

Modification of Silk Fibres with Acetic Anhydride and Phthalic Anhydride-Effects on Dyeability and Physio-Chemical Properties

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Abstract Silk fibres were chemically modified with acetic anhydride (AA) and phthalic anhydride (PA) to improve the tenacity, thermal properties, dye-abilities and colourfastness properties. Prior to the modification of silk with anhydrides, optimum modification conditions were established and modification was estimated on the weight gain. Improvements of tenacity were 7.56% for 13.63% acetic anhydride loading and 12.76% for 18.04% phthalic anhydride loading. Thermogravimetric analysis showed the improvement of thermal stability for the acetic anhydride modified silk whereas, phthalic anhydride modified silk showed inferior thermal property compared to that of the unmodified silk. Silk fibres modified with the both anhydrides showed better dye-ability to Direct Red 28 and Direct Orange 31, and improve colour fastness properties to the sunlight.

Keywords Silk fibre, Anhydride, Dyeability, Tenacity, Thermal properties

1. Introduction

Silk is continuous filament of protein fibre, for its unique characteristics of strength, fineness, length and luxury appeal, is called the “queen of fabrics” [1-4].

Silk fibres are valued for the outstanding characteristics that have exploited for the production of precious textile goods. However, silk possess some inferior textile performance, such as photo yellowing, an yellowing, wash and wear abrasion resistance, crease proofing properties, wrinkle recovery, rub resistance, colour fastness, dimensional stability, oil and water repellency etc [5, 6].

The characteristics of silk can be improved by chemical modification techniques. Among the various methods available for the modification of silk, chemical modification with anhydride appear attractive and are recently used in textile applications [6]. Modification enhance some properties such as crease recovery, tensile strength and elongation, light resistance, dyeing behavior, colour fastness, wash and wear behavior etc [7, 8].

The physico-chemical properties of modified silk fibres largely depend on the chemical structures and functional side groups of the loaded compound. In this study two

structurally different anhydrides such as acetic anhydride and phthalic anhydride were used for modification of degummed silk fibres. A comparative study was made on tensile strength, thermal property, dye-ability and colour fastness properties of modified and unmodified silk fibres.

2. Materials

Silk fibres were collected from Bangladesh Sericulture Research and Training Institute (BSR and TI), Rajshahi, Bangladesh. Reagent grade acetic anhydride (AA, $\text{CH}_3\text{-CO-O-CO-CH}_3$), phthalic anhydride (PA, $\text{C}_8\text{H}_4\text{O}_3$), sulphuric acid, sodium carbonate, ammonia solution, sodium hydroxide, sodium sulphate and Direct Red 28 were purchased from BDH (England). Glacial acetic acid, tartaric acid, potassium peroxodisulphate were purchased from Merck (Germany). Phthalic anhydride and Direct Orange 31 were received from Qualikems (India) and Sigma (USA) respectively. All the chemicals were used as received.

3. Methods

3.1. Degumming of Silk Fibre

Soap solution (wheel soap) of strength 3.5 g/L was prepared and its pH was adjusted to 10.0-10.5 by adding 1 g/L of soda ash (pH change was observed directly with Corning Model-7 pH meter). For each gram of silk fibre 30

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mL of liquor was taken and degumming was conducted at a temperature of 95-100 °C for 1 hour. During the operation, the pH of the bath falls and then silk fibre was transferred into second bath, and heated for 45 min at the same temperature. After degumming, the silk fibre was washed well with hot distilled water for 3 to 4 times.

3.2. Modification of Silk Fibre

Acid anhydride was dissolved in mixed solvent of water and alcohol, and modifications of silk were performed in that mixed solvent system. The modifying baths were prepared by adding required percentage of an anhydride (90% for acetic anhydride and 80% for phthalic anhydride) and the initiator (10% for acetic anhydride and 8% for phthalic anhydride) on the basis of weight of the fibre. The fibre-liquor ratio was maintained at 1 : 30. Modification was started at 30 °C and then the temperature was slowly increased almost to the boiling point within about 30 min and continued for 90 min with occasional, then allowed for further 30 min as the bath cools down. During modification, boiling distilled water was added to the modifying baths in order to maintain the fibre-liquor ratio constant. After modification, the fibres were washed with cold distilled water and dried at room temperature [9, 10].

Weight gain or anhydride loading and anhydride efficiency were calculated according to the following formula [9, 10]:

$$\text{Weight gain, \%} = \frac{B-A}{A} \times 100$$

$$\text{Anhydride efficiency, \%} = \frac{B-A}{C} \times 100$$

where A, B and C are the weight of degummed silk fibre before modification, weight of the silk fibre after modification, and weight of anhydride used, respectively.

