Radiation-Induced Graft Copolymerization of Methyl Methacrylate on Natural and Modified Wool. V. Crystalline and Morphological Structure

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Synopsis

X-ray diffraction patterns of the α- and β-crystalline phases of natural, chemically modified, and MMA-grafted wool fibers were investigated. In the grafted fibers variation of the equatorial and meridional scattering intensity during the α–β transformation was inhibited. This indicated that the grafting had stabilized the structure to the α–β transformation. The average crystallite size was found to increase with the extent of grafting, and the degree of orientation appeared to decrease with percent graft-on. SEM studies revealed little damage to the surface topography of wool fibers after chemical treatments. Graft copolymerization with MMA made the fiber surface regular and smooth, mainly because of deposition of polymer in the escarpment, thus reducing the sharpness of the scaly structure. Scanning electron micrographs of the peeled-off surface and cross sections of the grafted fibers indicated that a significant amount of polymer was deposited in the medullae of the fibers.

INTRODUCTION

Scanning electron microscopy has been used to study the surface topography and internal structure of natural wool.[1] Damage to wool fibers after treatment with different chemicals has been investigated by several workers.[1-5] Information about the internal (cortical) structure of the wool fiber has been reported[6,7] by examining the cross section of fibers and peeled surface of the extended and supercontracted fibers.[8] Anderson and Hoskinson[9] have used SEM to study the damage to wool fiber by attack of moth.

Needles[10] has studied the electron micrographs of wool grafted with poly(methyl methacrylate) and poly(*n*-butyl methacrylate). A uniform distribution of the polymer was observed throughout the fiber cross section by several authors[11-16] using light microscopy and transmission electron microscopy. The location of grafted polymer and change in intensity of the prominent equatorial and meridional reflections in the x-ray diffraction pattern of wool fiber grafted with polystyrene,[17] methyl methacrylate,[18,19] and ethyl, methyl, and *n*-butyl acrylate[20] has been reported.

Only little information is available regarding the structural changes taking place in chemical treatments or grafting of highly medullated wool fibers. This paper deals with the SEM and x-ray diffraction studies of Indian Malpura wool which is highly medullated. The aim of the present work was to locate the grafted polymer within the medullae of wool fiber, which has not been explored so far. Topological changes and α–β transformations taking place due to chemical treatment and grafting have been reported also. The method of

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grafting and the properties of the grafted fibers have been reported earlier.[21,22]

EXPERIMENTAL

Preparation of Grafted Sample

Indian Malpura wool fibers were chemically modified (i.e., oxidized, reduced, methylated, and crosslinked) by using hydrogen peroxide, sodium bisulfite, dimethyl sulfate, and formaldehyde. The graft copolymerization of natural and chemically modified wool with methyl methacrylate was carried out by mutual irradiation technique using ^{60}Co as source of the γ-radiation. The details of the chemical modification and grafting conditions used were reported in an earlier publication.[21] The graft-on was calculated as the percentage increase in weight over the original weight of the sample.

X-Ray Diffraction Photographs

Wide-angle x-ray diffraction photographs of natural, chemically modified, and grafted wool fibers were taken using a Norelco Philips x-ray generator with a flat plate camera. The specimen holder consisted of a pair of clamps which were capable of moving apart by a screw to stretch the fiber. The fibers in the bundle were kept as parallel and as straight as possible, and the specimen was built up to 1 mm in thickness. The x-ray diffraction photographs of the stretched fibers were also taken by extending the fibers to 15, 30, and 45%, respectively. The fiber bundle was stretched in water at 60°C and dried at room temperature. A sample to film distance of 4 cm was maintained. CuK_α radiation was employed at a voltage of 35 kV and a current of 20 mA. A fixed time of exposure of 5 hr was given in all the experiments. The specimen size and film processing techniques were standardized. The intensity of the various peaks was determined by taking equatorial, meridional, and azimuthal scans using a Joyce Loebl microdensitometer fitted with a polar table.

Average Crystallite Size

The average crystallite size in all the samples was calculated from the angular half-width of a particular reflection (at 20.4°) from the equatorial diffractograms using the relation given by Scherrer[23]:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where λ = wavelength of x-rays; β = angular diffraction width in terms of Bragg's angle 2θ; and K = shape factor, a constant whose exact value depends on the definition of β and D. For a relative measurement of the crystallite size, K can be taken as unity.

