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The Effect of Fixing Agents and Softner on Sericin Fixation of Trimethylolmelamine

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트리메틸올멜라민의 세리신 정착에 있어 정착제와 유연제의 영향

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Abstract The fixing behaviors of raw silk yarns treated with melamine and formaldehyde at a molar ratio of 1:3 for trimethylolmelamine were investigated. Sericin was fixed during the fixing process, but a part of sericin I was removed simultaneously by hot water. The weight losses by fixing and the degumming losses by degumming greatly decreased with increasing concentrations of melamine and formaldehyde. The silk yarns fixed with 0.011 M melamine and 0.033M formaldehyde were significantly degummed due to the insufficient fixation of sericin and the alkaline hydrolysis of sericin by sodium carbonate during the degumming process. On the other hand, the silk yarns fixed with 0.055M melamine and 0.165M formaldehyde were degummed slightly (the degumming losses of 3-8%) due to the strong fixation of sericin, which might result from the many cross-linkages between the sericin I molecules, which were formed by trimethylolmelamine. Those fixed with the fixing solution containing 15% owf softener showed the lowest weight and degumming losses because under the condition of 15% owf softener, the cation of the softener can effectively form ionic bonds with the negatively charged side chain of aspartic acid in sericin. In addition, van der Waals' forces may be also formed between the hydrophobic tail of the softener and the hydrophobic region of sericin, which may help inhibit the removal of sericin I.

요 약 트리메틸올멜라민에 의한 세리신 정착 거동을 고찰하기 위해 멜라민과 포름알데하이드를 몰 비 1:3으로 세리신정착액을 조성하여 실크 생사를 정착시켰고, 정련에 의해 세리신 정착 거동을 살펴보았다. 정착 과정에서 세리신의 정착이 일어나는 동시에 열수에 의해 세리신 I의 일부가 제거되었다. 정착 중의 감량과 정련에 의한 연감율은 멜라민과 포름알데하이드의 농도가 증가할수록 크게 감소했다. 0.011몰 멜라민과 0.033몰 포름알데하이드로 정착한 실크 생사는 불충분한 정착과 탄산나트륨에 의한 세리신의 알칼리 가수분해로 인해 많은 정련이 일어났다. 그러나 0.055몰 멜라민과 0.165몰 포름알데하이드로 정착한 실크 생사는 강한 세리신 정착으로 인해 3-8%의 매우 적은 연감율을 보였는데 이는 트리메틸올멜라민에 의해 세리신 I 분자 간에 많은 가교결합이 형성되었기 때문으로 사료된다. 또한 15% owf 유연제의 정착액으로 처리한 경우 정착에 의한 감량과 정련에 의한 연감율이 가장 작게 나타났는데 이는 유연제의 양이온이 세리신 중의 아스파르트산의 음이온과 이온결합을 형성하고 유연제의 소수부와 세리신의 소수성 영역 간에 반데르바알스력이 형성되어 세리신 I의 제거가 다소 억제된 것으로 사료된다.

Keywords : cross-linking, degumming, fixing sericin, formaldehyde, melamine, silk, trimethylolmelamine

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1. Introduction

The raw silk of the mulberry silkworm is composed of two major types of fibroin and sericin. Sericin constitutes about 23 % of raw silk, is hot water-soluble glycoprotein, and holds two fibroins together. Sericin is easily hydrolyzed. By hydrolyzation, the long protein molecule of sericin is broken down into smaller fractions which are easily dispersed and soluble in hot water. As the major amino acids groups in sericin is hydrophilic, the treatment of hot water destroys the hydrogen bonds between sericin molecules so that sericin dissolves into the water during the degumming process [1,2]. Sericin has been divided into various species based on relative solubilities. Four fractions of sericin are also designated by other researchers depending on their dissolution behaviour as sericin I, II, III, and IV [3,4].

