

# *In Vitro* Degradation Behavior of Carbon Fiber-Reinforced PLA Composites and Influence of Interfacial Adhesion Strength

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**ABSTRACT:** In the present study, carbon fiber-reinforced polylactide (C/PLA) composites with different interfacial conditions were prepared to determine the influence of interfacial adhesion strength (IAS) on *in vitro* degradation behavior of the C/PLA composites. Pure PLA and untreated and treated C/PLA composite samples were immersed in phosphate buffered saline (PBS; pH 7.4,  $37 \pm 0.5$  °C) for predetermined time periods. These samples were removed at each degradation time, measured to analyze molecular weight loss, weighed to assess water uptake and mass loss, and mechanically tested to obtain bending strength, modulus, and IAS. The matrixes in the C/PLA composites showed higher water uptake and lower mass loss in comparison with the pure PLA. Further, the PLA matrix in the treated composite absorbed less water and lost less mass and molecular weight than its counterpart in the untreated composite. Mechanical tests confirmed that the treated C/PLA composite exhibited a slower rate of decrease in bending strength, modulus, and IAS than the untreated one. The differences in degradation behavior between two composites can only be attributed to the difference in interfacial conditions because all other parameters were kept constant. The loss of bending strength and modulus was mainly caused by the interface degradation of the C/PLA composites. It can be concluded from our *in vitro* observations that the IAS had an obvious influence on the degradation characteristics of the C/PLA composites. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 150–158, 2001

**Key words:** carbon fiber; polylactide (PLA); composites; interfacial adhesion strength (IAS); *in vitro* degradation

## INTRODUCTION

A variety of bioabsorbable polymers have been used to date as internal fixation devices for bone fracture. Bioabsorbable devices offer at least two main advantages compared with conventional metallic implants: first, no retrieval of the devices is needed after fracture healing, and second, the

stress-shielding atrophy and weakening of the fixed bone that is associated with rigid metallic fixation can be alleviated.<sup>1,2</sup>

The most widely used bioabsorbable osteosynthesis materials are aliphatic polyesters of  $\alpha$ -hydroxyacid derivatives such as polylactide (PLA), polyglycolide (PGA), their copolymers (PGA/PLA), polydioxanone (PDS), and poly- $\beta$ -hydroxy butyric acid (PHBA).<sup>3–5</sup> PLA has been widely used because its degradation product, lactic acid, is biocompatible and can be incorporated in the tricarboxylic acid cycle.<sup>6</sup> However, non-reinforced

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PLA has low bending stiffness and shear strength and is not sufficient for fixing a high-load-bearing bone fracture. Accordingly, PLA-based composites reinforced with randomly oriented, chopped, or continuous carbon fibers have been used to produce high-strength osteosynthesis devices.<sup>7</sup> In our previous work,<sup>8</sup> carbon fiber-reinforced PLA (C/PLA) composites with different interfacial adhesion strength (IAS) were obtained, and the influence of the IAS on mechanical performance was investigated.

As materials for bone internal fixation devices, the degradation rates of these composites are of crucial importance from both biomedical and consumer applications points of view. Fast degradation of bioabsorbable devices will limit their application only to fast-healing fractures and may cause sterile sinuses. Slow degradation reduces the risk of sterile sinuses. However, too slow degradation means incomplete obviation of stress-shielding and may cause other problem. For example, a subcutaneous swelling and itching reported by Bergsma et al.<sup>9</sup> was caused by the presence of polymer debris 3 years after implantation.<sup>10</sup> Hence, the degradation rate is an important factor determining the nature and intensity of the inflammatory response and therefore the biocompatibility of an implanted polymer material.<sup>11</sup> It has been shown that the degradation rate of PLA is controlled by molecular weight,<sup>12</sup> pH value,<sup>12,13</sup> temperature,<sup>13</sup> device size,<sup>14</sup> enzymes,<sup>15</sup> crystallinity,<sup>10</sup> leachables and impurities,<sup>16</sup> etc. In addition, a heterogeneous degradation (faster degradation inside than at the surface) for PLA has been reported.<sup>17–19</sup> The enhanced degradation rate in the internal part was assigned to an “autocatalytic effect” due to generated carboxylic end groups. The degradation mechanism of PLA and other bioabsorbable polymers is being investigated worldwide because it is of paramount importance in biomaterial selection, design, and service. Nevertheless, up to now, there is little available literature regarding the degradation behavior of bioabsorbable polymer-based composites and the influence of interface characteristics. Zimmerman and Parsons<sup>7</sup> studied the degradation behavior of C/PLA composites, but did not consider the influence of the IAS, although they noted the “wicking effect” of the fiber–matrix interfaces. Slivka et al.<sup>20,21</sup> investigated the degradation behavior of C/PLLA, CaP/PLLA, and chitin/PLLA composites of different initial IFSS (i.e., IAS). However, a direct relation-

