Effects of Ozone Treatment on the Properties of Raw and Degummed Tassar Silk Fabrics

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ABSTRACT: Ozone is a powerful oxidizing agent and is widely used in various applications, which includes bleaching of cotton. Literature on the action of ozone on silk is almost not available. Therefore, an elaborate study was carried out to understand the effects of process parameters in the ozone treatment of raw and degummed tassar silk fabrics on their properties. The study was extended with a view to compare the ozone treatment with soap degumming and hydrogen peroxide treatment carried out on raw and degummed tassar silk fabrics, respectively. The treatment results in improvement in pliability of the fabric and reduction in color. Decrease in breaking strength, breaking elongation, and weight as well an increase in amino group content is also experienced by the material. The results obtained are substantiated with tyrosine content, scanning electron micrographs, and infrared spectroscopy of the treated materials. The effect of pH on the treatment is maximum upto pH 4 and then decreases. The treatment is more severe when the wet pickup used is 50% compared to 10 and 100%. With respect to treatment time, though the severity increases with time, it is maximum during the first 10 min of the treatment. Soap degumming of raw silk fabric results in little higher yellowness index and lesser loss in breaking strength and elongation and flexural rigidity compared to that of ozone-treated material. There is not much of difference between ozone and hydrogen peroxide treatments of degummed silk fabric, except for the lesser yellowness index obtained in the latter case. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 147–155, 2007

Key words: tassar silk fiber; breaking strength; elongation; FTIR spectroscopy; electron microscopy

INTRODUCTION

Tassar silk is a type of silk, produced by wild silk worms living on trees. It is a double thread filament, and in many respects it is very different compared to mulberry silk. It varies in quality, lacks the luster, and contains more mineral substances. It is irregular, coarse, and wiry but of almost negative elasticity. It is more difficult to process; their filaments possess an unusual strength and durability and do not absorb moisture. The color of the silk ranges from light to dark beige or brown. The color often penetrates to the core of the fiber and hence require powerful agent to bleach. It also does not absorb dyes as easily.

They also differ in their sericin content that varies from 8 to 15%, fiber cross section, and surfaces. The surface is striated. Degumming of tassar silk can be carried out using soap or synthetic detergents, alkali, and enzymes. Bleaching is normally carried out with hydrogen peroxide, and as alternative, potassium permanganate is used if the silk has strong self color.[1] Ozone, which is a known strong oxidizing agent, has never been attempted on tassar silk, though number of attempts have been made on wood pulp, cotton, and to an extent on wool.[2–5] Hence, a study was carried out to understand the effect of ozone on raw as well as degummed tassar silk fabrics. The study was carried out with known concentration of ozone, involving process parameters such as wet pickup (WP), pH, and treatment time (TT). The levels of the above variables were fixed on the basis of preliminary studies conducted. The effect was assessed in terms of color expressed as yellowness index, breaking strength and elongation, amino group content, weight, and flexural rigidity over the control sample. Test samples were also evaluated using scanning electron microscopy and infrared spectroscopy. The test results were also compared with the properties of soap-degummed and hydrogen peroxide-treated samples.

EXPERIMENTAL

Materials

Commercial grade plain woven gray tassar silk fabric with 30 × 30 yarns/cm, 80 × 65 denier single yarn in warp and weft and 45 g/m^2 was used. All the chemicals used except soap solution, which was a commercial grade agent, were of laboratory grade reagent and supplied by Qualigens Fine Chemicals Limited, India. Silkenz DGM was the enzyme used

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TABLE I
Percent Change in the Properties of Ozone-Treated Raw Silk Fabric

