

Preparation of Water-Repellent Silks by a Reaction with Octadecenylsuccinic Anhydride

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ABSTRACT: Silk fibers and membranes were acylated with octadecenylsuccinic anhydride (ODSA) at 75°C for different times. Swelling [*N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)] and nonswelling (xylene) solvent media were used for the reaction. Silk membranes that reacted in DMF or DMSO displayed faster reaction kinetics and attained higher weight-gain values than fibers. The effect of the solvent on the reaction yield was in the following order: DMSO > DMF >> xylene. The Fourier transform infrared spectra of acylated silk samples showed the characteristic absorption bands of the anhydride at 2990, 2852, 1780–1700, and 1170 cm⁻¹. The intensity of the latter band, which increased linearly with the weight gain, was used as

a marker for evaluating the reaction kinetics of the samples acylated in the nonswelling medium. The moisture regain and water retention of silk fibers acylated with ODSA decreased significantly, regardless of the solvent system used. Accordingly, the water repellency increased. Acylation induced an increase in the thermal stability of the silk fibers and membranes. Fine particles adhering to the surfaces of the silk fibers acylated in xylene were detected by scanning electron microscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 324–332, 2003

Key words: water repellency; silk fiber; acylation; solvent effect

INTRODUCTION

Textile finishing aims at improving the visual perception, handle, and functional properties of clothing articles, including easy-care, antistatic, antisoil, anti-staining, and anticrease behavior.¹ Many finishing products are commercially available, but their durability is not always long enough to maintain the desired property for the entire life span of the product. The goal of more durable finishing treatments can be achieved if the finishing agent is chemically bound to the fiber substrate.

As a protein fiber, silk possesses many acidic, basic, and hydroxy reactive sites belonging to the constituent amino acid residues. These can be exploited for reactions with selected chemical agents, the aim of which is to attain an effective and specific modification of the fibrous substrate and to impart to it the desired properties and performance. The chemical modification of silk with epoxides, isocyanates, and acid anhydrides has extensively been investigated.² The permanent incorporation of these reagents into

the fibers can be exploited to modulate the properties and functional performance of silk.

The acylation of silk with dibasic acid anhydrides has proven to be effective in improving chemical and thermal resistance and crease recovery and in reducing photoyellowing, in addition to changing the dye affinity.^{3–8} Silk acylated with ethylenediaminetetraacetic dianhydride has been exploited for the preparation of fibers with enhanced antimicrobial activity because of its high efficiency in absorbing and binding metal cations.⁹ In a recent study, anhydride molecules with long hydrocarbon pendant groups were used for the acylation of silk and wool.¹⁰ The reaction with these new acylating agents conferred enhanced hydrophobicity on the fibers and allowed waterproofed materials to be prepared. The results showed that extensive loading of the fibers with the reactant was not necessary for attaining an optimum degree of hydrophobicity and that a weight increase of 3–6% could ensure a high level of water repellency while keeping the intrinsic properties unchanged.

This study deals with the acylation of silk fibers and membranes with octadecenylsuccinic anhydride (ODSA) with both swelling and nonswelling solvent media. The former are the conventional dipolar aprotic solvents, *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), which are often used for these kinds of reactions onto protein fibers. Xylene, an apolar hydrocarbon solvent, was chosen and tested as

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a nonswelling medium for the acylation of silk. The assumption was that if the reaction was confined to the most external fiber layers, the surface barrier against water absorption and diffusion would noticeably be enhanced, and this would avoid possible drawbacks brought about by excessive loading of the modifying agents in the bulk of the fiber. Fibers and membranes were used to test the influence of the substrate morphology on the kinetics and yield of the reaction. The results allow us to envision the possibility of developing a new category of silk-based clothing and technical articles for applications that require water repellency.

EXPERIMENTAL

Materials

Reagent-grade ODSA (catalog no. 41,469-5) was purchased from Sigma-Aldrich K. K. (Tokyo, Japan) and used without further purification. Degummed silk (*Bombyx mori*) fibers and membranes, the latter prepared with casting techniques described in detail elsewhere,¹¹ were acylated with 20% (w/v) ODSA at 75°C for various periods of time. DMF, DMSO, or xylene (a mixture of isomers) was used as a solvent medium for the acylation. The reaction system was connected to a reflux condenser and held at a constant temperature in a thermostatic bath. A material-to-liquor ratio of 1:40 was maintained. At the end of the reaction, samples were washed first with pure solvent and then with acetone at 55°C for 1 h, for the removal of any unreacted anhydride, and were finally rinsed with water.

Measurements

The weight gain of silk fibers and membranes was calculated from the increase in the weight of the original samples after acylation. IR spectroscopy analyses were performed with a Nicolet 150P spectrometer (Nicolet Instruments, Madison, WI) equipped with an attenuated total reflection (ATR) diamond cell (Specac). The kinetics of moisture absorption were determined by the weighing of oven-dried samples at different time intervals, under standard conditions of temperature (20°C) and humidity (65%), until equilibrium (24 h). The water retention was determined with the centrifugal method according to ASTM Standard D 2402-78. The water drop absorption test 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. According to the time (t) taken for the drop to be absorbed, the samples were classified as follows: $- = t < 5$ min, $+ = 5 < t < 15$ min, $++ = 15 < t < 60$ min, and $+++ = t > 60$ min. Heat-flow differential scanning calorimetry (DSC)

measurements were performed with a Mettler-Toledo DSC 821 system (Greifensee, Switzerland) at a heating rate of 10°C/min. The open aluminum cell was swept with N₂ gas during the analysis. The surface morphology was examined with a Stereoscan 440 (LEO Electronic Microscopy, Ltd., Cambridge, England) scanning electron microscope at a 10-kV acceleration voltage, after gold coating.

