Investigation into the Effect of UV/Ozone Irradiation on Dyeing Behaviour of Poly(Lactic Acid) and Poly(Ethylene Terephthalate) Substrates

F. Fattahi[1], H. Izadan[2*], A. Khoddami[2]

[1]. M. Sc., Department of Textile Engineering, Isfahan University of Technology, P.O. Box: 84156- 83111, Isfahan, Iran.

[2]. Assistant professor, Department of Textile Engineering, Isfahan University of Technology, P.O. Box: 84156- 83111, Isfahan, Iran.

ABSTRACT

The effect of UV/Ozone irradiation together with the pretreatments using distilled water, hydrogen peroxide, and hydrogen peroxide/sodium silicate solutions on the dyeing depth of the poly(lactic acid), PLA, and poly(ethylene terephthalate), PET, fabrics by the application of disperse dyes were investigated and the results were compared with that of untreated fabrics. The results showed that the reflectance and the L* of the treated fabrics decreased and these reductions maximized by the pretreatment of the fabrics with the hydrogen peroxide/sodium silicate solution. The SEM images of the fabrics showed a change in the surface morphology of the treated fabrics which is attributed to the intensified etching effect of the UV/Ozone irradiation. Prog. Color Colorants Coat. 5(2012), 15-22. © Institute for Color Science and Technology.

1. Introduction

Surface modification of the fabrics with different methods, such as Plasma treatment [1-2], alkaline hydrolysis [3] and treatment with enzyme [4] are an active area of the research in the textile science. One of the effective and economical methods of surface modification of natural polymers and synthetic polymers, such as polyethylene, polypropylene, polyacetylene and PET, is ultraviolet/ozone (UV/O) irradiation. Excitation and dissociation of the polymeric molecules take place during exposing the surface to the UV/O treatment, which is known as a photosensitized oxidation process. This treatment, also, changes the surface morphology and topography of the polymer. The SEM (scanning electron microscopy) images of the sample showed a marked increase in the grain size and the surface roughness of the irradiated polymer in comparison to the surface of the untreated samples [5-11].

As the (UV/O) irradiation is done continuously under the atmospheric pressure, this is a proper finishing method for the polymers which are sensitive to the temperature and flame and would be damaged by the corona treatment [12].

PLA has applications in food packaging [13], biomedical applications [14] and etc. PLA fibre has also ecological advantages as well as excellent performance in textiles. It is an aliphatic polyester which can be

derived from 100% renewable resources such as corn [15-16] and therefore it is consider as an environmental friendly fibre [17].

The mechanical properties of PLA fibres are considered to be broadly similar to those of conventional PET fibres. Some typical properties of PLA fibres are compared with those of conventional PET fibres in Table 1 [15-16].

The specific gravity of PLA fibres is lower than that of PET fibres. The melting point of PLA fibres is between 130-170˚C, whereas that of PET fibres is in the range of 254-260˚C. Elastic recovery of PLA fibres at 5% strain is superior to that of PET fibres [15].

PLA fibres exhibit higher sensitivity to alkali than does PET. Some loss of fibre strength during subsequent wet processing is observed if care is not taken in the dyeing and finishing of the PLA fibre because of this sensitivity [15].

PLA fibre is a hydrophobic polymer and it is expected that disperse dyes have relatively high affinity for the fibre as is the case with other hydrophobic polymers such as PET fibres. Some special disperse dyes have been synthesized for the PLA fibres which show significantly better affinity to these fibres in comparison to the conventional disperse dyes used for the PET fibres [17]. However, whereas PET is conventionally dyed at around 130 °C in order to enable disperse dyes to diffuse at an acceptable rate into the material, PLA fibres must be dyed at lower temperatures for generally shorter times, typically 110 °C for 30 minutes. The use of excessive dyeing temperatures and/or extended dyeing times leads to fibre degradation, manifested as reductions in molecular weight, tensile strength and percentage elongation at break. In addition, other processes such as

heat setting, bleaching, and scouring, may have detrimental influences on the physical strength of PLA fibres [4].

It is claimed that dyed PLA fibres possess lower wash and crock fastness than dyed PET fibres at a given dye concentration in the substrate, while the reverse is true for light fastness [13, 18].

Due to having high refractive index of 1.54, PET fibers reflect a considerable amount of the incident light from their surface hence, making their dyeing difficult, especially black colors. Recently, many studies have been performed to obtain full color intensity on PET fibers surfaces by alkali treatment, low pressure plasma, sputter etching, low refractive index chemical resin coating, and liposome dyeing [15].