		10-min TT			20-min TT			30-min TT		
Properties	pH	10% WP	50% WP	100% WP	10% WP	50% WP	100% WP	10% WP	50% WP	100% WP
Yellowness index	2	−1	−2.7	−1.9	−1.2	−3.5	−2.5	−2.1	−4.3	−3.3
	4	−2.8	−7.2	−4.7	−3.9	−8.8	−5.6	−5.4	−9.5	−6.4
	6	−2.4	−6.3	4.1	3.4	−7.7	−4.7	4.1	−8.9	5.9
	7	−1.7	−5.9	−3.8	−3.2	−7.4	−4.5	−3.8	7.6	−5.6
	8	−1.5	−4.3	−3.5	−2.5	−6.5	−4.1	−3.4	−7	−5.1
	10	−1.2	−4.1	−3.2	−1.8	−5.7	−3.6	−3.2	−6.4	−3.8
	12	−0.8	−1.9	1.7	−1.4	−2.8	−2.2	−1.8	−3.2	−2.4
Breaking strength	2	−2	−5.2	−3.8	−3.8	−7	4.6	−4.8	−9.1	−6.3
	4	−5.2	−14.1	−9.5	−6.3	17.2	−10.8	−7.5	−28.2	−14.4
	6	−4.9	−12.2	−7.2	−6	−15.1	−8.3	−7.1	−21.4	−11.1
	7	−3.8	−8.8	−6.4	−5.4	−11.2	−7.6	−6.4	−17.3	−10.3
	8	−3.4	−7.1	−5.9	−4.2	−10	−6.4	−5.2	−15.1	−9.8
	10	−2.8	−6.5	−3.2	−3.2	−7.8	−5.3	−4.5	−9.8	−8.1
	12	−1.1	−3	−2.6	−1.9	−4.2	−3.7	−2.8	−5.7	−4.1
Breaking Elongation	2	−1.8	−4.2	−3.4	−3.1	−7	−4.1	−4	−8.6	−5.6
	4	−5.6	−11.1	−8.1	−6.6	−15.1	−9.2	−7.3	−24.8	−11.4
	6	−4.5	−10	−6.7	−5.8	−14.2	−7.8	−6.5	−20.1	−10.2
	7	−3.5	−8.9	−6.1	−5.1	−10.1	−6.4	−5.7	−18.6	−9.4
	8	−2.9	−6.8	−5.2	−4.1	−9.5	−5.9	−5.1	−15.4	−8.3
	10	−2.6	−5.6	−3	−3	−6.4	−5.1	−4.1	−14.1	−6.4
	12	−1	−3	−2.2	−1.5	−3.5	−2.8	−2.4	−4.5	−3.4
Amino group content	2	+0.9	+4.6	+3.7	+2.2	+5.3	+4.4	+3.3	+6.6	+6.8
	4	+4.9	+13.7	+11.6	+6.3	+15.1	+12.8	+8.4	+17.8	+14.6
	6	+4.1	+11.9	+9.9	+5.4	+14.4	+10.9	+7.1	+15.7	+12.8
	7	+3.2	+9.8	+8.7	+4.9	+13.6	+9.8	+6.5	+14.3	+11.7
	8	+1.6	+9.2	+8	+3.7	+12.1	+8.7	+5.4	+13.6	+10.2
	10	+1.2	+8.5	+7.5	+3.1	+11.4	+8.2	+3.9	+12.8	+9.4
	12	+0.4	+1.1	+1	+0.6	+1.5	+1.1	+0.9	+2.2	+1.2
Weight	2	−1.2	−2.3	−2	−1.5	−3.2	−2.2	−2.2	−4.8	−3.2
	4	−2.7	−4.7	−4	−3.2	−5.4	−4.1	−3.8	−7.2	−5.9
	6	−2.4)	−4.4	−3.8	−3	−5.1	−4	−3.1	−6.9	−5.2
	7	−2.2	−4.1	−3.6	−2.6	−4.9	−3.9	−3	−6.3	−5
	8	−2	−3.9	−2.8	−2.5	−4.2	−3.5	−2.8	−6.1	−4.8
	10	−1.8	−3.5	−2.6	−2.4	−3.9	−2.9	−2.7	−5.9	−4.2
	12	−1	−2	−1.9	−1.4	−2.5	−2.1	−1.9	−3.2	−2.7
Flexural rigidity	2	−2.5	−4.7	−4.5	−2.8	−5.6	−4.6	−3.5	−6	−5.6
	4	−5.2	−16.3	−13.4	−5.6	−16.9	−13.5	−6.3	−17.4	−15.1
	6	−3.6	−13.8	−12.1	−4.2	−14.4	−13.4	−4.3	−17.2	−14.5
	7	−3.4	−13.5	−11.9	−3.8	−14.2	−12.2	−4.2	−15.5	−13.2
	8	−3.2	−12.2	−10	−3.7	−13.6	−10.6	−4	−15.3	−10.7
	10	−3	−10.7	−9.8	−3.6	−12.2	−10.1	−3.9	−14	−10.2
	12	−2.3	−3.3	−3.1	−2.6	−3.7	−3.3	−3.2	−4.4	−3.9

in the study and supplied by Rossari Biotech India Pvt. Ltd., India.

Methods

Raw silk fabric

Preparation. The gray fabric was treated in an open bath having hot water at 70°C, using a liquor ratio of 40 : 1, for 10 min, to remove the impurities in it. Then the fabric was thoroughly washed and dried. This prepared raw silk fabric was used as control sample for the production of ozone-treated raw silk samples and soap-degummed sample.

Determination of sericin content. The sericin content in the silk was determined with a view to contain the degumming loss within this limit to protect fibroin from degradation, when the raw silk fabric is subjected to degumming operation. Enzymatic degumming technique was adopted for this purpose. The prepared raw silk fabric was treated repeatedly in a bath having 0.8% on the weight of material enzyme at pH 9–10 for 20 min at (55 ± 5)°C followed by 30 min at (85 ± 5)°C using a liquor ratio of 40 : 1 till a constant weight was achieved. The weight loss obtained in the above treatment was 7.87%, which gives the maximum sericin content in the silk.

Ozone treatment. Fabric strips cut in warp direction with various WP levels and pH are vertically hung inside the applicator of the laboratory ozonation apparatus and the treatment was carried out. A concentration of 60 g/m^3 of ozone with a flow rate of 0.5 L/min was used. The treated materials were washed with water and then soaped at 85°C, for 10 min, using 2 g/L solution, followed by washing, drying, and conditioning.
Soap degumming. The prepared material was degummed in a bath having 8 g/L soap and pH 10–11, for 90 min, at (85 ± 5)°C, using a liquor ratio of 60:1, taking precaution to keep the weight loss within the maximum sericin content. Then the fabric was thoroughly washed, dried, and conditioned. The weight loss was found to be 7.27%.

