

Nano-roughening of polyester via UV irradiation

Yong Gyun Jeong and Jinho Jang

School of Advanced Materials and System Engineering, Kumoh National Institute of Technology

1. 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. 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 three dimensional spring-like conformation of PTT chains in crystal structure. It has been known that PTT 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 higher heat shrinkage and processing difficulty in several steps including fiber spinning, dyeing and heat setting. 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. Several methods have been pursued to increase clarity and depth of shade in PET fabrics including modification of dyeability such as cation dyeable polyester, blending with brightly dyeable cellulose acetate, decreasing surface reflectance by either coating of low RI synthetic resin or surface roughening treatments. 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(400-800nm), it is required to introduce non-reflective coating of odd multiple thickness of 76nm to 156nm 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. 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. This study is to

generate nanoscale roughness on PET and PTT fabrics via UV/O₃ irradiation and to compare deep coloring effect of the irradiated polyester fabrics when dyed with black disperse dyes.

2. Experimental section

2.1 Materials

Scoured PET and PTT fabrics were a twill weave (190g/m²) and a knitted fabric (90g/m²) respectively. biaxially drawn PET film(SKC) of 100μm 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) as supplied by Clariant. Acetic acid, NaOH and Na₂S₂O₄ were used for pH adjustment and reduction clearing.

2.2. Continuous UV/O₃ irradiation and surface analysis

UV irradiation was carried out using an electrodeless UV irradiator(Fusion UV System Ltd) enclosing a H-bulb of 240W/cm intensity and UV dose was adjusted by repeated treatment of the samples at the constant conveyor speed of 10m/min. Micro-scale roughness of the treated surface was observed by a scanning electron microscope(SEM S-2400, Hitach), and nano-scale roughness was assessed by an atomic force microscope(Auto Probe M5, Thermo Microscopes Co.) in non-contact mode on 10 μm X 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 kept 60°C for 10 min and the temperature increased until 130°C and maintained for 40 minutes. After dyeing, surface-deposited dyes in the dyed samples were cleared reductively at 60°C for 20minutes using 2 g/L of NaOH and Na₂S₂O₄ 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 spectrophotometer (Kontron Instruments)was used for percent exhaustion by absorbance measurement of dyeing liquor at the maximum absorption wavelength before and after dyeing. For measurement of color before and after dyeing, reflectance and K/S were measured with a reflectance spectrophotometer(Gretag Macbeth) using illuminant D₆₅ 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 KS K 0430 A-1, A-3 at 120 K 0050

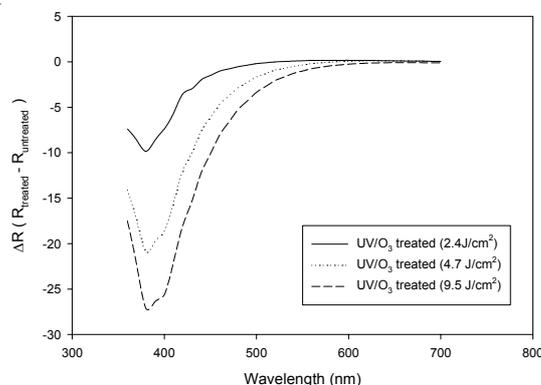
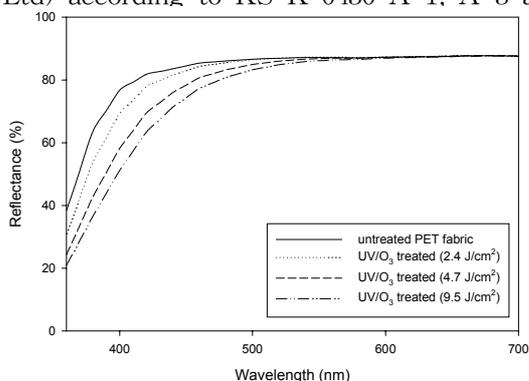


Figure 1. Effect of UV/O₃ irradiation on the reflectances of treated PET fabrics. **Figure 2.** Reflectance changes of UV/O₃ irradiated PET fabrics.

3. Results and Discussion

While surfaces of both fibers were photo-oxidized upon UV/O₃ irradiation, PET fiber was more susceptible to the treatment as represented by higher O(1s)/C(1s) ratio. It may be due to the fact that PET has inherently higher ratio of photo-oxidizable ester linkages per repeating unit compared with PTT. Photooxidation of polyesters are known to be largely related with 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 CO₂ gas evolution, peroxy group formation, etc.

Reflectance profile of the irradiated PET fabric showed that was given in *Figure 1*. With increasing irradiation doses, the reflectance of the treated fabric decreased proportionally at lower wavelength region, particularly at around 400nm. The reflectance difference between untreated and irradiated fabrics were obtained by subtracting reflectance of the treated fabrics by that of the untreated as shown in *Figure 2*. Surprisingly there was a minimum at the range of 380nm and 400nm implying nanoscale roughened surface. The pronounced decrease in about 400nm may be related with the height of surface roughness which can scatter short wavelength of visible spectrum.

Surface roughness decreases specular reflectance of a wavelength of light particularly at high angle of incidence, and the decrease in the reflectance are related with destructive interference due phase difference between top and bottom surfaces. It has been also known that the reflectance depends on not the lateral scale of roughness but its characteristic height of roughness. With normal incidence, anti reflection in the visible wavelength region may be achieved by lowest RMS roughness of from about 100 nm to 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 roughed surface.

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. RMS 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 upto 488nm destructively. Heights of most roughened surface increased from 43nm for the untreated to 85nm for the treated with 9.5 J/cm^2 suggesting that the irradiated surface can interfere longer wavelength than the untreated. However there must be several complicated factors influencing the observed reflectance difference such as not 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.

References

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