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Morphological and Spatial Effects on Toughness and Impact Damage Resistance of PAEK-toughened BMI and Graphite Fiber Composite Laminates

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Abstract

The microstructure property relationships have been studied in terms of glass transition behavior, phase morphology, and fracture toughness on thermoplastic polyetherketone with a phenolphthalein side group (PAEK) toughened bismaleimdes (BMI) resins, and in terms of interlaminar morphology and compression after impact (CAI) on the graphite fiber (T700SC), the reinforced BMI matrix composites that are toughened with a so-called ex-situ concept, respectively. The characteristic morphology spectrum has been found to occur as the concentration of PAEK is varied. In particular, the relationship between the morphology and the fracture toughness has been explored on the PAEK-BMI blends. The fracture micromechanism has then been used to explain the delamination and impact damage behavior on the graphite laminated systems, where the morphology properties relationship held true. The complex nature of the diffusion-controlled phase behavior has also qualitatively been studied, which served as a model for understanding the ex-situ toughening concept.

Keywords: bismaleimide; ex-situ concept; phase separation; structure; property relations; impact damage resistance

1. Introduction

The use of graphite fiber reinforced laminated composites for primary aircraft structures have significantly increased in recent years. As a kind of highperformance matrix resin, particularly for advanced military aircrafts where higher hot/wet temperature conditions are required, bismaleimdes (BMI) show many advantages, such as, excellent low coefficient of thermal expansion, low dielectricity, and excellent chemical and corrosion resistance over the state-ofthe-art epoxies. BMI resins can be processed in a manner similar to epoxies, but exhibit higher glass transition temperatures. However, BMI resins in general are inherently brittle^[1-2] because of their highly cross-linked structure. Therefore, BMI matrix composites reinforced with graphite fibers naturally tend toward delamination, by exterior impact or fatigue.

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A traditional approach to increase the fracture toughness of BMI resins and impact damage resistance of BMI matrix composites is to toughen them by incorporating high-performance engineering thermoplastics into the matrix to form a phase separated matrix structure^[3-6]. The impact damage resistance of the toughened laminates, characterized by compression after impact (CAI), can usually be enhanced to a level of the "second generation" of aircraft composites in the aerospace industry. However, dramatically increased matrix viscosity decreases the flow and impregnation ability, and the significantly changed prepreg handling and curing conditions are the price one has to pay.

After the traditional toughening technology was established, the concept of enhancing the impact damage resistance of graphite composites by interleaving thermoplastic films into each ply, was proposed and implemented by American Cyanamid^[7]. Composites containing special layers of a "high-strain polymer" between each ply exhibited obvious improvements in CAI compared to the traditionally toughened ones^[8-10]. The interleaved epoxy matrix laminates manufactured by Toray were then successfully qualified by Boeing,

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leading to the "third generation" of aircraft composites.

In recent times, an innovative concept has been developed, called the ex-situ concept, to significantly increase the CAI properties of thermosetting matrix graphite composites by specifically toughening the interlaminar regions between each graphite ply^[11-16]. It is noteworthy that the ex-situ concept needs to be distinguished from the technologies described earlier: thermoplastic toughened thermosetting resin with the characteristic phase separated and the inverted morphological structure spatially located specifically in the thin interlaminar regions, which further penetrates slightly into the neighboring graphite, plies to mechanically strengthen the bonding between the resinrich interlayer and the graphite ply, where the graphite plies themselves are still fully impregnated with the thermosetting matrix for the inherently high specific strength and modulus. The ex-situ concept has been successfully demonstrated for impact damage resistance improvements on epoxy matrix composites both for unidirectional graphite (UD) and cross-ply laminates^[11-14]. The industrial manufacturing procedure and curing conditions of the prepregged laminates remain as usual.

The present article extends the studies from the state-of-the-art epoxy matrix composites to the hightemperature BMI matrix composites and to the structure-properties relationship between the neat resin systems and the ex-situ toughened BMI matrix laminates. Although it has been long recognized that creation of a phase-separated morphology is an essential means of achieving fracture toughness improvement, however, effectively enhancing the fracture toughness of the neat resin systems usually does not come easy for the laminated composite systems. Thus, this study intends to understand the fundamental principles of toughening the unreinforced neat resins and the resin matrix composites reinforced with graphite fibers, with emphasis on the relationship between them.

