"*Ex Situ*" Concept for Toughening the RTMable BMI Matrix Composites, Part I: Improving the Interlaminar Fracture Toughness

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ABSTRACT: Aerospace-grade bismaleimide matrix composites was toughened based on a novel *ex situ* resin transfer molding (RTM) technique using a special manufactured ES^{TM} carbon fabrics. The toughening mechanism and toughening effect by the technique are studied using thermoplastic PAEK as toughener. Mode I fracture toughness (G_{IC}) of the composites toughened by *ex situ* RTM technique increased up to three times higher than that of the control system, and Mode II fracture toughness (G_{IIC}) increased two times higher as well. The composite without toughening was denoted as control system. The microstructure revealed that a reaction-induced phase decomposition and inversion happened in the interlaminar region, which resulted in a particles morphology that showed the thermosetting particles were surrounded with the PAEK phase. The plastic deformation and rupture of the continuous PAEK phase are responsible to the fracture toughness improvement. And the influence of PAEK concentration on toughness improvement was also investigated. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1625–1634, 2008

Key words: *Ex situ* RTM technique; resin transfer molding; fracture toughness; fractography; toughening mechanism

INTRODUCTION

Resin transfer molding (RTM) has been an efficient and economical technique to produce high-quality fiber-reinforced composite parts. This process combines the advantages of low injection pressure, short cycle time, and low-cost equipment with the ability to produce parts of complex shape. Practically, the operations in closed mold tool in a typical RTM process cycle include an injection of catalyzed resin into the mold and resin curing. The quality of RTM parts and the efficiency of the process depend strongly on the viscosity of the so-called RTMable resin system in the filling stage, however, the mechanical properties of the resulting parts are not only significantly affected by the inherent properties of resin but also by the reinforcing fiber, the fiber volume fraction, and the product qualities.

High toughness and impact damage resistance of the composites are required in aerospace applications, there is a compromise between the performance and affordability for RTM versus autoclave components. A traditional approach to improve the toughness of prepreg-grade composites is to toughen the matrix resin by introducing thermoplastic component into the matrix to form phase separated matrix structure.[1–5] However, a dramatic increase in matrix viscosity because of the addition of the toughening polymer with high molecular weight decreases the flow and impregnation ability, that is, the traditional toughening method works poorly for the RTM technique. The commercial RTMable resin systems are thus not toughened.[6] Over the past decade, few literatures have been reported to toughen the RTMable resins without sacrificing their flow characteristics.[7]

Cytec Company introduced a new toughening technology called Preform™ for RTM technology in 2003.[8] A special cowoven or cobraided fabric is produced with both the reinforcing carbon fibers and the thermoplastic toughening fibers obeying a well designed structure and volume fraction ratio between the fibers. During the mold filling stage, an untoughened thermosetting resin is injected at an appropriate temperature into the mold impregnating through the fabrics. After the filling stage is completed, the mold temperature is raised to a higher temperature to melt the thermoplastic fibers cowoven or cobraided

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with the reinforcing fibers and in the same time to initiate the crosslinking reaction of the thermosetting resin. Assuming that the thermoplastic fiber is soluble at the temperature in the thermosetting resin, the thermosetting matrix resin is consequently *in situ* and overall toughened. The toughening process is accompanied with the interdiffusion between the two components and curing conditions in the entire matrix.

An innovative concept, the so called *ex situ* was proposed by Yi in 2003.[9] The key advantage of *ex situ* technique is to significantly increase the interlaminar properties of thermosetting resin matrix carbon composites by toughening selective and specifically in the interlaminar regions.[10–14] ''*Ex situ*'' means in the context that, instead of using a thermoplastic toughened thermosetting matrix as an entity for the composite, the toughening polymer is first abstracted from the blend and used to coat the reinforcement. As the untoughened thermosetting resin is injected and the composite is cured, highly toughened thermoplastic-rich layers are established spatially in the thin interlaminar regions whereas the carbon plies remain thermosetting resin-rich. The microstructure of the interlaminar layers is characterized by the phase separated and inverted morphology. The *ex situ* concept has successfully been demonstrated for improvement in impact damage resistance for prepreg-grade composites based on epoxy,[10–12] BMI,[13] and PI[14] both for unidirectional carbon (UD) and cross-ply laminates cured in autoclave. The *ex situ* technique developed by this concept has been patented.[15]

Encouraged by the success for the state-of-the-art prepreg composites manufactured in autoclave, the study was extended to explore the *ex situ* RTM toughening concept.[16] Preliminary experiments validated that the *ex situ* RTM toughening technique worked well with RTMable low viscosity, untoughened epoxy (EP), bismaleimide (BMI), and polybenzoxazine (PBO) resins.[17] The key component in the study was the generically preformed carbon fiber reinforcements, trade-named as ES^{TM} fabrics patented by the National Key Laboratory of Advanced Composites.[15] The fabrics were sophisticatedly coated with the soluble polymer toughener based on the

TABLE I
Typical Mechanical Properties of BMI Resin

Properties	BMI (6421)
Tensile strength (MPa)	67.6
Tensile modulus (GPa)	2.28
Elongation at break (%)	1.88
Flexure strength (MPa)	119.5
Flexure modulus (GPa)	4.12
Impact strength (kJ/m^2)	14.3

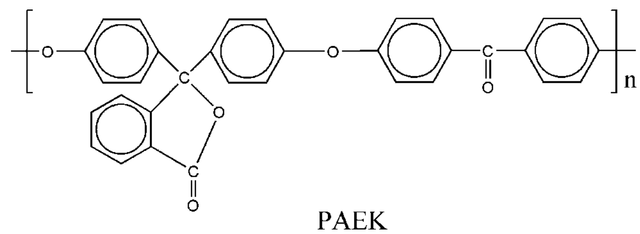

Figure 1 Molecular formula of the toughener PAEK.

ex situ RTM toughening technique, which provides also good tackifying ability.

