

Physical Properties and Dyeability of NaOH-Treated Silk Fibers

GIULIANO FREDDI,^{1,*} HIROSHI KATO,² MASUHIRO TSUKADA,² GIULIA ALLARA,¹
and HIDEKI SHIOZAKI³

¹Stazione Sperimentale per la Seta, via G. Colombo 81, 20133 Milano, Italy; ²National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan; ³Textile Institute of Kanagawa, Aikawa-machi, Kanagawa 240-03, Japan

SYNOPSIS

Domestic (*Bombyx mori*) and wild (tussah, *Antheraea pernyi*) silk fabrics were treated with diluted NaOH solutions by the pad/batch method. The equilibrium moisture regain of tussah silk fibers increased steadily with alkaline treatment, while that of *B. mori* did not change. *B. mori* tensile strength and elongation at break were slightly impaired. The average molecular orientation and crystallinity of both kinds of silk remained unchanged. Differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) showed that the thermal behavior of *B. mori* silk was almost unaffected, while that of tussah exhibited slight changes in the temperature range 250–300°C. By dynamic mechanical measurements (DMA) it was elucidated that both storage and loss moduli of *B. mori* silk fibers decreased following NaOH treatment. On the other hand, tussah silk exhibited a noticeable upward shift of the major loss peak. Alkali-treated tussah silk fibers, dyed with an acid dyestuff, attained a lower degree of dye-bath exhaustion. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The action of alkali toward silk has been the subject of several investigations.^{1,2} The intensity of the attack depends on the concentration of alkali, as well as on the time and temperature of treatment. Hydrolysis of peptide bonds is likely to occur, causing degradation of the fibroin molecules by main chain fission. Loss of hydroxyl amino acids and formation of amino acid derivatives, such as lysinoalanine, have also been reported.³

The use of alkali during silk processing is not rare. A typical example is silk degumming (that is, removal of sericin from raw silk), carried out on an industrial scale by means of boiling alkaline solutions.⁴ Though Vogt et al.⁵ reported that silk treated with hot aqueous solutions is more resistant to alkaline than acidic conditions, processing parameters should be carefully controlled in order to avoid the risk of extensive fiber degradation.⁴

A new method for chemical modification of silk fibers with epoxides has been recently proposed.^{6,7} According to this technique, silk fabrics are padded with an alkaline solution containing the modifying agent. The addition reaction of epoxide molecules toward silk takes place during batching at 30°C for 24 h. This method has proved to be quite effective, especially when applied to *B. mori* silk, and attractive for industrial application, since it permits significant savings of energy, water, and chemicals. The reaction system contains a strong alkali (NaOH). Though the concentration is rather low (< 0.3 M) and the reaction conditions are mild, the solution remains in the fibers for a long time before being washed off. It is therefore interesting to study its effect on the physicochemical structure of silk.

The chemical aspects related to the alkaline attack have been extensively studied by various authors.^{1–5} However, little attention has been paid so far to the changes induced in physical properties and fine structure of silk fibers. In the context of research into the effect of various physical and chemical treatments on the properties of silk fibers,^{8–10} we focused on the action of diluted alkaline solu-

* To whom correspondence should be addressed.

tions. The structural changes were studied by optical and tensile measurements, X-ray diffractometry, differential scanning calorimetry (DSC), and thermomechanical (TMA) and dynamic mechanical (DMA) analyses. The changes in fiber dyeability were investigated by measuring the extent of dye-bath exhaustion using a levelling acid dye.

EXPERIMENTAL

Materials

B. mori (plain woven, Habutae, 60 g/m²), and tussah (plain woven, Habutae, 98 g/m²) silk fabrics were used in this work. Samples were padded with aqueous solutions containing different amounts of NaOH from 2.0 to 12.0 g/L, referring to the optimum alkali concentrations determined for the chemical modification with epoxides by using the pad/batch method.^{6,7} The amount of wet pick-up was 100%. Padded silk fabrics were sealed in polyethylene bags, and stored for 24 h at 30°C. At the end of the batching period, samples were washed with distilled water and dried.

