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ENHANCED WETTING AND ADHESION OF POLYCARBONATE BY ULTRAVIOLET LIGHT SURFACE TREATMENT

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In this study, polycarbonate (PC) surfaces were treated with ultraviolet (UV) light irradiation at different treatment times (0 to 48 h) and at two UV wavelengths, i.e., at 365 nm (UVA) and at 254 nm (UVC). Morphological and surface properties were characterized by field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), and contact angle (CA) measurements. To check the shear strength of the treated polycarbonates, single-lap shear test was carried out. Both UVA and UVC treatment produced rougher PC surface compared to untreated PC, however, UVA did not affect much the wettability of PC. But for UVC treatment, the CA of PC decreased with increasing treatment time to a maximum reduction of 23% after 48 h. The shear strength of UVC-treated PC increased by 63% than that of untreated PC, which is attributed to the formation of functional groups at the surface making it hydrophilic and the rougher surface topography that gives more surface area for adhesion.

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Keywords: Ultraviolet; polycarbonate; wettability; surface treatment; adhesion

1. Introduction

Polycarbonate (PC) is a well-known, commercially available material used in various applications such as in automotive parts, data storages, corrective lenses, construction materials and biomaterials due to their many advantages including being light weight, its flexibility and non-toxicity [1-5]. However, its application in industry is restricted due to poor wetting property of the hydrophobic polycarbonate surface bacuse of low surface energy [6] causing adhesion problems between the polymer substrates and functional coatings [6, 7]. PC is chemically inert and, therefore, requires surface treatment to enhance their adhesion characteristics to other materials without changing its bulk properties. The surface modification techniques to improve the wettability of polymer surfaces include chemical treatment [8], ion beam irradiation [7, 9], laser [10], photochemical reaction [11], and plasma treatments [5, 12-14]. Zajickova et al. [13] reported a significantly improved thin film adherence of polycarbonate when it was pre-treated with plasma especially at low powers and short treatment times.

In this paper, we report the effect of ultraviolet (UV) light surface modification on the wettability and adhesion of polycarbonate surface at varying UV wavelengths and treatment times.

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UV treatment is one of the most multipurpose techniques in surface modification [15-18]. It has been widely used to alter the surface properties of applications such as enhancing biocompatibility of biomedical materials [15], improving adhesion of coatings to polymers , and increasing wettability and printability of polymers [2]. UV light surface treatment could help in removing loosely bonded impurities from the surface and also, it can create functional hydrophilic groups. The surface of a polymer is activated during UV treatment, which brings about the chain scission of the existing groups on the surface of the polymer and creates new functional groups such as –OH, -OOH, etc.

The objective of this study was to determine the effective UV wavelength and treatment time that can produce good hydrophilicity coupled with good adhesion of polycarbonates. Several surface characterization methods were conducted to test the samples such as scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and contact angle measurements. Single lap shear tests were carried out to check the adhesion performance of the UV-treated polycarbonates.

2. Experimental

2.1 Preparation and treatment of samples

Thermoplastic polycarbonates (Spolytech Inc. Korea) with 3 mm thickness were cut into 3 cm x 10 cm pieces. All samples were initially cleaned ultrasonically with distilled water and ethanol.

Fig. 1 shows a schematic of the present UV light treatment set-up. Samples were placed below the UV lamp (VL_4.LC, Vilber Lourmat, La Valle, France) at a distance of 50 mm. Two UV lamps (lamp length = 15 cm) with different wavelengths of 365 nm (UVA) and 254 nm (UVC) were used. UV at a constant intensity of 350 μW/cm^2 and 265 μW/cm^2 for UVA lamp and UVC lamp, respectively were irradiated on the polycarbonate surfaces at different treatment times: 0 h, 6 h, 12 h, 24 h, and 48 h. The results were compared to control samples (i.e., without treatment or untreated). The control and UV-treated samples were then subjected to different measurement and characterization techniques.

