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〈Research Paper〉

Surface Modification of Cellulose Acetate using UV/O_3 Irradiation

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Abstract— Upon UV/O_3 irradiation cellulose acetate (CA) films showed modified surface properties such as increased hydrophilicity and surface roughness as well as increased dyeability to cationic dyes. UV treatment induced photoscission of acetyl groups in the main chain of CA resulting in decreased degree of substitution from 2.2 to 1.3. The slight decreases in reflectance and transmittance were caused by remarkably increased nano-scale surface roughness of the CA surface as much as 20-fold, which can destructively interfere with visible lights of wavelength lower than 500nm. Water contact angle decreased from 54° to 14° with increasing UV energy. Surface energy also increased slightly. The surface energy change was attributed to significant contribution of polar component rather than nonpolar component indicating surface photooxidation of CA film. The increased dyeability to cationic dyes in terms of both K/S and %E may be due to photochemically introduced anionic and dipolar dyeing sites on the film surfaces.

Keywords: *Cellulose acetate, UV/O_3 irradiation, photooxidation, nano roughness, dyeability*

1. Introduction

Cellulose acetates(CA) in the forms of wovens, knits and nonwovens are used in various textile applications. These include women's linings, woven fashion, woven satins, circular knits, men's linings, tricot knits, woven velvet, home furnishings, medical and ribbons[1)]. CA is also an important material for industrial application fields in filter tow for cigarette, anti-reflection film for LCD polarizing plate, photographic film, osmotic membrane, security glass of automobiles, and electrical insulator film of condensers, etc. In spite of widespread usage of CA materials, studies on biodegradation and recycling of CA have been rarely reported[2-3)]. Among the related studies, effect of alkaline and cellulase treatments on mechanical strength and surface morphology of CA fabrics have been investigated. While alkaline treatment increased the drapability of CA fabrics, the cellulase treatment increased initially but decreased gradually with treatment time. The alkaline treatment improved the dyeability of CA fabrics to reactive dyes and deteriorated dyeability to disperse dyes. While the cellulase treatment lowered dyeability to both dyes.

Synthetic fibers often require high degree of multi-functional properties as well as inherent polymer properties. These include wettability, hydrophilicity, dye adsorption, antistaticity, antimicrobial property corresponding to increasing application fields, which closely related surface property of fiber. Therefore various surface modification methods are in use to change inert polymer surfaces. UV/O_3 irradiation has become increasingly popular due to increasing lamp intensity and compact irradiator comparable to corona and plasma treatment. Ultraviolet and ozone can break down and oxidize covalent bonds of organic molecules. In the case of hydrophobic fibers,

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*Corresponding author. Tel: +82-54-478-7715; Fax: +82-54-478-7710; e-mail: jh.jang@kumoh.ac.kr it is well known that UV irradiation increase fiber adhesion to high energy surface by increasing surface energy due to introduced photooxidized polar groups[4]. The continuous UV treatment mainly affect properties of surface region without influencing bulk properties and the choice of lamp and optical geometry can influence surface modification. Several surface modification studies by UV irradiation have been carried out including adhesion improvement of PET and PP[5], spectral irradiation influence on modification of PET film[6], cationic dyeable treatment of PET and PTT fabrics[7], effect of UV treatment on physical properties of the PET fabrics[8], dyeability change of PTT film[9] and nano-roughening and color deepening of PET fabrics[10]. Also UV curing of UV active chemicals on textiles have been investigated to impart functional property such as environmentally-friendly salt-free dyeing of cotton by improving dyeability via UV curing of cationic monomers[11], union dyeing of cationized cotton/wool blend fabrics[12] and preferential face coating of PET knit for water and oil repellent finish[13].

This study is to investigate effects of UV/O_3 treatment on surface properties of CA films such as contact angle, surface roughness, reflectance and transmittance, degree of substitution(DS), and to assess cationic dyeability of the irradiated CA films.

2. Experimental

2.1. Materials and chemicals

CA films were provided by EM Science of which degree of acetylation and degree of substitution were 36.6% and 2.17, respectively. Cationic dyes donated by Rifa Co. were Rifa Cationic Blue GRL 300(C.I. Basic Blue 41) and Rifa Cationic Pink FG(C.I. Basic Red 13) as shown in Scheme 1.

2.2. UV/O_3 irradiation

UVO-cleaner(Jelight Co., USA) with a maximum lamp intensity of 24mW/cm^2 was used to irradiate CA samples. Hg lamp was chosen to maximize surface modification effect due to more intense spectrum in shorter wavelength region compared with doped lamps. UV energy was adjusted to find optimal surface treatment condition for the samples by changing UV irradiation time.

