Fibers and Polymers 2014, Vol.15, No.11, 2313-2318 DOI 10.1007/s12221-014-2313-2

A Study of Pigment Application on Atmospheric Pressure Plasma Treated Cotton Fabric

C. W. Kan*, W. S. Man, and S. P. Ng[1]

Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
[1]*Hong Kong Community College, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*
(Received February 17, 2014; Revised May 4, 2014; Accepted July 6, 2014)

Abstract: Cotton fabric was treated with atmospheric pressure plasma under the influence of different degrees of discharge power (130 W, 140 W, 150 W, 160 W, and 170 W) and oxygen flow rates (0.2 *l*/min, 0.3 *l*/min, 0.4 *l*/min, 0.5 *l*/min, and 0.6 *l*/min). After plasma treatment, the cotton fabric was subjected to pigment dyeing. Experimental results revealed that plasma treatment with increasing discharge power and oxygen flow rate is able to achieve a better water absorbency and hence improve the pigment dyeing ability. In addition, the plasma treatment can improve the crocking performance of the pigment dyed fabric.

Keywords: Atmospheric pressure plasma, Pigment, Dyeing, Cotton

Introduction

Dyes are widely used in textile industry for imparting superior aesthetics. However, many environmental problems are encountered because of large volumes of effluents generated in the process. Pigment dyes show superior advantages, such as a shorter coloration process, low chemicals usage and less effluent formation [1]. In general, pigments offer good light and washing fastness but they always have comparatively poor color yield and evenness and rubbing fastness.

Pigments are water insoluble and inert to polymer surface due to the strong attractive force between pigment molecules. Pigment molecules are held mechanically in a solid binder polymer instead of forming bonding with polymer surface like dye molecules [2]. As a result, levelness and colorfastness of pigment coloration are highly correlated to physical and chemical properties of fabric and binders but not the structure of pigments.

Plasma treatment is one of the most environmentally friendly treatments since it is a dry treatment and consumes few chemicals [3]. Also, plasma treatment is an extremely short process and is easy to handle, which reduces production cost. Moreover, mechanical and physicochemical properties of the original material are retained. Depth of plasma modification of the subject material varies from 100 Å to several micrometers and the bulk of polymer remains the same [4].

Plasma modification can be done through polymerization, ablation and chemical reactions on the surface of the fabric. Plasma mechanism is determined by feeding gas under specific process conditions [5-10]. Plasma is a dynamic mix of ions, electrons, neutrons, excited molecules, free radicals, metastables and photons formed by plasma reactions such as ionization, excitation and dissociation which occur in front of electrodes. Helium-oxygen atmospheric plasma contains high concentration of active species [11]. During treatment, bombardment of active species causes surface atoms ejection when transferred energy is greater than atoms binding energy. A large number of cracks and grooves are generated on fiber surface by etching which modifies surface properties physically. Furthermore, during the treatment and/or immediately after plasma treatment on exposure to the atmosphere [12], free radicals insert new hydrophilic carboxylic and hydroxyl derivatives (e.g. -C=O, -C-O, -COOH, -OH) on fiber surface [13,14].

Previous research has reported that the hydrophility [15,16], hydrophobicity [17,18], dyeing ability [19,20], adhesion to different types of chemical finishing [21] and anti-microbial agents [22] etc. can be modified by plasma treatment. It has been pointed out that dyeability of pigments to different fabrics like polyester and silk can be improved by atmospheric pressure plasma [23], however, there is a lack of research on improving pigment coloration of cotton fabric by plasma technology. As a result, this paper investigates the effect of atmospheric pressure plasma treatment on cotton fabric for dyeing using pigment.

Experimental

Fabric

100 % ready-to-dye plain weave cotton fabric of 250 g/m^2 was washed with acetone (99 %, GR Grade) to remove surface dirt and was subsequently dried at room temperature. The dried fabric was conditioned at 65±2 % relative humidity and 20±2 ^{o}C for 24 h before plasma treatment.

