Structural Characteristics of Silk Fibers Treated with Epoxides

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SYNOPSIS

Structural characteristics of the silk fibroin fiber-modified with epoxide treatment were elucidated by refractive index measurement, differential scanning calorimetry, and thermomechanical analysis and on the basis of strength–elongation measurements. The four epoxides used were glycidol (G), ethylene glycol diglycidyl ether (E), tolyl glycidyl ether (T), and resorcinol diglycidyl ether (R). The values of the isotropic refractive index of the silk fiber increased by the action of T or R. The position of the endothermic peak attributed to the thermal decomposition and the position of the onset of the contraction of each of the samples treated with epoxides shifted to higher temperature, suggesting the more thermal stability. However, the values of the molecular orientation and the crystallinity of the specimen evaluated from X-ray diffraction analysis remained unchanged regardless of the epoxide treatment. These experimental results have been interpreted in terms of the cross-links between the adjacent silk fibroin molecules and of the hydrogen bonds between the hydroxyl groups of the epoxide molecules attached to the side chains of the silk fibroin.

INTRODUCTION

A considerable amount of work has been carried out on chemical modification onto silk with a view to improving its bulkiness, dyeability, and chemical resistance. Many researchers have performed on the grafting of vinyl monomers[1-4] onto silk fiber and tried to define the structural analysis[5-6] of the grafted silk fibers. It is elucidated that the silk fabric became soft and bulky in proportion to the air quantity ratio and the internal volume by the action of the methacrylamide onto the silk.[7] Among the chemical modifications, the epoxide treatment onto silk looks promising from the view of the experimental fact that physical properties are much improved by the action of epoxide. Shiozaki and Tanaka[8] have analyzed the reactivity of epoxide onto silk and demonstrated that the modifications with epoxide onto silk improve materially the fiber and the fabric, such as the physical properties, moisture absorption, chemical resistance, and wash and wear properties.

From the amino acid analysis[9] of the silk treated with epoxide, it may be concluded that the epoxide agents react with the side chains of the silk fibroin, such as lysine, histidine, arginine, and tyrosine, suggesting that most of the weight gain due to the fiber treatment distributes uniformly throughout the cross section and does not occur near the fiber surface.

It is well known that structural changes induced by the chemical modification have an important effect on the mechanical properties of the silk fibers. However, only limited information on the fine structural changes of silk fibers induced by the chemical modification is available. It is shown by one of the authors[10] that the refractive index is a practical measure to evaluate the structural changes, i.e., density and crystallinity, because the relationship between the isotropic refractive index (n_{iso}) and the density (ρ) of silk can be derived according to the following equation[11]:

$$K = (n_{iso} - 1)/\rho \qquad (1)$$

where $K = 0.357$. In addition, the technique of measuring the refractive index of the silk fiber is useful because the value of the refractive index[10,12] is very sensitive to the structural changes of the silk fibroin during the course of the chemical modification. However, the relationship between structural changes and physical properties of the chemically modified silk fiber has not been experimentally determined in detail. From this point of view, it is worthwhile to elucidate the structural changes of the silk fibroin fiber treated by the epoxide by measuring the refractive index.

We report in this paper structural characteristics including mechanical properties and thermal behaviors of silk fibroin fibers caused by the action of the epoxide onto silk fiber.

EXPERIMENTAL

Materials

Raw silk fibers were obtained from the reeling of cocoon threads of the domesticated mulberry silkworm, *Bombyx mori*. Two silk threads (21 d size) were twisted together mechanically. Silk fibroin fibers were pretreated with an 8.1 g/L NaSCN aqueous solution at 25°C for 5 min. Silk fibroin fibers pretreated were then dropped into a graduated glass tube containing different kinds of epoxides in tetrachloroethylene at 68–70°C for different periods of
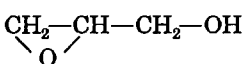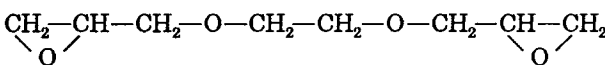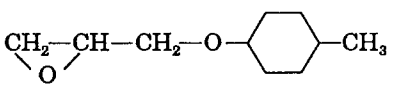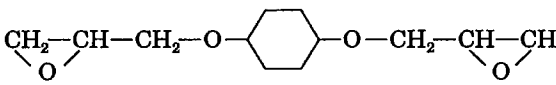
time; this was attached to a reflex condensor, held in a thermostatically controlled bath. The four epoxides used were glycidol (G), ethylene glycol diglycidyl ether (E), tolyl glycidyl ether (T), and resorcinol diglycidyl ether (R). Table I lists the epoxides used, the sample abbreviations, and the treatment conditions. At the end of the reaction, the samples were washed with boiling acetone for 30 min to remove the oligomers produced in the samples and washed successively with methanol, tap water, and, finally, distilled water. The weight gain was calculated from the oven-dried weights of the fibroin fiber. The samples were dried to constant weight and conditioned in air at 20°C, 65% relative humidity (RH) for 2 weeks.

