ISSN 1070-4272, Russian Journal of Applied Chemistry, 2018, Vol. 91, No. 8, pp. 1338−1344. © Pleiades Publishing, Ltd., 2018.

MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Antimicrobial Performance of Plasma Corona Modified Cotton Treated with Silver Nitrate[1]

S. Nourbakhsh

Textile Department, Islamic Azad University, Yadegar-e-Imam Khomeini (RAH) Shahre Rey Branch, Tehran, Iran
e-mail: nourbakhsh.sh@gmail.com

Received May 7, 2018

Abstract—Cotton fabric was treated by corona plasma discharge at different powers and numbers of passages. The carboxyl group content was determined by Methylene Blue staining and titration. Then, the untreated and treated cotton fabrics were treated with silver nitrate, and laundering test was carried out. The inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis for silver and antibacterial tests were done. The surface bonding and morphology were studied by FTIR/ATR spectroscopy and scanning electron microscopy (SEM), respectively. The plasma corona discharge treatment of cotton fabric increases the content of carboxyl groups. An increase in the power of plasma treatment increases the content of carboxyl groups and adsorption of silver ions. As a result, the antibacterial effect is enhanced and becomes more stable after repeated laundering.

Keywords: plasma corona discharge, cotton, antimicrobial effect, silver nitrate, carboxyl group

DOI: 10.1134/S1070427218080128

INTRODUCTION

Textile fibers are highly susceptible to attack by microorganisms. The growth of microorganisms on textiles occurs in the presence of moisture and nutrients and is enhanced at higher temperatures. The microbes affect not only the wearer, but also the textile itself [1, 2]. Synthetic fibers are resistant to attack of microorganisms because of their hydrophobicity, whereas cellulosic fibers under appropriate conditions act as a nutrient source for microorganisms and thus can degrade [1–3]. Cotton fibers are able to absorb moisture to become a suitable medium for bacterial growth [1, 2, 4, 5]. The microorganisms on cotton fibers cause generation of odor, stains, discoloration, damage, and deterioration. Therefore, it is necessary to prevent the growth of microbes on the fibers [1, 2]. Antimicrobial agents are used for inhibiting or killing microbes to reduce odor, damage, and undesirable effects. The common antibacterial agents used in textiles are silver, triclosan, polyhexamethylene biguanide (PHMB), and quaternary ammonium compounds. Silver metal is the most widely used antibacterial agent in textiles [1, 2, 6]. Heavy metals like silver kill bacteria by combining with intracellular proteins and activating them [1, 2, 7–9]. Silver-based products are more effective against bacteria than against fungi, mold, and mildew [2, 8].

Surface modification of textiles with silver particles is not permanent, and the antibacterial effect in this case decreases after repeated laundering. There are several methods for stabilizing materials on cotton fabric. These methods involve the use of a large amount of chemicals and water. The functionalization, drying, and curing processes are expensive and time-consuming [10–13]. Plasma discharge is a suitable method for modifying a polymer surface in a dry system without any pollution [14]. Surface modification of textiles [15, 16], polymers [17] including Nylon [18], polyethylene terephthalate [19, 20], and cotton fibers [21–26] by plasma discharge has been reported. Oxygen plasma treatment of cotton generates carboxyl and carbonyl groups, and the increase in the carboxyl group content makes the fiber functionalized and more wettable [27–30]. Coating of plasma-treated and untreated cotton and cotton/polyester fabrics with silver nitrate and silver nanoparticles was studied

[1] The text was submitted by the author in English.

previously [4, 31–36]. In this study, cotton fabric was treated by plasma corona discharge at different powers and numbers of passages. Methylene Blue staining and titration were used for determining carboxyl groups on untreated and treated cotton fabrics. Then, silver nitrate was deposited onto untreated and plasma-treated cotton fabrics. Laundering test was done to evaluate the durability of Ag ions on cotton fabric. Antibacterial test and ICP-OES analysis were carried out to determine the antibacterial effect and Ag ion content, respectively, before and after laundering. The scanning electron microscopy and FTIR/ATR were used for assessment of the surface morphology and functional groups.

