

# Physical Properties of Silk Fibers Treated with Ethylene Glycol Diglycidyl Ether by the Pad/Batch Method

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## SYNOPSIS

This paper deals with the epoxide treatment of silk fabrics by the pad/batch method. The optimum reaction conditions, i.e., NaOH concentration, and reaction temperature were 2.5 g/L and 30°C, respectively. A weight gain of 8.5% was attained at a reaction time of 6 h. This value slightly increased to 10% after 24 h. The reactivity of tyrosine and basic amino acid residues was dependent on the reaction time and did not significantly differ from the results of epoxide-treated silk fiber by the conventional method in tetrachloroethylene. The moisture regain slightly decreased at 4% weight gain and then increased with the epoxide content, exceeding the value of the untreated control. The crease recovery of the epoxide-treated silk fabrics measured in the wet state was significantly improved, whereas that in the dry state was almost unchanged. The rate of photoyellowing of the epoxide-treated silk fabrics by the pad/batch method was reduced significantly compared with that of the untreated control. Among the mechanical properties, elongation at break and tensile modulus remained unchanged, whereas the tensile strength slightly increased following the epoxide reaction. The thermal properties were evaluated by DSC and TGA and on the basis of the dynamic viscoelastic measurements. The DSC curve of the epoxide-treated sample showed a slight increase of the decomposition temperature of silk fibroin. The rate of weight loss determined by TGA remained unchanged regardless of the chemical modification, whereas the peak of loss modulus became broader and shifted to lower temperature. The X-ray diffractograms showed that the crystalline structure of silk fibers was not affected by the reaction with epoxides. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The reaction of epoxides with protein fibers, such as wool<sup>1,2</sup> and silk,<sup>3,4</sup> has been extensively studied since the end of the 1960s. As is well known, epoxides react with amines, alcohols, phenols, carboxylic acids, and thiols. Protein fibers contain amino acid residues with functional groups of all these types, whose reactivity toward epoxides has been the subject of several investigations.<sup>1-4</sup> The chemical modification of silk by reaction with epoxides was first introduced by Shiozaki and Tanaka<sup>4</sup> in 1969. Since then, techniques for the chemical finishing of silk

fabrics by treatment with epoxides, namely, ethylene glycol diglycidyl ether,<sup>5</sup> have been developed and are widely applied in Japan. This technique became quite popular, from the point of view of the industrial application, for its effectiveness in improving some inferior properties of silk fabrics, such as crease recovery in both the dry and wet states, light resistance, and color fastness to washing.<sup>6,7</sup>

The fine structural changes induced by reaction of epoxides with silk fibers have been extensively studied by Tsukada and co-workers.<sup>8-11</sup> The changes in physical structure, as well as in mechanical and thermal behaviors, were attributed to the formation of cross-links between adjacent fibroin chains and to the interactions by hydrogen-bond formation between the polar groups of epoxide molecules and functional groups of various amino acid residues.

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Moreover, the effect of the modification on the mechanical properties related to the hand and texture of epoxide-treated silk fabrics, i.e., bending, shearing, and compressional characteristics, has been reported.<sup>9</sup>

The epoxide treatment is conventionally carried out on silk fabrics, which are padded at about 100% wet pickup with a salt solution, usually 1*N* NaSCN, whose catalytic effect on the reaction of epoxides toward silk fibroin has been demonstrated.<sup>10</sup> The textile material is then treated in tetrachloroethylene with the required amount of epoxide at 60–80°C for different times, according to the desired weight gain. One of the major problems of this method is the use of the organic solvent, which is responsible for environmental pollution in work places and can be dangerous for the health of the exposed workers. Moreover, the treatment of silk fabrics at relatively high temperature for more than 2–3 h can sometimes enhance the risk of diminishing the intrinsic physicochemical and mechanical properties of the textile materials. Because of the above drawbacks, a comprehensive research program has been undertaken to study new modifying agents, such as dibasic acid anhydrides, as well as to develop new finishing techniques for silk fabrics.

The pad/batch method is widely used for textile processing, mainly for cellulosic and synthetic fibers, and it is highly appreciated because significant savings of water, energy, and chemical reagents can be achieved. The application of this method to silk processing is sometimes restrained, the limiting factor being usually represented by the small size of the silk lots processed at the same time. Nevertheless, a pad/batch treatment of silk fabrics with epoxides, aimed at many practical applications, appeared in a Japanese patent in 1989.<sup>6</sup>

The aim of the present article was to study the chemical reaction of epoxides with silk under the conditions adopted in the pad/batch method. The composition of the padding solution, as well as the reaction temperature and time, was studied in order to find the optimum parameters for silk treatment. Moreover, the physical, mechanical, and thermal properties of the resulting silk fabrics were investigated, in comparison with the results reported for silk prepared by using the conventional epoxide treatment.

