Toughening of BMI Based Graphite Laminates by *Ex-situ* Concept

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Abstract: High-performance bismaleimdes (BMI) matrix composites reinforced by graphite fibers were prepared and toughened with a thermoplastic component (PAEK) by using the *Ex-situ* concept. Experimental matrix was designed for overall toughening of the base resin, periodically interleaving thermoplastic films into each plies (*Ex-situ* concept) and for varying the film compositions. The highest impact damage resistance characterized by compression after impact (CAI) was obtained for the laminates toughened on the *Ex-situ* concept, especially, when two-component cast films of a special ration of PAEK/BMI 60∶40 were interleaved though the thermoplastic concentration for the overall toughening, interleaving the pure thermoplastic films and the two-component films was comparable. There were two peaks found in the DSC trace of the laminates toughened implying a phase separation process occurred. The glass transition temperature of the laminates toughened was slightly reduced due to the low-temperature PAEK. Morphological study revealed a typical granular structure just in the interplay region as a result of spinodal decomposition and coarsening process. This was in agreement of the result of DSC investigation.

Key words: bismaleimdes; compression after impact; *Ex-situ* concept
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Graphite fiber reinforced laminated materials with high stiffness and strength to weight ratios are widely used in skins structures of airframes. There is recently an increasing use of them for primary aircraft structures, particularly of advanced military aircrafts. Bismaleimdes (BMIs) are high-performance matrix resin with distinguished irradiation-proof and "hot-wet" properties, heat resistance and excellent mechanical property retention at elevated tempera-ture1s compared to epoxy systems. However, the use of BMI based graphite laminates in the primary structure has been limited by their poor impact damage resistance and the reduced compression strength after impact (CAI). A traditional method to improve the toughness of thermosetting matrix resin is incorporating a thermoplastic component into the system to form a toughened two-phase structure.

Recently, we developed an innovative concept to significantly increase the CAI properties of laminated graphite systems by periodically interleaving thermoplastic thin layers into graphite plies. This so-called *Ex-situ* concept has successfully been demonstrated in many epoxy based laminates[1-4]. It is likely an all-purposed concept for toughening any laminates independent on the chemistry of matrix resins. Hence, it was expected that the *Ex-situ* concept can also be applied for BMI based graphite laminates. This paper reports first result on BMI based laminates *Ex-situ* modified and demonstrates the success of new development[5].

1 Experimentals

1.1 Materials

In this paper, a model matrix of BMI resin system and the BMI based laminated graphite system were investigated. The matrix and the laminates were additionally toughened by a thermoplastic component.

The BMI used was a combination of N, N′-4, 4′-bismaleimdodiphenylmethane (BMPM), 0, 0′-diallyl-bisphenol A (DABPA) and some diluents. It is denoted as BMI 6421[6] and was an own development of the National Key Laboratory of Advanced Composites (LAC). Figure 1 show the molecular struc-

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ture of the BMPM and DABPA, respectively. Typical mechanical properties of BMI 6421 are listed in Table 1.

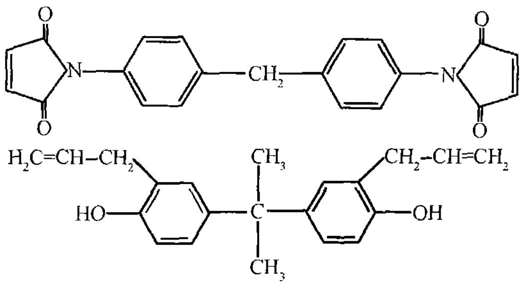

Fig. 1 Molecular formulae of the BMPM and DABPA used in the study

The thermoplastic component used was an amorphous polyetherketon with a phenolphthalein side group, developed in China (Xuzhou Engineering plastics Factory), denoted as PAEK[7]. Figure 2 shows its molecular structure. Neat PAEK has a glass transition temperature of about 240°C and its properties are very similar to PEEK in many aspects. PAEK is dissolvable in THF, making it suitable for manufacturing thin films and blending with BMI 6421 in solution.

The graphite fiber used was Toray T700.

1.2 Graphite Fiber/BMI Prepreg Manufacturing

Graphite laminates were manufactured by conventional prepreg technique. They were cured in an autoclave. Typical curing cycle is shown in Figure 3.