3.3. Measurement of Tenacity of Silk Fibres

Tenacity (Breaking strength) of silk fibres was measured by using the tensile strength tester (Torsees Schopper type-OS-100). For measuring the tenacity of silk fibre, at first the denier of the fibre was determined by the following equation.

$$D = \frac{W}{L} \times 9000$$

where D, W and L are the Denier of fibre, weight of fibre in grams and length of fibre in metre, respectively.

Silk fibres were cut into equal pieces with the length of 30 cm and weighed. From the above equation denier was measured for each test sample (fibre) and placed between two jaws of the tensile tester and maintained a length of 10 cm of each specimen. One twist per 2 cm was given along the length of the fibre between the jaws of the machine. The breaking load was observed at the point of break on the scale of the machine. In each experiment, tenacity for 10 specimens was taken and the mean of 10 readings gave the tenacity of the fibre. If 1000 g was required to break down 200 denier fibre then its tenacity will be

$$= \frac{1000}{200} = 5.0 \text{ g/denier}$$

Tenacity of raw, degummed, and modified silk fibres were also measured before and after exposure to sunlight in air.

3.4. Measurement of Thermal Properties

Thermal stabilities of the degummed and modified fibres were determined with the Thermogravimetric Analyser (Seiko-Extar TG/DTA-6300, Seiko, Japan). For the measurement, 4-8 mg of silk fibre was taken in the sample pan and 7.711 mg of alumina was taken in the reference pan. The measurement was conducted upto 600 °C with the heating rate of 10 °C/min in nitrogen atmosphere.

3.5. Dyeing of Silk Fibres with Direct Dyes

Direct dyestuffs were dissolved by first pasting with cold water and then by adding boiling water. The dye baths were prepared by adding 2% dye (Direct Orange 31 and Direct Red 28), 5% electrolyte and 3 - 5% Na₂CO₃ in aqueous solution on the basis of the weight of silk fibre. The fibre-liquor ratio was maintained at 1 : 30. Before immersing the silk fibre in dye bath it was soaked well in distilled water and squeezed for even absorption of dye particles. Dyeing was started at 40 °C and the temperature was then slowly increased almost to the boiling point within about 30 min and continued for 90 min with occasional stirring by a glass rod, then allowed for further 30 min as the bath cools down. During dyeing, boiling distilled water was added to the dye baths in order to maintain the fibre-liquor ratio constant. After dyeing, the fibres were squeezed over dye baths so that not a single drop of exhausted dye liquor was lost, rinsed in cold distilled water and dried at room temperature. The rinsed water was added to the exhausted dye bath and spectroscopic method was used to calculate the dye uptake by the fibres.

3.6. Colour Fastness to Sunlight [12]

Colour fastness test was carried out on raw, degummed, modified and modified dyed silk fibres. Specimens of the fibres were attached separately on a board by a glass rod and placed on the roof of a building for exposure in the open air under the sun without any protection from weathering, but was protected from rain, dews, etc. The specimens were exposed under the sun for seven hours each day continued for 300 h in the month of May to July. After every 50 hours, the fastness was assessed with the Grey Scale by comparing the change in colour of the specimen with that of the standard

4. Results and Discussion

4.1. Chemical Modification of Silk Fibre with Acetic Anhydride and Phthalic Anhydride

Degummed silk fibre was chemically modified with acetic anhydride (AA) and phthalic anhydride (PA) and a comparative study was made to see the responses of

modified fibres to sunlight in respect of loss of tenacity, colour fastness and thermal properties. As the weight gain of modified fibre considerably dependent on anhydride concentrations, initiator concentrations, temperature and reaction time, modification was conducted at optimized conditions.

It was seen that the percent weight gain of the silk fibre increased considerably with increasing anhydride concentration upto 90% for AA and 80% for PA. Beyond this condition, the percent weight gain started to decrease due to the decreased reactive sites of silk fibres at higher anhydride concentration. The optimized conditions for modification for acetic anhydride were 90% AA, 10% $K_2S_2O_8$, 60 min and 80 °C, and those for phthalic anhydride were 80% PA, 8% $K_2S_2O_8$, 80 min and 70 °C respectively and are listed in **Table 1**. Under optimized conditions, the maximum weight gains of AA and PA onto degummed silk fibre were 13.79% and 18.16%, respectively.

During modification of silk fibres with anhydrides, the initiator ($K_2S_2O_8$) generates active sites on the backbone of the silk fibres. As the created silk macroradicals are

immobile, the weight gain depends on the availability of the anhydride ions or radicals in the vicinity of fibre surface and weight gain become maximum at optimum anhydride and initiator concentrations [13].