## EXPERIMENTAL

### Materials

Silks were chemically modified with an epoxide compound by the pad/batch method. The silk fiber

and silk fabric were the same samples as used in a previous article.<sup>10</sup> Silk fiber and swatch (plain woven, habutae, 60 g/m<sup>2</sup>) were pretreated at different reaction temperatures and times, with aqueous solution (1000 mL) that contained 120 g ethylene glycol diglycidyl ether (EDGE) (Epiol E 100, Nihon Yushi Co.), 120 mL isopropanol, and different amounts of NaOH, in order to find the optimum conditions. Silk samples were padded with the epoxide reaction system to an approximate 100% wet pickup. Silk samples were then stored at 30°C (or at different temperatures in another experiment to find the optimum condition) for different periods of reaction time (0–24 h) in the closed system of a sealed polyethylene bag so as not to evaporate the epoxide reaction system that was absorbed within the silk fibers. Chemical modification of silk fiber with epoxide toward silk fibroin thus proceeded at 30°C, which is 50°C lower than that (68–79°C) for the conventional modification method. 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 tap water and, finally, with distilled water.

### Measurements

Dried silk fiber treated by the pad/batch method with different values of weight gain were hydrolyzed by heating at 110°C for 20 h in HCl 6*N* under vacuum. The hydrolyzed sample was filtered through a glass disk to remove small amounts of residues, dried in a rotary evaporator at 40°C, and dissolved in a buffer solution at pH 2.2 (1 mg/mL). The amino acid composition was determined using a Hitachi L-8500-type rapid amino acid analyzer. To analyze the minor and important basic amino acid residues related to the chemical modification with epoxide, a concentrated sample solution (five times higher) was used for the analyzer.

The crease recovery of silk fabrics was evaluated from measurements based upon the method described in the JIS standard L1079, 1966. Tensile strength and elongation at break of the epoxide-treated silk fibers were measured according to method described in a previous article.<sup>10</sup>

DSC measurements were performed on a Rigaku Denki instrument (DSC-10A) 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 aluminum cell was swept with N<sub>2</sub> gas during the course of the analysis. Thermogravimetric analyses (TGA) were run under nitrogen on a Rigaku Denki instrument programmed under isothermal conditions, raised at 10°C/min to 400°C.

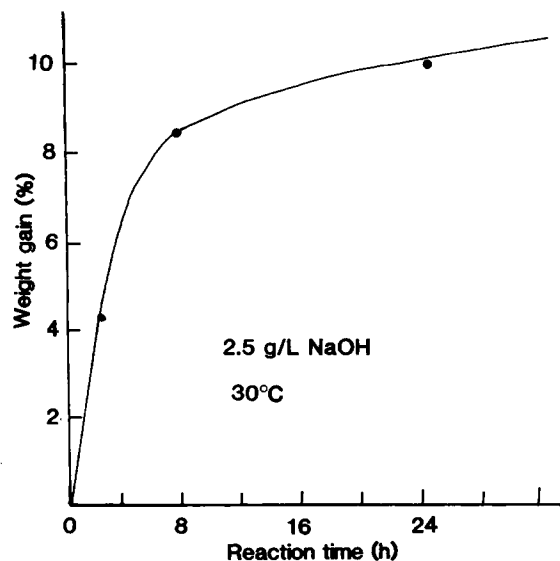
The dynamic moduli  $E'$  and  $E''$  were measured at 10 Hz with a Toyoseiki Rheograph Solid-S. The temperature range studied was from room temperature to 260°C and the samples were heated at 2°C/min. The sample length was 15 mm with an initial tension of 30 gf. The X-ray diffraction intensity curves were obtained at a scanning rate of 1 degree/min, time constant of 2 s, and counter range of 800. The voltage and current of the X-ray source were 30 kV and 20 mA, respectively.

Epoxide-treated silk fibers were irradiated from a carbon arc using a phadometer (WEL-25AX-HC-EC) of Suga Test Instrument Co. Whiteness values were calculated on a Color Computer (SM-3) of Suga Test Instrument Co. The whiteness ( $W$ ) of each sample was calculated according to the method described in a previous article.<sup>12</sup>  $L$ ,  $a$ ,  $b$ , lightness, blueness, and yellowness values were evaluated by a Suga Test Instrument AUD-SCH-2U colorimeter.

