

# Influence of Surface Treatment of Carbon Fibers on Interfacial Adhesion Strength and Mechanical Properties of PLA-Based Composites

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**ABSTRACT:** In the present study C/PLA composites with different fiber surface conditions (untreated and with nitric acid oxidation for 4 h and 8 h) were prepared to determine the influence of surface treatment on the interfacial adhesion strength and mechanical properties of the composites. A chemical reaction at the fiber–matrix interfaces was confirmed by XPS studies. Nitric acid treatment was found to improve the amount of oxygen-containing functional groups (particularly the carboxylic group, —COOH) on carbon fiber surfaces and to increase the surface roughness because of the formation of longitudinal crevices. The treated composites exhibited stronger interface adhesion and better mechanical properties in comparison to their untreated counterparts. There was a greater percentage of improvement in interfacial adhesion strength than in the mechanical properties. The strengthened interfaces and improved mechanical performance have been mainly attributed to the greater extent of the chemical reaction between the PLA matrix and the carbon fibers. The increased surface roughness also has had a slight contribution. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 367–376, 2001

**Key words:** carbon fiber; polylactide (PLA); composites; interfacial adhesion strength; surface treatment

## INTRODUCTION

It is well known that the properties of composites are significantly controlled by the interface region between the reinforcing fibers and the matrix. Most early work on the development of composite considered the fiber–matrix interfaces to be critical for ensuring good composite mechanical properties. Therefore, many studies have been carried out on the interfacial adhesion between the reinforcing fibers and the matrix.<sup>1–3</sup> However, most of

the studies focused on the system of carbon or glass fibers and engineering polymers.<sup>4–6</sup> There have been very few attempts to evaluate the interfacial adhesion between carbon fibers and resorbable polymers such as polylactide (PLA), polyglycolide (PGA), and polydioxanone (PDS) and their influence on the mechanical performance of the composites.

Biocompatible and resorbable poly(hydroxy acids) like PLA, PGA and so on have frequently been used as materials for internal fixation of bone fractures. However, nonreinforced PLA (or PGA or PDS) has low bending stiffness and shear strength and is not sufficient for fixing a long bone fracture. Accordingly, PLA composites reinforced with randomly oriented, chopped, or continuous carbon fibers are used to produce high-strength

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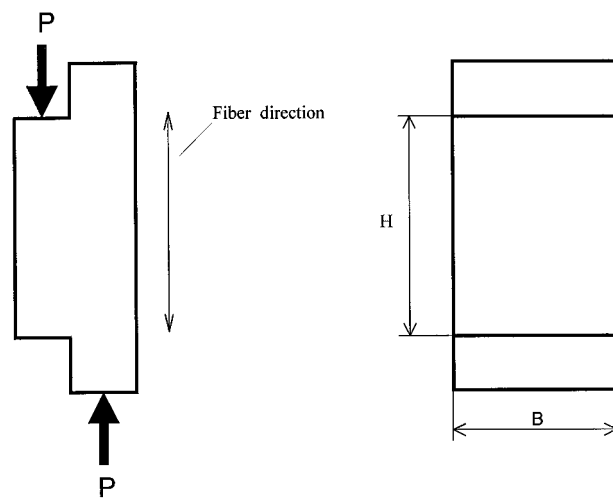
osteosynthesis devices.<sup>7</sup> Nevertheless, little information is available regarding the fiber-PLA interface and its influence on the performance of PLA-based composites.

A great deal of research has been devoted to surface treatment of carbon fibers in order to enhance the surface chemical reactivity, and thus improve their bonding to the matrix. In the case of a carbon fiber-reinforced polymer matrix composite system, one of the most effective surface treatments is liquid-phase oxidation, including oxidation in nitric acid and anodic oxidation in an aqueous electrolytic.<sup>8</sup> The former is simple without requiring a complex apparatus and can produce homogenous modified surfaces.<sup>9</sup> In this work C/PLA composite systems reinforced by carbon fibers with different fiber surface conditions were investigated to identify the surface chemistry of carbon fibers after an oxidation treatment using nitric acid and its influence on fiber-PLA adhesion and thus the performance of the composites. Concentrated nitric acid was employed to oxidize carbon fiber surfaces throughout this investigation.

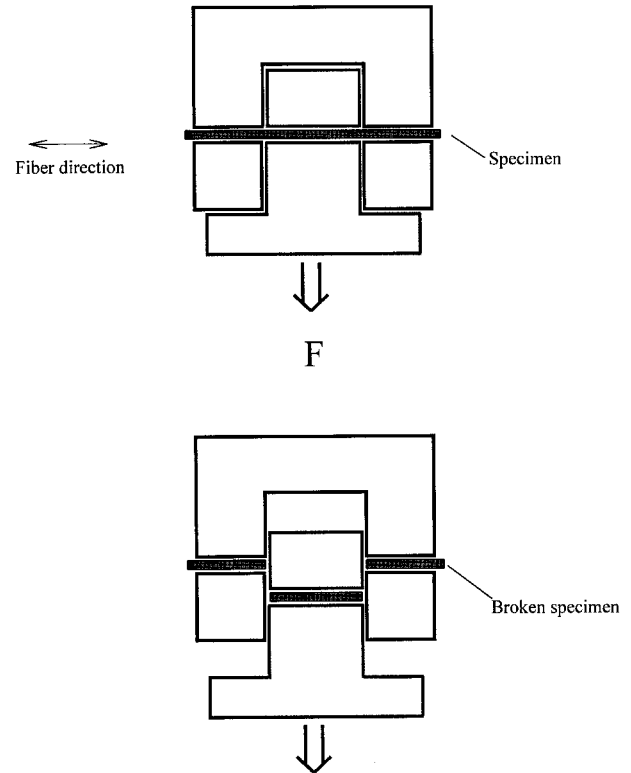
## EXPERIMENTAL

### Raw Materials

The medium-strength polyacrylonitrile-based (PAN-based) carbon fibers used in this experiment were supplied without a sizing finish and had the following characteristics: tensile



