

Materials Science and Engineering A 398 (2005) 227-232



www.elsevier.com/locate/msea

Characterization of three-dimensional braided carbon/Kevlar hybrid composites for orthopedic usage

Y.Z. Wan^{a,*}, G.C. Chen^b, Y. Huang^a, Q.Y. Li^a, F.G. Zhou^a, J.Y. Xin^c, Y.L. Wang^a

^a School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China
^b Aerospace Research Institute of Materials and Processing Technology, Beijing 100076, PR China
^c Department of Surgery, Tianjin Hospital, Tianjin 300211, PR China

Received 23 November 2004; received in revised form 10 March 2005; accepted 10 March 2005

Abstract

Three-dimensional (3D) braided carbon/Kevlar hybrid composites were fabricated by an RTM-aided vacuum solution impregnation plus in situ polymerization. The load–displacement behaviors, flexural properties, impact property, and shear strength of these 3D braided hybrid composites were studied as a function of Kevlar/carbon ratio. Composites of six different relative Kevlar fiber contents (0%, 20%, 40%, 60%, 80%, and 100% by volume) were prepared and characterized. Environmental scanning electron microscopy (ESEM) was used to examine the fracture surfaces of the hybrid composites. Hybrid effects for strain, flexural strength and modulus, shear strength, and impact property of the 3D braided composites were assessed. It was found that hybridization provided high flexural strength and modulus for the 3D braided composites. It is concluded that hybridization is an effective way of tailoring the properties of the 3D braided composites for orthopedic applications.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Three-dimensional (3D) braided; Carbon/Kevlar hybrid; Composite material; Mechanical properties

1. Introduction

During recent decades, there has been a tremendous growth in the use of composite materials in various fields of application, ranging from aerospace, automotive parts, boats to recreation equipment, office products, biomedical devices, etc. It is important to tailor their properties by adjusting fiber loading and architecture and fiber–matrix interface, by modifying matrix, and by hybridizing to meet different requirements.

Hybridization is one of the most effective approaches for adjusting the properties of composites. Hybrid composites are generally referred to as the materials that combine two or more fibers in a suitable binding resin. They offer a wide range of properties that cannot be obtained with a single kind of reinforcement. Unidirectional, short, and laminated hybrid composites have been extensively investigated [1–5] whereas much fewer studies have examined braided or woven hybrid composites. Furthermore, little literature is available for three-dimensional (3D) hybrid composites [6].

In our previous research [7], monomer casting (MC) nylon was chosen as the thermoplastic matrix. Carbon and Kevlar fibers were selected separately to prepare 3D fabricreinforced nylon composites. The mechanical properties of the two 3D composites were characterized and compared. The high stiffness of the carbon fiber composites and the low density and high damping performance of the Kevlar fiber composites were successfully demonstrated. Based upon these preliminary investigations it was concluded that hybridization of Kevlar fiber with carbon fiber would offer the potential of stiff, light, highly crashworthy composites suitable for orthopedics. The present paper reports the experimental results conducted on the 3D braided carbon/Kevlar hybrid composites.

^{*} Corresponding author. Tel.: +86 22 27405056; fax: +86 22 27404724. *E-mail address:* yzwan@tju.edu.cn (Y.Z. Wan).

 $^{0921\}text{-}5093/\$$ – see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.msea.2005.03.010

Sample definition	C _{3D} /MC	HF _{3D} /MC				K _{3D} /MC
		A	В	С	D	
Kevlar fiber volume fraction (%)	0	6	12	18	24	30
Carbon fiber volume fraction (%)	30	24	18	12	6	0
Relative Kevlar fiber volume fraction (%)	0	20	40	60	80	100

Table 1 Samples used in this study (total fiber volume fraction in the composites: 30%)

