Ex-situ Concept for Toughening the RTMable BMI Matrix Composites. II. Improving the Compression After Impact

Qunfeng Cheng,[1,2] Zhengping Fang,[1] Xiao-Su Yi,[2] Xuefeng An,[2] Bangming Tang,[2] Yahong Xu[3]

[1]*Institute of Polymer Composites, Zhejiang University/Key Laboratory of Macromolecular Synthesis and Functionalization, Ministry of Education, Hangzhou 310027, People's Republic of China*
[2]*National Key Laboratory of Advanced Composites/BIAM, Beijing 100095, People's Republic of China*
[3]*Research Institute of Aerospace Special Materials and Technology, Beijing 100074, People's Republic of China*

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ABSTRACT: The compression after impact (CAI) properties of bismaleimide (BMI) matrix composites manufactured by resin transfer molding (RTM) were significantly improved by *ex-situ* RTM technique. The thermoplastic polyetherketone with a functional group of phenolphthalein (PAEK) was used as toughener. The optical microscopy images of the cross-section of post-impact specimens revealed that the delamination resistance of specimens toughened through *ex-situ* RTM technique was dramatically improved. The energy absorption mechanism of composites toughened through *ex-situ* RTM technique was changed from the delamination to fiber fracture, which contributed to the improvement in CAI. The particle microstructure in interlaminar region of composites toughened through *ex-situ* RTM technique revealed that a reaction-induced phase decomposition and inversion happened in the interlaminar region. The BMI particles were surrounded with the PAEK phase, which can significantly improve the delamination resistance of composites. The in-plane static mechanical properties of G827/BMI composite toughened through *ex-situ* RTM technique were very well kept. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2211–2217, 2008

Key words: composites; *ex-situ* RTM technique; compression after impact; microstructure; mechanical properties

INTRODUCTION

Resin transfer molding (RTM) has been an efficient and economical technique to produce high-quality fiber-reinforced composite parts. However, the composites manufactured by RTM process suffer poor impact behavior. In the Part I,[1] a new interlaminar toughening method *ex-situ* RTM technique was applied to improve the interlaminar fracture toughness of G827/BMI composites manufactured by RTM process. The experimental results exhibited the G_{IC} and G_{IIC} value increased three and two times, respectively.

In this work, Part II, the compression after impact (CAI) properties, microstructure and in-plane static mechanical properties of composite laminates toughened through *ex-situ* RTM technique were investigated.

Correspondence to: X.-S. Yi (xiaosu.yi@biam.ac.cn).
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EXPERIMENTAL

Materials

An aerospace-grade bismaleimide resin BMI-6421, produced at National Key Laboratory of Advanced Composites (LAC)/BIAM, is used as the RTMable resin system. The commercial G827 carbon cloth (T300-3k, 160 g ± 7 g/m^2, Hexcel, France) is used as the reinforcement materials.

The toughening polymer was an amorphous engineering thermoplastic polyetherketone with a functional group of phenolphthalein (PAEK).[2–4] 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.

Specimen preparation

RTM technique was applied to manufacture the composite panels, and the ES^{TM} carbon fabrics was used as reinforcement material. The ES^{TM} carbon fabrics coated with the toughening polymer PAEK were provided by the LAC/BIAM using a patented special fabrication procedure.[5,6] The ES^{TM} carbon fabrics were placed in a closed RTM tool. Then the BMI-6421 was injected at 120°C under a pressure of 0.2 MPa into the mold to impregnate the porous

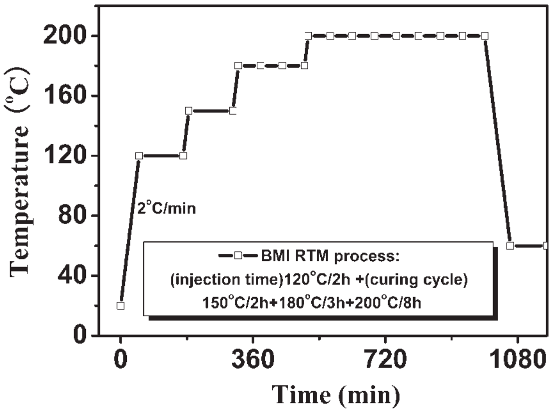


Figure 1 The RTM composite manufacturing process.

ES™ carbon preform. The proposed temperature and time is programmed as in Figure 1.

After curing, the mold was cooled down to 60°C and the composite panel was released. The RTM process practice was approved as easily performable. All the composite panels were finally ultrasonically C-scanned to check the molding defects and to evaluate the quality using the aerospace standard specifications.