E, 12 g, was dissolved in 100 mL of water containing 4 g of NaSCN at room temperature. The mixture was stirred for 3 h at 75–80°C. At the end of the reaction, the E oligomer was precipitated by pouring the solution into 500 mL of rapidly stirred water. After thorough washing with water and drying, the oligomer weighed 8.2 g.

Measurements

The refractive indices parallel to the fiber axis, $n_{\parallel}$, and those perpendicular to the fiber axis, $n_{\perp}$, were measured with Becke's line method using a polarized microscope under monochromatic light (Na light) at 20°C and 65% RH using the mixture system of diphenylamine and tricresyl phosphate for the refractive index range 1.555–1.595 or the mixture system of dibutyl phosphate and tricresyl phosphate

Table I   Characterization of Epoxides and Abbreviations for the Treated Silk Fibers

Epoxide	MW[a]	Molecular Form	Sample Abbreviation	Conc (%)	Treatment Time (h)
Glycidol	74	CH₂—CH—CH₂—OH (with O bridge)	G–1	10	1
			G–2	10	2
			G–3	10	3
Ethylene glycol DGE[c]	174	CH₂—CH—CH₂—O—CH₂—CH₂—O—CH₂—CH—CH₂ (with O bridges)	E–1	5	1
			E–2	5	2
			E–3	5	3
Tolyl GE[b]	164	CH₂—CH—CH₂—O—⟨ring⟩—CH₃ (with O bridge)	T–1	10	1
			T–2	10	2
			T–3	10	3
Resorcinol DGE[c]	222	CH₂—CH—CH₂—O—⟨ring⟩—O—CH₂—CH—CH₂ (with O bridges)	R–1	5	1
			R–2	5	2
			R–3	5	3

[a] Molecular weight.
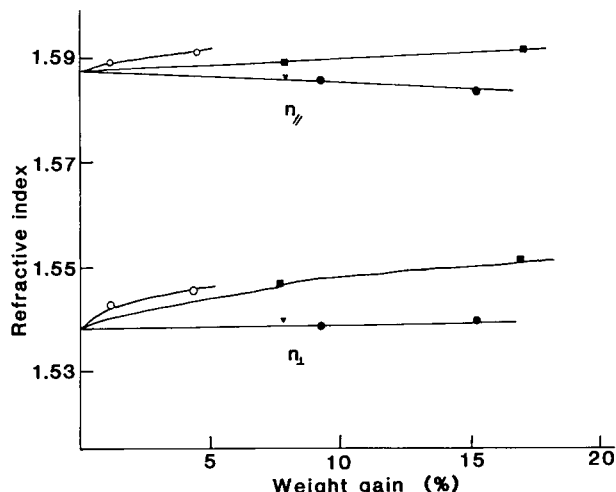[b] Glycidyl ether.
[c] Diglycidyl ether.

Figure 1 Refractive indices parallel to the fiber axis, $n_\parallel$, and perpendicular to the fiber axis, $n_\perp$, of the silk fibroin fiber treated with different epoxides in function of the weight gain. Epoxide: (▼) glycidol; (●) ethylene glycol diglycidyl ether; (○) tolyl glycidyl ether; (■) resorcinol diglycidyl ether.

for the range 1.500–1.555. The birefringence, Δn, and isotropic refractive index, n_{iso}, of the silk fiber were calculated according to the following equations:

$$\Delta n = n_\parallel - n_\perp \qquad (2)$$

$$n_{iso} = (n_\parallel + 2n_\perp)/3 = n_\perp + \Delta n/3 \qquad (3)$$

Load-elongation curves were obtained with an Instron testing machine (Toyo Baldwin Co.) at a constant rate of elongation of 30% per minute on specimens of 50 mm. The rupture strength and elongation at breaking point are the means of 20 tests carried out on the four sets of fibers.

