

## Effect of Processing Conditions on the Homogeneity of Partially Degummed Silk Evaluated by FTIR Spectroscopy

Hyun Ju Kim, Da Eun Chung, and In Chul Um\*

Department of Bio-fibers and Materials Science, Kyungpook National University, Daegu 702-701, Republic of Korea

### Abstract

The partial degumming of silk has recently attracted researchers' attention because of its ability to produce silk textiles with new tactile properties, intermediate between the softness of fully degummed silk and the hardness of raw silk. However, it is difficult to obtain partially degummed silk in a homogeneously degummed state due to the heterogeneous character of sericin removal. It is also difficult to examine the homogeneity of degumming. In the present study, Fourier transform infrared (FTIR) spectroscopy with attenuated total reflection (ATR) geometry was used to evaluate the effect of processing conditions on the degumming of silk yarns. The crystallinity index, calculated from FTIR spectra, showed an increase with the degumming ratio. Therefore, the homogeneity of degumming could be evaluated by the variation of crystallinity index for 30 different spots in silk yarns. The homogeneity of degumming was influenced by the total degumming time, the content of surfactant, and the liquor rate. No effect was observed upon changing the number of degumming cycles at the same total degumming time.

© 2013 The Korean Society of Sericultural Sciences  
Int. J. Indust. Entomol. 26(1), 54-60 (2013)

Received :  
18 March 2013  
Accepted :  
25 March 2013

**Keywords:**  
Silk, Partial degumming,  
FTIR, Crystallinity  
index, Homogeneity of  
degumming

### Introduction

Silk is an excellent textile material due to its high mechanical strength, excellent luster, and good touch feeling. Therefore, many researchers have tried to create silk-like fibers. Silk is composed of two proteins, fibroin and sericin; the removal of sericin, by degumming, improves the luster and handle of silk fabric. However, recently, raw silk without degumming has also attracted the attention of

consumers and researchers. This is because raw silk containing sericin is cool and can be utilized as a good textile material for summer clothing.

Partially degummed silk has been investigated in order to produce a textile whose handle is intermediate between the soft silk fibroin (fully degummed silk) and the hard raw silk (non-degummed silk). Lee *et al.* (2003) performed partial degumming of silk and found that both the abrasion resistance and the drape coefficient of silk decreased with

### \*Correspondence :

Hyun Ju Kim

Department of Bio-fibers and Materials Science, Kyungpook National University, Daegu 702-701, Republic of Korea

Tel: +82-53-950-7757 / FAX: +82-53-950-6744

E-mail: icum@knu.ac.kr

<http://dx.doi.org/10.7852/ijie.2013.26.1.054>

© 2013 The Korean Society of Sericultural Sciences

increasing degumming ratio. They also reported that sericin fixing was required in the case of partially degummed silk fabrics, due to their low colorfastness. Park (2010) conducted partial degumming of silk using soap and alkali solutions, and demonstrated the difficulties involved in dissolving and removing sericin homogeneously from the surface of raw silk.

This uneven degumming of silk is due to the fact that silk is a naturally produced material. Sericin is removed heterogeneously from raw silk during the degumming. Ko *et al.* (2013) controlled the degumming ratio of silk to produce regenerated silk with different residual sericin content. They observed the morphology of silk fibers as a function of degumming ratio (or residual sericin content). Scanning electron microscopy (SEM) revealed that sericin is removed from silk heterogeneously. That is, some areas of silk fiber retained large amounts of sericin, whereas other areas exhibited nearly complete elimination of sericin. This heterogeneous response to processing is common to natural materials, including cotton and wool. In the case of wool, when its cuticle scale is removed using formic acid and ultrasonication, the scale is removed heterogeneously, resulting in wool fibers with some areas completely free of scale and other areas showing normal scale (Bae and Um, 2012).

Thus, the heterogeneous degumming of silk yarn is a main obstacle in the development of partially degummed silk products. It is therefore necessary to improve the homogeneity of degumming. To detect and measure the degumming of silk, a simple and effective evaluation method is needed.