The interlaminar PAEK concentration was calculated as weight percentage. The G827/BMI composite panels for CAI test were controlled at a thickness of 4.0 ± 0.1 mm and the overall fiber volume fraction was controlled at 55% ± 2%. The G827/BMI composite panels for static mechanical properties test were controlled at a thickness of 2.0 ± 0.1 mm.

The control system was untoughened G827/BMI composites, which were fabricated by the same process with the G827/BMI composites toughened through *ex-situ* RTM technique.

Compression after impact test

The impact damage resistance of G827/BMI specimens was characterized by CAI according to the Boeing commercial airplane group method BSS 7260.[7] The size of the specimens were 150 mm × 100 mm × 4 mm quasi-isotropic rectangular laminates with plies of $[45/0/\text{–}45/90]_{3S}$ using the low-velocity impact energy of 4.45 J/mm.

After the impact, the damage area was evaluated by ultrasonic C-scan. Then the specimens were compressed to obtain the residual compression strength. Each CAI data reported was an average of three effective tests.

The static mechanical properties test of G827/BMI composites

The G827/BMI composite panels with plies $[0]_{12}$ was manufactured for mechanical properties tests. The size of the tensile specimen was 230 mm × 15 mm according to GB/T3554-1999.[8] The size of the compression specimen was 140 mm × 6 mm according to GB/T3856-2005.[9] The size of the flexure specimen was 75 mm × 12.5 mm according to GB/T3356-2005.[10] The size of the interlaminar shear strength specimen was 20 mm × 6 mm according to GB/T3357-2005.[11] Each mechanical data reported was an average of five effective tests.

Fractographic studies and cross-section observation

The fracture surface of specimens after CAI test was investigated using a scanning electron microscope (SEM, Hitachi S-3000N). The PAEK phase was chemically etched by tetrahydrofuran (THF) for 72 h to improve the contrast of the phase structure, then 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. The CAI specimens were cut and washed in an ultrasonic bath. The center cross-section was observed using optical microscopy (OM, LEICA DMRME, Germany).

RESULTS AND DISSCUSSION

Compression strength after impact properties

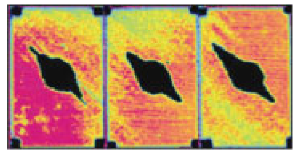
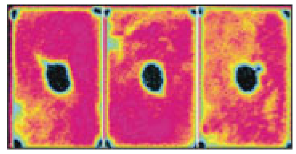
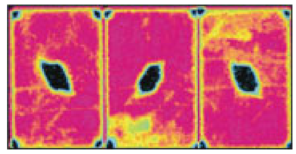
CAI data of G827/BMI is listed in Table I. The coefficient of variation, (C_V) was also reported, as well as the C-scan results. The color of C-scan results showed a good quality of composite specimens as-produced which indicated the *ex-situ* RTM technique was successful.

Table I shows that the CAI of the neat BMI matrix composites (control) is ∼ 155 MPa. The CAI of composites with an addition of 16.8 wt % PAEK through the *ex-situ* RTM technique increased from 155 to 254 MPa. Approximately 65% in CAI was improved. The highest increase in CAI is achieved at an addition of 20.2 wt % PAEK, as a result of ∼ 277 MPa, which was nearly 80% improvement. The damage area dropped from 1436 to 519 mm^2 of the control system. Specimens with the highest CAI had the lowest impact damage areas. The C-scan results of the post-impact specimens were in good agreement with the CAI and damage area data. Impact properties of composites demonstrated the high efficiency of *ex-situ* RTM technique in improving the impact damage resistance of the G827/BMI composites.

Cross section observation of the CAI specimens

A representative impacted specimen from each material system were cut along long axis in the center and polished to investigate the damage characteris-

TABLE I
CAI Values and C-scan Results of G827/BMI Laminates

Specimen	Matrix resin	CAI (MPa)/C_v%	Damage area (mm^2)	C-scan
1	Neat BMI (as control)	155/2.42	1436	
2	*Ex-situ* RTM technique toughened, with 16.8 wt % PAEK	254/3.34	527	
3	*Ex-situ* RTM technique toughened, with 20.2 wt % PAEK	277/2.93	519	

tic. Viewing by an optical microscope, all specimens showed a characteristic cone of damage.[12] Figure 2a showed the cross-section of post-impact control system of G827/BMI composite. The back surface (bottom in the figure) of the laminate showed a larger delaminated area with fibers fracture than that of the impacted surface. There were many transverse cracks in the failure area and considerable delamination propagation in the interlaminar regions. The delamination was wider through the thickness of the laminate and the fiber fracture appeared on the back surface of the laminate.

