Chemical Modification of *Bombyx mori* Silk with Calcium-Salt Treatment and Subsequent Glycerin Triglycidyl Ether Crosslinking

Jianxin He,[1,2] Guoxin Jia,[3] Shizhong Cui,[2] Shanyuan Wang,[1] Yaying Gao[1]

[1]*Key Laboratory of Textile Science and Technology (Ministry of Education), Donghua University, Shanghai 201620, People's Republic of China*
[2]*College of Textiles, Zhongyuan University of Technology, Zhengzhou 450007, People's Republic of China*
[3]*Textile Engineering Department, Henan Institute of Engineering, Zhengzhou 450007, People's Republic of China*

ABSTRACT: In this article, we propose a new modification method for obtaining porous silk fibers with excellent wet elastic resilience and flexibility. *Bombyx mori* silks were modified by calcium-salt treatment and subsequent epoxy crosslinking with glycerin triglycidyl ether. The effects of temperature, time, and catalyst (sodium carbonate) on the crosslinking reaction of the silk fibers were investigated, and the best conditions of reaction were determined as a temperature of 120°C, a crosslinking agent concentration of 7%, and immersion for 1 h with 2% Na_2CO_3 solution before the crosslinking reaction. The change in the structure and the physical properties of the silk fibers after calcium-salt treatment and epoxy crosslinking was studied. Separating behavior of the microfibers occurred on the surface of the silk fiber after calcium-salt treatment, and a porous structure formed in the interior of the silk. This porous structure of the silk was enlarged by subsequent epoxy crosslinking, and accordingly, the moisture conduction of the silk fibers improved remarkably. The breaking strength, breaking elongation, and wet elastic resilience of the silk fibers increased evidently after modification, and the modified silks exhibited a better flexibility. The conformation of silk fibroin fibers changed from β sheet to random coil after calcium-salt treatment, whereas the β-sheet content in the silk fibers increased after subsequent epoxy crosslinking. The significant reductions in the crystallinity and crystalline sizes in the silk fibers after the crosslinking reaction indicated that the crosslinking reaction occurred within the crystalline region because the calcium-salt treatment increased the reaction accessibility. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3260–3268, 2010

Key words: *Bombyx mori* silk; crosslinking; modification; structure–property relation

INTRODUCTION

Silk is one of the most favored textile materials and has been known as the queen of fibers since its discovery. Silk is highly appreciated for its outstanding characteristics, including its unique luster, comfortable hand, excellent softness, and good drape. However, it also suffers from some inferior properties, one of which is a low wet resiliency.[1] This disadvantage causes considerable inconvenience in the use of silk textiles; therefore, the world consumption of silk has been directly influenced.

The poor wet resiliency of silk fibers may be due to the lack of cystine residues and the resulting absence of chemical crosslinkages between silk fibroin molecules. When the fibers absorb water and swell, the salt linkages between the molecules, which give the fibers a high dry resiliency, are broken.[2] A considerable amount of work has been carried out on the chemical modification of silk with a view to improving its low wet resiliency. The modification processes have mainly included graft copolymerization,[3,4] dibasic anhydrides treatment,[5] aminoformaldehyde resin finishing such as with trimethylol melamine,[6] poly(carboxylic acid) crosslinking such as with citric acid and 1,2,3,4-butanetetracarboxylic acid,[7] and epoxy crosslinking.[8,9]

Among these modification processes, epoxy crosslinking seems likely to take a leading role in practical industrial applications with experimental results showing a great effectiveness in the improvement of some intrinsic properties of silk, especially its wet resiliency. Epoxides are known to react with amines, alcohols, phenols, carboxylic acids, and thiols. Silk

fibers contain amino acid residues with functional groups of all these types. The epoxy crosslinking of silk is based on the mechanisms of these reactions.

However, conventional treatment is carried out with an epoxide organic solution at 60–80°C. Because the use of organic solvents has drawbacks, such as environmental pollution and hazards to health, some alternative processes have been developed. Cai and coworkers[10,11] developed some new aqueous epoxy agents, including multiamino epoxy resin and multifunctional silicone-containing epoxide. Both of these significantly improved the wet resiliency of silk fabrics but resulted in a poorer fabric hand; in addition, high cost has also been a problem for industrial application. Tsukada et al.[12] developed an alternative pad-batch method, by which a high weight gain of silk fibers could be obtained and the wet resiliency could be improved; their study showed that there was no change in the crystalline structure of the silk fibers after epoxy crosslinking and crosslinked action did not occur in the interior of silk, especially in the crystalline region.

It is known that silk can be dissolved by stages in a neutral calcium-salt solution, and the priority of erosion and peeling off should be given to the weak structure within the silk.[13] Therefore, a micropore structure can come into being through the slight dissolution of silk in a calcium-salt solution. The micropore structure not only increase silk's air permeability and moisture conduction but also enhances the accessibility of the chemical reaction in the silk.

However, there is no information available on the effect of calcium-salt treatment on the epoxy crosslinking reaction of silk. In this article, we propose a new modification process of silk in which silk is dissolved slightly with calcium-salt solution and subsequently crosslinked with epoxide glycerin triglycidyl ether (GTGE). The changes in the structure and properties of the silk in the calcium-salt treatment and subsequent epoxy crosslinking were investigated in this study.

EXPERIMENTAL

Materials

Bombyx mori silks came from Henan Province, China. To remove the sericin, the silk fibers were degummed with a 0.5% Na_2CO_3 solution at 98°C three times. Deionized water was used throughout the experiment. All chemical reagents were reagent grade and were used without further purification.

