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A Study of the Structure and Properties of Male Silk

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Abstract
A new silk grade has been developed by separating silk cocoons according to gender using Ultra violet light (U-V) skill. Silk fibers from male cocoons structure and properties were tested using modern instruments which included the Scanning Electron Microscope (SEM), Fourier Transform Infrared (FT-IR), Thermo Gravimetric and Differential Thermo Gravimetric Analysis (TG-DTA) and single silk strength tester. Male silk fibers were found to pose superior physical properties, such as orientation degree, heat resisting properties and fracture strength. The superior properties of male silk fibers are set to expand the application of silk fibers.

1. Introduction

Silk fiber has long held the interest of man from the scientific, technological and aesthetic point of view. Silk has found applications in making yarn, cloth, decorative articles and biomedical because of its many outstanding attractions, including strength, dye ability, luster, and moisture absorption that distinguish them from other natural and synthetic fibers.

Despite the interest in the silk fibers, its application has been limited by the fibers weakness which includes crease recovery, rub resistance, color fastness, wash and wear properties. Attempts to improve silk properties by varying the physical and mechanical properties have been made, using diet variation, environmental conditions and filament preparation. Zhao et al, has reported that the physical and mechanical properties of silk have significant variations at both the intra-specific and intra-individual levels [1]. A study by Tsukada et al showed that the diameter of silk filament affects the physical, mechanical and dyeing properties of silk [2]. In the effort to try and understand the variation of chemical and mechanical properties of silk Vollrath used genetic modification of the silk worm [3]. While these approaches seem to have shown good chances of success, and have contributed to the improvement of the properties of silk, it is however clear that other approach must also be pursued.

The study of the properties of silk has also involved a review of the methodologies used to study silk properties. Smith et al has carried out a study on the testing conditions for the mechanical properties of silk, with a conclusion that some of the conventional testing methods are not reflective of the typical demands made on high-tensile materials during day to day application [4]. The analysis of the nano-structure and texture of polymer fibers which included silk was reported by Colomban and Gouadec, who used IR and Raman microscopes to try and understand not only the crystalline and amorphous regions of silk filament but also the progressive change from crystalline to amorphous regions in the structure of silk[5]. Another study of the structure of silk has been reported by Asakura and Nakazawa, who have used the solid state MNR method to try and study the Silk I and Silk II structures [6].

While much effort has been made to study the optimization of the properties, one area that seems to have received little attention is the classification of silk cocoons based on gender. Silk worms can be classified as male and female. Consequently the filament produced from female silk cocoons can be called female silk and the filament produced from male cocoons can be called male silk. The commonly available silk which will be referred to as normal silk consists of a mixture of both male and female silk. The study of Male silk may have been hindered by the problems encountered while trying to separate the male from the female cocoons. Chinese researchers have devised a novel technique of not only separating male silk from Female silk, but also producing Male silk at a commercial level [7]. In order to expand the male silk application, it is very important to understand its structure and properties. The purpose of this paper is to carry out an initial study on the structural and physical properties of Male and normal silk using the modern analysis instruments which include Scanning Electron Microscope (SEM), FT-IR spectrometer and TG-DTA analyzer.

2. Experimental

2.1. Materials

Reeled Male silk and Normal silk in filament form were supplied by JiangSu Minxing Cocoon Silk Stock Company, China. The silk samples were degummed as follows: The raw silk was boiled for 45 minutes in Boric Acid (0.2 mol/L) at 98-100ºC. Borax ($Na_2B_4O_5(OH)_4 \cdot 8H_2O$) was used to buffer the liquor. De-ionized water was used to rinse the samples twice. This degumming method is comparatively mild and can reduce the level of damage on raw silk [8].

2.2. Equipment and Testing

2.2.1. Scanning Electron Microscope (SEM)

Scanning Electron Microscope meter (HITACHI TM-1000, Japan) was used to test silk morphology. The silk samples were sputter-coated with a thin layer of gold to prevent electrical charging during the observation [9], two samples were used; one for longitudinal and another for cross section which involved a bundle of fibers.

