Development of Double Hydrophilic/Hydrophobic Surfaces of Wool Fabric

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Introduction

Wool fibre has a so-called skin–core structure. In this structure, the inner cortex is hydrophilic in nature due to the large number of polar groups contained in the polypeptide chains of the cortex. On the other hand, the outer surface of wool fibre is hydrophobic due to the presence of a high degree of disulphide cross-linkages in the cuticle and a film of fatty acids on the fibre surface which acts as a surface barrier against diffusion into wool fibres[1, 2]. Many chemical methods have been developed for modifying the wool fibre surface, such as chlorination and polymer deposition but these processes are often very harsh and modify bulk properties, besides creating effluent problems[3, 4]. As a result of increasing environmental awareness and tougher government legislation on effluent discharge around the world, alternative methods with lower environment impact need to be explored and one such method is surface modification by physical means. Different types of irradiation techniques have been utilized as alternatives to chemical processing of wool[5, 6]. UV irradiation has recently been used to modify the surface properties of wool and polyester fibre [7, 8]. In the current study focus is on the effect of 172nm UV excimer radiation on the properties of wool fibre have been reported. The effect of time and atmosphere (O_2, Air, and N_2) of irradiation on the properties of wool has been studied. Data is also presented for double hydrophilic/ hydrophobic properties of wool fabric.

Experimental

Materials

Wool used in the investigation is a scoured, unbleached plain weave, 96 GSM, 73 EPI, 66 PPI fabric. Finish chemical used are n-Tetradecane oil Made by Sid fine chemical limited, Mumbai , commercial formulation NUVA HPU made by Clariant Company, Arkofix NEC made by Clariant company and $Mgcl_2$

Pretreatment with UV radiation

Xeradex 20 UV Excimer lamp, (172 nm radiation) was mounted horizontally in an SS box (a). 10cm x 2cm strips of wool fabric (b) were placed under the lamp, at a distance of 5mm. Samples were exposed for 1min, 5 min and 15 min on each side in three different atmospheres namely air, O_2 and N_2.

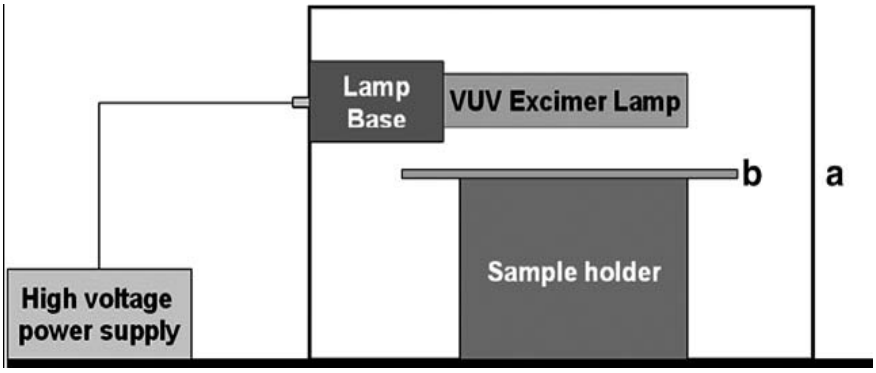

Figure1. Schematic diagram of 172 nm excimer lamp irradiation chamber [9]

Characterization of treated samples

Treated wool samples were tested for change in performance properties such as lipophilic behaviour, wicking behaviour and for change in surface topography brought about by UV exposure. All samples were conditioned for 24h in standard atmosphere before testing.

Oil absorbancy time was measured as the time taken for the absorption of an oil droplet by the fabric. Fabric was held horizontally at its two ends, with clamps, keeping it free of folds. A drop of oil was released onto it from a syringe from a height of 40 mm. Time taken for the complete absorption of drop by the fabric was recorded using a stop watch. This test was repeated on five different parts of the fabric and the average wetting time was calculated.

