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Special Issue

A Study on the Surface Degradation Mechanism of Polymer Insulator

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Abstract

This study analyzes the plasmasurface treatment of a composite material that was aimed at improving its interfacial property, after processing a simulated degradation under ultraviolet rays. The Fiberglass Reinforced Plastic (FRP) was produced under the optimal conditions after the surface treatment. In order to examine the changes in the fiberglass characteristics before and after the plasma surface improvement, an ultraviolet irradiator was used to accelerate a simulated degradation. The contact angle, surface potential and XPS assay were then used to measure the changes in the surficial and interfacial characteristics after the irradiation. The initial contact angles of the plasma treated samples produced under the optimal conditions and the non-treated ones were 78° and 72° respectively; but after the irradiation, those angles decreased remarkably to 23° and 17° respectively, as well as having surface hydrophilicity. The chemical change on the surface of the irradiated samples was found to be hydrophilicity caused by the decomposition of the hydrocarbon linkage and the creation of carboxyl on the surface relative to an increasing irradiating time. The surface potential decay of the samples which were electrically charged by a corona discharge showed that the accumulated charge decreased and the injected charge rapidly decreased relative to the increasing irradiating time.

In addition, upon the injection of positive (+) and negative (-) charges, the negative (-) charge rapidly decreased. It is supposed that this was due to the creation of the carboxyl that acts positive; thus, the creation of carboxyl was also examined. The fiberglass surface treatment through the use of plasma might be a very useful method in terms of the uniformity of the process and the protection of the environment.

Key Words: Plasma surface treatment, degradation, FRP, surface potential, XPS .

1. Introduction

FRP is a hybrid material in which fiberglass is impregnated with epoxy resin. Due to its excellent electrical and chemical characteristics, and its mechanical strength, this material is widely used in the electrical insulation of printed circuit boards, electric and electronic components, and in electrical and communication cables.

Also, thanks to its light weight and high strength, it is used in the aerospace, aviation and automobile fields [1,2].

However, a severe surrounding environment that places the components under very poor conditions may cause an interfacial change of the complex insulation material and lead to damage of the interfacial characteristics, which might damage the insulation property and result in an insulation breakdown.

The treatment of the reinforced material surface through plasma triggers the active species in the plasma (radical, ultraviolet, colliding electron, etc.) to form a polar group and a micro-broken surface. By the electrostatic charging effect, the hydrophilicity increases[3].

To improve FRP's interfacial property, this study used plasma to treat the surface of the fiberglass that is used in the reinforced material, and set the optimal conditions for the best wettability. Additionally, for the samples that were produced under the optimal conditions,it derived a surface degradation mechanism relative to a long-treatment under ultraviolet rays.

2. Experimental

The experiment used a plasma-treatment device system that consisted of a power supply part, discharging part and an air exhaust/vacuum detecting part. The device's schematic diagram and actual shape are shown in Figure 1. Regarding the conditions for the plasma-surface treatment of the fiberglass, a glass which has similar components to the fiberglass was used to determine the optimal conditions.

As a result, it was found that the sample produced under 0.1 Torr of pressure, 100 W of discharging power and 3 minutes of discharging time had the best wettability[4].

The fiberglass that was treated under the optimal conditions was then impregnated with epoxy resin to produce FRP. An ultraviolet irradiator (Q-Panel Lab Products) accelerated the simulated degradation for a maximum of 250 hours, with 50-hour intervals to examine the effects of the plasma-surface treatment relative to the discharge time. The contact angle, surface tension, XPS assay, surface potential decay and dielectric property were then used to measure the changes in the surficial and interfacial characteristics.

