# 산소 플라즈마 처리가 탄소섬유강화 복합재료의 충격특성에 미치는 영향

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# Influence of Oxygen Plasma Treatment on Impact Behaviors of Carbon Fibers-reinforced Composites

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## ABSTRACT

In this work, effects of oxygen plasma on surface characteristics of carbon fibers were investigated in impact strength of carbon fibers-reinforced composites. The surface properties of the carbon fibers were determined by acid/base values, FT-IR, and X-ray photoelectron spectroscopy (XPS). Also, the mechanical properties of the composites were studied by impact strength measurements. As experimental results, the $O_{1S}/C_{1S}$ ratio of the carbon fiber surfaces treated by oxygen plasma was increased compared to that of untreated ones, possibly due to development of oxygen-containing functional groups. The mechanical properties of the composites, including impact strength had been improved by the oxygen plasma on fibers. These results could be explained that the oxygen plasma resulted in the increase of the adhesion of between fibers and matrix in a composite system.

## 1. INTRODUCTION

From a technological point of view, the surface modification of carbon materials is great importance in a wide variety of fields, such as biomedical, electro chemistry microelectronics, and thin-film technology. The surface modification is accomplished through different types of treatments: thermal, wet chemical or electrochemical oxidation, plasma treatment, ion or cluster bombardment, ect. The ultimate goal of these treatments is to change the surface chemistry and microsructure of the material and thus modulate a number of properties: biocompatibility, roughness, reactivity, conductivity, etc[1-3].

In this context, surface modification of carbon fibers by oxidation is a topic of great interest. Particulary, low-temperature oxygen plasma provides a means of conveniently introducing surface oxygen function groups rapidlly and structural damage of both the bulk and the near surface. Oxygen functional group, many of which acidic and hydrophilic character, improve the surface properties by increasing the wettability, the chemisorption activity, the adhesion potential, ect., and are deemed to be highly relevant for the application of,

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e.g., carbon fibers as reinforcement of composite materials they can, for instance, control the chemical bonding with a phenoilc resin where the hydroxyl group can react with carboxylic group present on fiber surface and from a strong covalent, ester type bonding. Steady-state concentration of the oxygen groups is approached, presumably due to two competing effects; that is, the removal of surface atoms or clusters of atoms by etching reaction, and addition reaction between reactive sites and the reactant oxygen species in the plasma. In all cases, the plasma would only modify the outermost layers of the fiber: the low activation energy needed by atomic oxygen species to react with carbon atoms would not allow them to diffuse towards the internal surface[4-6].

Carbon surface oxidation by oxygen plasma would be somewhat easier on disordered carbon structures than on highly ordered ones such as graphite. The treatment time needed to achieve the desired changes in fiber surface chemistry is of the order of several seconds to a few minutes. Subsequently, upon exposure of the plasma treated material to the ambient, post reaction aging effects lead to a restructuring of the surface towards a new stable thermodynamic equilibrium in with the chemistry may differ somewhat from that originally created by the plasma. Carbon dangling bonds left behind by the plasma which and not chemisorbed oxygen when the treatment was over would be a source of further oxygen incorporation during storage.

In this work, effects of oxygen plasma on surface characteristics of carbon fibers were investigated in impact strength of carbon fibers-reinforced composites. And the replacement between the oxygen content and the fiber/matrix adhesion of the composites is investigated using a combination of surface analysis and impact strength.

## 2. EXPERIMENTAL

### 2.1 Materials and Sample Preparation

The fibers used in this work were polyacrylonitrile (PAN)-based carbon fibers (12K, TZ-607) manufactured by Taekwang of Korea. The epoxy resin used as a matrix was diglycidylether of bisphenol-A (DGEBA, YD-128 supplied from Kukdo Chem. Co. of Korea). Epoxide equivalent weight was 185-190 g.eq$^{-1}$ and the viscosity was 11500-13500 cps at 25℃. Diaminodiphenylmethane (DDM, purchased from Aldrich Co.) was selected as a hardener and methylethylketone (MEK) was used to reduce the high viscosity of DGEBA. The chemical structures of DEGBA and DDM were shown in Figure 1.

