Improvement of the Impact Damage Resistance of BMI/Graphite Laminates by the Ex-situ Method

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Abstract: High-performance bismaleimide (BMI) matrix composites reinforced with graphite fibers were prepared and toughened with a thermoplastic component (PEK-C) by using different toughening methods. Four experimental options were conducted using the neat BMI matrix, toughened BMI matrix with PEK-C, BMI laminates periodically interleaved with neat PEK-C films (Ex-situ concept 1) and BMI laminates periodically interleaved with BMI/PEK-C blend films (Ex-situ concept 2), respectively. The laminates were tested for compression strength after impact using an impact energy of 2 J mm^{-1}. The highest impact damage resistance was obtained for the laminates toughened using the Ex-situ concept 2, especially, when PEK-C/BMI two-component films, cast from a mixture of PEK-C : BMI = 60 : 40 were interleaved between the BMI laminate plies. Interleaving the pure thermoplastic film also gave good results (Ex-situ concept 1). There were two peak temperatures evident in the dynamic mechanical thermal analyses of the ex-situ toughened laminates implying that phase separation had occurred. The glass transition temperature of the toughened BMI laminates was slightly reduced due to the lower glass transition temperature of PEK-C. Morphological investigations revealed that a granular structure was present in the interply region presumably due to spinodal decomposition and coarsening. The results of this study are presented herein.

1. INTRODUCTION

Graphite fiber-reinforced laminated materials with high stiffness and strength to weight ratios are widely used in a variety of aerospace applications. The use of composites for
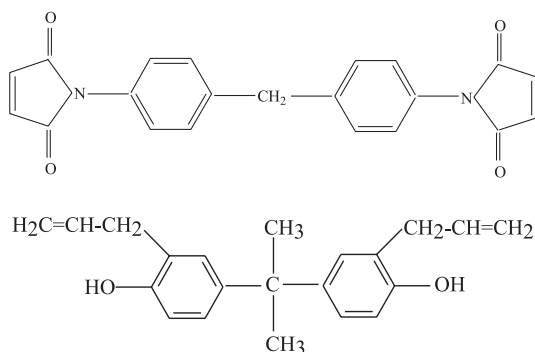
Figure 1. Molecular formula of the BMPM and DABPA used in the study.

primary aircraft structure, particularly on advanced military aircraft has increased significantly in recent years. Bismaleimides (BMIs) are high-performance structural matrix resins with distinguished processing characteristics, excellent chemical and corrosion resistance, "hot-wet" properties, heat resistance and excellent mechanical property retention at elevated temperatures compared to epoxy systems. However, the use of BMI-based graphite laminates in the primary structure has been limited to some degree by their poor damage resistance and the reduction in compression strength after impact (CAI). A traditional method to improve the toughness of thermosetting matrix resin is incorporating a thermoplastic component into the matrix system to form a toughened two-phase structure [1–3].

Recently, we developed an innovative concept to significantly increase the CAI properties of thermosetting matrix resin 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 [4–7]. It is probably an all-purpose concept suitable for toughening any composite laminates independent of the chemistry of matrix resins. The key factor for success is in the interlaminar morphological control. Hence, it was expected that the Ex-situ concept could also be applied to BMI/graphite laminates to effect improvements in damage tolerance. This paper reports preliminary results with BMI/graphite laminates modified by the Ex-situ method and demonstrates the success of approach [8].

2. EXPERIMENTAL

2.1. Materials

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 and was developed at the National Key Laboratory of Advanced Composites (LAC). Figure 1
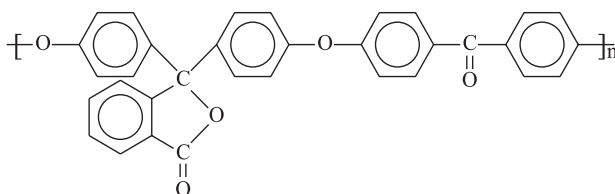
Figure 2. Molecular structure of PEK-C as toughness modifier.

shows the molecular structures of the BMPM and DABPA, respectively. BMI 6421 can be used as both a prepreg resin and a resin transfer moldable resin [9].

The thermoplastic component used was an amorphous polyetherketone with a phenolphthalein side group, developed in China [10], denoted as PEK-C. Figure 2 shows its molecular structure. Neat PEK-C has a glass transition temperature of about 230 °C according to the producer (Xuzhou Engineering Plastics Factory) and its properties are very similar to poltetheretherketone in many aspects. PEK-C is soluble in tetrahydofuran (THF), making it suitable for manufacturing thin films.

