Effect of Fluorination Treatment on Cotton Wettability, Dyeability and Mechanical Properties and Characterization of Surface Changes by XPS

S. Shekarriz[1]* and Z. Shariatinia[2]

[1.] Assistant Professor, Color and Polymer Research Centre, Amirkabir University of Technology, P.O. Box: 15875-4413, Tehran, Iran.

[2.] Assistant Professor, Chemistry Department, Amirkabir University of Technology, P.O. Box: 15875-4413, Tehran, Iran.

ABSTRACT

Cotton fabric was treated with fluorine gas in a nitrogen atmosphere. The effect of fluorination treatments on wettability, whiteness index, dyeability and mechanical properties of cotton fabrics were assessed. Kawabata analysis shows that fluorination treatment increases shear stiffness (G), shear hysteresis (2HG5), bending stiffness (B) and overall fabric stiffness (Koshi) on cotton fabric. Fluorination increases hydrophilicity of cotton by reducing the wetting time to less than 10 seconds for fluorinated cotton. In addition, the uniformity of wetting improves for the fluorinated samples. Fluorinated cotton dyed with two different direct dyes shows a slightly decreased exhaustion rate and color yield. X-ray Photoelectron Spectroscopy (XPS) was used to characterize untreated and fluorinated cotton. XPS indicates that oxidation, fluorination and formation bonds - COO and –CHF at 289.5 eV occurred on the fluorinated cotton surface. Prog. Color Colorants Coat. 7(2014), 85-93. © Institute for Color Science and Technology.

1. Introduction

Modification of fiber surface chemistry and morphology can be achieved by a number of "dry" techniques such as plasma, corona, fluorination etc. Through this route, reactive functionalities can be introduced into the materials surface to engineer the surface interface, whilst maintaining the bulk characteristic of the substrate material [1,2].

Direct modification of polymer surfaces yields a stable coating with fluorine atoms covalently linked to a substrate. The highly exothermal process can be controlled by lowering pressure and adjusting fluorine concentration (several volume percent of F2 in N2 or He). Direct fluorination is a well-known method for the surface modification of polymers [3,4]. The thickness of the modified layer of polymer is controlled over a 0.01-10 μm range. This technology is the so-called dry one with only gases being used, and materials of any shape can be modified. The process proceeds at or below room temperature and does not need initiation catalyst. One of the main advantages of direct fluorination is that only a thin surface layer of the material is modified, and hence, the bulk properties of the material are practically

unchanged [5].

Cotton needs pretreatment to make them suitable for dyeing or finishing. This pretreatment removes natural or added impurities.In conventional pretreatment of cotton woven fabric, desizing represents the main water emission source in the overall process. After desizing process, bleaching of fabrics with different chemicals is realized. Nowadays, for ecological reasons, the use of sodium hypochlorite and sodium chlorite as bleaching agents are now limited because of the AOX parameter [2]. Due to legislation introduced to control the level of absorbable organohalogens (AOX) released into the water supply, the replacement of wet finishing treatments with low or zero effluent processes is now a priority for textile industry. One example is the chlorine preparatory treatment for wool used prior to the addition of a shrink proofing polymer. One possible substitute for chlorine based wet finishing treatment is the use of another more reactive, halogen and fluorine. Gaseous fluorine renders wool shrink resistant [6]. Although organofluorides cannot be detected by the current AOX test methods, it is the strength of the carbon – fluoride bond that precludes the formation of carcinogenic species. Furthermore, as the fluorine reacts rapidly, primarily surface modification is occured. In the fluorination process, the formation of hydrogen fluoride is also limited, with no current effluent legislation covering fluoride ions restricting the commercial adoption of the process. The loss of gaseous fluorine or other species during the process can also be eliminated by careful design of the equipment and dry "scrubber" beds [7]. The present fluorination treatment basically involves exposure of the cotton fabric to an atmosphere of nitrogen containing 1% and 2% fluorine gas, with the exposure time as a function of fabric speed passing through the reaction chamber.

