# Thermal Properties of *Bombyx mori* Silk Fibers

**Han Zhang,[1] Jun Magoshi,[2] Mary Becker,[3] Jie Yu Chen,[1] Ryuji Matsunaga[1]**

[1] *Faculty of Bioresource Sciences, Akita Prefecture University, Akita 010-0146, JST, Japan*
[2] *National Institute of Agrobiological Resources, Tsukuba 305-8602, JST, Japan*
[3] *Department of Materials Science and Engineering, Fukui University, Fukui 910-8507, JST, Japan*

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**ABSTRACT:** The thermal properties of *Bombyx mori* silk fibers subjected to heat treatment were examined by thermogravimetry, differential thermal analysis, Fourier transform infrared absorption spectrometry (TG-DTA-FTIR) and scanning electron microscopy (SEM). The color, size, and shape of *B. mori* cocoon shells were observed as they were heated from 25 to 550°C. Only 1% of the original cocoon shell weight remains as cocoon ash after treatment at 550°C. Inorganic components, such as calcium, potassium, sulfur, magnesium, etc., were detected in the cocoon ash by energy dispersion fluorescent X-ray spectrometry. A sharp decrease in weight was observed in the TG data beginning around 280°C, and an endothermic peak appeared at 308°C, as evidenced by the DTA curves. The IR bands observed at 2380 $cm^{-1}$ (—OH stretching), 1760 $cm^{-1}$ (C═O stretching), 1503 (N—H stretching), 1085 $cm^{-1}$ (C—N stretching) and 965 $cm^{-1}$ (—$NH_2$ stretching) become stronger as an exothermic reaction beginning at 280°C takes place. This is probably due to cleavage of the main chain and the accompanying decomposition of the silk fibers. Similarly, a SEM micrograph of silk fibers treated at 300°C shows a microtubule in the middle of the silk fibers of about 25-$\mu$m diameter. This suggests that the thermal reactions starts in the middle of the silk fiber and forms a microtubule. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1817–1820, 2002

**Key words:** thermal properties; microstructure; fibers

## INTRODUCTION

*Bombyx mori* silk fibers consist primarily of two components, fibroin and sericin. Fibroin is the structural protein of the silk fiber, whereas sericin is the water-soluble proteinaceous glue that serves to bond the fibers together. The majority of fibroin's 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. Sericin, which comprises approximately 25 wt % of the silkworm cocoon, contains glycine, serine, and aspartic acid totaling over 60% of the overall composition.

Previous studies of the crystallinity of *B. mori* silk have revealed three different conformations, a random coil, an $\alpha$-form (or Silk I), and a $\beta$-form (or Silk II). Silk fibers have the well-oriented $\beta$-form conformation with an antiparallel pleated sheet structure, which is more stable than the $\alpha$-form. In recent years, extensive studies concerning silk fibroin molecules and their higher order structure,[1] crystallization of silk fibroin from solution,[2] dynamic and static light scattering of dilute aqueous solutions of silk fibroin,[3] mechanisms of conformational changes of silk fibroin,[4] the physical properties and structure of silk, as well as the thermal properties of cocoon shell treated from 25 to 180°C[5] have been performed.

Although there has been much research done on the physical properties and structure of silk fiber, there still remain some unanswered questions. In particular, the behavior of silk fibers that have been subjected to heat treatment needs to be studied.

In this work, the thermal properties of *B. mori* cocoon shell treated from 25 to 550°C were examined by TG-DTA-FTIR, and the inorganic compositions of cocoon ashes were evaluated using an energy dispersion X-ray fluorescence spectrometer. SEM micrographs showed a new microstructure of *B. mori* silk fibers and cocoon shell after heat treatment.

## EXPERIMENTAL

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, transfer line, and gas cell were temperature controlled to prevent condensation of the evolved gases. The FTIR used a MCT (Mercury cadmium telluride) detector.