An important method of decreasing the surface reflectance of PLA and PET fibres could possibly be the nanoscale surface roughening of the fibres using physico-chemical surface treatments via UV/O irradiation. It is believed that the roughening of the fibre surface increases the color depth of the fibre due to destructive interference and/or increasing the rate of dyeing [18-20].

This research was initiated in an effort to compare the change in the dyeing properties of PET and PLA fibres after UV/O irradiation in different conditions in terms of the sample's reflectance as well as the colorimetric properties of the dyed fibres. Also, to the best knowledge of the authors, there is no research published on the effect of the pretreatment of the UV/O irradiated fabrics with distilled water, Hydrogen peroxide and hydrogen peroxide plus sodium silicate solutions. Therefore, part of this research was dedicated to investigate the effect of these pretreatments.

Table 1: Properties of PLA and PET fibres [15].

Fiber properties	PLA	PET
Specific gravity	1.25	1.39
T_m (°C)	130-175	254-260
Tenacity (g/d)	6.0	6.0
Elastic recovery (5% strain)	93	65
Moisture regain (%)	0.4-0.6	0.2-0.4
Flammability	Continues to burn for 2 min after flame removed	Continues to burn for 6 min after flame removed
Smoke generation	63 m^2/kg	394 m^2/kg
Limiting oxygen index (%)	26	20-22
Refractive index	1.35-1.45	1.54

2. Experimental

All the chemicals used in the research except dyes were supplied from Merck. This study employed two sets of identically-constructed 'piqué' type of knitted fabrics provided by Nature Works LLC, USA and derived from 150/144 dtex/filament PLA (IngeoTM fibre) and 150/144 dtex/filament PET yarns, respectively. These kinds of products are generally used for outerwear garments such as socks, sportswear, activewear, women's dress, fashion wear and children's wear. "IngeoTM fibre" is the trademark of NatureWorks LLC's Poly (lactic acid) polymer produced from corn starch. The properties of the greige PLA and PET fabrics are shown in Table 2.

The fabric was scoured to remove any possible impurities which could potentially interfere with the subsequent surface treatment. Untreated PET and PLA fabrics were pre-scoured in a bath containing 1 g/l Kieralon Jet B conc. (non-ionic surfactant, BASF) and 1 g/l sodium carbonate ('soda ash') at 60 °C for 15 minutes. After scouring, the fabrics were rinsed with cold water for 10 min and flat dried at room temperature without any tension.

The pique knitted PLA and PET fabrics, were padded with 70% pickup after impregnating with three different solutions, which are as follows:

1- distilled water

2- 4 ml/l hydrogen peroxide (35%)

3- 4 ml/l hydrogen peroxide (35%) plus 7 g/l sodium silicate

Then, both sides of the fabrics were immediately irradiated with UV/O for 40 minutes. The treated samples were dyed with two disperse dyes, C.I. Disperse Blue 56 and Dianix Black S-R 200%. The pH of the dyeing bath was adjusted to 5 using an acetic acid/sodium acetate buffer solution and the L: R was equal to 40:1. As it is shown in Figure 1, the dyeing started at 40°C, and then ramped to the dyeing temperature ,110°C for the PLA and 130°C for the PET, at 2°C per minute and held in this temperature for 45 minutes, and then the bath cooled to 70°C at 3°C/min.

After dyeing, the fabrics were rinsed for five minutes with warm water and two minutes with cold water and then air-dried at room temperature. The reflectance spectra of all the dyed samples were measured using a 0/d Texflash spectrophotometer from Data Color in the visible region. In order to measure the spectral reflectance of the fabrics, the fabric folded four times and the measurement was done twice. In the second time the measurement was done after the 90 degrees rotation of the fabric, and then the average of these measurements were considered as the reflectance of the sample.
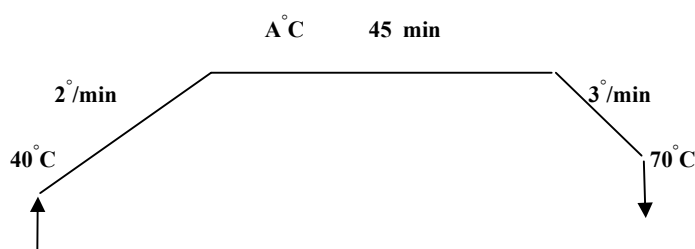

Figure 1: Dyeing profile of the PET and PLA fabrics, A: 130°C for the PET and 110°C for the PLA.

