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Effect of oxygen plasma-treated carbon fibers on the tribological behavior of oil-absorbed carbon/epoxy woven composites

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ABSTRACT

In this study, woven type carbon fibers were plasma-treated using oxygen gas, and the effect of the plasma treatment on tribological behavior of oil-absorbed carbon/epoxy woven composites was investigated. Chemical changes on the surface of the woven carbon fibers due to oxygen plasma treatment were determined by XPS analysis. Ball-on-disk wear tests were performed on untreated and plasma-treated carbon/epoxy woven composites that were fully oil absorbed. It was found that carbonyl functional groups were created on the carbon fibers due to oxygen-plasma treatment. In addition, the friction coefficient and wear rate of the plasma-treated carbon/epoxy composites were lower than that of untreated carbon/epoxy composites. SEM examination of the worn surface showed that the improved wear properties of the plasma-treated carbon/epoxy composites were attributed to enhanced adhesive strength, caused by the carbonyl functional groups between the carbon fibers and epoxy.

1. Introduction

The use of woven fabric reinforced polymer composites is increasing in automobile, aerospace, naval, and civil industries because they exhibit excellent mechanical properties in both longitudinal and transverse directions. Among them, carbon/polymer woven composites are prominent wear-resistant materials because carbon fabric offers good strength, stiffness, and thermal conductivity. Accordingly, many studies have examined the wear behavior of carbon/polymer woven composites [1–4]. Suresha and Chandramohan [5] compared friction and wear loss of carbon/epoxy woven composites with those of glass/epoxy woven composites. They reported that the carbon/epoxy woven composites showed both lower friction and slide wear loss compared to the glass/epoxy woven composites irrespective of load or speed. Wan et al. [6] investigated friction and wear behavior of three-dimensional braided carbon fiber/epoxy composites under dry sliding conditions. Their results showed that fiber volume fraction, normal load, and sliding speed affected wear behavior more significantly than the friction coefficient. Adhesion between the carbon fabric and matrix is crucial to the wear properties of carbon/polymer woven composites; however, carbon/polymer woven composites suffer from weak adhesion at the carbon/matrix interface due to the hydrophobic properties of carbon fabric. A number of reports have attempted to improve carbon/polymer composite wear properties by increasing interfacial strength between the carbon fiber and the matrix [7–9]. Rattan and Bijwe [10] applied three different carbon fabric textures (plain, twill, and satin) and investigated the effect of texturing on erosive wear behavior in carbon/polyetherimide woven composites. Zhang et al. [11] surface-treated carbon woven fabric with strong HNO_3 to improve friction and wear behavior of the carbon/polymide woven composites, and showed that surface treatment enhanced the carbon/polymide tribological properties due to improved adhesion between the carbon fabric and the polymide matrix. Zheng et al. [12] studied the effect of fiber oxidation on tribological behavior of 3D-braided carbon fiber/nylon composites and reported that the friction coefficient and wear rate of oxidized carbon/nylon composites were lower than those of untreated composites. To date, few studies have investigated the wear behavior of oil-absorbed carbon/polymer woven composites. Particularly, research on the effect of plasma-treated oil-absorbed carbon/epoxy woven composites on wear behavior has never been reported.

In the present study, woven type carbon fabrics were plasma-treated with oxygen gas and the effect of this plasma treatment on the wear behavior of oil-absorbed carbon/epoxy woven composites was investigated to apply the composites as the brake pad material of automobile. Ball-on-disk wear tests were performed on fully oil-absorbed carbon/epoxy woven composites that were made of untreated or plasma-treated carbon fabric, and SEM examination was conducted.

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Table 1
Specifications of woven type carbon fibers.

