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Different Surface Modification of Poly (Ethylene Terephthalate) and Polyamide 66 Fibers by Atmospheric Air Plasma Discharge and Laser Treatment: Surface Morphology and Soil Release Behavior

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Abstract

The wettability of poly (ethylene terephthalate) and polyamide fabrics is important for industrial use. This property can be obtained by treatment of fabrics using chemical and physical methods such as alkaline etching, plasma discharge treatments and laser irradiation. Some treatments change the surface of the fibers and fabrics so that causes negative effects of soil release in laundering process for costumer usage. In this research, poly (ethylene terephthalate) and polyamide 66 fabrics were exposed to atmospheric air plasma discharge and Excimer laser instrument. Wettability and soil release behavior of treated fabrics were determined and surface characteristics of atmospheric air plasma discharge and laser treated fabrics were assessed by SEM and FTIR/ATR analysis. Laser treatment of poly (ethylene terephthalate) fabric makes carboxylic acid groups which causes hydrophilicity on the poly (ethylene terephthalate) surface. Despite chemical changes on fiber surface and hydrophilicity of chemical groups, morphological changes on fiber surface are responsible for soiling behavior of poly (ethylene terephthalate) and polyamide 66 fabrics. Laser treated poly (ethylene terephthalate) and polyamide 66 fibers have ripple like structure so that soil can penetrate into the gaps and remained on the fiber surface. Plasma treatment causes uneven surface which soil remove easily during laundering process.

Keywords: Atmospheric air plasma discharge; Laser; Surface morphology; Soil release

Introduction

Surface properties of materials are often the important determinants of their usefulness. The important properties of polymer materials such as adhesion, friction, wetting and penetrability are strongly influenced by their surface characteristics and many of the chemical treatments now in use are aimed at modifying these properties [1]. Poly (ethylene terephthalate) and polyamide 66 fibers are hydrophobic, and textiles processing such as dyeing, printing, and finishing are based on wet treatments [2]. The wettability of poly (ethylene terephthalate) and polyamide fabrics is important for industrial use. This property can be obtained by treatment of fabrics using different methods such as alkaline etching, plasma discharge treatments and laser irradiation. Plasmas and lasers are useful methods for the surface treatment of materials without using water.

The possible applications of laser technology in the textile industry include removal of indigo dye of denim, heating threads, creating patterns on textiles to change their dyeability, producing surface roughness, welding, cutting textile webs [3-5]. The CO_2 laser has been used for investigation of surface degradation of linen textiles and physical modification on grey cotton in a laboratory scale [6,7]. Dyeing behavior of laser treated PET fabrics has been studied and the other research work consists of laser cleaning of artificially aged textiles [8,9]. Laser irradiation on polymer surface is used to generate a modified surface morphology. The smooth surface of polymers is modified by this technique to a regular, roll-like structure that can cause adhesion of particles and coating, wetting properties and optical appearance.

Corona and low temperature plasma are useful techniques for treating the surface of fibers or polymeric materials in a dry system. These technologies improve the surface of polymeric material without changing the bulk properties [10]. Some properties of materials change such as friction, adhesion, reflection of light, wetting and dyeing properties, water repellency, soiling behavior, soil release, printing and finishing processes [10-12]. Absorbed moisture content of polyamide fibers, AFM surface morphology characterization of PET fabrics and the other characterization of plasma processing for polymers such as poly(ethylene terephthalate) and polyamide 66 have been investigated [13-20]. Atmospheric air plasma discharge occurs when a high voltage is applied to electrodes. The electrons that were produced by this electrode are accelerated towards the isolator by a high voltage. The electrons collide with air particles, producing ozone and reach the substrate which splits chemical bonds, and produces radicals on the surface of the substrate [5].