Fourier transform infrared (FTIR) spectroscopy is a powerful tool to investigate the structure and conformation of silk polymers (Chen *et al.*, 2001; Ko *et al.*, 2010; Kweon *et al.*, 2001, Sonyama *et al.*, 1997). In the present study, we demonstrate that the homogeneity of sericin removal can be detected using FTIR spectroscopy with attenuated total reflection (ATR) geometry. Also, we examine the effect of processing conditions on the homogeneity of degumming, in order to provide preliminary guidelines for improving partial sericin removal from silk yarns.

## Materials and Methods

### Degumming

Silk yarns were degummed with purified water at 100°C for 10~60 min. After the degumming was completed, the degummed silk yarns were rinsed thoroughly in warm purified water to remove extra surface-associated sericin, and then dried. The purified water was obtained using a water purification system (RO50, Hana Science, South Korea) with a reverse osmosis membrane. To examine the effect of a surfactant, we used the non-ionic surfactant sorbitan monostearate (Span 60, Tokyo Chemical Industry Co., Ltd, Japan). The dry mass of the silk yarns was measured using a moisture analyzer (XM60, Precisa, Swiss).

The degumming ratio was calculated using the following equation:

$$\text{Degumming ratio (\%)} = \frac{1 - (\text{dry mass of degummed cocoons} / \text{dry mass of native cocoons})}{1} \times 100.$$

### FTIR measurement and determination of crystallinity index

FTIR-ATR spectra were obtained on a FTIR spectrometer (Nicolet 380, Thermo Fisher Scientific, USA). The crystallinity index was calculated as the intensity ratio of the 1260 and 1235 cm<sup>-1</sup> peaks in the FTIR spectrum, using the following equation (Bhat and Nadiger, 1980).

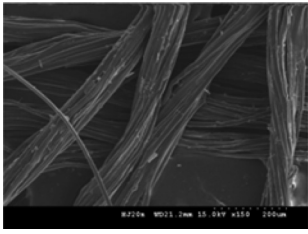
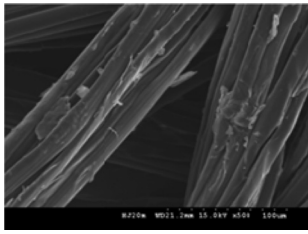
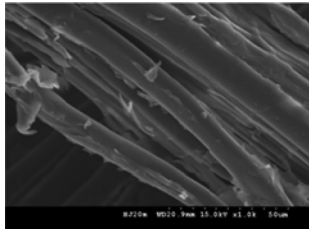
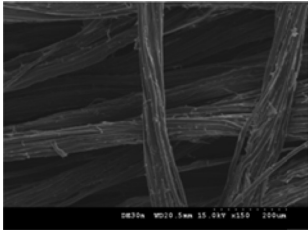
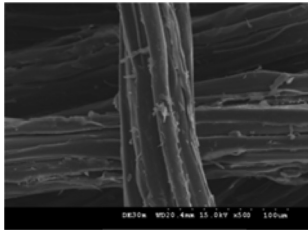
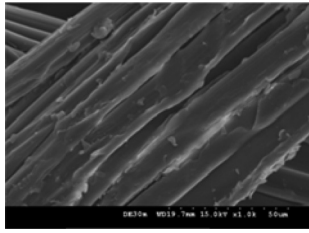
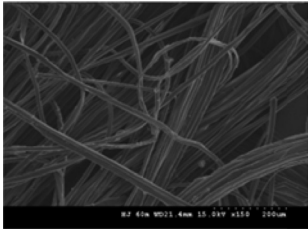
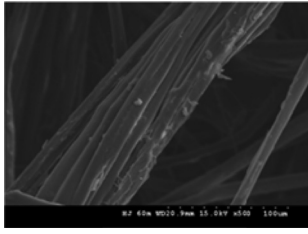
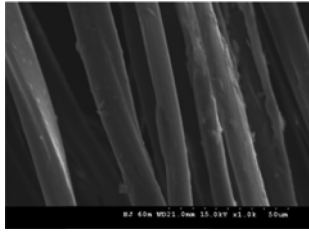
$$\text{Crystallinity index (\%)} = \frac{A_{1260\text{cm}^{-1}}}{A_{1235\text{cm}^{-1}}} \times 100$$

$A_{1235\text{cm}^{-1}}$ : Absorbance at 1235 cm<sup>-1</sup>

$A_{1260\text{cm}^{-1}}$ : Absorbance at 1260 cm<sup>-1</sup>

To determine the average and variation of the crystallinity index, FTIR measurement was performed at 30 different points along each silk yarn sample.