2. Experimental

The study was divided into two parts: the first part studied the matrix polymer systems and the second part studied the laminated composites.

2.1. Materials

The BMI used is a combination of N, N'-4, 4'-bismaleimdodiphenylmethane (BMPM), 0, 0'-diallyl-bisphenol A (DABPA), and some diluents. It is a commercial all-purpose grade of BMIs for prepregs, resin transfer molding (RTM), and resin film infusion (RFI), developed at and provided by the National Key Laboratory of Advanced Composites (LAC), Beijing Institute of Aeronautical Materials (BIAM), China, with the trademark of BMI 6421. The toughening polymer, PAEK, is an amorphous engineering thermoplastic polyetherketone with a phenolphthalein side group. It is a Chinese development^[17-19]. PAEK shows an intrinsic viscosity of 0.30 dl/g and a glass transition temperature T_g of 230 °C. The PAEK used in the present study has been supplied by the Xuzhou Engineering Plastics Factory, China. Fig.1 shows the molecular structure of the BMPM, DABPA, and PAEK, respectively.











Fig.1 Molecular formula of BMPA, DABPA, and PAEK.

2.2. Specimen preparation

PAEK modified BMI blends were prepared by traditional mechanical mixing. The PAEK concentration of the blends varied from 5 to 30 phr (parts per hundred resins). Cast bars were fabricated with the neat resin or the blends for morphological, thermal mechanical, and fracture toughness tests.

The graphite fiber used was a commercial Toray T700SC (Toray Co., Japan). BMI matrix graphite laminates were manufactured using the following procedure: the unidirectional graphite fibers were first pre-wet-winded and impregnated with the solvent-diluted BMI. The prepreg was cut into 16 plies, which were then laid up with $[45/0/-45/90]_{2S}$ on the mold. The laminate panels were autoclave cured and post-cured, following the temperature-time program recommended by the material supplier, the National Key Laboratory (Fig.2). The neat BMI matrix graphite laminates were made in the present study as a control for studying the structure-properties relationship between the matrix resin systems and the graphite com-

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posites.

Two laminated panels were ex-situ toughened and directly provided by the National Key Laboratory using a special patented fabrication procedure^[20]. The basic material components, the lay-up, and the curing conditions were identical, except that one panel was designed and fabricated to be initially PAEK-rich in the interlaminar regions and the other one initially rich in a special blend composition of PAEK to BMI of 60:40.

All composite specimens were controlled in their thickness. The global fiber volume fraction was determined from the knowledge of the fiber areal weight in the prepregs, fiber density, resin density, the lay-up, and specimen geometry. It was controlled in a range of $60\%\pm 2\%$ in the study.

Further experimental details and a complete identification of specimens can be found elsewhere^[15].



Fig.2 Curing and postcuring program for the graphite composites studied.

2.3. Morphology

The morphology of the specimens was investigated by using a scanning electron microscope (SEM, Hitachi S-3000N) and an optical microscope, respectively. The matrix resin specimens were fractured under cryogenic conditions using liquid nitrogen, whereas, for the graphite composites, the specimens were mechanically cut from the composite panel, followed by polishing the cross-section. To increase the contrast, all the fractured surfaces or the mechanical cut cross-sections were intensively chemically etched with tetrahydrofuran (THF) for 72 h, washed in an ultrasonic bath, and then dried for 4 h at 60 °C under vacuum. The fracture surface of the specimens was finally coated with a gold layer of about 200 Å thickness before the SEM examination.

2.4. Thermal mechanical test

Dynamic mechanical thermal analysis (DMTA) was conducted with TA Instruments DMA 800, operating in the single cantilever mode at an oscillation frequency of 1.0 Hz. The heating rate was 5.0 °C/min for a temperature range from room temperature to 350 °C. Matrix resin specimens for the analysis were rectangular bars of nominal 45 mm \times 8 mm \times 3 mm. The glass transition temperatures were taken to be the peak of the tan δ curve.

2.5. Fracture toughness measurement

The impact fracture toughness of matrix resins were tested on an Izod instrument in accordance with GB 2571–95 using un-notched specimens. The size of the impact specimens was, a length of 80 mm, a width of 10 mm, and a thickness of 4 mm, with a minimum of five successful specimens for each test.

