Dyeability of Silk Fabrics Modified with Dibasic Acid Anhydrides

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SYNOPSIS

Silk fabrics were chemically modified with different kinds of dibasic acid anhydrides. Samples with different acyl contents, ranging from 24 to 107 mol/10^5 g, were obtained by reaction with succinic (S), glutaric (G), phthalic (PA), and *o*-sulfobenzoic (OSBA) anhydrides. Dyeability with a cationic dye (Rhodamine B, C.I. Basic Violet 10) was determined by measuring dye uptake and K/S values. Following acylation, the absorption of basic dye was significantly enhanced for all samples. The maximum dye uptake was attained by OSBA-treated silk fabrics, while samples treated with S, G, and PA did not differ significantly. Dye uptake increased regardless of the acyl content, at least in the range examined. Reflectance measurements and K/S values confirmed the trend evidenced by dye uptake results. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

During the past two decades there has been a considerable academic and technological interest in the chemical modification of silk fibers. The use of dibasic acid anhydrides as modifying agents has been proposed by Tsukada and Shiozaki.[1] The optimum reaction conditions (temperature, time, concentration of modifying agent) for modification of silk fibers with aliphatic and aromatic dibasic acid anhydrides have recently been reported.[1-4]

Modified silk fibers showed increased resistance to photodegradation.[1] Moreover, a limited chemical modification carried out in mild conditions resulted in a drastic change in dyeing behavior.[1-3] Depending on the kind of anhydride used, the treatment changed the moisture content, improved crease recovery and imparted good transfer printing properties to silk fabrics.[3,5]

The fine structural changes of silk fibers modified with dibasic acid anhydrides have recently been reported.[6] Physical properties and fine structure (molecular orientation and crystallinity) of silk fibers modified with different kinds of dibasic acid anhydrides were largely unaffected by the chemical reaction.

Dyeability of silk is one of the most attractive topics for applied research, because the brilliancy of dyed and printed silk fabrics is a decisive factor for evaluating the quality of silk goods. Moreover, the development of new silk-based textile materials for expanding silk consumption and utilization requires blending with other fibers of natural, artificial or synthetic nature. Such developments are put back by the limits of the traditional dyeing and printing techniques.

Chemical modification of silk fibers by reaction with dibasic acid anhydrides has proved its effectiveness as a powerful tool for inducing drastic changes in dye affinity.[1-3] While the absorption of acid dyes is drastically reduced, that of cationic dyes is markedly enhanced. Moreover, significant changes in dye uptake are obtained by moderate modification, which means mild treatment (time, temperature), low amount of weight gain, preservation of outstanding silk fiber properties (hand, luster, etc.).

The aim of this work is to contribute to the development of new dyeing and printing techniques by studying the dyeing behavior of silk fibers modified with dibasic acid anhydrides. The effect of dif-

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ferent kinds of anhydrides and increasing acyl contents on the uptake of a cationic dye and on K/S values will be investigated. This study will provide a basic scheme for investigating dyeability of modified silk fibers in connection with the technological implementation of this modification technique.

EXPERIMENTAL

Materials and Measurements

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

Degummed samples of Habutae silk fabric (ca. 7.5 g/10 cm^2) were treated in dimethyl formamide (DMF), using the reaction conditions (reagent concentration, temperature, time) previously reported.[1,3] After treatment, the samples were washed with isopropanol, then with acetone at 55°C for 1 h in order to remove the unreacted anhydride, and finally with water. The weight gain was calculated from the weight of the fabric before and after chemical reaction.

The dyestuff used for the dyeing tests was Rhodamine B (C.I. Basic Violet 10). About 8 g of silk fabric were sealed in a Pyrex tube containing the dye bath (1% owf Rhodamine B and 10% owf Glauber's salt). The material–liquor ratio was 1 : 50. The dyeing temperature was gradually increased from 25 to 80°C over 1 h and kept constant for 1 h. The dye uptake (DU) was calculated by means of the following equation:

$$DU(\%) = (BC - AC)/BC \times 100$$

where BC and AC are the dye concentrations (g/l) before and after dyeing, respectively. Calibration curves were obtained spectrophotometrically by using standard solutions of dye at fixed concentration.

Reflectance curves were obtained with a Shimadzu multiphotometer (UV-3100S). Slit path, speed, illuminant, and view angle were 2.0 nm, 700 mm/min, C, and 2°, respectively. K/S values were calculated using the following equation:

$$K/S = (1 - R)^2/2R$$

where R is the reflectance of silk fabric dyed with Rhodamine B at 520 nm obtained from a reflectance curve.

