

Surface Composition Change of UV/Ozone Modified Polypropylene

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UV/오존에 의해 개질된 폴리프로필렌의 표면 조성 변화

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ABSTRACT : Polypropylene is oxidized with UV/ozone as a function of UV treatment time and ozone flow rate and its surface characteristics are investigated using contact angle measurements and XPS. The aging behavior of oxidized surface is investigated under air, water and ethylene glycol as the aging media. Adhesion strength is also investigated using a lap shear test. Polar surface energy increases with increasing UV/ozone treatment time as well as ozone flow rate. No polar surface energy change is observed under water aging, while under air aging it decreases significantly within 2-3 days and reaches the close value as that of the untreated PP. Adhesion strength increases with increasing UV/ozone treatment time as well as ozone flow rate.

요 약 : UV 조사시간과 오존유량을 변화시키면서 폴리프로필렌을 UV/오존 산화하였으며 이의 표면특성을 접촉각과 XPS를 이용하여 살펴보았다. 산화된 표면의 노화거동을 공기, 물, 에틸렌 글리콜 하에서 살펴보았으며, 또한 lap shear 실험을 통하여 접착력을 관찰하였다. 극성표면 에너지와 접착력은 UV/오존 처리시간과 오존유량이 증가함에 따라 증가함을 알 수 있었다. 물에서 노화실험을 한 경우 극성표면 에너지의 변화가 없었으나, 공기 하에서 실시한 경우 2-3일 이내에 급격히 감소하여 처리하지 않은 폴리프로필렌의 값에 근접하였다.

Keywords : Polypropylene, UV/Ozone treatment, Aging, Adhesion Strength, Contact Angle, X-ray Photoelectron Spectroscopy

I. Introduction

Polypropylene (PP) is one of the widely used commodity polymers and it has a non-polar characteristics. Non-polar property, i.e. low surface energy, of PP may cause problems in many com-

mercial uses such as adhesion and printing. To overcome this problem, surface oxidation method is used to modify the polymer surface. Corona discharge, plasma, flame and UV/ozone (UVO) treatments are commonly used to oxidize a polymer surface, and the oxidized polymer surfaces show improved wetting and adhesion properties compared to unmodified polymers.

The UVO treatment relies on the combined

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effects of UV light and ozone, and it has been shown to be very successful to modify polymer surfaces.¹⁻⁶ Surface oxygenation has been studied as a function of UVO treatment time, ozone concentration and intensity of UV. Contact angle, Fourier transform infrared attenuated total reflection (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS) are widely used to measure the degree of surface oxygenation.

The characteristics of oxidized surfaces of polymers alters when aged or washed.^{1,7,8} The aging behavior of the modified surface is a function of both the nature of polymer and aging medium. It is found that corona or oxygen plasma-treated PP is not changed significantly during aging, while poly(ethylene terephthalate) (PET) ages rapidly after corona, UVO or plasma treatments.^{1,9,10} Surface characteristics becomes nonpolar due to the rearrangement of oxidized molecules at the surface during air aging, while it remains as treated state under water aging. The aged PET showed migration of low molecular weight oxidized molecules from the surface into the bulk via interaction with functional molecules and reorientation of oxidized functionalities. Hill et al. found that change in PP surface during aging was primarily due to the rearrangements of oxidized molecules in the surface region, and it was attributed to the non-polar characteristics of bulk PP.¹

The objective of this work is to investigate the change of surface composition and adhesion strength depending on the UVO treatment time as well as on the ozone flow rate. The effects of aging media and aging time on the surface characteristics and adhesion strength are also studied.

II. Experimental

Polypropylene (B380J, SK Inc.) was used in this study. PP film was made with a hot press at 230 °C for 3 min. PP films were immersed in an ultrasonic bath containing distilled water for 30 min to clean their surfaces and then vacuum dried for 2 h before UVO treatment. PP film was treated for

various irradiation times and ozone flow rates at room temperature in a nitrogen purged quartz vessel with ozone generated in dry oxygen in an ozone generator (Pacific Ozone Inc.) under UV irradiation. A 400 W medium pressure mercury UV lamp was used, and it was placed 10 cm from PP film. The inlet oxygen flow rate into the ozone generator was 4.7 g/min and ozone concentration was controlled by changing voltage. Surface analysis of UVO treated films was carried out within 3 h after treatment to minimize the aging effect. UVO treated films were aged for different periods (2, 5, 7 and 28 days) to investigate the effect of aging on the surface composition. The aging experiments were done under three different media: air, ethylene glycol (EG) and water. In an air aging experiment, UVO treated films were exposed to the ambient, while UVO treated samples were immersed in distilled water or EG for immersion aging experiment. All immersed samples were vacuum dried at 30 °C for 30 min prior to surface analysis.

