# Spectroscopic studies of modified wool fibre surfaces

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The physicochemical properties of wool fibre surfaces are reviewed in terms of treatments used to increase surface polarity and promote aqueous wetting, dyability and shrink resistance. Use of a new UV ozone dry treatment, which is effectively effluent free, is shown to give levels of surface oxidation which leads to water wetting and dyeability which may be suitable for some industrial purposes.

Control of surface chemistry is an important factor in wool processing technology. Wool keratin fibres consist of a core of elongated cortical cells within an outer layer of overlapping cuticle cells each of which is covered by an epicuticle membrane. The latter is composed of proteinaceous material, which contains a high level of the amino acid cystine but, with a significant proportion (*ca.* 25%) of the lipid 18-methyleicosanoic acid. A schematic diagram of wool fibre structure according to Leeder[1] is shown in Fig. 1. The fibres have a low surface free energy, are hydrophobic and are characterised by relatively high inter-fibre friction due to the angularity of the cuticle cell edges. These characteristics are, to a large extent, undesirable from a textile viewpoint since (i) dyes, softening agents and shrink-proof treatments are usually applied from aqueous solution and therefore some degree of water wettability is desirable in the fibre surface, (ii) chemical treatments need to be strongly bound to the fibre surfaces in order to avoid removal during subsequent wash cycles and therefore strong physical, or chemical, adsorption is needed and (iii) free movement of fibres in clothing is desirable to aid restoration of shape after washing and to avoid shrinkage. It is therefore desirable to modify the surface properties of wool for textile applications.

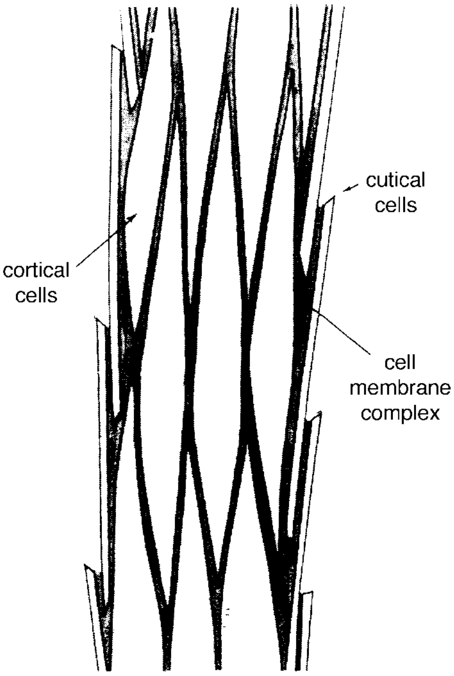

**Fig. 1** Schematic model illustrating the composite nature of wool fibre[1]

Modification of fibre surface chemistry, and particularly the lipid overlayer, plays an important role in this process. The method most widely used in the textile industry is an oxidation process, known as wet or Kroy chlorination which involves treatment of wool fibre top or woven fabrics with an aqueous solution of sodium hypochlorite (NaOCl). The process is aggressive and can cause some damage to the wool fibre but it does increase the wettability of the fibre surface and may also increase shrink resistance. The latter is thought to be due to loss of angularity at cuticle edges which leads to a more mobile network of fibres which allows relaxation back into shape after washing. Electron micrographs from untreated and Kroy treated wool fibres are shown in Fig. 2 which confirm the outer structure shown in Fig. 1 and also indicate the partial loss of cuticle relief after oxidation. The wet treatment does, however, produce chlorine-containing liquid effluent, which in the current climate of environmental awareness, may be difficult to dispose of. It has therefore, been necessary to identify replacement methods for the surface oxidation of wool materials which are acceptable from an environmental viewpoint and which can be used on a commercial scale. In particular, the use of dry methods of oxidation using lasers, oxygen plasmas, and corona discharge have been investigated.[2] Whilst each may be considered to have specific individual attractions, none has been found to be as effective as the wet method.

We have been involved in fundamental studies of the surface properties of wool fibres and their modification for a number of years and, after comparing the chemistry which results from the above processes, have developed a new method of textile fibre,[3] and thin film[4,5] oxidation, using low concentrations of ozone generated from atmospheric oxygen using UV light. Here, we review the physicochemical characteristics of wool fibres treated by the various oxidative methods mentioned with particular emphasis on results obtained using our own UV ozone system. Because this method of surface oxidation can be closely controlled we also present data for the progressive oxidation of fibre surfaces and link resulting changes to a series of experiments used to assess likely commercial performance.