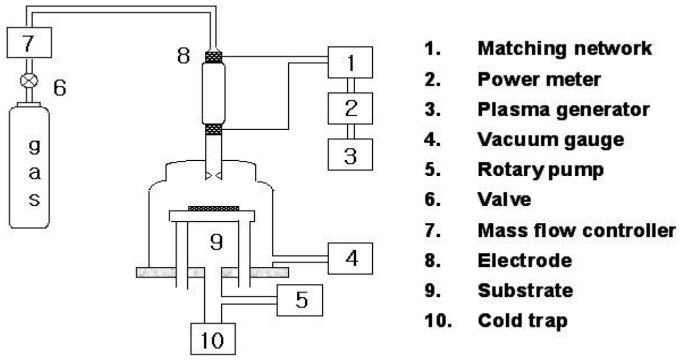


Figure 1: Schematic Diagram of Plasma Treatment System

3. UV Degradation Properties

Contact Angle and Surface Energy

The initial contact angles were found to be 70° for the non-treated samples and approximately 80° for the treated ones, indicating a hydrophobic surface on the materials. In addition, the surface energies which were measured by the contact angles were found to be approximately 40 mJ/m^2 for the non-treated samples and approximately 36 mJ/m^2 for the treated ones.

The changes in the contact angles following the ultraviolet irradiation are shown in Figure 2. As the irradiating time increases, the contact angle decreases, implying that the surface activation progresses alongside the ultraviolet irradiation. Usually, the photo-energy in a 340 nm area is 89.5 kcal/mol. This energy is larger than the C-H/C-C binding energies, and is able to decompose the chemical bond of a high hydrocarbon-bonded molecular surface. Thus, it can be supposed that the ultraviolet irradiation decomposes the C-C/C-H binding chains on the surface of the epoxy that has a 3D network structure and generates numerous radicals, which converts a non-active, stable surface to a highly-active, polar one while in an electronically excited state, and this in turn results in a low contact angle [5].

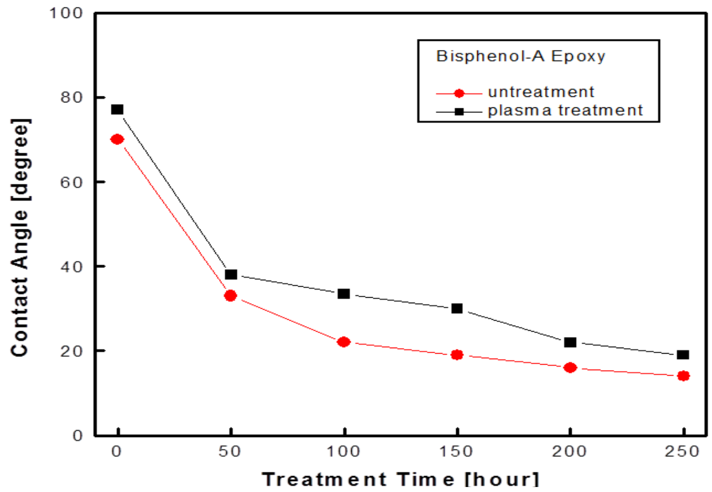


Figure 2: Contact Angle According to the UV Irradiation of FRP

Also, the surface energies were calculated from these measurements using the geometric mean approach of Owens-Wendt, as presented in Eqn. (1)

$$\gamma_1(1+\cos\theta)=2[(\gamma_S{}^d)^{1/2}\,(\gamma_1{}^d)^{1/2} / \gamma_1 + (\gamma_S{}^a)^{1/2}\,(\gamma_1{}^a)^{1/2} / \gamma_1\,] \qquad (1)$$

This equation permits the derivation of $\gamma_S{}^d$ and $\gamma_S{}^a$ via measurements of the contact angles θ of two liquids if γ_1, $\gamma_1{}^d$ and $\gamma_1{}^a$ of both liquids are known [6,7].

Further, contact angle values measured by dropping deionized distilled water and methylene solution and surface energy values obtained from Formula (1) are shown in Figure 3.

