JOURNAL OF MATERIALS SCIENCE 35 (2000) 2297–2303

# The effect of surface treatment on the performance improvement of carbon fiber/polybenzoxazine composites

JYONGSIK JANG*, HOJUNG YANG
*School of Chemical Engineering, Seoul National University, San 56-1, Shinlimdong, Kwanakku, Seoul, South Korea*
*E-mail: jsjang@plaza.snu.ac.kr*

The effects of surface treatments, such as oxygen plasma and nitric acid treatment, on the mechanical properties of carbon fiber (CF)/polybenzoxazine composites were investigated. Interlaminar shear strength (ILSS) and flexural strength of CF/polybenzoxazine composites were measured and correlated with surface area and surface functionality. Both oxygen plasma treatment and nitric acid treatment were efficient in the enhancements of the ILSS and flexural strength of CF/polybenzoxazine composites. However, nitric acid treatment was more efficient than oxygen plasma treatment due to large increment of surface roughness. Cohesive failure was observed in surface treated composite due to adhesion improvement. 

## 1. Introduction

Phenolic composites have been widely applied in aircraft interiors due to their good flame retardance and low smoke generation. Phenolic resins have low cost/performance index due to their cheap raw materials and easy synthesis. However, they release volatile by-products during the curing process so that it is hard to control the formation of micro voids and to design their molecular structure. They also have drawbacks such as limited shelf life and require the use of strong acids and alkalines as catalysts.

Novel phenolic resins have been synthesized to overcome these shortcomings. Ishida *et al*. synthesized polyfunctional monomer with a benzoxazine ring [1, 2]. The benzoxazine monomer is initiated by heat and polymerized by addition reaction so that there is no volatile by-product in the curing process. In addition, it has good dimensional stability due to the ring opening curing process, and its low viscosity enables the manufacture of complicated products [3, 4].

High performance composites used for the structural applications require good mechanical properties. Strong interfacial adhesion strength must be achieved to improve the mechanical properties of composites as it plays an important role in mechanical properties. However, carbon fiber often exhibits poor adhesion to polymers, because carbon fiber has inert surface. Much research has been conducted to enhance the adhesion between carbon fiber and polymer so that it is well known that the surfaces of carbon fibers can be modified by surface treatments.

A lot of approaches such as electrochemical oxidation, plasma treatment, and liquid phase oxidation of CF have been pursued in order to improve interfacial adhesion strength of CF composites. Especially, plasma treatment has been applied to modify the chemical and physical structures of the CF surface, tailoring fiber-matrix bonding strength, without influencing its bulk mechanical properties [5]. In addition, liquid phase oxidation of CF has been found to be quite effective in improving the shear properties of CF reinforced composites [6]. It has been suggested that this liquid phase oxidative treatment does not cause excessive pitting and degradation of CF and is mild compared to the high temperature gaseous phase oxidative treatment.

The enhancement of interfacial adhesion strength through surface treatments can be explained by several mechanisms [7–11]. These include fiber wetting, chemical bonding, and mechanical interlocking. Especially, good wetting is needed for good interfacial adhesion. Surface treatments enhance wettability by increasing the surface roughness. The enhancement of surface roughness aids fiber wetting by changing the contact angle. The change in the contact angle by roughness may be expressed by the following equation.

$$\cos \theta_f = r_f \cos \theta_s$$

where $r_f$ is the roughness factor (i.e. the ratio of the actual area to the projection area of the fiber) [12]. $\theta_f$ and $\theta_s$ are the contact angles on a rough surface and a smooth surface, respectively. The enhancement of surface roughness decreases the contact angle and increases the wettability. In addition, the polar components introduced by surface treatments improve wettability through the increase of surface energy. These

* Author to whom all correspondence should be addressed.

polar components may also react with matrix resin to make chemical bonding that enhances the interfacial adhesion strength.

Surface treatments of CF make micro-pittings on the fiber surface [13]. Micro-pittings allow more interpenetrating between fiber and matrix so that much mechanical interlocking will be achieved. Generally, it has been proposed that mechanical interlocking can provide the high bond strength even though other interactions may be weak [14–18].

The purpose of this work is to improve the mechanical properties of CF/polybenzoxazine composites using carbon fiber surface treatments. Low temperature oxygen plasma treatment and nitric acid oxidation methods were applied to CF surfaces to develop high performance from carbon fiber/polybenzoxazine composites. Plasma and nitric acid treatment times were correlated with surface functionality, surface area and interfacial adhesion between the carbon fiber and polybenzoxazine.

