

# Mechanical Properties of Tussah Silk Fibers Treated with Methacrylamide

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**ABSTRACT:** Tussah silk fibers were treated with methacrylamide (MAA). The polymerization of MAA onto tussah silk fibers and the mechanical properties of the MAA-treated tussah silk fibers were investigated. The tanning agent contained in tussah silk fibers acted as an inhibitor to the radical polymerization of MAA. The alkali treatment enhanced the swelling of noncrystalline regions of the tussah silk fibers and promoted the polymerization of MAA onto the tussah silk fibers. The cross-sectional area of the MAA-treated tussah silk fiber was given by the sum of the cross-sectional area of the original silk fiber and that of the MAA polymer. Breaking load of the fibers was almost unchanged by the MAA treatment, while rigidity was markedly increased. Young's modulus of the MAA-treated tussah silk fibers decreased with decreasing volume fractions of the fiber in the MAA-treated tussah silk fibers. Young's modulus of the MAA polymer in the MAA-treated tussah silk fibers was estimated by extrapolating the relation between Young's moduli and the volume fractions of the fiber to zero volume fraction. Young's modulus of the MAA polymer in the MAA-treated tussah silk fibers was significantly larger than the modulus of a MAA polymer plate. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2051–2057, 1997

**Key words:** tussah silk; mechanical properties; methacrylamide; polymerization; tanning agent

## INTRODUCTION

Among the wild silk fibers, tussah silk fibers are used commercially in the largest amount. Tussah silk fibers have useful properties that cannot be found in commercial mulberry silk fibers, such as high porosity<sup>1</sup> and high resistance to chemicals.<sup>2</sup> Therefore, increasing attention has been paid recently to tussah silk fibers to develop new textile products. Tussah silk fibers do present the textile technologist with a number of inferior properties, similar to those of mulberry silk, such as low crease resistance and low resistance to abrasion

during laundering. To improve these properties, chemical treatments with some kinds of vinyl monomers have been attempted. Kobayashi et al.<sup>3</sup> have reported that the treatment with methylmethacrylate enhances the crease resistance and the wrinkle recovery properties of silk fibers in the range of the polymer add-on from 30 to 40%. Methacrylamide (MAA) is one of the most promising vinyl monomers for the modification of silk fibers because large polymer add-on can be easily obtained because of the hydrophilic nature of the MAA. It has been previously reported that the treatment of tussah silk fibers with MAA is effective for reducing the damage to the fibers during laundering at the polymer add-ons higher than 50%.<sup>4</sup>

The MAA has a peculiarity that the silk fibers

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can be impregnated with this monomer up to quite high polymer add-ons without causing precipitation of the MAA polymer on the fiber surface. It is of interest to investigate the properties of the tussah silk fibers impregnated with MAA to high polymer add-ons.

The permeation of MAA into the noncrystalline regions of the silk fiber is faster for the fibers with a higher degree of swelling of this region. Because of the crosslinkings produced by the tanning agents, the tussah silk fibers show a lower degree of swelling than the mulberry silk fibers.<sup>5-7</sup> Thus, it is considered that tanning agents in the tussah silk fibers significantly influence the polymerization of MAA to the fibers.

In the present article, the polymerization of MAA to tussah silk fibers and the changes in the mechanical properties of tussah silk fibers, when the fibers were treated with MAA to high polymer add-ons, were studied.

## EXPERIMENTAL

### Materials

The raw silk fibers from tussah silkworm (*Antheraea pernyi*) and mulberry silkworm (*Bombyx mori*) were degummed by treatment with a commercial enzyme (SAL300, Rakutokasei Ltd.). The degumming bath contained 0.5% enzyme and 0.05% NaHCO<sub>3</sub>, and was maintained at a temperature of 50°C. The liquor-to-material ratio during the treatment was kept at 60 : 1. Each lot of raw silk was given three consecutive treatments of 1 h each with constant agitation; after each treatment the silk was quickly rinsed in boiling water and was then thoroughly rinsed with water. The weight losses of the fibers by the degumming were 11.6 and 22.0%, respectively, for these fibers. As described in the previous article,<sup>8</sup> these degumming treatments did not lower the tensile properties.