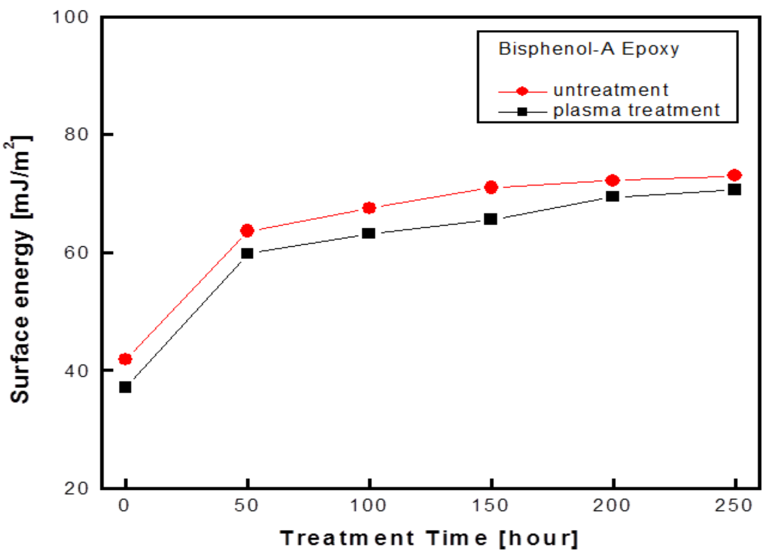


Figure 3: Surface Energy According to the UV Irradiation of FRP

As UV irradiation went on, the surface wettability increased, causing surface activation and increasing surface energy.

This indicates that, as UV irradiation went on, excessive irradiation energy might cause destruction of chemical bonds to produce lots of radicals and result in change of stabilized surface into activated one, leading to increase of surface wettability and surface energy.

XPS Analysis

As is shown in Figure 4, the XPS measurement indicates that the sizes of the carbon 1s (C1s) and oxygen 1s (O1s) peaks vary relative to the irradiating time.

However, according to the comparison of the non-irradiated and irradiated samples, when the irradiating time increased to 100 and 200 hours, the carbon peak decreased while the oxygen peak relatively increased. This result is indicating that UV irradiation caused oxidation and activation on the surface that led to increase of wettability.

This is the very factor resulting in hydrophilic surface and decrease of contact angle.

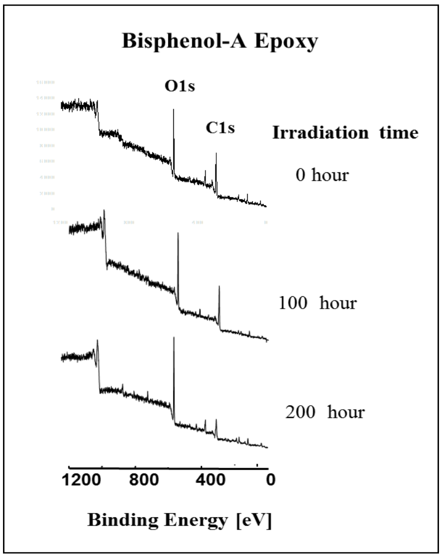


Figure 4: C1s and O1s Peaks According to the UV Irradiation of FRP

To find a more specific chemical structure of the surface, a sub-peak of the C1s peak was determined for a curve fitting. The results are shown in Figure 5. As was presented from the analysis of the C1s' internal peak through the curve fitting, while the main peaks of the non-irradiated surface were initially C-C and C-H, the surface peaks underwent various changes after the irradiation. As the irradiating time increased, the Ether (-CO), carbonyl (-C=O), and carboxyl (-COOH) peaks also increased. This is because the lengthy irradiation decomposed the hydrocarbon bonds and generated surficial radicals which rebounded with the oxygen molecules to produce a large amount of carbonyl. It was found that the carbonyl,and carboxyl which is formed from the bonding of carbonyl and atmospheric moisture,rapidly oxidized the surface[8,9].