Table 1. SEM images of degummed silk yarns with different degumming ratios and magnifications.

Magnification / Degumming ratio	150x	500x	1000x
6.8%			
10.4%			
11.3%			

## SEM observation

The morphology of the degummed silk yarns was observed by field emission SEM (FE-SEM, S-4300, Hitachi, Japan) after silver coating.

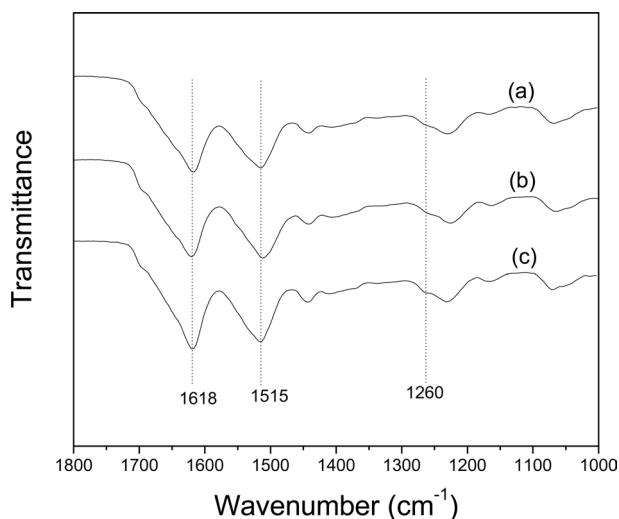
## Results and Discussion

### FTIR for determination of degumming homogeneity

Table 1 shows SEM images of degummed silk yarns with different degumming ratios, at different magnification. Although sericin removal from silk yarns can be confirmed by SEM observation, using this method it is almost impossible to evaluate the homogeneity of degumming, owing to the short

dimension range that can be observed by SEM. Although the images in Table 1 are taken over a wide range of magnifications, from 150× to 1000×, it is difficult to observe a sufficiently large area of the sample to evaluate homogeneity, under magnification that is high enough to detect sericin removal. That is, in the case of high magnification (1000×), sericin removal is clearly evident but the field of view is too small to evaluate the sample's homogeneity. For low magnification (150×), the field of view is still not large enough to evaluate homogeneity, and the sericin removal cannot be determined exactly. Thus, we conclude that SEM cannot be used to determine the homogeneity of degumming.

Fig. 1 shows FTIR spectra of degummed silk yarns with different degumming ratios and degumming time. All samples showed strong absorption peaks at 1618  $\text{cm}^{-1}$  and 1515  $\text{cm}^{-1}$  in the amide I and II bands,

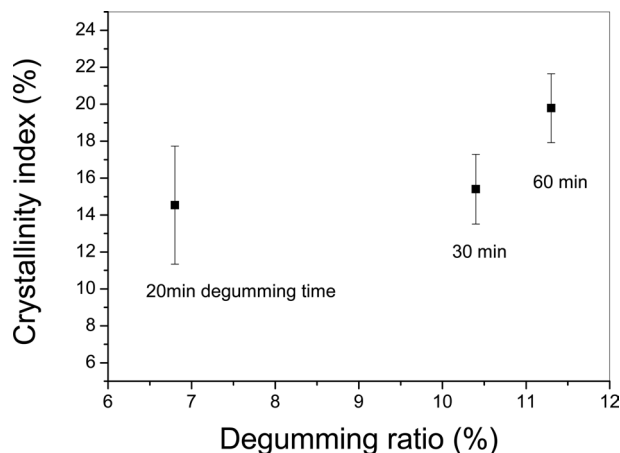


**Fig. 1.** FTIR spectra of silk yarn processed with different degumming ratios and degumming time: (a) 6.8 % (20 min degumming time), (b) 10.4 % (30 min) and (c) 11.3 % (60 min). Degumming was conducted with boiling purified water without other degumming agents.

