STRUCTURAL CHARACTERIZATIONS OF THREE-DIMENSIONAL CRIMPED SILK YARNS

by

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Silk yarns which are composed of two single yarns with different twist directions are treated with calcium nitrate solution at 95 °C, and a 3-D crimped structure is formed. The Fourier transform infrared spectroscopy spectrum is used to reveal the change of the secondary structures of silk fiber.

Key words: *3-D crimped silk yarn, Fourier transform infrared spectroscopy, secondary structure, twist*

Introduction

As a protein fiber, silk fiber has attracted much attention because of its exceptional properties. Silk fiber has excellent mechanical properties such as high modulus, high strength, and great extensibility, *etc.* [1]. Silk yarns are usually treated by nanosilver [2], nanozinc oxide [3] to embody the yarns with anti-bacterial or anti-ultraviolet property.

Recently, the secondary structure of silk fiber has been deeply studied to find the relationship between silk structure and excellent properties. Keten *et al.* [4] studied the size effect of β-sheet and found the smaller β-sheet structure led to a higher mechanical property. Du *et al.* [5] compared the β-sheet structure between silk and spider silk, and the results showed that high content of intermolecular β-sheet of spider silk led to a strain-hardening phenomenon. This paper tried to elucidate the forming mechanism of 3-D crimped silk yarns by their secondary structure.

Materials and experiments

Silk yarns with the fineness of 260 D were used in our experiment. Z-twist yarn and s-twist yarn were twisted together in z-direction to fabricate a needed sample, as illustrated in fig. 1(a), it was treated with 7.5 mol/L $Ca(NO_3)_2$ solution at 95 °C for 5 minutes, and then it was degummed with 2 g/L Na_2CO_3 solution at 98 °C for 1 hour. Finally it was washed with deionized water and dried at 95 °C for 3 hours. Figure 1 shows the structural changes of silk yarns. After such treatment, the silk yarns had 3-D crimped structure, which are referred as 3-D crimped silk yarns.

To find out the forming mechanism, Fourier transform infrared spectroscopy (FTIR) was employed to identify the interior structural changes of 3-D crimped silk yarns. The spectra were obtained with a Thermo Nicolet 5700 FTIR spectrometer, equipped with mercury cadmium telluride attachment. For each measurement, 32 scans were carried out with a resolution of 4 cm^{-1} and the wavenumber ranged from 500 to 4000 cm^{-1}.

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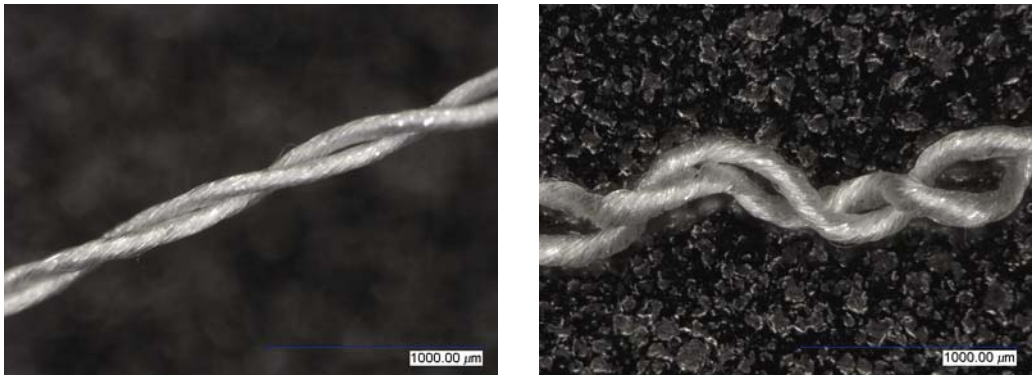