2. Experimental

2.1. Materials

The fabric was plain cotton bleached/mercerised fabric, 135 g/m², 60/60 warp/weft threads with a 20' carded weft supplied by Phoenix Calico Limited, UK.

2.2. Fluorination treatment

Elemental fluorination was carried out by Fluor Technik, GmbH, using current industrial scale equipment. Fluorinated samples were prepared in an atmosphere of 1% and 2% fluorine in a nitrogen atmosphere and each

sample processed at a rate of 10 m/minute.

2.3. KES-F testing

Shear and bending properties were determined using the Kawabata Evaluation System for fabric (KES-F) since bending and shear stiffness (B,G) and shear hysteresis (2HG5) have been previously identified as sensitive indicators of fabric softness and stiffness [8]. Prior to testing, the fabrics were conditioned for 24 hours at 65% R.H. and 20°C. Overall fabric stiffness (Koshi) was calculated on women's thin outerwear fabric.

2.4. Martindale abrasion test

The flat abrasion test of the fabric was performed using the martindale abrasion tester according to BS 5690: 1991.

2.5. Instron tensile testing

Fabric tensile testing was carried out according to method BS 2576: 1986 on an Instron 1122 (constant rate of elongation) under standard conditions.

2.6. Shirley crease recovery test

Crease recovery angle was measured using Shirley crease recovery tester according to BS 3086 (1972).

2.7. Wettability

Fabric wettability was determined by measuring the time that 0.05 ml distilled water was absorbed by conditioned samples.

2.8. X- Ray photoelectron spectroscopy (XPS)

XP spectra were obtained using a Vacuum Generators ESCA LAB-1 spectrometer. The samples were attached to the spectrometer probe with double sided adhesive tape and analysed with $Mg_{k\alpha}$ radiation (1253.6 eV). The spectrometer pressure was 4×10^{-8} torr. All values were calculated relative to the C (1s) photoelectron peak at 285.0 eV. The peak areas used to obtain the surface composition were corrected using Wagner's sensitivity factors [9]. The technique involves measuring the kinetic energy (KE) of the emitted photoelectron and calculating the electron binding energy (BE) using the relationship BE= hv – KE, where hv is the photon energy. The value of the electron binding energy enables the emitting atom to be identified and its oxidation state ascertained. In addition, the spectral line intensities allow the relative

abundance of species at the surface to be determined [10,11].

2.9. Whiteness measurement

Whiteness was measured on a MVE-P Macbeth reflectance spectrophotometer with 10° standard observer and illuminant D65.

2.10. Scanning electron microscopy (SEM)

scanning micrographs were obtained with an ISI 100A scanning electron microscope operating at a range of 5-10 kV. Magnification was 3000 times.

2.11. Dyeing with direct dyes

The following dyes and chemicals were used during dyeing: Solophenyl Red 4G (Direct Red), Solophenyl Blue 4GL (Direct Blue 78) and Glauber's salt anhydrous (Na$_2$SO$_4$)

Dyeing method: In this study, pretreated cotton with 1% fluorine and untreated cotton were dyed with two direct dyes. All dyeing were performed on Mathis Labomat dyeing equipment. The liquor ratio used throughout the study was 30:1 with a dye concentration of 2% o.w.f. The electrolyte was added in two portions

B, C in figure 1. The dyeing process was carried out according to the programme shown in figure 1 [12].

The exhaustion of the dye (E) referred to the percentage of the dye absorbed on the cotton to the total original amount of dye in the dyebath:

$$\% \ E = \frac{A_0 - A_1}{A_0} \times 100 \tag{1}$$

Where A_0 and A_1 are the absorbance (at λ_{max}) of dyes originally exist in the dyebath and residual dye in the exhausted dyebath, respectively. The absorbance of dyes was measured using PU 8720 UV/VIS scanning spectrophotometer, with the λ_{max} obtained for direct blue dye at 523 nm and for the direct red dye at 604 nm.