Degree of Orientation

For determining the degree of orientation of the α-crystallites, the azimuthal intensities in the vicinity of $2\theta = 9°$ were measured from the x-ray photographs. The degree of orientation π was calculated by eq. (2):

$$\pi = \frac{(180° - H)}{180°} \times 100 \tag{2}$$

where H is the half-width value.

SEM of Fibers

Surface Topography

Natural, chemically modified and grafted wool fibers were attached firmly by their ends with adhesive to a normal specimen holder (about 1 cm in diameter), a minimum amount of tension being applied to the fiber to prevent movement when it was subjected to the electron beam.

Internal Structure

Peeling of Fibers. The fiber was mounted on the specimen holder as mentioned earlier. With the aid of a stereo light microscope, a cut was made on the fiber surface, using a fresh razor blade, so that one edge of the cut could be held with a pair of tweezers and peeled along the longitudinal axis of the fiber.

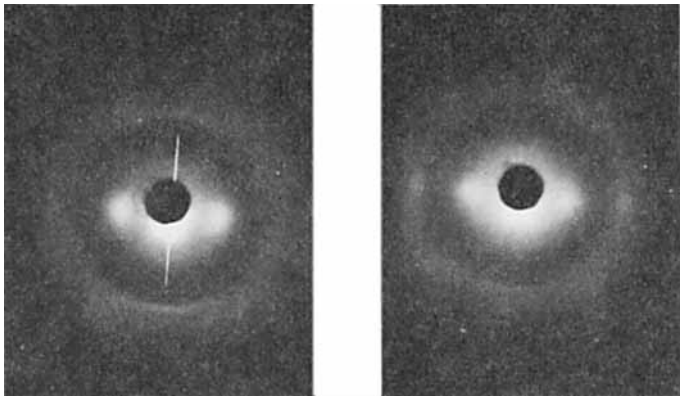
Cross Section of Fibers. The fiber bundles were embedded in epoxy resins. After the epoxy resin solidified, thick sections were cut by using a Huxley ultramicrotome fitted with a glass knife.

All the samples prepared by the above methods were coated with a layer of silver approximately 10 mm thick in an Edward coating unit to eliminate the effect of static charges. The specimens were then examined in SEM Cambridge Stereoscan model S4-10 with an accelerating potential of 5 kV and tilt angle of 45° (with reference to the optical axis).

RESULTS AND DISCUSSION

Two prominent reflections of α-keratin, viz., those at 9.8 Å equatorial and 5.1 Å meridional spacing, can be seen in natural wool fibers without any extensions. Reflection at 4.65 Å due to β-keratin can also be observed in the extended fibers. Further, the α-peak height at 9.8 Å decreased with increase in extension, and the β-reflection at 4.65 Å increased simultaneously. These observations for natural wool are in agreement with those already reported by Bendit[24] and Skretchly.[25]

Typical x-ray photographs of crosslinked and graft copolymerized crosslinked wool at various extensions are shown in Figures 1(a) and 1(b) and 2(a) and 2(b). On comparison of the x-ray diffraction pattern of the various grafted wool samples with that of natural and chemically modified wool, it was seen that the reflection due to α-keratin was retained in the grafted fibers. However, in grafted reduced and grafted methylated wool, a strong diffraction halo from the amorphous polymer appeared in the vicinity of $2\theta = 14°$.

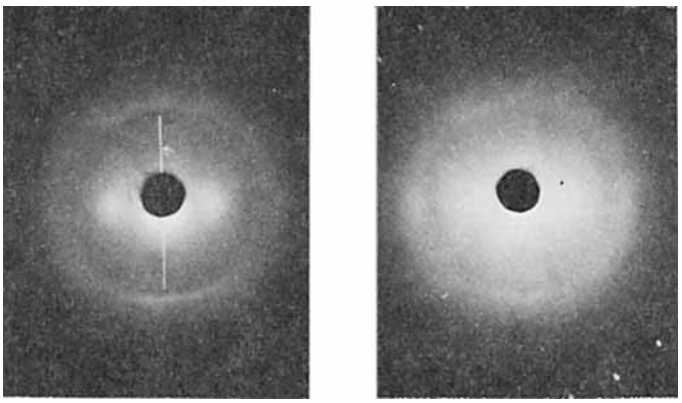


(a) (b)

Fig. 1. X-ray photographs of crosslinked wool at (a) 0% extension, (b) 45% extension.

