

Structure and Physical Properties of Epoxide-Treated Tussah Silk Fibers

MASUHIRO TSUKADA,*¹ YOKO GOTO,¹ GIULIANO FREDDI,² MASAOKI MATSUMURA,
HIDEKI SHIOZAKI,³ and HIROSHI ISHIKAWA⁴

¹National Institute of Sericultural and Entomological Science, Ministry of Agriculture, Forestry and Fisheries, Tsukuba City, Ibaraki 305, Japan, ²Stazione Sperimentale per la Seta, via Giuseppe Colombo 81, 20133 Milano, Italy,

³Textile Research Institute of Kanagawa, Aikawa-machi, Kanagawa 243-03, Japan,

and ⁴Shinshu University, Ueda, Nagano 386, Japan

SYNOPSIS

The structural characteristics and physical properties of epoxide-treated tussah silk fibers from *Antheraea pernyi* silkworm are discussed in relation to the increasing weight gain values. Ethyleneglycol diglycidylether (E) and glycerin diglycidylether (G) were used as modifying agents. The noticeably high weight gain values (about 140%) obtained were attributed to the catalytic effect of SCN⁻ anion absorbed by the fibers during the pretreatment under reduced pressure conditions. The amino acid analysis showed that epoxide G exhibited a slightly higher reactivity toward tyrosine, while arginine preferably reacted with epoxide E. The peak of loss modulus (E'') determined by dynamic viscoelastic measurements became broader and its position linearly shifted to lower temperature when the weight gain increased, and a minor peak appeared in the low-temperature region below 50°C. Differential scanning calorimetry (DSC) thermograms showed that the position of the decomposition peak of modified silk fibers shifted to lower temperature with increasing weight gain values. The minor and broad endothermic peaks, appearing in the reference sample at about 234 and 290°C, disappeared by epoxide treatment. X-ray diffraction patterns of tussah silk fibers suggested that the epoxide treatment does not affect directly the crystalline regions but causes a decrease of molecular orientation in the amorphous regions. Both birefringence (Δn) and isotropic refractive index (n_{iso}) of tussah silk fibers decreased by the reaction with epoxides, although with different rate and extent, confirming the decrease of average molecular orientation. The extent of decrease of strength and elongation depends on the kind of epoxide and on the weight gain value. Epoxide-treated tussah silk fibers did not show significant changes of surface characteristics as the weight gain values attained up to 60%.

INTRODUCTION

Over the last decade, there has been considerable interest in the improvement of the inferior textile properties such as antiyellowing, wash and wear (W&W) properties, and crease proofing of silk and wool by graft-copolymerization¹⁻⁵ and/or chemical modification^{4,6} techniques. Among the chemical modifying agents, epoxides have proved to be of particular interest when applied onto silk and ker-

atin fibers. It is now believed that the functional properties of silk fiber improve after epoxide treatment. The experimental results supporting this view were given by Shiozaki et al.,⁷ who elucidated that the silk fabrics treated with ethyleneglycol diglycidylether with weight gains of 15% exhibited a value of crease recovery angle higher than 140° in both dry and wet states, as well as decreased alkali solubility and improved color fastness to washing. The reactivity of epoxides toward *Bombyx mori* silk fibroin and the physical properties of the epoxide-treated silk fibers have been extensively studied.^{8,9} However, until recently little attention has been paid to the characterization of the epoxide-treated wild

* To whom correspondence should be addressed.

silk fibers^{8,9} such as *Philosamia cynthia ricini*¹⁰ and *Antheraea pernyi*, especially with regard to the modification of their physical properties and structure associated with the increase of weight gain value. We¹¹ recently elucidated the changes in the mechanical properties and handling of silk fabrics modified with ethyleneglycol diglycidylether and described their relationship with the fabric construction.

The chemical structure of tussah silk fibroin is rather different from that of *B. mori* silk fibroin. The alanine content is higher than that of glycine; furthermore, the amount of basic (lysine, histidine, and arginine) and acidic (aspartic and glutamic acid) amino acid residues of tussah silk is higher than that of *B. mori* silk fibers. It has been pointed out that basic and acidic amino acids as well as tyrosine have side groups reactive towards epoxides.^{8,9} The reactivity of functional amino acid residues of *P. cynthia ricini* toward epoxides has been recently studied with regard to the effect of the structure of epoxide molecule, nature of catalyst, reaction conditions, etc.¹⁰

This article elucidates the chemical reactivity and physical properties of tussah silk fibers treated with either ethyleneglycol diglycidylether or glycerin diglycidylether. The amino acid composition, thermal and viscoelastic behaviour, refractive indices, and crystalline structure, as well as tensile properties and surface characteristics, of tussah silk fibers were studied in relation to the weight gain. We believe that this study provides new perspectives in the field of the chemical modification of silk fibers and new tools for a better understanding of the chemical and structural effects induced by modifying agents.