Color strength of dyed fabrics were determined and expressed as the K/S value [13]. The K/S values were determined by a Macbeth reflectance spectrophotometer at the wavelength of minimum reflectance of dye being used. K is the absorption coefficient and S is the scattering coefficient. The higher the K/S value, the greater is the coloration of the fabric.
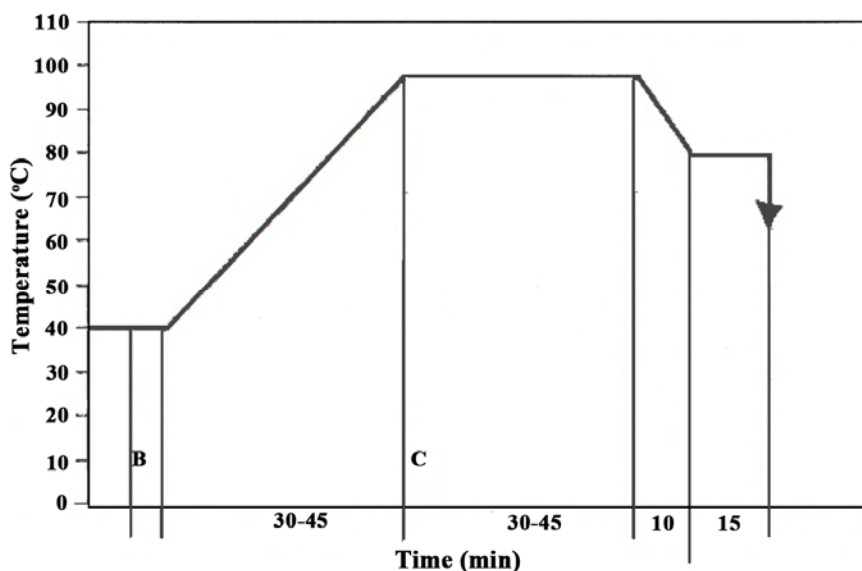

Figure 1: Cotton dyeing process with direct dyes. 2.0 g fabric, 2% (o.w.f) dye, liquor ratio 30:1, salt (10g/l), B=1/5th salt and C= 4/5th salt.

3. Results and discussion

3.1. Effect of fluorination treatment on the fabric mechanical properties, wettability and whiteness index

Fluorination pre-treatments increased the shear stiffness (G), shear synthesis (2HG5), bending stiffness (B) and overall fabric stiffness (Koshi). Table 1 indicates that the treatment imparts a harsher handle to the fabric relative to the untreated fabric. This is consistent with previous research, where an increase in fiber friction on exposure to corona discharge of cotton or fluorination of wool occurred [2,14-15].

Fluorinated sample shows an 8% increase in tensile strength. Fluorination doesn't affect the abrasion resistance/wrinkle recovery angle or whiteness of the fabric, Table1. Previous research showed that corona treatment of cotton fibers produces a number of beneficial effects such as increased yarn tensile strength and wettability properties [16,17].

Fluorination increased cotton's hydrophilicity by reducing the wetting time from 20 seconds for untreated to less than 10 seconds for fluorinated cotton, Table 2. In addition, the uniformity of wetting was improved for the fluorinated samples. Alteration of the primary wall morphology with chemical oxidation of fatty material and improved removal of any preparative material were probably primary reasons. Interestingly, the improvement in wettability appeared to be independent of the fluorine exposure time, highlighting the aggressive nature of the gas.

3.2. Dyeability of fluorinated cotton fabrics with direct dyes

The effect of the fluorination treatment on cotton dyeing was of interest. Hence both treated and untreated fabrics were dyed with representative direct dyes. It has been reported that both exhaustion rate, color yield of acid, pre-metallised and reactive dyes on wool can be considerably increased by fluorination treatment [18].