**Figure 1** Arrangement for interlaminar shear test.



**Figure 2** Arrangement for shear strength test.

strength, 2000 MPa; tensile modulus, 196 GPa; diameter, 6–8  $\mu\text{m}$ ; density, 1.75  $\text{g}/\text{cm}^{-3}$ . The matrix material, PLA, synthesized by ring-opening polymerization, was obtained from the Institute of Medical Devices of Shandong Province (Jinan, China). The PLA was of an amorphous nature with a glass-transition temperature of 56°C and a molecular weight of 100,000 (determined by viscosity measurement). The PLA was reinforced with three different carbon fibers: untreated fibers, nitric acid-oxidized fibers for 4 h, and nitric acid-oxidized fibers for 8 h. Hereafter these three fibers will be designated as UT-C, T4-C, and T8-C fibers, respectively, and the corresponding composites are denoted as UT-C/PLA, T4-C/PLA, and T8-C/PLA composites, respectively.

### Oxidation of Carbon Fibers with Nitric Acid

Nitric acid (65 wt %, analytical grade) was preheated and maintained at about 115°C in a 1000-mL beaker. Carbon fibers (10 g) wound onto a glass drum were immersed in the nitric acid for periods of 4 and 8 h. The oxidized fibers were then refluxed in acetone (analytical grade) for 12 h,

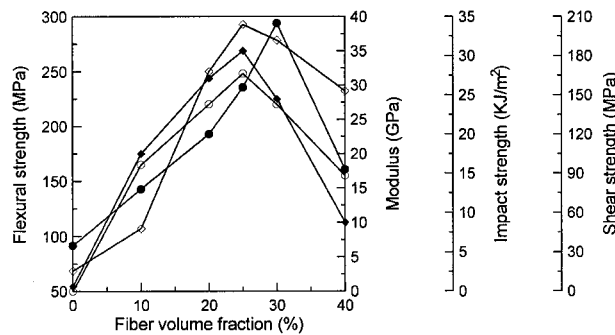
followed by rinsing with distilled water until the pH of the resulting wash water attained a constant value (pH  $\sim$ 6). The nitric acid-oxidized fibers were subsequently dried in an oven at 110°C for about 8 h.

### Extraction of Treated Carbon Fibers

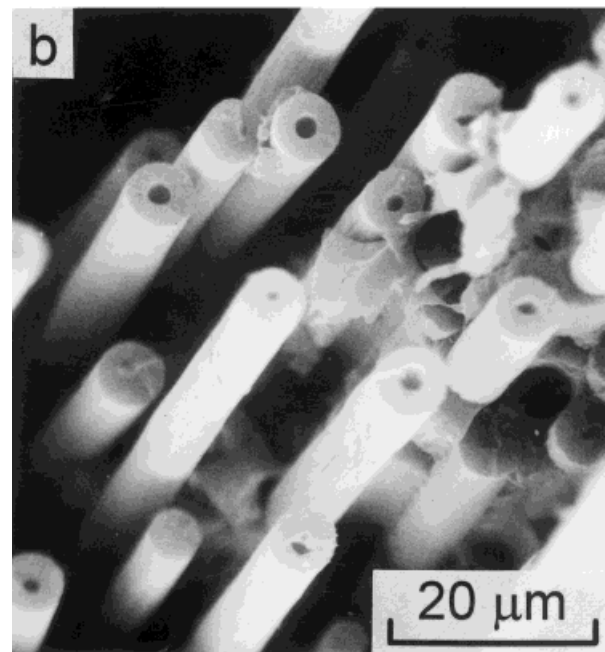
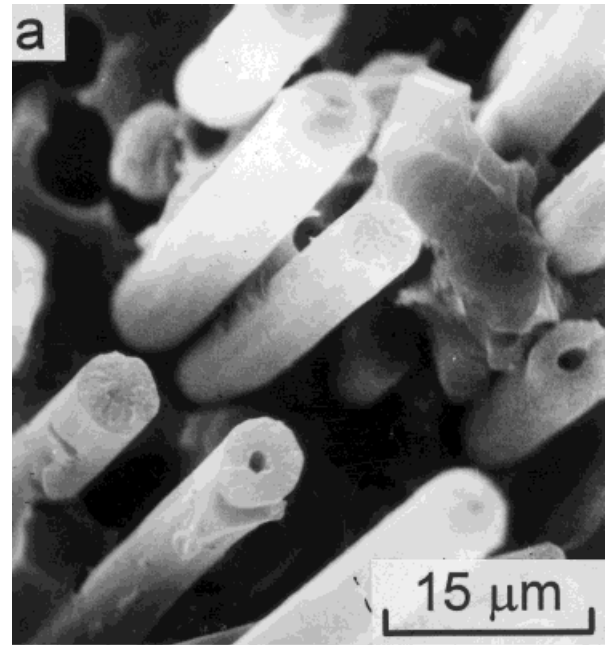
T8-C/PLA composite specimens were selected to determine the reactivity between the carbon fibers and the PLA. The PLA matrix was removed by extraction with acetone for 72 h until a constant weight. The extracted fibers were then resined with distilled water until the pH of the resulting wash water attained a constant value. The fibers were finally dried in a clean oven at 80°C for 24 h. The resulting fibers were denoted as EX-T8-C fibers.

