

# Evaluation of fiber surface treatment on the interfacial behavior of carbon fiber-reinforced polypropylene composites



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## ABSTRACT

Carbon fiber reinforced polypropylene (CFRPP) has been widely used in many engineering fields because of its high specific strength and stiffness. However, polypropylene (PP) does not adhere well with carbon fibers because it has a low free surface energy. In addition, high viscosity in the melted phase causes poor impregnation. In this study, surface treatment methods, i.e., coupling agents with plasma treatment on carbon fibers, were applied to increase the interfacial strength between the carbon fibers and the PP matrix. The modified carbon fiber surfaces were analyzed by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). To analyze the effectiveness of the surface treatment method, the interlaminar shear strength (ILSS) was measured using the three points bending test. From the test results, the ILSS of the specimens treated with the silane coupling agent after the plasma treatment increased by 48.7% compared to those of the untreated specimens.

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## 1. Introduction

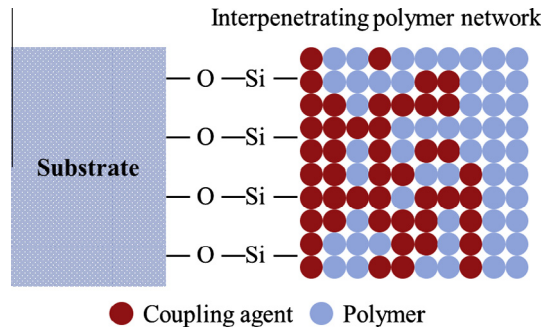
As environmental awareness gradually increases, thermoplastic polymers attract increased attention as a matrix for composite materials because of their recyclability and easy processability. The range of application for these polymers is also increasing, finding applications in everything from automobile parts to sports equipment [1–3]. Among various thermoplastic polymers, polypropylene (PP) is one of the more promising materials for the matrix because of its high flexural strength, low density and low price [4–6]. Carbon fiber reinforced PP (CFRPP) has been widely used in many engineering fields because of its high specific strength and stiffness. However, PP exhibits poor interfacial adhesion with carbon fibers (CF) because of low surface energy and a chemically inert surface. In addition, in its melted phase PP is very viscous and has difficulty impregnating dry fiber structures, such as fabrics. In that case, interfacial debonding is occurred by weak interfacial strength between the carbon fiber (CF) and PP. Therefore, various approaches have been investigated to increase the interfacial adhesion between the CFs and PP [7–9].

The functionalization of PP with polar molecules is the most attractive method to improve adhesion and compatibility [10–12]. However, the functionalization of PP such as maleic anhydride grafted PP leads to a decrease of the molecular weight. If the molecular weight of the PP becomes too low, the functionalized PP becomes quite brittle with reduced strength and stiffness [13].

The surface treatment of the fiber is another way to increase the interfacial adhesion except the functionalization of resin. Several techniques for surface treatments on fibers have been applied to improve the interfacial strength such as wet oxidation, sizing, whiskerization, thermal treatments, and coupling agent treatments. These surface modification methods either enhance the number of reactive functional groups or increase the surface roughness of the fiber to increase the physical bonding with the matrix. Coupling agent treatment is one of the most common methods for fiber surface treatment [14–16]. Silane coupling agents (CAs) improve interfacial strength between the glass fibers and the matrix. Cho et al. found that the interlaminar shear strengths of glass fabric/nylon 6 composites sized with various silane coupling agents were significantly improved compared with that of the commercially sized composites [17]. Gironès et al. investigated the effect of silane CAs on the properties of pine fibers/polypropylene composites [18]. Silane CAs form alkoxy silane groups, which, after hydrolysis, are capable of reacting with hydroxyl groups on the surface. There is a wide range of available functionalities for the organofunctional group. This organofunctional group is responsible for improving the compatibility between the reinforcing material and the polymer matrix, and can also establish covalent bonds between them. The interpenetrating polymer network that is formed between the organofunctional group of silane and the polymer matrix increases the interfacial strength in the case of thermoplastic resin, which is a difficult chemical-bonding material. An interpenetrating polymer network is defined as a blend of two physically cross-linked polymers. Fig. 1 shows interpenetrating polymer network structure created by the silane CA at

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**Fig. 1.** Interpenetrating polymer network structure created by the silane CA at the interphase between the substrate and the polymer matrix.

the interphase between the substrate and the polymer matrix. It does not necessarily involve cross-linking of the silane or other coupling agent and the polymer matrix [19].

