

Mechanical Properties of Silk Fibers Treated with Methacrylamide

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SYNOPSIS

Silk fibers were treated with methacrylamide (MAA), and changes in the mechanical properties of the silk fibers were investigated. The breaking load of the silk fibers was almost unchanged, whereas rigidity was markedly increased by the methylmethacrylate (MAA) treatment. Elongation at break of the silk fibers decreased significantly when the fibers were treated with MAA up to polymer add-on (ca. 300%). The cross-sectional area of the MAA-treated silk fiber was given by the addition of the cross-sectional area of the original silk fiber and that of the MAA polymer. The Young's modulus of MAA-treated silk fibers increased linearly with increasing volume fractions of fiber in MAA-grafted silk fibers. The Young's modulus of the MAA polymer in the MAA-treated silk fibers was estimated by extrapolating the relation between Young's moduli and volume fractions of fiber to the zero volume fraction of fiber. The Young's modulus of the MAA polymer in the MAA-treated silk fibers was larger than the sonic modulus measured for an MAA polymer plate.

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INTRODUCTION

Chemical treatment by using vinyl monomers such as methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), and methacrylamide (MAA) has been applied to silk fibers to increase the mass of silk fibers. Kobayashi et al.¹ have reported that the treatment with MMA enhances the crease resistance and the wrinkle recovery properties of silk fibers when the polymer add-on is in the range of 30–40%.

The industrially useful region of the polymer add-on for MMA and HEMA is less than 40% since polymers precipitate on the surface of the silk fibers at a higher polymer add-on.^{2–4} The good handle of silk fibers is extremely affected when the polymers precipitate on the fiber surface.

The MAA has a peculiarity in that the silk fibers 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

technological importance and scientific interest to investigate the properties of silk fibers impregnated with MAA to high polymer add-ons.

In the previous paper,⁵ the effects of MAA treatment on silk fibers have been studied within the range of the polymer add-on less than 150%, and it has been shown that durability to laundering and crease resistance of silk fibers are enhanced by the MAA treatment in this range of polymer add-on. In this paper, changes in the mechanical properties of silk fibers, when the fibers were treated with MAA to high polymer add-ons, were studied.

EXPERIMENTAL

Materials

The commercial raw silk fibers from the mulberry silkworm (*Bombyx mori*) were degummed with enzymes as described in the previous paper.⁶ The weight loss of the fibers by the degumming was 22.0%.

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MAA Treatment

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

$$G = \frac{W_2 - W_1}{W_1} \quad (1)$$

where W_1 and W_2 are the masses of the dry fibers before and after the treatment.

Preparation of an MAA Plate

In order to measure the density and elastic modulus of the MAA polymer, an MAA polymer plate was prepared. MAA was polymerized with ammonium persulfate in the aqueous solution at 50°C for 24 h, and the MAA plate was obtained by casting the polymer solution on a glass plate.

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 10 kV acceleration voltage.

Amino Acid Analysis

The MAA-treated silk fibers were hydrolyzed by heating them in 6N hydrochloric acid at 110°C for 24 h. During the hydrolysis treatment, contents of silk in the hydrochloric acid solution were kept constant. An undissolved residue of the fibers was filtered off from the hydrolysates. The amino acid contents in the hydrolysates were determined by using an amino acid analyzer ($L = 8500$, Hitachi Ltd.).

Density

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

Tensile Tests

Tensile tests of the silk fibers were carried out on single filaments 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 cross-head speed was 30 mm/min. The values represented in this paper were the average of 20 tests. Machine strain was negligibly small.

Sonic Modulus

The sonic modulus of an MAA polymer plate was obtained by measuring the time required for an ultrasonic wave to propagate between a certain gauge length of the MAA plate. The sonic modulus, E_p , of the MAA plate was calculated by using the equation

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

where ρ_p is the density of the MAA plate and C is the velocity of the ultrasound.

