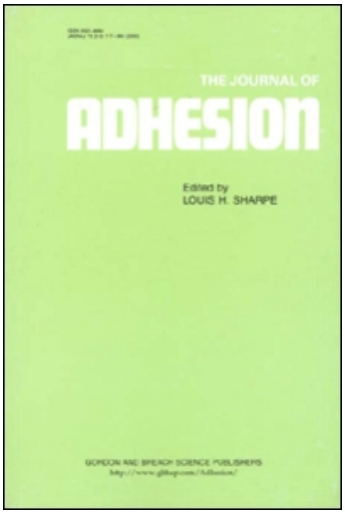

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Relationship Between Some Mechanical Strengths of CFRP and Interfacial Properties

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The relationships between microscopic properties such as interfacial shear strength (IFSS) and macroscopic properties such as flexural strength were investigated for CFRP prepared from carbon fiber and epoxy resin. Flexural, tensile and impact strengths all went through maximum values when plotted against the surface treatment time of the carbon fiber. The flexural strength of CFRP as a function of the treatment time of the carbon fiber behaved similarly to the adhesive strength of the resin and carbon fiber. Also, the results indicated that the bahavior of tensile and impact strengths varied with the treatment time in much the same way as the interfacial shear strength did. The occurrence of these two types of macroscopic and microscopic property effects can be understood by taking into account the chemical activity and roughness of the carbon fiber surface.

KEY WORDS Tensile strength; flexural strength; Charpy impact strength; CFRP; interfacial shear strength; adhesive strength; roughness; polar groups.

INTRODUCTION

Many papers have been written on surface analyses[1-4] and the characterization[5-11] of carbon fibers which have been treated under vairous conditions. In these papers, the surfaces of the fibers were mainly analyzed by XPS (X-ray photoelectron spectrometry), and it was observed that functional groups, especially oxygen-containing groups, were generated by various surface treatment processes. Investigations of surface-related properties have been sometimes carried out in relation to macroscopic properties such as flexural,[12-17] tensile[12-18] and impact[19-21] strengths of CFRP. For example, Lehmann *et al.*[12,15-17] showed that the behavior of flexural strength was similar to that of interlaminar shear strength (ILSS), which was determined by the short beam method. From these various studies, it is apparent that the mechanical properties of CFRP can be roughly correlated with the interlaminar ones. However, it cannot be said that the correlations are well established, because it is difficult to believe that all of these mechanical properties are correlated only with ILSS, in spite of the fact that the fracture mechanisms are expected to be different from each other. ILSS refers only to properties parallel to the fiber direction. Some of the experimental results obtained in the past are

doubtful. Furthermore, the mechanical properties should also be compared, for example, with the surface roughness of the carbon fiber, the adhesive strength, and so on. At any rate, more quantitative discussion must take place in order to confirm the correlation. Otherwise, we can not understand the complicated behavior resulting from surface treatment effects.

In this study, CFRP was prepared using epoxy resin and carbon fiber with various degrees of treatment, and the tests on flexural, tensile and impact strengths were carried out using test pieces prepared with various degrees of surface treatment. The effect of the surface treatment was clearly observed in these tests. At the same time, microscopic studies, such as for interfacial shear strength (IFSS) and adhesive strength, were performed. Finally, the relationship between macroscopic and microscopic properties was discussed in detail.

MATERIALS AND PROCEDURES

Materials

Carbon fiber having a 3.5 Gpa tensile strength and a 248 GPa tensile modulus of elasticity (High Carbolon, Asahi Chemical Co., Japan) was used. This fiber was supplied without any surface treatment. Epoxy resin used was Epikote 828, and MHAC-P (himic acid anhydride, (Methyl-3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalic anhydride) Hitachi Chemical Co., Japan) was used as hardener. The accelerator was 2E4MZ (Hitachi Chemical Co., Japan). CFRP was prepared using the impregnation method which took two hours at 150 °C. Since the glass transition temperature of this epoxy resin was around 150 °C, the residual stress was removed by keeping the specimens at 190 °C for two hours and allowing them to cool down slowly in the furnace.[22] The experimentally-determined volume fraction of carbon fiber in CFRP was 0.60 ± 0.05. This value was obtained from a microphotograph of the cross-section of the CFRP after a light treatment of the surface with 2 N nitric acid.

