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Preparation and characterization of three-dimensional braided carbon/Kevlar/epoxy hybrid composites

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Abstract Though unidirectional, short, and laminated hybrid composites have been extensively investigated because of their wider range of properties than non-hybrid composites, literature on three-dimensional (3-D) braided hybrid composites is very limited. In this work, Kevlar fibers were hybridized to carbon fibers to prepare 3-D carbon/Kevlar/epoxy composites with various carbon to Kevlar fiber volume ratios in an attempt to find alternative materials for osteosynthesis devices. The flexural, shear, and impact properties of the 3-D braided hybrid composites were measured in order to investigate the effect of carbon to Kevlar ratio and evaluate hybrid effects. In addition, residual flexural strength was tested for the impacted samples and the damage tolerance was assessed. Our experimental results revealed the existence of positive hybrid effects on the shear and flexural strengths flexural strain for the 3-D braided composites. The absorbed energy and flexural strength retention of the 3-D braided hybrid composites were found to decrease with relative carbon fiber content. It was shown that hybridizing ductile 3-D braided Kevlar fabric with stiff carbon fabric could result in the hybrid composites with flexural strength comparable to the all-carbon composite and impact damage tolerance superior to the all-Kevlar composite.

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Introduction

During recent decades, there has been increasing interest in hybrid composite materials made by combing two or more types of fibers in a matrix material or in two or more types of matrix materials. Compared to non-hybrid composites, hybrid composites offer a wider range of properties by changing the combinations of fibers and/or matrix materials in addition to regular adjustments of fiber loading and architecture, fiber-matrix interface, and so on.

Carbon fibers have been widely used reinforcement for metallic, ceramic, and polymeric matrices in light of their excellent properties and decreasing cost. The disadvantages of the carbon fibers are their low elongation at break and impact resistance. Hybridization provides an effective way of improving their composites by incorporating tough fibers. Kevlar fibers have a high elongation at break and their composites possess excellent impact performance. In addition, its biocompatibility was supported by Cochran et al. [1]. Therefore, hybridization of carbon and Kevlar fibers is believed an effective approach of creating hybrid composites possessing the combined advantages of both carbon and Kevlar fibers.

In our previous research [2, 3], carbon fibers were selected to prepare three-dimensional (3-D) braided carbon fabric-reinforced epoxy and nylon composites aimed to be used as orthopaedic implants. The high strength of the carbon fiber composites was successfully demonstrated. However, their low impact resistance is a concern when they are used as osteosynthesis devices. It is believed that hybridization of carbon fibers with Kevlar fibers will offer the potential of strong, light, and highly crashworthy composites suitable for osteosynthesis devices.

Though unidirectional, short and laminated hybrid composites have been extensively investigated [4–6], very little literature is available for 3-D braided hybrid composites [7]. As indicated in [7], the advantages of 3-D braided composites include the formation of a delamination resistant structure, the ability to fabricate thick and complex shapes, and single procedure, net-shape preforming. Furthermore, the braiding technique has been adopted by other researchers to make orthopaedic implants [8]. Therefore, 3-D braided fabrics were chosen as the reinforcement in the present study. The present paper reports the experimental results conducted on the 3-D braided carbon/Kevlar hybrid fabric-reinforced epoxy resin composites. The objective of the present study is to investigate the effect of the hybridization with Kevlar fibers on impact resistance and flexural properties of carbon fiber–epoxy resin composites.

Experimental

Materials

The reinforcements used in this work were PAN-based carbon fibers and Kevlar 49 fibers. The carbon fibers were 3 k fiber tow and the Kevlar fibers were 2,840 denier Kevlar 49 fiber tow. The matrix material used was a bisphenol-A type epoxy resin. The chemical structure of the epoxy resin was reported previously [9]. The physical properties of carbon fibers, Kevlar fibers, and epoxy resin employed in this study are presented in Table 1. The preforms, 3-D four-directional fabrics with a braiding angle of 16 were prepared by the Nanjing Fiberglass R&D Institute, Nanjing, China. According to the provider, the 3D braided preform was constructed by the intertwining or orthogonal interlacing of two sets of yarns–braiders and axials to form a fully integrated structure. Either carbon fibers, or Kevlar fibers, or carbon/Kevlar hybrids were used in the preparation of the 3-D braided preforms. For the hybrid fabrics, carbon to Kevlar fiber volume ratio was controlled by adjusting the yarn number of the carbon and Kevlar fibers. The total fiber volume fraction (V_f) of the composites used in the present study was kept at 45%. Table 2 gives designation of samples used in the present work. In Table 2, carbon to Kevlar fiber volume ratio, carbon fiber volume fraction in the composites, and relative carbon fiber volume fraction, which is volume of carbon fiber divided by total volume of carbon and Kevlar fibers in the composites, are given. As presented in Table 2, four 3-D braided hybrids with carbon to Kevlar fiber volume ratios of 1:2, 3:4, 3:2, and 3:1 were used to produce 3-D braided carbon/Kevlar/epoxy hybrid composites. Their photos are displayed in Fig. 1.

