플라즈마 에칭과 중합에 의한 탄소섬유의 표면 개질

강현민 • 김남일 • 윤태호

Plasma Etching and Polymerization of Carbon Fiber

H. M. Kang, N. I. Kim and T. H. Yoon

Key Words : Interfacial shear strength, Plasma etching & polymerization, acetylene, carbon fiber, vinyl ester resin

ABSTRACT

Unsized AS-4 carbon fibers were etched by RF plasma and then coated via plasma polymerization in order to enhance adhesion to vinyl ester resin. The gases utilized for the plasma etching were Ar, N_2 and O_2, while the monomers used for the plasma polymerization coating were acetylene, butadiene and acrylonitrile. The conditions for the plasma etching and the plasma polymerization were optimized by measuring interfacial adhesion with vinyl ester resin via micro-droplet tests. Among the treatment conditions, the combination of Ar plasma etching and acetylene plasma polymerization provided greatly improved interfacial shear strength (IFSS) of 69MPa compared to 43MPa with as-received carbon fiber. Based on the SEM analysis of failure surface and load-displacement curve, it was assume that the failure might be occurred at the carbon fiber and plasma polymer coating. The plasma etched and plasma polymer coated carbon fibers were subjected to analysis with SEM, XPS, FT-IR or Alpha-Step, and dynamic contact angles and tensile strengths were also evaluated. Plasma polymer coatings did not change tensile strength and surface roughness of fibers, but decreased water contact angle except butadiene plasma polymer coating, possibly owing to the functional groups introduced, as evidenced by FT-IR and XPS.

1. Introduction

Advanced polymer composites have been widely utilized in structural applications due to their high specific strength and stiffness, good corrosion resistance and low thermal expansion relative to conventional metallic materials [1]. However, composites materials still have drawbacks such as poor interfacial adhesion between fibers and matrix resins, which is one of critical factors on the properties of composites materials. In order to give better understanding on the interfacial adhesion, Sharpe [2] introduced 'interphase' which is said to be very different from adherend or adhesive layers, while Drzal proposed schematic diagram of interphase [3]. Drzal also concluded in his study that surface modifications of fibers is needed to remove weak boundary layer and to introduce polar groups so as to increase interactions with matrix resin [3].

During the past decades, there has been a great amount of research effort on the surface modification of carbon fibers which have been a major reinforcement for advanced composites [4-6]. A number of researchers have investigated surface modification by surface oxidation [7-9], polymer coating via electrochemical deposition [10] or solution method [11-12], monomeric or oligomeric sizing agents [13-14], plasma etching [15-20] and plasma polymerization coating [21-25]. Due to increasing environmental concerns, plasma polymerization coatings have received more attention than ever before.

Enhanced interfacial adhesion by plasma polymerization coating could be attributed to the functional groups introduced on to the fiber surface, which give rise interactions with functional groups in matrix resin [17-18].

Therefore, it would be nice to have reactive functional groups on fiber surface in order to have covalent bonding at the interface, which could be possible by careful selection of monomer for plasma polymerization depending on the matrix resin. In this study, acetylene, butadiene and acrylronitrile were utilized to form plasma polymer coating with C=C moieties in order to have covalent bonding with vinyl ester resin via free radical

reaction. FT-IR analysis confirmed that plasma polymer coatings of acetylene, butadiene and acrylronitrile contained C=C moiety as reported by Feith and Schwartz [23], and Weisweiler [25], and some other functional groups. Interfacial adhesion of plasma polymer coated carbon fibers were evaluated via micro-droplet tests with vinyl ester resin, and the conditions for plasma polymerization coating were optimized based on the adhesion results. Failure surface of carbon fiber after testing and load-displacement curves for adhesion test were analyzed in order to give better understanding on failure modes.

