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Nano roughening of PET and PTT fabrics via continuous UV/O_3 irradiation

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Abstract

Continuous surface treatment of PET and PTT fabrics was carried out to introduce nanoscale surface roughness using an electrodeless UV bulb for different periods of time. Reflectance of the irradiated fabrics decreased in the low wavelength regions of visible light, especially at 400 nm. The surface roughness of the irradiated fabrics was investigated to verify the scattering and destructive interference of visible light using SEM and AFM analyses. AFM images indicated that the treatment developed the nano-sized roughness on the polyester surfaces. The surface roughness increased by two-fold from 58 nm to 122 nm in terms of peak–valley roughness, which can interfere destructively the incident light of as high as 488 nm wavelength in the visible spectrum. The dyeability of the surface modified polyester fabrics to disperse dyes was similar to that of untreated fabrics. However, irradiation both after and before dyeing with black disperse dyes significantly decreased lightness of the dyed fabrics up to 8% with increasing treatment due to the enhanced surface roughness. Surprisingly color fastness of the dyed polyester fabrics was excellent because of surface-limited treatment of the polyester fabrics.

Keywords: PET; PTT; UV irradiation; Nano roughening; Disperse dyes; Color deepening

1. Introduction

Poly(ethyleneterephthalate) (PET) has been widely used as apparel and technical textile materials in the form of fibers, films and plastics due to excellent mechanical and physical properties. Recently poly(trimethyleneterephthalate) (PTT) has been introduced as a new promising polyester fiber due to its good resiliency, softness, and high stretchability comparable to spandex-containing fabrics due to 3D spring-like conformation of PTT chains in crystal structure [1]. It has been known that PTT also has superior properties such as low temperature dyeability to disperse dyes under atmospheric pressure and soft handle without alkaline treatment, etc. However, PTT has lower thermal stability than PET resulting in high heat shrinkage and processing difficulties in several steps including fiber spinning, dyeing and heat setting. However, it is hard to achieve deep and clear shade of color, particularly in polyester microfibers, due to large amount of reflecting light resulting from high refractive index (RI), flat surface, limited dyeability to other dyes of high extinction coefficient, etc. [2]. Several methods have been pursued to increase clarity and depth of shade in PET fabrics including cation dyeable polyester, blending

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with brightly dyeable cellulose acetate, decreasing surface reflectance by either coating of low RI synthetic resin or surface roughening treatments [3,4]. According to Fresnel's equation, PET (RI, 1.725) has surface reflectance of 7.1% at the interface of air and the polymer. Fluorocarbon or silicone resins are commercially applied for the non-reflective coating of PET. In order to minimize reflectance in visible wavelength region, it is required to introduce non-reflective coating of odd multiple thickness of 76–156 nm with a resin having low RI of about 1.313, where destructive interference can readily occur. However, it is difficult to adjust coating thickness to the specified range and to achieve appropriate durability of the coating during laundering [5–8]. Another method to decrease surface reflectance is to increase scattering and destructive interference either by roughening the PET surface to nanoscale using physico-chemical surface treatments, including plasma etching, sputter etching, etc., or by alkaline removal of embedded inorganic particles to form microcraters [9–12]. UV/O_3 treatment has been used for surface modification method for synthetic and natural polymers to increase wettability with water, surface energy, dyeability to cationic dyes, as well as UV curable chemical finishes such as wrinkle resistant and durable press finish, shrinkproofing treatment, pleat insertion, generation of patterned dyeing effect, etc. [13–17]. Recently, UV/O_3 treatment has become increasingly popular and practical because commercial introduction of powerful electrodeless mercury lamps as well as excimer lamps, has several advantages over other well-known surface modification techniques such as continuous operation, no vacuum and heat requirement, easy treatment on large 3D shaped objects, capable to create patterned treatment by area-selective irradiation, etc. The UV light shorter than 340 nm 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 PTT film. 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. 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. [18–21]. In addition, the UV/O_3 treatment may be beneficial in avoiding harsh handle and deteriorated elastic property of PTT fabrics caused by rapid recrystallization upon heating. This study is to generate nanoscale roughness on PET and PTT fabrics via UV/O_3 irradiation and to impart deep coloring effect of the irradiated polyester fabrics when dyed with black disperse dyes.