Surface Treatment

Surface treatment[22] was carried out in an electric furnace at 250 °C in air, after winding of the tow of carbon fiber on a spool. The electric furnace used in this study is a Model CE-25 (Tokaikanetsu Kogyou Co., Japan). The temperature in the furnace was controlled by measuring at three positions.

Macroscopic Properties

Flexural and tensile strengths were determined with a tension tester at the velocity of 1.0mm/min. In the tensile test, the locations where fractures occurred and the measured strengths were scattered when the Type 4 test piece in JIS K7113 was used. Satisfactory results were obtained by modifying the Type 1 test piece; this experiment was attained by attaching small pieces of commercial CFRP with adhesive to the both ends of the

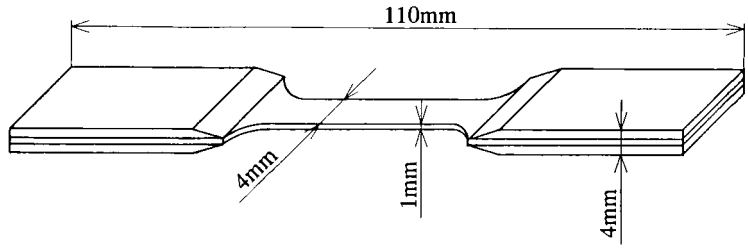


FIGURE 1 Test piece for tensile test.

test piece, as shown in Figure 1. Additionally, strain gauge was adhered to the test pieces and the elongation or strain at break was determined.

The Charpy impact test was conducted for test pieces of CFRP without notches using a Model CIEM-5-D impact tester (Tokyo Shikenki Co., Japan) according to JIS K7111. In this study, the energy (kJ/mm^2) absorbed by a specimen until the maximum load was adopted as the impact strength,[23] as shown in Figure 2, where the impact velocity was 2.4 m/s. The results were evaluated using the average of eight or more measured values.

Microscopic Properties

IFSS was determined by the microbond method.[24-25] A droplet of epoxy resin containing the hardener and the accelerator was deposited onto the surface of the fiber and cured under the same conditions as CFRP except that in this case a nitrogen atmosphere was used in order to prevent oxidation of the fiber. The final resin should be present in the shape of ellipsoids. The length covered with the resin was adjusted so as

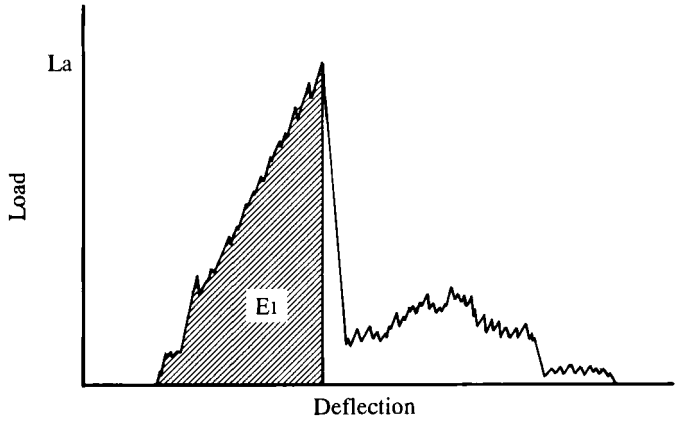


FIGURE 2 Load *vs.* deflection curve in Charpy impact test. E_1; impact strength expressed as kJ/m^2, L_a; impact strength expressed as GPa.

to become 30 ~ 50 μm using a hypodermic needle. IFSS (τ) was calculated from

$$\tau = \frac{F}{\pi DL} \tag{1}$$

where F is the pull-out force, D fiber diameter and L the covered length. However, since some resin remained on the surface without sliding, as shown in Figure 3, this calculation was modified somewhat. F and L were corrected according to the following equations. Namely, F_1 and L_1 were used for the calculation of τ instead of F and L, respectively.

$$F_1 = F - F_0 \tag{2}$$

$$L_1 = L - L_0 \tag{3}$$

where

$$F_0 = \sigma_0 \cdot A_0 \tag{4}$$

L_0 is the covered length remaining on the fiber surface which had not slid after measuring the IFSS. A_0 is the cross-sectional area of the broken resin. This value was determined from an electron micrograph of the droplet after the test by assuming that the broken surface had a circular shape. The σ_0 is the tensile strength of the resin. The value of 84 MPa was obtained for σ_0 by a tensile test of the test piece. This piece was prepared under the same conditions as the epoxy resin deposited on the fiber, though

