Chemical Modification of Bombyx Mori Silk with Epoxide EPSIB

Zaisheng Cai,[1] Guochuan Jiang,[1] Yiping Qiu[2]

[1]*Department of Textile Chemical Engineering, Textile Clothes and Materials Key Laboratory of National Education Ministry, Donghua University (China Textile University), Shanghai 200051, China*
[2]*Department of Textile Materials Science, Textile Clothes and Materials Key Laboratory of National Education Ministry, Donghua University (China Textile University), Shanghai 200051, China*

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ABSTRACT: Bombyx mori silk fabrics were chemically modified by EPSIB (a multifunctional silicone-containing epoxy crosslinking agent). The reactivity of the epoxy groups with silk fibroin was studied by using amino acid analysis. The physical properties of the modified silks such as resiliency (both wet and dry), moisture regain, dyeing behaviors, and solubility in a mixture solvent ($C_2H_5OH \times CaCl_2 : H_2O = 2 : 1 : 8$, molar ratio) were examined. The modified silk fabrics exhibited a significantly improved resiliency, a small increase in moisture regain and whiteness, and a slightly decreased tensile strength. The contents of Serine, Trosine, Lysine, and Histidine decreased linearly as the wet crease recovery angle (CRA) increased. The solubility in the mixture solvent also decreased as the wet CRA increased. The changes of physical properties, especially the wet CRA, were mainly due to the presence of stable crosslinks between silk fibroin and epoxy groups. The DSC and TGA analyses showed that EPSIB-modified silk fibroin had a higher thermal stability compared with the control. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3579–3586, 2004

Key words: epoxy resins; modification; proteins; fibroin; silk

INTRODUCTION

As a textile fiber, silk is highly appreciated for its outstanding characteristics such as unique luster, comfortable hand, excellent softness, and good drape. However, it also suffers from some inferior properties, one of which is low wet resiliency. It has been reported that the wet crease recovery angle (CRA) is generally only 42–57% of its dry CRA.[1] This may be due to the lack of cystine residues and the resultant absence of intermolecular chemical links in silk fibroin. The secondary intermolecular bonds that give silk fiber good dry resiliency are easily broken when silk is wet.[2] Therefore, silk creases easily during home laundry or when wet. The lower wet resiliency of silk could be improved by suitable chemical modification techniques, which create more permanent intermolecular bonds to prevent molecular movement when wet.

Besides the traditional use as a textile fiber, silk fibroin has been recently explored as a substrate for enzyme immobilization because of its good mechanical strength, chemical stability, and the presence of several functional groups that may be employed in various activation processes for enzyme immobilization.[3] Moreover, its good thermal stability is especially suitable for other applications. Therefore, the chemical reactivity[4–5] and the physico-chemical properties[6–10] of Bombyx mori silk fibroin have recently attracted considerable academic and commercial interest.

The chemical reactivity of silk with chemical finishing agents depends basically on the functional groups of the amino acid residues forming the sequence of the fibroin chains. Amines, alcohol, phenols, carboxyl, and thiols have been explored as potentially reactive sites for the chemical modification of silk. The modifying processes mainly include graft copolymerization,[6,11] dibasic anhydrides treatment,[12] amino-formaldehyde resin finishing such as trimethylol melamine (TTM),[13] polycarboxylic acids crosslinking [mainly citric acid and 1,2,3,4-butanetetracarboxylic acid (BTCA)],[14,15] and epoxide treatment.[4,5,16–28] Among the chemical modifications, the epoxide treatment for silk seems to be promising with experimental results showing a great effectiveness in improving some intrinsic properties of silk, especially its wet resiliency. The reactivity of monofunctional, functional, bifunctional, multifunctional, and silicone-containing epoxides with silk fibroin and the physical properties of epoxide-treated silk fibers have been extensively studied.[4,5,26,27]

The chemical modification of Bombyx mori silk by using epoxides is conventionally conducted with an epoxide solution in tetrachlorethylene at 60–80°C for different periods of time. Because the use of organic solvents may pose an environment threat, the indus-

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Correspondence to: Y. Qiu (Yqiu@tx.ncsu.edu).