EXPERIMENTAL

Materials

Ethyleneglycol diglycidylether (Denacol EX-810, Nagase Sangyo Co.; epoxide equivalent 115, viscosity 15 cps/25°C) and glycerin diglycidylether (Glycerol ED507, Asahi Denka Co.; epoxide equivalent 148, viscosity 165 cps/25°C), referred to as G and E, respectively, were both commercial products and were used without further purification.

Tussah silk fibroin fibers from *A. pernyi* were cleaned by acetone/ethanol mixture system to remove the wax, rinsed in distilled water, and dried to constant weight. Silk fibers (70 d/1 × 6 yarn) were degummed in aqueous solution containing sodium carbonate (3 g/L), sodium metasilicate (3 g/

L), and Marseilles soap (2 g/L) at 98–100°C to remove silk sericin prior to epoxide treatment.

The tussah silk yarns (ca. 1.0 g) were first immersed in 80 g/L NaSCN aqueous solution at 25°C under reduced pressure (700–720 mm Hg), squeezed to an approximate 115% wet pickup through a roller mangle, and finally treated in tetrachloroethylene (20 mL) containing either ethyleneglycol diglycidylether (2 mL) or glycerin diglycidylether (2 mL) at 80°C for different periods of reaction time (20 min–3 h) to obtain tussah silk fibers with varying values of weight gain. Samples were washed thoroughly with tetrachloroethylene, acetone, and distilled water to remove untreated epoxides and their oligomers. The weight gain increased monotonously with time and reached a maximum value at a certain reaction time. The weight gain of the fiber was calculated from the increase in weight of the original sample after chemical reaction.

Measurements

Dried silk fibers from *A. pernyi* silkworm, untreated and epoxide treated, were hydrolyzed by heating for 20 h at 110°C in 6N HCl. The hydrolyzates were filtered through a glass disk to remove small amount of residues and dried in a rotary evaporator at 40°C. The amino acid composition of silk hydrolyzates dissolved in a buffered solution (pH 2.2) was determined by using a Hitachi L-8500 Type Rapid Amino Acid Analyzer.

The dynamic moduli E' and E'' were measured at 10 Hz with a Toyoseiki Rheograph Solid-S. The temperature range studied was from room temperature to 270°C and samples were heated at 2°C/min. The sample length was 15 mm. The initial tension was 30 g.

The differential scanning calorimetry (DSC) measurements were carried out under nitrogen as described in a previous paper.⁵

X-ray diffraction patterns were obtained using an X-ray source with $CuK\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The conditions for the X-ray measurements have been described in detail elsewhere.⁵

The refractive indices were measured with the Beche's line method using a polarized microscope under the monochromatic light (Na light) at 20°C and 65% RH as previously described.¹²

The tensile properties of epoxide-treated silk 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 50 mm and strain rate of 20 mm/min.

The surface of the treated silk fibers was examined, after gold coating, with a JEOL JAX-333S scanning electron microscope at 15 kV acceleration voltage.

RESULTS AND DISCUSSION

Reactivity of Epoxides

Epoxide-treated tussah silk fibers with different weight gain values were prepared as described in the experimental section. The weight gain values ranged from 19.1 to 60.7% and from 8.8 to 139.9% for samples treated with epoxides G and E, respectively. The noticeably high weight gain values obtained in our experiments should be due to the pretreatment with NaSCN aqueous solution under reduced pressure conditions (700–720 mm Hg). The SCN^- anion absorbed by silk fibers exerted a catalytic effect¹³ enhancing the reactivity of some amino acid residues toward epoxides and consequently increasing the weight gain of silk fibers.

The reactivity of epoxides G and E toward tussah silk fibers was evaluated by the determination of the amino acid composition of two samples with similar weight gain value (about 60–64%). The results are listed in Table I. The amount of either tyrosine or basic amino acids (lysine, histidine, and arginine) of epoxide-treated silk fibers was markedly reduced,

indicating that their side chains are involved in the reaction with epoxides. These data agree with the observation of Tanaka et al.¹⁰ on monoepoxide-treated wild silk fibers. As expected, the amount of acidic amino acid residues (aspartic and glutamic acid) remained unchanged regardless of the epoxide treatment due to the fact that during the HCl hydrolysis the ester bond formed with epoxide molecules has been broken. The above results show that tyrosine exhibited a slightly higher reactivity toward epoxide G, while arginine preferably reacted with epoxide E.

On the basis of the amino acid composition, the tussah silk fibroin contains about $190\text{--}200\text{M}/10^5\text{g}$ amino acids possessing side groups reactive toward epoxides. The molar ratio between epoxides and reactive sites (roughly estimated from the weight gain value) was higher than 1 as the weight gain value exceeded about 40%. These findings suggest that, under the reaction condition adopted, either epoxide G or E should have reacted directly with the functional amino acid residues and should have partly formed dimers inside the silk fiber, enhancing the weight gain up to values not so far detected for other silk fibers, such as *B. mori* and *P. cynthia ricini*. The formation of dimers has been demonstrated by studying the hydrolysis products of *B. mori* silk fibroin after reaction with glycidol, a very highly reactive epoxide.¹⁴ Moreover, the extremely high weight gain value obtained for the epoxide E-treated tussah silk fiber (139.9%) should be partly attributed to the ring-opening polymerization mechanism.

