

Chemical Modification of Silk with Aromatic Acid Anhydrides

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SYNOPSIS

Bombyx mori silk fibers were chemically modified by acylation with aromatic acid anhydrides, such as phthalic and *o*-sulfobenzoic anhydrides. We examined the reactivity of these modifying agents toward silk fibers, the physical and thermal properties, and the dyeing behavior with acid and cationic dyes. The *o*-sulfobenzoic anhydride was more reactive toward silk fibroin than phthalic anhydride. The amount of both basic and acidic amino acid residues decreased after modification with aromatic acid anhydrides. The moisture regain of silk treated with phthalic anhydride remained almost unchanged, while that of the samples modified with *o*-sulfobenzoic anhydride increased linearly as the weight gain increased. Chemically modified silk fabrics showed improved crease recovery behavior, even though phthalic anhydride seemed more effective at comparatively low weight gain. The modification of silk with *o*-sulfobenzoic anhydride caused a drastic reduction of acid dye uptake and enhanced the affinity of silk for cationic dye. Silk fibers did not show any significant change in thermal behavior, regardless of the modification with *o*-sulfobenzoic anhydride. Silk fibers modified with phthalic anhydride showed on differential scanning calorimetry (DSC) curves a minor and broad endothermic peak at around 210°C, attributed probably to the breaking of the crosslinks formed between adjacent fibroin molecules.

INTRODUCTION

The application of graft copolymerization¹⁻⁴ or chemical modification⁵⁻⁹ techniques onto silk fibers has been the subject of several investigations and has recently attracted considerable academic and practical interest. Natural silk is highly appreciated for its mechanical properties and its outstanding characteristics, such as luster, handling, draping, etc. However, there is a scientific and applicative interest in exploiting silk for new articles in order to expand its consumption. Moreover, the requirements of the consumers for better maintenance properties have recently increased and put out a new challenge either for scientists or technologists. Vinyl monomers,¹⁻⁴ epoxides,⁵⁻⁸ and other modifying agents⁹ applied onto silk have proved effective for producing modification of fiber properties, such as dyeability, and

for improving some inferior textile performances, i.e., wrinkle recovery, wash and wear properties, and photoyellowing. Among the chemical modifying agents, epoxides⁵⁻⁸ have been extensively studied, and some of them are successfully applied for silk processing on an industrial scale. It has been demonstrated that silk fabrics modified with ethylene-glycol diglycidylether with a weight gain of 10–15% exhibited improved properties, such as crease proofing, wash and wear characteristics, and color fastness to washing.¹⁰

Nowadays, the development of textile materials by blending silk with other fibers, especially synthetic fibers, seems to be a potentially powerful approach to widen the use of silk beyond its traditional elitist market. Silk–synthetic fiber blends usually require the selection of specific dyeing techniques, often two-batch processes, in order to meet the different dye affinity of the individual components of the blend. One of the most serious problems that confront new developed silk blends is the uneven

dyeing and/or shade reproducibility. The modification of the dyeing properties of silk could be an interesting approach to exploit silk for new textile applications and for the improvement of the current dyeing techniques. Styrene-grafted silk fibers, due to the hydrophobic properties, showed affinity for disperse dyes and have been suggested suitable for heat transfer printing.¹¹ We have recently reported that silk fibers treated with ethoxyethylmethacrylate exhibited an increased uptake of acid dyes and a very interesting transfer printing behavior, compared to styrene-grafted silk fibers.¹² However, a relatively high weight gain value is usually required for an effective modification of the dyeing behavior by graft copolymerization with vinyl monomers. This fact could sometimes entail negative consequences on the tensile properties of silk fibers and on their handling and luster, especially when hydrophobic vinyl monomers were used as grafting agents.

The purpose of this work is to characterize silk fibers modified with two aromatic acid anhydrides, phthalic and *o*-sulfobenzoic anhydrides. We examined their reactivity toward silk fibroin as well as the physical and thermal properties and the dyeing behavior of the modified silk fibers. This work will provide new perspectives for the application of the chemical modification techniques and will contribute to expand the spectrum of silk utilization.

