

Surface Hydrophilic Treatment of Polyester Films via UV irradiation

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Abstract: Continuous surface treatment of polyester films was carried out to improve hydrophilicity and wettability by the irradiation of UV light. The effect of UV energy on the surface energy of the irradiated films using electrodeless UV bulb(H-type) was investigated by measuring contact angles of three different test liquids. ATR analysis showed that the ester bonds was broken and some new groups were produced such as carboxylic acid, phenolic hydroxy, and other esters, implying that ester bonds of polyester was responsible for the observed photo-oxidation effect.

Introduction

Poly(ethyleneterephthalate)(PET) has been widely used as apparel and technical textile materials in the forms of fibers, films and plastics due to excellent mechanical and physical properties. Also poly(trimethyleneterephthalate)(PTT) has been recently introduced as a new promising polyester fiber due to its good resiliency, softness, and high stretchability comparable to spandex-containing fabrics due to three dimensional spring-like conformation of PTT chains in crystal structure.¹ UV treatment has been used for surface modification method for synthetic and natural polymers to increase wettability to water, surface energy, dyeability to cationic dyes, as well as UV curable chemicals finishes, etc.²⁻³ Some polymer surfaces such as PE, PP, PS, PEEK, PET, PBT, etc. have been treated to impart special surface properties such as chemical composition, hydrophilicity, printability, bondability, roughness, electrical conductivity, etc. by wet and dry process including flame, corona discharge, plasma, and UV.⁴⁻⁵ Recently UV irradiation treatment became increasingly popular and practical because commercial introduction of powerful electrodeless mercury lamps as well as excimer lamps, which has several advantages over other well-known surface modification techniques: continuous operation, no vacuum and heat requirement, easy treatment on large 3D shape objects, capable to create patterned treatment by area-selective irradiation. The UV light shorter than 340nm emitted from UV bulb together with ozone is capable of breaking down the covalent bonds of C-C, C-O, and C-H present in many

organic materials, which can cause photoscission and photooxidation of polyester films. Molecular oxygen absorbs UV light emission and produces ozone with a reaction of the molecular oxygen and ground-state oxygen, and ozone absorption of 253.7 nm light results in singlet atomic oxygen production. This study is to increase hydrophilicity and surface energy of polyester films via continuous UV irradiation.

Experimental

Materials

Bi-axially oriented PET(100 μm) and PTT(20 μm) were used for untreated polyester films.

Continuous UV treatment

UV irradiation was carried out using an electrodeless UV irradiator(Fusion UV System Ltd) enclosing H- and D-bulb of 240W/cm intensity and UV energy was adjusted by repeated irradiation of the samples at the constant conveyor speed of 10m/min. To minimize IR heating of the polyester, air cooling method was adopted. Spectral irradiance of H- and D-bulb was shown in *Figure 1*.

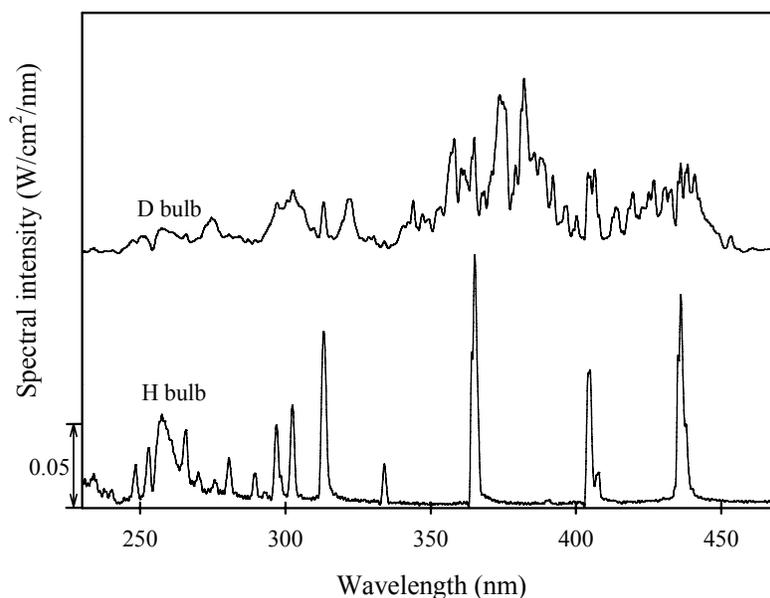


Figure 1 Spectral irradiance of H- and D-bulbs.