RESULTS AND DISCUSSION

Dye Uptake

Samples of silk fabrics modified with aliphatic (succinic and glutaric) and aromatic (phthalic and *o*-sulfobenzoic) dibasic acid anhydrides with different acyl contents were obtained by varying reaction temperature and time. Modified silk fabrics were then dyed with a cationic dye (Rhodamine B, C.I. Basic Violet 10) and dye uptake was estimated on the basis of dyebath exhaustion. Table I shows the values of dye uptake for the different samples of modified silk fabrics, together with the corresponding weight gain and acyl content values. The absorption of cationic dye increases following chemical

Table I Dye Uptake of Silk Fabrics Modified with Succinic (S), Glutaric (G), Phthalic (PA), and *o*-sulfobenzoic (OSBA) Anhydrides

	Weight Gain (%)	Acyl Content (mol/10^5 g)	Dye Uptake (10^{-5} g/g)
Control	—	—	947.5
S	6.3	55	966.5
S	8.8	75	967.5
S	12.5	107	968.0
G	7.5	58	965.0
G	10.3	79	967.5
G	13.2	102	969.0
PA	5.2	35	967.5
PA	5.9	40	967.5
PA	6.1	41	966.5
OSBA	4.4	24	992.5
OSBA	6.9	38	994.0
OSBA	11.5	63	995.5

modification with dibasic acid anhydrides. The increase is larger for samples modified with *o*-sulfobenzoic anhydride. It is noteworthy that the increase of dye uptake seems to be essentially independent of the kind of anhydride used and of the value of acyl content.

It has been reported in previous studies that free amine groups and hydroxyl groups of amino acid residues are the main reactive sites of silk fibroin toward anhydrides.[4] The acylation reaction gives rise to the formation of amide and ester bonds, while free carboxyl groups are introduced within the fiber, due to opening of the anhydride ring. The increasing amount of acid groups, together with the decrease of free amine groups has been considered responsible for the drastic change in dye affinity of silk fibers modified with dibasic acid anhydrides, that is, reduced uptake of acid dyes and increased uptake of cationic dyes.

In order to further investigate the dyeing behavior of modified silk fabrics, dye uptake values were plotted against acyl content (Fig. 1). Silk fabrics modified with succinic, glutaric, and phthalic anhydrides absorbed the same amount of dye, irrespective of acyl content. These results are quite interesting, because it appears that a threshold value exists for attaining a substantial change in dye affinity by acylation. From our results it can be inferred that the threshold for Rhodamine B is located below 35 mol/10^5 g, corresponding to the lowest acyl content obtained by reaction with phthalic anhydride (weight gain 5.2%). Moreover, on the basis of these results and other previously reported,[1-3] we think that this parameter is more dependent on the dye molecule used than on the chemical structure of the anhydride bound to the fibroin chains. In fact, while the side groups of succinic and glutaric anhydrides are characterized by hydrocarbon chains, phthalic anhydride has an aromatic ring.

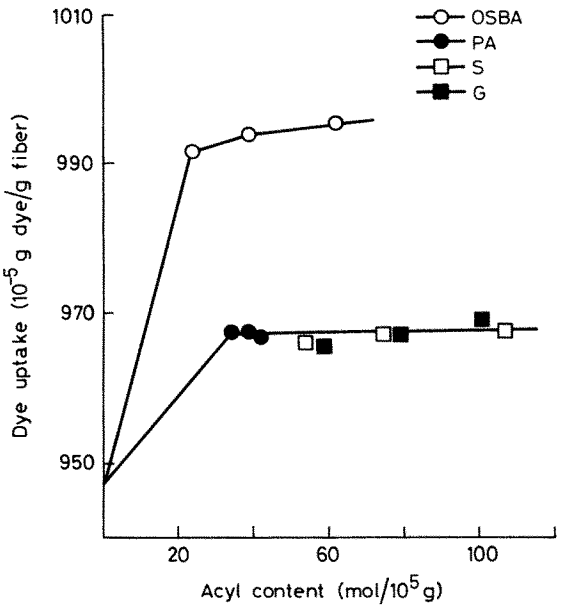

Figure 1 Dye uptake vs. acyl content of silk fabrics modified with succinic (S), glutaric (G), phthalic (PA), and *o*-sulfobenzoic (OSBA) anhydrides.

It has been suggested that glutarylation of silk may result in crosslink formation between adjacent fibroin chains,[1] leading to a smaller number of free pendant carboxyl groups. Since no differences in dyeing behavior have been observed between glutarylated and succinylated silk fibers, it can be inferred that dye uptake is not influenced by the different amount of free carboxyl groups in the silk fibers. The values of acyl content attained in our experiments largely exceeded the minimum required for an effective modification of dyeing behavior.

OSBA-treated silk fabrics showed the highest dye uptake among the samples examined. Even at an acyl content as low as 24 mol/10^5 g, the increase in dye absorption is about twice that of the other samples. Likewise for PA-, S-, and G-treated silk fabrics, no increased uptake of Rhodamine B was observed as the acyl content rose. The higher dye uptake of silk fabrics modified with *o*-sulfobenzoic anhydride can be attributed to the electronegativity of the sulfonic group formed as a result of the opening of the anhydride ring.