Dyeing tests were carried out in an acidic bath, using Suminol Fast Red B conc. (C.I. Acid Red 6) purchased from Sumitomo Chemicals Co., Ltd. The dye concentration was 1% owf (on the basis of fiber weight). Acetic acid (1% owf) and ammonium acetate (2% owf) were added to the dyeing bath. The material-to-liquor ratio was 1 : 50. The temperature was increased from 40°C to 80°C over 40 min, and maintained at 80°C for 30 min. Dyed samples were taken out and thoroughly rinsed with water.

Measurements

Equilibrium moisture regain was determined in standard conditions at 20°C and 65% relative humidity (RH).

Tensile strength and elongation at break were measured in standard conditions (20°C, 65% RH) with a Tensilon UTM-II (Toyo Baldwin Co., Ltd.) tensile tester machine.

The refractive indices, either parallel ($n_{||}$) or perpendicular (n_{\perp}) to the fiber axis, were measured with Beche's line method, using a polarized microscope under the monochromatic light (Na light) at 20°C and 65% RH.

The X-ray diffraction intensity curves were obtained at a scanning rate of 1°/min, with a diffractometer from Rigaku Denki Co., Ltd., using the CuK α radiation ($\lambda = 1.54 \text{ \AA}$). The voltage and cur-

rent of the X-ray source were 40 kV and 20 mA, respectively.

DSC measurements were performed on a Rigaku Denki Co., Ltd. instrument (model DSC 10-A) at a heating rate of 10°C/min. The DSC range and sample weight were 2.5 mcal/s and 2 mg, respectively. The open aluminium cell was swept with N₂ gas during the analysis.

A Rigaku Denki Co., Ltd. instrument (model CN-8361) for thermomechanical analysis (TMA) was used to detect the thermal contraction and expansion properties in the course of heating. The heating rate was 10°C/min, and dry N₂ gas provided the inert atmosphere. TMA full scale and initial load applied to the sample were $\pm 500 \mu\text{m}$ and 1 g, respectively.

Dynamic mechanical properties were measured using a Toyoseiki Rheograph Solid-S. The frequency of oscillation was adjusted to 10 Hz. The temperature range studied was from -50°C to 260°C, and samples were heated at 2°C/min. Sample length was 15 mm, with initial tension of 30 gf.

The dyeing behavior was determined by measuring the residual absorbance of the dyeing bath with a Shimadzu Seishakusho spectrophotometer (UV-3100S), at a wavelength of 505 nm.

RESULTS AND DISCUSSION

Moisture Regain and Tensile Properties

The values of equilibrium moisture regain measured before and after treatment with NaOH solutions are listed in Table I. *B. mori* silk fibers remained unchanged regardless of alkali treatment, while tussah exhibited an increase in moisture content. Since moisture regain is an important functional param-

Table I Equilibrium Moisture Regain and Tensile Properties of Alkali-Treated Silk Fibers

	Moisture Regain (%)	Strength (g/d)	Elongation (%)
<i>Bombyx mori</i> :			
untreated	8.2	4.6	20.2 \pm 1.2
2.5 g/L NaOH	8.2	4.1	22.4 \pm 1.7
Tussah:			
untreated	9.4	2.8	27.1 \pm 1.8
2.5 g/L NaOH	—	2.9	29.5 \pm 2.0
4.0 g/L NaOH	10.9	2.6	26.8 \pm 2.1
8.0 g/L NaOH	11.2	2.9	28.2 \pm 1.9

eter, which may influence such textile characteristics as crease recovery as well as the physical properties related to hand and comfort, the higher degree of hygroscopicity attained by tussah silk fibers is particularly remarkable. Therefore, the above results led us to envisage the possibility of modifying some functional properties of tussah silk fibers by means of a mild alkaline treatment.

The results of tensile measurements (Table I) show that *B. mori* silk fibers exhibited a decrease of tenacity, accompanied by a fairly higher extensibility. The values of energy of the untreated and alkali-treated samples were 6,566 and 5,302 (gf × mm), respectively, confirming that the treatment with NaOH resulted in a partial loss of the intrinsic tensile properties. On the other hand, alkali-treated tussah silk fibers proved to be more stable toward the alkaline treatment, showing only slight and random changes of both tenacity and elongation at break. This behavior should be primarily related to the differences in chemical (amino acid composition) and physical structure (amorphous, laterally ordered, and crystalline regions) between the two kinds of silk.¹¹

Refractive Indices and X-Ray Diffraction Curves

In an attempt to ascertain whether the alkaline treatment induced some structural changes, we studied the molecular orientation and crystallinity of untreated and alkali-treated silk fibers.