2.3. Contact angles measurement and surface energy calculation

Static goniometer attached with a CCD camera-(Phoenix 300, Ahtech) was used to measure contact angles of water and diiodomethane on UV irradiated samples by sessil drop method under constant temperature and humidity condition-(25°C, 65%RH). Five measurements or more were averaged to obtain contact angles on the samples. Surface energy was calculated using the contact angles of the two liquids according to the method of Owens Wendt *et al*[14-15]. Surface energy of solid surface is a sum of polar and nonpolar components. When a liquid wets on a solid surface Young' equation and work of adhesion(W_a) are as follows:

$$\gamma_L(\cos\theta) = \gamma_S - \gamma_{SL} \qquad (1)$$

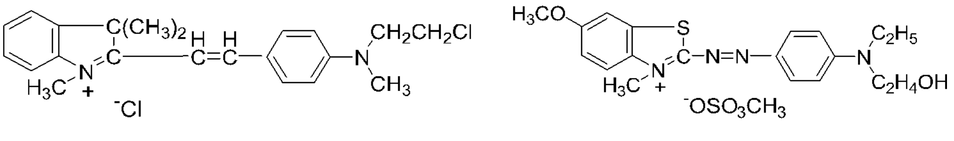
$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \qquad (2)$$

where γ_S, γ_L and γ_{SL} are interfacial energies of solid/air, liquid/air and solid/liquid interfaces respectively. Therefore surface energy of a solid surface can be calculated by the measured contact angles(θ) of two liquids as the following:

$$\gamma_L(1+\cos\theta) = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^p\gamma_L^p)^{1/2} \qquad (3)$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \qquad (4)$$

where γ_S^d and γ_S^p are dispersive and polar components of solid surface energy respectively.



C.I. Basic Blue 41 C.I. Basic Red 13

Scheme 1. Molecular structures of cationic dyes.

2.4. Instrumental analysis of modified CA surface

Reflectance and transmittance of treated CA films with different UV energies was measured with a Coloreye 3100 reflectance spectrophotometer(Gretag Macbeth) and a UV/VIS spectrophotometer(Agilent Technologies) respectively. ATR analysis was carried out using a Jasco FT-IR 300E spectrophotometer on the irradiated side of films attached with a KRS5 crystal. The subtracted spectra were obtained by subtracting absorbance of treated samples by that of the untreated after standardization. Nano-scale surface morphology was imaged using a Scanning probe microscopy (Auto Probe M5, Thermo Microscopes) in a noncontact mode.

2.5. Dyeability assessment

CA films treated with different UV energies were colored using an IR dyeing testing machine with two cationic dyes of C.I. Basic Blue 41 and C.I. Basic Red 13 at 3% shade and liquor to goods ratio of 50:1 under pH 5.5. After dyeing, the dyed fabrics were thoroughly rinsed with running water and dried. Evaluation of color yield(K/S) at the maximum absorption wavelength and % exhaustion based on absorbance of remaining dye liquor were made with the reflectance spectrophotometer and the UV/VIS spectrophotometer respectively.

2.6. Degree of acetylation and degree of substitution

Degree of acetylation(DA) were measured according to the method described in ASTM D-871-72 Method-B(heterogeneous saponification method). Degree of substitution(DS) of the sample was calculated from the DA values.

3. Results and Discussion

3.1. Effect on reflectance and transmittance

UV energy of 340nm wavelength or less can break down covalent bonds of C-C and C-O in CA films and the ozone generated under UV light oxidizes the polymer surface. The UV/O_3 treatment effect on reflectance change of the CA films was shown in Fig. 1 and 2. UV irradiation caused reflectance of the treated CA films to decrease, which can be seen particularly at the wavelength region below than 500㎚. With increasing UV energy, the reflectance proportionally decreased and slight yellowing was observed. The decrease in reflectance may be due to destructive interference of roughened surface caused by photooxidation of CA under UV irradiation. CA film is known for highly transparent to whole visible spectrum and is applied to optical films for polarizing films. Fig. 3 shows visible transmittances of CA films with increasing UV energy.

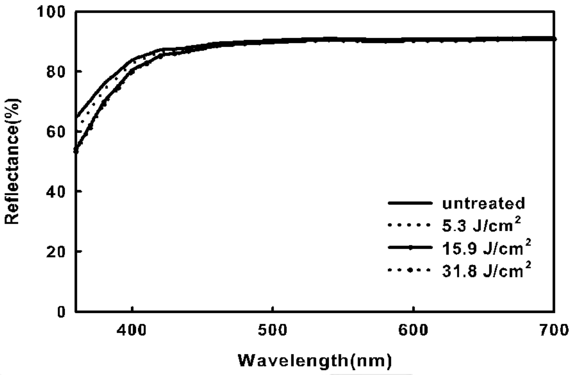


Fig. 1. Reflectance of UV-irradiated CA films.

