XPS Analysis of Corona-Treated PVdF Films with Air and Alkyl Methacrylate Monomer as a Coupling Agent

Kyu Seomoon[1*], Huikwon Moon[2], and Kisoo Kim[3]

Abstract— Polyvinylidene fluoride (PVdF) films were treated by dielectric barrier corona discharge coupling technique to enhance the interfacial adhesion of PVdF – polyvinyl chloride (PVC) films with air and alkyl methacrylate monomers as coupling agents. Effects of corona discharge voltage, film transfer speed in a roll-to-roll system on the surface properties of PVdF and interfacial adhesive force of PVdF-PVC are investigated with contact angle, ATR-FT-IR, XPS analyses and cross-cut tape test method. The contact angle decreased with an increasing corona discharge voltage and a decreasing film transfer speed in roll-to-roll system. As the discharge voltage increased, atomic composition of oxygen increased while that of fluorine decreased. The interfacial adhesion was enhanced when the PVdF film was treated in a mild corona condition; low discharge voltage, fast film transfer speed. The interfacial adhesion of PVdF-PVC films exhibited excellent results even at high discharge voltage when the PVdF film was corona-treated in alkyl methacrylate atmospheric condition.

Keywords— Alkyl methacrylate, corona anchoring, interfacial adhesive force, PVdF-PVC, XPS

I. Introduction

Polyvinyl chloride (PVC) is a widely used polymer in color sheets and wrapping sheets for a decoration and advertisement. PVC color sheets are usually used in exterior part and even in the architecture use; outer wall material of building, thus long-term weatherproof properties are needed for the outer surface of PVC film. Polyvinylidene fluoride (PVdF) is an excellent material for this outer surface film due to its excellent weatherproof property and relatively low working temperature among fluoropolymers [1, 2].

There is a great difference in surface polarity of two films, thus the interfacial adhesion between PVdF and PVC films is not good. In order to enhance the interfacial adhesion between PVdF and PVC film in commercial lamination products such as 3M Fixal film, very thin polymethyl methacrylate (PMMA) layer was used as an adhesive primer between PVdF and PVC films [3, 4]. The cast process is more simple and cheaper than the lamination process for manufacturing multi-layer film, and additional primer coating process makes unit cost high.

In this study, we tried new method to bond alkyl methacrylate monomers onto the PVdF surface by corona anchoring technic for enhancing the interfacial adhesive force between PVdF and PVC films. Methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BMA) were used as a precursor for corona anchoring.

II. Experiment

Fig. 1 is the schematic diagram of the dielectric barrier corona discharge apparatus used in this study. PVdF film was transferred into the corona discharge region with roll-to-roll system.

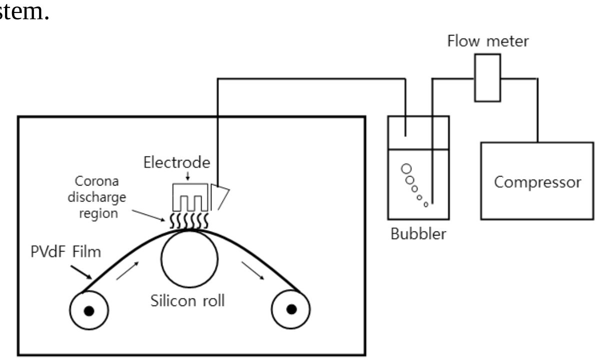

Fig. 1 Schematic diagram of corona discharge system

Air and alkyl methacrylate monomer vapor were fed to the corona discharge region through bubbler. Concentration of the alkyl methacrylate vapor was kept 1% by controlling bubbler temperature in water bath to maintain vapor pressure about 10 hPa (7.6 torr). Flow rate of air was 100 cm^3/min (sccm).

The surface energy, chemical composition and bonding state of the corona-treated PVdF films were analyzed using contact angle measurement, attenuated total reflection (ATR) FT-IR, and X-ray photoelectron spectroscopy (XPS).

PVC thin films were cast-coated on the corona-treated PVdF films. The interfacial adhesive force between PVdF and PVC film was analyzed by cross-cut test method (ASTM D3359) [5]. The cross-cut test is a method for determining the resistance of paints and coatings to separation from substrates by utilizing a tool to cut a right angle lattice pattern into the coating,

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penetrating all the way to the substrate. A quick pass/fail test can be accomplished through this method [6].

III. RESULTS AND DISCUSSION

A. Corona Treatment in Air Atmospheric Condition

Fig. 2 shows the effect of corona discharge voltage and film transfer speed in a roll-to-roll system on the contact angle of the corona-treated films.

