Degumming of Silk Yarn Using Alkali, Enzyme and Seidlitzia Rosmarinus

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Abstract— **In this study, silk yarns were degummed using alkali, enzyme (alcalase) and Seidlitzia Rosmarinus (Kelyab, an Iranian native product) to investigate the effectiveness of products as degumming agents. The efficiency of degumming was assessed in terms of weight loss and tenacity. Some physical properties of the degummed silk yarns, i.e. tensile strength and the yellowness index were also measured. Seidlitzia Rosmarinus (Kelyab) effectively removed sericin leading to maximum 22.73% weight loss. Degumming with alkali and Seidlitzia Rosmarinus (Kelyab) led to the highest weight loss among the samples while the strength of the yarn decreased with severity of the degumming treatments. Seidlitzia Rosmarinus (Kelyab) decreased the strength of the yarns at higher concentration and treatment time. The SEM micrograph showed that the Seidlitzia Rosmarinus (Kelyab) in the highest concentration could completely remove the sericin while no serious damage was observed.**

Key words: Silk, degumming, alkali, alcalase, Seidlitzia Rosmarinus (Kelyab).

I. INTRODUCTION

SILK is a well-known protein fiber and is appreciated as one of the most luxurious textile fibers. It possesses outstanding properties such as softness, strength, dye ability, and luster. In the literatures, a number of studies have focused on the physical and chemical structure of mulberry silk fiber. The silk filament is a composite material consisting of fibroin and sericin. The existence of pigments in the sericin layer causes the colors which remove through degumming process [1-4]. Both fibroin and sericin consist of proteins that have different compositions. Fibroin has highly oriented and crystalline structure therefore, is insoluble in water. Naturally, sericin has an amorphous structure and so can be easily removed in hot water without any fiber damages [5-8].

In raw silk production, degumming is a key step and the fibers glue should be totally removed in order to prepare the fiber to subsequent mechanical process and achieve a level dyeing and increase the softness, absorbency, and luster. Degumming is an expensive process and it causes about 20-25% weight loss, decreases the yellowness and strength. Consequently, the whiteness of the fibers can be increased due to the sericin removal. To preventing the fiber damages during the treatment, a number of parameters such as temperature, time and pH should be controlled. In the recent years, several investigations have been reported on the silk degumming processes with different materials [9-11]. The most important degumming methods can be categorized into few basic types, i.e. using boiling water bath [12-13], soap solution [5,14-15], alkaline bath [16-19], acidic solution [20-23] and enzymatic degumming [24-31]. The most recommended method for silk degumming is using Marseilles soap, an olive oil based soap. Due to some economic concerns, other degumming methods have been also developed during the past years.

"Seidlitzia Rosmarinus (Kelyab)" is a natural product of "Eshnan" or "Eshnoon" shrub (Persian words). The plant is a species of Chenpodiaceae family and grows in salty lands and deserts. The first step in production of Kelyab is the burning of tree branches. During the burning process, a dark viscous liquid is extracted and flows down on the ground. After cooling, it turns a greyish rough material similar to volcanic stones. This stone is called "Kelyab" that has alkaline properties. For degumming silk yarns, the stones should be milled into powder and then dissolved in soft water at the liquor to good ratio of 40:1 for 8 hours. In the next step, the bright liquid can be separated from residues and used for degumming purpose. The efficiency of the preparation process is about 51% while the rests are sand and other solid residues. The pH value of the liquid is about 11. According to the reported study, the Seidlitzia Rosmarinus (Kelyab) consists of nitrogen, phosphor, potassium, carbone groups and some organic materials [32].

This research compares various methods of silk degumming in terms of the efficiency of process with respect to weight loss and tensile strength breaking point of treated yarns. The article mostly focuses on the investigate the effect of Seidlitzia Rosmarinus (Kelyab) as a native Iranian botanical-based substrate, on degumming process and compare the results with those obtained with enzymatic and alkaline degumming treatments.