EXPERIMENTAL

Materials

Reagent-grade phthalic (PA) and *o*-sulfobenzoic (OSBA) anhydrides, purchased from Wako Pure Chemical Industries, Ltd., were used without further purification.

Samples of 0.5 g Habutae silk fabric (ca. 7.5 g/10 cm²) made of *Bombyx mori* silk treated with PA (2.25 g/15 mL) or OSBA (0.5 g/15 mL) in dimethyl formamide (DMF) at 80 and 65°C, respectively, for different periods of time. The reaction system was connected to a reflux condenser and held in a thermostatic bath. The material-to-liquor ratio was 1:30. At the end of the reaction, the silk samples were successively washed with DMF, then with acetone at 55°C for 1 h in order to remove the unreacted anhydride and finally with water. The weight gain (add-on value) was calculated from the increase in weight of the original silk fabric after chemical reaction. On this basis the acyl content was estimated.

The dyestuffs used for the dyeing tests were Aizencatilon Red GLH (C.I. Basic Red 38) and Kayanol Red RS (C.I. Acid Red 99). Dyeings were carried out at 85°C for 30 min in an acidic bath (acetic acid), with a material-to-liquor ratio of 1:40. The dyed samples were taken out and well rinsed with water.

Measurements

Dried silk fibers, either untreated or treated with PA and OSBA, were hydrolyzed by heating at 110°C for 20 h in HCl 6*N* under vacuum. The hydrolyzed samples were filtered through a glass disk to remove small amount 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 by using a Hitachi L-8500 Type Rapid Amino Acid Analyzer. Besides, four-times concentrated solutions were tested in order to precisely determine the amount of the amino acid residues (especially Lys, His, Arg, Met, etc.) whose amount in silk fibroin is very low.

The moisture regain was determined on dried samples kept at 20°C and 65% relative humidity for 7 days and expressed as grams of moisture per 100 g fibroin. Conditioned crease recovery angles were measured by using the Monsanto method as described in a previous paper.⁹

The dye uptake was measured with a Tokyodenshoku Color Analyzer 607 and expressed as *K/S* value.

The differential scanning calorimetry (DSC) measurements were carried out under nitrogen as described in a previous paper.³

RESULTS AND DISCUSSION

Reactivity of Anhydrides

Figure 1 shows the relationship between the reaction conditions (time, temperature, concentration of modifying agent) and the weight gain of silk fabrics treated with phthalic and *o*-sulfobenzoic anhydrides. The acylation of silk fibroin with *o*-sulfobenzoic anhydride easily proceeded at comparatively low temperature (65°C). Silk samples with a weight gain of 11.6%, corresponding to an acyl content of 62.7 mol/10⁵ g, were obtained after 3 h of reaction time. Since phthalic anhydride exhibited a very low reactivity toward silk fibroin, it was necessary to increase the reaction temperature (80°C) and the concentration

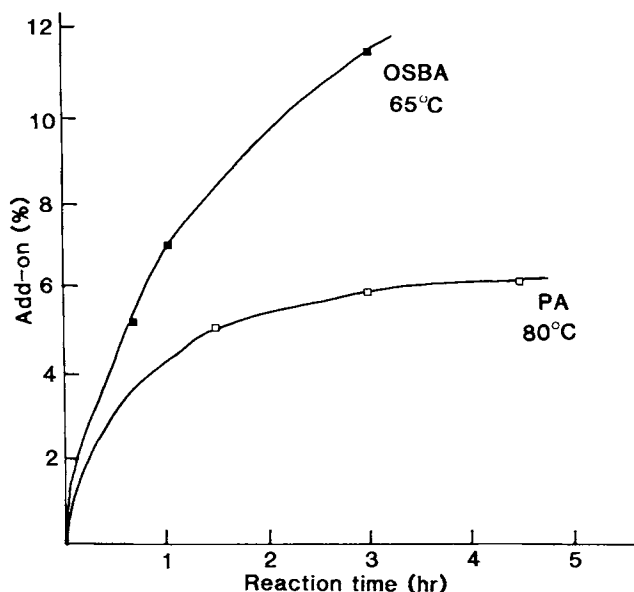


Figure 1 Relationship between the reaction time and the add-on value of silk fabrics modified with aromatic cyclic anhydrides: (□) silk (0.5 g) treated with 2.25 g of phthalic anhydride (PA) in 15 mL of DMF at 80°C; (■) silk (0.5 g) treated with 0.5 g of *o*-sulfobenzoic anhydride (OSBA) in 15 mL of DMF at 65°C.

of modifying agent in the reaction bath (about 4 times higher than OSBA) and to extend the reaction time to 4.5 h in order to attain a weight gain of 6.1% (acyl content: 41.1 mol/10⁵ g).