Calcium-salt treatment

Degummed silk fibers (1 g) were immersed in 100 mL of a calcium chloride solution ($CaCl_2/H_2O$ molar ratio = 1 : 8) and left at 70°C for a given time (0–60 min). Then, the silk fibers was added to a 5% ethylene diamine tetraacetic acid solution and heated at 100°C for 5 min to remove the remaining calcium ions. The collected fibers were washed extensively with deionized water and dried *in vacuo* at 60°C for 24 h. The weight loss of sample was calculated according to the difference in weight before and after treatment.

GTGE synthesis

Glycerin (1 mol) and 2% catalyst (on the basis of the mass of glycerin) were charged in a flask with a reflux condenser, dropping funnel, and thermometer. The synthesis of GTGE was performed at 80°C for 3 h by mechanical stirring after 3.06 mol of chloroepoxy propane was slowly added dropwise. Boron trifluoride ethylether was used as a catalyst in the reaction. The cooled product was then reacted at 40°C for 3 h under condition of stirring after the dropping of 3.06 mol 10% NaOH solution. After the reaction was completed, the product was neutralized with 10% HCl solution and then filtered to remove the generated sodium chloride. Pure GTGE was obtained by vacuum distillation. The reaction equation of GTGE synthesis is shown in Scheme 1.

Epoxy crosslinking reaction

Silk fibers obtained by the calcium-salt treatment were crosslinked in GTGE solutions with concentrations of 3–12% at a liquor ratio of 1 : 20, and Na_2CO_3 was used as the catalyst of the reaction. The epoxy crosslinking reaction was performed by three methods, as shown in Table I.

Silk fibers collected from the crosslinking agent solution were dried at 40°C for 1 h. After carding, the dried samples were cured for 10 min at a crosslinking temperature of 90–130°C. The crosslinked samples were washed extensively with deionized and dried *in vacuo* at 100°C for 24 h. The weight gain of samples was calculated according to the difference in weight before and after crosslinking reaction.

Measurement of the mechanical properties

The mechanical properties of the silk samples were measured on an Instron 5582 tensile tester (Canton, MA) with a gauge length of 10 mm and a stretching speed of 100 mm/min.

The elastic recovery percentage of elongation was used to represent the elastic resilience of the silk fibers. The measurement was performed on a LLY-06D fiber elasticity tester (Shandong Province, China) with a gauge length of 30 mm, a traction load of 250 mg, and a pretension of 5 mg. The silk
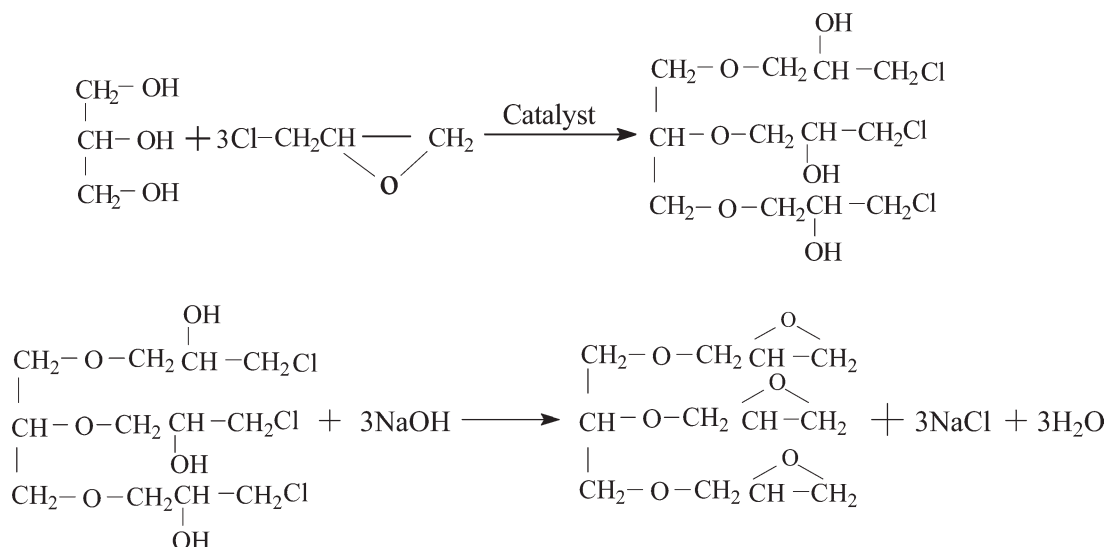
Scheme 1   GTGE synthesis reaction equation.

fibers were immersed in deionized water for 12 h at ambient temperature before testing, and the silk fiber was burdened for 3 min and subsequently recovered for 5 min at testing. The wet elastic resilience (R) of the samples was calculated with the following formula:

$$R = 1 - \frac{\varepsilon_1}{\varepsilon_0} \times 100\%$$

where ε_0 is the maximum fiber elongation at traction load and ε_1 is the residual elongation of the silk fiber after 5 min of recovery.

Measurement of the moisture conductivity

The moisture conduction of the silk fibers was determined by measurement of the vertical wicking height of the fiber assemblies. The test was conducted with a vertical wicking tester (from Donghua University, China) according to DIN 53924.[14] A fiber bundle of 80 fibers with 20 twists was suspended vertically with its lower end (10 mm) immersed in a reservoir of distilled water, to which 1% reactive dye (Prussian blue) was added to track the movement of the water. The height reached by water in the fiber bundle was measured by the clamped scale after immersion for 30 min to keep the water height stabile.

