Effect of Degumming Performed with Different Type Natural Soaps and Through Ultrasonic Method on the Properties of Silk Fiber

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ABSTRACT

Removal of sericin on the silk fibers is a surface modification process. Various chemical agents are used in the sericin removal process. In this article, effect of the sericin removal process performed in order to clear of the fiber surface from sericin through conventional and ultrasonic methods by using natural materials such as olive oil, daphne, turpentine soaps. The results obtained were examined with % weight loss values; bleaching properties, mechanical properties, morphological characteristics (SEM) followed by FT-IR. The most weight loss was observed in the sericin removal process performed with turpentine soaps through the ultrasonic method with a value of 28.9 %. Best results in terms of mechanical properties values and whiteness index values of the silk fibers were obtained in the ultrasonic method.

Key words: Olive oil soap, daphne soap, turpentine soap, degumming, conventional method, ultrasonic method, SEM

Introduction

Silk fiber is one of the most familiar, as well as being a very useful biopolymer and is universally acclaimed for most of the desirable properties of textile fiber: fineness, strength, elasticity, dyeability, softness, flexibility, smooth feeling, luster, elegance, grace and high rating [1,2].

Raw silk is composed of 22-25 % sericin, 62.5-67 % fibroin, water and mineral salts. Fibroin is a single protein that does not dissolve in the water and that has a fibrillar structure. As for sericin, it is available on the fiber and has an amorphous structure and this gummy protein dissolve in the water much more than the fibroin [3,4,5]. Thus, it is easy to remove this gum through various processes without causing any serious harm to the fiber [6,7].

Sericin hides the brightness and whiteness of the silk as well as causing it to have a hard handle. It also prevents its dyeability. Therefore, sericin existing on the silk fiber is made to dissolve by being hydrolyzed through different methods and with degumming agents [4,8]. Some degumming processes have been developed such as water, soap, soap-alkali boiling, enzymatic processes and boiling in the acidic solutions.

The most recommended method for degumming is the method where Marseille soap made out of olive soap is used. However, Marseille soap is rather expensive, it is generally sodium stearate based and its nonstandard household type productions are available [4]. Soap used in the degumming process blows sericin and then removes it from the filament by emulsifying it in the degumming bath [6,7]. Furthermore, combination of soap and alkali is not an environment-friendly method [6,7,9,10,11].

The textile industry uses large volumes of water in different wet processes and, therefore, produces enormous amounts of textile wastewater which is heavily charged with unconsumed dyes and other chemicals.

Ultrasonic sound waves have frequencies that human beings can not hear. While human ear can perceive sound waves between 16 Hz-16kHz, ultrasonic sound waves have a frequency range between 20kHz-20MHz. Power of the ultrasonic energy indicates its chemical effect through the cavitation event. As any sound wave, ultrasonic energy is also transmitted through the waves. These waves create compression and relaxation in the molecular structure of the medium through which they pass. When a sufficient amount of negative pressure is applied to the liquid, degradation is observed in the liquid and cavitation bubbles appear. In the successive compression periods, these bubbles crash to one another and generates a great amount of energy [12]. The use of ultrasonic energy in the textile wetting processes provides benefits in terms
of treatment time length, energy and chemical substance savings and increase of the product quality. An increase is observed in the mass transfer from the liquid to the solid material as a result of the cavitation emerging in the solid/liquid interface [13]. For the industrial use of the ultrasonic energy, such issues as the homogeneity and ultrasonic pressure distribution in the bath, position of the transducers, transition pattern of the fabric through the machine and bath temperature are attributed importance as regards to the machine design [14]. Ultrasound applications have high potential in such industries as chemistry, textile and leather [15,16]. Ultrasonic method enables an effective clearance in the degumming process and it facilitates the removal of the substances existing on the raw silk like dirt and sericin.

In enzymatic degumming, special proteins that have minimum effect on fibroin are used. With the use of these proteins, sericin dissolves through biological degradation. These substances are biodegradable and they eliminate the necessity to use soap in the enzymatic processes. Thus, dyeing-related non-level problems caused by the metallic soaps are also eliminated.