### MAA Treatment

The tussah silk fibers were immersed in an aqueous solution, consisting of MAA (0.8 mol/L) and ammonium persulfate (0.05 mol/L) adjusted to pH 3.0 by using sulphuric acid, at 50°C for various periods under a nitrogen atmosphere. The liquor-to-material ratio during the treatment was kept at 170 : 1. Then the fibers were thoroughly rinsed with water.

The tussah silk fibers, which were treated with

4% sodium hydroxide aqueous solution at 60°C for 30 min, were subjected to the MAA treatments. The MAA treatments were also made on mulberry silk fibers by adding a tanning agent, 2,5-dihydroxybenzoic acid, to the MAA solution by 0 to 1000 ppm.

The polymer add-on,  $G$ , was calculated from the increase in the mass of the fibers by using the equation

$$G = \frac{M_2 - M_1}{M_1} \quad (1)$$

where  $M_1$  and  $M_2$  are the masses of the dry fibers before and after the treatment.

### Preparation of a MAA Plate

To measure the density and Young's modulus of MAA polymer, a MAA polymer plate was prepared. MAA was polymerized from the aqueous solution with ammonium persulfate at 50°C and the MAA polymer solution was casted on a glass plate.

### Small-Angle X-ray Scattering Measurements on Wet Fibers

The samples used for small-angle X-ray scattering (SAXS) were prepared by winding tussah silk fibers 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 or a sodium hydroxide aqueous solution of 2–8% at room temperature for 24 h, and enclosed in a small cell with windows made of very thin polymethylmethacrylate film for the X-ray path. The scattering by this film was negligible. The top of the cell was wrapped with the film to keep the fibers under wet conditions. The equatorial 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 $\alpha$  X-rays. Because the SAXS of silk fibers was a narrow streak along the equator, the intensity,  $I(2\theta)$ , which was measured without using the height-limiting slit, was the intensity integrated with respect to the axis parallel to the fiber axis.

Because the absolute intensity of the incident beam was not measured, a parameter propor-

tional to the scattering power of swollen silk fibers,  $J$ , was estimated by using the equation<sup>9</sup>

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

where  $2\theta$  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.

### Amino Acid Analysis

Tussah silk fibers were treated with 4% sodium hydroxide aqueous solution at room temperature for 24 h. The weight loss of the fibers by the treatment was 18.5%. The concentrations of amino acids liberated from the fibers into the solution were determined by using an amino acid analyzer (L-8500, Hitachi Ltd.).

### Density

Densities of the MAA-treated silk fibers and the MAA polymer plate were measured by using a density gradient column with a NaBr aqueous solution.

### Scanning Electron Microscopy

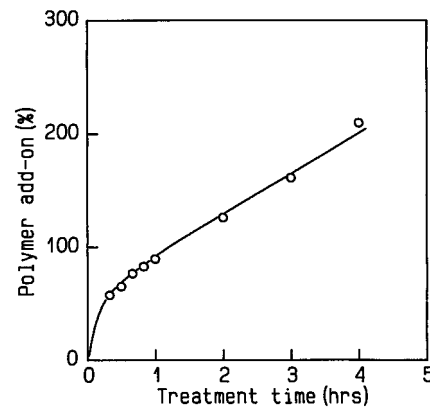
The MAA-treated silk fibers were coated with gold and the surface of the fibers was examined with a scanning electron microscope (JSM-T200, Nippondenshi Ltd.) at 5 kV acceleration voltage.

### Tensile Tests

Tensile tests of the single filaments of the tussah silk fibers were carried out at 20°C and 65% RH according to Japanese industrial standard R-7601, using an automatic Tensilon Tester (Toyo Baldwin Ltd.). The gauge length was 25 mm and the crosshead speed was 30 mm/min. Machine strain was negligibly small. The values represented in this article were the average of 20 tests.