Table I Amino Acid Composition (mol %) of Untreated and Epoxide-Treated Tussah Silk Fibroin with Different Weight Gain Values

	Tussah A	Tussah B	Tussah C
Asp	5.11	5.11	5.37
Thr	0.44	0.43	0.37
Ser	10.58	10.65	9.50
Glu	0.90	0.83	0.91
Gly	29.81	31.77	31.30
Ala	42.27	44.73	45.81
Val	0.88	1.24	1.09
Met	trace	trace	0.53
Ile	0.41	0.91	0.67
Leu	0.41	0.80	1.18
Tyr	5.11	1.02	1.37
Phe	0.34	0.65	0.66
Lys	0.13	trace	trace
His	0.90	trace	trace
Arg	2.72	1.86	1.24

Tussahs A, B, and C represent untreated, glycerin diglycidyl-ether-treated, and ethyleneglycol diglycidylether-treated tussah silk fibers with weight gain of 60.7 and 64.4%, respectively.

Dynamic Viscoelastic Behaviour

The dynamic viscoelastic properties of tussah silk fibers treated with epoxides G and E are shown in Figures 1–4. The dynamic storage modulus (E') curves (Figs. 1 and 3) show that the thermal stability of silk fibers treated with epoxides decreased as the weight gain value increased. At high weight gain values (above 60%), the thermal movement of fibroin molecules became evident at relatively low temperature, starting from about 100°C. On the basis of TMA measurements of *B. mori* silk fibroin membranes, it has been shown that the glass transition temperature is located at around 175°C.¹⁵ Assuming that the general thermal trend of tussah silk fiber is similar to that of *B. mori* silk, the behaviour of E' reported above suggests that the glass transition temperature shifted to lower values by reaction of epoxides into silk. The dynamic loss modulus (E'') curves (Figs. 2 and 4) of treated silk fibers show a major peak at about 200–210°C. The reference sam-

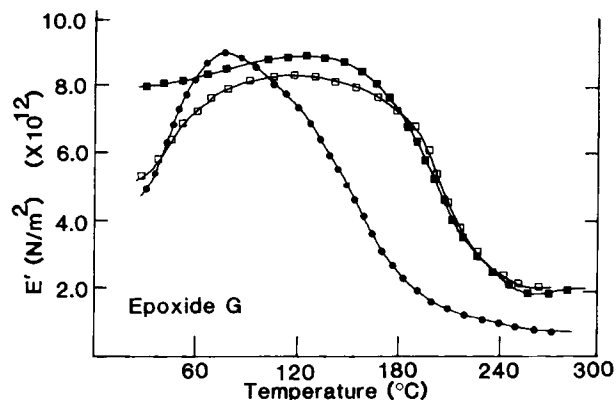


Figure 1 Plots of the dynamic mechanical storage modulus (E') for tussah silk fibers treated with G possessing different weight gain values. Weight gain (%): (\square) 19.1, (\blacksquare) 23.1, (\bullet) 60.7.

ple showed the maximum E'' peak at around 230°C (curve not reported). The temperature of loss modulus E'' shifted to lower values and the peak height decreased by epoxide treatment. The extent of shifting and broadening was significantly larger as the weight gain increased above 30%. Following the reaction of epoxides with tussah silk fibers, a newly induced minor peak appeared in the low-temperature region below 50°C . The position of the peak slightly shifted to higher temperature with increasing weight gain. The thermal movement appearing at low temperature seems to be related to the presence of epoxides in the amorphous regions of silk fibers and to the extent of fibroin-epoxide and epoxide-epoxide interaction, the latter becoming more important at high weight gain values.

As concerns the viscoelastic properties of tussah silk fibers, it has been elucidated that the peak of

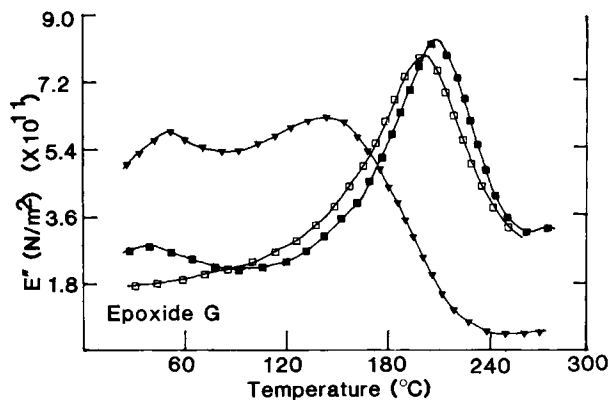


Figure 2 Plots of the dynamic mechanical loss modulus (E'') for tussah silk fibers treated with G possessing different weight gain values. Weight gain (%): (\blacksquare) 19.1, (\square) 23.1, (\blacktriangledown) 60.7.