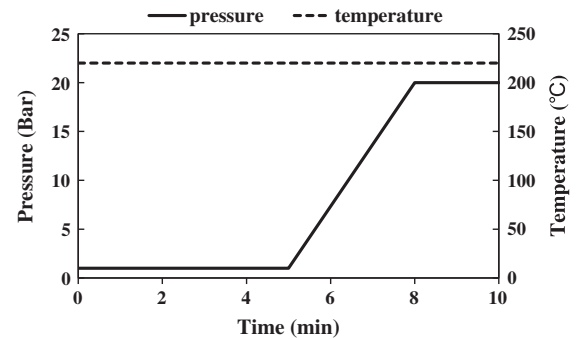
However, the silane CAs are not effective when applied to CFs because the CF does not contain a hydroxyl group [20]. However, the hydroxyl group can be attached on the fiber surface by plasma and wet chemical or electrochemical oxidation treatments. Shi et al. found that short CFs, which oxidized with nitric acid and then treated with silane CA, reinforced PTFE composites had better mechanical properties than untreated CF composite with the same content of CFs [21]. Wet chemical oxidation, however, produces environmental pollutants and the fiber must be thoroughly washed to remove by-products after treatment [20,21]. On the other hand, the plasma treatment is the simplest method and does not generate as many byproducts as the others. The plasma oxidation treatment often leads to the introduction of polar groups. Researchers have confirmed with XPS measurements that this may occur, even when using inert gases [22–24]. Park et al. found that plasma treatment led to a large quantity of reactive functional groups added to the CF surface [25].

In this study, the effect of a combined silane-CA/plasma treatment at atmospheric pressure on CFs in a PP composite matrix reinforced with CF fabrics was investigated. The surface morphology and mechanical properties of CFs treated with plasma and a silane CA surface treatment were characterized by a scanning electron microscope (SEM) and single filament tensile tests. The surface composition change of the CF surfaces with respect to the plasma treatment was investigated by X-ray photoelectron spectroscopy (XPS). The interlaminar shear strength (ILSS) of the

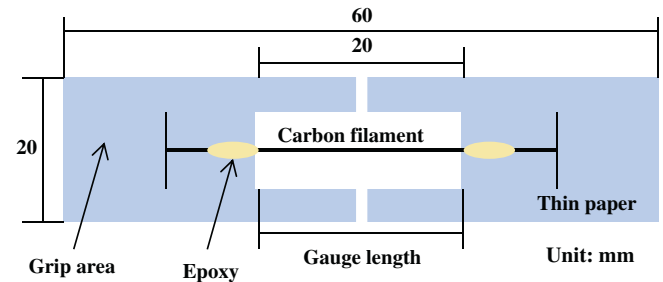
**Table 1**

Various surface treatments using plasma and silane CA.

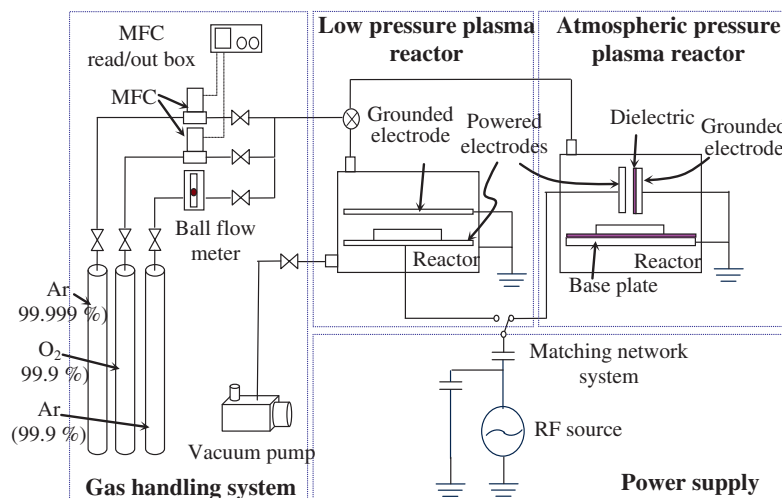
Specimen	Surface treatment	
	Plasma	Silane CA
U-0	–	–
U-P30s	30 s	–
U-P1min	1 min	–
U-P3min	3 min	–
S-0	–	1 wt.%
S-P30s	30 s	1 wt.%
S-P1min	1 min	1 wt.%
S-P3min	3 min	1 wt.%