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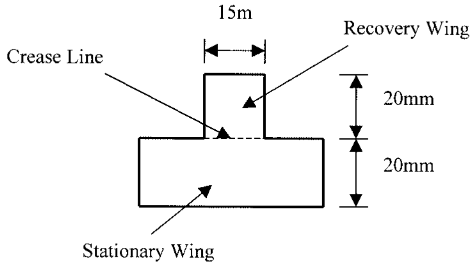

Figure 1 Sample for crease recovery angle measurement.

trial application of this epoxide treatment may be limited. Alternative treatments have always been sought. Therefore, a comprehensive research program was carried out in our laboratory to study new aqueous finishing agents and to successfully prepare aqueous epoxy agents such as TDEA (a multi-amino epoxy resin A) and TDEB (a multi-amino epoxy resin B).[23–25] Both of them can significantly improve wet resiliency of silk fabrics but result in a poorer fabric hand, which cannot be easily remedied by simple softening processes by using cationic, nonionic, and silicone softeners.[23–24] Therefore, alternative modifying agents such as EPSIA (a multifunctional silicone-containing epoxy crosslinking agent A) and EPSIB (a multifunctional silicone-containing epoxy cross-linking agent B)[26–28] have been developed.

We have recently reported the optimum conditions for EPSIA finishing of silk, the physical and dyeing properties, and the effect of EPSIA on the reactivity of silk fibroin. It is elucidated that changes of physical properties mainly resulted from the EPSIA-silk fibroin crosslinking reaction.[26–27] We also investigated the synthetic process of the silicone-containing epoxide and primarily discussed the application on silk crease-resist finishing using EPSIB.[28]

The objective of this study was to investigate the chemical modification of Bombyx mori silk by EPSIB. The reactivity of the modifying agent with silk was studied by means of amino acid analysis. The physical properties of the modified silk fabrics such as dry and wet CRA and the moisture regain were evaluated. Dyeing properties and the solubility of the silk fabrics in a mixture solvent ($C_2H_5OH : CaCl : H_2O = 2 : 1 : 8$, molar ratio) were also examined. Meanwhile, the thermal behavior was investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

White silk habutae fabrics (Bombyx mori, plain weave, weight = 52 g/m^2, warp/weft yarn denier = 42/84, warp/weft fabric count = 65/37/cm) supplied by Shanghai No. 1 Silk Dyeing and Finishing Factory (Shanghai, China) were used for all experiments.

EPSIB was synthesized in our laboratory. Dispersion agent JFC and Peregal O of industrial grade and other chemicals such as potassium thiocyanate and sodium carbonate of chemical grade were provided by Shanghai Chemical Reagent Purchasing Station (Shanghai, China).

Chemical modification

Silk fabric samples were padded twice with a finishing bath containing 100 g/L of EPSIB, 5 g/L of dispersion agent JFC, and 4 g/L of KCNS with an 85–90% wet pick-up. The fabrics were dried at 80°C for 2 min and finally cured at 130°C for 4 min.

Dyeing process

The dyeing behavior of the EPSIB-modified silk was investigated by using Lanaset Red G, Yellow 2R, and Grey G provided by Ciba (Shanghai) Chemical Co. The dyeing process was carried out in an oscillating sample machine manufactured by Wenzhou Textile Instrument Factory. Silk samples (20 × 30 cm) were used. Two percent (o.w.f.) dyestuff with a liquid ratio of 1 : 50 was employed and the pH 5.5 was adjusted by using acetic acid. The dyebath was kept at a temperature of 60°C for 5 min after adding auxiliaries and samples. The dyestuff was then added to the dyebath, which was maintained at 60°C for 5 min before raising the temperature to 90°C at a rate of 1°C/min. The

TABLE I
Amino Acid Composition (g/100 g) of the EPSIB-Modified Silk with Different Values of Wet CRA

	Wet CRA (W + F,°)			
	Control	EPSIB-modified		
Amino acid	217.2	255.3	275.6	294.8
Aspartic acid	1.86	1.85	1.87	1.86
Thyreonine	1.08	1.07	1.07	1.08
Serine	12.37	11.92	11.58	11.39
Glutamic acid	2.42	2.42	2.45	2.41
Glycine	34.86	34.85	34.86	34.86
Alanine	29.63	29.65	29.67	29.64
Valine	3.76	3.78	3.8	3.8
Methionine	0.35	0.37	0.4	0.41
Isoleucine	1.54	1.52	1.51	1.51
Leucine	0.89	0.87	0.87	0.86
Trosine	12.02	11.31	10.05	8.99
Phenylalanine	2.27	2.28	2.28	2.26
Lysine	0.49	0.38	0.26	0.18
Histidine	0.23	0.1	0.03	0
Arginine	0.56	0.55	0.55	0.56
Proline	0.68	0.63	0.69	0.67
Tryptophan	1.09	1.03	1.1	1.11
Total	106.1	105.06	103.84	102.56