2. Experimental

2.1 Materials

Unsized AS-4 carbon fibers with an average diameter of 8μm were received from Hercules and stored in a desiccator until needed. DERAKANE® 441-400 vinyl ester resin (33wt% styrene) donated by Dow was used as-received and benzoyl peroxide (Aldrich) was used as an initiator. Acetylene (99.5%), butadiene (99.9%, Kumho Petro Chemical) and acrylonitrile(99+%, Aldrich) were utilized for plasma polymerization, while Ar (99.9%), N_2 (99.9%) and O_2 (99.9%) gases were utilized for plasma etching.

2.2 Plasma Etching & Polymerization

A radio frequency (13.56MHz) plasma generator (HPPS-300, Hanatek, Korea), consisting of a bell-jar type Pyrex® chamber, manual impedance matching and mass flow controller (MFC), was used for plasma etching and plasma polymerization. The Pyrex® bell-jar was cleaned with acetone and then etched with O_2 plasma (90W, 10min, 30mtorr) prior to the experiments. The chamber was vacuumed to 1×10^{-3} mTorr and then flushed with the gas for plasma polymerization or plasma etching, followed by controlling the chamber pressure to desired level with MFC.

Unsized carbon fibers, 10cm long, were placed on the rectangular shape aluminum fixture, and staged horizontally in the center of the chamber and 15cm below of an electrode. Some fibers were only subjected to plasma etching with Ar, N_2 or O_2, while others were plasma etched and then plasma polymerization coated with acetylene, butadiene or acrylonitrile. Plasma etching conditions were optimized by measuring interfacial shear strength (IFSS) via micro-droplet tests as a function of plasma power (30-70 W), treatment time (1-10 min) and gas pressure (20-40mTorr). The plasma polymerization conditions were also optimized, but Ar plasma etched fibers were utilized due to the weak interfacial adhesion of plasma polymer coating to the as-received carbon fibers. The plasma polymerization conditions were optimized by varying treatment time (15-60 sec), plasma power (10-30 W), and gas pressure (20-40 mTorr). After optimizing the plasma polymerization conditions, adhesion of carbon fibers with plasma polymer coating was also evaluated.

2.3 Adhesive Property of Carbon Fibers

Interfacial adhesion of carbon fibers was evaluated with micro-droplet specimens which were prepared by the liquid method with vinyl ester resin as described previously [11].

For the interfacial adhesion measurements, three different types of fiber were evaluated; 1) plasma etched, 2) plasma polymer coated, and 3) plasma etched and plasma polymer coated. The tests were performed with the droplets ranged from 45 to 60μm in length. More than 20 specimens were tested and the results were averaged.

2.4 Characterization of Plasma Polymer Coating

Due to the difficulty in measuring the thickness of plasma polymer coating with the carbon fibers, silicone wafers were utilized. The thickness of the film was measured by Alpha-Step 500 with a scan length of 100 μm at a scan speed of 10 μm/sec and average of 5 samples is reported.

Water contact angles were measured by dynamic contact angle analyzer (Cahn DCA, Model 322) with plasma etched as well as with plasma polymer coated carbon fibers.

JASCO FT-IR-460 Plus was utilized to characterize the plasma polymer coating on the silicone wafers instead of the carbon fibers.

Plasma polymer coated carbon fibers were analyzed by a Perkin Elmer PHI 5400 X-ray photoelectron spectrometer (XPS) with Mg Ka x-ray source (1253.6 eV) at a take-off angle of 15 degree since plasma etched carbon fibers are well documented in the literature. Survey as well as high resolution spectra for elements were recorded at 14kV and 300W with an emission current of 25 *m*A obtained, while maintaining a vacuum level below 5x10-7. The C1s electron binding energy was referenced to 285.0eV and a Gaussian-Lorentian function was utilized for curve fitting of C1s peaks.

Tensile strengths of carbon fiber were measured according to ASTM-3379. Tensile tests were carried out at a crosshead speed of 0.3mm/min and load at break was measured via an electronic balance (BB2400, Mettler) connected to a personal computer. At least 20 samples were tested and the results were averaged.