The crack tip of delamination was observed by SEM, as shown in Figure 2(b,c). It was clear to see that the crack propagated along the single phase BMI matrix. The mechanism of delamination was similar to a mode I shear propagation in some certain sections of the failed laminate.[13] The stress state assigned by the shear loads in the interlaminar region caused tension in the orientation at angle of 45°, which resulted in crack coalesce to form delaminations with resin hackle crack, that occurred in the resin-rich interlaminar region.[14]

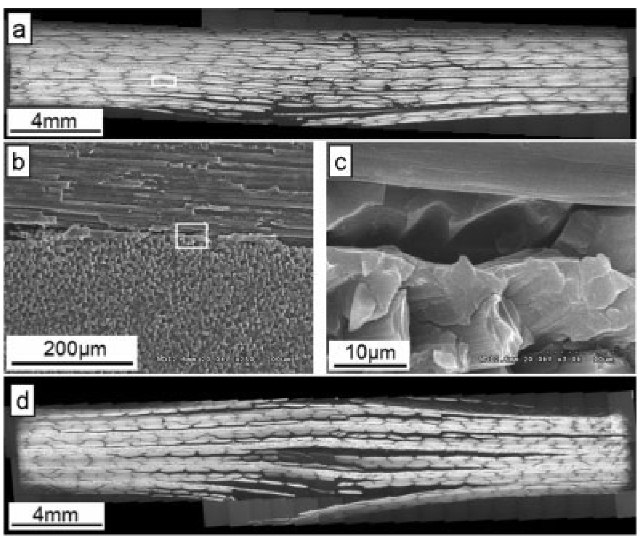


Figure 2 (a) The optical microscopy image of cross-section of the post-impact specimen of control system. (b,c) The SEM images of crack-tip propagation in interlaminar region. (d) The optical microscopy image of cross-section of control system after CAI test.

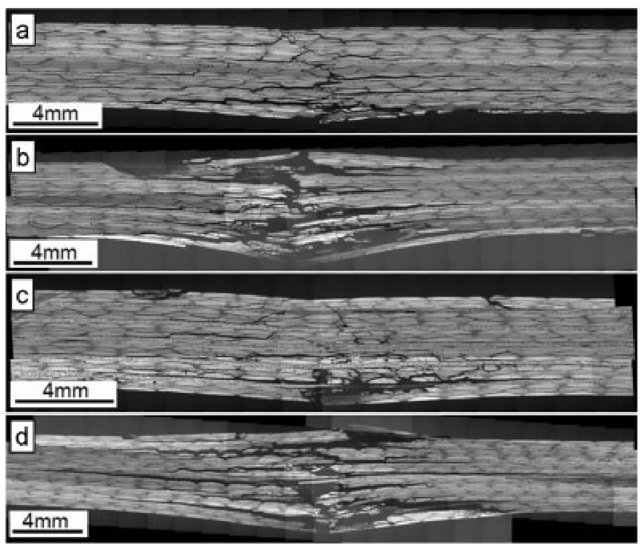


Figure 3 (a) The optical image of cross-section of the post-impact specimen 2 in Table I. (b) The optical image of cross-section of the specimen 2 after CAI test. (c) The optical image of cross-section of the post-impact specimen 3 in Table I. (d) The optical image of cross-section of the specimen 3 after CAI test.