The differential scanning calorimetry (DSC) measurements were performed on a Rigaku Denki instrument at a heating rate of 10°C/min. DSC range and sample weight were 2.5 mcal/s and 2 mg, respectively. Thermomechanical analysis (TMA) curves were obtained on a Rigaku Denki instrument at a heating rate of 10°C/min. TMA full scale was 500 μm.

X-ray diffractometric measurement was performed with a diffractometer (Rigaku Denki Co.) with a scintillation counter and a pulse height analyzer, using CuKα radiation. The voltage and current of the X-ray source were 40 kV and 20 mA, respectively. The diffraction intensity curves were measured at a scanning rate of 1°/min with a scanning region of 5–45°. Crystallinity was measured from X-ray diffraction curves according to the method proposed by Hermans and Weidinge.[13] Molecular orientation corresponding to the crystalline region and not to the amorphous region was estimated from the half-width of the X-ray diffraction curves.

RESULTS AND DISCUSSION

Refractive Index

Figure 1 shows the refractive indices, $n_\parallel$ and $n_\perp$, of the silk fiber treated with different epoxides to which

Table II   Add-Ons and Mechanical and Physical Properites of Silk Fibroin Fibers Modified by Various Epoxides

Sample	Add-On (%)	Strength (g/d)	Elongation (%)	Degree of Orientation (%)	Degree of Crystallization (%)
G-1	7.9	1.3	3.0	74.2	22.1
G-2	3.7	1.3	3.1	75.3	22.6
G-3	0.8	0.1	2.1	78.4	23.4
E-1	9.1	3.8	15.8	78.4	22.1
E-2	13.2	3.9	14.8	78.2	23.1
E-3	15.2	3.0	13.3	78.2	24.6
T-1	1.0	3.5	13.0	76.4	22.2
T-2	3.9	3.3	11.5	77.4	22.4
T-3	4.3	2.9	9.4	80.0	23.0
R-1	7.8	3.9	14.3	78.7	20.6
R-2	14.0	3.5	12.9	79.0	23.3
R-3	17.0	4.0	14.0	80.4	22.8
Control	—	3.1	12.2	80.4	22.3

various amounts of epoxides are contained. The symbol ▼ in Figure 1 indicates the value of the refractive index of the silk fiber treated with G for 1 h. Since the weight of the silk fiber decreased with the duration of the action of G for 2 and 3 h because of the degradation (Table II), their refractive indices are not given in Figure 1. The value of $n_{\parallel}$ of the fibers treated with G (with weight gain of 7.9%) and the silk fibers treated with E decreased gradually with an increase in the weight gain, whereas those values of $n_{\perp}$ were practically the same as was that value of the control sample.

Lysine and tyrosine were identified in the silk treated with glycidol, the latter being found by addition of a second molecule of glycidol to O-(dihydroxypropyl) tyrosine residues.[15] The changes in the above refractive index of the silk fiber treated with E can be, thus, well explained by considering the isotropic refractive index (n_{iso}) of the E oligomer, since the n_{iso} of the E dimer was 1.554–1.555, explaining why the apparent $n_{\parallel}$ decreases and $n_{\perp}$ increases slightly with treatment time.

The values of $n_{\parallel}$ and $n_{\perp}$ of the fibers treated with T and R increased with increasing weight gain. The increased amount of the values of $n_{\perp}$ of the silk fiber treated with T was greater than those values of $n_{\parallel}$ of the silk fiber.