2.6. Compression after impact test

The impact damage resistance of the composite laminates was evaluated by using QMW CAI specimens^[21] developed at Queen Mary College, Westfield University of London. They were quasi-isotropic rectangular laminates with a dimension of 89 mm \times 55 mm \times 2 mm. The specimens were impact loaded with an energy level of 2 J/mm. After the impact, the damaged area was evaluated with ultrasonic C-scan and the specimens were further compression loaded, following the procedure and conditions prescribed in the test protocol. Each CAI data reported was an average of three successful tests.

3. Results and Discussion

3.1. Thermal mechanical properties of matrix resin system

DMTA as a complementary method is usually used to study the phase separation behavior of polymer blends^[22]. For the PAEK modified BMI blends, it is apparent in Fig.3 that there are two relaxation peaks in the tan δ curves for the PAEK-rich and BMI-rich phases, respectively. These peaks represent T_{g} of the two phases. The higher temperature peaks are attributed to the BMI-rich phase and the lower one to the PAEK-rich phase. The two glass transition temperatures are listed in Table 1 for accurate comparison. As seen from the table, T_g of the curved neat BMI resin, at 1 Hz, is about 298.7 °C, whereas, that of the neat PAEK is about 230 °C. Because the presence of soluble PAEK lowers the glass transition temperature of the BMI, $T_{\rm g}$ of the BMI-rich phase declines slightly at first and then steadily, with the PAEK concentration steadily increasing. This steady decline is attributed to the increase in the total amount of PAEK added and dissolved in the BMI-rich phase. Correspondingly T_{g} of the PAEK-rich phase increases initially to about 10 °C because of the presence of dissolved BMI in this phase, and then slightly decreases for the higher PAEK concentrations. The effect of PAEK concentration on

the storage modulus of the PAEK-BMI systems is evident in Fig.3(b). A similar blending effect has also been found in the thermal-mechanical properties of polyetherimide (PEI) modified BMI blends^[4,23].



Fig.3 Loss factor (tan δ) and storage modulus against temperature plots for PAEK modified BMI systems with various PAEK concentrations.

Table 1 T_g of PAEK-rich and BMI-rich phase and corresponding phase morphology

	$T_{\rm g}$ /°C			
Specimens	PAEK phase	BMI Phase	Phase morphology (see Fig.4)	
Neat BMI	_	298.7	Single-phase	
Neat PAEK	230.0	_	Single-phase	
5 phr PAEK	240.5	297.4	Sea-island, with PAEK as island (Fig.4(a))	
10 phr PAEK	240.0	297.3	PAEK particles, partially continuous (Fig.4(b))	
15 phr PAEK	239.0	296.2	PAEK-BMI co-continuous, phase inverted (Fig.4(c))	
20 phr PAEK	238.6	295.9	PAEK-BMI co-continuous, phase inverted (Fig.4(d))	
30 phr PAEK	238.4	295.7	PAEK-BMI co-continuous, phase inverted (Fig.4(e))	

3.2. Morphological spectrum of matrix resin system

The series of micrographs in Fig.4 illustrate the

characteristic changes in the phase morphologies of the PAEK modified BMI blends with various PAEK concentrations by means of a SEM. The specimens were chemically etched as described earlier, prior to the examination, using SEM. The PAEK-rich phase had been preferentially etched away.

In the experiments, the amorphous PAEK was found to be soluble in the BMI resin to form a homogenous single-phase mixture until a critical concentration level was exceeded. At the PAEK concentration of about 5 phr, a second phase, rich in the thermoplastic polymer, was observed as shown in Fig.4(a). The chemically etched PAEK-rich domains, left holes with diameters of about 0.5-1.5 μ m uniformly dispersed in the BMI matrix. This was the typical "sea-island" phase morphology with the PAEK-rich phase as islands. The occurrence of the second-phase deposition typically obeys the chemical reaction-induced phase separation mechanism^[24-25].



