Effects of Ultraviolet Surface Treatment on Adhesion Strength of Carbon/Epoxy Composite

Jong Min Kim, Dai Gil Lee*

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ABSTRACT

In this work, the surface modification of carbon/epoxy composites was investigated using UV (ultraviolet ray) surface treatment to increase adhesion strength between the carbon/epoxy composites and adhesives. After UV surface treatment, XPS (X-ray photoelectron spectroscopy) tests were performed to analyze the surface characteristics of the carbon/epoxy composites. Comparing adhesion strengths with the surface characteristics, the effects of the surface modification of carbon/epoxy composites by UV surface treatments on the adhesion strengths were investigated.

1. INTRODUCTION

As composite structures were applied to many fields, various chemical surface treatment methods have been introduced to enhance adhesion performance and alter chemical and physical properties of polymer surfaces without affecting bulk properties. Common chemical surface modification techniques include treatments by flame, photons, plasma, electron beams, ion beams, X-ray, and γ-ray. These treatments have been applied to achieve the following purposes [1].

- to produce special functional groups at the surface for specific interactions with other functional groups.
- to increase surface energy.
- to increase hydrophobicity or hydrophlicity.
- to remove weak boundary layers or contaminants.

Among surface treatment methods above mentioned, UV surface treatment method is clean and inexpensive to set up experimental equipment and dose not require other peripheral devices like a vacuum chamber.

In this work, the effects of UV surface treatment on the adhesion strength of carbon/epoxy composites were investigated by performing peel tests, double lap shear tests and XPS analyses to verify surface modification of carbon/epoxy composites.

2. EXPERIMENTAL

2.1 Materials

Specimens for measurement of adhesion strengths were made from USN 150BX which was unidirectional carbon/epoxy prepreg (SK chemical, Korea). The mechanical properties of cured USN 150BX are listed in Table 1. Wrapped with nylon vacuum bag under temperature of 125 ℃ and pressure of 0.6 MPa, $[0]_{10T}$ stacked sheets of prepreg were cured in an autoclave. The cured carbon/epoxy composite plates were cut into pieces whose geometric sizes were 100 mm long, 20 mm wide and 1.4 mm thick, using a water-cooled diamond wheel cutter, and then the remnant impurities on the surface were wiped off using acetone.

DP460 structural epoxy adhesive (3M, USA) was used to make adhesion specimens. The specifications of this epoxy adhesive were listed in Table 2. After the epoxy adhesive was applied to the specimens, the adhesive was cured under 80 ℃ and 6 MPa for 150 min.

Department of Mechanical Engineering, Korea Advanced Institute of Science of Technology, 373-1, Gusong-dong, Yusong-gu, Daejon 305-701, Korea

*To whom correspondence should be addressed.

Table 1 Properties of carbon/epoxy composites

Elastic modulus (GPa)	Longitudinal	130
	Shear	5.06
Strength (MPa)	Longitudinal	2300
	Shear	60
Ply thickness (mm)		0.144
Fiber volume fraction		0.67

Table 2 Specifications of epoxy adhesive

Resin	Base	Epoxy
	Hardener	Amine
Elastic modulus (GPa)		2.7
Tensile strength (MPa)		37

2.2 Methodologies

Ultraviolet is classified into three parts, UV-A, UV-B and UV-C. The difference among them is which band of wavelength they have. The bands of wavelength of UV-A, UV-B and UV-C are 315-400, 280-315 and 100-280 nm, respectively. In this work, UV-A and UV-B lamps were used because most of the photo-oxidation or photo-degradation of polymeric materials takes place between 290-400 nm. UV-A and UV-B lamps employed for this work were TL40W/05 and TL40W/12RS (Philips, Netherlands), respectively. Using these UV-A and UV-B lamps, UV irradiation chamber was manufactured according to ASTM G53 and D5208.