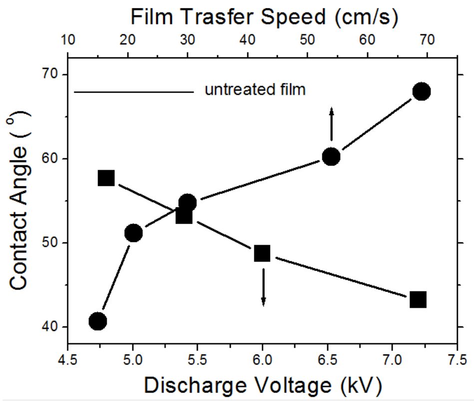

Fig. 2 Contact angle variation showing the effect of corona discharge voltage and film transfer speed

The water contact angle decreased with an increasing corona discharge voltage from 58° at 4.8 kV to 43° at 7.2 kV, while the angle increased with an increasing film transfer speed of roll-to-roll system from 41° at 15 cm/s to 68° at 69 cm/s. The water contact angle of untreated film was 68°. These results mean that corona discharge makes the corona-treated film surface more energetic and polar state, especially in the case of high discharge voltage and slow film transfer speed.

Atomic composition of the corona treated films analyzed using XPS are shown in Fig. 3. Atomic % of C:O:F in untreated film was 53:8:39. As the discharge voltage increased, atomic composition of oxygen increased from 8 to 17% at discharge voltage 9 kV, while atomic composition of fluorine decreased from 39 to 31% at discharge voltage 9 kV. The atomic composition of carbon was nearly constant about 51 to 53 %. These imply that oxygen atoms are incorporated into the film surface from the air, and fluorine atoms are ablated by the corona treatment. This is consistent with the water contact angle results in Fig. 2; the contact angle decreased with an increasing discharge voltage.

Fig. 4 shows the XPS C_{1s} spectra of corona-treated films. There are significant differences in the spectra about 293, 288.5, and 284.5 eV. In order to understand these differences in Fig. 4,

each C_{1s} spectrum is curve-fitted into several peaks as shown in Fig. 5 for a typical example.

Fig. 5 shows the curve fitting simulation result of XPS C1s spectrum of untreated PVdF film. Actually the untreated film is not a pure PVdF polymer, but a copolymer of 60% PVdF + 10% polyhexafluoro propylene (PHFP) + 30% polymethyl methacry- late (PMMA). PMMA was added for an adhesion with PVC film.

Each C_{1s} spectrum can be separated into 7 different peaks; general C*-C (284.5 eV), C*-O (286 eV, +1.5 eV to C*-C), C*=O (287.5 eV, +3.0 eV), O=C*-O (288.4 eV, +3.9 eV) in PMMA, C*-CF_2 (286.1 eV, +1.6 eV), C*F_2 (290.1 eV, +5.6 eV), and C*F_3 (293 eV, +8.5 eV) in fluoro-polymer [7, 8].

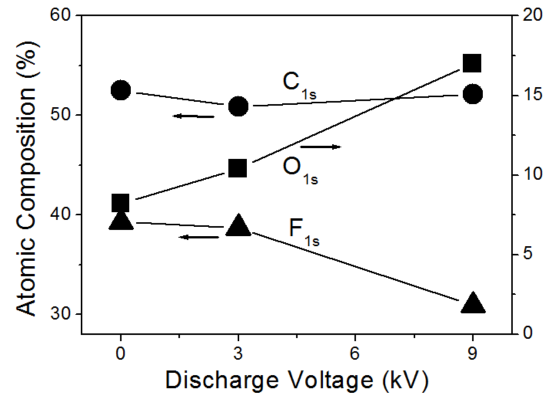

Fig. 3 Atomic composition of the corona-treated films in air atmospheric condition analyzed with XPS

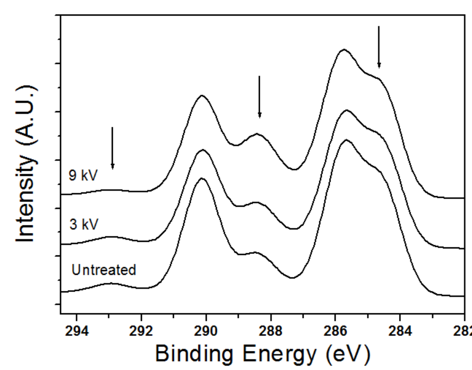

Fig. 4 XPS C_{1s} spectra of PVdF films corona-treated in air atmospheric condition (differences are marked with arrows)

