The X-ray diffraction patterns of natural and chemically modified wools of different varieties have been investigated. With chemical treatment, the degree of orientation decreases, whereas the average crystallite size increases. Scanning electron microscopic studies reveal that at the normal level of treatment there is little damage to the surface topography of wool fibres, but at higher levels of treatment the surface is badly damaged.

Oxidizing and reducing agents are used in a number of chemical finishes during the wet processing of wool. The conditions of treatment being very severe, the fibres are damaged, resulting in change in structure and increase in harshness. The importance of the scanning electron microscope (SEM) in wool research and processing was highlighted by Sikorski. Damage to wool fibres on treatment with different chemicals has been investigated. Hepworth et al. examined the topography of wool fibres after subjecting them to a large variety of chemical treatments commonly used in industrial finishing. Information about the internal (cortical) structure of the wool fibre was obtained by examining the cross-section of chemically modified fibres. Shrink-proofing treatment by pad chlorination modified the surface of the scales very slightly; there was no effect on the internal structure of the fibre. Electron micrographs of the peeled surface of the extended and supercontracted fibre were examined by Haly et al., Anderson and Hoskinson used SEM to study the damage to wool fibre by moth attack. Needles attempted to locate the polymer with the help of SEM after graft copolymerization of wool. X-ray diffraction studies on natural wool fibre revealed many structural features, but very few workers have investigated the structural changes in wool resulting from chemical treatment.

This paper reports the results of qualitative SEM studies on the modification of the fibre surface of Chokla, Rambouillet and crossbred wools through chemical treatment. The results of X-ray diffraction studies on these wools treated with thioglycollic acid are also given.

Materials and Methods
Chokla, Rambouillet, Rambouillet × Chokla (50%) white and Rambouillet × Chokla (50%) canary coloured wools were sorted out and heavy impurities like burr, dirt and dust were removed. These wools were then soxhlet extracted with diethyl ether and ethyl alcohol and finally washed with six changes of distilled water. The clean wools were dried at room temperature. The details of chemical modifications with thioglycollic acid, hydrogen peroxide and peracetic acid were reported earlier.

Scanning electron microscopy—Wool fibres were attached firmly by their ends with adhesive to a normal specimen holder (about 1 cm in diam), the minimum tension being applied to the fibre to prevent movement when it was subjected to the electron beam. All the samples were coated with a layer of silver (approx. 10 nm thick) in an Edward’s coating unit to eliminate the effect of static charges which lead to general loss of resolution and appearance of structure less bright patches. The specimens were then examined in SEM Cambridge stereoscan model S 4-10 with an accelerating potential of 5k V and tilt angle of 45° (with reference to the optical axis).

Wide angle X-ray diffraction pattern—Wide angle X-ray photographs of raw and thioglycollic acid-treated wools were taken using a Norelco Philips X-ray generator. The fibres in the bundle were kept as parallel and straight as possible and the specimen was built up to about 1 mm thickness. A sample to film distance of 4 cm was maintained and Cu Kα radiations were employed at a voltage of 35k V and a current of 20 mA. A fixed period of exposure (4 hr) was adopted for all the samples. The specimen size and film processing techniques were standardized. The intensity of the various peaks was determined by taking equatorial and azimuthal scans using Joyce Loebl microdensitometer fitted with a polar table.
Average crystallite size—The average crystallite size was calculated from the angular half-width of a particular reflection (20.4°) from the equatorial diffractograms using the following relation given by Scherrer:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where \( \lambda \) is the wavelength of X-ray, \( \beta \), angular diffraction width in terms of 2\( \theta \); and \( K \), shape factor, a constant whose value depends on the definitions of \( \beta \) and \( D \).

For a relative measurement of the crystallite size, \( K \) can be taken as unity. The instrumental line broadening was neglected, because it was minimized by the use of focusing techniques.