### Sonic Modulus

Sonic modulus of a MAA polymer plate was obtained by measuring the time required for an ultrasonic wave to propagate through the MAA plate of known length. Sonic modulus,  $E_p$ , of the MAA plate was calculated by using the equation



**Figure 1** Polymer add-on of tussah silk fibers treated with MAA plotted against treatment time.

$$E_p = \rho_p C^2 \quad (3)$$

where  $\rho_p$  is the density of the MAA plate, and  $C$  the velocity of the ultrasound.

## RESULTS AND DISCUSSION

### Polymerization of MAA onto Tussah Silk Fibers

The polymer add-on of the tussah silk fibers treated with MAA is plotted against the treatment time in Figure 1. The polymer add-on reached about 200% at a treatment time of 4 h. In the case of mulberry silk fibers, the polymer add-on reached about 400% at the same treatment time.<sup>4</sup>

The polymerization of MAA is initiated by radicals. It is known that tyrosine and histidine residues in wool<sup>10,11</sup> and primary alcohols in cellulose<sup>12</sup> are radicalized by persulfate. Silk fibers have primary alcohols at serine residues. Therefore, for silk fibers, tyrosine, histidine, and serine residues are considered to be radicalized by ammonium persulfate used for the MAA treatment. The amount of these amino groups does not differ significantly between mulberry and tussah silk fibers.<sup>13</sup> Therefore, it is difficult to explain the difference in the polymer add-on between tussah and mulberry silk fibers from the viewpoint of the amino acid composition. As is indicated by the native color of tussah silk fibers, the tussah silk fibers contain tanning agents,<sup>6</sup> which are not contained in mulberry silk fibers. The main component of the tanning agents is 2,5-dihydroxybenzoic acid. Thus, the influence of the tanning agents was investigated by adding 2,5-dihydroxybenzoic acid to the MAA solution for treating

**Table I Relation between the Concentration of 2,5-Dihydroxybenzoic Acid in the MAA Solution and the Polymer Add-On of the Mulberry Silk Fibers Measured at the Treatment Time of 1 h**

2,5-Dihydroxybenzoic Acid Conc. (ppm)	0	1	10	100	1,000
Polymer add-on (%)	274.4	167.4	19.0	7.5	3.2

mulberry silk fibers. The polymer add-ons measured at a treatment time of 1 h are listed in Table I. The polymer add-on of the mulberry silk fibers markedly decreased by the addition of 2,5-dihydroxybenzoic acid. It is clear that 2,5-dihydroxybenzoic acid acted as an inhibitor to the radical polymerization of MAA.

Tanning agents contained in tussah silk fibers bring about the crosslinkings between molecular chains of the fibers.<sup>6</sup> Thus, the degree of swelling of noncrystalline regions of the tussah silk fibers is smaller than the mulberry silk fibers.<sup>5,7</sup> The scattering power of tussah silk fibers, measured in water and a sodium hydroxide aqueous solution swollen states, is shown in Table II. As is known from the increase in the scattering power with increasing concentration of the sodium hydroxide, the degree of swelling of noncrystalline regions increases by this treatment.<sup>7</sup> Because the native color of tussah silk fibers was unchanged by the sodium hydroxide treatment, it is considered that the tanning agents still remained in the fibers. The amino acid contents liberated from the tussah silk fibers by the sodium hydroxide treatment are shown in Table III. The MAA polymer add-on of the tussah silk fibers treated with 4% sodium hydroxide solution is shown in Table IV. In this table, the MAA polymer add-on was measured at a treatment time of 1 h. The MAA polymer add-on is markedly increased by the sodium hydroxide treatment compared with the untreated fibers. Therefore, it can be concluded that the increase in the degree of swelling of noncrystalline regions of tussah fibers enhanced the MAA polymer add-on.