II. MATERIALS AND METHODS

A. Materials

1) Seidlitzia Rosmarinus (Kelyab)

Seidlitzia Rosmarinus (Kelyab) is a well-known native product for degumming silk yarns in Kashan provinc in Iran. So, the Kelyab was prepared from domestic market of Kashan.

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2) Yarn

Silk yarn from North Cocoon & Silk Co. was used in the experiments. This type of the yarn is mostly used in hand-woven carpet production as pile threads. A 16-folded silk yarn, 126 Tex with 200 twists per meter was taken for the experiments.

3) Chemicals

Conventional Sodium carbonate was obtained. Alcalase, type Dx was prepared from Novo Nordisk/Denmark. A non-ionic surfactant, N135 from Salis Chemicals Company was used. All the employed chemicals were of the laboratory reagent grade.

B. Methods

1) Degumming

Silk yarn samples were conditioned at 65%RH and 20°C, and measured for weight and then degummed under the conditions given in Table I. The commercial raw silk yarns were degummed by three different methods as follows:

Alkaline/Surfactant: Silk yarns were degummed in an alkaline solution containing 2.5 and 10 g/lit Sodium carbonate and 1 g/lit surfactant in a liquor to good ratio of 30:1 at boiling point for 30 and 60 minutes. After that the degummed silk yarns were thoroughly washed with water and left to dry at room temperature.

Enzyme: Degumming process was carried out with Alcalase enzyme at 0.5, 1 and 1.5 g/lit concentrations, at 7-8 pH using bicarbonate buffer and 5 g/lit surfactant for 30 and 60 minutes at 55°C. The degummed silk yarns were rinsed with water and dried at room temperature.

Seidlitzia Rosmarinus (Kelyab): The Seidlitzia Rosmarinus (Kelyab) used for degumming of silk yarns at 10, 15 and 20% concentrations for 30 and 60 minutes in boiling water bath. The yarns were thoroughly washed and samples allowed to be dried in air.

More details of degumming baths are given in Table I. The degummed samples were then subjected for some evaluation test such as weight loss, breaking strength changes, yellowness index, as well as SEM studies.

C. Measurement and Analysis

The weight loss, strength loss, yellowness index were measured for different degumming methods. The SEM images of silk yarns that were degummed with different techniques were also studied.

The weight loss was used to evaluate the degumming efficiency. Simply, the percentage of weight loss of the silk yarns after degumming process was calculated by measuring the differences in the weight of the raw and the degummed samples as shown by Eq. (1) [18].

$$\text{Weight loss}\% = \frac{W_1 - W_2}{W_1} \times 100 \qquad (1)$$

where, W_1 and W_2 are the weights of the silk yarn samples before and after degumming, respectively. All samples were conditioned at 20°C and 65% RH for 24 hours prior to weight measurements. To evaluate the degumming efficiency, the degumming process with 25% Marseilles soap at boil was taken as standard method and it was assumed that for such method the sericin was completely removed. The weight loss for this degumming method was 22.38%. Then, the degumming efficiency was calculated by using Equation 2.

$$DE\% = \frac{W_y}{W_s} \times 100 \qquad (2)$$

where W_y is the percentage of weight loss of sample and W_s is the weight loss obtained by soap degumming method.

Determination of breaking load of the samples was carried out using Uster tensorapid V3.9 TK/Shirley, at a gauge length of 250 mm and extension rate of 25 mm/min.

A scanning electron microscopy (XL30/Philips) was used for morphological characterization of silk yarns.

The CIELAB tristimulus values, i.e. L*a*b* values and the yellowness index of degummed silk yarns were measured by Ultra Scan Hunter spectrophotometer while D65 with illuminate and 1964 standard observer was used.