RESULTS AND DISCUSSION

Chemical reactivity

The chemical modification of silk fibers and membranes with ODSA was performed in different solvent systems. Besides the most conventional dipolar aprotic solvents, DMF and DMSO, an apolar hydrocarbon solvent, xylene, was used. Figure 1 shows the kinetics of the acylation of fibers and membranes in DMF and DMSO as a function of the reaction time. The weight gain of silk fibers increased rapidly within 30–90 min and then proceeded at a lower rate, tending to a plateau. Silk membranes showed sharper kinetics of acylation. Reaction times longer than 2 h caused extensive degradation and breakage of the membranes because of the harsh experimental conditions. Silk fibers and membranes acylated in xylene as the solvent, for different reaction times (until 7 h), did not show any significant change in the sample weight.

Silk membranes attained higher weight-gain values than fibers, regardless of the solvent used (DMF or DMSO). The reactivity of anhydrides toward silk depends on the number and accessibility of reactive sites. The latter are the amine and hydroxy groups of various amino acid side chains. Their concentration is supposed to be the same in fibers and membranes. However, it is reasonable to suppose that the accessibility may be drastically different. Fibers consist of a highly oriented fibrous texture, with fibroin chains held together by a dense network of interchain hydrogen bonds, not only in the crystalline regions but also in the amorphous regions; this limits the extent of longitudinal and transversal swelling when they are heated in a solvent.¹² However, membranes are isotropic in nature and more prone to swelling because of the lower degree of organization of the fibroin chains in the amorphous regions.¹¹ Therefore, the higher reactivity of ODSA toward silk membranes can reasonably be attributed to the easier diffusion of solvents and chemicals toward the available reactive sites.

The effect of the solvent on the yield of the reaction was in the following order: DMSO > DMF \gg xylene. The behavior of the two dipolar aprotic solvents is in good agreement with previously reported results.^{10,13} Because DMSO is able to induce an extent of volume swelling much higher than DMF, reagent diffusion occurred more efficiently and the reaction kinetics were

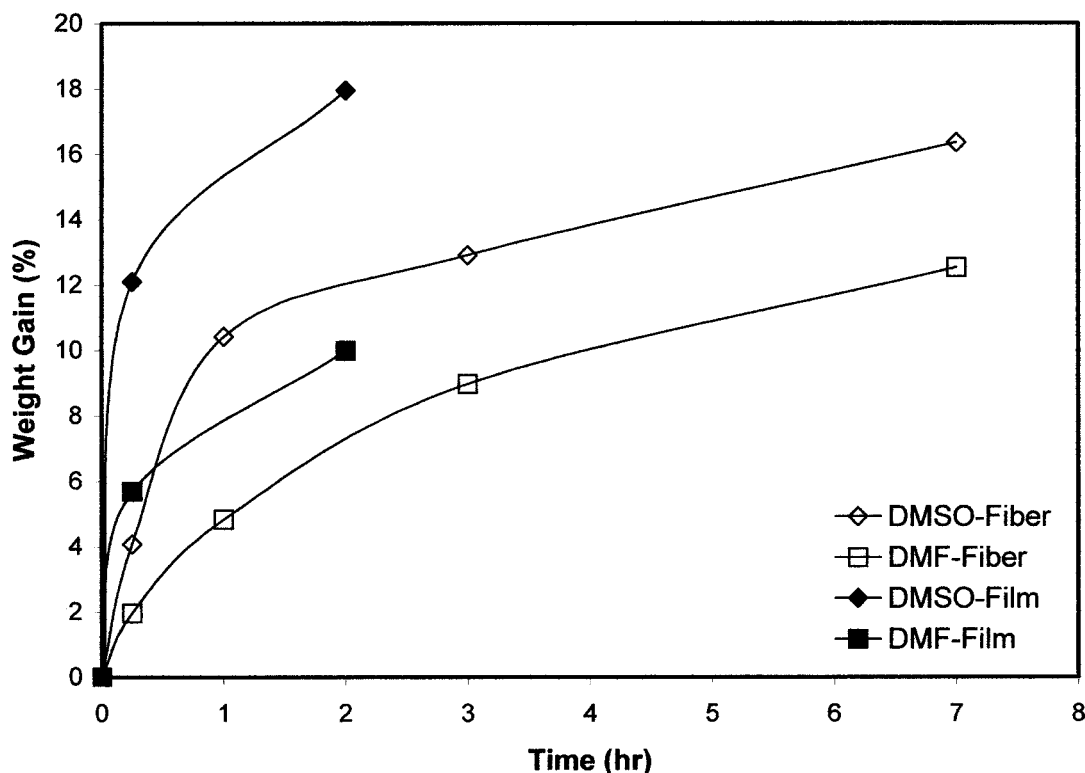


Figure 1 Weight gain versus the reaction time of silk fibers and membranes acylated with ODSA at 75°C in different swelling media (DMF or DMSO).

faster.¹⁴ Accordingly, the yield of the reaction attained higher values. Moreover, silk membranes displayed the same trend, despite the difference in substrate morphology. The very poor reaction yield with xylene can be attributed to the much lower ability of this solvent to induce fiber swelling. Like other apolar hydrocarbon solvents with similar solubility parameters, xylene can swell silk fibers to a very limited extent.¹⁴ It is, therefore, thought that the reaction in the bulk fiber and membrane probably occurred to a very limited extent.