One of the most important properties of textile products for costumer usage is soil release in laundering process. Some finishing processes change the surface of the fibers and fabrics so that causes negative effects on laundering process. Some researches have been done to investigate soil release of plasma treated poly (ethylene terephthalate) fabrics [21,22]. The aim of this study is to compare surface morphology and soil release behavior of synthetic fibers (Poly

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(ethylene terephthalate) and polyamide 66) under different surface treatment (Atmospheric air plasma discharge and laser ablation). For this purpose, poly (ethylene terephthalate) and polyamide fabrics were exposed to atmospheric air plasma discharge and Excimer laser. Wettability of atmospheric air plasma and laser treated fabrics were determined by AATCC -39-1980 test method. Surface characteristics of atmospheric air plasma discharge and laser treated fabrics were assessed by scanning electron microscopy (SEM) and Fourier Transform infrared/attenuated total reflectance (FTIR/ATR) analysis. Soiling behavior of poly (ethylene terephthalate) and polyamide fabrics was tested and the alterations were determined by colorimetric system.

Materials and Methods

Materials

The poly (ethylene terephthalate) fabric was a plain weave fabric and polyamide 66 (Polyamide) was knitted fabric. Non-ionic detergent (Persoftal PEN) were produced by BASF, carbon tetrachloride were reagent grade chemical supplied by Merck (Germany), carbon black and liquid paraffin were used for soiling of fabrics.

Methods

Atmospheric air plasma instrument was made by Azad Electrical Industries, Iran. Atmospheric air plasma equipment consists of 2 electrodes: metal electrode roll with silicone coating and aluminum electrode that is parallel with electrode roll. The experiments were carried out at atmospheric pressure and air. The power and velocity were set at 600 W and 2 m/min, respectively and the distance between electrodes was 3 mm. The number of passages used for poly (ethylene terephthalate) and polyamide fabrics was 20 passages.

Laser irradiation was performed using Excimer laser model: Lamba Physik LPX made by USA. The laser was operated with ArF gas and wavelength of 193 nm and the repetition rate of 1 Hz. The laser energy was 40 mJ/cm^2 and fabrics were placed in the distance of 2 meters from the instrument. The poly (ethylene terephthalate) and polyamide 66 fabrics were treated under 5 and 20 pulses of laser irradiation, respectively.

Wetting time of atmospheric air plasma and laser treated fabrics were determined by AATCC -39-1980 test method. A drop of water was poured on the surface of fabrics and Spreading time of a drop was determined by reporting the mean of 10 specimens. Infrared spectra were collected utilizing a Bruker-Equinox 55 system FTIR /ATR spectrometer. All data were recorded by means of a ZnSe Internal Reflective Element. Spectra were collected at a resolution of 4 cm^{-1} and 32 scans were collated. The morphology of fabric surface was determined by observation of the samples on a scanning electron microscope (SEM) (PHILIPS XL30) with an acceleration voltage of 20 kV at magnification of × 1000.

Soil release behavior test was carried out by preparing a stock solution of mixing 1gm carbon black and 9 gm liquid paraffin. Then this stock was added to 90 gm carbon tetrachloride. Untreated, atmospheric air plasma and laser treated samples were immersed in this solution for 1 minute, and then were dried in air for 24 hours. Every sample was divided to two parts. One part of fabrics was kept as non-washed samples then the second part of fabrics was washed in a detergent solution including 4 gm detergent per liter at temperature of 40°C for 90 minutes. Color parameters of washed and non-washed fabrics were determined and color change of them was compared. For presenting the data, color parameter of the fabrics were determined by Color Eye 7000 spectrophotometer [21].

The other test method of soil release was the AATCC test method 130-1995. This test method is used by fabric finishers to evaluate the performance of soil release finishes in actual use. This test was carried out by placing 5 drops of corn oil in specimen, then putting the glassine paper and weight on stained area for 60s. The washing procedure was carried out at temperature of 60°C, and then dried as the standard test method. For evaluation of soil release the fabrics were graded due to comparing with soil release scale.