The graphite fiber used was a commercial product of Toray T700SC of 12K tow. No additional fiber surface treatment was carried out for this study.

2.2. Graphite fiber/BMI laminate manufacturing

Unidirectional T700SC graphite fiber was impregnated with BMI solution by conventional wet-winding. 89 mm × 55 mm × 2 mm quasi-isotropic laminates of [45/0/ –45/90]2S were manufactured from the prepreg. The laminates were cured in an autoclave. The typical curing cycle is shown in figure 3. It can be seen that the specimens were post-cured at 200 °C for 4 h.

The fiber volume fraction in the final laminates was fairly constant at about 60 ± 2 for all specimens studied. Table 1 lists the typical mechanical data of the BMI 6421/T700 laminates tested. It is noteworthy that all laminates cured were non-destructively tested by means of ultrasonic scanning (C-scan) according to the standard manufacturing specification for composite laminates prior to mechanical testing. Mechanical testing was conducted only on those specimens that met the quality requirements [9]. Representative C-scan results are shown in table 2 for the impact-damaged specimens.

2.3. Experimental methodology

There were four experimental options for the comparative study. The experimental matrix is listed in table 2.

- Case 1, neat BMI 6421 matrix was used as control.
- Case 2, in this case, an overall toughened BMI matrix was used, i.e. the BMI matrix was first blended with about 17.5 wt.% PEK-C powders, and then the fibers were im-
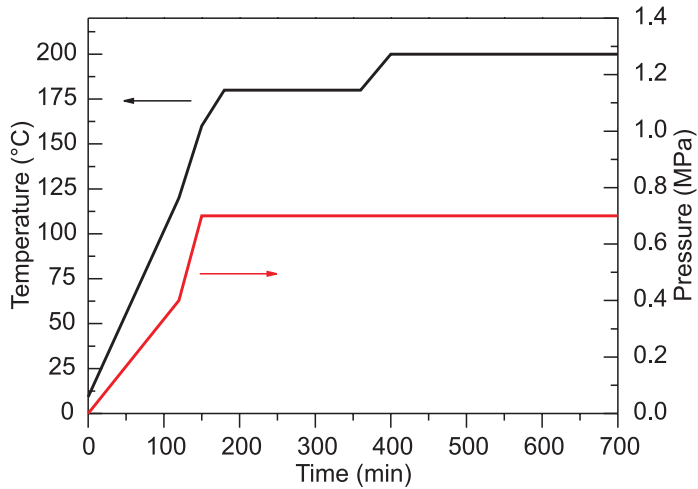
Figure 3. Temperature–time–pressure curing condition.

pregnated with the mixture in solution. The particles size was around a few hundred micrometers. It was basically nothing more than the conventional toughening technique, namely thermoplastic toughened thermosetting matrix. We called this toughening method in the study In-situ toughening.
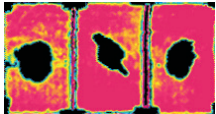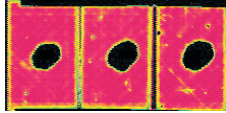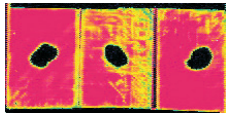
- Case 3 stands for the Ex-situ toughening concept 1. In this case the pure BMI prepreg was periodically interleaved with pure PEK-C films between each ply. The average PEK-C concentration in the laminate was also about 17.5 wt.%. However, it is obvious that the interply concentration of PEK-C for the Ex-situ approach should be higher than that for the In-situ one even when the average concentration for the final laminates in case 2 and 3 was comparable. This is due to the special location of the toughness modifier [5]. Therefore, Ex-situ toughening is a selective toughening method compared to the overall toughening concept.

- In case 4, the neat PEK-C films interleaved were replaced with PEK-C/BMI blend films. The composition ratio of the films could be varied from 0 to 100%. When PEK-C : BMI = 0 : 100 (0% PEK-C, neat BMI resin) it was reduced to case 1 as the control; and PEK-C : BMI = 100 : 0 (100% PEK-C, no BMI resin) was the same as case 3. Case 4 was called Ex-situ concept 2 in the study.

With regard to processing characteristics, it was found that in comparison with the non-toughened BMI composites (case 1), the handling, surface tack and drape, and processability became more difficult for the toughened materials (case 2), but not for those Ex-situ toughened (case 3 and 4). Quite the opposite, there were processing advantages if the proper manufacturing procedure was followed [8].

Table 1. The typical mechanical properties of BMI 6421/T700SC laminates.