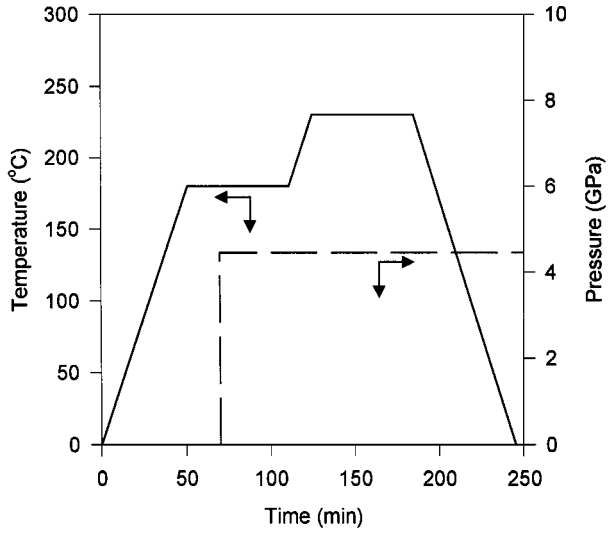



*Figure 2* Schematic diagram of cure cycle of CF/polybenzoxazine composite.

## 2. Experimental

### 2.1. Materials and monomer preparation

The benzoxazine monomer was synthesized by using bisphenol-A, formaldehyde and aniline. Aniline was purified by distillation and the other materials were used as received. The benzoxazine monomer was synthesized by the scheme in Fig. 1 [1, 2]. Carbon fiber was T300 grade plain fabric purchased from Toray Co. It was a high strength type and used as-received. CF was desized by the following procedure. It was refluxed in dichloromethane for 5 days and then in distilled water for 2 days. Desized CF was completely dried in *vacuo*, at 120 °C.

### 2.2. Plasma treatment

The desized CF was treated in the plasma reactor manufactured by Korea Vacuum Co. It has parallel electrode powered by 13.56 MHz RF generator. Oxygen was used as a carrier gas with $10^{-5}$ $m^3$/min flow rate. Plasma treatment time was varied from 1 min to 5 min and plasma discharge power was fixed at 100 W.

### 2.3. Acid treatment

The desized CF was refluxed in 60% nitric acid for varying time intervals at 100 °C and refluxed in distilled water to remove the nitric acid on the CF surface. It was completely dried in *vacuo*, at 120 °C.

### 2.4. Composites manufacturing

The CF fabric was impregnated with the THF solution. Benzoxazine was diluted in THF solvent and the solution concentration was fixed at 10 wt%. The prepreg was dried in *vacuo*, at 80 °C. Twelve plies were laminated and then cured at 180 °C for 1 hr and then postcured at 230 °C for 1 hr. The curing cycle is shown in Fig. 2. CF/polybenzoxazine composites were manufactured using the open leaky molding method.

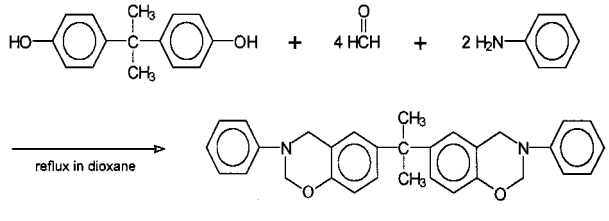



*Figure 1* Synthetic scheme of benzoxazine monomer.

### 2.5. Surface analysis

X-ray photoelectron spectroscopic (XPS) analysis of CF surface was performed with a 2830-S probe surface spectrometer from SSI Co. an Al anode X-ray source and a concentric hemispherical analyzer (CHA) detector were used.

The surface area of CF was measured by the Brunauer-Emmett-Teller (BET) method using Micromeritics ASAP-2010. Nitrogen gas was used as an absorbate.

### 2.6. Measurement of mechanical properties

ILSS of composites was measured according to ASTM D2344. In this case, the span to depth ratio was set at 6 and the crosshead speed was 1.3 mm/min.

The three point bending flexural test was performed according to ASTM D790M. The specimen was in the form of a rectangular bar with dimension $50 \times 20 \times 2.7$ mm. The span length was fixed at 32 mm and the crosshead speed was 0.85 mm/min.