Item	CF332NON (Plain)
Width (mm)	1020
Yarn	WTR-3K
Thread count (/inct)	(13 × 13)
Weight (g/m^2)	209 ± 13
Thickness (mm)	0.27

2. Experimental

A commercial carbon plain-woven fabric (CF332NON, Korea Carbon, Korea) with the specifications shown in Table 1 was used as a reinforcing material. Bisphenol-A type epoxy (YD-115, Kukdo Chemical, Korea) was used with a D-230 hardener (Dianiline, Kukdo Chemical, Korea) as the matrix resin. The epoxy resin and hardener were mixed in a 6:4 ratio by weight percent. The carbon fabric was placed in an acetone bath for 48 h and washed in distilled water with ultrasonication for 2 min to remove surface sizing agents on the surface. The desized carbon fabric was dried in an oven at 60 °C for 6 h, and subsequently surface treated with low-temperature atmospheric oxygen plasma using a Plasma-Preen II (Plasmatic Systems Ltd., USA). Oxygen gas was used to induce the plasma, and treatment times of up to 60 s were used to determine the optimal treatment. The carbon fiber contact angle was measured to determine change in surface tension and wettability after plasma treatment. The advancing angle of a single carbon fiber was measured by drawing the fiber in a distilled water solution. Chemical changes on the carbon fiber surface due to treatment were determined using X-ray photoelectron spectroscopy (XPS) analysis. The contact angle of basalt fibers was measured by K100SF (*Krüss Ltd., Germany*) to determine the change in surface tension and wettability after plasma treatment. Distilled water was used as the solution, and the advancing angle of a single basalt fiber was measured by drawing the fiber in the solution.

Wear specimens were made using four-plied carbon/epoxy woven composites with a fiber content less than 67% by weight. The carbon/epoxy woven composites were cured in an autoclave with a pressure of 2 kgf/cm^2 at 130 °C for 6 h. The cured composites were cut into 30 mm × 30 mm pieces using a diamond wheel cutter and immersed in commercial engine oil (ZIC A, SK lubricants, Korea) for 62 days. Then, they were removed from the oil solution, wiped to remove residual surface oil, and weighed to measure oil absorption. The oil-absorbed carbon/epoxy composites were adhered to a steel plate (Φ30 mm) and used for wear testing. Fig. 1 shows the schematic diagram of the wear specimens. Ball-on-disk wear tests, which used one zirconia (ZrO_2) ball, were conducted at room temperature using a Neotribo Friction & Wear test machine (Neo-Plus, Korea). The applied vertical load and rotational speed were 19.6 N and 10.6 m/min, respectively. Sectional shape of the wear track was measured using a surface profiler (Dektak 150, Veeco Ltd., USA) to determine wear volume loss. At least, five wear tests were performed for untreated and plasma-treated composites, respectively to ensure reproducibility of wear data.

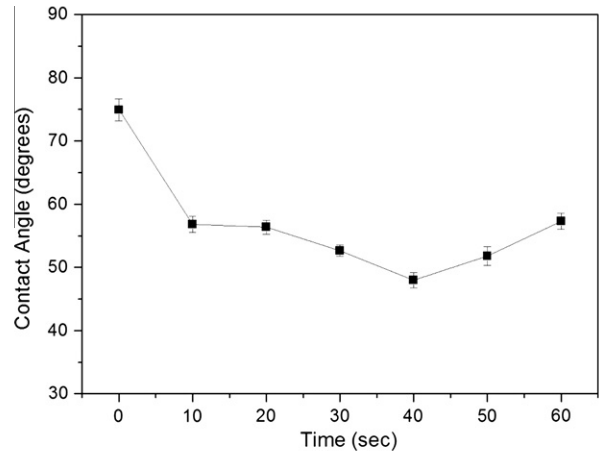

Fig. 2. Variation of contact angle as a function of treatment time.

3. Results and discussion

Contact angle was measured on the surface of a single carbon fiber as a function of time to determine the optimal plasma treatment. Fig. 2 shows the variation of contact angle measured on a single carbon fiber, on its advancing. As shown in the figure, the contact angle decreased sharply after oxygen plasma treatment, but rose, with small variations, as treatment time increased further. For example, the contact angle fell from ~76° to ~56° at 10 s, reached a minimum value of ~46° at 40 s, but rose to ~52° at 50 s. This could be due to the balance of plasma etching effect and surface oxidation; the former would increase the surface wettability while the later could lower the surface wettability. Since a

