STUDY ON THE INFLUENCE OF DEGUMMING TECHNOLOGICAL PARAMETERS ON SELF-DYED SILK

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Abstract - In this study, Marseille soap and Na_2CO_3 are used for self-dyed silk degumming and evaluated the influence of technological parameters on the degumming efficiency and color intensity of self-dyed silk. Self-dyed silk results from a new dyeing method; this is a green and without-water dye. Its mechanism is based on feeding silkworms with mulberry leaves supplemented by the Rhodamine B dyestuff; colored silk was then treated at different concentrations and time treatment. Xrite color i5 colorimeter, Scanning Electron Microscope (SEM), and Fourier transform infrared spectroscopy (FT-IR) were respectively used to evaluate the color intensity, the treatment efficiency, and the structural characterization of self-dyed silk. The results show that the higher the solution concentration and treatment time, the higher the weight loss ratio and the lower the color intensity. In addition, degumming with Na_2CO_3 retains the color of silk better than it with Marseille soap. The results are also for reference in selecting the appropriate treatment process for this new material.

Key words - Colored-silk; self-dyed silk; degumming; Marseille soap; Na_2CO_3

1. Introduction

With sustainability in fashion, eco-friendly materials, such as fabrics derived from natural or eco-treatment processes, are the most practical choice in the garment industry. Among them, the dyeing process is one of the pollutions causes [1-3]. The greening of the dyeing process has been researched and applied extensively in the textile industry, including research on natural dyes, dyeing by ultrasonic waves, and air dyeing [4, 5]. The self-dyed method, which uses fewer water resources and has no discharge, is also a method with great potential. Silk from silkworms has been a valuable material for textiles and garments for thousands of years until nowadays. A silk filament released from a silkworm has a structure of two filaments (fibroin) accounting for about 66-88% of the silk fiber composition, surrounded by a gum called sericin for about 11-32% [6]. Some studies on self-dyed silk have also been reported and show the feasibility and potential of this technology. Self-dyed silk is created based on the biological mechanism of silkworms after being fed dyes, then becomes self-dyed silk fabrics and used in apparel [6 - 8].

Usually, the degumming processes will remove the sericin of raw silk to increase softness, shine, and elasticity, then be dyed. Degumming with hot water, soap, alkaline, acid, enzymes, supercritical CO_2, ultrasonic pressure, and microwave ovens has been researched and developed recently [9, 10]. Although there are still limitations on environmental issues such as water and chemicals used, wastewater and chemical free, soap and alkali are still commonly used in silk degumming because of their feasibility and sound properties of the degummed silk [11–15]. In the self-dyed case, degumming self-dyed silk goes against the normal silk treatment process and reduces degummed self-dyed silk's color intensity. Kanita et al. [16] reported that the color intensity of self-dyed silk decreased after being treated with various degumming methods such as soap, alkaline, acid, and enzyme. However, more detailed reports on the influence of parameters on degummed self-dyed silk's intensity have yet to report.

Currently, studies on self-dyed silk treatment methods are limited. This paper presents the survey results of self-dyed silk by two popular methods: Marseille soap and Na_2CO_3. The results could evaluate the influence of technological parameters on the degumming efficiency and color intensity of self-dye silk, thereby selecting the appropriate treatment process for this new material.

2. Materials and Methods

2.1. Materials

Raw self-dyed silk (RS) from colored cocoons released by silkworms when tested by the method of feeding silkworms with mulberry leaves supplemented with the colorant Rhodamine B (RhB) (Figure 1); this is a commonly used colorant in the industry for fabric dyeing purposes. The RS sample used in this study was cultured and tested at the concentration of 1500 ppm pigment at Bao Loc silkworm farming facility - Lam Dong, Viet Nam.

Chemicals and machine: Na_2CO_3 (99%, Xilong-China), Marseille soap (France); Auto-chroma IR infrared dyeing machine - Mesdan Italia was used for degumming.

Figure 1. *a) Self-dyed silkworms and b) Self-dyed cocoons*

2.2. Methods

2.2.1. Silk degumming

Degumming with Na_2CO_3: Auto-chroma IR infrared dyeing machine - Mesdan Italia was used for degumming with the recipe: Na_2CO_3 at different concentrations (0.25 g/L and 0.5 g/L), L:R value of 30:1, 90°C in 30, 60 and 90 minutes. Treated samples were washed with water and dried by the drying chamber Mesdan at 70°C for 10 minutes.

Degumming with Marseille soap: Auto-chroma IR infrared dyeing machine - Mesdan Italia was used for de-gumming with the recipe: Marseille soap (MS) at different concentrations (2.5 g/L and 5 g/L), L:R value of 30:1, 90–95°C in 30, 60 and 90 minutes. Treated samples were washed with water and dried by the drying chamber Mesdan at 70°C for 10 minutes.

