

Acylation of Silk and Wool with Acid Anhydrides and Preparation of Water-Repellent Fibers

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ABSTRACT: Silk and wool fibers were acylated with two acid anhydrides, dodecenylsuccinic anhydride (DDSA) and octadecenylsuccinic anhydride (ODSA), at 75°C with *N,N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) as the solvent, the latter of which allowed higher weight gains to be reached. The weight gain and acyl content of wool was always higher than that of silk. Tensile properties of silk remained unchanged regardless of weight gain, whereas wool displayed a noticeably higher extensibility at high weight gain. Fine structural changes of acylated wool were detected by DSC analysis. Moisture regain and water retention of acylated silk and wool decreased significantly, whereas water repellency increased. SEM analysis showed the presence of foreign material firmly adherent to the surface of both silk and wool, whose amount increased with increasing weight gain. These deposits were attributed to the presence of the modifying agents at the fiber surface on the basis of the characteristic IR bands. The possible application of silk and wool fibers acylated with DDSA or ODSA for the preparation of water-repellent textile materials is discussed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2832–2841, 2001

Key words: *Bombyx mori* silk; wool; chemical modification; acid anhydride; water repellency

INTRODUCTION

The reaction of selected chemical agents with protein fibers, silk, and wool, is a particularly attractive system that can be used to obtain effective and specific modification of the fibrous substrate,

while keeping the intrinsic fiber properties unchanged.^{1,2} The market demand for clothing articles with superior easy care and wear properties, as well as the development of innovative textile products ("smart fibers") are some of the factors stimulating the research on chemical modification of fibers. Moreover, natural protein fibers are attracting considerable interest as starting materials potentially suitable for manufacturing various kinds of biomedical devices.³ In this context the desired functional performance can be optimized by selective chemical modification of the fibrous substrate.

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Acylation of silk^{1,4-8,12} and wool^{2,9-11} by reaction with acid anhydrides has been extensively investigated during the last three decades. The most striking feature of acylated silk and wool is the change in dye affinity. Acylated wool fibers display improved resistance to attack by acid, alkali, and oxidants; better shrink resistance; and increased settability. Crease recovery of silk slightly improves, although a certain degree of fiber stiffness may partly impair silk handle. Recently, silk modified with ethylenediaminetetraacetic dianhydride has been exploited for the preparation of fibers with antimicrobial activity because of the high efficiency in absorbing and binding metal cations.¹³

Textile finishing aims at improving visual perception, handle, and functional properties of clothing articles, such as antistatic, antisoil, antistaining, and anticrease behavior. Many finishing products are commercially available but their durability is not always long enough to maintain the desired property for the entire lifespan of the product. The goal of more durable finishing treatments can be achieved if the finishing agent is chemically bound to the fiber substrate. The acylation reaction can be exploited for binding chemicals onto protein fibers by means of the anhydride group and, by changing the chemistry of the anhydride substituent, it would be possible to confer new properties on fibers for either clothing or technical applications.

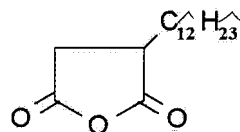
The present study deals with the chemical modification of silk and wool fibers with two acid anhydrides, dodecenylsuccinic anhydride (DDSA) and octadecenylsuccinic anhydride (ODSA), possessing a long alkyl chain as the pendant group. The reactivity of DDSA and ODSA in different solvents was studied. Modified silk and wool fibers were characterized for their physicochemical and morphological properties. The acylation reaction resulted in fibers with increased hydrophobicity. This property may address the development of new textile articles not only for clothing but also for innovative technical textile applications (such as medical textiles) where water repellency may be one of the required functions.

EXPERIMENTAL

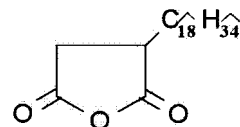
Materials

Reagent-grade dodecenylsuccinic anhydride (DDSA; cat. no. 44,327-1) and octadecenylsuccinic anhy-

dride (ODSA; cat. no. 41,649-5) were purchased from Sigma-Aldrich Japan K.K. and used without further purification. The general chemical structure of the acid anhydrides is as follows:



Dodecenylsuccinic anhydride (DDSA).



Octadecenylsuccinic anhydride (ODSA).

Degummed silk (*Bombyx mori*) and wool yarns were acylated with 20% (w/v) anhydride in *N,N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), which were purchased from Wako Pure Chemical Industries Ltd., at 75°C for various periods of time. The reaction system was connected to a reflux condenser and held at constant temperature in a thermostatic bath. The material-to-liquor ratio of 1 : 40 was maintained. At the end of the reaction, the fiber samples were washed first with DMF or DMSO and then with acetone at 55°C for 1 h, to remove any unreacted anhydride, and finally with water. The weight gain was calculated from the increase in weight of the original fibers after chemical reaction.

