Characterization of Microvoids in Mulberry and Tussah Silk Fibers Using Stannic Acid Treatment

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ABSTRACT: To investigate the volume, size, and number of microvoids in mulberry and tussah silk fibers, stannic acid gel was used as a contrasting medium to the small-angle X-ray scattering (SAXS). The influence of the stannic acid treatment on the structure of silk fibers was first investigated by using the wide-angle X-ray diffraction prior to characterization of the microvoids. The changes in crystallite size and degree of orientation with increasing stannic acid gel fraction in fibers are investigated, and it was found that the stannic acid treatment does not cause serious changes in crystallite size and degree of orientation. The changes in crystallinity indices were observed when the volume fractions of stannic acid gel in the fibers exceeded about 10%. Thus, it was confirmed that the structure of silk fibers was retained in the region of the stannic acid gel fraction less than 10%. SAXS measurements revealed that the number and the fraction of the microvoids are larger, while the sizes of the microvoids are smaller, for the mulberry silk fibers compared with the tussah silk fibers. The fraction macrovoids, however, is considered to be larger for the tussah silk fibers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 363–367, 1999

Key words: microvoid; silk fiber; mulberry; tussah; X-ray

INTRODUCTION

To develop new textile products from silk fibers, chemical modifications are necessary for the improvement of their inferior properties such as low crease resistance and low resistance to abrasion during laundering. For the modification of silk fibers with chemical agents, the degree of swelling of noncrystalline regions is a crucial factor because the reactions of the fibers with the chemical agents usually occur in the noncrystalline regions. In the case of graft treatments of mulberry and tussah silk fibers using methacrylamide, the amount of resin gained by the fibers is strongly related to the degree of swelling of noncrystalline regions, as determined by the small-angle X-ray scattering (SAXS) measurements.[1] That is, mulberry silk fibers that showed a larger degree of swelling of noncrystalline regions gained a larger amount of resin compared with tussah silk fibers.

It is well known that when the silk fibers are swollen with water or an aqueous solution of chemical agents, the cross-sectional area of the fibers markedly increases. This suggests that water and chemical agents penetrate into the voids in the silk fibers, and the voids are expanded due to dissociation of hydrogen bondings between fibrils. The voids having sizes less than several 10

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nm are detectable with SAXS and are called microvoids in this study.

In the previous study,[1] both the amorphous regions and the microvoids are treated as the noncrystalline regions, and the discrimination between these two components in the noncrystalline region was not made. This was because the electron density difference between the swollen amorphous regions and the microvoids containing water was so small that it was difficult to differentiate the SAXS due to these two components. Although a tremendous amount of investigation has been carried out so far on the wet fibers, only little information have been obtained with respect to the sizes and fractions of the microvoids into which water and chemical agents penetrated.[2–6]

To characterize microvoids in wet silk fibers, the present authors have applied the stannic acid treatment. The stannic acid treatment itself has a long history as a method to improve drapeability and to increase mass of the silk fibers. When the silk fibers are treated with an aqueous solution of stannic chloride, stannic acid gel is formed and fixed in the microvoids which have been expanded, in the swollen state, due to the dissociation of hydrogen bondings between molecules.[7] Because the electron density of stannic acid gel is extremely larger than other portions of the swollen silk fibers, stannic acid gel contrasts the microvoids. Thus, it is possible to characterize the microvoids, separately from the amorphous regions, in the swollen silk fibers by using the stannic acid gel as a contrasting medium to the SAXS.

This article reports the results of the characterization of the microvoids in mulberry and tussah silk fibers in the swollen state by using the stannic acid treatment. The difference in the swelling behaviors between these silk fibers was discussed.

EXPERIMENTAL

Materials

The raw silk fibers from mulberry silkworm (*Bombyx mori*) and Chinese tussah silkworm (*Antheraea pernyi*) were degummed with enzymes as described in a previous article.[8] The weight losses of these fibers by the degumming were 22.0 and 11.6%, respectively.

Stannic Acid Treatment

The fibers were immersed in an aqueous solution of 50% stannic chloride at a room temperature for 1 h, and then immersed in an aqueous solution of 6% disodium hydrogenphosphate at 65°C for 1 h. By repeating these procedures, the mass of fiber was increased. The volume fraction of stannic acid gel, v_g, fixed in the fibers were calculated by using the equation.

$$v_g = (\rho_f/\rho_{sn})\ W/(1 + W) \tag{1}$$

where W is the ratio of the weight gain by the treatment against the initial weight of the fibers, and ρ_f and ρ_{sn} are the densities of the treated fibers and stannic acid gel, respectively. The density of stannic acid gel[7] is 3.95 g/cm^3.