Typical results for the equatorial scattering intensity of the natural and 63.3% grafted natural wool fibers at different extensions are shown in Figure 3. The results of analysis of the equatorial scans are given in Table I. Two intensity peaks in the vicinity of $2\theta = 9$ and 20° are designated as A and B, respectively. Comparing the diffractograms of grafted wool with that of natural and chemically modified wool, it was found that the height of the first diffraction peak was decreased as a result of high graft-on of MMA onto the fibers. Over the level of about 70% grafting, a considerable decrease in the α-peak height at 0% extension was observed by Arai et al.[19] The ratio of the peak heights at two reflections was calculated for all the samples at various extensions, and the results are tabulated in Table I. There was only a slight decrease in this ratio in the grafted samples.

Further, a gradual increase in the peak height ratio with an increase in the percentage extension of the fiber was observed. In grafted fibers variation of the peak intensity during the α–β transformation was inhibited as compared to the ungrafted fibers. A slight change in the peak postion of reflection was observed with extension which shifted to lower 2θ.



(a) (b)

Fig. 2. X-ray photographs of 58.1% MMA grafted crosslinked wool at (a) 0% extension, (b) 45% extension.

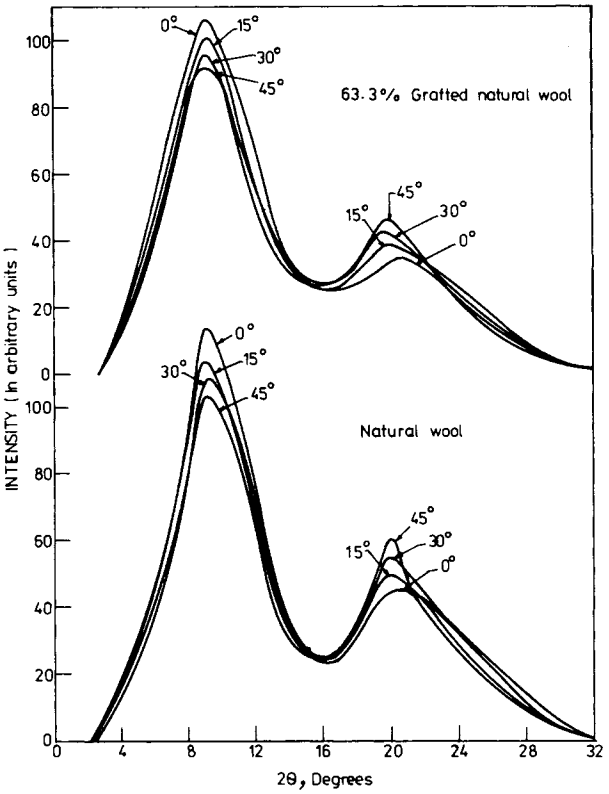


Fig. 3. Variation in equatorial scattering intensity in natural and grafted wool at various extensions.

The values of the average crystallite size calculated from the angular half-width and the degree of orientation are given in Table II. The average crystallite size was found to increase with the extent of grafting and degree of orientation appeared to decrease with percent graft-on.

Figure 4 shows the typical curves of the meridional scattering intensities of natural and 63.3% grafted natural wool at various extensions. Intensity variations for the 5.1 Å α-reflections were in agreement with the change in intensity for the equatorial α-reflection at 9.8 Å for all the samples. The sharp maxima of 5.1 Å reflection peak for natural, modified, and grafted fibers tended to disappear with increase in extension, and the peak position shifted to a higher 2θ angles. The variation in the peak intensity during the α–β transformation was decreased in the grafted fibers.

The inhibition in the transformation of the α-form to β-form in the grafted fibers may be due to the localization of the polymer within a region between the aggregates such as a microfibril and a matrix, and this leads to a marked stabilization of the α-crystallites in extension. With the help of the transmission electron microscope it was observed by Arai and Negishi[15] that some polymer occurs within the aggregated matrix in the partially reduced wool fibers. Decrease in the peak heights in the equatorial scan with the extent of grafting may be due to the disruption of the component of the α-helix by a rigid polymer like PMMA. Similar suggestions were given by Arai et al.[19] in their x-ray diffraction