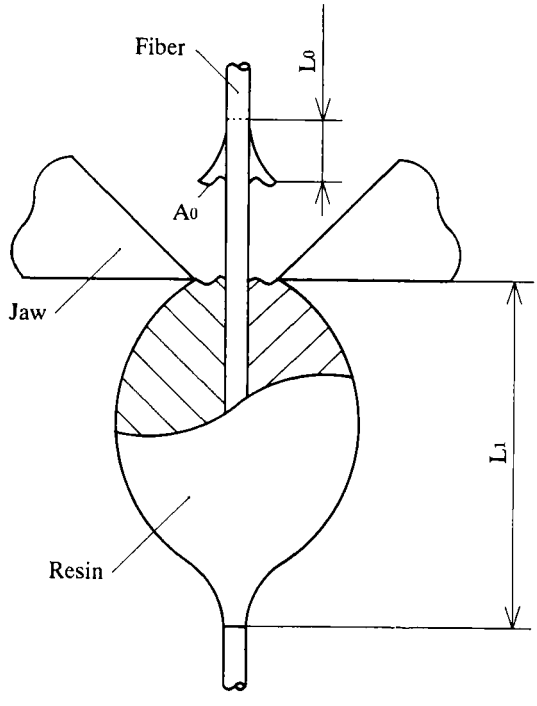


FIGURE 3 Fiber and resin in microbond test.

the shape was designed so as to be suitable for use in the tensile tester. The adopted value is the average of thirty to fifty measured values.

The surface free energy of the carbon fiber was obtained from the contact angles for n-hexadecane and ethylene glycol.[26-29] When the surface free energies are expressed by eqs. (5) and (6) for liquid (L) and solid (S), a contact angle θ can be correlated with the surface free energies by eq. (7) according to Young-Dupre's

$$\gamma_{LV} = \gamma_{LV}^{D} + \gamma_{LV}^{P} \tag{5}$$

$$\gamma_{SV} = \gamma_{SV}^{D} + \gamma_{SV}^{P} \tag{6}$$

$$(1 + \cos\theta)\,\gamma_{LV} = 2(\gamma_{LV}^{D}\,\gamma_{SV}^{D})^{1/2} + 2(\gamma_{LV}^{D}\,\gamma_{SV}^{P})^{1/2} \tag{7}$$

where the superscripts D and P stand for the contribution due to London dispersion forces and the polar contribution, respectively. The latter is largely made up of hydrogen bonding and dipole-dipole interactions. In this calculation, we adopted the following values for calculation; $\gamma_{LV}^{D} = 27.0$, and $\gamma_{LV}^{P} = 0$ for n-hexadecane, and $\gamma_{LV}^{D} = 31.6$ and $\gamma_{LV}^{P} = 15.9\ \mathrm{mJ/m^2}$ for ethylene glycol.[1)] We can obtain and γ_{SV}^{D} and γ_{SV}^{P} using eq. (7) from contact angles of the two liquids. The surface free energy of the fiber, γ_{SV}, can be obtained from eq. (6). The method for measurement of contact angles is described in detail elsewhere.[29]

In order to conduct the tensile testing of CFRP perpendicular to the direction of carbon fiber, CFRP was prepared in the same way as for the flexural test. The test specimens were obtained by cutting to the size of 10 × 70 mm, the longer dimension being in the direction perpendicular to that of carbon fiber. The tensile test was conducted in the longer direction of the specimens. The fracture occurred at the interface between the resin and carbon fiber. Of course, the area of the fractured surface is composed of those of the carbon fiber and the resin in the side in which carbon fiber remains. The fraction, S, of the resin in the fracture surface area can be expressed by eq. (8), when the carbon fibers are packed in a hexagonal arrangement.[30]

$$S = \left(\frac{\pi}{3.464\,V_f}\right)^{1/2} - 1 \tag{8}$$

When $V_f = 0.60$, $S = 0.230$. Further, the tensile strength of the resin prepared under the same conditions as for CFRP was 84 MPa, as already given. It is certain that the tensile strength observed in this experiment is mainly due to that of the resin ($0.230 \times 84 = 19$ MPa), and that the contribution of the adhesive strength between the carbon fiber and the resin is small. However, the change of the tensile strength always reflects that of the adhesive strength, because S is constant throughout this experiment. Therefore, this strength was conventionally regarded as the adhesive strength in this study.

