

Chemical and Property Modification of Silk with Dibasic Acid Anhydrides

MASUHIRO TSUKADA, *Sericultural Experiment Station, Tsukuba City, Ibaraki 305, Japan*, and HIDEKI SHIOZAKI, *Textile Research Institute of Kanagawa, Aikawa-Machi, Kanagawa 243-03, Japan*

Synopsis

In an attempt to provide information for improving silk fiber and fabric properties including crease recovery and yellowing, silk modification has been studied by using succinic and glutaric anhydrides. Glutarylation has been found to protect silk fibers from yellowing caused by the high energy radiation and to be more effective on increasing the crease proofing. The silk fabrics did not reduce the tensile properties such as strength and elongation at break even after the chemical modification with dibasic acid anhydrides. Thermal properties of the fibers remained unchanged in spite of the succinylation or glutarylation. From all the considerations of the survey of dye uptake, it would seem that the ester crosslinks are easily formed much more by the glutarylation than by the succinylation. The recovery values and yellowness indices of the modified silk fabrics and the measuring results of thermal and thermomechanical properties are explicable, taking into account of the different reactivity of the functional groups induced by the chemical modification with the dibasic acid anhydrides.

INTRODUCTION

Natural silks are one of the most beautiful and precious fibers, possessing excellent handling and outstanding mechanical characteristics as the clothing materials. However, they suffer from certain disadvantages such as antiyellowing, W & W, and crease proofing properties. Considerable effort has been expended in trying to improve these inferior properties of silk through chemical modification or by grafting techniques.¹⁻⁴ Epoxides,⁵⁻⁷ glutaraldehyde,⁸ and thiourea/formalin resin⁹ are the agents for the chemical modification for materially improving fiber and fabric properties. However, there is no information on the modification with dibasic acid anhydrides.

In a recent study, we¹⁰ reported the effect of moisture regain and the dyeing characteristics of the silk fibers modified with succinic anhydride and have considered the functionality of the groups introduced by the succinylation.

Our work was based on the assumption that crease resistance and antiphotoyellowing of silk fabrics could be improved by succinylation, which, owing to its reactivity groups, can induce crosslinking of silk fibroin. It seems of great interest to compare the results modified with succinic or glutaric anhydride because both anhydrides possess the possibility to combine the phenolic hydroxyl groups of Tyr residues, which play an important role in yellowing of the silk.

The purpose of our investigation was to see whether the chemical modification by using dibasic acid anhydrides would improve crease-proofing, antiphotoyellowing, and mechanical properties. We discussed further the susceptibility of the reactive sites and the modified molecular parts.

MATERIALS AND METHODS

Reagent grade succinic and glutaric anhydrides, purchased from Wako Pure Chemical Industries, Ltd., were used without further purification. Degummed and bleached silk fibroin fibers (21 den/1 × 2) or Habutae silk (ca. 7.5 g/10 cm²) was treated with 10% (w/v) succinic or glutaric anhydride in dimethylformamide (DMF) at 75°C for different periods of time; this was attached to a reflux condenser and held in a thermostatically controlled bath. The material-to-liquor ratio of 1:20 was maintained. At the end of the reaction, the samples were washed with isopropanol, then with acetone at 55°C for 1 h to remove the unreacted anhydride, and then successively with tap water.

The dyestuffs used were Kayanol Blue-N2G (C.I. Acid Blue 40) in the neutral bath and Kayaku Acid Orange II (C.I. Acid Orange 7) in the acidic bath (pH. 4.5).

Dyeing was carried out at 80°C for 90 min in the neutral bath or at 85°C for 30 min in the acidic one, keeping a material-to-liquor ratio of 1:80. The dye concentration was kept at 2.5% (owf). The dyed sample was taken out and rinsed well with fresh water. The dye uptake values were measured with a Hitachi Color Analyzer 607 and expressed in terms of *K/S* values.

Fiber strength and elongation at break were measured on a single thread with an automatic Tensilon tensile tester (UTM-II) at 20°C and 65% RH.

Conditioned crease recovery angles were measured by using the Monsanto method¹¹ on samples. The modification yield of the silk fabrics or fibers were calculated from the oven-dried weights of the samples before and after the treatment, a correction being made for the slight weight loss on the treatment with DMF alone.

Silk fabrics were irradiated from a Xenon lamp with using a photoemeter (WEL-25AX-HC-EC) of Suga Test Instrument Co., Ltd. Forced air cooling maintained the sample temperature at 35–38°C. Yellowness index was measured on a Color Computer (SM-3) of Suga Test Instrument Co., Ltd.