Results and Discussion

Results for poly (ethylene terephthalate) fabrics

Table 1 shows wetting time of untreated, atmospheric air plasma and laser treated poly (ethylene terephthalate) fabrics. Wetting time of

	L*		ΔE		K/S		Wetting time(s)	Soil release rate
	B	A	B	A	B	A		
control	83.67	83.67	-	-	-	-	-	-
untreated	78.10	81.842	5.57	1.834	1.78	1.64	5.9	4-5
Laser treated	78.738	81.412	5.31	2.27	1.89	1.47	2.21	4
plasma treated	78.424	81.598	6.25	3.45	1.83	1.21	0.57	4-5

Table1: Wetting time , color difference (ΔE) , color yield (K/S) and soil release rate of untreated , atmospheric air plasma and laser treated poly(ethylene terephthalate) (B; before washing, A; after washing , control; bleached cotton fabric, untreated: soil on bleached cotton fabric).

	L*		ΔE		K/S		Wetting time(s)	Soil release rate
	B	A	B	A	B	A		
control	70.078	70.078	-	-	-	-	-	-
untreated	58.842	74.412	11.26	4.39	1.70	1.52	3.52	4-5
Laser treated	60.936	73.108	9.142	3.304	1.85	1.67	0.52	4
plasma treated	60.946	69.993	9.29	2.586	1.82	1.28	0.85	4-5

Table2: Wetting time , color difference (ΔE) , color yield (K/S) and soil release rate of untreated , atmospheric air plasma and laser treated polyamide 66 fabrics (B; before washing, A; after washing , control; bleached cotton fabric, untreated: soil on bleached cotton fabric).

untreated poly (ethylene terephthalate) fabric was 5.9s. After laser and atmospheric air plasma treatment, wetting time decreased. According to previous works, the wetting time of laser treated fabric at low fluence irradiated poly (ethylene terephthalate) was reduced [23]. In this study, the used energy for the treatment was 40mJ/cm^2 and, 5 pulses were used for the treatment of poly (ethylene terephthalate) fabric. Under these conditions of treatment wetting time of a water drop on the surface of poly (ethylene terephthalate) decreased to 2.21s. The ripples induced by laser irradiation might be in the range of nanometer and air could not enter into the gaps between the ripples thus the water drop could enter into the gaps easily [23]. Wetting time for atmospheric air plasma treated poly (ethylene terephthalate) fabric was lower than laser treated fabric. The surface morphology of atmospheric air plasma and laser treated poly (ethylene terephthalate) fibers were different as shown in SEM micrographs (Figure 1). Under laser treatment, poly (ethylene terephthalate) fiber surface was rougher than atmospheric air plasma treated sample, and this surface roughness decreased the wettability of fiber [24].

SEM micrographs of poly (ethylene terephthalate) fibers are shown in Figure 1. Figure 1(a) showed the fiber surface of un-treated poly (ethylene terephthalate). As shown in the figures, un-treated fibers had a smooth surface. After the treatments, surface of fiber was different in atmospheric air plasma and laser treated fabrics. Laser treated samples (Figure 1c) had a ripple like structure, but atmospheric air plasma treated poly (ethylene terephthalate) (Figure 1b) showed some cracks and particles on the surface of the fiber. The physical changes on the surface of laser and atmospheric air plasma treated fabrics were different. High energy electrons in the atmospheric air plasma discharge could affect on the fiber surface and caused etching effect and atmospheric air plasma treatment increased the surface roughness, randomly. Laser treatment made a uniform roughness on the surface.

Figure 2 shows the FTIR/ATR analysis of the untreated, atmospheric air plasma and laser treated poly (ethylene terephthalate) fabrics. Despite previous works on plasma treatment that caused hydroxyl groups on the surface of poly (ethylene terephthalate) fabric [13], there was not any significant chemical change on the surface of atmospheric air plasma treated poly (ethylene terephthalate) (Figure 2). And the spectra of untreated poly (ethylene terephthalate) fiber and atmospheric air plasma treated fiber were similar. Untreated and atmospheric air plasma treated spectra showed a peak at the region of 1712 cm^{-1} which was related to ester groups of poly (ethylene terephthalate) fibers. The intensity of this peak reduced for laser treated poly (ethylene terephthalate) spectrum and there was a peak near this peak at the region of 1730 cm^{-1} which demonstrated carboxylic acid groups. These results showed that laser treatment of poly (ethylene terephthalate) fabric could oxidize the surface of the fiber and caused carboxylic acid groups which are the reason for hydrophilicity of the fabric.