Figure 1 shows that percent weight gain and its efficiency of AA and PA onto silk at optimized condition. The maximum weight gain for AA and PA was 13.63% and 18.04% at 80 °C and 70 °C respectively. At this temperature, the initiator ($K_2S_2O_8$) generates activated anhydrides and silk macroradicals on fibre surface, and combines themselves to give highest conversion. Again, the increase in temperature increased the rate of diffusion of anhydride into the fibre pores. Decreasing of percent weight gain and efficiency of AA and PA beyond the optimum temperature may be the result of degradation of silk during modification [14]. At temperatures over 80 °C for AA and 70 °C for PA, the reaction became reversible and, accordingly, ceiling temperature is established when the forward and backward reactions became equal. Consequently, at high temperatures, exceeding the optimum values, the weight gain started to decrease.

Table 1. Optimum modification conditions of degummed silk fibres

Anhydrides	Anhydride conc., %	Initiator conc., %	Temp., °C	Time, min	Weight gain, %	Anhydride efficiency, %
Acetic Anhydride	90	10	80	60	13.63	15.32
Phthalic Anhydride	80	8	70	80	18.04	22.70

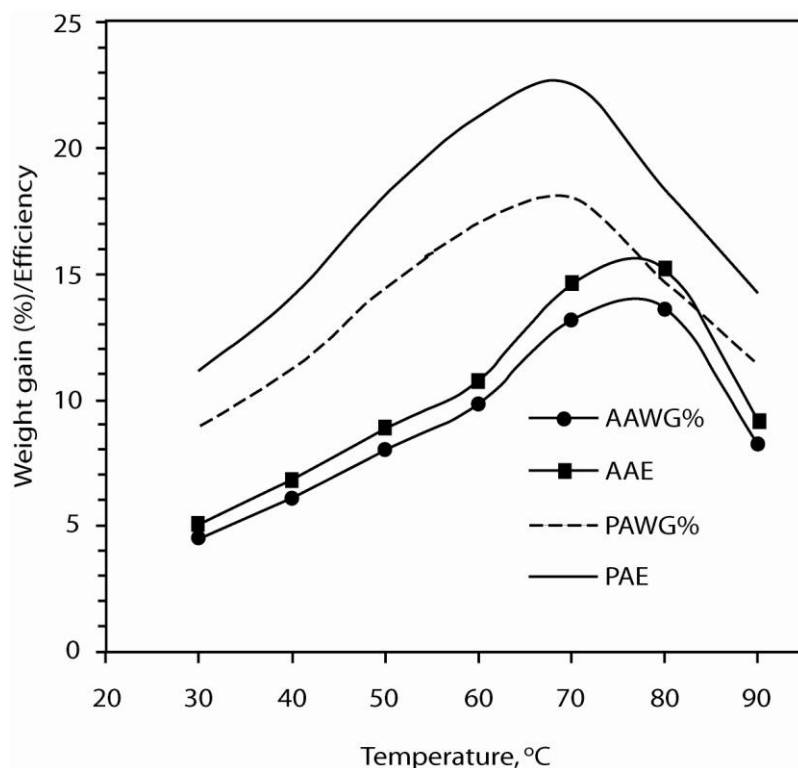


Figure 1. Modification of degummed silk fibres: Bath condition for acetic anhydride (AA) and phthalic anhydride (PA), 90% and 80%; initiator ($K_2S_2O_8$), 10% and 8%, reaction time, 60 and 80 min respectively. WG and E means weight gain percentage and anhydride efficiency

4.2. Tensile Strength

It is observed from the **Table 2** that tenacity of degummed silk fibre is 29.63 g/denier and modified silk fibre are 31.87 and 33.41 g/denier (for acetic anhydride and phthalic anhydride) respectively. On comparison between degummed and modified silk fibres, it is seen that the tenacity of modified silk fibres are higher than that of degummed silk fibre.

Table 2. Physical and thermal properties of untreated and treated fibres

Silk fibres	Weight gain, %	Tenacity, g/denier	Thermal stability ^a	
			weight loss, %	Temp., °C
Degummed	0	29.63	3-50	282-332
AA modified	13.63	31.87	7-53	292-345
PA modified	18.04	33.41	3-24-58	163-205-347

^aDetermined by TG at the heating rate of 10 °C/min.

This was caused due to weight gain of silk fibre with anhydrides; the crystallinity of silk fibre was reduced due to the incorporation of anhydride with the polypeptide chain and gave an additional strength to silk fibre [15]. Again, the tenacity of phthalic anhydride modified silk fibre is higher than that of acetic anhydride modified silk fibre. It may be explained that higher modification gives the higher strength to silk fibre as well as higher breaking strength of PA modified silk compared to that of AA modified silk fibres.