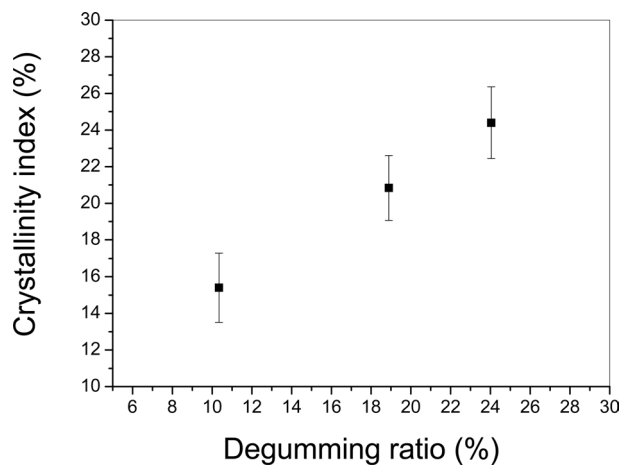
respectively. Also, a shoulder at 1260  $\text{cm}^{-1}$  appeared in the amide III band. These peaks and shoulder correspond to  $\beta$ -sheet crystallites of silk (Um *et al.*, 2001; Um and Park, 2007). The shoulder on the amide III peak became more evident by increasing degumming time and degumming ratio.

To examine the crystallinity of degummed silk with different degumming ratios, the crystallinity index was calculated from the FTIR spectra. The results are shown in Fig. 2. As the degumming ratio was increased, the crystallinity index also increased. Fig. 3 indicates similar trend among yarns processed at different degumming ratios and degumming conditions. The increased crystallinity index of degummed silk yarns may be related to the removal of sericin. In raw silk, sericin is amorphous, whereas silk fibroin is a highly crystalline material. Therefore, removal of the amorphous sericin increases the total crystallinity index of the silk (fibroin + sericin).

More importantly, Fig. 2 and Fig. 3 show that the crystallinity index of degummed silk yarn varies depending on the degumming conditions. In the



**Fig. 2.** Crystallinity index of silk yarns processed with different degumming ratios and degumming times. Degumming was conducted with boiling purified water without other degumming agents.



**Fig. 3.** The effect of degumming ratio on the crystallinity index of silk yarns degummed with different conditions.

present study, FTIR spectra of silk yarns were obtained using ATR geometry. Because a very small area of the silk sample is probed during each FTIR-ATR measurement, many different sites on the same silk yarn sample can be studied. FTIR spectra taken at different points along the degummed silk yarns can report upon the homogeneity of the degumming. In our study, 30 different points along degummed silk yarns were measured with FTIR-ATR and the corresponding crystallinity index was calculated from the FTIR spectrum of each point.

Because the crystallinity index is positively related to the degumming ratio, the variation among the 30 values of crystallinity index indicates the variation in degumming ratio along the silk yarn sample. A higher variation in the crystallinity index means that the degree of sericin removal (or degumming ratio) is more heterogeneous. The variation in the crystallinity index of degummed silk yarns was thus utilized to evaluate the homogeneity of degumming.

### Effect of degumming conditions on the homogeneity of degumming of silk

Fig. 2 also shows the effect of degumming time on the crystallinity index of silk yarns degummed with boiling purified water without any degumming agent. The variation of crystallinity index (i.e., height of the error bars) is the highest at a degumming time of 20 min, and was reduced with increasing degumming time. This result implies that the homogeneity of degumming is improved with increasing degumming time. For the degumming of silk, the silk yarn is first wetted, and the penetration of water into the silk yarns then dissolves the sericin. Evidently, 20 min is not sufficient for homogenous degumming of silk, considering (1) that degumming times of 30 min and 60 min resulted in a lower variation in crystallinity index than was observed after 20 min of degumming and (2) that the variation in crystallinity index remained nearly constant between degumming times of 30 and 60 min. This means that at least 30 min of degumming with hot purified water is necessary for homogeneous degumming of silk yarns.