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. The open aluminum cell was swept with N₂ gas during the course of the analysis. 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.

RESULTS AND DISCUSSION

Reactivity of Dibasic Acid Anhydrides

The previous papers^{10,12} described that the main reactive sites for the acylation onto the silk fibers are the amino groups of Lys residues and the hydroxyl groups of the Tyr and Ser residues of the silk fibroin and that the acylation onto silk fiber required more strict conditions than that for the wool keratin fibers, which is much abundant in the content of the Lys residues. The effect of the reaction time on the weight gains by treating with dibasic acid anhydrides at 75°C in DMF was examined (Fig. 1). Increase of the reaction time causes at first a rather steep rise of weight gains and reaches

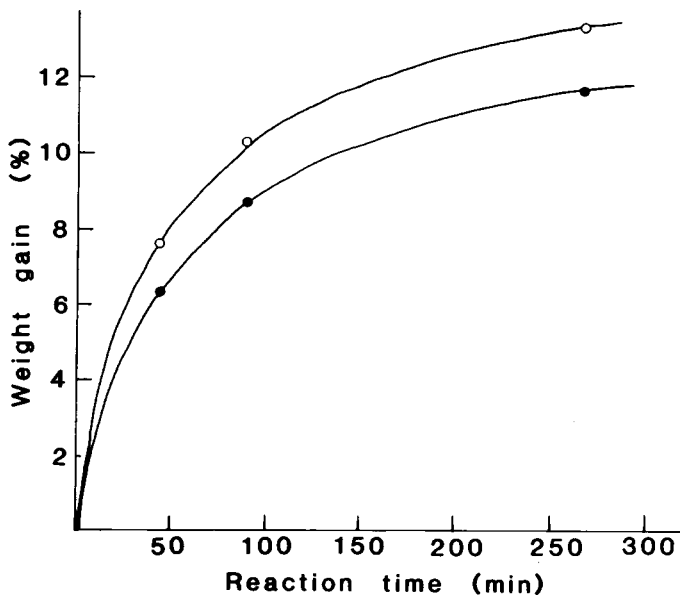


Fig. 1. Weight gains of the silk fibers treated in dimethylformamide solution contained 10% (w/v) succinic (●) or glutaric (○) anhydride at 75°C for different periods of time. The material-to-liquor ratio of 1 : 20 maintained.

maximum at about 270 min. It seems that glutarylated silk fibers showed a slightly greater modification yield than that of the succinylated. However, succinyl content of the modified silk fiber after attaining the equilibrium is similar to the content by the glutarylation, showing the saturated values of 115–120 mol/10⁵ g for both of the reactions.

Physical Properties of Modified Silk Fibers

The physical properties of the silk fibers modified with dibasic acid anhydrides are given in Tables I and II. The moisture regain of the silk fibers clearly increased by the succinylation onto silk, exhibiting simple increase with reaction time, while that of the glutarylated silk showed maximum at reaction time of 1 h, which exhibited a striking contrast to the succinylated silk.

It is considered that the rupture strength (g/d) of the silk fibers modified by graft-copolymerization decreased gradually, while the initial tensile resistance clearly increased.¹³ Mechanical properties of the silk modified with dibasic acid anhydrides remained unchanged compared with that of the original silk. The elongation at break of the silk tends to increase as the reaction proceeds. Therefore, the results obtained indicate that the original properties inherent in silk are not damaged even after the modification with dibasic acid anhydrides, the same as the modification with epoxides.⁷

The crease recovery values of the silk fabrics slightly increased by the succinylation (Table II) and remarkably increased by the glutarylation. Yellowness index values obtained by Xenon arc irradiation reduced remarkably for the glutarylated silk compared with control, while for the succinylated silk

TABLE I
Physical Properties of Modified Silk Fibers with Succinic
(S-1, S-2, S-3) and Glutaric Anhydride (G-1, G-2, G-3)

Sample	Moisture regain (%)	Strength (g/d)	Elongation at break (%)	Initial tensile resistance (g/d)
Control	9.4	3.5	12.3	77.9
Succinylated ^a				
S-1	12.5	3.8	14.3	79.2
S-2	13.1	3.6	13.5	81.2
S-3	14.4	3.4	14.5	79.4
Glutarylated ^b				
G-1	12.8	3.6	14.0	71.6
G-2	12.3	3.5	13.4	69.3
G-3	11.8	3.4	12.9	73.5

^aS-1, S-2, S-3 is the silk fiber treated with 10% (w/v) succinic anhydride in dimethylformamide at 75°C for 45, 90, and 270 min, respectively.

