Chemical Modification of Wool Fibers with Acid Anhydrides

GIULIANO FREDDI,[1] MASUHIRO TSUKADA,[2] HIDEKI SHIOZAKI[3]

[1]Stazione Sperimentale per la Seta, via Giuseppe Colombo, 83, 20133, Milano, Italy

[2]National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan

[3]Art Craft Technical Center of Kanagawa, 1-7-53, Honcho, Odawara, Kanagawa 250, Japan

ABSTRACT: Wool fibers were chemically modified by reaction with succinic and glutaric anhydrides. The weight gain (and acyl content) increased with increasing the reaction temperature (65–80°C) and time (1–2 h), attaining 18.9% (158.9 mol/10^5 g) and 23% (163.9 mol/10^5 g) for succinylated and glutarylated wool, respectively. Changes in the amino acidic pattern of acylated wool, i.e., decrease of basic amino acid residues and formation of ornithine, were observed by acid hydrolysis. The X-ray diffraction profiles of modified wool fibers remained essentially unchanged, suggesting that the crystalline structure was not affected by reaction with acid anhydrides. The degree of molecular orientation of acylated wool slightly decreased, especially at high weight gain. The viscoelastic response of wool modified with succinic and glutaric anhydrides was characterized by a shift to a lower temperature of both the drop of the storage modulus and the peak of the loss modulus. These features are indicative of a higher mobility of the keratin chians in the amorphous and crystalline domains. In fact, it is suggested that the chemical agent diffused into the accessible parts of α-crystallites, reaching the available reactive sites. This did not cause changes in the crystalline pattern of wool, but resulted in a different thermal behavior of fibers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1573–1579, 1999

Key words: wool; acylation; succinic anhydride; glutaric anhydride; structure; dynamic mechanical analysis

INTRODUCTION

The chemical modification of wool can be regarded as a powerful tool to improve some inferior textile performance of the fibers and to impart new physico-chemical and functional properties suitable for technological implementation, in order to meet market requirements for better wear and mainte- nance behavior of textile goods and for developing new textile products. The most popular chemical modification techniques are the graft copolymeriza- tion of vinyl monomers,[1,2] and the reaction of mod- ifying agents, such as epoxides[3–6] and acid anhy- drides.[7–9] Grafting implies the loading of fibers with large amounts of polymer, which are often needed to obtain the desired effect. On the other hand, the use of selected chemical agents permits achieving an effective and specific modification of the fibrous substrate, avoiding the drawbacks arising from ex- cessive polymer loading.

Various kinds of epoxides and acid anhydrides can be used as modifying agents for wool. The

first attempts to apply epoxides date back to the 1970s, thanks to the scientific contribution of Tanaka and Shiozaki.[3] Epoxide-treated wool fibers exhibited improved chemical resistance,[3] crease recovery,[5] and shrink-resist properties.[6] However, in spite of the evident improvement of fiber properties, the application to industrial-scale processing of the epoxide treatment is still limited. Studies on acylation of wool with acid anhydrides have been reviewed by Maclaren and Milligan.[9] Acylated wool fibers displayed improved resistance to attack by acid, alkali, and oxydants, better shrink resistance, and increased settability. Tsukada et al.[7,8] have recently investigated the kinetics of acylation of wool with succinic, glutaric, and itaconic anhydrides. The optimum temperature and time were 65°C and 2 h, respectively, which permitted to attain a weight gain of 15–18% and an acyl content of 110–140 mol/10^5 g, depending on the kind of chemical agent used. Free amine, hydroxyl, and phenol groups carried by variuos amino acid side chains are the most important reactive sites.[9] The crystalline structure of wool was not affected by acylation.[8] Accordingly, the tensile properties of acylated wool fibers, i.e., rupture strength and elongation at break, remained essentially unchanged.[7,8] The most stricking feature of acylated wool fibers was the change in dye affinity.[7] Absorption of acid dyes was noticeably reduced, while that of cationic dyes was markedly enhanced, due to introduction of extra acidic groups into the fiber.

In the present study wool fibers were acylated with succinic and glutaric anhydrides. Our interest focused on the reactivity of the modifying agents toward wool, as well as on the changes in crystalline structure, molecular orientation, and viscoelastic behavior induced by acylation. The results will be discussed with reference to those previously reported for wool,[7,8] as well as for silk,[10–15] another protein fiber that has been modified with various kinds of acid anhydrides.