Table II lists the values of refractive indices parallel (n_{\parallel}) and perpendicular (n_{\perp}) to the fiber axis, from which birefringence (Δn) and isotropic refractive index (n_{ISO}) were calculated. The optical properties of *B. mori* silk fibers did not change following the treatment with NaOH. The birefringence of tussah silk fibers remained almost unchanged, while the value of n_{ISO} increased slightly. These results confirm that the average molecular orientation of both kinds of silk was not significantly affected by the treatment with diluted NaOH solutions. The

Table II Refractive Indices of Alkali-Treated Silk Fibers

	n_{\parallel}	n_{\perp}	Δn	n_{ISO}
<i>Bombyx mori</i> :				
untreated	1.585	1.5385	0.0495	1.555
2.5 g/L NaOH	1.588	1.538	0.05	1.555
Tussah:				
untreated	1.565	1.531	0.034	1.542
4.0 g/L NaOH	1.570	1.536	0.033	1.548

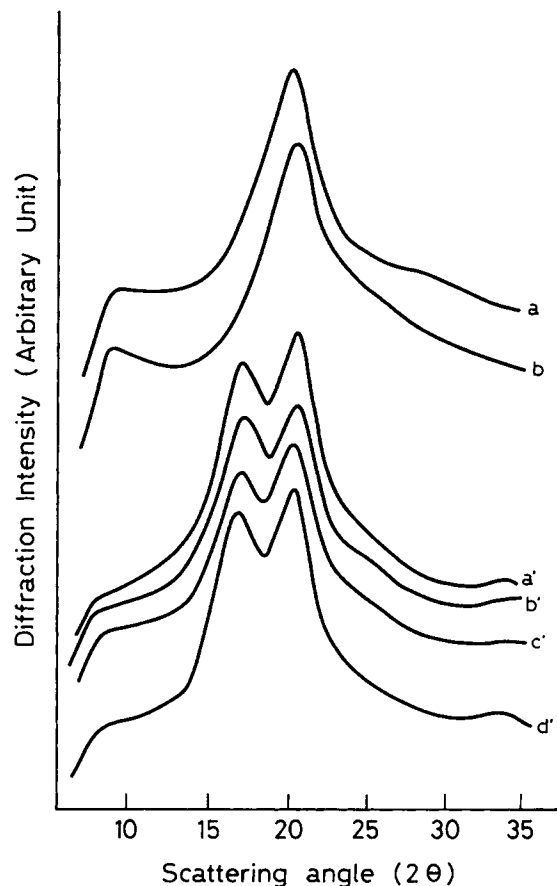


Figure 1 X-ray diffraction intensity curves of alkali-treated silk fibers. *B. mori*: (a) untreated; (b) 2.5 g/L NaOH. Tussah: (a') untreated; (b') 2.5, (c') 4.0, and (d') 8.0 g/L NaOH.

slight rise in n_{ISO} exhibited by tussah silk may be attributed to a change in fiber density, rather than to a higher degree of crystallinity (see below).

Wide-angle X-ray diffraction profiles were measured before and after NaOH treatment (Fig. 1). The diffraction curves, characterized by a single and broad peak at 20.2° (spacing of 4.56 Å) for *B. mori* [Fig. 1(a)], and by two peaks at 16.7° and 20.2° (spacing of 5.30 and 4.56 Å, respectively) for tussah [Fig. 1(a')], are typical of silk fibers with oriented β configuration.¹² The diffraction patterns remained unchanged regardless of alkaline treatment, confirming that the crystalline structure was not directly affected by the chemical agent. The degree of crystallinity did not change as well (data not shown).