### Preparation of Unidirectional C/PLA Composite Samples

The prepreg sheets were prepared by a similar method to that employed by Zimmerman et al.<sup>10</sup> Briefly, a fiber tow was drawn through a PLA solution bath and wound onto a cylindrical mandrel to form a single layer prepreg. The fiber volume fraction ( $V_f$ ) in the C/PLA composite was controlled by both the solution concentration and the pulling velocity of the fibers. After being in a ventilating cabinet for 24 h to allow the solvent to evaporate, the prepreg was cut into sheets and hand-laid in a metallic mold, keeping all sheets in one direction. The unidirectional C/PLA composite samples were compression-molded under a pressure of 2–3 MPa at  $110 \pm 5^\circ\text{C}$  for 20 min. The heating rate was 5 K/min and the cooling rate was



**Figure 3** Influence of  $V_f$  on mechanical properties for UT-C/PLA composites symbols: ○ Flexural strength, ◆ Flexural modulus, ◇ Impact strength, ● Shear strength.



**Figure 4** Fracture surfaces of UT-C/PLA composites: (a)  $V_f = 25\%$ , (b)  $V_f = 40\%$ .

approximately 4 K/min (furnace cooled). The pure PLA samples were prepared by the same procedure as that utilized for the C/PLA composites. All specimens had a thickness of 2 mm. All resulted samples were stored in a dessicator in order to prevent the absorption of moisture until use.

**Table I Interfacial Adhesion Strength and Mechanical Properties of Different Composites**

Materials	UT-C/PLA	T4-C/PLA	T8-C/PLA
Flexural strength (MPa)	248.0	252.6	280.0
Flexural modulus (GPa)	35.3	41.5	43.0
Impact strength (kJ/m <sup>2</sup> )	34.9	35.8	40.1
Shear strength (MPa)	155.8	160.4	180.2
Interlaminar shear strength (MPa)	18.1	25.1	29.5

### Measurement of Interface Adhesion

Many test techniques for interface adhesion have been reported, including the fragmentation test,<sup>11</sup> single-fiber pullout,<sup>12</sup> fiber-bundle pullout,<sup>13</sup> microcompression,<sup>14</sup> transverse tensile,<sup>15,16</sup> T-peel,<sup>17</sup> interlaminar shear strength (via a short-beam three-point bending test),<sup>18</sup> transverse flexural tests,<sup>19</sup> and others. As an alternative method, here we introduce a method to determine the fiber–matrix adhesion by measuring the interlaminar shear strength, which is considered to directly indicate the fiber–matrix adhesion strength by keeping a constant  $V_f$  via an interlaminar shear test according to Chinese National Test Standard GB 1450.1-83. The test arrangement is shown in Figure 1. The interlaminar shear strength,  $\tau$ , was calculated by

$$\tau = \frac{P}{BH} \quad (1)$$

where  $P$  is the applied load at the moment of fracture,  $B$  is the width of the test specimen, and  $H$  is the height of the plane subjected to shear force.

### Measurement of Mechanical Properties

The static mechanical properties of the composites were measured by doing a three-point flexural test on an DL-1000B electronic testing machine at a temperature of 25°C. Three-point flexural tests were carried out with a span-to-depth ratio of 16:1 at a crosshead speed of 1 mm/min. The flexural strength ( $\sigma$ ) and modulus ( $E$ ) were obtained with the following equations:

$$\sigma = \frac{3Pl}{2bh^2} \quad (2)$$

where  $P$  is the applied load at the moment of fracture,  $l$  is the span length,  $b$  is the width of the test specimen,  $h$  is the thickness of the test specimen; and

$$E = \frac{Pl^3}{4bh^3\delta} \quad (3)$$

where  $P$  is the load at a chosen point on the initial linear portion of the load-deflection curve and  $\delta$  is the deflection corresponding to the load,  $P$ .

The shear strength was measured with an DL-1000B electronic testing machine at a crosshead speed of 1 mm/min. The shear strength was measured with the help of a tool similar to that used by Kettunen et al.<sup>20</sup> and Majola et al.<sup>21</sup> Its test arrangement is depicted in Figure 2.

A X CJ-500 Impact Tester was used in this work to measure the impact properties of the C/PLA composites. Unnotched 80 × 6 × 2 mm bars were used at a span of 50 mm to measure the impact strength.

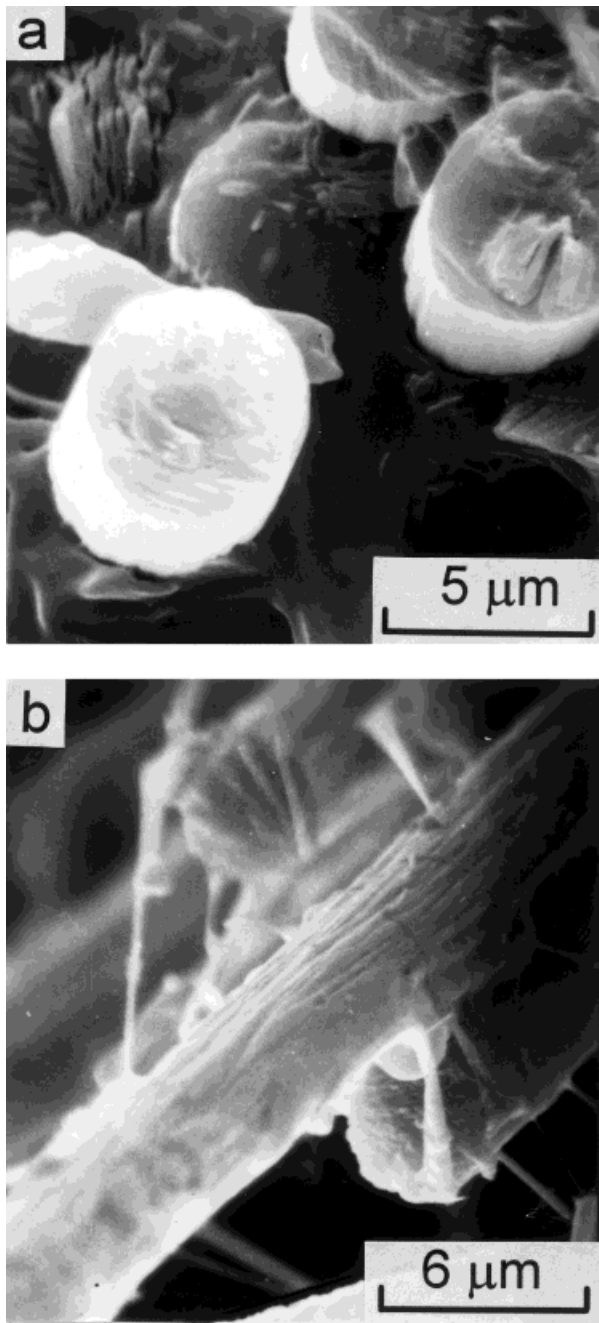
A minimum of five specimens was tested for each set of samples, and the average values are reported.