Density

Density of the fibers were measured at 23°C by using a density gradient column with a mixture of heptane and carbon tetrachloride or a mixture of carbon tetrachloride and bromoform.

X-ray Measurements

Wide-angle X-ray diffraction (WAXD) and SAXS were measured on aligned silk fibers by using a diffractometer (Rigaku Denki Ltd.), a position-sensitive proportional counter (PSPC, Rigaku Denki Ltd.), a pulse-height discriminator, and pinhole-collimated CuK_α X-rays. No height-limiting slit was attached to the PSPC. The X-ray specimens were prepared by aligning the fibers in parallel to each other into a bundle with a desirable thickness so that the volume of the fibers irradiated by the X-ray beam was kept approximately constant.

As shown later, the peak breadths of the equatorial and the azimuthal 201 WAXD intensity distributions were not changed by the stannic acid treatments. Thus, the peak intensity of the 201 diffraction, I_{201}, is in proportional to the crystallite fraction. Crystallinity indices of the fibers, C, were therefore calculated by using the equation.

$$C = \frac{I_{201}}{rL_1} \tag{2}$$

where r is the X-ray transmittance of the treated fibers and L_1 the thickness of silk part in the treated fibers. The optical path length in the treated fibers, t, is the sum of the thicknesses of the silk part and the stannic acid gel part. Thus, the value of L_1 was estimated as follows.

$$L_1\ \rho_0 + (t - L_1)\ \rho_{sn} = t\rho_f \tag{3}$$

$$t = -(\ln r)/(\rho_f \mu_f) \quad (4)$$

$$\mu_f = \mu_c(1 - W) + \mu_{sn} W \quad (5)$$

where ρ_0 is the density of untreated fibers, μ_{sn} and μ_c the mass absorption coefficients of tin and carbon, which are the major elemental components of the treated silk, respectively.

Crystallite size,[9] L_{201}, and degree of orientation,[10] Π, were calculated by using the following equations

$$L_{201} = (0.94\ \lambda)/(\beta \cos \theta_{201}) \quad (6)$$

$$\Pi = (\pi - \gamma)/\pi \quad (7)$$

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

From the SAXS intensity distributions, the microvoids volume fraction, v_p, the average area of the microvoid cross-section perpendicular to the fiber axis, S, and the number of microvoids per unit area of the fiber cross-section perpendicular to the fiber axis, n, were calculated by using the following equations.[11]

$$v_p = \{(2\pi\ m^2\ c^4)/(e^4\ \lambda^3\ \Delta\rho^2\ L\ t\ A_0)\} \int I(x)\ x\ dx \quad (8)$$

$$\ln I(x) = -k\ x^2 + \ln S + \ln\{(2\pi/\lambda^2/L^2) \int I(x)\ x\ dx\} \quad (9)$$

$$n = v_p/S \quad (10)$$

where $I(x)$ is the SAXS intensity at the scattering angle x, L the sample-to-receiver distance, m the electron mass, e the elementary electric charge, c the light velocity, and k the constant, respectively. The intensity of the primary beam, A_0, was determined by measuring the scattering of the standard sample, carbon fiber.[11] $\Delta\rho$ is the electron density difference between the voids and the surrounding solid, i.e., nearly equal to the electron density of the fiber. For the treated fibers, $\Delta\rho$ is given by the difference in the electron density between silk and stannic acid gel. The electron density of stannic acid gel was calculated from the gravimetric density of stannic acid gel by dividing with the atomic weight of tin and multiplying the number of electrons per tin atom. The electron density of silk was similarly calculated by considering the atomic contents in the unit cell of the silk crystallites.[12,13]

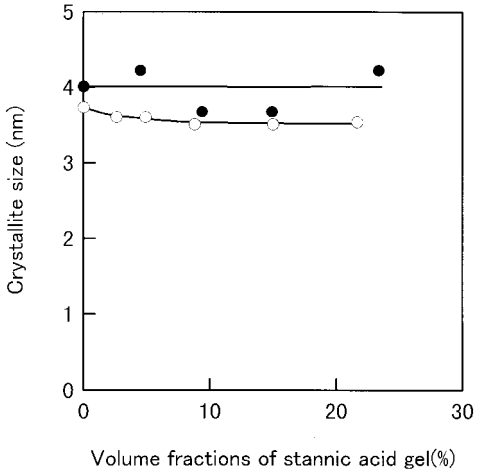

Figure 1 Crystallite sizes plotted against volume fractions of stannic acid gel in fibers for mulberry (open circle) and tussah (solid circle) silk fibers.

