Mechanical Properties of the Silk Degummed with Citric Acid and Ultrasound

Ruzica Brunsek, Ivana Schwarz and Mirta Than

Abstract Silk, called the "Queen of Fibers," is a continuous protein fiber produced by silkworm to form its cocoon. Raw silk fiber obtained by unwinding the cocoons of the silkworm Bombyx mori requires a great deal of handling and processing, which makes it one of the most expensive fibers. Because of the presence of sericin, raw silk is rough, hard, brittle, rugged, and without luster. The traditional method for silk degumming is with Marseilles soap, which is very expensive. Today, with new ecological and economic requirements, there are new methods for silk degumming, such as degumming with enzyme or with polycarboxylic acid, degumming with alkalis or with water. Recently, acid agents with the purpose to enhance the physical properties of silk replace soap. In general, the action of alkali is more aggressive than the action of organic acid. Citric acid, compared to the other organic acids, is cheaper, proven lack of toxicity, and ready availability. The aim of this paper is to investigate the influence of citric acid and ultrasound on silk degumming. For this purpose, silk fibers were degummed by the classic procedure, and with different concentrations of citric acid (15 and 30%), with and without ultrasound. The efficiency of the degumming was determined by measuring degumming ration and mechanical properties (fineness, tenacity, and elongation at break) of untreated and treated silk yarn.

Keywords Silk degumming · Citric acid · Ultrasound · Properties

1 Introduction

Silk is one of the oldest fibers known to man called the "Queen of Fibers" for its luster, luxury appeal, comfort, elegance, sensuousness, and glamour. Silk is a natural animal fiber, mainly made of protein fibroin. The greatest significance is the silk produced by the mulberry silk moth Bombyx mori and a few others in the same genus, which is cultivated for obtaining silk [1, 2].

R. Brunsek · I. Schwarz (✉) · M. Than
Faculty of Textile Technology, University of Zagreb, Prilaz Baruna Filipovica 28a, 10000 Zagreb, Croatia
e-mail: ivana.schwarz@ttf.hr

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Raw silk fiber obtained by unwinding the cocoons of the silkworm Bombyx mori requires a great deal of handling and processing, which makes it one of the most expensive fibers. Because of the presence of sericin, raw silk is rough, hard, brittle, rugged, and without luster. Raw silk is composed mainly of sericin, fibroin, water, and mineral salts. The proportion of fibroin in raw silk is 70–82% by weight, and it is insoluble in hot water. The sericin, which covers fiber in raw silk, is a compound of proteins with gum-resilient properties and acts as a gum binder to maintain the structural integrity of the cocoon. In addition, the sericin is more water-soluble than fibroin, and it is easily removable from the filaments through various processes without considerable damage to the filaments [3].

Silk processing from cocoons to the finished clothing materials consists of a series of steps (reeling, weaving, degumming, dyeing or printing, and finishing), but two most important processes of silk are degumming and dyeing. The sericin, natural gum, protects the fibers from mechanical injury and its removing improves the softness, color, and gloss of silk. To remove the sericin is necessary to conduct a process called degumming.

After removing sericin, the silk fibroin fibers get good brightness with excellent elasticity (45%) and tenacity reducing (30%). Properties of silk such as handling, luster, and rubbing behavior primarily depend on the quantity of sericin remained on the silk fibroin which shows that the degumming process is thus very important [4–7].

The traditional method for silk degumming is with Marseilles soap, which is very expensive. Today, with new ecological and economic requirements, there are new methods for silk degumming, such as degumming with enzyme or with polycarboxylic acid, degumming with alkalis or with water [8]. Recently, acid agents with the purpose to enhance the physical properties of silk replace soap. In general, the action of alkali is more aggressive than the action of organic acid. Citric acid, compared to the other organic acids, is cheaper, proven lack of toxicity, and ready availability [8–11].

Ultrasound has been used in processes of textile industry, especially in the processes of wet finishing which reduces processing time, saving energy and chemical substance, and increase the quality of the product [12, 13]. Ultrasound, in the degumming process, relieves the removal of the substances existing on the raw silk like dirt and sericin [14].