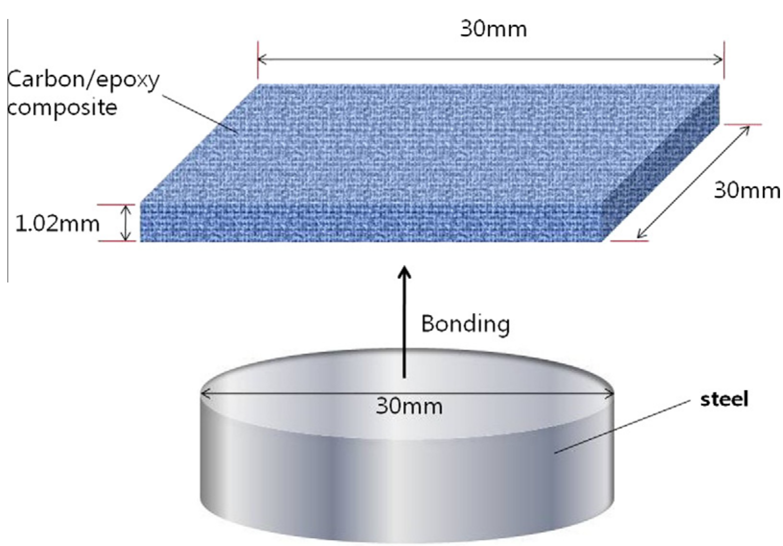

Fig. 1. Schematic diagram of wear specimen.

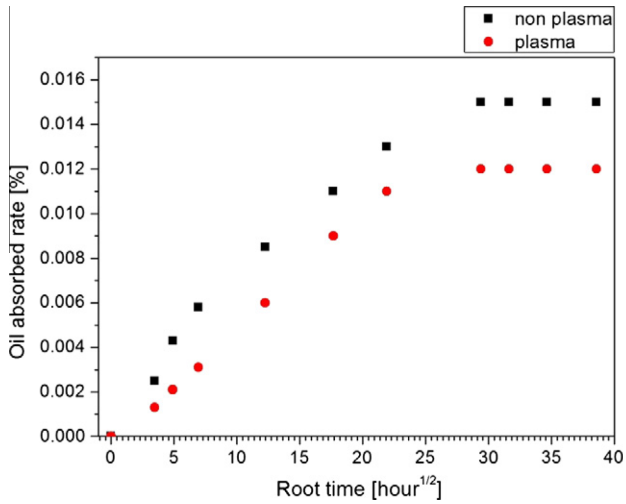

Fig. 3. Oil absorption rate for untreated and plasma-treated carbon/epoxy woven composites as a function of immersion time.

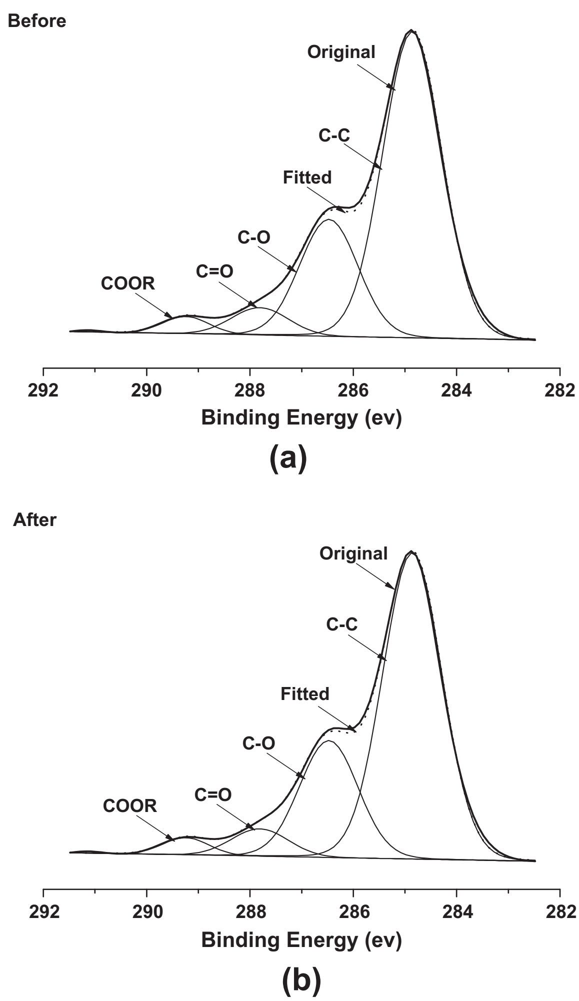

Fig. 4. XPS results of C1s peak with and without plasma treatment (a) before plasma treatment; (b) after plasma treatment.