Because soiling of fabrics may change the color of the white fibers, we evaluated color parameters of soiled fabrics before and after washing process using CIE L*a*b* system. Table 1 shows color parameters of soiled poly (ethylene terephthalate) fabric before and after washing process. L* value represents lightness of the samples. Increase of L* value demonstrates a lighter sample, thus lower amount of soil on the fiber surface, since the absorbed soil causes darker appearance of the fabric. After washing of the soiled samples, untreated poly (ethylene terephthalate) fabric showed increase between 78.10 and 81.84 in lightness (L*). In laser treated poly (ethylene terephthalate), there was

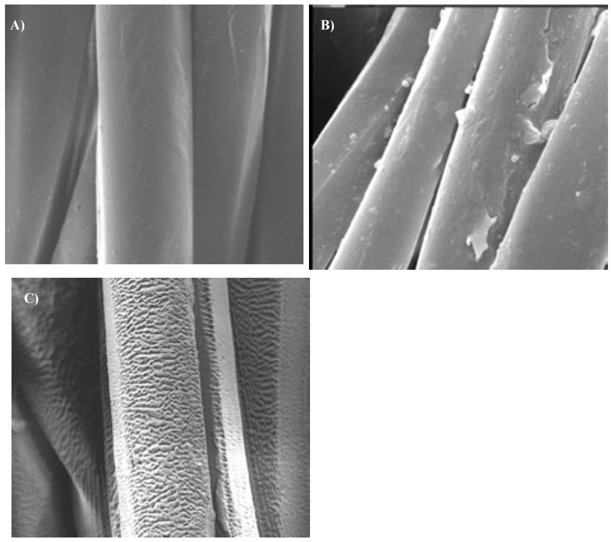

Figure 1: SEM micrographs of poly (ethylene terephthalate) fabric treated by laser and atmospheric air plasma discharge at magnification 1000: (a) untreated, (b) atmospheric air plasma treated, (c) laser treated.

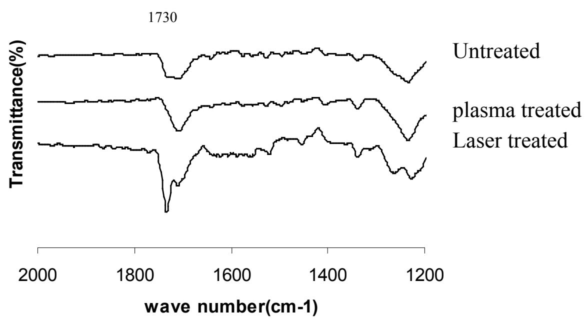

Figure 2: FTIR/ATR analysis of untreated, atmospheric air plasma and laser treated poly (ethylene terephthalate) fabrics.

an increase from 78.738 to 81.412 in lightness. As compared to untreated poly (ethylene terephthalate), laser treated poly (ethylene terephthalate) showed lower increase in lightness thus higher absorbance of soil. Despite the reported papers which soil repellency can be improved by low temperature plasmas [21] we observed increase in soil absorbance on laser treated fabric. Figures 1 (a) & (c) showed the SEM micrographs of untreated and laser treated poly (ethylene terephthalate). We could see that laser treated poly (ethylene terephthalate) had a ripple like structure. Therefore, soil could penetrate into the gaps and washing process was carried out difficultly and soil could not remove from the fabric easily. Surface of Porous fiber acts different from smooth surface [26] so that soil release behavior is different.

The CIE L*a*b* system provides a method for quantifying overall color difference between two specimens using one single term (ΔE), which incorporates the differences of the three individual color parameters as follows [27].