Degummed silk fabric

Preparation. A portion of soap-degummed silk material was taken and treated with bath having enzyme concentration of 0.5% on the weight of material, at pH 9–10, for 90 min, using a liquor ratio of 40 : 1. The treated material was then washed, dried, and conditioned. The weight loss was found to be 7.29%. This fabric was considered as control sample for the production of ozone-treated degummed tassar silk samples and hydrogen peroxide-treated tassar silk samples.
Ozone treatment. The treatment of degummed silk fabric with ozone was carried out on the same lines outlined for raw silk fabric. After the treatment, the material was washed only with water and then dried and conditioned.
Hydrogen peroxide treatment. The material was bleached in a bath prepared using 18 mL/L hydrogen peroxide (35% w/v) and 2 g/L of sodium silicate at pH 9 (adjusted with sodium carbonate) for 120 min at (85 ± 5)°C having liquor ratio of 60 : 1. Then the fabric was thoroughly washed, dried, and conditioned.

Test methods

Yellowness index[6] of the samples were calculated using reflectance values measured using Hitachi UV–vis Spectrophotometer U-3210. Breaking strength and elongation were found out,[7] in warp way using Instron tensile tester, model 4301. Weight[8] was determined using Mettler Toledo PB 303 balance. Flexural rigidity of the samples was found out in warp way using cantilever method.[9] Tyrosine and amino group contents were determined using 1-nitroso-2-naphthol,[10] and ninhydrin,[11] respectively. The scanning electron microscopy studies of selected samples were carried out using Hitachi S-310 scanning electron microscope,[8] and the infrared absorption spectra of the above samples were taken on a Perkin–Elmer Paragon 500 Fourier transform double beam spectrophotometer by using KBr disc method.[12,13]

RESULTS AND DISCUSSION

Effect of the treatment on raw and degummed tassar silk fabrics

The properties of raw and degummed tassar silk fabrics (control samples) and the effect of ozone treatment on these properties as percentage change are given in Tables I and II respectively, −ve and +ve signs indicate a decrease and an increase, respectively. All the test results obtained are statistically tested and the treatment is found to have significant effect on the properties. The various effects obtained are explained as follows.

The results indicate that the treatment decreases the yellowness index of both raw and degummed silk samples. Treatment of silk with oxidizing agents such as hydrogen peroxide, potassium permanganate and reducing agents namely sulfur dioxide and sodium hydrosulfite have shown removal of natural coloring matter and improvement in whiteness of the tassar silk.[14] Production of yellow color due to glycine, serine, and tyrosine present in silk by UV, hydrogen peroxide, and nitric acid is reported.[15–19] Raw and degummed tassar silk fabrics treated with 50% WP, pH 4, 30-min TT were taken as representative samples and their tyrosine contents were determined (Table III). The results show a reduction of more than 15% in both the cases. The reduction may be due to the formation of 3-4 dihydroxyphenylalanine and chromophoric products containing carbonyl groups from it, which are yellow in color.[20] Amino acids such as glycine, alanine, and tryptophan could have also contributed toward yellow color formation due to the production of chromophoric products containing carbonyl groups,[16] and formkynurenine,[21] respectively. In spite of the production of products contributing for yellow color during the treatment, the samples show a reduction in yellowness index. This clearly brings out the fact that the color reduction taking place due to bleaching of natural coloring matter in the tassar silk fiber is much higher than the color generation caused by the products of amino acid residues in the fiber.

The results on strength and elongation show that the treatment has adverse effect on both raw and degummed silk fabrics. A very good correlation of above 0.85 is found to exist between strength and elongation at all combinations of treatment conditions. For better understanding on the effect of the ozone treatment on these properties, scanning electron micrographs and infrared spectra were taken for the representative samples produced with 50% WP for 30-min TT at pH 4.

Scanning electron micrographs of treated raw and degummed silk compared to their respective control sample (Fig. 1) do not show any fibrillation but for some amount of disturbance in the distribution of sericin in the case of former. This clearly indicates