Table 1 Properties of carbon fibers, Kevlar fibers, and epoxy resin used in this study

Materials	Carbon fibers	Kevlar fibers	Matrix
Type	PAN	Kevlar 49	Bisphenol-A
Tensile strength (MPa)	2,800	3,260	60
Tensile modulus (GPa)	200	105	3.2
Elongation at break (%)	1.5	2.7	1.8
Density (kg m^{-3})	1,760	1,440	1,200
Filament diameter (μm)	7	12	/

Surface treatment of 3-D braided hybrid fabrics

The all-carbon fabrics were treated by liquid oxidization by immersing in $(NH_4)_2HPO_4$ solution (5 wt%) for one minute [10] The all-Kevlar fabrics were chemically treated in 10 wt% H_3PO_4 solution for an hour by referring to [11]. A two-step surface treatment process was used for the carbon/Kevlar hybrids. The 3-D braided carbon/Kevlar hybrid fabrics were first anodic-oxidized in 5 wt% $(NH_4)_2HPO_4$ solution for one minute, rinsed in distilled water, chemically treated in 10 wt% H_3PO_4 solution for an hour, and then washed in distilled water three times.

Composite manufacturing

3-D braided carbon fibers, Kevlar fibers, and carbon/Kevlar hybrid fabrics reinforced epoxy resin (denoted as C_{3D}/EP, K_{3D}/EP, and H_{3D}/EP, respectively hereinafter) composite specimens were prepared by the Vacuum Assisted Resin Transfer Moulding (VARTM) process. The VARTM process was described in detail elsewhere [12]. In brief, five braided fabrics with a nominal size of $160 \times 12 \times 2$ mm were placed in a mould. The epoxy resin and curing agent were thoroughly mixed at room temperature and freed from air bubbles by degassing at 70 °C for 30 min. The degassed mixed resin was then introduced into the mould under a pressure of 0.4–0.6 MPa and assisted by the vacuum.

Table 2 Relative fiber volume fraction in the hybrid fabrics (total fiber volume fraction in the composites: 45%)

Sample definition	K_{3D}/EP		HF_{3D}/EP		C_{3D}/EP	
	(1#)	2#	3#	4#	5#	(6#)
Carbon to Kevlar volume ratio	0	1:2	3:4	3:2	3:1	/
Carbon fiber volume fraction in the composite (%)	0	15	19	27	34	45
Relative carbon fiber volume fraction (%)	0	33.3	42.9	60	75.0	100

Fig. 1 Photos of 3-D braided hybrid fabrics with different carbon to Kevlar ratios (**a**) 3:2 (**b**) 1:2 (**c**) 3:1 (**d**) 3:4

The mould was then placed in an oven for curing (at 90 °C for 2 h) and postcuring (at 140 °C for 3 h).

Flexural tests

The flexural strength and modulus of the 3-D braided hybrid composites were measured using three-point bending test according to the ASTM standard method D 790. The composite specimens (60 × 12 × 2 mm) were tested using a support span of 32 mm at a cross-head speed of 2 mm/min. Load-displacement curves were recorded during flexural tests. All flexural properties were tested along the braiding direction. The flexural strength and modulus of each sample was determined from data on five test specimens.

Shear tests

The shear strength was measured with the help of a tool similar to that used by Kettunen et al. [13] and Majola et al. [14]. The dimensions of the shear testing samples were 60 × 12 × 2 mm. The shear strength was measured longitudinally (along braiding direction, i.e., the shear fracture surface was perpendicular to braiding direction).

Impact tests

The impact performance was tested using an XCJ-500 Impact Tester (pendulum type) with unnotched specimens. The specimens with dimensions of 100 × 12 × 2 mm were placed on two steel supports with a 40-mm span. The flexural strength of the impacted samples was tested to determine the strength retention with reference to unimpacted specimens, which indicates the ability to tolerate a specified amount of damage, i.e., damage tolerance [4, 15, 16].