low contact angle indicates a more hydrophilic surface state, the optimized treatment time was 40 s. Therefore, this time (40 s) was applied in investigating the use of carbon fabrics for carbon/epoxy woven composites.

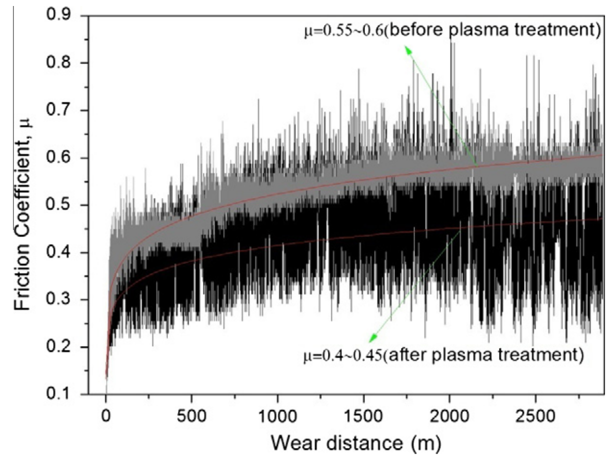

Fig. 5. Variation of friction coefficient of oil-absorbed carbon/epoxy composites with and without plasma treatment.

The carbon/epoxy woven composite oil content (C) was calculated from the specimen weight before and after oil absorption:

$$C = \frac{W_w - W_d}{W_d} \times 100(\%) \tag{1}$$

where W_w and W_d represent the weight of oil-absorbed and dry specimens, respectively. Fig. 3 shows measured oil content for untreated and plasma-treated carbon/epoxy woven composites as a function of immersion time. The oil absorption values agreed with the Fickian model dual-stage, which states that oil absorption follows a linear curve before the saturation point and then gradually reaches a fully saturated stage. Both samples were fully saturated after 36 days, but the oil content of carbon/epoxy woven composites without plasma treatment is higher than with the plasma treatment. Specifically, the oil absorption rate of untreated and plasma-treated cases are 0.14% and 0.12%, respectively when carbon/epoxy woven composites are fully saturated.

XPS analysis was performed to identify chemical reactions on the carbon fiber surface resulting from oxygen plasma treatment. Deconvolution analysis was conducted for the C1s peak. Fig. 4 shows original and deconvoluted C1s core level spectra of the untreated and plasma-treated carbon fibers. The C—C peak was located at 284.8 eV, C—O at 286.5 eV, C═O at 287.9 eV, and COOR group at 289.1 eV. The C═O and COOR peak area ratios increased, accompanied by a decrease of C—O peak area after the plasma treatment. This confirmed that the plasma treatment increased oxidation of the fiber surfaces, transferring C—O groups into C═O and COOR groups.

The effect of plasma treatment on the wear behavior of oil-absorbed carbon/epoxy composites was investigated by determining the change in friction coefficient as a function of wear distance. Fig. 5 shows the change in friction coefficient as a function of wear distance. As shown in the figure, plasma-treated carbon/epoxy woven composites had a lower friction coefficient compared to untreated carbon/epoxy woven composites. Specifically, the fraction coefficients of untreated and plasma-treated samples were 0.55–0.6 and 0.4–0.45, respectively. It is believed that debonding between fibers and epoxy matrix which occurs due to the weakness of the interfacial bonding works as a microcrack and develop as cracks or defects in the epoxy matrix. These defects increase surface roughness of epoxy matrix and the friction coefficient increases, which indicates that plasma-treated carbon/epoxy woven composites attain better interfacial bonding between the carbon fabric and the epoxy matrix.