RESULTS AND DISCUSSION

Surface of MAA-treated Silk Fibers

The polymer add-on by the MAA treatment is plotted against the treatment time in Figure 1. It is noted that the polymer add-on reached more than 400% at a treatment time of 5 h.

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

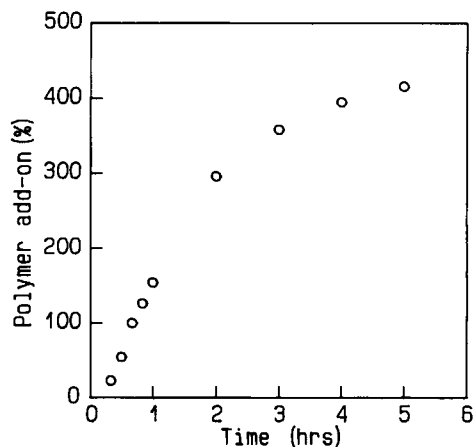


Figure 1 Polymer add-on of silk fibers by the MAA treatment plotted against treatment time.

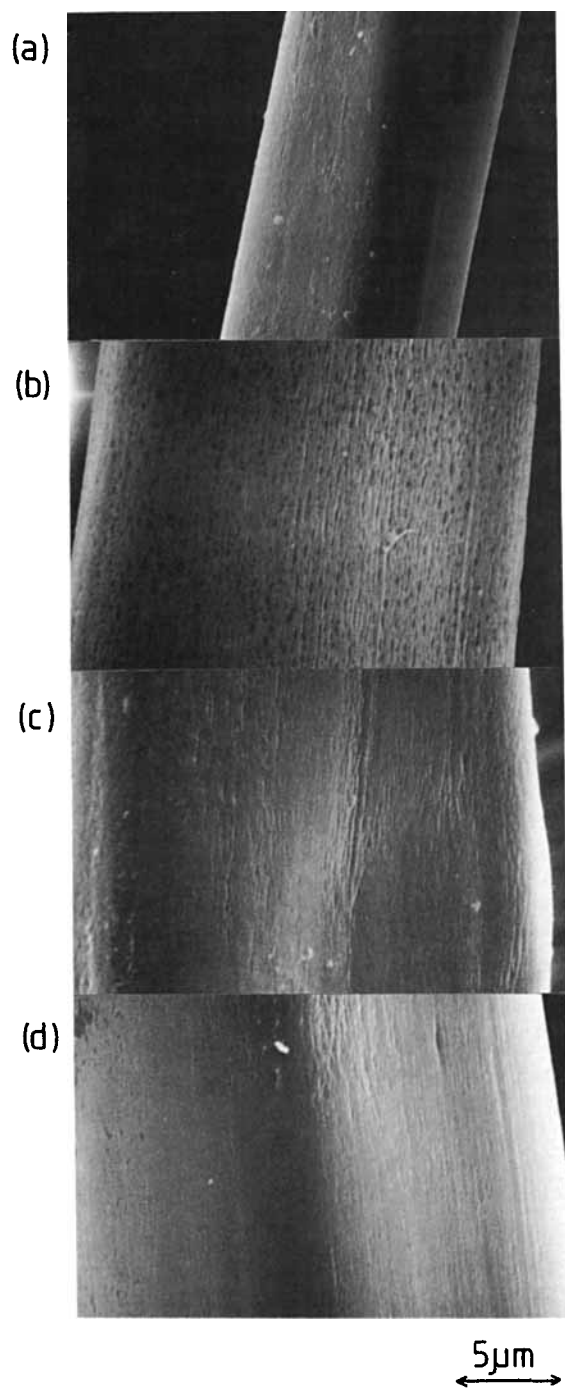


Figure 2 Scanning electron micrographs of (a) untreated silk fibers, and the silk fibers treated with MAA to the polymer add-on of (b) 100.2%, (c) 295.6%, and (d) 394.6%.

observed. It was reported previously that the polymerization of MAA infused in the noncrystalline regions of silk fibers destroyed the crystallites of silk fibers.⁷ The MAA tends to disperse into silk fibers.