Table 1 Mechanical properties of BMI 6421

Longitudinal tensile strength/MPa	Longitudinal tensile elastic modulus/GPa	Interlaminar shear strength /MPa	Flexural strength/MPa	Flexural elastic modulus/GPa
1670	143	92	1730	120

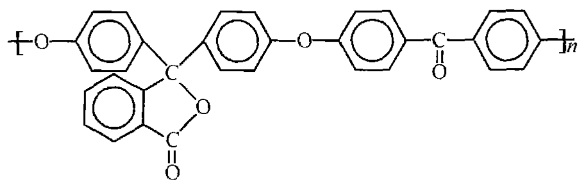

Fig. 2 Molecular structure of PAEK as toughness modifier

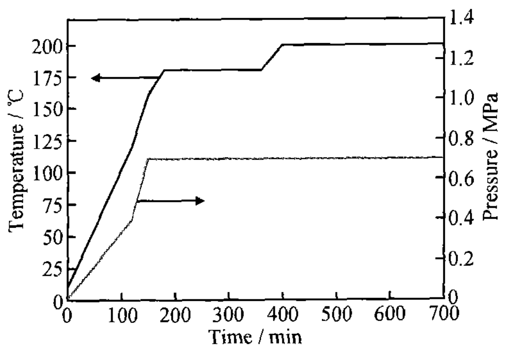

Fig. 3 Temperature-time-pressure diagram for curing

1.3 Experimental Methodology

As matrix resins there were four variants (Table 2): pure BMI 6421 as control (case 1), blended matrix of BMI 6421/PAEK with a PAEK concentration of about 17.5% (mass fraction) (case 2). Case 2 was basically nothing than the conventional toughening technique, namely thermoplastic modified thermosetting matrix. Case 3 stands for our *Ex-situ* concept, *i. e.* the pure BMI 6421 matrix based laminated system were toughened by periodically interleaving pure PAEK thin films into each plies. In principle, this is a "selective toughening concept" compared with the case 2, being better categorized to "overall toughening concept". In case 4, the pure PAEK films interleaved were replaced with those of PAEK/BMI 6421 two-component films. The composition ratio of the films could be varied from 0% to 100%. As PAEK ∶ BMI6421 = 0∶100 (0% PAEK), it reduced to case 1 as control; and for PAEK ∶ BMI 6421 = 100∶0 (100% PAEK), it returned to case 3. The experimental matrix is listed in Table 2.

1.4 Interleaving Film Prepararion

To produce PAEK/BMI 6421 two-component films for the case 4, PAEK and BMI 6421 were first mixed in THF at different ratios listed in Table 3; the mixed solution was then sprayed onto glass substrate to cast thin films. It is important to note that the PAEK concentration in each composition ratio was a constant of about 17.6% (mass fraction). Therefore, the film thickness decreased from 23μm for the ratio of 60∶40 to 18μm for the ratio of 100∶0 (Table 3).

1.5 Impact Damage Resistance

The impact resistance was evaluated by using QMW CAI specimens[8]. They were isotropic laminates with the plies of[45°/ 0°/ ~ 45°/ 90°] 2s, 89mm × 55mm in size. The impact energy used was 2J/ mm.

1.6 Morphology

The morphology of the specimens were investigated using a scanning electron microscopy (SEM, JSM-5610, JEOL Co.). The fracture surfaces of the specimens were etched with THF and dried, and coated.

2 Results and Discussion

2.1 Compression after Impact Properties

CAI data obtained is also listed and compared in Table 2. Each datum was an average of three specimens and C_V (%) stands for deviation.

As indicated in Table 2, the control (case 1)

Table 2 Experimental design and the test results of CAI data

Case	Matrix resin	CAI/ MPa	C_V /%	Remarks
1	BMI 6421 (control)	180	3.04	Pure BMI resin
2	BMI 6421/ PAEK (overall toughening)	199	0.789	Toughened resin
3	BMI 6421/ PAEK (*Ex-situ* concept)	254	8.70	Interleaving pure thermoplastic films
4	BMI 6421 / (BMI6421 / PAEK) (*Ex-situ* concept)	290	3.27	Interleaving two-component films

shows a CAI datum of about 180MPa, whereas for the blend matrix specimens (case 2) CAI is increased to about 199MPa. The toughness is enhanced, but the enhancement is relative. However, the toughness improvement resulting from the *Ex-situ* concept was much significant. CAI obtained in case 3 was about 254MPa even there was a big scatter among all specimens tested. The highest improvement of impact resistance was achieved by interleaving the two-component films into the plies (case 4), resulting in a CAI datum of about 290MPa, even when the quantity of PAEK added into the system was comparable with that in the blend (case 2) and in the pure PAEK film (case 3). This comparison demonstrates obviously the efficiency of *Ex-situ* concept in enhancement of impact damage resistance of graphite laminates even with intrinsically brittle matrix.