TABLE II
Percent Change in the Properties of Ozone-Treated Degummed Silk Fabric

		10-min TT			20-min TT			30-min TT		
Properties	pH	10% WP	50% WP	100% WP	10% WP	50% WP	100% WP	10% WP	50% WP	100% WP
Yellowness index	2	−0.5	−1.5	−1.1	−0.9	−1.9	−1.2	−1.9	−3.3	−2.5
	4	−2.6	−4.8	−3.8	−3.3	−6.9	−4.2	−3.4	−8.5	−5.5
	6	−2.4	−4	−3.7	−3.1	−6.1	−3.9	−3.2	−8	−5.1
	7	−1.5	−3.3	−3.1	−2.8	−5.5	−3.3	−3	−7.2	−4.6
	8	−1.4	−3	−2.6	−2.1	−5.2	−3	−2.7	−6.9	−3.1
	10	−0.9	−2.5	−2.2	−1.4	−4.3	−2.6	−2.2	−4.1	−2.2
	12	−0.2	−0.7	−0.3	−0.5	−1	−0.8	−0.7	−1.5	−1.0
Breaking strength	2	−0.8	−3.3	−2.6	−1.8	−4.7	−3.4	−2.4	−6.8	−4.8
	4	−4.1	−9.1	−7.2	5.4	−11.2	−8.3	−7.3	−15.8	−10.8
	6	−3.8	−8.1	−6.4	−4.6	−9.8	−7.7	−6.6	−13.6	−8.8
	7	−2.7	7.2	−6.2	−3.6	−8.5	−6.8	−5.4	−12.1	−7.2
	8	−2	−6.3	−5.6	−2.8	−7.7	−6.1	−4.1	−10.4	−6.3
	10	−1.4	−5.4	−3	−2	−6.3	−4.2	−3.5	−8.4	−5.6
	12	−0.7	−2.6	−1.5	−0.8	−3.7	−1.9	−1.7	−4.4	−3.4
Breaking Elongation	2	−1.7	−3.6	−2.5	−2.1	−5	−3.6	−3	−6.8	−4.4
	4	−4.4	−8.2	−7.1	−5.3	−9.7	−8	−6.1	13.6	−9.3
	6	−3.8	−7.9	−6.1	−4.4	−9	−7.1	−5.3	−11.3	−8.2
	7	−3	−7	−5.4	−3.8	−8.2	−6.3	−4.6	−10.1	−7.3
	8	−2.5	−6.1	−4.3	−2.9	−7.1	−4.9	−4.1	−9.2	−6.2
	10	−2	−4.9	−4	−2.6	−5.6	−4.4	−3.6	−8.3	−5.3
	12	−0.7	−2.4	−2	−1	−3.2	−2.6	−1.6	−4	−3.2
Amino group content	2	+0.4	+2.3	+1.3	+1	+2.4	+2	+1.6	+2.7	+2.6
	4	+2.2	+4.6	+3.4	+3	+5.8	+4.1	+3.2	+6.1	+4.9
	6	+1.8	+4	+3	+2.4	+4.6	+3.5	+3	+4.9	+4.2
	7	+1.4	+3.5	+2.6	+2	+4.1	+3	+2.4	+4.6	+3.7
	8	+1.2	+3.1	+2.3	+1.6	+3.8	+2.9	+2	+4.2	+3.5
	10	+1	+2.6	+1.7	+1.2	+3	+2.2	+1.8	+3.5	+2.8
	12	+0.1	+0.6	+0.4	+0.5	+0.9	+0.7	+0.6	+1.2	+3.2
Weight	2	−1	−2	−1.3	−1.2	−2.5	−1.6	−1.5	−2.2	−2.1
	4	−1.6	−2.7	−1.8	−1.7	−3.2	−2.1	−1.9	−3.6	−3.4
	6	−1.5	−2.5	−1.7	−1.6	−3.1	−2	−1.8	−3.3	−3.1
	7	−1.3	−2.4	−1.6	−1.5	−2.9	−1.9	−1.6	−3.2	−2.9
	8	−1.2	−2.3	−1.5	−1.4	−2.7	−1.8	−1.5	−2.9	−2.8
	10	−1.1	−2	−1.4	−1.3	−2.5	−1.7	−1.4	−2.8	−2.4
	12	−0.8	−1.6	−1.1	−1	−2.2	−1.4	−1.1	−2.4	−1.8
Flexural rigidity	2	−1.1	−3.1	−2.8	−1.3	−3.4	−3	−1.6	−3.7	−3.5
	4	−1.7	−5.5	−5	−1.8	−6.2	−5.8	−2.1	−9.1	−6.3
	6	−1.6	−5.4	−4.9	−1.7	−6.1	−5.6	−2	−8.8	−6.0
	7	−1.5	−5.2	−4.8	−1.6	−5.8	−5.5	−1.8	−7.4	−5.8
	8	−1.4	−5.1	−4.6	−1.5	−4.3	−5.4	−1.7	−7.1	−5.7
	10	−1.2	−4.8	−4.5	−1.4	−4.1	−5.1	−1.6	−7	−5.3
	12	−0.9	−3.1	−2.5	−1.1	−3.5	−2.9	−1.3	−4	−3.3

that the reason for loss in breaking strength and elongation resulting from the treatment is not because of fibrillation but due to some other reason.

When the above samples were taken for analysis using infrared spectroscopy, the following facts have been found out. Figure 2 shows spectra of these samples along with their representative samples. It can be said from the spectra of raw and degummed control samples that the degumming operation carried out on the raw silk did not damage the fibroin. The nature and intensity of polypeptide absorption bands at 1530 cm^{-1} of the spectra of the treated samples does not appreciably differ from those of control samples. It clearly indicates that the basic protein molecules in tassar silk fiber are retained as a major component. However, in the higher energy region, the broadening of envelope due to OH and NH vibration of the treated samples compared to

TABLE III
Tyrosine Content in Raw and Degummed Silk Samples Before and After Ozone Treatment

	Tyrosine content (mmol/100 g)		% Decrease in tyrosine content	
Sample	Raw silk	Degummed silk	Raw silk	Degummed silk
Control	1432.7	606.1	–	–
Ozone-treated[a]	1057.9	508.7	26.1	16.0

[a] 50% WP, 30-min TT at pH 4.