Plasma processing (ATMOSTM-Mulit, Plasmart in Korea) for the carbon fibers were carried out using atmospheric pressure and radiofrequency for Ar/O$_2$ (O$_2$ 1%) mixed gas. The radiofrequency generating Ar/O$_2$ mixture plasma was at 300 W and 13.56 MHz.

Unidirectional carbon fibers-epoxy matrix composites were prepared by continuous impregnation of the fibers using a drum winding technique for manufacturing prepreg with subsequent hot-pressing. Specimens were prepared from laminates composed of 22 plies and fabricated in a hot-press at 150℃ and 7.4 MPa for 150 min with a vacuum bagging method. The fiber volume fraction of bulk specimens was about 50 % (±2%), and the specimens were cut into test specimens to carry out mechanical testing.

### 2.2. Surface properties

The surface property changes of the carbon fibers before and after plasma treatment were characterized by the following techniques;

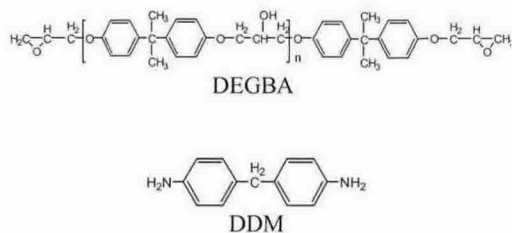The potential chemical activity of surface functional groups on plasma treated carbon fibers can be determined by measuring the pH according to the ASTM E-70 and by measuring acid-base values using the Boehm's method on the basis of adsorption of 0.1 N NaOH and HCl standard solutions.

The FT-IR instrument used was a Hartman & Brawn Model Bomen MB 102 Spectrophotometer. The scan range was 400 to 4000 cm$^{-1}$.

The X-ray photoelectron spectroscopy (XPS) experiment was performed using a VG Scientific ESCA LAB MK-II spectrometer equipped with a Mg-K α X-ray source. The base pressure in the sample chamber was controlled in the range of 10$^{-8}$ to 10$^{-9}$ torr.

### 2.3. Impact behaviors

Low-velocity impact test were performed with a drop-weight impact tester (ROSAND Insrtumented Falling Ewight Impact Tester, Type 4). Impact test specimens of dimensions 70 mm X 12.4 mm X 4 mm were used. The maximum drop height was 1m and maximum velocity of 108 m/s was attained.

**Table 1. pH and Acid-Base Values of the Carbon Fibers Studied**

| Specimens | pH | Acid value [meq·g$^{-1}$] | Base value [meq/g] |
|---|---|---|---|
| No treatment | 7.02 | 15.0 | 20.2 |
| CFP - 2 | 6.95 | 35.0 | 20.1 |
| CFP - 4 | 6.94 | 65.1 | 20.1 |
| CFP - 8 | 6.94 | 32.5 | 20.1 |
| CFP - 16 | 6.95 | 36.7 | 20.1 |
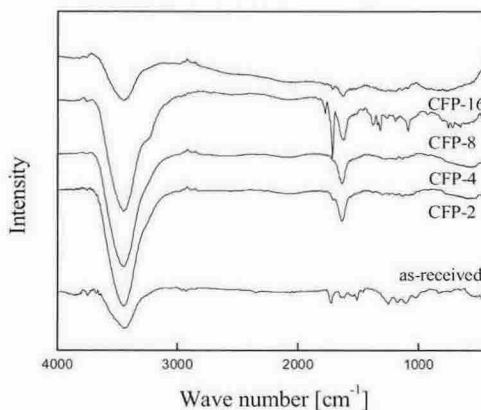


Fig. 2. FT-IR spectra of the plasma treated carbon fibers.