Contact angle and surface energy

Contact angle of the polyester films were measured by a sessile drop method using a static goniometer(Phoenix300, AhTech) attached with a CCD camera. Three test liquids of deionized water, diiodomethane and glycerin were used for the contact angle measurement. Five measurements under standard condition(20 \square , 65% RH) were averaged. Surface energy of the films were calculated

according to Owens *etal* 's method. Surface energy of a solid surface(γ_s) is a sum of a polar component(γ_s^p) and a nonpolar component(γ_s^d): $\gamma_s = \gamma_s^d + \gamma_s^p$. When a liquid wets a solid surface, work of adhesion is that $W_a = \gamma_s + \gamma_L - \gamma_{SL}$, where γ_L and γ_{SL} are interfacial energies of liquid/gas and solid/liquid boundaries respectively. Using Young's equation($\gamma_L \cos\theta = \gamma_s - \gamma_{SL}$), the equation mention above can be rearranged into the following equation: $\gamma_L(1 + \cos\theta) = 2(\gamma_s^d \gamma_L^d)^{1/2} + 2(\gamma_s^p \gamma_L^p)^{1/2}$. Therefore the surface energy of a solid surface can be calculated by measuring contact angles of two test liquids of known nonpolar and polar components.

ATR and ESCA analysis

Magna-IR spectrometer (Nicolet Instrument Corp., USA) with ATR accessory (45° ZnSe crystal) was used to detect the micron-scale chemical change of surface functional groups on films. Subtracted ATR spectra were obtained by subtracting absorbance of treated films with that of the untreated. X-ray photoelectron spectrometer (MT 500/1, VG Microtech) was used for quantify chemical composition change of the films at the nanometer scale.

Result and Discussion

Surface energy of PET films

Contact angles of three test liquids on UV-irradiated PET films were shown in Figure 2. The continuous UV irradiation decreased water contact angle proportionally with increasing UV energy level, implying significant photo-oxidation of the polymer surface. The surface energies of the treated films were calculated (*Table 1*). Total surface energy of the PET film increased with UV irradiation from 50.6mJ/m² to 61.1mJ/m². While the nonpolar component decreased from 39.3mJ/m² to 32.8mJ/m² with increasing UV energy, polar component increased more significantly from 11.3mJ/m² to 28.3mJ/m². The concomitant decrease in nonpolar component and increase in polar component suggested that increased hydrophilicity may be due to formation many photo-oxidated products from nonpolar groups such as ethylene and phenylene groups in repeating unit by the UV irradiation.

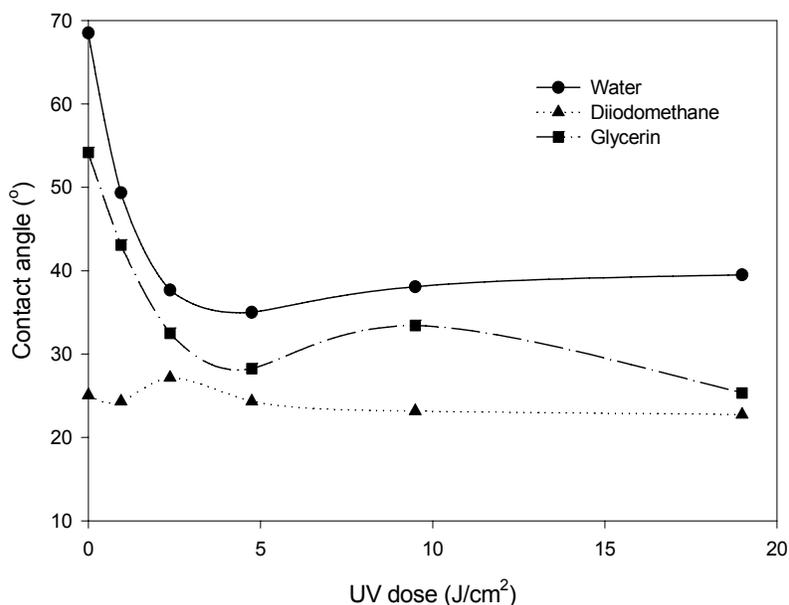


Figure 2 Effect of UV energy on contact angles of UV-irradiated PET films.

Table 1 Surface energy of UV/O₃ treated PET films.

UV dose (J/cm ²)	Surface energy(mJ/m ²)		
	γ^d	γ^p	γ^{TOT}
Untreated	39.3	11.3	50.6
0.95	36.5	18.9	55.3
2.37	33.9	25.8	59.7
4.75	33.7	26.9	60.7
9.49	32.8	30.6	63.3
18.99	32.8	28.3	61.1

ATR analysis of PET films

Figure 3 shows the subtracted ATR spectra of untreated and irradiated PET films. For untreated PET film, main chain ester of vibrates at 1716, 1247, 1101cm⁻¹ indicating stretching of C=O, C-O-C, O-C-C groups. In case of UV-irradiated sample the ester groups disappear and new bands appears which can be related with carboxy acid, phenolic hydroxyl, vinyl and other ester groups generated by photo-scission and photo-oxidation.