Tsukada et al.⁹ recently studied the modification of silk with aliphatic acid anhydrides, i.e., succinic and glutaric anhydrides. The optimum reaction temperature and time for silk acylation were 75°C and 270 min, respectively. Succinic and glutaric anhydrides showed almost the same reactivity toward silk fibroin, as expected from the fact that their chemical structure is very similar. The results reported in this paper showed that *o*-sulfobenzoic anhydride possessing the bulky benzoyl group exhibited a comparatively high reactivity, even if applied in relatively mild reaction conditions (Fig. 1). This behavior should be mainly attributed to the presence of the electronegative sulfonic group. These findings are in fair agreement with the results of Shiozaki and Tanaka.¹⁴ By studying the substituent effects of monocarboxylic acid anhydrides on silk acylation, they demonstrated that the reactivity decreased with increasing the size of the side chain and was enhanced by the introduction of SO₃H as substituent on the benzoyl group.

The main reactive sites for the acylation of pro-

tein fibers are the free amino groups of the basic amino acid residues (lysine, histidine, and arginine) and the hydroxyl groups of tyrosine, serine, and threonine.^{9,13-15} In order to evaluate the reactivity of aromatic acid anhydrides, we determined the amino acid composition of silk fibers modified with phthalic and *o*-sulfobenzoic anhydrides with weight gain of 6.1 and 11.6%, respectively (Table I). The amount of basic amino acid residues decreased by acylation. The loss of these reactive amino acids was 21 and 27 mol % for PA- and OSBA-treated silk fibers, respectively. The amount of hydroxylated amino acid residues remained almost unchanged, probably due to the fact that the ester bond once formed was broken during acid hydrolysis. It is particularly interesting to observe that the acidic amino acid residues seemed to be also affected by the reaction with aromatic acid anhydrides. The total decrease of aspartic and glutamic acid residues accounted for 22 mol % either for PA- or OSBA-treated silk fibers. The decrease in acidic amino acid residues should be further investigated in order to elucidate the role of these amino acid residues in the modification of silk with anhydrides because their involvement cannot be explained only by the acylation reaction mechanism.

Table I Amino Acid Composition (mole %) of Silk Fibroin Fibers Chemically Modified with Phthalic Anhydride and *o*-sulfobenzoic Anhydride

	PA ^a	OSBA ^b	Untreated
Asp	1.29	1.30	1.65
Thr	0.81	0.81	0.89
Ser	10.93	10.88	10.63
Glu	0.88	0.89	1.21
Pro	0.42	0.43	0.50
Gly	45.73	45.65	45.10
Ala	30.21	30.27	29.21
Val	2.20	2.23	2.42
Cys	trace	trace	trace
Met	0.10	0.08	0.14
Ile	0.53	0.53	0.71
Leu	0.41	0.43	0.54
Tyr	5.09	5.14	4.97
Phe	0.62	0.65	0.70
Lys	0.25	0.16	0.33
His	0.16	0.16	0.18
Arg	0.37	0.40	0.49

^a PA = phthalic anhydride (add-on; 6.1%).

^b OSBA = *o*-sulfobenzoic anhydride (add-on; 11.6%).