The exhaustion rate and color yield for fluorinated treated cotton was slightly lower than that for the untreated cotton using the blue and red direct dyes as we expected (Figures 2a,b and 3a,b). This is related to the effect of increasing the surface electronegativity of cotton fiber through fluorination. Therefore, anionic charges generated at the fiber surface may increase the repulsion of the negatively charged dye. This is similar to that observed for nylon 6 treated with oxygen plasma which was dyed with acid dyes, where the increase in fiber electronegativity caused by plasma treatment lowered the rate of dyeing with acid dyes but increased the rate of dyeing with basic dyes [19].

Table 1: Physical properties of Fluorinated cotton.

Sample	Abrasion performance no. of rubs	Tensile strength (kg)	CRA[a] (deg)	G[b]	2HG5 [c]	B[d]	Koshi (stiffness)
Untreated	6200	50.6 ± 1.22	135	1.32	5.32	0.113	7.5
1% F$_2$-10m.min	6300	55 ± 0.57	140	1.54	5.68	0.139	7.8
2% F$_2$-10m.min	6200	56 ± 0.92	137	1.68	5.92	0.152	7.9

[a] crease recovery angle, [b]shear stiffness(gf/cm.deg), [c]shear hysteresis(gf/cm), [d]bending stiffness (gf.cm^2/cm)

Table 2: Wettabillity and whiteness index launder (WI) of fluorinated cotton.

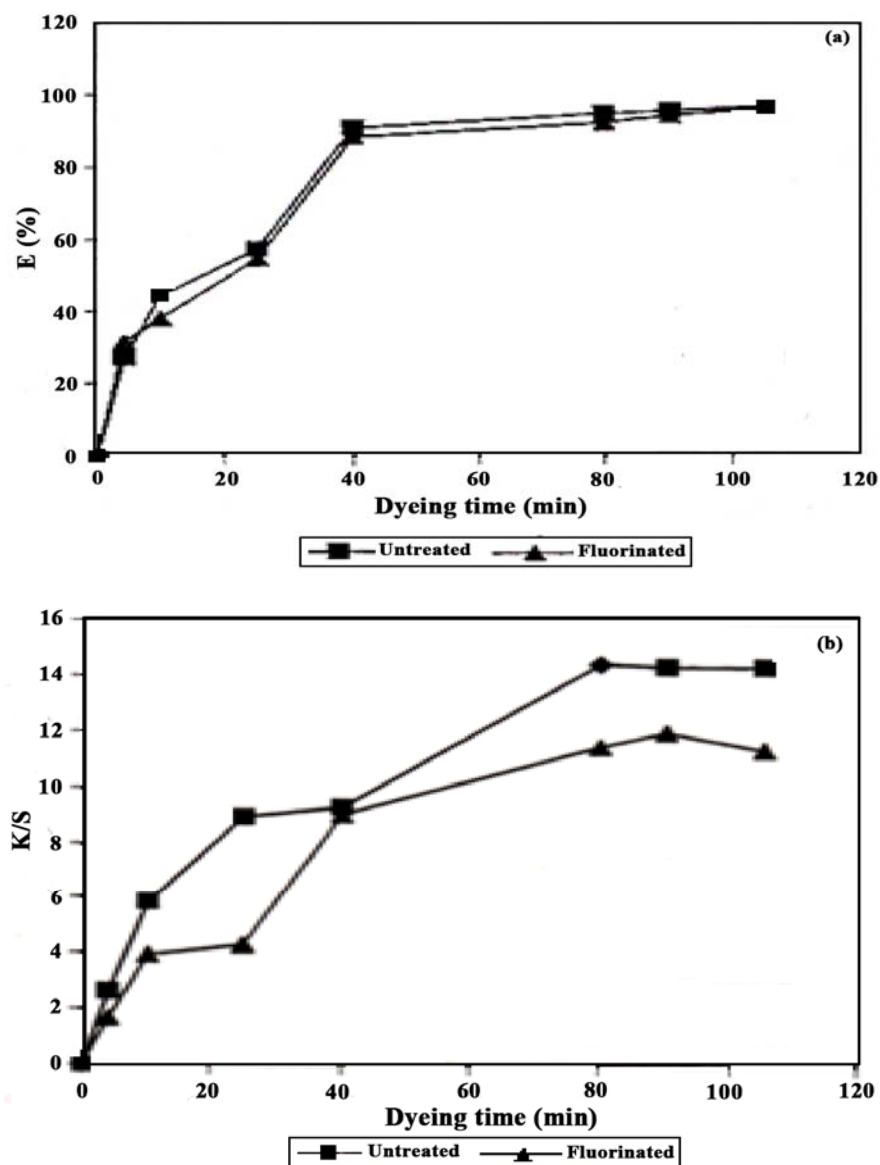| Sample	Untreated	1% F$_2$-10 m/min	2% F$_2$-10 m/min
Time (sec)	20	7	7
WI	68	67	68