Plasma Treatment

Atmospheric pressure plasma jet (APPJ) (Atomflo^{TM} 400) with rectangular nozzle (AH-500L, Surfx Technologies LLC, CA) was used for treatment of cotton (Figure 1) [24]. Helium (He, 99.995 % purity, flow rate: 30 *l*/min.) and oxygen (O_2, 99.7 % purity, flow rate: 0.2 *l*/min, 0.3 *l*/min,

*Corresponding author: tccwk@polyu.edu.hk

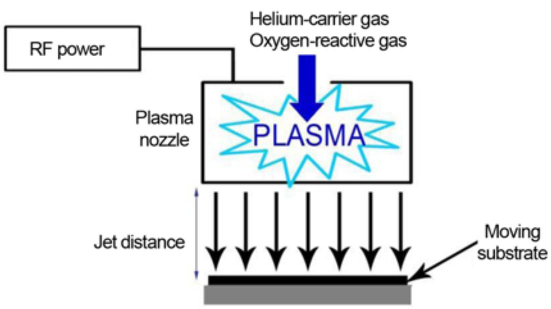

Figure 1. Schematic diagram of plasma treatment.

0.4 *l*/min, 0.5 *l*/min, and 0.6 *l*/min) were used as carrier and reactive gas, respectively. Plasma reactive species were generated at radio frequency of 13.56 MHz with different discharge powers (130 W, 140 W, 150 W, 160 W, and 170 W). The jet distance and jet moving speed were set at 3 mm and 5 mm/s, respectively. After APP treatment, the fabrics were conditioned at 65±2 % relative humidity and 20±2 °C for 24 h before pigment dyeing and evaluation.

Pigment Dyeing

Pigment dyeing solution was prepared by mixing 1 g blue pigment (Printofix Pigment, Clariant) and 30 g binder (Printofix Binder, Clariant) in 1 liter of deionized water. The cotton fabrics were padded by a horizontal padder (Weriner Mathis AG) for a dye uptake of 70 %. Padded samples were dried at 90 °C for 3 min and cured at 145 °C for 5 min by curing machine (Weriner Mathis AG). After dyeing, the fabrics were conditioned at 65±2 % relative humidity and 20±2 °C for 24 h before evaluation.

Water Absorbency

Water absorbency was measured by wicking rate measurement (standard DIN 53 923 (EDANA 10.1-72)) in warp and weft directions, 6 times. The sample edge was immersed in a large volume of distilled water and the time taken for the capillary ascension to reach 8 cm was measured. Wickability is presented by total wicking coefficient (W_c) of warp and weft directions [18]; it can be calculated by Lucas and Washbum equation (equation (1)). This equation describes the speed of a liquid which moves up or down in a capillary perpendicular to the free face of the liquid in the absence of gravity [25].

$$h = \sqrt{\frac{\gamma_c \cdot \gamma \cdot \cos\theta \cdot t}{2\eta}} = W_c \cdot t^{1/2} \quad (1)$$

where h is the height reached by the liquid at time t; r_c is the effective hydraulic radius of the capillaries; γ is the surface tension of the liquid-vapor interface; θ is the apparent contact angle of the fabric (in vertical wicking test, θ=180 °, thus cosθ=1); η is the viscosity of the liquid; W_c is the wicking coefficient; and t is the time.

Scanning Electron Microscopy (SEM)

Topographical features of surface of the plasma-modified cotton substrates were observed by scanning electron microscope (SEM, JSM-6490, JEOL Ltd., Japan). 4000X magnification images of substrates were captured at accelerating voltage of 20 kV.

Fourier Transform Infrared Spectroscopy (FTIR-ATR)

Perkin Elmer spectrophotometer (Spectrum 100, Perkin Elmer Ltd.) equipped with an attenuated total internal reflectance (ATR) accessory was used to analyze chemical functionalities of samples with 500 nm depth, qualitatively and quantitatively. Each FTIR spectrum was obtained after an average of 64 scans with a resolution of 4 cm^{-1}. For cotton fabric, the absorption peaks for -OH stretching at 3270 cm^{-1} and C-O stretching at 1313 cm^{-1} were indicated.