Table 3 Composition ratio of PAEK ∶ BMI 6421, the film thickness and the CAI data of the laminates interleaved with the films

Mass ratio of composition	Film thickness/ μm	CAI/ MPa	C_V/ %	Remarks
60 ∶ 40	23	290	3.27	Case 4 in table 2
80 ∶ 20	22	272	2.15	
90 ∶ 10	20	256	5.57	
100 ∶ 0	18	254	8.70	Case 3 in table 3

Table 3 reports CAI data in dependence on the PAEK/ BMI 6421 composition ratio for the laminates toughened by using the *Ex-situ* concept. It is clear that for the laminates with the highest CAI of 290MPa (case 4 in Table 2) two-component films were used alone with a special composition ratio of PAEK ∶ BMI 6421 = 60 ∶ 40, whereas for the laminates with CAI= 254MPa (case 3 in Table 2) only pure PAEK films were interleaved; this means that the composition ratio was 100 ∶ 0. As mentioned previously, the PAEK concentration was designed constant for the four different ratios. Why the CAI varies with the composition ratio is at the moment not clear.

2.2 Glass Transition Behavior

Figure 4 shows the glass transition behavior of neat BMI 6421 resin (a) and BMI 6421 graphite laminate (b) interleaved with the two-component films of a ratio of 60 ∶ 40 (case 4 in Table 2) by means of DMTA. High-temperature peak at about 285° C in Figure 4a is characteristic for the T_g of BMI 6421, which is, however, lowered down to about 271° C in figure 4b for the laminate. The lowering effect of glass transition temperature was not only found for BMI 6421, but also for the toughness modifier PAEK which, as shown in figure 4b, is slightly reduced from originally 240° C to about 234° C for the laminate. The exact cause for the lowering effect is at the moment unknown. Alone there were two characteristic temperatures recorded in figure 4b implies the existence of a two-phase structure for the matrix *Ex-situ* toughened.

2.3 Morphological Characteristics

Correspondingly to the glass transition behavior

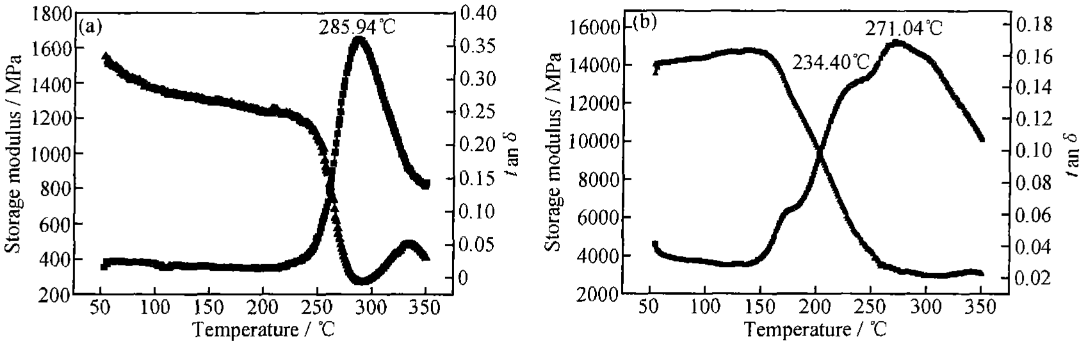

Fig. 4 Glass transition behavior of BMI 6421(a) and the graphite laminate (b) made by *Ex-situ* method

exhibited in Figure 4, morphological investigation revealed that a typical decomposition process occurred in the interlaminar regions (Figure 5). In the figure (a) one can easily find the horizon (0°) plies and the 45° plies of the laminate interleaved with the PAEK/BMI 6421 two-component films of a composition ratio of 60 : 40 (case 4 in Table 2). The PAEK component was prior the SEM study chemically etched-off with THF. The granular structure remained was BMI component cured. It could not be etched away. As shown in the figures, there is a characteristic granular morphology appears in the interplay region which is often observed on the thermal-reaction induced spinodal decomposition followed by a phase

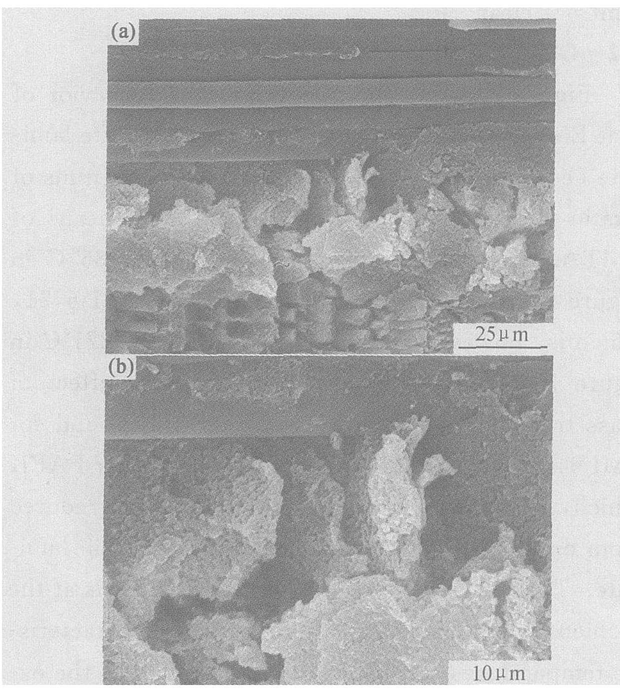

Fig. 5 (a) a representative of interply morphology of graphite laminate toughened by PAEK/BMI 6421 two-component film of a composition ratio of 60: 40 through *Ex-situ* concept. PAEK was chemically etched-off.
(b) a high magnification of (a)

coarsening process[9]. It is apparent that the granular structure is very fine, with an average diameter of or even lower than about 1μm.

