Structural Characteristics of Wool Fiber Modified with Itaconic Anhydride

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SYNOPSIS

The physicochemical properties of wool fibers chemically modified with itaconic anhydride in dimethylformamide were analyzed by DSC, TMA, and TGA and on the basis of measurements of the tensile characteristics. The acyl content in wool fiber increased even at the comparatively low reaction temperature ($65°C$) compared with that in silk fiber; this fact was due to the larger number of reactive sites in the wool than in silk such as basic amino acid residues. On the basis of DSC, TMA, and TGA analyses, the high thermostability of the modified wool fiber was evident. The molecular orientation, evaluated from the birefringence measurement, decreased slightly after the modification; however, tensile properties and surface characteristics of the wool fiber were not damaged. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The most striking characteristics of wool fibers are the excellent elasticity, moisture absorption, and dyeability due to their special primary chemical structure. In addition, they have good bulkiness attributed to the morphological structure, whereas wool fibers show some problems during the drying process of the wet fiber. In fact, the length of the fibers has bent to a contraction due to a low stability of the structure in the direction of fibrous axis. Therefore, chemical modification of the wool, useful tools to improve the setting,[1] microbiological resistance,[2] and physicomechanical stability, would be very important for a more wide utilization of the fiber. If the chemical modifications do not damage the original tensile and hydrophilic characteristics, they would give new properties to the wool fiber (e.g., washing and wearing properties) and improve its thermal stability.

Considerable interest has developed in the structural and morphological modification of wool fiber using reactive chemicals such as dibasic acid anhydrides[3] and epoxides.[4] Recently, we[3] also demonstrated that the mechanical properties of wool fiber were not changed even after the modification with dibasic acid anhydrides. In addition, our recent paper[3] shows that the succinylation onto the silk makes it easier to form free carboxyl groups while the ester cross-links are easily formed much more by the glutarylation than by the succinylation.

An interesting approach to the improvement of mechanical and morphological properties of natural fibers is the use of reactive epoxides and dibasic acid anhydrides. Bifunctional epoxides are generally more reactive than are monofunctional epoxides[4] toward animal protein fiber such as wool and silk fibroin. If the agents have unsaturated groups, the treatment would be more effective toward the improvement of structure and properties. The aim of the present work is to modify wool fiber with itaconic anhydride, a reagent with a vinyl group in its molecules; this is a new approach in the chemical modification of wool.

In this article, we describe the physicochemical properties of wool fiber after the chemical modification with itaconic anhydride.

EXPERIMENTAL

Materials

Wool fiber (2/48s) was cleaned by an acetone/ethanol mixture system in a Soxhlet extractor for 12 h, then rinsed in distilled water, dried to constant weight, and conditioned in air at room temperature.

Samples of known weight (about 1 g) were dried at 105°C for 2 h before treatment. Treatment in dimethylformamide (DMF) containing 10% itaconic anhydride was carried out at 65°C for different periods of time. Reagent-grade itaconic anhydride (MW = 112.08) (1), purchased from Wako Pure Chemical Industries, Ltd., was used without further purification:

$$CH_2=C \begin{matrix} CH_2-C \overset{O}{\underset{O}{\diagup}} \\ C \overset{O}{\underset{O}{\diagdown}} \end{matrix}$$

(1)
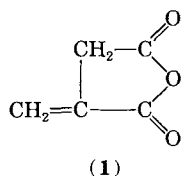
Samples treated in DMF without itaconic anhydride were also prepared. The control and modified samples were washed three times with DMF, three times with methanol, and five times with deionized water, then dried under the standard condition of 65% RH and 20°C and reweighted. Untreated sample before acetone/ethanol extraction was also used.

Measurements

The differential scanning calorimetry (DSC) measurement was carried out as described in a previous paper.[5] The thermomechanical analysis (TMA) was obtained on a Rigaku Denki instrument at a heating rate of 10°C/min. TMA full scale and initial force applied to the wool fiber were ±500 μm and 1 g, respectively.

Thermogravimetric analyses (TGA) were run under nitrogen on a Rigaku Denki thermogravimetric thermoflex system, raised at 10°C/min to 390°C. Sample weight and TGA full scale was 6 and 5 mg, respectively. All the measurements were repeated for reproducibility.

The surface of the treated samples was examined under a JEOL JAX-333S scanning electron microscope after gold coating.