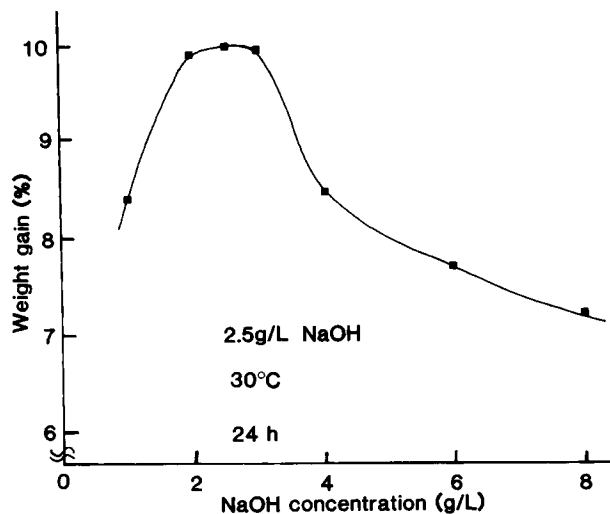
## RESULTS AND DISCUSSION

### Reactivity of Epoxide

The optimum conditions for the chemical modification of silk fabrics with EDGE by the pad/batch method were determined by studying the effect of different reaction conditions, i.e., reagent concentration, time, temperature, and the amount of weight gain attained. Figure 1 shows the behavior of the weight gain as a function of the reaction time, i.e.,



**Figure 1** Weight gain of the silk fibers prepared by the pad/batch method for different periods of reaction time in the reaction system (1000 mL) at 30°C containing 2.5 g NaOH, 120 g EDGE, and 120 mL isopropanol.

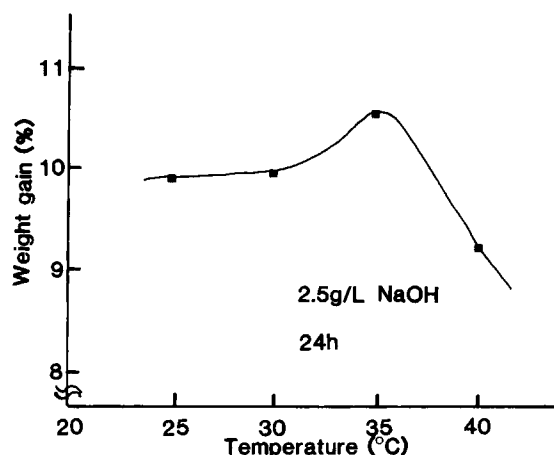


**Figure 2** Weight gain of the silk fibers prepared by the pad/batch method in the reaction system (1000 mL) at 30°C containing different amounts of NaOH and 120 g EDGE for 24 h.

the duration of the storage at 30°C after padding with a reaction mixture containing 2.5 g/L NaOH. The weight gain steadily increased up to about 8.5% during the first 8 h and then seemed to attain an equilibrium value at around 10% after 24 h. The same amount of weight gain can be attained in a shorter time (about 3 h, depending on the reaction conditions) using the conventional epoxide treatment. However, we would like to emphasize that the latter requires a reaction temperature of 75–80°C, which sometimes entails negative consequences on the physicochemical properties of the final product.

Figure 2 shows the relationship between the weight gain and the concentration of NaOH in the padding solution. All the samples were stored at 30°C for 24 h. The maximum weight gain was obtained in the range 2–3 g/L NaOH. The positive curve slope below 2 g/L NaOH concentration can be attributed to the catalytic effect exerted by the reagent, which enhanced the reactivity of EDGE toward silk fibroin. The decrease in weight gain above 3 g/L may be primarily caused by the strong alkalinity (pH 12) of the padding solution absorbed by the fibers and probably by the hydrolysis of oxirane ring and silk fibroin. The pH of the reaction system does not change in spite of the different NaOH concentrations examined. On the basis of the above findings, the optimum NaOH concentration ratios adopted was 2.5 g/L.

The effect of the reaction temperature on weight gain is shown in Figure 3. At 25–30°C, a constant weight gain of about 10% was obtained. This value slightly increased at 35°C, but when the temperature



**Figure 3** Weight gain of the silk fibers prepared by the pad/batch method in the reaction system (1000 mL) at different reaction temperatures containing 2.5 g NaOH for 24 h.

was raised up to 40°C, a quite sharp drop of the weight gain was registered. The optimum reaction temperature was therefore fixed at 30°C. Though a higher temperature could have permitted a slightly higher weight gain to be attained, the reaction conditions should have required a more accurate control, especially during industrial application, in order not to exceed the limit leading to the decrease of the reaction yield. With a reaction temperature of 7°C for 24 h we could obtain a weight gain of about 4% (data not shown), which is highly significant of the effectiveness of the pad/batch method compared with the conventional one.