For the same total period of degumming (30 min), a different number of degumming cycles can also be performed. That is, the silk yarns can be degummed for 30 min at once, or subjected to three 10-min cycles of degumming. Fig. 4 shows the effect of the number of degumming cycles on the homogeneity of degumming, for the same total degumming time (30 min). The crystallinity index of the two samples was quite similar, and the variation of crystallinity index remained almost constant with the number of

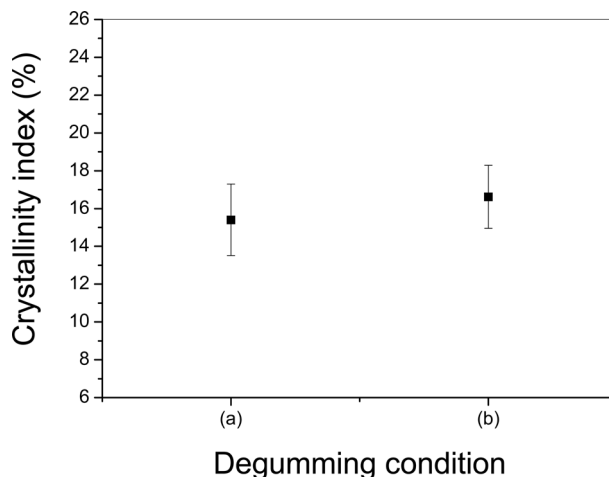
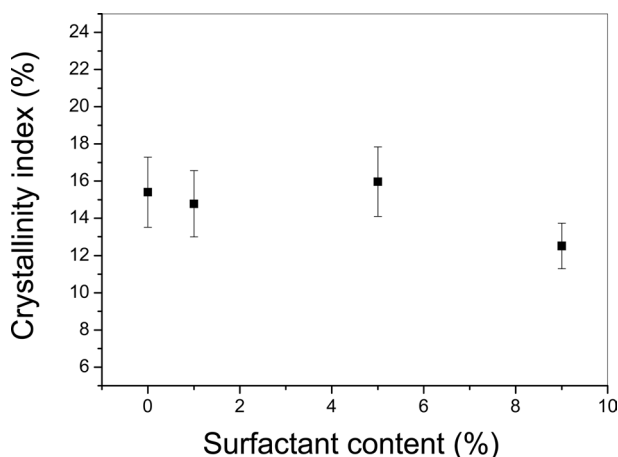


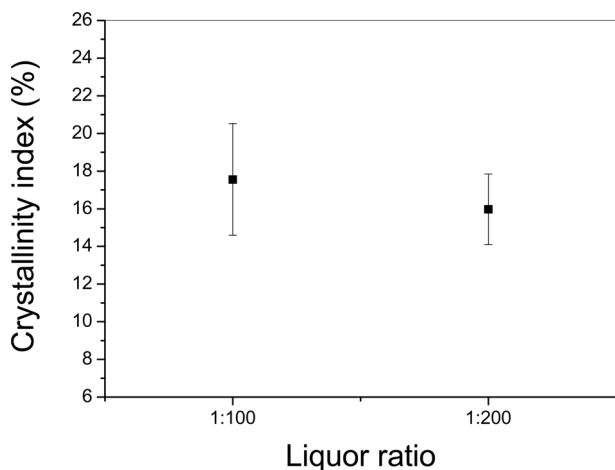
Fig. 4. Crystallinity index of degummed silk yarns upon changing the number of degumming cycles: (a) 30 min degumming performed once, and (b) 10 min degumming repeated three times. Degumming was conducted with boiling purified water without other degumming agents.

degumming cycles, indicating no significant effect on the degumming ratio and the homogeneity of degumming.

Controlling the penetration of water and degumming agents into silk yarn is also important for homogeneous degumming of silk. Surfactants have been used as wetting agents because of their ability to reduce the surface tension of a solid sample in the liquid medium. Therefore, it is expected that surfactant might improve the wetting of silk yarn during degumming, and thus, improve the homogeneity of degumming. Silk yarns were degummed in boiling purified water with different amounts of nonionic surfactant (sorbitan monostearate); the variation in their crystallinity index is shown in Fig. 5. Up to 5% surfactant, the crystallinity index variation showed nearly no change. However, when the content of surfactant was increased up to 9%, the crystallinity index showed less variation, implying that the homogeneity of degumming was improved. This result indicates that specific amounts of surfactant can help improve the homogeneity of silk degumming. Because the surfactant acts as a wetting agent for silk yarns, the hot water can penetrate the silk yarns evenly and remove the sericin



**Fig. 5.** Effect of surfactant content (% o.w.f.) on the crystallinity index of silk yarns degummed with boiling sorbitan monostearate (surfactant) aqueous solutions. The degumming time was 30 min.