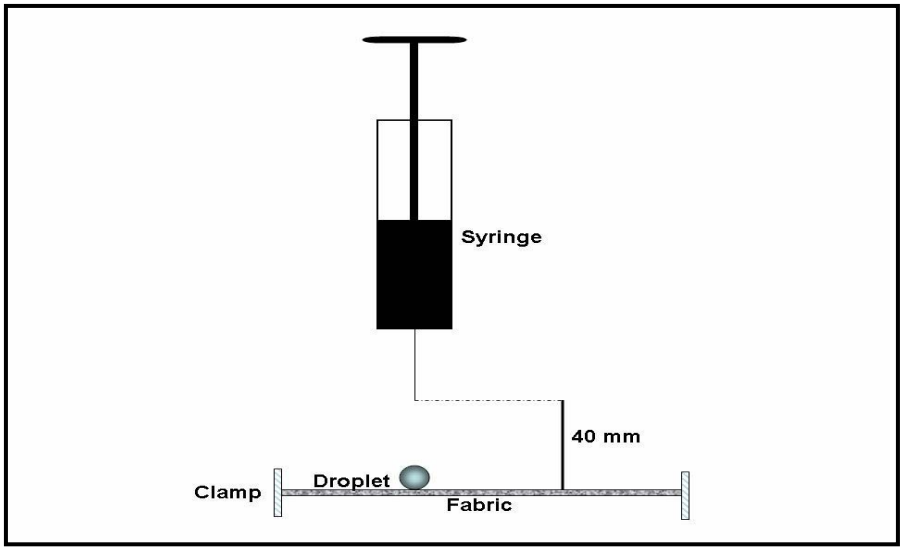

Figure2 Schematic of the set up used for measuring the oleophilic time of fabric [9]

Changes in surface morphology of wool fibre surface were studied with the help of a high resolution (up to 3 nm) scanning electron microscope (ZEISS EVO50) using SE detector, 20 kv power and gold coating of 100 Angstroms. ATR analysis was carried out to study the change in molecular composition of wool exposure to radiation. Perkin-Elmer 16PC FTIR spectrometer in ATR reflection mode with a zinc selenide crystal was used for the purpose.

Vertical wicking test

A rectangular wool sample (100mm x 20mm) was used for the wicking measurement. One datum line L1was marked along the longitudinal direction of the fabric, at a distance of 20 mm respectively from one end of the sample. The sample was immersed in water up to L1 and the distance covered by water with time was measured.

Finishing of wool

Wool fabric sample were padded with 2% o.w.f commercial formulation NUVA (Flurocarbon based chemical) and dry at 90^0C for 5 min and then cured at 120^0C for 1 min. Back side of this fabric was exposed under 172 nm UV light for 5 min, 10 min, 15 min, 20 min 25 min, 30 min.

Contact angle measurement

Treated wool fabric samples (10cm*2cm) were held horizontally at its two ends, keeping it free of folds. Colored water drop was released from a syringe at 40 mm height. Then we took photograph of it and transfer this picture to our computer. After that by protector and scale we measure contact angle. Such measurements were made on five different parts of the fabric and the average contact angle was measured.

Evaluation of tensile properties and bending length

Warp way and weft way breaking strength of untreated and treated wool fabric samples were determined after conditioning the samples by standard methods following the raveled strip method as per IS:1969:1968 procedure using Instron (model-1445) CRT universal tensile tester with a traverse speed of 100 mm/min and a pretension of 0.5N. The final gauge length of the fabric sample was 50mm* 20mm after raveling. The test results reported are an average of 10 tests for each sample.

Both warp way and weft way of untreated and treated wol fabrics have been measured as per 1S:6490-1971 (cantilever test) method using a Sasmira stiffness tester with a specimen size of 200mm*25mm.

Results and discussion

Physical changes in the surface of wool

The SEM micrograph of the surface structure of the untreated and the UV treated wool fabric in air, O_2 and N_2 atmosphere is shown in Figure 3. It can be observed that the untreated wool fibre has flat waxy smooth sharp scales with well defined scale edges. Boundaries separate the neighbouring cuticular cells are clearly resolved. Scanning

electron micrographs show that nano roughening of wool fiber surface has occurred on irradiation because of surface etching. Some raised scale edges, striations, nanopores along with increase in surface hydrophilic groups may significantly contribute to the adhesive forces between the wool fiber surface and oil molecules leading to increase in oleophlicity .It was clear that in O_2 atmosphere the sharp and round scale edge of the untreated fiber became non uniform and partially removed, indicating surface erosion of the wool fiber and there are some micropits on the surface. In case of O_2 atmosphere high energy photons breaks the molecular chains leading to formation of micropits. Sample irradiated at N_2 atmosphere shows different from other samples. Fat waxy smooth scale edges are broken and there are striations on the surface which could be due to the etching effect of the UV rays. These alterations of the fiber surface facilitate the capillary movement into the fiber and consequently improve the vertical wicking rate of the fabric.