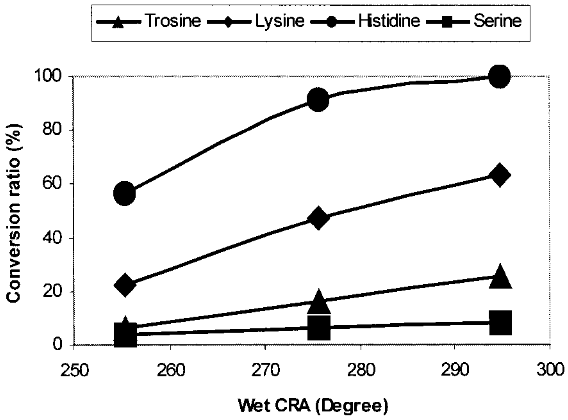

Figure 2 Conversion ratio of some amino acid residues of the Bombyx mori silk finished by EPSIB as a function of the wet CRA.

dyebath was kept at 90°C for 30 min. The sample was then boiled in a bath containing 2 g/L of a detergent (White Cat Brand) and 1 g/L of Na_2CO_3 for 15 min. Finally, the sample was rinsed twice with tap water.

Laundry (one-cycle process)

The chemically modified silk fabrics were washed in a washing machine at 30–40°C with a liquid to fabric ratio of 25 : 1 and a detergent (Mei Jia Jian brand) of 0.5–1 g/L for 5 min, then rinsed with tap water for 5 min, and finally air dried at room temperature.

Measurements

Crease recovery angle

Dry and wet CRAs were measured by using a ZST 80 Crease Recovery Apparatus according to ISO 2313–1972. The shape, dimension, and crease line of a specimen is shown in Figure 1. The specimen was creased under a weight of 500 g for 5 min and then allowed to recover for 5 min. Values of CRAs in both warp and weft directions were then determined. The samples were conditioned at 20°C and 65% relative humidity (RH) for at least 24 h before testing. The wet CRA was performed as described above except that fabric samples were immersed in 2 g/L of Peregal O at 40 ± 3°C for 5 min and then excess water was removed by sheets of blotting paper. The values (warp plus weft) reported are the averages of 10 specimens (five in the warp and five in weft).

TABLE II
Physical Properties of Bombyx mori Silk

Samples	CRA (W + F,°) Dry	Wet	Whiteness	Moisture regain (%)
Control	229.4	217.2	69.1	10.01
EPSIB-modified	291.4	294.8	71.1	10.84

TABLE III
Tensile Properties

Samples	Tensile strength (N) Warp	Weft	Failure strain (%) Warp	Weft
Control	535	587	7.4	10.3
EPSIB-modified	504	548	6.4	8.8

Fabric tensile strength

Fabric tensile strength was determined by using a YG 026 tensile testing machine following ISO 5081-77. Six specimens (three for warp and three for weft) were tested at a gauge length of 200 mm with a strain rate of 30 mm/min. The width of the specimen was 60 mm.

Moisture regain and whiteness

The moisture regain was evaluated as the percentage weight difference between conditioned (20°C and 65% RH for at least 24 h) and bone-dry fabric samples. Whiteness of silk sample was measured on a ZBD whiteness meter. Both moisture regain and whiteness values were the average values of 10 readings.

Amino acid composition analysis

Dried Bombyx mori silk specimens were hydrolyzed by heating at 110°C for 20 h in 6*M* hydrochloric acid under vacuum. Amino acid compositions of the hydrolyzed specimens were determined by using an 838 Type Amino Acid Analyzer.

Color fastness and K/S values

Color fastness was tested by using a Roaches Washing Fastness Machine and a Y571B Flat Abrasion Fastness Machine (Wenzhou Textile Instrument Factory) according to AATCC Test Method 119-1984. Color

TABLE IV
Crease Recovery Angle of Silk Fabrics after Washing

Number of washing cycles	Crease recovery angle (CRA) (°) Control Dry	Control Wet	EPSIB-modified Dry	EPSIB-modified Wet
0	229.4	217.2	291.4	294.8
5	213.2	224.1	280.9	273.5
10	214.0	212.0	285.8	273.2
20	190.9	217.6	268.4	269.5

TABLE V
Dye Uptakes in Terms of K/S Value of Silk Fabrics

Dyestuff	K/S Control	 EPSIB-modified	Note
Lanaset Red G	8.22	9.47	$\lambda_{max,Red} = 510$ nm
Lanaset Yellow 2R	4.5	8.88	$\lambda_{max,Yellow} = 450$ nm
Lanaset Grey G	5.08	8.98	$\lambda_{max,Grey} = 600$ m

changes due to washing and rubbing were determined by Gray Scale Method in five grades (grade 5 is the best fastness and grade 1 is the poorest). The K/S values of Bombyx mori silk fabrics were measured by using the MATCH-MATE 350 Micromatch Color Meter (DIANO Co.).