*Correspondence to:* H. Zhang (zhangh@akita-pu.ac.jp).

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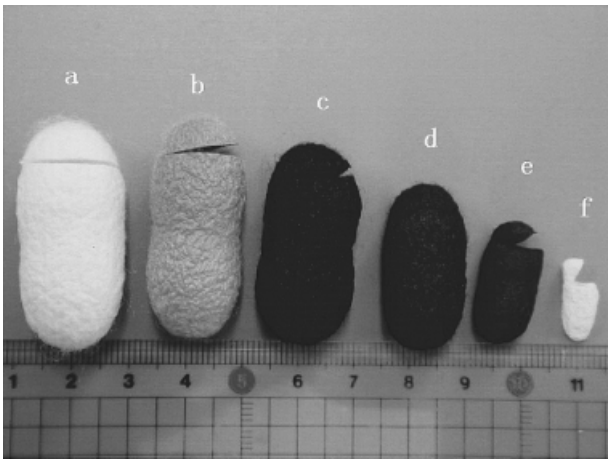


**Figure 1** The *B. mori* cocoon shells subjected to increasing heat treatments. (a) Untreated, (b) at 190°C for 0.5 h, (c) at 250°C for 0.5 h, (d) at 350°C for 1 h, (e) at 450°C for 3 h, (f) at 550°C overnight.

A JEOL JSM-5600 low-voltage, high-resolution SEM with a field emission gun was used to examine the morphology of cocoon shells and bundles of degummed silk 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.

Cocoon shells were individually placed in crucibles and combusted in a portable furnace using a heating profile of 190°C for 30 min, 250°C for 30 min, 350°C for 1 h, 450°C for 3 h, and then 550°C overnight. The inorganic compositions of cocoon ashes were evaluated using an energy dispersion fluorescent X-ray spectrometer (JSX-3201, JEOL Inc.). The detection range was from carbon to uranium, the resolution was 149 eV. Samples were placed in a 5-mm case and intensity measurements were obtained using an accelerating voltage of 30 kV. The data is reported in terms of weight percentage (wt %).

## RESULTS AND DISCUSSION

The cocoon's color changed from a whitish color (25°C) to light yellow (150°C), to black (200°C) and then back to a white color at 500°C during the course of heat treatment. Figure 1 shows the color, size, and shape of *B. mori* cocoon shells after heat treatment at increasing temperatures. 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 cocoon shell and silk fibers. The initial weight loss of 9% is attributed to the evaporation of water contained in cocoon shell at 105°C. This is followed by a sharp decrease of the cocoon weight from 150 to 450°C, and only 1% of the original cocoon shell weight remains as cocoon ash after heat treatment at 550°C. Similar results were found for silk fibers. The initial weight loss of 8.2% at 105°C is attributed to the evaporation of water contained in silk fibers. Both the cocoon and silk fibers follow similar trends in weight loss from 150 to 450°C as shown in Figure 2. The gradual weight loss of the silk fibers from 150 to 250°C and rapid weight loss from 250 to 450°C are represented, after which only 0.9% of the original silk fibers weight is left as silk fibers ash after heat treatment at 550°C.

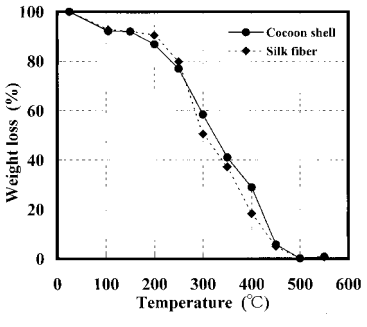


**Figure 2** The weight loss of *B. mori* cocoon shell and silk fibers by heat treatment from 25 to 550°C.

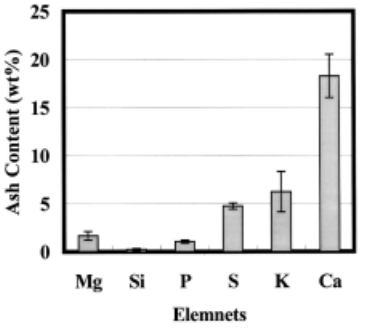


**Figure 3** The inorganic components of ash contents from *B. mori* cocoon shell.

Using energy dispersive X-ray fluorescence spectrometry, the inorganic components found in cocoon