Observation by STM

The surface of the carbon fiber was examined by scanning tunneling microscopy (STM) in order to confirm the change of roughness due to the surface treatment. A Digital Instrument STM Nano Scope II was used under the conditions of 1383 mV in bias and of $1 \sim 3$ nA in setpoint.

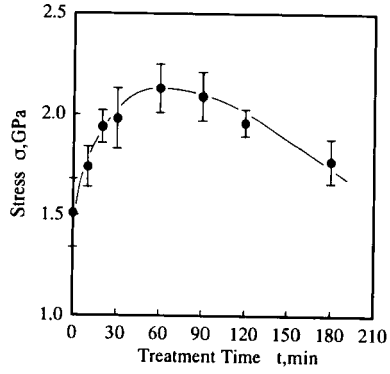


FIGURE 4 Flexural strength of CFRP as a function of treatment time of carbon fiber.

RESULTS AND DISCUSSION

Macroscopic Properties

The result for the flexural test of CFRP is shown as a function of treatment time of carbon fiber in Figure 4. The maximum strength was found at the treatment time of 60 min. As shown in Figure 5, the tensile strength varies with the treatment time in a manner similar to that of the flexural test. However, the treatment time for achieving the maximum strength in the tensile strength test is 20 min. These results are different from those of previous investigators such as Lehmann[12] and Manocha,[14] who insisted that the above mechanical properties had the same behavior as IFSS.

The impact strength of CFRP is shown in Figure 6. The maximum strength was about 65 kJ/m^2, which means that the strength was improved by 80%, in comparison with that of the untreated fiber. This value was obtained at around 10 min of treatment time. In that sense, the behavior of the impact strength is similar to that of tensile strength. The impact strength in the dimension of GPa, *i.e.*, the maximum value, was evaluated for convenience using the same equation as used in the flexural

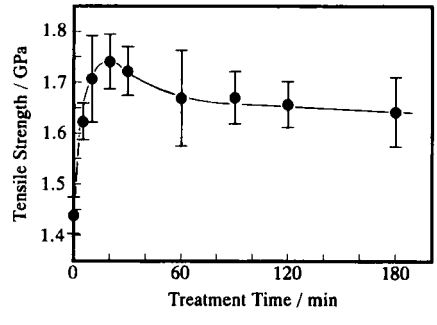


FIGURE 5 Tensile strength of CFRP as a function of treatment time of carbon fiber.

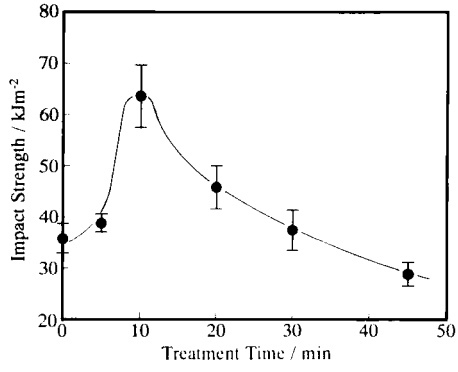


FIGURE 6 Impact strength of CFRP as a function of treatment time of carbon fiber. In this figure, the strength was evaluated by E_1 in Fig. 2.

test, namely,

$$\sigma = \frac{3Pl}{2bh^2} \tag{9}$$

where P is the maximum load, l the distance between the test piece holders, b the width of the test piece and h the height. As shown in Figure 7, the maximum strength appears at $10 \sim 20$ min in treatment time. This result is also similar to that in the tensile test, but it is different from the flexural one. The impact test is apparently similar to the flexural one, but this result suggests that the fracture mechanism is not the same. It was observed that the impact strength of CFRP with fibers treated for a long time becomes lower than the strength measured for CFRP with untreated fiber.

From the viewpoint of the effect of fiber treatment, macroscopic properties can be classified into two groups. Namely, the tensile and impact properties reached maximum values at $10 \sim 20$ min in treatment time, while the other property took 60 min to reach its maximum. In addition, the fiber properties such as modulus of elasticity

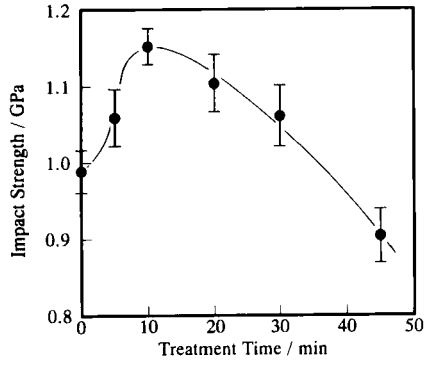


FIGURE 7 Impact strength of CFRP as a function of treatment time of carbon fiber. The strength is evaluated by L_a in Fig. 2.