## Experimental

Results are presented for woollen materials in either the untreated state or after application of a specific oxidative treatment. Wool was used as either carded fibre top or as

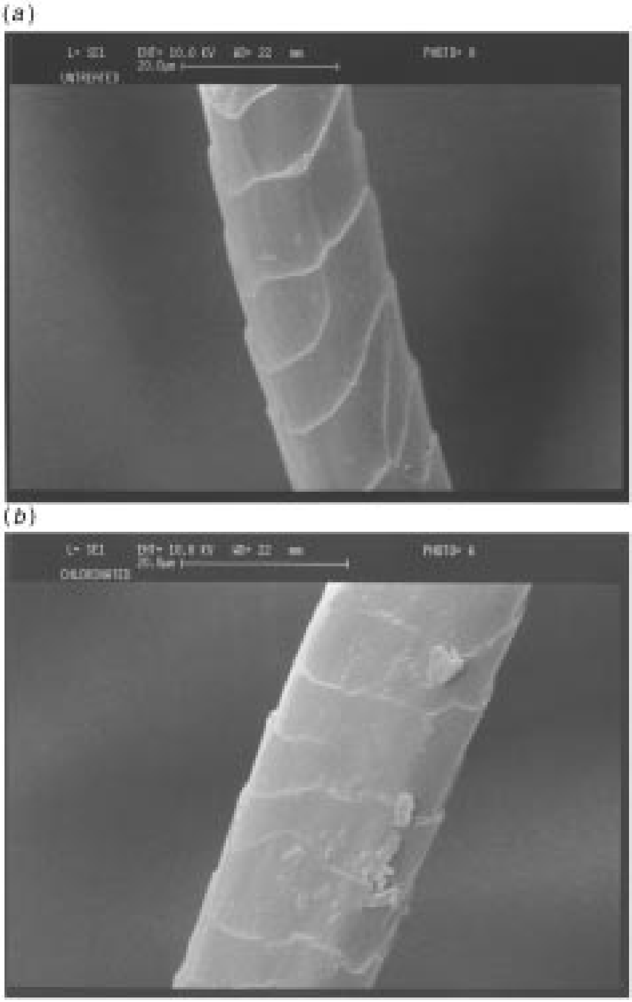

**Fig. 2** SEM images of (*a*) native/untreated and (*b*) wet/chlorine oxidised fibres

woven challis material, the specific form is given with individual results. Data are compared for wet 'Kroy' chlorination, laser, oxygen plasma, and UV ozone oxidation methods.

For Kroy chlorination samples of wool top or woven fabric were treated in a dynamic, continuous, bath system using an aqueous sodium hypochlorite–sulfuric acid mixture at pH 1.5–2.0, full details of this and other types of processing methods have been discussed elsewhere.[6]

Oxygen plasma treatments were carried out on woven samples at plasma densities of 200, 400 and 600 W m$^{-2}$ under atmospheric pressure (corona discharge). In addition a batch of wool fibres and a sample of woven material were treated for 30 s in a 240 V 0.15 A dc plasma under a flow of 25 cm$^3$ min$^{-1}$ oxygen and 80 cm$^3$ min$^{-1}$ argon at a pressure of $2 \times 10^{-4}$ Torr using a 160 cm$^2$ aluminium electrode (glow discharge). Samples of woven challis were treated with a defocused $CO_2$ pulsed laser of 248 nm or, on one occasion, 193 nm wavelength in the energy density range of 83–142 mJ cm$^2$.

For UV ozone treatment, fibres were exposed in a static batch treater for a range of exposure times up to 10 min or dynamically treated in a prototype reel-to-reel apparatus built in our own laboratory. Both apparatus were operated at ambient conditions of pressure and temperature. The batch treater is a stainless steel cell (280 × 300 × 80 mm) with a single element 180–400 nm wavelength UV lamp affixed to its roof and controlled by a timer to regulate exposure. Samples were treated on a plinth at varying separations from the lamp, the optimum distance was found to be 3 mm. The dynamic treater consists of two parallel arrays each of 12 × 30 W 180–400 nm wavelength lamps which are powered in groups of four by six 50 mA, 2.5 kV ballast units. Woven fabric is drawn between the arrays from a braked feed roll by a motorised pick-up roll. The rate of pass, controlled by a 0–12 V potentiometer on the pick-up motor, determines the fabric residence time in the active area of the lamps and hence the treatment level. Throughput rates of 4 to 70 cm min$^{-1}$ could be achieved with varying degrees of oxidation. By calculation of treatment power density throughput rates for an industrial scale treater were calculated at $<6$ m min$^{-1}$ for a 6 m bed single pass reactor. A schematic diagram of the treater is shown in Fig. 3.