The reactivity of EDGE toward the different amino acid residues of silk fibroin was evaluated by amino acid analysis. Silk fabrics were padded with a solution containing 120 g/L EDGE and 2.5 g/L NaOH and then stored at 30°C for different reaction times. Samples with a weight gain of 4.1, 8.5, and 10%, respectively, were taken after 3, 6, and 24 h of reaction time and were subjected to acid hydrolysis. The results obtained are listed in Table I, together with the composition of an untreated control. The amount of tyrosine and basic amino acid residues markedly decreased following the reaction with EDGE, whereas the others remained almost unchanged. As expected, the amount of acidic amino acid residues (aspartic and glutamic acid) did not change compared with the untreated sample, because the ester bond formed with the epoxide molecules is easily hydrolyzed under acid conditions. The reactivity of the aliphatic hydroxy groups (serine, threonine) was negligibly small, in good agreement

with the results reported for silk fibers treated in tetrachloroethylene by the conventional technique.<sup>11</sup>

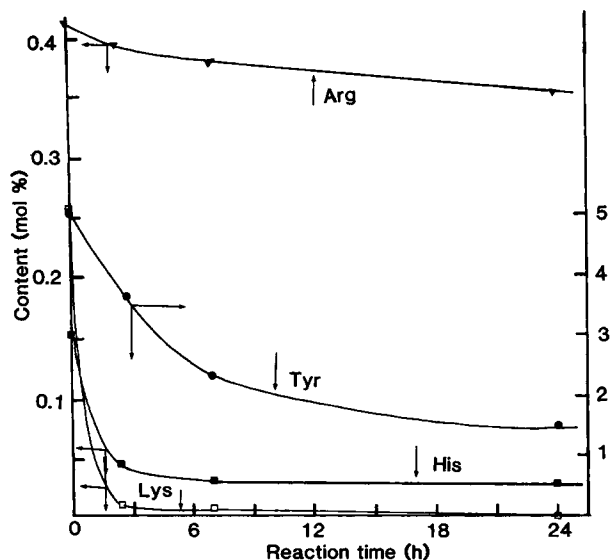
The time dependence of the addition reaction of EDGE to basic amino acid residues and tyrosine was studied by plotting their concentrations as a function of the reaction time (Fig. 4). Histidine and lysine showed a closely similar kinetics of reaction with EDGE, with only trace of both amino acids being detectable after 3 h of reaction time. On the other hand, the concentration of arginine changed very slowly over the entire range of reaction time examined. Tyrosine decreased almost linearly from 0 to 6 h, reaching about half the concentration of the untreated sample. As the reaction time increased from 6 to 24 h, the amount of tyrosine reacted decreased further on, though at a reduced rate. Since the amount of tyrosine is about 10 times larger than that of lysine and histidine (Table I), the reaction kinetics of EDGE toward silk fibroin can be described mainly in terms of addition to the tyrosine residues. From this point of view, we did not find any difference between the pad/batch method and the conventional method used for treating silk fabrics.

As for the reactivity of the basic amino acid residues, it has been reported<sup>2-5</sup> that it are influenced by several parameters, such as the solvent system used, the nature and concentration of the salt (nu-

**Table I** Amino Acid Composition (Mol %) of Chemically Modified Silk Fibers with EDGE with Different Amounts of Weight Gain

	Control	Epox-1 <sup>a</sup>	Epox-2	Epox-3
Asp	1.41	1.40	1.47	1.44
Thr	0.83	0.83	0.84	0.83
Ser	10.90	10.92	11.14	10.86
Glu	1.08	1.06	1.13	1.12
Gly	45.93	46.80	47.41	48.24
Ala	29.29	29.89	30.29	30.78
Val	2.20	2.37	2.45	2.51
Cys	trace	trace	trace	trace
Met	0.16	0.22	0.15	0.21
Ile	0.56	0.57	0.59	0.57
Leu	0.45	0.52	0.59	0.57
Tyr	5.18	3.71	2.36	1.57
Phe	0.60	0.62	0.63	0.69
Lys	0.25	—	—	—
His	0.14	—	—	—
Arg	0.37	0.35	0.37	0.36
Pro	0.64	0.73	0.55	0.58

<sup>a</sup> Epox-1, 2, and 3 represent the chemically modified silk fibers with EDGE with weight gain of 4.1, 8.5, and 10%, respectively.



**Figure 4** Changes in the amount of basic amino acid residues of the silk fibers prepared by the pad/batch method as a function of weight gain. Concentrated samples (five times larger compared with the normal analysis) were applied to the amino acid analyzer.

cleophilicity of the anion, acidity of the cation), as well as the shape and size of the substituent on the epoxide molecule. We can therefore attribute the sensibly lower reactivity of arginine to the reaction conditions adopted, i.e., to the type and concentration of reagents, time, temperature, etc.