In previous studies on sericin fixation using various N-hydroxymethylated compounds, it was found that the method of fixing sericin with melamine and formaldehyde was very effective. Melamine and formaldehyde showed an outstanding ability to fix sericin because of the cross-linking of sericin by the three methylol groups of trimethylolmelamine formed by the methylolation of melamine with formaldehyde [5,6].

This study was performed to investigate the effects of fixing agents containing a softener of cationic surfactant on sericin fixation of melamine and formaldehyde in a molar ratio of 1:3.

2. Experimental

2.1 Materials

The raw silk yarn (21 denier, China) bundles were prepared by folding 25 cm yarns in half. Melamine and formaldehyde (35% formalin) were in the first grade. Acetic acid and sodium carbonate were also in the first grade. The cationic surfactant was a commercial textile softener whose brand name was Pigeon (Pigeon Ltd., Korea) and the synthetic detergent was a commercial detergent whose brand name was Hanspoon (LG Household & Health Care Ltd., Korea).

2.2 Sericin Fixation

The raw silk yarn bundle was weighed before fixing sericin, and it was treated with the fixing solutions of melamine and formaldehyde in a molar ratio of 1:3 in order to fix sericin. The fixation of sericin was performed at a liquor-to-fiber weight ratio of 50:1, at a set temperature, and for a set time as shown in Figure 1. The silk yarn bundle was washed with water at 40℃ for 10 minutes followed by rinsing with cold water after fixing sericin. The treated silk yarn bundle was dried at 80℃ for 30 minutes in a hot-air drying machine, and it was weighed. The weight change of the silk yarn bundle which was treated with fixing solution was defined as next equation:

$$\text{Weight change by fixing (\%)} = \frac{WF_t - WF_0}{WF_0} \times 100$$

where WF_t was the weight of silk yarns after fixing sericin and WF_0 was the weight of raw silk yarns before fixing sericin.

2.3 Degumming

Degumming of sericin-fixed silk yarns was carried out in the degumming solution of detergent and sodium carbonate at 80℃ for 30 minutes at a liquor-to-fiber weight ratio of 50:1. The process of fixing sericin and degumming the sericin-fixed silk yarns was shown in Figure 1.

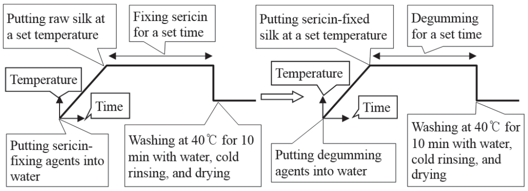

Fig. 1. The process of fixing sericin and degumming the fixed silk yarns.

The degummed silk yarns was washed with water at 40℃ for 10 minutes followed by rinsing with cold water after degumming. After washing, it was dried at 80℃ for 30 minutes in a hot-air drying machine and was weighed. The degumming loss of the silk yarns which was treated with degumming solution was defined as next equation:

$$\text{Degumming loss (\%)} = \frac{WD_0 - WD_t}{WD_0} \times 100$$

where WD_0 was the weight of raw silk yarns before fixing sericin and degumming, and WD_t was the weight of silk yarns after degumming.

3. Results and discussion

3.1 Melamine and formaldehyde

Figure 2 shows the weight changes of raw silk yarns by fixing sericin with various concentrations of melamine and formaldehyde in a molar ratio of 1:3 at 80℃ for 60 minutes and the degumming losses of sericin-fixed silk yarns by degumming with 15% owf detergent and 10% owf sodium carbonate at 80℃ for 30 minutes after sericin fixation.

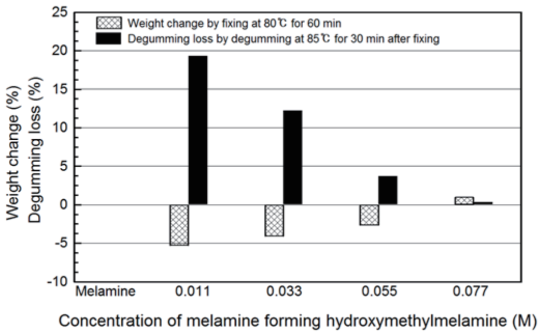

Fig. 2. Weight change of raw silk yarns by fixing sericin with various concentrations of melamine and formaldehyde in a molar ratio of 1:3 at 80℃ for 60 minutes, and degumming loss of sericin-fixed silk yarns by degumming with 15% owf detergent and 10% owf sodium carbonate at 80℃ for 30 minutes.