Fourier transform infrared (FTIR) spectroscopy

The chemical modification of silk entails the incorporation into the protein substrate of chemical groups characteristic of the modifying agent. In a recent article, we show that silk and wool acylated with dibasic acid anhydrides carrying long hydrocarbon chains display new absorption bands at 2990, 2852, 1780–1700, and 1170 cm^{-1} , which are attributable to the anhydride molecules linked to the fibrous substrate.¹⁰ In particular, the bands at higher wave numbers are due to the hydrocarbon chain pendant, those at 1780–1700 cm^{-1} arise from the free carbonyl group formed by the opening of the anhydride ring, and the band at 1170 cm^{-1} (C—O—C stretching) can be attributed to the formation of ester bonds following acylation of hydroxy amino acid residues.

Figure 2 shows the FTIR spectra of silk fibers acylated with ODSA in swelling and nonswelling media. As expected, the conformationally sensitive amide bands of silk remained unchanged, regardless of the chemical modification, and this indicated that the fiber structure was not affected by the reaction.² Compared with the control sample, those acylated in DMSO displayed new prominent bands falling at the wave numbers typical of the anhydride. The same comments apply to silk fibers modified in DMF (spectra not shown). Interestingly, the sample modified in xylene showed the presence of the same bands, although the intensity was lower, indicating that the reaction effectively occurred also in this solvent. Because the spectra were measured with the ATR technique, the signal came from the most external fiber layers, which were likely more involved in the reaction in the nonswelling medium. The FTIR spectra of silk membranes (Fig. 3) showed very similar features, in good agreement with the results reported for fibers.

The intensity of the IR bands typical of the anhydride tended to increase with an increasing weight gain of the fibers acylated in DMF or DMSO. The band at 1170 cm^{-1} was chosen as a marker for the reaction, and the I_{1170}/I_{1230} ratio was calculated and plotted as a function of the weight gain (Fig. 4). The linearity of the relation between the two variables allowed us to extend the same approach to the samples reacted in

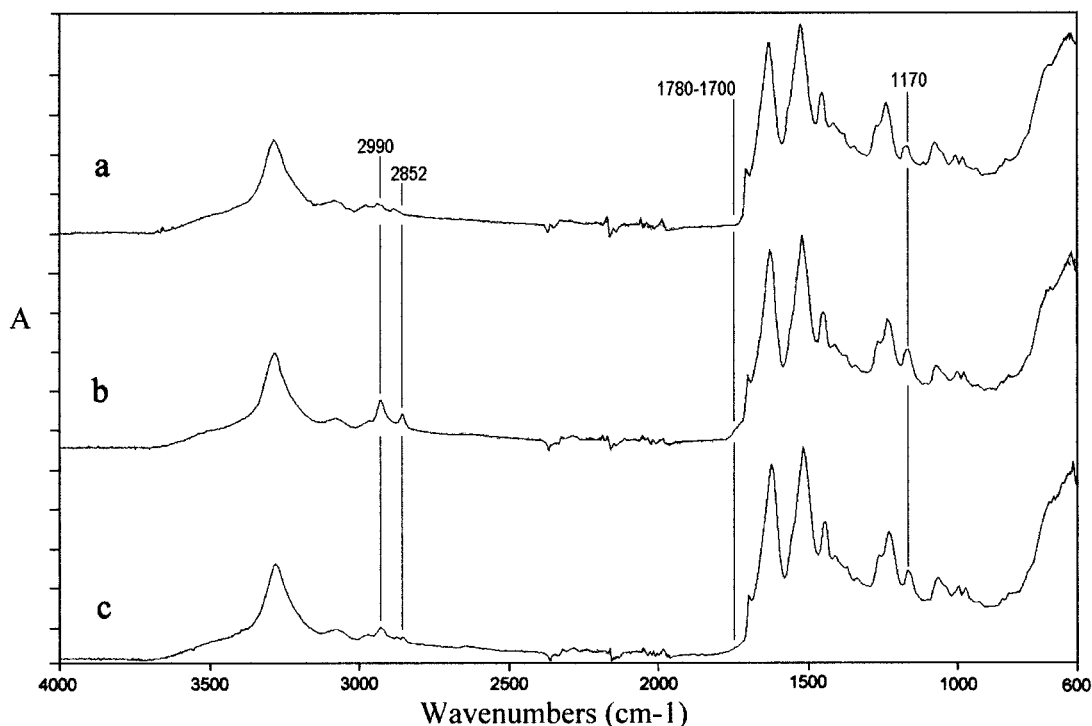


Figure 2 FTIR spectra of silk fibers untreated and acylated with ODSA: (a) control, (b) fibers acylated in DMSO at 75°C with a weight gain of 12.9%, and (c) fibers acylated in xylene for 2 h.