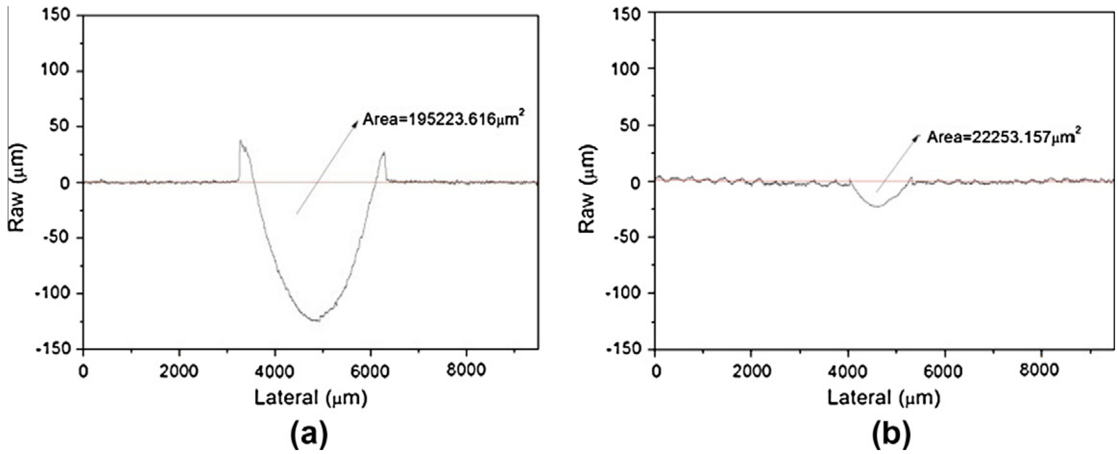

Fig. 6. Variation of depth profile (a) before plasma treatment; (b) after plasma treatment.

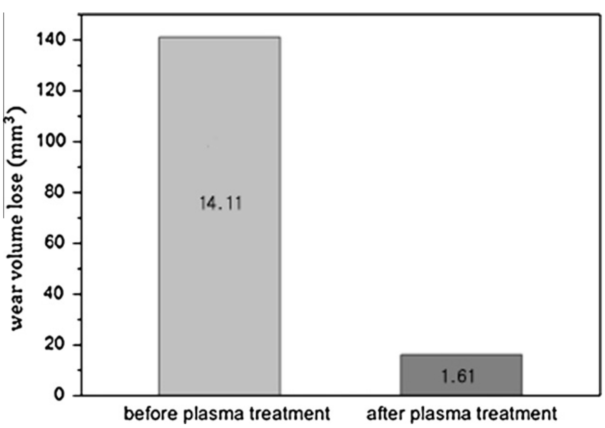

Fig. 7. Wear volume loss of carbon/epoxy woven composites with and without plasma treatment.

Sectional shape of the wear track was measured using a surface profiler and its worn area was calculated. Fig. 6 shows a comparison of the wear-depth profile for untreated and plasma-treated samples. As expected from the change of friction coefficient, the plasma-treated sample exhibited better wear-resistant behavior than the untreated sample. The maximum depth profiles of untreated and plasma-treated carbon/epoxy composites were 124 μm and 23 μm, respectively. Wear volume loss of the carbon/epoxy woven composites was calculated using the wear depth profile (Fig. 6). Fig. 7 shows a comparison of wear volume loss for untreated and plasma-treated samples. The plasma-treated sample exhibited better wear-resistant behavior than the untreated sample. The wear volume losses of the untreated and plasma-treated specimens were 14.11 mm^3 and 1.61 mm^3, respectively. This result occurred due to improvement of the interfacial adhesion between the carbon fabric and the epoxy matrix created by oxygen-plasma treatment of the carbon fabric surface.