### SEM Observation

The surface morphology of each filament before and after nitric acid treatment was examined with a Hitachi X-650 scanning electronic microscope (SEM). The fracture surfaces of the specimens were also examined to help identify the failure modes and to provide a qualitative assessment of the fiber–matrix adhesion.

### XPS Analyses

The UT-C, T4-C, and T8-C fibers were characterized with X-ray photoelectron spectroscopy (XPS). Analyses were performed on a PHI 1600 model surface analysis system with a 250 W MgK $\alpha$  X-



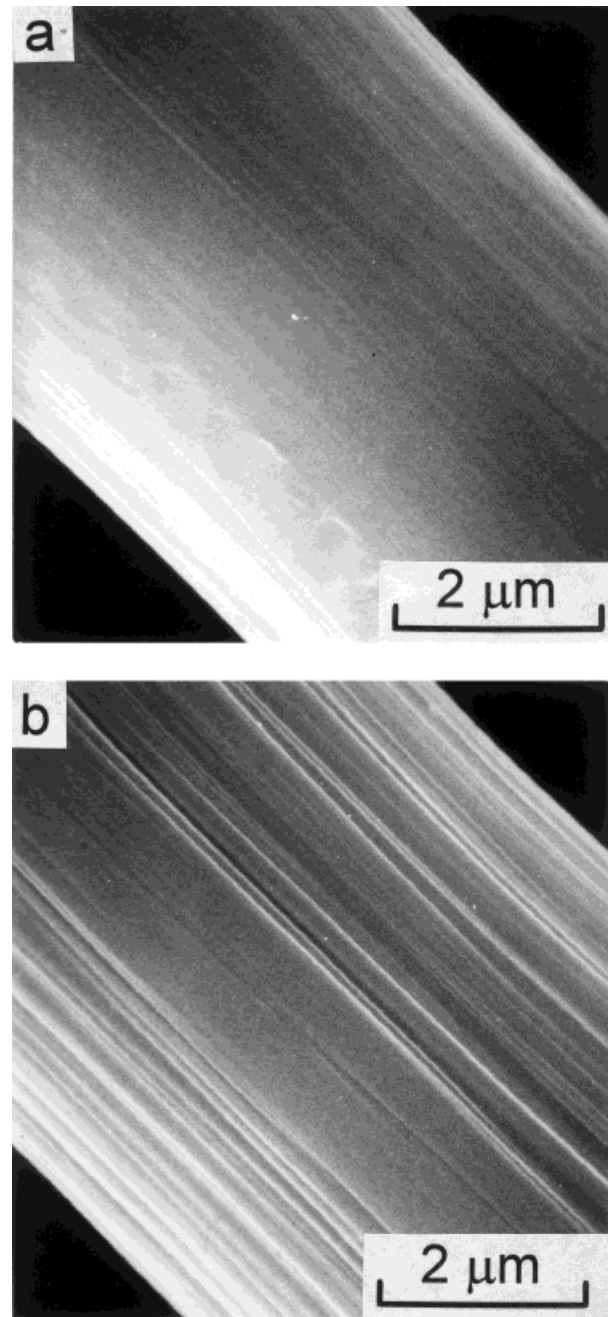
**Figure 5** Tensile fracture surfaces of C/PLA composites: (a) UT-C fibers, (b) T8-C fibers.

ray (1253.6 eV) source at a base pressure in the  $10^{-8}$ – $10^{-9}$  Torr range. All XPS spectra were average results from a surface area equal to  $0.8 \text{ mm}^2$ . All spectra of XPS were collected and fitted using PHI-MATLAB data-processing software. The surface group content was determined from the XPS peak area after subtraction of a linear background.

## RESULTS AND DISCUSSION

### Influence of $V_f$ on Mechanical Properties of Untreated Composite System

A typical plot of  $V_f$  versus flexural strength and modulus, impact strength, and shear strength is shown in Figure 3 for untreated composite sys-



**Figure 6** SEM micrographs of carbon fiber surfaces (a) before oxidation and (b) after 8 h oxidation in nitric acid.

**Table II Elemental Composition of Different Fiber Surfaces**

Fibers	C	O	N
UT-C	93.7	5.3	1.0
T4-C	86.1	12.0	1.8
T8-C	75.8	22.0	2.2

tem. It is obvious that all mechanical properties (flexural strength and modulus, impact strength, and shear strength) initially increase with  $V_f$ , reach maximum values, and then decrease with  $V_f$ . The optimum  $V_f$  for flexural strength, modulus, and impact strength is 25%, but the shear strength exhibits its maximum value at  $V_f = 30\%$ . The increase of these mechanical properties with  $V_f$  is anticipated and can be easily explained by the rule of mixtures. An interpretation of the reducing trend above the optimum  $V_f$  is provided by Figure 4, which shows that a higher  $V_f$  (40%) leads to fiber contacts, as shown in Figure 4(b). Of course, this lower value of the optimum  $V_f$  may reflect that improvements are needed in the composite preparation process, particularly, the fiber dispersion technique.