xylene to evaluate the reaction kinetics. Figure 5 shows the plot of the I_{1170}/I_{1230} ratio versus the reaction time of silk fibers and membranes in xylene. The IR index increased gradually with the reaction time for

silk membranes, whereas that of fibers rose sharply at very short reaction times and then decreased slightly, attaining a plateau. The difference in the texture and morphology of the silk fibers and membranes may

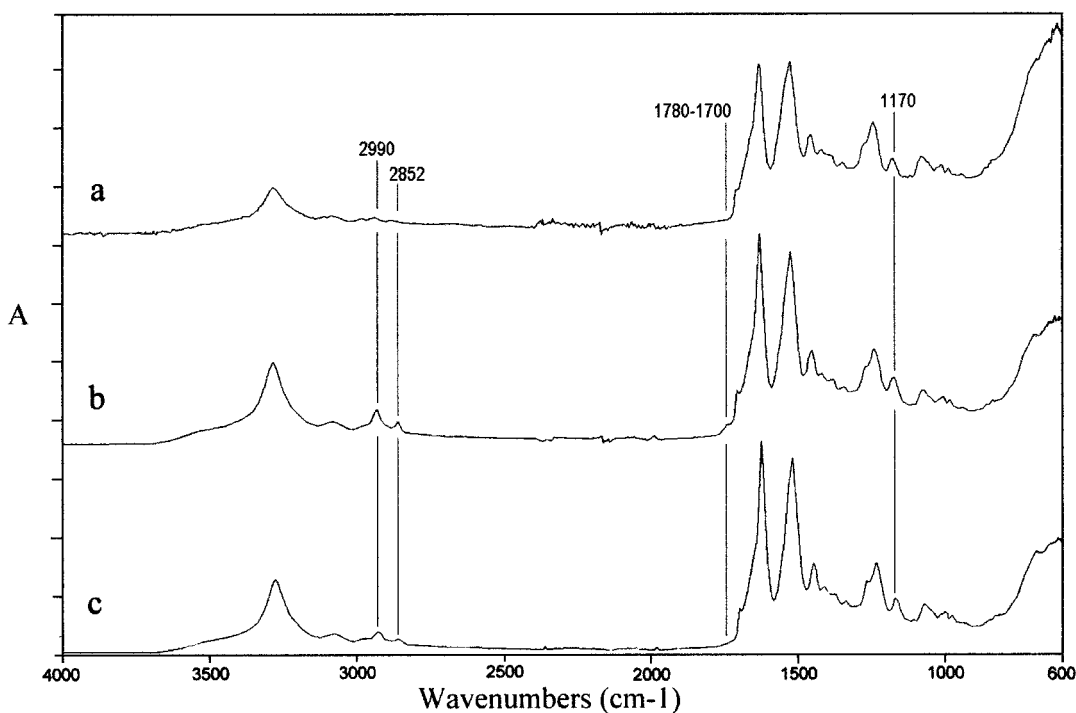


Figure 3 FTIR spectra of silk membranes untreated and acylated with ODSA: (a) control, (b) membranes acylated in DMSO at 75°C with a weight gain of 18.0%, and (c) membranes acylated in xylene for 30 min.

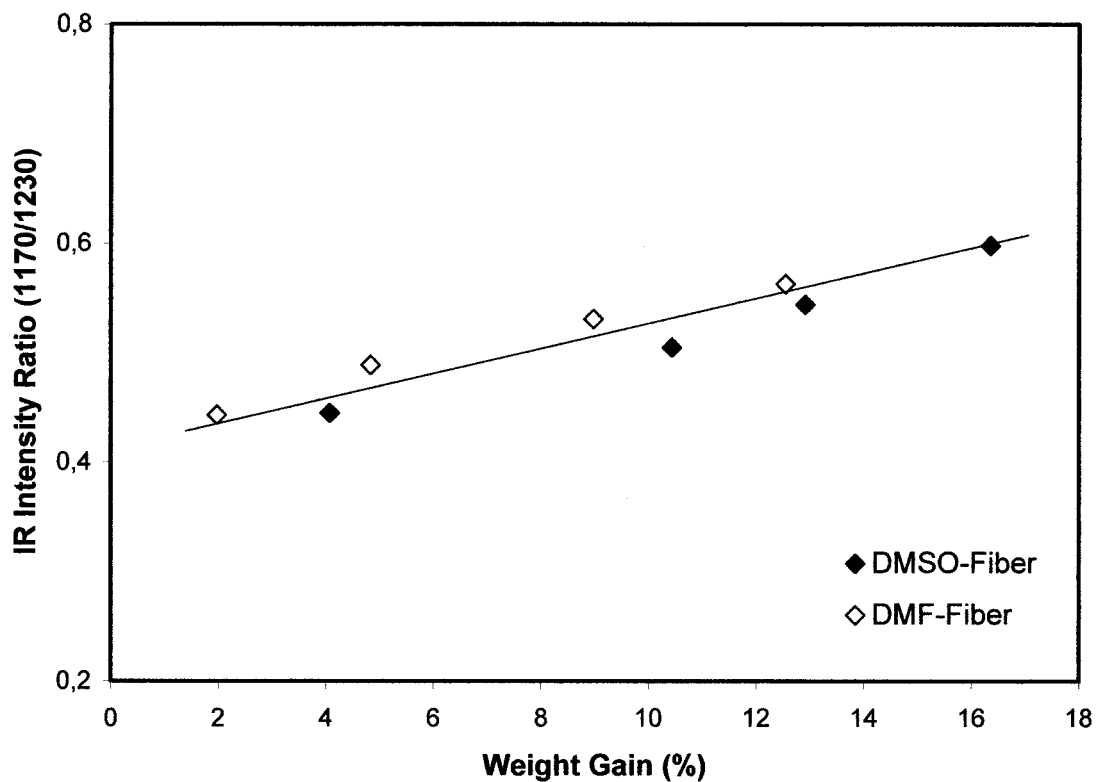


Figure 4 IR I_{1170}/I_{1230} ratio versus the weight gain of silk fibers acylated with ODSA in DMF and DMSO.