Physical Properties and Dyeability

Figure 2 shows the changes in moisture regain of silk fabrics treated with phthalic and *o*-sulfobenzoic anhydrides with different weight gains. The OSBA-treated silk fibers exhibited a linear increase of water absorption as the weight gain increased, while PA-treated silk fibers did not show significant changes in moisture content compared to the untreated sample. The hydrophilic character of the SO₃H substituent introduced into the fiber by reaction with *o*-sulfobenzoic anhydride played a positive role in hindering the hydrophobicity of the benzoyl group and resulted in enhancing the water absorption of the modified fibers. On the other hand, the carboxyl group freed by phthalic anhydride after reaction with fibroin could only partly contrast the hydrophobicity of the benzoyl group, which has been demonstrated to be markedly effective in lowering the moisture regain of acylated silk fibers.¹⁴

The crease recovery behavior of silk fabrics modified with aromatic acid anhydrides with respect to the weight gain is given in Figure 3. These chemical modifications have been found to be effective in improving the crease-proofing properties of silk fabrics, even if with different rate and extent. The increase in crease recovery should be mainly attributed to the presence of the bulky benzoyl substituent introduced into the fiber substrate by acylation.¹⁴ It is worthwhile to note that phthalic anhydride significantly enhanced the crease recovery value at lower weight gain than *o*-sulfobenzoic anhydride. These results could be explained taking into account the relationship between moisture regain and crease re-

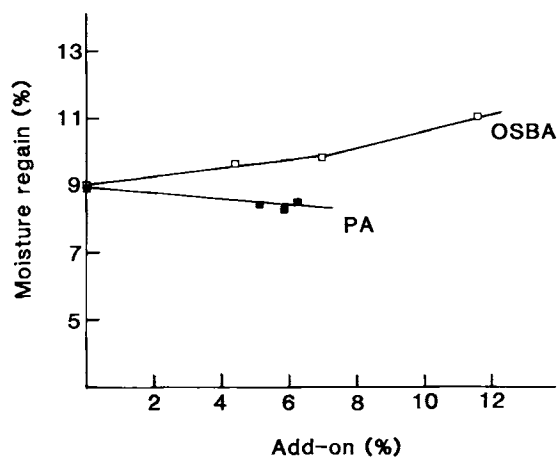


Figure 2 Relationship between moisture regain and add-on values of silk fabrics modified with different aromatic cyclic anhydrides: (■) phthalic anhydride; (□) *o*-sulfobenzoic anhydride.

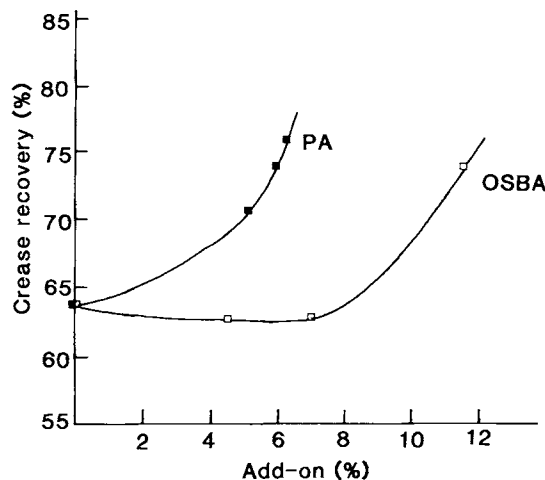


Figure 3 Relationship between crease recovery the add-on values of silk fabrics modified with different aromatic cyclic anhydrides: (■) phthalic anhydride; (□) *o*-sulfobenzoic anhydride.

covery of silk fabrics. Shiozaki and Tanaka¹⁴ showed that the crease recovery values of both untreated and acylated silk fabrics decreased when the moisture content increased. We can therefore suggest that the lower crease recovery of the OSBA-treated silk fabrics should be partly attributed to their slightly increased moisture content. These results coincide with those reported in a previous paper on succinylated and glutarylated silk fabrics.⁹ The latter showed lower moisture regain but higher crease recovery values than the former.