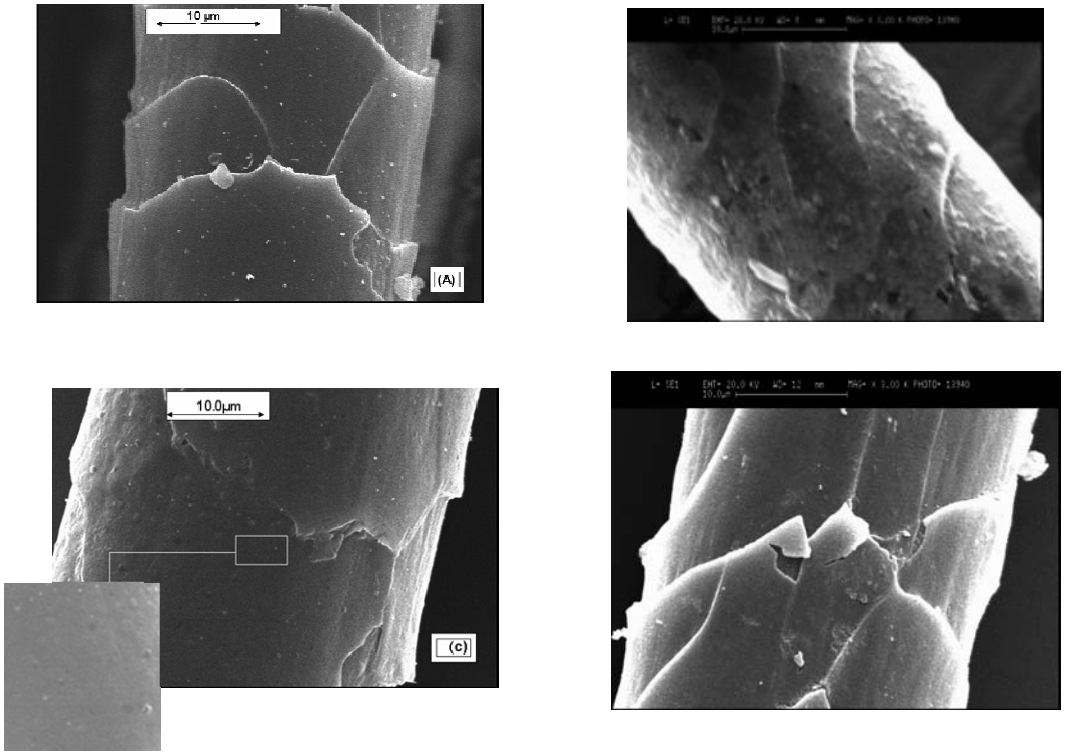

Figure3 SEM micrographs of wool fibre treated with UV Excimer lamp for 15 min (A) Untreated (B) Air (C) O_2, and (D) N_2 atmosphere.

Oleophilicity of wool

Oleophilicity of a surface can be defined as the time taken for a drop of oil to be completely absorbed by a fabric. Wool is a fiber characterized by a hydrophilic core protected by an outer surface rendered hydrophobic by the presence of a thin (0.9 nm) layer of fatty acids on its epicuticular surface [6]. This layer does not get removed even during the scouring of wool and the fibre continues to be hydrophobic on the surface thus making it difficult to dye and process it using aqueous industrial processes.

Several physical and chemical reactions are responsible for the observed lipophilicity of wool after UV exposure. The first phenomenon is commonly known as the ozone–oxygen cycle [8]. Oxygen from the atmosphere absorbs high-energy photons from the excimer to form highly reactive excited oxygen O (1D) either directly or first forming O_3 (ozone) and then dissociating into O (1D) and O_2. The presence of nitrogen in air plays an important role in the production of such reactive excited oxygen species [8]. The excited oxygen O (1D) in turn oxidizes the fatty layer and reacts with the fibre surface to form oxygen containing polar groups i.e hydroxyl (-OH) and carbonyl (-C=O) groups.

