of resins for applications in advanced composites, electronics and aerospace. BMI resin matrix composites can offer a performance temperature range between epoxies and polyimide [1, 2].

However, the high cost of advanced composite parts is the key limit for their extensive utilization in aerospace industry, weapon system and naval vessel field. In the last 10–15 year as an industry we have worked at alternative manufacturing methods to reduce the cost of a given quality of composite structure. One aspect of this overall effort has been to develop composite materials that can be processed to a high quality without use of an autoclave [3–5]. An autoclave is a heated pressure vessel used extensively in the aerospace industry for the manufacture of composite parts. Many smaller composite companies would like the quality of part routinely produced by autoclave processing but cannot justify the expenditure that installing an autoclave would entail. Composite structures are getting larger and finding an autoclave of correct size can be a major logistical problem that makes the design and production engineer look to alternative methods of manufacture. One potential solution to these problems would be a hypothetical composite material as strong, as stiff and as cosmetically perfect as an autoclave part but requiring only low pressure and low temperatures to achieve the desired results [6, 7]. Unfortunately, we never saw the report that the BMI resin matrix composites could be made by using vacuum bag cure only technique to prepare autoclave quality BMI resin matrix composites. However, advances in our understanding of processing of BMI composite materials and improvements in formulations and formatting of BMI prepregs have resulted in major improvements in the quality of oven heated, vacuum consolidated laminates.

The initiative of reducing cost led authors of this paper to develop vacuum-bag curable BMI/carbon fibe prepreg with high performance. High performance thermoplastic

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polymer modified polyetherketone (PEK-C) toughened typical two-component system based on the 4,4′-bismaleimidodiphenyl methane (MBMI)/O,O′-diallybisphenol A (DABPA), a popular BMI resin formulation (BMI-B) with excellent mechanical properties and outstanding processability, is selected here as the baseline formulation. The mechanical properties of the BMI-B/T700 composite manufactured by using an autoclave are excellent, however, there were always some voids and even delaminations could be found in the vacuum consolidated composite laminates. In order to obtain high performance BMI matrix composite fabricated by vacuum bag cure only technique, one kind of additive WD-01 was selected to modify above toughened BMI-B resin system. Why was the WD-01 selected? WD-01 is a toluene solution of alkylammonium salt of polyacrylate/polyacryamide copolymer, the copolymer is amphoteric in nature with a resin compatible tail and a filler-seeking head group (see Fig. 1). According to theoretic analyses, the filler-seeking group will be anticipated to have excellent adhesion to carbon fiber while the organic tail will have good compatibility with resin matrix, the fiber-matrix interfacial adhesion would be enhanced. On the other hand, the viscosity of WD-01 is just about 300 cPa s at room temperature, the low viscosity of WD-01 would be also very helpful to improve the fiber impregnation by the resin matrix and remove the bubbled trapped in the resin and fiber bundles. The analyses of anticipated functions from the WD-01 led the authors of this paper to select and add it into the BMI-B resin system. The quality and properties of the WD-01 incorporated BMI/T700 (BMI-WD/T700) composite have been investigated, and significant results have been achieved.

Experimental

Raw materials

WD-01 (a toluene solution of alkylammonium salt of polyacrylate/polyacryamide copolymer, Yantai Science and Technology Cor., China); PEK-C (see Scheme 1, Suzhou Institute of Engineering Plastics, China), MBMI (Hubei Honghu bismaleimide factory), DABPA (Hubei Institute of Chemistry, China), carbon fiber T700SC-12000-50C (Abbr. T700, Toray Company, Japan). The weight ratio of the components in BMI-B resin was MBMI:DABPA:PEK-C = 100:87:20. BMI-WD resin system was the same matrix as BMI-B but was filled with 1 wt.% WD-01 based on total resin weight.

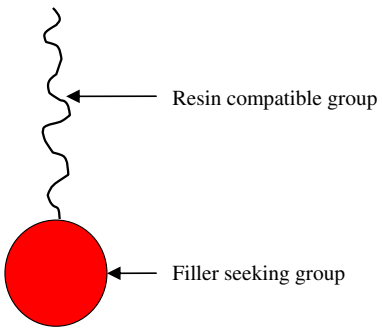
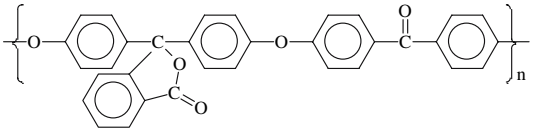