Property	Typical value	Test procedure
Tensile strength (MPa)	2110	GB/T 3354–1999
Tensile modulus (GPa)	125	
Compression strength (MPa)	1180	GB/T 3856–1983
Flexural strength (MPa)	1570	GB/T 3356–1999
Flexural modulus (GPa)	125	
Interlaminar shear strength (MPa)	100	JC/T 773–1996

Table 2. Experimental variables, CAI values and C-scan results in comparison.

Case	Matrix resin	CAI (MPa)	C-scan after impact	Damage area (mm^2)	Remarks
1	Neat BMI (as Control)	180		544	Pure BMI matrix
2	BMI/PEK-C blend (In-situ toughening)	199		408	Toughened BMI matrix with 17.5 wt.% PEK-C
3	BMI/PEK-C films interleaved (Ex-situ toughening concept 1)	254		345	Interleaving pure PEK-C films, average PEK-C concentration 17.5 wt.%
4	BMI/(BMI/PEK-C blend films interleaved) (Ex-situ toughening concept 2)	290		220	Interleaving BMI/PEK-C blend films, average PEK-C concentration $\cong$ 17.5 wt.%

2.4. Blend film preparation

To produce PEK-C/BMI 6421 blend films for use in case 4, PEK-C and BMI were first mixed in THF at the different ratios listed in table 3. The mixed solution was then sprayed onto glass substrate to cast thin films of the blends. The concentration of PEK-C was controlled at about 20 g m^{-2} in the films. Therefore the film thickness decreased from 23 μm for PEK-C : BMI = 60 : 40 to 18 μm for 100 : 0 (table 3).

Table 3. Effect of the blend film composition on the film thickness and CAI strength.

PEK-C : BMI ratio (in weight)	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 2

2.5. Impact damage resistance

The impact damage resistance was evaluated by using QMW CAI specimens [11] developed at Queen Mary College, Westfield, University of London. They were 89 mm × 55 mm × 2 mm quasi-isotropic rectangular laminates with plies of [45/0/–45/90]$_{2S}$. The impact energy used was 2 J mm^{-1}. Delamination after impact was investigated using an ultrasonic scan (C-scan).

2.6. Morphological observations

The morphology of specimens was investigated using a scanning electron microscopy (SEM; JSM-5610, JEOL Co.). The fracture surfaces of the specimens were chemically etched with THF for 72 h. Then the fracture surfaces were coated with a layer of gold about 200 Å thick before examination.

2.7. Dynamic mechanical thermal analysis

Dynamic mechanical measurements were carried out on a Dynamic Mechanical Thermal Analyzer (DMTA) 800 (TA Instruments) using the single cantilever mode at a heating rate of 5 °C min^{-1} and a frequency of 1 Hz. The specimen size was 45 mm × 8 mm × 3 mm. The glass transition temperatures were taken to be the peak of the tan δ curve.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties of BMI 6421/T700SC laminates

Table 1 reports the typical mechanical properties of BMI 6421/T700SC laminates studied.

3.2. Compression strength after impact properties

Compression strength after impact data (CAI) obtained is listed and compared in table 2 for the four experimental options. Each CAI datum was an average of three specimens.

The data scatter was less than 5% on average. The C-scan results are also shown in the Table, indicating the impact damage area of each of the three specimens tested.

As indicated in table 2, the control (case 1) showed a CAI strength of about 180 MPa, whereas for the blend matrix specimens (case 2) the average CAI was increased to about 199 MPa. The toughness was enhanced, but the enhancement was relative. However, the toughness improvement resulting from the Ex-situ toughening was more significant. The CAI obtained in case 3 was about 254 MPa for Ex-situ toughening concept 1. The highest improvement of impact resistance was achieved by interleaving the BMI/PEK-C two-component blend films between the plies (case 4), resulting in a CAI average of about 290 MPa, even when the quantity of PEK-C added into the system was comparable with those in the blend matrix (case 2) and in the pure PEK-C films interleaved laminates (case 3). This comparison demonstrates the efficiency of Ex-situ toughening in enhancing the impact damage resistance of BMI/graphite laminates, particularly for the experimental case 4 of Ex-situ toughening concept 2.

The C-scans after impact were consistent with the measured CAI results. As shown in the table quantitatively, with an observed decrease in the damage area, the CAI value increased. Specimens with the highest CAI corresponded to those with the lowest impact damage area.