### 2.7. Fractographic analysis

Fracture surfaces of CF/polybenzoxazine composites were observed by scanning electron microscope (SEM, Jeol 840A) and all specimens were coated with a thin layer of gold to eliminate charging effects.

## 3. Results and discussion

### 3.1. Oxygen plasma treatment

The CF surface was oxygen plasma treated to improve the interfacial adhesion strength of CF/polybenzoxazine composites. First of all, the effect of oxygen plasma treatment on surface morphology of CF was studied.

Fig. 3 summarizes the surface area and the ratio of $O_{ls}$ to $C_{ls}$ atom of plasma treated CF according to plasma treatment time. The BET surface area increases with increasing plasma treatment time and shows the maximum value at 3 min. After 3 min, the CF surface area is reduced. The increase of surface area results from micro-pittings on the CF surface caused by oxygen plasma treatment. Generally, it has been proposed that active species in the plasma gas aggressively attack the defect-rich or the edge-carbon site, resulting in the increase of CF surface area [19, 20]. On the contrary, severe plasma treatment of CF reduces the specific surface area due to overall smoothing of the CF surface.

The ratio of $O_{1s}$ to $C_{1s}$ atom of CF increases slightly with plasma treatment time. In general, oxygen plasma treatment produces the oxygen containing functional groups such as hydroxyl, carbonyl and carboxylic groups. However, the weak boundary layer of CF is removed by oxygen plasma treatment so that the increment of $O_{1s}/C_{1s}$ ratio is relatively small.

ILSS and flexural strength of plasma treated CF/polybenzoxazine composites were measured to relate the surface morphology of CF with interfacial adhesion of the composites. Fig. 4 shows the ILSS of CF/polybenzoxazine composites with plasma treatment time. The ILSS of CF/polybenzoxazine composites increases with increasing treatment time and decreases after 3 min. The maximum ILSS of CF/polybenzoxazine composites shows 73% improvement compared with that of the untreated one.

This result can be explained by the enhancement of wettability and mechanical interlocking. As represented in Fig. 3, plasma treatment increases the surface area. The surface roughness is proportional to the surface area because surface density (i.e. the mass per projection area) of CF is almost same in spite of surface treatments. The increased surface roughness aids wetting of polybenzoxazine.

On the other hand, oxygen-containing groups increase slightly by oxygen plasma treatment, so that the wettability improvement and chemical bonding by polar components cannot contribute to the enhancement of interfacial adhesion strength considerably.

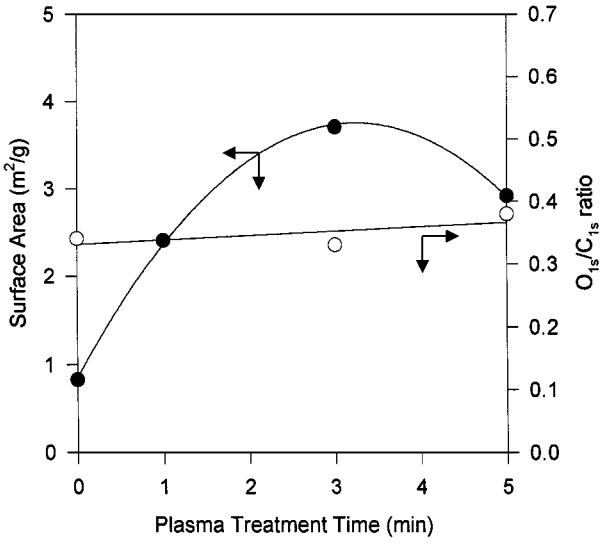



*Figure 3* BET surface area and $O_{1s}/C_{1s}$ ratio of oxygen plasma treated CF as a function of oxygen plasma treatment time.