This study deals with the interaction of the toughening polymer with the RTMable BMI resin. The aerospace-grade RTM composites panels were fabricated based on the *ex situ* RTM technique with the ES^{TM} carbon fabrics. The interlaminar toughness was characterized by G_{IC} and G_{IIC} and the fractographic features. The impact resistance and damage tolerance of composites toughened through *ex situ* RTM technique and the effect of *ex situ* RTM technique on the in-plane properties of composites were also studied and will be reported in a subsequent article*, which will be published soon. The whole work belongs to programs carried out at the National Key Laboratory of Advanced Composites (LAC/BIAM) to promote the wide application of advanced composites in aerospace industry.

EXPERIMENTAL

Materials

A bismaleimide (BMI) under a trade-name of 6421 was produced at the National Key Laboratory of Advanced Composites and used as the RTMable resin system in the study. The typical mechanical properties of the cured BMI are listed in Table I. The resin is commercialized by the Beijing Institute of Aeronautics Materials (BIAM).

The commercial G827 carbon cloth (T300-3k, 160 g $\pm$ 7 g/m^2, Hexcel) is used as the reinforcement materials.

The toughening polymer was an amorphous engineering thermoplastic polyetherketone with a functional group of phenolphthalein (PAEK).[18–20] It has an intrinsic viscosity of 0.30 dL/g and a glass transition temperature (T_g) of 230°C. The PAEK was supplied by Xuzhou Engineering Plastics Factory, China. The molecular structure of the PAEK is shown in Figure 1. The amount of PAEK used to toughen composite was calculated by wt % in matrix resin. There were two variable amounts of the PAEK concentration namely 16.8 and 20.2 wt %, respectively.

*''*Ex situ*'' Concept for Toughening the RTMable BMI Matrix Composites, Part II: Improving the Compression After Impact.

Specimen preparation

RTM technique was applied to manufacture the composite panel, the ES™ carbon fabrics was used as reinforcement material. The ES™ carbon fabrics coated with the toughening polymer PAEK were provided by the LAC using a special fabrication procedure patented.[15,16]

The ES™ carbon fabrics were first placed in a closed RTM mold tool. Then the RTMable resin was injected at 120°C under a pressure of 0.2 MPa into the mold to impregnate the porous ES™ carbon fabrics. The mold temperature was raised at a rate of 2°C/min to the two step curing temperatures, followed by a postcuring. After that, the mold was cooled down to 60°C and the composite panel was released. The profile for temperature control is given in Figure 2. All the RTM panels were finally ultrasonically C-scanned to check for molding defects and to examine the quality according to the aerospace standard specifications.

The interlaminar PAEK concentration was calculated by wt % in matrix resin. The composite panel's RTM-manufactured with G827 were controlled in the thickness of about 3.0 ± 0.1 mm. The overall fiber volume fraction was controlled at 55% (±2%).

For comparison, control systems were manufactured. The basic lay-up of the carbon fabrics and the injection and curing conditions were identical with the control systems using uncoated fabrics.

Fracture measurements

All specimens for both Mode I and Mode II fracture toughness tests were cut from the *ex situ* RTM technique toughened panels. Fracture toughness experiments were performed on a MTS 880 testing machine.

A standard double-cantilever beam (DCB) specimen was used to measure Mode I interlaminar fracture toughness, according to Chinese Aviation Industry Standard HB 7042-96,[21] as shown in Figure 3. The DCB specimens were 25 mm wide, 180 mm long, and 3.0 ± 0.1 mm thick. A PTFE film of 25 μm thick was inserted in the mid-plane to create an initial crack. A load was applied in the perpendicular direction to upper surface of the sample at a speed of 2 mm/min. During each loading cycle, the displacement and the crack length were monitored.

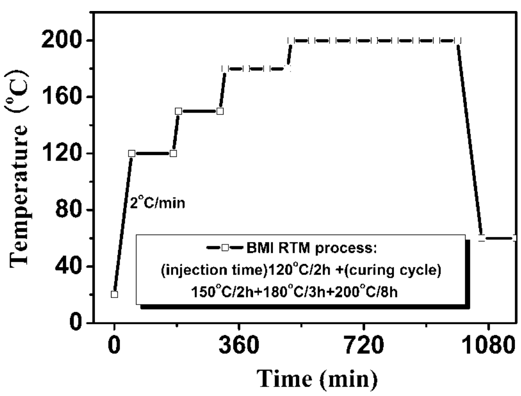

Figure 2 The RTM composite manufacturing process.

