Three-Dimensionally Braided Carbon Fiber–Epoxy Composites, A New Type of Materials for Osteosynthesis Devices. II. Influence of Fiber Surface Treatment

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ABSTRACT: Interfacial adhesion between carbon fiber and epoxy resin plays an important role in determining performance of carbon–epoxy composites. The objective of this research is to determine the effect of fiber surface treatment (oxidization in air) on the mechanical properties (flexural strength and modulus, shear and impact strengths) of three-dimensionally (3D) braided carbon-fiber-reinforced epoxy (C_{3D}/EP) composites. Carbon fibers were air-treated under various conditions to improve fiber–matrix adhesion. It is found that excessive oxidation will cause formation of micropits. These micropits are preferably formed in crevices of fiber surfaces. The micropits formed on fiber surfaces produce strengthened fiber–matrix bond, but cause great loss of fiber strength and is probably harmful to the overall performance of the corresponding composites. A trade-off between the fiber–matrix bond and fiber strength loss should be considered. The effectiveness of fiber surface treatment on performance improvement of the C_{3D}/EP composites was compared with that of the unidirectional carbon fiber–epoxy composites. In addition, the effects of fiber volume fraction (V_f) and braiding angle on relative performance improvements were determined. Results reveal obvious effects of V_f and braiding angle. A mechanism was proposed to explain the experimental phenomena. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1040–1046, 2002

Key words: three-dimensionally (3D) braided; carbon fiber; composites; interfacial adhesion; surface treatment

INTRODUCTION

Conventional biomedical metals, such as stainless steel, titanium, and its alloy, cobalt-chromium alloy, are not ideal materials for fracture fixation because of their much higher stiffness than the underlying bone. The stiff osteosynthesis devices can lead to long-term stress or strain shielding, prevent formation of callus, delay unions and nonunions, and cause bone atrophy and thus may result in refracture after the removal of fracture devices.[1–4] Another problem in using metallic fixation systems is the corrosion that produces metallic ions and thus causes hypersensitivity. To overcome the major disadvantages of metallic devices and retain their high strengths, three-dimensional (3D) carbon fiber–epoxy (C_{3D}/EP) composites were prepared. The C_{3D}/EP composites can offer lower stiffness than

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metals, higher impact damage and delamination tolerances, and superior fracture toughness to unidirectional fiber composites.[5] More importantly, the use of the C_{3D}/EP composites allows us to tailor their mechanical properties such as elastic modulus to match that of bones to provide a state of stress in bones close to physiological level, as well as strength to meet the requirements of bone fixation.

It is well known that the surfaces of carbon fiber can be modified by surface treatment. A literature search has shown that a study on the effect of fiber surface treatment on properties of 3D composites has not been published, although much research has been conducted to enhance the adhesion between carbon fiber and polymer matrix for unidirectional and short-fiber composites.[6–9] The aims of this study are, thus, to investigate the influence of carbon fiber surface treatment on mechanical properties of the C_{3D}/EP composites as well as to determine the effects of fiber volume fraction (V_f) and braiding angle on performance improvement caused by fiber surface treatment.

EXPERIMENTAL

Materials

The matrix material (epoxy resin) and the 3D fabrics used here were the same as that applied earlier.[5]

Preparation of Composite Samples

The preparation procedures of the C_{3D}/EP composite samples were described in the first part of this series of articles.[5] Unidirectional carbon fiber–epoxy resin (C_L/EP) composite samples were also prepared in the present work to determine the effect of fiber architecture on performance improvement. Similar to the C_{3D}/EP composite samples, the C_L/EP composite samples were also prepared by vacuum impregnation technique. Instead of the 3D fabrics for the preparation of the C_{3D}/EP composite samples, the unidirectional fibers were placed parallel to long axis of the specimen to produce the C_L/EP composite samples. The fiber volume fraction (V_f) of the C_L/EP composites was controlled by the amount of fiber bundles. Other processing parameters were identical to those applied to the C_{3D}/EP composite samples. The fiber volume fractions of the C_{3D}/EP and C_L/EP composites were kept 39 ± 2 and 40 ± 1%, respectively, unless noted.