2. Experimental

2.1. Materials

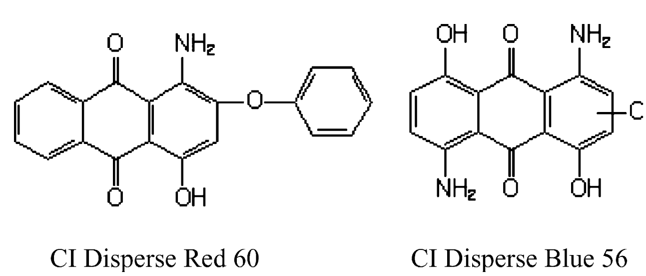
Scoured PET and PTT fabrics were a twill weave (190 g/m^2) and a knitted fabric (90 g/m^2), respectively. Biaxially drawn PET film (SKC) of 100 μm in thickness was used for evaluation of surface roughness. Four kinds of disperse dyes were used including Foron Black RD-BRE 300, Foron Black RD-3GE 300, Foron Br. Red E-2BL (C.I. Disperse Red 60), Foron Blue E-BL 150 (C.I. Disperse Blue 56) (Scheme 1) as supplied by Clariant. Acetic acid, NaOH and $Na_2S_2O_4$ were used for pH adjustment and reduction clearing.

2.2. Continuous UV/O_3 irradiation and surface analysis

UV irradiation was carried out using an electrodeless UV irradiator (Fusion UV System Ltd) enclosing an H-bulb of 240 W/cm intensity and UV dose was adjusted by repeated treatment of the samples at constant conveyor speed of 10 m/min. Micro-scale roughness of the treated surface was observed by a scanning electron microscope (SEM S-2400, Hitach), and nanoscale roughness was assessed by an atomic force microscope (Auto Probe M5, Thermo Microscopes Co.) in non-contact mode on 10 μm × 10 μm area. Roughness values were calculated by averaging over five sample areas.

2.3. Assessment of reflectance and dyeing

All the dyeing was carried out at pH 5.5. Polyester fabrics were dyed in a laboratory-scale dyeing machine (Daelim Engineering). Dyeing liquor of LR 50:1 was kept at 60 °C for 10 min and the temperature was increased until 130 °C and maintained for 40 min. After dyeing, surface-deposited dyes in the dyed samples were cleared reductively at 60 °C for 20 min using 2 g/L of NaOH and $Na_2S_2O_4$, respectively. Subsequently the samples were rinsed with tap water. C.I. Disperse Red 60 and C.I. Disperse Blue 56 were dyes with 2% owf shade, Foron Black RD-BRE 300 and Foron Black RD-3GE 300 were dyes with 6% owf. A UV/VIS



Scheme 1. Molecular structures of disperse dyes used in the study.

spectrophotometer (Kontron Instruments) was used for percent exhaustion by absorbance measurement of dyeing liquor at the maximum absorption wavelength (λ_{max}) before and after the dyeing. For measurement of color before and after dyeing, reflectance and K/S at λ_{max} were measured with a reflectance spectrophotometer (Gretag Macbeth) using an illuminant D_{65} and 10° observer. Color fastness to laundering and rubbing was tested using a Launder-O-meter (Daelim Engineering) and Crock meter (Korea Science Co., Ltd) according to ISO 105-CO2 and ISO 105-X12, respectively.

3. Results and discussion

3.1. Reflectance change of UV/O_3 irradiated polyester film and fabrics

While surfaces of both fibers were photooxidized upon UV/O_3 irradiation, PET fiber was more susceptible to the treatment as represented by higher O(1s)/C(1s) ratio [19]. It may be due to the fact that PET has inherently higher ratio of photooxidizable ester linkages per repeating unit compared with PTT. Photooxidation of polyesters are known to be largely related to the presence of light absorbing aromatic ester linkages in main chain, which results in direct chain-scission by irradiation of 315 nm and some secondary reactions such as decarboxylation, CO or CO_2 gas evolution, peroxy group formation, etc. [21].