Fig. 1 Illustration of copolymer in WD-01



Scheme 1 PEK-C (n = 15~25)

Preparation of resin blends and neat resin castings

Slurry mixing process was used to prepare BMI-B resin. First, an air flow pulverizer made by Shanghai Factory of Chemical Equipment was used to process the MBMI and PEK-C into powders with average particle size no more than 40 μm. Then, the pulverized MBMI and PEK-C powders were mixed with DABPA at 85 °C, and a mechanical mixer was then used to mix the mixture for 5 min. Last, a three-roller machine was used to mix the mixture for three times and controlled the temperature of the rollers no more than 80 °C. 1 wt.% WD-01 was incorporated right after the addition of PEK-C for BMI-WD system, and all the other processing conditions were the same as those for BMI-B system.

The blends of various BMI components were heated and degassed immediately in a vacuum oven at 130–140 °C for 30–60 min, then cured at 135 °C for 2 h and 195 °C for 3 h.

Prepreg

The BMI/T700 and BMI-WD/T700 prepregs were prepared by hot/melt technique using a home-made prepreger at Beijing Institute of Aeronautical Materials (BIAM). The resin film was prepared at 80 ± 5 °C, the initial impregnation temperature was 105–125 °C, the pressures of the front, middle and rear pressing rollers were 0.1 MPa, 0.2 MPa and 0.3 MPa, respectively, and the producing speed limit was 2 m/min.

Laminates

All the composite laminates were manufactured with vacuum bag cure only process in a heated air oven. The thermal cycle was: 135 °C/2 h + 190 °C/3 h, the heating rate was 2 °C/min.

Characterization and determinations

Differential scanning calorimetry (DSC) tests were performed using Pekin–Elmer Pyris 1 DSC (Perkin–Elmer Cetus Instruments, Norwalk, CT), the temperature was ramped at 10 °C/min, and nitrogen with a flow rate of 20–30 mL/min was used as a purge gas during the measurement. Prior to each set of runs, the calorimeter was calibrated with Indium. The glass transition temperature (T_g) of composite was evaluated by dynamic mechanical thermal analysis (DMA), the heating rate was 5 °C/min and the frequency chosen was 1 Hz. T_g was reported as the peak in tanδ. Ultrasonic C-scanning detection of laminates was performed on a home-made apparatus, the frequency selected was 5 MHz. All the mechanical properties of laminates were tested according to Chinese Standards using a 10T Instron machine, see Table 1. The compression strength after impact (CAI) was detemined according to BSS 7260, the size of the sampe was 150 mm by 100 mm with the lay-up form of $[45/0/–45/0/90]_{4S}$, the impact energy was 4.45 J/m. Micrographic inspections were performed to examine the coupons for voids. Microsections were prepared by placing a piece machined from the laminate, approximately 20 mm by 20 mm, into a sample holder and mounting it with epoxy. The specimen was then grounded and polished using typical metallographic procedures and then examined using an optical microscope. Cure shrinkage rate of resin was obtained by volumetric change after cure by water displacement method descirbed in [8]. Void volume content in laminate was determined according to ASTM D3171.

Results and discussion

Influence of WD-01 on neat resin

One of the obstacles for composite applications is the dimension infidelity. The constituent materials of a composite react differently to the changes in environmental conditions encountered during processing. Chemically, the reinforcing fibers do not experience significant change during the process cycle. The thermoset polymer matrix on the other hand contracts during crosslinking by as much as 6% [9]. Consequences of the cure shrinkage can induce stress which can alter the final geometry of composite part, and this adversely affecting final properties of the composite structure.

Table 1 Test standards for composite laminates

Test	Standard
Tensile test	GB/T 3354–1999
Flexural test	GB/T 3356–1999
Compression test	GB/T 3856–1983
Short beam shear test	JC/T 773–1996
Compression strength after impact	BSS 7260

The cure shrinkage rates of BMI-B and BMI-WD neat resin were determined. As shown in Fig. 2, the cure shrinkage rate of BMI-B neat resin was reduced from 4.0% to 1.8% by incorporation of 1 wt.% WD-01. WD-01 is a toluene solution of alkylammonium salt of high molecular weight copolymer with very low viscosity (300 cPa s at room temperature), the copolymer includes a resin compatible group and a organic filler seeking group, so it will improve the resin to wet out the fiber surface, reduce the surface tension between the resin and reinforcing fiber, accelerate the dispersion of reinforcing fibers and decrease the viscosity of resin. As illustrated in Fig. 1, because of the amphoteric structure, WD-01 will not only reduce the interactive forces between the carbon fibers, but also reduce the interactive forces among the molecules during the cure process of resin, so it will prevent the volume contract of the resin and the cure shrinkage rate of cured resin will be reduced. The appearances of the BMI-B neat resin castings with and without addition of 1 wt.% WD-01 are shown in Fig. 3. Significant change had happened since the