Air-Oxidation of Carbon Fibers

A lot of approaches such as gas-phase oxidation (in air, O_2, O_3, CO_2, SO_2, etc.), liquid phase oxidation (HNO_3, NaClO, HClO, $KMnO_4$, etc.), plasma treatment, and grafting of carbon fibers were pursued to enhance the fiber–matrix bond. The advantages of oxidation in air including low cost, ease of operation, lack of pollution, and excellent homogeneity make it one of the best approaches. The carbon fibers used in this work were oxidized in air under different conditions, that is, 673K/1h, 723K/1h, and 723K/2h.

Measurements

Fracture Strength of Fibers

The fracture strength of the treated and untreated fibers were tested at room temperature in a DL-1000B tensile test machine at a cross speed of 1 mm min^{-1} and a gauge length of 40 mm, according to the national standard testing method of China GB 3362-82.

BET Surface Areas

The Brunauer–Emmett–Teller (BET) surface areas of the treated and untreated carbon fibers were determined by a ASAP-2400 automatic physical adsorber by using highly purified nitrogen gas. The details were reported in ref 10.

Mechanical Properties

The measurement procedures of the mechanical properties (flexural strength and modulus, shear and impact strengths) of the C_{3D}/EP and C_L/EP composite samples were identical to those described in Part I of this series of articles.[5] For C_L/EP composite samples, flexural, shear, and impact test samples were tested longitudinally, and C_{3D}/PLA composite specimens were tested along warp tows. At least five samples were tested for each sample group from which the mean values and the standard deviations were reported.

Interfacial Bonding Strength

Many test techniques for interface adhesion were reported, including fragmentation test,[11] single fiber pull-out,[12] fiber-bundle pull-out,[13] microcompression,[14] transverse tensile,[15] T-peel,[16] in-

terlaminar shear strength (via a short-beam three-point bending test),[17] and transverse flexural tests.[18] Here, an interlaminar shear test with the C_I/EP composite was carried out to measure the interlaminar shear strength according to Chinese national test standard GB 1450.1-83, which was considered to directly indicate the fiber/matrix adhesion strength by keeping a constant fiber content.[19] The test arrangement was reported elsewhere in detail.[19]

SEM Observation

The surfaces of the untreated and treated carbon fibers were observed by a XL-30 model environmental scanning electronic microscope (ESEM). The scanned surfaces were coated with a thin layer of gold to eliminate charging effects particularly at high magnifications.

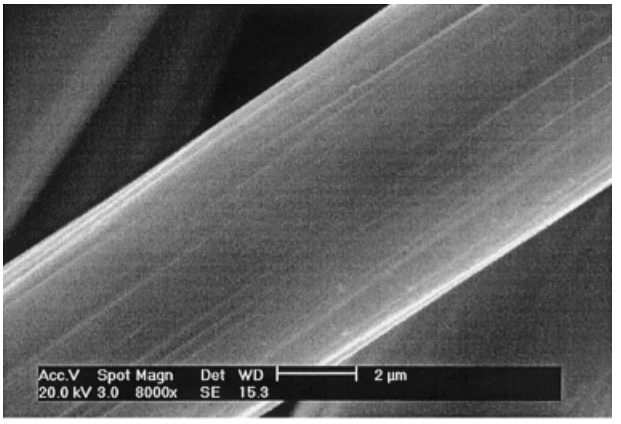
RESULTS AND DISCUSSION

SEM Observation

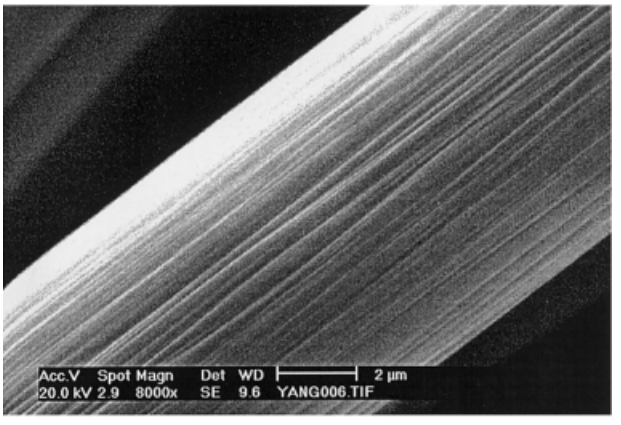
First of all, the effect of air oxidation on fiber surface morphology was studied. Changes in fiber surface morphology as a result of air oxidation are depicted in Figure 1. Clearly, the surfaces of the untreated fibers seem to be smooth; only a few shallow crevices can be found. After surface treatment, the longitudinal crevices deepen and the roughness of the fiber surface increase [see Fig. 1(b)]. A typical high-magnification view (×40) of fiber surface [see Fig. 1(c)] shows some deep micropits. It is interesting to note that the micropits are found on all fiber surfaces we have observed. Precisely, all these micropits are located in crevices of fibers. The site-selectiveness of the micropits in fiber crevices may suggest that there are more defects in carbon fiber crevices because the formation of micropits occurs preferably in defect-rich sites.