The isotropic refractive index and the birefringence of the silk fibroin treated with epoxide are shown in Figure 2. The values of n_{iso} of fiber treated with E remained unchanged regardless of the epoxide treatment. The values of n_{iso} of the silk fiber treated with T or with R increased with increasing the weight gain, which is in contrast to those values of the silk fiber treated with E or R, whose results
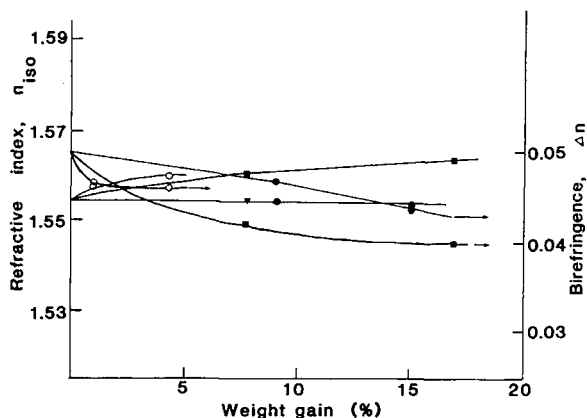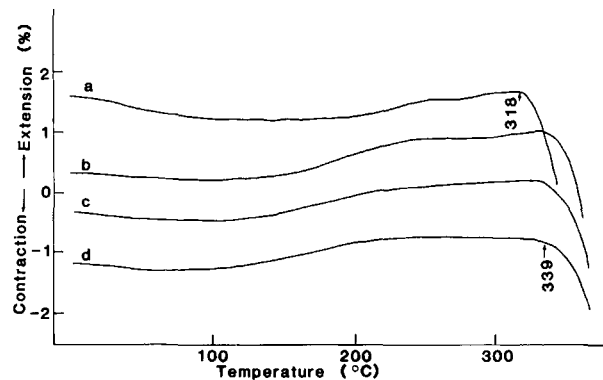

Figure 3 TMA curves of the silk fiber treated with ethylene glycol diglycidyl ether for different periods of treatment time. Time (h): (a) 0; (b) 1; (c) 2; (d) 3.

seem to reflect the structural difference of the epoxide molecules; that is, R and T epoxide possess an aromatic group in their structure, whereas E and G epoxide do not possess one. On the other hand, the birefringence of all fibers treated with epoxides decreased gradually.

The values of birefringence of the fiber treated with T decreased rapidly in the weight gain range 0–4%. The decreased amount of refractive index of the fiber treated with R was greater than that treated with E. The above measuring results of the refractive index should be attributed to the structural change of silk fibroin induced by the action of epoxide. It is worthwhile to note that the birefringence of the silk fiber treated with bifunctional epoxides, i.e., R and E, clearly decreased with the duration of the epoxide reaction onto silk fibroin. The increasing of the values of n_{iso}, which presumably are attributed to the increasing of the values of $n_{\perp}$, can be assigned to an increase in sample density as is obvious from

Figure 2 Isotropic refractive index, n_{iso}, and the birefringence, Δn, of the silk fiber treated with different epoxides in function of the weight gain. Symbols are the same as in Figure 1.
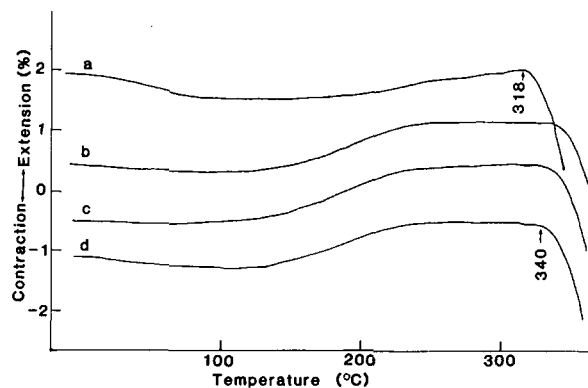

Figure 4 TMA curves of the silk fiber treated with resorcinol diglycidyl ether. Time (h): (a) 0; (b) 1; (c) 2; (d) 3.

eq. (1) and to an increase in the molecular aggregation. It can therefore be presumed that the cross-links are formed between the adjacent silk fibroin molecules by the epoxide treatment.

Mechanical Behavior

A study of the effect of changes in the structural changes of silk fibroin on mechanical behavior was undertaken using a fibrous sample treated with various kinds of epoxides. The tensile strength and elongation at breaking point of the silk fiber treated with epoxide are shown in Table II. The strength and elongation of the control silk fiber is 3.1 g/d and 12%, respectively. Strength and elongation of the silk fiber treated with G reduced rapidly, especially above the treatment time of 2 h. The elongation at breaking point of the fiber treated with E increased up to 15.8% and decreased down to the value of the control sample when the treatment time was 2–3 h. The increase in the strength of the silk fiber treated with epoxide seems to imply the formation of the cross-links between the adjacent silk fibroin molecules, which was in accord with the estimation from the refractive index measurement.