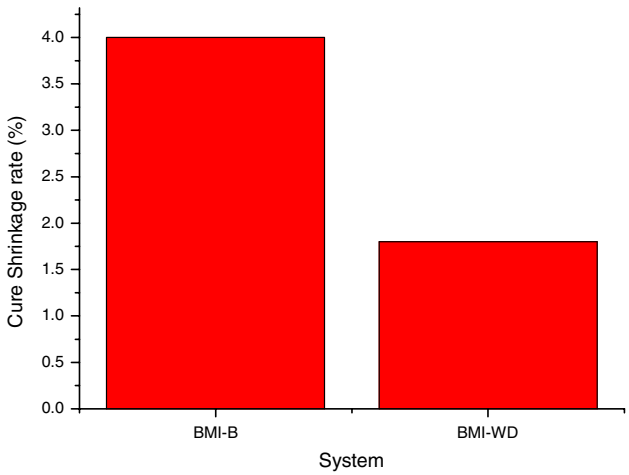


Fig. 2 Cure shrinkage of BMI resins

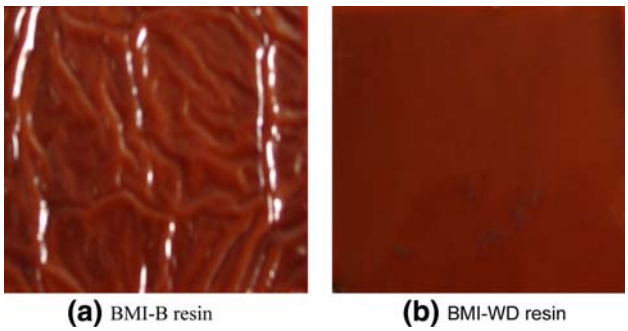


Fig. 3 Appearances of neat resin castings

incorporation of WD-01. There were a lot of wavy striations on the surface of the BMI-B neat resin casting (see Fig. 3a) because serious shrinkage happened during the resin cure process. But the surface of BMI-WD neat resin casting was very smooth (as seen in Fig. 3b). These indicate the interaction between the formed molecules during cure process has been greatly decreased because the amphoteric characteristics of WD-01 molecules. This further verify the cure shrinkage rate of BMI neat resin can be decreased significantly by incorporating 1 wt.% WD-01. However, mechanism of resin cure shrinkage is complicate and detailed investigation and analyses on the effect of WD-01 to different resins are needed to be carried out further.

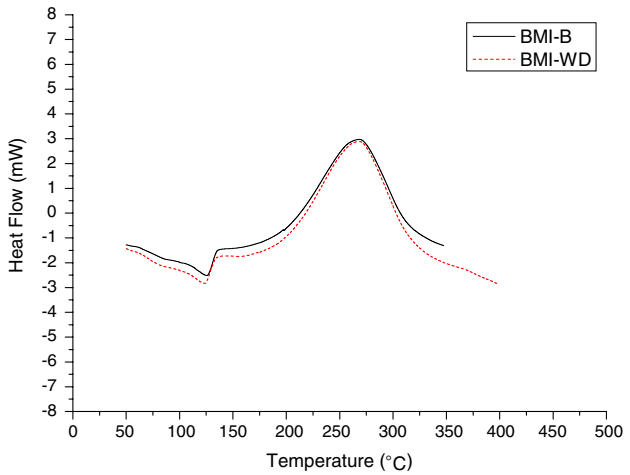


Fig. 4 DSC curves of BMI-B and BMI-WD resin systems

Figure 4 gives the DSC cure curves of BMI-B and BMI-WD resin systems. As shown in Fig. 4, there are no significant differences between the initiative reaction temperatures, reaction peak temperatures, and final reaction temperatures of the two systems. These indicate that the incorporation of WD-01 has no significant influence on the chemical cure behavior of the resin system. The endothermic peak before the initiation of the reaction corresponds to the endothermic character of MBMI particles melting and PEK-C particles dissolving into the resin system.