Changes in Fracture Strength of Fibers

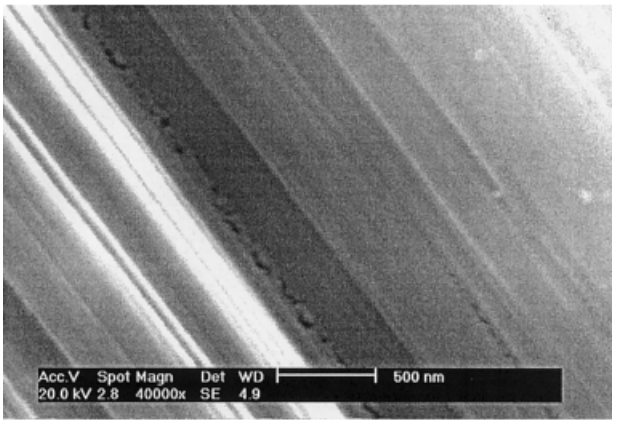
Changes in characteristics (fracture strength, BET surface area) of carbon fibers caused by air-oxidization are listed in Table I. As expected, the improvement in surface roughness results in the increase of fiber surface area, which has been confirmed by BET surface area measurement presented in Table I. The increase of fiber surface area results from deepened crevices and formation



(a)



(b)



(c)

Figure 1 SEM micrographs of carbon fibers: (a) untreated; (b) and (c) air-oxidized at 723K/2h.

of micropits in crevices of fiber surfaces. It is found that air oxidation at 673K/1h, 723K/1h, and 723K/2h enhances the interfacial adhesion strength (IAS) of the C_I/EP composites by 73, 107, and 113%, respectively. The IAS measured with the C_I/EP

Table I Influence of Air Oxidation on the Properties of Carbon Fibers and Their Composites

	Air Oxidation Conditions			
	Untreated	673K/1h	723K/1h	723K/2h
BET surface area (m^2/g)	0.78 ± 0.02	1.37 ± 0.08	1.91 ± 0.12	2.98 ± 0.15
Fracture strength loss (%)	0.0 ± 0.0	0.5 ± 0.1	11.0 ± 1.1	32.2 ± 1.2
Interfacial adhesion strength (MPa)	15 ± 1.0	26 ± 1.1	31 ± 1.2	32 ± 1.2

composites can reflect the fiber–matrix bond conditions of the C_{3D}/EP composites because the fiber–matrix adhesion may be not related to fiber architecture. The improvement in IAS can be easily explained by the enhancement in mechanical interlocking due to rougher surface (more contact points between fibers and matrices), as well as by the improvement in wettability due to higher surface energy, which was verified by other research.[20]

Data in Table I obviously show that air oxidation degrades carbon fibers. Air oxidization at 723K for 2 h lost 32% of their initial fracture strength. This large reduction in fracture strength is attributed to the large number of micropits on fiber surfaces. Therefore, it is reasonable to conclude that severe oxidation in air will cause many deep micropits and thus result in great strength loss of fibers, which will be deleterious to the overall mechanical performance of corresponding composites (see below).