Therefore, the aim of this paper is to investigate the influence of citric acid and ultrasound on silk degumming. For this purpose, silk fibers were degummed by the classic procedure, and with different concentrations of citric acid (15 and 30%), with and without ultrasound. The efficiency of the degumming was determined by measuring degumming ration and mechanical properties (fineness, tenacity, and elongation at break) of untreated and treated silk yarn.

2 Experimental

2.1 Testing Samples

Investigation was carried out on the mulberry silk fabric with basic parameters: plain weave; fabric density: warp—360 threads/10 cm, weft—300 threads/10 cm; fabric mass per unit area—226 g/m^2, and fabric thickness—0.33 mm.

2.2 Traditional Degumming

Silk fabric was traditional degummed at 80 °C for 2.5 h in the degumming solution containing 15% Marseilles soap, 1.5% sodium carbonate (Na_2CO_3), 0.05% nonionic detergent, and liquor ratio was 1:30. After degumming, the sample was treated at 80 °C for 5 min with 0.2% Na_2CO_3 to remove soap, which remains on the surface of the sample. Then, degummed samples were washed first with cold and then with warm water and finally dried immediately at 80 °C for 1 h, and then kept at room temperature for 48 h.

2.3 Citric Acid Degumming

Silk fabric was degummed in the degumming bath containing citric acid solutions at the concentration of 15 and 30%, respectively, and 0.2% nonionic detergent SVN at 80 °C for 2.5 h, and liquor ratio was 1:20 in laboratory apparatus with mechanical agitation.

2.4 Ultrasound Degumming

Silk fabric was degummed with and without ultrasound employing ultrasound unit tt. Elmasonic with ultrasound frequency 80 kHz and different media (water, 15% Marseilles soap, 15 and 30% citric acid) at constant temperature (80 °C) for 2.5 h.

Due to the analysis of the effectiveness of the different degumming processes, raw silk fabric was referred as untreated control sample, and silk fabric treated in water containing without soap and citric acid at the same treatment condition with and without ultrasound was referred as “Blank” sample.

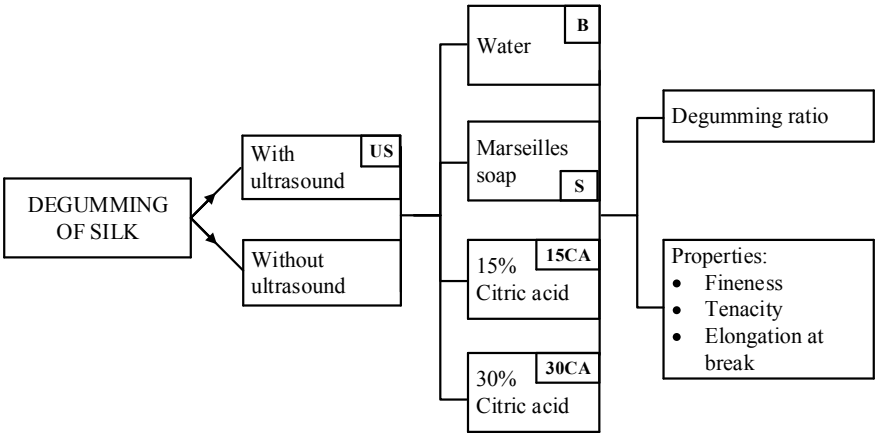

Fig. 1 Protocol of investigation of silk degumming

2.5 Determining the Treatment Efficiency

Determining of degumming ratio. Degumming ratio, i.e., the amount of sericin removed by different degumming treatment, was calculated from the weight loss of silk fiber before and after degumming treatment.

Determining of textile technology properties. Fineness (ISO 1973:1995), tenacity, and elongation at break (ISO 5079:1995) determined on tensile testers Vibroscop and Vibrodyn 400. Measurements of samples of tested properties were performed on conditioned samples.

The protocol of investigation was carried out as it is shown in Fig. 1.

3 Results and Discussion

A large number of measurements ($n = 50$) of the silk yarn properties are performed. Therefore, statistical indicators are shown: arithmetic mean ($\bar{X}$), standard deviation (σ), variation coefficient (CV), and practical limit of error (p_{gg}). The degumming ratio was calculated comparing silk fabric degumming in hot water with samples degumming with Marseilles soap, 15 and 30% citric acid solution with and without ultrasound. Differences (%) are expressed as percentages and are shown in Fig. 2.