EXPERIMENTAL

Material. The fabric used in this study was a desized, scoured, and bleached plain weave cotton weighing 109 g m^{-2} (Testfabrics style 400), produced by Testfabrics, West Pittston (the United States). Laventin LNB nonionic detergent (BASF, Germany) was used. Silver nitrate, nitric acid, sodium chloride, sodium hydroxide, and hydrogen chloride were purchased from Merck (Germany). The AATCC standard detergent without optical brightener and Methylene Blue dye from Merck (Germany) were used.

Methods. The plain weave cotton fabric was washed with the nonionic detergent and dried to prepare for plasma discharge treatment. Cotton fabric was treated by plasma corona discharge at different powers and number of passages (500 and 1000 W; 40 and 60 passages). The atmospheric air plasma corona instrument was made by Azad Electrical Industries (Iran). It has two electrodes: metal electrode roll with silicone coating and aluminum electrode parallel with electrode roll [37]. The experiments were carried out at atmospheric pressure in air. The power and velocity were set at 500 or 1000 W and 2 m min^{-1}, respectively. The distance between the electrodes was 3 mm. The untreated and plasma-treated cotton fabrics were stained with Methylene Blue dye (C.I. basic blue 9) for determining carboxylic acid groups on cotton. The staining was carried out with a 1 % (w/v) Methylene Blue solution for 5 min at room temperature, after which the fabric was dried [27]. The color parameters of the stained fabrics were determined with a Color Eye 7000 A spectrophotometer (D_{65}/10°).

The color yield (*K/S*) of the dyed fabrics was calculated using the Kubelka–Munk equation

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

where R is the reflectance. The color difference (ΔE) of the untreated and corona plasma discharge treated cotton fabrics was calculated by Eq. (2) [38]:

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

The carboxyl group content (mg-equiv L^{-1}) [27, 39] was determined by titration. For this purpose, the cotton fabrics samples were ground to a powder, dried in an oven, acidified with an HCl + NaCl solution, and titrated with an NaOH + NaCl solution (25 ± 0.5°C) using a precision burette.

The untreated and plasma corona discharge treated cotton fabrics were coated with a 2% silver nitrate solution at ambient temperature for 30 min, after which the samples were passed through pad rollers, dried at 100°C, and cured at 150°C for 1 min. Then, the samples were washed with distilled water to remove the nonabsorbed fragments from the cotton surface. The coated fabric samples were divided in two portions. One portion was kept as control, and the other portion was used for the laundering test. The cotton fabrics were washed according to the AATCC 124-1996 standard test method at 46°C with five cycles of washing using AATCC standard detergent.

The antibacterial test was carried out according to the AATCC 100 standard test method. Two kinds of bacteria (Escherichia coli and Staphylococcus aureus) were used for the test, and the samples were incubated for 24 h. After 24 h of bacterial growth, the photos were taken from agar plates, the colonies were counted, and the bacteria reduction was calculated using Eq. (3):

$$\text{Reduction (\%)} = [(C - A)/C] \times 100, \quad (3)$$

where C denotes the counted colonies on cotton fabric and A, the counted colonies on $AgNO_3$-coated plasma-treated and untreated cotton.

The IR spectra were taken with a Bruker-Equinox 55 FTIR/ATR system. All the data were recorded using a ZnSe internal reflective element. The spectra were collected at a resolution of 4 cm^{-1} with 32 scans. The fiber surface morphology was examined with a Philips XL30 scanning electron microscope (SEM) at an acceleration voltage of 20 kV and magnification of ×7500.