Structural characterization

The silk samples were coated with gold film to observe the surface morphology and the microstructure. The instrument was a JEOL JSM-5600LV electron microscope (Tokyo, Japan) with an accelerating voltage of 15 kV.

Fourier transform infrared (FTIR) spectra of the silk samples were recorded with a Nicolet Nexus 670 FTIR spectrometer (Madison, WI) with the KBr disc technique (1 mg of powder of the samples/300 mg of KBr). One hundred scans were taken with a resolution of 2 cm^{-1}.

X-ray diffraction was recorded at room temperature from 5 to 50° at a scanning speed of 0.02°/s with a Rigaku-D/Max-2550PC diffractometer (Tokyo, Japan) with Ni-filtered Cu Kα radiation at a wavelength of 0.1542 nm. The operating voltage and current were 40 kV and 30 mA, respectively.

The diffraction profile of silk fibers was fitted by the Lorentzian function and ranged from 5 to 50° of the corresponding Bragg angle (2θ; reflection angle). The crystallinity (X_d) was calculated by the following equation:[15]

$$X_d = \left[1 - \frac{S_a}{S_a + S_{cr}}\right] \times 100\%$$

where S_a is the amorphous integrated area and S_{cr} is the sum of the integrated areas of the crystalline peaks.

The average size of the crystallites was calculated from the Scherrer equation with the method based on the width of the diffraction patterns obtained in

TABLE I
Methods for the Epoxy Crosslinking Reaction

Method 1	The silk sample was immersed in deionized water for 1 h and then immersed in a crosslinking agent solution without a catalyst for 1 h.
Method 2	The silk sample was immersed in deionized water for 1 h and then immersed in a crosslinking agent solution with 2% Na_2CO_3 for 1 h.
Method 3	The silk sample was immersed in a 2% Na_2CO_3 solution for 1 h and then immersed in a crosslinking agent solution without a catalyst for 1 h.

the X-ray reflected crystalline region. In this study, the crystallite sizes were determined with the diffraction pattern obtained from the lattice planes at a 2θ of $20.4°$:

$$L = \frac{k\lambda}{\beta \cos \theta}$$

where L is the size of the crystallite, k is the Scherrer constant (0.89), λ is the X-ray wavelength, and β is the full width at half-maximum of the measured reflection.

RESULTS AND DISCUSSION

Calcium-salt treatment

Dissolution behavior occurred on the *B. mori* silks after the calcium-salt treatment, and the weight loss of the silks increased linearly with the time of calcium-salt treatment, as shown in Figure 1. Calcium ions could impregnate into the silk and coordinate with the polar lateral groups, such as hydroxyl, carboxyl, and amido, of the amino acid to form a chelate compound.[16] Therefore, the secondary bonds between the silk fibroin molecules were destroyed, and the intermolecular force weakened, which resulted in the dissolution of silk fibroin molecules, especially in amorphous region.

The calcium-salt treatment had a major effect on the tensile properties of the silk fibers, as shown in Figure 2. The tensile strength of the fibers decreased with increasing treating time, and the breaking strength appeared to have twice the obvious reduction after calcium-salt treatments for 10 and 30 min, which may have been because of the destruction of the amorphous and crystalline regions in the fibers, respectively. The breaking elongation of the silk fibers exhibited a reduced trend with the calcium-
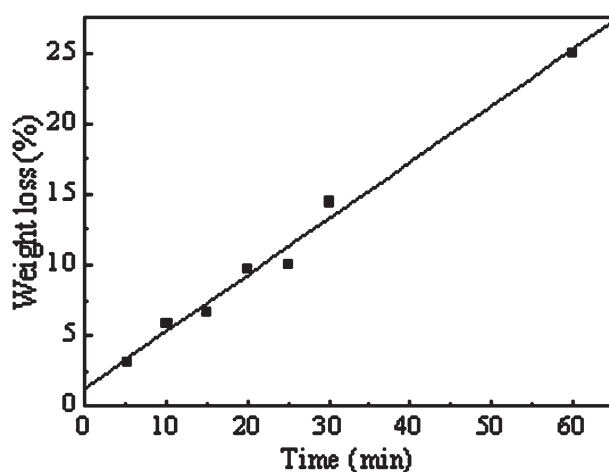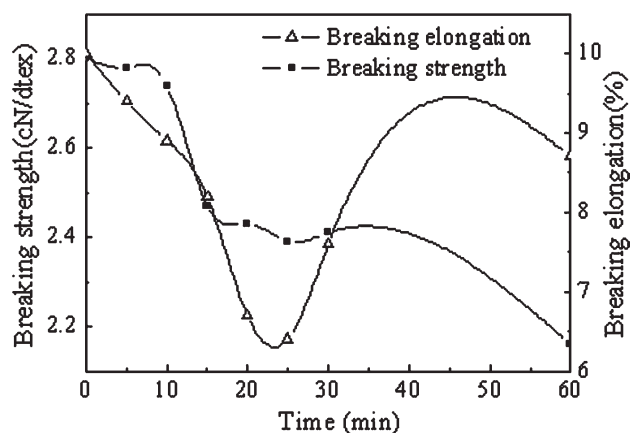

Figure 2 Effect of the time of the calcium-salt treatment on the tensile properties of the silk fibers.

salt treatment, especially after 10 min of treatment, whereas the breaking elongation increased with treatment time. Therefore, the breaking strength and elongation of the silk fibers decreased less within 10 min of calcium-salt treatment.