Table I Concentrations of Amino Acid in Hydrolysate of MAA-Treated Silk Fibers

Amino Acid	Polymer Add-on (%)		
	0	23.3	100.2
Aspartic acid	24.7	24.4	28.3
Glutamic acid	23.7	24.9	26.2
Lysine	7.5	5.5	8.9
Arginine	11.3	11.4	19.8
Histidine	4.7	4.1	6.7
Serine	134.6	132.7	140.2
Tyrosine	106.7	108.2	109.5

Concentration of amino acid in ng/10 μ L.

Mechanical Properties of MAA-Treated Silk Fibers

The polymerization of MAA is initiated by radicals. It is known that tyrosine and histidine residues in wool^{8,9} and primary alcohols in cellulose¹⁰ 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 concentrations of these amino groups and polar amino groups in the hydrolysates obtained from the MAA-treated silk fibers were listed in Table I. The concentrations of amino groups were almost unchanged independent of the polymer add-on. Thus, the molecular chains of MAA polymer are not likely to be grafted to the molecular chains of silk. The occurrence of crosslinkings between the molecular chains of silk fibers by the MAA polymer can hardly be expected.

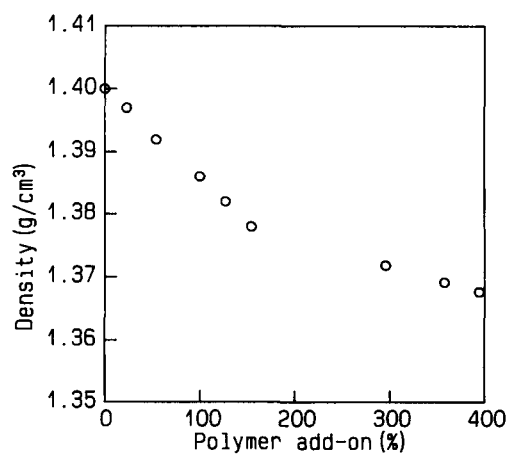


Figure 3 Density of MAA-treated silk fibers plotted against polymer add-on.

Table II Density and Sonic Modulus of an MAA Plate

Density (g/cm ³)	Sonic Modulus (GPa)
1.350	1.42

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

If the cross-sectional area of the MAA-treated silk fiber is given by the sum of the cross-sectional area of original silk fiber and that of the MAA polymer, the ratio of the cross-sectional area of the MAA-treated silk fiber, S_t , against that of the original silk fiber, S_f , is given by the equation

$$\frac{S_t}{S_f} = \frac{S_f + S_p}{S_f} = 1 + \frac{G\rho_f}{\rho_p} \quad (3)$$

where S_p is the cross-sectional area of the MAA polymer, G the polymer add-on, ρ_f and ρ_p the densities for original silk fiber and the MAA polymer, respectively. ρ_p is listed in Table II. The values of S_t/S_f were calculated from eq. (3) by using the density of bulk MAA polymer as ρ_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 density of the MAA-treated 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 silk fi-

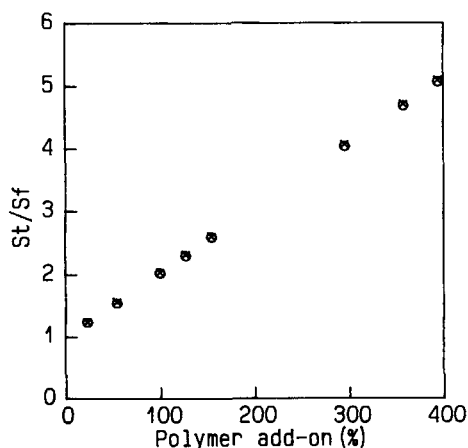


Figure 4 Ratio of cross-sectional area of the MAA-treated silk fibers against that of the original silk fibers, S_t/S_f , plotted against polymer add-on. O; experimental values, X; calculated values.