The difference in loss of mass was established between the blank sample and samples treated with Marseilles soap, 15 and 30% citric acid solution. The degumming ratio of silk fiber treated with hot water, soap solution, 15 and 30% citric acid solution was 3.47, 18.56, 9.36, and 12.69%, respectively.

As expected, almost all of the sericin was removed after degumming with soap solution. Initially, the degumming ratio of silk fibers increased gradually with raising

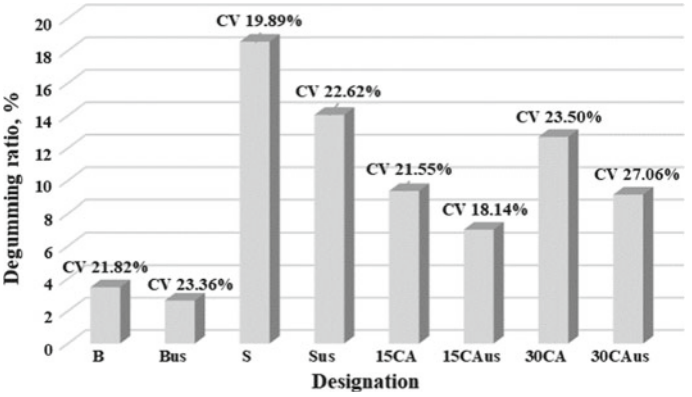

Fig. 2 Degumming ratio of degummed silk

Table 1 Fineness of silk yarn—warp and weft

Designation	$\bar{X}$ (dtex)	σ (dtex)	CV (%)	p_{gg} (%)	$\bar{X}$ (dtex)	σ (dtex)	CV (%)	p_{gg} (%)
	Without ultrasound				With ultrasound			
Warp								
N	196.6	45.9	23.4	6.5	196.6	45.9	23.4	6.5
B	186.5	54.1	29.0	8.0	220.7	87.9	39.8	11.0
S	184.2	49.8	27.1	7.5	251.7	116.3	46.2	12.8
15CA	194.2	57.9	29.4	8.1	222.2	77.6	34.9	9.7
30CA	193.3	41.7	21.6	5.9	225.6	96.5	42.8	11.9
Weft								
N	215.9	58.9	27.3	7.6	215.9	58.9	27.3	7.6
B	206.7	47.1	19.9	5.5	251.8	73.7	29.3	8.1
S	188.4	57.7	30.6	8.5	219.3	70.8	37.0	10.3
15CA	205.9	46.6	22.6	6.3	222.5	65.1	29.3	8.1
30CA	198.0	46.5	23.5	6.5	227.2	78.4	34.5	9.6
n	50							

the concentration of citric acid and the amount of residual sericin, which remains, on the raw silk fiber decreased with increasing citric acid concentration. After degumming with ultrasound, degumming ratio decreased, and amount of residual sericin on the raw silk increased in all treatments carried out.

Test results of fineness of silk yarn (Table 1) indicate a little change in silk yarn fineness, degummed without ultrasound, in relation to the untreated sample. The yarn becomes slightly finer. Comparing the degumming processes with and without ultrasound, results show that fineness of yarn degummed with ultrasound little bit increased which is in accordance with the results for degumming ratio.

Table 2 Tenacity of silk yarn—warp and weft

Designation	$\bar{X}$ (cN/tex)	σ (cN/tex)	CV (%)	p_{gg} (%)	$\bar{X}$ (cN/tex)	σ (cN/tex)	CV (%)	p_{gg} (%)
	Without ultrasound				With ultrasound			
Warp								
N	27.1	4.9	17.9	4.9	27.1	4.9	17.9	4.9
B	22.4	3.9	15.0	4.2	23.7	6.4	27.0	7.5
S	6.2	2.9	47.9	13.3	21.8	5.5	25.3	7.0
15CA	26.6	4.4	19.7	5.5	28.9	7.4	31.5	8.7
30CA	15.7	2.8	18.1	5.0	27.5	5.9	24.9	6.9
Weft								
N	21.6	3.7	16.9	4.7	21.6	3.7	16.9	4.7
B	20.4	3.8	16.4	4.6	20.7	4.8	23.2	6.4
S	9.4	3.9	41.6	11.5	11.6	4.2	35.9	9.9
15CA	20.9	3.6	16.6	4.6	24.9	5.9	23.8	6.6
30CA	16.2	3.5	21.8	6.1	24.2	4.8	19.9	5.5
n	50							

Morphological and structural changes have occurred after exposure of fibers to the ultrasound treatment. The fiber structure is loose, and cross-linking with citric acid is much better. Therefore, the cross-link distribution is uniform, and as a result, fiber fineness increased.