Reflectance profile of the irradiated PET fabric is given in Fig. 1. With increasing irradiation doses, the reflectance of the treated fabric decreased proportionally at lower wavelength region, particularly at around 400 nm. The reflectance difference between untreated and irradiated fabrics was obtained by subtracting reflectance of the treated fabrics by that of the untreated as shown in Fig. 2. Surprisingly there was a minimum at the range of 380–400 nm implying nanoscale roughened surface. The pronounced decrease in about 400 nm may be related to the height of surface roughness which can scatter short wavelength of visible spectrum. When a randomly rough surface for which the distribution of surface heights is defined by a Gaussian probability distribution, reflectance of rough surface can be related by the following relation [22]:

$$R_r = R_s \exp[-(4\pi\sigma \cos i/\lambda)^2]$$

where R_s and R_r are specular reflectances of perfectly smooth and rough surfaces, respectively, σ is RMS deviation of the surface from its mean level, i and λ are incident angle and wavelength of light.

Therefore surface roughness decreases specular reflectance of a wavelength of light particularly at high angle of incidence and the decrease in the reflectance is related to destructive interference, due to phase difference between top and bottom surfaces. It has been also known that the reflectance depends not only on the lateral scale of roughness but also its characteristic height of roughness. With normal incidence, anti reflection in the visible wavelength region may be achieved by lowest RMS roughness of about 100–200 nm in case of surface reflected light because minimal height of roughened surface must be multiples of a quarter wavelength of incident light to produce destructive interference. SEM and AFM analysis were carried out to observe the roughened surface. As can be seen in Fig. 3, laterally several micron-sized craters were appeared upon irradiation. However, it was difficult to calculate the vertical height of craters which may be partly responsible to observed scattering effect. Fig. 4 and Table 1 are AFM images and roughness data of untreated and irradiated PET films. Therefore RMS

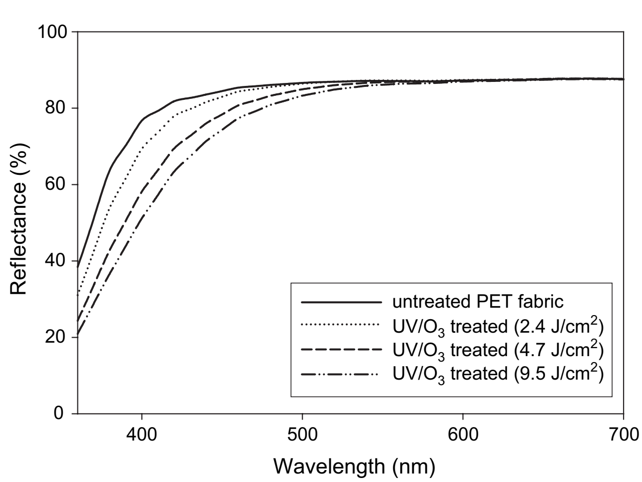


Fig. 1. Effect of UV/O_3 irradiation on the reflectances of treated PET fabrics.

