Modification of Cellulose Fiber with Silk Sericin

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ABSTRACT: Cellulose fiber surface was modified with silk sericin (or simply, sericin). Sericin fixation on cellulose was confirmed by environmental scanning electron microscopy (ESEM) and Fourier transform infrared spectrophotometry–attenuated total reflectance (FTIR-ATR). Sericin content in finished samples was estimated by dyeing treated fabrics with an acid dye, Supranol Bordeaux B, and determining *K/S* and *L* values of the dyed fabrics. The treated fabrics were tested for free formaldehyde content, crease recovery, tensile strength, electrical resistance, water retention, and biocidal activity. From ESEM and FTIR-ATR results, it was found that sericin coated onto cotton surfaces as a film. Increasing sericin content in the finishing solution increased the amount of coated sericin, and a greater depth of color in dyed samples and reduced free formaldehyde content in treated samples were observed. The sericin content in samples was found to have a negligible influence on tensile strength and crease recovery angle. With increasing sericin content, electrical resistivity of the samples dramatically decreased and water retention increased, indicating that sericin-treated fabrics may be comfortable to wear because of its maintenance of moisture balance with respect to human skin. Because cotton textile coated with sericin exhibited low formaldehyde content and no biocidal activity against *Klebsiella pneumoniae* and *Staphylococcus aureus*, the fabric may reduce skin irritation and disturbance of physiological skin flora arising from textile contact. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1421–1428, 2005

Key words: surface modification; sericin; biomaterials; cellulose; dyes/pigments

INTRODUCTION

Atopic dermatitis, a chronic inflammatory skin disease, has undergone a widespread increase in recent years, especially in children and people with sensitive skin. The disease is generated by numerous factors, such as food, inhalant allergy, climate, dust, dust mites, and chemical and physical irritants. Contacting skin with clothes can aggravate atopic dermatitis, possibly from residual detergents, formaldehyde released from finishing agents, and harsh clothes (particularly wool and synthetic fibers). Wearing clothes of smooth surface is one method of avoiding the disease because it has been established that special cloths made from silk improve atopic dermatitis in children.[1]

Sericin, produced by silkworms, primarily contains hydroxyl, carboxyl, and amino groups, and its blend or copolymers show special reactivities and properties. Today, sericin is widely exploited in many applications such as cosmetics, membranes, supports for immobilized enzyme, supplementary food, medical materials, and functional fibers.[2] Dietary absorption of sericin elevates intestinal adsorption of iron, zinc, calcium, and magnesium.[3] Sericin exhibits antibacterial and antioxidant properties in cigarette filters.[4] It has been found to exert a photoprotective effect against ultraviolet-B (UVB)–induced tumor promotion and damage to the skin.[5] In natural and synthetic fibers, sericin is used to improve moisture absorbency and impart a soft hand to fabrics.[6–8] Moreover, it has been shown to prevent abrasive skin injuries and rashes, and to enhance crease recoverability, tear resistance, and dyeability to direct dye.[9–11] As mentioned, sericin has been used for textile finishing in numerous investigations, although reactions during the finishing process have not yet been elucidated.

Preparation of clinical textiles that are effective against skin irritation is essential. Comfortable clothes, characterized by high moisture sorption and smooth surface, and are free of formaldehyde, are designed to ameliorate inflammatory reactions. Sericin was the investigative focus of interest to be used for modifying

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TABLE I
Compositions in Finishing Solution

Sample code	Composition in finishing solution			
	Sericin (g/L)	DMDHEU (mL/L)	Magnesium chloride (g/L)	60% Acetic acid (mL/L)
UT	—	—	—	—
Blank	—	40.0	10.0	1.0
2.5	2.5	40.0	10.0	1.0
5	5.0	40.0	10.0	1.0
10	10.0	40.0	10.0	1.0
25	25.0	40.0	10.0	1.0
50	50.0	40.0	10.0	1.0

cellulose fiber surface, not only because of its available properties and reactivities, but also because of the benefits of using waste sericin from silk industries.

In this investigation, sericin was used as a finishing agent with the commonly used system for cotton processing, that is, the methylol derivative of ethyleneurea/magnesium chloride. The presence of sericin and its reactivity on cotton fabric surface were analyzed using Fourier transform infrared spectrophotometry–attenuated total reflectance (FTIR-ATR), environmental scanning electron microscopy (ESEM), and dyeing with Supranol Bordeaux B acid dye. Effects of sericin content on fabric properties, such as crease recovery angle, tensile strength, water retention, electrical resistivity, and free-formaldehyde and biocidal activity of treated fabrics, were studied.