(a) 5 phr



(b) 10 phr



(c) 15 phr

(d) 20 phr



(e) 30 phr



As the amount of PAEK was further increased, the phase-separated PAEK-rich particles became larger and were associated. In the meantime, the BMI-rich particles were first observed to form with these second-phase particles (Fig.4(b)), resulting in the development of a partially continuous, complex morphology. Then, as further PAEK was mixed to a level of about 15 phr, a phase-inverted morphology occurred that consisted of the distributed and partially connected BMI-rich particles and nodules in a continuous PAEK- rich phase (Fig.4(c)). The sizes of the BMI particles and/or the statistical periodic distances between the particles were approximately 3.5-4.0 µm (Fig.4(c)). It is believed that, around this threshold concentration of PAEK modification, a larger-scale network of BMI- rich domains was first established, forming a characteristic PAEK-BMI cocontinuous microstructure in nature.

For the further increase of PAEK, higher than 15 phr, the co-continuous phase morphology developed in a self-similar manner. However, the BMI particle sizes and/or the statistical periodic distances between them declined as shown in Fig.4(d) and Fig.4(e).

The BMI particle sizes and/or the statistical periodic distances were then carefully determined. The result is shown in Fig.5 and Table 2. It is obvious that the diameter of the BMI-rich particles and nodules or the statistical periodic distances decrease with an increase in the PAEK concentration. An average diameter D of about 3.58 µm was measured for a 15 phr PAEK concentration, 1.75 µm for the 20 phr, and 1.21 µm for the 30 phr, respectively. The standard deviation δ was also determined using a statistical analysis Eq.(1) and reported in Table 2.

$$\delta = \left[\begin{array}{c} \sum_{i=1}^{n} (D_i - D)^2 \\ \frac{1}{n-1} \end{array} \right]^{1/2}$$
(1)

where D_i stands for the average diameter of the BMI particles or the statistical periodic distance n for the



Fig.5 Statistical determination of diameters of BMI- rich domains (statistical periodic distances) for phaseinverted PAEK-BMI blends.

Table 2Statistical determination of D of BMI-rich do-
mains and δ

Specimens	D/µm	<i>δ</i> /μm
15 phr PAEK	3.58	0.531
20 phr PAEK	1.75	0.262
30 phr PAEK	1.21	0.228

statistical number of BMI particles. With the PAEK concentration increasing, δ becomes smaller, implying that the BMI-rich particles or the statistical periodic distances behave more uniformly.

Thus, a series of different morphologies were generated as the PAEK concentration varied and these, in turn, could be seen to strongly influence the thermal mechanical characteristics of these systems (refer to Table 1).

3.3. Structure-property relationship of matrix resin system

Fracture toughness of the PAEK modified BMI blends was studied as a function of the concentration of PAEK added and the results are shown in Fig.6. There is an initial steady increase in the fracture toughness because of the presence of dissolved PAEK in the BMI matrix, and then an accelerated increase begins at a PAEK concentration of about 5 phr. This is consistent with the onset of phase separation. The maximum toughness is reached at a PAEK concentration of about 15 phr. As is known in Section 3.1 and referred to Fig.4, at this threshold concentration, the phase-separation, the initial phase-inversion, and the phase-co-continuity occurs simultaneously in the blend. It appears that both the phase separation and the initial inversion are required to achieve a significant increase in the fracture toughness of the PAEK modified BMI systems.



Fig.6 Plot of impact fracture toughness against PAEK concentration for PAEK-BMI systems.

However, this rapid increase is interrupted and a significant toughness drop is found in Fig.6 as the

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PAEK concentration is going higher than 15 phr. Over this threshold value the toughness decreases rapidly. Many researchers^[4,22-23] studied PEI toughened epoxies and BMIs separately, and reported a similar behavior in the toughness versus PEI concentration. As they reported, the epoxy-rich domains of the phase-inverted systems gradually decreased with the increase of PEI and there was no further improvement in toughness over a critical threshold of PEI concentration. It was generally understood that the effect of thermoplastic toughening would not be obtained unless the thermoplastic was added at 20 wt% or greater, depending on the two-phase systems. For the PAEK toughened BMI, the critical PAEK threshold seemed to be around 15 phr for the toughness improvements.

As far as the basic micromechanism responsible for the increase in measured toughness in thermoplastic toughened thermosetting polymers is concerned, C. B. Bucknall, A. H. Gilbert^[26] and J. L. Hedrick et al.^[27] have concluded that ductile tearing in the thermoplastic-rich phase is the major mechanism, where no plastic yielding of the thermosetting-rich phase was observed. In the present study, it is evident that the crack growth occurs through both the phases and the crack process is essentially brittle in nature. As shown in Fig.7 for a 20 phr the PAEK toughened the BMI blend over the threshold value for phase inversion. There is no clearly identifiable toughening mechanism, plastic drawing, deformation, or ductile failure found. A fracture toughness of about 17 kJ/m² has been measured for the blend. It is apparent that the complex nature of the materials precludes a straightforward interpretation between the microstructure and fracture properties.