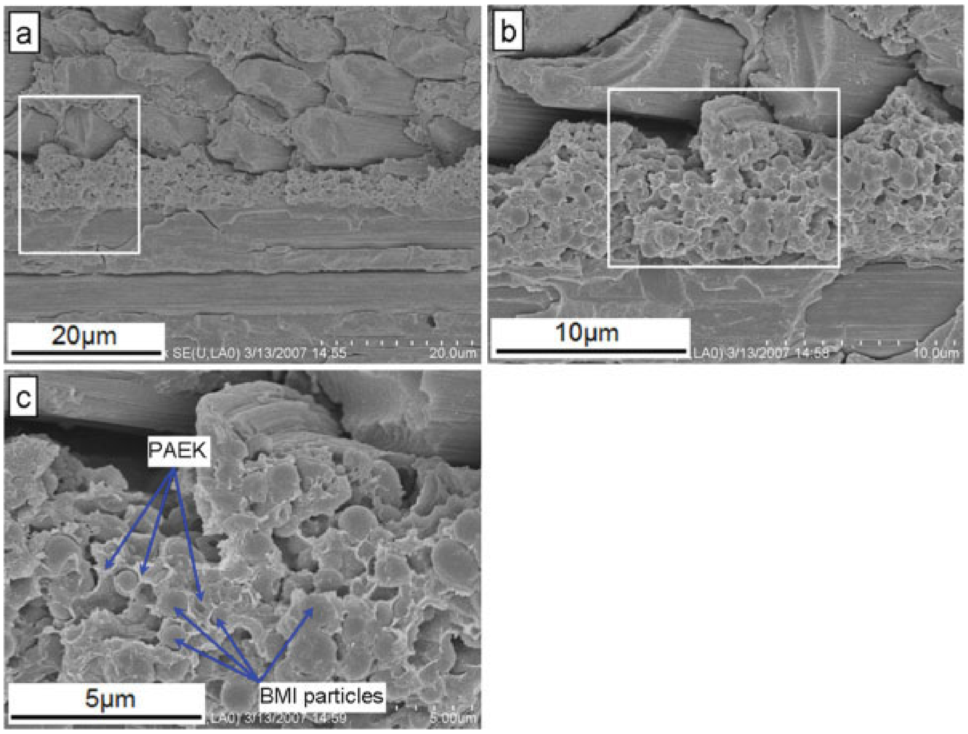


Figure 4 The SEM images of interlaminar section of the specimen 2 in Table I: (a) 2000×, (b) 5000×, and (c) 10000×. PAEK was chemically etched in part. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

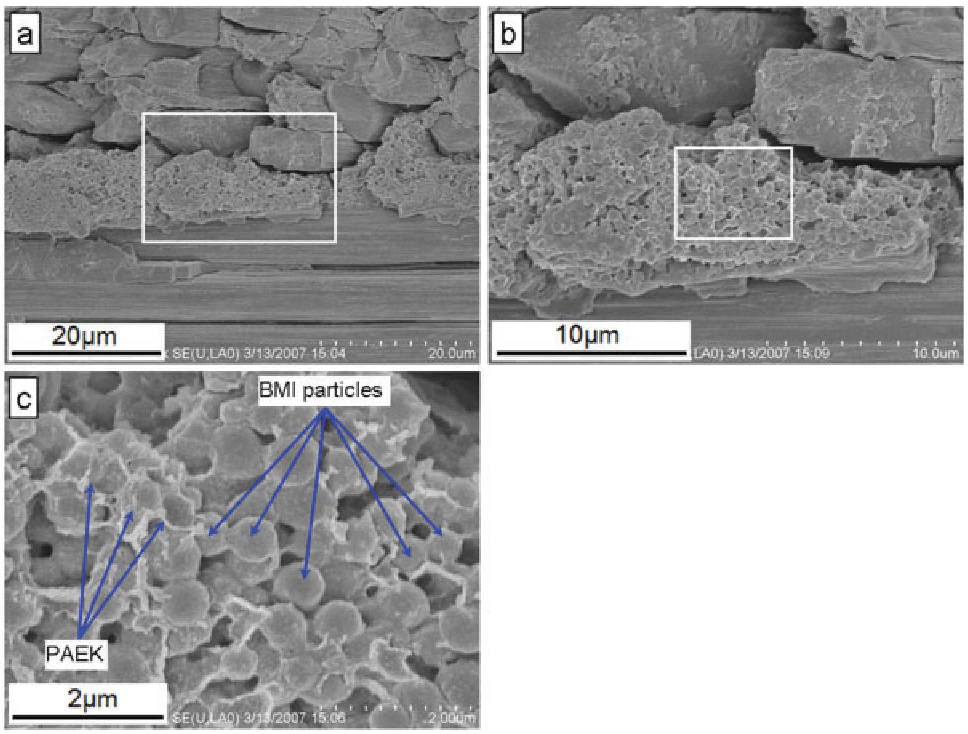


Figure 5 The SEM images of interlaminar section of specimen 3 in Table I: (a) 2000×, (b) 5000×, and (c) 20,000×. PAEK was chemically etched in part. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Static Mechanical Properties of G827/BMI Laminates