Epoxy crosslinking reaction

Silk samples treated by the calcium-salt solution for 10 min were crosslinked by epoxide GTGE, and Figure 3 shows the weight gain of silk fibers with three methods under various crosslinking temperatures at 7% crosslinking agent solution. The weight gain at each temperature in methods 2 and 3 was more than that in method 1, in which no catalyst was used. When Na_2CO_3 was used as a catalyst, the epoxy groups of GTGE were opened to form active centers by nucleophilic attack of negative ions in alkalescent solution on them, which reacted with some groups,
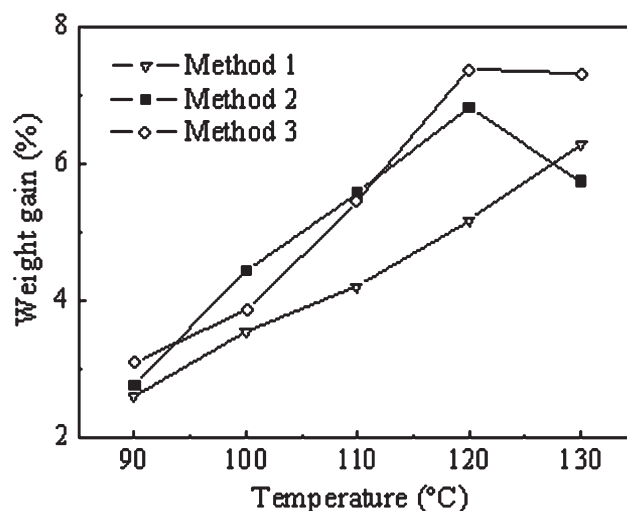

Figure 1 Effect of the time of the calcium-salt treatment on the weight loss of the silk fibers.

Figure 3 Effect of the epoxy crosslinking temperature on the weight gain of the silk fibers at a GTGE concentration of 7%.
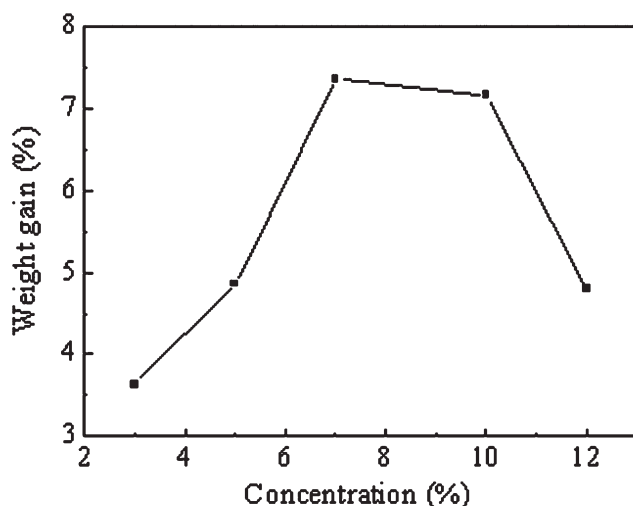
Figure 4 Effect of the GTGE concentration on the weight gain of the silk fibers by method 3 at a crosslinking temperature of 120°C.

such as amines, alcohols, phenols, and carboxylic acids, in the side chain of silk fibroin to form a crosslinking structure.[17]

The weight gain of the silk fibers increased almost linearly with the elevation of crosslinking temperature; however, the weight gain decreased when the temperature was more than 120°C in methods 2 and 3 with Na_2CO_3 as a catalyst (Fig. 3). This was because more active centers formed in the high-temperature-initiated ring-opening polymerization of themselves in the condition with the catalyst. In addition, the high-temperature hydrolysis reaction of GTGE in the alkalescent solution was another reason.

We found by comparing the results from methods 2 and 3 that the adding mode of the catalyst Na_2CO_3 also affected the weight gain of the silk fibers. Immersion first in Na_2CO_3 solution was favorable for improving the crosslinking effect of the silk fibers at a high crosslinking temperature of more than 110°C (as shown in method 3 of Figure 3). A possible explanation was that carbonate broke the secondary bonds between the silk fibroin molecules, and the bulk effect of the silk fibers resulted in the increase of the accessibility of the crosslinking agent.

Figure 4 shows the relationship between the concentration of GTGE and the weight gain of the silk fibers in method 3 at a crosslinking temperature of 120°C. The weight gain of the silk fibers increased first with the concentration of crosslinking agent. However, when the concentration was more than 7%, the silk fibers demonstrated a decreasing weight gain, which could have been due to the increased chance of the ring-opening polymerization of crosslinking agent itself at the high concentration.

Property analysis

The property results for the degummed, calcium-salt-treated, and crosslinked silk fibers are shown in Table II. Calcium-salt treatment for 10 min had no apparent effect on the mechanical properties of the silk fibers, and the cause may have been that calcium-salt treatment for a shorter time only dissolved a small part and did not apparently destroy the structure of the silk fibers. However, noticeable variations were observed in the mechanical properties after the epoxy crosslinking reaction. The

TABLE II
Physical Properties of the Degummed, Calcium-Salt-Treated,
and Epoxy-Crosslinked Silk Fibers