Surface analysis of samples was done by X-ray photoelectron spectroscopy (XPS), static contact angle measurements. To measure the oxygen content, the XPS spectra were obtained on an ESCA 2803-S (VG Microtech) using Al K α photon source. An electron take-off angle of 37° was used. Binding energies were referenced to the hydrocarbon component peak at 285 eV. The chemical information indicating changes in the UVO treated PP was obtained by curve fitting the carbon 1s (C1s) spectra. Static contact angles were measured using PCHM-575 instrument (First Ten Angstroms, Inc.). Deionized water and methylene iodide were used to calculate the dispersive and polar components of the surface free energy using the harmonic mean method.¹¹

A lap shear test was used to investigate the effect of adhesion characteristics of the PP film to aluminum. Araldite AW10 and HV 953K were used as adhesive and hardener, respectively, and these were mixed 1:1 weight ratio prior to use. The thickness of PP film was 5 mm and an aluminum

tape was attached to the backside of the PP film to prevent damage to PP film during the lap shear test. Crosshead speed of tensile tester (Tensilon/UTM III-500, Toyo Baldwin) was 50 mm/min. In case of water aged PP, PP was vacuum dried at 30 °C for 30 min before attaching to aluminum.

III. Results and Discussion

The C1s XPS spectra of the PP film before and after UVO treatment are shown in Figure 1. The tail on the high binding energy side of the main C1s peak shows that oxygen incorporation into the PP surface gives rise to a variety of functional groups such as -C-O-, -C=O, -COOH which correspond to binding energies of 286.1, 287.6, 289.1 eV, respectively. Even though it is not easy to decide the exact oxygen functional groups from the XPS spectra, earlier studies reported that the polar

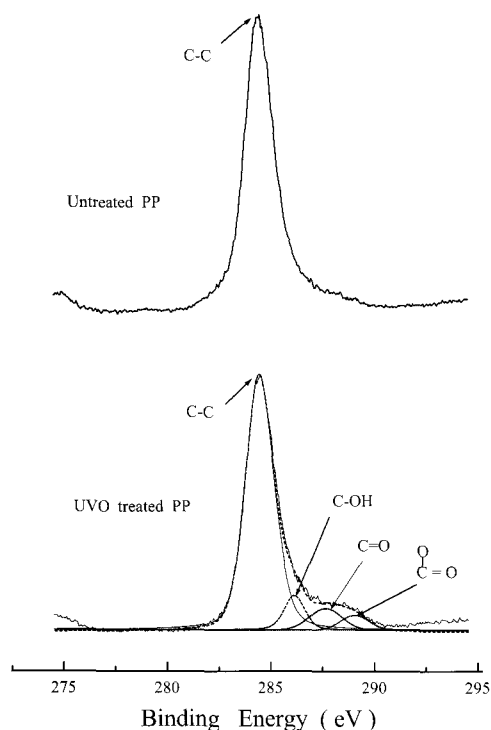


Figure 1. Carbon 1s XPS spectra of (a) UVO treated PP and (b) untreated PP.

characteristics of a PP surface increased with increasing amount of functional groups. O1s/C1s has been widely used to compare the extent of surface oxygenation. The difference in the O1s/C1s between the treated and untreated PP, Δ O1s/C1s, is used to investigate the extent of surface oxygenation.

1. Effect of UVO treatment time and Ozone flow rate

The increase in extent of surface oxygenation with UVO treatment time under same ozone flow rate (6.7 g/hr) is observed by different characterization methods. (Figures 2 and 3) The XPS results show that O1s/C1s, i.e. the extent of surface oxygenation, increases with UVO treatment time in the early reaction stage and it tends to level off after 20 min. (Figure 2) Figure 3 shows that the polar surface free energy increases up to 10 min UVO treatment and then tends to level off. These results indicate that surface oxygenation occurs at the surface of PP film by UVO and it agrees with previous works. A different trend of oxygenation with respect to UVO treatment time is observed depending on the characterization methods, and it can be attributed to the different detectable depth