The refractive indices parallel to the fiber axis, $n_{\parallel}$, and that perpendicular to the fiber axis, $n_{\perp}$, were measured with Becke's line (Na light) at 20°C and 65% RH according to the method reported in a previous paper.[6]

The fibers were tested on an Instron tensile tester (Toyo Baldwin Co., UTM-II). In all tests, the fibers were extended at a constant rate of 10%/min. Temperature and humidity were maintained at 20°C and 65% RH, respectively. Each value is the average of 25 test results.

The moisture regain was determined by measuring the weight of samples kept at 20°C and 65% RH for 7 days and the weight of the dried sample at 105°C for 2 h, then was expressed as g moisture/100 g wool fiber.

RESULTS AND DISCUSSION

Reactivity of Itaconic Anhydride

Table I summarizes the effect of the reaction time on the weight gains and acyl contents by treating with itaconic anhydride at 65°C in DMF. By increasing the reaction time, the values of weight gain and acyl content increased in the very beginning of the reaction, whereas their values increased very slowly after 3 h. It was clearly shown that the amount of acyl group, introduced onto wool fiber during the reaction with itaconic anhydride at 65°C, was much higher than that onto silk fiber treated in DMA at 75°C.[5] These results suggest that the itaconic anhydrides can react easily with the reactive sites of the amino acid residues of the wool fiber compared with those of silk fiber.

It is of particular interest to note that the acylation of wool fiber with itaconic anhydride proceeded at a comparatively low temperature compared with the silk fiber. It should be due to the large number of reactive sities of wool fiber toward itaconic anhydride, i.e., basic amino acid residues such as Lys, Arg, and Hist. In fact, our recent study showed that

Table I Weight Gain Acyl Content of the Wool Fiber Treated in DMF Solution Containing 10% (w/v) Itaconic Anhydride at 65°C as the Function of the Reaction Time, with the Material-to-Liquor Ratio of 1:20 Maintained

Reaction Time (h)	Weight Gain (%)	Acyl Content (mol/10^5 g)
1	9.9	76.7
2	14.0	108.5
4	17.4	134.9

the amount of these reactive amino acid residues in wool fiber and in silk fiber (unpublished data) is 111 and 13 mol %, respectively.

To evaluate the reactivity of wool fiber toward itaconic anhydride, we determined the amino acid composition of the modified wool fibers with different values of weight gain (Table II). The amount of basic and oxy amino acid residues, which are the reactive sities in the wool fiber, remained almost unchanged even after the chemical modification, suggesting that the ester bond once formed was broken during acid hydrolysis. The reactive mechanism of itaconic anhydride toward wool fibers presents a similality to that of dibasic acid anhydride such as succinic and glutaric anhydride,[3,5] as is obvious from Table II. It is therefore confidently expected that the cationic dye uptake for the treated wool fiber increases significantly, whereas the anionic dye uptake decreases considerably because of the repulsion between the anionic dye and the acidic carboxyl groups that were introduced in the wool fiber by the chemical modification.

DSC Thermograms

The DSC curves for the wool fibers modified are shown in Figure 1. Control sample (a) showed a

Table II   Amino Acid Composition (Mol %) of Wool Fibers that Are Chemically Modified with Itaconic Anhydride with Different Amounts of Weight Gain

	Control	Wool[a]	Wool[b]
Asp	6.42	6.46	6.45
Thr	6.46	6.42	6.41
Ser	11.16	10.87	10.87
Glu	12.21	12.33	12.33
Gly	9.37	9.31	9.38
Ala	5.75	5.81	5.88
Val	6.23	6.44	6.46
Cys	5.38	5.61	5.64
Met	0.53	0.50	0.55
Ile	3.40	3.51	3.49
Leu	8.20	8.18	8.21
Tyr	3.94	3.57	3.77
Phe	2.95	2.97	3.00
Orn	Trace	0.062	0.079
Lys	3.00	2.89	2.76
His	0.80	0.63	0.59
Arg	7.34	7.18	6.80
Pro	6.80	7.23	7.30