2. Experimental

2.1. Materials

The fibers used in this work were T300 carbon fiber (tensile strength 3530 MPa, tensile modulus 230 GPa, density 1760 kg m^{-3} , strain at break 1.5%) and Kevlar 49 fiber (tensile strength 3260 MPa, tensile modulus 105 GPa, density 1440 kg m^{-3} , strain at break 2.7%). The preforms, 3D fourdirectional fabrics with a braiding angle of 16° were provided by the Nanjing Fiberglass R&D Institute, Nanjing, China. Carbon fiber, Kevlar fiber, and carbon/Kevlar hybrids were used in the preparation of the 3D braided preforms. The carbon fiber was 3k fiber tow and the Kevlar fiber was 2840 denier Kevlar 49 fiber tow. For the hybrid fabrics, the Kevlar to carbon volume ratio (see Table 1) was adjusted by changing the yarn numbers of the carbon and Kevlar fibers. The total fiber volume fraction (V_f) of the composites used in the present study was controlled at 30%. As presented in Table 1, the absolute Kevlar and carbon fiber volume fractions in the composites were, respectively, 0% and 30%, 6% and 24%, 12% and 18%, 18% and 12%, 24% and 6%, and 30% and 0%. The relative Kevlar fiber volume fraction was thus 0%, 20%, 40%, 60%, 80%, and 100%.

2.2. Composite manufacturing

As described previously [7], an RTM-aided vacuum solution impregnation plus in situ anionic polymerization technique was employed to prepare the 3D braided carbon, Kevlar, and hybrid fabrics-reinforced MC nylon (denoted as C_{3D}/MC , K_{3D}/MC , and HF_{3D}/MC , respectively) composites. The preparation procedures were similar to those described elsewhere [8].

2.3. Mechanical tests

Measurement of flexural properties and shear and impact strengths was carried out in this study. A three-point bending fixture was chosen to test the flexural strength and modulus of the 3D hybrid composites. The testing procedures of the flexural properties, as well as the shear strength were identical to those described in [9]. The flexural strength and modulus were calculated following ASTM D 790. Load–displacement curves were recorded during flexural tests. The impact strength was tested using an XCJ-500 Impact Tester (pendulum type) with notched specimens. The sample dimensions were $80 \text{ mm} \times 12 \text{ mm} \times 2 \text{ mm}$ with a support span of 40 mm.

All mechanical properties were tested along the braiding direction. For each sample group, five specimens were tested, and the average values are reported.

2.4. SEM observation

After impact tests, the fracture surfaces were examined using an XL30 environmental scanning electron microscope (ESEM). All fracture surfaces were coated with a thin layer of gold to eliminate charging effects.

3. Results and discussion

3.1. Load-displacement curves

Fig. 1 compares the typical load–deflection curves from the three-point bending tests for different samples. The initial parts of all the load–displacement curves were linear. Afterwards (after the plateau), linearity was still observed for the samples with high carbon fiber contents (80% and 100% by volume), but non-linearity was observed in the composite samples with high Kevlar fiber contents (80% and 100% by volume) probably due to damage development, such as interfacial failure, plastic deformation of the matrix, and crack propagation. The flexural strain of the hybrid composites was higher than that of the C_{3D}/MC composite and increased with the Kevlar fiber volume fraction. Consequently, we concluded that a positive hybrid effect for the strain existed for



Fig. 1. Load-displacement curves of the 3D braided carbon/Kevlar hybrid composites.

carbon kevlar fabric

the current 3D 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 [10,11].

It was found from Fig. 1 and experiments that the allcarbon fiber (C_{3D}/MC) composite showed rapid load rise and the highest maximum load. Conversely, the all-Kevlar fiber composite showed slow load rise and the lowest maximum load, and the failure occurred in ductile manner because of the high elongation property of the Kevlar fiber. The hybrid composite with a high carbon fiber content (Sample A) resembled the C_{3D}/MC composite, whereas the hybrid composite with a high Kevlar fiber content (Sample D) followed the behavior of the K_{3D}/MC composite. This was likely due to the fact that carbon fiber dominated in Sample A and Kevlar fiber dominated in Sample D. Fiber breakage was the dominant failure for the C_{3D}/MC composite and Sample D with a high carbon fiber content (80% by volume), while no fiber breakage was observed on either the tensile or the compressive side for the K_{3D}/MC composite and Sample A with a high Kevlar content (80% by volume). This indicated that the high Kevlar materials yielded a better ductility than the C_{3D}/MC and carbon fiber-dominated composites. It was noted that fiber buckling, which caused an irreversible deformation, was a typical failure mode for the hybrid composites with high Kevlar fiber contents. Compared to the carbon fiber-dominated samples, the Kevlar fiber-dominated samples failed gradually at larger deflections, indicating higher energy absorption and better damage tolerance.

