NOTES

Crystallite Orientation in Wool Fibers

The main features of the wide angle X-ray patterns in wool are[1]: meridional α-arc associated with group of reflections at about 0.51 nm ($2\theta = 17.8°$), the equatorial spot at 0.465 nm ($2\theta = 19°$) associated with β-form, and the equatorial spot at 0.98 nm ($2\theta = 9°$) common to both α- and β-forms. The various reflections observed in the X-ray patterns indicate good crystallite orientation in the direction of fiber axis.

Wools of different biological origin are known to show differences in their properties, which, in turn, are related to differences in the structure and morphology.[2-9] The birefringence values of three different wools, namely Merino, Chokla, and Lincoln, have been shown to correlate well with their morphology and various physical properties.[3,5] Birefringence in wool arises predominantly from its crystallites, and their orientation is therefore of considerable interest. However, there is hardly any reported study on the changes in crystallite orientation as related to such differences. In the present work, the X-ray diffraction technique was used to characterize crystallite orientation in these wool fibers stretched to different degrees.

EXPERIMENTAL

Types of Wool Samples. The studies were conducted on clean wool samples obtained from three different breeds of sheep, viz., Merino (64^s quality, Australian breed), Chokla (44^s quality, Indian breed), and Lincoln (40^s quality, U.K. breed). Besides the unstretched samples, which were designated as control samples, X-ray diffraction studies were also made on stretched samples.

Stretching of Samples. To stretch the fiber bundles, a stretch frame was fabricated. Bundles of parallel fibers were stretched manually while held in the stretch frame in water at room temperature. After stretching, the bundle was left in water in the stretched condition for about 12 h, after which it was left in the laboratory atmosphere (40% RH) for another 12 h before the X-ray test. To obtain maximum diffracted intensity, following Skertchly's observations,[10] all the bundles were prepared so that in the stretched condition they had an approximate linear density of 10 mg/cm. Such bundles, while held taut, were nearly 1 mm thick.

Flat Plate Patterns. A flat plate X-ray diffraction camera was used to obtain diffraction patterns of wool fiber bundles. The sample to film distance was 3.5 cm and the exposure time was 4 h.

X-ray Diffraction Studies. X-ray diffraction studies were made on a Phillips X-ray diffractometer equipped with a texture goniometer assembly. The texture goniometer was used for obtaining azimuthal intensity scan of equatorial reflections at 0.98 nm ($2\theta = 9°$) and 0.465 nm ($2\theta = 19°$), and meridional reflection at 0.51 nm ($2\theta = 17.8°$). Nickel-filtered CuK_α radiation generated at 45 kV and 35 mA was used. The incident beam was collimated through a line slit 1 mm wide and 2 mm long and the diffracted beam was received through a 1-mm-wide slit. The scans were obtained at a scan speed of 0.6° (2θ)/min. All the X-ray scans were obtained in a laboratory maintained at 40 ± 5% RH and 22 ± 2°C.

RESULTS AND DISCUSSION

Flat Plate X-Ray Patterns of Wool. To illustrate the crystallographic features of wool, flat plate X-ray patterns of the Lincoln wool, control and stretched (40% extension), are presented in Figure 1. The equatorial (0.98 nm) and meridional (0.51 nm) reflections are typical of α-kerain and the second equatorial reflection (0.465 nm) suggests that the transformation from α- to β-conformation has occurred on stretching.

Limitations on Interpretation of Azimuthal Patterns. An approximate measurement of the orientation of the crystallites is provided by the half width of an azimuthal intensity scan of a crystalline reflection obtained from a parallel fiber bundle. In wool there are two important problems that make it difficult to quantify crystal orientation in terms of half-width and these are:

(i) The prominent crystalline reflections do not originate from a single crystallographic family of planes.
(ii) The crystalline reflections from the α and β crystalline phases either show an overlap between themselves or between them and the prominent amorphous halo.

Due to the first limitation stated above, quantitative measurement of orientation in terms of the Hermans ori-

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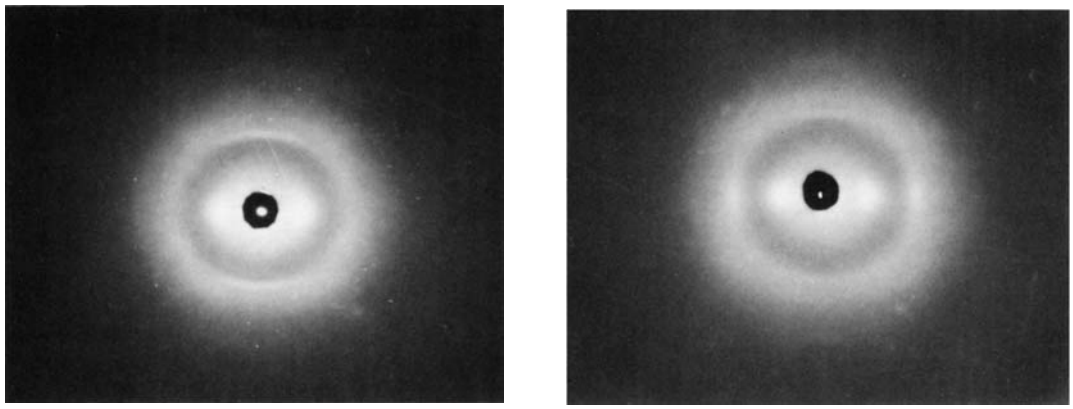

(a) (b)

Figure 1 Flat plate X-ray patterns for Lincoln wool: (a) control; (b) stretched to 40% extension.

entation factor from the meridional reflection is also not very meaningful. However, it is of obvious interest to attempt to measure crystallite orientation in the stretched wool samples, particularly as the crystallinity measurements do not give a clear indication of the changes that take place on stretching.[5] The birefringence data on these fibers[3] is also not very conclusive on the orientational changes that take place on stretching. This is so because, with phase transformation, the intrinsic birefringence changes and the changes in measured birefringence in stretched samples cannot give an insight into the orientational changes taking place in these samples.