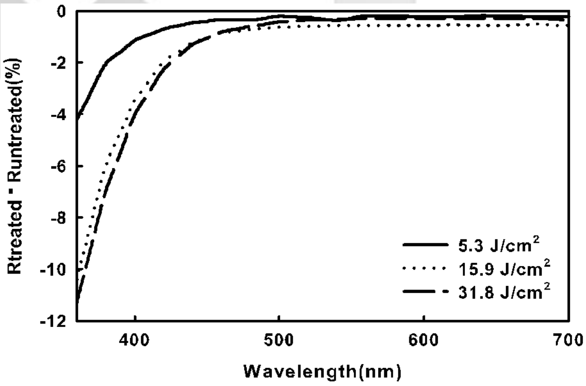


Fig. 2. Subtracted reflectance of UV-irradiated CA films.

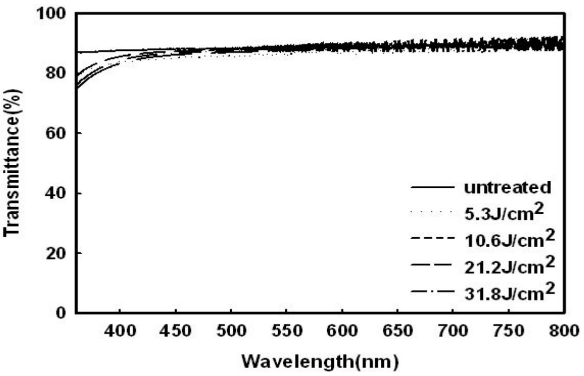


Fig. 3. Transmittance of UV-irradiated CA films.

The reduced transmittance appeared at 500nm or less comparable to the decreased reflectance, implying that observed transmittance may originate from the disappearance of the interfered light of lower wavelength in particular by nanoscale roughness of the CA surface, which will be discussed later.

3.2 Hydrophilicity and surface energy

Surface hydrophilic property of the treated CA film was evaluated by the measurement of contact angles on irradiated CA surfaces using water and diiodomethane as test liquids(Fig. 4).

While contact angle of nonpolar diiodomethane increased slightly with increasing UV dose, contact angle of water decreased significantly from 54° to 14°. From the measured contact angles surface energies of the irradiated CA were calculated based on the method proposed by Owens *et al.* as shown in Fig. 5. The surface photooxidation by UV/O_3 increased total surface energy of CA film where polar component increased remarkably and nonpolar componenet decreased at a less extent compared with polar component with increased UV irradiation.

Therefore the increased surface energy resulted from the increase in polar component rather than decrease in nonpolar component suggesting that photo-scission of cellulose acetate linkage produced both disappearance of nonpolar groups and generation of oxidized products: e.g. conversion of nonpolar C-C to polar C=O and C-O.

3.3 ATR analysis and degree of acetylation

Surface chemical composition of the irradiated CA film was estimated by ATR analysis(Fig. 6 and 7). Upon UV irradiation, stretching vibration bands such as C=O, C-C-O, O-C-C located at 1732, 1215, 1024cm^{-1} of ester groups in CA diminished respectively. Also bending peak of methyl($-CH_3$) at 1364cm^{-1} in acetate group decreased simultaneously.

Therefore the imparted hydrophilic property ofCA film is proved to be the elimination of acetyl

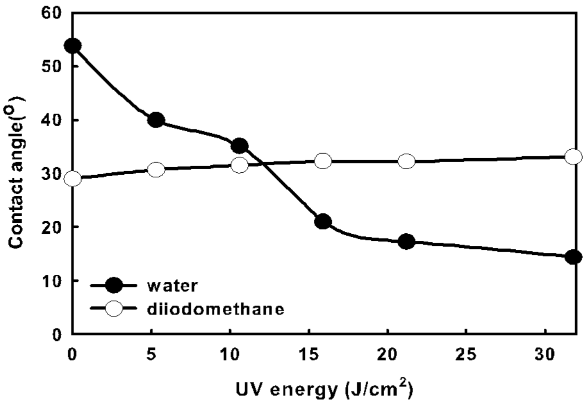


Fig. 4. Contact angles of UV-irradiated CA films.