The dyeing properties of silk fabrics modified with *o*-sulfobenzoic anhydride were examined using two different dyes, an acid and a cationic dye applied in acidic bath (Table II). The decrease in acid dye uptake was about 80% for the sample with an acyl content of 23.8 mol/10⁵ g and reached the value of 98% when the acyl content exceeded 38 mol/10⁵ g. The data shown in Table II are quite consistent with

Table II Dyeability of Sulfobenzoylated Silks in Relation to Add-on Value

Sample Add-on (%)	Acyl Content (mole/10 ⁵ g)	K/S Value	
		C.I. Basic Red 38	C.I. Acid Red 99
0	—	4.15	14.64
4.4	23.8	14.17	3.00
7.0	38.0	14.64	0.22
11.6	62.7	15.68	0.063

the results of the dyeing behavior of silk fabrics modified with aliphatic acid anhydrides.⁹ Another important feature of OSBA-treated silk fabrics is the large increase in cationic dye absorption. The silk fabric with an acyl content of $23.8 \text{ mol}/10^5 \text{ g}$ exhibited a K/S value 3.4 times higher than the untreated sample. The K/S value did not change significantly in the acyl content range from 38 to $62.7 \text{ mol}/10^5 \text{ g}$, suggesting that a saturation value has already been attained.

The dyeing behavior of OSBA-treated silk fibers should be attributed to the drastic change of their chemical properties induced by reaction with the modifying agent. An important part of the free amino groups carried by the fibroin side chains reacted with the anhydride (Table I) and, as a consequence of the reaction, a relatively high number of sulfonic groups was introduced in the fibrous substrate. These strong acidic groups are supposed to play the major role in decreasing the uptake of acid dye (mainly because of the repulsive effect of their negative charge) and in increasing the affinity for the cationic dye.

We would like to emphasize the importance of the above experimental results from the point of view of their technological application for silk dyeing and printing, either alone or in blend with other natural and/or synthetic fibers. A limited chemical modification carried out in very mild conditions, i.e., the treatment of silk fabrics with OSBA for 45 min at 65°C , could result in a significant change of the dyeing behavior, without affecting the physical and mechanical properties as well as the handling and luster. In addition, it has been already reported that the introduction of the benzoyl group in silk fibers by acylation enhanced their transfer printing behavior with disperse dyes.¹⁴ We believe that the chemical modification techniques will represent a powerful method for producing silk fibers possessing "new" properties. By a specific selection of the modifying agent and a careful control of the treatment conditions, we will be able to impart the desired characteristics to the silk fibers, in order to develop new textile products and/or renew the processing techniques.

Thermal Properties

Figure 4 shows the DSC curves of silk fibers modified with phthalic anhydride. The DSC measurements demonstrated that the position and the shape of the major decomposition peak at 318°C of PA-treated silk fibers remained unchanged and that a minor broad endothermic peak (Fig. 4, arrow) appeared at

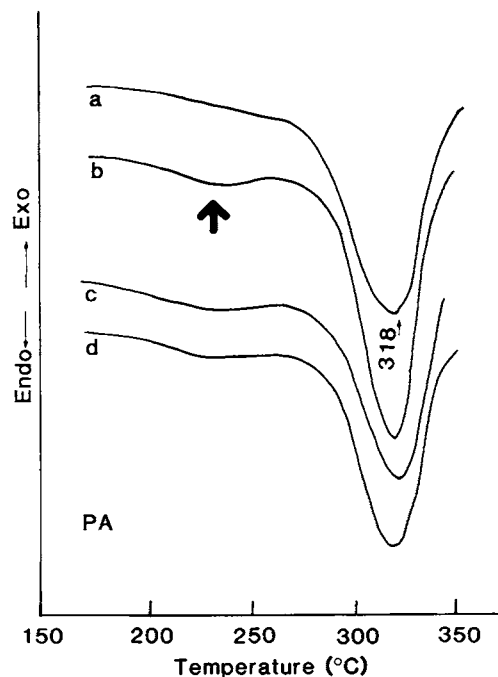


Figure 4 DSC curves of silk fibers treated with phthalic anhydride possessing different values of add-on: (a) 0, (b) 5.2, (c) 5.9, (d) 6.1%. For the arrow (\uparrow) see the text.

above 210°C . It is of interest to note that the DSC curves [Fig. 4, (b)–(d)] present an almost complete similarity to those of silk samples modified with glutaric anhydride.⁹ In a previous paper, we estimate that the shoulder peak was due to the disruption of the intermolecular crosslinks formed by glutaric anhydride.