Thermomechanical Analysis

To define the contraction and extension of the silk fibroin fiber in the course of the heating process, TMA curves of the silk fiber treated with epoxide were obtained. Since each of the silk fibers shows a striking resemblance in thermal behaviors, we have shown representative TMA curves of silk fiber treated with E and R in Figures 3 and 4, respectively.
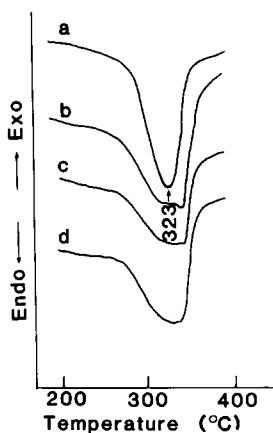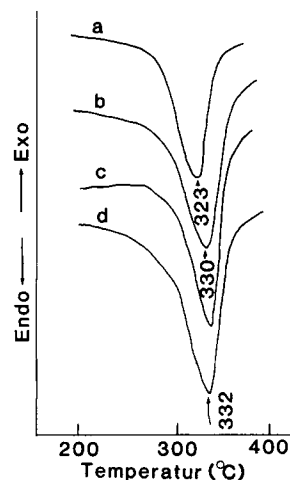

Figure 6   DSC thermograms of silk fiber treated with ethylene glycol diglycidyl ether for different periods of treatment time. Time (h): (a) 0; (b) 1; (c) 2; (d) 3.

The control sample demonstrated the slight contraction of about 0.4% in a temperature range between 30 and 230°C; then the length of the specimen was retained unchanged up to 300°C. The control sample exhibited an abrupt contraction in length above 318°C. Silk fiber treated with E exhibited similar TMA curves to those of the control. However, silk fiber began to contract at above 330°C. The shift to higher temperature of the onset of the contraction of the silk fiber can probably be explained by the thermal behavior of enthropic elasticity resulting in the thermal movement of the silk fibroin molecules in the amorphous region, suggesting that the more thermal stability can be accounted for by the strong interaction between silk fibroin
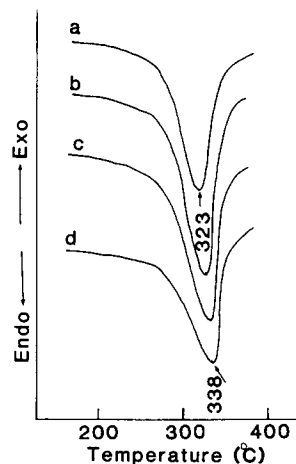

Figure 5   DSC thermograms of silk fiber treated with glycidol for different periods of treatment time. Time (h): (a) 0; (b) 1; (c) 2; (d) 3.

Figure 7   DSC thermograms of silk fiber treated with tolyl glycidyl ether for different periods of treatment time. Time (h): (a) 0; (b) 1; (c) 2; (d) 3.
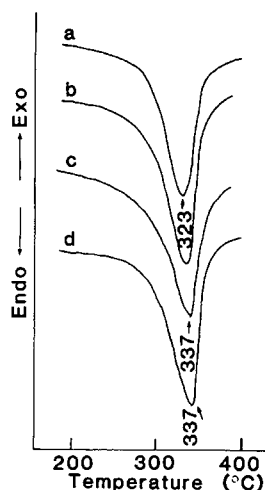
Figure 8   DSC thermograms of silk fiber treated with resorcinol diglycidyl ether for different periods of treatment time. Time (h): (a) 0; (b) 1; (c) 2; (d) 3.

molecules resulting from the epoxide treatment onto silk fibroin.