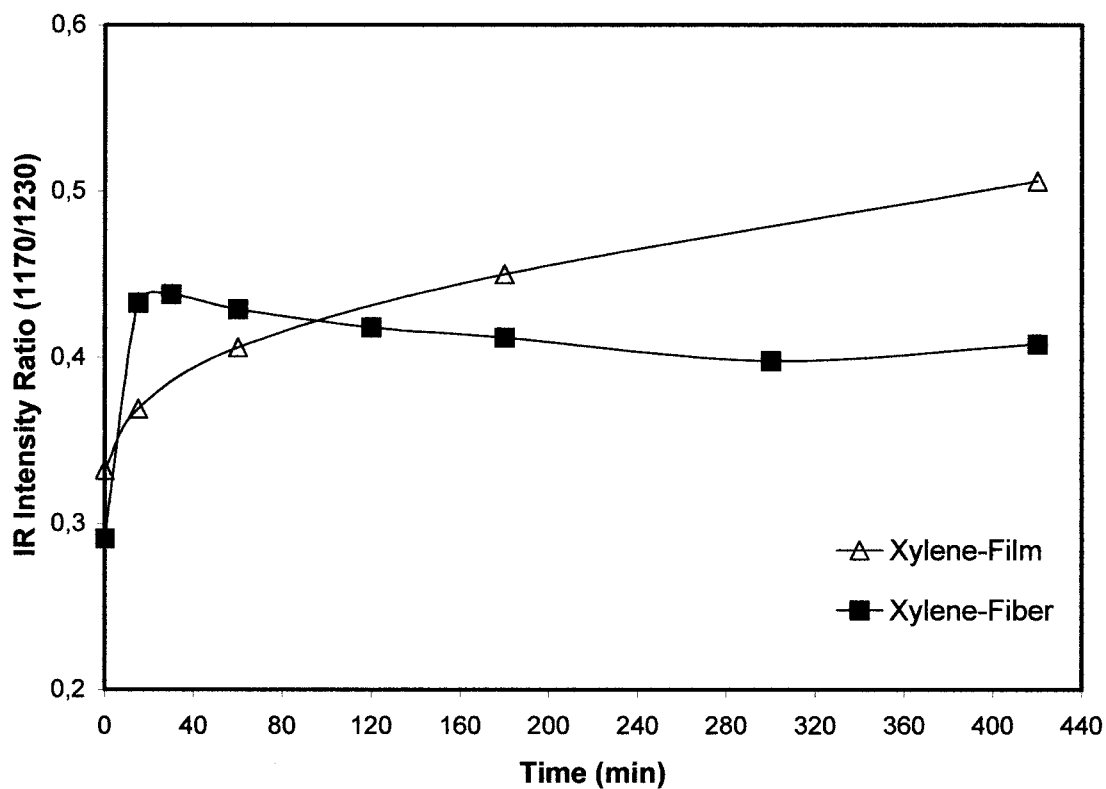


Figure 5 IR I_{1170}/I_{1230} ratio versus the treatment time of silk fibers and membranes acylated with ODSA in xylene.