### Influence of Surface Treatment on Mechanical Properties of C/PLA Composites

The interfacial adhesion strengths obtained from the interlaminar shear test are listed in Table I. The interlaminar shear strength for nitric acid-oxidized composite systems was found to be higher than that of the untreated one. The interlaminar shear strength for the treated system increased by 38.7% and 63.0% after 4 h and 8 h, respectively, of oxidization in nitric acid compared with that of the untreated one. This suggests that surface treatment substantially improves the fiber-matrix adhesion and therefore improves the mechanical properties of the composites (Table I). Nevertheless, because of the surface treatment the percentage increase of these strengths is much lower in comparison to that of interlaminar shear strength, suggesting that the interlaminar shear strength, whose measurement was derived from the interlaminar shear test, is sensitive to the fiber-matrix adhesion. Similar to other fiber-matrix adhesion-controlled parameters such as transverse tensile strength and interlaminar shear strength (from the short-beam three-point bending test), this in-

terlaminar shear strength can also be used to indicate the interfacial adhesion strength. Further, the interlaminar shear test may be applied to assess the relative interfacial adhesion strength in other fiber composite systems.

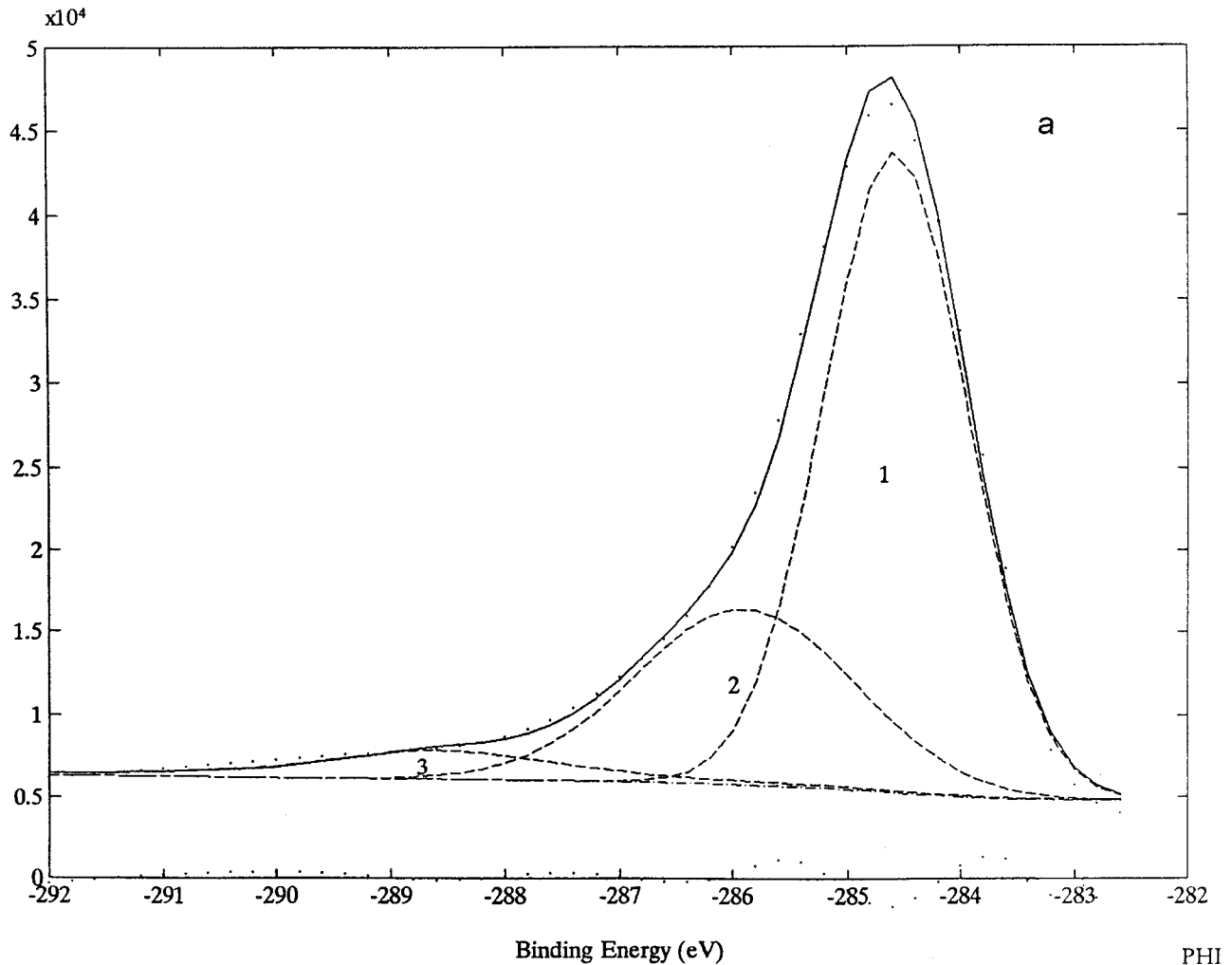
It can be observed in our experiments that all strength values rise after nitric acid oxidation, and the longer the oxidation time, the higher the strength values. It should be noted that too long an oxidation time—beyond 8 h—is not suitable because of excess fiber degradation during the oxidation process.

Interlaminar shear strength is a matrix- and interface-dominated mechanical parameter, implying that the observed improvement in interlaminar shear strength for the treated composite systems is only attributable to the strengthening of the fiber-matrix interfaces because the matrix is unchanged.