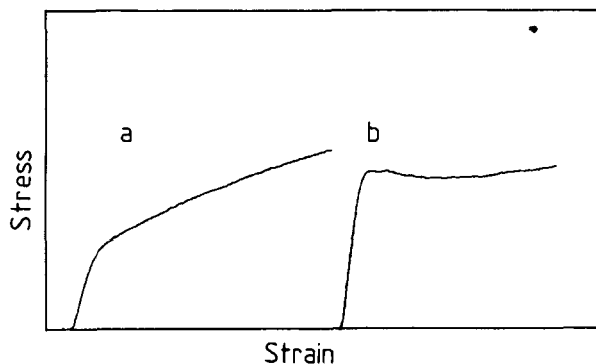


Figure 5 Typical stress-strain curves for (a) untreated silk fiber and (b) MAA-treated silk fiber with the polymer add-on of 154.7%.

ber is equal to the addition of the cross-sectional area of the original silk fiber and that of the MAA polymer.

Figure 5 shows the typical stress-strain curves for the untreated and MAA-treated silk fibers. The untreated silk fibers do not show a yield point [Fig. 5(a)]. The MAA-treated silk fibers, however, showed a yield point when the polymer add-on was more than 154.7% [Fig. 5(b)].

In Figure 6, breaking load and strength of MAA-treated silk fibers are shown against polymer add-

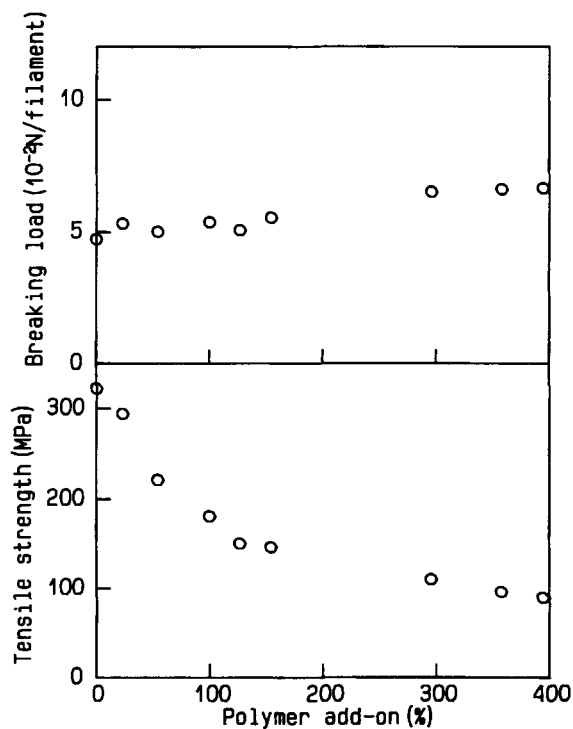


Figure 6 Breaking load and strength of MAA-treated silk fibers plotted against polymer add-on.

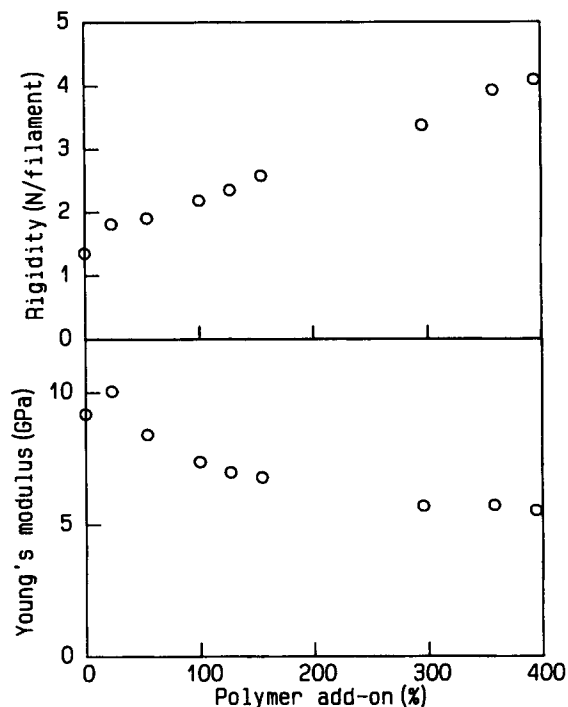


Figure 7 Rigidity and Young's modulus of MAA-treated silk fibers plotted against polymer add-on.