Measurements

The tensile properties of modified silk and wool fibers were measured with a Tensilon UTM-II (Toyo Baldwin Co.), using the standard technique at 20°C and 65% RH at a gauge length of 100 mm and strain rate of 40 mm/min.

Heat-flow differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo DSC 821 system at a heating rate of 10°C/min. The open aluminium cell was swept with N₂ during the analysis.

Kinetics of moisture absorption was determined by weighing oven-dried samples at different time intervals, in standard conditions of temperature and humidity, until equilibrium (24 h).

Water retention was determined by using the centrifugal method according to the standard ASTM D 2402-78. The water drop absorption test

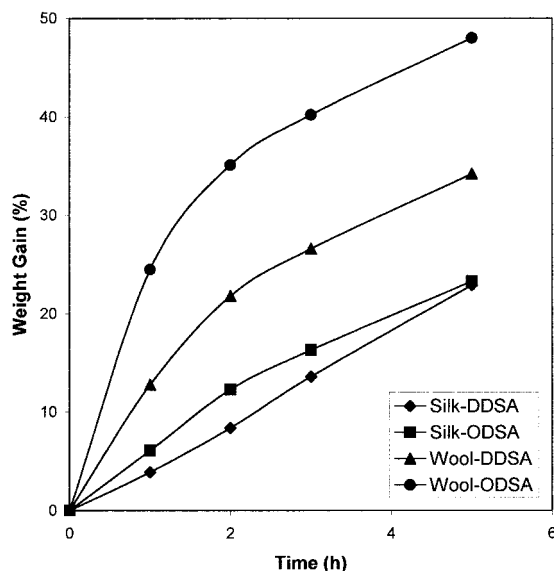


Figure 1 Weight gain versus reaction time of silk and wool fibers acylated with 20% w/v DDSA or ODSA, in DMF at 75°C (material-to-liquor ratio 1 : 40).

was performed with the following procedure: a drop of water was placed on the surface of the sample through the needle of a microsyringe and the time of liquid absorption was monitored. Following the time (t) taken for the drop to be absorbed, samples were classified as follows: (–) for $t < 5$ min; (+) for $5 < t < 15$ min; (++) for $15 < t < 60$ min; (+++) for $t > 60$ min.

Surface morphology was examined with a Stereoscan 440 (LEO) scanning electron microscope, at 10 kV acceleration voltage, after gold coating.

IR spectroscopy analyses were performed with a Nicolet-150P spectrometer (Nicolet Instruments, Madison, WI), equipped with an ATR diamond cell (SPECAC).

RESULTS AND DISCUSSION

Chemical Reactivity

Figure 1 shows the kinetics of acylation of silk and wool with DDSA and ODSA, at 75°C, in DMF for different periods of time, as determined from the weight increase of the fibers.

The weight gain of silk increased almost linearly as a function of the reaction time, whereas that of wool increased more rapidly during the first 2 h and then proceeded at a lower rate. The apparent difference in the reaction order between silk and wool, as well as the difference in the

extent of weight gain attained by the fibers may depend on various factors related to morphological, chemical, and structural properties of the fibrous substrate. Wool has a complex cellular structure, whereas silk is a fibrous secretion consisting of few protein components (i.e., sericins and fibroin). Surface and internal morphologies are drastically different, and these features might significantly affect adsorption and diffusion of chemicals. Additionally, the different amino acid compositions entail that different numbers of functional groups potentially reactive toward anhydrides are available within the fiber matrix. Amine groups of basic amino acid residues (lysine, histidine, and arginine), hydroxy groups of serine and threonine, and phenyl groups of tyrosine are the most important reactive sites for anhydrides.^{1,2} The free-SH cysteine groups of wool may react as well.² On the basis of the amino acid composition, the total amount of potentially reactive sites can be estimated to be 228.3 and 399.2 mol/10⁵ g for silk and wool, respectively. Although not all of them are accessible to reagents, because they are buried into the fiber structure and remain inaccessible to chemicals, wool is richer than silk in reactive sites, and this might have partly contributed to the constantly higher weight gain of wool compared to that of silk.

DDSA and ODSA possess a closely similar chemical structure, the only difference being the length of the aliphatic chain linked to the anhydride group. Data listed in Table I permit a comparison between the reactivity of the two anhydrides toward silk and wool.

The extent of acylation of wool fibers was almost the same with the two acylating agents, implying that the difference in chemical structure was irrelevant for the reaction in terms of both reagent diffusion and accessibility of reactive sites. On the other side, silk treated with DDSA exhibited a slightly higher acyl content, partly attributable to the lower size of the hydrocarbon pendant.

Solvent Effect

The effect of solvent on the reactivity of ODSA toward silk and wool was examined using DMSO and DMF as the solvent for chemical modification. Figure 2 shows the behavior of weight gain as a function of reaction time.

