

Physical Properties and Structure of Silk. XI. Glass Transition Temperature of Wild Silk Fibroins

Silk filament is spun by domestic silkworm, *Bombyx mori*. Wild silkworms also produce the same type of fibrous proteins, fibroins, which are practically used for silk gut or spinning yarn. Previously, we have reported the glass transition temperatures of fibroins obtained from domestic silkworm^{1,2} and tussah silkworm, (*Antheraea pernyi*),³ a wild silkworm. In the present study, we used three wild silkworms, i.e., kusakan (*Dictyoploca japonica*), erisan (*Attacus ricini*), and tensan (*Antheraea yamamai*), and determined the glass transition temperatures of their fibroins by differential scanning calorimetry (DSC) and compared with that of domestic silk fibroin. The effects of methanol treatment on the glass transition temperatures were also investigated.

EXPERIMENTAL

Liquid silk was obtained from the posterior division of the silk gland in full-grown larvae (one day before spinning) of wild silkworms. Aqueous solutions of wild silk fibroins were prepared by dispersing liquid silk in deionized water and diluting to a concentration of about 20%.

Films for DSC measurements were cast from the solutions onto thin polyethylene films and air-dried at 20°C. These wild silk fibroin films were all identified to be in the random-coil conformation containing a small amount of the α -helix conformation from X-ray diffraction patterns. For comparison the domestic silk fibroin films were also prepared as reported previously.^{1,2} Treatment with methanol was carried out by immersing fibroin films in methanol for 48 h at 20°C and then drying at room temperature.

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-II differential scanning calorimeter at a constant heating rate of 10 K/min under nitrogen.

RESULTS AND DISCUSSION

Figure 1 shows DSC curves of wild silk fibroins before and after immersion in methanol. The glass transition temperatures observed as endothermic shifts of the base lines were determined for untreated kusakan, erisan, and tensan fibroins to be 198, 191, and 201°C, respectively. The glass transition temperature of untreated domestic silk (*Bombyx mori*) fibroin was observed at 172°C, which agrees well with 175°C reported previously.^{1,2}

On treatment with methanol, the glass transition temperatures shifted to 208, 202, and 203°C for kusakan, erisan, and tensan fibroins, respectively. The rise of the glass transition temperatures of these wild silk fibroins is attributed to the increase in the crystallinity which restricts molecular motions in the amorphous region. The glass transition was not observed for domestic silk fibroin on treatment with methanol due to the random coil \rightarrow β -form conformational transition accompanied by crystallization and the resulting significant loss of amorphous region.^{4,5}

CONCLUSIONS

The glass transition temperatures of three wild silk fibroins, kusakan, erisan, and tensan, were determined as 198, 191, and 201°C, respectively. These values are higher than 172°C for domestic silk fibroin and 162°C for kusakan. The glass transition temperatures of wild silk fibroins were raised by treatment with methanol due to the increase in crystallinity.

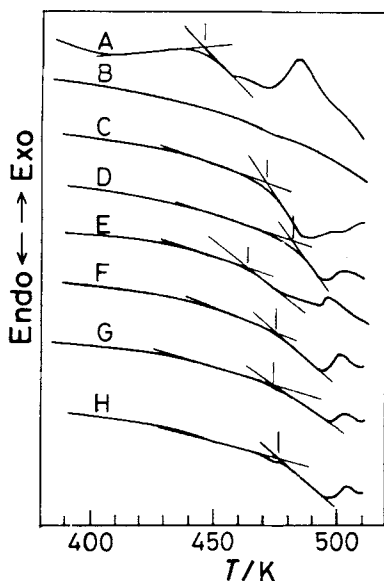


Fig. 1. DSC curves of silk fibroin films untreated and treated with methanol: (A) untreated and (B) treated domestic silk; (C) untreated and (D) treated kusun; (E) untreated and (F) treated erisan; (G) untreated and (H) treated tensan fibroins.

References

1. J. Magoshi and S. Nakamura, *J. Appl. Polym. Sci.*, **19**, 1013 (1975).
2. J. Magoshi, Y. Magoshi, S. Nakamura, N. Kasai, and M. Kakudo, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1675 (1977).
3. J. Magoshi, Y. Magoshi, and S. Nakamura, *J. Appl. Polym. Sci.*, **21**, 2405 (1977).
4. M. Shimizu, *J. Sericult. Sci. Jpn.*, **20**, 155 (1951).
5. J. Magoshi, Y. Magoshi, and S. Nakamura, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 185 (1981).

SHIGEO NAKAMURA
YASUO SAEGUSA
YOSHIO YAMAGUCHI

Department of Applied Chemistry
Faculty of Engineering
Kanagawa University
Kanagawa-ku, Yokohama, Japan

JUN MAGOSHI
SUMIE KAMIYAMA

National Institute of Agrobiological Resources
Yatabe, Ibaraki, Japan

Received March 19, 1985
Accepted May 22, 1985