TABLE 1
Analysis of Equatorial Diffraction Scans

Sample	% Extension	Intensity of peak heights, (arbitrary units) Reflection A	Reflection B	B/A
Natural wool	0	122	44	0.36
	15	112	48	0.43
	30	107	53	0.50
	45	101	59	0.58
MMA (63.3%)–*g*–natural wool	0	106	35	0.33
	15	101	39	0.39
	30	96	42	0.44
	45	91	46	0.51
Oxidized Wool	0	116	29	0.25
	15	111	33	0.30
	30	104	39	0.37
	45	97	48	0.50
MMA(87.1%)–*g*–oxidized wool	0	108	31	0.28
	15	105	32	0.30
	30	101	35	0.35
	45	97	38	0.39
Reduced wool	0	123	32	0.26
	15	119	35	0.29
	30	114	39	0.35
	45	101	41	0.41
Methylated wool	0	119	35	0.29
	15	116	36	0.31
	30	110	40	0.36
	45	103	43	0.43
Crosslinked wool	0	112	41	0.37
	15	105	44	0.42
	30	101	54	0.53
	45	97	58	0.59
MMA(53.1%)–*g*–crosslinked wool	0	100	41	0.41
	15	98	43	0.44
	30	93	47	0.50
	45	86	50	0.58

studies on MMA–*g*–wool with different chemical initiators. The grafted polymer chains have been suggested to be linked to the low sulfur proteins, and the growing polymer ends might be diffused in part into the α-phase, thus disrupting the α-material. When the polymer is deposited in the region which is chemically or physically laterally crosslinked, stress might be produced locally by the lateral swelling resulting from the deposition of the polymer. This stress might be transferred to the fibril through the crosslinks and open up the α-helix. The rigid polymer phase would restrict rotation of the polypeptide segments which had been deformed by the graft copolymer. As a result, it is most likely that these chains would be prevented from forming the β chain crystal during stretching.

To study the modified surface features of the wool fibers, the terminology

TABLE II
Degree of Orientation and Average Crystallite Size of the Various Grafted Fibers

Sample	% Graft-on	Crystallite size D, Å	π, %
Natural wool	0	9.85	79.1
	17.6	10.40	76.0
	63.3	11.44	73.2
Oxidized wool	0	10.10	78.3
	35.8	10.90	75.6
	87.1	10.60	76.3
Reduced wool	0	10.38	77.9
	47.5	11.50	74.0
Methylated wool	0	9.75	79.5
	74.3	12.41	75.5
Crosslinked wool	0	9.76	79.1
	21.9	10.20	75.2
	53.1	10.84	74.7

suggested by other workers[26] was adopted. The surface characteristics of the natural and chemically modified wool fibers as revealed by electron micrographs showed that the escarpments were prominent and well defined. There were

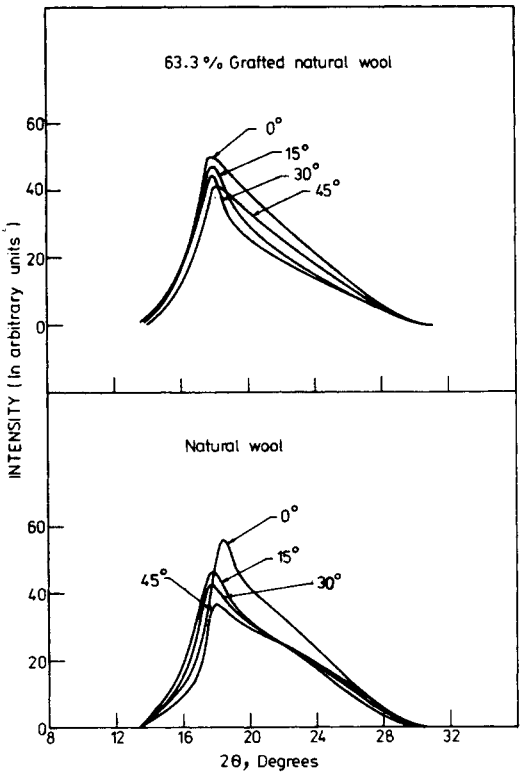


Fig. 4. Variation in meridional scattering intensity in natural and grafted wool at various extensions.

small asperities on the faces of the fiber which were particularly pronounced at the escarpments. There was no significant change in the fiber surface after the chemical treatment under prescribed conditions. Attack of the reagent leads to a slight smoothening of the fiber as the small asperities are removed. It has been reported earlier[5] that treatment with hydrogen peroxide in severe conditions causes the distal edges of cuticular cells to lift, and in some cases the clefts are totally removed. The escarpments are also severely attacked. Even in our studies, though the conditions used for oxidizing were not so severe, the sharpness of the edges of the cuticular cells were decreased to some extent showing thereby an attack on the escarpments. In case of attack with sodium bisulfite and formaldehyde, the distal edges of the cuticular cells were lifted slightly. The fiber surface became smooth after the formaldehyde treatment. There was not much difference in the fiber surface after the treatment with dimethyl sulfate except that the asperities were removed. A typical scanning electron micrograph of 35.8% grafted oxidized wool is shown in Figure 5. As is evident from the micrographs, there is a general loss of the scale structure of the wool fibers as compared to the ungrafted fibers. Further, the deposition of the polymer in the escarpments was observed. One of the common features in all the grafted samples was the decrease in the sharpness of the scaly structure. This effect was most obvious in the grafted oxidized wool. A thin coating of the polymer took place all over the fiber surface which could not be removed by prolonged Soxhlet extraction. The high molecular weight homopolymer may be occluded within the highly crosslinked keratinous materials covered with an epicuticle which is semipermeable in nature.