Changes in Mechanical Properties of Composites by Air-Oxidation

Flexural Properties

The effect of air oxidation on flexural strength and modulus of the C_{3D}/EP composites is depicted in Figure 2. Included are the C_L/EP composites for comparison purposes. The maximum flexural strength and modulus for the C_{3D}/EP composites are observed at 723K/1h treatment and they decrease when the treatment time increases to 2 h, owing to great fiber strength loss. This trend is inconsistent with that of the IAS that enhances monotonically with increasing oxidation time or temperature. This result indicates that the flexural properties of a composite depend on not only the IAS, but also on fiber strength. Hence, it is reasonable to consider that a suitable extent of surface treatment should be selected to get an optimum match between IAS and fiber strength. Excessive fiber surface treatment will seriously damage fiber and cannot result in performance improvement of the corresponding composites, although a very strong fiber–matrix bond can be obtained, which is right for other surface treatment methods, such as liquid oxidation and even plasma treatment,[21] as well as for metallic matrix composites.[22]

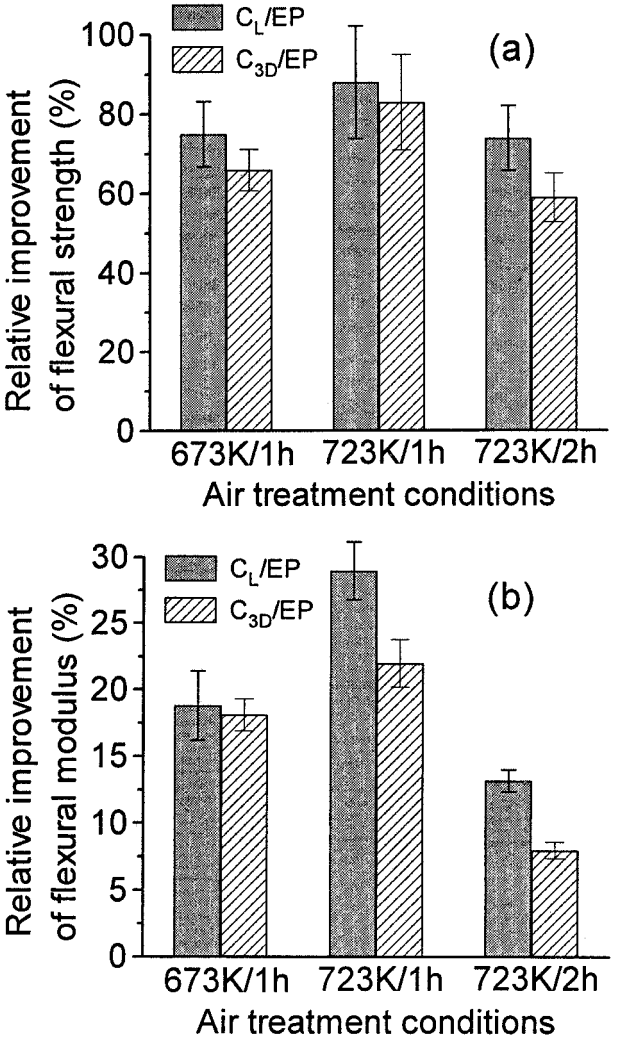


Figure 2 Relative improvements of flexural strength (a) and modulus (b) for the C_{3D}/EP and C_L/EP composites by air oxidation.

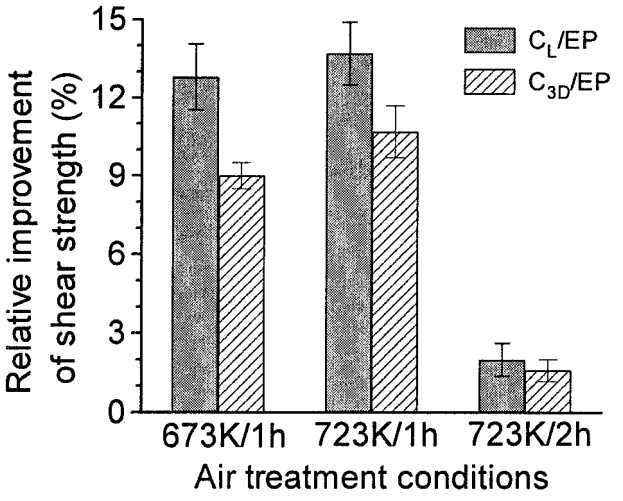


Figure 3 Relative improvements of shear strength for the C_{3D}/EP and C_L/EP composites by air oxidation.