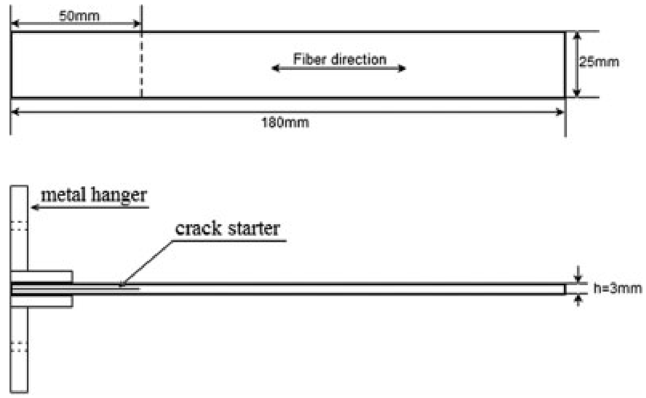

Figure 3 Schematic of specimen used for DCB delamination resistance testing.

The critical strain energy release rate, G_{IC}, is calculated by the following equation:

$$G_{IC} = \frac{mP\delta_e}{2aW}$$

where m is an exponent of the experimental compliance, P is the applied critical load, δ_e is the displacement corresponding to P, a is the crack length, and W is the specimen width, respectively.

An end notch flexure (ENF) test specimen was used to measure Mode II interlaminar fracture toughness according to the Chinese Aviation Industry Standard HB 7043-96[22] as shown in Figure 4. The ENF specimens were 25 mm wide, 140 mm long, and 3.0 ± 0.1 mm thick. A PTFE film of 25 μm thick was also inserted in the mid-plane of laminates.

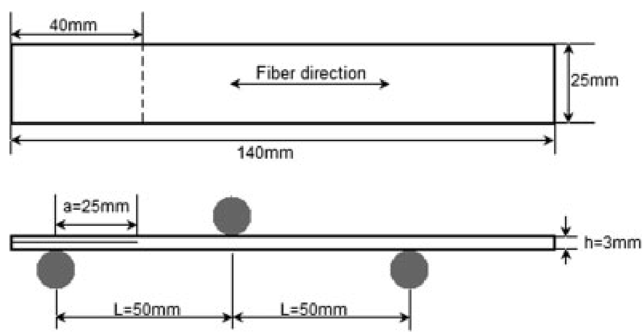

Figure 4 Schematic of specimen used for ENF delamination resistance testing.

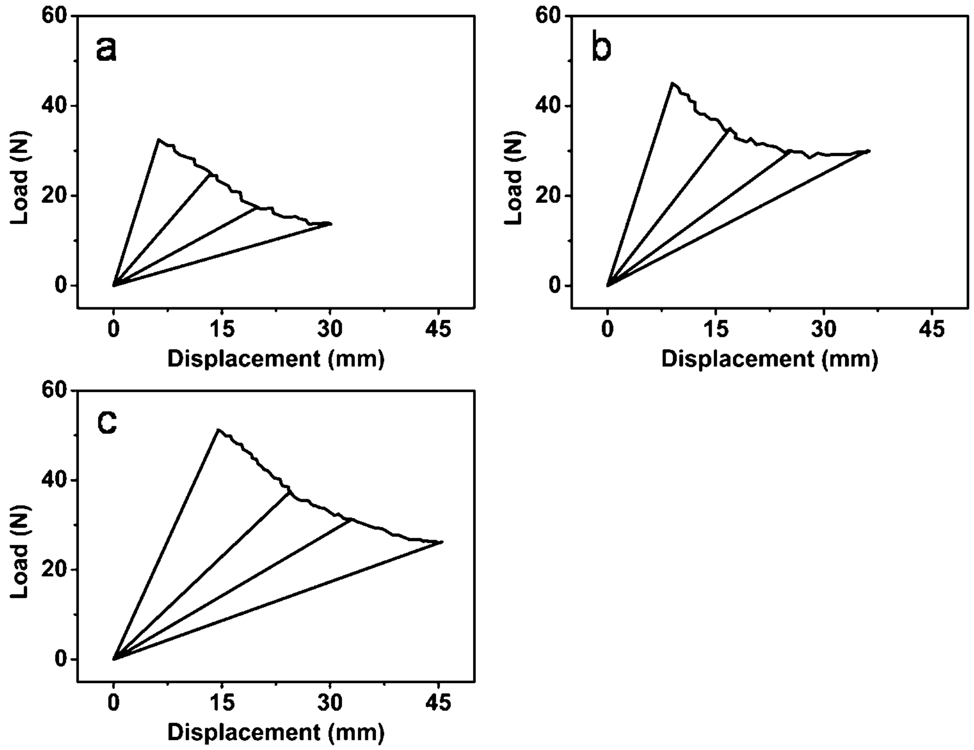

Figure 5 Typical load-displacement curves of the specimens in the Table II under Mode I test: (a) Specimen 1; (b) Specimen 2; and (c) Specimen 3.