Figure 2: Solophenyl Red 4G on untreated and fluorinated cotton: (a) exhaustion profile and(b) color yeild.

3.3. XPS analysis of cotton modified by gaseous fluorine

XPS survey scan of cotton treated with gaseous fluorine revealed that the surface of treated cotton was composed of C, O and F (Figure 4(a-d)). The gaseous fluorine was incorporated in to the fiber surface as indicated by the fluorine (1s) peak around 685 eV,

Figure 4(d). The C (1s) and O (1s) peaks in the XP spectra of cotton treated with gaseous fluorine accord with binding energy values of 285 eV and 532 eV, respectively, Figures 4(a,b). There is no sign of nitrogen in the treated cotton, Figure 4(c).
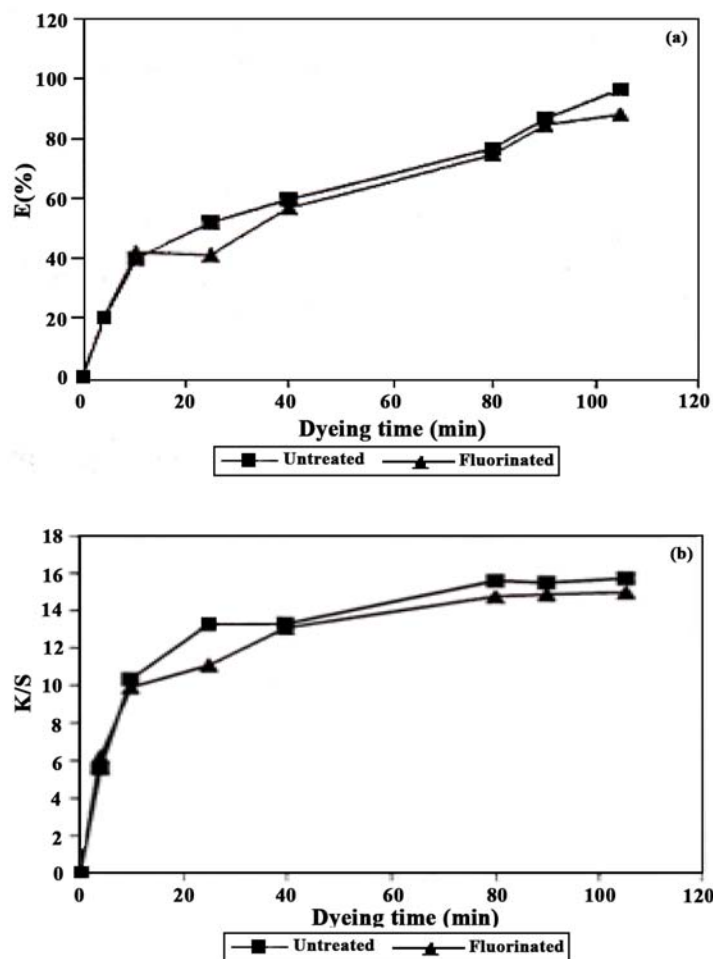
Figure 3: Solophenyl Blue 4GL on untreated and fluorinated cotton: (a) excxhaustion profile and (b) color yeild.
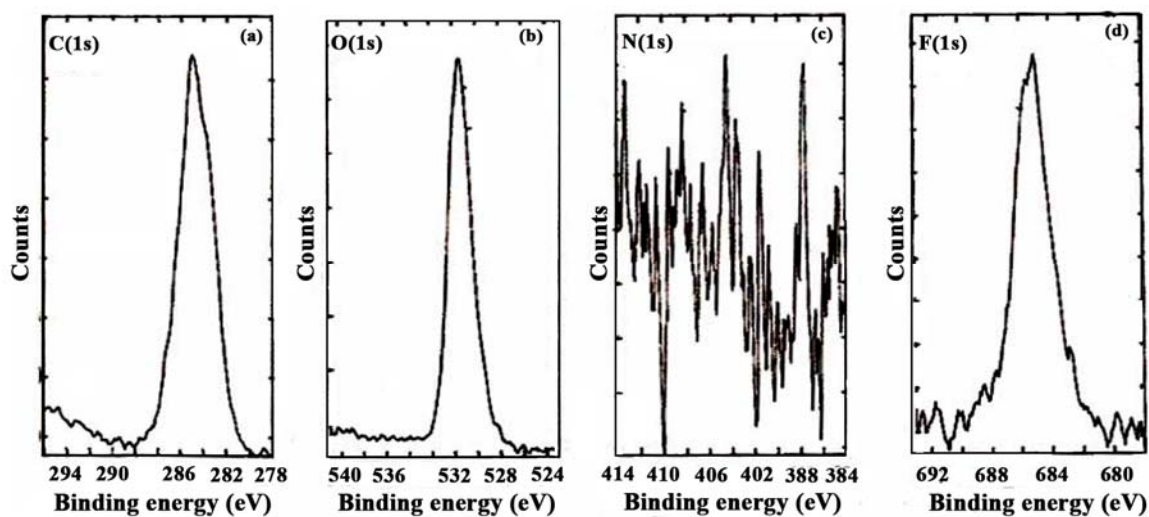