RESULTS AND DISCUSSION

Influence of the Stannic Acid Treatment on the Crystallite Structure

The influence of the stannic acid treatment on the structure of silk fibers was first investigated by using WAXD prior to characterization of the microvoids. The changes in crystallite size and degree of orientation with increasing stannic acid gel fraction in fibers are shown in Figures 1 and 2. Tussah silk fibers show slightly larger crystallite sizes than mulberry silk fibers. It is known that the stannic acid treatment does not cause serious changes in crystallite size and degree of orientation. Figure 3 shows the changes in crystallinity indices by the treatment. When the volume fractions of stannic acid gel exceed about 15%, crystallinity indices decrease for mulberry silk fibers, suggesting destruction of crystallites. The decrease of the crystallinity indices, however, was no more than 20%. On the other hand, crystallinity indices for tussah silk fibers increase when the volume fractions of stannic acid gel exceed about 10%. The increase in crystallinity for tussah silk fibers was also observed when the fibers were treated with a dilute aqueous solu-

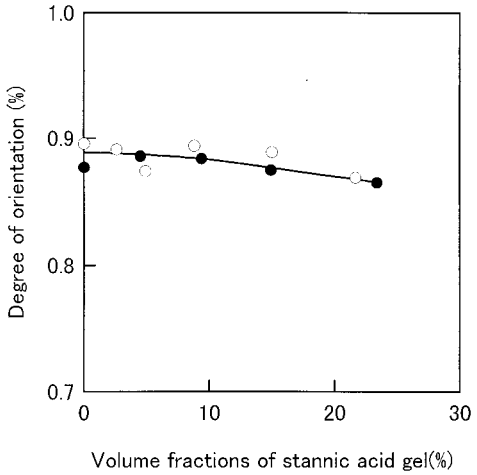

Figure 2 Degree of orientations plotted against volume fractions of stannic acid gel in fibers for mulberry (open circle) and tussah (solid circle) silk fibers.

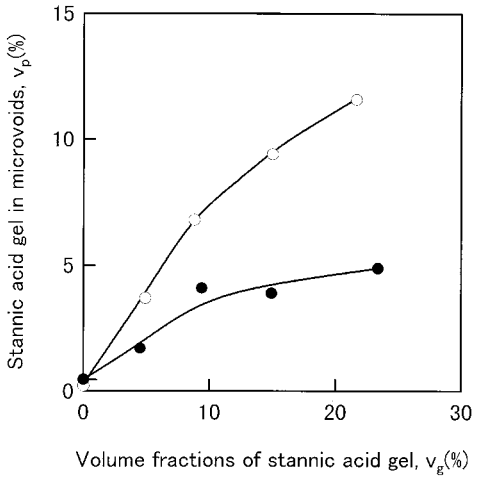

Figure 4 Microvoid volume fractions plotted against volume fractions of stannic acid gel in fibers for mulberry (open circle) and tussah (solid circle) silk fibers.

tion of hydrochloric acid.[14] Thus, it is confirmed that the structure of silk fibers was retained in the region of the stannic acid gel fraction less than 10%.

Microvoids Containing Stannic Acid Gel

The stannic acid-treated fibers produced narrow streak-type SAXS similar to the untreated silk fibers, while the intensity of the SAXS was intensified by the contrasting effect of the stannic acid gel fixed in the microvoids.

Figure 4 shows the volume fractions of stannic acid gel fixed in microvoids, v_p, as a function of the stannic acid gel fraction in the fibers, v_g. It is known that the volume fraction of stannic acid gel fixed in the microvoids is smaller than the fraction fixed in the whole fibers. This indicates that part of stannic acid gel was trapped in the macrovoids of the fibers. In effect, a large number of macrovoids with diameters of about 0.2 μm have been observed by the scanning electron microscope in the cross-section of tussah silk fibers.[15] Although such large macrovoids have not been observed for the mulberry silk fibers, the difference between v_p and v_g values indicates that part of the stannic acid gel was trapped in the voids beyond the sizes detectable with SAXS. It is known from Figure 4 that at an equivalent value of v_p, tussah silk fibers show a larger stannic acid gel fraction in the fibers compared with mulberry silk fibers. This result is in accordance with the microscopic observation showing that tussah silk fibers contain larger amount of macrovoids. With increasing values of v_g, the microvoid fraction becomes saturated for tussah silk fibers. For the mulberry silk fibers, the increment of v_p value is, although not saturated, also depressed. At this level, the mulberry silk fibers shows larger v_p value than the tussah silk fibers. This indicates that mulberry silk fibers have a larger amount of microvoids accessible with stannic acid gel compared with the tussah silk fibers.