It is stated that enzymatic treatment especially increases the affinity of the reactive dyestuffs against silky material [17]. It is asserted that alkaline and neutral proteases are effective in degumming process and degumming kinetics depends on the enzyme dosage and treatment time length [4]. Enzymatic method is a controlled process as it has the capability to enter into reaction with the specific points of sericin [11].

In order to reduce the risk of environmental pollution from such wastes, it is necessary to treat them properly before discharging to the receiving environments.

In this study, sericin removal process was performed through the conventional and the ultrasonic methods by using the olive oil, turpentine and daphne soaps.

### Material and Method

#### 2.1. Material:

Silk fibers used in this research were specially produced in the province of Bursa of Turkey. They were conditioned 48 hours prior to testing under 20±2 °C and 65±2 RH% condition. Properties of the fibers are indicated in the Table 1.

<table>
<thead>
<tr>
<th>Table 1: Properties of the silk fibers.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stiffness (dtex)</td>
</tr>
<tr>
<td>Tensile strength (cN/tex)</td>
</tr>
<tr>
<td>Elongation (%)</td>
</tr>
</tbody>
</table>

#### 2.2. Chemical Treatments of Silk Fibers:

Silk fibers were exposed to two different methods. Experimental details of the conventional and the ultrasonic methods of the degumming process are given below.

##### 2.2.1. Conventional Method:

In the study, Polimat HT Sample Dyeing Machine (Type A11612N-Emsey) was used. A treatment of 60 minutes was conducted at 95°C at a 1/30 flotte ratio with marsille, daphne and turpentine soap solutions prepared at 0.7 % ratio with distillate water. At the end of the process, test samples were washed for 5 minutes in 1.5L hot water and then rinsed for 5 minutes in 1.5L cold water.

##### 2.2.2. Ultrasonic Method:

Ultrasonic method Branson B2200B E4 was carried out at (220 volt and 205 Watt) ultrasonic bath with 20 kHz frequencies. A treatment of 20 minutes was conducted at 60°C at a 1/30 flotte ratio with marsille, daphne and turpentine soap solutions prepared at 0.7 % ratio with distillate water. At the end of the process, test samples were washed for 5 minutes in 1.5 L hot water and then rinsed for 5 minutes in 1.5 L cold water.

##### 2.3. Determination of the Weight Loss:

Raw and degummed fibers used in the experiments were conditioned under laboratory conditions and then, average weight was determined by making 5 measurements for each test sample according to ASTM D5848-10E1[18]. Weight loss was found by measuring the weight difference between the untreated samples and the samples treated with soaps of different origins. After the treatment, samples were dried in the drying oven at 95°C until they reached to the fixed weighting. Weight loss was calculated and the initial weight was indicated as %. Amount of the weight loss was calculated with the following formula:

\[
\%WL = \frac{W_1 - W_2}{W_1} \times 100 \quad \text{Equation (1)}
\]

WL: Weight loss  
W₁ : Raw Silk Weight  
W₂ : Degumming Silk Weight
2.4. Testing and Characterization of Silk Fibers after Chemical Treatments:

Applying the conventional, microwave energy and ultrasonic energy methods on silk fibers (single fiber length is 250 mm), mechanical characteristic values were determined based on ASTM D 3822 with Instron 4411 (50 N load, speed of 10 mm/min) resistance device [16]. Besides, morphological properties were analyzed by JEOL JSM-5410 LV operated at 20 kV.

3. Results:

3.1. Effect of ultrasound on silk degumming:

It was observed that more weight loss occurred in the sample where degumming process was performed through the ultrasonic energy technique with the olive oil soap. It was detected that degumming processes performed through the ultrasonic energy technique by using the other soap types did not have an important effect on the weight loss. Ultrasonic energy had a positive effect on the increase of the tensile strength and elongation values.

3.2. Weight Loss:

Weight losses occurring in the surface processes applied to silk fiber through 2 different methods and with 3 different natural soaps are indicated in the Figure 1 by percentages.