The weight loss (i.e. the additive inverse of weight change) of raw silk yarns by fixing sericin with 0.011M melamine and 0.033M formaldehyde was about 5% due to the removal of sericin by hot water during the fixing process.

Sericin consists of significant amounts of serine (about 38%) along with aspartic acid (about 15%) [7]. It was reported that the sericin of raw silk fiber exists in 4 different forms classified as sericin I, II, III, and IV based on their solubility in hot water [8,9]. Sericin I is the outermost layer of sericin and sericin IV adheres fibroin. The order of solubility in hot water decreased from outer to inner layer. Thus, the weight losses occurring during fixing sericin were caused by the removal of sericin I due to hot water.

In sericin which is a globular protein, most hydrophobic amino acids may be located among twisted chains deep within the molecule, and by contrast, polar and charged amino acids tend to occupy positions on the outside surface, where they contact the surrounding water molecules. Thus, polar and charged amino acids attract water molecules and promote to dissolve sericin.

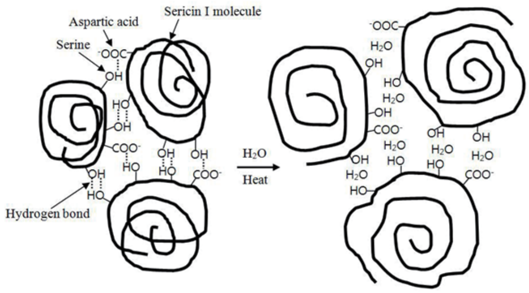

Fig. 3. Schematic description on the predictable cleavage of the hydrogen bonds between sericin I molecules in hot water.

Figure 3 shows that the polar side chains of serine and the negatively charged side chains of aspartic acid occupy the positions on the outside surface of sericin I. The molecular conformation of sericin I is random coil and attracts water molecules. The hydrogen bonds between sericin molecules are broken by water molecules and subsequently sericin molecules are swollen by water to dissolve easily in hot water. These may be the reason for the weight losses occurred during the fixing process.

But as shown in Figure 2, the weight losses decreased with increasing concentrations of melamine and formaldehyde. The weight of silk yarns fixed with the aqueous fixing solution of 0.077M melamine and 0.231M formaldehyde rather increased slightly more than that of raw silk yarns due to the large amounts of fixing agents to form trimethylolmelamine which could effectively fix sericin enough to endure hot water.

The degumming loss by fixing with 0.011M melamine and 0.033M formaldehyde was about 19%. This result may be caused by the insufficient and incomplete fixation of sericin due to the relatively small amounts of fixing agents. The degumming losses greatly decreased with increasing concentrations of melamine and formaldehyde. Especially the silk yarns fixed with 0.077M melamine and 0.231M formaldehyde were hardly degummed, which may be caused by the sufficient and strong fixation of sericin.

3.2 Cationic softener in fixing solution

Cationic softener in the fixing solution might bind by electrostatic attraction to the negatively charged groups on the surface of sericin and neutralize their charge, and the long aliphatic chains of softener might be then oriented towards the outside of the fiber. Thus, in this study, the effect of softener in fixing solution on the fixation of sericin was investigated.