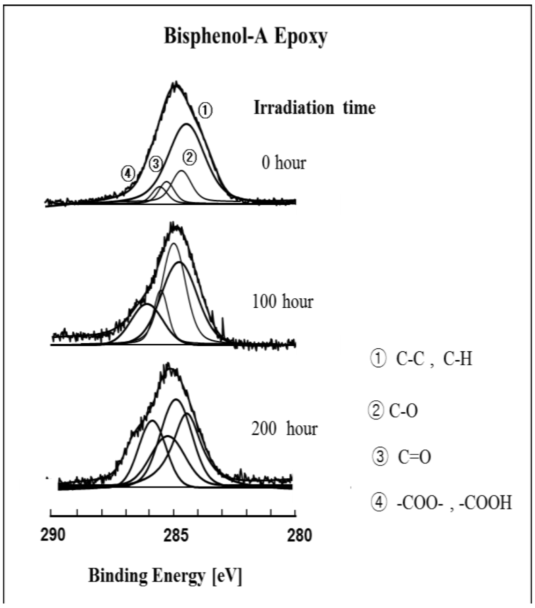
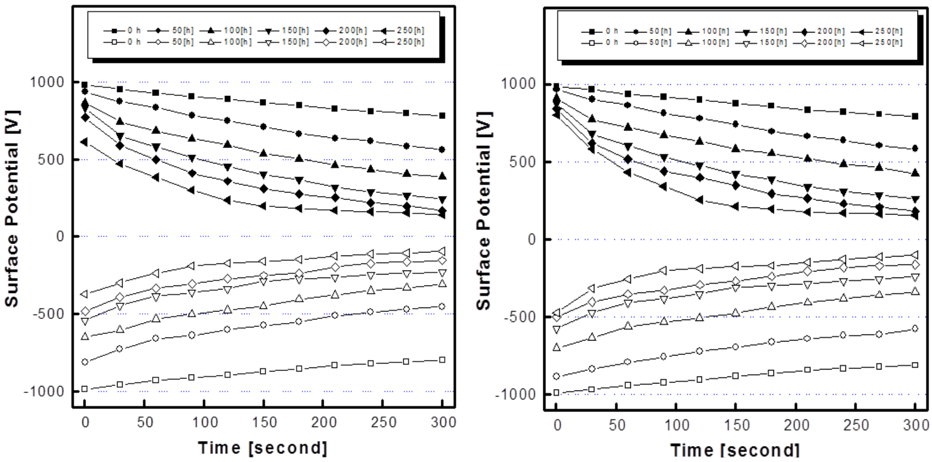


Figure 5: The Change of C1s Sub-Peaks According to the UV Irradiation of FRP

Surface Potential Decay

Surface potential decay arising from UV irradiation is shown in Figure 6. It was found that the electric charge supplied to the surface decreased as UV irradiation went on, which is considered that hydrophilic polar groups formed on the surface by UV irradiation might elevate the activation degree of surface molecular bonds and increase of surface free energy. In other words, the surface's electrical insulating property became deteriorated because lots of radicals, including oxygen, generated by irradiation energy were supplied to the surface or movement and binding of free charges were facilitated. Further, in the analysis of polarity changes arising from corona application, the surface potential decay by negative charge application was faster than that by positive charge application. As analysis went on, specimen initially showing negative polarity was changed to have activated surface of high energy because, as UV irradiation went on, the high-energy surface and the low-energy sub-surface were re-positioned due to energy difference between them. In other words, it is considered that electrical double layers corresponding to electrical charges formed on the surface were made inside the specimen by UV irradiation and they were mutually re-positioned by thermodynamic reaction [10]. As a result, it is considered that surface activation leads to increase of surface energy, which results in increase of wettability and finally dramatic surface potential decay in short period.