[a] Modified wool fiber with weight gain of 9.9%.
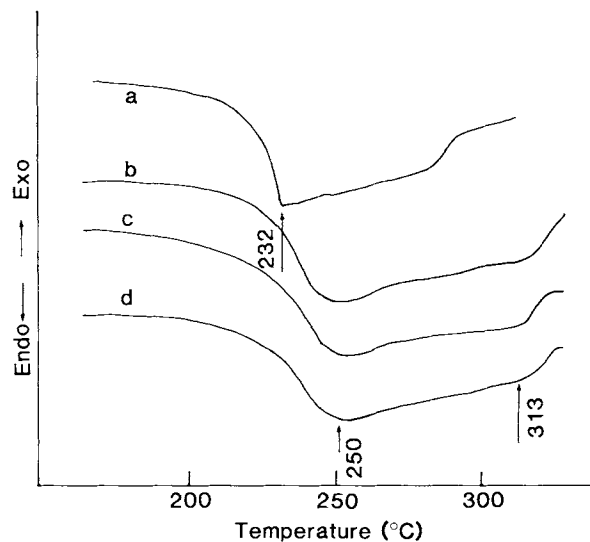[b] Modified wool fiber with weight gain of 17.4%.

Figure 1   DSC curves of control wool (a) and modified wool fibers with itaconic anhydride with different amounts of weight gain. Weight gain (%): (b) 9.9; (c) 14.0; (d) 17.4.

shoulder-form endothermic peak at 232°C with a broad endothermic peak in the higher temperature range from 230 to 270°C and then the DSC curve shifted toward to the exothermic reaction. The endothermic peaks at about 220°C and at 250–270°C are attributed to the melting of the α-helix structure and of the β-structure of the microfibrils and matrix protein,[7] respectively. The endothermic peak that appeared at 232°C for the control sample became broad and shifted to higher temperature (248–250°C) for the modified wool samples [Fig. 1(b)–(d)]. These thermal behaviors suggest the greater thermal stability of the wool fiber treated with itaconic anhydride. In addition, the DSC curves of wool fiber with a weight gain of 9.9% was similar in form to that for the sample with a weight gain of 17.4%, implying that no significant changes in thermal behavior can be detected in the weight gain range from 9.9 to 17.4%.

TMA Curves

To define the thermomechanical properties in a heating process, TMA curves for the modified samples were obtained (Fig. 2). Untreated (a) and control sample (b) exhibited the gradual extension of about 1% in the temperature range of 50–230°C. Beyond this temperature range, a maximum contraction peak was observed on the TMA curves of control fiber (b) at 240–243°C and a slightly higher peak compared to the temperature of the endo-
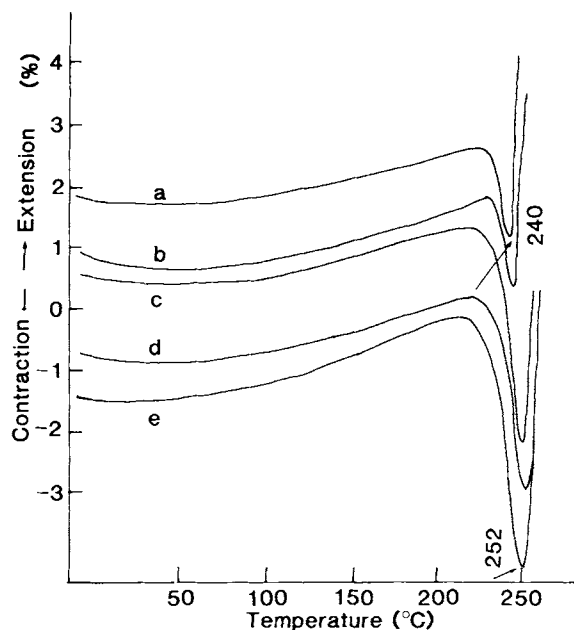
Figure 2 TMA curves of (a) untreated, (b) control, and wool fibers modified with itaconic anhydride with different amounts of weight gain. Weight gain (%): (c) 9.9; (d) 14.0; (e) 17.4.

thermic peak appeared on DSC curves of the corresponding sample [Fig. 1(a)]. On the other hand, the contraction peak of the wool fibers [Fig. 1(c)–(e)] modified with itaconic anhydride occurred consistently at 10°C higher than the peak temperature of the control [Fig. 1(b)]. These results were in agreement with the results of DSC measurements (Fig. 1). In addition to the shifting of the contraction

peak to higher temperature, the contraction peak became intense by the chemical modification.