For each mechanical test, at least five samples were tested for each sample group from which the mean values and the standard deviations were obtained.

Microstructure observation

A BX51RF optical microscope (Olympus Company) was used to observe the microstructure of the 3-D braided composites and to assess internal damage of impacted specimens. In order to obtain good resolution of the microstructures, specimens were frozen in liquid nitrogen for 24 h to keep the epoxy resin brittle so as to avoid any coverage by the worn debris during polishing.

SEM observation

The observation of fracture surfaces of the hybrid composites was performed on an XL30 scanning electron microscope (Philips, the Netherlands).

Results and discussion

Microstructure of 3-D braided carbon/Kevlar/epoxy hybrid composites

Figure 2 shows typical microstructure of a 3-D braided carbon/Kevlar/epoxy hybrid composite (Sample 4#). As shown in this figure, carbon and Kevlar fibers were distributed uniformly within each fiber bundle, without obvious fiber aggregations. The transverse view (see

Fig. 2b) revealed the existence of resin-rich areas (areas among fiber bundles) that may cause strain inhomogeneities.

Load-displacement curves

Typical load-displacement curves from the three-point bending tests for the all-carbon, all-Kevlar, and hybrid composites are shown in Fig. 3. The all-carbon fiber composite (C_{3D}/EP) showed a rapid load rise, the highest maximum load, and catastrophic failure, indicating a brittle manner of this composite. The all-Kevlar fiber composite (K_{3D}/EP) showed a slow load rise, high yield displacement, and the lowest maximum load. This behavior suggested that the composite possessed certain ductility because of the high elongation property of the Kevlar fibers. The hybrid composite with a high carbon fiber content (Sample 5#) showed a similar behavior to the all-carbon composite, whereas the hybrid composite with a high Kevlar fiber content (Sample 2#) followed the behavior of the all-Kevlar composite. This was due to the fact that carbon fibers dominated in Sample 5# and Kevlar fibers dominated in Sample 2#.

It was found that the flexural strain of the hybrid composites was higher than that of the all-carbon composite and increased with Kevlar fiber loading. As a result, a positive hybrid effect for the strain existed for the current 3-D braided hybrid system as a positive hybrid effect for the strain can be identified when the strain of a hybrid composite is greater than that of a low-elongation, non-hybrid composite [17, 18]. Khatri and Koczak also observed a positive hybrid effect for the flexural strain in their unidirectional E-glass/AS4 graphite fibers/PPS composites [19].

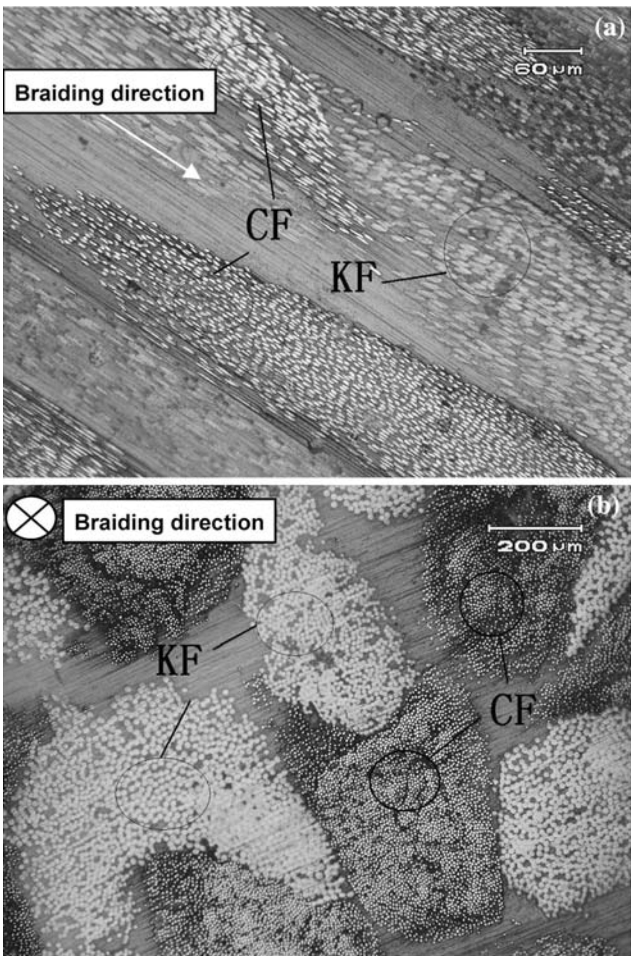

Fig. 2 Microstructure of a 3-D braided carbon/Kevlar/epoxy hybrid composite (**a**) Longitudinal (**b**) Transverse (CF = Carbon fiber; KF = Kevlar fiber)