Interface adhesion quality can also be assessed qualitatively through SEM fractography. For example, Ibarra and Panos<sup>22</sup> interpreted their experimental results in terms of the fiber-matrix interface, which was characterized by SEM. Fracture surfaces of the C/PLA composites clearly demonstrate the effect of nitric acid oxidation on the interfacial adhesion. Different failure modes can be observed in Figure 5. The fiber surfaces from the UT-C/PLA composites are clean, indicating extensive interfacial failure; while for T8-C/PLA composite specimens, the failure mode is mainly matrix failure since some adhering PLA are observed on fiber surfaces. This result indicates that treated composites exhibit stronger interfaces than untreated ones, which is in agreement with the result from interlaminar shear test. Similar observations and analyses were reported elsewhere.<sup>23,24</sup>

### SEM Observation of Fiber Surfaces

Typical surface topographical features of carbon fibers, with and without nitric acid oxidation, are shown in Figure 6. The surfaces of UT-C fibers seem to be smoother, with no pits and crevices found, as shown in Figure 6(a). After 4 h of surface treatment, some longitudinal crevices are obvious. With a long treatment time (e.g., 8 h), the crevices on fiber surfaces seem to deepen [Fig. 6(b)] because of the continuous etching effect of nitric acid. That is, the fiber surfaces become increasingly rough in the form of crevices when the treatment time is extended. It is believed that the increased fiber roughness and thus the improved



**Figure 7** XPS spectra of C1s region: (a) UT-C fibers, (b) T4-C fibers, and (c) T8-C fibers; for each: (1) C—C, (2) C—OH, (3) —COOH, and (4) new functionality.

surface area should promote the mechanical interlocking effect between the fibers and the matrix. In addition, removal of oily contaminants and other organic species may also have a slight effect in improving fiber–matrix adhesion since the fiber surfaces that have been cleaned, a condition confirmed by the increased electrical conductivity measured with the fiber bundles,<sup>25</sup> are believed to enhance the wettability between the fibers and the matrix. This is thought to permit a more intimate fiber–matrix contact and therefore to enhance the van der Waals and/or dipole–dipole interactions.

#### XPS Results

In principle, good adhesion of most matrix materials with carbon fibers mainly comes from a

chemical interaction between the matrix materials and functionalized carbon fiber surfaces during composite synthesis process because van der Waals and dipole–dipole interactions are relatively weaker than chemical bonds.

In order to further determine the mechanisms of adhesion promotion by nitric acid treatment, UT-C, T4-C, and T8-C fibers were studied by XPS. A summary of the surface elemental analyses is given in Table II. Comparisons of the results for T4-C and T8-C with untreated fibers indicate that surface treatment yields a significant increase in the oxygen level. Apparently, the concentration of oxygen measured on the surfaces of T4-C and T8-C fibers is, respectively, more than 2 and 4 times greater than the level measured on the untreated counterparts. The increase in the surface nitrogen content resulting from an oxidation