Figure 5 shows the DSC curves of silk fibers either untreated or modified with *o*-sulfobenzoic anhydride. The untreated sample [Fig. 5 (a)] exhibited a single endothermic peak at around 318°C , which is attributed to the thermal decomposition of silk fibroin with oriented β' configuration.¹⁶ As shown by the DSC curves [Fig. 5 (b)–(d)] of OSBA-treated silk fibers with increasing weight gain, the thermal behavior was not affected by the reaction with the anhydride. From these results it was elucidated that the modifying agent reacted with the active sites in the fibrous substrate without inducing a remarkable perturbation of the arrangement and of the mutual interaction between the fibroin chains in the amorphous regions.

We can therefore estimate that the acylation of silk fibers with phthalic anhydride resulted in the formation of crosslinks (mainly hydrogen bonds and/or hydrophobic interactions) between the side group of the aromatic acid and active sites located on adjacent fibroin chains. The slight decrease of

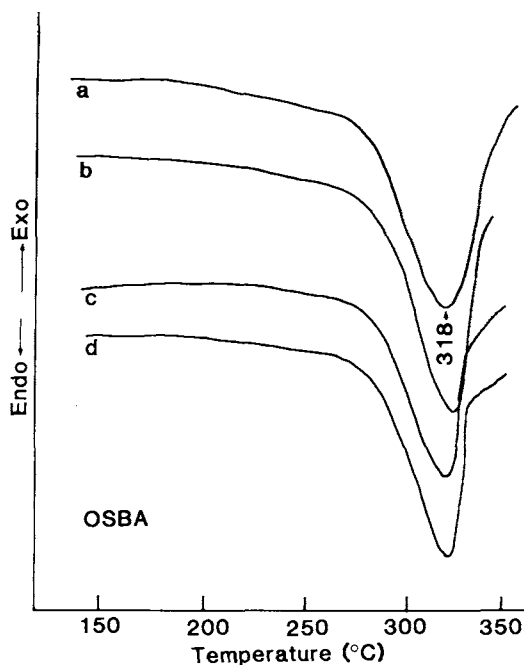


Figure 5 DSC curves of silk fibers treated with *o*-sulfolobenzoic anhydride possessing different values of addition: (a) 0, (b) 4.4, (c) 7.0, (d) 11.6%.

moisture content and the relatively high value of crease recovery exhibited by the PA-treated silk fibers (Figs. 2 and 3) seemed to support this hypothesis.

REFERENCES

1. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 965 (1988).
2. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 2133 (1988).
3. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **39**, 1289 (1990).
4. M. Tsukada, *J. Seric. Sci. Jpn.*, **53**, 380 (1984).
5. M. Tsukada and H. Shiozaki, *J. Seric. Sci. Jpn.*, **58**, 15 (1989).
6. Y. Tanaka and H. Shiozaki, *Makromol. Chem.*, **129**, 12 (1969).
7. Y. Tanaka and H. Shiozaki, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 2741 (1974).
8. M. Tsukada, H. Shiozaki, H. Urashima, and M. Yokozawa, *J. Text. Inst.*, **80**, 547 (1989).
9. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **37**, 2637 (1989).
10. H. Shiozaki, Y. Tanaka, H. Iida, and K. Nishina, *J. Seric. Sci. Jpn.*, **41**, 33 (1972).
11. T. Kako, A. Katayama, and N. Kuroki, *J. Seric. Sci. Jpn.*, **46**, 103 (1977).
12. M. Tsukada, G. Freddi, M. Matsumura, H. Shiozaki, and N. Kasai, *J. Appl. Polym. Sci.*, to appear.
13. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.* **41**, 1213 (1990).
14. H. Shiozaki and Y. Tanaka, *J. Seric. Sci. Jpn.*, **49**, 307 (1980).
15. H. Shiozaki, M. Tsukada, and M. Matsumura, *J. Seric. Sci. Jpn.*, **57**, 165 (1988).
16. H. Ishikawa, M. Tsukada, I. Toizume, A. Konda, and K. Hirabayashi, *Sen-i Gakkaishi*, **28**, 91 (1972).

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