EXPERIMENTAL

Materials

Twill-woven, mercerized, and bleached cotton fabrics (40 × 30 cm) were used. Magnesium chloride, 33.5% formaldehyde solution (Merck, Darmstadt, Germany), 96% acetic acid, ammonium acetate, glacial acetic acid (Riedel-de Haën, Seelze, Germany), and acetylacetone (Fluka Chemie, Buchs, Switzerland) were all analytical grade. Supranol Bordeaux B acid dye (DyStar, Frankfurt, Germany) *N*,*N*′-dimethylol-4,5-dihydroxyethylene-urea (DMDHEU-based reagent) (Arkofix NDF, Clariant Switzerland, Muttenz, Switzerland), and silk sericin powder with average molecular weight of 20,000 (Seiren, Tokyo, Japan) were used in the investigation.

Methods

Preparation of treated fabrics

Solutions for fabric finishing were prepared according to the compositions in Table I.

Cotton fabrics were padded through finishing solutions on a laboratory padder (Werner Mathis AG, Zurich, Switzerland), squeezed under a pressure of 2.6 bar, and run at a speed of 2.0 m/min (pickup 68–70%). Fabrics were then dried and cured in a laboratory dryer (Werner Mathis lab dryer) according to the manufacturer's recommendation. Each treated fabric was cut in two halves, one of which was retained without further treatment, whereas another was washed with distilled water at 70°C for 30 min (liquor ratio of 1 : 50).

Analysis of sericin fixation on fabric surface

Analysis of fabric surface was performed on selected chemically treated samples using environmental scanning electron microscopy (ESEM; FEI/Philips, Acht, The Netherlands) and a Vector 22 FTIR spectrophotometer (Bruker, Darmstadt, Germany), equipped with attenuated total reflectance (ATR; MIRacle™, PIKE Technologies, Madison, WI). DMDHEU-based reagent, in the original form of a viscous liquid, was padded directly on KBr pellet and characterized using FTIR.

Determination of sericin content

Samples were dyed with 2.5% [on weight of fabric (owf)] solution of Supranol Bordeaux B solution at a liquor ratio of 1 : 50, at pH 3.1 (in acetic acid), for 30 min at 60°C. *L*-values of the samples were measured using a tristimulus colorimeter (sample diameter 10 mm; Chroma-Meter CR 210, Konica Minolta GmbH, Unterföhring, Germany). K/S values were calculated according to the Kubelka–Munk function from reflectances of dyed samples measured at 541 nm [SP8-100 double-beam spectrophotometer, diffuse reflectance sphere 0°/d; Philips, Inc., Melville, NY (formerly Pye Unicam)]. Change in sericin content on the sample surface was evaluated using $(K/S)_{corr}$ from the following equation:

$$\left(\frac{K}{S}\right)_{corr} = \left(\frac{K}{S}\right)_{sample} - \left(\frac{K}{S}\right)_{blank} \quad (1)$$

Determination of free formaldehyde content

Levels of free formaldehyde from freshly treated samples were determined according to LAW112.[12] A 1-g sample was extracted with 100 mL of distilled water in a closed bottle, at 40°C for 1 h. The extract was then filtered, after which a 5-mL aliquot was added to 5 mL of reagent prepared from 15% (w/v) ammonium acetate, 0.2% (v/v) acetylacetone, and 0.3% (v/v) glacial acetic acid; the mixed solution was kept at 40°C for 30 min. Absorbance of solutions was then spectrometrically measured at 412 nm. The formaldehyde content was obtained using a calibration curve constructed with defined amounts of formaldehyde.

Determination of physical properties of finished fabrics

Physical properties of tensile strength, crease recovery angle, electrical resistivity, and water retention of unwashed and washed samples were determined. A set of identical determinations was conducted on untreated samples, which were collectively treated as control. All samples were conditioned in a standard atmosphere of 65% relative humidity at 20°C for a minimum of 48 h before determination.

Tensile strength of 20 warp yarns from each sample was measured, according to DIN 53834, using a universal strength tester (Instron TM-M, Instron Corp., Canton, MA): 7 cm of gauge length, 5 cN of pretension, force of 10 N, and load speed of 20 cm/min were applied.

Crease recovery angle (CRA) of the samples was performed according to DIN 53890 at 5 and 30 min. CRA of specimens in warp (W) and fill (F) directions was measured separately; the CRA°(W + F) value of specimens was evaluated.

Electrical resistance of treated samples was measured using a teraohmmeter (7 KA 1100; Siemens AG, Karlsruhe, Germany). The samples were placed between two plate electrodes of 11 cm diameter, and the electrical resistivities were measured at a constant voltage of 100 V.