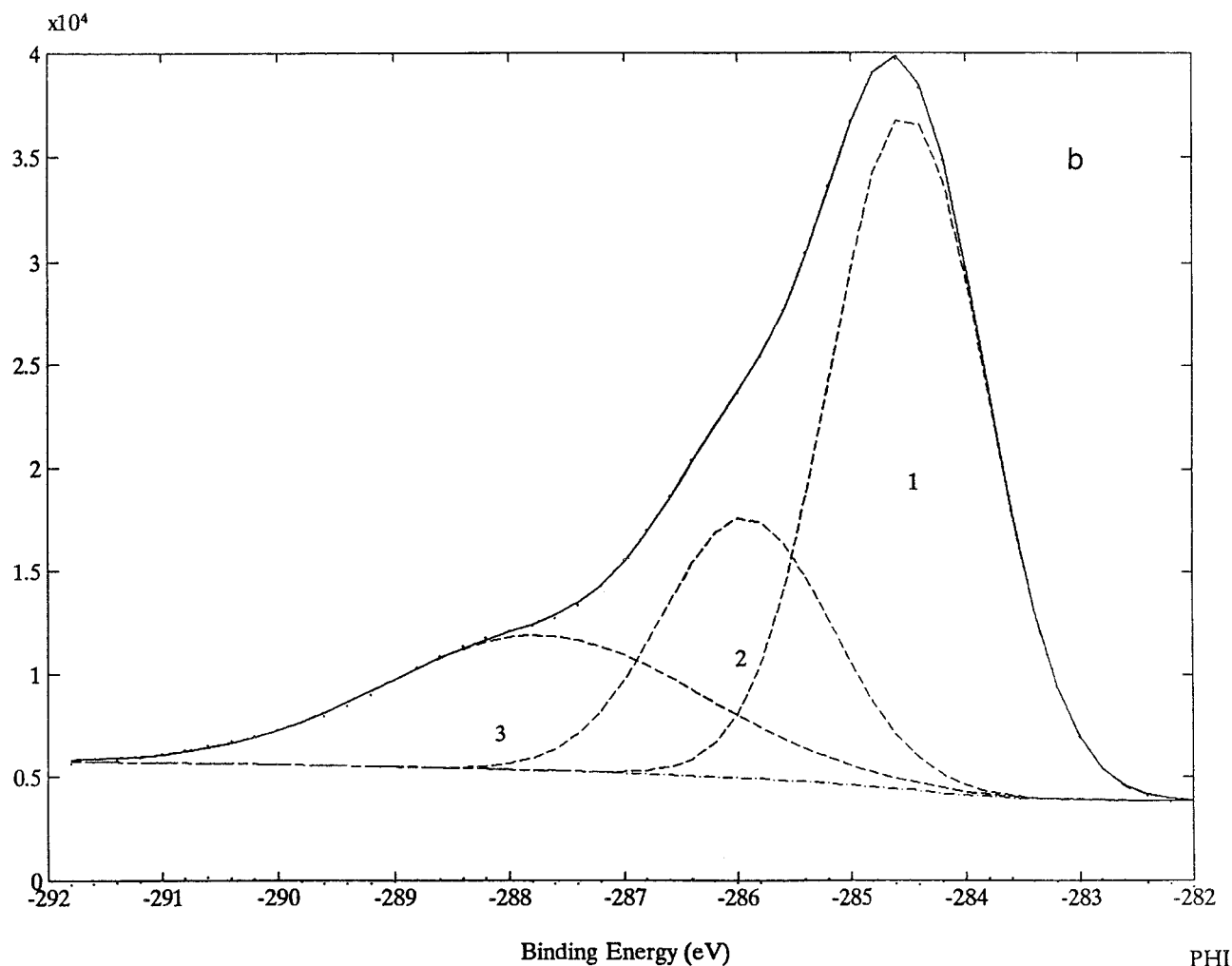


Figure 7 (Continued from the previous page)

treatment in nitric acid is also obvious. The surface nitrogen content of T8-C fibers is twice that measured for the untreated ones.

It may be more important to detect the variations in functionality on fiber surfaces before and after oxidation. We do not show an overall spectrum for any of those fiber samples because they are all essentially similar, showing C1s, O1s, and N1s. Rather, we show the curve-fitted spectra of an individual region. The curve-fitted C1s spectra for carbon fibers under different conditions are illustrated in Figure 7. The surface functional groups and their contents are listed in Table III. The surface functional groups have been determined to be C—C, C—OH and —COOH groups for both untreated and treated (T8-C) fibers, which is consistent with previous results obtained by Jones and Sammann for PAN-based carbon fibers.<sup>26</sup> As expected, a significant increase in the

amount of —COOH and C—OH was observed for an oxidation treatment in nitric acid. Similar observations have been made by other researchers.<sup>27</sup> Obvious differences clearly exist in the spectra between T8-C and EX-T8-C fibers. The C—C and C—OH groups are present on those two fibers, but their contents differ. More important, it can be seen that after synthesizing with the PLA matrix, the —COOH group disappears and is substituted for by a new group—that is, the —COOH functionality has in some way been consumed and converted into another functional group during composite synthesis process, possibly through an esterification reaction.<sup>28</sup> The exact reaction mechanism will have to be determined by other surface analyses, including Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), and Raman spectroscopy, but without a doubt a chemical reaction



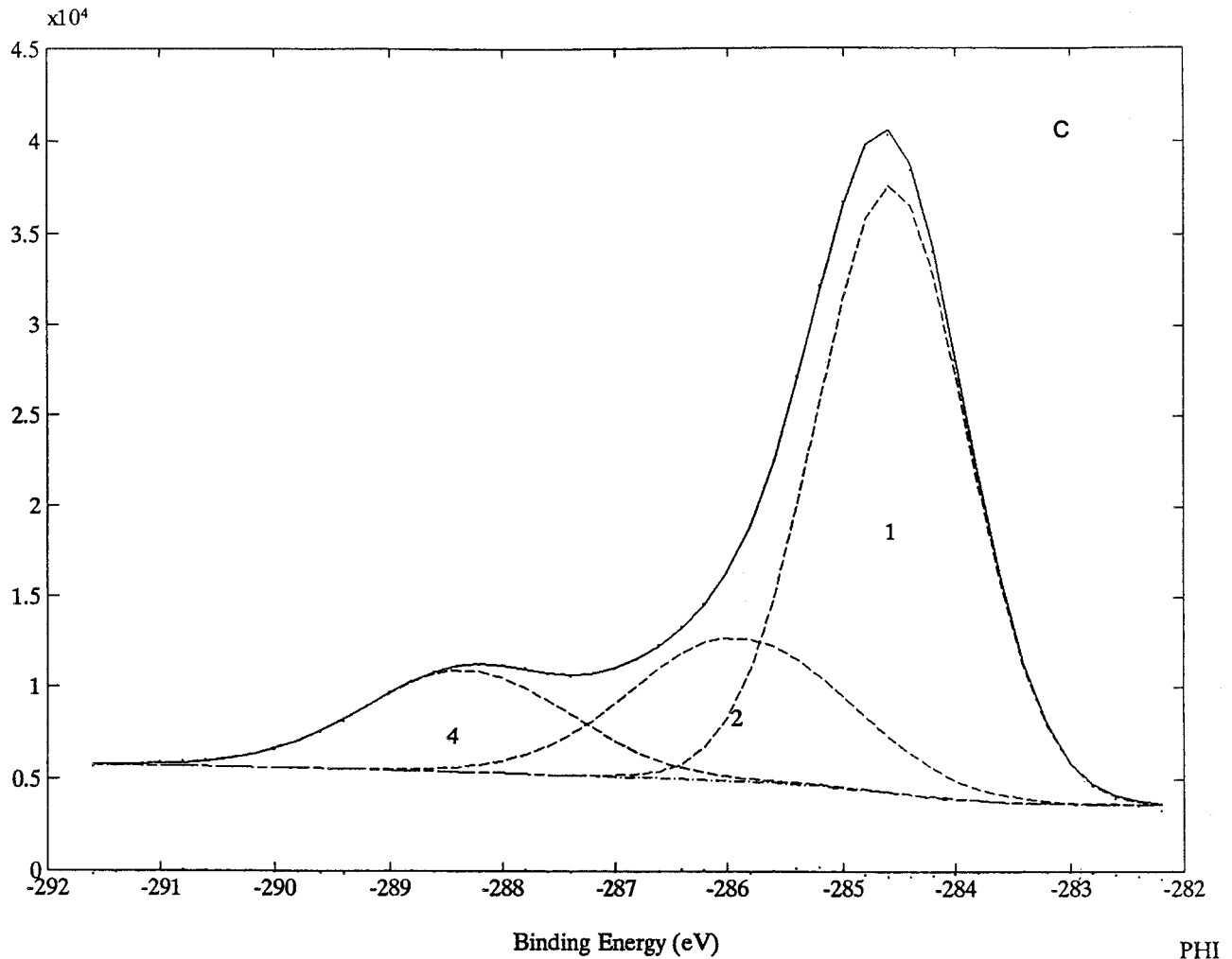


Figure 7 (Continued from the previous page)

does occur at the fiber-PLA interfaces. Therefore, it is reasonable to deduce that a chemical reaction that has occurred at the fiber-PLA interfaces is the main contributor to improvement in the interfacial adhesion strength and the overall performance for C/PLA composites.