3.2. Flexural properties

450

400

350

300

250

200

0

20

Flexural strength (MPa)

Fig. 2 shows the flexural properties of the HF_{3D}/MC composites as a function of relative Kevlar fiber content. As expected, the K_{3D}/MC composite showed lower flexural strength and modulus than the C_{3D}/MC composite. It was believed that the lower flexural properties of the K_{3D}/MC composite were attributed to the lower mechanical properties of



60

80

Strength

Modulus

40

Kevlar fiber volume fraction (%)

the Kevlar fiber than the carbon fiber (when fiber/matrix adhesion was not taken into account). However, it was interesting to note that the HF_{3D}/MC composites of 20%, 40%, and 60% Kevlar fiber by volume showed higher flexural strength and modulus than the C3D/MC composite. Of which, Sample A had the highest flexural strength at 442 MPa, which was 11% higher than the C_{3D}/MC composite and Sample B had the highest modulus at 25 GPa, 19% higher than the C_{3D}/MC composite, showing positive deviations from the Rule of Mixture. Even for Sample C, with a relative Kevlar fiber volume content of 60%, its flexural strength was still higher than the C_{3D}/MC composite. Similarly, the three 3D hybrid composites with 20%, 40% and 60% Kevlar fiber by volume showed higher flexural modulus than the 100% carbon fiber composite. These results confirmed the existence of the positive hybrid effect, which is common for various composites. Khatri and Koczak obtained the maximum flexural strength for both unidirectional and cross-plied composites containing 75% (by volume) AS4 fiber and 25% E-glass fiber [12]. Fu et al. gained a positive hybrid effect on the elastic modulus with their hybrid particle/short-fiber composites [13]. A positive hybrid effect was also found in a polyethylene–glass fibers/PMMA hybrid system [14].

The positive hybrid effect for flexural strength and modulus observed in this study could be attributed to the combination of the Kevlar and carbon fibers. As mentioned early, fiber buckling on the surface of the all-Kevlar composite dominated its failure. It was believed that the presence of stiff carbon fiber could prevent the Kevlar fiber from buckling. On the other hand, the Kevlar fiber could help the carbon fiber resist breaking, which led to a higher maximum stress.

3.3. Shear strength

The shear strength as a function of the Kevlar fiber content of the 3D braided hybrid composites is presented in Fig. 3. The shear strength of the hybrid composites showed a different trend from the flexural strength and modulus. No obvious



Fig. 3. Shear strength of the 3D braided carbon/Kevlar hybrid composites.

Flexural modulus (GPa

20

16

12

100

positive hybrid effect was observed for the shear strength. The C_{3D}/MC composite had the lowest shear strength and the K_{3D}/MC composite showed the highest value among all samples tested. The shear strength of the 3D hybrid composites enhanced with increasing Kevlar fiber content.

3.4. Impact strength

Impact resistance of a composite is the measure of total energy absorbed in the material before final failure. The fiber kinds and their hybrids in the composites were found to have a significant effect on the energy absorption capability [15]. Sreekala et al. observed a positive hybrid effect in glass and oil palm fibers-phenol-formaldehyde hybrid composites [16]. By adding a small amount of glass fiber, they noted a 100% improvement in impact strength for their hybrid composites. The positive hybrid effect on impact property was also reported by Peijs et al. [17].

The impact strength obtained in this study is depicted in Fig. 4 as a function of relative Kevlar fiber loading. Clearly, the Kevlar fiber-reinforced composite exhibited higher impact strength than the carbon fiber composite. The impact strength increased with the volume fraction of the Kevlar fiber. The increase in the impact strength was at least partially due to the high energy absorbing ability of the Kevlar fiber. As can be seen from Fig. 4, the 3D braided hybrid composites had less significant energy absorbing capability when compared to the K_{3D}/MC composite, but improved impact property when compared to the C3D/MC composite. This was understandable as the Kevlar fiber possessed higher energy absorbing capability than the carbon fiber. The Kevlar fiber underwent extensive deformation before final break; while no deformation occurred for the carbon fiber. This was clearly shown from the impact fracture surfaces of typical samples (see Fig. 5). Generally, impact energy is primarily dissipated through plastic deformation of matrix, fiber pull-out and fiber breakage. The fracture surfaces shown in Fig. 5(c) revealed another mechanism of impact failure, which was the plastic



Fig. 4. Impact strength of the 3D carbon/Kevlar hybrid composites plotted against relative Kevlar fiber content.