2.2.2. FT-IR Spectroscopy Measurement

Fourier transform infrared (FT-IR) spectra of silk samples were recorded on a Nicolet 5700 to analyze the chemical structure of the fibers. KBr disk technique with a resolution of 4cm^{-1} in a spectral range of 4000~200cm^{-1} with 16 scans per sample were used [10].

2.2.3. Mechanical Property Testing

Tensile properties were measured under standard testing conditions using LLY-06 electric single-fiber tensile apparatus. The samples were cut into 5 cm on the aluminum frame, the tensile tests were performed with gauge length of 10mm. All tests were conducted at a strain rate of 10 mm/min. Each recorded value was an average of 5 measurements.

2.3. Thermo Gravimetric Analysis

Thermal gravimetric (TG) analysis was performed on degummed normal and male silk with a Penkin-Elmer thermo gravimetric analyzer (American -PE co.). The analyzer settings were: a continuous nitrogen flow (30 ml/min) and a heating rate of 10 ºC /min from 25 to 700 ºC. The sample was approximately 2–3 mg.

2.4. Moisture Regain Measurement

Silk samples were oven dried at 140- 150 for 2 hours to remove all the moisture. They were then placed in a controlled room with a temperature of 20±2ºC and a relative humidity of 60±5% and weight change recoded every after 10 minutes until the fibers attained equilibrium weight.

3. Results and Discussion

3.1. Surface Morphology of Male Silk Fibers

Scanning electron microscope was used to observe the longitudinal and cross section surface morphology of degummed male silk fibers, the results are as shown in Figure 1.

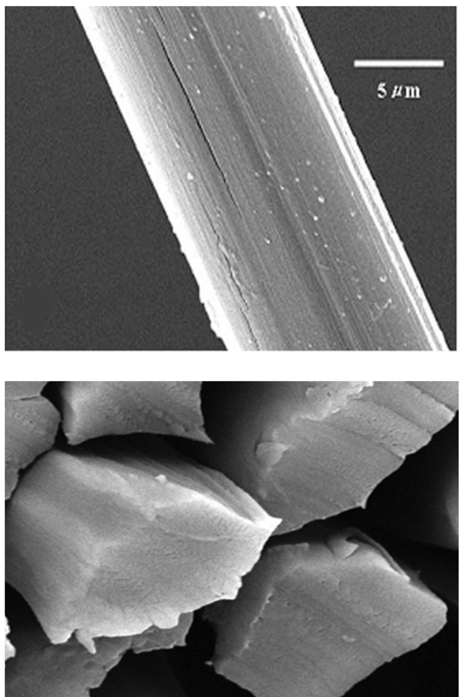

Figure 1. *Scanning electron micrographs (5000x magnification) of Cross sectional surface (a) and longitudinal (b) of Male silk fibers*

From Figure 1, it can be seen that cross section surface of male silk was compact blocks which had very tiny pores sparsely distributed. A smooth compact surface was observed when the fiber was viewed in the longitudinal direction. Based on this observation we can reasonably suggest that male silk filaments are compact and crystalline. The pore size and number shows that the molecular structure of male silk are well arranged reducing the amorphous regions.