However, by far the most important oxidation reaction is the oxidation of disulphide protein linkages (-S-S-) to give S^{VI} in the form of anionic sulphonic acid groups ($–SO_3H$) accompanied by intermediate products like cystine monoxide and cystine dioxide [10] .These all physicochemical phenomenon increases the surface energy of the fabric and have a linear relationship with its lipophilic behavior. In Figure 4 shows the results of oleophilicity of wool when exposed to 172 nm UV radiation in air, oxygen or nitrogen atmosphere It can be observed that oil spread time for the control wool fabric is very much less . This may be due to the presence of hydrophobic fatty layer on the surface of wool fabric. Hydrophobic oil attracts the hydrophobic fatty layer on the surface of wool fabric and makes the surface of wool fabric lipophilic. UV irradiated wool fabrics in air, O_2 and N_2 atmosphere also shows very less oil spread time. It may be due to the increase in surface roughness, surface energy and surface area of wool fabrics after irradiation. Additionally it is also known that the main mechanism of oxygen incorporation is due to cleavage of disulphide protein linkages also lead to creation of cystic acid on wool. Together all these phenomena help to make the surface of irradiated wool highly lipophilic. Air and O_2 atmosphere UV treated wool fabric samples show almost similar oil spread time but in case of N_2 atmosphere oil spread time is slightly less compared to air and O_2 atmosphere.

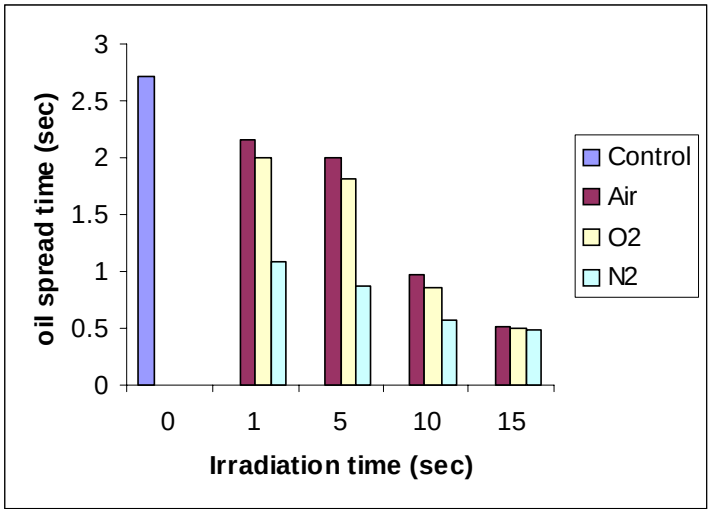

Figure4 Oleophilicity test of UV irradiated wool fabrics

Wickability of wool

Wicking behaviour can be explained with reference to the capillary action of water which is defined as the upward movement of water against gravitational force within the spaces of a porous material. it is a function of the forces of adhesion (attraction between water molecules and the substrate due to intermolecular forces of attraction), cohesion (attraction between water molecules), and surface tension. Capillary action occurs when the adhesive inter molecular forces between the liquid and the substrate is stronger than the cohesive intermolecular forces within the liquid. The irradiation of wool by Excimer lamp damages the fatty layer and also develops hydrophilic groups on the surface. These two changes contribute significantly to the adhesive forces between the wool surface and water molecules, leading to an increase in wickability[11]. Moreover if the pore size is small and relatively uniform, water level can rise to higher level by capillary action than if the pore size is large and non uniform[11, 12].

As we see in the Figure 5, 6, 7 there is a significant improves in wickability of UV treated fabrics, as indicated by relatively short time, less than 10 sec to achieve a height of 2 cm in comparison with 2 cm reached after 2 mins for untreated wool fabrics Increased wickability of the irradiated fabrics caused by the changed surface properties with the 172 nm UV treatment in Air, O_2 and N_2 atmosphere. Wickability increases with increase in exposure time in different atmosphere. It can be seen from the figures that irradiation increases the wickability of wool up to 15 min of exposure time, beyond which it stabilizes. In case of N_2 atmosphere wickability is slightly more than air and O_2 atmosphere. This may be due to the formation of striations on the fibre surface which help in capillary movement of water.