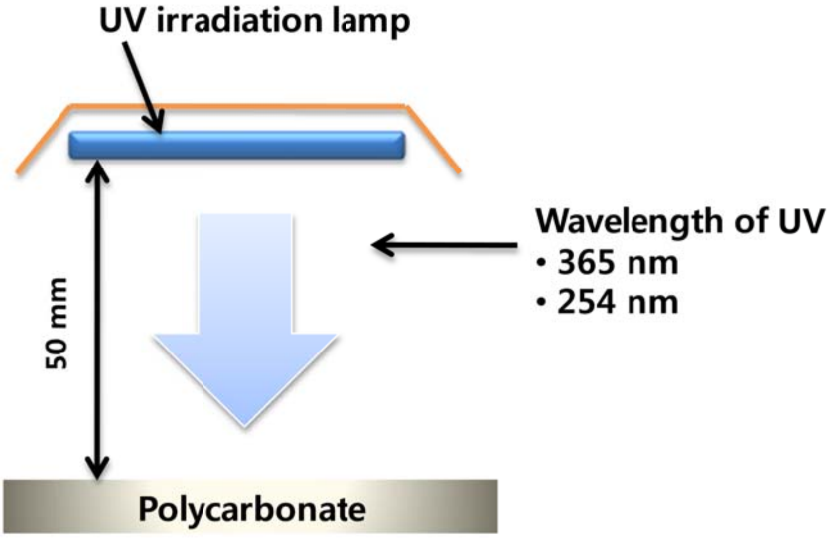

Fig. 1. Schematic layout of the present UV light irradiation surface treatment system.

2.2 Measurements and characterization

Contact angle measurements were carried out using a GBX, Digidrop (France) contact angle meter. Dieonized water and glycerol with a drop diameter of 6 μm were automatically dropped onto the PC surface. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface chemistry of the untreated and UV-treated polycarbonate surface. The XPS data were obtained using a K-Alpha (Thermo Fisher Scientific, US) using a Al Ka (hv = 1486.6eV) X-ray radiation source. The X-ray source power was 300 W (12kV × 2.5 mA), with a spot diameter of 400 um. The analyzer pass energy was 200 eV. Base pressure during analysis was about 5×10^{-7} torr. The spectra obtained were referred to the C1s peak (286.4 eV) of carbon. Atomic concentrations were calculated using an Advantage system. The surface structure and morphology of the present samples were studied by field emission scanning electron microscopy (FE-SEM, S-7400, Hitachi, Japan).

Single lap shear tests were conducted in a universal testing machine (Unitech-M, R&B) according to ASTM D3164 - 03. The single lap shear test specimens (Fig. 2) were composed of two PC boards and DP460 epoxy adhesive as shown in Fig. 2. The test speed was maintained at 1 mm/min. At least 3 specimens for each sample were tested and the average values are reported in this paper.

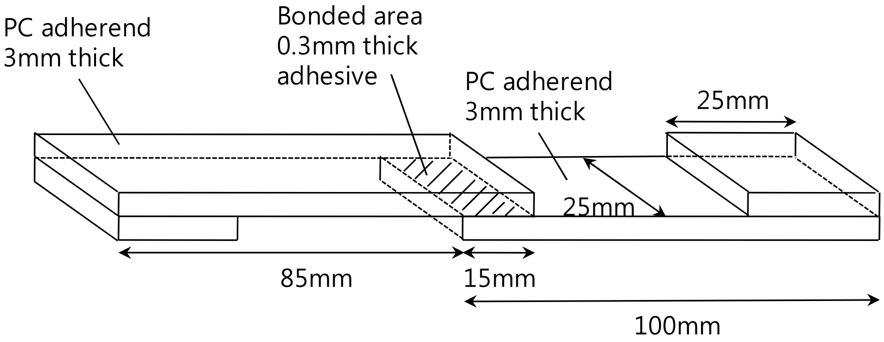

Fig. 2. Design and dimensions of the specimen for single-lap shear test.