Viscoelasticity

Figure 3 shows the behavior of the dynamic storage (E') and loss (E'') modulus curves of wool fibers in the temperature range of 25–250°C. The two major changes in the E' value are apparent: one slightly increasing beginning in the temperature range of 25–100°C and the other decreasing beginning above 208°C for the wool fibers with a lower value of weight gain. The position corresponding to the start position of the E' decrease shifted toward lower temperature when the weight gain increased. On the other hand, the E'' value of the wool fiber with a low value of weight gain began to increase at above 200°C. The broad loss modulus (E'') peak appeared at about 235°C for the wool specimen with a lower value of weight gain. However, the position of the E'' peak shifted toward to lower temperature when the weight gain increased. These results imply that the thermal molecular movement corresponding to the increase of the E'' value occurred at relatively low temperature at about 200°C when the weight gain increased. Therefore, the thermal movement of the wool keratin molecules is accelerated by the thermal movement of the itaconic anhydride combined to the wool keratin molecules.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis curves for wool fiber and modified wool fiber are shown in Figure 4. It is obvious that two major weight changes occurred, one
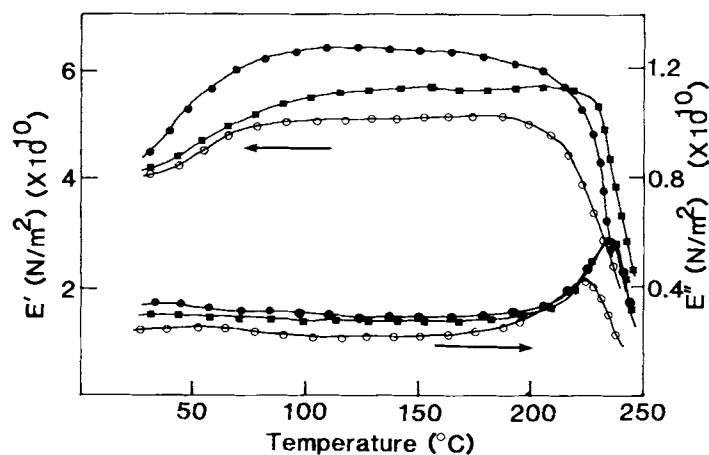

Figure 3 Dynamic storage (E') and loss (E'') modulus curves of (●) control and wool fibers modified with itaconic anhydride with different amounts of weight gain. Weight gain (%): (■) 9.9; (○) 17.4.
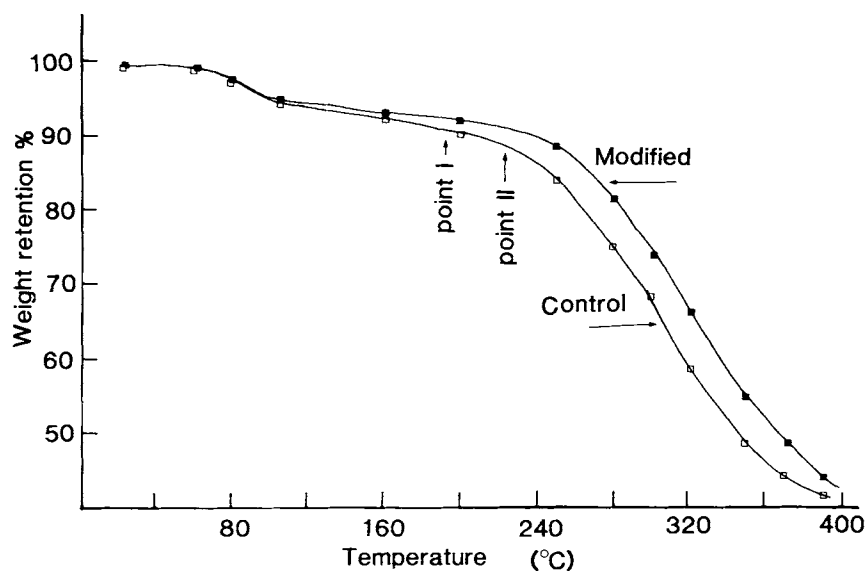
Figure 4 Thermogravimetric analysis curves of control (□) and modified wool fibers (■) with itaconic anhydride with weight gain of 17.4%. For points I and II, see the text.

beginning at 70–100°C, which corresponds to the evaporation of absorbed water, and the other beginning at about 160–200°C, which corresponds to thermal decomposition. In a nitrogen atmosphere, the control fiber exhibited a slight weight loss beginning at ca. 195°C (point I) and then a more drastic weight loss at above 220°C (point II). On the other hand, modified wool fiber, with a weight gain of 17.4%, showed the former and latter weight loss at 240 and 245°C, respectively. These findings suggest that the modified wool fiber has a high thermostability.