Department of Materials Science and Engineering
Kwang-ju Institute of Science and Technology
Kwang-ju, 506-712 Korea

3. Results and Discussion

3.1 Adhesive property of carbon fibers

The interfacial adhesion of carbon fibers was marginally increased by Ar plasma etching (50.2±6.7MPa, 17% increase), followed by O_2 etching (47.0MPa) and N_2 etching (46.4MPa), compared to as-received fibers (43.0±4.2MPa). Compare to Ar plasma etching, N_2 and O_2 plasma etchings are known to be generating more nitrogen or oxygen containing moieties, which may not interact well with vinyl ester resin.

Since the optimizations of plasma polymerization conditions were carried out with Ar plasma etched carbon fibers, it may be interesting to evaluate the adhesion of as-received carbon fibers with plasma polymer coating only. Carbon fibers coated with plasma polymers of acetylene, butadiene or acrylonitrile at the optimized conditions provided IFSS values of 50.0, 46.4 or 32.5MPa, respectively. As expected, acetylene plasma polymer coating provided the highest adhesion, owing to possible chemical reaction of C=C with C=C bond in vinyl ester resin. It is interesting to note that acrylonitrile plasma polymer coating exhibited even lower adhesion than the as-received carbon fibers (43.0MPa) although strong polar moieties in acrylonitirle are expected to increase adhesion.

At the optimum conditions, acetylene plasma polymerization coating with Ar etching provided IFSS of 69.4MPa (61% increase), followed by 52.4MPa with butadiene and 47.0MPa with acrylonitrile plasma polymerization coatings. These values can be compared to 50.0, 46.4 or 32.5MPa with plasma polymer coating of acetylene, butadiene or acrylonitrile, respectively, or 50.2MPa with Ar plasma etching. It is interesting to note that the interfacial adhesion of plasma polymer coated carbon fibers was further enhanced by Ar plasma etching prior to the plasma polymerization coating, indicating Ar plasma etching enhanced adhesion between fiber surface and plasma polymer coating.

Since it was not easy to speculate failure mode, the gas for the plasma etching prior to plasma polymerization of acetylene was changed form Ar to N_2 or O_2 gas and compared to Ar plasma etching. As shown in Figure 8, the carbon fibers which were etched with N_2 and O_2 and then coated with acetylene plasma polymers provided IFSS of 59.5 and 57.3 MPa, respectively, which were are much lower than that with Ar plasma etching (69.4MPa).

3.2 Tensile strength of plasma coated carbon fiber

Tensile strengths of carbon fiber slightly decreased by gas plasma etching of Ar, N_2 and O_2 gases. Ar plasma treated carbon fibers exhibited tensile strength of 3.74, 3.55 and 3.23GPa at 1, 5 and 10 min of treatment time, respectively, compared to 4.03GPa with as-received fibers at a gauge length of 10mm. The tensile strength of N_2 and O_2 plasma etched carbon fibers also decreased in a similar manner as the treatment time increased

3.3 Thickness of plasma polymer coating

The acetylene plasma polymer coating provided approximately 6.5nm at 15sec and increased almost linearly to approximately 41.2nm at 90sec, while butadiene and acrylonitrile plasma polymerization showed approximately 5.8 nm and 4.6nm at 15 sec, and 35.4nm and 29.7nm at 90 sec, respectively. Fairly large difference in the thickness at 90 sec may depend on the nature of monomer structure; how easy to polymerized with plasma energy at a given conditions.