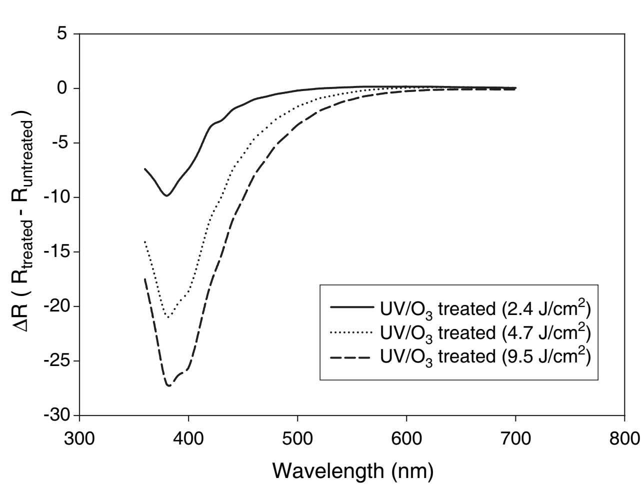
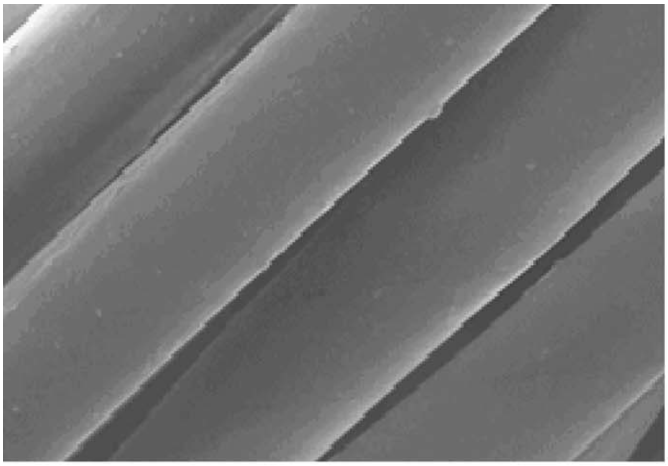
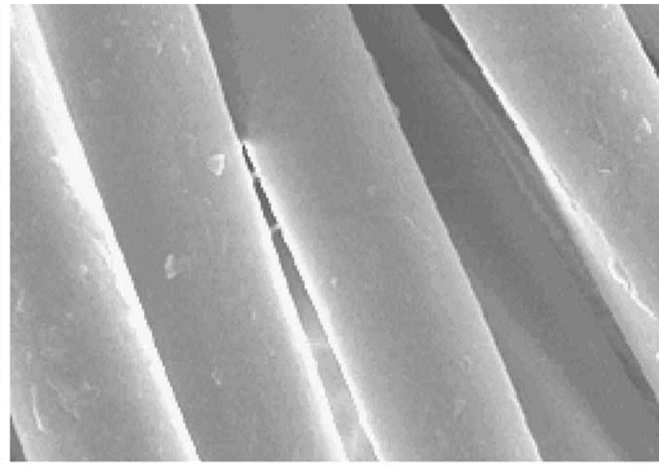


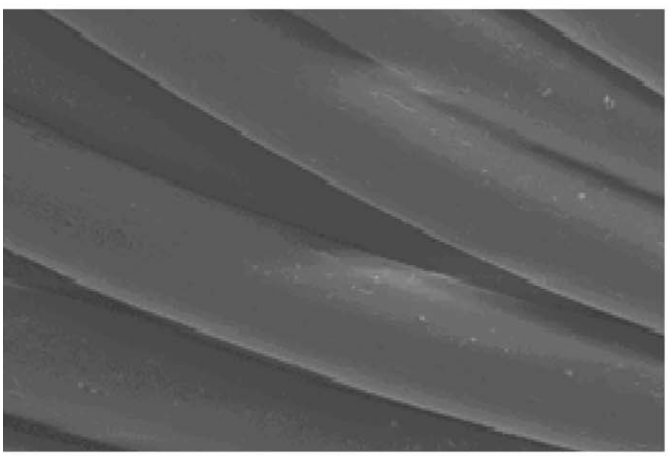
Fig. 2. Reflectance changes of treated PET fabrics.



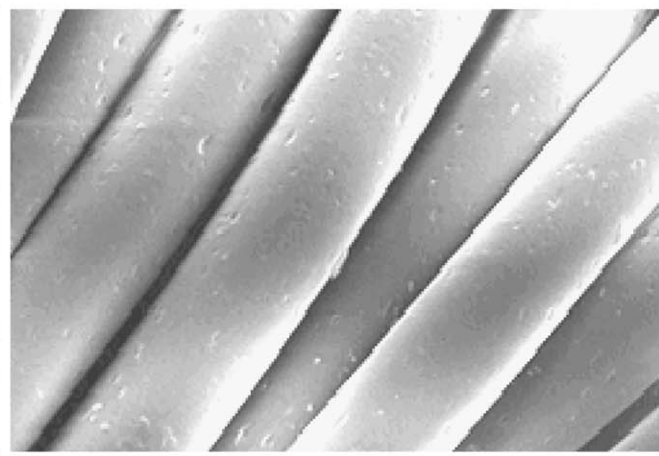
(a) untreated PTT fabric



(b) UV/O_3 irradiated PTT ($1.9 J/cm^2$)