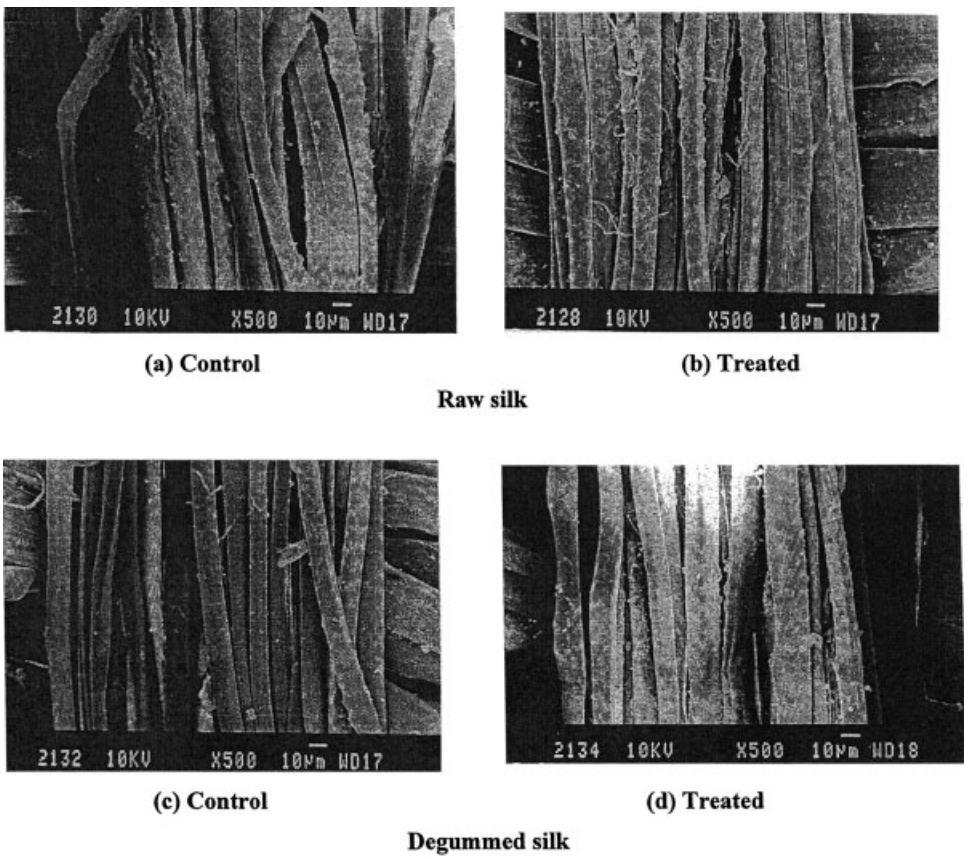
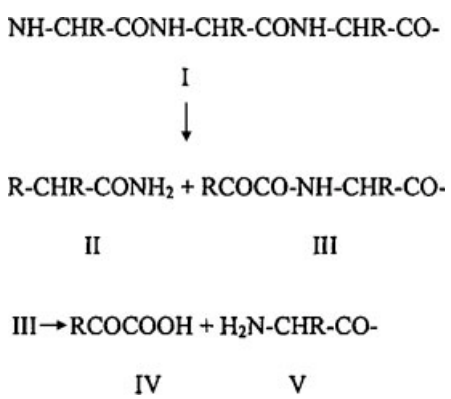


Figure 1 Scanning electron micrographs of control and ozone-treated (50% WP, 30-min TT at pH 4) samples.

control samples reveals breaking of peptide backbone into fragments possessing more free amino and carboxyl groups. Further strong absorption band at 2400 cm^{-1} reveals a high conversion of amide groups into amino group either in the form of free or primary amine salts (ethanolate) in the treated samples. The above explanation proves that the ozone treatment results in generation of new amino groups in the tassar silk. The increase in amino group content of treated samples (Tables I and II) confirms the above fact.

The oxidation mechanism proposed toward the introduction of amino groups in the chemical structure[16] (I) of tassar silk is given below:



The above mechanism clearly indicates the rupture of silk macromolecules, causing reduction in breaking strength and elongation. The breaking strength is found to have a good correlation of −0.85 with breaking elongation and amino group content of the treated samples at all combinations of treatment conditions. One another reason for loss in strength and elongation is the weight loss (Tables I and II) experienced by raw and degummed silk fabrics. Breaking strength and elongation is found to have a correlation of above 0.80 with weight loss at all combinations of treatment conditions. The reasons for the weight loss are discussed below.

Both raw and degummed silk give a maximum weight loss of 7.2 and 3.6% respectively, when the treatment conditions were 50% WP at pH 4 for 30-min TT. The weight loss may be due to the formation of nitrates from serine and glutamic acid present in sericin.[22] The maximum sericin content in the tassar silk fiber was found to 7.87%. During the degumming operation the sample had lost 7.29%, leaving a residual sericin content of 0.58% in the sample. The weight loss of 3.6% occurred in the sample at the time of ozone treatment clearly indicates that fibroin also has suffered a weight loss.