Table 2: Specifications of the knitting PLA and PET fabrics.

Fibre type	Yarn linear density	Fabric structure	Tickness (mm)	Weight (g/m^2)
PLA	150/144 dtex/filament	Pique	0.781	18.45
PET	150/144 dtex/filament	Pique	0.801	19.5

The L*a*b* of the samples were calculated using D65 standard illuminant and 10 degrees standard observers. L*a*b* color specification system was defined by CIE in 1976 for which L* represent the lightness (black/white) of the colored sample and a* and b* represent the opponent signals red/green and yellow/blue, respectively.

Also, for the analysis of the change in the surface morphology of the fabrics, the image of the surface of the PET fabrics were obtained using a scanning electron microscope.

3. Results and discussion

Figures 2 and 3 show the reflectance spectra of all the black dyed fabrics with clear reduction in the reflectance spectral values of the treated fabrics in comparison to the untreated one. Figure 2 shows a slight reduction in the reflectance of the treated PET fabrics which is fairly uniform across the visible wavelengths. In the case of the PLA fabrics dyed with the black dye (Figure 3), the reduction across the visible wavelengths is not uniform and significantly higher reduction over the range of 660 to 700 nm can be observed.
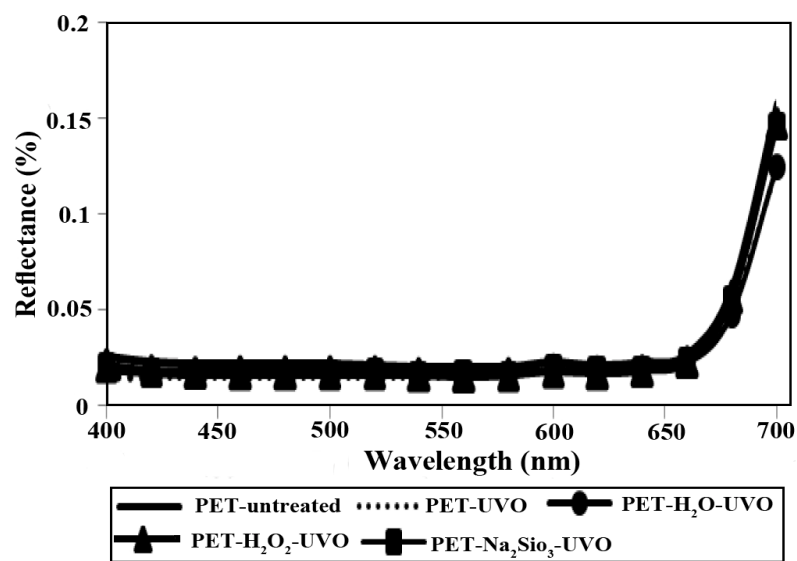

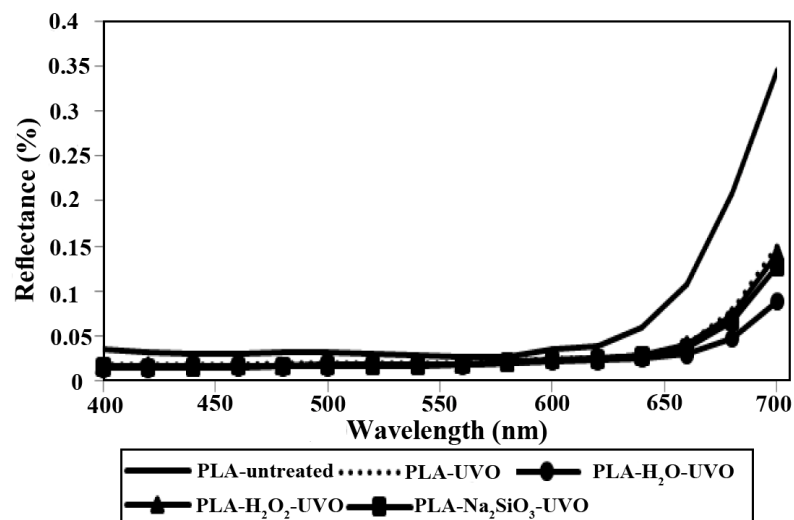**Figure 2:** Reflectance of the PET fabrics dyed with Dianix Black S-R 200%.

Figure 3: Reflectance of the PLA fabrics dyed with Dianix Black S-R 200%.