Three-point bending apparatus with two stationary support posts of 100 mm apart was used to create shear fracture in the mid-plane. The loading point was in the center between the two stationary posts and the crack tip was at 25 mm from the stationary post, as shown in Figure 4. A displacement rate of 2 mm/min was used to load the specimen in flexure until the load decreased upon crack propagation.

Mode II fracture toughness, G_{IIC}, is calculated as:

$$G_{IIC} = \frac{9P\delta a^2}{2W(2L^3 + 3a^3)}$$

where P is the applied critical load, δ_e is the displacement corresponding to P, a is the crack length, W is the specimen width, and L is the half span length.

Fractographic studies and cross section observation

The fracture surface of specimens after Mode I and Mode II tests was observed using a scanning electron microscope (SEM, Hitachi S-3000N). The crack propagation tip was observed using optical microscope (OM, LEICA DMRME Germany).

The specimens were washed in an ultrasonic bath and dried for 4 h at 60°C under vacuum. All specimens for SEM were coated with a gold layer of 200 Å thick.

RESULTS AND DISSCUSSION

Fracture energy properties

All specimens were cut from the *ex situ* RTM technique toughened panels. The investigation was carried out with the PAEK content as the variable. The load-displacement curves of the G827/BMI laminates under Mode I test are shown in Figure 5, where each triangle represents one loading/unloading cycle. The applied critical load P increased with

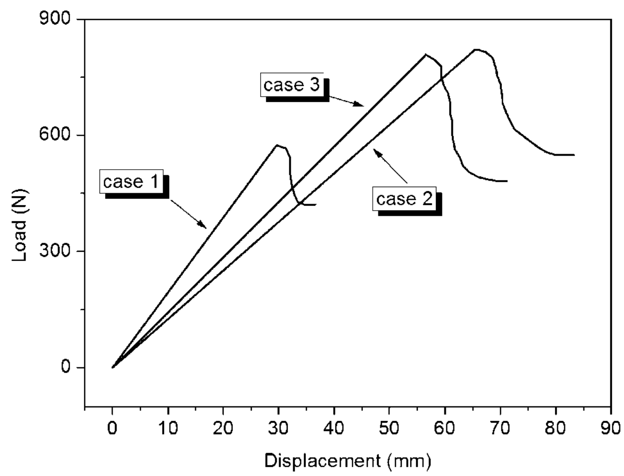

Figure 6 The load-displacement curves of the specimens in Table II under Mode II test.

TABLE II
The Interlaminar Fracture Toughness G_{IC} and G_{IIC} of Composite Laminates Manufactured with G827/BMI Carbon Cloth

Specimen	Matrix Resin	G_{IC} (J/m^2)/C_v (%)	G_{IIC} (J/m^2)/C_v (%)
1	Neat BMI (as control)	215/11.6	510/2.75
2	*Ex situ* RTM technique toughened, with 16.8 wt % PAEK	453/9.13	971/3.26
3	*Ex situ* RTM technique toughened, with 20.2 wt % PAEK	627/3.19	905/5.37

PAEK content, which indicated that the energy needed for crack propagation increased with PAEK content.

Figure 6 shows the load-displacement curves of the G827/BMI laminates under Mode II test. For the control system, the drop is sharp, which indicates that the crack, once initiated, propagated quickly. For the toughened composites, the drop in the load-displacement curves is less steep and the critical load is high, which indicates that the crack propagation in these composites encountered higher resistance.

The G_{IC}, G_{IIC}, and the coefficient of variation (C_V) are listed in Table II. The G_{IC} and G_{IIC} for the neat BMI matrix composites are 215 and 510 J/m^2, respectively. Both values are typical for the traditional brittle BMI matrix composites reinforced with the high volume fraction of carbon fibers. However, both values rise significantly after that the composites are toughened through the *ex situ* RTM technique and as the PAEK content increased. An addition of 16.8 wt % PAEK gives a G_{IC} of 453 J/m^2 and addition of 20.2 wt % gives a G_{IC} of 627 J/m^2; both are twice higher than that of the control system. The toughening mechanism of the improvement in G_{IC} and G_{IIC} will be discussed in section ''Fracture surface characteristics.''

A remarkable increase in the G_{IIC} is also found. However, the relationship of G_{IIC} versus PAEK content is nonlinear. The similar result in Mode II test has been reported by Woo and Mao[23] and Kim and Kim.[24] In conclusions, the efficiency of the *ex situ* RTM technique in toughening the high performance BMI matrix RTMable composites in terms of the interlaminar fracture toughness, G_{IC} and G_{IIC} have been confirmed.

Fracture surface characteristics

The crack propagation in cross section and the morphology of fracture surface of G_{IC} and G_{IIC} specimens were investigated. The crack-tip trace in Mode I loading test for all specimens were shown in Figure 7. There is no crack bifurcation and deflection in control specimen, as shown Figure 7(a). The crack propagated along the interface between the fiber and the matrix, and ended in the BMI-rich region. The cracks of the toughened composites propagated in the interlaminar region, as shown in Figure 7(b,c). The crack deflection, bifurcation, blunting occurred in the toughened composites.