![Weight Loss Graph](image)

**Fig. 1:** Weight loss properties as a result of the degumming process performed with conventional and ultrasonic methods.

When the weight loss ratios of the process performed with conventional method are evaluated in terms of methodology, they are seen within the limits specified in the literature [20].

However, degumming processes performed with all of three natural soaps yielded good results in both the conventional and the ultrasonic energy methods and a great amount of sericin was removed. In the degumming process conducted through the ultrasonic energy method, time was shortened, weight loss increased, a contribution was made to the amount of the water that was used. Positive effect and power of the environment-friendly ultrasonic energy method became clear with sonication [21, 22, 23].

3.3. Mechanical Properties:

When the changes in the resistance properties at the end of the degumming process performed through the conventional and the ultrasonic energy methods by using the daphne soap, turpentine soap and olive oil soap are evaluated according to Figure 2, resistance properties of the treated silk fibers are higher than the untreated fibers. An overall decrease is observed in the resistance values at the end of the degumming processes conducted through the conventional and the ultrasonic energy methods. The reason of this decrease is the removal of the sericin and thus the emerging weight loss. This decrease observed in the resistance values is less in the degumming process performed with the ultrasonic energy method. Moreover, H bonds order in the polymer chain structure of the silk fibers is not distorted due to sonication effect thanks to the microwave energy and even the order in the beta chain structure of the silk fiber is not distorted. This effect is more obvious to be observed in the turpentine soap.
An overall increase is observed in terms of elongation values when the Figure 3 is analyzed. This increase results from the fact that the fibers possess a more amorphous structure after the removal of the sericin. This effect can also be attributed to the amino acid groups of the polymer chain. This is because of the positive effect of the turpentine soap on the resistance properties and the fact that ultrasonic energy creates a perfect cavitation in the water.

3.4. Degree of Whiteness:

% Remission values measurement of the dyed samples was performed through Datacolor Spectra Flash 600 plus reflectance spectrophotometry according to CMC 2:1 CIELab and CIELch system. Color measurements were conducted by using D65 light source with 10° observer. Degrees of whiteness were calculated with Berger Whiteness formula [24] with the use of remission values. Measurements of the raw silk fibers and those undergoing a degumming process through the conventional and microwave energy methods with different soaps were performed in the spectrophotometry at 10 nm range for 400-700 nm wavelengths and % Remission values of the samples are given in the Table 2. Degrees of whiteness determined according to Berger Whiteness Index Formula with the use of % Remission values are also indicated in the Figure 4.

It is already known that an overall increase is observed in the remission percentages obtained at the end of the removal of the sericin through the conventional and the ultrasonic methods when compared to the untreated materials (Table 2 and Figure 4). Perfect increases are observed in the remission values when the treatment is performed through the ultrasonic energy rather than the conventional method. Beside to the increase in the remission values obtained with each of the three soaping, an additional positive increase is observed in the remission values obtained at the end of the degumming performed through the ultrasonic method with the turpentine soap.
Table 2: % Remission values obtained at the end of the degumming process performed through the conventional and ultrasonic methods