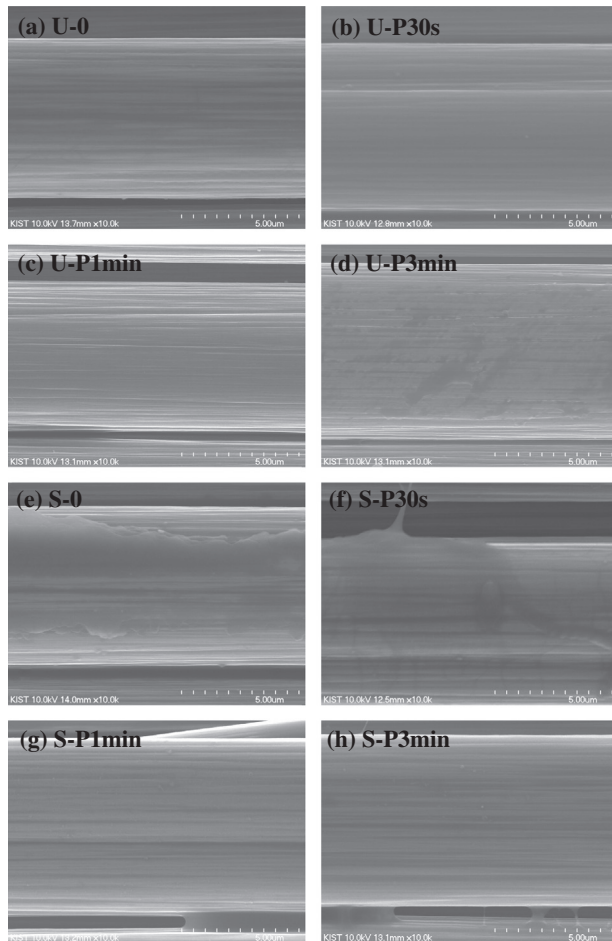
**Fig. 3.** Pressure–temperature–time diagram of the molding cycle.



**Fig. 4.** Single filament tensile test specimen.



**Fig. 2.** Plasma surface treatment system.



**Fig. 5.** SEM topographies of the CF surface with respect to surface treatment methods; (a) untreated, (b) plasma 30 s, (c) plasma 1 min, (d) plasma 3 min, (e) silane CA, (f) silane CA after plasma 30 s, (g) silane CA after plasma 1 min, and (h) silane CA after plasma 3 min.

CF/PP composites with the surface treatment method was measured using the short beam shear test.

## 2. Experiments

### 2.1. Surface treatments

PAN-based CF fabric (12k plane weave, AKSA, Turkey) sized with bisphenol A diglycidyl ether epoxy by the manufacturer was

used as the composite reinforcing material. The average diameter of the carbon fiber is 7  $\mu\text{m}$ . The silane CA, 3-methacryloxy propyltrimethoxy silane (KBM-503, Shin-Etsu Chemical Co., Ltd., Japan), was used for the treatment.

#### 2.1.1. Silane CA treatment

1 wt.% of the silane CA was prepared in distilled water as per the recommendations of the manufacturer. The pH of the CA solution was brought to 4.2 by adding acetic acid. The solution was stirred for 1 h before use to ensure complete silane hydrolysis. The fabrics were immersed in the silane CA solution for 20 min, and the treated fabrics were dried in air at 80  $^{\circ}\text{C}$  for 1 h [26].

#### 2.1.2. Plasma treatment

The plasma system used in this study consisted of a gas handling system, an atmospheric pressure plasma reactor, and a power supply, as shown in Fig. 2. The capacitively coupled atmospheric pressure plasma system had two parallel electrodes, the grounded electrode coated with a dielectric material ( $\text{Al}_2\text{O}_3$ ) and the powered electrode, and a base plate coated with the same dielectric material. The area of the electrodes and the width of the gap between them were  $170 \times 50 \text{ mm}^2$  and 1 mm, respectively. The distance between the electrodes and the base plate was adjustable [27]. In this study, the atmospheric plasma treatment on the CF surface was performed with argon gas. Plasma treatment with argon gas primarily affects the surface of the substrate, thus the materials are relatively safe from internal damage at long exposure times compared to the treatment with oxygen gas [28]. The gas flow rate was set at 10 LPM and the power was 150 W.