EXPERIMENTAL

Materials

Wool fibers (2 × 48s yarn) were cleaned by an acetone/ethanol mixture system in a Soxhlet extractor for 12 h, then rinsed with distilled water, dried to constant weight and conditioned in air at room temperature. Reagent grade succinic and glutaric anhydrides were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification.

Samples of known weight (ca. 1 g) were dried at 105°C for 2 h before teatment. Acylation was carried out in dimethylformamide (DMF) containing 10% w/v succinic or glutaric anhydride, at 65 and 80°C for 1 and 2 h. The material-to-liquor ratio was 1:30. At the end of the reaction, wool fibers were washed with DMF, then with acetone for 1 h at 55°C in order to remove the unreacted anhydride, and finally with water. The weight gain was calculated from the increase in weight of the wool sample after reaction. On this basis the acyl content was estimated.

Measurements

Dried wool fibers were hydrolyzed in HCl 6 N at 110°C for 20 h under vacuum. The hydrolyzed samples were filtered through a glass disk to remove small amounts of residue, dried in rotary evaporator at 40°C, and dissolved in a buffer solution at pH 2.2 (1 mg/mL). The amino acid composition was determined by using a Hitachi L-8500 rapid amino acid analyzer.

X-ray diffraction measurements were performed with a Rigaku Denki Co. RU-200 diffractometer, using CuKα radiation.

The refractive indices were measured with the Beche's line method using a polarized microscope under the monochromatic light (Na light) at 20°C and 65% relative humidity as previously described.[16]

Dynamic mechanical measurements (DMA) were carried out with a Toyoseiki Rheolograph Solid-S. The temperature range studied was from −50 to 260°C. Specimens of 15-mm length were heated at 2°C/min. The temperature dependence of storage (E') and loss (E'') moduli was measured at a frequency of 10 Hz, with an initial tension applied to samples of 30 gf.

RESULTS AND DISCUSSION

Reactivity of Anhydrides

The reactivity of succinic and glutaric anhydrides was evaluated on the basis of weight gain and amino acidic analysis of modified wool fibers. In a previous study[7] it was reported that weight gain and acyl content of wool fibers modified with both succinic and glutaric anhydrides increased with

Table I   Weight Gain and Acyl Content of Wool Fibers Modified with Succinic and Glutaric Anhydrides

Reaction Conditions	Succinic Anhydride		Glutaric Anhydride	
	Weight Gain (%)	Acyl Content (mol/10^5 g)	Weight Gain (%)	Acyl Content (mol/10^5 g)
65°C,1h	12.6	111.8	9.6	76.8
80°C,2h	18.9	158.9	23.0	163.9

increasing reaction temperature and time, without significant differences in the kinetics of acylation between the two modifying agents. Optimum conditions for acylation of wool were a temperature in the range 65–80°C and a reaction time of 1–2 h. The results listed in Table I are consistent with those previously reported,[7] showing that an appreciable increase in weight gain could be achieved even in very mild conditions (for 1 h at 65°C). It is noteworthy that higher reaction temperatures (75–80°C) and times (2–4 h) were required to attain about 10–13% weight gain with silk, by acylation with the same chemical agents.[14] This may depend on the physicochemical and morphological differences between wool and silk, i.e., amount and accessibility of potentially reactive sites, rate of diffusion of the chemicals within the fiber matrix, steric factors, etc.

The amino acid composition of acylated wool fibers (Table II) showed a slightly lower recovery of basic amino acid residues. In particular, arginine decreased by reaction with both succinic and glutaric anhydrides and lysine decreased only in the sample modified with succinic anhydride. Histidine remained almost unchanged. A limit in this approach for evaluating the reactivity of anhydrides is that several N-, O-, and S-acyl groups formed by acylation are broken during acid hydrolysis.[9] In fact, from the amino acid composition we can calculate an acyl content of ca. 20 mol/10^5 g, which accounts for only 13% of the total acyl content (see Table I). However, even though only a partial view arises from the amino acidic analysis, some differences in the reactivity of basic amino acid residues can be noticed. These findings agree with previous observations emerging from the acylation of silk.[12–14] The reactivity of different anhydrides depends on both morphological and steric factors of the fibrous substrate, as well as on chemical factors related to the characteristics of the anhydride substituent.[10,11] In fact, it has been demonstrated that the bulkier the side chain, the lower the reactivity,

while the presence of electronegative groups usually enhances the rate of reaction. A detectable amount of ornithine was observed in the acid hydrolysates of acylated wool. It has been suggested that it arises from acylated arginine residues during acid hydrolysis.[17]