The fracture surfaces of the control system under Mode I and Mode II test were observed by SEM, as

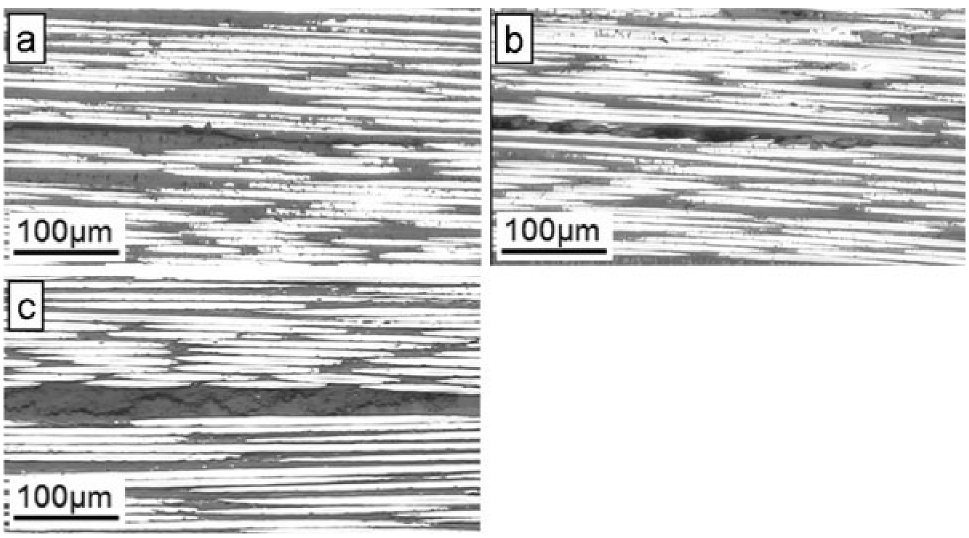

Figure 7 Optical images of the crack-tips: stands for the (a) Specimen 1, (b) Specimen 2, and (c) Specimen 3 in Table II, respectively. The crack propagates from left to right.

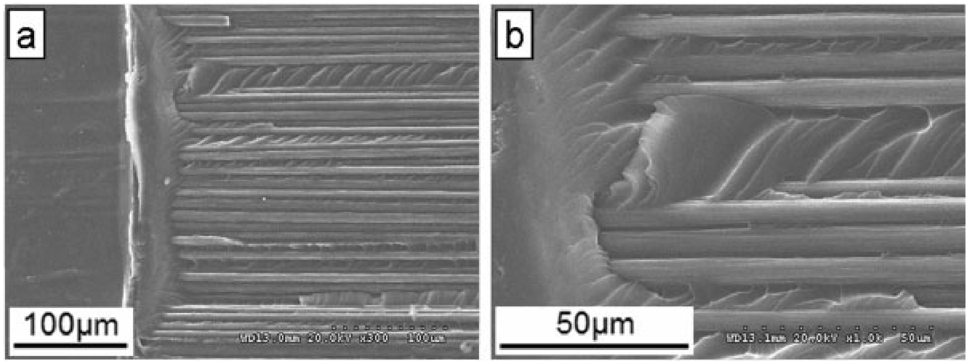

Figure 8 SEM images of the onset of crack propagation of the Specimen 1 in Table II under Mode I test: (a) ×300; (b) ×1000. The crack propagates from left to right.

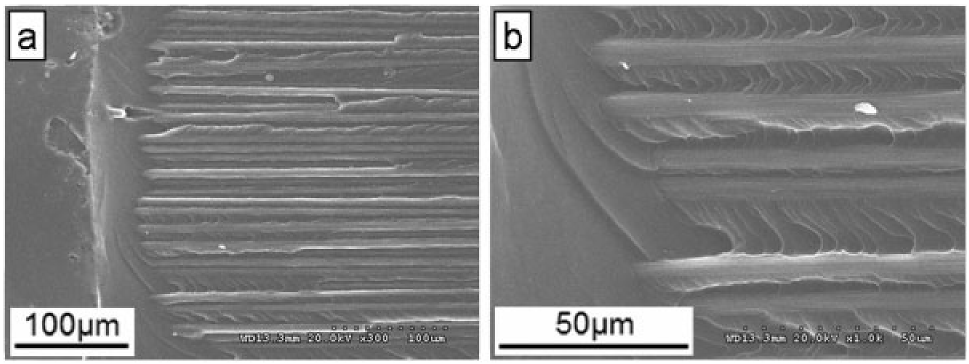

Figure 9 SEM images of the onset of crack propagation of the Specimen 1 in Table II under Mode II test: (a) ×300; (b) ×1000.