Thermal Properties

The thermal behavior of *B. mori* and tussah silk fibers treated with NaOH was evaluated on the basis

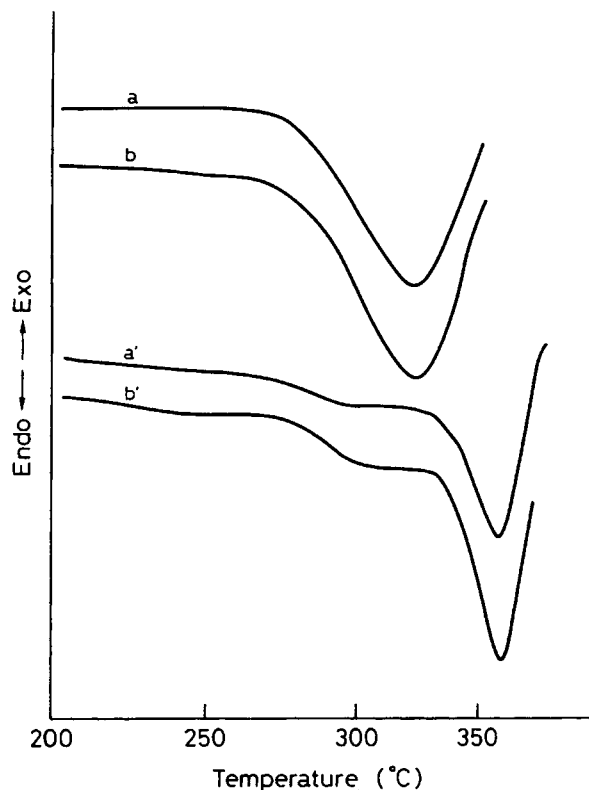


Figure 2 DSC curves of alkali-treated silk fibers. *B. mori*: (a) untreated; (b) 2.5 g/L NaOH. Tussah: (a') untreated; (b') 4.0 g/L NaOH.

of differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). The DSC curves of the two kinds of silk (Fig. 2) are characterized by a prominent endothermic transition whose temperature peak is located at 320°C and 358°C for *B. mori* [Fig. 2(a)] and tussah [Fig. 2(a')], respectively. This transition, attributed to the thermal decomposition of silk fibers with oriented β -form structure,¹³ remained unchanged regardless of the alkaline treatment. In the case of tussah, however, the intensity of the minor and broad endothermic transition appearing at around 300°C increased for the sample treated with NaOH [Fig. 2(b')]. Most thermal events occurring at above 200°C have been attributed to the molecular motion of the fibroin chains not only in the amorphous but also in the crystalline regions of tussah silk fibers.¹⁴ However, taking into account the above X-ray results, the less-ordered fibrous domains (amorphous and laterally ordered regions) should have been primarily affected by the NaOH treatment, for example by rearrangement of the intermolecular network of hydrogen bonds.

The influence of diluted NaOH solutions on the expansion and contraction properties of silk fibers was studied by thermomechanical measurements (Fig. 3). Both untreated [Fig. 3(a)] and alkali-treated [Fig. 3(b)] *B. mori* silk fibers behaved similarly, showing a weak contraction of 0.7% from room tem-

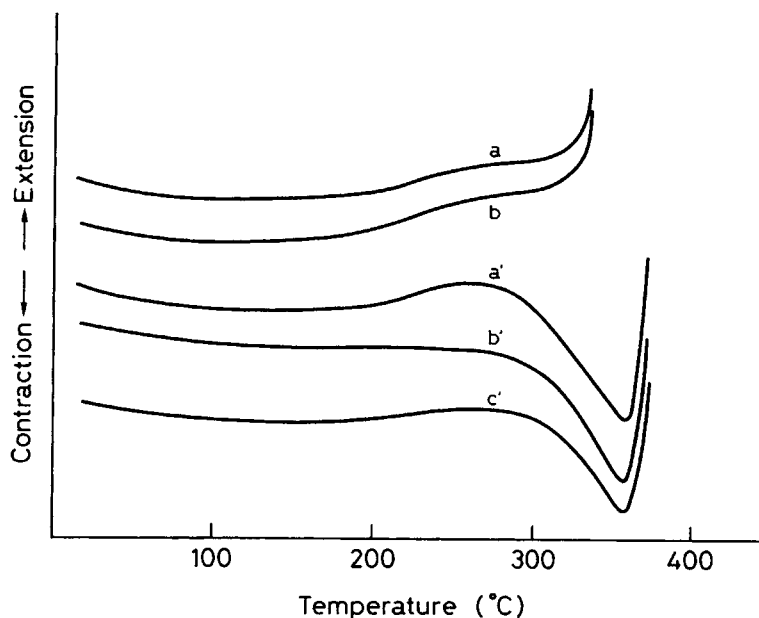


Figure 3 TMA curves of alkali-treated silk fibers. *B. mori*: (a) untreated; (b) 2.5 g/L NaOH. Tussah: (a') untreated; (b') 4.0, and (c') 8.0 g/L NaOH.