Color Yield Measurement

The color of pigment dyed material was characterized by reflectance measured at given wavelength intervals throughout the visible spectrum by reflectance spectrophotometer (Macbeth Color-Eye 7000A) with illuminant D65 and 10 ° standard observer. The fabric was folded four times to ensure opacity and reflectance measurement from 400 nm to 700 nm with 20 nm interval was obtained eight times. Percent reflectance values were converted into *K/S* values in accordance with the Kubelka-Munk equation (equation (2)).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (2)$$

where K is the absorption coefficient of the colorant, S is the scattering coefficient of the colored substrate, and R is the reflectance of the colored sample. The higher the *K/S* value, the more the pigment uptake is, resulting in better color yield.

Levelness

Relative unevenness index (RUI) [20] was found by measuring color reflectance values at 8 random locations on the sample by reflectance spectrophotometer (Macbeth Color-Eye 7000A) with illuminant D65 and 10 ° standard observer spectrophotometer with D65 Illuminant and 10 ° standard observer from 400 nm to 700 nm with 20 nm interval. RUI of the colored sample was calculated by equations (3) and (4).

$$S_\lambda = \sqrt{\frac{\sum_{i=1}^{n}(R_i - R_m)^2}{n-1}} \quad (3)$$

where S_λ is standard deviation of reflectance values, R_i is reflectance value of the ith measurement for each wavelength, and R_m is mean of reflectance values of n measurements for each wavelength.

$$RUI = \sum_{400}^{700} C_\lambda V_\lambda = \sum_{400}^{700} \frac{S_\lambda}{R} V_\lambda \quad (4)$$

where V_λ is photopic relative luminous efficiency function.

Table 1. Suggested interpretations of RUI values [20]

RUI	Visual appearance of levelness
<0.2	Excellent levelness
0.2-0.49	Good levelness
0.5-1.0	Poor levelness
>1.0	Bad levelness

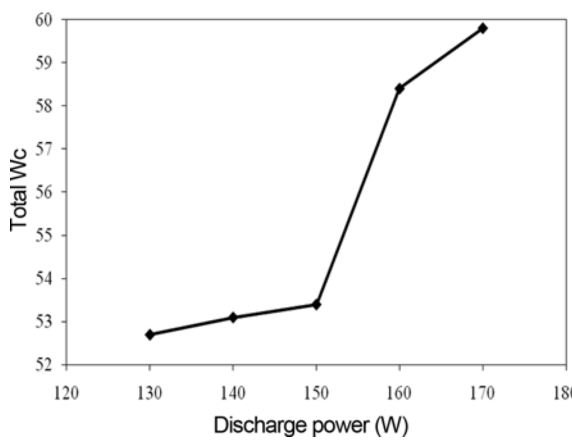

Figure 2. Relationship between wicking coefficient and discharge power.

The degree of evenness is described according to the RUI value obtained; suggested interpretations of RUI values are shown in Table 1 [26].

Colorfastness to Crocking

Colorfastness to crocking was measured by Crockmeter method (AATCC 8) with dry and wet conditions. Other than conventional grey scale assessment, the *K/S* value of the stained white test cloth was also measured.

Results and Discussion

Water Absorbency

The results of wicking test are summarized in Figure 2; wickability is increased with the increase of discharge power and reaches the highest value at treatment power 170 W. Progressive wicking includes wetting of fiber surface, transportation of liquid to assembly of fibers and adsorption liquid on fiber surface or diffusion of liquid into interior of the fibers [26]. The wickability is governed by the properties of the liquid-solid surface interactions and geometric configuration of the pores structure [27,28]. SEM images of fibers (Figure 3) suggest that higher discharge power of plasma treatment can form more cracks on fiber surface. A higher discharge power can attain a higher rate of plasma active species formation so that the number of active species reactive to cotton fiber surface increase, leading to increased etching rate [29]. In addition, a higher discharge power allows more active species with higher energy to bombard