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

Color difference (ΔE) of soiled untreated poly (ethylene terephthalate) fabric before washing was 5.57, and after washing, it reached to 1.834. The difference of decrease was 3.74.. For laser and Color difference (ΔE) of soiled untreated poly (ethylene terephthalate) fabric before plasma treated poly (ethylene terephthalate) fabrics, this decrease was 3.04 and 4.42, respectively. Lower decrease in color difference after washing process shows lower effect of washing process, and soil remained into the gaps. Soiled laser treated poly (ethylene terephthalate) fabric showed lower effect of washing and soil release, as compared with plasma treated poly (ethylene terephthalate) fabric.

The color strength (K/S value) was established according to the following Kubelka-Munk equation, where K and S represent the absorption and scattering coefficient, respectively [22] and R represents reflectance.

$$K/S = (1-R)^2 / 2R$$

The K/S value shows color yield of dyed or stained fabric, and higher amount of K/S value shows higher concentration of dye or stain. For soiled laser treated poly (ethylene terephthalate) fabric, after washing process, the K/S value reduced from 1.89 to 1.47. Whereas it reached from 1.83 to 1.21 for plasma treated one. It seems that plasma treatment of poly (ethylene terephthalate) fiber was more effective than laser treatment for soil release processes of polymer. The obtained results of soil release rate in Table 1 showed this effectiveness. We can see that laser treated poly (ethylene terephthalate) fabric showed lower rate of soil release compared to the plasma treated and untreated poly (ethylene terephthalate).

Soiling behavior of untreated, laser and atmospheric air plasma treated poly (ethylene terephthalate) fabrics are shown in Table 1. L*(Lightness) values for soiled laser and atmospheric air plasma treated fabric were higher than untreated fabric; therefore showed slightly lighter soiled fabric by laser and atmospheric air plasma treatment. But this difference is not very significant for anti-soiling properties of treated fabrics.

Results for polyamide 66 fabrics

Wetting time of untreated, atmospheric air plasma and laser treated polyamide 66 fabrics is shown in Table 2. Untreated polyamide 66 fabrics showed the wetting time of 3.52 s whereas laser treated fabric had a 0.52 s wetting time. Laser treated polyamide fabric showed higher wettability (85%) than untreated fiber and slightly lower wetting time than atmospheric air plasma treated fiber. Roughness in hydrophilic surface causes increase in wettability [24] and therefore wetting time for polyamide fiber decreased by laser and atmospheric air plasma treatment.

Figure 3(a) shows the surface of un-treated polyamide 66 fiber. The surface of polyamide 66 fiber showed a smooth surface. After the treatments, Laser treated polyamide 66 fibers (Figure 3c) had a ripple like structure, but atmospheric air plasma treated polyamide 66 (Figure 3b) showed some cracks on the surface of the fiber. Plasma discharge consists of high energy electrons which can affect on the surface of polyamide 66 fibers so that produce an etched surface. The physical changes on the surface of laser and atmospheric air plasma treated polyamide 66 fabrics were different. Plasma treatment caused uneven surface on the fiber. But laser treatment made a uniform ripple like structure on the polyamide 66 fiber surfaces.

Functional groups alterations of polyamide fiber are shown in Figure 4. It was found that ATR spectrum of laser treated polyamide 66 showed different peaks from untreated and atmospheric air plasma treated polyamide 66 fibers. At laser treated polyamide 66 fiber, a peak was appeared at the region of 1733 cm^{-1} which is responsible for increasing the concentration of acid end groups in polyamide 66 [25].