Table 1. Results of methylene blue staining

Parameter	Untreated	1000 W		500 W	
		40 passages	60 passages	40 passages	60 passages
L	41.39	37.54	36.93	38.91	38.60
a	1.17	–2.13	–2.45	–2.01	–2.35
b	–35.13	–35.34	–35.46	–35.47	–35.65
K/S	0.49	0.71	0.78	0.59	0.66
ΔE	–	5.07	5.75	4.04	4.52

Inductively coupled plasma optical emission spectroscopy analysis (ICP-OES) of $AgNO_3$-coated cotton fabrics was carried out using a Varian Vista-Pro instrument (the United States). Each sample (0.03 g) of cotton fabric was placed in a furnace (Nabertherm, Germany) at 600°C for 1 h, after which nitric acid (5 mL) and distilled water were added to a total volume of 25 mL. The silver ion concentration was calculated from the calibration curve obtained using standard solutions.

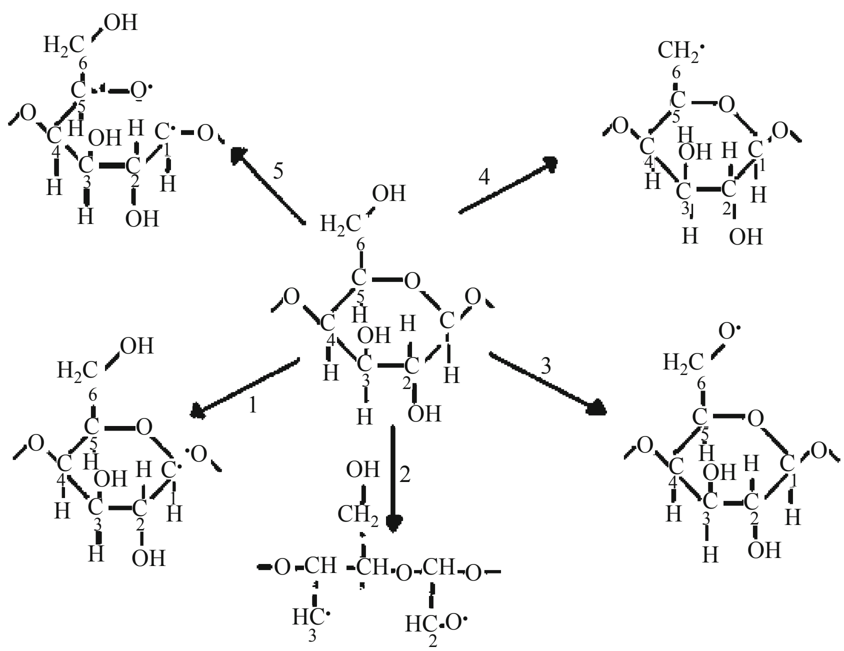
RESULTS AND DISCUSSION

Carboxyl group content. *Methylene Blue staining.* Methylene Blue dye (C.I. basic blue 9) is a cationic dyestuff. It is absorbed on the anionic $–COO^–$ groups of cotton. These groups appear on cotton fiber upon oxidation of cellulose [27–29]. Higher amount of carboxyl groups leads to higher Methylene Blue dye absorption and thus to higher K/S value. The color parameters after Methylene Blue staining show that plasma treatment of cotton fabric produced carboxyl groups on the fiber surface (Table 1), as the K/S value increased upon plasma treatment compared to the untreated cotton. The untreated cotton showed the color yield (K/S) of 0.49; i.e., the untreated cotton adsorbs Methylene Blue dye, probably because of the presence of carboxyl groups in untreated cotton. The color yield reached 0.78 after corona plasma treatment at 1000 W with 60 passages. The K/S value increased as the plasma energy was increased. The L value indicates the lightness of dyed fabrics. Lower L values correspond to darker fabric. The L value for the untreated cotton was 41.39, and it decreased to 36.93 at the highest parameters of corona plasma treatment (1000 W, 60 passages). These results are in agreement with those of the previous studies involving the use of corona discharge in air to alter the chemical and physical properties of cotton fiber. This leads to an increase in wetting and to a decrease in pH of water in contact with the cotton [29, 37]. This acidic pH is due to the presence of carboxylic acid groups in cotton. The atmospheric plasma corona discharge produces high concentration of chemically active species such as excited oxygen, oxygen radicals, free electrons, and oxygen ions. These species attack the fiber surface and generate free radicals (Scheme 1) [28, 40–42]. The bond cleavage between C1 and glycosidic oxygen (1), dehydrogenation at C6 (3), or bond cleavage between C1 and ring oxygen (5) result in the formation of carbonyl (aldehyde) group, which has higher polarity than the hydroxyl group; these are possible mechanisms of corona plasma discharge action on cotton fabric [28, 42]. The increase in reactive sites on cellulose by generating free radicals leads to further reactions yielding carboxyl groups on cotton.