**Table II Scattering Power of Tussah Silk Fibers Measured in the Swollen State with Water and a Sodium Hydroxide Aqueous Solution**

Concentration of NaOH Aqueous Solution (%)	0	2	4	8
Scattering power	1	1.3	2.3	3.7

### Surface of MAA-Treated Tussah Silk Fibers

Figure 2 shows the scanning electron micrographs of the surface of MAA-treated tussah silk fibers. The smooth surface of the untreated silk fibers was retained and no precipitation of MAA polymer was observed.

### Mechanical Properties of MAA-Treated Tussah Silk Fibers

In Figure 3, densities of MAA-treated tussah silk fibers are shown against polymer add-on. The density of the fibers decreased with increasing the polymer add-on.

If the cross-sectional area of the MAA-treated tussah silk fiber is given by the sum of the cross-sectional area of an original fiber and that of the MAA polymer, the ratio of the cross-sectional area of the MAA-treated silk fiber,  $St$ , against that of the original fiber,  $Sf$ , is given by the equation

$$\frac{St}{Sf} = \frac{Sf + Sp}{Sf} = 1 + \frac{G\rho_f}{\rho_p} \quad (4)$$

where  $Sp$  is the cross-sectional area of the MAA polymer, and  $\rho_f$  and  $\rho_p$  the densities of original silk fibers and a MAA polymer, respectively.  $\rho_p$  is shown in Table V. The values of  $St/Sf$  were calculated from eq. (4) by using the density of bulk MAA polymer as  $\rho_p$ , and the results were shown in Figure 4 as a function of polymer add-on. The experimental values determined from the linear density and the density of the MAA-treated

**Table III Concentrations of Amino Acids Liberated from Tussah Silk Fibers by the Treatment with a Sodium Hydroxide Aqueous Solution**

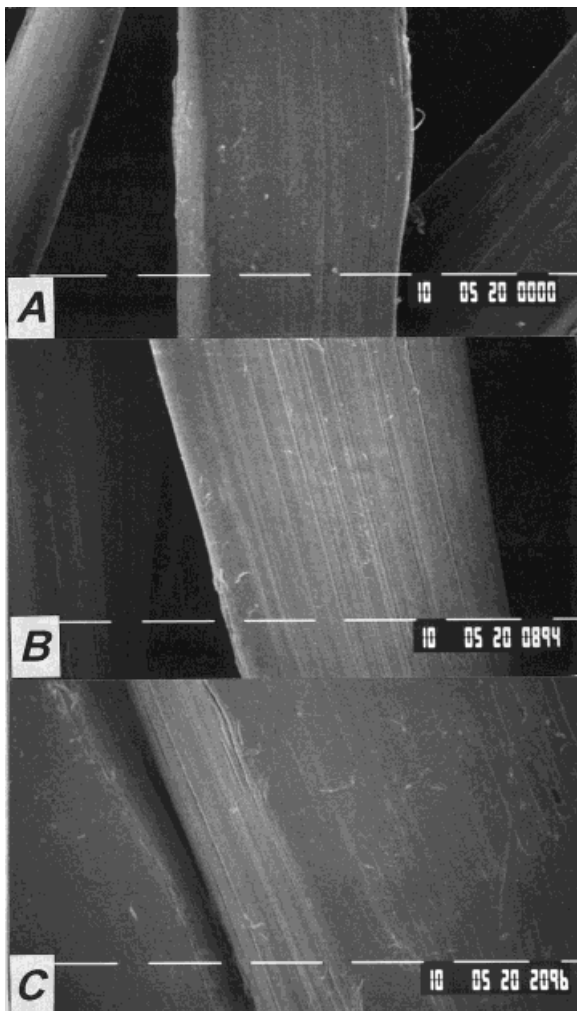
Glycine	Serine	Tyrosine	Alanine	Glutamic Acid
115.9	33.3	25.0	16.2	6.1

Concentrations in mg/100 mL.