### Equilibrium Moisture Regain

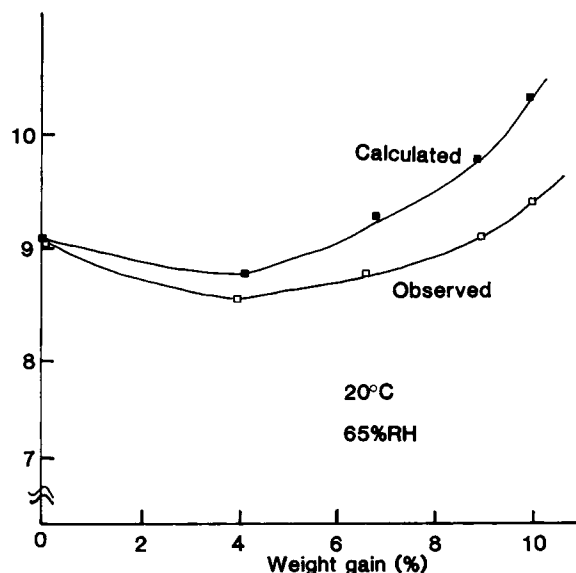
The equilibrium moisture regain values of silk fabric treated with EDGE by the pad/batch method were plotted as a function of the weight gain. Figure 5 shows the "observed" curve, obtained by referring the water regain to the total sample weight (silk + EDGE), and the "calculated" curve, in which the humidity content is referred to the amount of silk in the sample. Both curves exhibited the same behavior, the gap between them increasing linearly with the amount of weight gain.

The curves showed a minimum at about 4% weight gain, above which the equilibrium regain gradually began to increase, exceeding the corresponding value of the untreated control. These results can be partly attributed to the decrease in the number of the hydrophilic reactive sites, i.e., basic and/or acidic amino acid residues, which react preferentially in the initial reaction stage with epoxide, and, subsequently, with less hydrophilic sites such

as Tyr react with epoxide, resulting in an increase of the equilibrium moisture regain.

The rise of equilibrium regain following the treatment of silk fibers with EDGE has been already reported by other authors.<sup>10,11</sup> This effect can be attributed to the hydrophilic properties of the epoxide molecules inserted into the fibroin matrix, which contribute to increase the amount of water absorbed.

An interesting feature of the above results is that the observed equilibrium regain of EDGE-treated silk fabrics did not exceed the reference value of the untreated sample until the weight gain reached about 8%. The behavior can be tentatively attributed to the reaction conditions adopted for the pad/batch treatment. It has been reported<sup>10</sup> that intermolecular cross-links are formed by the reaction between bifunctional epoxide and reactive amino acid residues such as Lys, His, Arg, Tyr, and Asp. The formation of cross-links may subtract polar and ionized groups to the balance of the amino acid side chains effective in promoting the absorption of water by silk fibroin. At low weight gain, the hydrophilic properties of the bonded EDGE molecules can only partly compensate the decreased capability of absorbing water by the modified silk fibers. However, as a certain limit of weight gain is attained (about 8%), their contribution to the equilibrium regain becomes substantial. The hypothesis that the reaction conditions of the pad/batch treatment promote intermolecular



**Figure 5** Equilibrium regain of the silk fibers prepared by the pad/batch method. The (■) calculated and (□) observed equilibrium regain are expressed in terms of g/silk and g/silk + attached amount of EDGE within the silk fiber, respectively.

cross-linking, rather than the formation of pendant epoxide groups, is in good agreement with the crease recovery data discussed in a following section.

### Crease Recovery

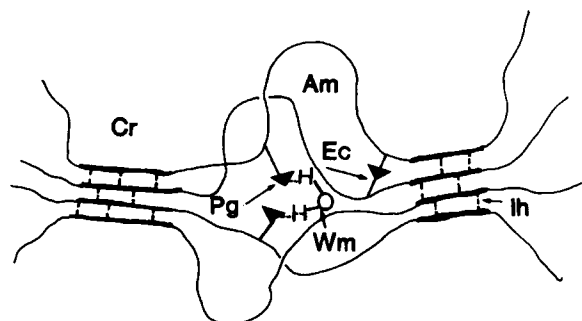
The crease recovery behavior is one of the weak points of silk fabrics, which should be improved in order to meet the increasing requirements for better textile performances. Table II shows the crease recovery values, measured in both the dry and wet states, of EDGE-treated silk fabrics with increasing amounts of weight gain, as obtained by the pad/batch method. Whereas in dry state the percentage of crease recovery remained essentially unchanged compared with the untreated control sample, the values measured in the wet state significantly increased for all the fabrics tested, regardless of the epoxide content.

The significant improvement of the crease recovery behavior in the wet state is particularly interesting and is in good agreement with the results reported by Kamiishi et al.,<sup>13</sup> who studied the cross-linking structure and the mechanical properties of epoxide-treated silk fabrics obtained by the conventional method. In fact, they<sup>13</sup> found that the crease recovery both in the dry and wet states is largely dependent on the water content of the fabric before treatment. The higher the water content, the higher the crease recovery in the wet state, whereas in the dry state, the values remained unchanged or became even worse than those of the control. Since in our study the padding is carried out in a water solution, it follows that a selective improvement of the crease recovery behavior in the wet state should be expected.