Water retention values of samples were determined according to DIN 53814. Two specimens (4 × 4 cm) of each sample were immersed in water for 24 h, after which excess water from adsorption was extracted by centrifugation at 2790 rpm for 20 min. Moist samples were weighed, dried in an oven at 105°C for 4 h, and further dried in a phosphorus pentoxide desiccator for 1 week, after which the samples were reweighed. Water retention value (*WRV*, %) was calculated from the following equation:

$$WRV = \frac{W_m - W_D}{W_D} \times 100 \qquad (2)$$

where W_M is weight of moist fabric (g) and W_D is weight of dried fabric (g).

Assessment of biocidal activities

The assessment of biocidal activities was performed according to AATCC test method 147-1998 (Parallel Streak Method), with *Klebsiella pneumoniae* and *Staphylococcus aureus* as test organisms. Sample specimens (25 width) were placed on nutrient agar; diluted cultures of *K. pneumoniae* and *S. aureus* were streaked in three parallel lines. The cultures were incubated for 24 and 48 h. The intensity of bacterial growth was evaluated.

RESULTS AND DISCUSSION

Fixation of sericin on fabric surface

ESEM micrographs in Figure 1(a)–(d) show images of washed samples treated with DMDHEU alone, and combinations of DMDHEU and sericin (10, 25 and 50 g/L), respectively. It can clearly be seen that sericin, coated as a film onto the fiber surface, and the film thickness increase with increasing amounts of sericin in the finishing solution. Therefore, this outcome provides evidence of the chemical fixation of sericin onto the fiber surface.

Figure 2 shows FTIR-ATR spectra of untreated and treated samples. The patterns of samples spectra changed when different recipes of finishing solution were used. The absorption band at 1706 cm^{-1} (peak I) in Figure 2(b) is observed for the sample treated with DMDHEU-based reagent alone. In comparison to DMDHEU-based reagent spectra, given in Figure 3, this band corresponds to ν(C=O) in DMDHEU. A slight shift of this band to 1695 cm^{-1} is observed for samples finished with a combination of DMDHEU and various amounts of sericin, whose intensities are independent of the amount of sericin, and so this band corresponds to ν(C=O) in DMDHEU. Reactions between *N*-methylol groups in DMDHEU and amino groups in the sericin main chain may cause this band shift. The small shoulder of the absorption band at approximately 1745 cm^{-1} (peak III) is more obvious when 50 g/L sericin is used, possibly attributed to the ν(C=O) of ester group generated from the reaction between *N*-methylol groups in DMDHEU and carboxylic groups in the side chain of sericin (with approximately 20 mol % of constituted aspartic acid and glutamic acid together). With increasing sericin on the fabric surface, absorption bands at 1652 (peak II), 1540–1520 (peak IV), and 1457 cm^{-1} (peak V) corresponding to ν(C=O), δ(N—H), and δ(C—H), respectively, show greater intensities. From FTIR-ATR results, the reactions occurring in this investigation are similar to those between DMDHEU and carboxylic acid group or amino group in aspartic acid and glutamic acid in the presence of aluminum sulfate, reported earlier.[12]

Sericin was fixed onto the cotton fabric surface by chemical bindings of reactions between sericin, DMDHEU, and cellulose. The possible reactions are schematically shown in eqs. (3) and (4) [Fig. 4(a) and (b), respectively].

Interestingly, free *N*-methylol group reacted to carboxylic acid in the side group or amino group backbone of sericin, instead of being released as formaldehyde, as in the proposed reaction in eq. (5) (Fig. 5).[13–15] Therefore, sericin plays an important role in the de-