Soiling behavior of hydrophobic fibers is different from natural fibers because of their electrostatic charges on their surface [21]. Some surface treatment such as plasma treatment changes functional groups on the surface of the hydrophobic fibers therefore creates hydrophilic groups. Increasing hydrophilic group increases moisture content of fibers thus reducing soiling tendency. Surface treatment by laser irradiation showed different results for soil release behavior compared to plasma treatment. Table 2 shows color parameters of soiled polyamide 66 fibers before and after washing process. Before washing process L* value was 58.842 for un-treated polyamide and after washing it reached to 74.412. Laser and atmospheric air plasma treated polyamide fabric showed lower increase for lightness as compared with untreated sample. It seems that atmospheric air plasma and laser

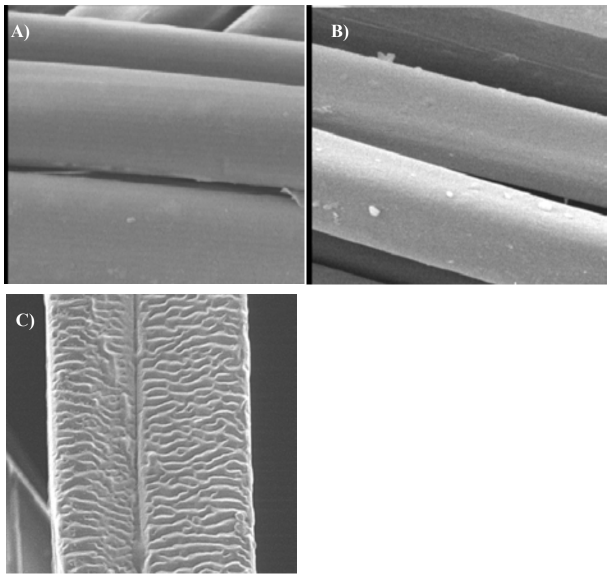

Figure 3: SEM micrographs of polyamide 66 fabric treated by laser and atmospheric air plasma discharge at magnification of 1000: (a) untreated, (b) atmospheric air plasma treated, (c) laser treated.

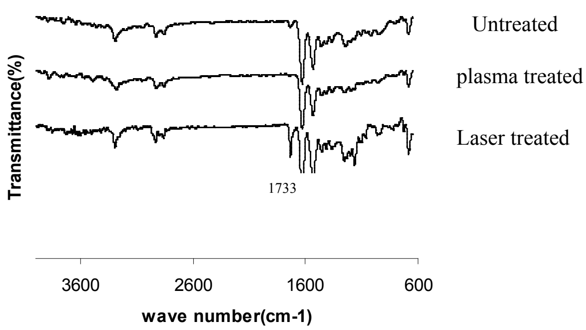

Figure 4: FTIR/ATR analysis of untreated, atmospheric air plasma and laser treated polyamide 66 fabrics.

treated samples showed lower soil release behavior despite making functional groups (hydrophilic groups) on the fiber surface, therefore morphological properties of treated surface plays significant role in soil release behavior. We could see this difference in Figure 3 which showed laser treated polyamide (Figure 3c) had ripple like structure. In table 2 we can see color difference (ΔE) and K/S value (color yield) results of soiled polyamide 66 fabrics. After washing process of soiled plasma treated polyamide 66 fabrics K/S value reduced from 1.82 to 1.28. The K/S value for soiled laser treated was 1.67 by washing process. The higher K/S value for laser treated polyamide 66 fabrics shows high concentration of soil, and therefore lower soil release effect on laser treated polyamide 66 fibers. The color difference (ΔE) of laser treated polyamide 66 fabric after washing showed higher difference as compared with plasma treated polyamide 66 fabrics. These results indicated that laser treatment on polyamide 66 fibers caused lower effect of soil release after washing process, since the rate of soil release test showed it. Soil release rate for laser treated polyamide 66 fabric was 4 and it increased to 4-5 for plasma treated fibers.

Conclusions

Plasma discharge and laser treatment of polyamide 66 and poly (ethylene terephthalate) fibers increased wettability of the fabric. Laser treatment of poly (ethylene terephthalate) made carboxylic acid groups which caused hydrophilicity on the poly (ethylene terephthalate) surface. Despite chemical changes on the fiber surface and hydrophilicity of chemical groups, morphological changes on the fiber surface are responsible for soil release behavior of poly (ethylene terephthalate) and polyamide 66 fabrics. The surface morphology of plasma and laser treated fibers are different. Laser treated poly (ethylene terephthalate) and polyamide 66 fibers have uniform ripple like structure and soil can penetrate into the gaps, thus washing process is carried out difficultly and soil remains in the fabric, whereas plasma treatment of polymers causes uneven surface on the fibers that soil removes from the surface easily.