**Fig. 6.** Effect of liquor ratio on the crystallinity index of silk yarns degummed with boiling 5% (o.w.f.) sorbitan monostearate aqueous solution. The degumming time was 30 min.

in a homogeneous manner.

The degumming of silk yarns can also be affected by the liquor ratio, which indicates the ratio of silk yarn to degumming solution. Fig. 6 shows the effect of liquor ratio on the crystallinity index variation of degummed silk yarns. As the liquor ratio was changed from 1:100 to 1:200, the crystallinity index varied to a lesser extent, indicating an improvement in degumming homogeneity. Increasing the relative

amount of hot water, which acts as a solvent for sericin, improves the accessibility of hot water into the silk yarn. In contrast, as less water (or degumming bath) is used in degumming, silk yarns become more closely assembled and the hot water becomes less accessible to the silk yarns. Thus, a lower liquor ratio (a larger volume of water) can be helpful to promote homogeneous degumming of silk yarns.

This study demonstrates that the crystallinity index calculated from FTIR-ATR spectra of silk yarns is positively related to their degumming ratio, and it can be a powerful and convenient method for evaluating the homogeneity of silk degumming. The silk yarns were degummed under various conditions, including degumming time, number of cycles, amount of surfactant, and liquor ratio. The homogeneity of the silk yarn was improved by increasing the total degumming time, the content of surfactant, and the liquor ratio, whereas the homogeneity did not change upon increasing the number of cycles at the same total degumming time.

## Acknowledgement

This work was supported (Grant No. C0055432) by Business for Cooperative R&D between Industry, Academy, and Research Institute funded by Korea Small and Medium Business Administration in 2012.

## References

- Bae CH, Um IC (2012) The effect of ultrasonication on the micro-splitting of wool fiber. *Fiber Polym* 13, 943-947.
- Bhat NW, Nadiger GS (1980) Crystallinity in silk fibers: Partial acid hydrolysis and related studies. *J Appl Polym Sci* 25, 921-932.
- Chen X, Shao ZZ, Marinkovic NC, Miller LM, Zhou P, Chance MR (2001) Conformation transition kinetics of regenerated Bombyx mori silk fibroin membrane monitored by time-resolved FTIR spectroscopy. *Biophys Chem* 89, 25-34.

- Ko JS, Lee KH, Bae DG, Um IC (2010) Miscibility, structural characteristics, and thermal behavior of wet spun regenerated silk fibroin/nylon 6 blend filaments. *Fiber Polym* 11, 14-20.
- Ko JS, Yoon K, Ki CS, Kim HJ, Bae DG, Lee KH, Park YH, Um IC (2013) Effect of degumming condition on the solution properties and electrospinnability of regenerated silk solution. *Int J Biol Macromol* 55, 161-168.
- Kweon H, Ha HC, Um IC, Park YH (2001) Physical properties of silk fibroin/chitosan blend films. *J Appl Polym Sci* 80, 928-934.
- Lee EM, Lee HJ, Yoo HJ (2003) The physical properties and dyeability of degummed and sericin fixed silk fabrics. *J Kor Soc Cloth Text* 27, 517-523.
- Park GY (2010) Half-degumming Behaviors of Raw Silk Yarns Degummed with Soap and Alkalis. *Text Color Finish* 22, 349-355.
- Sonyama M, Miyazawa M, Katagiri G, Ishida H (1997) Dynamic FT-IR spectroscopic studies of silk fibroin films. *Appl Spec* 51, 545-547.
- Um IC, Kwon H, Park YH, Hudson S (2001) Structural characteristics and properties of the regenerated silk fibroin prepared from formic acid. *Int J Biol Macromol* 29, 91-97.
- Um IC, Park YH (2007) The effect of casting solvent on the structural characteristics and miscibility of regenerated silk fibroin/poly(vinyl alcohol) blends. *Fiber Polym* 8, 579-585.