Tables 3 and 4 show the L*a*b* of the PET and PLA fabrics dyed with the black disperse dye, respectively. The values of the L* in these tables support the results obtained from the corresponding reflectance spectra of the fabrics. The reduction in the reflectance of the treated fabrics could also be observed from the visual depth of the fabrics.

The SEM images of the PET fabrics in Figure 4 show that the untreated fabric has fairly smooth surface, and the existence of few small particles on the surface of the fibres are probably due to the insufficient removal of the chemicals durin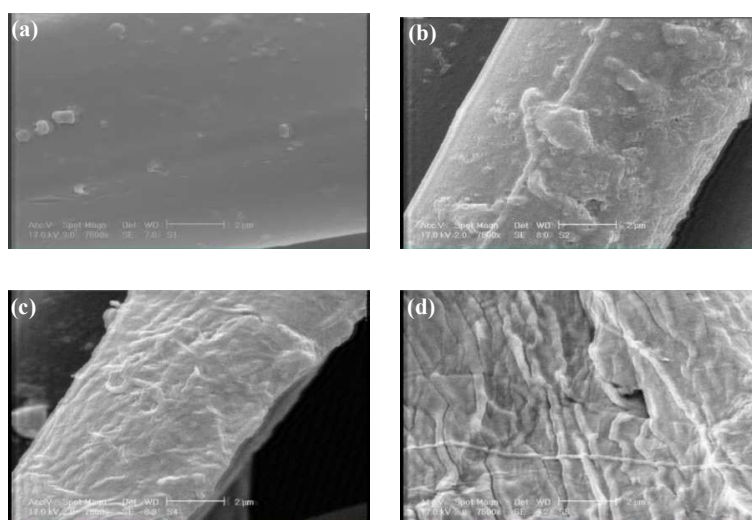g the washing stage. However, the surface morphology of the treated fabrics has change dramatically and there are different features on the surface of the fibres, such as grooves and voids. This surface modification may be owed to the etching of the fibre surface happened after the bombardment of the surface of the fibres with ions and free radicals. This surface roughening effect leads to either a light trapping phenomenon due to destructive interference or increase in the dyeing rate of the fibre, which is a consequence of increasing the surface area of the fibre. Both of these effects may be the reason for the decrease in the reflectance and the L* of the fabrics after the treatment.

Table 3: The L*a*b* of the PET fabrics dyed with the black disperse dye.

	Untreated	UV/O	H_2O-UV/O	H_2O_2-UV/O	H_2O_2-Na_2SiO_3-UV/O
L*	16.1	13.4	13.6	13.7	13.9
a*	1.6	2.7	2.23	1.8	2.0
b*	-0.8	1.4	0.3	-0.6	-0.4

Table 4: The L*a*b* of the PLA fabrics dyed with the black disperse dye.

	Untreated	UV/O	H_2O-UV/O	H_2O_2-UV/O	H_2O_2-Na_2SiO_3-UV/O
L*	19.9	15.2	14.5	15.3	15.3
a*	5.75	4.0	3.5	4.3	4.2
b*	2.7	2.3	3.7	3.3	3.5

Figure 4: The SEM image of the PET fabrics, (a) Untreated, (b) UV/O, (c) H_2O_2-UV/O, (d) H_2O_2-Na_2SiO_3-UV/O, the scale of the images is 2μm at magnifications of 7500x.

As it is well known, most of the black disperse dyes used in order to dye the PET fibres, are a mixture of more than one dye and they are formulated by the dye maker companies to produce acceptable black color on the PET fibres and therefore they may show unpredictable behaviour on the PLA fibres. The blue disperse dye, Disperse Blue 56, was used in this research to further support the results obtained from the dyeing of the fabrics with the black disperse dye. Figures 5 and 6 show the reflectance of the PET and PLA fabrics, respectively, dyed with the blue disperse dye. The L*a*b* of the corresponding fabrics also can be obtained from Tables 5 and 6, respectively. It can be inferred that the reflectance and L* of the samples have decreased considerably in comparison to that of the untreated fabrics. Figure 5 shows that the reflectance values of the PET fabrics have been decreased roughly below 580 nm,

especially for the fabric treated with the H_2O_2/Na_2SiO_3 solution. A similar effect but in a less extent happened for the wavelengths roughly above 670 nm, while the rest of the wavelengths show no significant change.

The PLA fabric dyed with the blue dye showed a similar trend in the fabric reflectance and L* after the treatments; however, in this case, the UV/O irradiated samples showed a decrease for all the visible wavelengths.