perature to about 150°C, followed by a region of gradual extension at around 200°C. The final abrupt extension occurred at 320°C, coinciding with the thermal decomposition of the fibers. The TMA curves of tussah silk showed a broad and weak contraction (0.7%) in the temperature range 25–200°C. Afterward, a prominent contraction peak, whose maximum is located at 358°C, occurred before the final extension. It is interesting to note that the untreated sample [Fig. 3(a)] extended slightly between 200°C and 250°C, while NaOH-treated samples [Fig. 3(b', c')] exhibited a higher thermal stability in the same temperature range. From these results we can infer that the alkaline treatment influenced the rubber elastic behavior of tussah fibers above T_g ,¹⁵ resulting in a partial restriction of the molecular motion of the fibroin chains. This feature might be related to the changes observed in the DSC thermograms of the same samples.

Dynamic Mechanical Behavior

The thermal behavior of alkali-treated silk fibers was further investigated by means of dynamic mechanical measurements (DMA). In previous papers,^{16–17} it has been shown that DMA is very sensitive in detecting fine-structure changes induced by various kinds of treatments.

Figure 4 shows the dynamic storage (E') and loss (E'') modulus curves of *B. mori* silk fibers, measured in the range from –50°C to 260°C. The storage modulus of the untreated sample remained stable

from room temperature until about 170–180°C, and then dropped sharply. On the other hand, the NaOH-treated sample exhibited a gradual decrease of E' , as shown by the continuous negative slope of the curve. Accordingly, the E'' curve changed significantly. The intensity of the prominent loss peak at 229°C (untreated sample) decreased; the peak broadened and shifted to lower temperature. The changes in viscoelastic behavior should be attributed to the effect of the alkali agent, which remained within the fiber matrix long enough to cause not only breaking of hydrogen bonds, but also localized main chain fission by hydrolysis of the more sensitive peptide bonds (usually those formed by hydroxyl amino acid residues²). The observed loss of tenacity seems to support this hypothesis.

The E' and E'' curves of tussah silk fibers are shown in Figure 5. The untreated sample is characterized by a sharp drop of storage modulus at about 190–200°C, and a prominent loss peak at 235°C. Alkali-treated samples exhibited an upward shift of the above transitions. This is particularly evident for the loss peak, whose maximum shifted to 250°C and 256°C for the samples treated with 2.5 and 4.0 g/L NaOH, respectively. This behavior is primarily attributable to a restriction of the thermally induced molecular movement of fibroin chains. These findings are in good agreement with TMA data, which showed a lower degree of fiber extensibility at above 200°C. Moreover, the slight increase of n_{ISO} confirms that alkali-treated tussah silk fibers attained a denser and more compact fiber structure.

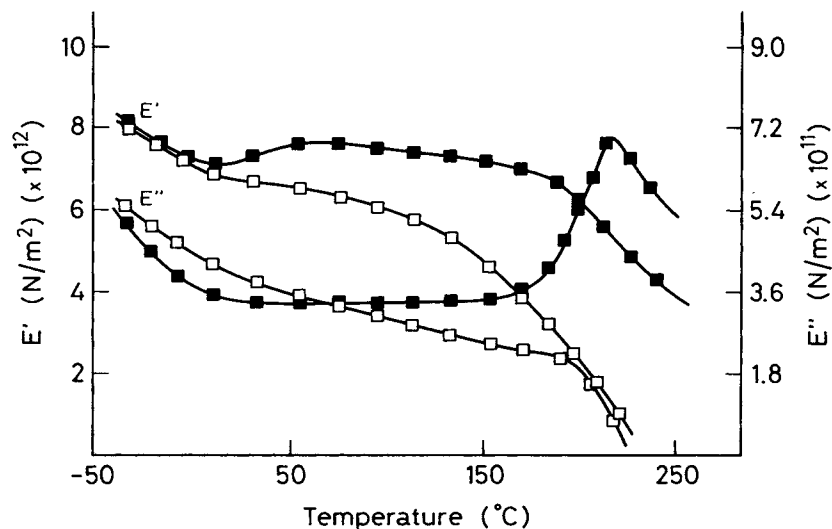


Figure 4 Dynamic storage (E') and loss modulus (E'') curves of *B. mori* silk fibers untreated (■) and treated with 2.5 g/L NaOH (□).