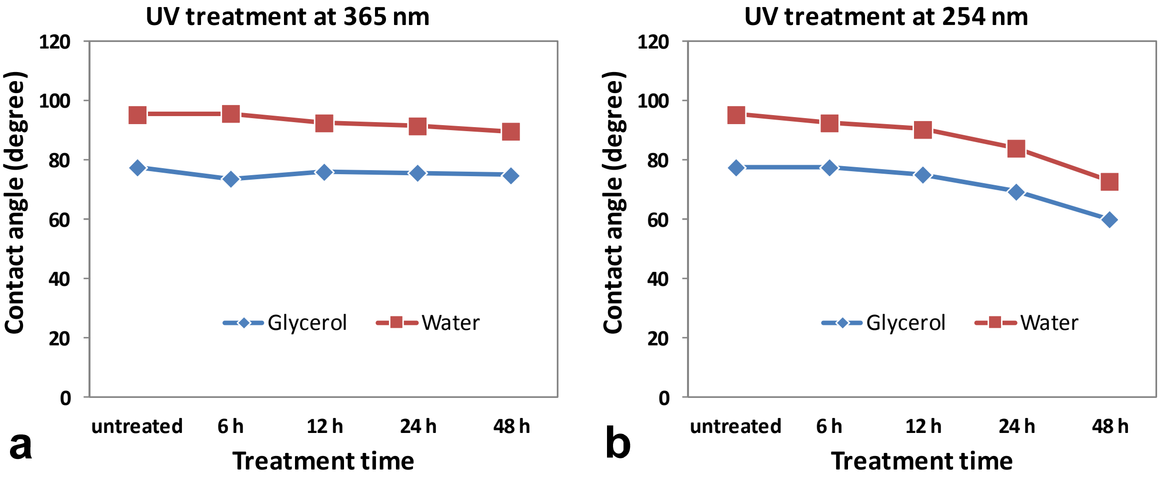

Fig. 3. Variation of the water and glycerol contact angle values of the untreated and (a) UVA-treated (365 nm) and (b) UVB-treated (254 nm) PC surfaces at different treatment times.

3. Results and discussion

Fig. 3 shows the water and glycerol contact angle (WCA and GCA, respectively) values of the UV-treatment polycarbonates as a function of UV wavelength and treatment time. The PC control WCA and GCA values were found to be 95.3° and 77.5°, respectively indicating poor wettability of the PC surface. The UVA-treatment showed very little effect on the WCA and GCA of PC even after 48 h of treatment time (Fig. 3a). However, we can see that there was a noticeable decrease in both WCA and GCA of PC after treating with UVC (Fig. 3b). After 48 h of UVC treatment, the WCA and GCA decreased by 23.6% and 22.6%, respectively from the control condition. The present results showed the clear effect of shorter wavelength, which carried higher photon energy, to the improvement of wettability of polycarbonate. To help explain the changes in CA of the present samples, we obtained XPS spectra of the different samples. Table 1 gives the oxygen to carbon (O/C) atomic ratio of the PC polymers based from the XPS spectra with different treatment conditions. From Table 1, we can see that the O/C ratio of PC showed a large increase from 15.89 to 24.59 in UVC treatment condition with respect to the untreated condition, but not very big change in O/C ratio was noticed after UVA treatment. This indicates that more oxygen was present at the PC surface after UVC treatment, thus enabling a more hydrophilic surface. Maattanen et al. [19] also reported enhanced wettability of pigment-coated papers when they were treated with UVC irradiation.

Table 1. O/C ratio on polycarbonate surface for the untreated case and UV-treated cases at 365 nm (UVA) and 254 nm (UVC) at different treatment times.