Degumming efficiency: Evaluate the degumming efficiency of colored silk by assessing the percent weight loss as the following formula:

$$Weight\ loss = \frac{M_0 - M_1}{M_0} \times 100\ (\%)$$

Where M_0 and M_1 are the weights of the raw silk and degummed silk.

Color intensity: The color intensity of raw and degummed silk was determined by using an X-rite Color i5 Benchtop Spectrophotometer. The K/S value is a function of color depth and is calculated according to Munk's Kubelka equation as below:

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

Where: R is the Reflectance value.

2.2.2. Morphological structure

The morphology of degummed silk fibers was observed with scanning electron microscopy (SEM) (S–4800, Hitachi, Japan) at Chemical Technology Institute, Vietnam.

2.2.3. FT-IR analysis

Fourier-transform infrared spectroscopy (FT-IR-Jasco 4700, Japan) was used for the analysis of components of silks at the Chemical Technology Institute, Vietnam. Measurement was done within the spectral range 400 – 4000 cm^{-1}.

3. Results and Discussion

3.1. Effect of concentrations and time treatment on degumming efficiency

Degumming efficiency is assessed by the weight loss percentage of treated samples, equivalent to the amount of sericin removed from silk.

A common degumming is a process that hydrolyze the sericin, breaking the peptide linkage of amino acid into small molecules and ultimately dissolving the sericin; it uses water and degumming agent such as soap, alkali, synthetic detergent, or organic acid [6].

Soap is an anionic surfactant used in conjunction with water for washing and cleaning. The fats and oils used in soap-making come from animal or plant sources (Fat + NaOH → glycerol + sodium salt of fatty acid–soap) [24]. Soaps are alkaline majorly, the degumming action of soap solution is due to the alkaline formed on hydrolysis of soap and then produced soda salt [25]. The swollen sericin was separated by the soap in the bath and dissolved in water due to the emulsification action of the soap [14]. By Na_2CO_3, hydrolysis of sodium carbonate in an aqueous solution gives hydroxide ions. Hence, the solution is alkaline; it is absorbed to $COO{-}Na^+$ and gets solubilized, then the alkali sericin compound undergoes progressive decomposition in combination with more alkali. The presence of Na^+ results in the formation of the sodium salt of the amino acids containing COOH groups, which are soluble and removed. In addition, the OH groups of serine may also be converted to $O{-}Na^+$, increasing sericin solubility [17].

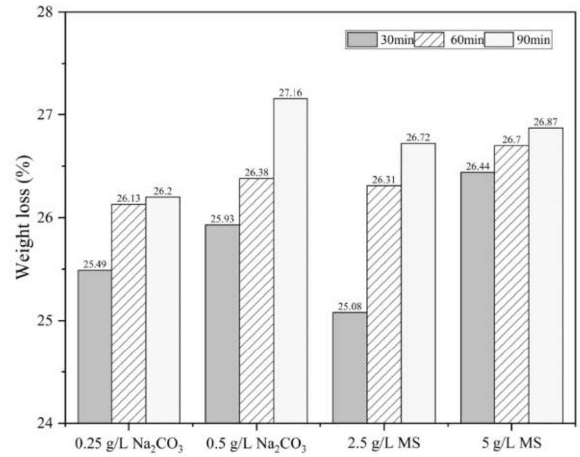

Figure 2. *Degumming efficiency of degummed self-dyed silk*

Figure 2 displayed the degumming efficiency; the weight loss was lowest at the treatment concentration of 0.25 g/L Na_2CO_3 (25.49 %) and 0.25 g/L MS (25.08 %) treated in 30 minutes, highest at the concentration of 0.5 g/L Na_2CO_3, (27.16 %) and 5 g/L MS (26.87 %) treated in 90 minutes. It shows that higher concentrations and longer times of treatment lead to better sericin removal. Besides, the results also showed that silk degummed with Na_2CO_3 or MS gave a similar weight loss ratio. In addition, various studies reported that silk treatment had good results with Na_2CO_3, applied at 0.5 g/L or MS at 5 g/L, treated in 90 minutes at 90ºC [18-21].

3.2. Effect of concentrations and time treatment on color intensity

Figure 3 displayed the visual external color of raw and treated self-dyed silk results from the different degumming methods. The treatment increased the gloss but decreased color intensity. Treated silk with Na_2CO_3 resulted in higher color intensity than MS. On the other hand, Figure 3b shows the pink color sample from RhB dyestuff, indicating that the remaining color molecules are bound to the fibroin of silk.