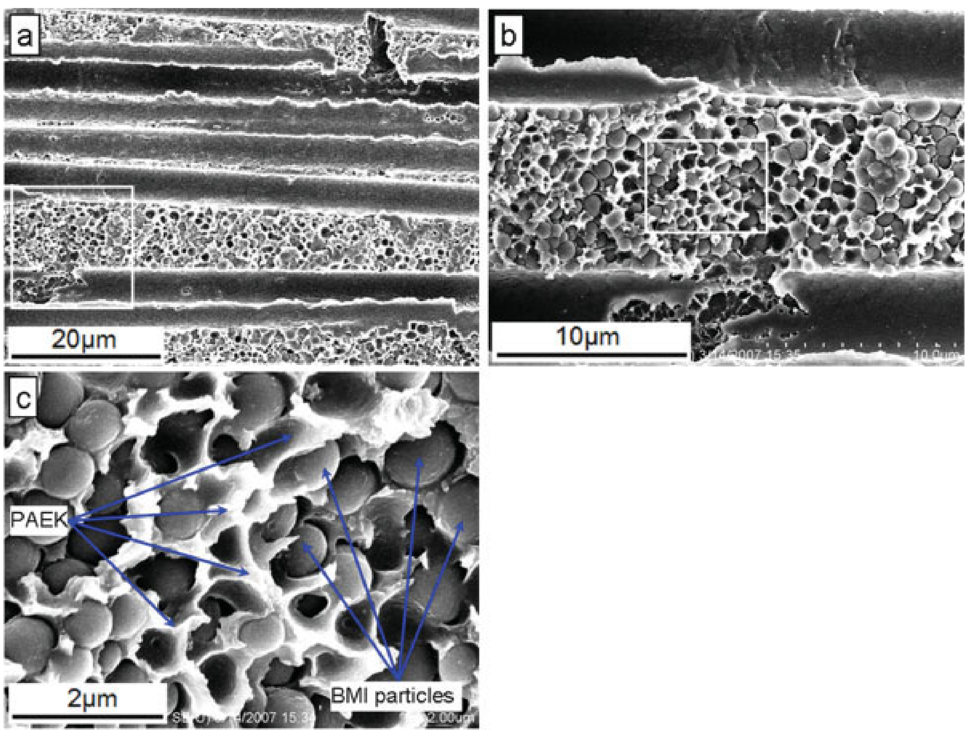

Figure 10 SEM images of fracture surface of the Specimen 2 in Table II under Mode I test: (a) ×2000; (b) ×5000; (c) ×20,000. The crack propagates from left to right. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

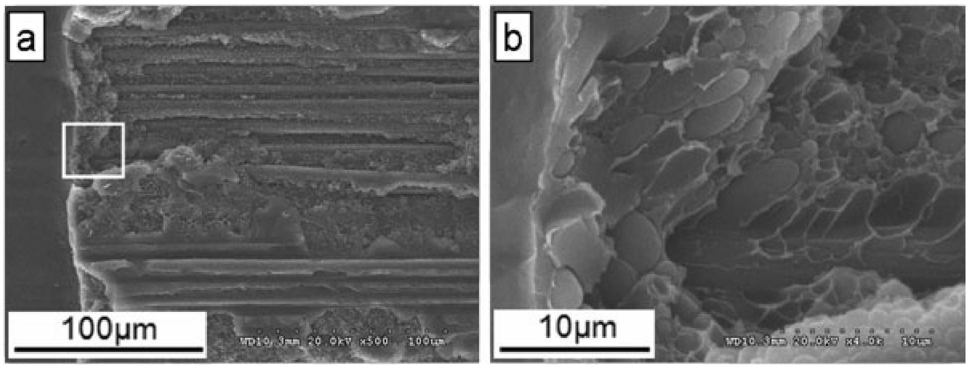

Figure 11 SEM images of the onset of crack propagation of the Specimen 2 in Table II under Mode I test: (a) ×500; and (b) ×4000. The crack propagates from left to right.

shown in Figures 8 and 9, respectively. The characteristic hackle marks are observed on the fracture surfaces, which are typical in samples tested under conditions leading to shear delamination.[25] The matrix resin failed by a series of parallel cracks, which are at an around angle of 45° to the fibers. There is no fiber pullout on the fracture surface, which indicated that no fiber bridging happened.

The fracture surface of composites toughened with *ex situ* RTM technique was much rough, as shown in Figure 10. The typical phase inverted particles structure was confirmed. The BMI-rich particles are surrounded by continuous PAEK-rich phase. The particle is in a small diameter of 0.8 μm. The cavitations or debonding of the particles phases and the plastic yielding of the BMI-rich or PEAK-rich phases is recognized as toughening mechanism. To further explore the toughening mechanism, the onset of crack propagation was investigated by SEM, as seen in Figure 11. Under the G_{IC} test, the crack propagation resulted in the plastic deformation of BMI particles from a shape of globular to elliptical. The