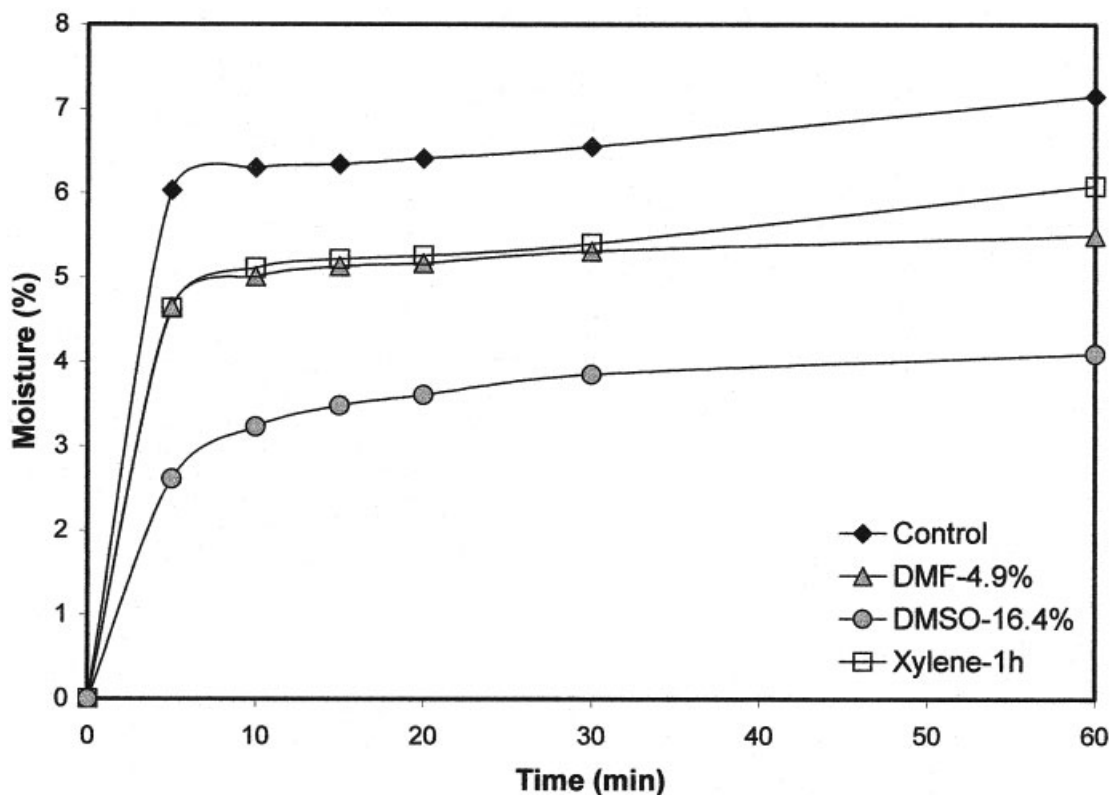


Figure 6 Kinetics of the moisture absorption of silk fibers untreated and acylated with ODSA in different solvent media.

account for the different trends of the two curves. Prolonging the reaction time could favor swelling and diffusion of the modifying agent into the membranes. However, the same could not happen for the fibers because of the constraints caused by the close and dense fiber structure.

Moisture regain, water retention, and water repellency

The introduction of a long hydrocarbon chain by acylation is thought to enhance the hydrophobicity of silk fibers.¹⁰ This property was measured with a series of specific tests. Figure 6 shows the kinetics of the moisture absorption of untreated and acylated silk fibers. The latter displayed lower rates of initial moisture uptake and tended to attain lower levels of equilibrium moisture regain than the control sample (Table I). Both the rate of moisture absorption and equilibrium moisture regain decreased with an increasing weight gain of silk fibers acylated in swelling media.

With reference to the silk fibers acylated in xylene, it is interesting to note that the curve of moisture absorption after 1 h of reaction with ODSA overlapped that of the sample acylated in DMF with about a 5% weight gain; this suggests that a remarkably high degree of hydrophobicity was attained, even with a very limited extent of modification in terms of the weight increase. The values of the equilibrium moisture re-

gain were lower for short reaction times and then tended to increase, gradually approaching that of the control sample (Table I). IR results (Fig. 5) showed that reaction times longer than 1–2 h did not significantly increase the yield of acylation. Therefore, it is reasonable to consider that the permanence of silk in xylene for longer times probably caused negative side effects on the reaction yield and fiber performance.

The water retention of the acylated silk fibers overall decreased significantly, regardless of the solvent used (Table I). The extent of decrease was higher for the samples acylated in swelling media and was dependent on the weight gain, suggesting the contribution of both surface and bulk hydrophobicity. The samples acylated in xylene showed a similar trend, but the amount of water retained was higher, probably because the bulk of the material was only slightly modified and the hydrophobicity of the fibers mostly depended on the shielding effect of the acylating agent present at the surface level, which acted as a barrier against water diffusion during the wetting step. The longer the reaction time was, the more water was retained, in good agreement with the moisture regain data.

The water repellency tests highlighted the high degree of surface hydrophobicity attained by silk fibers acylated with ODSA. The samples acylated in xylene performed better than the others, even after very short

TABLE I
Moisture Regain, Water Retention, and Water Repellency of Silk Fibers Acylated with ODSA in Different Solvent Systems

Sample	Weight gain (%)	Treatment time (min)	Moisture regain (%)	Water retention (%)	Water repellency ^a
Silk control	0		8.0	85.7	—
DMF	4.8	60	6.2	48.8	+
	8.9	180	6.5	36.2	+
	12.5	420	—	35.4	++
DMSO	10.4	60	—	40.1	++
	12.9	180	5.2	36.7	+++
	16.4	420	4.3	34.3	+++
Xylene	—	30	6.1	51.3	+++
	—	60	6.2	51.3	+++
	—	120	5.9	45.9	+++
	—	180	7.3	49.8	+++
	—	300	—	54.7	+++
	—	420	7.6	56.2	+++

^a — = < 5 min; + = 5 < t < 15 min; ++ = 15 < t < 60 min; +++ = t > 60 min.

reaction times, whereas weight-gain values higher than 10–12% were needed for the samples acylated in DMF or DMSO for the same level of performance to be reached. These results draw the attention to the superior effectiveness of a selective surface modification

over that occurring in the bulk material. The shielding effect of the long hydrocarbon chains inserted within the most external layers of silk fibers allowed the material to contrast the diffusion of water and conferred a noticeably waterproof performance on them.