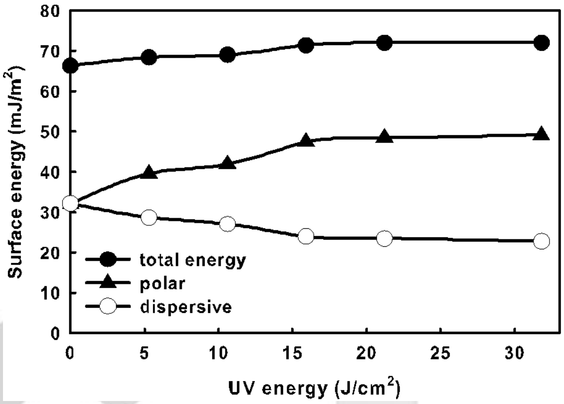


Fig. 5. Surface energy of UV-irradiated CA films.

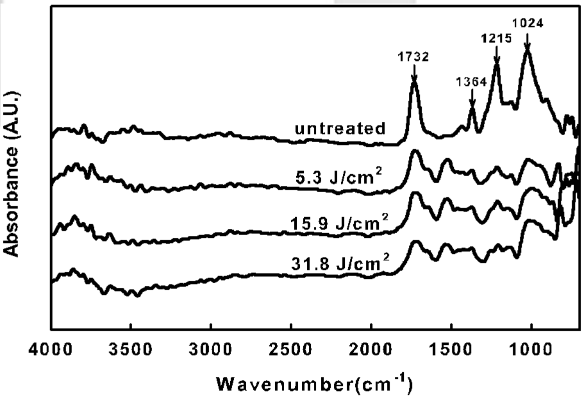


Fig. 6. ATR spectra of UV-irradiated CA films.

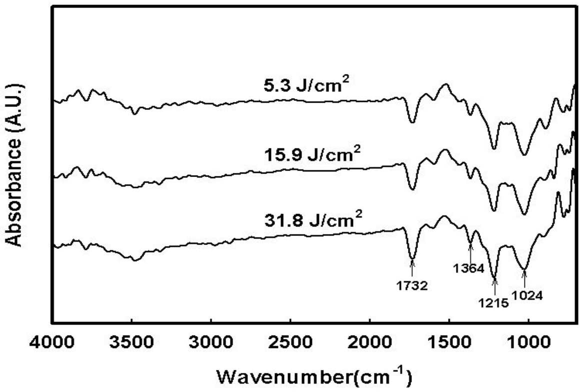


Fig. 7. Subtracted ATR spectra of UV-irradiated CA films.

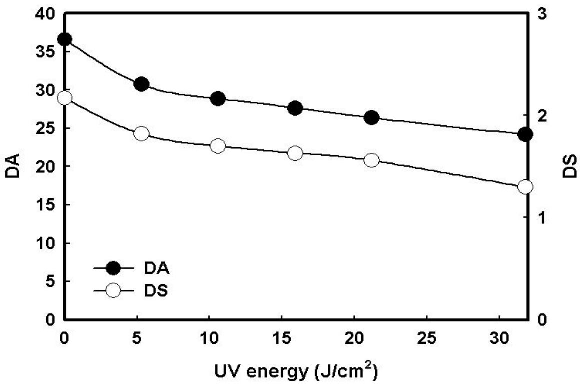


Fig. 8. DA(degree of acetylation) and DS(degree of substitution) of UV-irradiated CA films.

groups(CH_3COO-) in CA by UV irradiation. The increasing peaks located at 1520cm^{-1} may be attributed to the stretching of nonpolar C=C groups.

Although vibration of photooxidized products was not observed in IR spectrum, significant photo-oxidation may occur at outermost surface. The photoscission of acetyl groups as indicated in ATR analysis was again confirmed by DA measurement of the irradiated CA films(Fig. 8). While degree of acetylation(DA) and degree of substitution(DS) of untreated CA film were 36.6% and 2.17 respectively. The irradiated samples showed increased DA and DS upto 24.2% and 1.3 with increasing UV energy. This suggests that surface cellulose diacetate was changed to cellulose monoacetate or even cellulose.

3.4. Surface roughness

Effect of UV treatement on surface roughening which caused destructive interference of short visible spectrum in the treated samples as indicated in Fig. 2 was investigated by AFM analysis as shown in Fig. 9 and Table 1. With increasing UV energy upto 31.8J/cm^2, remarkably ca. 20-fold increase in surface roughness values of treated film was observed e.g. R_{pv} from 6.3 nm to 111.9 nm. This indicates that UV irradiation break down and oxidize surface layer of CA film inhomogeneously depending on the crystalline nature of the surface. In other words, UV etching effect concentrated more on amorphous-rich region compared to more crystalline region resulting in peak and valley morphology.