Titration method. The carboxyl group content was measured by titration; the results are shown in Fig. 1. The untreated cotton has the 1.25 mg-equiv $L^{–1}$ content of carboxyl groups, and the corona plasma discharge treatment at the highest energy level increased it to 2.73 mg-equiv $L^{–1}$. An increase in the power and number of passages led to higher carboxyl group content (Fig. 1). These results agree with the results obtained by Methylene Blue staining.

Silver ion content (ICP-OES analysis). Table 2 shows the results of determining the silver ion content by ICP-OES analysis. The cellulosic fibers like cotton can absorb silver ions because of the presence of polar groups. The hydroxyl groups of cellulose can absorb silver ions, so that 0.82% silver ions was absorbed onto untreated cotton, and after repeated laundering the silver ion content decreased to 0.51%. This result agrees with the data obtained for the untreated cotton fabric by the methods of Methylene Blue staining and titration. The corona plasma discharge treatment increased the

Scheme 1.



carboxyl group content; therefore, the silver ion content on the cotton fabric increased also, reaching 1.38% at the highest levels of power and number of passages (1000 W, 60 passages). The increase in the silver ion amounts on plasma corona discharge treated cotton is due to the presence of the anionic groups on cotton fabric. These anionic groups include carboxylic acid groups produced by oxidation of the fibers [27–29]. The possible reaction that occurs in the system is shown in Scheme 2:

Scheme 2.

$$\text{Cell}--\text{COO}^- + \text{Ag}^+ \rightarrow \text{Cell}-\text{COOAg}$$

Antibacterial effect. Silver metal has antibacterial effect, and the antibacterial properties of silver-loaded cotton fabrics were studied using AATCC 100 standard test method. The antibacterial action of silver ions is due to their penetration inside the bacteria cell and death of the cell. Also, heavy metals react with proteins by linking

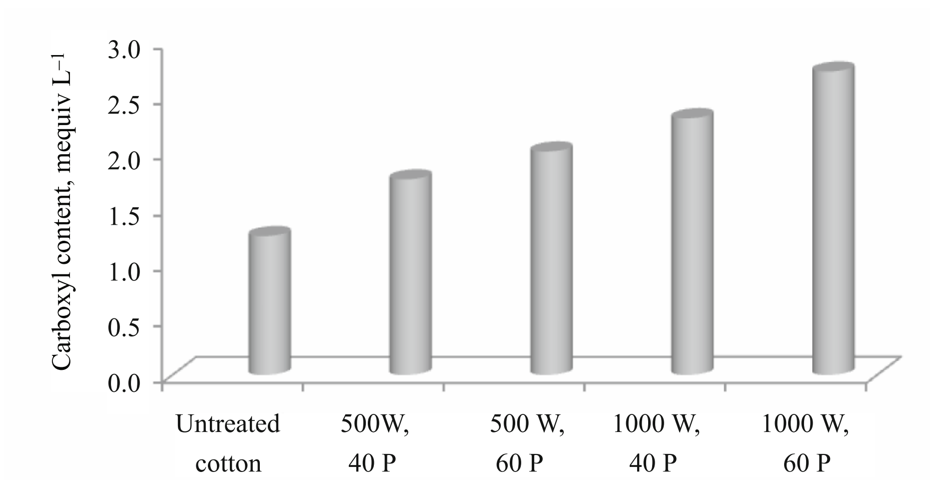


Fig. 1. Carboxyl content of untreated and corona plasma discharge treated cotton fabrics.