Figure 4: XPS survey scan of fluorinated cotton.

Table 3 also illustrates the surface changes after fluorination treatment where there is an increase in oxygen and fluorine content and reduction in carbon content. The increased O/C ratio indicates that not only the cotton fiber is fluorinated, but it is simultaneously oxidised.

Table 3: XPS elemental composition of treated cotton fibers.

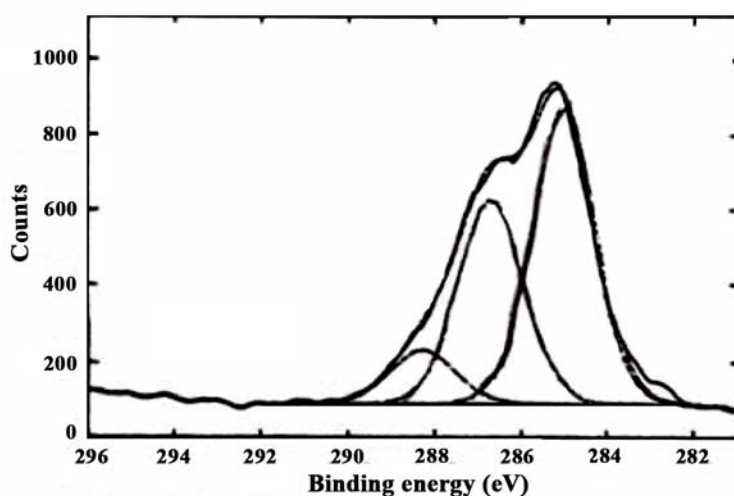|	Atomic composition (%)						Atomic ratio
	C	O	Ca	N	Na	F	O/C
Untreated	67.1	32.9	-	-	-	-	0.49
1% F_2-10m.min	54.8	35.9	-	-	-	9.4	0.65
2% F_2-10m.min	55.2	36.7	-	-	-	8.1	0.66