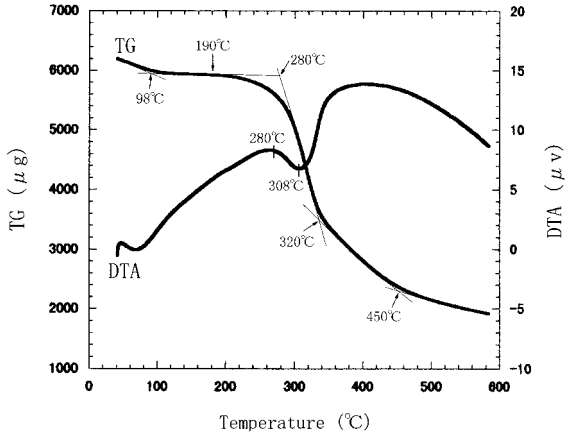


**Figure 4** TG and DTA curves for *B. mori* silk fiber from 20 to 580°C.

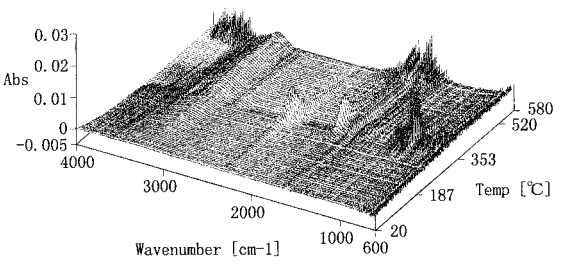


**Figure 5** FTIR spectra of silk fiber were observed from 20 to 580°C at a heating rate of 10°C $min^{-1}$.

ashes are shown in Figure 3. The calcium content represents 18.3 wt % of the total cocoon ash, 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 %. The weights of the elements are directly proportional to the cocoon shell weight with the exception of calcium. The shape of cocoon shell does not collapse because of the carbon and inorganic content of the coon ash.

From the TG-DTA-FTIR data, the thermal degradation process of *B. mori* silk fibers is shown in Figure 4. In the TG curve, the weight loss during the degradation process of silk fiber occurs in four steps from 22 to 580°C. The first step is attributed to the evaporation of water at the inflection point around 98°C followed by no weight change from 98 to 190°C; however, this is where the color turns yellow. The second step is marked by a sharp decrease in weight beginning at 280°C. In the DTA curve, a peak appears at 308°C, which starts gradually at around 280°C; it is an endothermic peak corresponding to the thermal decomposition of silk fibers. The third and fourth steps in weight decrease in the TG curve from 320 to 450°C, and from 450 to 580°C, occurred at lower rates.

The FTIR spectra observed from 20 to 580°C, at a heating rate of 10°C $min^{-1}$, are shown Figure 5. A peak at 2380 $cm^{-1}$, attributed to the —OH group, is observed after being heated to 308°C. Similarly, a peak at 1760 $cm^{-1}$ (C═O) appears at 346°C, the peak at 1503 $cm^{-1}$ attributed to N—H stretching appears at 328°C, the 1085 $cm^{-1}$ peak attributed to the C—N stretching appears at 357°C, while the 965 $cm^{-1}$ peak attributed to the —$NH_2$ stretching begins at 342°C.