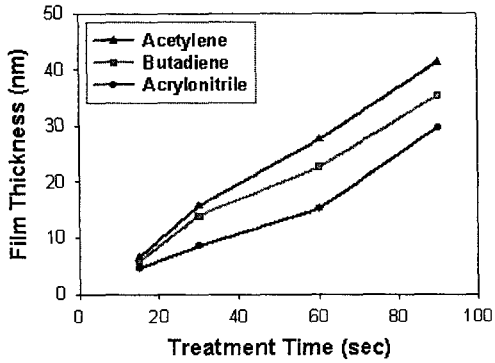

Figure 1. Thickness of plasma polymer coating

3.4 FT-IR analysis

In FT-IR analysis of the acetylene plasma polymer coating, strong peaks at around 2900 and 1400 cm^{-1} can be assigned to CH_3 asymmetric stretching (2960 cm^{-1}), CH_2 stretching (2928 cm^{-1}) and CH_3 symmetric stretching (2870 cm^{-1}), C=O stretching (1715 cm^{-1}, 1680 cm^{-1}), C=C stretching (1585 cm^{-1}), CH_2 bending (1450 cm^{-1}) and CH_3 bending (1375 cm^{-1}). Those C=C moieties could involve in free radical reaction in vinyl ester resin, resulting in improved interfacial adhesion of carbon fibers.

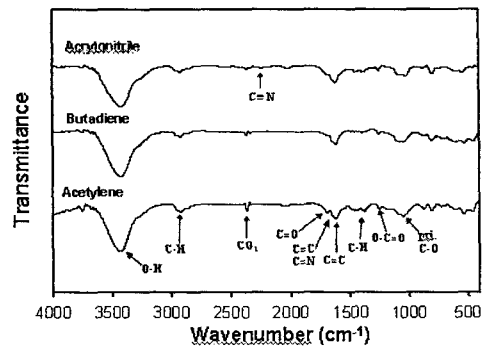

Figure 2. FT-IR analysis of Plamsa Polymer Coating

3.5 XPS analysis

In XPS anlysis, all plasma polymer coatings of acetylene, butadiene and acrylonitrile exhibited similar spectrum in wide scan. However, in a deconvoluted C 1s peak, a number of peaks were observed, which can be assigned to C-C, C=C, C-O, C=O and C-OOH type functional moieties in acetylene and butadiene plasma polymer coating, while C-C, C-N, C=C, C-O, C=O and C-OOH functional moiety in acrylonitrile plasma polymer coating. As expected from FT-IR analysis and the results reported in the literature, C=C moieties were observed in all polymer coating, while C-N functional groups were also found in acrylonitile plasma polymer coating. Plasma etching of carbon fiber prior to plasma polymerization of acetylene, butadiene and acrylonitrile did not changed chemical nature of plasma polymer coating.

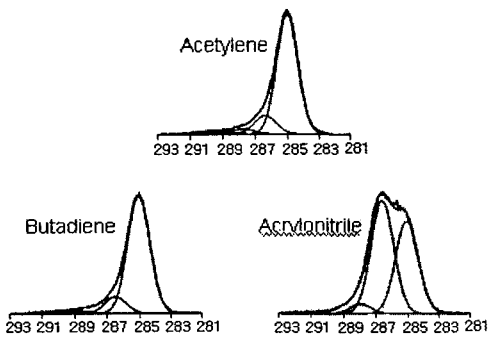

Figure 3. XPS analysis of Plasma Polymer Coating

4. Conclusions

The adhesion of carbon fibers to vinyl ester resin was greatly enhanced by the plasma etching and plasma polymerization coating. The combination of plasma polymerization coating with Ar plasma etching provided even higher interfacial adhesion of carbon fibers compared with plasma polymer coating only.

The enhanced adhesion of carbon fiber with plasma etching and plasma polymerization coating can be attributed to cleaning effect, mechanical interlocking, and/or covalent bonds by free radical reaction of C=C moieties in plasma polymer coatings and vinyl ester resin, which may from chemical bond to vinyl ester resin. Combination of plasma etching and plasma polymerization does not seem to change the chemistry of plasma polymer coating, based on water contact angle, FT-IR and XPS results.

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