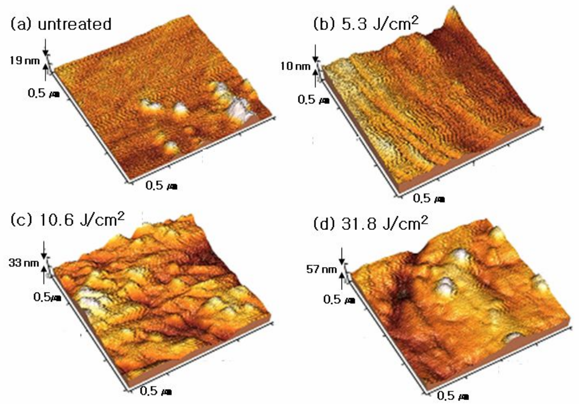


Fig. 9. AFM image of UV-irradiated CA films.

Table 1. Roughness parameters of untreated and treated CA films

Roughness UV energy	Average (R_a)	RMS (R_q)	Peak-to-valley (R_{pv})
untreated	0.8	1.1	6.3
5.3 J/cm^2	3.9	4.6	14.2
10.6 J/cm^2	5.1	6.9	34.0
21.2 J/cm^2	10.2	12.5	50.8
31.8 J/cm^2	19.1	25.4	111.9

3.5 Cationic dyeability

The effect of surface treatment on dyeability of treated CA film was assessed with two cationic dyes of C.I. Basic Blue 41 and C.I. Basic Red 13 in Fig. 10 and 11. The irradiated CA exhibited excellent increases in both K/S and % Exhaustion. The dyeability increase was proportional to UV energy indicating electrostatic interaction of the dyes. It also introduced anionic surface coupled with stronger polar interaction of CA films because of the more polar groups, presumably such as carboxylic acid, brought about by higher degree

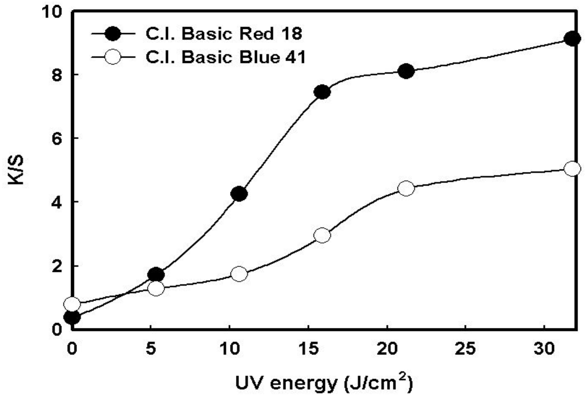


Fig. 10. K/S of CA films dyed with basic dyes.

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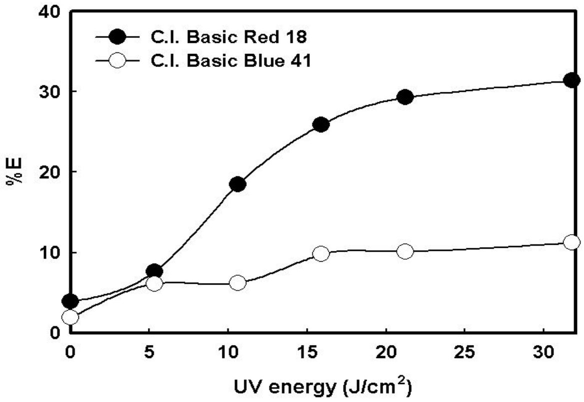

Fig. 11. Exhaustion of CA films dyed with basic dyes.

of photooxidation and photoscission. And the red dye is more sensitive to the anionic dyeing sites produced by the surface modification compared with the blue dye. Also the higher exhaustion of irradiated films may correspond to the higher concentration of the anionic dyeing sites on the CA surface of different surface polarity without significantly influencing bulk property.

4. Conclusions

Surface of CA films was modified with UV/O_3 irradiation and the changed surface properties depending on UV energy were characterized in terms of optical property, surface chemical composition, contact angle and surface energy, nano-scale roughness and dyeability to cationic dyes. Following conclusions are made based on the investigation. UV treatment resulted in scission and oxidation of acetyl groups in the main chain of CA resulting in decreased degree of acetylation.

The treatment slightly decreased reflectance and transmittance by producing nanoscale roughened surfaces, which destructively interfere with short wavelength region of visible spectrum. The enhanced hydrophilic property such as decreased water contact angle and increased surface energy were observed. This resulted from more significant contribution of increased polar component rather than that of decreased nonpolar component. The increased dyeability of the modified CA film to cationic dyes with increasing UV energy may be attributed from electrostatic and dipolar interaction between cationic dyes and anionic dyeing sites in the film surface of more polar nature.

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