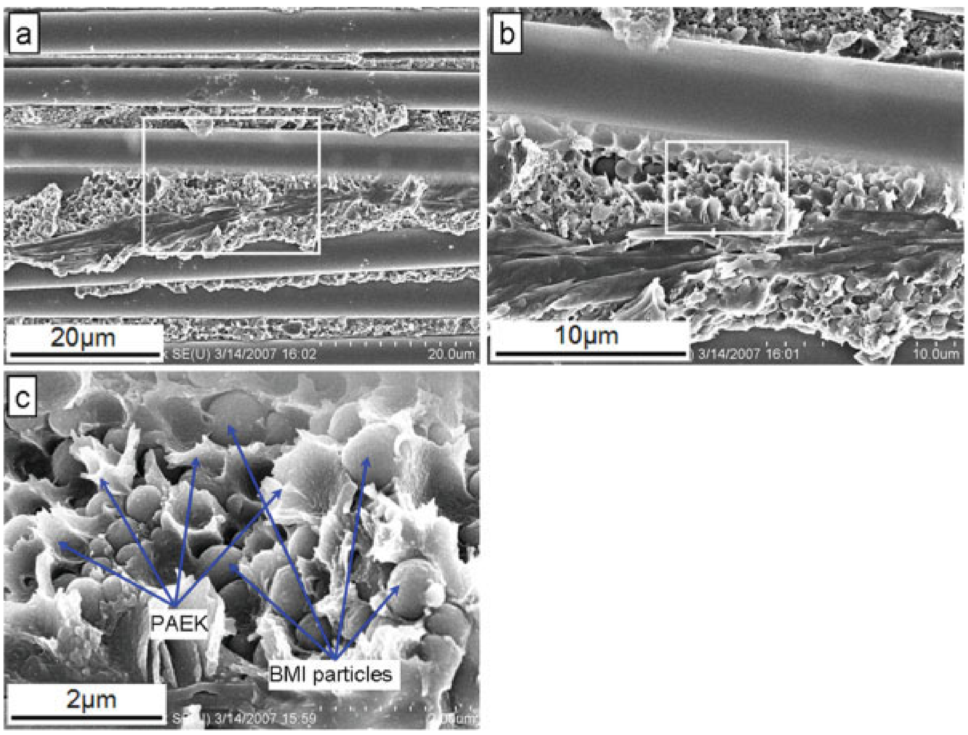

Figure 12 SEM images of fracture surface of the Specimen 3 in Table II under Mode I test: (a) ×2000; (b) ×5000; and (c) ×20,000. The crack propagates from right to left. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

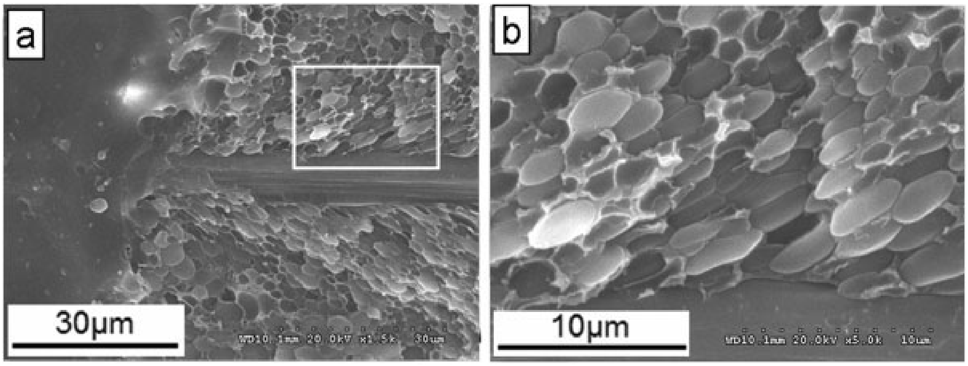

Figure 13 SEM images of the onset of crack propagation of the Specimen 3 in Table II under Mode I test: (a) ×1500; (b) ×5000. The crack propagates from left to right.

orientation of the BMI particles was at an angle of 45° to the fibers, which was similar to matrix hackle marks occurred in control system. The deformation of BMI particles and the plastic tearing of PAEK phase resulted in the increase in G_{IC}.

The G_{IC} increases with an increase in the PAEK content from16.8 to 20.2 wt % correspondingly. The resultant fracture surface is shown in Figure 12. The diameter of BMI-rich particles decreases to 0.4 μm. The decrease in particle size is in a good agreement with the reaction-induced phase separation and coarsening mechanism.[26] The cracks propagate through fracture of the continuous PAEK-rich phase by tearing under the local tensile loading conditions. Higher crack energy may be absorbed by this phase compared to Specimen 2 in Table II. The fracture surface at onset was shown in Figure 13. The fracture morphology was similar to Figure 11.

Similar micrographs for Specimens 2 and 3 in Table II are shown in Figures 14 and 15, respectively. The phase separation and inversion is also observed on the specimens in Mode II tests. Under the three-point bending PAEK phase was obviously torn as a result of the shear deformation