Tensile Properties

Some details of the mechanical properties and moisture regain of the wool fiber modified with itaconic anhydride are listed in Table III. It is relevant to note that these authors have not normalized tensile strength and thus a comparison was difficult as wool fiber weight changes by chemical modification. However, it is quite possible to compare the tensile properties as qualitative measurements. It can be seen that the mechanical properties of the wool fiber modified with itaconic anhydride remained unchanged compared with that of the control sample. Therefore, the results obtained indicate that the original properties inherent in wool fiber are not damaged even after the modification with itaconic anhydride, which is the same behavior as for the modification of silk with dibasic acid anhydride.[5]

Surface Characteristics

The surface characteristics of the wool fiber modified with itaconic anhydride were investigated by scanning electron microscopy (SEM). Figure 5 shows the SEM micrographs of the wool fibers before and after modification with itaconic anhydride. The wool fiber modified with itaconic anhydride showed the typical feature of the scale as that of the control sample. It is suggested that the itaconic anhydride did not damage the surface characteristics of the original wool fiber.

Table III   Physical Properties and Moisture Regain of the Wool Fibers Treated with Itaconic Anhydride (2/48 s) with Different Amounts of Weight Gain

Sample	Strength (g)	Elongation (%)	Moisture Regain (%)
Control	351	35.3	14.5
Untreated	358	36.1	13.2
Modified			
WG[a] 9.9%	354	35.3	9.1
WG 14.0%	400	39.0	9.6
WG 17.4%	366	38.9	10.0

Sample length 50 mm; chart speed 300 mm/min; drawing speed 20 mm/min. Full scale 500 g. Moisture gain was expressed in terms of g moisture/100 g wool fiber.
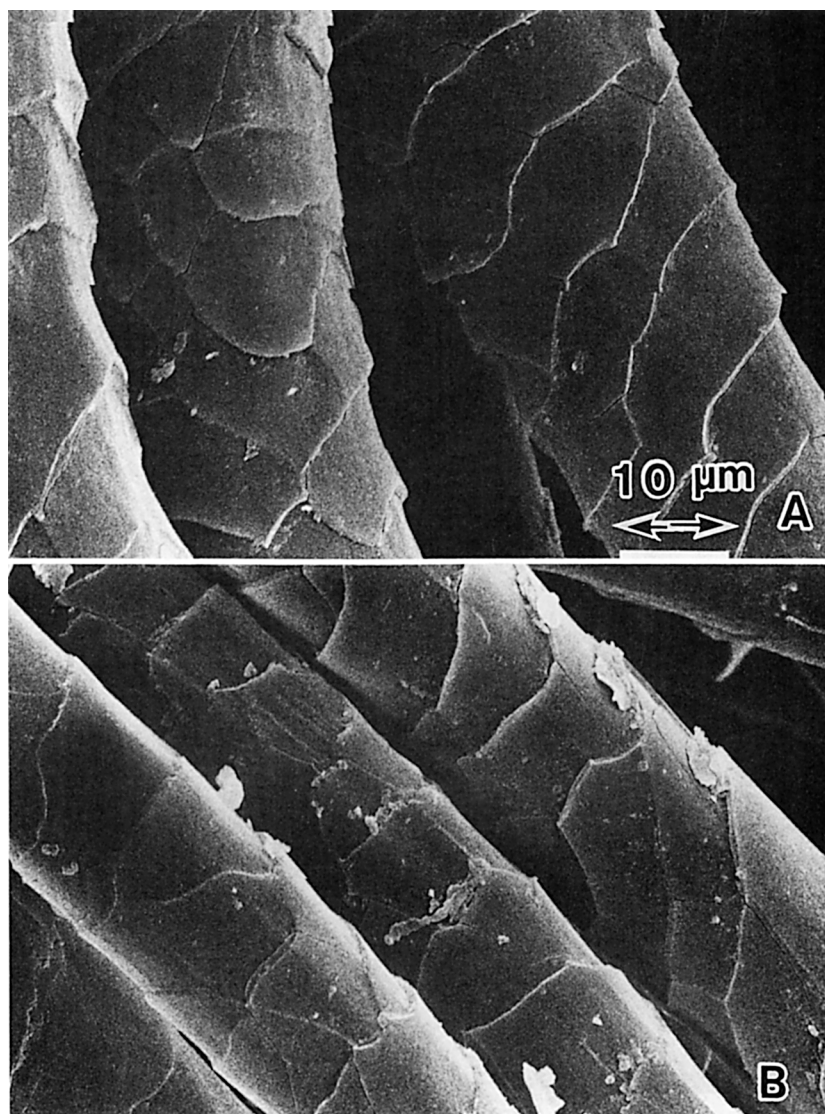
[a] Weight gain (%).