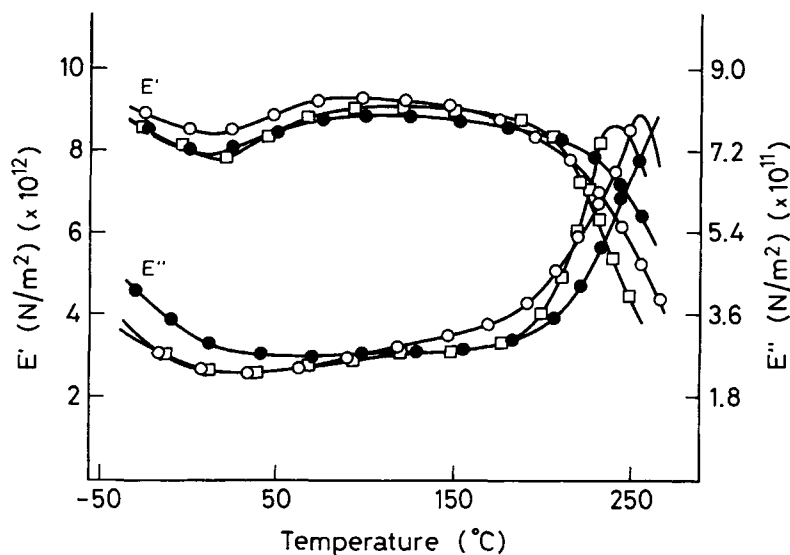


Figure 5 Dynamic storage (E') and loss modulus (E'') curves of tussah silk fibers untreated (\square) and treated with 2.5 (\circ), and 4.0 g/L NaOH (\bullet).

We⁷ recently reported that tussah silk fibers, modified with epoxides by the pad/batch method, exhibited an upward shift of the loss peak, in striking contrast with previous results from epoxide-treated tussah silk.¹⁸ The above DMA data elucidate that the alkaline agent contained in the padding solution was mainly responsible for the upward shift of the E'' peak.

Dyeing Behavior

Untreated and alkali-treated silk fibers were dyed with an acid dyestuff of the levelling type. The results (Table III) show a rather different behavior between *B. mori* and tussah silk fibers. While the former showed only slight changes compared to the untreated sample, the latter exhibited a lower degree

of dye-bath exhaustion following the alkali treatment.

The dyeing behavior of NaOH-treated tussah silk fibers cannot be attributed to chemical changes induced by the alkali agent, since the amino acid composition (i.e., the amount of basic amino acid residues) did not change after the treatment (data not shown). Other parameters of the dye-fiber system should have played the major role in decreasing dye-bath exhaustion. It has been recently reported that the specific surface area of tussah silk fibers increased by NaOH treatment.¹⁹ This effect, however, which usually promotes the absorption of dye molecules, should have been overcome by other factors. On the basis of thermal (TMA, DMA) and optical (n_{150}) results, we suggest that the structural changes that occurred within the amorphous and laterally ordered regions might have led to a restriction of dye diffusion by steric hindrance. The denser the structure, the lower the accessibility of some reactive sites potentially available for binding dye molecules. The mechanism of microvoid reduction and strong molecular aggregation, suggested by Kawahara²⁰ for tussah silk fibers treated with various chemical agents, might apply to the samples examined in this work.