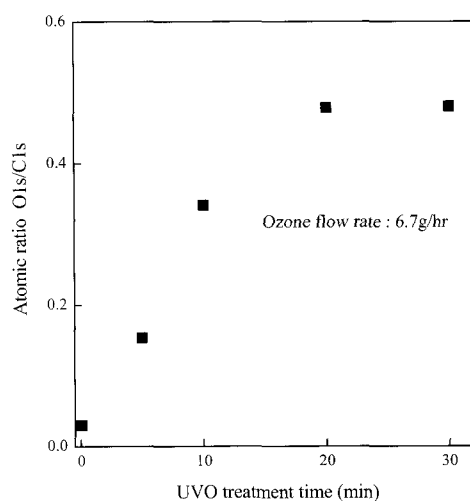


Figure 2. O1s/C1s atomic ratio of PP as a function of UVO treatment time.

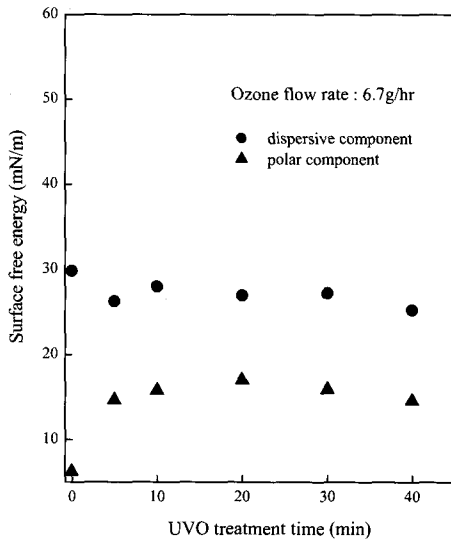


Figure 3. Surface free energy of PP as a function of UVO treatment time.

of each characterization method.

The detectable depths of contact angle, XPS and FTIR-ATR are 2-3 Angstrom, 100 Angstrom and 10^4 - 10^5 Angstrom, respectively.^{12,13} The leveling off of polar surface free energy and O1s/C1s after 10 min and 20 min treatments, respectively, means that the concentration of polar groups by oxygenation reaches its equilibrium concentration up to detectable depth of contact angle measurement and XPS at that treatment time. Ozone diffuses into the PP film from the surface during UVO treatment and its concentration at a given depth of PP film increases with time until it reaches maximum concentration. The film thickness is thin enough to neglect the variation of UV intensity with the depth of film. Thus, it is found that ozone diffusion is a determining factor in UV/ozone treatment to control the thickness of fully oxygenated layer at the given irradiation time. Walzak et al.¹⁴ and Gongjan et al.¹⁵ also reported that O1s/C1s and contact angle of PP tends to be level ed off after 10-15 min UVO treatment. These results also show that the UVO treatment occurs not only on the surface but also to a certain depth.

Figures 4 and 5 show the effect of ozone flow

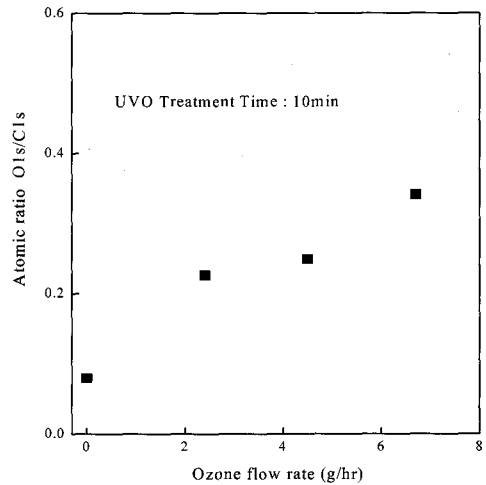


Figure 4. Effect of ozone flow rate on O1s/C1s atomic ratio of PP

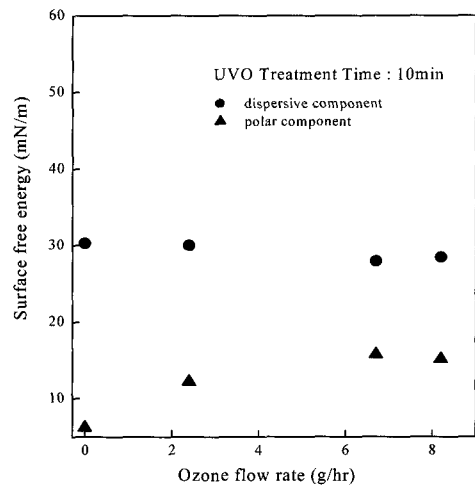


Figure 5. Effect of ozone flow rate on the surface free energy of PP

rate on the surface characteristics at 10 min UVO treatment time. O1s/C1s increases linearly with ozone flow rate, while polar surface free energy tends to be level ed off at 6.7 g/hr. Thus it can be concluded that an optimum ozone flow rate exists to obtain a fully oxygenated PP surface.