Figure 5   Scanning electron micrographs of (A) control and (B) modified wool fibers with itaconic anhydride with weight gain of 17.4%.

Molecular Orientation

We determined the birefringence (Δn) and isotropic refractive index (n_{iso}) of the wool fiber modified with itaconic anhydride (Table IV). Table IV shows the refractive index of the wool fiber in relation to the different weight gains. As the weight gain increased, the Δn value and the isotropic refractive index slightly decreased and exhibited the tendency to saturate when the weight gain reached above 14%. Since the birefringence and the isotropic refractive index are a measure of the molecular orientation and crystallinity, respectively, it is evident that the molecular orientation slightly decreased after modification with itaconic anhydride.

Table IV   Refractive Index of the Wool Fibers Treated in DMF Solution Contained 10% (w/v) Itaconic Anhydride at 65°C with Different Amounts of Weight Gain

Sample	$n^{\|\|}$	$n^{\perp}$	Δn^{a}	$n_{iso}{}^{b}$
Control	1.560	1.550	0.010	1.559
Untreated	1.559	1.550	0.009	1.553
Modified				
WG 9.8%	1.561	1.552	0.009	1.555
WG 14.0%	1.560	1.552	0.008	1.555
WG 17.4%	1.560	1.552	0.008	1.555

[a] Birefringence.
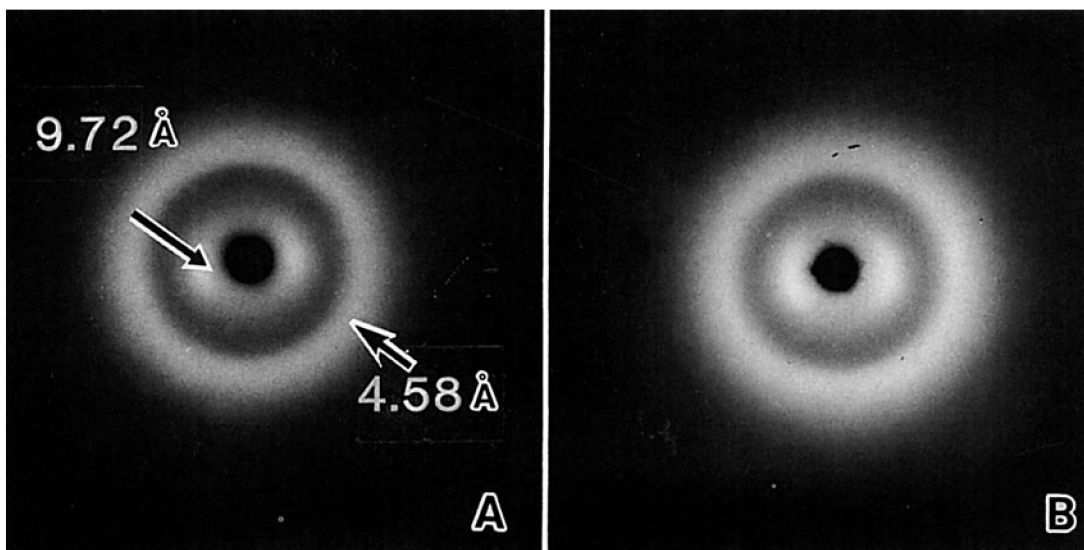[b] Isotropic refractive index.

Figure 6   X-ray diffraction patterns of (A) control and (B) modified wool fibers with itaconic anhydride with weight gain of 17.4%.

Crystalline Structure

X-ray diffraction photographs of wool fiber are presented in Figure 6. The wool fiber shows the broad diffraction pattern oriented toward the equator and the Deby–Scherrer ring corresponding to a spacing of 9.72 and 4.58 Å, respectively, which are characteristic of the β pattern of wool fiber.[8] The X-ray diffraction of wool fiber stayed unchanged even after chemical modification with itaconic anhydride, suggesting that the itaconic anhydride did not break the crystalline structure of the wool fiber.

It is obvious that the tensile and morphological properties as well as TMA characteristic of modified wool are not damaged; nevertheless, the TGA measurements are in agreement with the DSC results, demonstrating that modified wool fiber is more resistant to decomposition compared with the control fiber.

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