There is greater reactive functionality ( $-\text{COOH}$ ) on the treated fiber surfaces than on the untreated ones. In other words, more sites

exist to form chemical bonds per unit of surface space for the treated fibers than exist for their untreated counterparts, causing the treated composites to exhibit stronger interfaces. As mentioned above, since van der Waals forces and dipole-dipole interaction are much weaker than chemical bonds, the significant improvement in interfacial adhesion strength and the obvious enhancement in overall mechanical properties for the treated systems can be mainly attributed to an increased level of chemical reaction.

Table III Functional Groups of Different Carbon Fiber Surfaces and Their Contents

Fibers	C—C	C—OH	—COOH	New Group
UT-C	65.9	27.5	6.6	0
T8-C	63.9	21.1	15.0	0
EX-T8-C	54.8	23.1	0	22.1

## CONCLUSIONS

1. XPS analyses demonstrate that a chemical reaction between the carbon fibers and the PLA matrix occurs during the composite synthesis process.

2. The degree of fiber-surface roughness increases as the duration of oxidation treatment increases. Increased roughness in the form of crevices helps to a limited extent to enhance fiber-matrix adhesion.
3. When treated with nitric acid, surfaces of the carbon fibers exhibit an increased concentration of the reactive group ( $-\text{COOH}$ ), that is, the number of the bonding sites, which significantly improve the adhesion of carbon fibers to the PLA matrix via an interfacial chemical reaction.
4. Surface treatment improves the overall mechanical properties of the C/PLA composites, which can be directly attributed to improvement of the fiber-matrix adhesion. The improved interfacial adhesion strength and the overall mechanical properties for the treated C/PLA composite systems can be mainly attributed to the increased chemical-reaction level.

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## REFERENCES

1. Cho, K.; Kong, T.; Lee, D. *Polym J* 1997, 29(11), 904.
2. Noobut, W.; Koenig, J. J. *Polym Compos* 1999, 20(1), 38.
3. Keusch, S.; Haessler, R. *Composites* 1999, 30A, 997.
4. Dilsiz, N.; Akovali, G. *Composite Interfaces* 1996, 3, 401.
5. Lee, S. M. *Compos Sci Technol* 1992, 43, 317.
6. Hoecker, F.; Karger, K. J. *Composites* 1994, 25, 729.
7. Corcoran, S.; Koroluk, J.; Parson, J. R.; Alexander, H.; Weiss, A. B. In *Current Concepts for Internal Fixation of Fractures*; Uthoff, H. K., Ed.; Springer-Verlag: New York, 1981; p 136.
8. Park, S. J.; Park, B. J. *J Mater Sci Lett* 1999, 18, 47.
9. Wu, Z.; Pittman C. U.; Gardner, S. D. *Carbon* 1995, 33(5) 597.
10. Zimmerman, M.; Parsons, J. R. *J Biomed Mater Res* 1987, 21, 45.
11. Dai, S. R.; Piggott, M. R. *Compos Sci Technol* 1993, 49, 81.
12. Miller, B.; Gaur, U.; Hirt, D. E. *Compos Sci Technol* 1991, 42, 207.
13. Domananovich, A.; Peterlik, H.; Kromp, K. *Compos Sci Technol* 1996, 56, 1017.
14. Chen, E. J. H.; Young, J. C. *Compos Sci Technol* 1991, 42, 189.
15. Keusch, S.; Haessler, R. *Composites* 1999, 30A, 997.
16. Fitzer, E.; Weiss, R. *Carbon* 1987, 25, 455.
17. Yamashita, Y.; Nakao, K. *J Reinforced Plastic Composites* 1999, 18(9), 862.
18. Jang, B. Z. *Compos Sci Technol* 1992, 44, 333.
19. Upadhyaya, D.; Tsakiroopoulos, P. *J Mater Processing Technol* 1995, 54, 17.
20. Kettunen, J.; Makela, E. A.; Miettinen, H.; Nevalainen, T.; Heikkila, M.; Pohjonen, T.; Tormala, P.; Rokkanen, P. *Biomaterials* 1998, 19, 1219.
21. Majola, A.; Vainionpaa, S.; Rokkanen, P.; Mikkola, H. M.; Tormala, P. *J Mater Sci Mater Med* 1992, 3, 43.
22. Ibarra, L.; Panos, D. *Polym Int* 1997, 43, 251.
23. Wan, Y. Z.; Wang, Y. L.; Luo, H. L.; Cheng, G. X.; Yao, K. D. *J Appl Polym Sci* 2000, 75, 987.
24. Ageorges, C.; Friedrich, K.; Ye, L. *Compos Sci Technol* 1999, 59, 2101.
25. Wan, Y. Z.; Wang, Y. L.; Li, G. J.; Luo, H. L.; Cheng, G. X. *J Mater Sci Lett* 1997, 16, 1561.
26. Jones, C.; Sammann, E. *Carbon* 1990, 28, 509.
27. Gardner, S. D.; Singamsetty, C. S. K.; He, G.; Pittman, C. U. *Appl Spectrosc* 1997, 51, 636.
28. Qi, J. G. Masters Thesis, Tianjin University, 2000.