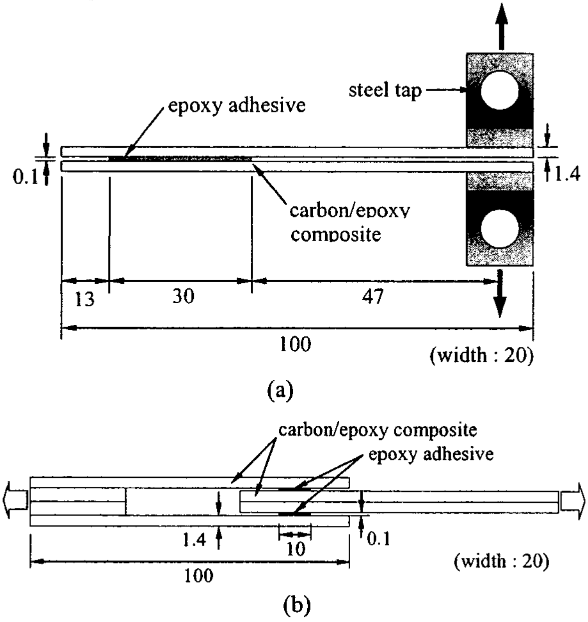


Fig. 1 Dimensions of specimens for (a) peel test and (b) double lap shear test, (units in mm).

To measure adhesion strengths, peel and double lap shear tests were performed using INSTRON 4206 UTM (Instron Corp., USA) at a crosshead speed of 2mm/min. Fig. 1 shows the geometric sizes of specimens for peel and double lap shear tests, respectively. When applying adhesive to carbon/epoxy composites, to maintain adhesion layer thickness of 0.1 mm, thickness gauges with thickness of 0.1 mm and width of 13 mm were attached to the end parts of adhesive layer. After epoxy adhesive was fully cured in the autoclave, the thickness gauge were removed. Fig. 2 (a) shows peel test results. The maximum peel strength of 4,000 N/m was obtained from UV-B 12 hr treated specimens and the peel strength of UV-B 3 hr treated specimens reached 90 % of the maximum peel strength. However, when UV-B irradiation time was longer than 12 hr, the peel strengths were decreased gradually because excessive UV irradiation caused the degradation of carbon/epoxy composites.

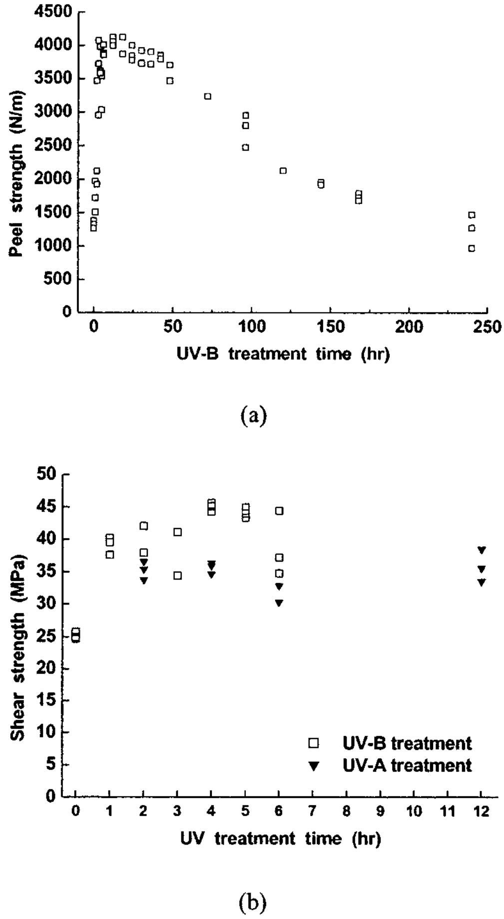


Fig. 2 Adhesion strengths of carbon/epoxy composite adhesive joints with respect to UV treatment conditions, (a) peel strength, (b) shear strength.

Double lap shear test results for carbon/epoxy specimens are shown in Fig. 2(b). Comparing shear strengths of UV-A and UV-B treated specimens, UV-B treated specimens surpassed UV-A treated specimens in shear strengths. Consequently, as the wavelength of UV got shorter and irradiation time got longer, the adhesion strength was increased. However, excessive UV irradiation caused adverse effect on the adhesion strength of carbon/epoxy composites due to the degradation.