**Table II** Crease Recovery of the Epoxide-treated Silk Fabrics in Both the Dry and Wet States That Were Prepared by the Pad/Batch Method with Different Amounts of Weight Gain

Sample	Crease Recovery (%)	
	Dry	Wet
Control	72.7	59.4
Epox-1 <sup>a</sup>	69.3	79.4
Epox-2	68.8	81.7
Epox-3	69.7	86.0

The crease recovery angles were measured by using the Monsanto method in both the dry and wet states. See Table I for legend.



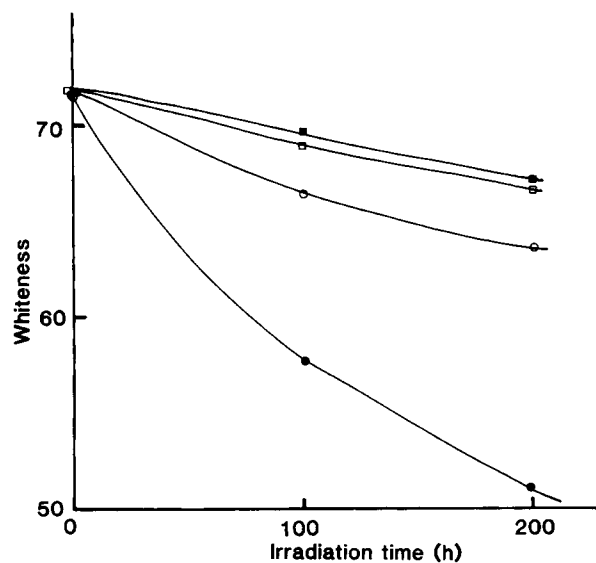
**Figure 6** Schematic representation to explain the improved crease recovery of the pad/batch epoxide-treated silk fiber in the wet state. A higher value of crease recovery is explained in terms of the stable intermolecular cross-links. Notation: Cr, crystalline region; Am, amorphous region; Wm, water molecule; Ec, epoxide cross-linking; Pg, pendant epoxide group; Ih, intermolecular hydrogen bond.

To achieve a deeper insight into the molecular mechanism of the fabrics, we should take into account the intermolecular cross-links formed by the bifunctional epoxide molecules (Fig. 6). Besides linking adjacent fibroin chains, it is expected that the epoxides form, with the absorbed water molecules, a three-dimensional network of hydrogen bonds, which stabilize the fiber structure by conferring on it the capability of recovering from mechanical deformations. This effect is larger in the wet than in the dry state mainly because of the plasticizing effect of the layer of hydrogen-bonded water.

The above findings are important from the point of view of the industrial application of the pad/batch method, because a significant improvement of the physical properties of silk fabrics can be attained by a limited chemical modification carried out in mild conditions, which do not affect the intrinsic properties of silk.

### Changes in Whiteness Following Irradiation

Figure 7 shows the changes in whiteness of silk fabrics with different epoxide contents prepared by the pad/batch method. The whiteness values of the untreated control (a) exhibited a rapid decrease following carbon arc irradiation for 100 and 200 h. The rate of the photoyellowing of the silk fabric with 4.1% weight gain (b) was reduced slightly, compared with the untreated sample. As the weight gain increased further on, the rate of photoyellowing markedly reduced, as demonstrated by the curves of the samples with 8.5% (c) and 10% (d) weight gain.



**Figure 7** Changes in whiteness of silk fabrics with different amounts of weight gain following carbon arc irradiation. Weight gain (%); (●) 0; (○) 4.1; (□) 8.5; (■) 10.

We would like to draw attention to these data, which demonstrate that with slight increasing epoxide weight gain (4.1%) the rate of loss of whiteness was greatly decreased. It was concluded that the epoxide treatment onto silk fabrics has a marked influence on sustaining the whiteness of irradiated silk fibers/fabrics.