UV treatment condition	Treatment time			
	Untreated	12 h	24 h	48 h
365 nm (UVA) → O/C ratio	15.89	18.95	18.26	17.12
254 nm (UVC) → O/C ratio	15.89	15.47	23.44	24.59

We further checked the surface properties by high magnification XPS and the results are shown in Fig. 4 and Table 2. The untreated and UV-treated PCs showed three species of C1s spectrum corresponding to C-C and C-H groups (285.0 eV), C-O-H groups (286.5 eV) and the very low intensity $\pi \rightarrow \pi^*$ interaction (shake up) (291.0 eV) [20]. However, the UVC-treatment showed an increase in C-O-H species (286.5 eV), created additional oxidized carbon-oxygen moieties (C=O at 287.6 eV, O-C=O at 288.8 eV) and caused a decrease in the $\pi \rightarrow \pi^*$ interaction peak (291.0 eV). The creation of C=O and O-C=O groups, which have hydrophilic property, is attributed to the breaking down of C-C and C-H groups due to the effect of UVC irradiation at high photon energy and oxygen in air [21]. Yaghoubi and Taghavinia [22] also reported the formation of functional groups on the surface of polycarbonate after treatment with atmospheric plasma and increased surface roughness, making the PC surface more hydrophilic.

Table 2. Percentage of species on polycarbonate surface for the untreated case and UV-treated cases at 365 nm (UVA) and 254 nm (UVC) based from XPS results at different treatment times.

	Treatment condition						
Species	Untreated	365 nm (UVA)			254 nm (UVC)		
	0 h	12 h	24 h	48 h	12 h	24 h	48 h
C-H, C-C (285.0° eV), %	75.61	73.3	74.43	70.82	75.01	58.26	57.1
C-O-H (286.5° eV), %	15.77	18.29	17.27	20.43	16.2	25.14	19.58
C=O (287.6° eV), %	-	-	-	-	-	8.6	8.84
O-C=O (289.0° eV), %	-	-	-	-	-	-	7.05
π-π^* (291.0° eV), %	8.62	8.41	8.30	8.75	8.79	8.0	7.43