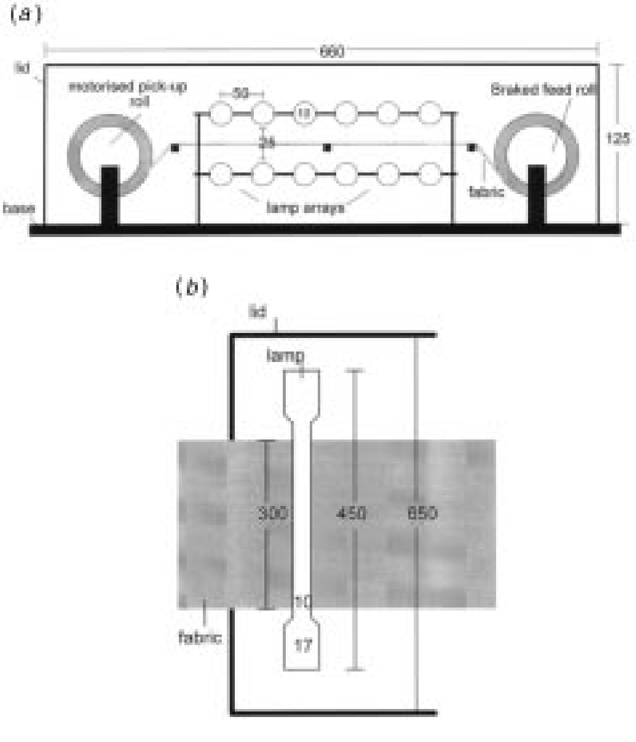

**Fig. 3** Side elevation (*a*) and, plan view (*b*) of dynamic UV ozone treater

Sample compositions and chemical state information have been obtained using X-ray photoelectron spectroscopy (XPS). Experiments have been carried out using a VG ESCALAB Mk 1 using Al-K$\alpha$ X-rays of energy 1486.6 eV, at a residual pressure of $10^{-8}$ Torr. Measurements were made in fixed analyser transmission and with the analyser normal to the plane of the sample at pass energies of 85 eV for broad scan spectra and 25 eV for high-resolution scans of S 2p and C 1s peaks. All peaks have been charge referenced to the major C—C/C—H 1s peak at 285.0eV (assumed to be proteinaceous/lipid in origin). Surface compositions have been calculated using the areas of the respective photoelectron peaks after subtraction of a Shirley type background. Correction has been made for the angular asymmetry of photoemissions,[7] transmission of the energy analyser,[8] photoionisation cross-section[9] and the inelastic mean free path of the photoelectrons.[10]

Chemical shift data for UV ozone treated samples have also been obtained using a Scienta ESCA300 spectrometer with a monochromated aluminium X-ray source. These spectra have been recorded at a pass energy of 150 eV, slit width of 0.5 mm, 0.05 eV per channel and a dwell time of 0.1 s per channel and an anode power of 2.8 kW. Samples of either woven cloth or rafts of fibres (both 20 × 20 mm), from different sources, were affixed to aluminium sample stubs using a copper frame which also helped to minimise sample charging. No Al or Cu peaks were detected in the spectra from any of the samples indicating that only the wool surface was being analysed.

The water wetting characteristics of woven challis have been assessed by floating a 2 × 2 cm square of the material on the surface film of distilled water at room temperature and measuring the time for the water to advance over the upper surface and sink the sample. This method was found to allow easy relative assessment of wetting characteristics where the sessile drop method is inappropriate, owing to the topographical and capillary effects in woven materials, and performing the single fibre micro Whilhelmy test on the low modules wool fibres is not possible.

Depth of colour for printed samples was measured using absorbance in the visible (400–700 nm wavelength) spectral region using an ICS-Texicon spectrophotometer. Berger whiteness and yellowness indices were compared for UV ozone, plasma and corona oxidations using the same method.

## Results and Discussion

Typical XPS spectra from untreated and oxidised (challis/UV ozone) wool materials are shown in Fig. 4. Major peaks due to carbon and oxygen and lower intensity peaks due to sulfur and nitrogen are evident. The surface compositions of all treatment types and their levels of application are given in Table 1. The effects of the individual treatments are reported and discussed below.

### Wet (Kroy) chlorination

As shown in Table 1 there is a marked increase in surface oxygen from *ca.* 12 to 24 atom%. The chemical effects of this treatment have been investigated and reported by a number of workers[2,11] who have shown that the main mechanism of oxygen incorporation is by the oxidative cleavage of disulfide protein linkages ($-S-S-$) to give $S^{VI}$ in the form of sulfonic acid groups ($-SO_3H$). This process is characterised by a shift in binding energy of the sulfur 2p peak from 164 eV for the native disulfide to 168 eV for the $S^{VI}$ shown in Fig. 5 for fibre top. These spectra clearly show that no peak corresponding to $S^{IV}$ is evident in the spectrum from the untreated wool. Furthermore no disulfide sulfur appears to be present in the wet chlorinated material indicating that the oxidation is 100% effective. Oxidation of all the S detected in the untreated material (*ca.* 3 atom%) to sulfonic acid would lead to a 9 atom% increase in oxygen and hence an approximate total of 22% and, since the levels observed are slightly higher than this figure, it appears that some oxidation also occurs at either carbon or nitrogen atoms. Small decreases in surface carbon levels, detectable after treatment, are thought to be due to the removal or modification of the lipid layer since this is often associated with slight increases in signal from proteinaceous nitrogen and sulfur. These chemical changes give rise to an increase in the polar component to the surface free energy of the fibres.