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Untreated</th>
<th>Olive Oil Soap</th>
<th>Daphne Soap</th>
<th>Turpentine Soap</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional</td>
<td>Ultrasonic</td>
<td>Conventional</td>
<td>Ultrasonic</td>
</tr>
<tr>
<td>400</td>
<td>73.35</td>
<td>76.56</td>
<td>76.83</td>
<td>76.69</td>
</tr>
<tr>
<td>420</td>
<td>76.59</td>
<td>79.42</td>
<td>79.87</td>
<td>79.33</td>
</tr>
<tr>
<td>440</td>
<td>79.38</td>
<td>81.70</td>
<td>82.41</td>
<td>81.54</td>
</tr>
<tr>
<td>460</td>
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<td>84.54</td>
<td>83.38</td>
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<tr>
<td>480</td>
<td>83.82</td>
<td>85.03</td>
<td>86.17</td>
<td>84.82</td>
</tr>
<tr>
<td>500</td>
<td>85.42</td>
<td>86.28</td>
<td>87.51</td>
<td>85.95</td>
</tr>
<tr>
<td>520</td>
<td>86.61</td>
<td>87.27</td>
<td>88.49</td>
<td>86.78</td>
</tr>
<tr>
<td>540</td>
<td>87.49</td>
<td>88.02</td>
<td>89.17</td>
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</tr>
<tr>
<td>560</td>
<td>88.23</td>
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<td>89.76</td>
<td>87.91</td>
</tr>
<tr>
<td>580</td>
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<td>600</td>
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</tr>
<tr>
<td>640</td>
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<td>660</td>
<td>90.37</td>
<td>90.13</td>
<td>91.21</td>
<td>89.42</td>
</tr>
<tr>
<td>680</td>
<td>90.74</td>
<td>90.42</td>
<td>91.54</td>
<td>89.73</td>
</tr>
<tr>
<td>700</td>
<td>91.28</td>
<td>90.89</td>
<td>92.02</td>
<td>90.24</td>
</tr>
</tbody>
</table>

Fig. 4: Degrees of Whiteness obtained at the end of the degumming process performed through the conventional and the ultrasonic methods.

3.5. SEM Observation of Silk Fibers:

Sem photographs of the untreated silk fibers are seen in the Figure 9 and Figure 10. In the Figure 11 and Figure 12, removal of the sericin through different methods by using the daphne soap is indicated, in Figures 13 and 14, removal of the sericin through different methods by using the turpentine soap and in the Figures 15 and 16, removal of the sericin through different methods by using the olive oil soap are indicated.

If a degumming process is insufficient and incompatible, residual sericin should appear as deposits on the surface of the filaments and nonuniformity over the surface of the yarn must be observed [25]. When an overall assessment of the SEM photographs is made, it is observed that degumming processes performed with the ultrasonic energy are more successful than those performed through the conventional method. Power of the ultrasonic energy became clear once more in the surface morphology. Sericin of the exterior surface was removed completely. In the light of the other results, it was found out that sericin layer available on the exterior surface was removed completely in the ultrasonic energy method where the turpentine soap was used and the fibrillary structure of the silk fiber became more apparent.

Conclusion:

In the degumming processes conducted through both the conventional and ultrasonic energy methods with three different natural soaps, degumming process performed with the turpentine soap yielded positive results in terms of weight loss, whiteness degree and mechanical properties. Ultrasonic energy method yielded the best positive results in the degumming processes performed with the turpentine soap. The reason of the success of the ultrasonic energy processes is the strength that is achieved by Sonication. Thanks to Sonication, ultrasonic energy process provides both energy and time saving. In this study, % weight loss increase is outstanding with the success of ridding the impurities. Weight loss results can be correlated with mechanical test results, which can be regarded as a proof for more enhanced
interfacial interactions with ultrasonic energy than the conventional method.

When the conventional method is replaced by sonicator process in the degumming process with natural soaps, we can demonstrate an example of cleaner production. In order to ensure long-term benefit of individual factory in abating groundwater pollution, the overall steps have been as follows:

- Environment-friendly natural soaps were used instead of synthetic based soaps.
- Conventional method was replaced by the ultrasonic energy method and the process was made energy-saving and economical.

Moreover, beyond all results, it is rather evident that chemical substance, energy, water and time savings are provided thanks to the environment-friendly ultrasonic energy method.

Fig. 9: Untreated silk fibre.

Fig. 10: Untreated silk fibre.

Fig. 11: Treated silk fibre with laurel soap by conventional process.

Fig. 12: Treated silk fibre with laurel soap by ultrasonic process.

Fig. 13: Treated silk fibre with turpentine soap by conventional process.

Fig. 14: Treated silk fibre with turpentine soap by ultrasonic process.
Fig. 15: Treated silk fibre with olive oil soap by conventional process.

Fig. 16: Treated silk fibre with olive oil soap by ultrasonic process.

References

18. ASTM D5848-10E1, “Standard Test Method for Mass Per Unit Area of Pile Yarn Floor Coverings”.