The weight gain of both silk and wool increased more when acylation was performed in DMSO,

Table I Weight Gain and Acyl Content of Silk and Wool Acylated with Dodecenylsuccinic (DDSA) and Octadecenylsuccinic (ODSA) Anhydrides

	Silk			Wool	
	MW (Da)	Weight Gain (%)	Acyl Content (mol/10 ⁵ g)	Weight Gain (%)	Acyl Content (mol/10 ⁵ g)
DDSA	266.38	22.9	86	34.2	137
ODSA	350.54	23.3	66	48	128

the effect of which was particularly evident for wool, as shown by the twofold weight gain reached in this solvent. Both DMSO and DMF are dipolar aprotic solvents with moderate hydrogen-bonding tendency. Their solubility parameter δ does not differ too much, although DMSO has higher values of dipole moment and dielectric constant than those of DMF.¹⁴ This characteristic is believed to play an important role in reducing electrostatic attractive forces within the fibers and enhancing solvent penetration and diffusion.¹⁵ Accordingly, it was reported that the swelling volume induced by DMSO onto silk¹⁶ and wool¹⁵ is much higher than that induced by DMF. The higher the ability of the solvent to swell the fibers, the lower the restriction to diffusion of reagents and the higher the reaction efficiency. It is noteworthy that after a 7-h reaction in DMSO, wool reached an acyl content of 208.8

mol/10⁵ g, about half the theoretical amount of functional groups available for acylation. In the same reaction conditions the acyl content of silk was 73 mol/10⁵ g, corresponding to about one-third of the total number of potentially reactive sites.

Mechanical Properties

The functional performance of textile fibers is mostly determined by their tensile properties. Because chemical treatments at fairly high temperature are likely to affect the intrinsic fiber properties,^{2,17} it is of interest to control their effect on the fibers. Table II lists the results of tensile measurements of silk and wool acylated with DDSA and ODSA with increasing weight gain.

Silk acylated with DDSA or ODSA up to a 23% weight gain did not exhibit any detectable change in breaking load, elongation at break, and energy compared to that of the control sample. These results are consistent with others previously reported,¹ indicating that acylation with acid anhydrides does not induce adverse effects toward the intrinsic tensile properties and can be considered a safe chemical modification technique for silk.

Wool showed a different behavior, the most interesting aspect of which was the significant increase of elongation at break as a function of increasing weight gain with both DDSA and ODSA. This effect is not completely new. For example, it was previously reported that the introduction of acetyl groups makes wool easier to extend in water.¹⁸

Acylation with itaconic anhydride resulted in a slightly higher extensibility of wool in standard conditions of temperature and humidity.¹⁰ Wool fibers acylated with succinic and glutaric anhydrides did not show remarkable changes in their tensile properties,⁹ although a partial loss of fiber stiffness, a higher degree of fiber swelling, lower molecular orientation, and enhanced thermally induced molecular motion of the keratin chains

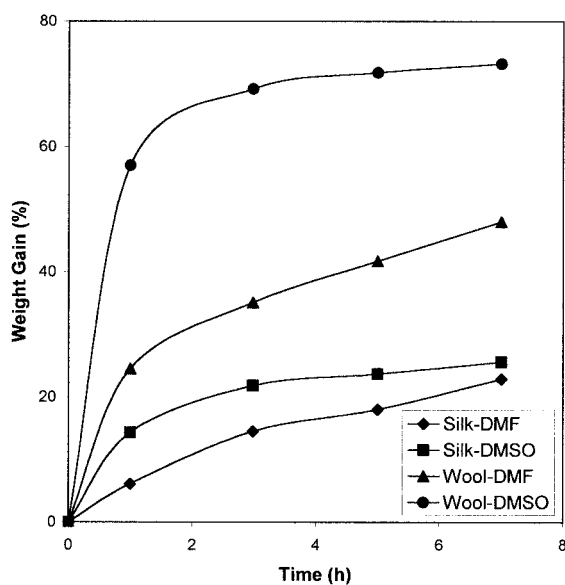


Figure 2 Weight gain versus reaction time of silk and wool fibers acylated with 20% w/v ODSA in DMF or DMSO at 75°C (material-to-liquor ratio 1 : 40).

Table II Tensile Properties of Silk and Wool Acylated with Dodecenylsuccinic (DDSA) and Octadecenylsuccinic (ODSA) Anhydrides

Sample	Weight Gain (%)	Breaking Load (gf)	Elongation at Break (%)	Energy (gf/mm)
Silk Control	0	439 ± 21	18.7 ± 1.2	3302 ± 576
DDSA	8.4	463 ± 29	19.5 ± 1.3	3587 ± 665
	13.6	428 ± 21	19.0 ± 1.1	3361 ± 335
	23.3	436 ± 12	19.3 ± 1.0	3241 ± 401
ODSA	6.1	388 ± 25	18.9 ± 1.3	3062 ± 478
	14.5	435 ± 17	19.7 ± 1.1	3517 ± 400
	22.9	432 ± 14	18.9 ± 0.6	3172 ± 299
Wool Control	0	288 ± 33	29.0 ± 5.5	4109 ± 770
DDSA	12.8	292 ± 28	34.0 ± 2.3	4738 ± 880
	21.8	324 ± 39	42.2 ± 1.6	5530 ± 1000
	34.2	363 ± 23	53.3 ± 1.1	6702 ± 462
ODSA	24.5	293 ± 32	37.8 ± 2.9	4872 ± 786
	35.1	311 ± 32	46.2 ± 1.5	5381 ± 632
	40.2	314 ± 29	53.9 ± 1.5	5844 ± 735