2. Aging Effect

The change in surface composition under

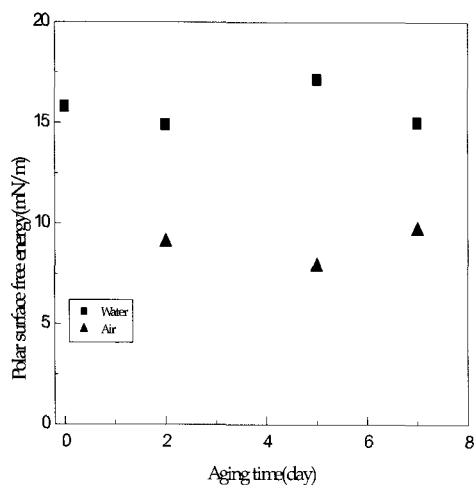


Figure 6. Change in polar surface free energy of UVO treated PP under various aging media

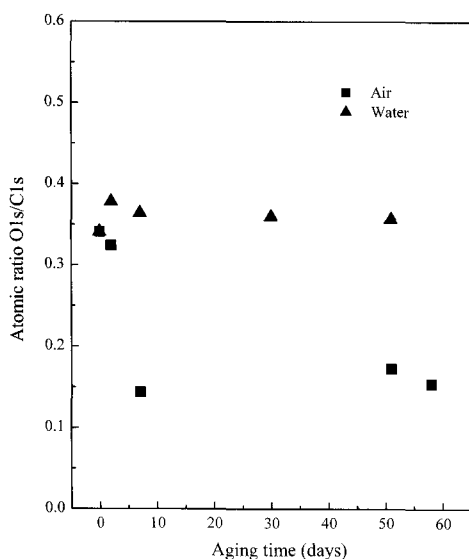


Figure 7. Change in O1s/C1s atomic ratio of UVO treated PP aged under air and water

different contact materials has been reported by several workers.^{1,7,8} Figures 6 and 7 show the variation of polar surface free energy and O1s/C1s ratio of UVO treated PP as a function of aging time and aging medium. Aging media used are air, ethylene glycol (EG) and water, and surface energies of EG and water are 48 mJ/m² and 72.8 mJ/m², respectively. Polar surface free energy of air

aged UVO treated PP decreases rapidly within 2 days, while it decreases rather slowly under EG. In both cases, polar surface energy reaches close to the value of untreated PP (1-2 mN/m higher than untreated PP). Polar surface free energy shows more or less constant values under water aging. It is found that surface composition changes into less polar state, i.e. more hydrophobic composition, under low surface energy aging medium. Garbassi and coworkers found that no change in O1s/C1s for oxygen plasma treated PP, while the advancing contact angle had returned to the value of untreated PP within 10 days in air aging.^{9,10} It was attributed to the macromolecular rearrangements in the top 5 nm. Static secondary ion mass spectroscopy data also showed the macromolecular motions leading to burial of oxygen-containing groups away from the surface.¹⁰ When it was aged in water, the rearrangement of molecules at the surface was not reported. Strobel and coworkers reported a very slight change in O1s/C1s and contact angles on air aged UV/air or UV/air/ozone oxidized PP.^{1,8}

O1s/C1s ratios under air and water aging also shows similar trend as polar surface free energy. (Figure 6) The difference in aging behavior between polar surface free energy and O1s/C1s is aging time to reach the constant value. In air aging O1s/C1s ratio needs 7 days to be level ed off, while only 2 days are needed for polar surface free energy. The change in O1s/C1s under air aging shows a different behavior from the previous worker's results, and it is rather similar to the aging behavior of oxidized PET. O1s/C1s ratio of photo-oxidized PET drops rapidly within several days, and it appeared to be stable after that in air aging.¹⁻³ Contact angle also changed a little. The aging behavior of corona-treated or photo-oxidized PET showed a migration of low molecular weight oxidized material into the bulk and the reorientation of oxidized functionalities that were formed on relatively immobile polymer chains.^{3,17} The migration of low molecular weight oxidized material is enhanced due to the interaction between ester