Fig.7 SEM micrographs showing crack propagation in the PAEK-BMI system (20 phr PAEK).

3.4. Surface-diffusion controlled morphology spectrum of matrix resin system

Another aspect in the present study was to study the surface-diffusion controlled morphology development of the PAEK-BMI systems. As a model, the PAEK film was bonded in close contact with the bulk uncured BMI. As the temperature rose to an appropriate degree, both the low molecular BMPM and DABPA began to diffuse into PAEK. The amount, diffusion rate, depth, and distribution of BMPM and DABPA that diffused into PAEK depend on the time and temperature conditions, and especially on the mutual dissolvability of the respective components. The diffusion process was additionally accompanied with the curing reaction of BMPM and DABPA, and the reaction-induced spinodal phase separation of PAEK from BMI^[28].

Fig.8(a) shows a representative global cross-section of the interface region of the model system between PAEK and cured BMI. The initial thickness of the PAEK film was about 18 μ m. However, as mentioned before, the PAEK film itself was chemically fully etched away. The remainder in the micrograph was the fully cured BMI.

There are approximately four regions of different characteristic morphology spectrum identifiable in the micrograph. They include, from left to right, the surface region (Fig.8(b)), the transition region, the region rich in larger BMI particles (Fig.8(c)), and the bulk BMI region (Fig.8(d)), respectively.



Fig.8 Cross-section of PAEK-BMI laminated specimen with morphology spectrum. ((b), (c), and (d) are the high magnification micrographs of (a))

At a higher magnification of the surface region where the previous PAEK film is located in Fig.8(b), it is obvious that a co-continuous nodular BMI structure is established. The morphology and the nodule sizes look roughly very similar to those shown in Fig.4(b) or Fig.4(c) and/or in a stage in-between. This result reveals that the low molecular BMPM and DABPA had diffused into and penetrated throughout the entire PAEK film, reacted with each other in PAEK and phase- separated simultaneously from PAEK, even when the BMI concentration must have been the lowest on the surface region in this section, by taking the direction of the diffusion, from right to left in the micrograph, into consideration.

From Fig.8(c), it is clear that there are many considerably larger BMI particles, about 7-8 μ m in diameter, concentrated to form a rough line in a location about 40-50 μ m from the previous surface of the PAEK film. Because the previous PAEK film was only 18 μ m thick, it is evident that the low molecular BMPM and DABPA had made the PAEK film swell in thickness from the initial 18 μ m to about 75 μ m, thereby lowering the PAEK density and enhancing the BMI diffusevity to form larger BMI particles. In the PAEK-rich region among the larger BMI particles, there is a connected granular morphology observed. The fine sizes of the BMI granular domains were found to be about 2.5-3.0 μ m to 0.5-1.0 μ m. As mentioned previously, this microstructure should result from the reactioninduced phase separation and inversion, depending additionally on the component densities and concentrations. The broad and contrasted spectrum of the sizes of BMI granules is characteristic for this region.

It is interesting to note that the macromolecular PAEK had also possibly penetrated into the bulk BMI resin to form the "islands" in the continuous BMI "sea" (Fig.8(d)).

The one-side diffusion controlled phase morphology can also be found in the "sandwich" specimens with a central PAEK thin film symmetrically covered by two thick BMI resins on both sides (Fig.9). In this model, the swelling effect of the low molecular uncured BMI in the PAEK film was slightly constrained and inhibited. As shown in Fig.9, the previous 18 μ m thick PAEK film had swelled to a thickness of about 60 μ m. On both the near-boundary regions the co-continuous nodular and granular phase structure was clearly observed again (Fig.9(b) and Fig.9(c)).



Fig.9 Morphology spectrum of the BMI-PAEK-BMI "sandwich" ((b), (c) are the high magnification micrographs of (a)).

