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Inorganic Composition and Thermal Properties of Cocoon Fiber

Han ZHANG*, Jun MAGOSHI**, Yoshiko MAGOSHI**, Hirohisa YOSHIDA***,

JieYu CHEN* and Kazuto SAIKI****

*Faculty of Bioresource Sciences, Akita Prefecture University, Akita 010-0195, JST, Japan
**National Institute of Agrobiological Resources, Tsukuba 305-8602, JST, Japan
***Faculty of Engineering, Tokyo Metropolitan University, Tokyo 192-0397, Japan
****Faculty of Engineering and Resource Science, Akita University, Akita, 010-8502, Japan
E-mail : zhangh@akita-pu.ac.jp

The changes of color, size and shape of *Bombyx mori* cocoon shells were observed from 25℃ to 550℃. Only 1 % of the original cocoon shell weight remains as cocoon ash after treatment at 550℃. The inorganic components were detected in the cocoon ashes such as calcium, potassium, sulfur, magnesium etc., using energy dispersion fluorescent X-ray spectrometer analysis system. The thermal properties of *B. mori* cocoon shell subjected to heat-treatment were examined by thermogravimetry-differential thermal analysis-Fourier transform infrared absorption spectrometry (TG-DTA-FTIR) and scanning electron microscopy (SEM). Chemical changes started gradually at around 180℃, and a sharp decrease in weight was observed around 280℃ by TG curves. The IR bands appearing around 2380 cm^{-1} (-OH stretching), 1760 cm^{-1} (C=O stretching), 1503 cm^{-1} (N-H stretching), 1085 cm^{-1} (C-N stretching) and 965 cm^{-1} (-NH_2 stretching) become stronger as an exothermic reaction around 280℃ takes place. This is probably due to the cleaving of the main chain and the accompanying decomposition of the cocoon fibers. Similarly, a SEM micrograph of raw silk fibers treated at 300℃ shows a microtubule in the middle of the fibers of about 25 μm diameter. This suggests that the thermal reactions starts in the middle of the fiber and forms a microtubule.

Key Words : Inorganic composition, Thermal properties, Cocoon shell, Cocoon fiber

Introduction

Cocoon fiber is a long double monofilament produced by silkworm. Silkworms construct the cocoons to protect themselves during metamorphosis.

Cocoon fibers consist primarily of two components, fibroin and sericin; fibroin is the structural protein of the silk fiber, and sericin is the water-soluble glue that serves to bond the fibers together. The majority of fibroins composition is highly periodic with simple repeating sections broken by more complex regions containing amino acids with bulkier side chains. The highly repetitive sections are composed of glycine (45%), alanine (30%), and serine (12%) in a roughly 3:2:1 ratio and dominated by $[Gly\text{-}Ala\text{-}Gly\text{-}Ala\text{-}Gly\text{-}Ser]_n$ sequences. The sericin protein, which comprise approximately 25 wt% of the silkworm cocoon, contain glycine, serine, and aspartic acid totaling over 60%.

Previous studies of the crystallinity of *B. mori* silk have revealed three different conformations, a random coil, an α-form (termed Silk I), and a β-form (termed Silk II). Cocoon fibers have the well-oriented β-form conformation with a antiparallel pleated sheet structure, which is more stable than the α-form. In recent years, extensive studies have been performed concerning the microscopic structure of silk fibroin molecules and their higher order structure by atomic force microscopy (AFM),[1,2] using X-ray diffraction and differential scanning calorimetry (DSC) carried out to clarify the crystallization mechanism of silk fibroin from liquid silk,[3] the size of fibroin in a random-coil conformation measured by dynamic light scattering (DLS).[4] These studies explained the mechanism of how fibroin gel transforms into a solid state and proceeds to the spinneret and extrudes to form the silk fiber in the silk gland of the silkworm. While the physical properties and structure of silk, as well as the thermal properties of cocoon shell treated from 25℃ to 180℃ has been reported,[5] there still remain some properties no detailed studies have been made on the cocoon fiber.