^bG-1, G-2, G-3 is the silk fiber treated with 10% (w/v) glutaric anhydride in dimethylformamide at 75°C for 45, 90, and 270 min, respectively.

increased clearly (Table II). It may be noted that the glutarylation onto silk has been found to protect silk from yellowing caused by the UV irradiation. The characteristics variations observed in the crease recovery value and yellowness index should be due to the difference in the mode of the modified molecular parts, and further study will be needed to elucidate the facts.

The dyeing behavior of the silk modified with dibasic anhydrides was evaluated for their dyability characteristics using two kinds of dyestuffs (Table III). A significant decrease in the dye (C.I. Acid Blue 40) uptake for the succinylated silk was observed, compared with that of glutarylated silk. That is to say, the *K/S* values of the glutarylated silk dyed with Acid Blue 40 in a neutral bath were half of the control, while those of the succinylated silk became 1/3 of the control. The succinylated silk dyed with Acid Orange 7 at pH 4.5 also showed a slightly greater decrease in the dye uptake than the glutarylated. These results demonstrating the differences in dye uptake ap-

TABLE II
Crease Recovery of the Silk Fabrics Treated with Succinic (S-1, S-2, S-3) and Glutaric
Anhydride (G-1, G-2, G-3) and Change of the Yellow Index of the Silk Fabrics
Irradiated for 100 h by Xenon Lamp

Sample	Crease recovery (%)	YI
Control	77.2	6.01
Succinylated		
S-1	79.3	7.92
S-2	78.4	8.98
S-3	78.3	9.33
Glutarylated		
G-1	87.4	4.82
G-2	88.5	4.61
G-3	89.3	4.43

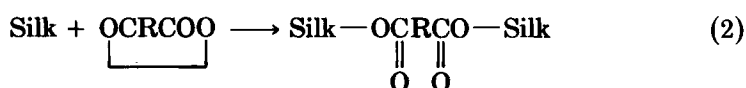
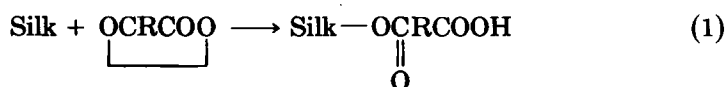
TABLE III
The K/S Values of the Succinylated ($115.6 \text{ mol}/10^5 \text{ g}$) and Glutarylated Silk
Fibers ($116.5 \text{ mol}/10^5 \text{ g}$) Dyed with Acid Dyestuffs

Sample	Acid Blue 40 ^a	Acid Orange 7 ^b
Control	13.303	19.845
Succinylated	4.480	14.168
Glutarylated	6.168	16.256

^aSamples were dyed in a neutral bath at 80°C for 90 min (2.5% owf).

^bSamples were dyed in an acid bath (pH 4.5) at 85°C for 30 min (2.5% owf).

pear to have made a considerable contribution to the increased interaction between the dye molecules and carboxyl groups present in the modified chains. As might be expected, the succinylation onto the silk makes it easier to form the free carboxyl groups (1), while the ester crosslinks (2) are easily formed much more by the glutarylation than by the succinylation:



Thermal Properties of the Modified Silk Fibers

In order to define the thermomechanical properties, TMA curves for the modified silk were obtained (Figs. 2 and 3). Control silk showed the contraction of about 0.4% in the temperature range between 30 and 100°C; then the

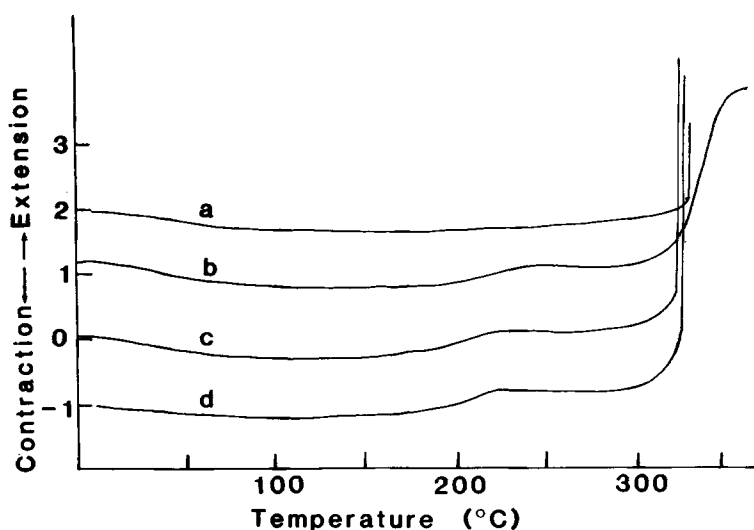


Fig. 2. Thermomechanical analysis curves of silk fibers treated with succinic anhydride in dimethylformamide at 75°C for different periods of time. Time (min): (a) 0; (b) 45; (c) 90; (d) 270.