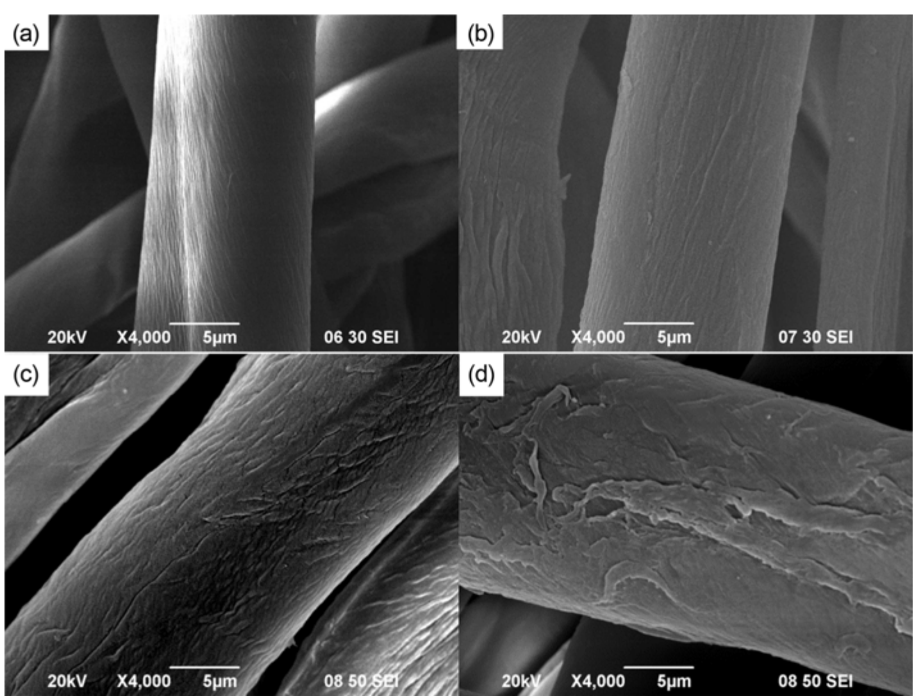

Figure 3. SEM pictures of (a) untreated cotton fiber, plasma treated cotton fiber with (b) 130 W, (c) 150 W, and (d) 170 W discharge power.

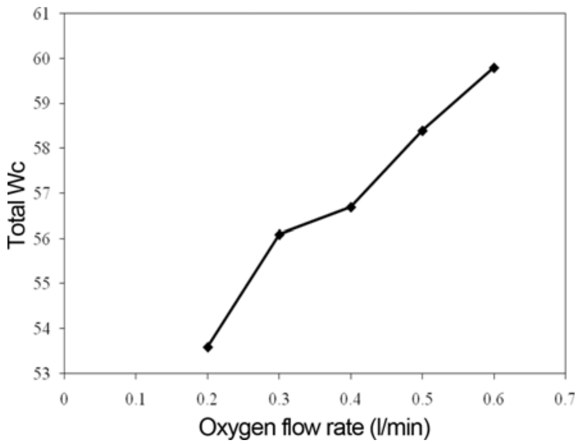

Figure 4. Relationship wicking coefficient and oxygen flow rate.

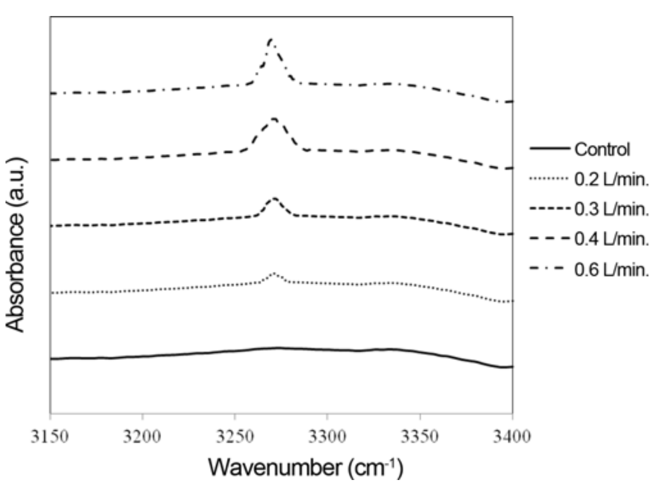

Figure 5. FTIR spectra of -OH groups in cotton fiber with different flow rate (170 W, jet moving speed: 5 mm/s, and 3 mm jet-to-substrate distance).