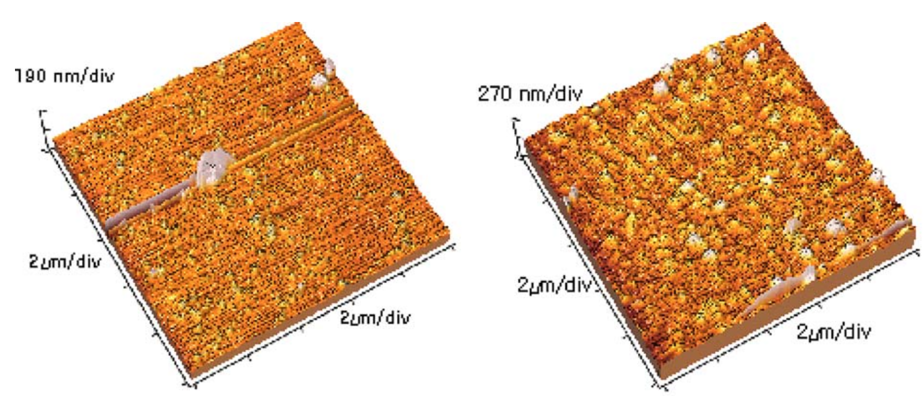
(c) untreated PET fabric



(d) UV/O_3 irradiated PET ($1.9 J/cm^2$)

Fig. 3. SEMs of untreated and UV/O_3 irradiated PET and PTT fabrics.

roughness increased by nearly two-fold from 12 nm to 21 nm. Peak-to-valley distance increased from 58 nm to 122 nm, which can interfere the surface reflected visible light of short wavelength up to 488 nm destructively. Heights of most roughened surfaces increased from 43 nm for the untreated to 85 nm for the treated with $9.5 J/cm^2$ suggesting that the irradiated surface can interfere with longer wavelength than the untreated. However, there must be several complicated factors influencing the observed reflectance difference such as



(a) (b)

Fig. 4. 3D views of non-contact mode AFM images of PET films. (a) Untreated surface; (b) UV/O_3 irradiated surface ($9.5 J/cm^2$).

Table 1
The roughness parameters of untreated and treated PET films

Treatment	Roughness (nm)					
	R_a [a]	R_q [a]	R_p [a]	R_v [a]	R_{pv} [a]	Height
Untreated	9	11	36	21	58	43
9.5 J/cm^2	16	21	72	50	122	85

[a] R_a, R_q, R_p, R_v and R_{pv}, denote roughness of average, root mean square, peak, valley and peak-to-valley, respectively.

non normal incident light, horizontally not planar surface of the fabric, large distribution of height profile of roughened surface, and contribution of scattered and refracted light to the reflectance, etc. However, the reflectance change of the treated fabric seemed to be related to the more roughened surface rather than new chromophore formation.

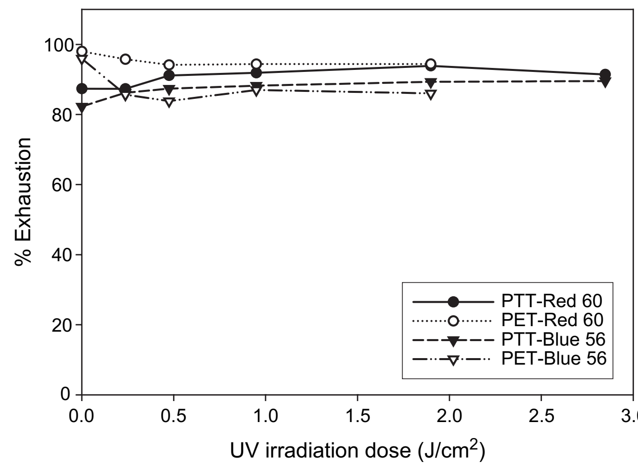


Fig. 6. Percent exhaustion of PTT and PET fabrics dyed with C.I. Disperse Red 60 and Blue 56.