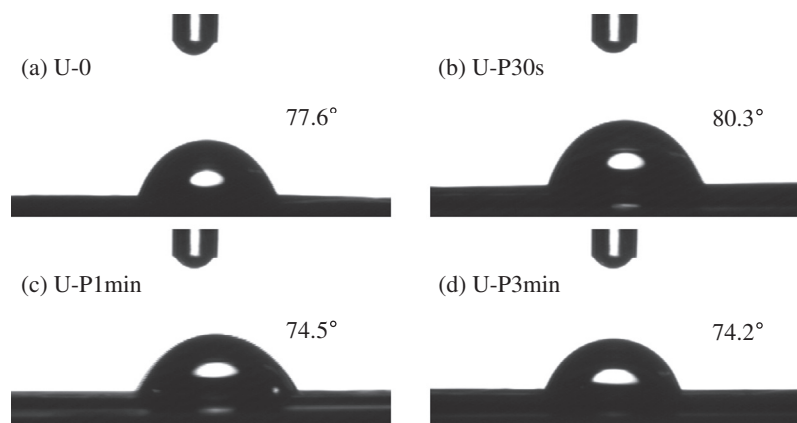
#### 2.1.3. Silane CA treatment after plasma treatment

The silane CA treatment, as previously described, was applied to the plasma-treated CF.

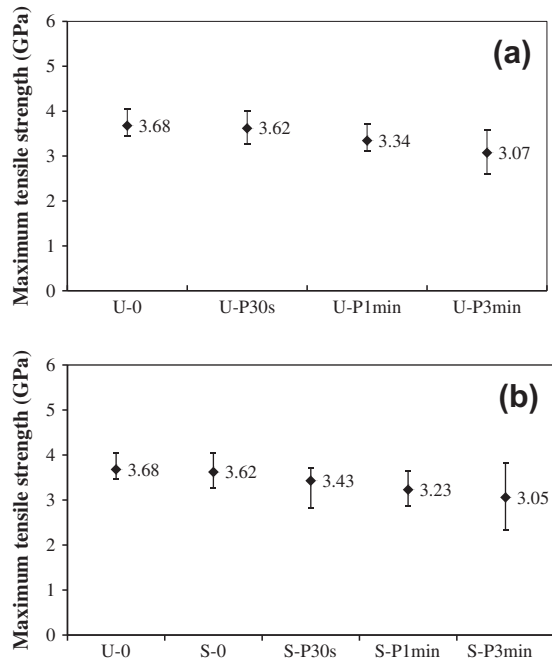
The surface-treated specimens were labeled according to the treatment method, as shown in Table 1. Investigation of the surface change after treatment was performed by scanning electron microscope (SEM) (Jeol, USA) and X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Scientific, UK) and contact angle measurement (DIGIDROP, GBX, France). The XPS spectra were obtained using an Al K $\alpha$  (1486.6 eV) X-ray source. The pass energy was set at resolution 200 eV and the analysis was carried out under vacuum conditions of  $5 \times 10^{-7}$  Torr.

### 2.2. CF/PP composite fabrication

The CF/PP composites were fabricated using the film stacking method in the molding cycle. Isotactic PP (427888, Sigma-Aldrich Co., LLC., USA) pellets were used to make a PP film, 0.2 mm thick,



**Fig. 6.** Contact angle with respect to plasma treatment time; (a) untreated, (b) plasma 30 min, (c) plasma 1 min, and (d) plasma 3 min.



**Fig. 7.** Single filament tensile strength of the CF with respect to surface treatment on the CF; (a) plasma treatment, (b) silane CA-treated specimens after plasma treatment.

by a hot press. Seven sheets of PP film and 6 sheets of CF fabric were stacked alternately. The stack was then pressed at 220 °C under 20 bars of pressure for 10 min. Fig. 3 shows the molding cycle of the CF/PP composite. If high pressure is abruptly applied, resin cannot be impregnated into the fabric and squeezed out from the inter-layer. Therefore, pressure was applied steadily during the cycle. The fiber volume fraction of the fabricated composites was approximately 54%.