In general, the morphology spectrum in the interface-diffusion controlled PAEK-BMI specimens is controlled by the BMI concentration, which, in turn, is governed by the simultaneous diffusion of low molecular components, swelling of PAEK, cross-linking reaction of BMI, and the BMI concentration dependent phase-separation and inversion behaviors. In other words, the diffusion model can ideally be used to study the complex behavior of composition dependent diffusion, swelling, reaction, phase decomposition, and inversion of thermoplastic modified thermoset systems at the same time, with only one specimen.

3.5. Interlaminar morphology spectrum in graphite fiber laminated composite system

The basic idea of the ex-situ concept is to maximize the potential of thermoplastic-toughening effect by a sophisticated spatial design for laminated composite systems^[20,29-32] where the interlaminar regions are intentionally highly toughened (inter-laminar toughening), whereas, the graphite plies are nontoughened. Thus, the ex-situ concept is in principle a spatially localized toughening concept. Many important aspects and conditions in prepreg handling and fabrication-like processability, drapability, and so on, of the traditionally over-all-toughened prepregs can be considered and even improved. According to this concept, the PAEK-toughened BMI must be placed in the inter-laminar regions for the BMI matrix graphite composites instead of replacing the interlaminar BMI resin by pure PAEK, whereas, the graphite plies should merely be impregnated with the neat BMI as usual.

Fig.10 shows a representative cross-section of the $0^{\circ}/45^{\circ}$ interlaminar region of such an ex-situ toughened BMI laminate composite by means of SEM. As seen, the interlaminar region is about two to three fibers thick.



Fig.10 Representative of interlaminar morphology of pure PAEK-toughened BMI-graphite fiber laminates through ex-situ concept ((b) is the high magnification of (a)).

According to the provider's information, the BMI matrix prepregs were previously coated with pure PAEK. However, after the autoclave curing and specimen preparation, this continuous PAEK phase had chemically been washed out prior to the SEM examination. Higher magnification (Fig.10(b)) revealed that the continuous BMI granular domains occurred in the entire interlaminar region, implying that during specimen curing the BMI components diffused throughout the PAEK-rich interlaminar layers. A global network of the BMI granular and nodular morphology was thereafter established in the interlaminar regions as desired for the ex-situ concept. This process reflects the complex behavior of diffusion, reaction, phase separation and inversion, and impregnation as studied on the model system described in Section 3.4. The phase morphology is thus identical in many aspects to

that shown in Figs.9(b) and 9(c). However, the statistical periodic distances and/or the nodule sizes, about 0.5 μ m, in the interlaminar region seem to be finer than that in the model system. The size reduction might be attributed to the vacuum/pressure conditions during the composite specimen fabrication. It might also be caused by the constrained volume between the graphite plies compared to the model system (Fig.9), cured in open conditions where the PAEK layer was swellable.

If the pure PAEK coated prepregs were replaced with a coating of PAEK toughened BMI resin with a ratio of 60:40, there was generally no significant difference in the phase morphology observed, compared with that of the pure PAEK coating. A representative micrograph is shown in Fig.11 for comparison with Fig.10.



Fig.11 Representative of interlaminar morphology on PAEK toughened BMI (60:40) laminates through ex-situ concept ((b) is the high magnification of (a)).

3.6. CAI properties—structure relationship

The CAI for the nontoughened and ex-situ toughened BMI graphite laminates are listed and compared in Table 3. As is known, the BMI matrix composites are intrinsically brittle. The CAI of the neat BMI composite specimen is about 180 MPa. The laminates, ex-situ toughened with initial pure PAEK coating, show a much higher CAI of about 254 MPa. However, the highest CAI is achieved by specimens ex-situ toughened with the initial coating of the PAEK-BMI blend, with a ratio of 60:40. It is as high as 290 MPa, about 160% higher than that of the control.

Table 3 CAI data	of	composite	laminates	studied
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Specimen	Toughening method	CAI /MPa	Data deviations /%
1	None-toughened	180	2.13
2	Ex-situ toughened with pure PAEK	254	8.70
3	Ex-situ toughened with PAEK-BMI blend of 60:40	290	3.27

It was evident in the fracture toughness tests on the resin systems that there is a strong relationship between the phase morphology and toughness of the PAKE toughened BMI blends. As also reported by X. S. Yi^[24], co-continuous nodular morphology at the threshold of the phase inversion is the hallmark for the high toughness of the PAEK toughened epoxies blends. The behavior held true for the impact tests of the BMI graphite composites ex-situ toughened. It is thought that the co-continuous nodular and granular morphology spectrum takes responsibility for the high impact damage resistance characterized by CAI. However, it is not clear why the CAI improvement on the specimens ex-situ toughened initially with the PAEK-BMI blend, with a ratio of 60:40, is about 20% higher than that of the pure PAEK modification, even though their morphologies appear very close to each other.