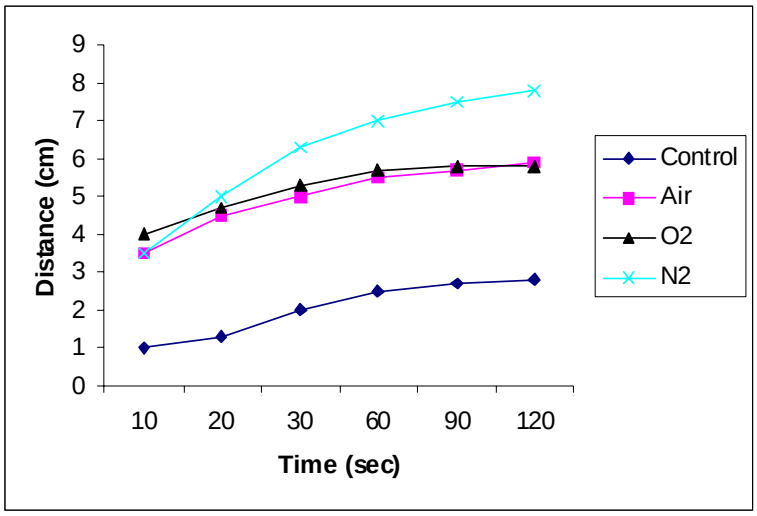

Figure5 5 min irradiated wool fabric

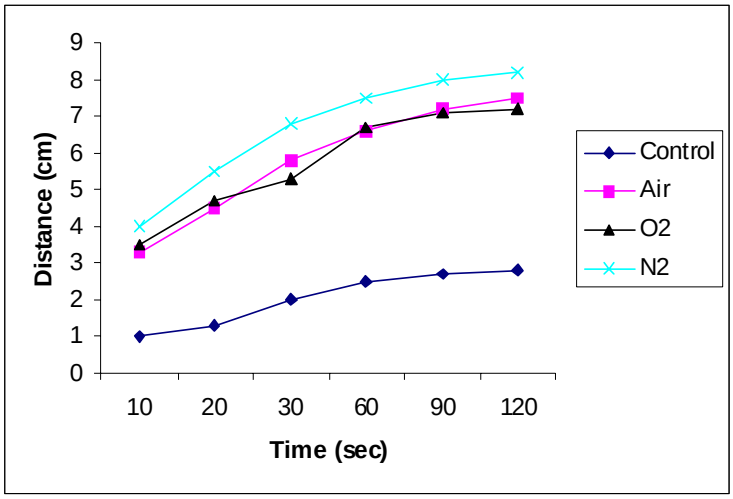

Figure6 10 min irradiated wool fabric

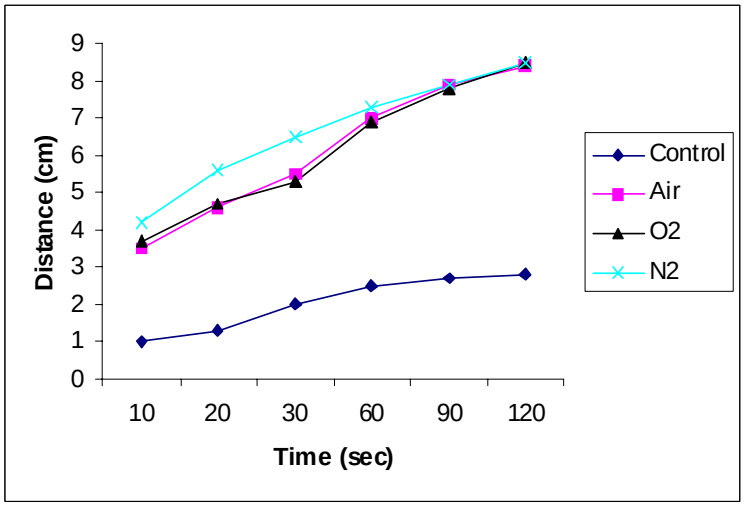

Figure7 15 min irradiated wool fabric

Development of special finishes on wool

Preparation of double hydrophobic/ hydrophilic surfaces

A multifunctional wool fabric having hydrophobic property on one face and hydrophilic property on the opposite face was prepared by first padding with fluorocarbon based chemical NUVA HPU and then irradiating on one side with the 172 nm UV Excimer lamps. Treated samples were characterized by contact angle measurements.