Flexural properties

The effect of relative carbon fiber volume fraction on the flexural properties of the 3-D braided carbon/Kevlar hybrid composites is shown in Fig. 4. The all-carbon composite exhibited the highest values of flexural strength and modulus while the all-Kevlar composite showed the lowest values. The lower flexural properties of the all-Kevlar composite stemmed from the lower mechanical properties of the Kevlar fibers than the carbon fibers. It was noted that the flexural modulus of

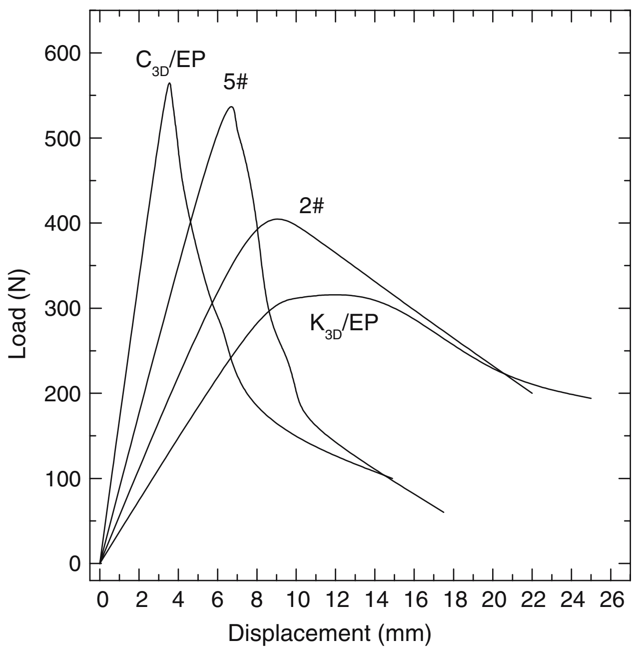

Fig. 3 Load-displacement curves of the 3-D braided carbon/Kevlar/epoxy hybrid composites

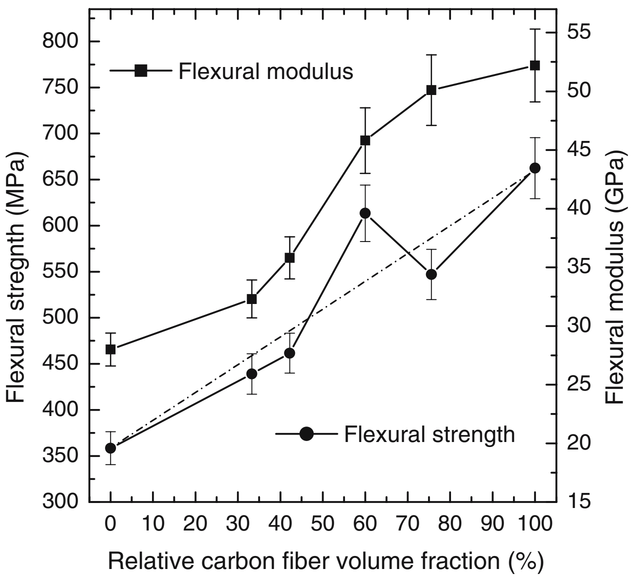

Fig. 4 Variations of flexural properties with relative carbon fiber volume fraction for the 3-D braided carbon/Kevlar hybrid composites (total fiber volume fraction: 45%)

the hybrid composites increased monotonically with relative carbon fiber volume fraction. By contrast with the trend for the flexural modulus, the flexural strength of the 3-D braided composites showed a maximum value (613.4 ± 30.7 MPa) at a carbon to Kevlar ratio of 3:2 (Sample 4#) which was 12% higher than that (547.0 ± 27.4 MPa) of a hybrid composite (Sample 5#) containing more carbon fibers. Figure 4 shows that flexural modulus and strength of the all-Kevlar composite enhanced when carbon fiber was hybridized. A similar result was reported by Kostar et al. who observed improved tensile modulus and strength for their epoxy resin composites by hybridizing carbon fiber to Kevlar fiber [7].