Other possibilities for the occurrence of weight loss are due to removal of gaseous products such

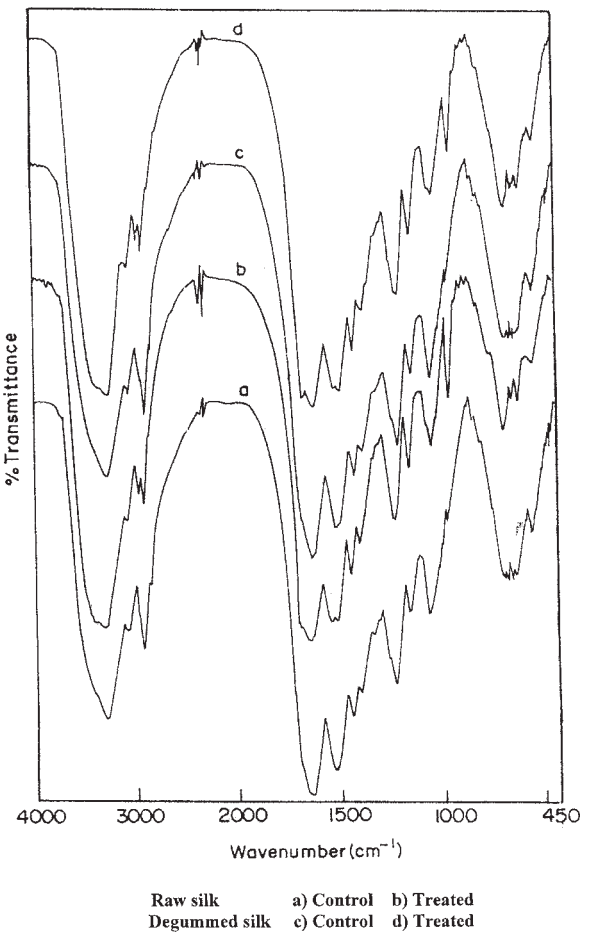


Figure 2 FTIR spectra of control and ozone-treated (50% WP, 30-min TT at pH 4) samples.

as ammonia, carbon dioxide, and aldehydes.[23] The proposed reactions involved are indicated below.

$$\text{II} + \text{V} \rightarrow \underset{\text{VI}}{\text{H}_2\text{N-CHR-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-CHR-CO-NH}_2}$$

$$\text{II} + \text{V} \rightarrow \underset{\text{VII}}{\text{H}_2\text{N-CHR-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-NH}_2}$$

$$\underset{\text{VI}}{\text{H}_2\text{N-CHR-COOH}} \rightarrow \underset{\text{VIII}}{\text{NH}_3} + \underset{\text{IX}}{\text{CO}_2\text{+RCHO}}$$

$$\underset{\text{VII}}{\text{H}_2\text{N-CHR-COOH}} \rightarrow \underset{\text{VIII}}{\text{NH}_3} + \underset{\text{IX}}{\text{CO}_2\text{+RCHO}}$$

Tassar silk contains 0.48%[24] of waxes on the weight of its sericin content. Formation of smaller acids, aldehydes, ketones by the action of ozone on these waxes would have also resulted in weight loss.[25]

The treatment causes reduction in flexural rigidity of both raw and degummed fabrics. The weight loss experienced by the material during the treatment and the drop in interfilament forces due to the removal of sericin are the cause for such a reduction.[26,27] The production of pyruvic acid, ammonia, carbon dioxide, and aldehydes during the treatment is already explained. The loss of the above products from fibroin could have resulted in removal of fragments (short chains) from silk macromolecules. Moreover, the possibility of removal of fragments from fibroin molecular chains would have caused reduction in flexural rigidity. Similar effect arising out of alkaline hydrolysis of fabric made from PET polymer is also reported.[28]

Effect of process conditions on raw and degummed silk fabrics

The effect of process conditions namely WP, pH, and TT on the properties of ozone-treated silk samples can also be seen from the Tables I and II. Statistical treatments of the results indicate that all the above process parameters significantly affect the properties of raw and degummed silk samples.

Effect of pH

The results show that for a given % WP and TT, the action of ozone increases from pH 2 to 4 and then decreases. The reason for such a trend is explained taking into account the decomposition behavior of ozone.

The action of ozone on silk depends on the treatment pH. In acidic pH, it reacts predominantly as parent ozone molecule,[29,30] and in alkaline pH, it forms secondary oxidants such as OH°, HO_2°, HO_3°, and HO_4°. The oxidation potential of ozone and OH° are 2.07 V[31] and 2.80V.[32] Ozone looses its oxidation potential from 2.08 to 1.4 V with increase in pH.[33] Moreover, it is reported that the dissolved ozone concentration in water decreases from 4.3×10^{-4} mol/L at pH 4 to 1.5×10^{-4} mol/L at pH 10.[34] It is clear from the above facts that the efficiency of ozone treatment is maximum up to pH 4 and then decreases, irrespective of its availability as ozone or OH°. A point to be noted here is that though OH° has higher oxidation potential than ozone, the efficiency of the treatment in the alkaline region is lower than acidic region, since lesser amount of dissolved ozone is available for the generation of OH°.

However, the treatment indicates that the action of ozone at pH 2 is lower than that that of pH 4. This behavior can be explained as follows.