Table III Dye-Bath Exhaustion of Alkali-Treated Silk Fibers

	Dye Conc. (10 ⁻⁵ g Dye/g Fiber)	pH
<i>Bombyx mori</i> :		
untreated	1.25	4.47
2.0 g/L NaOH	1.27	4.69
4.0 g/L NaOH	1.23	4.64
Tussah:		
untreated	0.82	4.66
4.0 g/L NaOH	2.01	4.77
12.0 g/L NaOH	2.18	5.04

CONCLUSIONS

The treatment of *B. mori* and tussah silk fibers with diluted NaOH solutions resulted in slight-to-marked

changes in physical properties and dyeability, whose extent was strongly dependent on the different physico-chemical structure and reactivity of the two kinds of silks towards the alkali agent. *B. mori* silk showed a loss of tenacity accompanied by noticeable changes in viscoelastic behavior, probably due to a limited hydrolytic degradation of the fibroin backbone, while dyeability did not change significantly, compared to the untreated sample. On the other hand, tussah silk exhibited marked changes in physical properties and thermal behavior, as well as in dye uptake. The NaOH treatment was effective in improving moisture absorption, which might result in better handling and comfort of textiles based on tussah silk fibers. The thermal stability increased by the action of the alkali agent, which induced either a collapse of the microvoids present in the fiber matrix, or a stronger molecular aggregation of the fibroin chains in the amorphous regions. The extent of dye-bath exhaustion decreased, resulting in a lower depth of shade in dyed samples. This aspect of the NaOH treatment should be carefully considered in view of its application to silk processing.

REFERENCES

1. F. Lucas, J. T. B. Show, and S. G. Smith, *Adv. Prot. Chem.*, **13**, 107 (1958).
2. M. S. Otterburn, in *Chemistry of Natural Protein Fibers*, R. S. Asquith, Ed., Plenum Press, New York, 1977.
3. A. Robson, and Z. H. Zaidi, *J. Text. Inst.*, **55**, 267 (1967).
4. A. Svilokos Bianchi and G. M. Colonna, *Melliand Textilberichte*, **73**, 68 (1992).
5. B. Vogt, U. Altenhofen, and H. Zahn, *Textilveredlung*, **20**, 90 (1985).
6. M. Tsukada, H. Shiozaki, Y. Goto, and G. Freddi, *J. Appl. Polym. Sci.*, **50**, 1841 (1993).
7. G. Freddi, H. Shiozaki, G. Allara, M. Tsukada, Y. Goto, and H. Yasui, *J. Appl. Polym. Sci.*, to appear.
8. M. Tsukada, H. Kato, G. Freddi, N. Kasai, and H. Ishikawa, *J. Appl. Polym. Sci.*, **51**, 619 (1994).
9. M. Tsukada, G. Freddi, and N. Minoura, *J. Appl. Polym. Sci.*, **51**, 823 (1994).
10. M. Tsukada, H. Shiozaki, and G. Freddi, *Melliand Textilberichte*, **74**, 778 (1993).
11. M. Tsukada, G. Freddi, M. Nagura, H. Ishikawa, and N. Kasai, *J. Appl. Polym. Sci.*, **46**, 1945 (1992).
12. R. D. B. Fraser and T. P. MacRae, in *Conformation in Fibrous Proteins and Related Synthetic Polypeptides*, Academic Press, New York, 1973.
13. H. Ishikawa, M. Tsukada, I. Toizume, A. Konda, and K. Hirabayashi, *Sen-i Gakkaishi*, **28**, 91 (1972).
14. M. Nagura, M. Urushidani, H. Shinohara, and H. Ishikawa, *Kobunshi Ronbunshu*, **35**, 81 (1978).
15. S. Nakamura, Y. Saegusa, Y. Yamaguchi, J. Magoshi, and S. Kamiyama, *J. Appl. Polym. Sci.*, **31**, 955 (1986).
16. M. Tsukada, G. Freddi, P. Monti, A. Bertoluzza, and H. Shiozaki, *J. Appl. Polym. Sci.*, **49**, 1835 (1993).
17. H. Shiozaki, M. Tsukada, Y. Goto, N. Kasai, and G. Freddi, *J. Appl. Polym. Sci.*, to appear.
18. M. Tsukada, Y. Goto, G. Freddi, M. Matsumura, H. Shiozaki, and H. Ishikawa, *J. Appl. Polym. Sci.*, **44**, 2203 (1992).
19. Y. Kawahara, *J. Silk Sci. Tech. Japan*, **2**, 51 (1993).
20. Y. Kawahara, *Sen-i Gakkaishi*, **50**, 93 (1994).

Received April 25, 1994

Accepted June 26, 1994