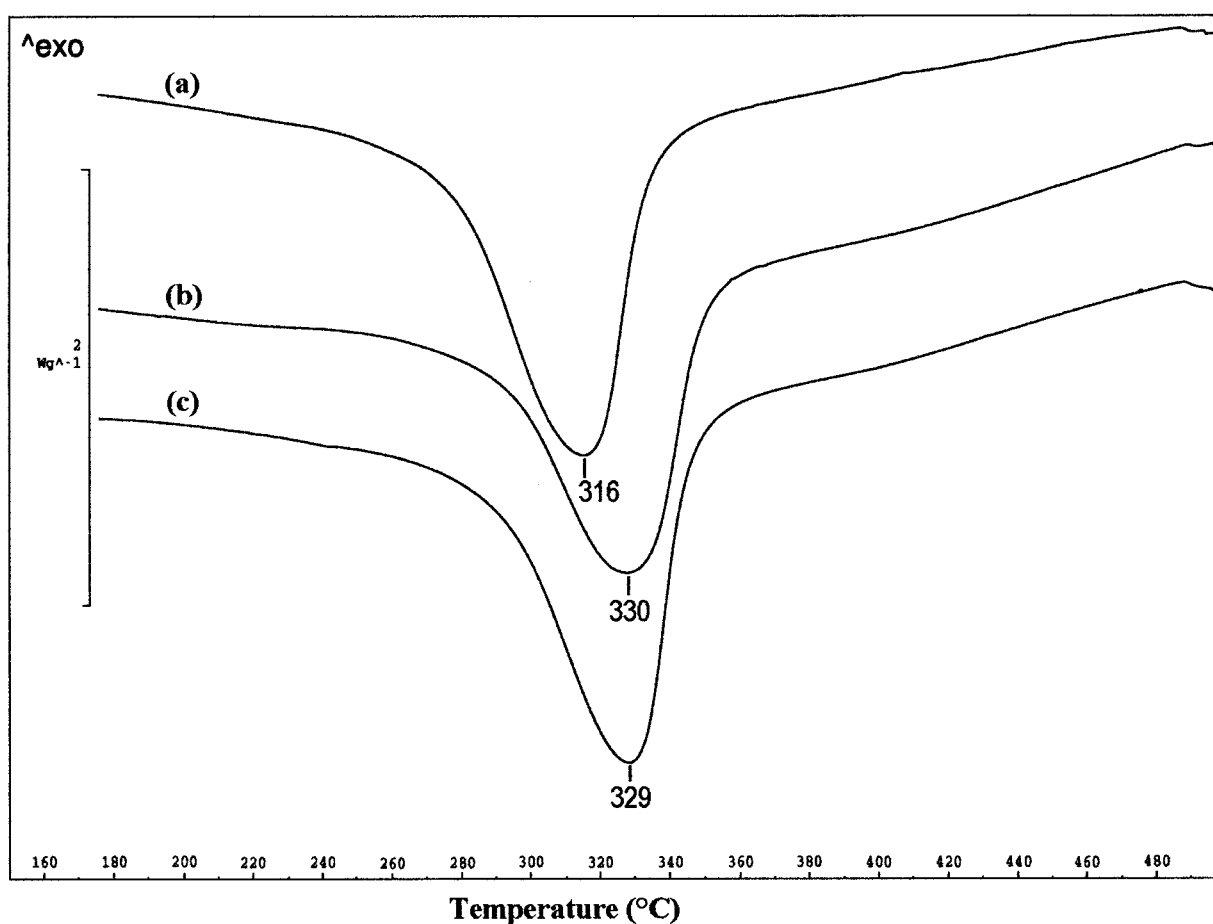


Figure 7 DSC curves of silk fibers untreated and acylated with ODSA: (a) control, (b) fibers acylated in DMSO at 75°C with a weight gain of 16.4%, and (c) fibers acylated in xylene for 3 h.