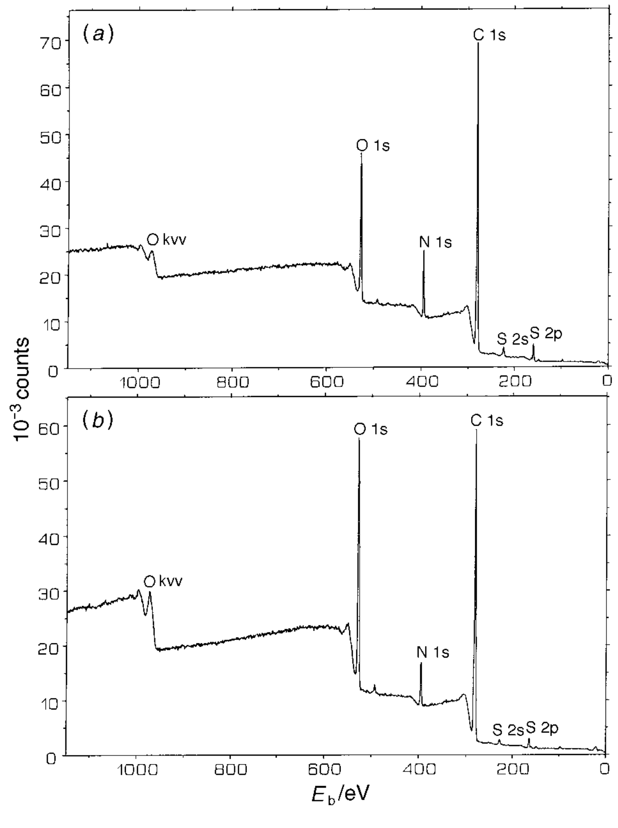

**Fig. 4** XPS survey spectra from (*a*) native and (*b*) UV exposed surfaces

**Table 1** Surface composition (atom%) of wool samples

| sample | C | O | S | N |
|---|---|---|---|---|
| untreated top | 79.3 | 11.8 | 2.7 | 6.2 |
| untreated challis | 76.0 | 12.1 | 3.1 | 6.8 |
| plasma | | | | |
| challis: 200 W m$^{-2}$ | 66.6 | 20.8 | 3.4 | 9.2 |
| challis: 400 W m$^{-2}$ | 64.2 | 21.0 | 3.8 | 10.0 (Na 1.0) |
| challis: 600 W m$^{-2}$ | 60.3 | 21.5 | 3.4 | 11.8 (Si 3.0) |
| top: 2.25 kW m$^{-2}$ | 74.4 | 17.6 | 1.5 | 6.5 |
| challis: 2.25 kW m$^{-2}$ | 65.6 | 18.8 | 3.4 | 12.2 |
| UV–ozone | | | | |
| UVO5 | 67.0 | 24.7 | 2.3 | 6.0 |
| UVO10 | 61.9 | 27.5 | 2.8 | 7.8 |
| wet chlorination | 62.6 | 24.1 | 3.1 | 9.2 |

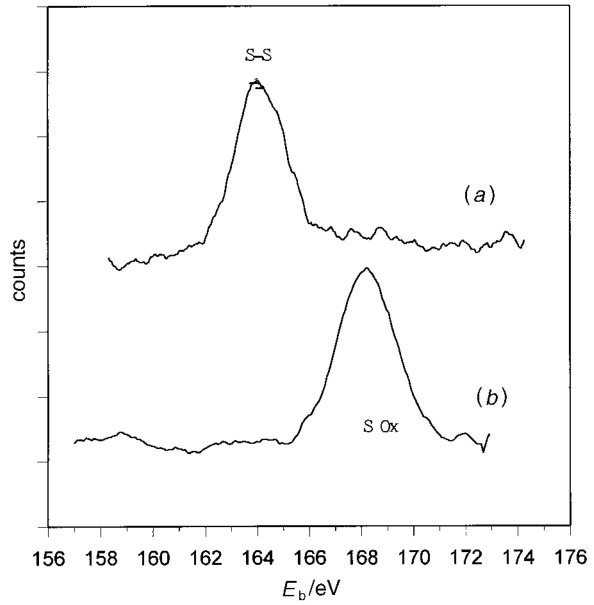

**Fig. 5** Sulfur 2p spectra from (*a*) native and (*b*) wet/Cl treated wool, showing disulfide (164 eV) and oxidised sulfur (sulfonic acid) peaks (168 eV)

The anionic $-SO_3H$ species produced by the process, coupled with the modification of the lipid layer, lead to a more hydrophilic surface, with a time to wet for a 2 × 2 cm square of challis of 15 s. The untreated materials are hydrophobic and do not wet by this method. The oxidised surface is also found to have greater attraction toward cationic surfactants such as amino functional polysiloxanes (*e.g.* Lanalux) used as softening agents.