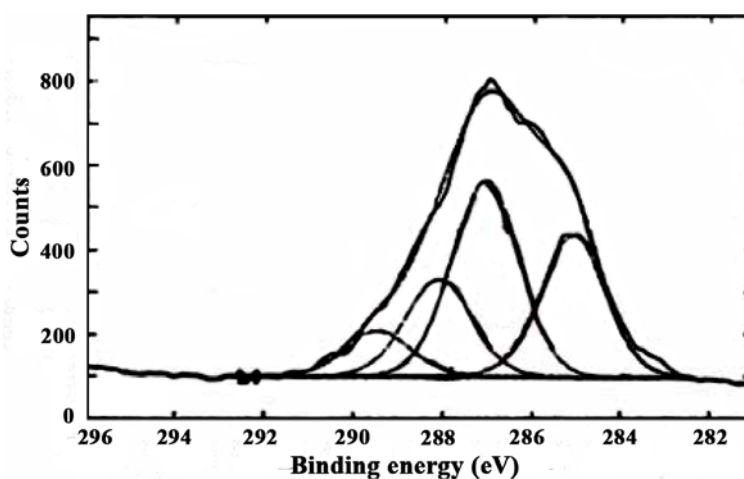**Figure 5:** XPS C(1s) spectra of untreated cotton.

Figure 6: XPS C(1s) spectra of fluorinated cotton.

The increase in oxygen content may be caused by the presence of oxygen during the treatment or may be caused by post-oxidation of unstable species on exposure to air. The simultaneous oxidation of cotton after fluorination caused the same effects as other fluorinated polymers such as polyethylene, polypropylene, polyester and wool. Fluorine treatment raises significantly the surface energy and hence the wettability of these polymeric materials [20-24].

The high resolution and C (1s) spectral scan of untreated cotton shows that the surface carbon can be divided to three distinct peaks (Figure 5):

(a) 285.0 ev   -C-C-, C- H species;
(b) 286.5 eV   -C-OH, -C-O-C- species;
(c) 288.0 eV   -C=O, O-C-O species

The high resolution C (1s) spectrum of fluorinated cotton indicates an increase in high binding energy intensity due to oxidation and fluorine incorporation onto the fiber surface (289.5 eV – COO, -CHF), Figure 6 and Table 3 relative to the untreated cotton in Figure 5.

The relative reduction in the peak intensity 285.0 eV may be due to volatilisation of the surface hydrocarbron after oxidation. SEM revealed no major topographic changes due to fluorination treatments.

4. Conclusion

Kawabata analysis of fluorinated cotton showed increased shear stiffness, shear hysteresis and bending stiffness of the fabric, indicating that the treatment imparts a harsher handle to the fabric in comparison with the untreated fabric. Gaseous fluorination of cotton produced an increase in tensile strength of fabric but had no effect on wrinkle recovery or abrasion resistance relative to untreated cotton. Fluorination treatment of cotton increased wettability and uniformity of the wetting due to surface oxidation. The wetting effect and mechanical properties of fluorinated cotton appear to be independent of the gaseous fluorine concentration, highlighting the aggressive nature of fluorine attack.

Fluorinated cotton dyed with direct dyes showed a slightly decreased exhaustion rate and color yield. This may be related to the effect of fluorination which increases surface electronegativity of cotton fiber. Therefore, anionic charges generated at the fiber surface increase the repulsion of the negatively charged dye.

XPS measurement of fluorinated cotton showed an increase in surface oxygen and fluorine levels, resulting in enhanced surface wettability.

5. References

1. M. Ueda, Tokino, Physico-chemical modifications of fibers and their effect on coloration and finishing, *Rev. Prog. Color. Relat. Top.,* 26(1996), 9-19.

2. S. Perincek, I. Bahtiyari, A. Korlu, K. Duran, New techniques in cotton finishing, *Text. Res. J.,* 79(2009), 121-128.

3. J. P. Hobbs, P. B. Henderson, M. R. Pascolini, Assisted permeation through surface fluorinated polymers, *J. Fluorine Chem.*, 104(2000), 87-95.

4. P. A. B. Carstens, S. A. Marais, C. J. Thompson, Improved and novel surface fluorinated products, *J. Fluorine Chem.,* 104(2000), 97-107.