References

1. Joanne Yip C, Chan K , Sin KM, Lau KS (2002) Study of plasma-etched and laser-irradiated polyamide materials**.** Mater Resea Innov 6: 44.
2. El-Nagar BK , Saudy MA, Eatah AI , Masoud M M (2006) DC pseudo plasma discharge treatment of polyester textile surface for disperse dyeing. J th Text Inst 97: 111-117.
3. Dascalu T, Acosta-Ortiz S, Ortiz-Morales M, Compean I (2000) Removal of the indigo color by laser interaction. Opt Lasers Eng 34: 179-189.
4. Ortiz-Morales M, Poterasu M , Acosta-Ortiz S, Compean I , Hernandez-alvardo M R (2003) A comparison between various laser-based denim fading. Opt Lasers Eng 139: 15-24.
5. Rouette H K (2001) Encyclopedia of Textile Finishing, Springer, Germany.
6. Ferrero F, Testore F, Tonin C , Innocenti R (2002) Autex Research Journal 2.
7. Chow YL, Chan CK , Kan CW (2011) Fibers and Polymers 12: 275.
8. Shaohua L, Xiang Z (2003) Coloration Technology 119: 19.
9. Belli R, Miotello A , Mosaner P, Toniutti L (2006) Applied Physics A 83: 651.
10. Oktem T, Seventekin N (2002) Improvement of surface related properties of poly (ethylene terephthalate)/cotton fabrics by glow discharge treatment. Indian journal of fibre & textile research 27: 161-165.
11. Yip J, Chan K, Sin KM, Lau KS (2002) Study of physico-chemical surface treatments on dyeing properties of polyamides. Colo Techn 118: 26-30.
12. Gupta A, Hilborn J, Hollenstein Ch, Plummer JG, Houriet R, et al. (2000) Surface modification of polyester films by RF plasma. J Appl Polym Sci 78: 1083-1091.
13. Zhu L, Wang C, Qiu Y (2007) Surf Coat Techn 201: 7453.
14. Poletti G, Orsini E, Raffaele-addamo A, Riccardi C, Selli E (2003) Appl surf sci219: 311.
15. Poll HU, Schladitz U, Schreiter S (2001) Surf Coat Techn142: 489.
16. Verschuren J, Kiekens P (2005) Autex Research Journal 5.
17. Leroux F, Campagne C, Perwuelz A, Gengembre L (2009) Surf Coat Technol 203: 3178.
18. Raffaele-addamo A, Riccardi C, Selli E, Barni R, et al (2003) Surf Coat Technol 174: 886 .
19. Chernik VN, Paskhalov AA, Gaidar AI (2009) J surf invest 3**:** 215.
20. Mitrofanov AV, Karban OV, Sugonyako A and Lubomska M (2009) J surf invest 3: 519.
21. Seventekin N, Oktem T, Ayhan H, Piskin E (2000) Modification of polyester and polyamide fabrics by different in situ plasma polymerization methods. Turkish journal of chemistry 24: 275.
22. Oktem T, Aylan H, Seventekin N, Piskin E (1999) Coloration Technology 115:274.
23. Kan CW (2008) Impact of textile properties of polyester with laser. Optics & Laser Technology 40: 113-119.
24. Parkin IP, Plagrave RG (2005) Self-cleaning coatings. J Mater Chem 15: 1689-1695.
25. Lewin M (2007) Hand book of fiber chemistry. (3rd edition) Taylor and Francis-New York.
26. Schindler WD, Hauser PJ (2004) Chemical finishing of textiles, Woodhead publishing limited, England.
27. Collier BJ , Epps HH (1999) Textile Testing and Analysis, Merrill, Upper Saddle, New Jersey.