Elastic modulus of the crystalline regions of Tussah silk

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The elastic modulus E_l of the crystalline regions of Tussah silk of *Antheraea pernyi* parallel to the chain axis was determined by X-ray diffraction. The E_l value was 20 GPa for both (0 0 2) and (0 0 6) reflections (*c* axis; chain direction), which is smaller than that of *Bombyx mori* (23 GPa). The small E_l for silk fibroin of *A. pernyi* is attributed to the large cross-sectional area of one molecule in the crystal lattice.

(Keywords: elastic modulus; crystalline regions; Tussah silk; *Antheraea pernyi*; crystal structure; mechanical property)

Introduction

The elastic modulus E_l of crystalline regions in polymers provides important information on the molecular conformation in the crystal lattice[1–5]. We have measured the E_l of various polymers parallel to the chain axis using X-ray diffraction. The data so far accumulated have led us to relate the E_l value, the extensivity of a polymer molecule, both to the molecular conformation and to the mechanism of the deformation in the crystal lattice. The high E_l values for polymers with a fully extended planar zigzag conformation, i.e. polyethylene (PE) with $E_l = 235$ GPa and poly(vinyl alcohol) (PVA) with $E_l = 250$ GPa, are attributed to the high force constants of bond stretching and bond angle bending.

Silk is a most important fibrous substance with unparalleled qualities for textiles, etc. It was reported that the molecular chain of silk fibroin has a large scale zigzag conformation in which the zigzag unit is composed of amino acid residues, in the so-called pleated sheet conformation[6,7]. The crystalline regions of *Bombyx mori* are composed of glycine, alanine and serine residues (3:2:1). In a previous paper[8], we measured the value of E_l for silk fibroin of *B. mori* by X-ray diffraction (23 GPa). We discussed the E_l value in relation to both the crystal structure and the specimen modulus.

Here we report the value of E_l for Tussah silk of *Antheraea pernyi* by X-ray diffraction. Silk fibroin of *A. pernyi* is similar to that of *B. mori* in its skeletal structure in the crystalline regions[9], but is mainly composed of alanine residues.

Experimental

Degummed and annealed (200°C, 1 h at constant length) silk fibroin of *A. pernyi* was used. The density of the specimen was 1.308 g cm^{-3}, as measured by the flotation method in benzene–carbon tetrachloride at 30°C. The specimen's modulus was 8.9 GPa, as measured from the initial slope of the stress–elongation curve using a tensile tester (Shimadzu Autograph SD-100) at 20°C. The initial length of the specimen was 20 mm, and the extension rate was 2 mm min^{-1}.

Figure 1 shows the X-ray fibre photograph of degummed and annealed silk fibroin of *A. pernyi*. *Figure 1* shows the high crystallinity and high degree of orientation of the crystallites.

The lattice extension under a constant load was measured by means of an X-ray diffractometer (Rigaku Denki Co. Ltd, RAD-B System) equipped with a stretching device and a load cell. The strain ε of the fibre identity period was estimated by measuring the diffraction peak shift induced by an applied constant stress.

Marsh *et al.*[9] reported that the pseudo crystal structure of silk fibroin of *A. pernyi* belongs to an orthogonal system. The unit cell parameters were $a = 9.46$ Å, $b = 10.54$ Å, c (fibre axis is converted from b to c axis) $= 6.92$ Å measured by equatorial and meridional reflections. In this study, (0 0 2) and (0 0 6) reflections were employed for the measurement of E_l. The experimental error in measuring the peak shift was evaluated ordinarily to be $< \pm 1/100°$ in 2θ angle.

This X-ray method is based on the assumption of homogeneous stress distribution, in other words, stress σ in the crystalline regions is equal to that applied to the specimen (externally applied stress). This assumption has been proven for PE, PVA, cellulose, poly(*p*-phenylene terephthalamide), poly(ethylene terephthalate), etc.[1–5].

The elastic modulus E_l was calculated as:

$$E_l = \sigma / \varepsilon$$

All the measurements were performed at 25°C and 60% relative humidity. More detailed descriptions have been given in earlier papers[1–5].