were evidenced by both optical and thermal measurements.¹¹ Therefore, the observed changes in the tensile behavior of acylated wool should be primarily related to the reaction with DDSA or ODSA, which probably altered the internal balance of charge density and distribution, hydrogen bonding, and hydrophobic interactions of untreated wool.

Differential Scanning Calorimetry

Thermal measurements are a powerful tool for detecting fine structural changes of fibers. The DSC curves of untreated and acylated silk did not show significant changes in the shape and intensity of the prominent decomposition peak of silk fibroin, apart from a slight shift to high temperature (from 316 to 321°C; curves not shown), in good agreement with previously reported results.¹ On the other hand, the DSC profiles of acylated wool displayed interesting changes (Fig. 3).

Following acylation with DDSA or ODSA, the endothermic shift associated with the onset of the thermally induced molecular motion of keratins (T_g)¹⁹ started at lower temperature. The endotherm with peak temperature at 232°C for untreated wool, attributed to α -helix melting,²⁰ became broader; a shoulder appeared at lower temperature; and its intensity in the high-

temperature range decreased. These features suggest the presence of α -helical components with lower thermal stability.⁹ Acylation altered the inter- and intramolecular interactions in the amorphous regions, leading to an enhanced molecular motion of nonhydrogen-bonded chain segments. Moreover, the anhydride molecules diffused into the less laterally ordered α -crystallites induced local disordering of keratins' arrangement and lower thermal stability of these α -helical domains.²⁰ These fine structural changes may be

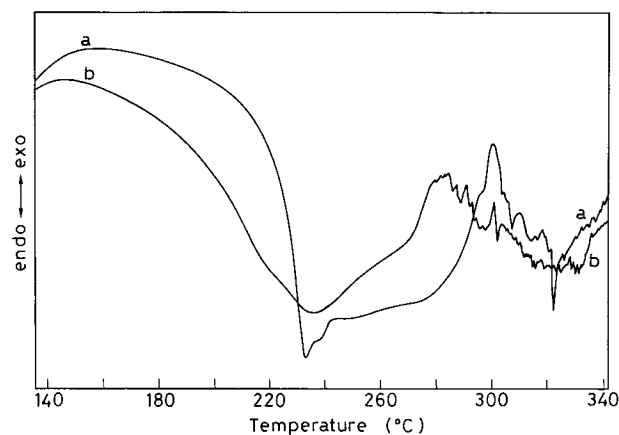


Figure 3 DSC curves of wool untreated (a) and acylated with DDSA with 34.2% weight gain (b).

closely related to the above-discussed changes in tensile properties of acylated wool.

Moisture Regain, Water Retention, and Water Repellency

The kinetics of moisture absorption of untreated and acylated silk and wool fibers is shown in Figures 4 and 5, respectively.

The initial rate of moisture absorption was slightly lower for acylated silk and wool, which tended toward equilibrium values significantly lower than those of the corresponding untreated samples (see Table III). These findings account for a reduced affinity toward water, probably attributed to reduction of available binding sites following reaction with the anhydrides, as well as to the shielding effect brought about by the long hydrophobic side chains. The difference in the initial rate of moisture absorption seems to suggest a possible barrier effect of the modifying agent toward moisture diffusion into the fibers.

The results of water retention and water drop absorption tests are listed in Table III. The values of water retention of silk acylated with DDSA or ODSA dramatically decreased, irrespective of weight gain and kind of acylating agent. A noticeable decrease of water retention was observed for acylated wool as well, although the extent was lower compared to that of silk. The water drop absorption test highlighted the high degree of water repellency attained by acylated fibers. The

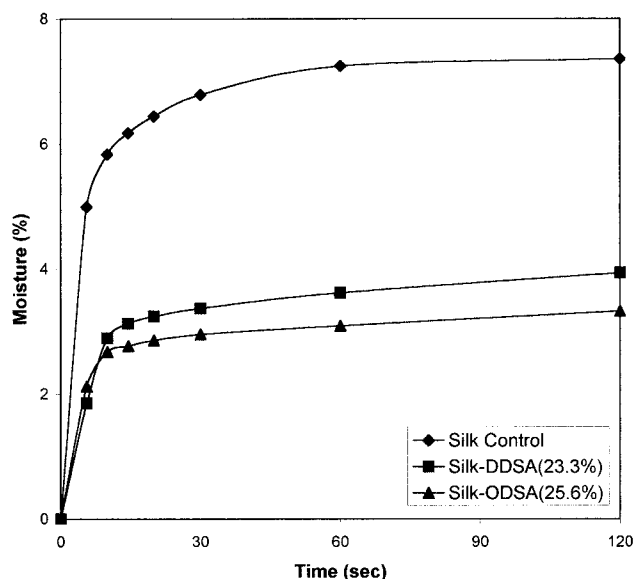


Figure 4 Kinetics of moisture absorption of untreated and acylated silk fibers at 20°C and 65% RH.