5. J. Maity, P. Kothary, E. A. O'Rear, C. Jacob, Preparation and comparison of hydrophobic cotton fabric obtained by direct fluorination and admicellar polymerization of fluoromonomers, *Ind. Eng. Chem. Res.*, 49(2010), 6075-6079.

6. K. J. Dodd, C. M. Carr, B. Kidd, K. Byrne, Fluorination-a novel pretreatment for wool to impart shrink resistance*, J. Soc. Dyers Color.,* 111(1995), 63-66.

7. B. M. Mueller, Adsorbable organic halogens in textile effluents, *Rev.Prog. Coloration,* 22(1992),14-21.

8. E. Finnimore, Instrumental assessment of fabric softness, part 1 correlation of instrumental measurement and manual assessment, *Melliand Textilber.*, 67(1986), 514-516.

9. C. D. Wagner, Sensitivity of detection of the elements by photoelectron spectrometry, *Anal. Chem.,* 44(1972), 1050-1053.

10. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, R. Bergmark, S. E. Karlson, I. Lindgren, B. Lindberg, Atomic molecular and solid-state structure studied by means of

electron spectroscopy, *Nova Acta Regiae Soc. Sci. Ups.*, 20(1967), 208-282.

11. S. Shekarriz, P. Cohen, C. M. Carr, R. Mictchell, C. Jones, Surface chemical analysis of 1,2,3,4 butane tetracarboxyic acid modified cotton, *J. Mater. Sci.,* 38(2003), 2945-2951.

12. Technical data: Solophenyl dyes, dyeing methods, CIBA-GIEGY.

13. S. Gorji Kandi, F. Ameri, N. Khalili, Instrument dependency of Kubelka-Munk theory in computer color matching, *Prog. Color Colorants Coat.*, 5(2012), 85-90.

14. W. J. Thorsen, Temporary and permanent fiber-friction increases induced by corona treatment, *Text. Res. J.*, 41(1971), 331-336.

15. A. E. Pavlath, K. S. Lee, Pretreatment of textiles under plasma conditions, *Proc 5th Int Wool Text. Res. Conf. Aachen,* 3(1975), 263.

16. J. Verschuren, P. Kiekens, C. Leys, Textile-specific properties that influence plasma treatment, effect creation and effect characterization, *Text. Res. J.*, 77(2007), 727-733.

17. W. J. Thorsen, Modification of the cuticle and primary wall of cotton by corona treatment, *Text. Res. J.*, 6(1974), 422-429.

18. J. Shao, Surface modification of wool by novel dry finishing to impart shrink resistance, improved dyeability and printability, PhD Thesis, UMIST, 1998.

19. T. Wakida, M. Lee, Y. Sato, S. Ogasawara, S. Niu, Dyeing properties of oxygen low-temperature plasma-treated wool and nylon 6 fibers with acid and basic dyes, *J. Soc. Dyers Color.,* 112(1996), 233-236.

20. L. J. Hayes, D. D. Dixon, Direct fluorination of polyamide, *J. Fluorine Chem.,* 10(1977), 17-28.

21. K. J. Dodd, C. M. Carr, B. Kidd, K. Byrne, Fluorination-a novel pretreatment for wool to impart shrink resistance, *J. Soc. Dyers Color.,* 111(1995), 63-66.

22. L. J. Hayes, D D. Dixon, Direct fluorination of polyamide, *J. Fluorine Chem.*, 10(1977), 17-28.

23. L. J. Hayes, D. D. Dixon, Direct fluorination of polyester and related compounds, *J. Fluorine Chem.*, 10(1977), 1-16.

24. A. P. Kharitonov, G. V. Simbirtseva, V. M. Bouznik, M. G. Chepezubov, M. Dubois, K. Guerin, A. Hamwi, H. Kharbache, F. Masin, Modification of ultra-high-molecular weight polyethylene by various fluorinating routes, *J. Polym. Sci.*, part A: polymer chemistry, 49(2011), 3559-3573.