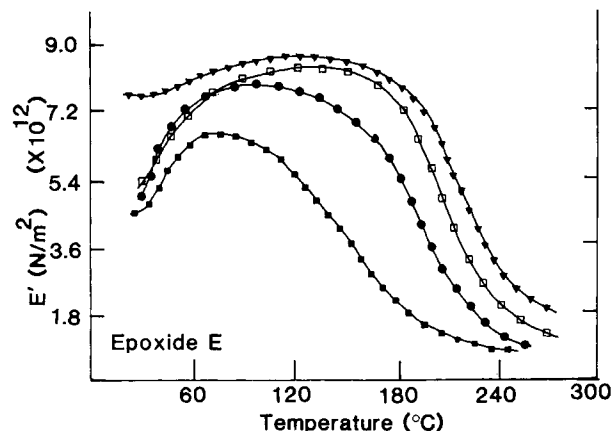


Figure 3 Temperature dependence of the E' of tussah silk fibers treated with E with different weight gain values. Weight gain (%): (\blacktriangledown) 8.8, (\square) 17.8, (\bullet) 25.5, (\blacksquare) 64.4.

loss modulus (E'') starting at 190°C upward, which is closely related to the loss modulus (E''), should be attributed to the crystalline disperse peak, i.e., the molecular motion of the crystalline regions, because the spacings [d_{002}] corresponding to the intersheet distance expand gradually at above 190°C .¹⁶ Figure 5 shows the relationship between the peak temperature of loss modulus (E'') and the weight gain values. The E'' peak shifted linearly to lower temperature as the weight gain value increased, suggesting that the molecular motion of the crystalline regions is noticeably influenced by the epoxide reaction with silk fibroin molecules. These results of the dynamic viscoelastic behaviour of tussah silk fibers indicate that the segmental molecular motion of the crystalline regions becomes less restrictive after epoxide treatment with increasing weight gain, suggesting that epoxides bound to the side chains

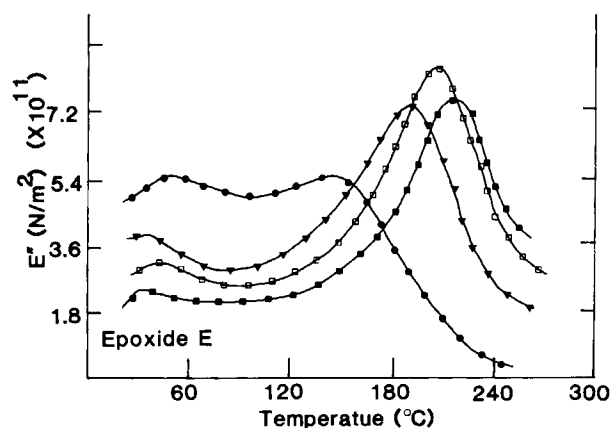


Figure 4 Temperature dependence of the E'' of tussah silk fibers treated with E with different weight gain values. Weight gain (%): (\blacksquare) 8.8, (\square) 17.8, (\blacktriangledown) 25.5, (\bullet) 64.4.

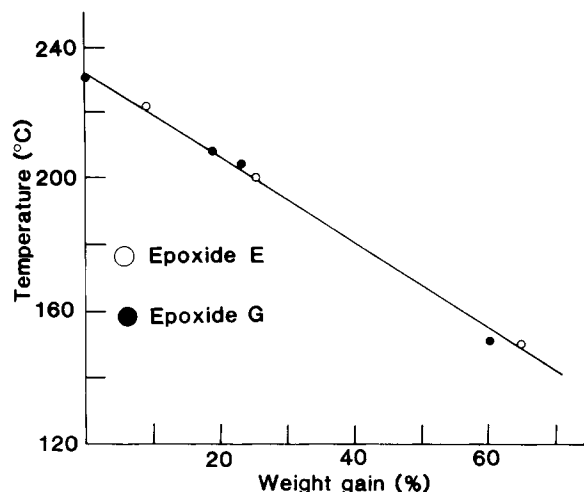


Figure 5 Relationship between the weight gain value and the E'' peak temperature of epoxide-treated tussah silk fibers determined by dynamic viscoelastic measurements. Epoxide: ○, E; ●, G.

of reactive amino acid residues not only in the amorphous regions but also in the laterally ordered (directionally crystallized) regions of the silk fibers.