on. The breaking load was almost unchanged. The strength decreased with increasing polymer add-on. In Figure 7, rigidity and Young's modulus of MAA-treated silk fibers are shown 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 8, elongation at the break of the MAA-treated silk fibers is shown against polymer add-on. When the polymer add-on reached about 300%, the elongation of the fibers decreased significantly.

Young's Modulus of MAA Polymer in the MAA-Treated Silk Fibers

In Figure 9, Young's moduli of MAA-treated silk fibers are shown 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

$$V_f = 1/[1 + (G\rho_f/\rho_p)] \quad (4)$$

The Young's modulus of MAA-treated silk fibers increased linearly with increasing volume fractions of fiber. By extrapolating the relation between Young's moduli and volume fractions of the silk fiber to the volume fraction of zero, the Young's modulus

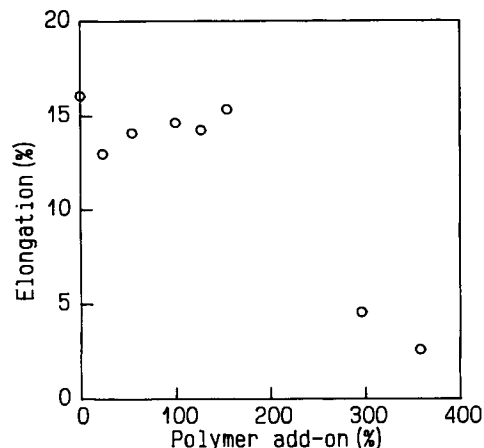


Figure 8 Elongation at break of MAA-treated silk fibers plotted against polymer add-on.

of the MAA polymer in the MAA-treated silk fibers can be estimated. The Young's modulus of the MAA polymer estimated in this way was 4.6 GPa. This value is three times as large as the value of a MAA polymer plate listed in Table II.

CONCLUSIONS

With the MAA treatment of silk fibers, the polymer add-on more than 400% was easily obtained. The cross-sectional area of the MAA-treated silk fibers corresponded with the sum of the cross-sectional area of original silk fibers and that of the added polymer. The precipitation of the MAA polymer on the surface of the silk fibers, however, was not observed. The rigidity of the fibers increased, while the breaking load was almost un-

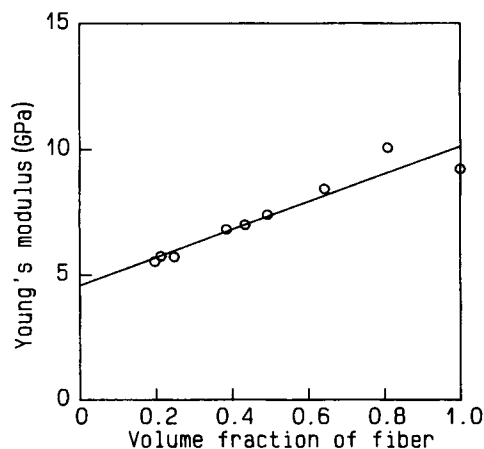


Figure 9 Young's modulus of MAA-treated silk fibers plotted against volume fraction of fiber.

changed by the MAA treatment. A linear relationship was found between the Young's modulus of the MAA-treated silk fibers and the volume fraction of the fibers. By extrapolating this relationship to zero volume fraction, the Young's modulus of the MAA polymer in the fibers was estimated to be 4.6 GPa, which was three times larger than the Young's modulus of bulk MAA.

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