### Laser treatment

As shown in Table 2 the 193 nm wavelength treatment applied at an energy density of 83 mJ m$^{-2}$ for 100 pulses gives the highest degree of disulfide to $S^{VI}$ oxidation at 56%. The most effective of the 248 nm wavelength treatments is the

**Table 2** Laser treatment conditions and resulting disulfide oxidation

| sample no. | fluence/mJ cm$^{-2}$ | $\lambda$/nm | pulses | % S$^{VI}$ |
|---|---|---|---|---|
| 1 | 142 | 248 | 100 | 46 |
| 2 | 114 | 248 | 50 | 0 |
| 3 | 114 | 248 | 200 | 53 |
| 4 | 142 | 248 | 100 | 34 |
| 5 | 83 | 193 | 100 | 56 |
| 6 | 114 | 248 | 50 | 17 |

114 mJ m$^{-2}$ treatment applied for 200 pulses. This gives a similar level of sulfur oxidation (53%). The other levels of oxidation achieved are generally low and are not of sufficient level for commercial applications.

### Oxygen plasmas

The quantitative effects of plasma treatment upon the surface compositions of the samples are shown in Table 1 compared to the untreated and wet chlorinated surfaces. The increase in surface oxygen in these instances is again approximately 9 atom% giving a final level of *ca.* 21 atom%.

The sulfur chemistry of these materials has been discussed in detail elsewhere.[2] The high-resolution S 2p spectra obtained from the 200, 400 and 600 W m$^{-2}$, and the 240 V/0.15 A plasma-treated samples all show evidence for the presence of at least two sulfur species at the surfaces *i.e.* all contain a major peak at *ca.* 164 eV, which is due to the presence of native disulfide, and a minor peak at *ca.* 168 eV attributable to oxidised S$^{VI}$ in the form of sulfonic acid. These treatments are not therefore as effective as the wet chlorination process for sulfur oxidation.

Calculation of the amounts of S$^{VI}$ present, from the relative peak areas, indicates that the extent of sulfur oxidation is not markedly energy dependent for the conditions used and that only about 20–30% of the total surface sulfur (*ca.* 3 atom%) is oxidised to the S$^{VI}$ state. A lower level of oxidation (18% of total) was observed for the 240 V/0.15 A fibres and was thought to be due to shadowing effects during treatment, whereby fibres at the centre of the treated web receive a lower exposure to the plasma than fibres at the web surface. Subsequent rearrangement of the fibre web during mounting for XPS, meant that some of these lesser treated/unoxidised fibres are included in the analyzed area. For the other samples the general level of oxidation observed accounts for an increase in surface oxygen of only about 3%. However, since, as shown in Table 1, the total surface oxygen levels of the plasma-treated samples are almost as high as those recorded from the wet chlorinated sample it appears that although the plasma is only partially effective in oxidising the sulfur component of the wool surface, oxygen is being introduced at some other surface sites, most probably carbon atoms present as either lipid or protein. This was confirmed by the presence of a shoulder to the higher binding energy side of the main C 1s (C—C/C—H) photoelectron peak at 284.6 eV for these materials which was of greater intensity than that observed in curves from unoxidised wool. This additional structure was shown to be due to the presence of hydroxy and carbonyl groups.[2,3]

### UV–ozone

As shown in Table 1 the UV ozone treatment leads to levels of surface oxygen which are more than a factor of two higher than those recorded for the untreated surface. Indeed the value shown for the 10 min UV ozone treated sample (27.5 atom%) is higher than that generally achieved by the wet chlorination process (*ca.* 24%) which has been shown to oxidise all disulfide sulfur to S$^{VI}$.

The S 2p spectra from these materials (Fig. 6) also show two peaks, again at *ca.* 164 and *ca.* 168 eV, but in this instance the most noticeable feature of the curves is the much higher intensity of the higher binding energy peaks, due to oxidised sulfur (sulfonic acid groups). These indicate that *ca.* 90% of the total surface sulfur is oxidised to the S$^{VI}$ state which is a significant improvement on the levels of oxidation obtained using the other dry treatments (*e.g.* Table 2). As shown in Table 1, the total increases in surface oxygen for the treated samples appear to be at least as high as those which might be expected for 100% oxidation of all of the sulfur present and again it is likely that oxygen is also being introduced at proteinaceous/lipid carbon sites on the wool surface.