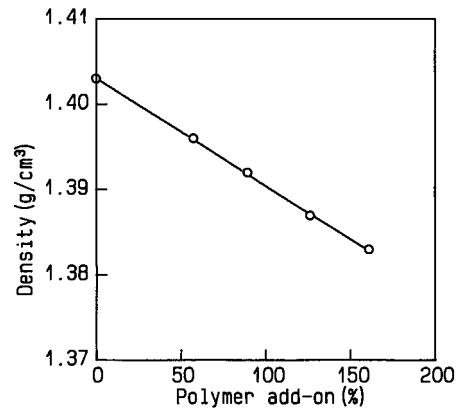
**Table IV Weight Loss of the Tussah Silk Fibers by the Treatment with 4% NaOH and the Polymer Add-On of the Tussah Silk Fibers Measured at the Treatment Time of 1 h**

	Untreated	Treated
Weight loss by (%)		
NaOH treatment	—	1.8
Polymer add-on (%)	99.8	231.2

tussah silk fibers are also shown in Figure 4. The calculated values agree well with the experimental values. Therefore, the cross-sectional area of the MAA-treated tussah silk fiber is given by the sum of the cross-sectional area of the original silk fiber and that of the MAA polymer.



**Figure 2** Scanning electron micrographs of (a) untreated tussah silk fibers, and the tussah silk fibers treated with MAA to the polymer add-on of (b) 89.4%, (c) 209.6%. Scales in figures correspond to 10 μm.



**Figure 3** Density of MAA-treated tussah silk fibers plotted against polymer add-on.

In Figure 5, breaking load and tensile strength of MAA-treated tussah silk fibers are plotted against polymer add-on. The breaking load was almost unchanged. The strength decreased with increasing polymer add-on. In Figure 6, rigidity and Young’s modulus of MAA-treated tussah silk fibers are plotted against polymer add-on. Rigidity is defined as the value of Young’s modulus multiplied by the cross-sectional area of the fiber. The rigidity was markedly increased by the treatment. In Figure 7, elongation at break of the MAA-treated tussah silk fibers is plotted against polymer add-on. At the polymer add-on of about 150%, the elongation of the fibers decreased significantly.

**Young’s Modulus of MAA Polymer in the MAA-Treated Tussah Silk Fibers**

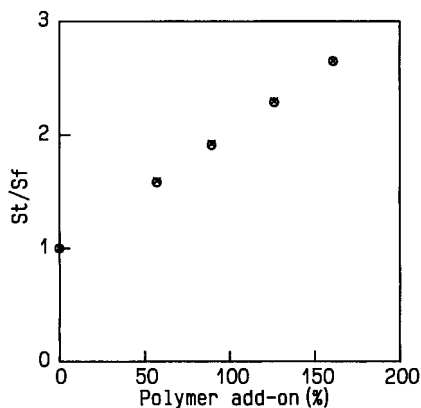
In Figure 8, Young’s moduli of MAA-treated tussah silk fibers are plotted against the volume fractions of the silk fiber in the MAA-treated silk fibers,  $V_f$ . The volume fraction,  $V_f$ , is defined by the equation

$$V_f = \frac{Sf}{St} \tag{5}$$

The Young’s modulus of tussah silk fibers decreased with decreasing volume fractions of the

**Table V Density and Sonic Modulus of a MAA Plate**

Density (g/cm³)	Sonic Modulus (GPa)
1.350	1.42

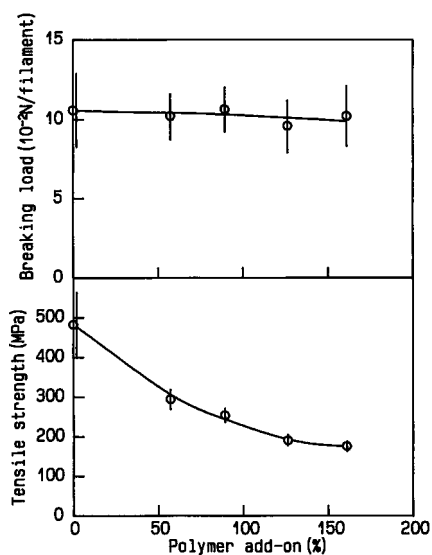


**Figure 4** Ratio of cross-sectional area of the MAA-treated tussah silk fibers against that of the original fibers,  $St/Sf$ , plotted against polymer add-on. (○) experimental values; (×) calculated values.