DEGBA



DDM

**Fig. 1. Chemical structures of DEGBA and DDM.**

## 3. RESULTS AND DISCUSSION

### 3.1 Surface properties

Table 1 shows the experimental surface properties of the carbon fibers treated by oxygen plasma. The results

of pH show that the surface properties of untreated carbon fibers are a slight excess of basic properties. This is probably due to the existence of basic groups on the fiber surfaces through high manufacturing treatment time. Both the pH and the acid values of plasma treated carbon fibers acidity to that of the untreated fibers, and indicate that the treatment time at 4 min provides an optimum condition to the surface acidity of the fibers.[5]

Fig. 2 shows the FT-IR results of plasma treated carbon fiber specimens. As a result, the oxygen functional groups (C=O, COOH, and C-O) at 1600-1800 cm$^{-1}$ and hydroxyl group (O-H) at 3450 cm$^{-1}$ are increased in the plasma treated carbon fibers. Moreover, the hydrocarbon group (CH) at 2980 cm$^{-1}$ is decreased with increasing the treatment time. This result affects the surface characteristics of the fibers, resulting in improving the interfacial adhesion between the fibers and the matrix resins, due to the increase of oxygen functional groups on carbon fiber surfaces.

Wide scan spectra in the binding energy range 0~1000 eV are obtained to identify the surface elements present and carry out a quantitative analysis. XPS wide scan spectra of the plasma treated carbon fiber specimens are shown in Fig. 3. The intensity scale factors for the plasma treated carbon fibers are higher than that of the as-received carbon fiber specimen. The XPS spectra show distinct carbon and oxygen peaks, representing the major constituents of the carbon fibers investigated. Relatively weak peaks of other major elements, such as nitrogen are also observed. No other major elements are detected from wide scan spectra on the surface of the carbon fibers. The resulting surface element concentrations of the plasma treated carbon fiber specimens are listed in Table 2. It is found that the surface carbon concentrations of the as-received and CFP-4 carbon fiber specimens are 74.3 at% and 68.8 at%, respectively. A lower surface carbon concentration in the CFP-4 carbon fiber specimen compares to that of the as-received specimen can be attributed to the bonding of oxygen on the carbon surfaces produced by the plasm treatment. The surface concentration of oxygen in the CFP-4 specimen is relatively similar to that of the as-received carbon fiber. The broad carbon peak that is observed in the binding energy, due to the several carbon-based surface functional groups which have different binding energies[6].
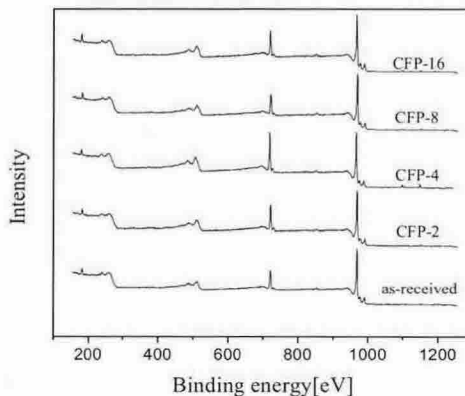


Fig. 3. XPS spectra of plasma treated carbon fibers.

## 3.2 Impact behaviors

Fig. 4 shows the impact strength of the composites. As a result, a good relationship between the characters of plasma treated carbon fiber surfaces and the resulting fibers-matrix adhesions on impact strength of the composite is existed in this experimental condition. That is, impact value is increased with increasing the wettability of the fibers for the degree of adhesion at interfaces due to the plasma treatment, resulting from increasing the polarity and oxygen functional groups of the fiber surfaces. And the maximum strength value of impact is obtained at the oxygen plasma treated carbon fiber specimen, CFP-4. This result is in good agreement with surface analyses of the carbon fibers studied.
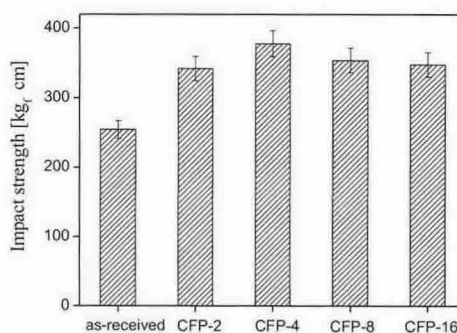


Fig. 4. Impact strength of plasma treated carbon fibers reinforced composites.