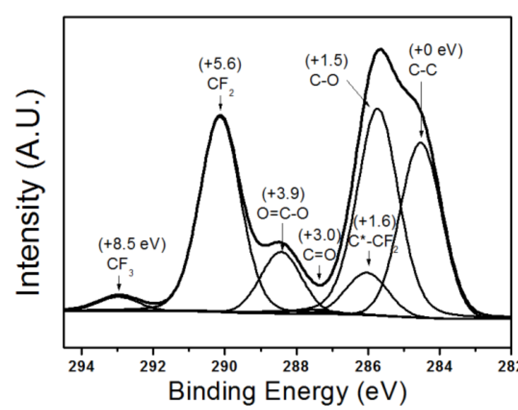

Fig. 5 Typical example of curve fitting simulation result of C_{1s} peak of untreated film obtained by XPS analysis. Numbers in parenthesis mean chemical shift of carbon bonded in each functional group

Chemical bonding states of carbon atoms in the corona-treated film surface were divided into two groups as shown in Fig. 6. One group decreased with an increasing discharge voltage; general C*-C and F-bonded C*. The other group increased with an increasing discharge voltage; O-bonded C*. These results are consistent with the results of Fig. 2 and Fig.3. The corona discharge makes oxygen atoms incorporated into the film surface in the form of O=C-O, C-O and C=O, thus the film surface is changed to more polar state by incorporated oxygen atoms.

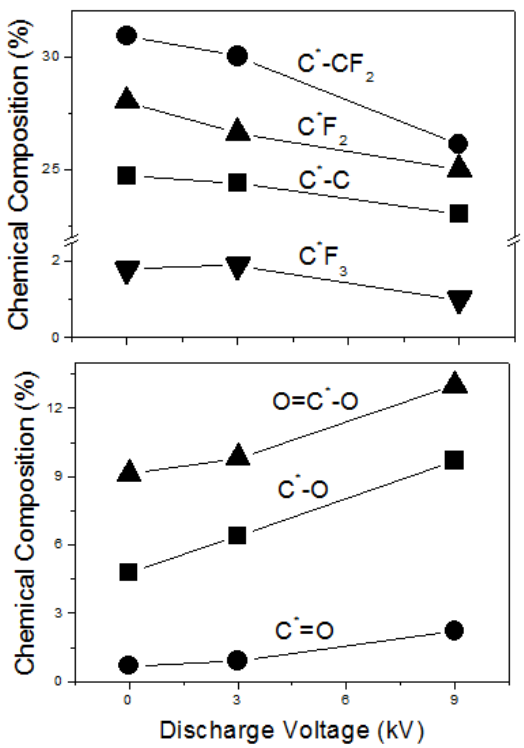

Fig. 6 Chemical bonding states of the corona-treated films simulated by curve fitting of XPS C_{1s} peaks

B. Corona Treatment in Air + Alkyl methacrylate Atmospheric Condition

Alkyl methacrylate (MMA, EMA and BMA) monomer vapor was delivered into the corona discharge region with air through bubbler as shown in Fig. 1. Concentration of alkyl methacrylate vapor in air was 1%.

Fig. 7 shows the contact angle of the corona-treated films in air and alkyl methacrylate monomer atmospheric conditions. The water contact angle decreased with an increasing corona discharge voltage regardless of alkyl methacrylate monomer.

Fig. 8 shows atomic compositions of the corana–treated films in the air + BMA atmospheric condition alanyzed by XPS. Effect of corona discharge voltage on the atomic composition of the corona-treated films were similar trend to the result of air atmospheric condition. As the corona discharge voltage increased, atomic composition of oxygen increased from 8 to 14 %, while atomic composition of fluorine decreased from 39 to 30%. But atomic composition of carbon slightly increased from 53 to 57% due to incorporation of BMA molecules onto the film surface.