### 2.3. Tensile tests with single filaments

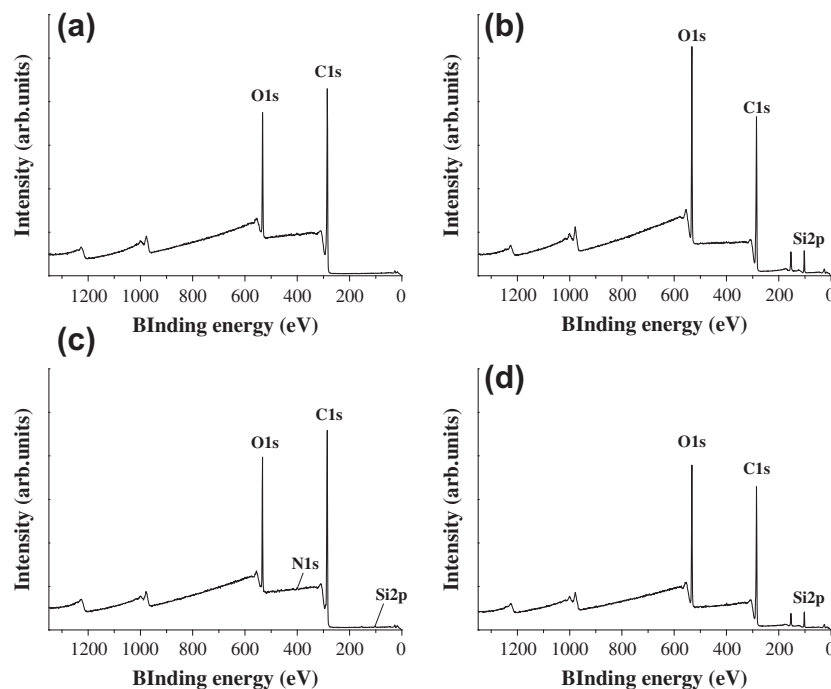
The tensile strength of a single carbon filament was measured using a universal testing machine (INSTRON 5567A, MA, USA) based on the ASTM D 3379-75 standard test method for high-modulus materials. A schematic diagram of the single filament test specimen is shown in Fig. 4. A single filament was bonded by adhesive to a thin paper, which had a central longitudinal slot of a fixed gauge length. The epoxy resin used to fix the filament was extended along the longitudinal direction to avoid any concentration of stress on the fixed section if the filament is out of alignment. Once the specimen was clamped in the grips of the tensile testing machine, the backing strip was cut away, allowing the filament to transmit the applied tensile load. The specimen was pulled to failure, the load and elongation were recorded, and the tensile strength and modulus were calculated from the usual formulas. Each samples measured for 20 times were averaged.

### 2.4. Short beam shear test on the composites

Generally, the single fiber test method is used to measure the interfacial bonding strength between the fiber and the matrix. However, this method often results in considerable data scatter. Therefore, the short beam shear test was used to measure the interlaminar shear strength (ILSS). The ILSS of the CF/PP composites was measured using a universal testing machine (INSTRON 4469, MA, USA), based on the ASTM D2344. The rectangular-shaped specimen was 24 mm × 6.5 mm × 4 mm and the loading speed was 1 mm/min. The maximum shear stress ( $\tau$ ) was calculated according to the following equation:

$$\tau = 0.75 \times \frac{P_m}{bh}$$

where  $P_m$  is the maximum load during the test (N),  $b$  is the measured specimen width (mm), and  $h$  is the measured specimen thickness (mm). Each samples measured for 5 times were averaged.



**Fig. 8.** XPS survey scan of the CF surface with respect to surface treatment methods; (a) untreated, (b) silane CA, (c) plasma 1 min, and (d) silane CA after plasma 1 min.

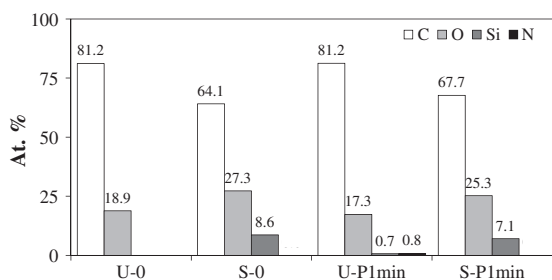


Fig. 9. Atomic concentrations of the CF surface with respect to the surface treatment methods.

### 3. Results and discussion

The surfaces of the specimens were examined by SEM to compare the surface morphologies with respect to the surface treatment methods as shown in Fig. 5. The untreated fiber surface was smooth with shallow longitudinal grooves. In the case of the U-P30s and U-P1min, the surface grooves distributed along the fiber were slightly deeper, but no other significant change was observed. In the U-P3min case, the CF surface was damaged by the long exposure to the plasma treatment, as shown in Fig. 5(d). In the case of the S-0 and S-P30s, silane CA aggregated on the CF surface, but in the cases of S-P1min and S-P3min, the samples had smooth surfaces, as shown in Fig. 5(e–h). These data imply that the S-P1min and S-P3min specimens were uniformly treated with silane CA without aggregation, compared to the other specimens.