III. Results and Discussion

A. Degumming Efficiency

The alcalase was used under the optimal conditions of pH and temperature and the degumming treatment with alkali was also carried out and the degumming results by Seidlitzia Rosmarinus (Kelyab) was compared to them as well as the soap bath as standard method. The values of weight loss, strength, degumming efficiency and yellowness index of the treated samples are shown in Table II. To investigate the rate of degumming treatment for different methods, the graph obtained for weight loss was considered. Figure 1 shows that the weight loss increases with the increase in concentration within certain treatment time for all methods. The specifications of employed cods in Figures 1 and 2 are detailed in Table III.

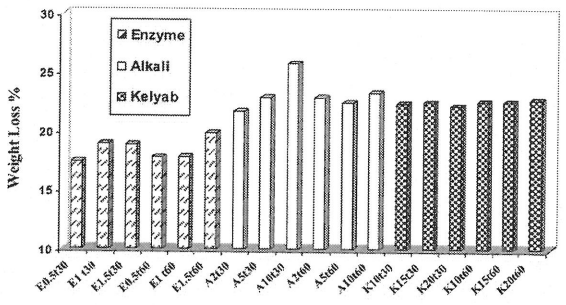

Fig. 1. Effect of different treatments on the weight loss.

The effect of enzyme concentration on the extent of degumming at different treatment times is between 17-20%. It is noteworthy that variation of enzyme concentration does not significantly affect on the removal of sericin and the weight loss would be happened in at lower concentration, too. According to Table II, the degumming efficiency has increased with increasing the treatment time and enzyme concentration to some extent.

Degumming of silk yarns with alkaline solution results in weight loss varies from 21.7 up to 25.8%. It was

TABLE I
EXPERIMENTAL CONDITIONS USED FOR DEGUMMING OF SILK YARNS

Material	Concentration	Time, (min)	Temperature, (°C)	pH
Sodium Carbonate	2,5,10 (g/lit)	30,60	Boiling	10-11
Surfactant	1 (g/li)			
Alcalase	0.5,1,1.5 (g/lit)			
Sodium Bicarbonate	5 (g/lit)	30,60	55	7-8
Surfactant	5 (g/lit)			
Seidlitzia Rosmarinus (Kelyab)	10, 15, 20%	30,60	Boiling	9-11

TABLE II
EFFECT OF TREATMENTS ON THE PHYSICAL PROPERTIES OF THE YARNS.

Time, min	Method	Concentration	Weight loss%	Strength g/tex CV%	Degum efficiency%	Yellowness index
30	Alcalase	0.5 (g/lit)	17.44	39.73 3.8	77.9	4.87
		1 (g/lit)	18.95	40.05 1.1	84.6	4.16
		1.5 (g/lit)	18.55	37.84 1.9	82.9	4.10
	Alkali	2 (g/lit)	21.7	39.70 1.5	96.9	4.81
		5 (g/lit)	22.9	37.70 3.3	93.3	4.10
		10 (g/lit)	25.8	33.62 3.7	115.2	25.80
	Kelyab	10%	22.48	38.38 2.2	100.4	5.12
		15%	22.52	37.53 1.9	100.6	5.06
		20%	22.19	37.41 2.1	99.1	5.26
60	Alcalase	0.5 (g/lit)	17.82	38.40 1.1	79.6	4.84
		1 (g/lit)	17.84	36.34 1.5	79.7	3.67
		1.5 (g/lit)	19.87	35.77 1.9	88.8	3.41
	Alkali	2 (g/lit)	22.9	40.24 1.9	102.3	4.12
		5 (g/lit)	22.5	37.21 1.2	91.6	4.36
		10 (g/lit)	23.3	37.68 2.5	102.2	23.3
	Kelyab	10%	22.57	38.99 2.4	100.8	4.85
		15%	22.58	36.95 3.7	100.8	4.73
		20%	22.73	36.73 1.3	101.5	4.06

observed that by increasing the alkali concentration for 30 minutes bath, the weight loss increased respectively. This may be due to the hydrolysis of sericin and its solubilisation in the treatment bath. However the variation for 60 minutes bath was relatively constant. It seems that, more than 100% degumming efficiency could originate from the removal of sericin and the fibron damage through alkaline degumming. In alkaline degumming process, sericin is degraded into sericin peptide or hydrolyzed sericin with a molecular weight loss.