Table 2. Bacteria reduction percentage and ICP-OES data for silver-loaded untreated and plasma corona treated fabrics (B: before laundering, A: after laundering)

Bacteria, parameter	Sample	1000 W		500 W		Untreated
		40 passages	60 passages	40 passages	60 passages	
Escherichia coli	B	100	100	100	100	21.6
	A	99.95	100	99.2	99.9	0
Staphylococcus aureus	B	96.25	99.9	86.5	96.15	50
	A	74.35	90.45	53.95	95.1	25
Ag concentration, wt %	B	1.29	1.38	1.23	1.29	0.82
	A	1.24	1.33	1.17	1.24	0.51

with the thiol group, leading to the protein inactivation [8, 9]. The results we obtained are presented in Figs. 2 and 3 and in Table 2. Figures 2 and 3 show the content of E. coli and S. aureus colonies on untreated and corona plasma discharge treated cotton fabrics. The figures also show the content of the colonies before and after repeated laundering. The *E. coli* colonies were approximately zero for corona plasma treated cotton fabric (Figs. 2a, 2b), whereas on untreated cotton (Figs. 2e, 3e) and silver-loaded untreated cotton (Figs. 2c, 2d, 3c, 3d) their content was the highest. The bacteria reduction percentage is given in Table 2. The reduction of E. coli bacteria was 100% at all powers and passages of plasma corona discharge treatment. After repeated laundering, the reduction percentage remained on the 99–100% level. For untreated cotton fabric, silver nitrate could reduce *E. coli* bacteria by only 21.6%, and the reduction percentage reached zero after repeated laundering. The reduction of *S. aureus* bacteria reached 99.9% after plasma corona discharge treatment at 1000 W and 60 passages. Enhanced antibacterial properties of corona-treated fabrics can be attributed to higher hydrophilicity, which made them more accessible to silver ions [43]. The results of antibacterial tests show that silver remained on cotton fabric after repeated laundering, and high bacteria reduction of silver-loaded fabric after repeated laundering may be due to physical bonding to the cotton fabric [4].

FTIR/ATR analysis. The FTIR/ATR spectra are shown in Fig. 4. The spectra of the untreated and corona plasma treated cotton fabrics were similar, although we expected to see the existence of carboxyl groups according to the results of Methylene Blue staining and the titration methods. The IR spectra of Ag–cotton and Ag–corona treated cotton systems showed no evidence of binding of Ag ions with cotton fabric; however, Ag ions are difficult to detect by IR spectroscopy [44].

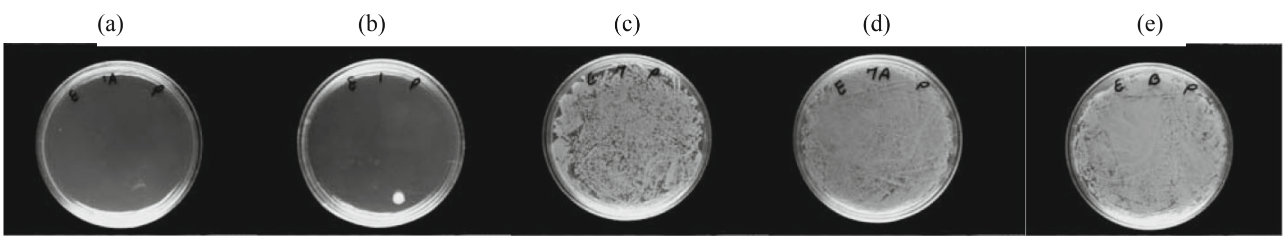


Fig. 2. The grown colonies of *E. coli* on cotton fabrics. Sample: (a, b) Ag-loaded plasma corona discharge treated, (c, d) Ag-loaded untreated, and (e) cotton without Ag. (a, c) Before and (b, d) after laundering.