ship between IFSS and degradation behavior cannot be derived because of the difference in the nature of those reinforcing fibers. For example, CaP fiber can degrade, chitin fiber can swell, and carbon fiber is nonabsorbable.<sup>20,21</sup> A composite system with varying IAS and identical fiber and matrix should be provided to examine the influence of the IAS on degradation properties.

It is believed that the properties of composites are significantly controlled by the interface conditions. So, interfacial adhesion between the reinforcing fiber and the matrix, and its influence on mechanical performance have been investigated by many researchers.<sup>22–24</sup> Our previous studies on metal matrix composites had demonstrated that the IAS not only affected the mechanical properties, but also affected physical properties, like thermal expansion behavior.<sup>25,26</sup> In the first part of this series,<sup>8</sup> we obtained C/PLA composites with different IAS values by fiber surface treatment in nitric acid. The only difference among these composites was interface condition. The purpose of this additional study is twofold: to investigate the *in vitro* degradation of C/PLA composites and to evaluate the influence of interface conditions on the *in vitro* degradation behavior.

## EXPERIMENTAL

### Raw Materials

The medium-strength polyacrylonitrile (PAN)-based carbon fibers used in this experiment were supplied, without a sizing finish, by Shanghai Xingxin Carbon Ltd. (Shanghai, China). They have the following characteristics: tensile strength, 2000 MPa; tensile modulus, 196 GPa; diameter, 6–8  $\mu\text{m}$ ; density, 1.75  $\text{g cm}^{-3}$ . 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  $1 \times 10^5$  (determined by viscosity measurement). The PLA was reinforced with untreated and nitric acid-oxidized fibers. For simplification, the resulting composites were referred to as untreated and treated C/PLA composites, respectively.

### Oxidation of Carbon Fibers with Nitric Acid

Nitric acid (65 wt %, analytical grade) was preheated and maintained at  $\sim 115^\circ\text{C}$  in a 1000-mL

beaker. Carbon fibers (10 g) wound onto a glass drum were immersed in the nitric acid for 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. The nitric acid-oxidized fibers were subsequently dried in an oven at 110 °C for ~8 h.

### Preparation of Unidirectional C/PLA Composite and Pure PLA Samples

Both the untreated and treated C/PLA composites were manufactured using a solvent casting plus compression molding technique, as previously described.<sup>8</sup> Briefly, a fiber tow was drawn through a PLA solution bath and wound onto a cylindrical mandrel to form a single layer prepreg. After air-drying for at least 24 h, the prepreg was cut into sheets and hand laid-up in a metallic mold, keeping all sheets in a direction. The unidirectional C/PLA composite samples were compression molded under 2–3 MPa at 110 ± 5 °C for 20 min. The resulting samples were stored in a dessicator to prevent the absorption of moisture until use. The fiber volume fraction in all C/PLA composite samples was kept constant at ~25%. The pure PLA samples were prepared by the same solvent casting plus compression molding technique as utilized for the C/PLA composites to avoid differences in structure and performance between the pure PLA and the PLA matrixes in the C/PLA composites.

### In Vitro Degradation Tests

The pure PLA and C/PLA composite samples were divided into two groups. Group A (6 × 6 × 2 mm), cut from compression-molded specimens, were designed to have water uptake, mass loss, and molecular weight loss. Group B (80 × 6 × 2 mm), also cut from compression-molded specimens, were designed to obtain changes in mechanical properties. All specimens from Group A were placed in glass tubes (without stirring), each containing 50 mL of phosphate buffered saline (PBS, pH 7.4, 37 ± 0.5 °C). Each sample from Group B was hung at one end with a silk thread, to avoid deformation resulting from its own weight during the degradation test, and immersed in PBS (pH 7.4, 37 ± 0.5 °C) in a big glass beaker (1000 mL). All samples were degraded *in vitro* for predetermined periods of 0, 5, 10, 15, 20,

or 25 days. A few specimens from Group A were taken out at 2 days to determine mass loss. The PBS was changed every 5 days.