In this work, our purpose was to examine the microstructure of *B. mori* cocoon shells before and after high-treatment to obtain information about their physical properties as well as shape, size and color by using digital camera and SEM. We also wanted to investigate the thermal properties of *B. mori* cocoon shell treated over 180℃ by TG-DTA-FTIR, This information is vital to understand fully how these factors influence the microstructure of cocoon fibers. The inorganic compositions of cocoon ashes were also examined using an energy dispersion fluorescent X-ray spectrometer analysis system. We anticipate that the results obtained in this work will be useful in the understanding a new microstructure evolution during high-treatment in the cocoon fiber.

Experimenting

Bombyx mori cocoon shells (Tyu 9.0 x Nichi 9.0) have been sponsored by National Institute of Agrobiological Resources.

The inorganic compositions of cocoon ashes were evaluated using a energy dispersion fluorescent X-ray spectrometer analysis system (JSX-3201, JEOL Inc.). The detection range is from carbon to uranium; the resolution is 149 eV. Samples were placed in a 5 mm case and measurements were obtained under a 30 kV. The data was reported in terms of weight percentage (wt%).

Thermal analysis measurements were carried-out using a Seiko Exstar 6000 thermal analysis system with a Seiko TG/DTA 6200 connected to a Jasco FTIR 620 using a Seiko TG-IR interface to create an integrated TG-DTA-FTIR system. The evolved gases were introduced into a gas cell in the TG-DTA-FTIR interface from the furnace tube of the TG-DTA through a heated transfer line with a glass-coated inside surface. The TG-DTA furnace tube, a transfer line and the gas cell were temperature controlled in order to prevent condensation of the evolved gases. The FTIR used a MCT (Mercury cadmium telluride) detector.

A JEOL JSM-5600 low voltage, high resolution SEM with a field emission gun was used to examine the morphology of the cocoon shell and the bundles of degummed cocoon fibers. Cocoon sections or fibers were attached to sample stubs using conductive double-sided stick tape and coated with approximately 15 nm of Au-Pd alloy prior to being imaged at 5-20 kV.

Figure 1 The *B. mori* cocoon shells subjected to increasing heat treatments.
a) Untreated, b) At 150℃ for 0.5 hr , c) At 190℃ for 0.5 hr,
d) At 250℃ for 0.5 hr, e) At 350℃ for 1 hr, f) At 450℃ for 3 hr, g) At 550℃ overnight.

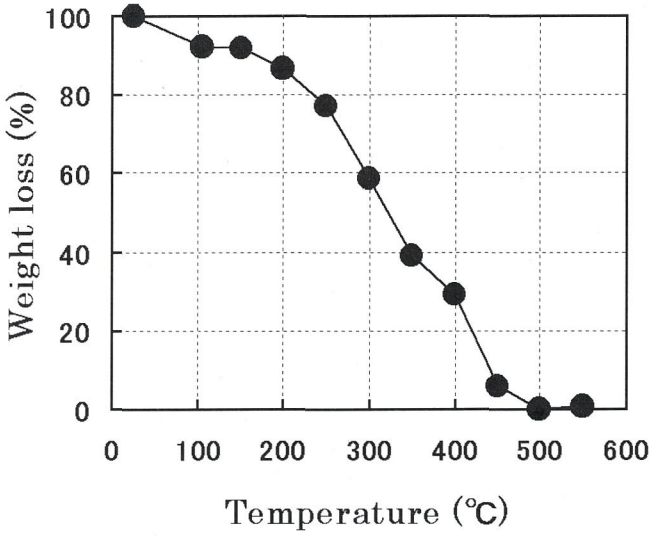

Figure 2 The weight loss of *B. mori* cocoon shell by heat treatment from 25℃ to 550℃.