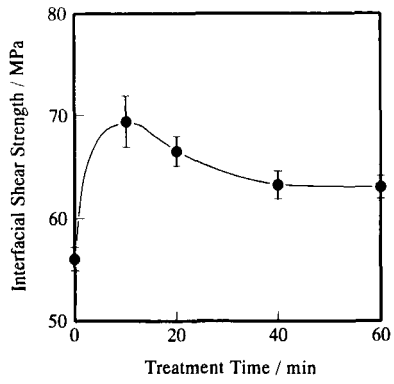


FIGURE 8 Interfacial shear strength (IFSS) as a function of treatment time of carbon fiber.

changed with the surface treatment. The effect was reported in detail by us in another paper.[31] It is easily predicted by the strength of materials that the engineering performance of CFRP is not influenced as much as obtained in this study.

Microscopic Properties

Microscopic properties were also examined. The results for IFSS are shown in Figure 8. The maximum value of 70 MPa was attained at around 10 min in treatment time at 250 °C. In this case, IFSS was improved by around 20% as compared with that of untreated fiber. This extent of improvement is almost equal to the increase of 21% in tensile strength. In addition, ILSS also showed the maximum value at around 15 min in treatment time, as described elsewhere.[32] The result for surface free energy of carbon fiber is shown in Figure 9. The surface free energy leveled off at around 30 min, after increasing significantly after 20 min of treatment time. On the other hand, the adhesive strength between the fiber and the resin increased with treatment time and reached the maximum at around 60 min, as shown in Figure 10. From these results, we can see that there are also two types of microscopic properties. Namely, one type is IFSS and

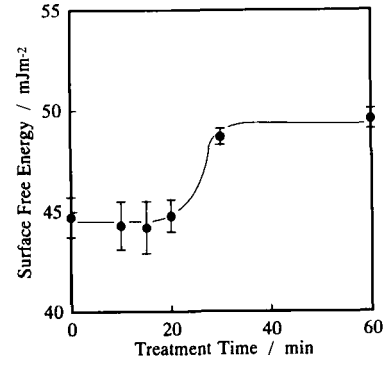


FIGURE 9 Surface free energy of carbon fiber as a function of treatment time.

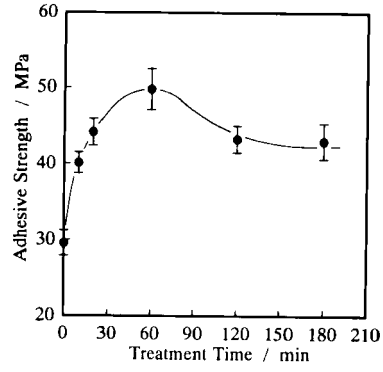


FIGURE 10 Adhesive strength as a function of treatment time of carbon fiber.

surface free energy, the maximum value of which appears at 15 ~ 30 min in treatment time, and the other one is adhesive strength, the maximum value of which appears at 60 min. It is hard to explain these phenomena only by considering the chemical activity of the fiber surface. The maximum treatment time of IFSS should coincide with that of adhesive strength, if only the chemical activity is concerned with these surface phenomena. However, as pointed out by Drzal[33] and other investigators,[31,34,35] not only the surface chemical activities, but also surface roughness must be taken into account, when we consider the surface effect of the carbon fiber. It was difficult to observe the change of surface roughness with respect to the treatment time by using an electron microscope. The method of STM (scanning transmission electron microscopy)

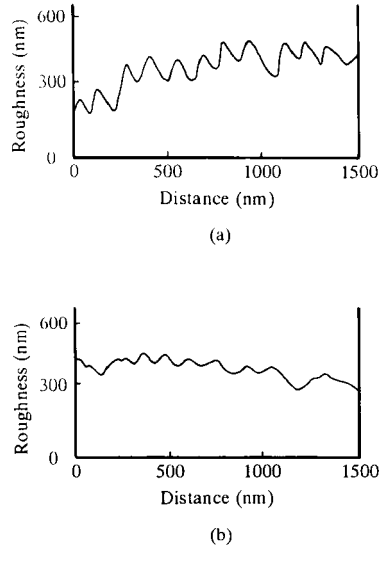


FIGURE 11 Surface roughness of carbon fiber observed by STM. (a); untreated, (b); treated for 60 min.

was adopted for this purpose. As shown in Figure 11, it is clear that there is a large difference in surface roughness between the untreated and treated fibers.