Padding liquor composition
Nuva HPU 30gpl
Arkofix NEC 8 gpl
$Mgcl_2$ - 5 gpl
Acetic acid- 0.5 gpl

Wool fabric padded with previous chemical at 70% pick up and dries at 90^0C, 2 min and cure at 120^0C for 1 min. Then after 1 day conditioning this fabric undergoes contact angle measurement.

Contact angle

Measurement of contact angle is one of the effective methods to distinguish between a hydrophobic and a hydrophilic surface. On many hydrophilic surfaces, water droplets exhibit contact angles of around 30^0 while on highly hydrophobic surfaces, which are incompatible with water, it shows a contact angle of 140^0 and above. Therefore in this study the contact angle measurement method was adapted to quantify the hydrophobicity and hydrophilicity of the wool surface. Table2 shows the contact angle of wool fabric treated with water repellent flurocarbon finish, followed by irradiation of one side of the fabric with the 172 nm UV Excimer lamp.

Table 2 Contact angle measurement

Contact angle measurement (^{0})		
Untreated wool	90	
Treated wool		
Irradiation time (min)	Non irradiated side	Irradiated side
5	140	60
10	138	50
15	138	40
20	138	25
25	140	20
30	140	10

From the Table2 it can be observed that the contact angle on the irradiated side of the fabric (hydrophilic side) decreases with increase in irradiation time. The contact angle decreases markedly up to irradiation time of 30 min, after which it stabilizes. An interesting observation is that, on the non irradiated side of the fabric, the surface remains completely hydrophobic and continues to show a very high contact angle of around 130^0. Thus a wool fabric, having one side hydrophobic and the other side hydrophilic has been produced.

Studies on irradiation of fluropolymers exposed to UV (<200 nm) radiation have been carried out. These studies show that on irradiation with VUV excimer lamp the fluorocarbon finish undergoes photo oxidation which involves defluorination of the surface and incorporation of oxygen as $CF\text{-}O\text{-}CF_2$, $CF_2\text{-}O\text{-}CF_2$ and $CF\text{-}O\text{-}CF_3$ moieties.

The strength of C-F bond is very high e.g., C-F bond in carbon tetra fluoride has bond dissociation energy of 124kcal/mol[15]. Hence modification of the fluorocarbon polymers is effective when irradiated with 172 nm excimer lamp which emits photons of 7.2 ev. These high energy photons are capable of breaking even C=C bond whose bond dissociation energy (146kcal/mol) is higher than C-F bond[16]. Hence the incidence of high energy photons may break the –CH-, -CF-, -CC bonds of the fluorocarbon finish present on the surface of the treated wool fabric leading to generation of free radicals on the surface. These highly reactive free radicals may further react with oxygen in the gas phase (air), and thus substitute the fluorine by oxygen containing groups and made the surface of wool fabric hydrophilic.

ATR analysis

In Figure 8 Fluorocarbon treated and untreated wool samples were subjected to ATR analysis with a view to confirm the presence of functional groups mentioned above. ATR investigations provide information about the chemical nature of the outer 10^{-6} m of the modified fibre surfaces. In curve C the most intense bands in this analysis are observed at 1202 and 1150cm^{-1} and can be assigned to the CF_2 symmetric and asymmetric stretching vibrations. Analysis also exhibits strong carbonyl absorption at 1738cm^{-1} [17]. This carbonyl group is part of ester linkage connecting the CF_2 chains to the backbone. In curve E and F a small peak has been observed at 1045cm^{-1}. This may be due to UV rays in presence of O_2 atmosphere produce Cystic acid which is the oxidation product of disulphide groups present in untreated wool. In curve A and B no intense CF_2 stretching vibrations has been observed and also no peak has been observed at 1738cm^{-1} which may be due to the oxidization of ester linkages between wool fabric and fluorocarbon polymer.