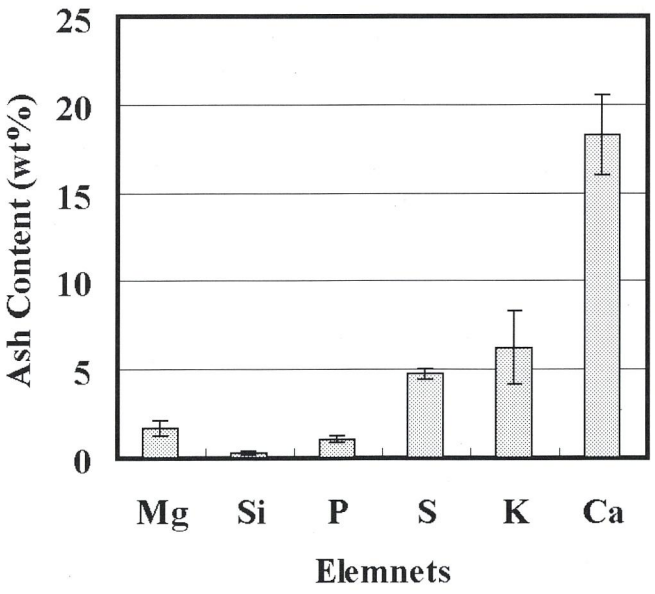

Figure 3 The inorganic components of ash contents from *B. mori* cocoon shell.

Results and Discussion

Cocoon shells were individually placed in crucibles and combusted in a portable furnace using a heating profile of 150℃ for 30 min, 190℃ for 30 min, 250℃ for 30 min, 350℃ for 1 h, 450℃ for 3 h, and then 550℃ overnight. *Figure* 1 shows the color, size and shape of *B. mori* cocoon shells after heat-treatment at increasing temperatures. The cocoon's color changed from a white color (25℃) to light-yellow (150℃), to brown (190℃), to black (200℃) and then back to a white color at 550℃. The size and shape decreased with an increase in the temperature and weight loss from the cocoon shell. *Figure* 2 shows the relationship between the heating temperature and the weight loss of the cocoon shells. The weight loss of 9 % is attributed to the evaporation of water contained in cocoon shell at 105℃. This is followed by a sharp decrease of cocoon weight from 150℃ to 450℃, after which only 1 % of the original cocoon shell weight is left as cocoon ash after heat-treatment at 550℃.

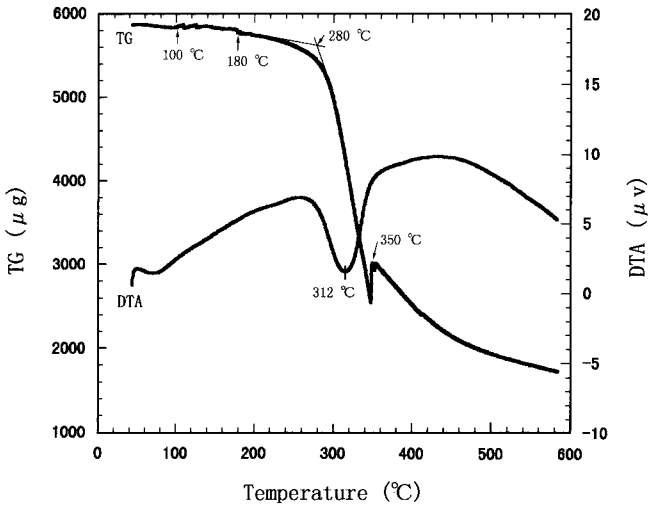

Figure 4 TG and DTA curves for *B. mori* cocoon shell.

We used an energy dispersive X-ray fluorescence. The inorganic components measured for cocoon ashes are shown in *Figure* 3. The calcium content represents 18.3 wt% of the total cocoon ash weight percentage; the potassium content represents 6.3 wt%; the sulfur content represents 4.8 wt%; the magnesium content represents 1.7 wt%; the phosphorus content represents 1.2 wt%; and the silicon content represents 0.3 wt%.

Similar results were observed by TG-DTA-FTIR. The TG-DTA results of the thermal degradation process of *B. mori* cocoon shell are shown in *Figure* 4. In the TG curve, the weight decreases of cocoon shell are four steps from 20℃ to 580℃. The first step is attributed to the evaporation of water around 100℃. In the TG curve, the weight decreases of cocoon shells are four steps from 20℃ to 580℃. The first step is attributed to the evaporation of water around 100℃. The second step turned the color to brown at 180℃. The third step is marked by a sharp decrease in weight beginning at 280℃, and a peak appeared at around 345℃ in the TG curve. The fourth step is from 350℃ to 580℃, at which point a relaxation of weight decrease in the TG curve appeared. Another endothermic peak was observed about 312℃ in the DTA curve. It corresponds to the thermal decomposition in cocoon fiber.