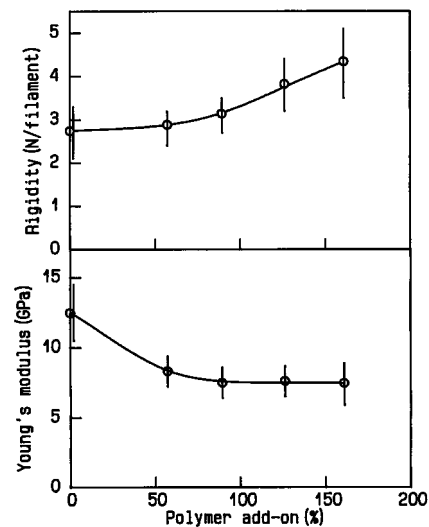
fiber. By extrapolating the relation between Young's moduli and volume fractions of the silk fiber to the volume fraction of zero, Young's modulus of the MAA polymer in the MAA-treated tussah silk fibers will be estimated. Young's modulus of the MAA polymer estimated in this way was no less than 5 GPa. This value is significantly larger than the value of a MAA polymer plate shown in Table V.

## CONCLUSIONS

The tanning agent contained in tussah silk fibers acted as an inhibitor to the radical polymerization



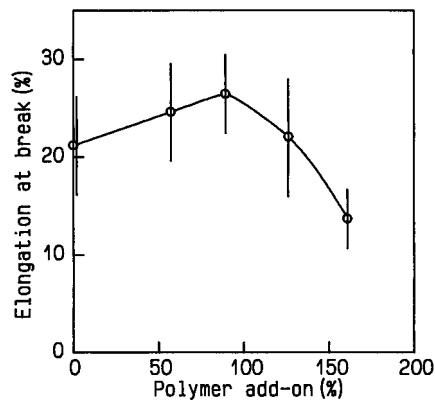
**Figure 5** Breaking load and tensile strength of MAA-treated tussah silk fibers plotted against polymer add-on.



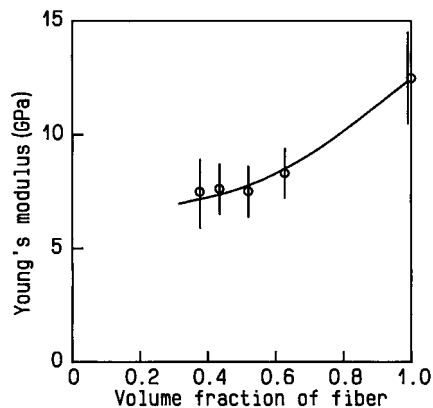
**Figure 6** Rigidity and Young's modulus of MAA-treated tussah silk fibers plotted against polymer add-on.

of MAA. The degree of swelling of noncrystalline regions of tussah fibers was increased by the sodium hydroxide treatment, and the MAA polymer add-on of tussah silk fibers was enhanced.

The cross-sectional area of the MAA-treated tussah silk fibers corresponded with the sum of the cross-sectional area of an original fiber and that of the added polymer. The precipitation of the MAA polymer on the surface of the tussah silk fibers was not observed. The rigidity of the fibers increased while breaking load was almost unchanged by the MAA treatment. By extrapolating the relationship between Young's modulus of the MAA-treated tussah silk fibers and the volume fraction of the fibers to zero volume fraction, Young's modulus of the MAA polymer in the MAA-treated tussah silk fibers was estimated.



**Figure 7** Elongation at break of MAA-treated tussah silk fibers plotted against polymer add-on.



**Figure 8** Young's modulus of MAA-treated tussah silk fibers plotted against the volume fraction of the fiber.

Young's modulus of the MAA polymer was extremely larger than that of a MAA polymer plate.

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