deformation of fibers. It was therefore readily understood that the observed higher impact strength of the carbon/Kevlar hybrid composites than the C_{3D}/MC composite was ascribed to the plastic deformation of the Kevlar fiber, which consumed large amounts of energy. Accordingly, the more the Kevlar fiber, the higher the impact strength of the HF_{3D}/MC composites (as shown in Fig. 4). It should be mentioned that the presence of the carbon fiber in the hybrid composites was likely to restrict the extent of the plastic deformation of the Kevlar fiber, which caused lower impact strength of the hybrid composites than the K_{3D}/MC composite. Additionally, fiber/matrix interfacial failure was evident in all the composite samples studied. This was probably due to weak interfacial bonding because no fiber surface treatment was carried out. It was found that the impact strength of the hybrid composites was nearly a weighted sum of the impact strength of all the individual components. Therefore, we deduced that the hybrid system did not show a hybrid effect on impact strength. This agrees with results reported by Park and Jang, who investigated the impact behavior of glass/aramid hybrid composites and did not declare any hybrid effect [18].

3.5. Practical importance of hybridization in orthopedics

An osteofixation implant should at least meet certain physical and medical demands to be safe for clinical applications, including good biocompatibility, sufficient strength, and suitable stiffness (close to human bones). Metallic osteosynthesis devices are associated with problems such as stress shielding, corrosion, and artifacts in computed tomography (CT) and magnetic resonance imaging (MRI) [19–21]. Bioabsorbable surgical devices offer certain advantages over metallic ones-elimination of stress shielding, avoidance of second surgical operation, etc. However, the use of internal fixation devices consisting of bioabsorbable polymers, such as polyglycolide (PGA), polylactide (PLA), and copolymers of lactide and glycolide (PLGA) has been linked to such complications as transient fluid accumulation or sterile sinus formation in late stages [22,23]. Furthermore, their relative low strength allows bioabsorbable devices to be used only in nonload-bearing bones. The advantages of non-absorbable fibrous composites have gained wide acceptance [24,25]. Compared to other fibrous composites, 3D composites present more advantages [9,26]. To date, various 3D composites have been made for osteosynthesis devices [7,27]. Their mechanical properties are summarized in Table 2. As can be seen from this table, the 3D braided carbon fiber-epoxy (C_{3D}/EP) composites demonstrated the highest strength and the K_{3D}/MC the lowest strength among all the 3D composites listed. By combining carbon fiber and Kevlar fiber a reduction in impact strength was traded for increased strength and modulus when compared to an all-Kevlar fiber composite. More importantly, the hybrid composites of both higher strength and modulus (due to a positive hybrid effect) and higher impact strength than the all-carbon fiber composite were obtained.



Fig. 5. SEM micrographs of impact fracture surfaces (a and b) C_{3D}/MC , (c) Sample A, (d) Sample D (e–g) K_{3D}/MC .

Table 2

Comparisons of mechanical properties of 3D braided composites with biomedical metals and human cortical bone

Materials	Flexural strength (MPa)	Flexural modulus (GPa)
Cortical bone	180	20
Ti-Al-V	380	120
Stainless steel	280	200
Co–Cr	480	240
C _{3D} /EP	756	47
C _{3D} /MC	395	21
K_{3D}/MC	205	14
HF _{3D} /MC		
Sample A	442	22
Sample B	421	25
Sample C	277	24
Sample D	243	21

Comparisons of various 3D composites with biomedical metals and human cortical bone seem to indicate that Sample A is promising in terms of its high strength and close modulus to human bones. It should be mentioned that no positive hybrid effect for impact strength was obtained for the current carbon–Kevlar–MC composite system. A deep insight on hybridization may allow us to design a better hybrid system so we can tailor the mechanical properties of the 3D braided composites to meet the requirements of orthopedic usage.

4. Conclusions

3D braided carbon/Kevlar hybrid composites possessing advantages of both the carbon and Kevlar fibers were created by hybridization. The high carbon fiber content 3D hybrid composites exhibited load-displacement curves similar to that of the all-carbon composite. In the same way, the high Kevlar fiber content composites resembled the all-Kevlar fiber composite in load-displacement behavior. The positive hybrid effect for the strain was found for the 3D hybrid composites. Results of flexural tests revealed the existence of a positive hybrid effect in strength and modulus for the 3D braided hybrid composites. However, we found no hybrid effect for shear strength and impact property. SEM observations indicated that the Kevlar fiber deformed in a highly plastic manner during impact, which absorbed a lot of energy, while no plastic deformation was discernible for the carbon fiber case. This can interpret the experimental results that the 3D hybrid composites displayed higher impact strength than the all-carbon composite. Hybridization was found to yield the 3D braided hybrid composites with high strength, with a modulus close to that of human bones and with moderate impact strength. It is concluded that hybridization is an effective method of tailoring the mechanical properties of the 3D braided composites to meet the needs of orthopedics.