The quality of vacuum consolidated laminates

Ultrasonic C-Scan, optical microscopy, void volume content analyses were applied to check the quality of unidirectional and symmetric cross-ply laminates.

As shown in Fig. 5, the ultrasonic C-Scanning pictures of WD-01 incorporated laminates are much better than those without WD-01, and significant delamination can be found at the cross-section corresponding to the dark area in the $[45/0/–45/90]_{4S}$ BMI-B/T700 laminate (Fig. 5b). In order to further confirm the quality of those laminates, optical observation of the microstructure of the laminates was carried out (samples were taken from marked areas shown in Fig. 5). Figure 6 shows typical optical micrographs of laminates manufactured from BMI-B/T700 and BMI-WD/T700 prepregs by vacuum bag cure only technique. Voids were found in the laminates manufactured from BMI-B/T700 prepreg (see Fig. 6a), it is difficult to

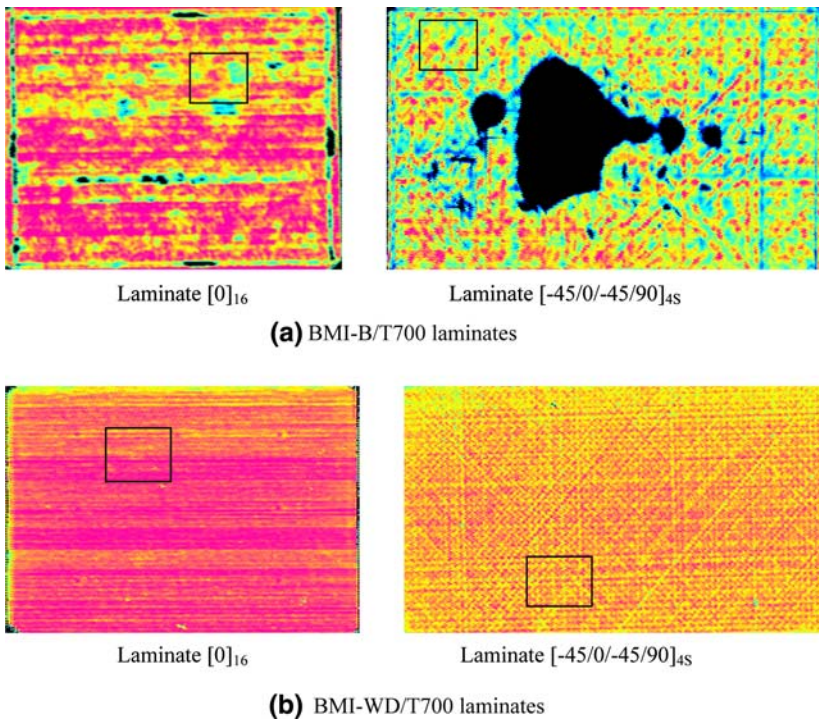


Fig. 5 Ultrasonic C-scanning pictures of BMI-B/T700 and BMI-WD/T700 laminates

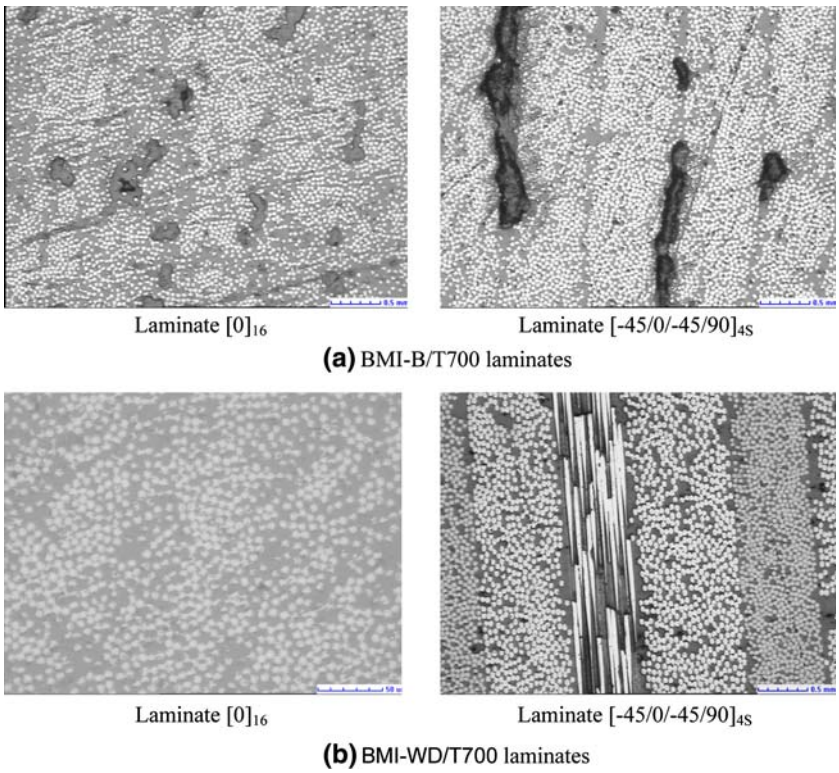


Fig. 6 Optical micrographs of BMI-B/T700 and BMI-WD/T700 laminates

find voids in those laminates corresponding to BMI-WD/T700 system (Fig. 6b). Void volume content was determined according to ASTM D3171 testing method here. As shown in Table 2, the vacuum consolidated BMI-WD/T700 laminates have very low void volume content (<1%). BMI-WD/T700 composite laminates with autoclave cure quality (usually <1%) have been manufactured successfully by using vacuum bag cure only technique.

According to reference [3], most of the voids in composites were caused by entrapped air and volatiles (include absorbed water) in the prepreg. Both the entrapped air and volatile should be released before the gelling point of resin. As seen in Fig. 6a, all the voids are very small and exist between the adjacent layers and in the filament bundles. It is difficult to remove those small voids. As we mentioned above, the structure of WD-01 is amphoteric with low viscosity, the special amphoteric characters and low viscosity behavior will improve the resin to wet out the fiber surface, reduce the surface tension between the resin and reinforcing fiber, accelerate the dispersion of reinforcing fibers and decrease the viscosity of resin. So the bubbles entrapped in the resin can go through the fiber layers and be removed efficiently by the incorporation of WD-01.

Table 2 Main properties of BMI-B/T700 and BMI-WD/T700 composites

Contents	BMI-B/T700		BMI-WD /T700	