Thermal Properties

Figure 6 shows the DSC curves of tussah silk fibers treated with epoxides G and E together with untreated tussah silk fibers. The untreated sample exhibited two minor and broad endothermic peaks (shoulder form), one at about 234 and another at around 296°C. This thermal behaviour is characteristic of tussah silk fibroins and differentiates them from *B. mori* silk fibers, which show a single endothermic peak at about 320°C. The reference sample (a) showed a major endothermic peak at 362°C attributed to the thermal decomposition of tussah silk fibroin.¹⁶

Compared to the reference sample, the DSC curves of G-treated tussah silk fibers (b and c; weight gain 46.0 and 60.7%, respectively) showed a quite interesting thermal behaviour. The position of the decomposition peak shifted to lower temperature down to about 356°C; moreover, the intensity of the two minor endothermic peaks decreased significantly and their temperature seemed to shift to lower values. Comparing the thermal behaviour of silk fibers treated with epoxides G (c) and E (d) with almost the same weight gain value (60.7 and 64.4%), the latter exhibited a rather noticeable shift to lower temperature of the major endothermic peak. This tendency has been confirmed by the DSC analysis

of silk fibers treated with epoxide E with a weight gain value of 139.9%. The temperature of the decomposition peak shifted down to 322°C, about 40°C lower than the reference sample; moreover, the two minor endothermic peaks became almost undetectable.

From our results, it is elucidated that the reaction that occurred between silk fibroin and epoxides affects their thermal properties, even though epoxide E seemed to have a markedly higher effect on decreasing the decomposition temperature of epoxide-treated silk fibers. Assuming that either epoxide G or E react with silk fibroin with almost the same reaction mechanism, we suggest that their different effect revealed by thermal analysis should be partly related to the chemical properties of the epoxide molecules and to the mutual interactions with silk fibroin chains. The hydroxyl group carried by epoxide G might contribute to a certain extent to maintain the thermal stability of modified silk fibers by the formation of hydrogen bonds with fibroin chains and/or near epoxide molecules. This fact seemed to contrast with the tendency of decreasing the decomposition temperature following the reaction of epoxides with silk fibers, as demonstrated by silk samples treated with epoxide E with increasing weight gain values.

As concerns the minor endothermic peaks appearing at about 234 and 290°C in the reference

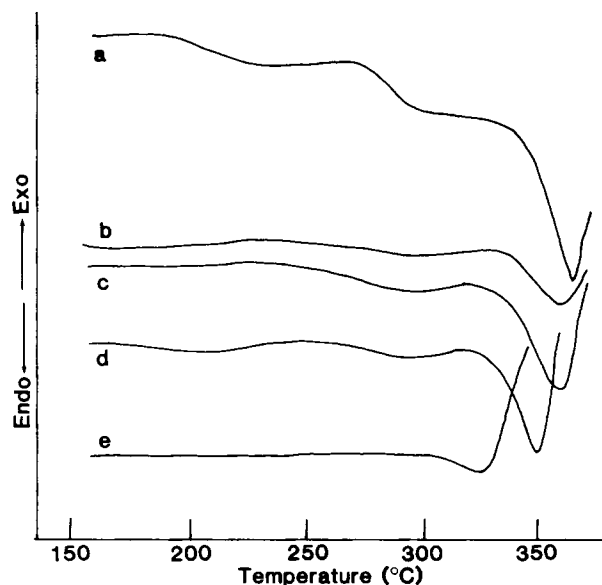


Figure 6 DSC curves of epoxide-treated tussah silk fibers with different weight gain values. (a), untreated sample; (b) and (c), G-treated samples with weight gain of 46.0 and 60.7%, respectively; (d) and (e); E-treated samples with weight gain of 64.4 and 139.9%, respectively.

sample and shifting to lower temperature after epoxide treatment, their meaning and behaviour have not yet been clearly elucidated. Nagura et al.¹⁵ re-

ported the structural changes of regenerated tussah silk fibroin membranes induced by heat treatment and demonstrated that the interhelical interactions