It was interesting to study the compositional effect for the Ex-situ concept 2 (case 4) on the CAI response. The results are reported and compared in table 3. The thickness of BMI/PEK-C blend films as produced varied from 18 μm (PEK-C : BMI = 100 : 0) to 23 μm (PEK-C : BMI = 60 : 40). However, when the specimens with the interleaved films of different initial thickness were cured in an autoclave under the same temperature–time–pressure conditions, the flow behavior of the materials was different. In the case of the initially thicker laminates, more BMI resin flowed out of the laminate. Therefore, the resulting laminate thicknesses were closer to each other. They were about $2.0 + 0.2$ mm for all specimens tested, implying that they had roughly comparable fiber volume fractions. It was experimentally difficult to measure the PEK-C concentration in the final interlaminar regions.

It is clear by comparing the CAI data to the various blend compositions that the increase of PEK-C concentration in the initial cast films did not result in an increase in the CAI strength of the laminates. The highest CAI strength of 290 MPa was obtained on the specimens with a PEK-C : BMI blend ratio of 60 : 40 (case 4 in table 2).

3.3. Glass transition behavior

Figure 4 shows representative DMTA results for a neat BMI resin (a) and a BMI/PEK-C composite laminate (b) with the blend films interleaved (case 4 in table 2). The peak temperature at about 318 °C in figure 4(a) is characteristic for the T_g of neat BMI 6421, which is, however, reduced to about 296 °C in figure 4(b) for the composite laminate. In contrast to this lowering effect on the BMI, the glass transition temperature of the PEK-C component was found to increase from 230 °C for the neat resin to about 239 °C in the composite
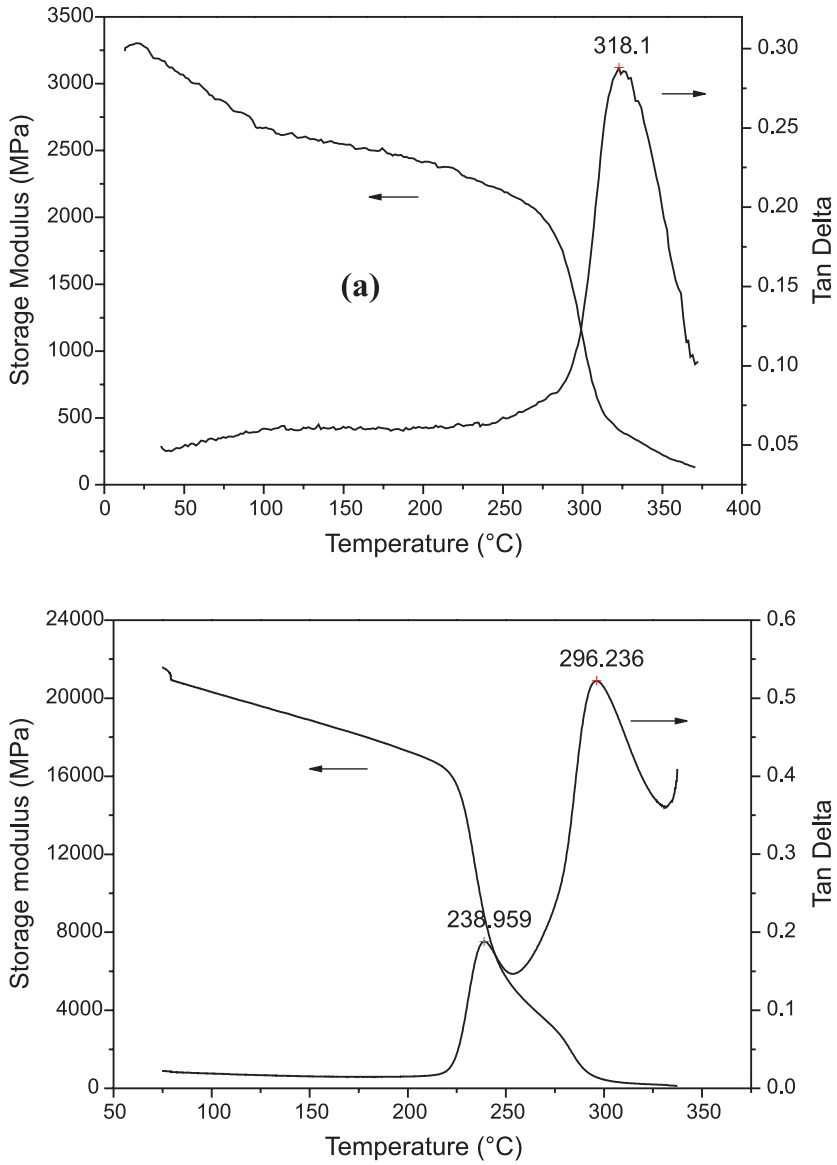
Figure 4. Glass transition behavior of (a) the neat BMI; and (b) the composite laminate of case 4 in table 2.