Crystalline Structure and Molecular Orientation

Figure 1 shows the wide-angle X-ray diffraction profiles of untreated and acylated wool fibers. The control sample [Fig. 1(a)] showed the typical diffraction pattern of α-keratins,[18] with a prominent 2θ peak at 20.2° and a minor peak at 9°, corresponding to the crystalline spacings of 4.39 and 9.82 Å, respectively. The position and intensity of

Table II   Amino Acid Composition of Wool Fibers Untreated and Modified with Succinic and Glutaric Anhydrides with 18.9 and 23.0% Weight Gain, Respectively

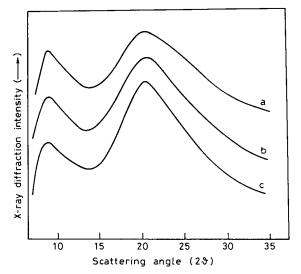| Amino Acid (mol %)	Untreated	Succinic Anhydride (18.9%)	Glutaric Anhydride (23.0%)
Aspartic acid	6.43	6.48	6.44
Threonine	6.38	6.44	6.39
Serine	10.96	10.89	10.73
Glutamic acid	12.23	12.24	12.29
Glycine	9.44	9.39	9.37
Alanine	5.76	5.72	5.80
Valine	6.38	6.60	6.40
Cystine	5.65	5.75	5.59
Methionine	0.59	0.50	0.60
Isoleucine	3.45	3.46	3.46
Leucine	8.08	8.14	8.18
Tyrosine	3.51	3.68	3.63
Phenylalanine	2.93	2.95	2.93
Ornithine	—	0.36	0.36
Lysine	3.01	2.87	3.04
Histidine	0.80	0.81	0.80
Arginine	7.30	6.77	7.03
Proline	7.08	6.92	6.90

Figure 1 X-ray diffraction curves of untreated (a), succinylated (b), and glutarylated (c) wool fibers with 18.9 and 23% weight gain, respectively.

the diffraction peaks remained unchanged for succinylated [Fig. 1(b)] and glutarylated [Fig. 1(c)] wool fibers with high weight gain (18–23%), suggesting that the reaction of the modifying agents with keratins did not cause significant changes in structure of the fibrillar elements forming the crystalline regions of wool. We may, therfore, infer that acylation primarily occured in the less ordered fiber regions, where the potentially reactive sites are probably more accessible to chemicals. Similar results have been reported for wool fibers modified with itaconic anhydride,[8] as well as for silk.[14]

Optical measurements (Table III) are a useful source of information about the overall fiber structure. Birefringence (Δn) may be regarded as an estimate of the average molecular orientation of a fibrous polymer, because it reflects the orientation of both the polymer chains in the amorphous regions and the polymer crystals in the crystalline regions. Untreated fibers showed a Δn value of 0.0095, which places wool within the group of the poorly oriented textile fibers.[19] From the results listed in Table III it is possible to see that acylation induced a slight decrease of birefringence, whose extent was dependent on the weight gain. This implies a slightly lower degree of molecular orientation for acylated wool fibers, attributable to the reaction with the modifying agent, which induced swelling of the fiber matrix and disordering of the arrangement of the keratin chains. The values of isotropic refractive index (n_{ISO}), a parameter related to structural and morphological features of the fiber, such as crystal content, density, etc., showed a tendency to decrease with increasing the weight gain. Because the X-ray diffraction data showed that the crystalline structure was not affected by acylation, we can conclude that its behavior may account for a slight decrease in fiber density.

A common feature emerging from the results of X-ray diffraction and optical measurements is that acylation induced only slight changes in the fine structure of wool. Similar results were obtained with acylated silk fibers, the extent of changes being always small and being related to the kind of reagent used and to the weight gain attained.[12–14] These findings suggest that the reaction of selected chemical agents with wool (as well as with silk) permits obtaining a specific chemical modification of the fibrous substrate, without noticeably affecting its fine structure and the related physico-mechanical properties.[20]

Dynamic Mechanical Behavior

The temperature dependence of the dynamic (E') and loss (E'') modulus of untreated, succinylated, and glutarylated wool fibers was studied in the range from −50 to 260°C. The storage component of dynamic modulus of untreated wool (Fig. 2) decreased in the low temperature

Table III Optical Properties of Wool Fibers Modified with Succinic (S) and Glutaric (G) Anhydrides