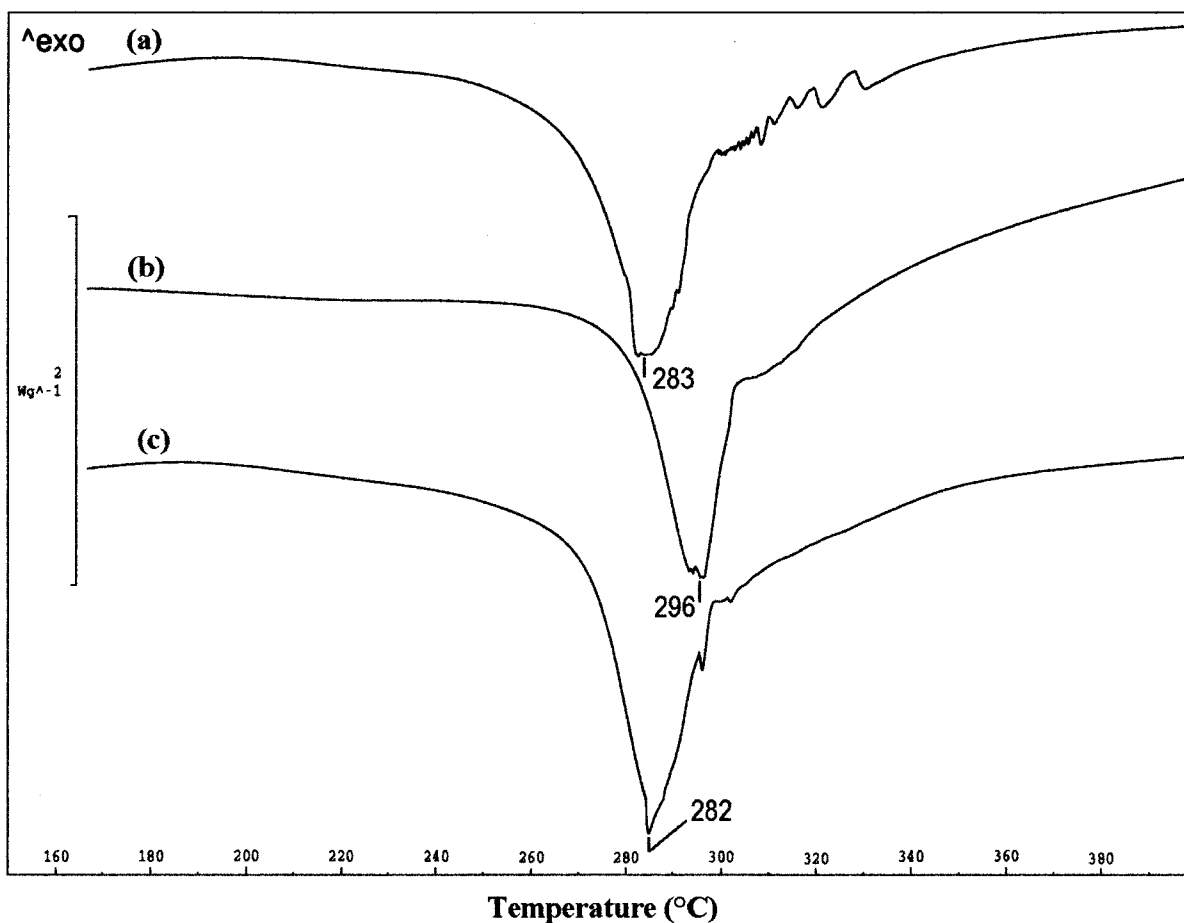


Figure 8 DSC curves of silk membranes untreated and acylated with ODSA: (a) control, (b) membranes acylated in DMSO at 75°C with a weight gain of 18.0%, and (c) membranes acylated in xylene for 3 h.

DSC

The thermal behavior of silk acylated with ODSA in swelling and nonswelling media was studied by DSC. DSC profiles of silk fibers are shown in Figure 7. The common feature of acylated silk fibers was an upward shift of about 15°C of the prominent endothermic peak appearing over 300°C, which corresponded to the melting and thermal degradation of oriented silk fibroin with a β -sheet crystalline structure.¹⁵ This trend was displayed by all the acylated samples, regardless of the weight gain and solvent used.

Like the fibers, silk membranes acylated in swelling media melted and decomposed at 296°C (Fig. 8), a higher temperature than that of the untreated membrane, which showed an endothermic peak at 283°C, which is typical of nonoriented silk fibroin with a β -sheet crystalline structure.¹¹ Membranes acylated in xylene did not show any shift of the peak endotherm, which tended to broaden in the high-temperature range.

These observations suggest that the acylation of silk fibers and membranes with ODSA conferred improved thermal stability on the resulting materials.

Surface morphology

The surface morphology of silk fibers acylated with ODSA in different solvents was examined by scanning electron microscopy. The surface of the fibers acylated in DMF or ODSA was as smooth as that of the untreated sample (picture not shown). No significant morphological changes were observed. However, the use of xylene resulted in the presence of finely dispersed particles tightly adhering to the surfaces of the fibers (Fig. 9). This feature characterized all the samples reacted in the nonswelling solvent system. It is reasonable to assume that the poorly swollen fibers did not allow effective penetration of the reagents into the bulk, and the reaction mainly occurred in the most external fiber layers, resulting in the surface deposition of foreign matters. Their presence may also account for the high degree of surface hydrophobicity displayed by these samples.

CONCLUSIONS

The chemical modification of silk fibers and membranes with ODSA, an acylating agent possessing a

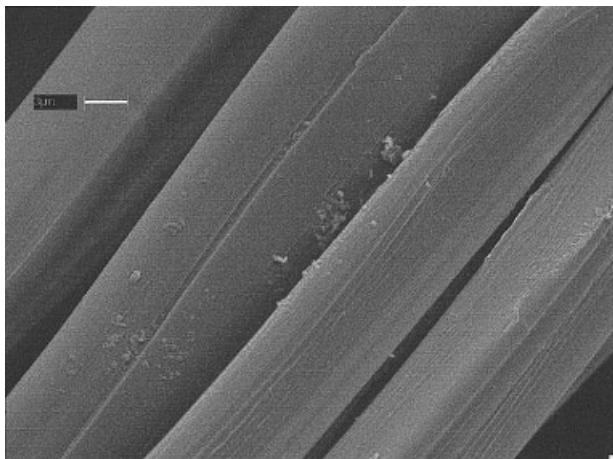


Figure 9 Scanning electron microscopy photograph of silk fibers acylated with ODSA in xylene for 2 h.

long hydrocarbon chain, resulted in silk materials with enhanced hydrophobicity. Evidence of the reaction was obtained with FTIR measurements, which showed the effective incorporation of the acylating agent in fibers and membranes treated in both swelling and nonswelling media. The latter solvent system was particularly attractive because the reaction was confined to the most external layers of the substrate; this avoided possible drawbacks related to excessive loading of the acylating agent in the bulk.

The reaction of ODSA with silk fibers can be exploited for the preparation of effective waterproofed textiles, whereas silk membranes with enhanced hy-

drophobicity can be applied as substrates for the adhesion and growth of living cells, with the aim of preparing biomedical devices for tissue regeneration.

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