To understand the effect of the phase morphology effect on the impact damage resistance and particularly the effect of ex-situ interlaminar toughening on the CAI in the graphite laminates, the cross-section of the laminate specimens impacted and compression loaded was studied using an optical microscope. The representative global micrographs are presented in Fig.12, each of them with a local magnification. It is clear that the crack propagation occurs smoothly along many resin-rich interlaminar layers between the graphite plies for the nontoughened specimen, leading to delamination and microbuckling of the laminated graphite system (Fig.12(a)). This appearance implies that the interlaminar resin remains naturally brittle and the bond strength between each ply appears to be relatively weak. Fig.12(b) shows that the delamination tendency is obviously suppressed by numerous transverse cracks through the graphite plies for the ex-situ toughened specimen, with the initial PAEK-BMI blend coating in the ratio of 60:40. It is suggested that the energy required for the cracks to grow and coalesce is not high enough to form delamination, because of the energy being absorbed by the typical co-continuous granular domains formed specifically in the interlaminar regions by the ex-situ concept. Higher crack propagation resistance in the crack path is thus thought to be the major mechanism for the ex-situ concept.



(b) Ex-situ toughened specimen

Fig.12 Representative cross-sections of the BMI/graphite laminates impacted and compression loaded in the CAI test.

4. Conclusions

The ex-situ concept has been demonstrated as a highly successful technique for toughening in the present study on BMI matrix/graphite composites, by using a spatial arrangement of the phase separated and inverted morphological microstructure specifically placed in the interlaminar regions. The phase separated and inverted morphology at the threshold has been proven as a characteristic hallmark for the efficient toughening of the inherently brittle BMI resins, toughened with the amorphous thermoplastic PAEK. The graphite plies themselves have been fully impregnated with the BMI as usual for the intrinsically high specific strength and modulus of the laminated systems. As a preliminary result, the BMI matrix laminates ex-situ toughened initially with the pure PAEK coating exhibit an increase in compression after an impact of about 40%, and for the laminates initially coated with a PAEK-BMI blend of a ratio of 60:40, an increase of about 60%, when compared with the untoughened control specimens.

The micromechanisms of impact fracture have been studied and there has been no indication of plastic yielding of the BMI-rich or PEAK-rich phases on the model specimens. However, the crack must clearly be deflected as it advances into the co-continuous and phase-inverted BMI-PAEK material. This will lead to an increase in toughness for the unreinforced material. Also, in the graphite composites, the crack must advance by fracture of the co-continuous BMI-PAEK phases into the interlaminar region. It is considered that, first, in this two-phase microstructure, when they dissolve partially with each other, to toughen the inherently brittle BMI, it will undoubtedly be tougher than the BMI-rich phase. The limited mutual solubility between PAEK and BMI has been confirmed by the thermal mechanical analysis. Second, the energy required for the cracks to grow and coalesce is not high enough to form a delamination, because of the energy being absorbed by the typical co-continuous, twophase, granular domains formed specifically in the interlaminar regions by the ex-situ concept. Thus, when the characteristic microstructure forces the crack to advance through the co-continuous phase, this leads to an increase in the measured delamination resistance.

Considering the structure-property relationships it appeared that phase separation and inversion at the threshold were required to achieve a significant increase in the toughness of the PAEK modified BMIs. This relationship held true for the ex-situ toughened graphite composites.

A special feature of the ex-situ concept is the diffusion-induced phase behavior. It has been shown that the composition dependent nature of simultaneous diffusion of the low molecular BMPM and DABPA into the high molecular PAEK to make it swell, the cross-linking reaction of BMPM and DABPA in PAEK, phase-separation and inversion in the BMI-PAEK blend, and finally the flow and impregnation ability, which prevents the voids and fabrication defects are very complex. For the complex behavior a quantitative study is obviously needed to establish the relationship. This investigation is ongoing at LAC of BIAM in Beijing.

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