Solubility

The solubility of the silk was determined by boiling silk samples (3 × 3 mm square) in a mixture solvent ($C_2H_5OH : CaCl_2 : H_2O = 2 : 1 : 8$, molar ratio) for 10 or 30 min. The solubility rate of the silk was measured with an UV-365 Type Ultraviolet Spectraphotometer.

DSC and TGA analysis

The DSC analysis was carried out in nitrogen (gas flow rate of 50 ml/min) on a 2910 Modulated DSC System (TA Co.) at a heating rate of 10°C/min. TGA was performed in nitrogen (gas flow rate of 60 ml/min) on a HI-RES TGA 2950 Thermogravimetric Analyzer (TA Co.) at a heating rate of 50°C/min.

RESULTS AND DISCUSSION

Chemical reactivity of EPSIB with bombyx mori silk

TABLE VII
The Relationship Between Wet CRA and Solubility of Silk in the Mixture Solvent

	Control	EPSIB-modified		
Wet CRA (°)	217.2	255.3	275.6	294.8
Solubility rate (%)	100	28.5	13.7	9.85
Refluxing time (min)	10	30	30	30

The amino acid analysis of the modified silk with different values of wet CRA was performed to evaluate the chemical reactivity of EPSIB with silk fibroin. Table I shows that the contents of some amino acid residues such as Serine, Tyrosine, Lysine, and Histidine were affected by EPSIB modification. Figure 2 shows the relationship between the wet CRA and the conversion ratios of the amino acid residues. There was an almost linear relationship between conversion ratios of Serine, Tyrosine, Lysine, and Histidine and the wet CRA, which agreed with those already reported by other researchers.[23,26] This confirms that the active groups of these amino acid residues are the main reactive sites between silk and EPSIB. Epoxy groups should react with the hydroxyl group of Serine, phenol hydroxyl group of Tyrosine, amino group of Lysine, and imino group of Histidine.

Physical properties

Tables II and III show the changes in resiliency, moisture regain, whiteness, and tensile strength of the silk fabrics. Fabrics modified with EPSIB did exhibit a substantial improvement of both dry and wet resiliency (i.e., dry CRA was increased from 229.4° to 291.4°, and wet CRA was raised from 217.2° to 294.8°). In addition, the modified silk fabrics showed a small increase in both whiteness and moisture regain, a decrease of 6.4% ($P < 0.05$) in tensile strength, and a decrease of 14% in failure strain ($P < 0.05$) in both warp and filling directions (Table III). These changes of physical properties are mainly because EPSIB-silk crosslinking reaction occurred in the more accessible amorphous regions of silk fibroin.

TABLE VI
Color Fastness of EPSIB-Modified Bombyx mori Silk

Dyestuff	Samples	Soaping fastness (Grade) Fading	 Stained cotton	 Stained silk	Rubbing fastness (Grade) Dry	 Wet
Lanaset Red G	Control	4	4–5	3	4	4–5
	Modified	4–5	5	3–4	4	4
Lanaset Yellow 2R	Control	5	5	4	4–5	4–5
	Modified	5	5	4	4	4–5
Lanaset Grey G	Control	5	4–5	4	4	4
	Modified	5	4–5	4	3–4	4