3. XPS ANALYSIS

3.1 Chemical Shift and Surface Modification

XPS (X-ray photoelectron spectroscopy) is one of the most versatile techniques used for analyzing surfaces chemically and provides information about the chemical state and concentration of elements comprising the outermost layers of a solid.

XPS analyses were performed using ESCALAB MK II (VG Scientific, UK) which irradiates specimens with Mg Kα X-rays (1253.6 eV). XPS survey spectra of carbon/epoxy composites with respect to UV irradiation conditions were shown in Fig. 3. The spectra were composed of several peaks, major peaks were C 1s and O 1s and minor peaks were nitrogen, chlorine, fluorine and silicon. The atomic contents on the surface of carbon/epoxy composites were listed in Table 3. Carbon and oxygen occupied around 70 % and 20 % of entire contents, respectively, and other minor elements occupied less than 3 %. A little amount of nitrogen contents came from amine which was used for the hardener of epoxy resin. During epoxy resin cure, the amine and epoxy ring of resin construct strong cross-linking chains. Other elements like fluorine and silicon would be impurities, however, chlorine content listed in Table. 3 showed some outstanding tendency. The variation of chlorine contents was closely analyzed apart from chemical shifts.

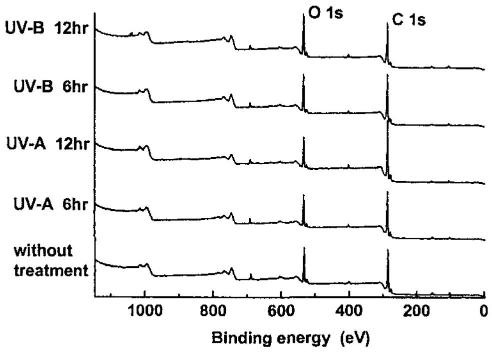
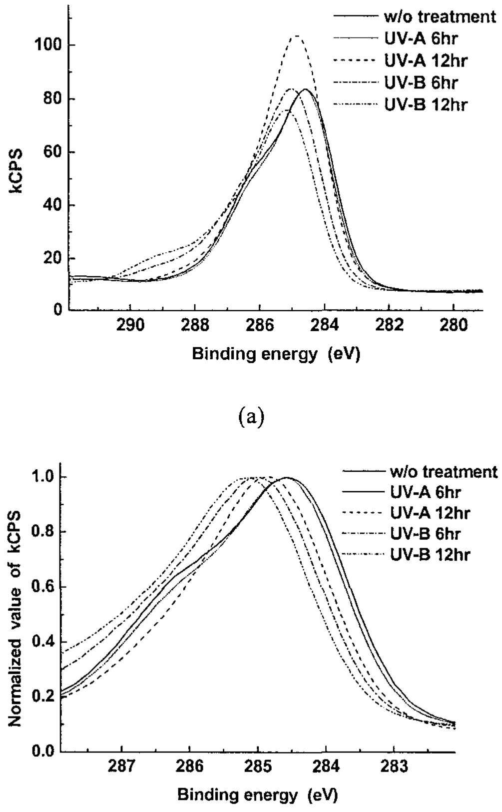


Fig. 3 Survey spectra of the surface of carbon/epoxy composites with respect to UV irradiation conditions.

Table 3 Atomic contents on the surface of carbon/epoxy composites

(%)	C	O	Cl	N	F	Si
Without treatment	70.04	22.09	0.26	2.57	2.06	2.98
UV-A 6hr	72.12	20.38	0.26	2.74	1.86	2.64
UV-A 12hr	75.81	16.24	0.20	3.50	1.83	2.42
UV-B 6hr	70.20	22.29	0.17	2.96	2.13	2.26
UV-B 12hr	66.29	26.02	0.15	3.16	1.92	2.46



(a)

(b)

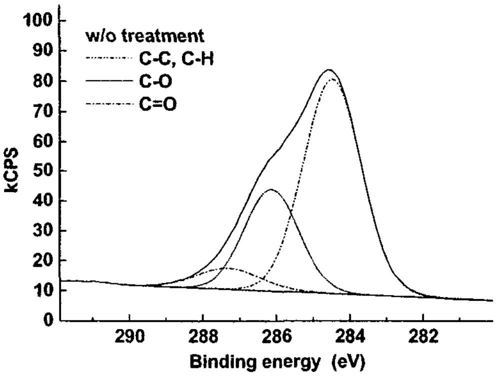
Fig. 4 C 1s spectra of carbon/epoxy composites, (a) original spectra, (b) normalized spectra.