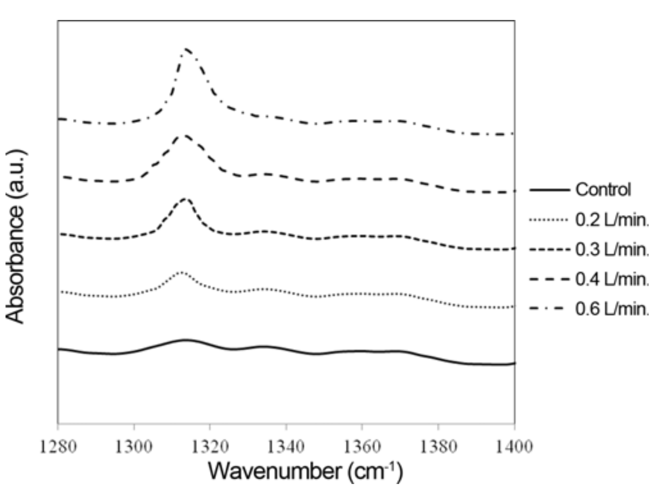

Figure 6. FTIR spectra of -C-O groups in cotton fiber with different flow rate (170 W, jet moving speed: 5 mm/s, and 3 mm jet-to-substrate distance).

the substrate. As a result, the water absorption rate is highly increased [29].

Obviously, an increasing trend of wicking coefficient with increasing oxygen flow rate is showed in Figure 4 and the wicking coefficient is the largest at 0.6 *l*/min oxygen flow rate. Under high discharge power, oxygen-containing polar groups further advance the wickability of cotton. Active oxygen active species like ground-state $O(^3P)$, metastables, $O_2(a^1\Delta_g)$, O_2 $(b^1\Sigma_g^+)$, and ozone O_3 are generated with sufficient energy for effective collision [25]. High oxygen population thus gives a higher concentration of plasma active species which enhance the plasma effect.

Oxidation of cotton fiber surface caused by reactive oxygen plasma species greatly enhances the adhesion force between polymer surface and water molecules by inducing new functional groups -OH (Figure 5) and -C-O (Figure 6) [24]. The concentration of surface hydrophilic groups is amplified continuously during the course of treatment. The peak area indicates that oxygen containing function groups present increase as oxygen flow rate changes from 0.2 *l*/min to 0.6 *l*/min. It is obvious that when the oxygen flow rate increases, more oxygen plasma species are generated to interact with fiber surface leading to increase in the amount of newly formed hydrophilic function groups on the fiber surface [24].

Color Yield and Levelness

Generally speaking, plasma treated samples show a better color yield than the untreated sample (Table 2). Plasma treatment results in great improvement of water absorption of cotton fabric by morphological modification and hydrophilic group insertion [22,23], as shown in Figures 2 and 3. The color yield increases when the discharge power increases. As shown in Figure 3, high discharge power can deteriorate the fiber surface more rapidly than low discharge power. In addition, as the discharge power increases, the number and activity of active species in plasma increases and the interaction on the fiber surface increase, leading to formation of polar groups and changes in fiber morphology. The difference in fiber morphology suggests that water absorbability improvement is caused by larger surface-volume ratio. Discharge power of 170 W gives the highest color yield. Meanwhile, it is noted that under the same discharge power of 170 W, color yield of fabric increases continuously with the flow rate of oxygen and reaches the highest (0.6 *l*/min). At low flow rate, the amount of oxygen species in plasma is not sufficient to enhance surface hydrophility. Meanwhile, at low flow rate, oxidation due to air impurities such as nitrogen and water vapors prevails over the surface modification with oxygen because the plasma treatment was conducted at atmospheric pressure, which is not an air-free environment. As the oxygen flow rate increases, the amount of oxygen supplied increases accordingly. The increased amount of oxygen species in plasma can introduce oxygen-containing groups on the

Table 2. Color yield of blue pigmented cotton fabric

Sample	Untreated	130 W/0.3 *l*/min	150 W/0.3 *l*/min	170 W/0.3 *l*/min	170 W/0.2 *l*/min	170 W/0.4 *l*/min	170 W/0.6 *l*/min
Color yield	12.89	13.10 (↑7.2 %)	13.17 (↑7.8 %)	13.23 (↑8.3 %)	13.17 (↑7.8 %)	13.66 (↑11.8 %)	13.74 (↑12.4 %)