Fig. 6 shows the image of the water contact angle on the CF bundle with respect to the plasma treatment time. In the case of the U-P30s, the contact angle increased because the epoxy sizing on the CF surface was removed by the plasma treatment. This means that the inert CF surface was exposed by plasma treatment. After 1 min of the plasma treatment time, the contact angle decreased because the CF surfaces were functionalized by plasma treatment after removing the epoxy sizing perfectly.

Fig. 7 shows the single filament tensile test results of the CF as a function of the surface treatment. The tensile strength of the specimens treated with plasma decreased with treatment time, because the surface damage of the CF increased as the plasma treatment time increased. The tensile strength of the U-P3min specimen decreased by 16.6% compared to that of the untreated specimen, as shown in Fig. 7(a). The tensile strengths of the silane CA-treated specimens after plasma treatment were similar to those of the plasma-treated specimens because silane CA treatment does not affect the tensile strength of the CF.

XPS analysis was performed to investigate the atomic concentration and chemical bonding changes of the treated CF surface. The XPS spectra of the CF surface, corresponding to binding energies between 0 eV and 1350 eV, are shown in Fig. 8. The carbon and oxygen peak represent the major constituents of the CF surface. Silicon was detected from the silane CA-treated specimens. In the plasma-treated specimens, small amounts of nitrogen and silicon are regarded as impurities. The atomic properties of the CF with respect to the surface treatment are listed in Fig. 9.

Fig. 10 shows the C1s peak of the XPS spectra on the CF surfaces with respect to plasma treatment time. Table 2 shows the binding energies of the functional groups used for the decomposition of the C1s peak [29–31]. Many peaks, such as  $sp^2C$ ,  $sp^3C$ , hydroxyl group ( $C-O(H)$ ), and carboxyl group ( $COO(H)$ ), were detected on the untreated CF surface from the epoxy sizing material in the CF, shown in Fig. 10(a). In the plasma 30 s-treated CF, the  $sp^2C$  peak is smaller but the  $sp^3C$  peak is larger. Some of the carbonyl group ( $C=O$ ) were also detected, as shown in Fig. 10(b). These results are attributed to the change in epoxy sizing on the CF by plasma treatment. After 1 min of plasma treatment, the hydroxyl group increased, but the carboxyl group disappeared. However, in the plasma 3-min-treated CF, the hydroxyl group decreased but the carboxyl group increased.

Table 3 shows the relative quantities of the functional groups on the CF surfaces, which were observed in XPS spectra. The hydroxyl group is an important component because silane CA forms a strong chemical bond with the hydroxyl group. The hydroxyl group was detected from the untreated CF surface. This may have been induced by the epoxy sizing on the fiber surface. Then the hydroxyl