Reflectance Measurements and *K*/*S* Values

The color appearance of dyed fabrics is better expressed in terms of K/S values, obtained by reflectance measurements. These values are related to the amount of dye absorbed and are a direct measure of hue, intensity, and depth of shade of dyed samples.

Figure 2 shows the reflectance curves of silk fabrics modified with *o*-sulfobenzoic anhydride. As the acyl content increases, the curves shift slightly toward lower reflectance values, which is a direct measure of the more intense shade attained by the samples.

K/S values of silk fabrics modified with different kinds of dibasic acid anhydrides were calculated on the basis of reflectance measurements at 520 nm by means of the equation shown in the experimental part. Results obtained are listed in Table II, together with weight gain and acyl content values.

The trend observed for dye uptake is clearly confirmed by these results. Following chemical modification with dibasic acid anhydrides, K/S values

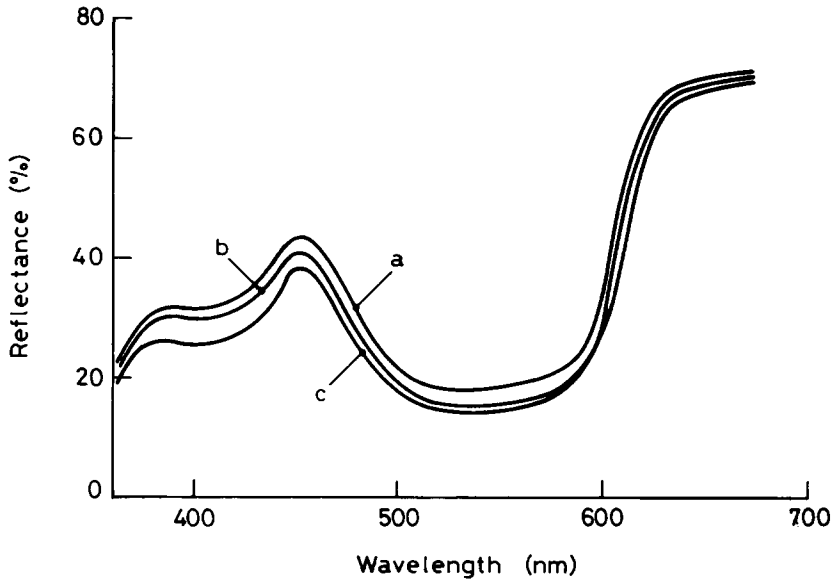

Figure 2 Reflectance curves of OSBA-treated silk fabrics with different amount of weight gain: (a) 4.4%, (b) 6.9%, (c) 11.5%.

increased, the highest levels being attained by OSBA-treated silk fabrics. Like dye uptake values, K/S values did not change significantly in relation to the acyl content of the various samples. PA-, S-, and G-treated silk fabrics exhibited almost the same color intensity and shade, irrespective of the amount of weight gain and of the kind of anhydride molecule used.

CONCLUSIONS

The results reported in this study provide further evidence for the phenomena observed in previous studies on the dyeability of silk fabrics modified by reaction with dibasic acid anhydrides.[1-3] This chemical modification technique has proved to be a powerful tool for changing the dyeing behavior of silk. The main findings emerging from this work can be summarized as follows:

1. Affinity toward acid dyes decreases.[1,3]
2. Uptake of Rhodamine B and other cationic dyes[3] is significantly enhanced.
3. The dyeing behavior seems to be more affected by the chemical structure of the dye molecule than by the side group of the anhydride molecule.

Table II K/S Values of Silk Fabrics Modified with Succinic (S), Glutaric (G), Phthalic (PA), and *o*-sulfobenzoic (OSBA) Anhydrides

	Weight Gain (%)	Acyl Content (mol/10^5 g)	K/S
Control	—	—	1.17
S	6.3	55	1.74
S	8.8	75	1.71
S	12.5	107	1.74
G	7.5	58	1.70
G	10.3	79	1.71
PA	5.2	35	1.66
PA	5.9	40	1.73
PA	6.1	41	1.67
OSBA	4.4	24	1.89
OSBA	6.9	38	1.91
OSBA	11.5	63	1.96

4. The modification seems to attain its maximum effect at very low acyl content.
5. The presence of free pendant groups, more electronegative than carboxyl groups, such as in the case of *o*-sulfobenzoic anhydrides (free sulfonic group), can be used as modulating parameter for inducing further changes in dye uptake.

In view of a technological implementation of this modification technique, a systematic study is necessary in order to find optimum modification conditions, in relation to the kind of dye used and to the functional performances of the end product.

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