Mechanical properties	Specimen 1: Neat BMI (as control)	Specimen 2: *Ex-situ* RTM technique toughened (16.8 wt % PAEK)	Specimen 3: *Ex-situ* RTM technique toughened (20.2 wt % PAEK)	Test standard
0° Tensile strength (MPa)	1392	1500	1550	GB/T 3354-1999
0° Tensile modulus (GPa)	102	105	112	
Poisson ratio	0.32	0.30	0.34	
0° Compression strength (MPa)	1135	1117	1071	GB/T 3856-2005
0° Compression modulus (GPa)	101	104	110	
Flexural strength (MPa)	1684	1806	1749	GB/T 3356-2005
Flexural modulus (GPa)	108	115	113	
Interlaminar shear strength (MPa)	103	108	104	GB/T 3357-2005

Figure 2(d) showed the cross-section of the control specimen after CAI test. The failure mode was mainly delamination accompanied with little fiber fracture. The delamination was the key mechanism of energy absorption in the control system, only little the fiber fracture, which may be a reason of the control system with the low CAI value.

The cross-sections of G827/BMI composite toughened through *ex-situ* RTM technique with 16.8 and 20.2 wt % PAEK shown in Figure 3. For the G827/BMI composite toughened through *ex-situ* RTM technique, both the size of damage cone and the amounts of delamination decreased with an increase in the toughening polymer PAEK concentration. The reason was the increase in the resistance of delamination of composites. The cross-section of specimens after CAI test revealed that the key energy absorption mechanism of G827/BMI composites toughened through *ex-situ* RTM technique was changed from delamination to fiber fracture compared with the control system.

A representative interlaminar cross section of G827/BMI composite toughened through *ex-situ* RTM technique with 16.8 wt % PAEK was shown in Figure 4. The horizon (0°) ply and the 45° ply appeared in the SEM micrograph. The thickness of interlaminar region was ~ 7.5 μm. In the interlaminar region there was a typical cocontinuous, phase separated and inverted particle microstructure. The PAEK phase was chemically removed in part using THF before the SEM analysis. The BMI particles with a diameter of 0.8 μm were clearly embedded as dispersed phase in the continuous PAEK phase.

With the PAEK concentration increasing to 20.2 wt %, the thickness of interlaminar region increases from 7.5 to ~ 10.0 μm in Figure 5. However, the size of BMI-rich particles decreased from 0.8 to 0.4 μm. As shown in Figure 5(c), the BMI particles were densely interconnected with each other. It should be noted that the crack propagation caused by out-of-plane impact can be efficiently deflected or bifurcated by BMI particles or stopped by tearing of PAEK phase.

By taking the CAI data into consideration, it is believed that the cocontinuous BMI particles morphology in interlaminar region formed by the reaction-induced phase decomposition and inversion can dramatically improve the interlaminar fracture toughness, which was demonstrated in Part I. When the specimens toughened through *ex-situ* RTM technique encounter impact out-of plane, the energy absorption mechanism is changed from delamination to fiber fracture. As a result, the CAI property of G827/BMI toughened through *ex-situ* RTM technique is significantly improved.

Mechanical properties

The objective of *ex-situ* technique is to improve the interlaminar fracture toughness and impact damage resistance of composites. The other interlaminar toughening techniques[15] also improve the impact damage resistance but will reduce the stiffness and strength of composites due to the toughener with low stiffness and strength. Thus, the in-plane static mechanical properties of G827/BMI composites

TABLE III
The Thickness and V_f of G827/BMI Laminates

Specimen	Matrix resin	Thickness (mm)	Lamina V_f (%)	Overall V_f (%)
1	Neat BMI (as control)	2.05	55.7%	54.3%
2	*Ex-situ* RTM technique toughened, with 16.8 wt % PAEK	2.12	60.2%	52.5%
3	*Ex-situ* RTM technique toughened, with 20.2 wt % PAEK	2.14	61.3%	52.2%