3.2. Dyeability of UV/O_3 treated PET and PTT fabrics to disperse dyes

Dyeing results of the untreated and treated fabrics with 2% owf C.I. Disperse Red 60 and C.I. Disperse Blue 56 are shown in Figs. 5 and 6. Both the anthraquinone dyes gave similar dyeability to the treated fabrics irrespective of UV dose implying that photodegraded surface did not deteriorate dyeability and can have enough intermolecular interactions, such as van der Waals force and hydrogen bond, because nonionic disperse dyes were not disturbed by the presence of carboxy acid groups and phenolic hydroxy acid groups of the photooxidized outer surface layer of the treated fabric. However, it has been reported that the treated surface has significant improvement of dyeability to cationic dyes, where main dyeing mechanism is due to electrostatic interaction between the anionic fiber and cationic dyes [19,20]. Similar to red and blue disperse dyes, two black disperse dyes showed similar K/S and percent exhaustion when dyed to deep shade. However, it was surprising that the treated PET and PTT fabrics decreased proportionally lightness up to 6% and 8%, respectively, with increasing irradiation (Fig. 7). The color deepening effect of the irradiated fabrics can be understood as the following: while exhaustion and color yield were measured and calculated from the reflectance change at maximum absorption wavelength, the lightness include the reflectance contribution in the short wavelength region which was significantly changed after the UV/O_3 treatment. Similar color deepening effect of irradiation treatment was observed when UV/O_3 treatment was carried out after the dyeing of PET and PTT fabrics with black disperse dyes (Fig. 8). The treated fabrics still decreased lightness up to 6% in case of treated PTT fabric but prolonged irradiation caused the lightness to increase above certain level of dose resulting in significant degradation of the

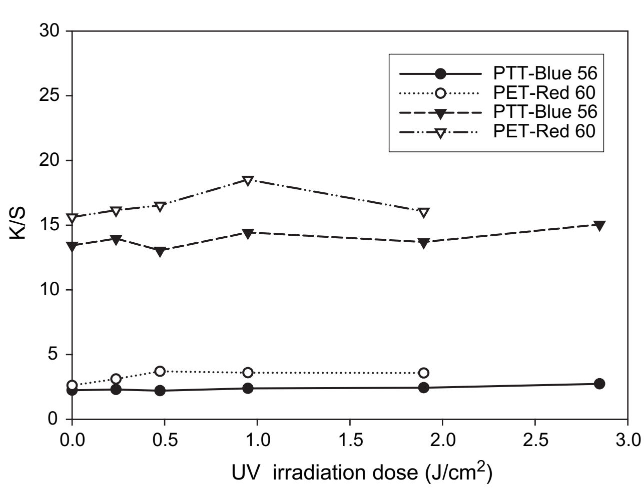


Fig. 5. K/S of PTT and PET fabrics dyed with C.I. Disperse Red 60 and Blue 56.

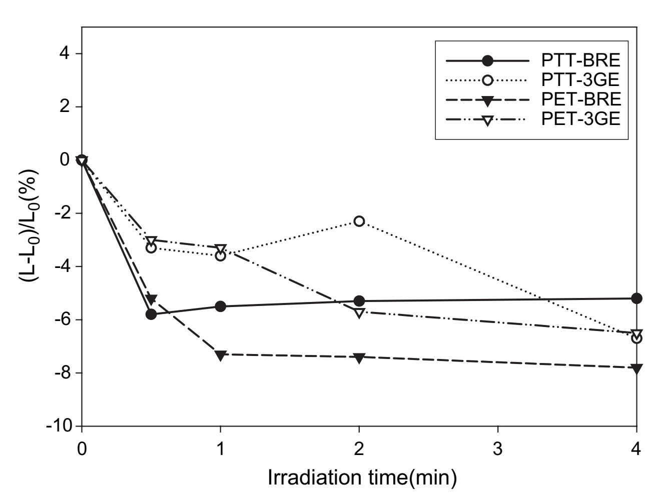


Fig. 7. Lightness change of black-dyed polyester fabrics, UV/O_3 pretreatment before dyeing.

