

Influence of Swelling of Noncrystalline Regions in Silk Fibers on Modification with Methacrylamide

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SYNOPSIS

The degrees of swelling of noncrystalline regions of domestic and tussah silk fibers were investigated by measuring the small-angle X-ray scattering intensity of the fibers in wet conditions and analyzing the scattering intensity based on a two-phase model, i.e., crystalline regions and water-swollen noncrystalline regions. The influence of the degree of swelling of noncrystalline regions on the graft treatment of these fibers with methacrylamide was investigated. The changes in the structure caused by the graft treatment were also analyzed using the wide-angle X-ray diffraction measurements. As compared with the tussah silk fibers, the domestic silk fibers showed a larger degree of swelling of the noncrystalline regions, and gained a larger amount of resin by the graft treatment. The crystallites with smaller sizes in the tussah silk fibers were destroyed preferentially by the graft treatment. For the domestic silk fibers, the crystallites were destroyed more seriously and rather homogeneously independent of the crystallite sizes. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

To develop new textile products from silk fibers, several inferior properties of these fibers such as low-crease resistance and low-resistance to abrasion during laundering should be modified. For the modification of silk fibers with chemical agents, the swelling property of the noncrystalline regions is an important factor since the reactions of the chemical agents with the fibers usually occur in the noncrystalline regions of the fibers.

The graft copolymerization with some kinds of vinyl monomers has been applied for silk fibers.^{1,2} Methacrylamide (MAA) is one of the most attractive vinyl monomers since large polymer add-on can be easily obtained because of the hydrophilic nature of MAA. Furthermore, the authors have found that the graft copolymerization with MAA effectively improves crease resistance and resistance to abrasion of silk fibers.^{3,4}

In this paper, the degrees of swelling of noncrystalline regions in domestic and tussah silk fibers were

investigated and the influence of the swelling property on the graft treatment of these fibers with MAA was discussed.

EXPERIMENTAL

Materials

The raw silk fibers from domestic silkworm (*Bombyx mori*) and Chinese tussah silkworm (*Antheraea pernyi*) were degummed with enzymes as described in the previous paper.⁵ The weight losses of the fibers by the degumming were 22.0 and 11.6%, respectively, for these fibers.

Graft Treatment

The graft treatments were performed by using methacrylamide (MAA) and ammonium persulfate of reagent grade. The fibers were immersed in a resin aqueous solution, consisting of MAA (0.8 mol/L) and ammonium persulfate (0.05 mol/L) adjusted at pH 3.0 by using sulphuric acid, at 50°C for various periods under a nitrogen atmosphere. The liquor-to-material ratio was kept at 170 : 1. Then the fibers

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were thoroughly rinsed with water. The polymer add-on, G , was calculated from the increase in the weight of the fibers by using the equation

$$G = \frac{M_1 - M_0}{M_0} \quad (1)$$

where M_0 and M_1 are the weights of the dry fibers before and after the graft treatment.

Small-Angle X-Ray Scattering Measurements on Wet Fibers

The fibers were wound in parallel with each other on small rectangular frames made of thin metal wire. By adjusting the number of layers wound on the frame, the volume of the fibers irradiated by the X-ray was kept approximately constant. The frame was soaked in water at room temperature for 24 h, and then enclosed in a small cell with windows made of very thin polymethylmethacrylate film for the X-ray path. The top of the cell was wrapped with the film to keep the fibers under wet conditions. The equatorial small-angle X-ray scattering (SAXS) intensity distributions were measured with a diffractometer (Rigakudenki Ltd.), a position sensitive proportional counter (PSPC, Rigakudenki Ltd.) and a pulse height discriminator using pinhole-collimated CuK_α x-rays.

No height-limiting slit was attached to the PSPC. Blank exposure of the cell filled with water showed negligible scattering as compared with the scattering by the sample. Since the SAXS of silk fibers was a narrow streak along equator, the intensity, $I(2\theta)$, measured without using the height-limiting slit, was the intensity integrated with respect to the axis parallel to the fiber axis. Since the absolute intensity of the incident beam was not measured, a parameter proportional to the scattering power of swollen silk fibers, J , was estimated by using the equation⁶

$$J = \int_0^\infty I(2\theta) 2\theta d\theta \quad (2)$$

where 2θ is the scattering angle. In calculating eq. (2), the intensity distribution at very small angles was obtained by extrapolating the experimental scattering curves to zero angle by using a Guinier plot.