Relationship Between Properties

The macroscopic and microscopic properties can be understood by the following idea. First, the microscopic properties can be controlled by two factors,[33] namely, polar effect and surface roughness. The surface free energy will be directly reflected by the former effect. However, the effect of surface roughness may not be simple to predict, although it is certain that the effect will decrease with treatment time. So we considered the scheme for the surface of the fiber, as shown in Figure 12. IFSS is determined by the force parallel to the fiber. Therefore, the surface roughness is expected to be sensitive to IFSS as well as to the effect of polar groups. The surface effect in this case can be considered to be analogous to the friction problem.[36] Adhesive strength and IFSS will be the sum of stresses at break, σ_s, due to polar group and of σ_R, due to roughness. The relation can be expressed by eq. (10).

$$\text{Adhesive strength or IFSS} = \sigma_s + \sigma_R \ldots\ldots \tag{10}$$

Carbon fiber is always "gripped" by the resin, since the resin shrinks in the curing process of CFRP. In terms of adhesive strength, the polar group will also have the same effect as that for IFSS. However, the surface roughness has a weak effect on the strength, as shown schematically in Figure 12. In fact, in our experiment the value of IFSS is almost twice as much as the adhesive strength in the case of untreated fiber, as shown in Figures 8 and 10. This fact has been also recognized for various PAN-based carbon fibers by Nakanishi and Sawada.[37] Therefore, the behavior of IFSS can be expressed by Figure 13(a). According to this consideration, tensile and impact strength are closely correlated with IFSS. In other words, the surface roughness is very important in IFSS, tensile and impact strengths. On the other hand, the behavior of adhesive strength can be expressed as Figure 13(b). The treatment time showing the maximum value becomes longer due to the weak effect of roughness and to a slow decrease of the effect relative to the treatment time. In addition, when we observed the

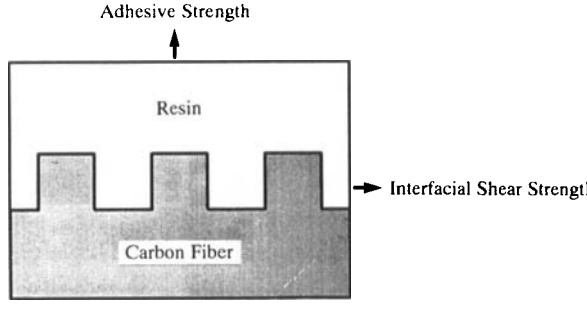
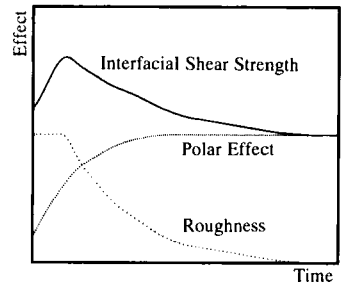
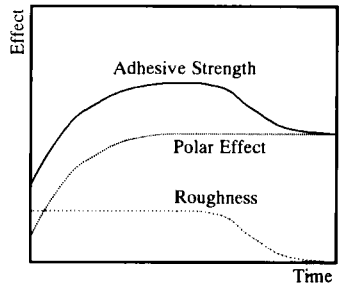


FIGURE 12 Directions of stress at interface for adhesive strength and IFSS.



(a)



(b)

FIGURE 13 Effects of polar group and roughness on IFSS and adhesive strength. (a); IFSS, (b); adhesive strength.

treated surface of the carbon fiber by XPS, only a slight increase of oxygen was detected even after a treatment for 180 min at 250 °C. At this stage, it is not clear whether or not the polar effect is completely attributable to the increase of oxygen on the surface. The surface may be activated only by exposing the fiber to air at high temperatures without oxidation. More detailed studies are required for better understanding the surface of carbon fiber.

CONCLUSIONS

The relationship between microscopic and macroscopic properties was investigated for CFRP prepared from carbon fiber and epoxy resin. The flexural properties of CFRP behaved similarly to the adhesive strength of carbon fiber and the resin. The tensile and impact properties of CFRP behaved similarly to the interfacial shear strength (IFSS). The occurrence of these two types of behavior can be understood based on the chemical activity and roughness of the carbon fiber surface.

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