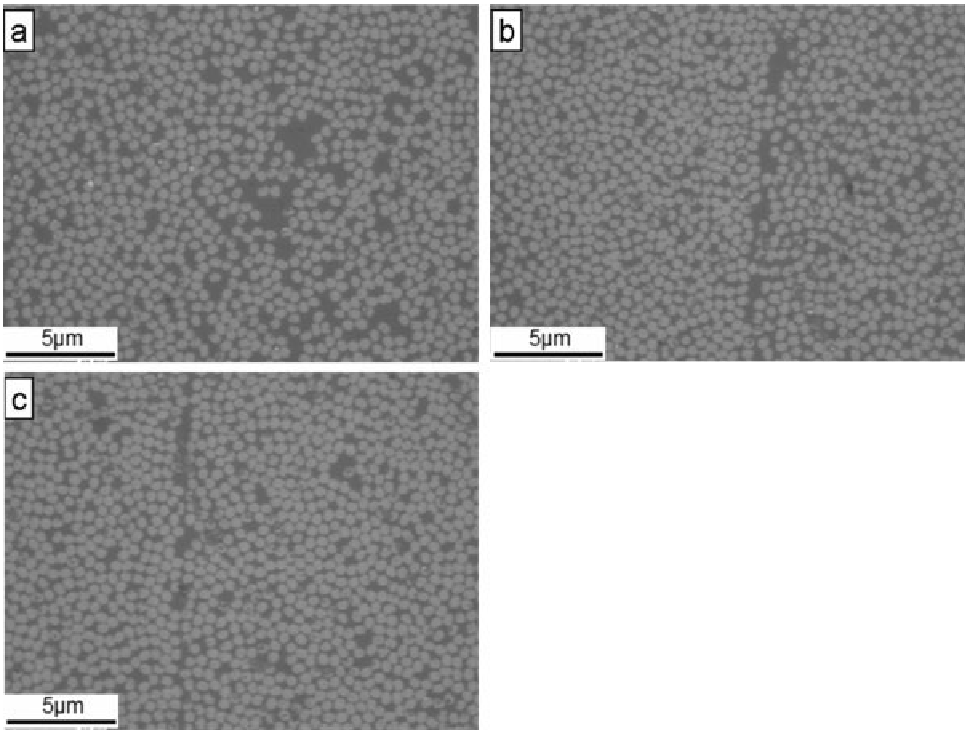


Figure 6 The optical microscopy images of lamina section of specimen in Table III: (a) specimen 1, (b) specimen 2, and (c) specimen 3.

toughened through *ex-situ* RTM technique were performed to evaluate the advance of this novel technique applied in RTM manufacturing process. The results were given in Table II. Most of mechanical properties of composites such as, tensile strength, tensile modulus, flexural strength, flexural modulus, increased a little, even when the overall fiber volume fraction decreased slightly because of the limited increase in thickness of composites. The increase in interlaminar shear strength was attributed to the interlaminar fracture toughness improvement, which was investigated in Part I.

The thickness was controlled to keep the overall fiber volume fraction. The thickness of G827/BMI composites was given in Table III. Since the PAEK was introduced into the interlaminar region, the thickness of laminate composites for mechanical test increased from 2.05 to 2.12 mm and 2.14 mm, respectively. The nominal overall fiber volume fraction decreased from 54.3 to 52.5% and 52.2%. However, the average lamina fiber volume fraction of G827/BMI composites according to GB/T 3366-1996[16] was much higher, given in Table III. The increase is attributed to the denser compaction (Fig. 6). To control the thickness of G827/BMI composites toughened through *ex-situ* RTM technique, the lamina was pressed hardly.

The concept of *ex-situ* involves increasing the ductility of the region between the plies, which allows inter-ply stresses formed under impact to be relieved and flexure to appear without the formation of large delamination. The typical cocontinuous particle microstructure is designed to stop transverse cracks forming delamination at the ply interface, which results in the improvement in interlaminar fracture toughness. When the post-impact specimens toughened through *ex-situ* RTM technique are compressed, the main energy absorption mechanism is changed from delamination to fiber fracture. So the CAI value significantly increases.

CONCLUSIONS

1. The *ex-situ* RTM technique has been demonstrated as a highly successful technique of toughening RTMable composites via ES^{TM} carbon fabrics. The CAI exhibited significant increase from 155 to 277 MPa for G827/BMI composites with 20.2 wt % toughening polymer PAEK.
2. SEM observation revealed that the BMI particles were surrounded with the PAEK phase, which was formed by the reaction-induced phase decomposition and inversion. The crack propagation was deflected or bifurcated by BMI particles or stopped by tearing of PAEK phase, which resulted in the improvement in delamination resistance of G827/BMI composites toughened through *ex-situ* RTM technique.
3. The energy absorption mechanism of G827/BMI composites toughened through *ex-situ* RTM technique was changed from the delamina-

tion to fiber fracture, which contributed to the significant improvement in CAI. The main reason is supposed to be the cocontinuous BMI particles morphology formed in interlaminar region.

4. The in-plane static mechanical properties of G827/BMI composites toughened through *ex-situ* RTM technique were well kept compared with the control system, which indicated the advance of *ex-situ* RTM technique.

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