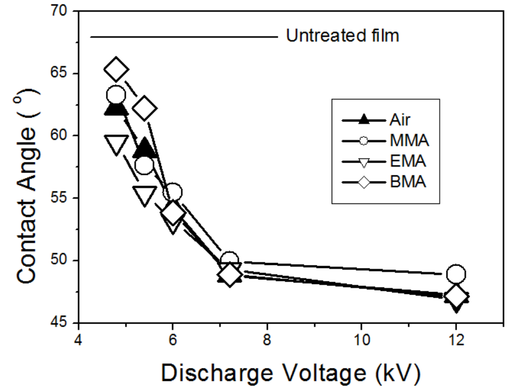

Fig.7 Contact angle variation of corona-treated films in air and alkyl methacrylate monomer atmospheric conditions

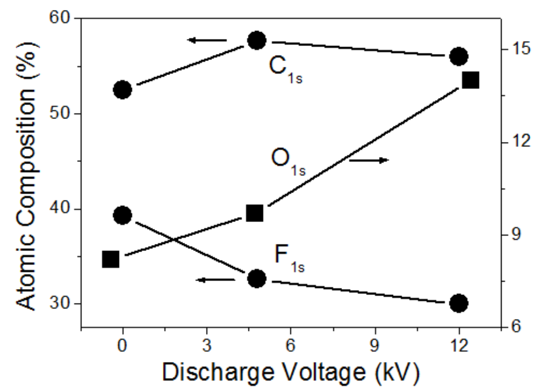

Fig. 8 Atomic composition of the corona-treated films in air + BMA atmospheric condition analyzed with XPS

C. Interfacial Adhesive Force of PVdF-PVC Films

About 75 µm thickness of PVC thin films were coated on the corona-treated PVdF films. The interfacial adhesive forces between PVdF and PVC film were analyzed by cross-cut test method (ASTM D3359) [5].

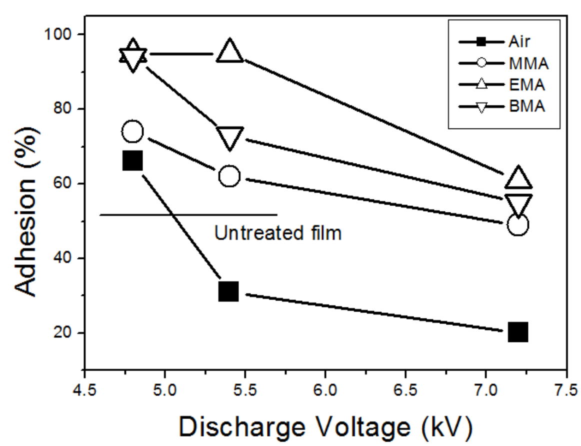

Fig. 9 Cross-cut tape test results of the corona-treated films by the ASTM D3359 method

Fig. 9 shows the effect of corona discharge voltage on the interfacial adhesion of PVdF-PVC films. Corona treatments were carried out at various atmospheric conditions; air, MMA, EMA and BMA. Adhesion % means that remained part after take-off the test tape. Adhesion % of the untreated PVdF film was 52%.

At 4.8 kV of discharge voltage, all corona-treated films exhibited good adhesion; 66% in Air condition, 74% in MMA, 95% in EMA, 94% in BMA. But increasing discharge voltage resulted in decreasing interfacial adhesion, especially great decreasing in air atmospheric condition, thus even worse adhesion than corona-untreated sample. However in alkyl methacrylate atmospheric condition, interfacial adhesion of PVdF-PVC films exhibited excellent results even at high discharge voltage.

These results could be understood in terms of surface free energy of related polymers represented in TABLE I. There is a great difference of an 11.2 mN/m in surface free energy between PVdF and PVC films, thus adhesion of two films is not good. Therefore proper materials such as alkyl methacrylate which have intermediate surface free energy between PVdF and PVC was anchored on the interface, the interfacial adhesive force can be enhanced.

TABLE I
SURFACE FREE ENERGY OF RELATED POLYMERS

Polymer	SURFACE FREE ENERGY (MN/M)
PVdF	30.3
PVC	41.5
PMMA	41.1
PEMA	35.9
PBMA	31.2

IV. CONCLUSION

PVdF films were treated by corona anchoring method with air and alkyl methacrylate monomers as coupling agents to enhance the interfacial adhesione between PVdF and PVC. The contact angle decreased with an increasing corona discharge voltage and a decreasing film transfer speed in roll-to-roll system. As the discharge voltage increased, atomic composition of oxygen increased while that of fluorine decreased. The corona discharge makes oxygen atoms incorporated into the film surface in the form of O=C-O, C-O and C=O, thus the film surface is changed to more polar state by incorporated oxygen atoms. At a high discharge voltage over 5 kV, corona-treated PVdF films in air exhibited poor adhesion to PVC film rather than untreated film. However, the interfacial adhesion of PVdF-PVC films exhibited excellent results when the PVdF films were corona-treated in alkyl methacrylate atmospheric condition even at high discharge voltage.

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