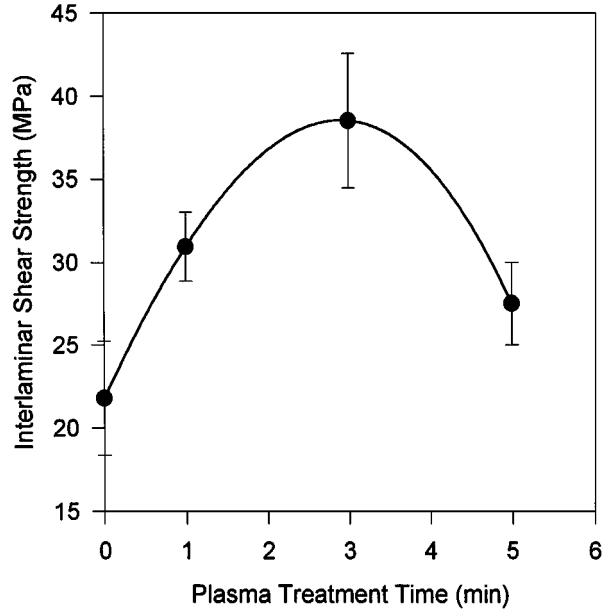



*Figure 4* ILSS of CF/polybenzoxazine composites as a function of oxygen plasma treatment time.

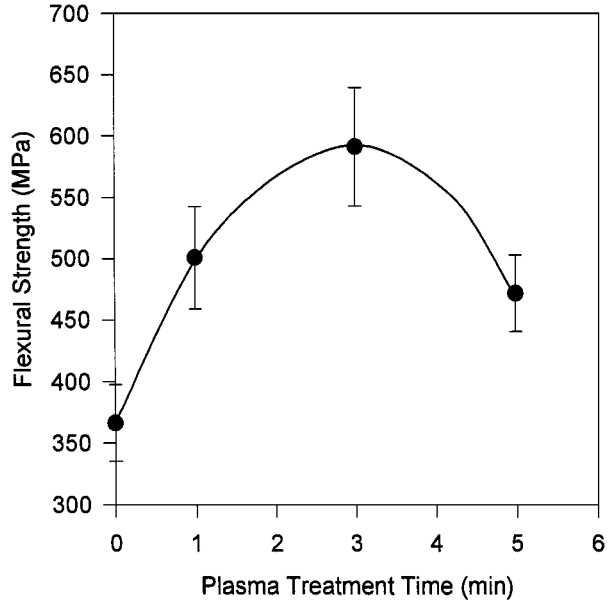
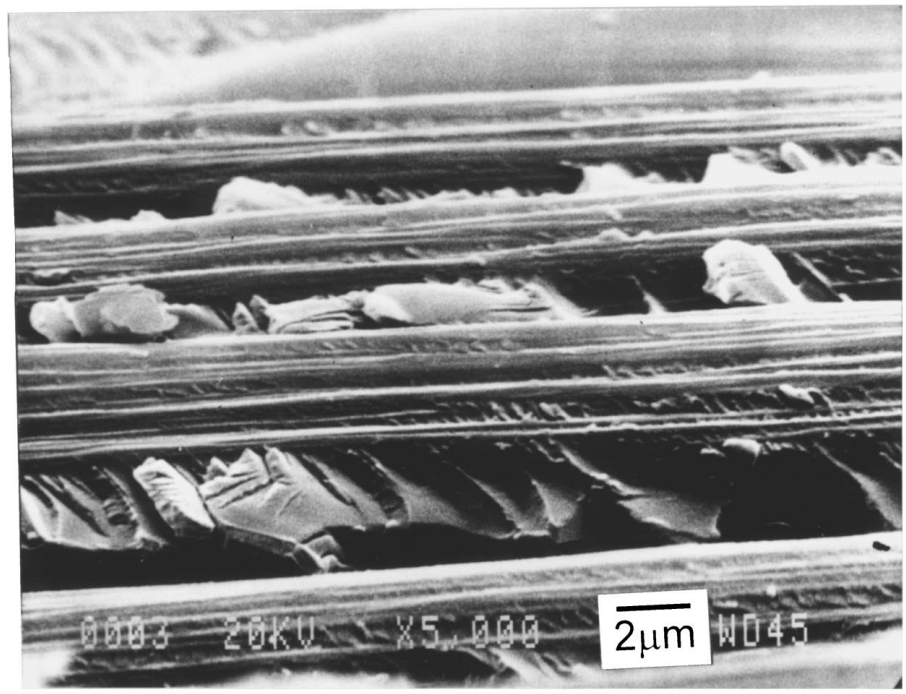