Table 3. Levelness of blue pigmented cotton fabric

Sample	Untreated	130 W/0.3 *l*/min	150 W/0.3 *l*/min	170 W/0.3 *l*/min	170 W/0.2 *l*/min	170 W/0.4 *l*/min	170 W/0.6 *l*/min
Levelness	0.29	0.28	0.21	0.19	0.22	0.15	0.12

Table 4. Crocking fastness of blue pigmented cotton fabric

Sample	Untreated	130 W/0.3 *l*/min	150 W/0.3 *l*/min	170 W/0.3 *l*/min	170 W/0.2 *l*/min	170 W/0.4 *l*/min	170 W/0.6 *l*/min
Dry crocking rating*	4-5*	5	5	5	5	5	5
(*K/S* value)#	(0.32)#	(0.23)	(0.23)	(0.22)	(0.23)	(0.21)	(0.22)
Wet crocking rating*	3-4*	4	4	4-5	4-5	4-5	4-5
(*K/S* value)#	(0.90)#	(0.52)	(0.48)	(0.36)	(0.37)	(0.32)	(0.31)

*Grey scale: 5 and 1 represent the best and the worst color fastness rating, respectively and #the higher the *K/S* value, more color is transferred to the white test cloth and poorer is the color fastness.

cotton surface leading to enhanced water absorbency and then improves the color yield.

Evenness of color in pigment dyeing is a common problem, which is caused by pigment molecules migration and agglomeration. Water insoluble pigment molecules easily aggregate in aqueous solution and migrate to a little bit higher temperature area during drying. However, plasma treated cotton gives a more uniform color depth in blue pigment dyeing (Table 3). The possible reason of higher evenness may be due to trapping of pigment and binder in the cracks induced by plasma treatment (Figure 3). When comparing the RUI standard in Table 1, evenness of 1 g/*l* pigment dyeing to plasma treated cotton is acceptable.

Color Fastness to Crocking

The grey scale rating and color yield of the stained white test cloth sample are presented in Table 4. In the crocking test, the color transferred to the white test cloth was normally assessed by comparing it with the grey scale for staining, and a grey scale rating was assigned. However, comparison of standard grey scale rating by human eyes was subjective and inaccurate. Therefore, the transferred color on the white test cloth was evaluated by reflectance spectrophotometer, the same as for color yield measurement. The crocking fastness of blue pigment dyed fabric shows good fastness in dry condition but with a relatively poor performance in wet crocking. In pigment dyeing, pigments particles only show strong attractive force to one another in their solid crystal lattice structure and attachment of pigment depends on the mechanical adhesion force between binder and polymer surface. As a result, detachment of pigment in wet condition is serious when binders dissolve into water. Generally speaking, plasma treated fabric can achieve better crocking fastness and the improvement is directly proportional to the level of power and oxygen flow rate [12,30,31]. One explanation for this is that the linkage in polymer-binder-pigment system is strengthened physically by cracks and chemically by the oxygen containing group, which results in reduction of pigment detachment. Overall, plasma treatment gives a significant improvement in crocking [12,30,31].

Conclusion

Cotton fabric was treated with oxygen plasma with different degrees of discharge power and oxygen flow rates. Experimental results revealed that high discharge power and oxygen flow rate contribute to better water absorbency improvement on cotton fabric. In addition, the plasma treatment showed a positive influence on increasing color yield and rubbing fastness of blue pigment application on cotton fabric. Especially, the rubbing fastness is greatly improved.

Acknowledgements

The work was supported by a research grant from the Hong Kong Polytechnic University.