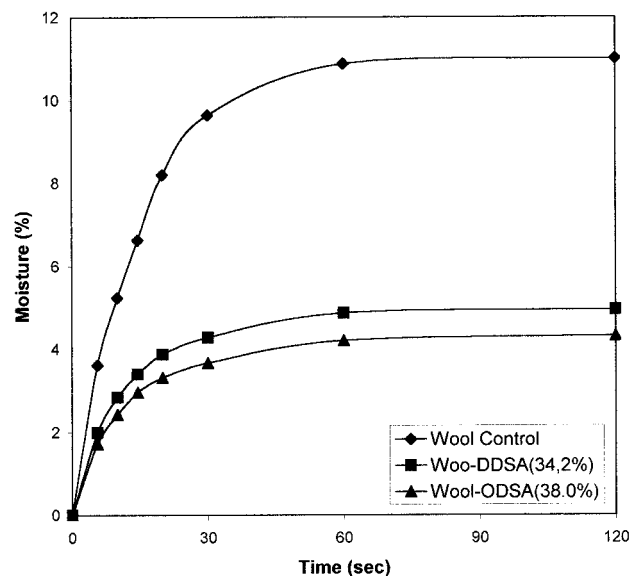


Figure 5 Kinetics of moisture absorption of untreated and acylated wool fibers at 20°C and 65% RH.

natural surface hydrophobicity of wool was enhanced by acylation. However, the most significant changes were observed for silk. Although untreated silk absorbed the water drop as soon as it was deposited onto its surface, the acylated samples displayed a high persistence of the drop, whose shape and volume remained unchanged for a very long period of time.

The preceding accumulated results are indicative of the extremely high degree of bulk and surface hydrophobicity induced by acylating silk and wool with DDSA or ODSA. This effect was particularly significant for silk, which behaved like a waterproofed material even at low weight gain of the acylating agent.

Surface Morphology

Surface morphology of acylated silk and wool was examined by SEM to highlight eventual local changes induced by reaction with the modifying agents. Figure 6 shows the SEM micrographs of acylated silk.

In striking contrast with the surface smoothness of untreated silk [Fig. 6(a)], fibers treated with both DDSA and ODSA showed the presence of variable amounts of foreign material deposited onto their surface. Low weight gain resulted in a finely dispersed deposition of particles tightly adherent to the fiber surface [Fig. 6(b)]. At higher weight gain, the deposit became thicker and the

Table III Moisture Regain, Water Retention, and Water Repellency of Silk and Wool Acylated with Dodecenylsuccinic (DDSA) and Octadecenylsuccinic (ODSA) Anhydrides

Sample	Weight Gain (%)	Moisture Regain (%)	Water Retention (%)	Water Repellency ^a
Silk Control	0	7.7	96.7	—
DDSA	3.9	4.4	45.6	+++
	8.4		44.4	
	13.6			
	23.3			
ODSA	6.1	3.8	55.3	+++
	14.5		43.5	
	22.9			
	25.6			
Wool Control	0	12.0	51.2	+
DDSA	12.8	5.7	34.1	+++
	26.6		38.1	
	34.2			
ODSA	24.5	5.0	30.2	+++
	38.0		25.7	
	48.3			

^a See the Experimental section for the symbol meaning.

distribution onto the fiber surface was rather inhomogeneous [Fig. 6(c)].

The morphological features of acylated wool fibers were slightly different (Fig. 7). Instead of covering the entire fiber surface, the deposit tended to accumulate at the scale edge [Fig. 7(b)]. The higher the weight gain, the higher the amount and inhomogeneity of the deposit [Fig. 7(c)].

On the basis of the SEM results it is reasonable to assume that the presence of these deposits may be considered responsible for the high degree of surface hydrophobicity displayed by acylated fibers. This phenomenon was much more evident for silk, which showed the presence of an almost continuous coating at high weight gain.

FTIR Spectroscopy

To confirm the nature of the surface deposit observed by SEM analysis, acylated silk and wool fibers were examined by IR spectroscopy, using the ATR technique. FTIR spectra of silk and wool are characterized by strong bands at above 3000 cm^{-1} (O—H and N—H stretching vibrations) and various amide bands in the range 1700–600

cm^{-1} , which are typical of polypeptides and proteins and allow their conformational characterization.²¹ The anhydride molecules are characterized by strong absorptions at 2950–2750 cm^{-1} (C—H stretching), 1775 cm^{-1} (C=O stretching), and 1200–900 cm^{-1} [C(O)—O—C(O) asymmetric stretching].