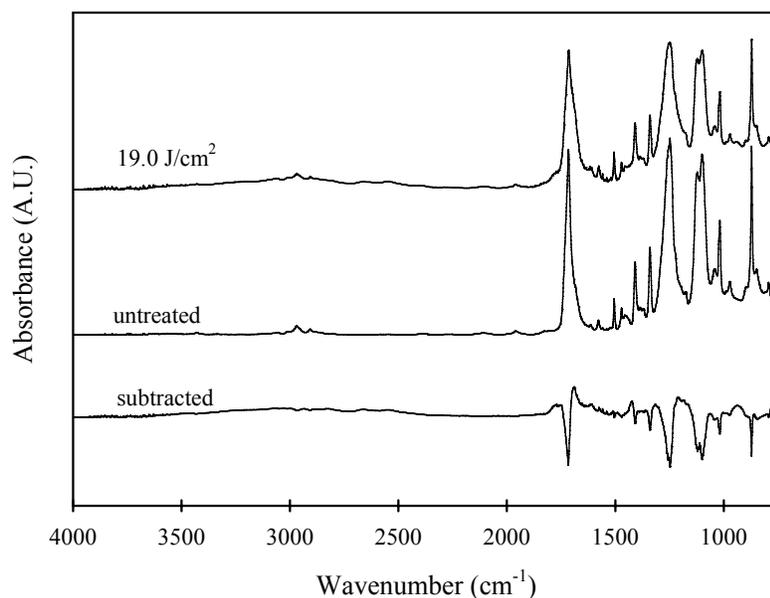


Figure 3 Subtracted ATR spectra of UV irradiated PET films.

ESCA analysis of PTT films

Figure 4 and 5 shows the C_{1s} spectra of untreated and treated PTT films. Change in chemical composition of surface-modified PTT surface at nanometer-scale level was examined by ESCA. As expected, increased hydrophilicity of the UV-irradiated polyester film was also substantiated by increased O_{1s}/C_{1s} ratio, which represents abundant photo-oxidized byproducts on the surface such as $C=O$, $HO-C=O$, OH , etc.

Conclusions

Surface of polyester films was more wettable to water after continuous UV irradiation. Surface energy of the treated film increased with higher UV energy and increase of polar component was more significant than the decrease in nonpolar component. ATR and ESCA analysis verified the increased hydrophilicity resulted from photo-scission of the main chain ester groups and successive photo-oxidation of the polyester films. Simple UV irradiation may be employed in the printing, coating, and other industrial fields as a viable alternative as well as other surface treatments.

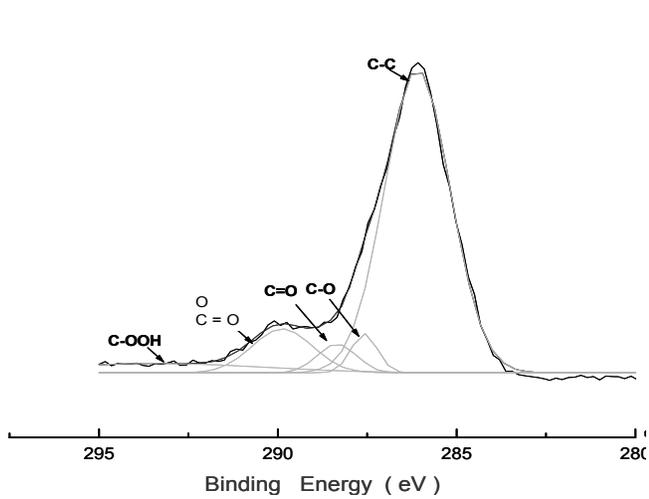


Figure 4 C_{1s} spectra of untreated PTT films.

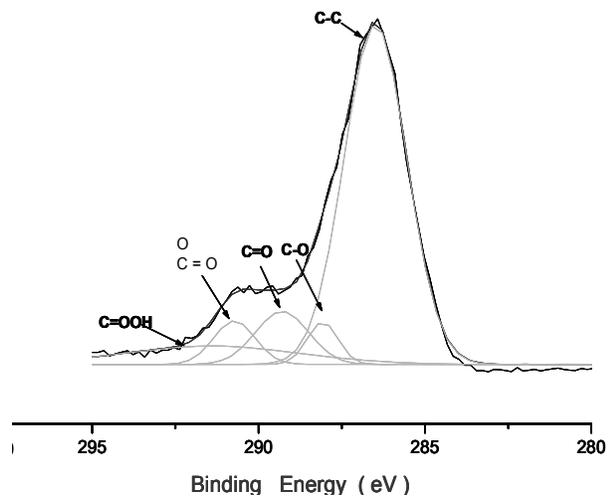


Figure 5 C_{1s} spectra of treated PTT films.

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