3.2. FT-IR Spectroscopy

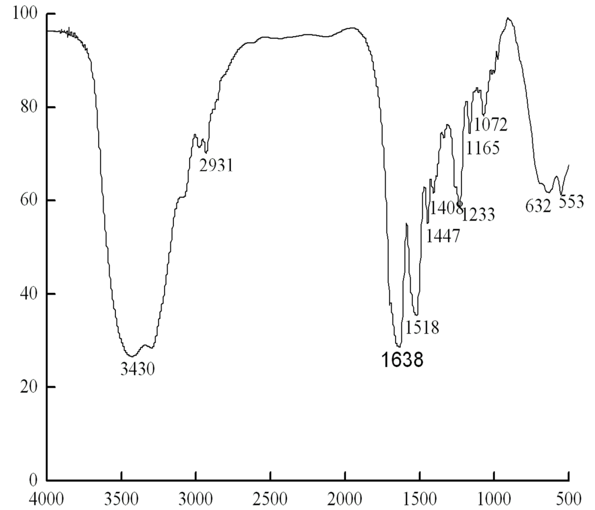

Figure 2. Fourier transform infrared (FT-IR) spectra of degummed male silk fibers.

FT-IR spectra of degummed male silk samples were investigated to establish the existence of various type of chemical bonds. The spectras are as shown in Figure 2. Comparing the bands on the spectra with those of normal silk, all the stretching and bending vibrations and there absorption bands appear in similar region. This is an indication that there is no chemical difference between the two fibers. There was a marked significant broadening of the vibration bonds in the region 3420 of male silk, this indicates that there is an increase of the OH vibrations. This OH bonds increase may have an influence in making the male fibers have additional strength through hydrogen bonding. [11, 12] Amide groups are the dye site of silk fibers, they are mainly present in amorphous regions of the fiber which is hydrophilic and allows adsorption. In male silk the crystalline regions have been increased at the expense of amorphous regions, this is the cause of reduction in the amide groups.

3.3. Thermo Gravimetric Analysis

Two types of silk fibroin were tested using the Thermo gravimetric analyzer and TG diagrams are as shown in Figure 3.

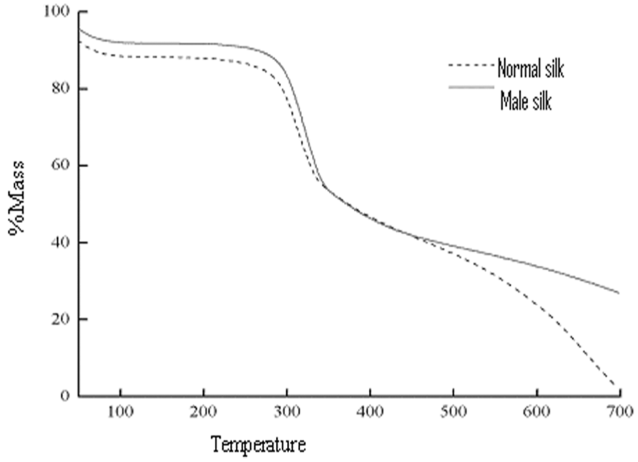

Figure 3. TG curves of Male and Normal silk

In the range of 25～100 ºC, both Male and normal silk fibroin releases water molecule, accompanied by minor weight loss. The major weight is between the range 250ºC～320ºC. The highest temperature of weight loss of Male silk is higher than that of normal silk, while the final temperature quality regain ratio in Male silk is higher than normal silk. This shows that Male silk has better heat stability than that of normal silk. This result agrees to the fact that the degree of crystallinity and orientation of male silk is higher than normal silk unanimously.

3.4. Breaking Strength and Elongation

Since the sericin in the silk has no contribution to the mechanical properties of the filament, the mechanical test was performed on un-degummed silk to avoid damage on the fibroin protein. Conditioning of the two types of silk was done by putting them in the room temperature 20±2ºC and relative humidity 60±5% for 8 hours, testing of the mechanical properties was listed in Table 1.

Table 1. Mechanical properties of male and normal silk

Sample	Breaking strength ($cN.dtex^{-1}$)	Elongation (%)	Initial modulus ($cN.dtex^{-1}$)
Male silk	4.289	32.035	79.1
Normal silk	3.911	33.239	75.3

It is well known that fiber mechanical properties are closely related to their degree of crystallinity and degree of orientation, if they are higher, the breaking strength of the fiber is high. From Table 1, the breaking strength and initial modulus of Male silk is higher than that of normal silk. This is mainly caused by their internal structural difference, and especially the degree of orientation of silk fiber has a great effect. Most of Male silk fiber macro fibroin molecules are arranged parallel to the fiber axis. So there are more macro molecules to endure the higher breaking stress. The normal silk degree of orientation is lower than that of Male silk, and only part of molecules endure the external stress in the direction of fiber axis and this causes the breaking strength to be lower[8].