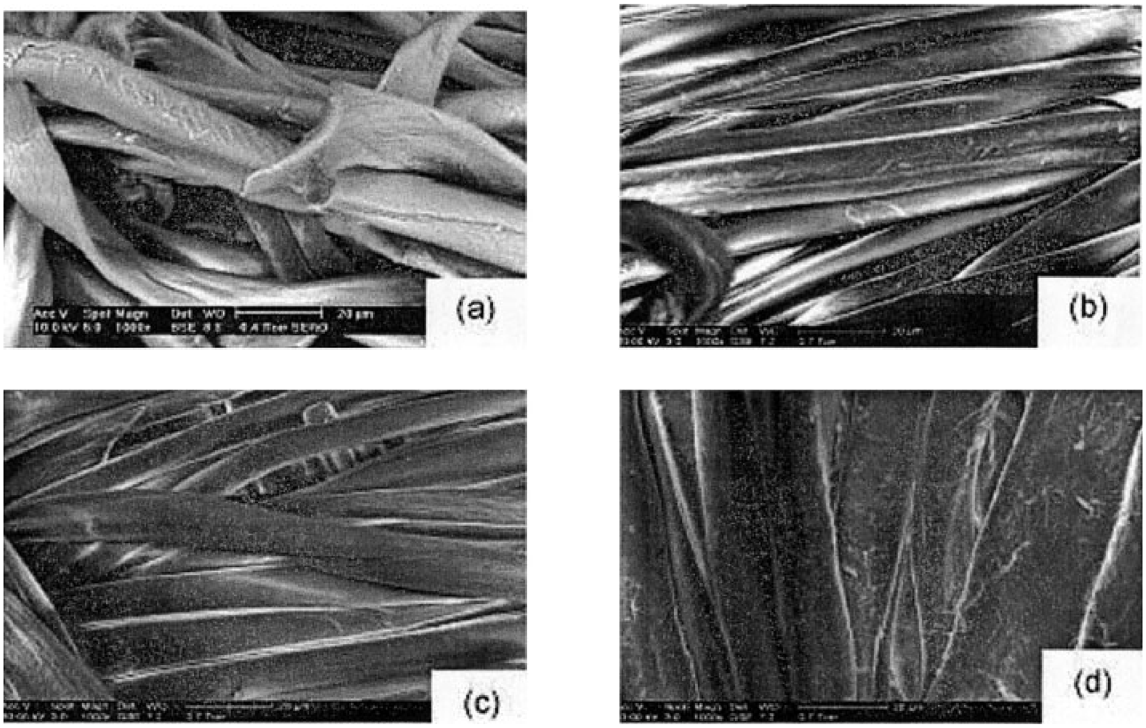

Figure 1 ESEM micrograph of sample treated with DMDEHU alone (a); and combination of DMDHEU and sericin (in g/L) 10 (b); 25 (c) and 50 (d).

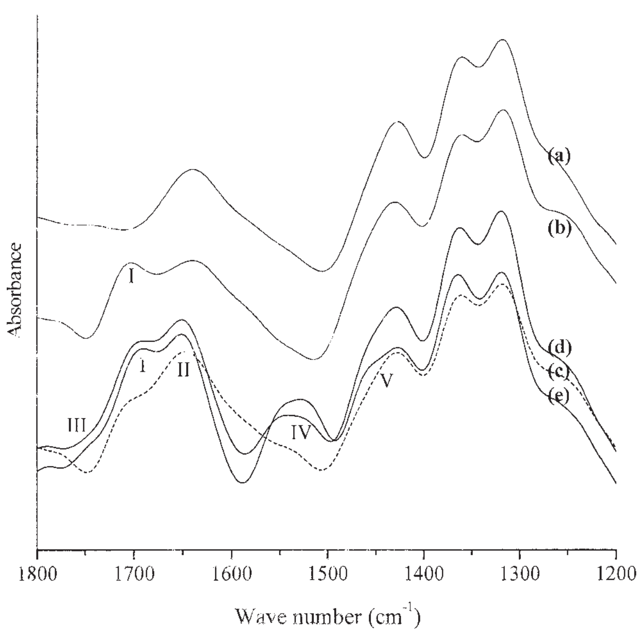

Figure 2 FTIR-ATR spectra of untreated sample (a); sample treated with DMDHEU alone (b); and combination of DMDHEU and sericin in g/L) 10 (c), 25 (d), and 50 (e).

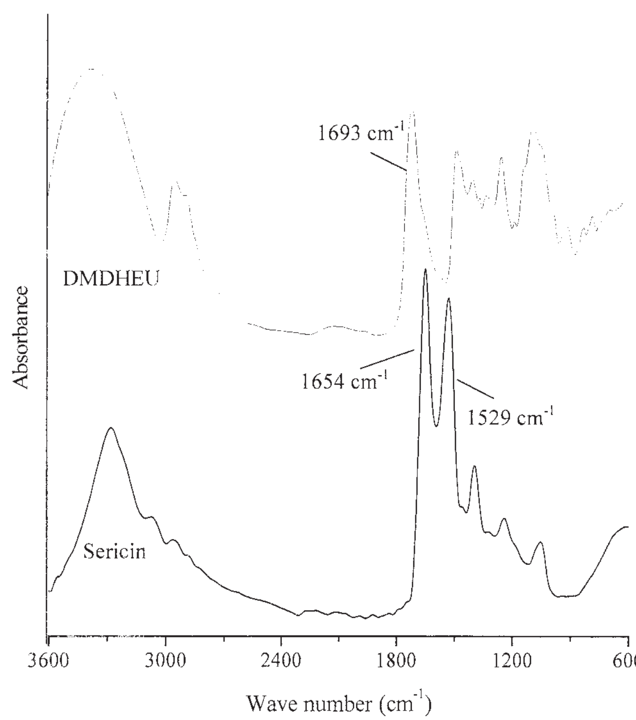

Figure 3 FTIR spectra of DMDHEU-based reagent (on KBr pellet) and sericin powder (FTIR-ATR).