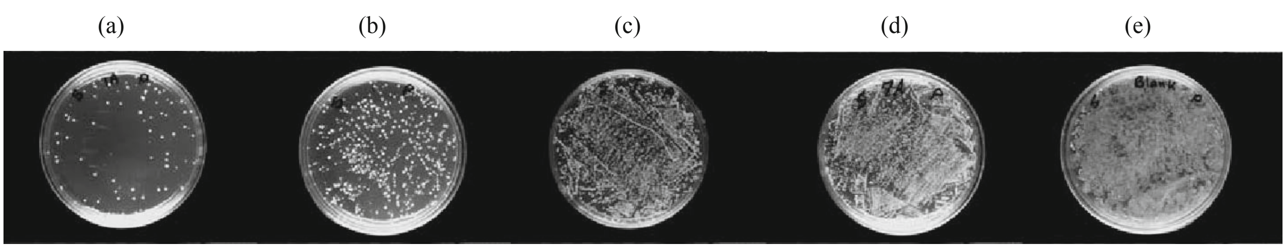


Fig. 3. The grown colonies of *S. aureus* on cotton fabrics. Sample: (a, b) Ag-loaded plasma corona discharge treated, (c, d) Ag-loaded untreated, and (e) cotton without Ag. (a, c) Before and (b, d) after laundering.

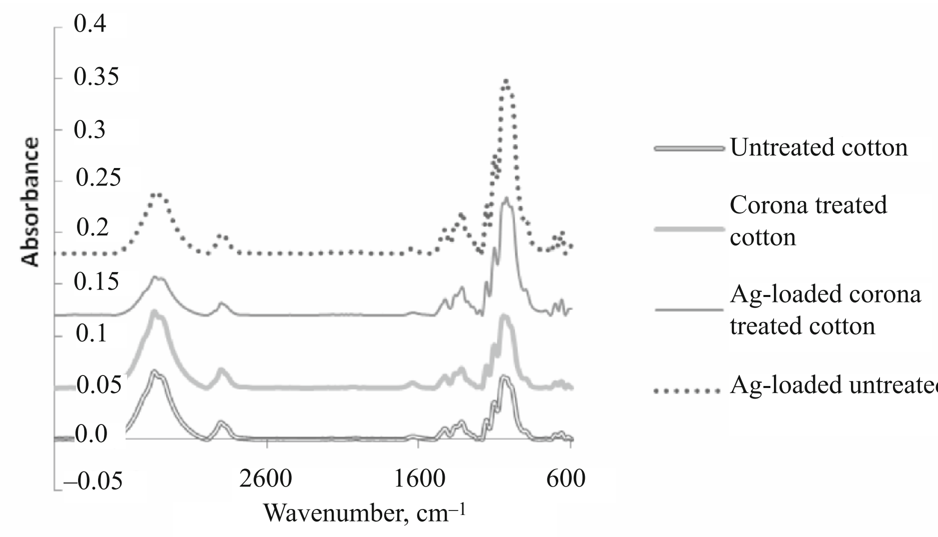


Fig. 4. FTIR/ATR analysis of untreated, corona treated, Ag-loaded untreated, and Ag-loaded corona treated cotton.

Fig. 5. SEM micrographs of $AgNO_3$ coating on (a) untreated cotton before laundering, (b) untreated cotton after laundering, (c) plasma-treated cotton before laundering, and (d) plasma-treated cotton after laundering.

SEM morphology. The SEM micrographs of silver coating on untreated and plasma corona discharge treated cotton are shown in Fig. 5. Figures 5a and 5c show Ag loading on untreated and corona treated cotton; some particles appearing upon coating can be seen. After repeated laundering, these particles are removed from the surface (Figs. 5b, 5d). Although SEM micrographs did not show significant amount of silver particles on corona treated fabric after repeated laundering, we can attribute the preservation of the antibacterial effect to penetration of silver particles into the cracks and etching caused by corona discharge treatment of cotton fabric.