The impact energy of composites is a major mechanical property for evaluating the degree of toughness of composite materials. When materials are impacted, the transferring load is absorbed into the material and it affects the residual mechanical properties.

**Table 2. Compositions of the Carbon Fibers Studied by XPS Measurements**

[unit: at %]

| Specimens | XPS | | | |
|---|---|---|---|---|
| | C$_{1S}$ | N$_{1S}$ | O$_{1S}$ | O$_{1S}$/C$_{1S}$ |
| As-received | 74.3 | 1.4 | 24.3 | 0.327 |
| CFP-2 | 73.5 | 1.4 | 25.1 | 0.342 |
| CFP-4 | 68.8 | 0.7 | 30.6 | 0.445 |
| CFP-8 | 72.1 | 1.4 | 26.5 | 0.368 |
| CFP-16 | 69.7 | 1.5 | 28.9 | 0.414 |

The total impact energy measured during the test, $E_t$, is the sum of the initiation energy, $E_i$, and the propagation energy, $E_p$. If the specimen is adequately described by simple beam theory, than the initiation energy in a unidirectional composite reinforced with one type of fiber is given by[7]

$$E_i = \frac{Lwt}{18} \cdot V_f \cdot \frac{\sigma_f^2}{E_f} \qquad (1)$$

Where $L$ is the span length, $w$ the specimen width, $t$ the specimen thickness, $V_f$ the fiber volume fraction, and $\sigma_f$ and $E_f$ the fiber stress and the fiber modulus at failure by tension or compression, respectively.

The second portion of the impact energy, $E_p$, is more complex since $E_p$ is dependent on material fracture mechanisms that in turn, are influenced by specimen geometry as well as by material properties. For specimens having a similar geometry, the relative percentage of energy absorbed in fracture initiation and propagation provides an indication of the ductility of the materials. The ductility index ($DI$) can be defined as the ratio of the propagation energy to the initiation energy[8]

$$DI = \frac{E_p}{E_i} \qquad (2)$$

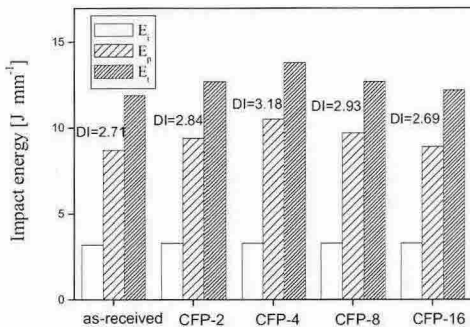Therefore, brittle materials have low $E_p$ and, as a result, low $DI$, as deduced from eq. (1).



**Fig. 5. Impact energy and ductile index (DI) of plasma treated carbon fibers reinforced composites.**

The results for $E_p$, $E_i$, and $DI$ are shown in Fig. 5. The total energy adsorbed during the impact test, i.e. both the impact energy and the $DI$ of plasma treated carbon fibers-reinforced composites. This is probably due to the presence of CFP-4, resulting in increased ductile behavior of the composites[9]. Therefore, the increase in impact properties is equal to that of the mechanical interfacial properties, which can improve the entire mechanical properties of carbon fiber-reinforced composites.

## 4. CONCLUSION

In this work, the $O_{1s}/C_{1s}$ ratio of the carbon fiber surfaces treated by oxygen plasma was increased compared to that of untreated ones, possibly due to the development of oxygen-containing functional groups. The mechanical properties of the composites, including impact strength had been improved in the oxygen plasma on fibers. These results could be explained that the oxygen plasma resulted in the increase of the adhesion between fibers and matrix in the composite systems.

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