It was clearly shown in Fig. 4 that there was a positive deviation from the Rule of Mixtures, suggesting the existence of the positive hybrid effect on the flexural strength. Hybrid effect was reported by various researchers for different composite systems when two or more reinforcements with distinct properties were used [20–23]. The positive hybrid effect for the flexural strength observed in this study can be attributed to the "synergistic effect" of the flexible Kevlar fibers and the stiff carbon fibers. As proposed by Zweben [24], high elongation fibers in the hybrid composites enhanced the strain level required to propagate cracks through the composites, i.e., high elongation fibers behaved like crack arrestors on a micromechanical level. On the other hand, high strength fibers in the composites improved the stress level at break. It should be mentioned that the current experimental results are not sufficient to reveal the differences in the hybrid effects between 3-D braided composites and composites reinforced with fibers of other architectures since hybrid effects are dependent on many factors such as matrix and fiber properties, nature of fiber-matrix interface, structure of hybrids and so forth [7, 25–27]. Therefore, more experiments should be carried out in our further work to address this issue.

Shear strength

Figure 5 shows dependence of the shear strength of the 3-D braided hybrid composites on the relative carbon fiber volume fraction. The average shear strength increased initially with carbon fiber content and then showed a reduction. Sample 4#, showing the highest flexural strength, also exhibited the highest shear strength among all hybrid samples tested. Furthermore, it was shown in Fig. 5 that the shear strength of the hybrid composites was higher than that predicted by the Rule of Mixtures (the dotted lines in Fig. 5). This indicates a positive hybrid effect on the shear strength for the carbon/Kevlar/epoxy hybrid composites.

Figure 6 shows typical shear fracture surfaces of the hybrid composites. Different features can be observed for the 3-D braided hybrid composites with varying

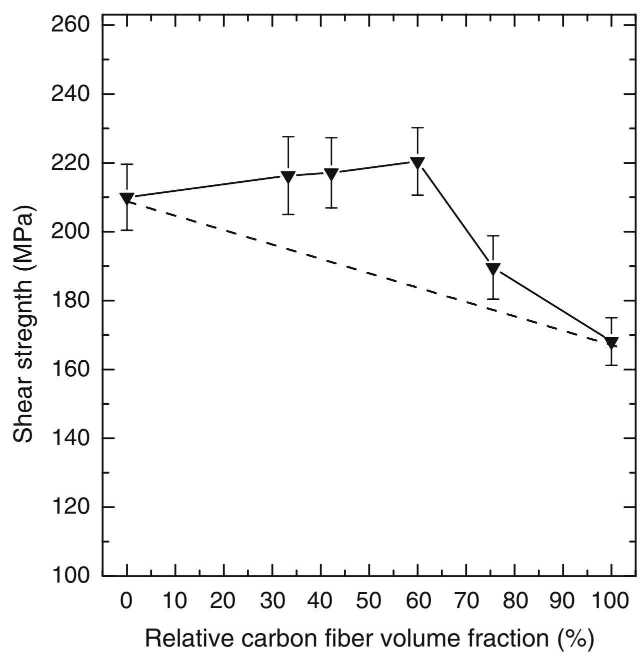

Fig. 5 Dependence of shear strength on relative carbon fiber volume fraction for the 3-D braided carbon/Kevlar/epoxy hybrid composites

carbon fiber content. Figure 6a clearly showed that under the action of a shear load extensive plastic deformation occurred to the Kevlar fibers in the hybrid composite of a carbon to Kevlar ratio of 1:2 (Sample 2#). In contrast, no plastic deformation happened to the carbon fibers as clearly shown in Figs. 6a and b. The positive hybrid effect on the shear strength indicates that a certain degree of plastic deformation is necessary to obtain high shear strength.

Impact properties

Impact resistance of a composite is the measure of total energy absorbed in the material before final failure. Type of fibers and their hybrids in the composites were found to have a significant effect on the energy absorbing capability [28]. In this work, absorbed energy was measured for various samples and post-impact samples were used to measure residual flexural strength. In Fig. 7 the absorbed energy and flexural strength retention of the hybrid composites are plotted versus the relative carbon fiber volume fraction. Obviously, the all-Kevlar fiber composite absorbed the most energy in all samples tested. The all-carbon composite samples broke after impact and therefore, its data were not given in this figure. The all-Kevlar composite and the hybrid composites with higher Kevlar fiber loadings still kept integrity, but damage on sample surface was discernible.