		Silk sample		
		Degummed	Calcium-salt-treated for 10 min	Epoxy-crosslinked[a]
Breaking strength	Mean (cN/dtex)	2.80	2.74	3.31
	CV (%)[b]	11.67	14.21	15.16
Breaking elongation	Mean (%)	9.8	8.9	13.6
	CV (%)	22.44	20.61	14.24
Initial modulus	Mean (cN/dtex)	53.0	51.2	46.7
	CV (%)	14.95	10.43	15.06
Breaking work	Mean (cN/dtex)	0.17	0.15	0.24
	CV (%)	27.86	29.71	26.12
Wet elastic resilience	Mean (%)	64	64	81
	CV (%)	21.58	25.30	29.12
Moisture regain	Mean (%)	9.1	8.9	8.6
	CV (%)	5.5	5.0	4.8
Wicking height	Mean (mm)	37	71	164
	CV (%)	6.7	7.0	5.9

[a] Method 3 was used at 120°C with a GTGE concentration of 7% for 10 min.
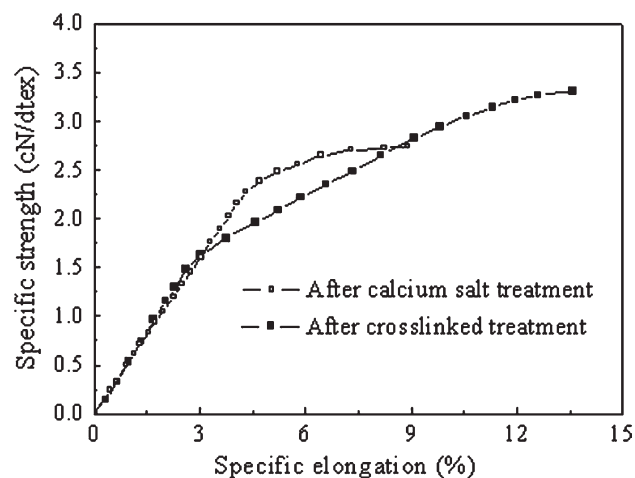[b] CV represents coefficient of variation.

Figure 5 Comparison of the tensile curves of the calcium-salt-treated and epoxy-crosslinked silk fibers.

crosslinking reaction of silk fibers was carried out for 10 min with method 3 at a temperature of 120°C and a GTGE concentration of 7%. The breaking strength and breaking elongation of silk fibers increased evidently, but the initial modulus decreased slightly after the epoxy crosslinking reaction, and the breaking strength increased from 2.74 to 3.31cN/dtex, and the breaking elongation increased from 8.9 to 13.6%. Furthermore, there was a noticeable improvement in the wet elastic resilience of the silk fibers after the epoxy crosslinking reaction, which increased from 64 to 81% (Table II).

Figure 5 exhibited the tensile curves of the silk fibers treated by the calcium-salt solution and crosslinked subsequently with epoxy GTGE. The yield point position of the silk fibers shifted downward from 5 to 2.8% after epoxy crosslinking; meanwhile, a high elastic deformation region appeared in its tensile curve. The silk fiber obtained after epoxy crosslinking reaction exhibited a better flexibility.

Obviously, these changes in the mechanical properties were mostly due to the structural changes induced by the epoxy crosslinking reaction. The secondary bonds of silk fibroin could be destroyed by the polar epoxy groups, and the crystallinity of silk fibers decreased after epoxy crosslinking (see later discussion). Thus, the silk fibers modified exhibited a greater elongation and a lower modulus. At the same time, the crosslinking structure formed in the amorphous region, and the crystallites as a reinforced phase were distributed over the crosslinked amorphous region, which led to increases in the breaking strength and wet elastic resilience of the silk fibers after the crosslinking reaction.

No obvious change was found in the hydroscopic properties for the silk fibers obtained after the calcium-salt treatment and subsequent epoxy crosslinking; however, the moisture conduction of the silk

fibers was improved markedly by the two processes, for the wicking height of the silk fibers increased by 92% after calcium-salt treatment and then increased by 1.3 times further after subsequent epoxy crosslinking (Table II).

Fiber morphology

The morphological changes in the silk fibers obtained after the calcium-salt treatment and subsequent epoxy crosslinking were observed by scanning electron microscopy and are shown in Figure 6. The degummed silk fiber showed a cross section with only a few pores and a smooth surface, except for some residual sericin [Fig. 6(a,b)]. The silk fibers were composed of crystalline microfibers, among which an amorphous region was present. The coordination between the calcium ions and the polar lateral groups in the peptide chain destroyed the secondary bonds between the silk fibroin molecules, which resulted in the swelling and dissolution of the amorphous region. Therefore, after calcium-salt treatment, a separating microfibrillar structure appeared on the surface of the silk fibers, and an enlarged cross section presented the apparent pore structure [Fig. 6(c,d)].

Epoxy crosslinking also affected fiber morphology. An apparent accretion at the cross sections of the silk fibers was observed after the epoxy crosslinking reaction, and the pores in the interior enlarged in size and increased in number [Fig. 6(e)]. The secondary bonds of silk fibroin were also destroyed by the polar epoxy groups, and the pore structure formed after the calcium-salt treatment enhanced the accessibility of GTGE in the interior of the silk fibers, which resulted in further swelling and dissolution of the silk fibers.