The extensibility of Male silk is lower than that of normal silk, this is mainly because the normal silk degree of orientation is lower and its macro molecules link are arranged randomly and loosely, leaving internal bond angle of macro molecule larger space for extension and the wavy and interwoven peptide chain section can become straight and extend, making the extensibility of normal silk to be higher.

The initial modulus of Male silk is higher than that of Normal silk, this is related to the curve and contraction of fiber and its fine filament characteristic, in addition it is also related to the high orientation degree of molecules in amorphous region of silk fiber. The degree of orientation of Male silk is higher than that of normal silk, so the macro molecules are arranged more orderly, making the force of interaction between molecules of material bigger and internal hole ratio smaller, the activity space for motion of each unit become smaller, and it is hard to cause micro-Brownian motion , so it is hard to change molecule's structure.

3.5. Moisture Absorption

From equilibrium weight at standard conditions the weight of silk fibers was recorded every after 10 minutes, until the fiber absorption reached equilibrium, the results are as shown in Figure 4. Calculation for moisture regain rate were done using standard formula.

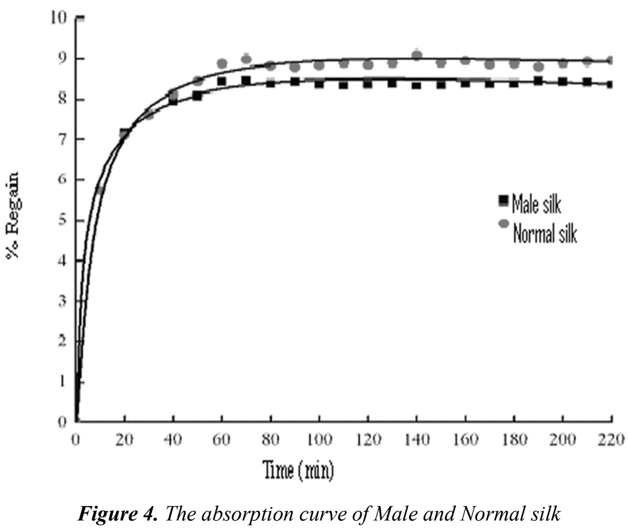

Figure 4. The absorption curve of Male and Normal silk

From Figure 4, we can see that the absorption curves of Male and normal silk are very similar. The absorption rate in initial section is similar, but between 20 min~50min, the absorption rate of normal silk is faster than that of Male silk. Both the two types of fiber reached absorption equilibrium in about 50 min. But the moisture regain rate of normal silk was faster than that of Male silk, this is because the degree of crystallinity of Male silk is higher than that of normal silk. The hydrophilic groups of molecules form interlocking key between molecules in crystalline region and makes the arrangement of molecules more compact, so it is hard for water molecules to enter the crystalline region. Generally, fibers with bigger amorphous region have more absorption ability [12]. At equilibrium, the moisture regain rate of Male silk is 8.5% and that of normal silk is 9.1%.

4. Conclusion

Male silk surface structure is compact and has smaller holes and few in number compared to normal silk. Male silk fiber surface morphology showed a compact fiber. Crystallinity, breaking strength and initial module of Male silk are higher than the ordinary silk while crystal structure is the same. Male silk exhibited better heat stability than that of normal silk. The moisture regain rate of normal silk changed faster than that of Male silk. This could be due to the fact that the degree of crystallinity of Male silk is higher than that of normal silk. At equilibrium, the moisture regain of Male silk is 8.5% and that of normal silk is 9.1%.

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