The quantity of bound acid or alkali in silk is almost zero between the pH range 4 and 9,[35,36] which is an isoelectric region of silk. In this region, silk represented as $NH_2—S—COOH$ would be available as $^+NH_3—S—COO^-$. Below pH 4 and above pH 9, it would be converted as $^+NH_3—S—COOH$ and $NH_2—S—COO^-$, respectively.[36] As the reactivity of ozone is depressed by COOH group,[37] the action of ozone on silk at pH 2 is lowered. The effect of ozone at pH 4, 6, and 7 is higher than that at pH 2, since at these levels silk contains only COO^- group, which is reactive toward ozone,[37] unlike COOH group.

Another reason for less severity of ozone at higher alkaline levels is given below. The sodium carbonate used in the treatment for achieving required pH exists as CO_3^- in strong basic conditions and as bicarbonate ions (HCO_3^-) in weak basic conditions.[38] Carbonate and bicarbonate ions are inhibitors capable of consuming OH° produced from ozone decomposition.[37] The rate constants for reaction of OH° with carbonate and bicarbonate ions is 4.2×10^8 $M^{-1}s^{-1}$ and 0.15×10^8 $M^{-1}s^{-1}$, respectively. Since at strong basic conditions carbonate ions predominates and due to its higher rate constant, consumption of hydroxyl radical is more compared to weak basic conditions in which bicarbonate ions are prevalent. Hence, the action of ozone on silk is less severe at higher alkaline pH.

Effect of WP

The results show that at any given pH, the effect of ozone treatment is maximum at 50% WP, followed by 100 and 10% WP levels. A similar trend is obtained in the action of ozone on cellulose wherein it is reported that the oxidation is maximum when the water content is between 45 and 50%.[39] The trend obtained in the present study is explained based on the distribution of water molecules at different regions in the silk fiber polymer matrix. Figure 3 gives the schematic representation of ozone path from gas phase to reaction site. The ozone gas, O, is separated from the reaction site, R, in the silk polymer matrix by a certain distance, which can be divided into four regions. These regions are (i) the distance between O and fiber surface or distance occupied by surface water (d_1), (ii) the distance occupied by mobile water phase i.e., water molecules present in the voids in the fiber (d_2), (iii) immobile water phase i.e., water molecules attached to the hydrophilic groups (d_3), and (iv) the distance between the immobile water phase and R (d_4).

When sufficient water is not present i.e., at low WP levels, d_1 and d_2 are absent and hence O is transported by convection across the distances d_1 and d_2 and then by diffusion across d_3 and d_4. Since sufficient water is not supplied, entire hydrophilic group in the fiber is not hydrated and hence the extent of attack at R is low.

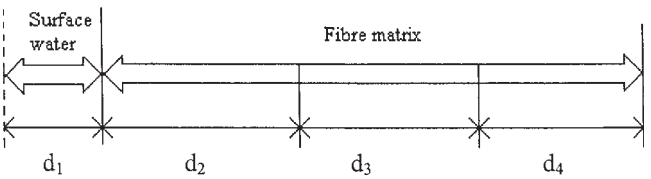


Figure 3 Schematic representation of ozone path from gas phase to reaction site.

When sufficient water is supplied i.e., at medium WP levels, d_1 is absent and d_2 is either fully or partially absent depending on the quantity of water available and hence O is transported by convection across d_1 and convection or diffusion across d_2 followed by diffusion across d_3 and d_4. Since sufficient water is supplied, entire hydrophilic group in the fiber is hydrated and hence the extent of attack at R is maximum.

When excess water is present i.e., at high WP levels, d_1 and d_2 are present and hence O is transported by diffusion across d_1, d_2, d_3, and d_4. Since excess water is present at d_1 and d_2, dilution of ozone takes place and hence ozone attack at R is lower in spite of complete hydration at d_3.

Effect of TT

A representative picture given in Figure 4 shows the effect of time of treatment carried out at various WP levels at pH 4 for raw and degummed silk samples. It clearly indicates that as the TT increases, the severity of the action of ozone on both raw and degummed silk increases. A similar kind of trend is observed for all the properties at various levels of WP and pH (Tables I and II).

Further, it can be observed from the figure that the action of ozone is of the highest order during the first 10 min compared to second and third 10 min.

Comparison of soap-degummed and ozone-treated raw tassar silk samples

The properties of soap-degummed and ozone-treated silk samples for a specific weight loss of (7.2 $\pm$ 0.07)% is given in Table IV. All the test results obtained are statistically tested and found to be significant. The table clearly shows that treatment with ozone shows a higher reduction in color and breaking strength and elongation than that of soap-degummed sample. The reduction in color in soap-treated sample is due to removal of sericin, whereas in ozone-treated sample it is due to the dominating bleaching action over the yellow color generation action of ozone, which is explained already. The drop in breaking strength and elongation is due to