### Tensile Properties

The values of tensile strength, elongation at break, and tensile modulus of silk fabrics with different amounts of epoxide content are listed in Table III. The samples with 4.1, 8.5, and 10% weight gain were prepared by padding the fabrics with the epoxide solution containing 2.5 g/L NaOH and by storing them at 30°C for 3, 6, and 24 h, respectively. Fol-

**Table III** Tensile Strength and Elongation at Break of the Silk Fibers Modified with EDGE with Different Amounts of Weight Gain

Sample	Strength (g/d)	Elongation (%)	Tensile Modulus (g/d)
Control	2.9	21.7	44.8
Epox-1	3.3	21.3	49.0
Epox-2	3.3	21.9	46.2
Epox-3	3.4	20.4	48.3

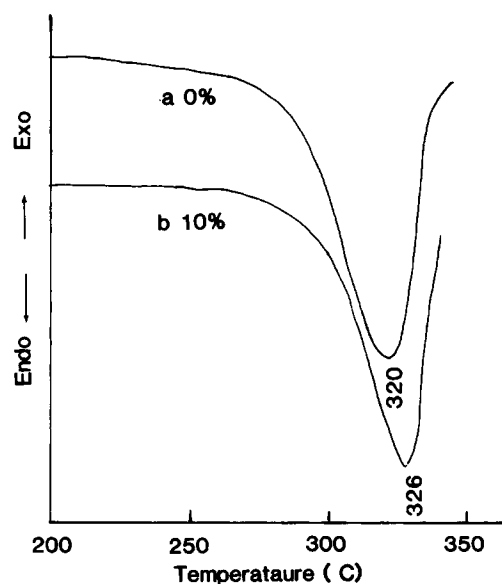
1 g/d =  $1.22 \times 10^3$  kgf/cm<sup>2</sup>. See Table I for legend.

lowing the epoxide treatment, the tensile strength slightly increased compared with the untreated control and remained essentially unchanged in the range of weight gain examined. The slight but constant increase of strength can be attributed to the formation of intermolecular cross-links between adjacent fibroin chains by reaction of the bifunctional epoxide molecules. It is noteworthy that the cross-linking effect is noticeable at relatively low weight gain (4.1%), confirming the above-discussed data on crease recovery and supporting the hypothesis that the reaction conditions adopted for the pad/batch method favor the formation of cross-links, limiting the presence of pendant epoxide side groups. A less noticeable increase in strength is conferred on silk fibers by the conventional epoxide treatment. However, a fall in strength has been reported for samples treated at 75–80°C for 3 h or longer.

As for the values of elongation at break and tensile modulus, two other important characteristics that determine the functional performances of textile materials, the data listed in Table III show that the EDGE-treated silk fabrics do not significantly differ from the untreated control, exhibiting almost the same mechanical behaviors.

### Thermal Behavior

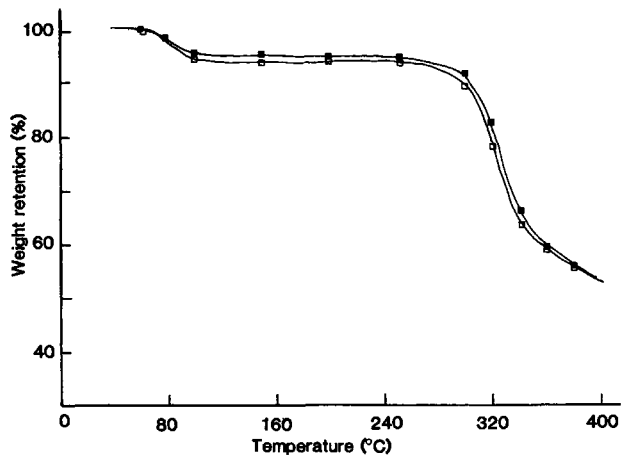
Figure 8 shows the DSC curves of untreated and EDGE-treated silk fabric prepared with the pad/



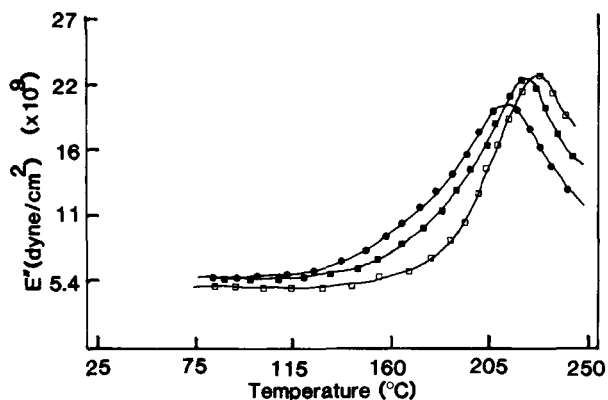
**Figure 8** DSC curves of the (a) control and (b) epoxide-treated silk fiber prepared by the pad/batch method. Weight gain (%): (a) 0; (b) 10.

batch method. The untreated control (a) showed a single endothermic peak at about 320°C, attributed to the thermal decomposition of silk fibroin with oriented  $\beta$  configuration.<sup>14</sup> The silk fabric modified with EDGE (b) exhibited a similar thermal behavior, with a single and prominent endothermic transition whose peak temperature slightly shifted upward to 326°C. No additional thermal transitions were detected in the DSC curve of the silk fabric after reaction with EDGE. These findings, i.e., the presence of a single endothermic peak and the shift of the decomposition temperature to higher values, are in good agreement with the results reported for silk fabrics treated by the conventional method with different bifunctional epoxide molecules,<sup>10</sup> the extent of peak temperature shift being characteristic of the kind of epoxide used. The slightly higher decomposition temperature can be related to the presence of intermolecular cross-links rather than to a modification of the crystallinity and/or orientation of silk fibers.