FTIR spectra of acylated silk and wool fibers showed changes in the spectral regions where the characteristic absorptions of the anhydride molecules fall (Figs. 8 and 9). With increasing weight gain, the intensity of the absorptions at 2920, 2852, 1780–1700, and 1170 cm^{-1} increased. These bands are clearly attributable to the presence of the anhydride molecules linked to the fibrous proteins. In particular, those at higher wavenumbers are ascribed to the hydrocarbon chain pendant, the shoulder at 1780–1700 cm^{-1} arises from the free carbonyl groups formed by opening of the anhydride ring, whereas that at 1170 cm^{-1} (C—O—C stretching) could be attributed to the formation of ester bonds following acylation of hydroxy amino acid residues. The characteristic amide bands of silk and wool remained unchanged, indicating that acylation did

not induce any appreciable structural and conformational change, at least from the spectroscopic point of view.

These results are of particular interest because they confirm that the most external fiber layers

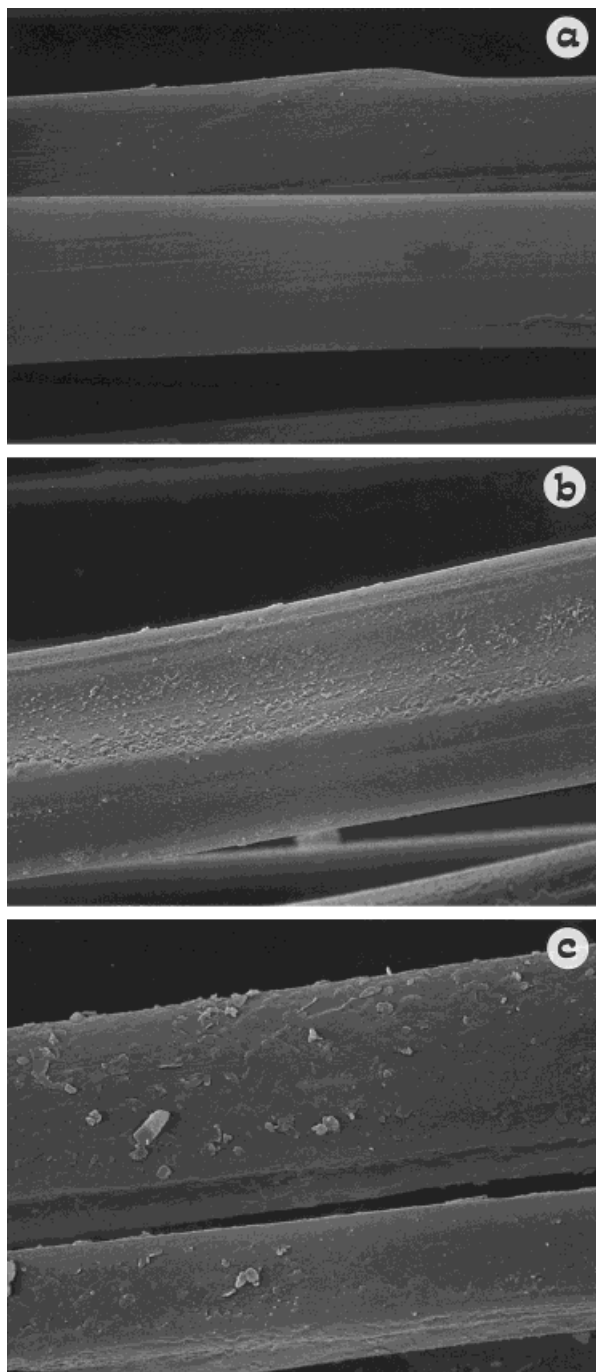


Figure 6 SEM photomicrographs of untreated and acylated silk fibers. (a) Control; (b) DDSA-silk with 3.9% weight gain; (c) ODSA-silk with 22.9% weight gain. Magnification $\times 2500$.