	Refractive Indices		Birefringence	Isotropic Refractive Index
Sample	Parallel ($n\parallel$)	Perpendicular ($n\perp$)	(Δn)	(n_{ISO})
Untreated	1.5575	1.548	0.0095	1.551
S-12.6%	1.555	1.546	0.0090	1.549
S-18.9%	1.553	1.546	0.0070	1.548
G-9.6%	1.555	1.547	0.0080	1.549
G-23%	1.552	1.545	0.0070	1.547

Figure 2 Dynamic mechanical curves of untreated and succinylated wool fibers with 12.6 and 18.9% weight gain.
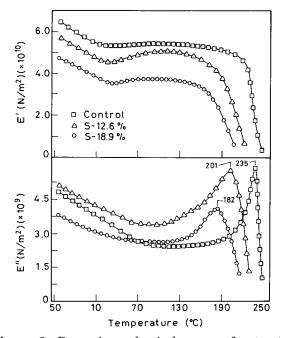

Figure 3 Dynamic mechanical curves of untreated and glutarylated wool fibers with 9.6 and 23% weight gain.

range, from −50 to about 20°C, and then remained stable over a wide temperature range, until about 190°C. Beyond this temperature the E' curve showed a sharp fall in response to various molecular relaxation processes attributable to exceeding of the softening temperature (T_g)[21] and α-helix melting.[22] Accordingly, a prominent relaxation peak appeared in the imaginary part of the modulus (loss peak at 235°C). Following chemical modification with both succinic (Fig. 2) and glutaric (Fig. 3) anhydrides the viscoelastic behavior of wool fibers showed significant changes. The main features were a decrease in the value of modulus with increasing the acyl content, an anticipated drop of storage modulus and a shift to lower temperature of the loss peak, the extent of shift being linearly related to the amount of weight gain (Fig. 4).

The viscoelastic measurements are a powerful tool for detecting changes in the fine structure of fibers. From the E' and E'' curves of untreated wool it is possible to observe that major changes in modulus occurred in the low and high temperature range. At low temperature (from −50°C to about 20°C) the value of modulus decreased as a consequence of microbrownian motions of wool backbone chains, with partial contribution of side-chain motions in the higher temperature
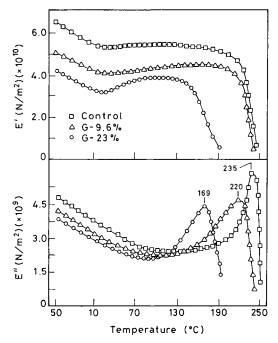
range.[22] At high temperature (from 190°C upwards), the storage modulus dropped sharply, and a strong loss peak appeared due to disordering and melting of α-helix crystallites.[21,22] Following acylation, the low-temperature pattern was almost unaffected, while remarkable changes appeared in the high-temperature viscoelastic pattern of both succinylated and glutarylated
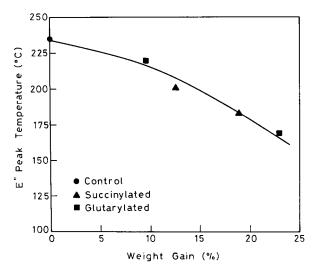

Figure 4 Loss peak temperature versus weight gain of acylated wool fibers.

wool fibers. From the viscoelastic response it is possible to assume that the thermally induced molecular motions of the keratin chains in both amorphous and α-helix domains were enhanced by acylation, resulting in a decrease of T_g and in a lower thermal stability of the α-crystallites. The decrease in modulus of acylated wool fibers as a function of the weight gain may be related to the swollen state induced by the reaction, which resulted in a lower degree of fiber stiffness and density, in agreement with otpical measurements.

The complexity of wool fiber morphology makes it difficult to attribute the above changes to a specific fiber compartment. However, we suggest that acylation might have perturbed the inter- and intramolecular interactions (hydrogen bonds) in the amorphous regions, resulting in an enhanced molecular motion of nonhydrogen bonded chain segments. This hypothesis is consistent with the results of optical measurements (decrease in average fiber orientation), as well as with previously reported thermomechanical results,[7] showing that succinylated and glutarylated wool fibers exhibited a tendency to extend more easily than untreated fibers above 100°C, the onset temperature of final extension shifting downwards of about 40–50°C for fibers with high weight gain. Concerning the α-helix crystallites, the X-ray diffraction results showed that they were not directly affected by acylation, as evidenced by the position and intensity of the diffraction peaks. However, it has been shown that α-crystallites consist of two different regions, one of which is less laterally crosslinked and is more accessible to chemical agents.[22] We, therefore, suggest that anhydride molecules probably diffused into these fiber domains and reacted with available reactive sites, inducing limited but detectable structural changes, which were monitored by DMA analysis. The presence of a less thermally stable α-helix fraction is confirmed by previously reported DSC data,[7] showing the appearance of an additional endothermic peak at about 215–220°C for succinylated and glutarylated wool fibers, in addition to that at 230–235°C attributed to melting of α-helices in untreated wool.