Wide-Angle X-Ray Diffraction Measurements for Dry Fibers

The wide-angle X-ray diffraction (WAXD) was measured with a diffractometer, a PSPC, and a pulse height discriminator using pinhole-collimated CuK_α X-rays. No height-limiting slit was attached to the PSPC.

Crystallinity index, C , was calculated by the equation⁷

$$C = \frac{\iint I(\theta, \phi) \sin^2 \theta \cos \theta \sin \phi d\phi d\theta}{rt} \quad (3)$$

where

$$t = -\frac{\ln r}{\rho\mu} \quad (4)$$

$I(\theta, \phi)$ is the intensity distribution of the overlap of 002 and 201 diffractions, r and t are the X-ray transmittance and the thickness of the specimen, ρ is the density of the fibers, and μ is the mass absorption coefficient of carbon. Since the changes of the Jacobian for the integration of $I(\theta, \phi)$ with respect to θ and ϕ , i.e., $\sin^2 \theta \cos \theta \sin \phi$, were relatively small in the angle region to be measured, the Jacobian was assumed to be one. The orientation of the crystallinities in these fibers was high, thus, the intensity, $I(\theta, \phi)$, measured without using a height-limiting slit, was the intensity integrated with respect to the azimuthal angle.

Crystallite size,⁸ L_c , and degree of orientation,⁹ Π , were calculated by using the following equations:

$$L_c = \frac{0.94\lambda}{\beta \cos \theta_{201}} \quad (5)$$

$$\Pi = \frac{\pi - \gamma}{\pi}, \quad (6)$$

where θ_{201} is the peak Bragg angle, β the full width at half maximum of the equatorial intensity distribution, γ the full width at half maximum of the azimuthal intensity distribution, respectively, for the 201 diffraction, and λ is the X-ray wavelength.

RESULTS AND DISCUSSION

Swelling of Silk Fibers

Figure 1 shows the equatorial SAXS intensity distributions of the swollen fibers. The SAXS intensity

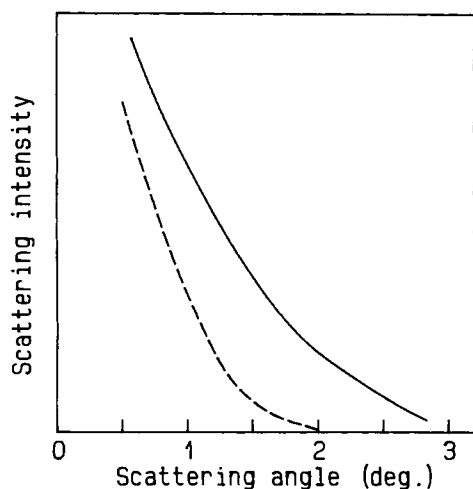


Figure 1 Equatorial small-angle X-ray scattering profiles. Solid curve, swollen domestic silk fibers; dashed curve, swollen tussah silk fibers.

for swollen domestic silk fibers is markedly stronger than the swollen tussah silk fibers. The ratio of J values for swollen tussah silk fibers against that for swollen domestic silk fibers was 0.38.

Hermans et al.¹⁰ have reported that the scattering power for the swollen cellulose fibers can be explained by using a two-phase model, i.e., crystalline regions and noncrystalline regions containing water. The scattering power, S , is given by the equation

$$S = (\sigma_1 - \sigma_2)^2 w_1 w_2 = KJ \quad (7)$$

where σ_1 and σ_2 are the electron densities of the two regions and w_1 and $w_2 = (1 - w_1)$ are the volume fractions of these regions. K is a constant depending on the intensity of the incident beam. By assuming that the electron density is proportional to the gravimetric density, the scattering power for water swollen silk fibers was calculated by using the following equation:

$$S = K'(d_c - d_a)^2 w_1 (1 - w_1) \quad (8)$$

where K' is a constant, d_c and d_a are the gravimetric densities of the crystalline regions and noncrystalline regions in the silk fibers containing water, and w_1 in this case is the volume fractions of the crystalline regions of silk fibers containing water. By assuming that water was absorbed only in noncrystalline regions and the noncrystalline regions were expanded by the volume equal to the volume of water absorbed, d_a and w_1 can be calculated by using equations