Data on Orientation Function. The azimuthal scans of the reflections at 0.98 nm and 0.465 nm (both equatorial) and at 0.51 nm (meridional) were obtained for the three wool types stretched to different extensions in water at room temperature and held taut during the X-ray measurement. The crystallite orientation was calculated in terms of an arbitrary orientation function ϕ, defined as follows:

$$\phi = (180 - dw)/180$$

where dw is the half-width, i.e., at half the peak height (in degrees) of the azimuthal intensity scan. This orientation factor varies from 0 for an unoriented sample to 1 for a fully oriented sample.

The data for the control and the stretched wool fibers are shown in Table I. In the case of 0.465 nm reflection, the control sample and 20% stretched sample do not give measurable intensity at this position. Hence the orientation factor could only be obtained for higher extensions. Similarly in the case of 0.51 nm reflection, the data could only be obtained for the control sample and for samples stretched up to 30% extension. The azimuth of the 0.51 nm reflection shows only small improvement on stretching. Possibly, this may also indicate that the orientation of the microfibrils remains unaffected during stretching. However, the 0.51 nm reflection is not resolved and the limitation (i), as stated earlier, should be kept in mind. The crystallite orientation measured using the azimuthal scan of the 0.98 nm composite reflection was found to decrease with increase in stretch level. A similar observation was reported by Bendit.[11] Obviously, since the measurement of orientation from the 0.98 nm reflection

Table I Orientation Function of the Crystalline Reflections in Stretched Wool Samples

Extn (%)	0.98 nm			0.465 nm			0.51 nm		
	L	C	M	L	C	M	L	C	M
0	0.82	0.81	0.77	[a]	[a]	[a]	0.67	0.66	0.66
20	0.81	0.79	0.74	[a]	[a]	[a]	0.69	0.67	0.68
30	0.80	0.74	0.74	0.81	0.82	0.67	0.70	0.70	0.67
40	0.79	0.76	0.71	0.84	0.83	0.71	[a]	[a]	[a]
65	0.77	0.76	0.70	0.86	0.85	0.75	[a]	[a]	[a]

[a] Insufficient intensity to resolve from the background.

suffers from both the limitations stated above, it cannot be expected to give an accurate measurement of crystallite orientation. The 0.465 nm reflection is free from these limitations and hence represents true changes in the orientation; the data on this reflection suggest that the crystallite orientation improves with stretching.

The crystallite orientation factor determined from azimuthal scans comes out to be around 0.8. However, this could be an underestimate in view of the multiple nature of the reflection.

It is generally believed[12-14] that in wool fiber the microfibrils show very high orientation in the direction of the fiber axis. This is easily seen in electron micrographs. Since the α-helices are within the microfibrillar cylinders, the crystallite orientation of wool would be expected to be very high and would in fact relate to the orientation distribution of the cylindrical microfibrils. On this model, the crystallite orientation of wool fiber would be higher than that reflected by the azimuthal intensity measurements, as reported here. This may be due to the intrinsic nature of the X-ray diffraction patterns of wool, which are highly complex and unlike other fibers, discrete reflections originate from more than one set of planes.

When Lincoln fibers stretched to 30% extension were allowed to relax in free condition, the orientation function calculated for the 0.465 nm reflection decreased from 0.81 to 0.79. This perhaps arises from the greater freedom of mobility due to larger free volume generated in the transformed region.[15] Besides, under the present experimental conditions the set is low and in the absence of stable crosslinks the extended configuration collapses when the fiber is allowed to relax in the free condition. However, detailed studies on the effect of relaxation of stretched and stretch-set fibers were not made.

Differences in the Three Wools Studied. In spite of the approximate nature of the orientation factor and in view of the limitations of this method as applied to wool, relative comparison of the orientation of the crystallites in the three wool types may still be valid. As shown in Table I, a significant observation can be made, viz., that Merino fiber has relatively lower crystallite orientation compared to the other two fibers. It is interesting to recall that Merino fiber had also the lowest crystalline content[5] and also shows low molecular orientation measured from birefringence,[3] which primarily originates from the crystalline phase. Wool fiber may be visualised as a simple two phase composite containing 7.5-nm-diameter microfibrils which are composed of well-aligned α-helices embedded in an essentially isotropic matrix, believed to be present in the form of small globules consisting of bulky side chains, which apparently have no global orientation.

These differences could arise from the structural and morphological differences among the three wools. Merino fibers show bilateral structure, i.e., ortho and para type cells in near 2:1 proportion whereas the other two wools are predominantly para type.[5] Since ortho cells are known to show relatively poor microfibrillar packing[16] and a higher proportion of bulky side groups,[8] ortho-rich Merino fibers will be expected to show low molecular orientation compared to the other two wools, as is found to be the case (Table I). Further, this agrees with the other structure–property relationships observed for these three wools.[3-6]

CONCLUSIONS

In the wide angle pattern, authentic data on orientation can be obtained from the azimuthal intensity of 0.465 nm equatorial reflection only as the other reflections are composite and difficult to resolve. It was found that the orientation of the crystalline phase increases on stretching and its magnitude depends on relaxation conditions.

Among the three wools studied, Merino fibers show the lowest crystallite orientation as compared to that of Lincoln and Chokla wools, and this agrees with the other structure–property relationships observed for these three wools.

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