Figure 6 shows a SEM micrograph of a *B. mori* cocoon shell and silk fibers that has been treated at 350 and 300°C for 3 h. The silk fibers of the cocoon shell appear to swell [see Fig. 6(a)], it is thought that gas accumulated inside the fibers by diffusion result in the microtubule present in the middle of the silk fibers (see Fig.6-b). *B. mori* raw silk fibers that were treated at

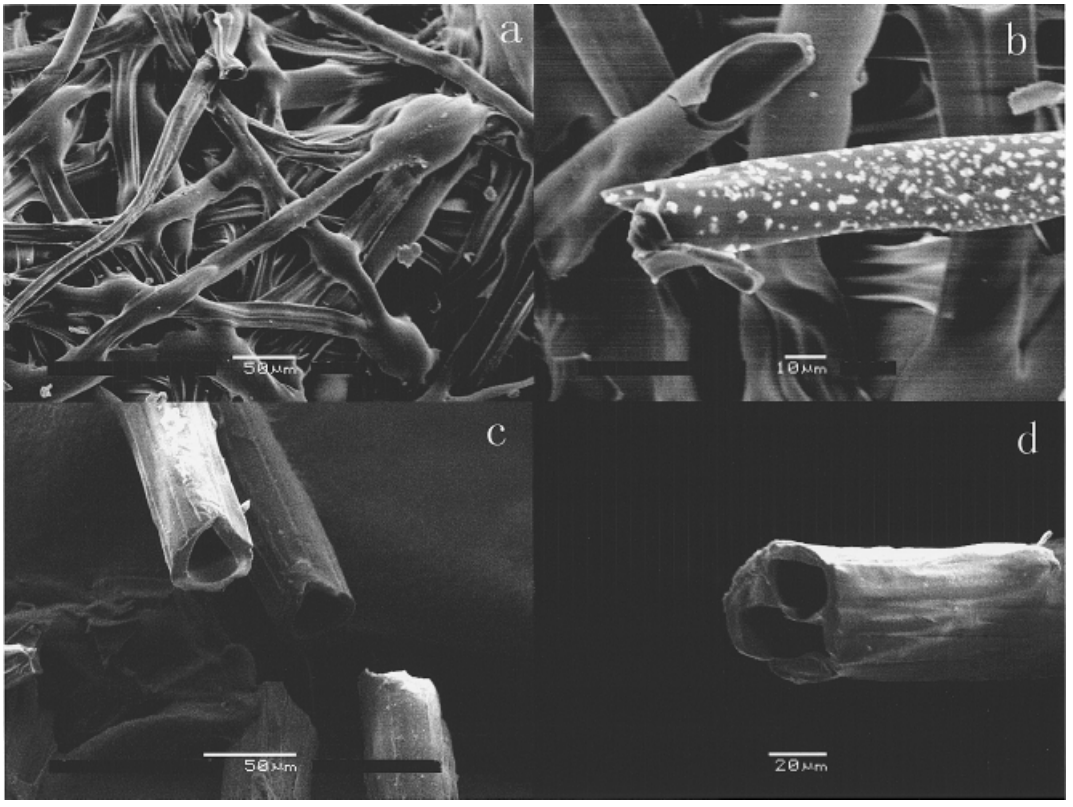


**Figure 6** SEM images of surface of cocoon shell and section of raw silk fibers. (a,b) Shows *B. mori* cocoon shell treated at 350°C for 3 h; (c,d) shows *B. mori* raw silk fibers treated at 300°C for 3 h.

300°C for 3 h are shown [Fig. 6(c) and (d)]. Similar microtubules were formed in the middle of these silk fibers, and are approximately 25 $\mu$m in diameter.

Therefore, chemical changes started gradually at around 190°C, as evidenced by the TG curve. In addition, a large endothermic reaction corresponding to a substantial weight decrease started at around 280°C. Two exothermic reactions also occurred. The exothermic reaction below 280°C is thought to be due to oxidation and the exothermic reaction at around 308°C due to cleavage reaction of the —OH chain of the silk fibers. These are thought to be associated with the decomposition and reorganization reactions undergone during heat treatment of the *B.mori* silk fiber and the microtubule formation.

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