functionalities and oxidized material. Strobel and coworkers also reported the presence of low molecular weight oxidized molecules on the UV/air or UV/air/ozone treated surface similar to those on corona treated PP and those were removable by water washing.^{1,8} In case of UV/air/ozone treatment, no change of O1s/C1s ratio was reported even after washing low molecular weight oxidized molecules. Hill et al. argued that the modification taking place farther from the surface did not result in low molecular weight oxidized molecules that can be removed by water washing.¹ The amount of material removed is dependent on the type of surface oxidation and the extent of modification. Strobel et al. attributed the stability of PP on aging to the high molecular weight of the base PP and the lack of interaction between the corona treated surface and the unmodified bulk and surface migration, and the reorientation are also hindered by the high molecular weight nature of the bulk PP.⁸ It means that sufficient modification depth and the presence of low molecular weight oxidized molecules in oxidized layer can induce the migration and reorientation at the surface. Even though Strobel and coworkers also reported the presence of low molecular weight oxidized molecules on the surface, they did not report how much molecular weight decreases by UV/ozone. Kim et al. found that molecular weight of bulk PP decreases significantly by 10 min UVO treatment, while only a slight molecular weight decrease was observed with UV/nitrogen.¹⁶ This indicates that the decrease in molecular weight of UV/ozone treated PP is largely dependent on the chain scission in ozone penetration depth, i.e. oxidized layer. Significant modification of surface by UVO occurred in the top 1-2 μm^1 , and it gives an idea that lots of low molecular weight oxidized molecules are produced in the surface oxidized layer by UVO treatment. High molecular weight oxidized molecules, which have immobile characteristics, can interact with low molecular weight oxidized materials and it can enhance the potential of migration of low molecular weight

oxidized materials at surface to the bulk as oxidized PET.

From the above discussion our results indicate that the increase of dispersive surface energy and decrease of polar surface energy under air aged PP are likely due to a reorientation as was the case for plasma treated PP and interfacing with high energy medium, such as water, changes reorientation patterns, because polar groups are attracted to the surface by its contact with water. The decrease in O1s/C1s ratio during air aging in our results indicates that some oxidized materials exhibit migration of low molecular weight oxidized molecules into the bulk similar to the behavior of photo-oxidized PET. For water aging, water interacts with surface polar groups and orientation of surface polar groups to the water occurs at the surface. Water diffuses into PP and it enhances the mobility of low molecular weight molecules toward surface rather than bulk. Occhiello and coworkers also reported the enhanced chain mobility due to the diffusion of water during water aging of plasma treated PP.¹⁰ Those two factors are responsible for the constant O1s/C1s ratio during water aging. Migration in water aging also can induce the removal of low molecular weight oxidized molecules at the surface. An evidence for migration of low molecular weight material in UV/ozone treated PP also can be found from the change in adhesion strength upon aging.

3. Adhesion Strength

Figures 8 and 9 show the effect of ozone flow rate and UVO treatment time on the adhesion strength. Adhesion strength increases up to 7 times of untreated film for 5 min treatment, and it shows constant adhesion strength after 10 min. Polar surface free energy and adhesion strength show similar behavior against UVO treatment time as shown in Figures 3 and 9. It is quite reasonable because a contact angle measurement monitors the outermost surface properties and adhesion strength is strongly dependent on the surface characteristics.

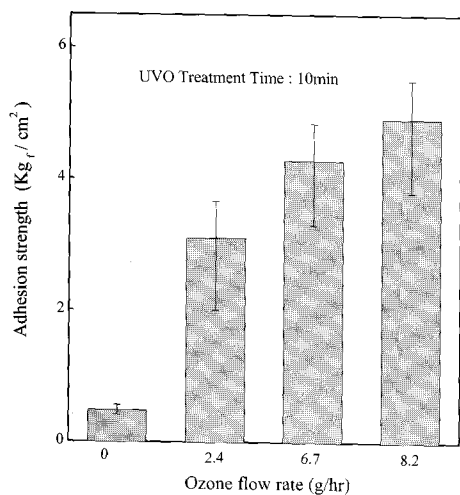


Figure 8. Effect of ozone flow rate on the adhesion strength of UVO treated PP/aluminum