References

1. J. R. Aspland, *Text. Chem. Color.*, **5**, 31 (1992).
2. R. M. Christie, R. R. Mather, and R. H. Wardman, "The Chemistry of Color Application", pp.5-30, Blackwell Science, Malden, Mass, 1999.
3. H. A. Karahan and E. Özdoğan, *Fiber. Polym.*, **9**, 21 (2008).
4. K. K. Samanta, M. Jassal, and A. K. Agrawal, *Surf. Coat. Tech.,* **203**, 1336 (2009).
5. H. Höcker, *Pure Appl. Chem.*, **74**, 423 (2002).
6. R. Morent, N. De Geyter, J. Verschuren, K. De Clerck, P. Kiekens, and C. Leys, *Surf. Coat. Tech.*, **202**, 3427 (2008).

7. M. Parvinzadeh and I. Ebrahimi, *Appl. Surf. Sci.,* **257**, 4062 (2011).
8. M. Parvinzadeh and I. Ebrahimi, *Radiat. Eff. Defect. S.*, **166**, 408 (2011).
9. I. Ebrahimi, A. Kiumarsi, M. P. Gashti, R. Rashidian, and M. H. Norouzi, *Eur. Phys. J. Appl. Phys.*, **56**, 10801 (2011).
10. M. P. Gashti, D. Hegemann, M. Stir, and J. Hulliger, *Plasma Process. Polym.,* **11**, 37 (2014).
11. S. K. Hodak, T. Supasai, B. Paosawatyanyong, K. Kamlangkla, and V. Pavarajarn, *Appl. Surf. Sci.*, **254**, 4744 (2008).
12. F. Leroux, C. Campagne, A. Perwuelz, and L. Gengembre, *Surf. Coat. Tech.*, **254**, 3902 (2008).
13. Z. S. Cai and Y. P. Qiu, *J. Appl. Polym. Sci.*, **99**, 2233 (2006).
14. Ľ. Černákorá, D. Kováčik, A. Zahoránová, M. Černák, and M. Mazúr, *Plasma Chem. Plasma P.*, **25**, 427 (2005).
15. M. Šimor, J. Ráhel, M. Černák, Y. Imahori, M. Štefečka, and M. Kando, *Surf. Coat. Tech.*, **172**, 1 (2003).
16. M. Kostić, N. Radić, B. M. Obradović, S. Dimitrjević, M. M. Kuraica, and P. Škundrić, *Chem. Ind. Chem. Eng. Q.*, **14**, 219 (2008).
17. M. Radetic, D. Jocia, and P. Jovancic, *AATCC Rev.*, **32**, 55 (2002).
18. C. M. Zhang and K. J. Fang, *Surf. Coat. Tech.*, **203**, 2058 (2009).
19. D. Knittel and E. Schollmeyer, *J. Text. Inst.*, **91**, 151 (2000).
20. A. Schütze, J. Y. Jeong, S. E. Babayan, J. Park, G. S. Selwyn, and R. F. Hicks, *IEEE Trans. Plasma Sci.*, **26**, 1685 (1998).
21. K. K. Wong, X. M. Tao, C. W. M. Yuen, and K. W. Yeung, *Text. Res. J.*, **71**, 49 (2001).
22. Y. Ren, C. X. Wang, and Y. P. Qiu, *Surf. Coat. Tech.*, **202**, 2670 (2008).
23. Y. Shin and D. I. Yoo, *J. Appl. Polym. Sci.*, **108**, 785 (2008).
24. C. W. Kan, C. W. M. Yuen, and W. Y. Tsoi, *Cellulose,* **18**, 2949 (2011).
25. N. R. S. Hollies, M. M. Kaessinger, B. S. Watson, and H. Bogaty, *Text. Res. J.*, **16**, 829 (1957).
26. C. L. Chong, S. Q. Li, and K. W. Yeung, *J. Soc. Dyers. Colour.*, **108**, 528 (1992).
27. Y. L. Hsieh, *Text. Res. J.*, **65**, 299 (1995).
28. J. M. Marchal, *Text. Res. J.*, **71**, 813 (2001).
29. N. V. Bhat and Y. N. Benjamin, *Text. Res. J.,* **69**, 38 (1999).
30. K. J. Fang and C. M. Zhang, *Appl. Surf. Sci.,* **255**, 7561 (2009).
31. E. Özdogan, R. Saber, H. Ayhan, and N. Seventekin, *Color. Technol.,* **118**, 100 (2002).