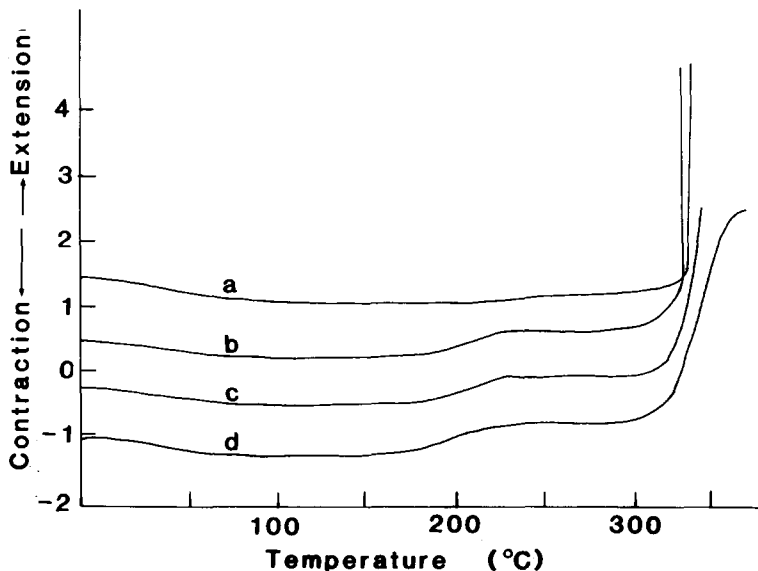


Fig. 3. Thermomechanical analysis curves of silk fibers treated with glutaric anhydride in dimethylformamide at 75°C for different periods of time. Time (min): (a) 0; (b) 45; (c) 90; (d) 270.

length of the specimen remained unchanged up to 300°C. The control specimen exhibited the abrupt extension in length above 320°C. TMA curves of the succinylated silk (Fig. 2) are similar to that of the control, except for showing a slight extension of about 0.3% for the succinylated silk. Glutarylated silks (Fig. 3) also exhibited similar TMA curves to those of control and succinylated silk. It is noted that the changing length of the glutarylated silk stops temporarily above 300°C, which is contrasted to the succinylated silk, suggesting the greater thermal stability of the glutarylated silk.

Figures 4 and 5 show the DSC curves of the modified silk fibers. Succinylated silk showed a single endothermic peak at around 317°C, which is attributed to the thermal decomposition of the silk fibroin with oriented β' orientation,¹⁴ exhibiting the same DSC curves of the control. Therefore, it is considered that the abrupt extension in the length observed in Figures 2 and 3 is due to the thermal decomposition of the silk fibroin. DSC curves for the glutarylated silk shifted slightly toward to the endothermic reaction above 210°C (Fig. 5), which formed a striking contrast to the succinylated and control silk, although the temperature corresponding to the thermal decomposition of the modified silk remained unchanged in spite of the succinylation or glutarylation.

On the basis of the survey of crosslinking reaction produced by the difluoro-dinitro-sulfones, Zahn and Hammoudeh¹⁵ suggested that crosslinks are more easily formed in wool keratin compared with the silk, because wool keratin possesses abundant reactive sites, i.e., Lys and Tyr residues. It is elucidated that glutaric anhydride forms more easily the crosslinks between the side chains of silk fibroin. The difference in the crease recovery values and yellowness indices (YI) between the succinylation and glutarylation would imply that the crosslinks formation contributes to improving crease proofing

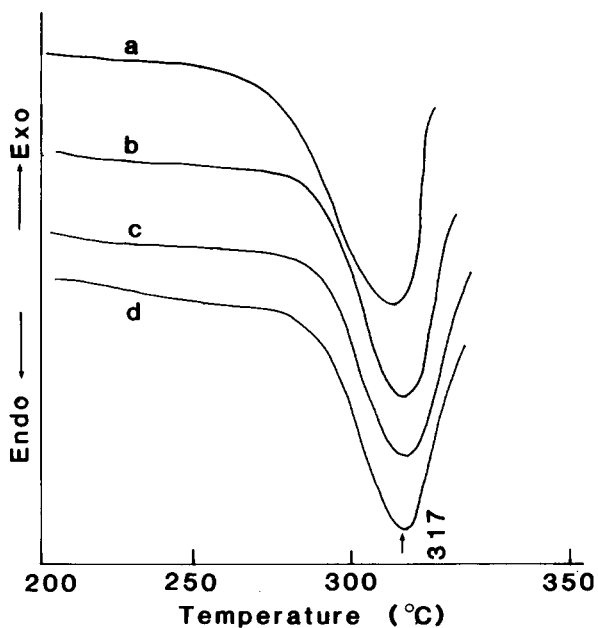


Fig. 4. DSC curves of succinylated silk fibers in dimethylformamide at 75°C for different periods of time. Time (min): (a) 0; (b) 45; (c) 90; (d) 270.