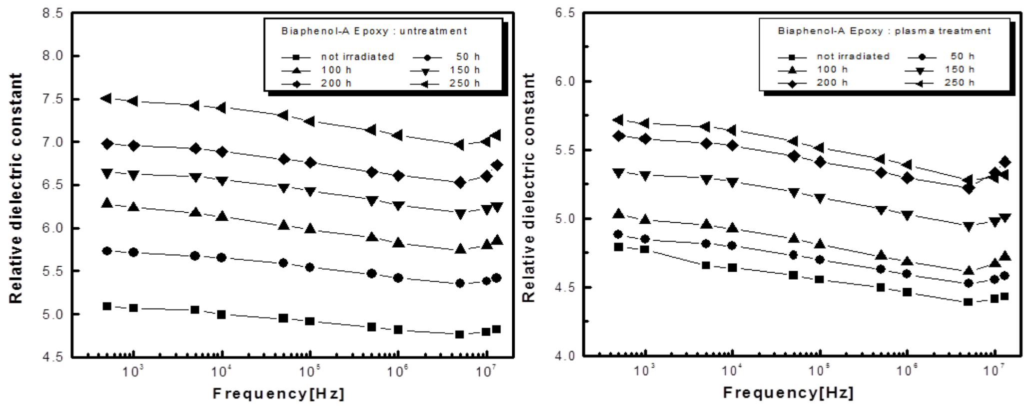


(a) Untreatment (b) Plasma Treatment

Figure 6: Surface Potential Decay According to the UV Irradiation of FRP

Dielectric Property

The non-hereditary rates relative to the ultraviolet irradiation are shown in Figure 7. As is presented in the figure, when the irradiating time increased, the non-hereditary rates also increased. In the case of Bisphenol type A epoxy resin after the 250-hour irradiation, the treated samples produced under 10 kHz increased to 5.6, and the non-treated ones increased from 4.9 to 7.4.



(a) Untreatment (b) Plasma Treatment

Figure 7: Relative Dielectric Constant vs Frequency According to the UV Irradiation of FRP

It is considered that UV irradiation might cause change of its structure maintained by Van der Waals force, including orientation polarization of dipoles, destruction of interfacial bonds by excessive light energy, and thermal expansion of its constituents. Such structural changes and difference of thermal expansivity between epoxy resin and glass fiber might result in the increase of dielectric constant. Further, increase of dielectric constant was higher at lower frequency. It is considered that UV irradiation might cause the interfacial polarization and dipole's orientation polarization, which is the reason for increase of dielectric constant at lower frequency band[11].

4. Conclusion

This study set the conditions for the plasma-surface improvement of a composite material. Ultraviolet irradiation was performed on the plasma-treated surface. The surficial degradation mechanism was analyzed through a comparison of the electronic and chemical inter-relations. The results are as follows.

1. The optimal conditions for the plasma-surface treatment in an oxygen atmosphere were 100 W, 0.1 Torr and 3 minutes. The plasma treatments were performed under the optimal conditions.
2. After the irradiation, the surface of the treated samples were activated by the contact angle and surficial energy to create a hydrophilic surface. By irradiating the treated composite material, it was found that the surface becomes hydrophilic due to the presence of -CO, -C=O and -COOH radicals.
3. When the specimens exposed to UV irradiation or not exposed to UV irradiation were electrically charged by the corona discharge, the electrical charges accumulated on the surface decreased as UV irradiation went on. Further, UV irradiation caused generation of positive polar radicals on the surface and dramatic decrease of negative polar charges applied to the surface.
4. In the case of bisphenol-A type epoxy resin, it was increased to 5.6 (treated with plasma) or 7.4 (not treated with plasma). It can be concluded that UV irradiation causes increase of dielectric constant.

Plasma treatment of glass fibers is a dry method that can overcome deterioration problems found when a wet surfactant treatment method is employed. It is a highly useful method for surface treatment in view of uniform treatment effects and environment-friendliness. It is important to identify the relationship between various environmental factors' deterioration effects through comprehensive further investigation and analysis.

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