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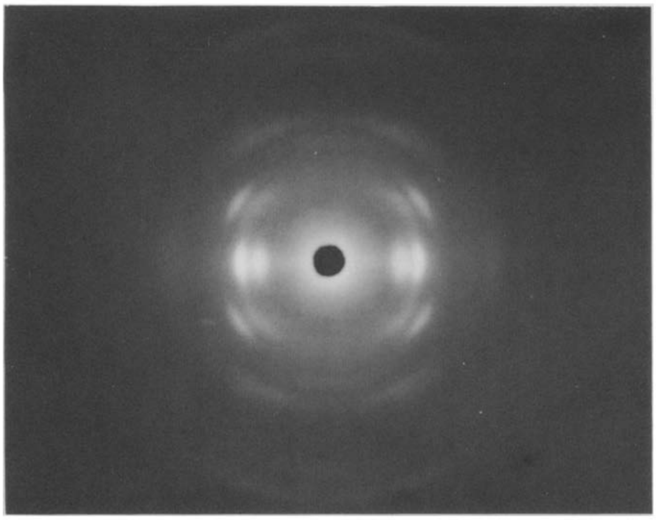

Figure 1 X-ray fibre photograph of silk fibroin of *A. pernyi*

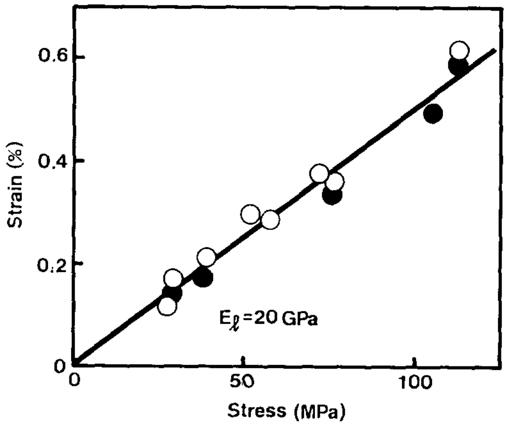

Figure 2 Stress–strain curves for the (0 0 2) plane (○) and the (0 0 6) plane (●) of silk fibroin of *A. pernyi*

Results and discussion

Figure 2 shows the stress σ–strain ε curves for the (0 0 2) and (0 0 6) planes of silk fibroin of *A. pernyi* at 25°C. Plots from the (0 0 2) plane coincided with those of the (0 0 6) plane within experimental error. They could be expressed by a straight line through the origin, and the lattice extensions were always reversible. From the initial slope of the curve, the E_l value obtained was 20 GPa.

Table 1 shows the E_l value, the f value, that is, the force required to stretch one molecule by 1%, and the cross-sectional area, S, of one molecule in the crystal lattice of silk fibroins of both *A. pernyi* and *B. mori*[8]. The E_l values of these silk fibroins were very low compared with those of PE, PVA (~one-tenth). The low E_l values of silk fibroins can be attributed to their contracted conformation, which are shrunk 5.6–5.8% compared with the fully extended conformation owing to the internal rotation around C–C single bonds. For the deformation of these conformations, the mechanism of the change in the internal rotation angle plays an important role, with the force constant being smaller than those of bond stretching and angle bending. More detailed descriptions have been given in a previous paper[8]. As shown in *Table 1*, the E_l value of *A. pernyi* was slightly smaller than that of *B. mori*. The S value is larger for the silk fibroin of *A. pernyi*. The crystalline regions of silk fibroin of *B. mori* consist of glycine, alanine and serine (3:2:1), while that of *A. pernyi* is mainly composed of alanine[10]. In the latter case, the methyl group of alanine lies in the *b*-direction (perpendicular to the hydrogen bonds) and the higher bulkiness of the methyl group than that of hydrogen increases the *b*-dimension. This brings the increment of S and the decrement of E_l for silk fibroin of *A. pernyi*. Accordingly, by correcting the effect of S of one chain, the f values were equal to each other. This indicates that the difference in S of one molecule in the crystal lattice, or the number of chains passing through per unit area, is the origin of the difference of E_l for these two silk fibroins. Marsh *et al.*[9] reported a real, though small, difference in the fibre identity periods between silk fibroin of *A. pernyi* (9.65 Å) and *B. mori* (9.67 Å). This implies a larger twist in the chains of silk fibroin of *A. pernyi*. However, this contraction does not seem to influence the mechanical properties of the chain judging from the similarity in f values.

Table 1 Elastic modulus E_l, the cross-sectional area S and the f values of silk fibroin of *A. pernyi* and *B. mori*

	E_l (Gpa)	S (Å^2)	f ($\times 10^{-10}$) (N)
A. pernyi	20	25.0	0.50
B. mori	23	21.7	0.50

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