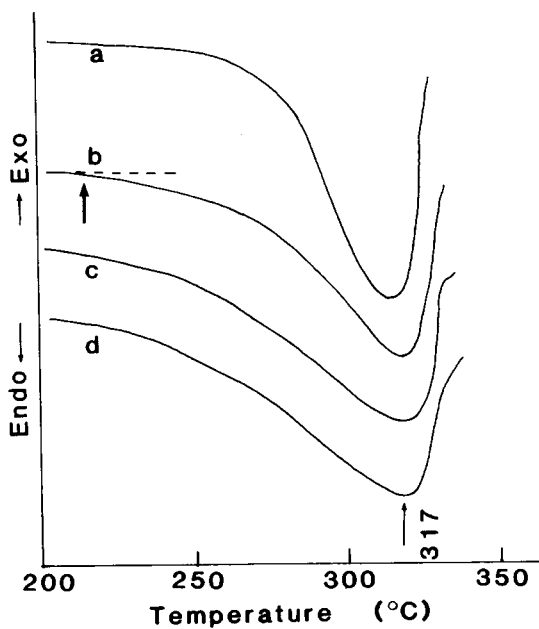


Fig. 5. DSC curves of glutarilated silk fibers in dimethylformamide at 75°C for different periods of time. Time (min): (a) 0; (b) 45; (c) 90; (d) 270; (↑) Shifting of DSC curve toward to the endothermic reaction.

and antiyellowing properties (Table II). As illustrated in Figure 5, a slight shifting of the DSC curve of the glutarylated silk toward the endothermic reaction at around 210°C may be attributed to the disrapture of the ester crosslinks and the thermal stability observed on the TMA curves of the glutarylated silk [Fig. 3(d)] is explicable, taking into account of the ester crosslinks. It should not be concluded, however, from what has been mentioned that the crosslinks formed between the adjacent silk fibroin molecules by the glutarylation have an effect on the increase of recovery values and yellowness indices (Table II) of the modified silk fabrics.

References

1. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 965 (1988).
2. S. Samal and G. Sahu, *J. Macromol. Sci. Chem.*, **A21**, 725 (1984).
3. S. Samual, G. Sahu, and P. L. Nayak, *J. Appl. Polym. Sci.*, **29**, 3283 (1984).
4. N. Mohanty, S. N. Torasia, M. C. Mohanta, D. K. Rout, and H. K. Das, *J. Macromol. Sci. Chem.*, **A20**, 409 (1983).
5. H. Shiozaki and Y. Tanaka, *Makromol. Chem.*, **152**, 217 (1972).
6. H. Shiozaki and H. Tanaka, *J. Seric. Sci. Jpn.*, **45**, 74 (1976).
7. M. Tsukada, H. Shiozaki, and M. Nagura, *J. Seric. Sci. Jpn.*, **56**, 323 (1987).
8. M. Tsukada and H. Shiozaki, *J. Seric. Sci. Jpn.*, **55**, 257 (1986).
9. S. Serafimov, M. Cheshmedzhiv, and A. Arsov, *Tekhnol. Tekst. Prom. No. 6*, 100 (1970); *Chem. Abstr.*, **74**, 113095 (1971).
10. H. Shiozaki, M. Tsukada, and M. Matsumura, *J. Seric. Sci. Jpn.*, **57**, 165 (1988).
11. Am. Soc. Testing and Mater., Method D1295-67, *Book of ASTM Standards*, Philadelphia, 1967.
12. H. Shiozaki and H. Tanaka, *J. Seric. Sci. Jpn.*, **49**, 307 (1980).
13. M. Tsukada, unpublished results.
14. H. Ishikawa, M. Tsukada, I. Doizume, A. Konda, and K. Hirabayashi, *Sen-i Gakkaishi*, **28**, 91 (1972).
15. H. Zahn and M. M. Hammoudeh, *Kolloid Z.*, **2511**, 289 (1974).

Received December 21, 1987

Accepted May 18, 1988