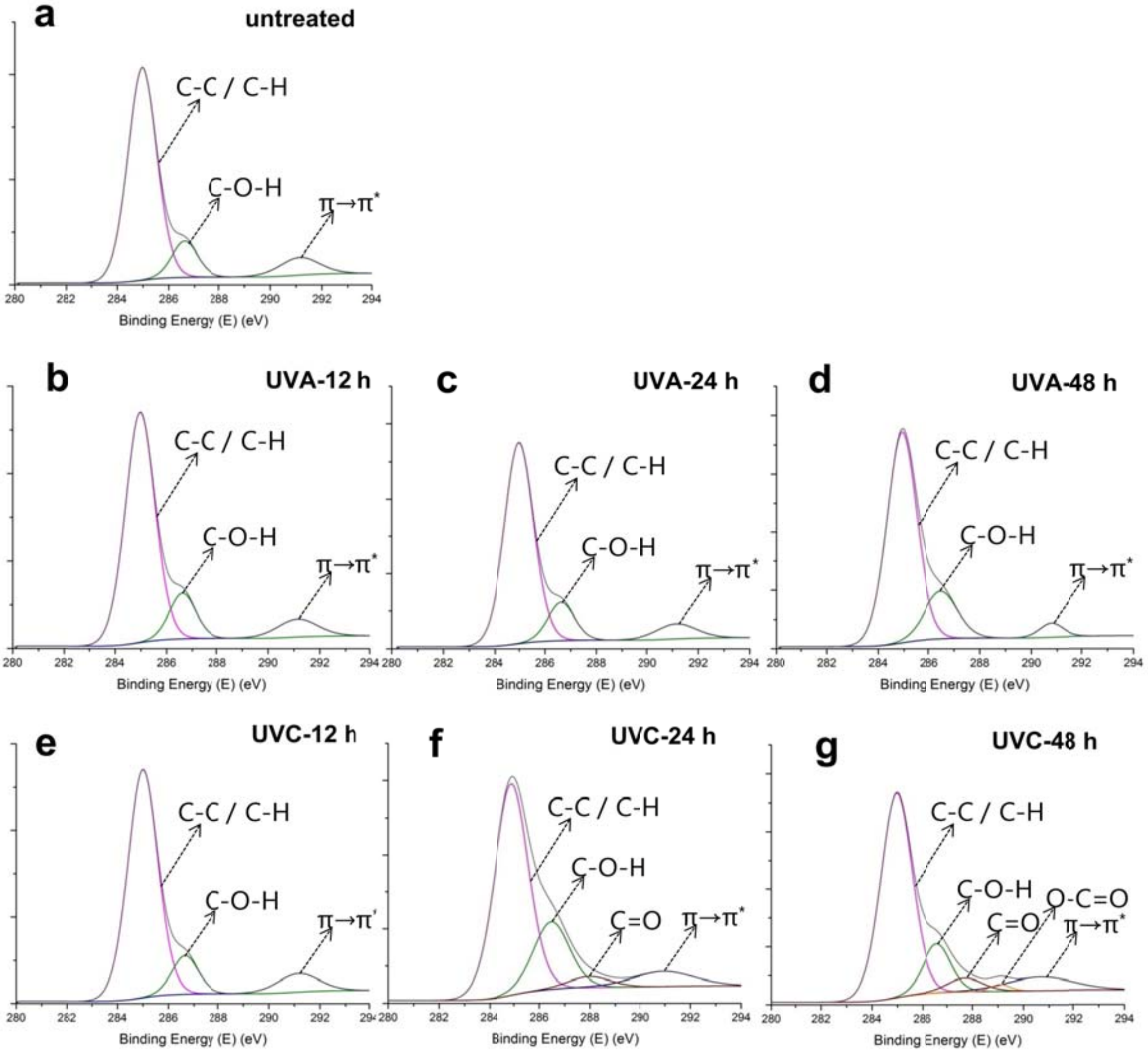

Fig. 4. C1s XPS spectrum of the surface of polycarbonate with respect to ultraviolet treatment conditions: (a) untreated, (b-d) UVA-treated (365 nm) and (e-g) UVC-treated for (b,e) 12h, (c,f) 24 h, and (d,g) 48 h.

Fig. 5 shows the FE-SEM images of (a) the untreated PC surface, (b) 48 h UVA-treated PC surface, and (c) 48 h UVC-treated PC surface. Here, we can see that the untreated PC showed generally smooth surface with some impurities. However, when UV was irradiated after 48 h, the impurities on PC were almost removed and a rough surface was produced for both UVA and UVC treatment; however, it can be observed that a much rougher surface was produced after UVC treatment. The UVC-treated surface showed protuberances and caves, which increase the surface roughness and consequently increased the surface energy, making the surface more hydrophilic. As already checked by XPS, this increased wettability is attributed to the oxidation and the chemical etching leading to increased surface roughness from UVC irradiation (i.e., at 254 nm).

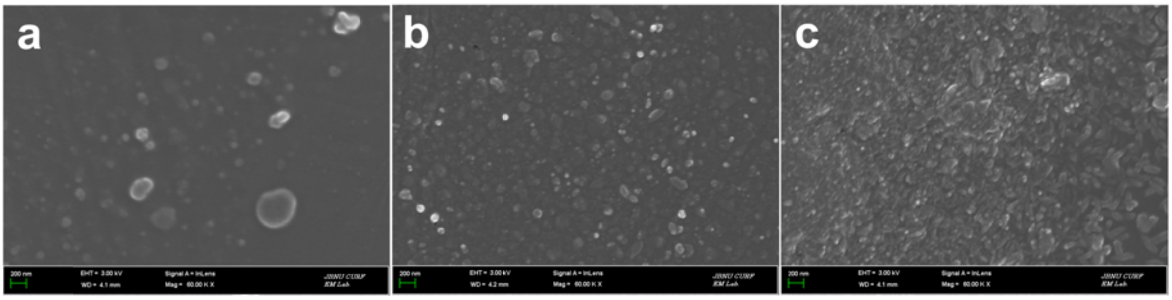

Fig. 5. FE-SEM images of (a) the untreated PC surface, (b) 48 h UVA-treated PC surface (365 nm) and (c) 48 h UVC-treated PC surface (254 nm).