CONCLUSIONS

The cotton fiber contains carboxyl groups –COOH, and the oxygen plasma treatment of cotton increases their amount, as shown by the Methylene Blue staining and titration methods. The increased content of –COOH groups leads to more efficient binding of Ag in the form of Ag salt of –COOH. The increase in the power of plasma treatment increases the silver adsorption. The absorption of Ag significantly reduces the growth of two kinds of bacteria on cotton.

REFERENCES

1. Gao, Y. and Cranston, R., *Textile Res. J.*, 2008, vol. 78, p. 60.
2. Purwar, R. and Joshi, M., *AATCC Rev.*, 2004, vol. 4, p. 22.
3. Dring, T., *Textile Finishing: Antimicrobial, Rotproofing, and Hygiene Finishes*, Heywood, D., Ed., Hampshire (UK): SDC, 2003, p. 353.
4. Ilic, V., Saponjic, Z., Vodnik, V., Potkonjak, B., Jovancic, P., Nedeljkovic, J., and Radetic, M., *Carbohydr. Polym.*, 2009, vol. 78, p. 564.
5. Gorensek, M. and Recelj, P., *Textile Res. J.,* 2007, vol. 77, p. 138.
6. Williams, J.F., Halosource, V., and Cho, U., *AATCC Rev.*, 2005, vol. 5, pp. 17–21.
7. McDonnell, G. and Russel, A.D., *Clin. Microbiol. Rev.*, 1999, vol. 12, p. 147.
8. Rai, M., Yadav, A., and Gade, A., *Biotechnol. Adv.*, 2009,