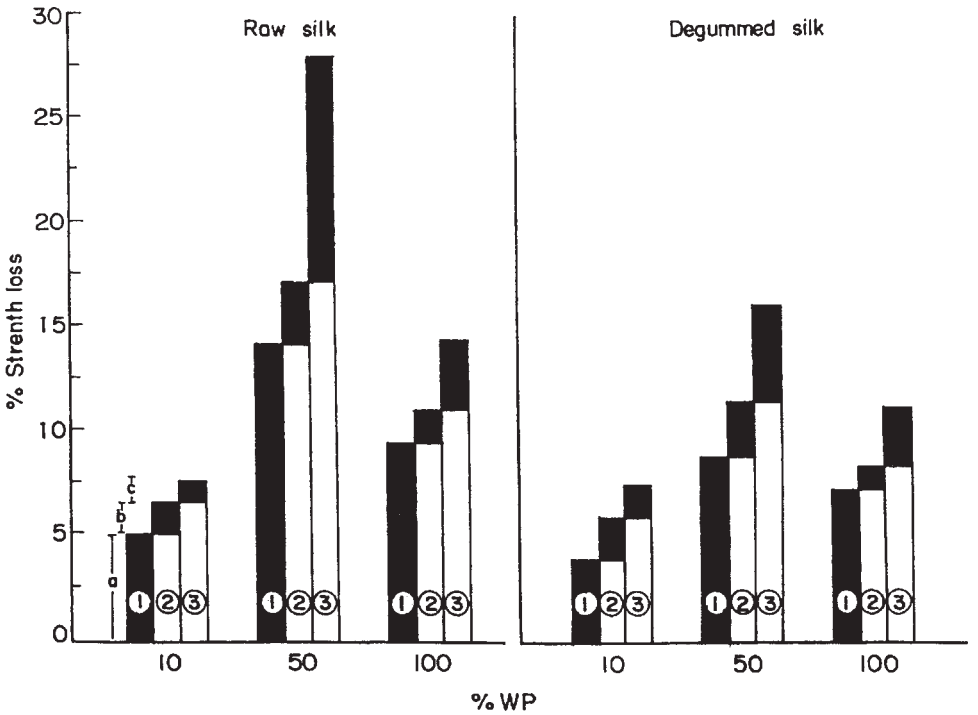


Figure 4 Effect of TT on strength loss of ozone-treated raw and degummed silk samples.

removal of sericin from raw silk but for ozone-treated sample it is due to the rupture in the silk macromolecule as explained earlier. The effect is also quite evident from the amino group content of soap-degummed and ozone-treated samples. Soap-degummed sample shows a higher reduction in flexural rigidity due to lowering of interfilament forces resulting from removal of sericin. Since complete removal of sericin is not achieved in ozone treatment, flexural rigidity is higher in ozone-treated materials.

Comparison of hydrogen peroxide and ozone-treated degummed tassar silk samples

The properties of hydrogen peroxide and ozone-treated degummed tassar silk samples are shown in Table V for a particular breaking strength and elongation loss of (8.9 ± 0.2)% and (8.1 ± 0.1)% respectively. All the test results are found to be statistically significant. It shows that only in respect of yellowness index, the difference is very high compared to all other properties. The poor reduction of yellowness index in ozone treatment is due to the generation of yellow color-causing carbonyl groups, which suppresses the bleaching action of ozone.

CONCLUSIONS

The present study clearly indicates that the ozone has significant effect on the properties of raw and degummed tassar silk fabrics. In spite of the production of products contributing for yellow color during the treatment, both the silk fabrics show a reduction in color.

The loss in breaking strength and elongation resulting from the treatment is due to the generation of new amino groups as indicated by infrared spectra and ninhydrin estimation technique. The treatment does not produce fibrillation in the material, which is

TABLE IV
Properties of Soap-Degummed and Ozone-Treated Raw Silk Fabrics with Weight Loss (7.2 ± 0.07)%

Properties	Soap-degummed sample	Ozone-treated sample
Yellowness index	−5.1	−9.8
Breaking strength	−18.0	−28.2
Breaking elongation	−13.9	−24.8
Amino group content	−12.8	+17.8
Flexural rigidity	−23.8	−17.4

TABLE V
Properties of Hydrogen Peroxide-Treated and Ozone-Treated Samples with Strength and Elongation Loss (8.9 ± 0.2)% and (8.1 ± 0.1)%, Respectively

Properties	Hydrogen peroxide-treated	Ozone-treated
Yellowness index	−37.0	−4.8
Weight	−1.5	−2.7
Amino group content (mol/g)	−1.0	+4.6
Flexural rigidity (mg cm)	−3.5	−5.5

evident from scanning electron micrographs. The weight loss occurring in the treatment is due to the removal of gaseous products such as ammonia, carbon dioxide, aldehyde, ketones, and nitrates. The flexural rigidity of both the materials decreases due to the treatment.

All the process parameters chosen have significant effect on the properties of both the materials. Since the efficiency of ozone is low above pH 4, these materials are less affected by it above this pH. On the contrary, the action of ozone is found to be low even at pH less than 4, which is due to the inhibiting action of COOH groups generated in silk at lower pH levels in this condition of treatment. The effect of ozone at pH 12 is very low, which is due to predominant inhibiting action of carbonate ions over bicarbonate ions liberated from sodium carbonate used in the treatment at this condition.

For the ozone to act completely on silk, sufficient supply of water is required, which neither results in inadequate dissociation of the gas nor dilution. Further, the action of ozone increases with time and it is severe during the initial phase of the reaction.

Soap treatment of silk is found to be less severe than ozone treatment. Hydrogen peroxide treatment results in lower yellowness index compared to ozone treatment.

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