A simple comparison of Figure 2(a) and (b) demonstrates that the relative improvement of flexural strength as a result of air oxidation is greater than that of the modulus. The maximum flexural strength (851 MPa) of the C_{3D}/EP composites is 1.8 times as high as that of the untreated ones (466 MPa); whereas the maximum modulus (33 GPa) only enhances by 20% as compared with that of the untreated one (27 GPa). This is of paramount importance for the materials used as osteosynthesis devices because 851 MPa means a strength much higher than that of the natural load-bearing (cortical) bone (200 MPa)[23] and 33 GPa means a modulus very close to that of the natural load-bearing (cortical) bone (20 GPa),[23] which is the basic requirement for an ideal osteosynthesis device (with a modulus close to the underlying bone and a high enough strength). It is suggested that fiber surface treatment seems to be more suitable to fracture fixation materials than to conventional engineering materials that need high modulus in addition to high strength.

The effects of air oxidation on flexural strength and modulus of the C_L/EP composites are similar to those of the C_{3D}/EP ones. It is noteworthy that the relative improvements in flexural strength and modulus are lower for the C_{3D}/EP composites in comparison to their C_L/EP counterparts.

Shear Strength

Figure 3 displays the relative improvements of the shear strength for both the C_{3D}/EP and the C_L/EP composites. The shear strengths of the C_{3D}/EP and C_L/EP composites are obviously enhanced by air oxidation treatment. Compared with the relative improvements in flexural strength and modulus, the increments in shear strength are slighter, suggesting the shear strength is less sensitive to interfacial conditions because it depends on matrix properties to a larger extent. Similar phenomenon was found for the carbon–PLA composite system.[19] Figure 3 still seems to show that the relative improvement in shear strength of the C_{3D}/EP composites is less significant than the C_L/EP ones.

Impact Strength

Figure 4 shows the relative improvements in impact strength for the C_{3D}/EP and C_L/EP composites after fiber surface treatment in air. It is noted that evident decreases in impact strength caused by air oxidation are observed. The impact strengths of the C_{3D}/EP composites air-treated at 673K/1h, 723K/1h, and 723K/2h are decreased by 2.6, 5, and 15%, respectively. This can be attributed to the strengthened interfaces. It is known that higher IAS will cause higher impact strength if the interface is very weak. On the contrary, further improvement in IAS will result in lower impact strength if IAS exceeds a definite value. The concrete mechanism can be found in ref. [24]. It is also found that the changes in impact strength for the C_{3D}/EP and C_L/EP composites are different. The former exhibits less change than the latter does, which is in agreement with these for flexural strength, modulus, and shear strength.

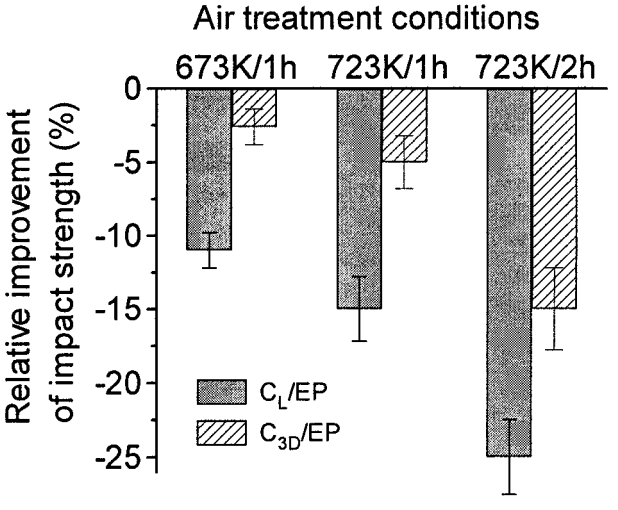


Figure 4 Relative improvements of impact strength for the C_{3D}/EP and C_L/EP composites by air oxidation.

Table II Effect of V_f on Relative Performance Improvements Caused by Surface Treatment

	V_f			
	0.30	0.39	0.46	0.65
Relative improvement of flexural strength (%)	61 ± 11.5	83 ± 12.0	102 ± 13.0	91 ± 18.0
Relative improvement of flexural modulus (%)	12 ± 3.0	22 ± 1.8	56 ± 8.0	42 ± 6.6

The differences in relative improvements of the flexural strength and modulus, shear and impact strengths between the C_{3D}/EP and C_L/EP composites suggest that the effect of surface treatment on the mechanical performance is related to fiber architecture to some extent.