DSC Thermograms

Lastly, we will refer to the changes in the thermal properties in relation to the structural change of the silk fibroin fiber treated with epoxide. DSC thermograms were recorded for the silk fiber treated with different epoxides over the temperature range 200–400°C at a heating rate of 10°C/min (see Figs. 5–8). The control silk fiber showed a single endothermic peak at around 323°C, which was attributed

to the thermal decomposition of the silk fibroin with oriented β' configuration.[5] The endothermic peak of the silk fibroin broadens with the duration of the G treatment. The position of the endothermic peak of the silk fiber treated with E, T, and R shifted slightly to higher temperature. The increased amount of the shifts for the fiber treated with T was 15°C higher than that for the control, whose value is larger than any other values of the specimen. According to the DSC study of the silk fibroin fiber, we[14] estimated that the position of the endothermic peak attributed to the thermal decomposition shifts to higher temperature with an increase in the degree of the molecular orientation. These results are believed to show an increase in the molecular orientation of silk fibroin caused by the action of the epoxide. To make sure that the degree of molecular orientation increases, we therefore measured the degree of the molecular orientation and the degree of crystallinity (Table II). No significant difference in the degree of molecular orientation and the degree of the crystallinity can be detected regardless of the epoxide treatment, suggesting that the molecular orientation and the crystalline size of silk fibroin molecules remained unchanged regardless of epoxide treatment. Thus, the changes of mechanical behavior, refractive index, and thermal properties of the silk fibroin fiber treated with epoxide are largely caused by structural changes such as formation of cross-links between the adjacent silk fibroin molecules and of hydrogen bonds between the hydroxyl groups of the epoxide molecules attached to the side chains such as lysine, arginine, aspartic acid, glutamic acid, serine, and
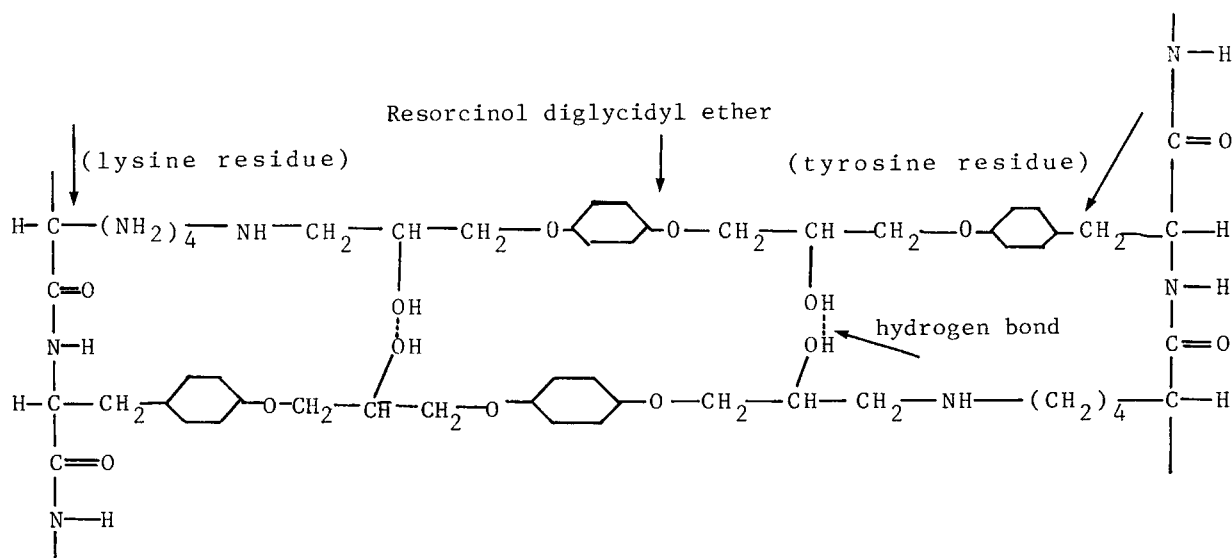

Figure 9   Schematic of our model system. Note that the model is one-dimensional.

tyrosine residues[8] of the silk fibroin. Our model schematically displayed in Figure 9 consists of a number of epoxides attached to the side chains of the silk fibroin. These effects result in the changes of mechanical properties, thermal properties, and refractive indices.

It should be pointed out here that molecular orientation and the crystallinity evaluated from the X-ray diffraction analysis and the mechanical properties of the treated silk fiber stayed unchanged regardless of the epoxide treatment, suggesting that the decrease in the birefringence of the silk fiber with the duration of the epoxide reaction may be attributed to the decreasing of the molecular orientation corresponding to the amorphous region and not to the crystalline region and may be due to the value of the refraction of the epoxide reacted toward the silk fibroin used in the investigation.

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