Degree of orientation—For determining the degree of orientation of the \( \alpha \)-crystallites, the azimuthal intensities of the reflection in the vicinity of \( 2(\theta) = 9^\circ \) were measured from the X-ray photographs. The degree of orientation was calculated using the equation:

\[ \pi = \frac{(180^\circ - H^\circ) \times 100}{180^\circ} \]

where \( H^\circ \) is the half-width value.

Results and Discussion

To study the modified surface features of the wool fibres, the terminology suggested by Dobb et al. has been adopted. The external surface of the wool fibre is accordingly considered to be divided into faces contained in some of the following boundaries: ‘clefts’.

Fig. 1—Scanning electron micrographs of the surface of natural wools (a) Chokla wool (x 810); (b) Rambouillet wool (x 1560); (c) Ramb. x Chokla (50%) white wool (x 900); and (d) Ramb. x Chokla (50%) canary coloured wool (x 780).
'escarpments' and 'ridges'. Clefts separate two faces (clearly two adjacent cells) at the same radial distance from the fibre axis. Escarpments may form boundaries between faces of the same cuticular cell at different radial distances from the fibre axis, or at the distal edges of cuticular cells. Ridges separate faces at the same or different radial distances from the fibre axis.

Fig. 1 (a-d) shows the electron micrographs of the untreated Chokla, Rambouillet, Ramb. x Chokla (50%) white and Ramb. x Chokla (50%) canary coloured wools. The escarpments are well defined and cleft lines are generally ill-defined. The only features of significance on the faces of the fibres are small asperities which are particularly pronounced in Chokla wool. In general, the details of the progress of chemical attack were revealed clearly by the scanning electron micrographs. The initial attack of a particular reagent leads to a slight smoothening of the fibre as the small asperities are removed. Under severe conditions, escarpments are lifted and the clefts become wider, because they represent regions in which penetration becomes progressively easier. The escarpment becomes badly damaged and in some cases of severe attack of the chemicals, the faces become etched and in certain cases the damage is manifested as deep cavities in the cuticle. From the electron micrographs of the chemically treated wools, it has been observed that Rambouillet wool is damaged to a greater extent compared to Chokla or Ramb. x Chokla (50%) wool.

At lower levels of treatment with thioglycolic acid (0.2 M), the attack on the fibres is extremely mild and the fibre surface gets smoothened. At higher levels of treatment (1.0 M TGA), the clefts are widened and the escarpments are lifted. Fig. 2 (a-c) shows the electron micrographs of TGA-treated Chokla, Rambouillet and Ramb. x Chokla (50%) canary coloured wools at higher concentration of TGA. It is seen that by the use of 0.2 M TGA at pH 4.5, there is practically no change in the fibre surface, but at higher concentration, the surface is damaged.

Treatment with hydrogen peroxide causes the distal edges of cuticular cells to lift and the clefts are widened markedly (Fig. 3 a-c). In some cases, the clefts are totally removed and the attack is severe at the escarpments. Even under normal commercial bleaching conditions, the disintegration of escarpments is quite severe and in some cases faces are also damaged in a similar manner, which leads to the removal of the imbricate nature of the cuticular surface.

Milder treatment with peracetic acid (1.0% at 25°C for 4 hr) causes a slight change in the fibre surface, but at higher concentrations (5% peracetic acid), the fibre surface is damaged badly (Fig. 4 a-d). The faces are deeply etched and in certain cases striated horizontally. Earlier studies by Hepworth et al.5 showed that with...
peracetic acid – hypochlorite, the faces are striated longitudinally.