vol. 27, p. 76.
9. Feng, Q.L. Wu, J., Chen, G.Q., Cui, F.Z., Kim, T.N., and *Kim,* Jo., *J. Biomed. Mater.,* 2000, vol. 52, no. 4, p. 662.
10. Dastjerdi, R., Montazer, M., and Shahsavan, S., *Colloids Surf. A: Physicochem. Eng. Aspects*, 2009, vol. 345, p. 202.
11. Cheng, Q., Li, C., Pavlinek, V., Saha, P., and Wang, H., *Appl. Surf. Sci.,* 2006, vol. 252, p. 4154.
12. Man, X., Jun-Qiang, F., and Xiao-Long, C., *J. Shanghai Univ.* (Engl. Ed.)., 2008, vol. 12, no. 1, p. 85.
13. Xu, B., Niu, M., Wei, L., Hou, W., and Liu, X., *J. Photochem. Photobiol. A*: *Chemistry,* 2007, vol. 188, no. 1, p. 98.
14. Rouette, H.K., *Encyclopedia of Textile Finishing*, Germany: Springer, 2001.
15. Poll, H.U., Schladitz, U., and Schreiter, S., *Surf. Coat. Technol.*, 2001, vol. 489, p. 142.
16. Verschuren, J. and Kiekens, P., *Autex Res. J.,* 2005, vol. 5, p. 154.
17. Raffaele-Addamo, A., Riccardi, C., Selli, E., and Barni, R., *Surf. Coat. Technol.*, 2003, vol. 886, p. 174.
18. Zhu, L., Wang, C., and Qiu, Y., *Surf. Coat. Technol.*, 2007, vol. 201, p. 7453.
19. Poletti, G., Orsini, E., Raffaele-Addamo, A., Riccardi, C., and Selli, E., *Appl. Surf. Sci.*, 2003, vol. 219, p. 311.
20. Leroux, F., Campagne, C., Perwuelz, A., and Gengembre, L., *Surf. Coat. Technol.*, 2009, vol. 203, p. 3178.
21. Karahan, H.A., Ozdogan, E., Demir, A., Ayhan, H., and Seventekin, N., *Fibre Textiles East. Eur.*, 2009, vol. 17, p. 19.
22. Pandiyaraj, K.N. and Selvarajan, V., *J. Mater. Process. Technol.*, 2008, vol. 199, p. 130.
23. Karahan, H.A. and Ozdogan, E., *Fibers Polym.*, 2008, vol. 9, no. 1, p. 21.
24. Inbakumar, S., Morent, R., De Geyter, N., Desmet, T., Anukaliani, A., Dubruel, P., and Leys, C., *Cellulose*, 2009, vol. 17, no. 2, p. 417.
25. Andreozzi, L., Castelvetro, V., Ciardelli, G., Corsi, L., Faetti, M., Fatarella, E., and Zulli, F., *J. Colloid Interface Sci*., 2005, vol. 289, no. 2, pp. 455–465.
26. Lam, Y.L., Kan, C.W., and Yuen, C.W.M., *Fibers Polym.*, 2013, vol. 14, no. 1, p. 52.
27. Malek, R.M.A. and Holme, I., *Iran. Polym. J.*, 2003, vol. 12, p. 4.
28. Agostino, R., *Plasma Processing of Polymers*, Italy: Kluwer Acad., 1997, pp. 348–350.
29. Carneiro, N., Souto, A.P., Silva, E., Marimba, A., Tena, B., Ferreira, H., and Magalhães, V., *Color. Technol.*, 2001, vol. 117, no. 5, p. 298.
30. Prysiazhnyi, *V.,* Kramar, A., Dojcinovic, B., Zekic, A., Obradovic, B.M., Kuraica, M.M., and Kostic, M., *Cellulose*, 2013, vol. 20, no. 1, p. 315.
31. Kostic, M., Radic, N., Obradovic, B.M., Dimitrijevic, S., Kuraica, M.M., and Skundric, P., *Plasma Process. Polym.*, 2009, vol. 6, no. 1, p. 58.
32. Lee, H.J., Yeo, S.Y., and Jeong, S.H., *J. Mater. Sci.*, 2009, vol. 38, no. 10, p. 2199.
33. Shahidi, S., Rashidi, A., Ghoranneviss, M., Anvari, A., Rahimi, M.K., Bameni Moghaddam, M., and Wiener, J., *Cellulose*, 2010, vol. 17, no. 3, p. 627.
34. Yuranova, T., Rincon, A.G., Bozzi, A., Parra, S., Pulgarin, C., Albers, P., and Kiwi, J., *J. Photochem. Photobiol. A: Chemistry*, 2003, vol. 161, p. 27.
35. Nourbakhsh, A. and Ashjaran, A., *Materials*, 2012, vol. 5, no. 7, p. 1247–1257.
36. Gorjanc, M., Bukosek, V., Gorensek, M., and Mozetic, M., *Textile Res. J.*, 2010, vol. 80, no. 20, p. 2204.
37. Nourbakhsh, S. and Yazdanshenas, M.E., *Color. Technol.*, 2008, vol. 124, pp. 43–47.
38. Collier, B.J. and Epps, H.H., *Textile Testing and Analysis, Upper Saddle River*, NJ (USA), Prentice Hall, 1999, pp. 209–211.
39. Yang, C.Q. and Bakshi, G.D., *Textile Res. J.,* 1996, vol. 66, no. 6, p. 377.
40. McCord, M.G., Hwang, Y.J., Qiu, Y., Hughes, L.K., and Bourham, M.A., *J. Appl. Polym. Sci*., 2003, vol. 88, p. 2038.
41. Ward, T.L., Jung, H.Z., Hinojosa, O.R., and Benerito, R.J., *J. Appl. Polym. Sci.,* 1979, vol. 23, p. 1987.
42. Vaideki, K., Jayakumar, S., Thilagavathi, G., and Rajendran, R., *Appl. Surf. Sci.*, 2007, vol. 253, p. 7323.
43. Radetic, M., Ilic, V., Vodnik, V., Dimitrijevic, S., Jovancic, P., Saponjic, Z., and Nedel, J.M., *Polym. Adv. Technol.*, 2008, vol. 19, no. 12, p. 1816.
44. Rincon, A.G., Pulgarin, C., Laub, D., and Xantopoulos, M., *J. Photochem. Photobiol.* A: C*hemistry*, 2006, vol. 181, p. 363.