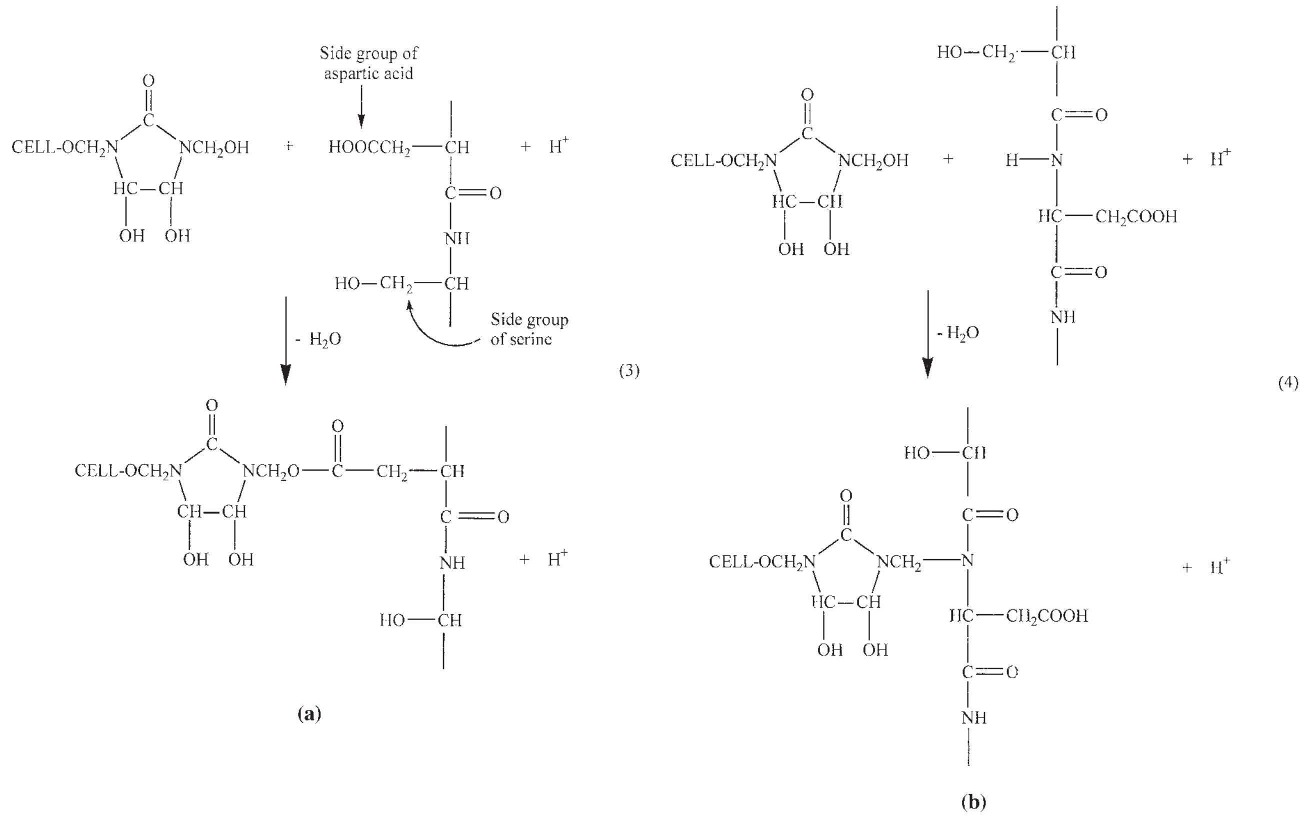

Figure 4 Schemes of possible reactions between *N*-methylol group in DMDHEU and carboxylic group in side group of sericin (a); and amino group in main chain of sericin (b).

creased amount of free formaldehyde in treated fabrics. Sericin, which has a chemical structure similar to that of urea, ethylene urea, and dicyandiamide, which have all been used as a formaldehyde scavenger,[16] may assume this function as well. Figure 6 shows the drastic reduction in free formaldehyde content in the samples when sericin was added to the finishing solution. With increasing amounts of sericin, free formaldehyde substantially decreases. Free formaldehyde reaches minimum values of 40–50 ppm, which are under the limit for ecotextiles (e.g., 75 ppm for shirt), particularly in fabrics treated with 25–50 g/L sericin.[17] However, the amount of free formaldehyde in the fabric treated with DMDHEU-based reagent is dependent on DMDHEU content in the finishing solution, pad–dry–cure condition, and washing process applied. Fabrics treated with low amounts of DMDHEU-based reagent, high curing temperature, and an additional washing step have been shown to have low amounts of formaldehyde.[16,18] Therefore, low-formaldehyde textile is possibly produced with consideration to adjustments in the finishing condition.