### Water Uptake

At each time point, part of the pure PLA and C/PLA composite samples were removed from PBS, quickly wiped, and weighed with a TG-328A microbalance with an accuracy of 0.1 mg to determine water uptake. The water uptake,  $W$ , of the pure PLA was determined by the following mass equation:

$$W = \frac{m - m_0}{m_0} \times 100\% \quad (1)$$

where  $m$  is the mass of a degraded sample measured at time  $t$ , and  $m_0$  represents the initial mass of a dried sample.

The water uptake of the C/PLA composite samples was normalized to the initial weight of the PLA matrix in a composite, which was expressed as

$$W = \frac{m_c - m_{c,0}}{m_{m,0}} \times 100\% \quad (2)$$

where the subscripts m and c stand for PLA matrix and composites, respectively.

### Mass Loss

After selected degradation times, the degraded pure PLA and composite samples were taken out, completely dried, and then weighed. The mass loss,  $M$ , of the pure PLA samples was calculated from

$$M = \frac{m_0 - m}{m_0} \times 100\% \quad (3)$$

where  $m_0$  is the initial sample mass, and  $m_t$  is the mass of dried residual samples.

In the case of the C/PLA composites, mass loss was normalized to the initial mass of the PLA matrix in a composite, which was

$$M = \frac{m_{c,0} - m_c}{m_{m,0}} \times 100\% \quad (4)$$

where the subscripts m and c stand for PLA matrix and composites, respectively.

### Molecular Weight Loss

Molecular weight was determined by viscometric measurements on diluted chloroform/PLA (carbon fibers were filtered) solutions in an Ubbelohde viscometer at 25 °C. The viscosity average molecular weight ( $\bar{M}_v$ ) of the samples was estimated from the intrinsic viscosity  $[\eta]$  of the PLA matrixes in the C/PLA composites by using the following formula:

$$[\eta] = K\bar{M}_v^a \quad (5)$$

where  $K$  and  $a$  are empiric constants. To investigate the molecular weight degradation rate of the C/PLA composites of different IAS, the normalized molecular weight,  $\bar{M}_v/\bar{M}_{v,0}$ , was reported (where  $\bar{M}_{v,0}$  is the initial viscosity average molecular weight of the pure PLA).

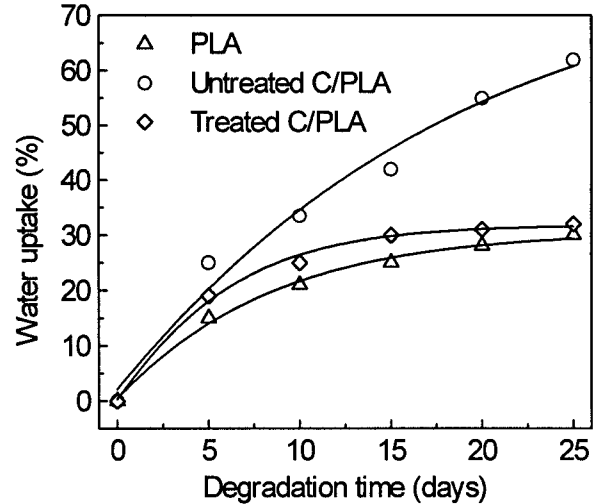
### Measurement of Mechanical Properties

The degraded pure PLA and composite samples from Group B were removed from PBS at day 0, 5, 15, 20, and 25, and then were completely air dried. The static mechanical properties of the initial and degraded pure PLA and C/PLA composite samples were measured at ambient temperature to get the bending strength ( $\sigma$ ) and modulus ( $E$ ), and IAS (except the pure PLA samples). The measured bending strength, modulus, and IAS were normalized to their initial values ( $\sigma_0$ ,  $E_0$ , and  $IAS_0$ , respectively). The normalized values,  $\sigma/\sigma_0$ ,  $E/E_0$ , and  $IAS/IAS_0$ , were added in bending strength versus time, modulus versus time, and IAS versus time curves, respectively. The measurement of these properties was described in detail in the first part of this series.<sup>8</sup> A minimum of five specimens was tested for each set of samples, and the average values are reported.