laminate. There were two characteristic peak temperatures observed in figure 4(b), imply-ing the existence of a two-phase morphology for the toughened composite system.
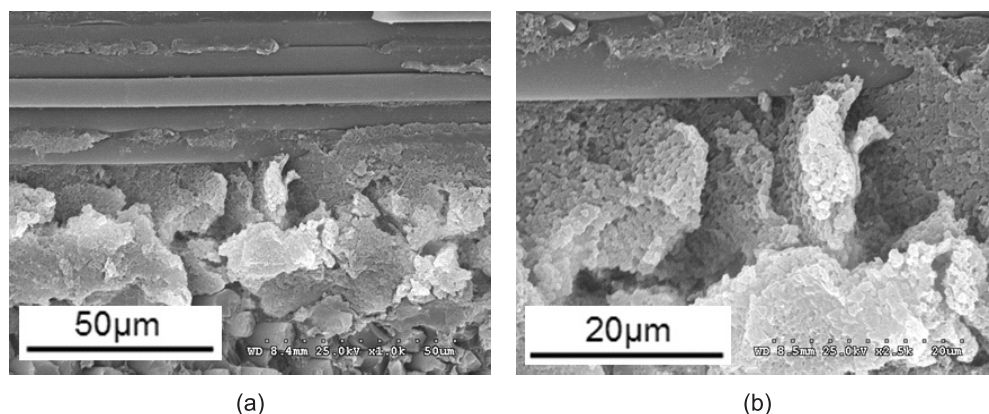
(a) (b)

Figure 5. (a) A representative of interlaminar morphology of the laminate toughened with PEK-C/BMI blend film (magnification: × 1500; case 4 in table 2). The PEK-C was chemically etched-off. (b) A higher magnification (× 2500) of (a).

3.4. Morphological characteristics

Correspondingly to the glass transition behavior exhibited in figure 4, a morphological investigation by SEM indicated that a typical decomposition process occurred in the interlaminar regions (figure 5). In figure 5(a) the horizon (0°) plies and the 45° plies of the laminate interleaved with the PEK-C/BMI 6421 two-component films (60 : 40, case 4 in table 2) are readily apparent. The PEK-C component was chemically removed using THF prior to the SEM analysis. The granular structure remaining (figure 5(b)) is the cured BMI component. As expected, it could not be removed by the solvent treatment. As shown in the figures, there is a granular morphology present in the interply region which is often observed in thermally induced spinodal decomposition, followed by a phase coarsening process [12]. It is apparent that the granular structure is very fine, with an average diameter of about 1 μm (figure 5(b)).

However, the results were different for the laminate interleaved with pure PEK-C films as shown in figure 6 (case 3 in table 2). After the same chemical etching conditions as described above, an overlapped nodular structure of cured BMI remained. 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 [12]. This is a complex process that is influenced by many properties, for instance, the diffusion, the solubility of the components, the rate competition, the viscosity and the surface tension.

By taking into consideration the CAI and the morphological characterization results, it is conceivable that the co-continuous, but not overlapped granular structure may be a good morphology leading to high toughness and thus high impact damage resistance. It is also believed that the two-component films help to facilitate the spinodal decomposi-
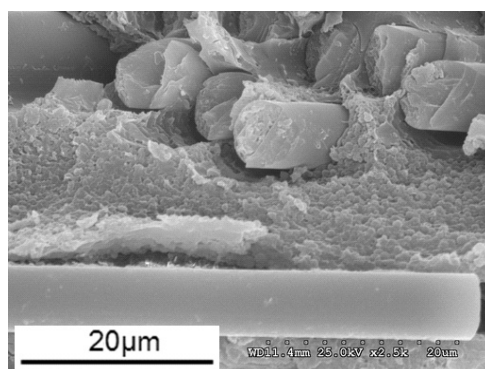
Figure 6. A representative of interlaminar morphology (× 2500) of the laminate toughened with pure PEK-C film (case 3 in table 2). PEK-C was chemically etched-off with THF.

tion and coarsening process, leading to a desirable granular structure. However, a more intensive investigation to this structure–property relationship is needed to understand this phenomenon.

4. CONCLUSION

In conclusion, in terms of compression after impact (CAI) behavior the *Ex-situ* concept has successfully been demonstrated for BMI 6421/PEK-C laminated graphite systems, particularly if the two-component films of a specific composition ratio of PEK-C : BMI = 60 : 40 were periodically interleaved (Ex-situ concept 2).

NOTE

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