Among the different pretreatments applied for achieving deep coloring, the H_2O_2/Na_2SiO_3 method have the highest effect on the surface reflectance spectra of the PET and PLA fabrics dyed with Blue dye. This result could be the possible effect of Na_2SiO_3 that acts as a H_2O_2 stabilizer by which H_2O_2, a photosensitizer that increases UV absorption, remained longer in touch with the fibres surface before its dissociation.
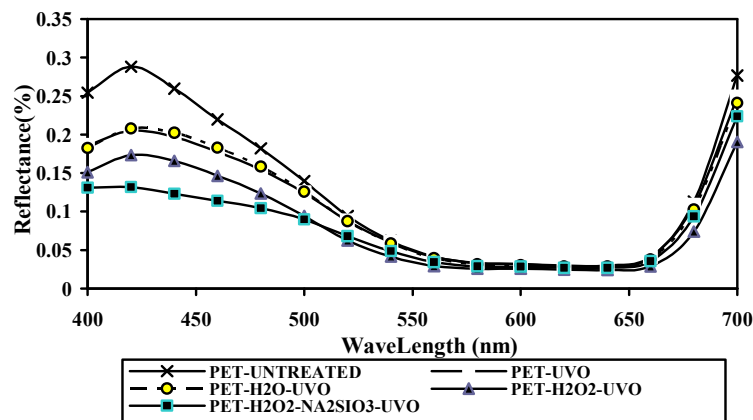

Figure 5: The reflectance of the PET fabrics dyed with C.I Disperse Blue 56.
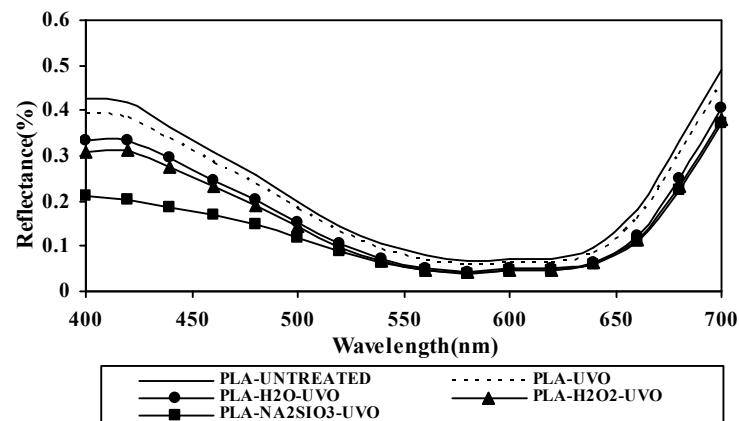

Figure 6: The reflectance of the PLA fabrics dyed with C.I Disperse Blue 56.

These results may also be related to the surface roughening happened due to the different pre-treatments of the UV/O irradiated fabrics. Again, the resultant surface roughness may contribute to the decrease of reflectance values of the dyed PET and PLA fabrics by the two possible reasons already explained for the PET fabrics.

It is important to note that some changes in the a* and b* of the treated samples can be observed in Tables 3 and 4, however, as the study of a preferred black is not the subject of this paper, no comments made on this topic.

Table 5: The L*a*b* of the PET fabrics dyed with the blue disperse dye.

	Untreated	UV/O	H$_2$O-UV/O	H$_2$O$_2$-UV/O	H$_2$O$_2$-Na$_2$SiO$_3$-UV/O
L*	32.6	31.2	31.1	27.0	27.2
a*	4.1	-0.3	-0.1	3.2	-2.3
b*	-39.1	-31.6	-32.8	-32.1	-32.1

Table 6: The L*a*b* of the PLA fabrics dyed with the blue disperse dye.

	Untreated	UV/O	H$_2$O-UV/O	H$_2$O$_2$-UV/O	H$_2$O$_2$-Na$_2$SiO$_3$-UV/O
L*	41.6	39.5	35.7	34.4	32.3
a*	8.3	8.5	9.2	9.3	4.3
b*	-38.6	-38.6	-39.0	-38.4	-28.6

4. Conclusions

The color depth of the PLA and PET fabrics were increased by three different pre-treatment methods followed by the UV/O irradiation. This increase in the depth of dyeing is believed to be due to the surface roughening of the fabrics produced by the UV/O irradiation. This effect of the UV/O treatment has the potential to be used in the preparation of so called formal black polyester clothing. Further research is being carried out to apply this method of surface modification of PET and PLA fabrics in industrial scale.