## RESULTS AND DISCUSSION

### Water Uptake

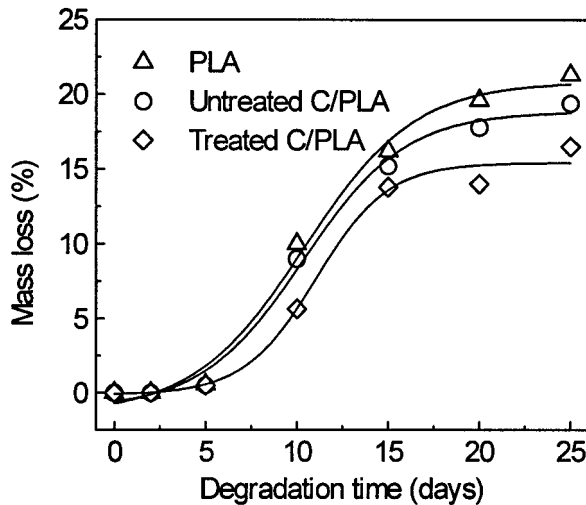
All samples absorbed a certain amount of water during the degradation process as reported in Figure 1. Comparing the pure PLA with the PLA matrixes in the C/PLA composites, the PLA matrixes showed higher water uptake at each time



**Figure 1** Water uptake as a function of degradation time for C/PLA composites with different IAS.

point. The apparent difference in water uptake for these samples suggested that the fiber–matrix interfaces exerted an effect. This phenomenon can be explained by taking into account the “wicking effect” of the fiber–matrix interfaces. As already reported for the degradation of the C/PLA composites, the fibers (more precisely, the interfaces), exposed to the degradation medium served to wick fluid into the composite plate.<sup>7</sup> In other words, the fiber–matrix interfaces were the part of the composites most vulnerable to moisture attack. In the present study, all C/PLA composite samples were cut from compression-molded plates, indicating fiber ends (i.e., interfaces) were exposed to the degradation medium. Thus, the interfaces could wick water and result in higher water uptake of the PLA matrixes in the C/PLA composites compared with that of the pure PLA.

It is of interest to note that the PLA matrix in the treated composite took up less water than the PLA matrix in the untreated one. This difference can only be attributable to the difference in the IAS (the IAS values for the untreated and treated C/PLA composites were 18.1 and 25.1 MPa, respectively<sup>8</sup>) because all other parameters were identical for the two composite systems. This result suggests that higher IAS helped to resist absorbing water. In fact, this mechanism has already been indicated in literature:<sup>27</sup> “The plasma surface treatment should also be expected to retard the hydrolytic degradation rate of the reinforcing fibers (CaP) and their matrix (PLLA), because the improved interfacial bonding would re-



**Figure 2** Mass loss as a function of degradation time for C/PLA composites with different IAS.

duce the wicking of water into the interfacial space.” Our results confirmed that higher IAS could reduce the water amount penetrated into the composite through fiber–matrix interfaces, and therefore could reduce the water uptake of the matrix in a composite.

#### Changes in Mass Loss

The mass loss data for the untreated and treated composites and the pure PLA are plotted in Figure 2. It is clear that the dynamics of mass loss for all samples were similar to each other. Data in Figure 2 show that no mass loss occurred during the first 2 days. There was very little mass loss (<0.6%) before 5 days for each sample. From day 6 to 15, all samples lost mass at a very fast rate; the degradation rates were estimated at 1.57, 1.47, and 1.33% per day for the pure PLA and PLA matrix in the untreated and treated composites, respectively. All samples showed a reduced mass loss rate after 15 days of degradation. From day 16 to 25, the degradation rates were 0.51, 0.42, and 0.27% per day for the pure PLA, PLA matrix in the untreated and treated composites, respectively. Evidently, the pure PLA showed a faster mass loss than the C/PLA composites. After 25 days of degradation, 78.7, 80.6, and 83.5% of their initial mass remained for the pure PLA and PLA matrixes in the untreated and treated composites, respectively. It is noted that the PLA matrix in the untreated composite showed a faster and greater mass loss compared with its