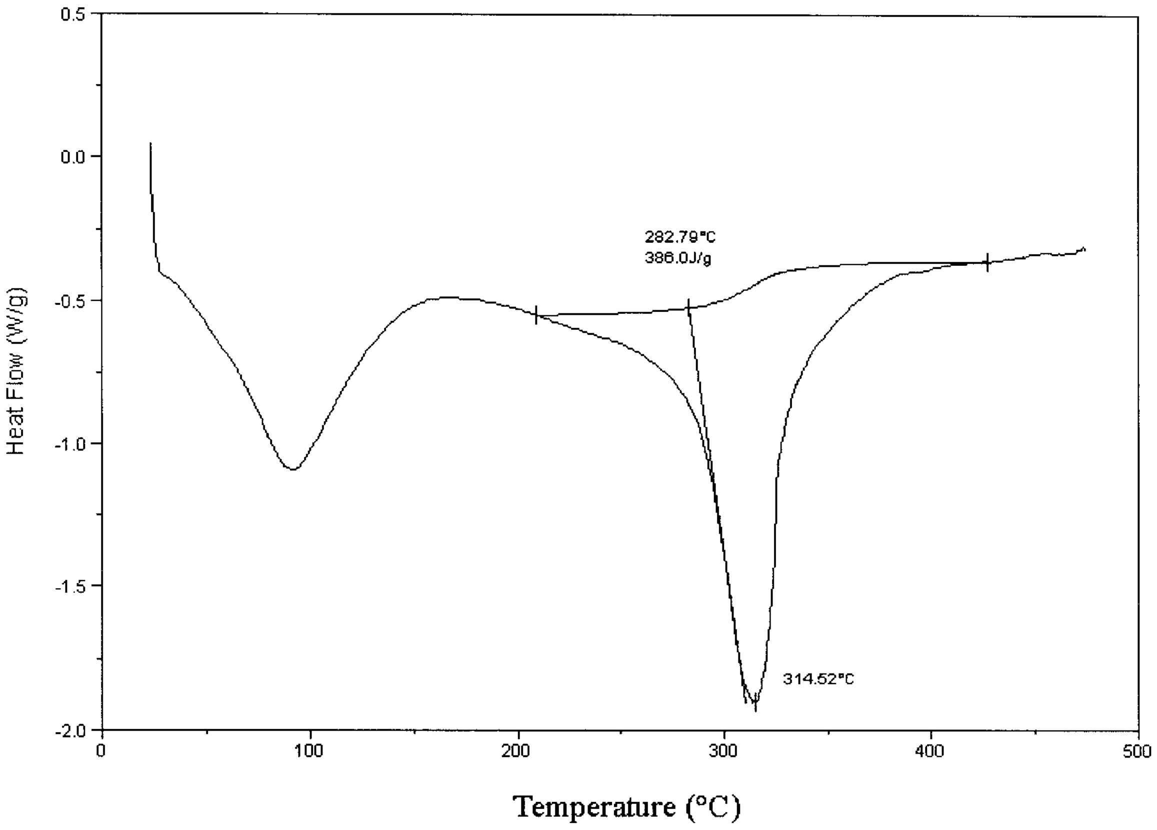

Figure 3 DSC curve of the control bombyx mori silk fibroin.

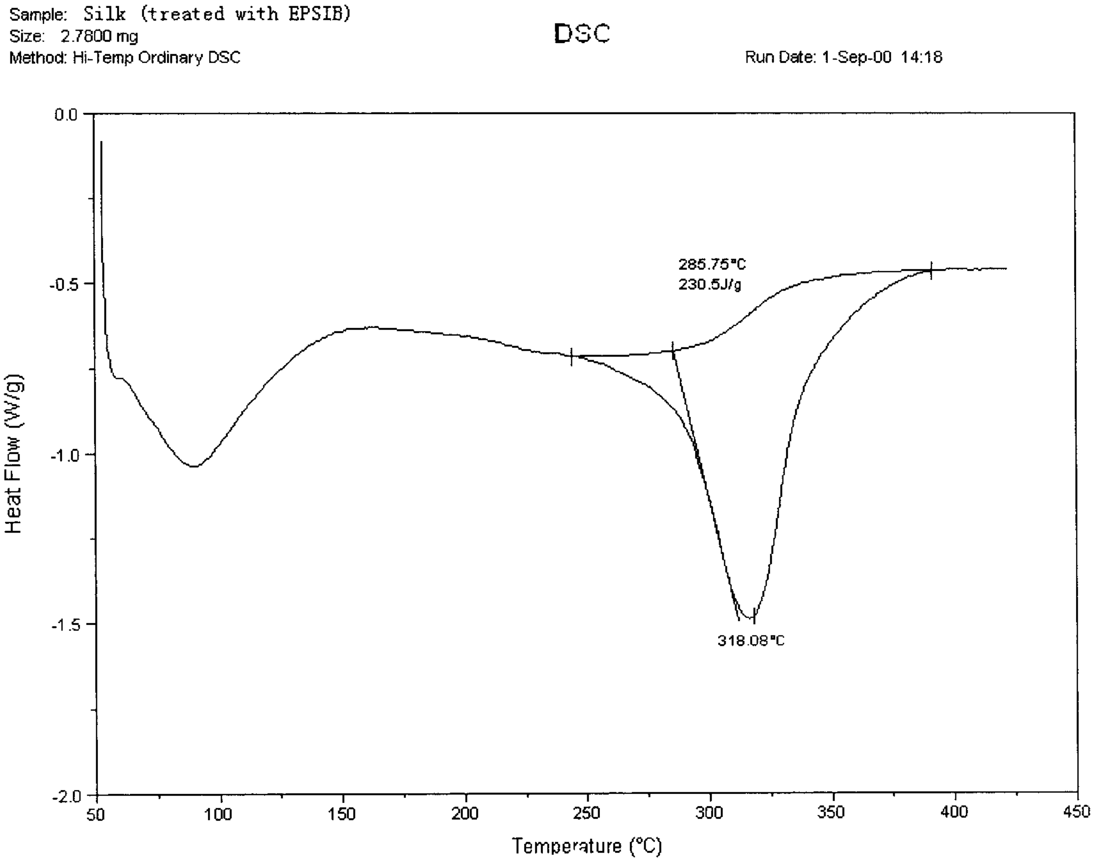
Sample: Silk (treated with EPSIB)
Size: 2.7800 mg
Method: Hi-Temp Ordinary DSC
Run Date: 1-Sep-00 14:18