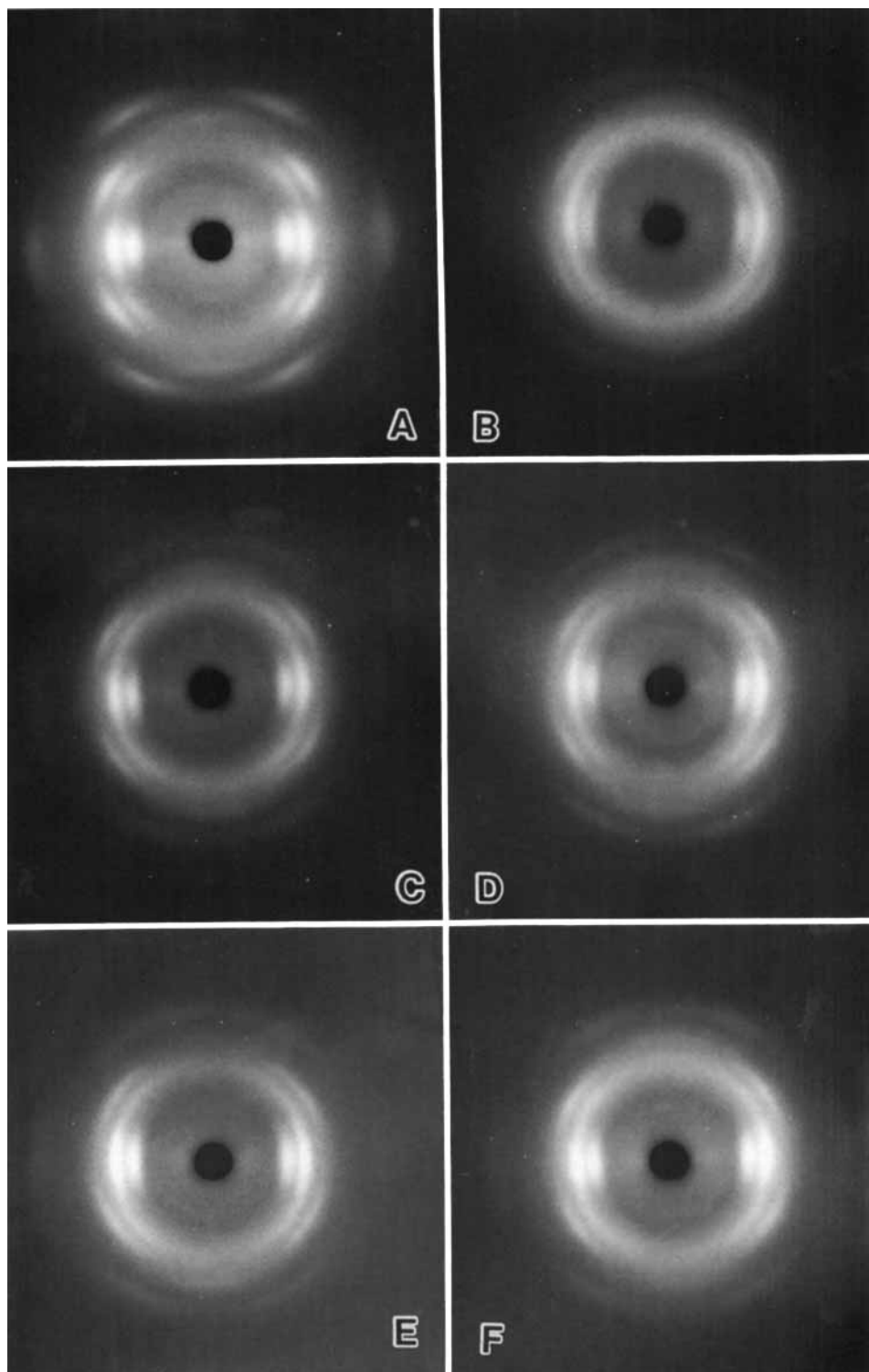


Figure 7 X-ray diffraction patterns of tussah silk fibers treated with epoxides G and E with different weight gain values. A, control; B, E—17.8%; C, E—64.4%; D, G—19.1%; E, G—46.0%; F, G—60.7%.

in the α -helix crystal were weakened suddenly above about 190°C; moreover, at a temperature of 220°C the β -sheet crystals grow from random coil at high crystallization rate. Further investigation should be carried out to elucidate if there are some relationships between these conformational changes and the endothermic transitions exhibited by tussah silk fibroin, particularly that at 234°C. Therefore, we would like to emphasize that the reaction with epoxides entails some modification of the arrangement of fibroin molecules, not only in the amorphous regions but also in more ordered parts of the fiber close to the crystalline regions, and affects their thermal movement, as detected by DSC analysis and dynamic viscoelastic measurements.

Crystalline Structure

To evaluate the crystalline structural changes of tussah silk fibers induced by reaction with epoxides G and E, X-ray diffraction patterns were analyzed (Fig. 7). Untreated tussah silk fibers showed diffraction patterns oriented toward the equator and corresponding to the spacings of 4.47 and 5.65 Å, which are characteristics of the oriented β' configuration. These spacings are attributed to the diffraction from the [002] and the [201] planes of tussah silk fibroin. The fibers treated with epoxides G and E showed the same diffraction pattern associated with the β' configuration as the reference tussah silk. It is of interest to note that the diffraction pattern corresponding to the [002] spacing of the intersheet distance remained unchanged regardless of the epoxide treatment; however, the diffraction pattern due to the [201] became broader, suggesting

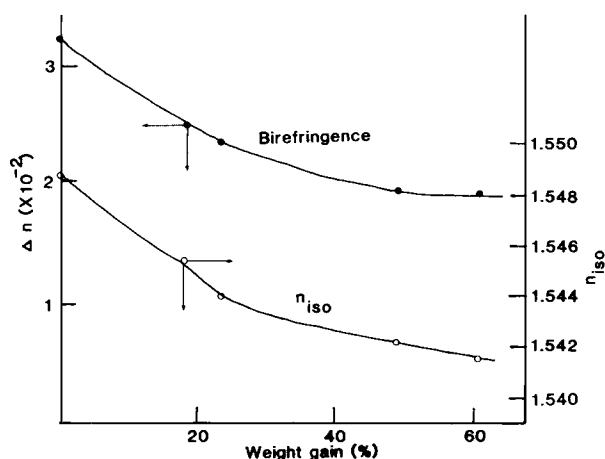


Figure 8 Birefringence (●) and isotropic refractive index (○) of tussah silk fibers treated with epoxide G.