After the calcium-salt treatment and epoxy crosslinking, the remarkable improvement in the moisture conductions of the silk fibers should have been related to the formation and increase of the pore structure. However, the surface of the epoxy-crosslinked silk fibers exhibited a continuous coating layer, and the former microfibrillar structure could hardly be observed. In addition, some granules deposited onto the fiber surface could also be found [Fig. 6(f)]. The observed surface morphology was due to the epoxy crosslinking process, which caused the bonding between the silk and the epoxy.[18]

FTIR spectroscopy

FTIR spectra of the degummed, calcium-salt-treated, and crosslinked silk fibers are shown in Figures 7 and 8. The band of silk fibers at 856 cm^{-1} attributed to the absorbance of tyrosine disappeared after calcium-salt treatment (Fig. 7); this indicated that the
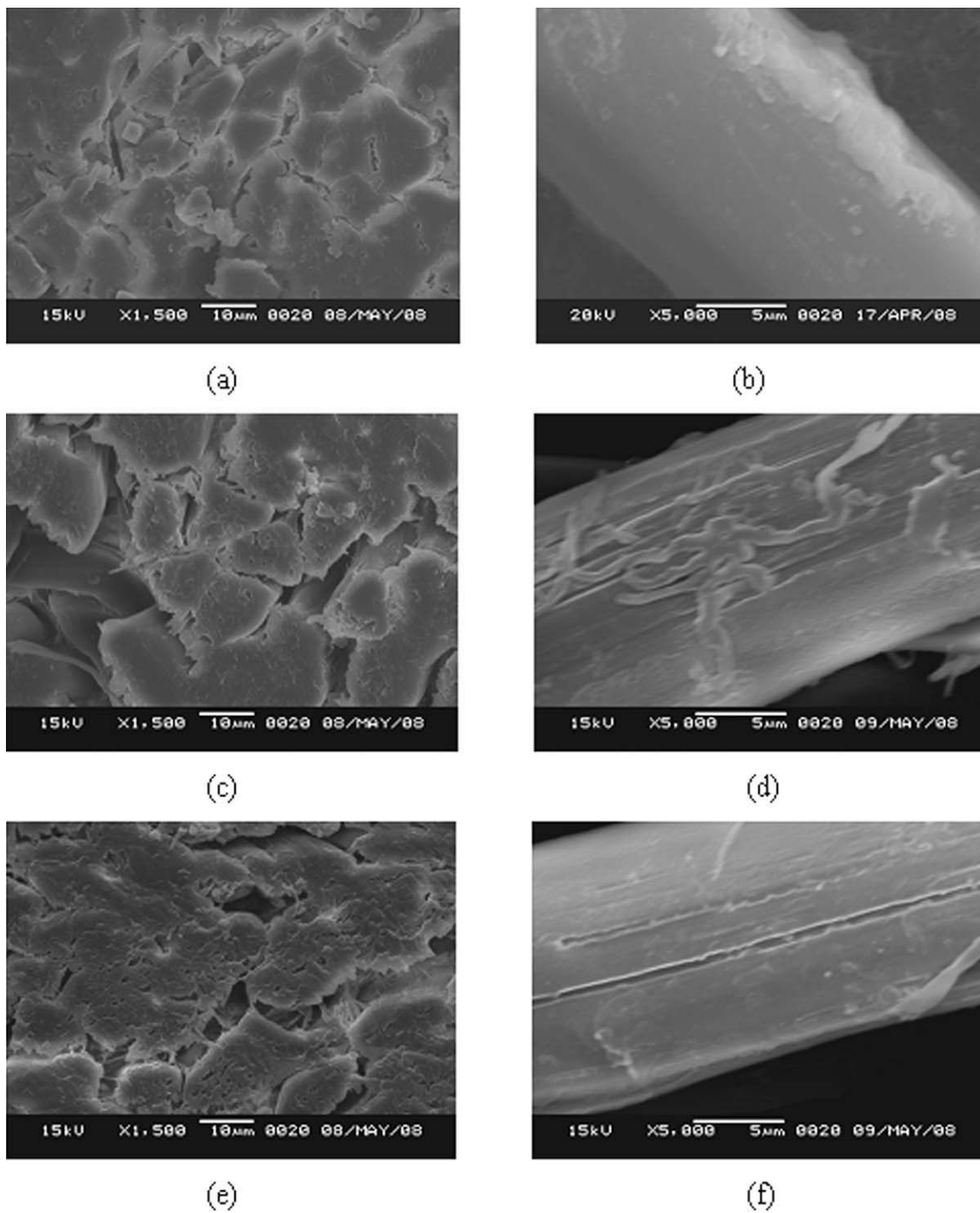
Figure 6 Scanning electron microscopy photographs of the (a,b) degummed, (c,d) calcium-salt-treated, and (e,f) epoxy-crosslinked silk fibers (1500× magnification at the cross section and 5000× magnification at the longitudinal).

dissolution of silk fibers occurred in the amorphous region because tyrosine was located in the amorphous region.[19]

The amide I region of the degummed silk fibers showed a triplet at 1699, 1639, and 1618 cm^{-1}, which was wholly assigned to β-sheet conformation. After the calcium-salt treatment, the peak at 1618 cm^{-1} disappeared, and the absorbance of the peak at 1699