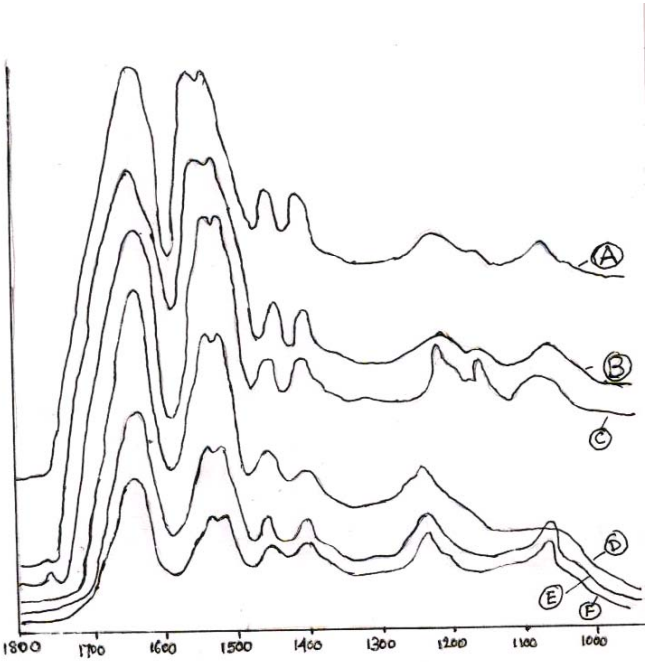

Figure 8 ATR spectra of UV treated wool in different conditions (A) One side of FC treated fabric irradiated by excimer lamp for 30 minutes in air atmosphere (B) One side

of FC treated fabric irradiated by excimer lamp for 20 minutes in air atmosphere (C) FC treated wool fabric, (D) Untreated, (E) O_2 atmosphere for 20 min, (F) Air atmosphere for 20 min .

Vertical wicking of irradiated/ non irradiated surfaces

Vertical wicking test was conducted on hydrophobic and hydrophilic wool fabric and the results are shown in Figure 9 .Unexposed samples and those exposed to short term irradiation (0 to 15 min) have poor wicking. In the case of samples irradiated for 25-30 min, the wickability is good. However, for samples exposed to VUV radiation for 30 min the Wickability improves significantly.

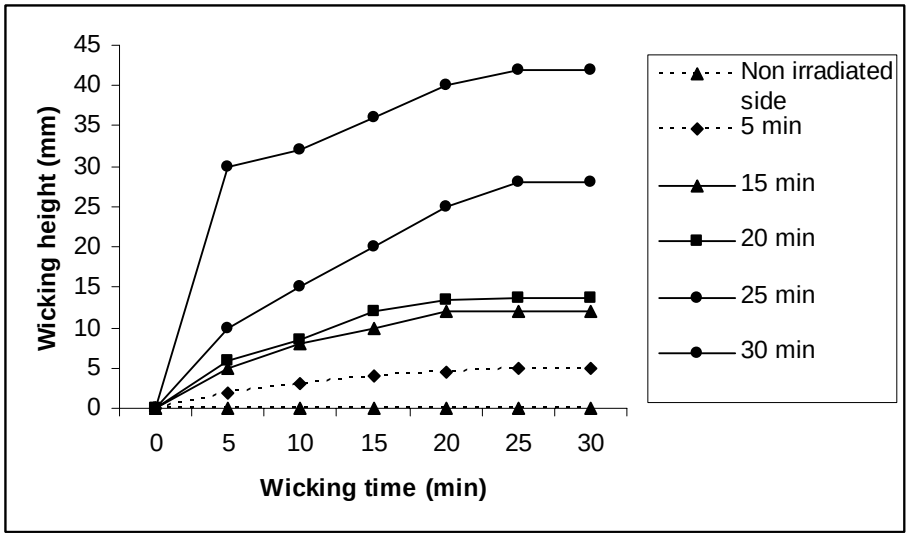

Figure 9 Wicking property of irradiated/ non irradiated surface.