To analyze chemical shifts, C 1s spectra were separated from survey spectra as shown in Fig. 4 (a). Since it is not easy to read chemical shifts from original raw spectrum data, all spectra were normalized by dividing whole data by each maximum electron counting rate (kCPS; kilo-counts per second). Fig. 4 (b) shows the normalized spectra of each C 1s spectrum.

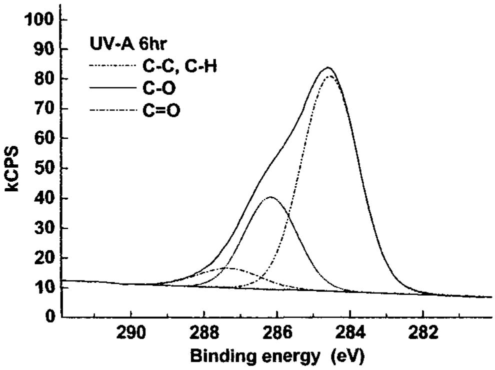
The spectra of the specimens both without treatment and with UV-A 6hr treatment show almost similarly, however, some trends can be found in the graphs. The longer UV treatment time and the short UV wavelength (the wavelength of UV-B is shorter than that of UV-A) gave rise to leftward chemical shifts. In the normalized graphs, it is easy to observe that the binding energies of peak points moved leftward. These chemical shifts mean that the surface characteristics of carbon/epoxy composites were altered by UV irradiation. So, the decompositions of carbon chains were performed in order to analyze surface characteristics of carbon/epoxy composites. By using binding energies of some functional groups listed in Table 4, each C 1s spectrum was decomposed as shown in Fig. 5.

Table 4 Binding energies of functional groups

Functional groups	Binding energy (eV)
C-C, C-H	284.6
C-O	286.2
C=O	287.5



(a)



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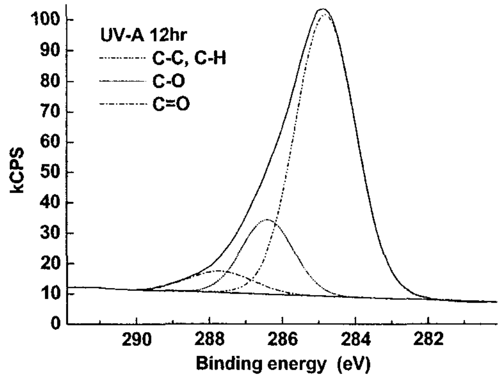

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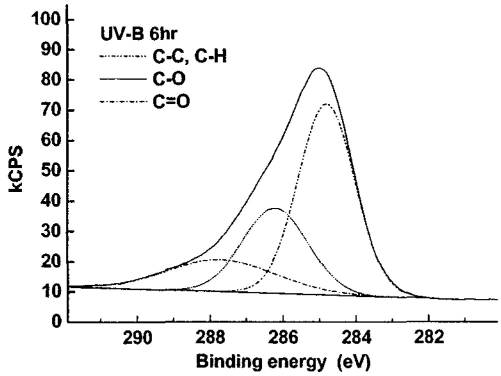

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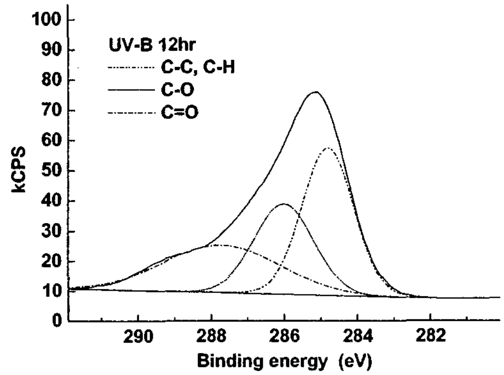

(e)

Fig. 5 Decomposition of C 1s spectrum of carbon/epoxy composite surfaces, (a) without treatment, (b) UV-A 6hr, (c) UV-A 12hr, (d) UV-B 6hr, (e) UV-B 12hr

Each chemical bond composition on the surface of specimens listed in Table 5 was analyzed by calculating the ratio of area below the original curve to area below the individual decomposed curve.