Figure 4 DSC curve of the EPSIB-modified bombyx mori silk with wet CRA of 294.8°.

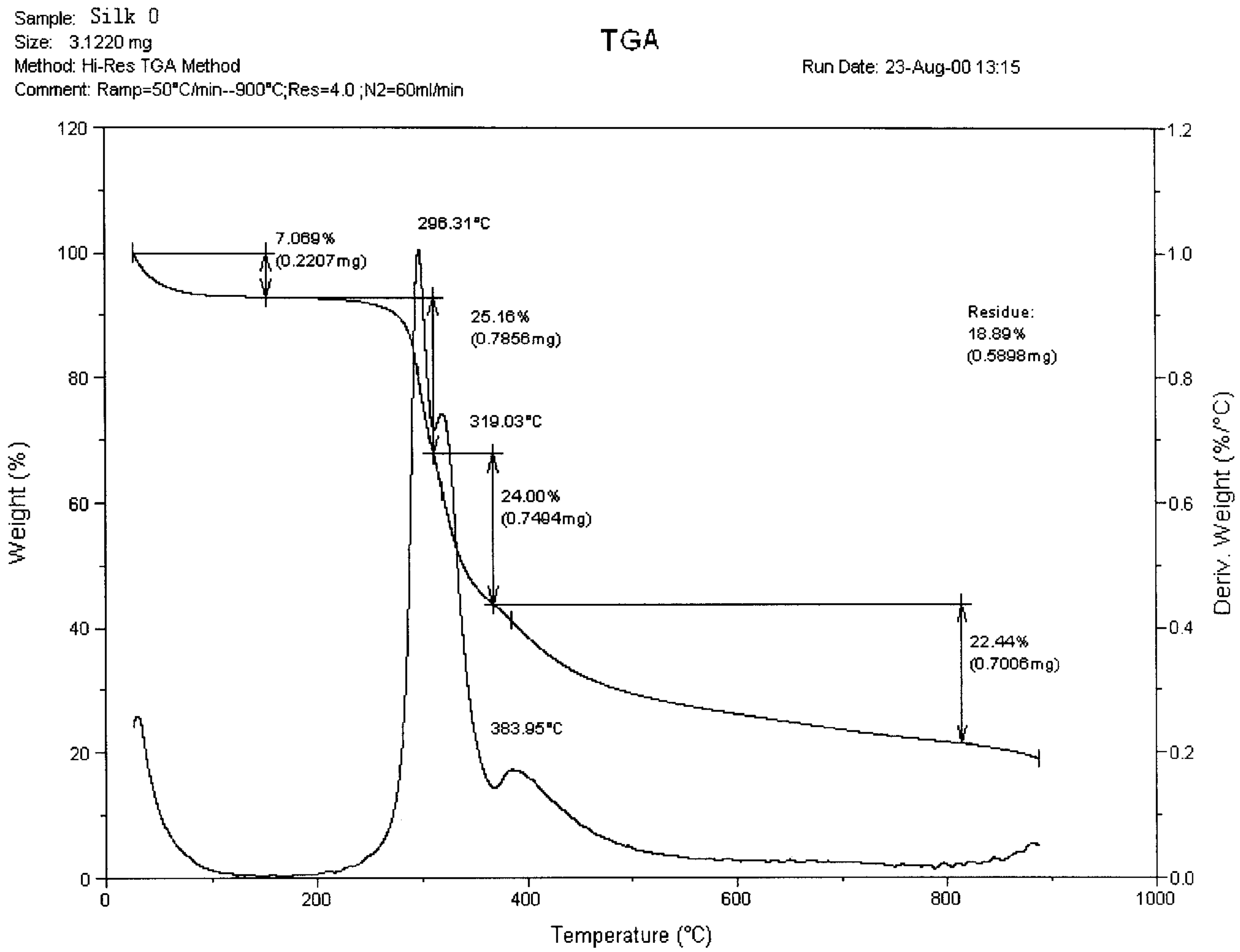

Figure 5 TGA curve of the unmodified silk in nitrogen.

Table IV gives the CRAs and their changes with the number of washing cycles. Both dry CRA and wet CRA still remained 268.4° and 269.5° after 20 washing cycles, which are 92.1 and 91.4% of the original CRA, respectively. These results indicate that the modified silk fabrics had good laundry durability. It was again due to the presence of covalent bonds between EPSIB epoxy groups and silk fibroin.

Dyeing behavior of the EPSIB-modified silk fabrics

The modified silk fabrics exhibited an increase in dye uptake of all three dyestuffs under the same dyeing conditions as the control sample (Table V). EPSIB was a weak cationic epoxide, and the modified silk fabrics generally carried more or less positive charges. Therefore, the modified silk fabrics have stronger affinities for ionic dyes. The dye uptakes of the modified silk fabrics were higher than the control fabrics. The soaping fastness of modified fabrics was either slightly higher or the same as the control fabrics, while the opposite was true for the rubbing fastness (Table VI).

Solubility of silk fibroin

The solubility properties are very useful and important for identifying and evaluating the occurrence of chemical modifications on silk fibers and estimating whether there are covalent bonds between EPSIB epoxy group and silk fibroin. Table VII represents the solubility rate of the modified silk in the mixture solvent as a function of wet CRA. The data show that all control specimens were dissolved on refluxing for only 10 min, whereas the solubility rates of the modified samples decreased almost linearly with the increase of wet CRA. This was still likely due to the presence of crosslinks between epoxy groups and silk fibroin that decreased the soluble fraction in the mixed solvent.

Thermal properties

Figures 3 and 4 show the DSC curves of the control and modified samples, respectively. For the control