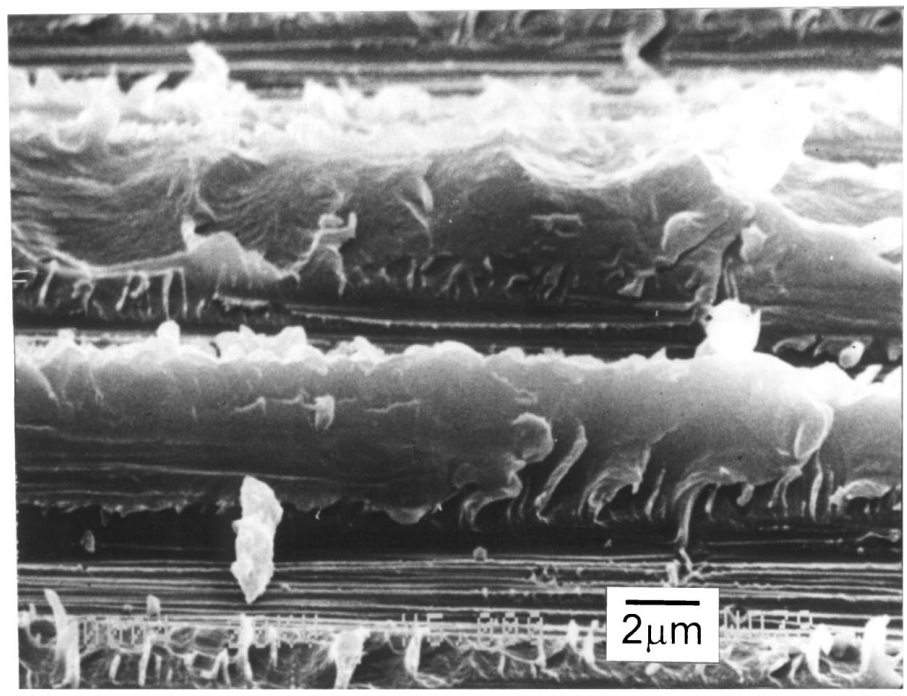

*Figure 5* Flexural strength of CF/polybenzoxazine composites as a function of oxygen plasma treatment time.

Plasma treatment of CF made micro-pittings on the CF surface [13]. Micro-pittings allow more interpenetration between CF and polybenzoxazine, so that the maximum mechanical interlocking would be achieved at 3 min plasma treatment. Therefore, the increase of surface roughness is the major contribution to adhesion enhancement through improving wettability and mechanical interlocking. The decrease of ILSS after 3 min is ascribed to the decrease of CF surface area (see Fig. 3). Excess plasma treatment smoothes the CF surface, reducing mechanical interlocking and wettability, so that the ILSS of composites decreases.

Fig. 5 shows the flexural strength of the oxygen plasma-treated CF/polybenzoxazine composites as a function of treatment time. The maximum flexural




(a)




(b)

*Figure 6* SEM photographs of the fractured surface of CF/polybenzoxazine composite after flexural test according to oxygen plasma treatment time: (a) untreated, (b) 3 min.

strength is observed at 3 min treatment and it decreases when the treatment time is over 3 min. Flexural strength of CF/polybenzoxazine composites is well correlated with ILSS, which confirms the mechanical properties of the composites mainly depend on the composite's interfacial adhesion strength between the fiber and matrix. The decrease of flexural strength after 3 min is attributed to not only the decrease of ILSS but also the deterioration of the fiber itself. Donnet *et al*. investigated the effect of plasma treatment on the mechanical properties of T300 carbon fiber [13]. According to their result, the tensile breaking load of T300 carbon fiber is lowered by plasma treatment. In addition, excess plasma treatment smoothes the CF surface to reduce mechanical interlocking and wettability so that the ILSS and flexural strength of composites decrease.

Fig. 6 represents SEM photographs of the fracture surface of CF/polybenzoxazine composites after flexural test. The fracture surface of untreated CF/polybenzoxazine composite has little remnant of polybenzoxazine, showing a lot of groovings and crevices of bare fiber itself (Fig. 6a). This result implies