Table I Crystallinity, v_c , Density of Crystallites, d_c , and Density of Noncrystalline Regions, d_{a0} , for Dry Domestic and Tussah Silk Fibers

Fiber	v_c (%)	d_c (g/cm ³)	d_{a0} (g/cm ³)
Domestic silk	59.9	1.410	1.26
Tussah silk	54.9	1.357	1.20

$$d_a = \frac{d_{a0}(1 - v_c) + d_w v_w}{1 - v_c + v_w}, \quad (9)$$

$$w_1 = \frac{v_c}{1 + v_w}, \quad (10)$$

where d_{a0} and d_w are the gravimetric densities of noncrystalline regions of dry silk fibers and water, v_c is the volume fractions of crystalline regions of dry silk fibers, and v_w , the ratio of volume of water absorbed in noncrystalline regions of the fibers against the volume of dry fibers. For d_c , the value reported by Marsh et al.^{11,12} was used, and for d_{a0} and v_c , the values determined in the previous works^{13,14} were used. The density of water, d_w , was assumed to be 1 g/cm³. These values are summarized in Table 1. For various values of v_w , d_a and w_1 were calculated by using eqs. (9) and (10), and then $(d_c - d_a)^2 w_1 (1 - w_1)$ in eq. (8) was calculated. The values of $(d_c - d_a)^2 w_1 (1 - w_1)$ are plotted against v_w in Figure 2. The scattering power showed a maximum at $v_w = 1$.

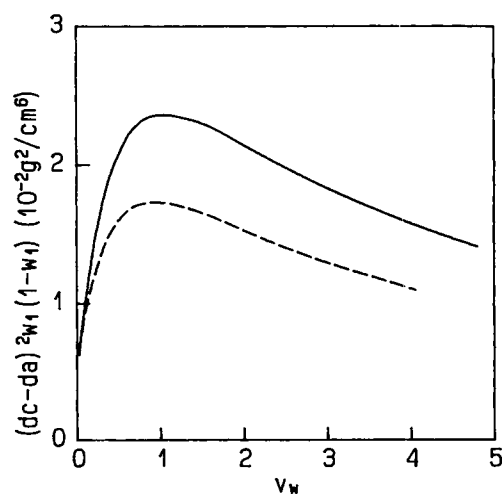


Figure 2 $(d_c - d_a)^2 w_1 (1 - w_1)$ against v_w . Solid curve, swollen domestic silk fibers; dashed curve, swollen tussah silk fibers. v_w is the ratio of volume of water absorbed in noncrystalline regions of the fibers against the volume of the dry fibers.

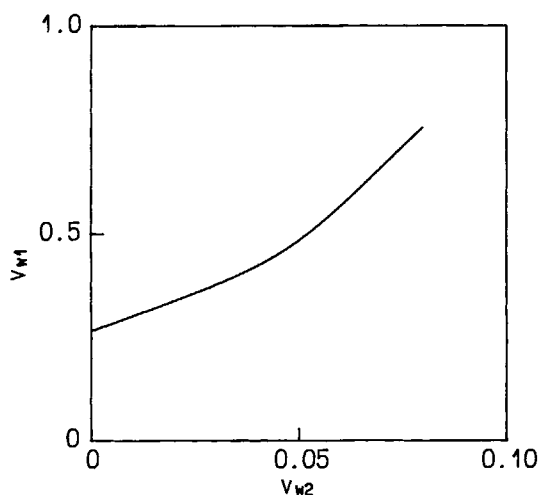


Figure 3 Relation between v_{w1} and v_{w2} , which make the relative scattering power of the tussah silk fibers against domestic silk fibers equal to 0.38. v_{w1} and v_{w2} are the ratios of volume of water absorbed in noncrystalline regions against the volume of the dry fibers for domestic silk fibers and tussah silk fibers, respectively.