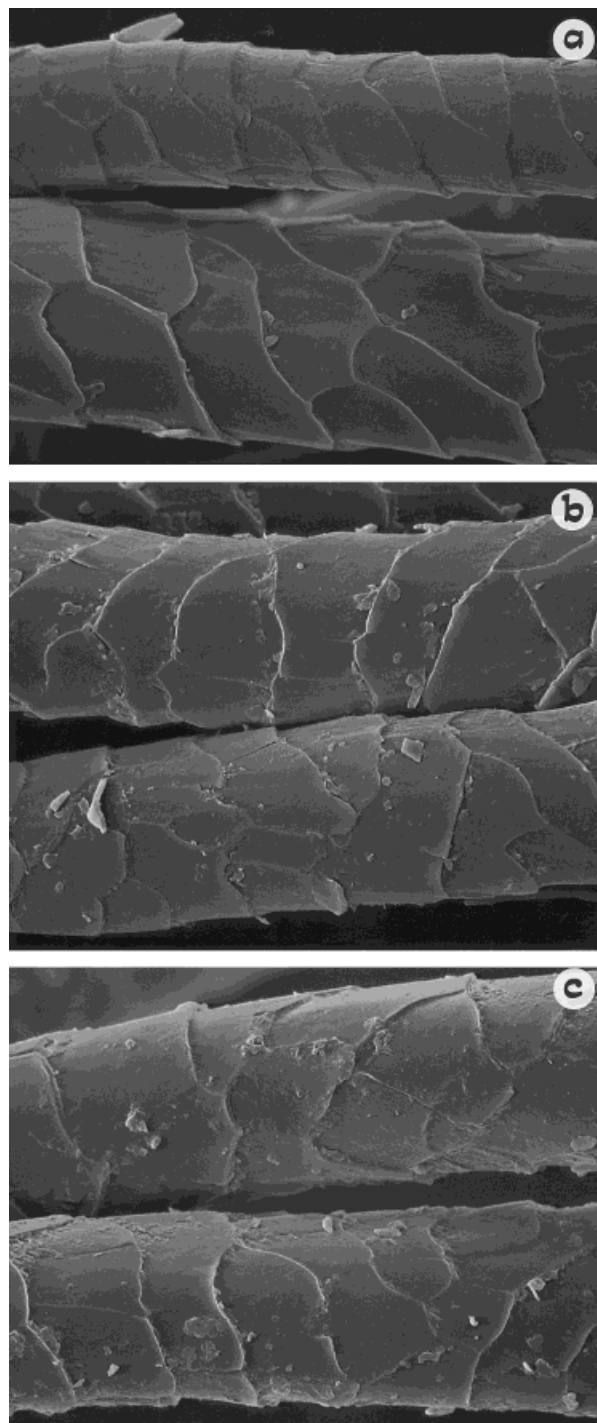


Figure 7 SEM photomicrographs of untreated and acylated wool fibers. (a) Control; (b) DDSA-wool with 12.8% weight gain; (c) ODSA-wool with 48.3% weight gain. Magnification $\times 2100$.

were chiefly involved in the reaction with the anhydrides, without excluding the possibility that acylation also occurred in the bulk (see DSC and

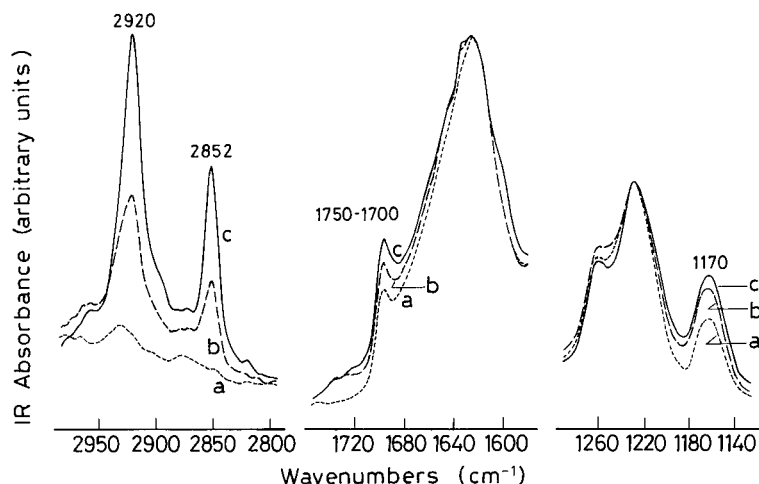


Figure 8 FTIR spectra of untreated and acylated silk fibers. (a) Control; (b) ODSA-silk with 6.1% weight gain; (c) ODSA-silk with 14.5% weight gain.

tensile measurements). This behavior may be attributed to the properties of the modifying agent (i.e., size and hydrophobicity of the hydrocarbon side chain), which probably limited its diffusion into the most internal fiber domains potentially reactive toward chemicals. The presence of the modifying agent in the most external fiber layer also accounts for the enhanced surface hydrophobicity displayed by acylated silk and wool.

CONCLUSIONS

Protein fibers were modified by reaction with acid anhydrides possessing a long hydrocarbon chain as the side chain. The reaction with these new

acylating agents conferred enhanced hydrophobicity on both silk and wool and allowed water-proofed fibers to be prepared. SEM and FTIR analyses showed that the most external fiber layers were particularly involved in the reaction, although bulk modification occurred as well, as indicated by tensile and DSC measurements.