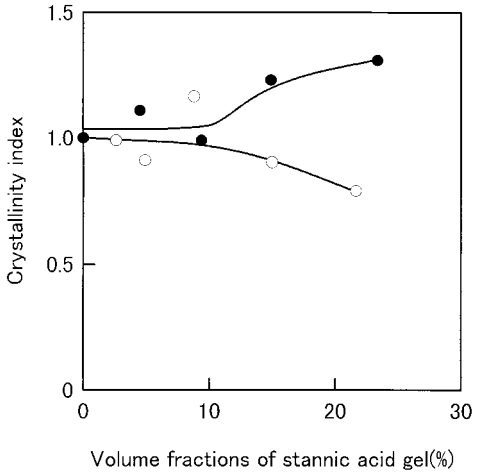

Figure 3 Crystallinity indices plotted against volume fractions of stannic acid gel in fibers for mulberry (open circle) and tussah (solid circle) silk fibers.

The cross-sectional area of the microvoids and the number of the microvoids per unit cross-section area of fibers are shown in Figures 5 and 6 as a function of the stannic acid gel fraction in fibers. At the beginning of the stannic acid treatment, the number of the microvoids increases while the size of the microvoid cross-section decreases up to the

stannic acid fraction of about 10%. This indicates that microvoids with smaller sizes are gradually accessed by stannic acid gel and produces SAXS. Beyond the stannic acid gel fraction of about 15%, the number of the microvoids decreases while the cross-section size increases for the mulberry silk fibers. This would be related to the destruction of the crystallites at this higher stannic acid gel fraction, as shown in Figure 3, where the association of the adjacent microvoids resulting in the increase in the microvoid cross-section area and decrease in the number of microvoids takes place. Thus, it would be suitable to compare the microvoids in the mulberry and the tussah silk fibers at the stannic acid gel fraction of about 10% where the microvoids of smaller sizes have already been accessed but the association of the microvoids has not occurred yet. By comparing the microvoid parameters at this stannic acid gel fraction, it is known that the number and the fraction of the microvoids are larger, while the sizes of the microvoids is smaller for the mulberry silk fibers compared with the tussah silk fibers. These microvoids are considered to be produced by the dissociation of hydrogen bondings between molecules in the fibers. The fraction macrovoids, however, are considered to be larger for the tussah silk fibers.

The reactivity of the silk fibers with a chemical agents is positively correlated to the largeness of the internal surface area as well as the external surface area. Because mulberry silk fibers show a larger volume fraction and a smaller sizes of the microvoids, it is expected that the internal surface area for mulberry silk fibers is larger than the tussah silk fibers. This results is in accordance with the difference of the weight gain by the graft treatment with methacrylamide between the mulberry and the tussah silk fibers. That is, the mulberry silk fibers gained a larger amount of resin than the tussah silk fibers.[1]

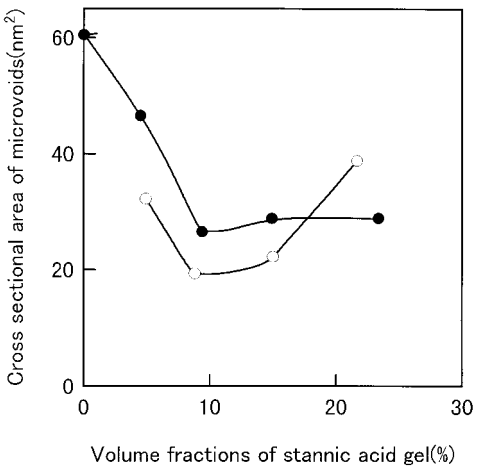

Figure 5 Cross-sectional area of microvoids plotted against volume fractions of stannic acid gel in fibers for mulberry (open circle) and tussah (solid circle) silk fibers.

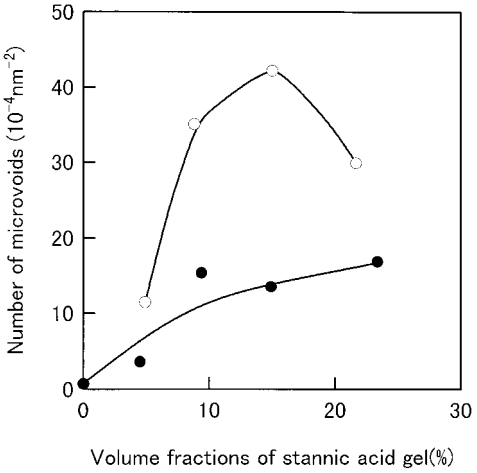

Figure 6 Number of microvoids per unit cross-sectional area of fibers plotted against volume fractions of stannic acid gel in fibers for mulberry (open circle) and tussah (solid circle) silk fibers.

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