The TGA curves shown in Figure 9 refer to the untreated control (a) and to the EDGE-treated silk fabric with 10% weight gain (b). Both of them proceed parallel to each other over the temperature range examined, displaying two inflection points; the first at about 50°C, corresponding to the loss of moisture regain, and the second at 280°C, steeper and more prominent than the former, which coincides with the beginning of the thermal degradation of silk fibers. The above findings imply that the rate and extent of weight loss of silk fibers in the heating process is not significantly influenced by the epoxide treatment.

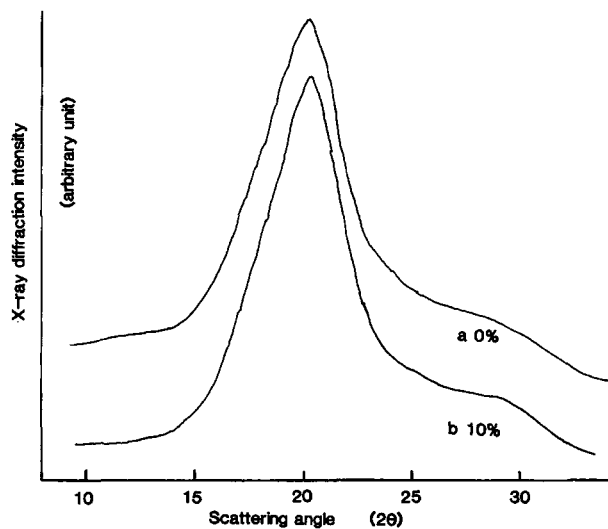


**Figure 9** Thermogravimetric analysis (TGA) curves of the silk fiber prepared by the pad/batch method. Weight gain (%); (□) 0; (■) 10.



**Figure 10** Dynamic loss modulus ( $E''$ ) of the silk fibers with different amounts of weight gain. Weight gain (%): (□) 0; (■) 8.5; (●) 10.

To further investigate the thermal behavior of EDGE-treated six fabrics, we studied the viscoelastic properties by measuring the temperature dependence of the dynamic loss ( $E''$ ) modulus (Fig. 10). The  $E''$  curve of the untreated control showed a prominent peak at 229°C, which has been attributed to the crystalline disperse peak, i.e., to the molecular motion within the  $\beta$  crystals, because the spacings [ $d_{(002)}$ ] corresponding to the intersheet distance<sup>15</sup> gradually expand at above 190°C. The loss modulus curves of silk fabrics with an epoxide content of 8.5% (b) and 10% (c) showed a shift to lower values of the peak temperature (223 and 213°C, respectively).



**Figure 11** X-ray diffraction intensity curves of silk fibers with different amounts of weight gain. Weight gain (%): (a) 0; (b) 10.



Moreover, the peaks broadened and their onset temperature decreased with the weight gain.

The viscoelastic properties of epoxide-treated silk fabrics were significantly affected by the reaction with EDGE. Similar results were reported for tussah silk fibers, following treatment with different kinds of epoxides.<sup>10</sup> The molecular motion of the fibroin chains in the amorphous regions is noticeably influenced by the reaction with the epoxide molecules, which induce an apparent decrease of the glass transition temperature,<sup>16</sup> as shown by the lower onset temperature of the  $E''$  peak. Moreover, the segmental motion within the crystalline regions becomes less restrictive after the epoxide reaction, suggesting that the EDGE molecules bound to the reactive side groups of the amino acid residues not only in the amorphous regions, but also in the laterally ordered regions of silk fibers even at relatively low weight gain.

#### X-ray Diffraction Curves

The X-ray diffraction intensity curves of untreated and EDGE-treated silk fabrics with 10% weight gain were measured to ascertain whether fine structural changes in the crystalline regions were induced by the reaction with the epoxide (Fig. 11). The untreated control (a) showed a major X-ray diffraction peak at 20.5 degrees, corresponding to the specific crystalline spacing of 4.39 Å, which is characteristic of silk fibers with a highly oriented  $\beta$  structure. The EDGE-treated silk sample (b) exhibited a diffraction curve essentially similar to the untreated sample, as concerns the position and intensity of the major diffraction peak at 20.5 degrees, which remained almost unchanged.

The above results are consistent with those reported for tussah silk fibers modified with epoxides, demonstrating that the crystalline structure with oriented  $\beta$  crystals remained essentially unaffected

by the chemical reaction occurring inside the silk fibers.

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