Content of sericin in treated fabrics

Table II shows *K/S* and *L* values of untreated and treated–dyed samples. The samples treated with various sericin contents yielded different *L* and *K/S* values. Increased *K/S* and decreased *L* values of dyed samples are observed with increasing amounts of sericin in the finishing solution. The increased amount of sericin affects greater numbers of ammonium groups

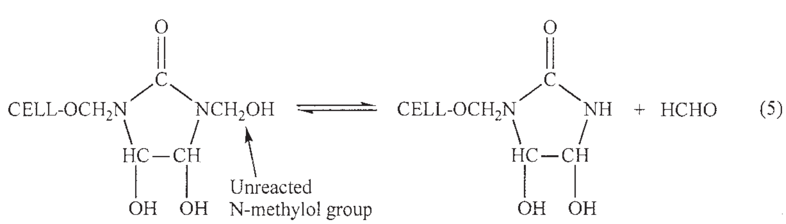

Figure 5 Reaction of formaldehyde released from unreacted *N*-methylol group.

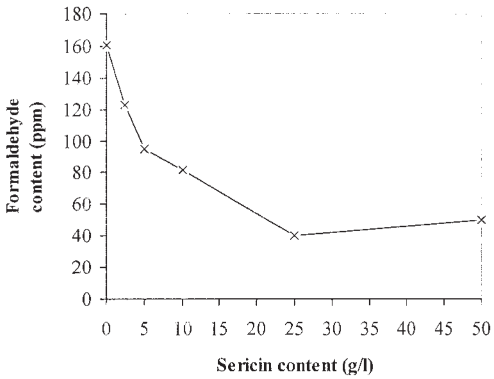

Figure 6 Free formaldehyde content in samples treated with sericin.

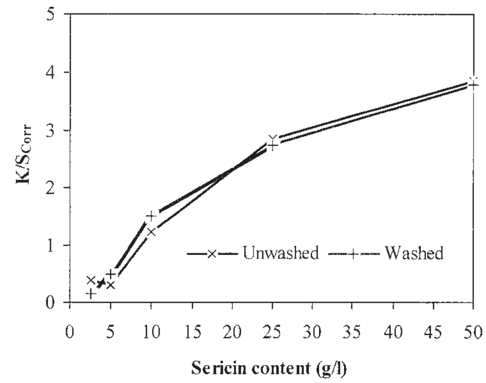

Figure 7 Color depth of samples treated with sericin (K/S_{corr}).

in sericin (at low pH) that are attracted to the Supranol Bordeaux B acid dye. Samples treated with DMDHEU alone show lower K/S values than those of samples treated with a combination of DMDHEU and sericin because DMDHEU crosslinks onto the fabric surface and thus reduces dye accessibility. Calculation of $(K/S)_{corr}$ is a function of sericin content in the finishing solution, as shown in Figure 7. The values of dyed samples increase with increasing sericin. Small differences in $(K/S)_{corr}$ between unwashed and washed samples are observed. Hydrolysis of sericin on a sample surface during washing and dyeing may affect these varied values. The lower the number of ammonium groups on the surface of samples with washing, the paler the color observed.

Physical properties of treated fabrics

Tensile strengths of warp yarns of untreated and treated samples are shown in Table II. Samples treated with DMDHEU alone yield lower tensile strength by 26% for unwashed and 21% for washed samples compared to that of untreated samples. Strength losses by 24–36% and 21–33% are found for unwashed and washed samples treated with combinations of DMDHEU and sericin, respectively. In comparison among treated samples, sericin does not significantly affect tensile strength. However, random changes in values are observed when the amounts of sericin are varied, possibly from undistributed crosslinked and acid hydrolysis reactions of cellulose molecules.

CRA (warp + fill) of samples is shown in Figure 8. Samples treated with DMDHEU alone show a significant improvement in CRA, by 38% at 5 min and 33% at 30 min. With sericin, the CRA of samples seems to increase with increasing sericin content. However, by adding up to 50 g/L sericin a slight reduction in CRA of sample is observed.