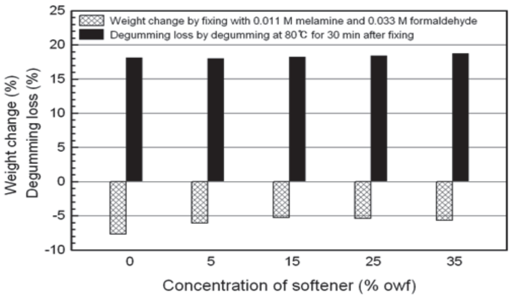

Fig. 4. Weight change by fixing with 0.011M melamine and 0.033M formaldehyde containing 25% owf acetic acid and various concentrations of softener at 80℃ for 60 minutes, and degumming loss by degumming with 15% owf detergent and 10% owf sodium carbonate at 80℃ for 30 minutes after fixing sericin.

Figure 4 shows the fixing and degumming behaviors of raw silk yarns fixed with 0.011M melamine and 0.033M formaldehyde containing 25% owf acetic acid and various concentrations of softener at 80℃ for 60 minutes and subsequently degummed with 15% owf detergent and 10% owf sodium carbonate at 80℃ for 30 minutes.

Even though the differences between the weight changes according to the concentration of softener were small (weight losses of 5-8%), the fixation with the fixing solution containing 15% owf softener showed the lowest weight loss. This indicates that 15% owf softener in the fixing solution can be a little bit effective in restraining the removal of sericin during the fixing process. However, the degumming losses by degumming the sericin-fixed silk yarns were in the range of 18-19% regardless of the concentration of softener. It is expected that the large amount of sericin may be hydrolyzed by sodium carbonate in the degumming solution because of the insufficient and incomplete fixation of sericin due to the relatively small amounts of fixing agents (Figure 5).

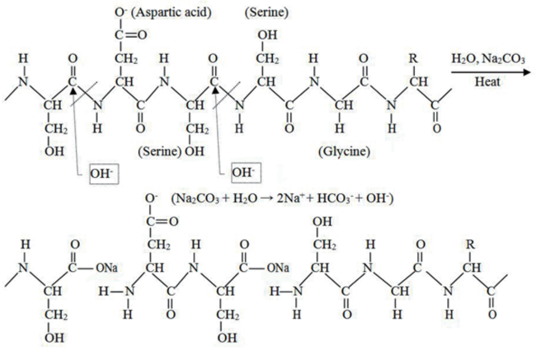

Fig. 5. Predictable mechanism for the alkaline hydrolysis of sericin in hot water containing sodium carbonate during the degumming process (symbol R stands for a side chain of amino acids).

Figure 6 shows the fixing and degumming behaviors of raw silk yarns which were fixed with 0.055M melamine and 0.165M formaldehyde containing 25% owf acetic acid and various concentrations of softener at 80℃ for 60 minutes and degummed with 15% owf detergent and 10% owf sodium carbonate at 80℃ for 30 minutes.

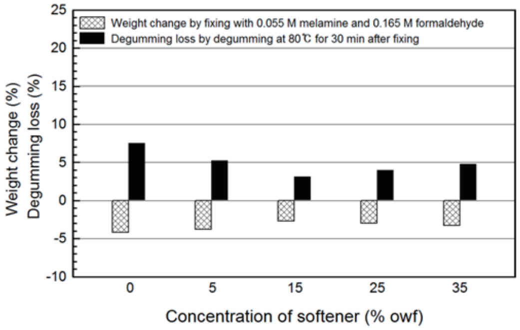

Fig. 6. Weight change by fixing with 0.055M melamine and 0.165M formaldehyde containing 25% owf acetic acid and various concentrations of softener at 80℃ for 60 minutes, and degumming loss by degumming with 15% owf detergent and 10% owf sodium carbonate at 80℃ for 30 minutes after fixing sericin.

The weight changes by fixing sericin showed small weight losses of 2-4% by comparison with the fixation of sericin with 0.011M melamine and 0.033M formaldehyde. Also, the silk yarns fixed with 0.055M melamine and 0.165M formaldehyde were slightly degummed by below 8% due to the strong fixation of sericin. The silk yarns fixed with the fixing solution containing 15% owf softener showed the lowest degumming loss, which might result from the low weight loss and the effective sericin fixation during fixing process.