Typical X-ray photographs of natural and TGA-treated wools are shown in Fig. 5 (a,b). Due to the highly amorphous nature of the fibre, clearly defined reflections are not obtained. However, two prominent reflections of the α keratin structure, viz. those at 9.8 Å equatorial and at 5.1 Å meridional spacing1 can be seen. On comparing the photographs of different varieties of wool it appears that there is a shift in the peak position at 5.1 Å in the meridional spacing in the case of Chokla and Ramb. × Chokla as compared to the Rambouillet wool. To study quantitatively the variation of peak intensity from a particular reflection, equatorial X-ray diffractograms were plotted. A typical X-ray diffractogram is shown in Fig. 6. The results of analysis of the equatorial scans are given in Table 1. There are two major intensity peaks at angles 9.8 Å and 20.4 Å. These are designated as reflections A and B respectively. The ratio of the peak heights at two reflections is calculated for each of the samples. This ratio increases after chemical treatment, indicating perhaps an increase in the degree of order. The degree of orientation and average crystallite size have also been calculated and are summarized in Table 1. The degree of orientation decreases after the chemical treatment, whereas the average crystallite size increases.

**Conclusion**

At normal levels of treatment, there is little damage to the surface topography of wool fibres, but at higher levels the surface is damaged badly. X-ray diffractograms reveal that the degree of orientation decreases after the chemical treatment, whereas the average crystallite size increases.

![Fig. 3—Scanning electron micrographs of the surface of wools treated with hydrogen peroxide (2 vol.) at 80°C for 3 hr (a) Chokla wool (× 720); (b) Rambouillet wool (× 1440); and (c) Ramb. × Chokla (50%) white wool (× 780)].
Fig. 4—Scanning electron micrographs of the surface of wools treated with 5% peracetic acid for 4 hr [(a) Chokla wool (x 780); (b) Rambouillet wool (x 750); (c) Ramb. x Chokla (50%) white wool (x 1560); and (d) Ramb. x Chokla (50%) canary coloured wool (x 780)].

Fig. 5—X-ray photograph of Ramb. x Chokla (50%) white wool [(a) Untreated, and (b) TGA-treated].
Table 1—Analysis of the Equatorial Diffraction Scans of the X-ray Photographs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intensity of peak heights (arbitrary units)</th>
<th>B/A</th>
<th>Degree of orientation ° D</th>
<th>Crystallite size D Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reflection A</td>
<td>Reflection B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chokla</td>
<td>100</td>
<td>39</td>
<td>0.39</td>
<td>74.8</td>
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<tr>
<td>Chokla treated with TGA (1.0 M) at 35°C for 20 hr</td>
<td>113</td>
<td>51</td>
<td>0.45</td>
<td>69.6</td>
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<td>Rambouillet</td>
<td>94</td>
<td>47</td>
<td>0.50</td>
<td>67.1</td>
</tr>
<tr>
<td>Ramb. treated with TGA (1.0 M) at 35°C for 20 hr</td>
<td>93</td>
<td>53</td>
<td>0.57</td>
<td>65.8</td>
</tr>
<tr>
<td>Ramb. x Chokla (white)</td>
<td>82</td>
<td>31</td>
<td>0.38</td>
<td>68.7</td>
</tr>
<tr>
<td>Ramb. x Chokla (white) treated with TGA (1.0 M) at 35°C for 20 hr</td>
<td>91</td>
<td>52.5</td>
<td>0.57</td>
<td>66.1</td>
</tr>
<tr>
<td>Ramb. x Chokla (canary coloured)</td>
<td>92</td>
<td>36</td>
<td>0.39</td>
<td>73.6</td>
</tr>
<tr>
<td>Ramb. x Chokla (canary coloured) treated with *TGA (1.0 M) at 35°C for 20 hr</td>
<td>115.5</td>
<td>52.5</td>
<td>0.53</td>
<td>73.2</td>
</tr>
</tbody>
</table>

Acknowledgement

The authors wish to thank Dr. R.M. Acharya, Director, CSWRI, Avikanagar, for permission to publish this paper and Prof. D.S. Varma, Textile Technology Department, IIT, New Delhi, for permission to utilize the SEM and X-ray facilities at IIT and for the encouragement provided by him throughout this work.

References