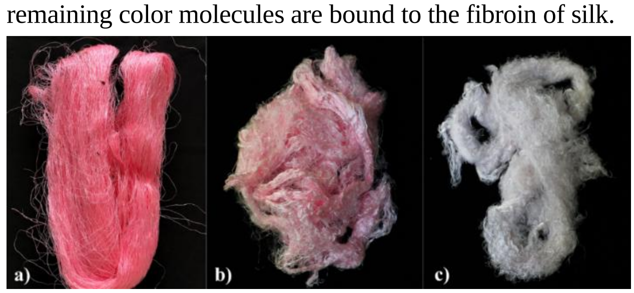

Figure 3. *a) Raw self-dyed silk; b) Degummed with Na_2CO_3, (0.5 g/L, 90 min); c) Degummed with Marseille soap (5 g/L, 90 min)*

The color intensity (K/S) used to evaluate the amount of pigment present in silk is shown in Figure 4, peaking at 540 wavelengths. At high concentrations (0.5 g/L Na_2CO_3 or 5 g/L MS) treated in 90 minutes, the color intensity decreased the most; that is because of some of the removal of dyestuffs in the silk along with sericin during the degumming process.

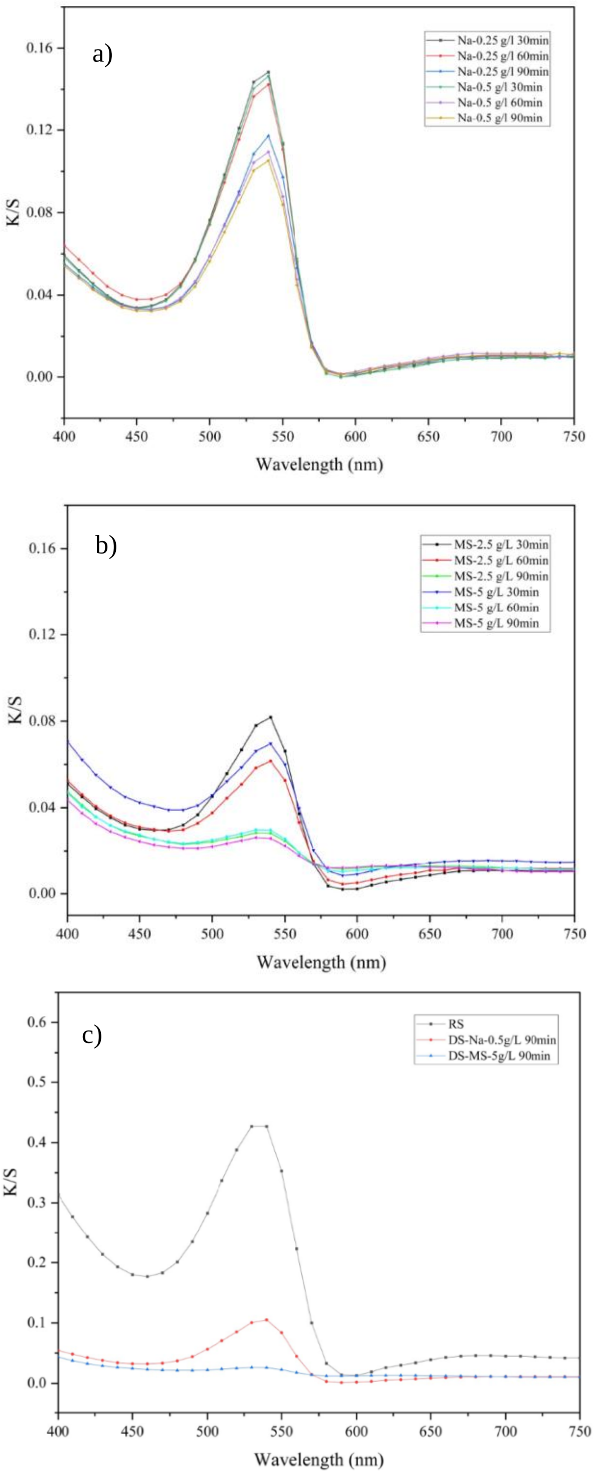

Figure 4. *Color intensity (K/S) of: (a) DS at various Na_2CO_3 concentration and time; (b) DS at various Marseille soap (MS) concentration and time; (c) raw silk (RS), degummed silk with Na_2CO_3 (DS-Na) and degummed silk with Marseille soap (DS-MS)*

Soaps hydrolyze in high temperatures to give free alkali and "acid soap." The scouring action of soap upon silk could be divided into two parts: First, the degumming action removes sericin from raw silk. Second, soap solution effect on degummed silk, fibroin also absorbs 'acid soap' in soap degumming solution, causing variation in silk color [14], which affected degummed self-dyed silk's color intensity in this case, more than Na_2CO_3 treatment.

The results also show that concentration and treatment time in both methods is inversely proportional to the color intensity of self-dyed silk.

3.3. Morphology of silk fibers

The degumming process removed sericin that covered two fibroin filaments. Observation of the morphology and fiber surface allows for evaluating the degumming process's effect on self-dyed silk.