4.3. Thermal Properties

The thermal behavior of degummed, AA and PA modified fibres were examined by thermogravimetric analysis which is shown in the **Figure 2**. It can be observed from **Figure 2** that the loss in weight for degummed, AA and PA-modified silk fibres are around 3%, 7% and 3% at 282 °C, 292 °C and 163.5 °C respectively in nitrogen which implies that only moisture were removed with no degradation in these temperature. Actually for degummed silk, T_d^{1st} occurred with 50% weight loss in the temperature range 282-332 °C for AA modified silk, T_d^{1st} occurred with 53% weight loss in the temperature range 292-345 °C, whereas, for PA modified silk, first pyrolysis degradation T_d^{1st} occurred in the early stage with 24% weight loss in the temperature range 163-205 °C. Second degradation T_d^{2nd} for PA modified silk with 58% weight loss occurred at the temperature range around 300-347 °C. For PA modified silk fibre, weight loss was found twice. The first degradation occurred in linkage between silk fibroin and PA unit and, next degradation occurs in fibroin backbone of silk fibre.

From the **Figure 2** it is seen that the thermal stability of AA modified fibre is higher than unmodified fibre; which may be happened due to the incorporation of anhydride molecule onto the silk fibre [16]. The anhydride molecule caused a protective layer onto the active surface of the silk fibre which first worked against the applied heat and ultimately decreased the heating strength on the fibroin

backbone. So the modified fibre showed higher thermal stability. **Figure 2** also shows that PA modified silk exhibits the lowest thermal stability among all the modified and unmodified silk fibres. It might be attributed that at the high temperature, phthalic anhydride unit undergoes exothermic degradation which enhances the early degradation of the silk fibroin.

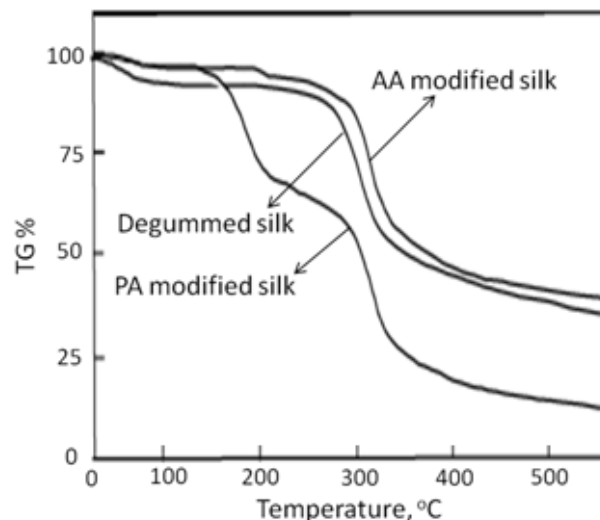


Figure 2. TG analysis of degummed, acetic anhydride and phthalic anhydride modified silk with the heating rate of 10 °C/min

4.4. Dyeing of Modified and Unmodified Silk

The degummed and modified (AA and PA modified) fibres were dyed with Direct Red 28 and Direct Orange 31 with the condition given in the footnote of the **Table 3**. From the **Table 3**, it can be seen that the dye exhaustion of modified silk fibre is higher than that of unmodified (degummed) silk fibre. The anhydride molecule make the fibre hydrophobic, and due to their hydrophobic properties the dye ability of the silk fibres increases. From the experiment it was observed that the dyed modified silk fibre was more lustrous, soft, pleasant at appearance, attractive in hue and gave more uniform shade than the dyed unmodified (degummed) silk fibres in case of all the dyes used.

Table 3. Dyes uptake by the degummed, AA modified and PA modified silk

Name of dye	Dye exhaustion, %		
	Degummed silk fibre	Modified silk fibre	
		Acetic anhydride	Phthalic anhydride
^a Direct Red 28	70.22	80.91	84.38
^b Direct Orange 31	77.58	88.83	91.00

Bath condition: Fibre-liquor ratio, 1:30; reaction time, 90 min; conc. of dye, 2%; electrolyte, 5%; and Na₂CO₃ (3%)^b or (5%)^a on the basis of the weight of silk fibre.