Effect of V_f

Mechanical tests were conducted on the C_{3D}/EP composite samples with high or low V_f. The 3D fabrics used here were air-treated at 723K/1h. The experimental procedures and specimen dimensions were the same as those discussed previously. Table II presents the results of mechanical tests for the C_{3D}/EP composites with different V_f. As can be seen from the data in Table II, the percentages of the increase in flexural strength and modulus because of the improvement of fiber–matrix adhesion enhance monotonically with the increase of V_f up to 0.46, after which they decrease. The explanation is that the composites with a high V_f have a high total interfacial area between fiber and matrix. Accordingly, the composites become more sensitive to the difference in fiber–matrix adhesion. The unusual low performance improvement for a composite with a V_f of 0.65 is related to its high V_v (see below).

Effect of Braiding Angle

The data from mechanical tests (see Table III) show obvious differences in relative improvements of mechanical performance for the C_{3D}/EP composites with various braiding angles [the air-oxidation condition for 3D fabrics was identical (723K/1h)]. It is observed that the lower the braiding angle, the higher the relative improvements of flexural strength and modulus. Data in Table III further confirm that fiber structure exerts an effect on the percentage of performance improvement caused by fiber surface treatment.

Actually, this result agrees well with the result discussed above; that is, the C_L/EP composites show higher relative improvements than the C_{3D}/EP counterparts at an identical V_f level. For an understanding of the variations of relative performance improvements with V_f and braiding angle observed in Tables I and II, we may put forward a proposal: the relative improvements in mechanical properties are proportional to the effective fiber–matrix interface area, A_E. For a C_L/EP composite (considering its properties along fiber axis), A_E is the total interface area, A, if there are no fiber contacts and interface voids within a composite, that is, $A_E = A$. In the case of a C_{3D}/EP composite (considering its properties along warp direction as is in this work), A_E can be calculated with the following equation (neglecting the angle of inclination along z axis because the samples are thin)

$$A_E = A \cos \alpha \leq A \tag{1}$$

where α is the braiding angle of the 3D fabric. Hence, the relative performance improvements of

Table III Effect of Braiding Angle on Relative Performance Improvements Caused by Surface Treatment

	Braiding Angle (°)			
	15	20	27	41
Relative improvement of flexural strength (%)	88 ± 9.0	83 ± 12.0	72 ± 6.0	65 ± 4.2
Relative improvement of flexural modulus (%)	28 ± 1.2	22 ± 1.8	16 ± 1.0	13 ± 1.0

the C_{3D}/EP composites are less than these of the C_L/EP ones at the same V_f level. Similarly, it is easy to understand that the relative improvements of mechanical performance should enhance with decreasing braiding angle and with increasing V_f for the C_{3D}/EP composites. The unusual low relative improvements for a C_{3D}/EP composite with a V_f of 0.65 is attributed to its low A_E as a result of fiber contacts and high V_v.

Of course, the exact mechanism may be more complicated. This proposal should be modified in further studies even if it can explain our experimental results.

CONCLUSIONS

1. Air oxidation of carbon fibers can considerably improve the flexural strength, slightly increase the flexural modulus and shear strength, but reduce the impact strength of the C_{3D}/EP composites.
2. The improvements in flexural strength, modulus, and shear strength, and the reduction in impact strength caused by air oxidation are less significant for the C_{3D}/EP composites than with their C_L/EP counterparts.
3. The mechanical properties of the C_{3D}/EP composites with a higher V_f and lower braiding angle are more sensitive to the improvement of fiber–matrix adhesion than those with a lower V_f and higher braiding angle, respectively. It is proposed that the relative performance improvements for a 3D composite are related to its effective interface area.
4. Excessive fiber surface treatment causes great fiber strength loss due to the presence of micropits. The formation of micropits is site-selective; the preferred site is in fiber crevices. It is inferred that a treatment under moderate oxidation condition can produce the optimum mechanical properties for the C_{3D}/EP composites. It is also inferred that air oxidation treatment of carbon fibers is particularly suitable to the materials for osteosynthesis devices.

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