SEM images (Figure 5) show that the sericin is removed and makes the surface smoother. Moreover, there is no damage to the fibroin composition of degummed silk fibers with two different degumming methods. Figures 5a and 5c show that the silk surface is still rough, and debris of sericin is distributed along the fiber axis when degumming at low concentrations and fewer times. That is different from the case of higher concentrations. Observing Figures 5b and 5d could see a smooth silk surface, rarely the appearance of sericin particles. It shows that the higher concentration of Na_2CO_3 and MS, specifically at 0.5 g/L Na_2CO_3 or 5 g/L MS, the higher the efficiency of removing sericin. However, higher concentrations can damage silk fiber, as some studies have reported previously [21]. In addition, there was no important difference among the degumming approaches used in this study.

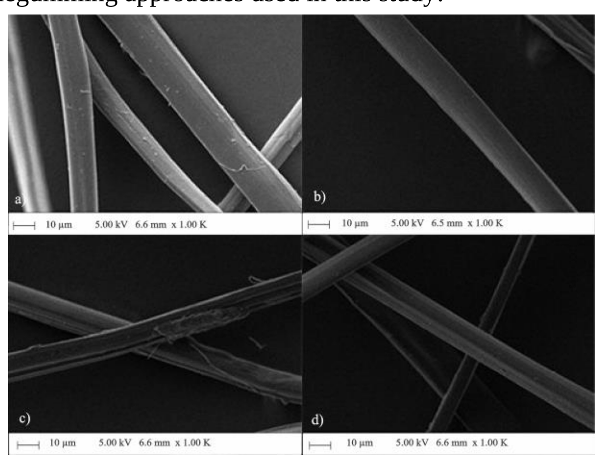

Figure 5. *SEM image of a) Degummed silk with Na_2CO_3 0.25 g/L-30min; b) Degummed silk with Na_2CO_3 0.5g/L -90min; c) Degummed silk with MS 2.5g/L-30min, d) Degummed silk with MS 5.0g/L-30min*

3.4. Fourier infrared spectroscopy

FT-IR evaluated the effect of degumming on the molecular structure of silk fiber. Figure 6 shows the spectrum of raw and degummed silk. The strong absorption at the band 1053 cm^{-1} (C–OH stretching), 1398 cm^{-1} (C–H and O–H bending), and 3500-3200 cm^{-1} (O–H stretching) of raw silk are due to the side chains of serine, which is up about 30% of the amino acids of sericin [22].

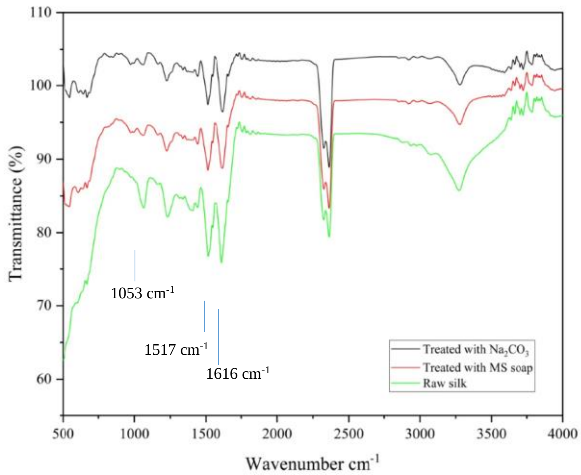

Figure 6. *FT-IR of raw and degummed self-dyed silk*

Their intensity decreased after treatment, indicating a decrease of sericin in degummed silk. The peak at 1517 cm^{-1} (N–H) corresponds to amide II, and the peak at 1616 cm^{-1} (stretched C=O) corresponds to amide I, assigned to β-sheet (crystalline). These are two characteristic peaks of silk [23] observed clearly on treated samples, demonstrating that both degumming methods do not damage the molecular structure of self-dye-silk.

4. Conclusions

The results show higher the solution concentration and treatment time, the higher the weight loss ratio and the lower the color intensity, specifically at 0.5 g/L Na_2CO_3 or 5.0 g/L MS treated in 90 minutes. To remove sericin from self-dyed silk, both methods using Na_2CO_3 and MS yield similar results. However, degumming with Na_2CO_3 retains the color of silk better than it with MS. In addition, the decreation of the color intensity of degummed silk also helps to guide applications for different types of self-dyed silk, such as raw-organza, half-degumming, or "lustre" silk. Based on the different physical and mechanical properties (especially gloss and shedding) of various silk types, they're applied for many purposes in Textile production. In order to limit the wet treatment such as degumming, bleaching, weight gain, etc., self-dyed silk fabrics are suggested to be used in raw type; research on the application of raw self-dyed silk fabric for clothes has been reported. Finally, this paper serves as a reference for self-dyed silk degumming technology parameters to create different types of silk fabrics with different color intensities.

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