Figure 7 shows the predictable interactions between sericin I molecules and cationic softener in fixing solution. Cationic softeners tend to be based on quaternary ammonium salts with one or two long alkyl chains [10]. Quaternary ammonium cation of softeners can be attracted at the negative site of fiber to form ionic bond [11]. The cation of softener forms ionic bond with negatively charged side chain of aspartic acid in sericin. And van der Waals' forces are also formed between the hydrophobic tail of softener and the hydrophobic region of sericin. It was expected that these interactions could slightly restrain the removal of sericin I in the fixing solution containing 15% owf softener during the fixing process.

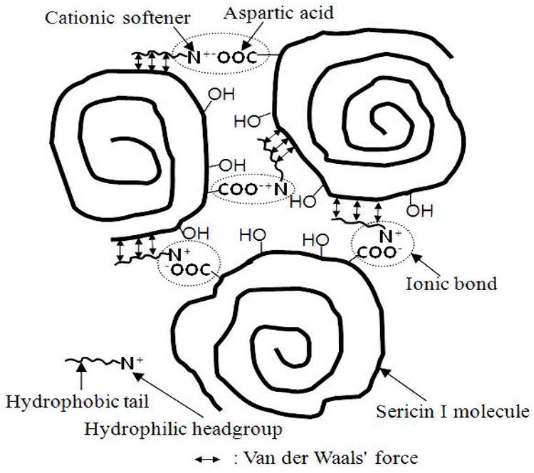

Fig. 7. The predictable interactions between sericin I molecules and cationic softener in fixing solution.

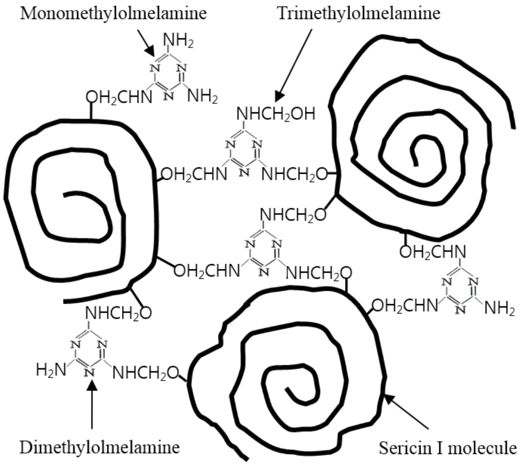

Fig. 8. The predictable cross-linking of sericin I molecules with hydroxymethylated derivatives of melamine and formaldehyde in a molar ratio of 1:3.

Figure 8 shows the cross-linking of sericin I molecules with hydroxymethylated derivatives (mono-, di-, and tri-methylolmelamine) of melamine produced by hydroxymethylation of melamine with formaldehyde. It was commonly predicted that the hydroxymethylation of melamine with formaldehyde in a molar ratio of 1:3 might mainly produce trimethylolmelamine [12,13]. The hydroxyl group of serine in sericin links up with the methylol group of methylolmelamine under loss of a molecule of water [14].

In the case of fixing sericin with 0.055M melamine and 0.165M formaldehyde, as shown in Figure 6, 65-87% of sericin (degumming losses of 3-8%) was fixed because the many cross-linkages between sericin I molecules were formed by trimethylolmelamine.

4. Conclusions

When raw silk yarns were fixed with various concentrations of melamine and formaldehyde in a molar ratio of 1:3 and then the sericin-fixed silk yarns were degummed with detergent and sodium carbonate, the silk yarns fixed with 0.011M melamine and 0.033M formaldehyde were significantly degummed because of the insufficient fixation of sericin and the alkaline hydrolysis of sericin, but those fixed with 0.055M melamine and 0.165M formaldehyde were slightly degummed due to the strong fixation of sericin resulted from the many cross-linkages of sericin I molecules by trimethylolmelamine. Fixing sericin with the solution containing 15% owf softener showed the lowest weight and degumming losses due to the interactions such as ionic bond and van der Waals' forces between sericin I and softener.

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