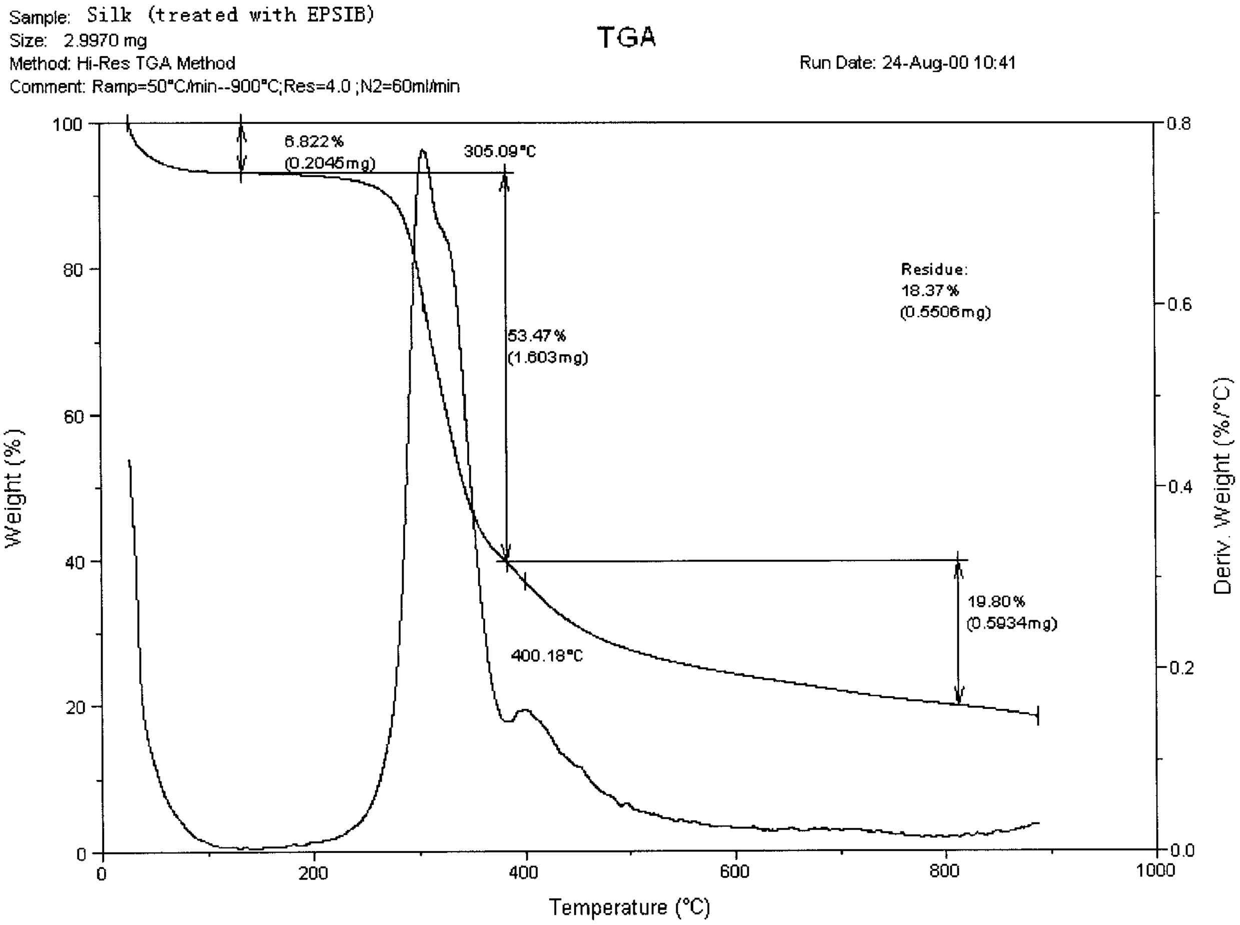

Figure 6 TGA curve of the EPSIB-modified bombyx mori silk fiber with wet CRA of 294.8°.

sample, the endothermic peak initiated at 282.79°C, about 3°C lower than that of the modified samples. Moreover, the modified silk exhibited major endothermic peak at 318.08°C, corresponding to the thermal decomposition of silk with β-configuration.[29] The position of the above endothermic peak was more than 3°C higher than the control sample. Meanwhile, the shapes of the decomposition endothermic peaks of the EPSIB-modified samples became slightly broader and more asymmetric compared with that of the control sample. This phenomenon showed that the chemical modification with EPSIB had an obvious effect upon the thermal stability of silk fibroin. In addition, the TGA curves show that the modified silk specimens exhibited a slightly higher thermal stability. There were three peaks at 296.31, 319.03, and 383.95°C in the TGA curve of the control sample (Fig. 5), while only two peaks at 305.09 and 400.18°C in that of the modified sample (Fig. 6). It seemed that the first and the second peaks were merged into one peak after silk was modified by EPSIB. Moreover, the peak at the biggest weight loss of the modified sample appeared at 400.18°C, which is 16°C higher than the control. These results indicate that the crosslinking covalent bonds formed by the reaction between silk and EPSIB led to a more thermally stable structure in silk.

CONCLUSION

From the results and analysis above it is concluded that Bombyx mori silk fabrics modified with the multifunctional silicone-containing epoxide EPSIB showed a rather significant change of physical and chemical properties. Resiliency of the modified silk fabrics exhibited a dramatic improvement; moisture regain and whiteness showed a small increase, whereas tensile strength and failure strain were slightly decreased. The uptakes of dyes on the modified silk increased. The soaping fastness was either the same or slightly increased, whereas the rubbing fastness was either slightly decreased or the same for the modified silk. All of these will provide new perspectives for the use of silk as a traditional textile material.

The contents of major amino acid residues (Serine, Tyrosine, Lysine, and Histidine) in the modified silk fibroin were decreased linearly with the increase of wet CRA. It indicates that EPSIB had reacted with the active sites on those amino acid residues to form stable covalent bonds, which were attributed to the solubility decrease in the mixed solvent, resulting in a good laundry fastness and all other physical and chemical changes.

The results of DSC and TGA show that Bombyx mori silk exhibited an obvious higher thermal stability after being modified with EPSIB. This result means that the modified silk could be more suitable for specific nontextile applications, such as enzyme immobilization for which the large number of reactive groups such as carboxyl and thiol remained as the base.

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