Figure 1 also shows that at higher concentration of Seidlitzia Rosmarinus (Kelyab) and treatment time of 30 minunte, sufficient weight loss is obtained. It was observed that the variation at higher concentration and treatment time is linear. Silk is nearly degummed completely in such condition and the amount of removed gum can be compared to those of alkaline treatment. The highest weight loss for Seidlitzia Rosmarinus (Kelyab) was obtained at 20% concentration and 60 minute treatment time which was about 22.73%. According to results, the increasing of weight loss is proportional to the concentration of Seidlitzia Rosmarinus (Kelyab). While the efficiency of enzyme method is higher than Seidlitzia Rosmarinus (Kelyab) method, the later benefits from economic advantages due to lower cost.

Some researchers studied on the effect of different substances on chemical components of silk. Gulrajani *et al.* [20] investigated the effect of organic acids on the

chemical structure of silk during the degumming process. Tímár Balázy [33] reported the effect of alkalis and Nalankilli [34] and Cavaco [8] discussed on the effects of proteolytic enzymes on silk. It can be assumed that Seidlitzia Rosmarinus (Kelyab), with alkaline basis, could degrade proteins by the hydrolysing of -CO-NH- Linkage. Solution of Seidlitzia Rosmarinus (Kelyab) in degumming bath attacks at the silk chain and remove sericin.

TABLE III
SPECIFICATIONS OF SAMPLES OF FIGS. 1 AND 2.

Sample	Material	Concentration	Time, min
E0.5t30		0.5 (g/lit)	
E1t30		1 (g/lit)	
E1.5t30		1.5 (g/lit)	30
	Enzyme		
E0.5t60		0.5 (g/lit)	
E1t60		1 (g/lit)	60
E1.5t60		1.5 (g/lit)	
A2t30		2 (g/lit)	
A5t30		5 (g/lit)	
A10t30		10 (g/lit)	30
	Alkali		
A2t60		2 (g/lit)	
A5t60		5 (g/lit)	60
A10t60		10 (g/lit)	
K10t30		10%	
K15t30		15%	
K20t30		20%	30
	Seidlitzia Rosmarinus (Kelyab)		
K10t60		10%	
K15t60		15%	60
K20t60		20%	

B. *Physical Properties*

The results of strength loss and yellowness index of silk yarns after different degumming processes are given in Table II. Alcalase enzyme acts selectively and attacks to the given parts of the fibres. As shown in Figure 2, the strength decreases with the increasing of treatment duration and concentration. Also, the decrease in the yellowness index may originate from the existence of natural yellow colorants in sericin structure that were removed during the degumming treatment.

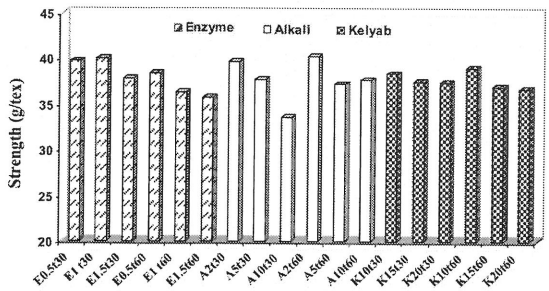

Fig. 2. Effect of different treatments on the yarns strength.

The employed alkali provided a pH, ranging between 10 and 11. The concentration of sericin at the surface of the fibers is high and gradually tends to decrease during the degumming process. In fact, alkali removed the sericin and hydrolyzed the protein and consequently reduced the strength of the fibers. The damages become severer at higher treatment times and concentrations. It can be concluded that increasing the alkali concentration results in higher strength loss as seen in Figure 2. Yellowness index decreased at higher concentration. It is clear that at higher concentration of alkali, the fibroin could be also attacked and the values of yellowness index can be more affected. These findings are in agreement to the degumming efficiencies values. The highest values of yellowness index was achieved by using 10 g/lit of alkali.