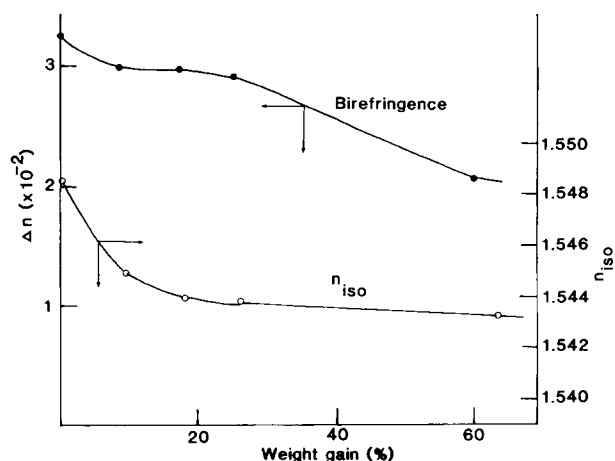


Figure 9 Birefringence (●) and isotropic refractive index (○) of tussah silk fibers treated with epoxide E.

that the molecular orientation partly became disordered after epoxide treatment.

Refractive Indices

The birefringence (Δn) and isotropic refractive index (n_{iso}) of treated tussah silk fibers are reported in Figures 8 and 9, respectively. Silk fibers treated with epoxide G (Fig. 8) showed a parallel and gradual decrease of either Δn and n_{iso} as the weight gain value increased up to 60%. It is interesting to note that the decrease of refractive index values is not linearly related to the weight gain, confirming there exists a mutual interaction between epoxide and silk fibroin. Silk fibers treated with epoxide E (Fig. 9) showed a rather different behaviour: The birefringence remained almost unchanged as the weight gain increased up to 30% and then decreased gradually, attaining a final value similar to that of silk fibers treated with epoxide G. The n_{iso} value decreased very quickly as the weight gain increased to 15–20% and then remained almost unchanged. The silk fibers with a weight gain of 60% showed an n_{iso} value higher than that of the corresponding sample treated with epoxide G.

Birefringence may be regarded as a molecular property related to the configuration of the molecules and to their orientation in a fibrous polymer. The above results show that the reaction of epoxide E with tussah silk fibroin molecules causes a lower decrease of orientation compared to the fibers treated with epoxide G, suggesting that epoxide E molecules introduced into silk fibers, at least for relatively low weight gain values, do not disturb the average molecular orientation.

Since the isotropic refractive index ($n_{i\text{so}}$) is related to the degree of order and crystallinity of the silk fibers, it seemed that both epoxides G and E affected the crystallinity of tussah silk fibers, although to a different extent, following the increase of weight gain value. This effect may be regarded mainly as a decrease of the degree of order rather than a modification of the crystalline structure, as elucidated by X-ray analysis.

Surface Characteristics

The surface characteristics of tussah silk fibers after treatment with epoxides were investigated by scanning electron microscopy (SEM) analysis. Figure 10 shows the SEM micrographs of tussah silk fibers treated with epoxides G and E with different weight gain values ranging from 46 to 139.9%. No significant differences were detected between the silk fibers treated with the two kinds of epoxides. Compared to the untreated fibers (micrograph not shown), the

reaction with epoxides did not seem to affect the surface characteristics as the weight gain increased up to 40–45% (A). The typical longitudinal streaks with regular spacing of about 0.2 μm , one of the morphological characteristics of wild silks, appeared clearly on the fiber surface (A, B). As the weight gain value increased to 60–65% (C), the streaks became less visible and the silk fibers appeared swollen as a consequence of the introduction of epoxides inside them. Only a few small granules were detected on the epoxide-treated silk fibers with the highest weight gain value (D; 139.9%).

Tensile Properties

The mechanical properties of tussah silk fibers treated with epoxides G and E, as well as the water absorption values, are listed in Table II.

The average water absorption value of epoxide-treated silk fibers is slightly higher than that of the reference sample. The differences among the sam-