5. References

1. R. H. Wardman, A. Abdrabbo, Effect of plasma treatment on the spreading of micro drops through polylactic acid (PLA) and polyester (PET) fabrics, *AUTEX Research Journal*, 10(2010), 1-7.
2. M. Parvinzadeh**,** I. Ebrahimi, Atmospheric air-plasma treatment of polyester fiber to improve the performance of nanoemulsion silicone, *Appl. Surf. Sci.*, 257(2011), 4062-4068.
3. N. A. Ibrahim, M. A. Youssef, M. H. Helal, M. F. Shaaban, Exhaust dyeing of polyester-based textiles using high-temperature- alkaline conditions*, J. Appl. Polym. Sci.,* 89(2003), 3563-3573.
4. S. H. Lee, W. S. Song, Enzymatic hydrolysis of polylactic acid fiber, *Appl. Biochem. Biotechnol.*, 164(2010), 89-102.
5. C. Ton-That, D. O. H. Teare, P. A. Campbell, R. H. Bradley, Surface characterisation of ultraviolet-ozone treated PET using atomic force microscopy and X-ray photoelectron spectroscopy, *Surf. Sci.,* 433-435(1999), 278-282.
6. E. M. Kim, J. Jang, Surface modification of meta-aramid films by UV/Ozone irradiation, *Fibers Polym.*, 11(2010), 677-682.
7. P. Kuang, J. H. Lee, C. H. Hwang-Kim, K. Constant, Improved surface wettability of polyurethane films by ultraviolet ozone treatment, *J. Appl. Polym. Sci.,* 118(2010), 3024-3033.
8. *G. H. Koo, J. Jang, Surface modification of*

poly(lactic acid) by UV/Ozone irradiation, *Fibers Polym.*, 9(2008), 674-678.

9. S. L. Gao, R. Häßler, E. Mäder, T. Bahners, K. Opwis, E. Schollmeyer, Photochemical surface modification of PET by excimer UV lamp irradiation, *Appl. Phys. B,* 81(2005), 681-690.

10. H. Y. Nie, M. J. Walzak, B. Berno, N. S. McIntyre, Atomic force microscopy study of polypropylene surfaces treated by UV and ozone exposure: modification of morphology and adhesion force, *Appl. Surf. Sci.,* 144-145(1999), 627-632.

11. L. F. Macmanus, M. J. Walzak, N. S. Mcintyre, Study of ultraviolet light and ozone surface modification of polypropylene, *J. Polym. Sci., Part A: Polym. Chem.,* 37(1999), 2489-2501.

12. C. W. Tsao, L. Hromada, J. Liu, P. Kumar, D. L. DeVoe, Low temperature bonding of PMMA and COC microfluidic substrates using UV/Ozone surface treatment, *Lab Chip*, 7(2007), 499-505.

13. O. Avinc, A. Khoddami, Overview of poly(lactic acid) (PLA)fibre- Part I: production, properties, performance, environmental impact, and end-use applications of poly(lactic acid) fibres, *Fibre Chem.,* 41(2010), 391-401.

14. J. Y. Park, I. H. Lee, Controlled release of ketoprofen from electrospun porous polylactic acid (PLA) nanofibers, *J. Polym. Res.*, 18(2010), 1287-1291.

15. O. Avinc, A. Khoddami, Overview of poly(lactic acid)(PLA)fibre- Part II: wet processing; pretreatment, dyeing, clearing, finishing, and washing properties of poly(lactic acid) fibres, *Fibre Chem.*, 42(2010), 68-78.

16. R. E. Drumright, P. R. Gruber, D. E. Henton, Polylactic acid technology*, Adv. Mater.,* 12(2000), 1841-1846.

17. L. He**,** S. F**.** Zhang**,** B. T**.** Tang, L. L**.** Wang**,** J. Z. Yang**,** Dyes with high affinity for polylactide, *Chin. Chem. Lett.*, 18(2007), 1151-1153.

18. J. Jang, M. Kim, Y., Jeong, Cationic dyeable treatment of PET and PTT fabrics by continuous UV/O$_3$ irradiation, *J. Korean Fibre Soc.,* 40(2003), 424-430.

19. M. Kim, J. Jang, Y. Jeong, Effect of continuous UV/O$_3$ irradiation on the physical properties of PET and PTT fabrics*, J. Korean Fibre Soc.,* 41(2004), 80-85.

20. J. Jang, Y. Jeong, Nano roughening of PET and PTT fabrics via continuous UV/O$_3$ irradiation, *Dyes Pigm.*, 69(2006), 137-143.