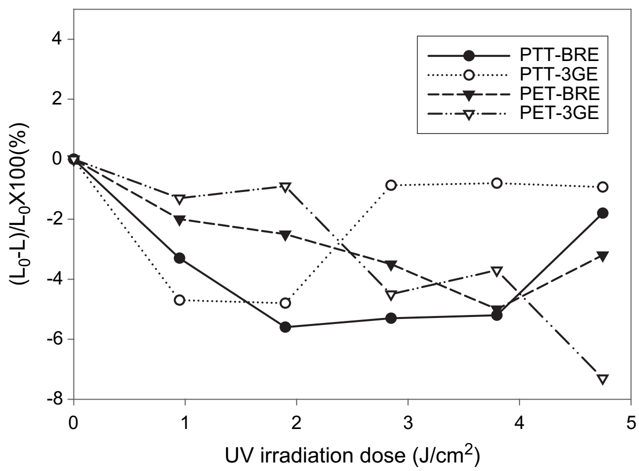


Fig. 8. Lightness change of black-dyed polyester fabrics, UV/O_3 post-treatment after dyeing.

black dyes. Although the irradiation can cause not only surface roughening of the fabrics but also the photodegradation of dyes, the photodegradation of dyes seemed to be negligible at low treatment level because of high depth of shade applied to the fabrics.

3.3. Color fastness of UV/O_3 treated PET and PTT fabrics

PET and PTT fabric samples for color fastness test were irradiated for 6 min and 4 min, respectively. Color fastness to laundering and crocking is shown in Tables 2 and 3. As expected both treated fabrics had similar fastness to the untreated fabrics under laundering despite UV/O_3 treatment. Also the treated fabric showed excellent stability to both dry and wet crocking. Therefore, it can be said that the UV/O_3 treatment did not deteriorate color fastness property of the disperse dyes because the treatment may change only outer surface layer of the polyester fabrics.

4. Conclusions

The optical properties of the UV/O_3 irradiated PET and PTT fabrics were investigated in terms of surface roughening and reflectance change. The dyeability of the irradiated fabrics to reactive dyes and color deepening of black dyed fabrics were explained by the reflectance change caused by the irradiation. UV/O_3 treatment produced micro-sized and nano-sized surface roughness by selective photodegradation which can encourage light to scatter and interfere destructively depending on the height of the surface roughness. According to AFM analysis, surface roughness increased from 58 nm to 122 nm at UV dose of 9.5 J/cm^2. The resultant surface was able to decrease reflectance of short wavelength range of visible spectrum. While the irradiated polyester fabrics did not change the dyeability to disperse dyes, the lightness decreased due to the treatment both before and after the dyeing was observed when dyed with black disperse dyes. The dyed fabric had excellent color fastness to laundering and rubbing. Therefore the UV/O_3 treatment could be used as nano-roughening method for color deepening of the polyester fabrics which can substitute current plasma and sputter etching techniques.

Table 2
Color fastness to laundering

Dyes	PTT			PET		
	K/S	PET	Cotton	*K/S*	PET	Cotton
Red 60	2.7	4	4/5	3.6	4/5	4/5
Blue 56	15.1	4/5	4/5	16.1	4/5	4/5
Black BRE	32.8	4/5	4/5	24.3	4/5	4/5
Black 3GE	28.3	4/5	4/5	24.3	4/5	4/5

Table 3
Color fastness to rubbing

Dyes	PTT				PET			
	PET		Cotton		PET		Cotton	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Red 60	4/5	4/5	4/5	3/4	3	4/5	4/5	3/4
Blue 56	4/5	4/5	4/5	3/4	4/5	4/5	4/5	4/5
Black BRE	4/5	4/5	4/5	4/5	4/5	4/5	4	4/5
Black 3GE	4/5	4/5	4	4/5	4/5	4/5	4/5	4/5

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