Figure 1. Silk yarns; (a) untreated, (b) 3-D crimped

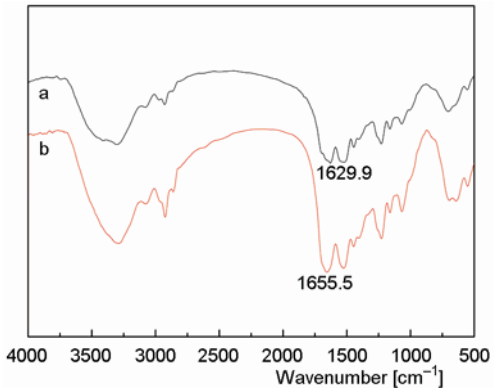

Figure 2. FTIR spectra; (a) untreated, (b) 3-D crimped

Results and discussions

Figure 2. depicted the FTIR results of untreated silk yarns and 3-D crimped silk yarns. It was easy to find out that the absorption peaks were similar to each other. However, the absorption peak at the wavenumber of 1629.9 cm^{-1} of untreated silk yarns corresponds to the wavenumber of 1655.5 cm^{-1} of 3-D crimped silk yarn, which means the β-sheet structure of untreated silk yarns is changed into random coil of 3-D crimped silk yarns.

Further, part of the FTIR spectra were fitted in ten peaks for various secondary structures including random coils at 1647 cm^{-1}, helical conformation at 1659 cm^{-1}, β-turns at 1666, 1678, and 1685 cm^{-1}, β-sheet at 1616, 1624, 1635, and 1697 cm^{-1}, and tyrosine side chains at 1604 cm^{-1} [6]. The Gauss function was selected as the fitting function. The fitted results were shown in fig. 3.

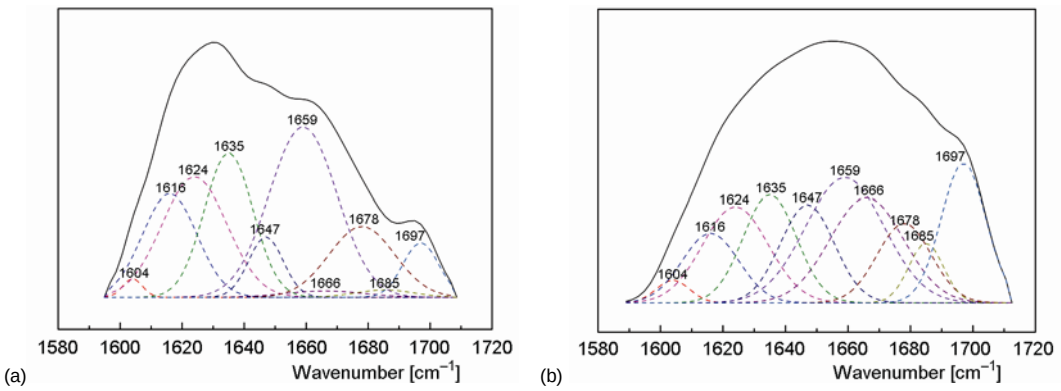

Figure 3. The FTIR spectra fitted with 10 peaks for various structure; (a) untreated, (b) 3-D crimped

The area of each fitted curve corresponds to the content of each secondary structure. The contents of each kind of secondary structure of silk yarns were shown in tab. 1. It was clear to find that the secondary structure of the helical conformation, β-sheet, and tyrosine side chains decreased after treatment, while random coil, and β-turns increased. Originally, for the untreated silk yarn, the β-sheet was connected with each other by hydrogen bonding. When the silk yarns treated with $Ca(NO_3)_2$ solution at a high temperature, the Ca^{2+} ion and high temperature would break the hydrogen bonding. Therefore, the β-sheet structure would be changed into β-turns, while the helical conformation structures would be changed into random coils. The results were similar to our previous observation [7], the number of hydrogen bonding decreases with the increase of treating temperature.

Table 1. A comparison of the structure of silk yarns

Items	Untreated silk yarn	3-D crimped silk yarn
Random coil	5.3138	10.4624
Helical conformation	24.36	18.32
β-turns	14.5311	27.3369
β-sheet	53.6074	42.5985
Tyrosine	2.1865	1.482

The changes of the secondary structure made the silk fibers loose. However, the centripetal force by twisting of silk yarns restrains silk fibers becoming loose. The two forces interact with each other to produce the 3-D crimped structure of silk yarns.

Conclusions

The forming mechanism of 3-D crimped silk yarns was discussed. The Ca^{2+} ion and high temperature broke the hydrogen bonding which connected β-sheet structure together. Some of the β-sheet and helical conformation structures changed into β-turns and random coil. The changes of the secondary structure made the silk fibers loose. However, the centripetal force by twisting of silk yarns restrain silk fibers becoming loose. Interacting of the two kinds of force made silk yarns 3-D crimped structure.

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