Acknowledgements

This study was supported by the Tianjin Municipal Natural Science Foundation (Grant No. 013604211), Key Project Program (Grant No. 0113111711), and Municipal Science and Technology Development Program (Grant No. 043111511).

References

- J. He, M.Y.M. Chiang, D.L. Hunston, C.C. Han, J. Compos. Mater. 36 (2002) 2653–2666.
- [2] M.L. Dunn, M. Taya, H. Hatta, J. Compos. Mater. 27 (1993) 1493–1519.
- [3] R. Park, J. Jang, Compos. Sci. Technol. 58 (1998) 1621-1628.
- [4] M.M. Thwe, K. Liao, J. Mater. Sci. Lett. 19 (2000) 1873-1876.
- [5] M.L. Dunn, M. Taya, H. Hatta, J. Compos. Mater. 27 (1993) 1493–1519.
- [6] T.D. Kostar, T.W. Chou, P. Popper, J. Mater. Sci. 35 (2000) 2175–2183.
- [7] Y.L. Wang, Y.Z. Wan, B.M. He, Z.Q. Zhang, K.Y. Han, J. Mater. Sci. 39 (2004) 1491–1494.
- [8] L.Y. Zheng, Y.L. Wang, Y.Z. Wan, F.G. Zhou, X.H. Dong, J. Mater. Sci. Lett. 21 (2002) 987–989.
- [9] Y.Z. Wan, Y.L. Wang, G.X. Cheng, K.Y. Han, J. Appl. Polym. Sci. 85 (2002) 1031–1039.
- [10] H. Fukuda, J. Mater. Sci. 19 (1983) 974-982.
- [11] G. Kretsis, Composites 18 (1987) 13-23.
- [12] S.C. Khatri, M.J. Koczak, Compos. Sci. Technol. 56 (1996) 473-482.
- [13] S. Fu, G. Xu, Y. Mai, Composites 33B (2002) 291-299.
- [14] N. Saha, A.N. Banerjee, Polymer 37 (1996) 699-701.
- [15] C.H. Chiu, K.H. Tsai, W.J. Huang, Compos. Sci. Technol. 59 (1999) 1713–1723.
- [16] M.S. Sreekala, J. George, M.G. Kumaran, S. Thomas, Compos. Sci. Technol. 62 (2002) 339–353.
- [17] A.A.J.M. Peijs, R.W. Venderbosch, P.J. Lemstra, Composites 21 (1990) 522–530.
- [18] R. Park, J. Jang, J. Mater. Sci. 36 (2001) 2359-2367.
- [19] P. Ciappetta, S. Boriani, G.P. Fava, Clin. Neurol. Neurosurg. 99 (1997) \$174.
- [20] K.L. Wapner, Clin. Orthop. Relat. Res. 271 (1991) 12-20.
- [21] C. Zannoni, M. Viceconti, L. Pierotti, A. Cappello, Med. Eng. Phys. 20 (1998) 653–659.
- [22] O.M. Bostman, J. Bone Joint Surg. 73A (1991) 148-152.
- [23] E.K. Partio, O. Bostman, R. Hirvensalo, S. Vainionpaa, K. Vihtonen, H. Patiala, P. Tormala, P. Rokkanen, J. Orthop. Trauma 6 (1992) 209–215.
- [24] J. Kettunen, E.A. Makela, H. Miettinen, T. Nevalainen, M. Heikkila, T. Pohjonen, P. Tormala, P. Rokkanen, Biomaterials 19 (1998) 1219–1228.
- [25] J. Krysa, K. Balik, J. Krena, J. Gregor, Mater. Chem. Phys. 57 (1998) 156–161.
- [26] Y.Z. Wan, Y.L. Wang, H.L. Luo, X.H. Dong, G.X. Cheng, Mater. Sci. Eng. 326A (2002) 324–329.
- [27] Y.Z. Wan, Y.L. Wang, Y. Huang, F.G. Zhou, B.M. He, G.C. Chen, K.Y. Han, Compos. Sci. Technol, in press.