Table 5 Composition of functional groups

(%)	C-C, C-H	C-O	C=O
Without treatment	64.6	28.5	6.9
UV-A 6hr	66.8	26.4	6.7
UV-A 12hr	76.9	17.1	6.1
UV-B 6hr	54.5	27.8	17.63
UV-B 12hr	41.5	28.8	29.8

As UV treatment time got longer and wavelength of UV got shorter, the composition of C-C and C-H bond was decreased but that of C=O increased rapidly and C-O had little difference. However, the composition of UV-A 12hr treated specimen showed somewhat low C=O fraction, the reason was estimated due to exposed carbon fiber on the surface or much denser carbon fiber near the surface. So, compared to the previous adhesion strength tests, increase in the composition of C=O and decrease in that of C-C and C-H bond of the carbon/epoxy surface could result in higher adhesion strength.

The photon energy of shorter wavelength than 350 nm is strong enough to break most chemical bonds such as C-C and C-H on the epoxy [2], and the photochemical process typically consists of C-H scission, C-C scission. Chemical surface modifications of carbon/epoxy composites induced by UV irradiation are the result of a complex set of processes involving the combined effect of UV and oxygen in the air. Zhang et al. [3] suggested that the carbonyl bonds (C=O) were apparently formed in the initial stage of photodegradation and then decomposed upon further aging and their idea that C=O bonds increased by UV irradiation agreed well to this work.

3.2 Chlorine Contents

The most widely used epoxide monomer is the diepoxide prepared by treatment of one mole of bisphenol A (BPA) with two moles of epichlorohydrin. The reaction of BPA with epichlorohydrin leads to the most common epoxy resin, the diglycidyl ether of bisphenol-A (DGEBA).

Although pure DGEBA would have no chlorine contents, commercial resins may have up to about 1 % chlorine. The active chlorine may block reaction of lower base catalysts, such as tertiary amines, and hence its concentration may be critical. When organically-bound chlorine is present the resin will have a reduced functionality and hence the cured resin will have a less tight network. The organically bound chlorine will be in the forms known as (i) hydrolysable and (ii) inactive. The presence of the former is due to incomplete dehydrochlorination and the latter to either reaction of epichlorohydrin with the secondary alcohol or abnormal addition of the phenolic hydroxyl group (C-OH) [4].

The measured chlorine contents on the surface of carbon/epoxy composites with respect to UV treatment conditions were listed in Table 3. The shorter wavelength of UV and the longer UV treatment time resulted in the less chlorine contents. This downward tendency in the chlorine content coincided with the former test results of adhesion strengths. So, it could be estimated that the variation of chlorine contents on the surface of the carbon/epoxy composites was one of the crucial factors that affected the adhesion strengths.

4. CONCLUSIONS

In this work, the interrelations between adhesion strength and surface modification by UV irradiation on the surface of carbon/epoxy composites were investigated.

Through the experimental results of adhesion strength, UV-B surface treatment resulted in superior adhesion strength to UV-A surface treatment. Also, as the wavelength of UV got shorter and irradiation time got longer, the adhesion strength was increased. However, excessive UV irradiation caused adverse effect on adhesion strength of carbon/epoxy composites.

XPS analyses were performed to verify the surface modification of carbon/epoxy composites and chemical shifts due to variation of functional groups on the surface were observed. By decomposition of C 1s spectra, as the wavelength of UV got shorter and irradiation time got longer, it was found that the content of C=O bonds on the surface increased rapidly, but the content of C-C and C-H bonds decreased and C-O bonds showed little difference. The other result derived from XPS analyses was the variation of chlorine content. Though the atomic content of chlorine was slight, its variation provided similar tendency to the chemical shifts.

In conclusion, it was possible to increase C=O bonds and decrease chlorine content on the surface of carbon/epoxy composites by UV irradiation and these phenomena could result in the enhancement of adhesion strength of carbon/epoxy composites.

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