The analysis of the tenacity results, given in Table 2, of silk yarn after degumming without ultrasound shows significant variations in relation to the untreated sample. As expected, traditional degummed samples in the soap show a significant decrease in tenacity. It can be concluded that samples degummed with 15% citric acid have the lowest tenacity reduction, 1.8%, while samples degummed with 30% citric acid have tenacity reduction for 6.6%. The reason for tenacity reduction is the process of cross-linking that is performed in an acid medium (pH 2.5), which aggressively acts on fiber structure and damages fibers.

The results of ultrasound degumming indicate a positive impact of ultrasound on the mechanical properties of the silk yarns tested. During the ultrasound treatment, it occurred changes in the fiber structure and fiber tenacity increased. Because of ultrasound vibrations, the segment of macromolecules come close each other and forming new area with better-arranged structure and reduction of internal stresses.

Samples degummed with ultrasound loose less of their tenacity, while the loss of tenacity of samples degummed without ultrasound treatment is higher. By analyzing the obtained results, it is evident that tenacity of the yarn degummed with 15% citric acid and with ultrasound is increased for 6.2%, and samples degummed with ultrasound and 30% CA slightly increased for 1.5%.

In addition, the results of tenacity (Table 2) are in accordance with change of fineness (Table 1) and degumming ratio (Fig. 2) of silk yarn. It can be observed that

Table 3 Elongation at break of silk yarn—warp and weft

Designation	$\bar{X}$ (%)	σ (%)	CV (%)	p_{gg} (%)	$\bar{X}$ (%)	σ (%)	CV (%)	p_{gg} (%)
	Without ultrasound				With ultrasound			
Warp								
N	14.3	1.6	11.2	3.1	14.3	1.6	11.2	3.1
B	14.2	1.4	10.0	2.8	12.9	2.7	20.6	5.7
S	5.0	1.3	25.1	6.9	11.4	2.4	20.6	5.7
15CA	11.3	1.7	15.2	4.2	10.8	2.1	19.8	5.5
30CA	7.8	0.9	12.6	3.5	12.2	1.8	14.5	4.0
Weft								
N	17.2	2.2	12.6	3.5	17.2	2.2	12.6	3.5
B	15.0	1.7	11.1	3.1	13.3	2.1	15.6	4.3
S	5.2	1.5	29.1	8.1	5.7	1.5	25.7	7.1
15CA	10.9	1.5	14.1	3.9	13.1	2.6	19.8	5.5
30CA	7.8	1.1	14.4	4.0	12.4	1.5	12.4	3.4
n	50							

performed degumming silk with citric acid and with ultrasound have influenced fiber tenacity.

For all the samples, the elongation is continuously, but not significantly reduced what is shown in Table 3. The test results of the samples degummed with ultrasound have the lowest reduction of elongation at break in comparing with samples degummed without ultrasound.

4 Conclusion

The raw silk fabric was degummed with different concentration of citric acid and ultrasound to investigate their influence on silk degumming and mechanical properties. Based on the results of the investigations, which have been carried out under the same degumming conditions, with and without ultrasound, a positive effect of ultrasound treatment on the fineness of silk yarn cannot be confirmed with certainty.

However, a positive effect of ultrasound treatment during degumming on the tenacity of silk yarn should be pointed out. Samples degummed with ultrasound loose less of their tenacity, while the loss of tenacity of samples degummed without ultrasound treatment is larger. The results obtained by conducted treatments have shown that samples degummed with 15% citric acid, with or without ultrasound, have the lowest tenacity reduction.

It may be concluded that the use of ultrasound and citric acid, as an environmentally and economically acceptable degumming process in comparison with the

traditional method, results in a successful removal of sericin, with significant savings of time and energy.

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