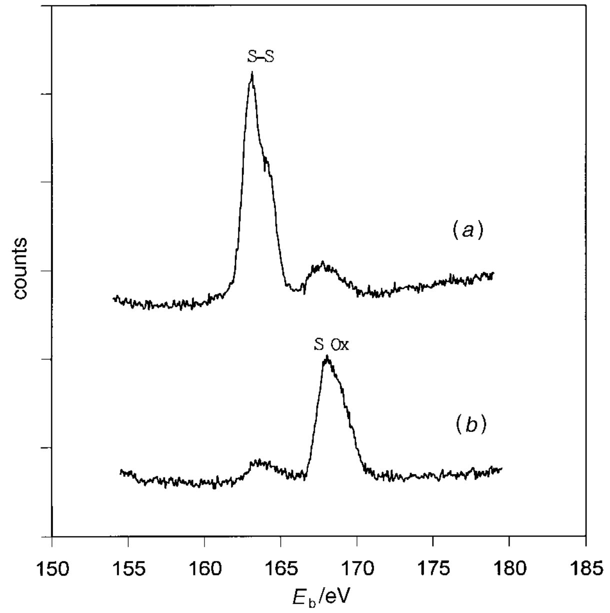

**Fig. 6** Sulfur 2p spectra from (*a*) native and (*b*) UV exposed surfaces

The carbon 1s data shown in Fig. 7 supports this in that differences between the envelopes from the untreated and treated surfaces are markedly different. The envelope from the untreated material is characterised by a major peak at a binding energy of 285 eV which is due to C—C/C—H bonding of the main protein and lipid structures of the material, a shoulder to the higher binding energy side of this peak, at an

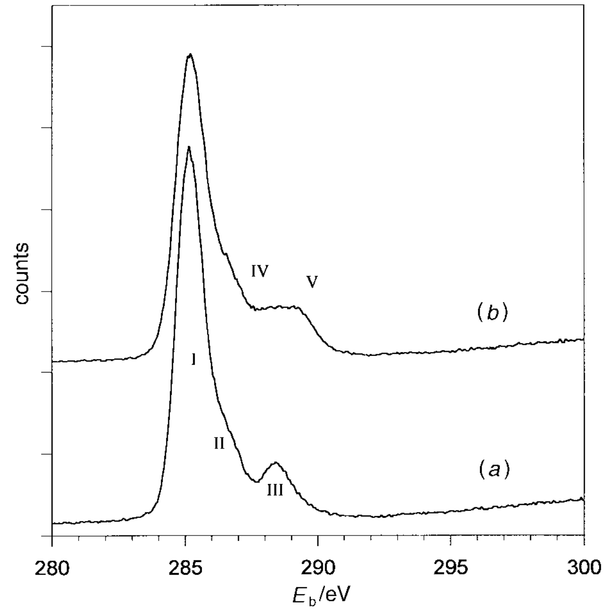

**Fig. 7** Carbon 1s peak envelopes from (*a*) native and (*b*) 9 min UV exposed surfaces

**Table 3** Peak assignments and binding energies for Fig. 7

| peak | $E_b$/eV | assignment |
|---|---|---|
| I | 285.5 | C—C/C—H |
| II | 287 | C—N |
| III | 288.5 | N—C=O |
| IV | 287.5 | N—C—O ? |
| V | 289.5 | COOH/COOR |

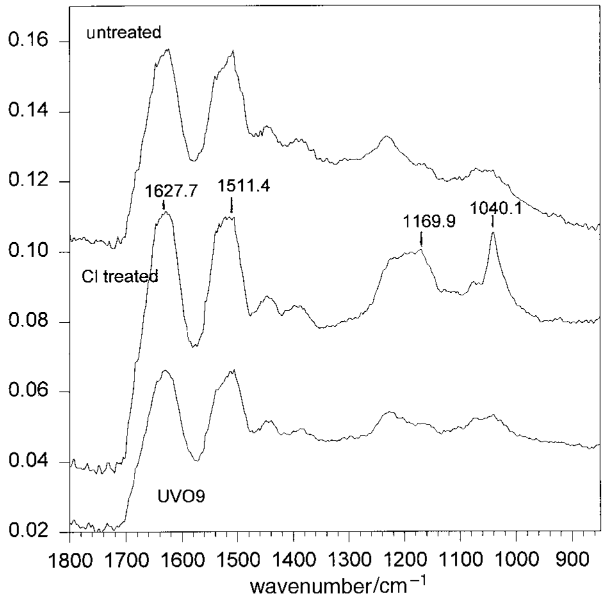

**Fig. 8** FTIR spectra from native (untreated), wet/Cl treated wool and 9 min UV exposed surfaces

approximate chemical shift of 1.5 eV, which is due to C—N, C—S and C—O— groups, and a partially resolved peak at a shift of 3.0 eV due to N=C=O groups of the cystine. The envelope is typical of those recorded in our own laboratory for native wool[2] and of those reported by other workers for such material.[12,13]

The envelope from the oxidised material contains additional structure in the form of an unresolved peak at a shift of 2.0 eV which may be due to N—C—O— groups, and a further partially resolved peak at a shift of 4.0 eV which is consistent with the formation of carboxylic acid or ester groups (COOH/COOR) as a consequence of oxidation. Peak asignments are given in Table 3.