Water-sorption behavior of samples is shown in Figure 9. Water-retention values of treated samples are less than those of untreated samples because of the reduced accessibility of DMDHEU to water. The substantial reduction in water-retention values of treated samples is approximately 35 and 28% for unwashed and washed samples, respectively. However, increasing amounts of sericin in samples seem to improve the water-retention value because slightly increased values are observed.

The results of electrical resistivity of the samples are shown in Table II. The value of electrical resistivity of untreated samples is intermediate between those of unwashed and washed–treated samples. Washing is

TABLE II
Properties of Samples: Untreated (UT), Unwashed (UW), and Washed (W)

Sample code	*K/S*		*L*-value		Tensile strength of warp yarn (N)		Electrical resistivity ($\times 10^7$ ohm)	
	UW	W	UW	W	UW	W	UW	W
UT	1.26	—	57.36	—	3.06	—	123.3	—
Blank	1.08	0.75	57.42	65.01	2.24	2.41	20.8	1112.3
2.5	1.47	0.89	55.72	62.94	2.22	2.09	14.0	1300.0
5	1.38	1.25	56.83	58.85	2.32	2.37	15.0	1166.7
10	2.33	2.27	48.91	49.90	2.22	2.02	17.2	1296.7
25	3.81	3.60	41.74	44.29	2.01	2.17	6.03	95.3
50	4.86	4.60	41.09	37.65	2.24	2.26	7.7	80.0

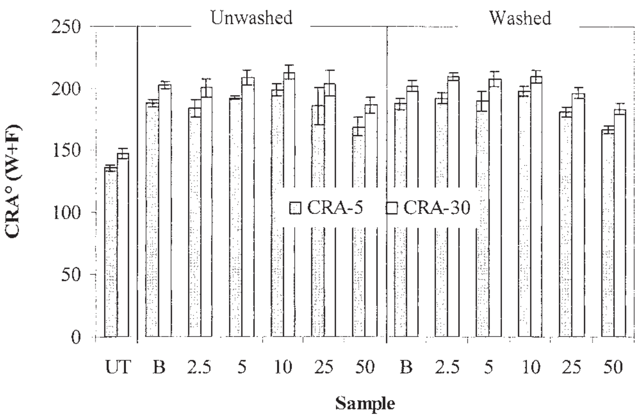

Figure 8 CRA (warp + fill) of untreated and samples treated with sericin. B = blank (no sericin added).

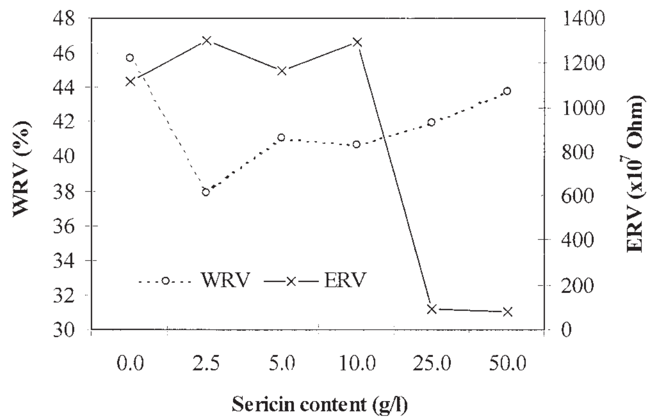

Figure 10 Relationship between water retention and electrical resistivity values of washed samples.

an important process in changing the electrical resistivity of treated samples. Washed samples yield lower electrical resistivity values than those of unwashed samples because of removal of a hydroscopic conductive substance (i.e., magnesium chloride). In washed samples, polar groups in sericin play an important role in improvement of moisture absorption. Increasing the amount of sericin causes greater absorption of moisture on the fiber surface, and thus slightly lower electrical resistivity is observed. When sericin was used up to 25 g/L, a drastic decrease in electrical resistivity was observed. The electrical resistance property is related to water retention, and the relationship between these two values of washed fabrics and sericin content is shown in Figure 10. Electrical resistivity of washed samples treated with sericin dramatically decreased, whereas water retention dramatically increased, especially in samples treated with high amounts of sericin, up to 25 g/L.

Biocidal activity of sericin-modified fibers (fabric)

The results of biocidal activity tests of sample treated with sericin are shown in Table III. No growth of *K. pneumoniae* is observed in all samples. In the case of *S. aureus*, it grows slightly on an untreated sample (control), a washed sample treated with DMDHEU alone (blank), unwashed and washed samples treated with a combination of DMDHEU and 10 g/L sericin, and full growth on unwashed and washed samples treated with a combination of DMDHEU and 50 g/L sericin. No growth of *S. aureus* is observed on the unwashed sample treated with DMDHEU alone (see Fig. 11). The results indicate that free formaldehyde in the sample exhibits biocide activity because there was no evidence of bacterial growth on the unwashed samples and enhanced bacterial growth on the washed sample and samples treated with high amounts of sericin (with low free formaldehyde content).