4.5. Colour Fastness to Sunlight

Raw silk, degummed silk, modified silk and dyed silk fibres were exposed to sunlight for up to 300 h and colour

changes were observed in every 50 h exposure. From the **Table 4** it is observed that with the progress of exposure time to sunlight in open air, colour of raw silk fibres changes from golden yellow to dull yellow. But in case of degummed silk fibres, colour changes appears to be very slight from white to yellowish white. That means, raw silk fibre undergoes degradation faster than degummed silk fibre. This is possibly, due to the presence of greater amount sericin in raw silk fibre than that in the degummed silk fibre. Xanthophylls is responsible for yellow colour of raw silk. But the effect of UV-light in air exanthoproteic reaction occurs, hence, yellow colour of raw silk turns to dull yellow. A yellowing mechanism is also postulated that by the effect of UV-light, *p*-hydroxyl- phenylpyruvyl peptide, a chemical component of yellowing of silk is converted to *p*-hydroxyl phenylpyruvic acid and amino acids such as alanine, glycine, valine, leucine etc [17].

From the **Table 4** it is also observed that the colour change of the degummed silk and modified silk (fibroin) is slight compare to raw silk. That was because of the formation of glycidyl radicals in silk fibroin by the irradiation in sunlight, which reacted with atmospheric oxygen and change of peroxy radicals [18, 19]. That oxidation reaction occurred at the earlier time of light exposure. When the reaction was completed the change in colour or fading did not occur. The colour fastness of the modified silk fibre was better than that of degummed silk fibre, because, modification with AA and PA formed a protective layer on the silk surface which itself partially protected UV-radiation and decreased the rate of UV-light penetration into the fibre backbone. This effect decreased the action of the UV-light on the change of the colourfastness. The protective layer of AA and PA modified fibres also reduced the rate of moisture diffusion to the site of fading causing the decreasing rate of yellowing.

Table 4. Colourfastness and change in colour of raw, degummed, AA modified and PA modified silk on exposure to sunlight in air

Exposure Period, hours	Fastness grade and colour			
	Raw silk	Degummed silk	AA modified silk	PA modified silk
0	5 Golden yellow	5 White	5 Cream white	5 White
50	3 Pale yellow	5 White	5 Cream white	5 White
100	3-2 Pale yellow	5-4 Yellowish white	5 Cream white	5-4 Whiteness decrease
150	3-2 Pale yellow	5-4 Yellowish white	4 Cream white	4 Whiteness decrease
200	2 Dull yellow	5-4 Yellowish white	4-3 Whiteness decrease	4 Whiteness decrease
250	2 Dull yellow	4 Yellowish white	3 Slightly yellowish white	4-3 Slightly yellowish white
300	2-1 Dull yellow	4-3 Yellowish white	3 Slightly yellowish white	3 Slightly yellowish white

Table 5. Colour fastness and change in colour of degummed, AA modified and PA modified silk dyed with Direct Red 28 and Direct Orange 31 on exposure to sunlight in air

Exposure Period (hrs)	Firstness grade and colour					
	Degummed silk		AA modified silk		PA modified silk	
	Direct Red 28	Direct Orange 31	Direct Red 28	Direct Orange 31	Direct Red 28	Direct Orange 31
00	5 (Bright red)	5 (Bright Orange)	5 (Bright red)	5 (Bright Orange)	5 (Bright red)	5 (Bright Orange)
50	5-4	5-4	5	5-4	5-4	5-4
100	5-4	5-4	5-4	5-4	5-4	5-4
150	5-4	4	5-4	4	4	4
200	4-3	4-3	4	4	4	4
250	3	4-3	4-3	4	4-3	4-3
300	2-1	3	3-2	4-3	3	4-3

Colourfastness properties of degummed and modified silk fibres dyed with Direct Red 28 and Direct Orange 31 are tabulated in the **Table 5**. From the **Table 5**, it is observed that modified dyed silk fibres give better colour fastness properties than that of degummed dyed silk fibre when they are exposed to sunlight in air. It might be explained that after modification, the $-NH_2$ groups on silk backbone were blocked by modification reaction, as a result the atmospheric oxygen could not react with the $-NH_2$ group of silk fibre to form peroxy radicals. So, the change in colour or fading did not occur or slightly occurred [20].

5. Conclusions

Degummed silk fibres were chemically modified with acetic anhydride and phthalic anhydrides with optimum anhydride concentration, initiator concentration, time and temperature. Both the acetic anhydride and phthalic anhydride modified fibres showed superior tenacity, dye-abilities and colour fastness properties compared to that of unmodified silk fibres. Among the modified and unmodified silk fibres, acetic anhydride modified silk showed the best thermal stability and phthalic anhydride modified silk showed the worst thermal stability. Dye-ability of the modified fibres with Direct Red 28 and Direct Orange 31 were higher than unmodified fibres. The dyed modified fibres were more lustrous, uniform and pleasant at appearance than degummed silk fibre.

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