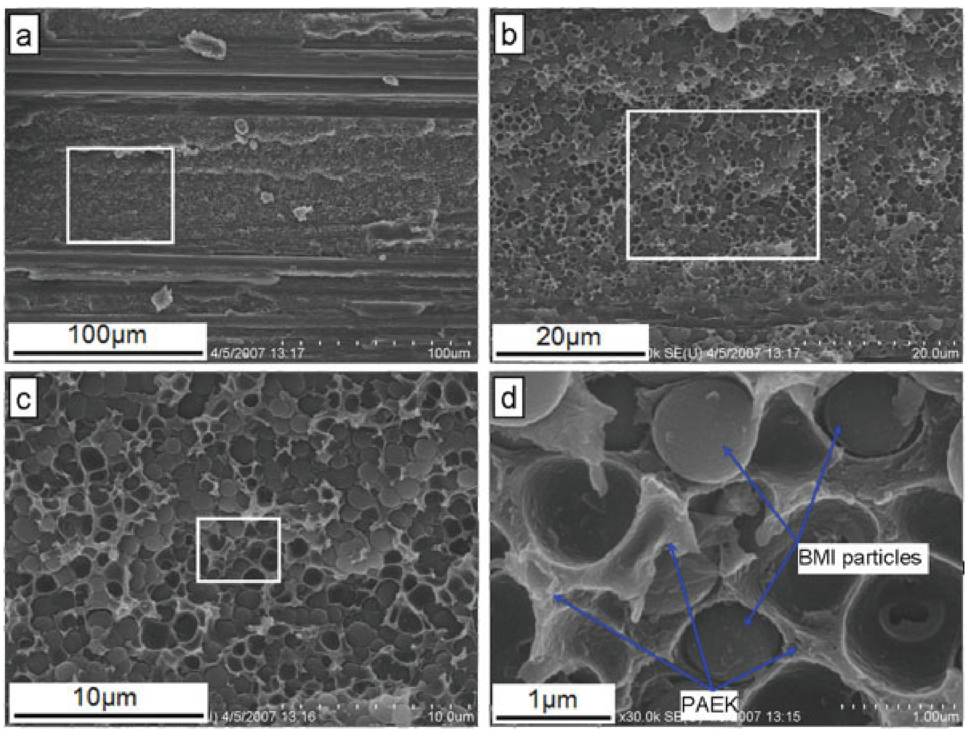

Figure 14 SEM images of fracture surface of the Specimen 2 in Table II under Mode II test: (a) ×500; (b) ×2000; and (c) ×5000; (d) ×30,000. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

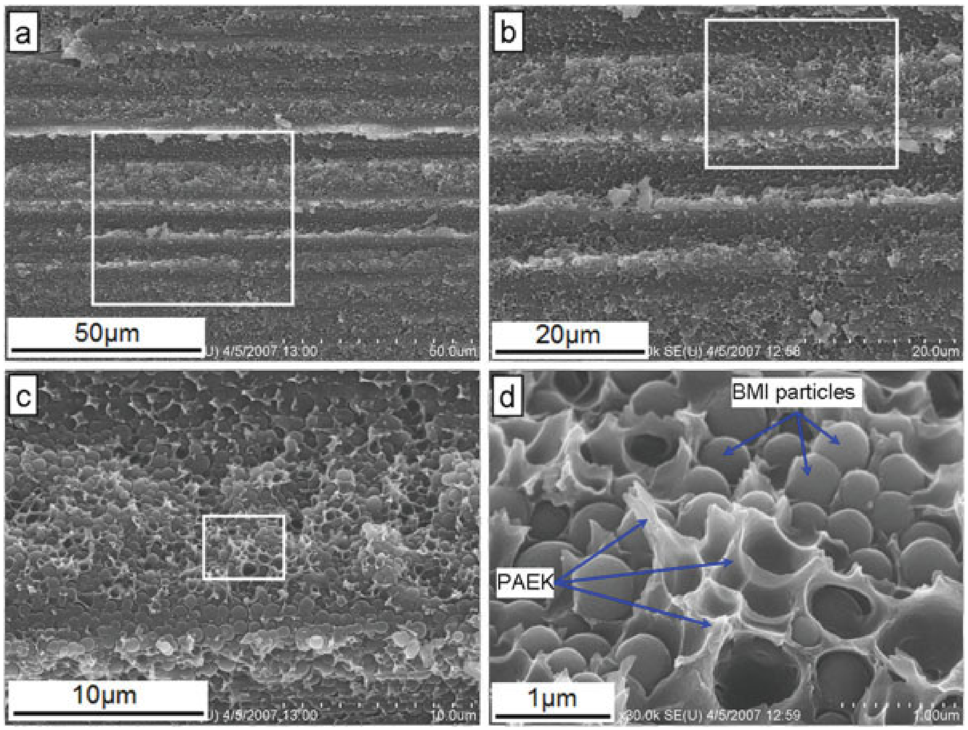

Figure 15 SEM images of fracture surface of the Specimen 3 in Table II under Mode II test: (a) ×1000; (b) ×2000; (c) ×5000; and (d) ×30,000.[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in the interlaminar region of composites. No evident was found in the deformation of BMI-rich particles. At a higher magnification [Figs. 14(d) and 15(d)], the PAEK-rich phase shows to be sheared or torn under Mode II loading conditions instead of cavitation or debonding.

CONCLUSIONS

The *ex situ* RTM technique has been proved as a highly effective technique of toughening RTMable BMI matrix composites via ES^{TM} carbon fabrics.

The interlaminar fracture toughness showed significant increase from 215 to 627 J/m^2 in G_{IC} and from 510 to 905 J/m^2 in G_{IIC}, respectively. The increases in interlaminar fracture toughness are believed to attribute to the relief of plastic constraint at the crack tip by PAEK-rich phases in the BMI matrix composites. Fractographic evidence of the plastic deformation and rupture along the crack paths is presented for both Mode I and Mode II tests. The phase separation and inversion continuous particles microstructure are responsible for the improvement.

This investigation was carried out at the National Key Laboratory of Advanced Composites (LAC/BIAM) in cooperation with Zhejiang University, China. The authors thank Dr. Ling Wang of the LAC/BIAM for the assistance and discussion.

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