The FTIR spectra was observed from 20℃ to 580℃ at a heating rate of 10℃min^{-1}, and are shown in *Figure* 5. One peak presented at 2380 cm^{-1} is observed after being heated to 306℃, it is attributed to the -OH. Similarly, peaks presented at 1760 cm^{-1} are attributed to the C=O at 335℃, 1503 cm^{-1} are attributed to the N-H stretching at 310℃, 1085 cm^{-1} are attributed to the C-N stretching at 351℃, and 965 cm^{-1} are attributed to the -NH_2 stretching at 321℃.

Figure 6 shows SEM micrograph of *B. mori* cocoon shell which were treated at 350℃ for 3 hrs. The cocoon fibers present states of swelling out. It is thought that gas occurred in the inside of the cocoon fibers by the dissolution (see Fig.6-a), and the microtubule present in the middle of the cocoon fibers (see Fig.6-b). The *B. mori* raw silk fibers which were treated at 300℃ for 3 hrs are shown in *Figure* 6-c and *Figure* 6-d. Similarly, the microtubule formed in the middle of the raw silk fibers is about 25 μm in diameter.

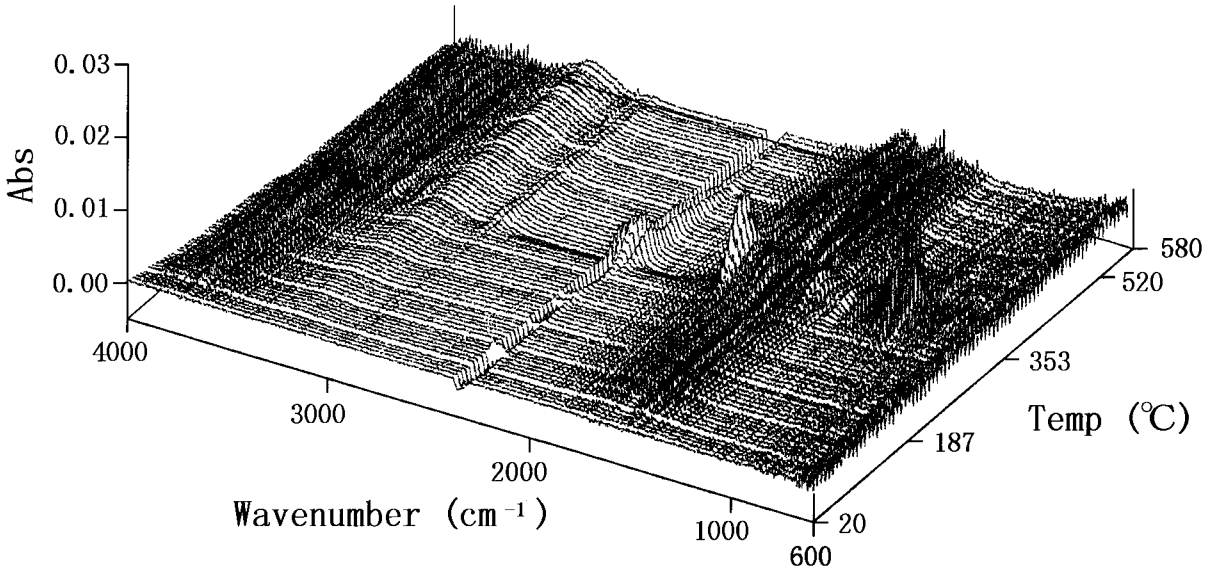

Figure 5 FTIR spectra of cocoon shell were observed from 20℃ to 580℃ at a heating rate of 10℃min^{-1}.