Worn surfaces of the untreated and plasma-treated carbon/epoxy woven composites samples were examined using SEM to investigate the wear mechanism. Silver paste was applied to clearly visualize morphology of the wear track for each specimen. Figs. 8 and 9 show the worn surfaces of untreated and plasma-treated carbon/epoxy woven composites, respectively. Typical wear mechanisms of fiber-reinforced woven composites, including matrix microcracks, fiber breakage and debonding at the interface, occurred at many spots for both samples. For the untreated sample, fibers were broken and dispersed randomly in the epoxy matrix. In addition, fibers peeled off from the epoxy, and the surface of the peeled fibers, were relatively clean due to weak adhesion forces between the carbon fibers and epoxy matrix (Fig. 8). For the plasma-treated sample (Fig. 9), the fibers and epoxy matrix remained well adhered, despite the presence of local cracking, indicating that more energy was required to wear the oxygen plasma-treated specimen than the untreated specimen.

4. Conclusions

In the present study, the effect of oxygen-plasma treatment on the wear behavior of oil-absorbed carbon/epoxy woven composites was investigated. Ball-on-disk wear tests were performed on fully oil-absorbed carbon/epoxy composites that were made of un-

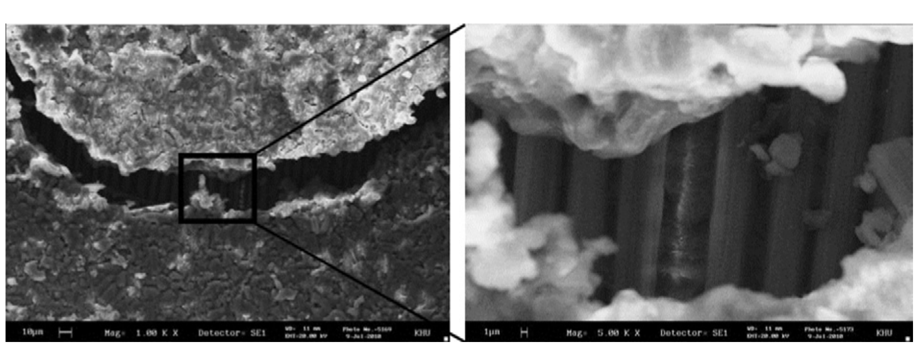

Fig. 8. SEM photographs of worn surfaces of carbon/epoxy woven composites without plasma treatment.

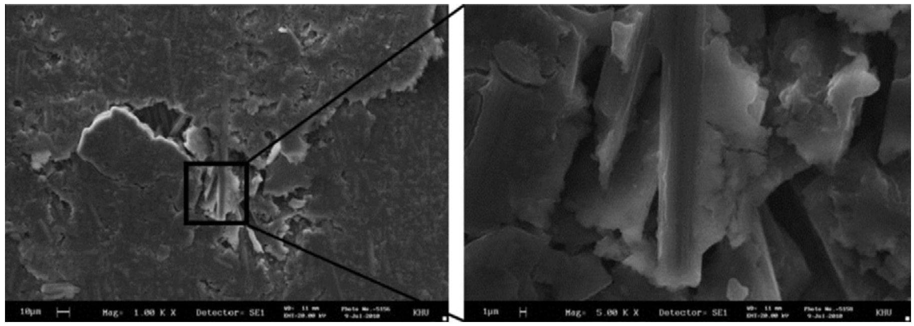

Fig. 9. SEM photographs of worn surfaces of carbon/epoxy woven composites with plasma treatment.

treated and plasma-treated carbon fibers. The following conclusions can be drawn from this study:

(1) Oxygen-plasma treatment of the carbon fabric resulted in improved wear properties of the carbon/epoxy woven composite. The friction coefficient and wear volume loss of oil-absorbed carbon/epoxy composites were reduced by 26% and 88%, respectively, by plasma treatment.
(2) Significant difference on the worn surface between untreated and plasma-treated samples occurred at the interface of the carbon fiber and the epoxy matrix. In untreated samples, fibers peeled off from the epoxy, and the surface of the peeled fibers was relatively clean. Fibers and epoxy remained adhered at the interface for the plasma-treated sample.
(3) The increase in interfacial adhesion strength of the plasma-treated sample was caused by the formation of new polar functional groups, especially C=O and COOR groups.
(4) However, a wear test is an indirect and unreliable way to understand mechanical properties, and tensile and mode I fracture tests of oil-absorbed carbon/epoxy woven composites with and without plasma treatment are under way.

Acknowledgments

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