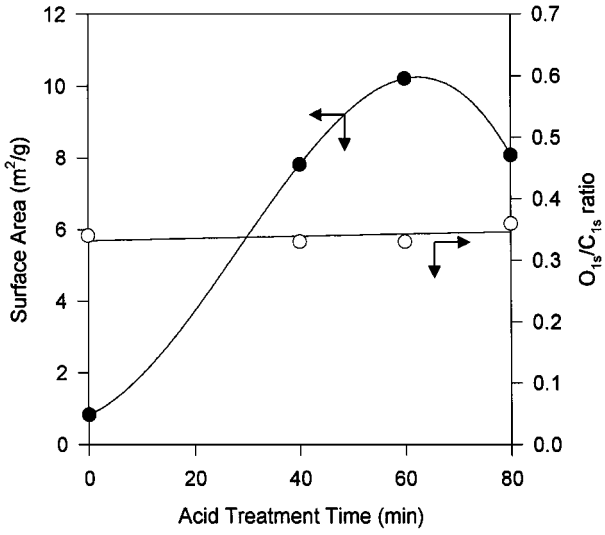



*Figure 7* BET surface area and $O_{1s}/C_{1s}$ ratio of nitric acid treated CF as a function of nitric acid treatment time.

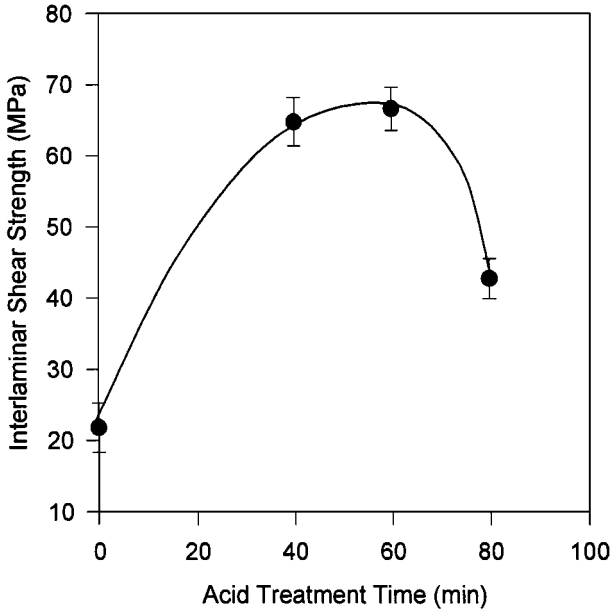



*Figure 8* ILSS of CF/polybenzoxazine composite as a function of nitric acid treatment time.

that fracture occurs in the interface between the CF surface and the matrix because of poor interfacial adhesion strength. On the other hand, the fracture surface of 3 min plasma treated CF/polybenzoxazine composite is covered with polybenzoxazine (Fig. 6b). This indicates that plasma treatment significantly improves the interfacial adhesion strength, which induces cohesive failure in the matrix region. The observation of SEM photographs is coincident with the enhancement of mechanical properties.

## 3.2. Nitric acid treatment

The nitric acid treatment has been known to be an effective method to modify the CF surface, especially to improve the shear properties of the composite. Therefore, CF was modified with nitric acid for the improvement of shear property of CF reinforced composite.

Fig. 7 displays the surface area and the $O_{1s}/C_{1s}$ ratio of nitric acid treated CF according to acid treatment time. The BET surface area increases with acid treatment time up to 60 min and then decreases due to smoothing by excessive oxidation. The BET surface area of 60 min treated CF is 10 times as large as that of untreated CF. The increment of BET surface area by nitric acid treatment was larger than that by plasma treatment, which implies that nitric acid treatment can be more efficient than plasma treatment in improving interfacial adhesion between CF and polybenzoxazine through promotion of wettability and mechanical interlocking. The $O_{1s}/C_{1s}$ ratio increases with the acid treatment time, which represents the introduction of polar functional groups that usually aid good wetting. The $O_{1s}/C_{1s}$ ratio increment with the nitric acid treatment is not much different from that with the plasma treatment.

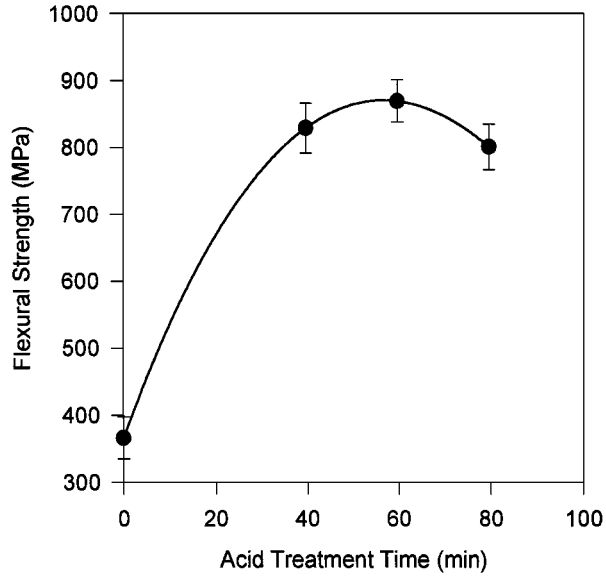



*Figure 9* Flexural strength of CF/polybenzoxazine composite as a function of nitric acid treatment time.