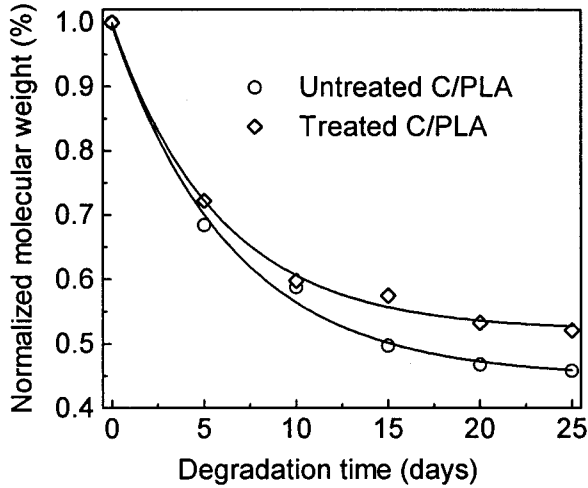
counterpart in the treated one at all time points. This result suggests that the IAS had an obvious effect on degradation rate of a composite and that the higher the IAS, the lower the degradation rate.

The relative constant mass during the early degradation stage was consistent with the results observed by other research groups<sup>28,29</sup> and could be interpreted by the fact that the oligomers can diffuse through bulk and dissolve, causing mass loss only when the molecular weights of the chains are decreased to a critical value.<sup>30–33</sup>

The lower degradation rate of the PLA matrixes in both composites than that of the pure PLA seemed to be contrary to the water uptake trend shown in Figure 1. The higher water uptake of the PLA matrixes in composites would be expected to lead to a faster degradation rate than the pure PLA. However, the result shown in Figure 2 was completely in contrast with the anticipated trend. It is reasonable to consider that this phenomenon is related to the presence of fiber–matrix interfaces. On one hand, interfaces serve to wick water into the composite plate, accelerating the degradation of the PLA matrix. On the other hand, the degradation products can easily flow out through interfaces, which helps to decrease the “autocatalytic effect”, thus retarding the degradation of the PLA matrix. The result shown in Figure 2 indicates that the latter was dominant for the two opposite effects.

It is believed that the degradation rate is proportional to water and ester concentrations and autocatalyzed by the generated carboxylic end group.<sup>32</sup> It is not difficult to understand that the higher degradation rate of the PLA matrix in the untreated composite might be attributed to its higher water content when compared with the PLA matrix in the treated composite, provided the IAS influence on the release of degradation products was limited. It should be stated here that the exact mechanism governing this phenomenon is not very clear at the present time. Further research is necessary to explore this phenomenon.

The slower degradation of the treated composite, which yielded lower concentrations of degradation products per unit time, was advantageous because higher concentrations of degradation products often cause sterile sinuses and bone resorption around implants and exert a toxic influence on cell culture.<sup>34–36</sup> Therefore, surface treatment of carbon fibers designed to increase the IAS



**Figure 3** Changes in normalized molecular weight with degradation time for C/PLA composites with different IAS.

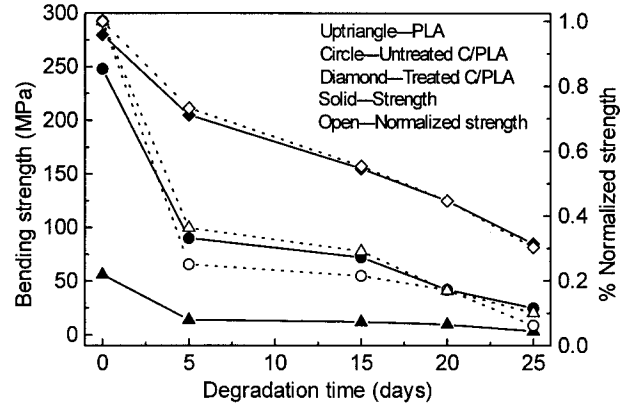
of the C/PLA composites is beneficial to improve the initial mechanical performance<sup>8</sup> and to restrain the degradation.

