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Studies on Physical Properties and Structure of Silk. Glass Transition and Crystallization of Silk Fibroin

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Synopsis

Amorphous silk fibroin with random coil conformation shows endothermic and exothermic peaks and endothermic shift on the DSC (differential scanning calorimetry) curve. The endothermic shift observed at 175°C was due to the glass transition. The exothermic peak at 212°C is recognized to be the crystallization, which later was confirmed by x-ray diffraction pattern. The endothermic peak at 280°C is shown to be the degradation.

INTRODUCTION

The crystallization and the glass transition and melting temperatures of many synthetic polymers have been investigated by means of differential scanning calorimetry (DSC) and differential thermal analysis (DTA). However, a few studies on natural polymers, especially silk fibroin, have been reported. We reported previously that the degradation peak[1,2] of the α-form, β-form, and well-oriented β-form of silk fibroin occurs at 294°, 296°, and 300°C, respectively. In the present work, we investigated the thermal properties of the silk fibroin using a differential scanning calorimeter and determined the temperature of glass transition and crystallization of amorphous silk fibroin with random coil conformation.

EXPERIMENTAL

Silk fibroin solution was obtained from the posterior part of the middle division of the silk gland in full-grown larvae (one day before spinning) of *Bombyx mori*. The sericin was removed by washing the silk gland thoroughly with deionized water. The aqueous solution of silk fibroin was dialyzed against the deionized water and diluted to a concentration of about 0.8%, then the films (10% moisture contents) for DSC measurement were cast from the solution onto thin polyethylene films and dried at 20°C. The random coil conformation[3] (amorphous) of silk fibroin molecules in these specimens was identified by means of x-ray diffraction and IR absorption spectroscopy.

Differential scanning calorimetry was performed on a Perkin-Elmer DSC-1B differential scanning calorimeter under nitrogen. A heating rate of 8°C/min was used.

A Rigaku x-ray diffraction apparatus (Type 4042) was operated at 35 kV and 20 mA, and wide-angle x-ray diffraction patterns were recorded on a cylindrical film camera by using nickel-filter Cukα radiation.

RESULTS AND DISCUSSION

Figure 1 shows DSC curves of amorphous silk fibroin with random coil conformation. Two endothermic peaks were observed at about 100° and 280°C. An exothermic peak at 212°C and an endothermic shift at 175°C were also observed.

The endothermic peak at about 280°C was prominent, suggesting the degradation[1] of silk fibroin with random coil conformation, since an abrupt weight loss[4] (TG curve) of silk fibroin had been obtained at about 250°C. The broad endothermic peak observed at about 100°C seems to be attributable to the evaporation of water in the specimens, for when the specimens were kept in a desiccator containing silica gel for two weeks, the peak (Fig. 1b) becomes smaller

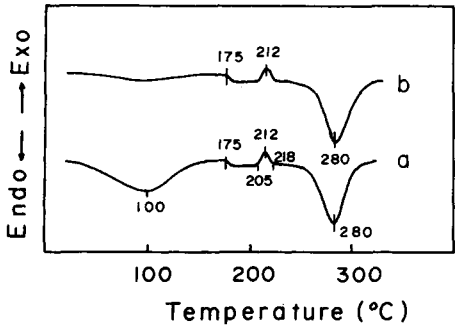
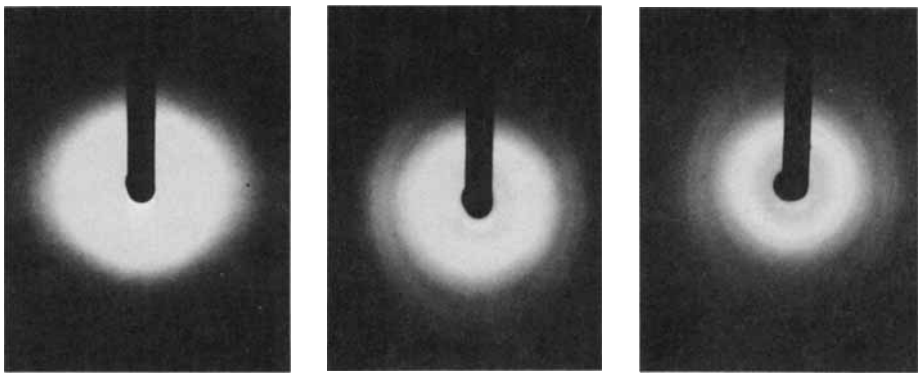


Fig. 1. DSC curves of amorphous silk fibroin with random coil conformation: (a) untreated; (b) kept in desiccator containing silica gel for two weeks.



(a) (b) (c)

Fig. 2. X-Ray diffraction patterns of silk fibroin film: (a) amorphous silk fibroin with random coil conformation; (b) heat-treated silk fibroin at 220°C; (c) β-form silk fibroin treated with methanol at 20°C for 2 hr.

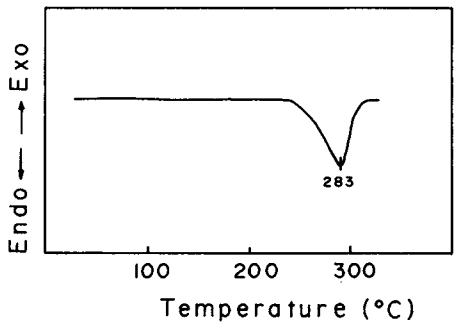


Fig. 3. DSC curve of silk fibroin film heat-treated at 220°C.

than before drying. The results were coincided with those obtained previously from TG curves.[4] In Figure 1 the glass transition of the silk fibroin (amorphous) was also observed as the endothermic shift at 175°C. As reported in the previous papers,[1,5] the dynamic dispersion and dielectric absorption of amorphous silk fibroin was also observed nearly at the same temperature (180°C).

The original exothermic peak at about 212°C was further investigated by x-ray diffraction (Fig. 2). This exothermic peak was confirmed to be due to the crystallization of silk fibroin, namely, the conformational change of the random coil to the β-form, by comparison with the x-ray diffraction patterns of silk fibroin with and without heat treatment at 220°C (Figs. 2a and 2b). In addition, x-ray diffraction pattern of the specimen with heat treatment was identified to be the β-form of silk fibroin (Fig. 2c), as reported by earlier investigators.[6]

Figure 3 shows a DSC curve of silk fibroin with heat treatment at 220°C. The glass transition and crystallization peak were unrecognizable. This is due to the conformational change from the random coil to the β-form. In this case, only the endothermic peak appeared at about 283°C. The fact suggests the degradation of silk fibroin with the β-form.

From these results, we concluded that glass transition and crystallization are present in the amorphous silk fibroin film as well as in synthetic polymers. In this case, the crystallization of amorphous silk fibroin was estimated to be 1.2 kcal/res[7] by using DSC.

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