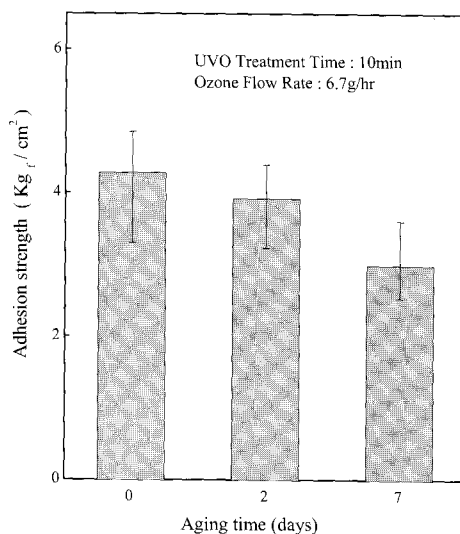


Figure 10. Effect of aging time on the adhesion strength of UVO treated PP/aluminum under air

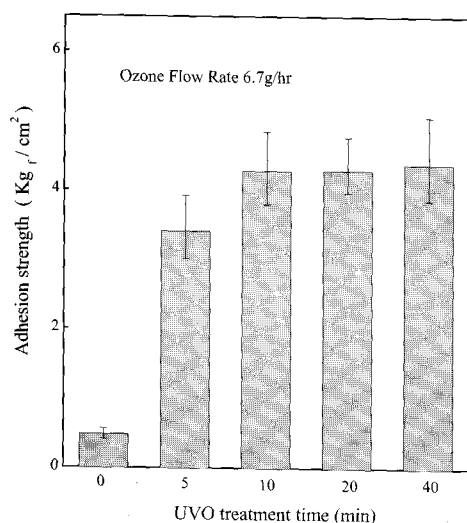


Figure 9. Effect of UVO treatment time on the adhesion strength of UVO treated PP/aluminum

Gongjian et al. also reported similar results.¹³ Adhesion strength is also strongly affected by ozone flow rate. (Figure 8) Adhesion strength increases rapidly even at low ozone flow rate (2.4 g/hr) and its increasing rate decreases with increasing ozone flow rate. Improvement in adhesion strength is due to the increasing concentration of polar species at the surface. Adhesion strength also depends on the

aging period. (Figure 10) The UV/ozone treated PP is aged for 2 and 7 days under air before making lap shear test specimens and it is found that adhesion strength decreases with aging period. In case of water aging, adhesion strength is not measured due to the low adhesion strength. Adhesion strength is strongly related to the concentration of polar groups and chain length, i.e. molecular weight, of molecules at the surface. Low concentration of polar groups and/or high concentration of low molecular weight molecules at the surface will deteriorate the adhesion strength. The concentration of surface polar groups, i.e. polar surface free energy, becomes low for air aged PP as shown in Figure 6 due to the rearrangement, and it causes low adhesion strength. For water aging, water interacts with surface polar groups and orientation of surface polar groups to the water occurs at the surface. Meanwhile, water diffuses into the PP film during water aging and it again attracts the underlying oxidized molecules to the surface. This will enhance the migration of low molecular weight oxidized molecules to the surface. Thus, level of low molecular weight oxidized materials is increased at the surface and it deteriorates the adhesion strength,

while increased concentration of surface polar groups tends to enhance the adhesion strength. Our results indicate that the level of low molecular weight in the surface affects the adhesion strength more significantly.

IV. Conclusions

The polar surface energy, i.e. the degree of oxygenation, increases with increasing UV/ozone treatment time as well as ozone flow rate. The surface characteristics of UV/ozone treated PP change depending on the aging medium. As the surface energy of aging medium increases, surface polar energy changes less. No change of surface polar energy is observed under water aging, while it changes significantly within 2-3 days and reaches to the same value of untreated PP under air aging. XPS results show the similar behavior. It is attributed to the rearrangement and migration of low molecular weight oxidized material during aging. This aging behavior is similar to photo-oxidized PET. Adhesion strength increases with increasing UV/ozone treatment time and ozone flow rate. However, adhesion strength of air aged oxygenated PP decreases with increasing aging time due to the reorientation of polar groups at the surface. It is too low to measure the adhesion strength of water aged PP and it is attributed to the high concentration of low molecular weight materials at surface due to the migration of low molecular weight molecules. Migration can be enhanced by the penetration of water into PP during water aging.

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