Investigation of the surface chemistry of the wool, carried out using FTIR spectroscopy, results in the spectra shown in Fig. 8 in which data for untreated material and wool that has been either Kroy or UVO oxidised are compared. The strongest peaks in all these spectra occur at 1627 and 1511 cm$^{-1}$ and are attributable to secondary amide (—CONH). Absorbency in the range 1000–1450 cm$^{-1}$, which contains the sulfur–oxygen bands of sulfonic acid, is significantly less for the untreated wool than for the two oxidised materials. The spectrum from the Kroy treated sample contains very strong peaks at 1040 and 1170 cm$^{-1}$, due to S—O and $SO_2$ stretching respectively, which are of much lower intensity in the spectrum from the UV ozone sample and even lower intensity in the spectrum from the untreated material.

The magnitude of depth probed by FTIR experiment is of the order $10^{-6}$ m whereas the inelastic mean free path of photoelectrons in solids is $10^{-9}$ m giving a maximum depth probed by XPS of *ca.* 10 nm. The information given by the two techniques is therefore characteristic of significantly different levels of the sample surface in molecular terms and the surface reactivity of the materials might be expected to be more accurately reflected by the XPS experiment.

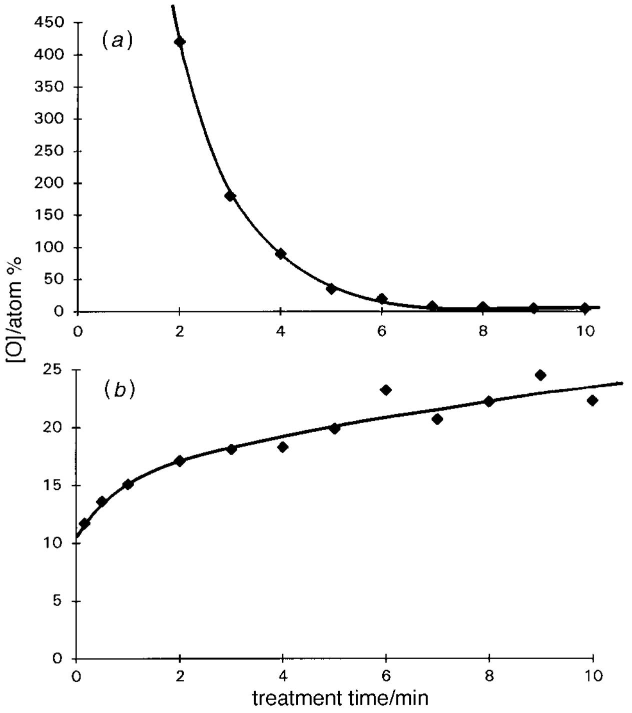

**Fig. 9** Relationship between wool aqueous wetting time ($T_w$) and UV exposure time ($T_t$) resulting in eqn. (1)

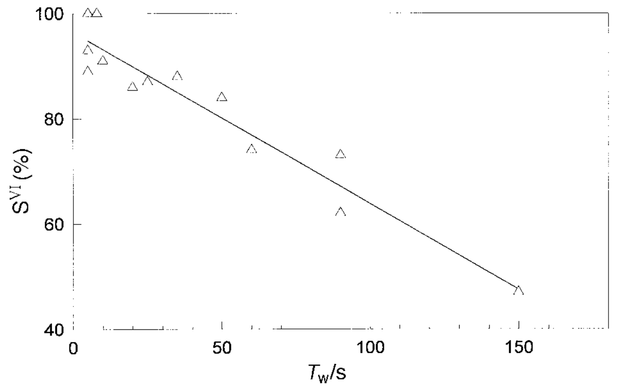

**Fig. 10** Relationship between ($T_w$) and disulfide oxidation (%) leading to eqn. (2)

The aqueous wetting behaviour of the UV ozone treated wool is shown in Fig. 9(*a*) to be an inverse function of treatment time related to the wool surface oxygen level as shown by Fig. 9(*b*). From Fig. 9(*a*) the time to wet ($T_w$) is given by the exponential term:

$$T_w/\text{s} = \exp(7.3 - 0.73T_t) \qquad (1)$$

The % oxidation of disulfide sulfur to the $S^{VI}$ state has a linear relationship with wetting time, as shown in Fig. 10, and in this instance $T_w$ is given by expression (2)

$$T_w/\text{s} = (100 - [S^{VI}])/0.33 \qquad (2)$$

where $[S^{VI}]$ is the % of total native disulfur oxidised.