However, the situation changed for the laminate interleaved with pure PAEK films in Figure 6 for case 3 in Table 2. At the same chemical etching conditions, an overlapped nodular structure of remained BMI component appeared. The average diameter of the nodular structure seems much larger than the correlation length so that the particles were strongly interconnected to form a rough morphology. As known, there are many factors affecting the spinodal decomposition and coarsening mechanism[9], for instance, the diffusion behavior, the dissolubility behavior, the speed competition behavior, the viscosity behavior and the surface tension behavior, *etc*. However, an exact explanation for the change in morphology can at the moment not be given.

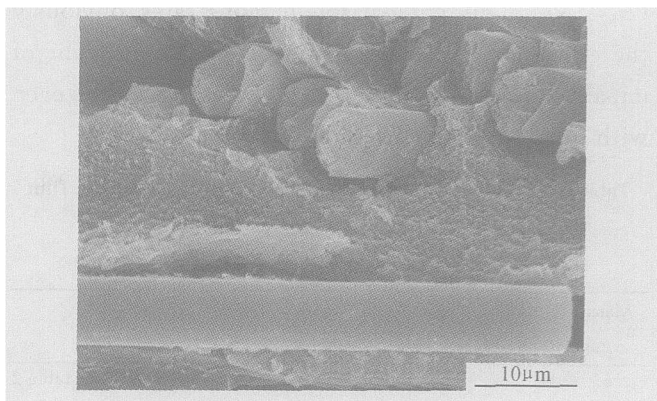

Fig. 6 A representative of interlayer morphology of graphite laminate toughened by pure PAEK film through *Ex-situ* method. PAEK was chemically etched-off.

By taking CAI data in conjunction with the morphological characteristic into consideration, it is conceivable that the completely grown and co-continuous, but not overlapped granular structure must be a good sign for high toughness and thus for the high impact damage resistance. It is also believed that the two-component films help to facilitate the spinodal decomposition and coarsening process, leading to the granular structure. However, an intensive investigation to this structure-property relationship is certainly needed.

3 Conclusion

In conclusion, in terms of compression after impact (CAI) behavior the *Ex-situ* concept has successfully been demonstrated for BMI 6421 / PAEK laminated graphite systems, particularly if the two-component films of a specific composition ratio of 60∶40 were periodically interleaved.

Acknowledgements

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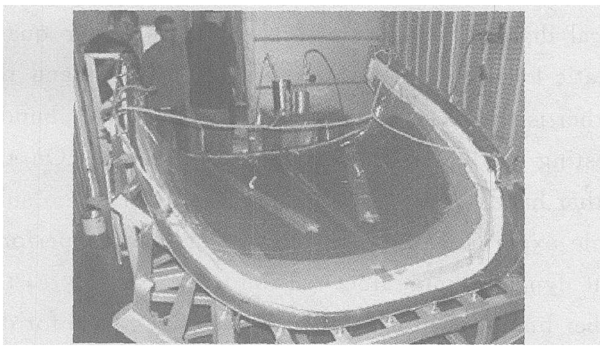

Fig. 8 Infusion procedure

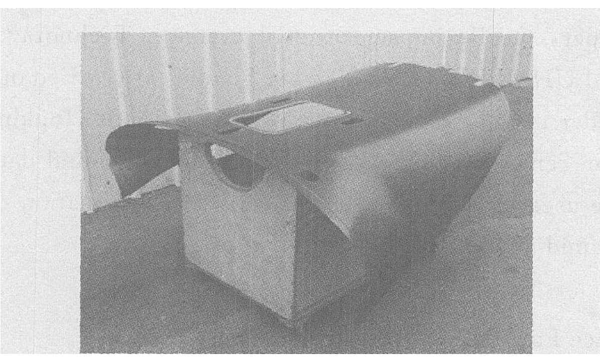

Fig. 9 Cured and trimmed part

6 Conclusion

In conclusion, it can be state that high performance PMI foams meet the demands of the match mould press, autoclaving and any kind of resin infusion processes.

The excellent creep compression resistance and outstanding temperature resistance of PMI foams make it possible to use them for all common cure cycles. Post-curing temperatures up to 225 ℃ are allowed. PMI foam core can be used with cost effective cocuring processing technology and it is easy to be shaped.

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