The longitudinal structure of the core of the fiber was studied by peeling. Figure 6 shows the peeled surface of the oxidized wool. From the electron mi-

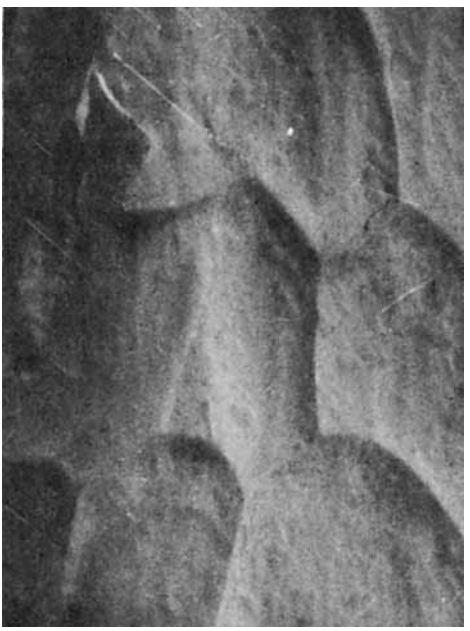


Fig. 5. Scanning electron micrograph of the surface of 35.8% MMA-grafted oxidized wool (1030 ×).

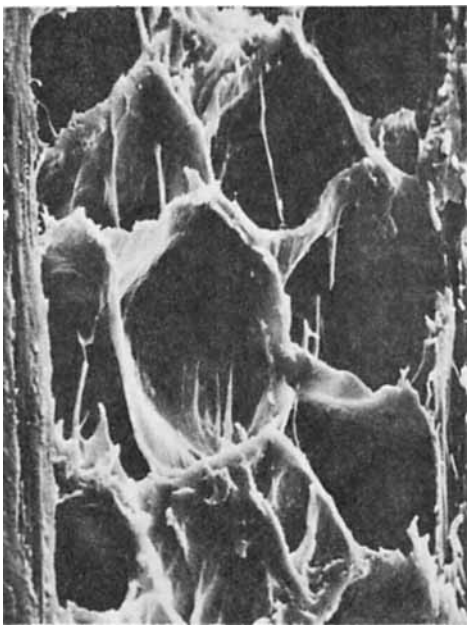


Fig. 6. Scanning electron micrograph of the peeled surface of oxidized wool (820 ×).

crograph of the natural wool, the cortical cells were quite clearly visible. Medullae were observed in all the other chemically treated fibers. The shape and the size of the medullae were the same in oxidized, reduced, and methylated wool but were different in crosslinked wool. It is well known that different types of medullae are found in medium and coarser qualities of wool, and wool from the same breed may have two different types of medullae. There was no visible difference in the medullae or the cortical cell of the chemically treated wool.

The SEM of the peeled-off surface of the graft copolymerized methylated wool is shown in Figure 7. After grafting the fibers were observed to be considerably swollen and the percentage of medullated fibers was quite high; hence it was thought that a good amount of polymer might have penetrated into the medullae and deposited on the collapsed cells which are polyhedral in shape in the original fibers. Figure 7 indicates no regularly shaped polyhedral cells. These cells are disrupted, indicating the penetration of the polymer to the medullae, though the exact location of the grafts could not be confirmed from these micrographs.

The cross sections of the fibers were also studied to locate the grafts in the cortex or the medullae. Figure 8 shows the cross section of the natural wool fiber. It was observed that the polyhedral shapes of the collapsed cells in the medullae of the natural wool were quite clear and shapely. But the cross sections of the grafted natural wool and grafted oxidized wool (Fig. 9) show the disruption of these cells, and small deposits on the collapsed cells could be observed in both cases.