Single-lap shear tests were conducted to check the effect of UV treatment on the adhesive joint strength (adhesion) of two polycarbonate surfaces. Based from our CA results, only the UVC treatment have shown large effect on the wettability of PC surface, thus we only tested for the single-lap shear strength of the UVC-treated PCs and the result is shown in Fig. 6. The UVC-treated PCs showed better adhesive shear strength compared to the untreated case. The UVC treatment at 6 h, 12 h, 24 h, and 48 h increased the shear strength of 2.18 MPa from the untreated case to 2.7 MPa, 3.16 MPa, 3.23. MPa, and 3.55 MPa, respectively. The results here relate well with the CA results, where increasing CA gave better adhesive strength based from single-lap shear test. Furthermore, the increased roughness of the UVC-treated PC surface could have also provided larger surface area for adhesion of adhesives, thus resulting to higher shear strength. The optimum result in the present study was achieved at a UVC-treatment of 48 h.

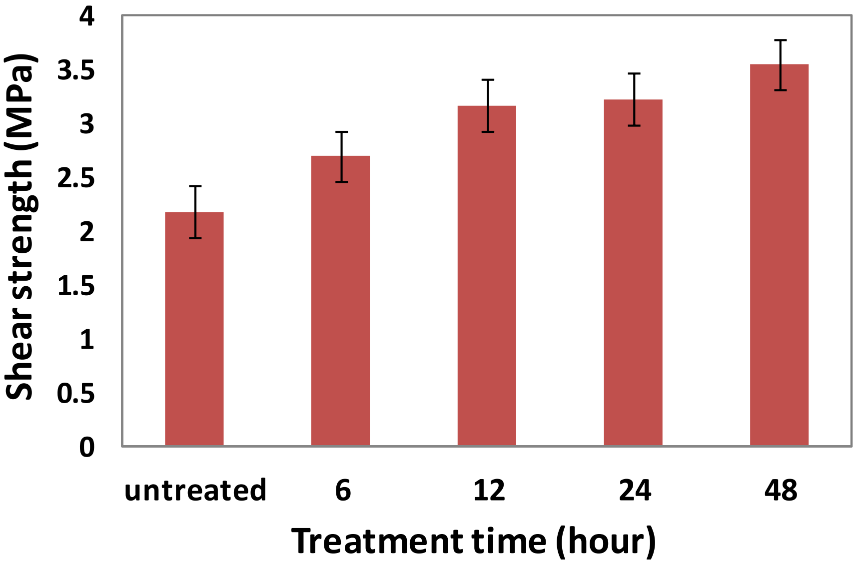

Fig. 6. Shear strength of polycarbonate adhesive joint with respect to UVC surface treatment time.

4. Conclusions

Here, we treated the polycarbonate (PC) surface with ultraviolet (UV) light at two different wavelengths, i.e., UVA (~365 nm) and UVC (254 nm) to investigate their effect on the wettability and adhesion of PC surfaces. The UV-treatment time was varied from 0 h to 48 h. The UVA treatment showed not much change in water and glycerol contact angle (CA) measurements even after 48 h, however, the UVC treatment showed a decreasing trend in CA values with the increase in UVC-treatment time, achieving up to 23% reduction in CA values after 48 h. The increase in hydrophilicity and better wettability behavior of UVC-treated PC surface compared to both untreated and UVA-treated surface are attributed to the higher O/C ratio and the formation of C=O (287.6° eV) and O-C=O (289.0° eV) groups at the PC surface after UVC treatment. Morphological characterization also showed rougher surface for UVC treatment compared to both untreated and UVA-treated PC surface. The improved hydrophilicity and higher roughness of the UVC-treated PC resulted to a 63% increase in shear strength compared to the untreated PC. Thus, in this study, we found that UVC treatment could enhance the wettability and adhesion of PCs.

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