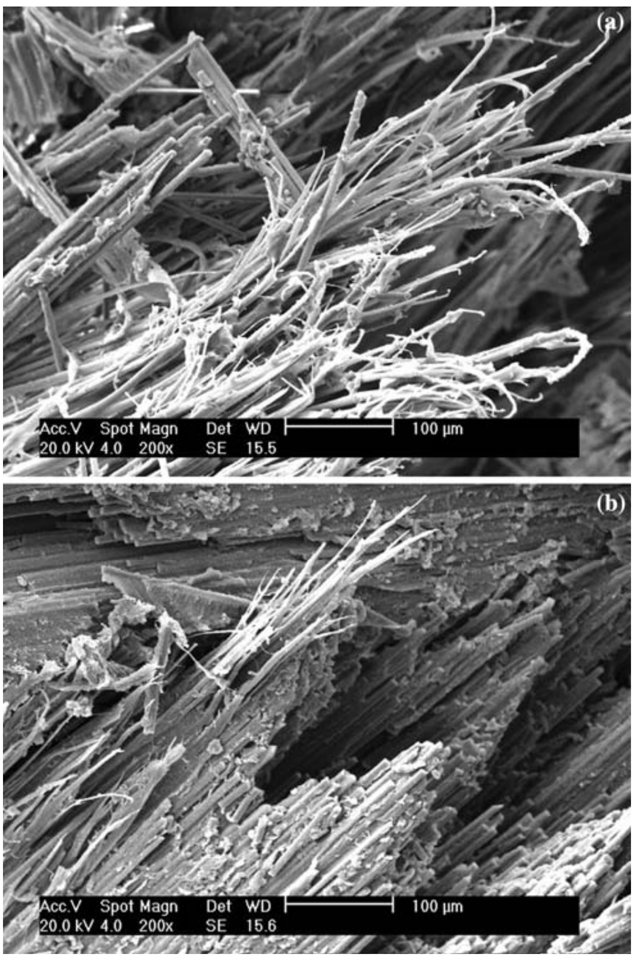

Fig. 6 Typical shear fracture surfaces of the 3-D braided carbon/Kevlar/epoxy hybrid composites (**a**) Sample 2# (**b**) Sample 5#

It was also found in Fig. 7 that the absorbed energy decreased steadily with relative carbon fiber loading. The decreasing trend was at least partially due to the low energy absorbing capability of the carbon fibers. As expected, the 3-D braided hybrid composites had lower energy absorbing capability when compared to the all-Kevlar fiber composite because of the brittle nature of the carbon fibers in the hybrids. Karbhari et al. declared a similar result for their 2-D-braided glass/Kevlar hybrid composites. They noted that the highest level of energy was absorbed by the all-Kevlar architecture, and the lowest by the all-glass [29]. Likewise, the hybridization of brittle carbon fibers with ductile polyethylene fibers was proven to be highly effective in improving the impact properties of the unidirectional carbon composite [30, 31].

It is recognized that impact energy is absorbed through both elastic deformation and creation of damage through various failure modes including delaminations, interfacial debonding, fiber rupture, matrix cracking, surface microbuckling, fiber structure, and the like [32–35]. Generally, matrix crack is initiated when lamilated composites are impacted, which

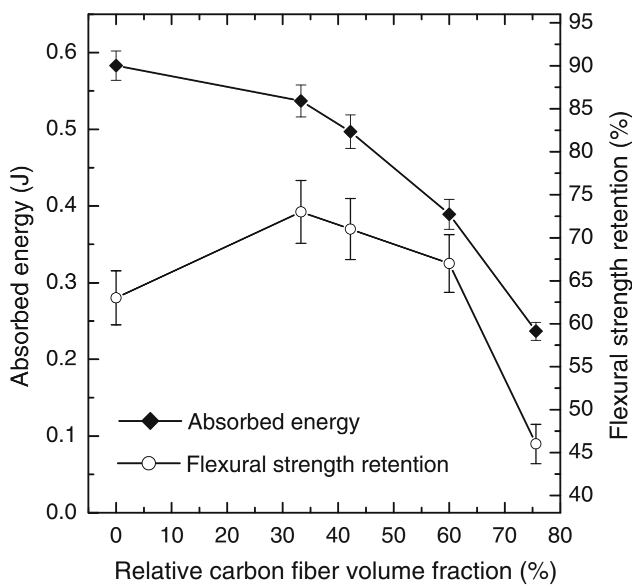

Fig. 7 Absorbed energy and flexural strength retention of the 3-D braided carbon/Kevlar hybrid composites plotted against relative carbon fiber content

