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Physical Properties and Structure of Silk. III. The Glass Transition and Conformational Changes of Tussah Silk Fibroin

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Synopsis

The glass transition, crystallization, and α–β transition of the Tussah silk fibroin were studied by means of DSC (differential scanning calorimetry) and infrared spectroscopy. The endothermic shift due to the glass transition was observed at 162°C. The endothermic peak at 220°C was attributed to the α–β conformational transition from the infrared spectra. The exothermic peak due to the crystallization occurred at 230°C.

INTRODUCTION

In the previous report,[1] the glass transition temperature of amorphous silk fibroin with random coil conformation has been determined by differential scanning calorimetry (DSC), and the exothermic peak at 212°C in the DSC curve has also been assigned to the crystallization of amorphous silk fibroin by recording the x-ray diffraction patterns of silk fibroin before and after heat treatment at 220°C.

The present work was intended to investigate the glass transition, conformational transition and crystallization of Tussah silk fibroin by DSC and infrared spectroscopy.

EXPERIMENTAL

Silk fibroin solution was obtained from the posterior division of the silk gland in full-grown larvae (one day before spinning) of *Antheraea pernyi.* After the aqueous solution of silk fibroin was dialyzed against deionized water and diluted to a concentration of about 0.1%, films for DSC and IR measurements were cast from the solution onto thin polyethylene films and dried at 20°C.

Differential scanning calorimetry was performed on a Perkin-Elmer DSC-II differential scanning calorimetry under nitrogen. Infrared spectra were obtained using a JASCO Model IR-G-type infrared spectrometer at 4000–400 cm^{-1}.

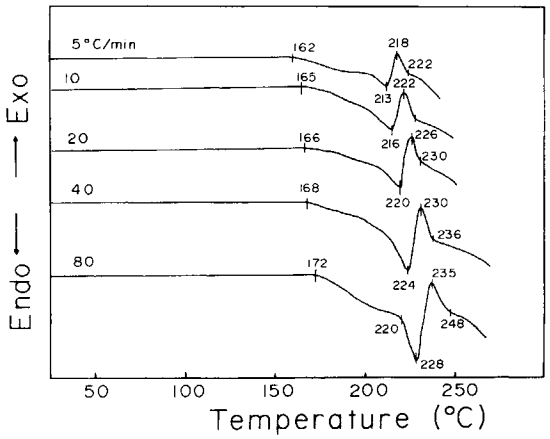

Fig. 1. DSC curves of Tussah silk fibroin at various heating rates.

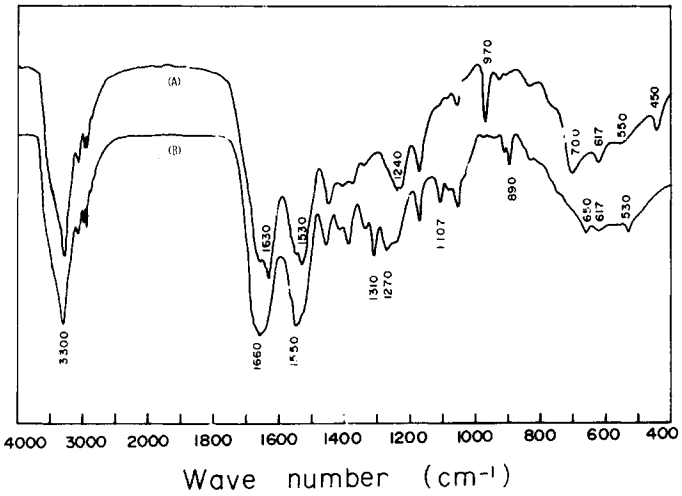

Fig. 2. Infrared spectra of Tussah silk fibroin: (a) untreated, (b) heat treated at 220°C for 30 min.

RESULTS AND DISCUSSION

Figure 1 shows DSC curves at various heating rates of Tussah silk fibroin film. The specimen was dried in a sample pan at 120°C for 10 min under nitrogen before measurement. For each curve, an exothermic and endothermic peak and an endothermic shift are observed. Both peaks shift to higher temperatures with increasing heating rate, namely, the exothermic peak shifts from 218° to 235°C and the endothermic peak, from 213° to 228°C. The endothermic shift also moves from 162°C at 5°C/min to 172°C at 80°C/min. An abrupt increase in linear thermal expansion was observed at this temperature.[2] Accordingly, the glass transition temperature of Tussah silk fibroin was determined to be 162°C from the endothermic shift at the slowest heating rate of 5°C/min.

In order to clarify the origin of the exothermic and the endothermic peaks, infrared spectra of Tussah silk fibroin were recorded before and after heat treatment at 220°C for 30 min (Fig. 2). The infrared spectrum of untreated silk

fibroin film shows bands characteristic of the α-helix of silk fibroin, 1660, 1550, 1310, 1270, 1107, 890, and 617 cm^{-1}, and a band characteristic of random coil conformation at 650 cm^{-1}. After heat treatment at 220°C, the bands attributed to the extended β-form of silk fibroin are found at 1630, 1530, 1240, 970, and 700 cm^{-1}, and that of the α-helix at 617 cm^{-1} in the infrared spectrum. The band at 650 cm^{-1} due to the random coil conformation and most of the bands due to the α-helix disappear as a result of the heat treatment at 220°C.

This result indicates that the conformational transitions from random coil to β-form and from α-helix to β-form are induced by heat treatment at 220°C. Green et al.[3] reported that a α–β transition of poly(β-alkyl-L-aspartates) such as the methyl, ethyl, and benzyle esters are endothermic in character. Therefore, the endothermic peaks in the range of 213° to 228°C are attributed to the conformational transition from α-helix to extended β-form. The exothermic peaks ranging from 218° to 238°C are assigned to the crystallization of the amorphous region of Tussah silk fibroin to β-form crystals.

References

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