Mechanical properties of nitric acid treated CF/polybenzoxazine composites were measured and compared with those of oxygen plasma treated composites. Fig. 8 shows the ILSS of the CF/polybenzoxazine composites manufactured after nitric acid treatment. The ILSS value increased with increasing treatment time and decreased after 60 min. The increment of polar functionality and surface roughness can advance the interfacial adhesion strength between resin and CF surface, which causes the increase of the ILSS. The flexural strength of composites oxidized with nitric acid is displayed in Fig. 9. A significant increase of flexural strength caused by nitric acid treatment is observed. The flexural strength of 60 min oxidized CF/polybenzoxazine composites is 2.4 times as high as that of untreated ones and is even more than that of plasma-treated ones. This is attributed to the considerable increase of surface area caused by nitric acid treatment. (see Figs 3, 7)

Fig. 10 presents the SEM photographs of the fracture surfaces of composites modified with nitric acid oxidation for 60 min. The fracture surface is extensively embedded with matrix. This suggests that cohesive failure occurred in the matrix region due to the improvement

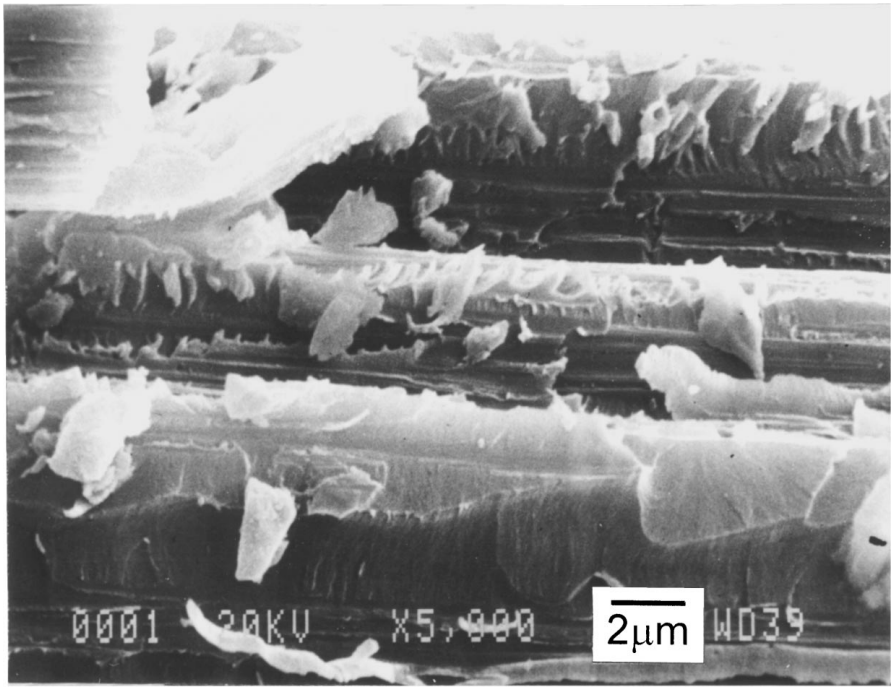



*Figure 10* SEM photograph of the fracture surface of CF/polybenzoxazine composite nitric acid treated for 60 min after flexural test.

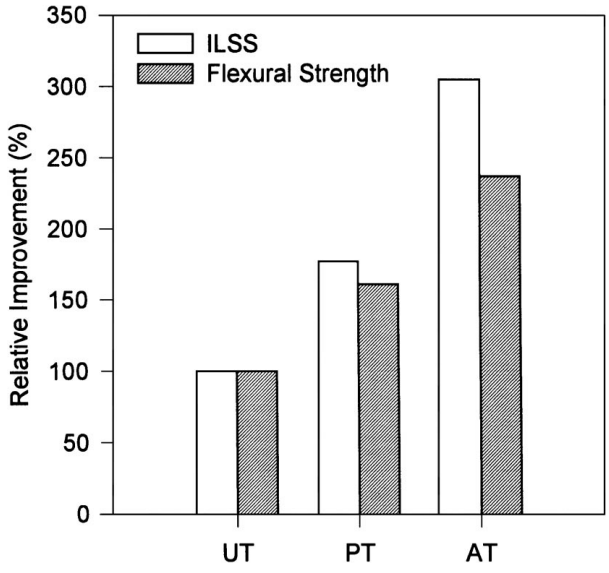



*Figure 11* Relative improvements of flexural strength and ILSS of CF/polybenzoxazine composite by surface modification: (a) untreated (UT), (b) oxygen plasma treatment (PT), (c) nitric acid treatment (AT).