Performance properties of treated fabric

The fluorocarbon finish and UV irradiation may affect some of the essential properties of a fabric like handle, feel, strength etc. Therefore, some critical physical properties of the treated fabric such as bending length, tensile strength have been studied. Results are summarized in Table 3

Table3. Performance property measurement

Time of irradiation (min)		Bending length (cm)		Tensile strength (N/Tex)	
		Warp way	Weft way	Warp way	Weft way
Untreated sample		3.4	3.2	270	225
FC treated fabric		4.1	3.9	255	200
One side of treated fabric irradiated by UV lamp	5	3.8	3.8	265	230
	15	4.1	3.7	263	228
	20	4.3	3.7	264	225
	25	4.4	3.6	260	220
	30	4.5	3.5	255	225

It can be seen from the results that on treatment with fluorocarbon finish there is a slight increase in bending length i.e stiffness of the fabric and tensile strength slightly reduces because of stiffness of the fluorocarbon treated fabric. If we compared the result almost 5% loss of tensile strength has been observed on the treated sample compared to the untreated wool fabric sample. Irradiation did not affect strength parameter much more. This may be because of it effect only micrometer surface of the fabric.

Conclusion

Monochromatic UV irradiation of 172 nm can modify the surface properties of wool to an appreciable extent. 15 minutes of exposure time brings about notable changes in the surface morphology as well as surface chemistry of wool as seen by the SEM and ATR analysis. It also improved wicking and lipophilic behaviour of all treated samples. Most dramatic effects are observed for treatment in N_2 atmosphere for 15 min. SEM of these samples shows striations on the surface and wicking rate is also higher compare to Air and O_2 atmosphere. Understanding of surface physicochemical changes on wool due to VUV radiation paves a path for developing value added finishes for wool fabric. For instance, the study of morphological changes on one side irradiation has shown that the irradiation modifies only the side being irradiated but not the back side due to strong absorption of photons of 172 nm light within the submicron structure of the surface. It may hence be concluded that UV radiation has the potential to be exploited in design and development of cleaner, more effective and more efficient commercial processes for finishing and processing of textiles.

About the Author

The author is working as assistant executive in Vardhman Fabrics, process product development department.

References

1. Maclaren, Milligan, *Woo Science,* Vol 3, 1996, pp345.
2. Thomas, Hocker, *9th International Wool Textile Research Conference,* Vol 4, 1995, pp351**.**
3. J.H. Xin, R.zhu, J. Hua, *Coloration Technology,* Vol 118, 2002, pp169-173
4.J Odvarka and J Hunkova, *Society of Dyers and Colorists.,* Vol 99**,** 1983, pp207.
5. K R Millington, *Textile Research Journal,* Vol *68,* 1998, pp413
6. C.Wai, C.Kwong, M.U.Chuan-Wah, Autex *Research.Journal, Vol* 3, 2003, pp195-200
7. S.Periyasamy, M.L.Gulrajani, D.Gupta, *Europian Polymer Journal*, 2007, Vol 43, pp4573
8. S.Periyasamy, M.L.Gulrajani, D.Gupta, *Journal of Applied Polymer Science*, 2007, Vol 103, pp410
9.D.Gupta, S.Basak, *Journal of Applied Polymer Science*, Vol.117, 17 January 2010, pp 3448-3453.
10. M.R.Adams, A.Garton, *Advanced Chemical Technology*, Vol 3, 1996, pp 249

11. P. Guiong, Y.Dezhaung, L.Jincheng, *Journal of Applied Polymer Science*, Vol 90,2003, pp115,
12.F.A. Rasaoul, D.J.T. Hill, G.A.George, *Polymer Advance Technology*. Vol 9, 1998, pp24,
13. K R Millington and J S Church, *Journal Photochemistry Photobiology*, Vol 39, 1997, pp204
14. C.W. Chan, K. Yuen, C.W.M. Miao, M.H., *Textile Research Journal*., Vol 69 ,1999, pp 407–416 .
15. Periyasamy, M.L.Gulrajani, D.Gupta, *Surface Coating Technology*, Vol 201, 2007, pp 7288-7290
16. N.J.Harrick, John *Wiley and Sons*, Vol 23, 1967, pp30.
17. Jeffrey S. Church, David J. Evans, *Journal of Applied Polymer Science*, Vol. 57, 25 February1995, pp1585-1594.