cm^{-1} decreased. In addition, a broad peak presented at 1643 cm^{-1}, which was attributed to random coil conformation (Fig. 7).[20] This indicated that calcium-salt treatment led to the conformation transition of silk fibroin from β sheet to random coil, which was confirmed by the change from the amide III region. After the calcium-salt treatment, in the amide III region, the shoulder peak at 1260 cm^{-1} decreased,
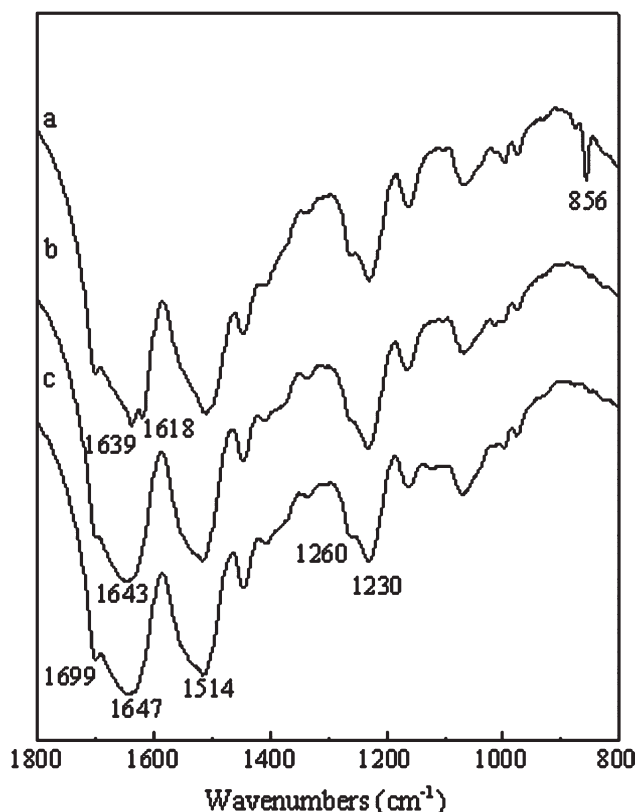
Figure 7 FTIR spectra of the (a) degummed, (b) calcium-salt-treated, and (c) epoxy-crosslinked silk fibers (1800–800 cm^{-1}).

Figure 8 FTIR spectra of the (a) degummed, (b) calcium-salt-treated, and (c) epoxy-crosslinked silk fibers (4000–2000 cm^{-1}).

whereas the peak at 1230 cm^{-1} increased; the former was assigned to β sheet, and the latter was assigned to random coil.[21]

The evidence of the epoxy crosslinking reaction was provided by the enhancement of the band at 2933 cm^{-1}, assigned to the C—H stretching vibration, for the C—H groups were rich in GTGE (Fig. 8). By comparing the spectra of the silk fibers obtained after the calcium-salt treatment and epoxy crosslinking, we found that the epoxy crosslinking reaction resulted in the conformation transition of the silk fibroin from random coil to β sheet because of the enhancement of the peaks at 1699 and 1260 cm^{-1} (Fig. 7), which were attributed to the β-sheet structure. As mentioned previously, the hydrolysis reaction of GTGE was a side reaction during the epoxy crosslinking process of the silk fibers, which could have resulted in the formation of alcohol. It is known that an alcohol solution can induce silk fibroin to change from random coil to β sheet.[22]

X-ray diffraction analysis

No change in the shape of the diffraction curves of the silk fibers was observed after the calcium-salt treatment and subsequent epoxy crosslinking (Fig. 9); this suggested that the crystalline phase of silk II
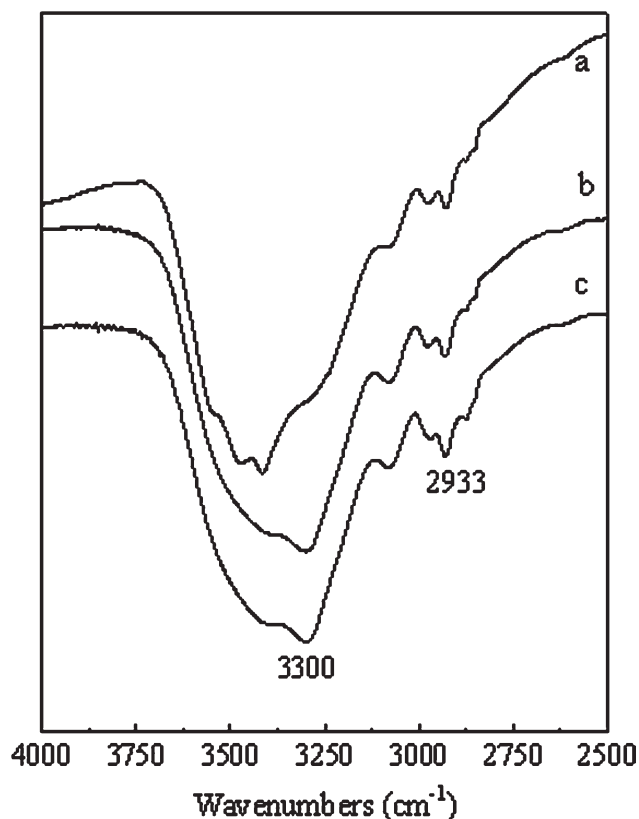
was not affected by the two processes. However, the crystallinities of the silk fibers exhibited different variation tendencies after the two processes. There was no obvious change in the crystallinity of the silk fibers after the calcium-salt treatment, whereas the crystallinity decreased after the epoxy crosslinking reaction (Table III). The calculated results demonstrate that the crystallite size of the silk fibers
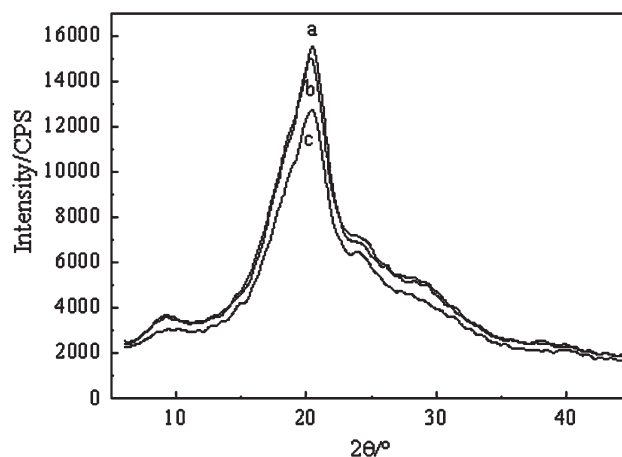

Figure 9 X-ray diffractograms of the (a) degummed, (b) calcium-salt-treated, and (c) epoxy-crosslinked silk fibers.