of the interfacial adhesion strength between CF and matrix by the nitric acid treatment.

Fig. 11 shows the relative improvements of the ILSS and flexural strength of CF/polybenzoxazine composites after surface treatments. ILSS and flexural strength are largely enhanced by both the plasma treatment and acid treatment. The increment of surface area produced by the nitric acid treatment was larger than that by the oxygen plasma treatment. This is the reason why nitric acid treatment is more effective than oxygen plasma treatment in improving the mechanical properties of CF/polybenzoxazine composites. From the view point of surface treatment, the ILSS of CF/polybenzoxazine composite was improved effectively compared to the flexural strength of CF/polybenzoxazine composite.

## 4. Conclusion

The influences of oxygen plasma treatment and nitric acid treatment on the mechanical properties of CF/polybenzoxazine composites were studied and correlated with surface characteristics of modified CF. Oxygen plasma treatment and nitric acid treatment were effective in improving the mechanical properties of CF/polybenzoxazine composites. The flexural strength of CF/polybenzoxazine composites increased with oxygen plasma treatment and nitric acid treatment. Interfacial adhesion strength was affected by both the surface roughness and the functionality of CF. However, surface roughness is thought to be the major factor of mechanical performance improvement of CF/polybenzoxazine composites. Nitric acid treatment enhanced the mechanical properties of CF/polybenzoxazine composite compared to the oxygen plasma treatment due to a large increase of fiber surface roughness.

## References

1. X. NING and H. ISHIDA, *J. Polym. Sci.* **32** (1994) 921.
2. *Idem.*, *ibid.* **32** (1994) 1121.
3. J. JANG and S. SHIN, *Polym. J.* **27** (1995) 601.
4. H. ISHIDA and D. J. ALLEN, *J. Polym. Sci.* **34** (1996) 1019.
5. R. LI, L. YE and Y. W. MAI, *Composites Part A* **28A** (1997) 73.
6. J. B. DONNET and R. C. BANSAL, "Carbon Fiber," 2nd ed. (Marcel Dekker Inc., New York, U.S.A.) p. 188.
7. L. Y. YUAN, S. S. SHYU and I. Y. LAI, *J. Appl. Polym. Sci.* **42** (1991) 2525.
8. C. Y. YUE and W. L. CHEUNG, *J. Mater. Sci.* **27** (1993) 3843.
9. L. S. SCHADIER and C. LAIRD, *ibid.* **27** (1992) 4024.
10. D. J. BLUNDELL, R. A. CRICK, B. FIFE, J. PEACOCK, A. KELLER and A. WADDON, *ibid.* **24** (1989) 2057.
11. S. SAIELLO, J. KENNY and L. NICOLAIS, *ibid.* **25** (1990) 3493.
12. R. N. WENZEL, *Ind. Eng. Chem.* **28** (1936) 988.
13. J. B. DONNET, M. BRENDLE, T. L. DHAMI and O. P. BAHL, *Carbon* **24** (1986) 757.

14. J. R. EVANS and D. E. PACKHAM, *J. Adhesion* **9** (1978) 267.
15. *Idem., ibid.* **10** (1979) 39.
16. *Idem., ibid.* **10** (1979) 177.
17. P. J. HINE, S. EI MUDDARRIS and D. E. PACKHAM, *ibid.* **17** (1984) 207.
18. J. KALANTAR and L. T. DRZAL, *J. Mater. Sci.* **25** (1990) 4186.
19. R. J. SMILEY and W. N. DELGASS, *ibid.* **28** (1993) 3601.
20. W. P. HOFFMAN, W. C. HURLEY, T. W. OWENS and H. T. PHAN, *ibid.* **26** (1990) 4545.

*Received 3 September 1998*
*and accepted 6 October 1999*