CONCLUSIONS

The reaction of wool with acid anhydrides is favored by the presence of many reactive sites (amine, hydroxyl and phenol groups) carried by the amino acid side chains of keratins. Therefore, a high degree of acylation can be attained even in mild reaction conditions (65°C).

The crystalline structure of wool remained essentially unchanged by acylation. Fine structural changes in specific fiber domains were detected by viscoelastic measurements, suggesting that the thermal response of the fibers was partially modified by reaction with succinic and glutaric anhydrides. These findings are in good agreement with previously reported data.[7]

The changes in viscoelastic behavior can be controlled through the acyl content (see Fig. 4). For example, if a degree of acylation corresponding to about 10–12% weight gain is reached, the physical properties undergo only slight changes, while the dyeing behavior, which remains the most stricking characteristic of acylated wool fibers, has already shifted towards a higher affinity for cationic dyestuffs.[7]

We think that these results might offer new opportunities for the development of finishing techniques, leading to expand wool consumption by widening the range of textile application.

REFERENCES

1. Arai, K. In Block and Graft Copolymerization; Ceresa, R., Ed.; John Wiley and Sons: London, 1973, Vol. 1, p. 193.
2. Maclaren, J. A.; Milligan, B. In Wool Science. The Chemical Reactivity of Wool Fiber; Science Press: Marrickville, NSW, 1981, p. 235.
3. Tanaka, Y.; Shiozaki, H. Sen-i Gakkaishi 1982, 38, T-491.
4. Tanaka, Y.; Shiozaki, H. Proc. 7th Int. Wool Text. Res. Conf., Tokyo, 1985, Vol. IV, p. 441.
5. Kamiishi, Y.; Tanaka, Y.; Arai, K. Proc. 8th Int. Wool Text. Res. Conf.; Cranshaw, G. H., Ed., WRONZ: Christchurch, 1990, Vol. I, p. 346.
6. Ito, H.; Muraoka, Y.; Umehara, R.; Shibata, Y.; Miyamoto, T. Text Res J 1994, 64, 440.
7. Tsukada, M.; Shiozaki, H.; Konda, A. J Appl Polym Sci 1990, 41, 1213.
8. Tsukada, M.; Gotoh, Y.; Romanò, M.; Hishikawa, H.; Shiozaki, H. J Appl Polym Sci 1992, 46, 1477.
9. Maclaren, J. A.; Milligan, B. In Wool Science. The Chemical Reactivity of the Wool Fibre; Science Press: Marrickville, 1981, p. 135.

10. Shiozaki, H.; Tanaka, Y. J Seric Sci Jpn 1980, 49, 307.
11. Shiozaki, H.; Tsukada, M.; Matsumura, M. J Seric Sci Jpn 1988, 57, 165.
12. Tsukada, M.; Gotoh, Y.; Freddi, G.; Shiozaki, H. J Appl Polym Sci 1992, 45, 1189.
13. Tsukada, M.; Gotoh, Y.; Freddi, G.; Shiozaki, H.; Ishikawa, H. J Appl Polym Sci 1992, 45, 1719.
14. Tsukada, M.; Gotoh, Y.; Shiozaki, H.; Freddi, G.; Crighton, J. S. J Appl Polym Sci 1994, 51, 345.
15. Freddi, G.; Tsukada, M.; Kato, H.; Shiozaki, H. J Appl Polym Sci 1994, 52, 769.
16. Tsukada, M.; Nagura, M.; Ishikawa, H.; Shiozaki, H. J Appl Polym Sci 1989, 37, 2637.
17. Milligan, B.; Wolfram, L. J. J Text Inst 1973, 64, 170.
18. Arai, K.; Negishi, M. J Polym Sci Part A-1, 1971, 9, 1865.
19. Morton, W. E.; Hearle, J. W. S. In Physical Properties of Textile Fibers; The Textile Institute: Heinemann, London, 1975, p. 564.
20. Tsukada, M.; Freddi, G. In Polymeric Materials Encyclopedia; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996, Vol. 10, p. 7728.
21. Menefee, E.; Yee, G. Text Res J 1965, 35, 801.
22. Arai, K.; Ishikawa, M. Sen-i Gakkaishi 1983, 39, T14.