TABLE III
Crystallinity and Crystallite Size of the Degummed,
Calcium-Salt-Treated, and Epoxy-Crosslinked Silk Fibers

Silk sample	Crystallinity (%)	Crystallite size (nm)
Degummed	50.35	3.52
Calcium-salt-treated	51.55	3.27
Epoxy-crosslinked	47.37	2.90

decreased evidently after the calcium-salt treatment and epoxy crosslinking (Table III).

Tsukada et al.[23] investigated the modification of the silk fibers with ethylene glycol diglycidyl ether by the pad-batch method, and their research results showed that the diffraction curves of ethylene glycol diglycidyl ether modified silks were similar to that of the original sample in terms of both peak position and intensity. Their research results confirmed that the crosslinking reaction of epoxy did not occur in the crystalline region of the silk fibers. However, in this research, the fact was that the crystallinity and the crystallite size of the silk fibers decreased after the epoxy crosslinking reaction. This demonstrated that the calcium-salt treatment increased the accessibility of the subsequent crosslinking reaction, which could proceed in the crystalline region of the silk fibers and promoted the conversion from crystalline region to amorphous.

Compared with the degummed silk fibers, the modified fibers presented a structure with a lower crystallinity and fewer crystallites, and the crystallites as a reinforced phase distributed over the crosslinked amorphous region. As described previously, the crystalline region of silk fibers obtained after the calcium-salt treatment was accessible for epoxy GTGE; thus, the chemical crosslinking points could come into being on the surface of the newly formed crystalline region. Accordingly, a good connection could be established between the crystalline and amorphous regions. Therefore, the silk fibers modified in this study exhibited better flexibility.

CONCLUSIONS

An effective process for modifying silk fibers was presented in this article. *B. mori* silks were treated first by calcium salt and then crosslinked with GTGE. Porous silk fibers with excellent wet elastic resilience and flexibility were obtained. The research showed that the calcium-salt treatment increased the accessibility of the subsequent crosslinking reaction; this led the breaking strength and wet elastic resilience of the silk fibers to increase evidently. In addition, a porous structure formed in the interior of the silk fibers through the calcium-salt treatment, which was further enlarged in the subsequent crosslinking reaction, which resulted in a remarkable improvement in the moisture conduction. The new modification method has no extra requirement for manufacturing equipment and is economical and practical for mass production. All of these will provide new perspectives for the use of silk as a traditional textile material.

References

1. Lee, W. K.; Sin, K. M. Text Asia 1991, 22, 86.
2. Yang, Y.; Li, S. J Text Inst 1993, 84, 638.
3. Tsukada, M. J Appl Polym Sci 1988, 35, 2133.
4. Shiozaki, H.; Tanaka, Y. J Polym Sci Part A: Polym Chem 1970, 8, 2791.
5. Tsukada, M.; Shiozaki, H. J Appl Polym Sci 1989, 37, 2637.
6. Yang, Y.; Li, S. Text Asia 1992, 7, 72.
7. Yang, Y.; Li, S. Text Chem Col 1994, 26, 25.
8. Hu, C.; Sun, K. J Soc Dyer Col 1998, 114, 359.
9. Cai, Z.; Jiang, G.; Yang, S. Coloration Technol 2001, 117, 161.
10. Cai, Z.; Jiang, G.; Qiu, Y. J Appl Polym Sci 2004, 91, 3579.
11. Cai, Z.; Wang, F.; Yang, S. J China Text Univ (Eng Ed) 2000, 17, 56.
12. Tsukada, M.; Shiozaki, H.; Goto, Y.; Freddi, G. J Appl Polym Sci 1993, 50, 1841.
13. Miyaguchi, Y.; Hu, J. Food Sci Technol Res 2005, 11, 37.
14. Das, B.; Das, A.; Kothari, V. K.; Fanguiero, R. Fibers Polym 2008, 9, 225.
15. He, J.; Cui, S.; Wang, S. J Appl Polym Sci 2008, 107, 1029.
16. Ha, S.; Park, Y. H.; Hudson, S. M. Biomacromolecules 2003, 4, 488.
17. Hu, C.; Jin, Y.; Sun K. J Soc Dye Col 2000, 116, 204.
18. Prachayawarakorn, J.; Boonsawat, K. J Appl Polym Sci 2007, 106, 1526.
19. Arp, Z.; Autrey, D.; Laane, J.; Thomas, G. J. Biochemistry 2001, 40, 2522.
20. Holloway, P. W.; Mantsch, H. H. Biochemistry 1989, 28, 931.
21. Bhat, N. V.; Nadiger, G. S. J Appl Polym Sci 1980, 25, 921.
22. Li, M. Z.; Tao, W.; Kuga, S.; Nishiyama, Y. Polym Adv Technol 2003, 14, 694.
23. Freddi, G.; Shiozaki, H.; Allara, G.; Coto, H.; Tsukada, M. J Soc Dye Col 1996, 112, 88.