Astrazone Blue dye, which reacts with sulfonic acid groups, has been used to probe the actual surface distribution of oxidised sulfur. This gives a less intense coloration with the UV ozone treated wool than with the Kroy treated material. We believe that this is due to a greater depth of oxidation obtained with the Kroy method. The UV ozone treatment, which is more surface specific, is therefore accurately characterised in terms of depth, by XPS data which would explain the agreement between the chemical data from that technique and the aqueous wetting data.

**Table 4** Absorbances at 680 nm for UVO, chlorinated, plasma and corona treated wool

| treatment colour ($\lambda_{max}$/nm) | absorbance at $\lambda_{max}$ |
|---|---|
| turquoise (680) | |
| Kroy | 25.64 |
| corona[a] | 24.45 |
| DUVO10[b] | 23.72 |
| plasma | 23.63 |
| DUVO5[c] | 22.58 |
| light turquoise (680) | |
| DUVO10 | 21.40 |
| Kroy | 21.02 |
| DUVO5 | 19.24 |
| plasma | 18.57 |
| corona | 18.33 |
| brown (400) | |
| DUVO10 | 7.54 |
| corona | 7.43 |
| plasma | 6.95 |
| DUVO5 | 6.86 |
| Kroy | 6.64 |
| beige (400) | |
| DUVO10 | 2.61 |
| corona | 2.35 |
| plasma | 2.36 |
| DUVO5 | 2.33 |
| DUVO1 | 2.30 |
| dark olive (640) | |
| corona | 20.99 |
| DUVO10 | 19.97 |
| plasma | 19.93 |
| Kroy | 19.55 |
| DUVO5 | 18.06 |
| mid olive | |
| DUVO10 | 5.87 |
| plasma | 5.79 |
| Kroy | 5.30 |
| DUVO5 | 5.01 |
| dark grey | |
| corona | 15.23 |
| DUVO10 | 14.70 |
| plasma | 14.50 |
| Kroy | 14.41 |
| DUVO5 | 12.66 |
| mid grey | |
| corona | 3.41 |
| DUVO10 | 3.36 |
| plasma | 3.16 |
| Kroy | 3.11 |
| DUVO5 | 3.11 |

[a] Corona conditions were 640 W $m^{-2}$ $min^{-1}$. [b] $[S^{VI}] = 70\%$ of total S, $[O] = 18.1$ atom%. [c] $[S^{VI}] = 50\%$ of total S, $[O] = 17.0$ atom%.

**Table 5** Berger whiteness and yellowness index E313 for treated challis

| treatment | Berger whiteness | yellowness index |
|---|---|---|
| DUVO1 | 28.0 | 21.4 |
| DUVO5 | 20.7 | 24.2 |
| DUVO10 | 16.2 | 26.0 |
| Kroy | 17.7 | 25.4 |
| plasma | 26.8 | 21.8 |
| corona | 33.8 | 19.3 |

The printability of UV ozone treated samples has been compared with that of Kroy chlorinated and corona treated materials using a set of standard print conditions. The results are given in Table 4. The print definition *i.e.*, the sharpness of the boundary between printed and unprinted fabric, was good and the colour intensity compared favourably with the plasma and Kroy treated surfaces. Since any discolouration (*e.g.* yellowing) of the wool fabric is likely to affect the final printed colour, Berger whiteness and yellowness figures have been measured and are given in Table 5. The degree of discolouration is seen to be comparable with, but no worse than, the wet method.

## Conclusions

XPS study of the wool fibre surfaces indicates that they are 75–80% carbon, 10–12% oxygen, 2–3% sulfur and 6–9% nitrogen. The N and S are due to cystinic protein. The C and O are in part proteinaceous but there is also a contribution from a surface lipid layer. This must be either very thin (< 10 nm) and/or incomplete for the proteinaceous N and S photoelectron lines to be detectable. The wool fibres themselves are hydrophobic.

All of the oxidative treatments appear to result in cleavage of cystine disulfide bonds to give oxidised sulfur species thought to be sulfonic acid groups. Some oxidation also occurs at cystine/lipid carbon sites.

The UV ozone treatment increases the surface oxygen levels of fibres and woven material by a factor of approximately two, the precise level being dependent upon exposure time. The water wetting time of woven material is an inverse function of treatment time and is shown to decrease linearly with oxidative cleavage of disulfide S to $S^{VI}$.

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