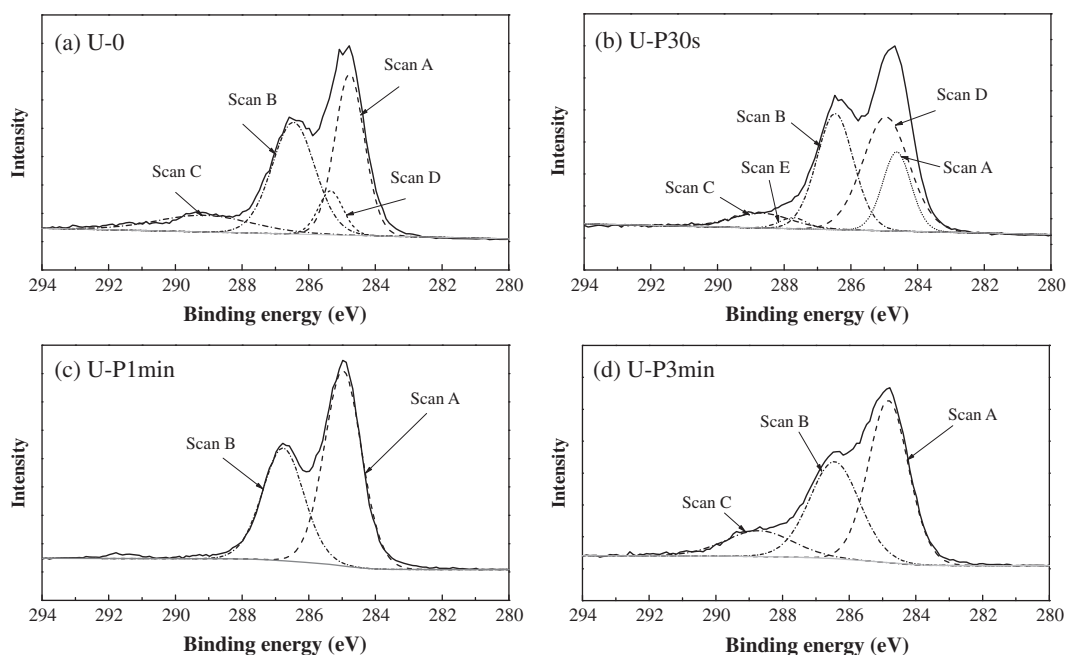


Fig. 10. C1s XPS spectra of CF surfaces with respect to plasma treatment; (a) untreated, (b) plasma 30 min, (c) plasma 1 min, and (d) plasma 3 min.



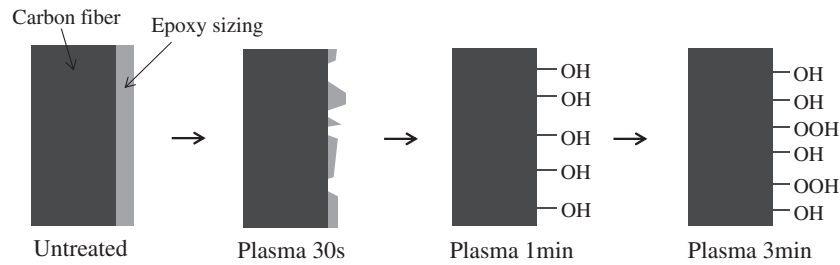


Fig. 11. Schematics of the mechanism of plasma treatment on CF surface.

Table 2

Binding energies of the functional groups of the XPS C1s peaks.

Peak	Functional group	Binding energy (eV)
Scan A	sp <sup>2</sup> C	284.6 (±0.1)
Scan B	C—O(H)	286.2 (±0.1)
Scan C	COO(H)	288.6 (±0.1)
Scan D	sp <sup>3</sup> C	285.2 (±0.1)
Scan E	C=O	287.4 (±0.1)

Table 3

Contents of the functional groups of the CF surfaces with respect to the plasma treatment time.

	Scan A	Scan B	Scan C
	sp <sup>2</sup> C 284.6 (±0.1) (%)	C—O(H) 286.2 (±0.1) (%)	COO(H) 288.6 (±0.1) (%)
U-0	38.9	39.1	8.9
U-P30s	40.5	32.9	6.9
U-P1min	60	40	—
U-P3min	49.5	37.1	13.4

group decreased with time until the treatment time of 30 s, when the epoxy sizing on the surface of the treated CF was partially removed by the plasma treatment. After 1 min of plasma treatment time, the hydroxyl group on the CF surface began to increase, after all of the epoxy sizing was removed, decreasing again after 3 min of plasma treatment time. The reason it decreased is that the hydroxyl group is primarily formed on the CF surface during short plasma treatment times, but the portion of hydroxyl group on the CF surfaces decreases as the portion of carboxyl group increases with increasing treatment time [32]. The mechanism of this phenomenon based on the results in Table 3 is explained in Fig. 11.

The short beam shear test results of the CF/PP composites are shown in Fig. 12. The ILSS of the plasma-treated specimens increased as the treatment time increased, because the wettability of the CFs and introduction of functional groups increase with the treatment time. These factors are favorable to form strong chemical bonds between CF and polymer matrix of the composite [33]. In the silane CA-treated specimens, after plasma treatment, the ILSS of the S-P1min was higher than that the others, as shown in Fig. 12(b). The maximum shear stress of S-P1min with maximum hydroxyl bond density increased by 48.7% compared to that of the untreated specimen. This result shows that the hydroxyl group on the CFs, generated by plasma treatment, reacted with the silane CA, strengthening the interface between the fibers and the matrix. However, when the plasma treatment time was 3 min, the ILSS decreased compared to that at 1 min of plasma treatment time. This result implies that the hydroxyl groups on