	$\overline{X}$	S	$\overline{X}$	S
0° Tensile strength/MPa	2347	79	2350	58
0° Tensile modulus/GPa	128	4.5	128	3.2
Flexural strength/MPa	1400	78	1764	57
Flexural modulus/GPa	103	4.4	110	4.0
0°Compressive strength/MPa	1001	80	1220	55
Short beam shear strength/MPa	78	4.5	102	3.4
Compression strength after impact/MPa	–	–	230	10
Glass transition temperature (T_g)/°C	220	–	216	–
Void volume content/%	4.5	0.4	0.8	0.06

Properties of vacuum consolidated laminates

Basic mechanical properties of BMI-B/T700 and BMI-WD/T700 laminates had been determined. As shown in Table 2, an improvement of mechanical properties of BMI-WD/T700 composite can be seen because of the reduced voids in this system. The CAI of BMI-WD/T700 composite is 230 MPa, this indicates that the vacuum consolidated BMI-WD/T700 composite system own excellent toughness. The high toughness of BMI-WD/T700 composite is beneficial from the high content of high performance thermoplastic PEK-C in the resin system. The CAI value for BMI-B/T700 composite was not determined because significant delamination was found in the laminate for CAI test, as shown in Fig. 5b.

The T_g of BMI-B/T700 composite was decreased slightly from 220 °C to 216 °C by adding 1 wt.% WD-01, however, because the content of WD-01 was very low (1 wt.% based on total resin weight) and the solvent in WD-01 had been removed from the resin system during the cure process, so the influence of WD-01 on the heat resistance of BMI-B/T700 composite was very weak.

From above results, we can deduce that vacuum bag cure only technique can produce BMI-WD/T700 laminates with excellent mechanical properties, excellent toughness, low void volume contents (about 1%) and good heat resistance, and these properties approach those typically expected of autoclave cured prepreg materials.

Conclusions

The cure shrinkage rate of BMI-B resin was decreased from 4.0% to 1.8% by incorporation of additive 1 wt.% WD-01, and the surface morphology of neat resin casting was changed significantly. The quality of BMI-B/T700 laminates has been improved significantly by incorporating WD-01. The main mechanical properties of composite were improved by incorporation of 1 wt.% WD-01, and the T_g of BMI-B/T700 composite was not effected significantly. The laminates manufactured from BMI-WD/T700 prepreg by using vacuum bag cure only technique have excellent mechanical properties with autoclave cure quality to meet aerospace application requirements.

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