**Changes in Molecular Weight**

Unlike the profiles for mass loss, the viscosity average molecular weight,  $\bar{M}_v$ , of all C/PLA composite specimens decreased immediately after placement in PBS and continued to decrease throughout the time course (see Figure 3). The  $\bar{M}_v$  decreased for PLA matrixes in both composites at approximately the same trend. As seen in Figure 3, the  $\bar{M}_v$  decreased exponentially with degradation time. Five days after degradation, the  $\bar{M}_v$  of the PLA matrixes in the untreated and treated C/PLA specimens decreased to  $6.8 \times 10^4$  and  $7.2 \times 10^4$ , respectively, the latter having an obviously lower degradation rate. Moreover, the difference in degradation rates seemed to enlarge with degradation time. At the end of 25 days, 52% of its initial  $\bar{M}_v$  remained for the PLA matrix in the treated C/PLA composite and only 45% remained for the PLA matrix in the untreated composite. The results of molecular weight measurements further indicated that the degradation rate of the C/PLA composites could be engineered by varying their IAS.

**Changes In Mechanical Properties**

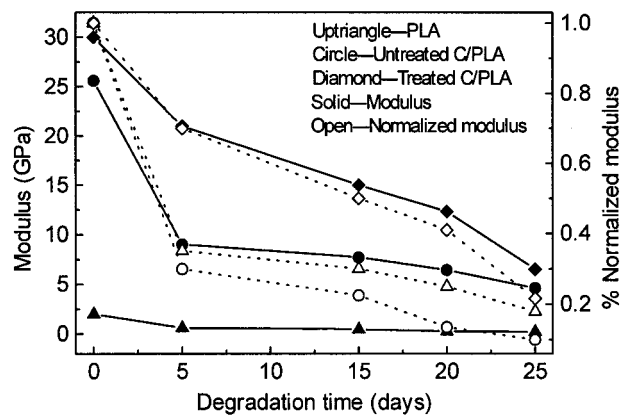
The bending strength of both C/PLA composites and pure PLA samples as a function of degrada-



**Figure 4** Effect of degradation time on bending strength and normalized bending strength for C/PLA composites with different IAS.

tion time is depicted in Figure 4. Also shown in Figure 4 is the normalized bending strength to compare the rate of decrease in bending strength for different materials. The variations of the bending modulus, as well as normalized modulus, with degradation time are illustrated in Figure 5. As seen from Figures 4 and 5, the bending strength and modulus for the pure PLA and both composites declined continuously with degradation time.

Obviously, the pure PLA exhibited much lower bending strength and modulus than both composites. More importantly, it lost bending strength and modulus at a rate greater than the C/PLA composites, simply because carbon fibers cannot degrade.



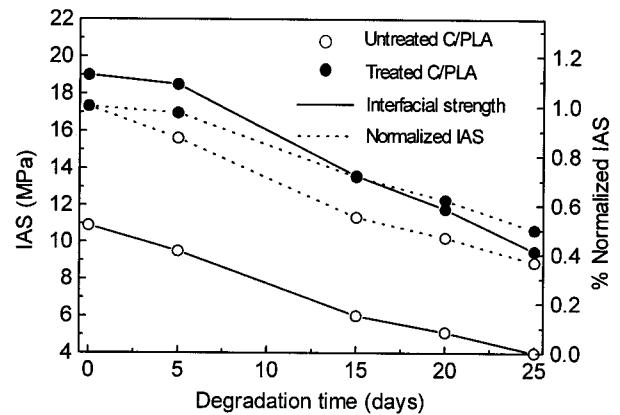
**Figure 5** Effect of degradation time on bending modulus and normalized modulus for C/PLA composites with different IAS.