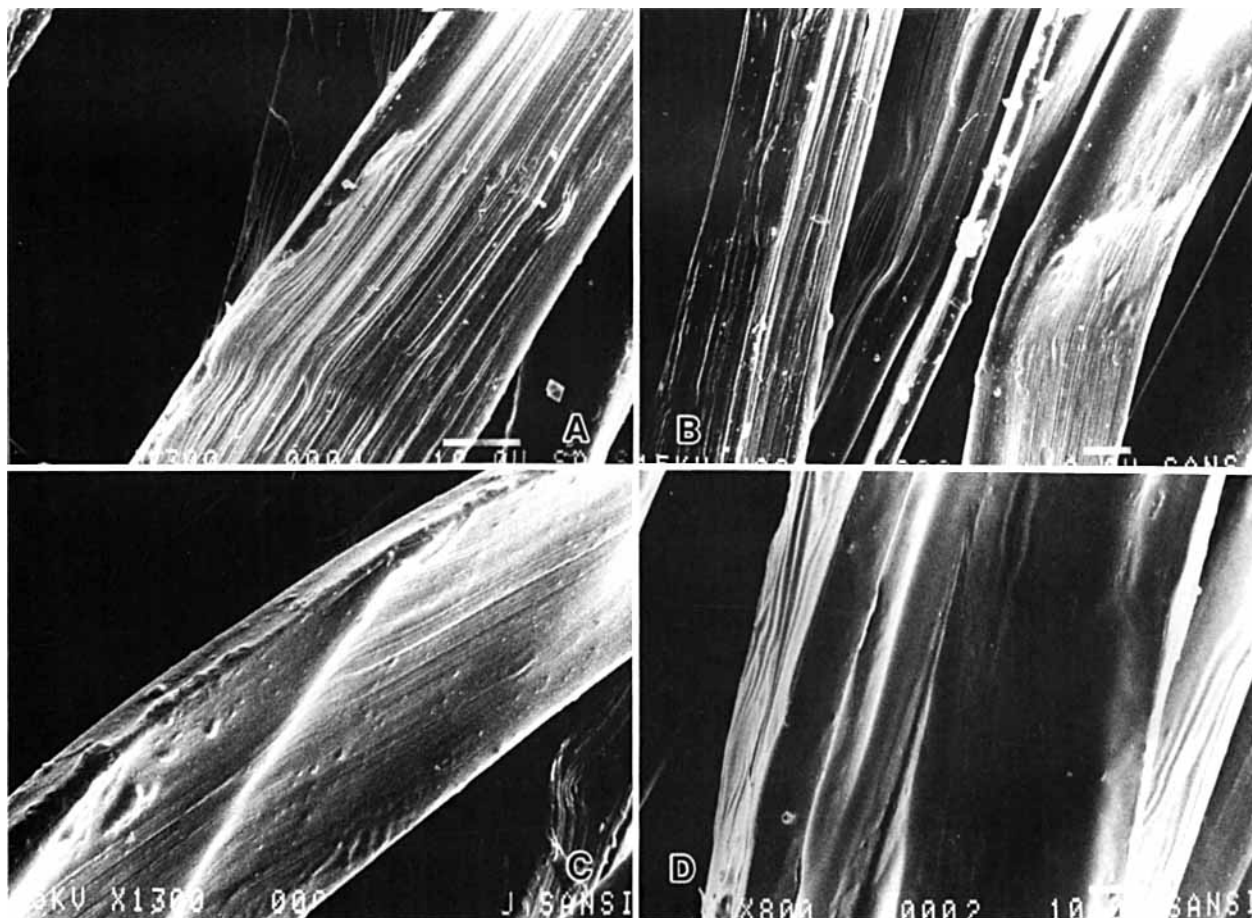


Figure 10 Scanning electron micrographs of tussah silk fibers treated with epoxides G and E with different weight gain values. A, G—46%; B, E—64%; C, G—60%; D, E—139.9%.

Table II Physical Properties of Tussah Silk Fibroin Fiber from *A. pernyi* Treated with Glycerin Diglycidylether (G) and Ethyleneglycol diglycidylether (E) Possessing Different Weight Gain Values

Sample	Weight Gain (%)	WA ^a (%)	Strength (g/d)	Elongation (%)
Control	—	7.7	3.6	40.6
Epoxide G treated	19.1	7.7	2.5	32.4
	23.1	8.4	2.3	30.8
	29.0	8.1	2.5	30.2
	46.0	7.9	2.6	25.0
	60.7	7.5	2.5	24.26
Epoxide E treated	8.8	8.9	3.0	31.6
	17.8	8.9	2.9	29.0
	25.5	8.7	2.8	28.8
	64.4	7.3	1.8	20.8
	139.9	8.8	1.7	21.6

^a WA, water absorption (%).

ples treated with the same kind of epoxide seem quite randomly distributed and not directly related to the increase of weight gain values.

Following the reaction of tussah silk fibers with epoxide G, the strength attained a lower value that remained almost unchanged regardless the increase of weight gain from 19.1 to 60.7%. On the other hand, the elongation showed a linear decrease with increasing weight gain values. As concerns the tussah silk fibers treated with epoxide E, their strength remained constant for weight gain values up to 25.5% and then decreased to about one half, compared to the reference sample. The elongation showed a linear decrease for weight gain values until 64.4%. The increase of weight gain value from 64.4 to 139.9% did not seem to markedly affect the tensile properties of tussah silk fibers. It is reasonable to consider that the decrease of the tensile properties of the epoxide-treated silk fibers can be explained by the increase of fiber size associated with the swelling behaviour of the samples, especially when the weight gain value reached 60% as shown in Figure 10.

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