Acylated fibers, especially silk, exhibited extensive surface coating, which became inhomogeneous at high weight gain. Although this aspect might be optimized by suitable changes of the reaction conditions, the results reported demonstrate that there is no real need to attain high levels of weight gain for the fibers to display a high degree of hydrophobicity. Fibers with good performance as water-repellent materials can be

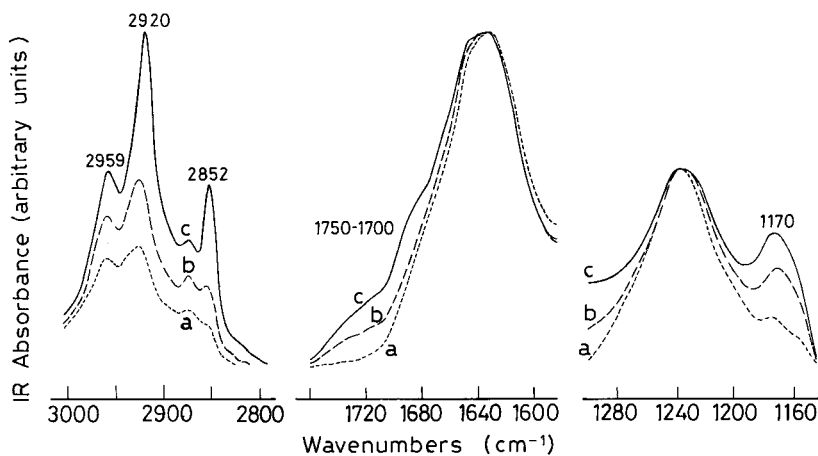


Figure 9 FTIR spectra of untreated and acylated wool fibers. (a) Control; (b) DDSA-wool with 12.8% weight gain; (c) DDSA-wool with 26.6% weight gain.

prepared by limiting the weight increase in the range of 3–6 wt %, which can be considered safe for keeping the intrinsic fiber properties unchanged (tensile properties, handle, luster, etc.). Moreover, to further confine the acylation reaction within the most external fiber layer it would be advisable to use the solvent with the lowest swelling effect toward the fibers.

Waterproofed fiber materials may find application not only for the production of specific clothing articles, but also in the field of technical textiles. The latter cover a wide range of applications (medical and health care, protection, furnishing, etc.), offering a real opportunity for expanding the consumption of natural protein fibers. Preliminary results obtained in our laboratory showed that protein fibers acylated with DDSA or ODSA are less prone to water staining and bacterial contamination than untreated ones. Studies in this field are in progress.

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REFERENCES

1. Tsukada, M.; Freddi, G. in *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 10, p. 7728.
2. MacLaren, J. A.; Milligan, B. *Wool Science: The Chemical Reactivity of Wool Fiber*; Science Press: Marricksville, NSW, 1981; pp. 135, 235.
3. Furuzono, T.; Ishihara, K.; Nakabayashi, N.; Tamada, Y. *Biomaterials* 2000, 21, 327.
4. Shiozaki, H.; Tanaka, Y. *J Seric Sci Jpn* 1980, 49, 307.
5. Shiozaki, H.; Tsukada, M.; Matsumura, M. *J Seric Sci Jpn* 1988, 57, 165.
6. Tsukada, M.; Gotoh, Y.; Freddi, G.; Shiozaki, H. *J Appl Polym Sci* 1992, 45, 1189.
7. Tsukada, M.; Gotoh, Y.; Freddi, G.; Shiozaki, H.; Ishikawa, H. *J Appl Polym Sci* 1992, 45, 1719.
8. Tsukada, M.; Gotoh, Y.; Shiozaki, H.; Freddi, G.; Crighton, J. S. *J Appl Polym Sci* 1994, 51, 345.
9. Tsukada, M.; Shiozaki, H.; Konda, A. *J Appl Polym Sci* 1990, 41, 1213.
10. Tsukada, M.; Gotoh, Y.; Romanò, M.; Ishikawa, H.; Shiozaki, H. *J Appl Polym Sci* 1992, 46, 1477.
11. Freddi, G.; Tsukada, M.; Shiozaki, H. *J Appl Polym Sci* 1999, 71, 1573.
12. Freddi, G.; Tsukada, M.; Kato, H.; Shiozaki, H. *J Appl Polym Sci* 1994, 52, 769.
13. Arai, T.; Freddi, G.; Colonna, G. M.; Scotti, E.; Boschi, A.; Murakami, R.; Tsukada, M. *J Appl Polym Sci* 2001, 80, 297.
14. Van Krevelen, D. W. *Properties of Polymers*; Elsevier Science: Amsterdam, 1990; p. 774.
15. Koenig, N. H. *J Appl Polym Sci* 1977, 21, 455.
16. Kitamura, A.; Sibamoto, A.; Demura, M. *J Seric Sci Jpn* 1990, 59, 43.
17. Vogt, B.; Althenhofen, U.; Zahn, H. *Textilveredlung* 1985, 20, 90.
18. Atkinson, J. C.; Speakman, J. B. *J Text Inst* 1964, 55, T433.
19. Menefee, E.; Yee, G. *Text Res J* 1965, 35, 801.
20. Arai, K.; Ishikawa, Sen-i Gakkaishi, M. 1983, 39, T14.
21. Krimm, S.; Bandekar, J. *Adv Protein Chem* 1986, 38, 181.