From the values shown in Figure 2, the values of v_w for the domestic and the tussah silk fibers, v_{w1} and v_{w2} , respectively, were calculated so that the relative values of the scattering power became 0.38. Since the amount of water absorbed by the silk fibers is several tens of percents of the fiber volume at maximum,¹⁵ the calculation was made in the range $v_{w1}, v_{w2} < 1$. The results are shown in Figure 3. The increase in the cross sectional area of the domestic silk fibers by the swelling in water was measured to be 18.2%.¹⁴ In Figure 3, the value of v_{w1} takes a minimum value of 0.27 at $v_{w2} = 0$. Therefore, it is known that the tussah silk fibers scarcely absorb water in the noncrystalline regions. However, the increase of the cross sectional area of the tussah silk fibers by the swelling in water was measured to be 15.9%.¹⁴ In the cross section of tussah silk fibers, a large number of voids with diameter of about 0.2 μm have been observed by the scanning electron microscope.¹⁶ For the domestic silk fibers, these voids with large sizes were not observed. Therefore, it is considered that the cross section of tussah silk fibers was increased by the water entered in these large voids. The sizes of these voids are so large that SAXS caused by them is limited in a very low scattering angle and was not detected by the SAXS measurements in this study.

Tussah silk fibers have several noticeable properties such as high resistance to chemicals, high glass transition temperature, and high thermolysis temperature. Domestic silk fibers shrink readily in so-

lutions of lithium salts while tussah silk fibers withstand this treatment. The glass transition temperature of tussah and domestic silk fibers are 201¹⁷ and 175°C,¹⁸ respectively. The thermolysis temperatures of tussah and domestic silk fibers determined from DSC thermal analysis¹⁹ are 362 and 320°C, respectively. As is indicated by the native color of tussah silk fibers, the tussah silk fibers contain tanning agents,²⁰ which are not found in domestic silk fibers. It is well known that tanning agents tend to gum proteins. Brunet and Coles²⁰ have pointed out the high resistance to chemicals can be explained by the crosslinkings between molecular chains of tussah silk fibers brought about by the tanning agents. The occurrence of crosslinkings also increases the glass transition and thermolysis temperatures. The authors¹⁴ have shown that thermolysis temperature is increased by fixing the tanning agents in domestic silk fibers. Therefore, it is considered that the occurrence of crosslinkings by tanning agents has contributed to the high resistance against thermal decomposition of tussah silk fibers. Crosslinkings in noncrystalline regions of tussah silk fibers are considered to prevent water from penetrating into noncrystalline regions of the fibers and lower the degree of swelling.

Graft Treatment of Silk Fibers with Methacrylamide

The polymer add-on for the silk fibers by the graft treatment with methacrylamide (MAA) is plotted against the treatment time in Figure 4. Larger polymer add-on was obtained for the domestic silk fibers

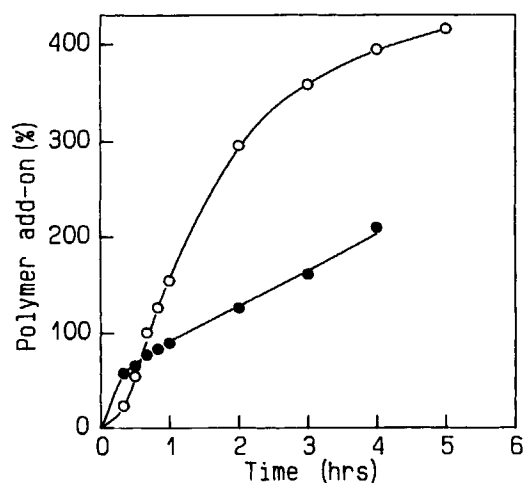


Figure 4 Polymer add-on against graft treatment time. Open circles, domestic silk fibers; solid circles, tussah silk fibers.

as compared with the tussah silk fibers. The reactions of MAA with silk fibers are accelerated by radicals derived in the fibers. It is known that tyrosine, tryptophan, and histidine residues in wool^{21,22} and primary alcohols in cellulose²³ are radicalized by the decomposition of persulfate. Silk fibers have primary alcohols at serine residues. Therefore, for silk fibers, tyrosine, tryptophan, histidine, and serine residues are considered to be radicalized by the decomposition of ammonium persulfate used for MAA treatment. The amount of these amino groups, however, does not differ significantly between domestic and tussah silk fibers.²⁴ Therefore, it is difficult to explain the difference in polymer add-on between domestic and tussah silk fibers by the difference in the amino acid composition.