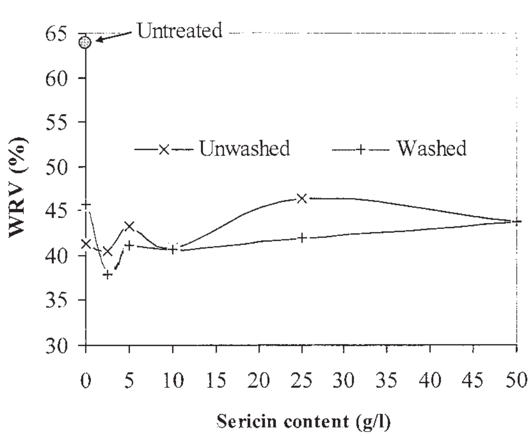

Figure 9 Water retention values of samples treated with sericin.

CONCLUSIONS

Surface modification of cellulose fiber with sericin was successful using a pad–dry–cure process. Sericin was chemically fixed onto the surface of cotton and its presence on washed samples was analyzed using ESEM and FTIR-ATR. The extent of fixed sericin on fiber surfaces was a function of sericin content in the finishing recipe. A greater color depth of dyed samples with increased sericin content in the finishing solution was observed. By increasing the amount of sericin, the free formaldehyde content in treated fabrics dramatically decreased. Free formaldehyde (40 ppm) was found in the sample treated with a combination of 40 mL/L DMDHEU-based reagent and 25 g/L sericin. The formaldehyde content is possibly lowered even further if the finishing conditions are adjusted, such as by reducing the amount of DMDHEU and by increasing the curing temperature. In the presence of sericin, tensile strength and crease recovery of cotton fabrics were not affected, although moisture sorption properties, with indications of an in-

TABLE III
Biocidal Activities of Samples[a]

Sample code	*Klebsiella pneumoniae*		*Staphylococcus aureus*	
	24 h	48 h	24 h	48 h
Control	−, −, −	−, −, −	+, +, −	+, +, +/−
Blank (unwashed)	−, −, −	−, −, −	−, −, −	−, −, −
Blank (washed)	−, −, −	−, −, −	+, +/−, −	+, +/−, −
10 (unwashed)	−, −, −	−, −, −	+, +, +/−	+, +, +/−
10 (washed)	−, −, −	−, −, −	+, +, +	+, +, +
50 (unwashed)	−, −, −	−, −, −	+, +, +	++, ++, ++
50 (washed)	−, −, −	−, −, −	+, +, +	++, ++, ++

[a] −, no growth; +/−, little growth; +, growth; and ++, full growth (the interpretation corresponds to each strike of bacteria).

crease in water retention and reduction in electrical resistivity, were substantially influenced.

Silk allergy arising from the presence of sericin is still a debatable issue[1,19–21]: allergic reactions, whether among workers in the silk industry or silk sutures, have been recognized, but are very rare for wearers. Dust from sericin, presents on fibroin fibers, may be the cause. Allergic reactions attributed to the textiles used in this investigation would not occur from the sericin coated onto a fiber surface as film. The textile attained advantages of moisture sorption from the coated sericin; wearing clothes made from this textile may control the moisture balance between fabric and skin. The low formaldehyde content and absence of biocidal activity against microorganisms indicated that this textile was specifically suitable in reducing irritation and avoiding a disturbance of the physiological skin flora from textile contact.

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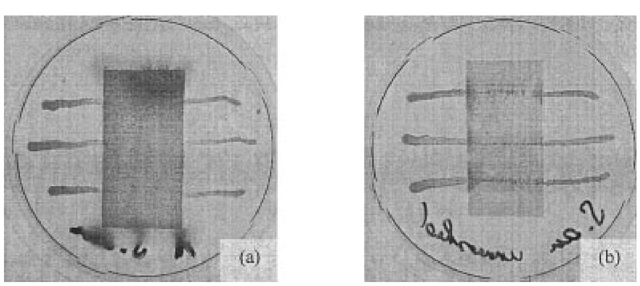

Figure 11 Growth of *Staphylococcus aureus* on (a) unwashed sample treated with DMDHEU alone and (b) unwashed sample treated with combination of DMDHEU and 50 g/L sericin.

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