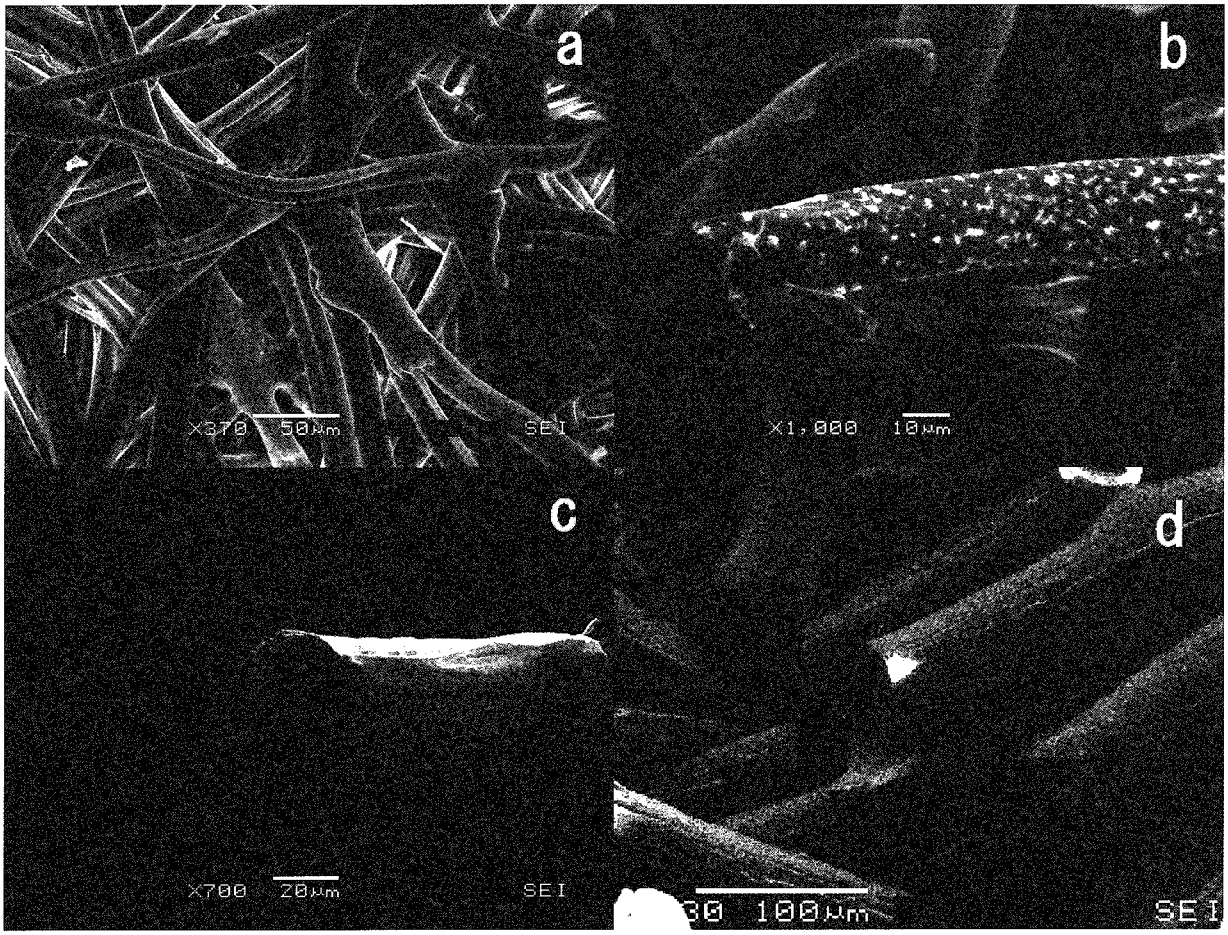

Figure 6 SEM images of surface of cocoon shell and section of raw silk fibers.
a) and b) shown *B. mori* cocoon shell treated at 350℃ for 3 hr, c) and d) shown *B. mori* raw silk fibers treated at 300℃ for 3 hr.

Therefore, chemical changes started gradually at around 180℃ as evidenced by the TG curve. In addition, a large endothermic reaction corresponded to the substantial weight decrease starting at around 280℃. Two exothermic reactions occurred. The exothermic reaction below 280℃ is thought to be due to oxidation and the exothermic reaction at around 280℃ due to cleavage reaction of the -OH chain of the cocoon fibers. These are thought to be associated with the decomposition and reorganization reactions created during heat-treatment of the *B. mori* cocoon fiber and the microtubule was formed.

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