The crystallinity index, the crystallite size, and the degree of orientation are plotted against polymer add-on of the silk fibers in Figure 5. If it is assumed that the amount of the crystallites is unchanged by the graft treatment, then the crystallinity index of the treated fibers, C , is calculated from the crystallinity index of the untreated fibers, C_0 , by using the equation

$$C = C_0 \frac{B_0}{B_1} \quad (11)$$

where B_0 and B_1 are the volume of the dry silk fibers before and after graft treatment. The values of C calculated in this way are shown in Figure 5, top, by a dashed curve. Experimental values of the crystallinity index were smaller than the calculated values. Thus the crystallites were destroyed by the graft treatment. The crystallite size increased with increasing polymer add-on for tussah silk fibers, whereas the crystallite size was almost unchanged for domestic silk fibers (see Fig. 5, middle). The increase in the crystallite size and the decrease in the crystallinity for tussah silk fibers suggest that the crystallites with smaller sizes were destroyed preferentially by the MAA graft treatment. The degree of orientation decreased by the graft treatment (see Fig. 5, bottom). From these results, it is known that polymerization of MAA infused in the noncrystalline regions of the fibers disturbed orientation of the crystallites caused the internal strain, and finally destroyed the crystallites. The permeation of MAA into the noncrystalline regions will be serious for domestic silk fibers since the degree of swelling of the noncrystalline regions is larger for domestic silk fibers as compared with tussah silk fibers as shown in the previous section. It is concluded that domestic silk fibers that showed a larger degree of swelling of

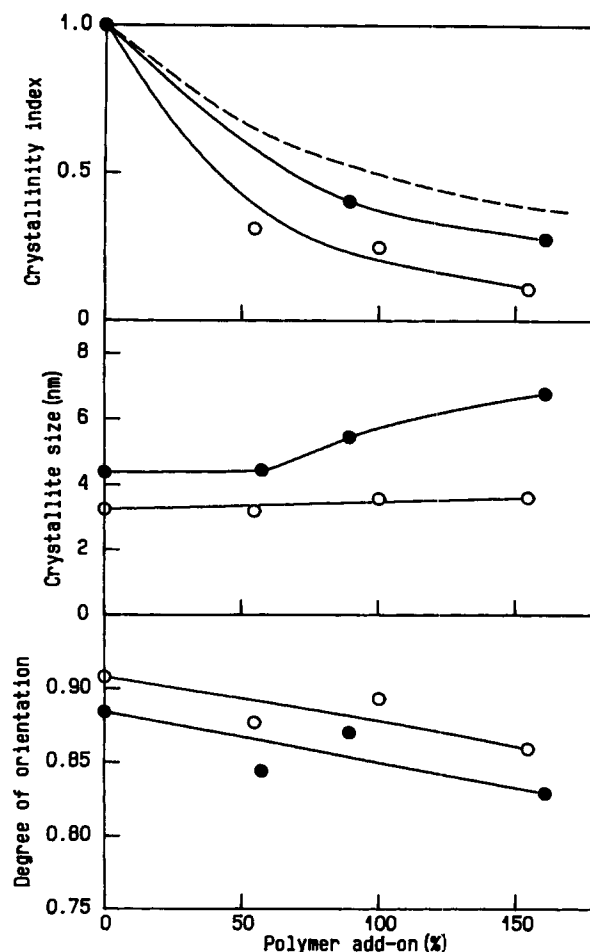


Figure 5 Crystallinity index, crystallite size, and degree of orientation against polymer add-on. Open circles, domestic silk fibers; solid circles, tussah silk fibers. Dashed curve shows crystallinity index calculated by assuming that the amount of crystallites is unchanged.

the noncrystalline regions gave larger polymer add-on and suffered serious destruction of the crystallites.

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