The strength of the yarn decreased with the increasing of Seidlitzia Rosmarinus (Kelyab) concentration as well as the treatment time. However, Figure 2 shows that the variation is somehow linear. Degumming process showed that the yellowness index decreases at higher concentration. The lowest value was found at the 20% Seidlitzia Rosmarinus (Kelyab) and 10 minutes treatment time.

C. *Morphological Characterization*

The surface morphologies of the silk yarns of different treatments, i.e. alcalase, alkali and Seidlitzia Rosmarinus (Kelyab) are shown in Figure 3. The surface morphological properties of the degummed yarns were studied by the scanning electron microscopy (SEM) and revealed the removal of sericin. The separation of silk filaments adhering to each other happened during degumming process. To evaluate the efficiency of Seidlitzia Rosmarinus (Kelyab) degumming, SEM micrographs reveal that even at the highest concentration no damage could happen to the fiber surface and as a result a complete sericin removal can be enhanced.

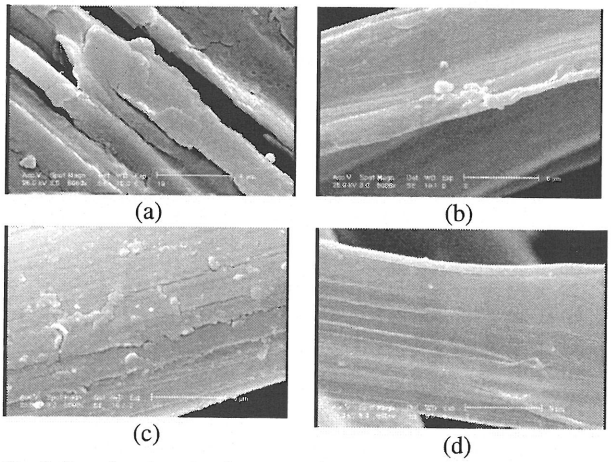

Fig. 3. Scanning electron microscopy photography of silk samples. a) raw silk b) degummed with sodium carbonate 5 g/lit, 60 min c) degummed with enzyme 1 g/lit, 60 min d) degummed with Seidlitzia Rosmarinus (Kelyab) 20%, 60 min.

IV. CONCLUSIONS

Three different silk degumming treatments were studied and it was shown that all methods can effectively remove sericin leading to weight loss. The evaluation of data was carried out through the measurement of the weight loss, strength, and the yellowness index of the samples. The weight loss occurred due to the sericin content of raw silk

that decreases during degumming treatments to some extent and the degradation of products of fibroin was achieved. The employed degumming stuffs, i.e. alkali, enzyme, and Seidlitzia Rosmarinus (Kelyab) effectively removed the sericin and resulted in about 17-25% weight loss. Degumming with alkali and Seidlitzia Rosmarinus (Kelyab) led to the highest weight loss. It was shown that, the degree of the hydrolysis of fibroin depends on the pH and the concentration of the solution bath. The strength of the treated samples decreased with the severity of the degumming treatments. The weight loss trends for all three agents were similar but the samples treated with alkali at higher treatment time showed lowest values. The results were comparable with those obtained from yellowness indexes as well. The yellowness index decreased with increase in treatment temperature. It was discussed that, the decrease in the yellowness index could relate to removing of colored substances in sericin. Based on results, it was claimed that the results of strength lost and yellowness index are with good agreement with the weight loss results.

SEM images of silk fibers approved the removal of the sericin in degumming treatment. In an incomplete degumming, residual sericin still was observed on the surface of the fibers and irregularity over the surface of the yarn was evident. However, the higher cost of enzymes in comparison to the other chemicals should be considered. The alkali substrates successfully degummed silk however, the damage of silk fibroin could be the drawback of these methods. Totally, the Seidlitzia Rosmarinus (Kelyab) as a natural product, showed reasonable results in terms of degumming efficiency, yarn properties and the cost.

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