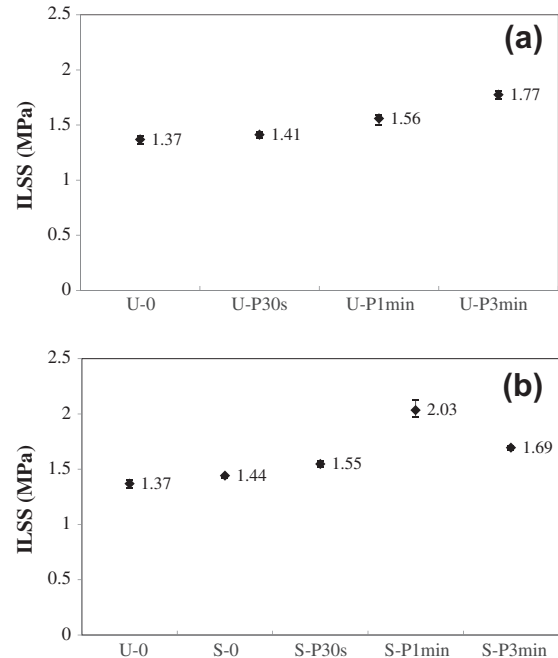


Fig. 12. ILSS of the CF/PP composite specimens with respect to surface treatment on the CF; (a) plasma treatment, (b) silane CA treated specimens after plasma.

the surface of S-P3min could not react intensively with the silane CA because the hydroxyl groups were reduced by the long plasma treatment time. In the case of the S-0 and S-P30s, the increase in ILSS was slight because the epoxy sizing on the CF was not completely removed. Therefore, the hydroxyl group could not be generated directly onto the CF surface, and only a weak bond was formed.

Fig. 13 shows the SEM images of the composite fracture surfaces. In case of the untreated specimen, the PP and the carbon fibers were separated from each other due to weak adhesion between PP and untreated carbon fiber surfaces as shown in Fig. 13(a). In case of the S-P1min specimen with maximum ILSS, improved impregnation state was observed compared to the untreated specimen and PP was stuck on the carbon fiber surfaces as shown in Fig. 13(b). It contributed to the improvement of ILSS in the short beam shear test.

The silane CA treatment applied after the plasma treatment increased interfacial bonding between the CF and PP more efficiently than the plasma treatment alone. Plasma treatment contributed to the improvement of the mechanical interlocking and wettability, which increases interfacial bonding between the CF and PP. However, in the case of silane CA treatment applied after plasma treatment, not only does this treatment have the effects of plasma treatment, but a strong interpenetrating boundary layer is also

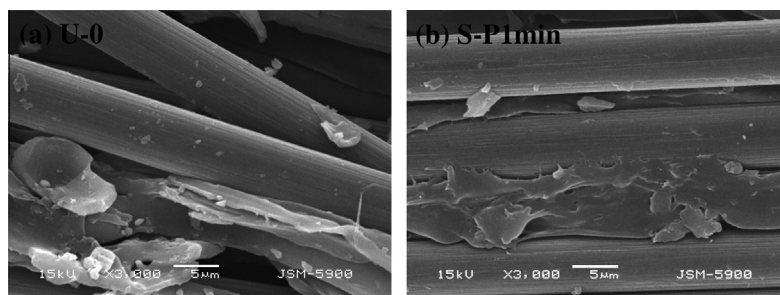


Fig. 13. SEM topographies of the composite fracture surfaces: (a) untreated, (b) silane CA after plasma 1 min.

formed by the interpenetrating polymer network between the silane layer and PP.

#### 4. Conclusions

In this study, a CF surface treatment was performed to improve the interfacial strength between the fibers and the PP matrix using CAs combined with plasma treatment. The following conclusions were derived from the results.

- (1) The single filament tensile strength of the specimens treated with the plasma at atmospheric pressure decreased as treatment time increased because the surface damage of the plasma-treated CF increased with treatment time. The tensile strength of the plasma 3-min-treated specimen decreased by 16% compared to that of the untreated specimen. The tensile strengths of the silane CA-treated specimens after plasma treatment were similar to those of the plasma-treated specimens.
- (2) When the plasma treatment time was 1 min, the density of the hydroxyl group showed the highest among the specimens, but it decreased at 3 min of plasma treatment time.
- (3) The ILSS of the specimens increased 29.7% with 3 min of plasma treatment compared to that of untreated specimens because the wettability of the CFs and introduction of functional groups increased with plasma treatment time. These factors are favorable to form strong chemical bonds between CF and polymer matrix of the composite.
- (4) The ILSS of the specimens increased 48.7% with the silane CA treatment, after 1 min of plasma treatment compared to that of the untreated specimen, because the hydroxyl group on the CFs generated by plasma treatment reacted with the silane CA, strengthening the interface between the CF and the PP through an interpenetrating polymer network. In this case, impregnation state was improved compared to the untreated specimen and the PP was stuck on the carbon fiber surface.

From these results, the combination of plasma and CA treatments is one of the promising methods that can be used to enhance the interfacial strength between a CF and PP matrix.

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