extends to the interface of two laminae and progresses as delamination [33]. In comparison, theoretically, the 3-D braided fabric composites offer considerable advantages. In 3-D braided fabric composites, fibers run in different directions and are braided together. When a 3-D braided composite is subjected to impact loading beyond threshold energy level, propagation of cracks will be hindered by fiber tows, which slows down the crack propagation. When impact energy is further increased, fiber tows may fracture. In the 3-D braided hybrid composites containing two types of fiber tows, the brittle carbon fiber tows break first while the ductile Kevlar fiber tows may remain unbroken. This phenomenon was observed in our experiments as revealed by a typical optical micrograph of impacted specimens shown in Fig. 8, where fractured carbon fibers were observed.

As shown in Fig. 7, the hybrid composite with the highest Kevlar fiber content (Sample 2#) presented the highest flexural strength retention among all samples studied. Even Samples 3# and 4# demonstrated larger flexural strength retention than the all-Kevlar fiber composite, indicating that the carbon fibers played a role in reducing the damage of the hybrid composites. The higher retention of the hybrid composites than the all-Kevlar composite can be attributed to the ‘‘synergistic effect’’ between the carbon and Kevlar fibers. Interestingly, similar to the absorbed energy, the residual flexural strength of the 3-D hybrid composites also dropped with increasing relative carbon fiber volume fraction. This is likely to be ascribed to the increased carbon fiber loading and thus increased fiber breakage under impact loading due to the low impact resistance of the carbon fibers.

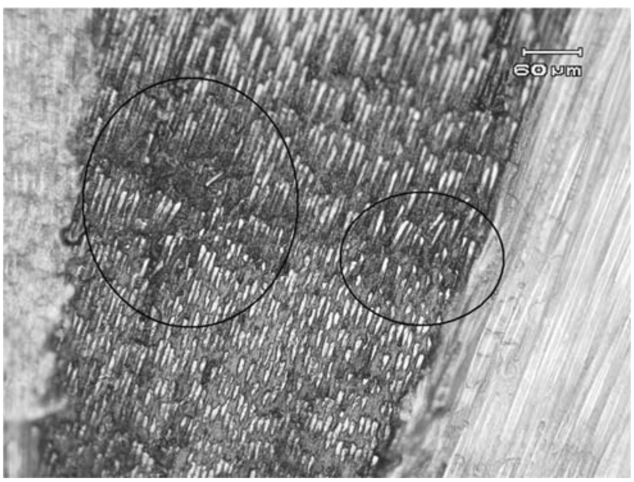

Fig. 8 A typical optical micrograph of a 3-D braided hybrid specimen after impact test showing fiber breakage

It was reported that the impact damage tolerance of composites could be improved significantly by stitching in the through-thickness direction using high-tensile-strength yarns of glass, carbon or Kevlar [36]. The reason for the stitched composites possessing improved damage tolerance and post-impact mechanical strength was their enhanced interlaminar resistance [37, 38]. It is therefore reasonable to believe that the 3-D braided composites will show higher residual flexural strength than unidirectional and laminated composites, which is of practical importance when used as osteosynthesis devices. Comparisons among composites with different fiber architectures should be made under identical impact testing condition in further studies to experimentally show the advantages of 3-D braided composites.

Conclusions

Mechanical properties of 3-D braided carbon fiber-epoxy composite could be effectively adjusted by hybridizing Kevlar fibers. It was observed that positive hybrid effects existed on the shear strength and flexural strain and strength for the 3-D braided composites. On the one hand, the absorbed energy and flexural strength retention of the 3-D braided hybrid composites were found to decrease with carbon fiber content as a result of the brittle nature of carbon fibers. On the other hand, the carbon fibers helped resist damage of the composites such that the 3-D braided hybrid composites showed higher damage tolerance than the composite containing 100% ductile Kevlar fibers. The results presented in this work demonstrated that hybridization with certain amount of ductile Kevlar fibers could create hybrid composites with flexural and modulus comparable to the corresponding all-carbon composite. Furthermore, hybridization remarkably promoted the shear strength, impact energy absorption characteristics and damage tolerance of the 3-D braided carbon fiber composite.

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