Comparison between the treated and untreated C/PLA composites suggested that the former exhibited higher bending strength and lower decreasing rate at all degradation periods. The untreated composite had 36% of its initial bending strength left at 5 days. It declined further to 29, 17, and 10% at days 15, 20, and 25, respectively. The treated composite exhibited 73, 55, 44, and 30% of its initial bending strength after 5, 15, 20, and 25 days, respectively, in PBS. Bending strengths of 25 and 85 MPa were measured at day 25 for the untreated and treated composites, respectively. Thus, the untreated composite demonstrated a significantly greater decrease in bending strength than the treated one. The higher degradation rate in bending strength for the untreated composite resulted from its higher water uptake, because higher water absorption led to lower mechanical properties.<sup>7,36</sup>

The changes in bending modulus over time demonstrated a pattern similar to bending strength. The treated C/PLA composite with stronger interfacial bonding showed higher normalized modulus than the untreated counterpart during the whole degradation process. At day 5, 15, 20, and 25, the untreated composite lost, respectively, 65, 70, 75, and 82% of its initial modulus, whereas the corresponding values were 30, 50, 59, and 78%, respectively, for the treated one. Both the bending strength and modulus of the treated composite decreased slower than the untreated one, indicating the C/PLA composite with higher IAS possessed a lower degradation rate in bending strength and modulus, which is in agreement with its slower decrease in mass and lower water uptake.

### Interface Degradation and Influence of IAS

The interface degradation was characterized by the reduction of the IAS with degradation time, as shown in Figure 6. The untreated composite presented 87, 55, 47, and 37% of its original IAS, whereas the treated composite still possessed 97, 72, 62, and 50% of its initial IAS by 5, 15, 20, and 25 days, respectively. Clearly, the treated composite had higher remaining IAS, indicating it possessed slower interface degradation rate in comparison with the untreated counterpart. In addition to matrix degradation, the interface degradation was responsible for the decrease in bending strength and modulus for the two composites.



**Figure 6** Changes of IAS and normalized IAS with degradation time for C/PLA composites with different IAS.

Furthermore, a simple estimation with the rule of mixture can deduce that the interface degradation is a dominant factor decreasing the bending strength and modulus of the C/PLA composites because contribution of the degradation of the PLA matrix is very limited. Therefore, the faster loss of bending strength and modulus for the untreated composite was caused by its higher interface degradation rate.

The difference in interface degradation rate could only be attributed to the difference in IAS because all other parameters were identical for the two composites; that is, the interface condition had an effect on the interface degradation rate. It is reasonable to consider that the interface degradation was directly caused by water intrusion into the interface. The penetrated water could break the bonding between the fiber and the matrix, probably by forming hydrogen bond with carbon fiber. It has been proposed that breakage of interfacial bonding by water was related to the interface structure for carbon fiber/polymer composites.<sup>37</sup> As reported in our previous paper,<sup>8</sup> the fiber/matrix bonding was caused by mechanical interlocking, van der Waals force, and a slight chemical bonding for the untreated composite, whereas for the treated one, its interface adhesion was bonded via mainly chemical bonding. This difference in interfacial bonding could account for the different interface degradation rate, considering mechanical interlocking and van der Waals forces could be debonded easily by water, whereas the debonding of chemical linkage was slower and difficult and occurred under longer immersion time. A similar analysis was carried out by

Noobut and Koenig.<sup>37</sup> However, as suggested in literature,<sup>38</sup> how water and the fiber–matrix interfaces interact is still not fully clear even for nonabsorbable matrix composites. It is thought that the mechanisms of water–interface interactions are much more complex for bioabsorbable matrix composites than in the case of nonabsorbable matrix ones. Further investigation is under work to disclose the concrete mechanisms.

## CONCLUSIONS

1. The pure PLA samples absorbed less water than the PLA matrixes in the C/PLA composites because of the wicking effect of the fiber–matrix interfaces. The treated C/PLA composite of higher IAS took up less water than the untreated one of lower IAS.
2. The PLA matrixes in the C/PLA composites showed slower mass loss than the pure PLA because of the reduced autocatalysis. Furthermore, the PLA matrix in the treated composite possessed a lower mass loss rate in comparison with its counterpart in the untreated composite.
3. The viscosity average molecular weight loss of the PLA matrix in the treated C/PLA composite was obviously lower than that of its counterpart in the untreated composite.
4. The interfaces of the C/PLA composites degraded consistently during *in vitro* degradation, and the rate of decrease in IAS was dependent on the interfacial characteristics.
5. The bending strength and modulus of the pure PLA and both composites, as well as the normalized values, declined as the degradation time increased. For both composites, the loss of bending strength and modulus was mainly caused by the interface degradation. It was confirmed that the IAS of the C/PLA composites had an obvious effect on the decreasing rate of bending strength and modulus.

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