It is believed that the grafted copolymer resides in the keratinous matrix between the microfibrils within the cortical cells. Preferential grafting in the ortho-cortex has been observed. Macrofibrils are closely packed in the para-cortex, whereas in the ortho-cortex a sufficient amount of matrix exists between

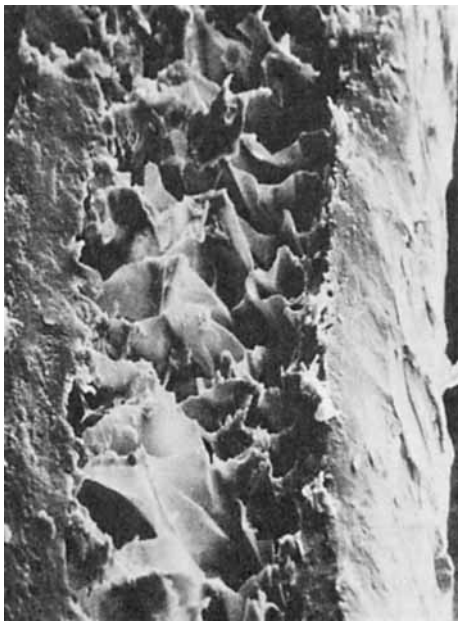


Fig. 7. Scanning electron micrograph of the peeled surface of 129% MMA-grafted methylated wool (300 ×).

the macrofibrils. Also, the para-cortex is more keratinized than the ortho-cortex. Hence the diffusion of monomer into the noncrystalline α-helices constituting the macrofibrils. This may be one of the plausible reasons of the preferential grafting in the ortho-cortex. Medullae in coarse wool consist of a number of polyhedral collapsed cells with air spaces between. Monomer can diffuse into

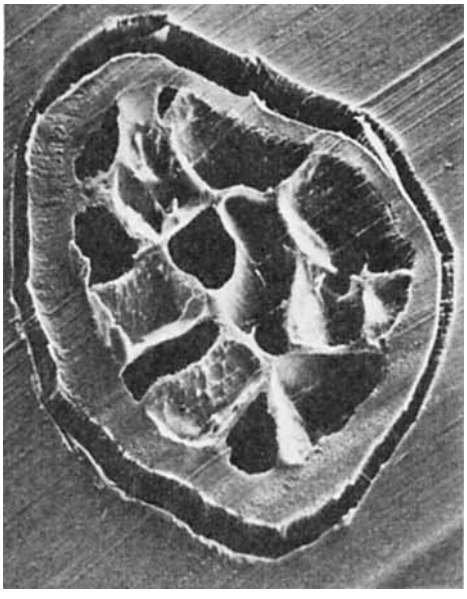


Fig. 8. Scanning electron micrograph of cross section of natural wool (350 ×).

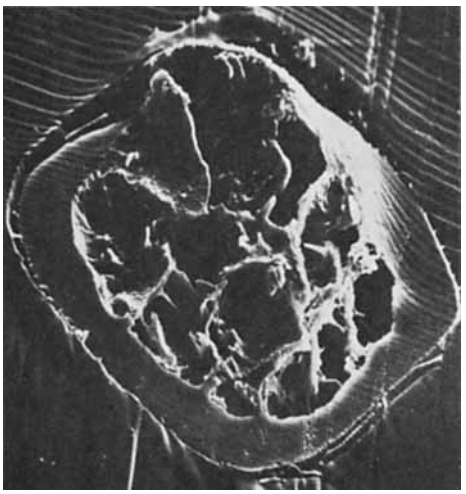


Fig. 9. Scanning electron micrograph of cross section of 63.3% MMA-grafted natural wool (540 ×).

this region (which is again noncrystalline) and may polymerize. Whether this polymer will be grafted or not is difficult to say, but once formed inside the medullae it will be difficult to extract it.

The SEM photographs of peeled surface (Fig. 7) and fiber cross section (Fig. 9) clearly show a distortion in the polyhedral cells of the medullae. The presence of deposited polymer in the medullae will not affect the x-ray diffraction pattern of the grafted fibers. It has been reported that more than 50% grafting of MMA onto wool by chemical methods reduces the α-component in the grafted fibers by about 50–60% of the native fiber, indicating that an appreciable amount of α-helical aggregates has been deformed or disrupted by deposition of polymer. A reduction in the intensity of the 9.8 Å reflection was observed in the present work. However, the decrease in intensity was less than 20% in 63.3% MMA–*g*–wool. This evidence along with the SEM results indicates that a significant amount of polymer has been deposited in the medulla of the fiber.

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