

# Changes in Physical Properties of Methacrylonitrile(MAN)-Grafted Silk Fibers

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## SYNOPSIS

Changes in physical properties of silk fibers, grafted with methacrylonitrile (MAN), were investigated as a function of the weight gain. The weight gain increased steadily during the first 60 min of reaction and gradually attained an equilibrium value (60%) after about 4 h. The initial tensile resistance of silk fibers decreased by MAN grafting. The crystalline structure of silk fibers remained unchanged, regardless of MAN grafting, however, a minor and broad peak appeared in the X-ray diffraction curves of MAN-grafted silk fibers with a weight gain of 60%, corresponding to the unoriented MAN polymer attached inside the fibers. Molecular orientation of silk fibroin chains in the crystalline regions, evaluated from X-ray diffraction curves, did not change significantly, while both birefringence and isotropic refractive index decreased as the weight gain increased, implying that MAN polymer attached preferentially to the amorphous and not to the crystalline regions. Dynamic viscoelastic measurements showed that the position at which the  $E'$  value began to decrease shifted to a lower temperature as the weight gain increased. These findings suggest that the thermal movement of silk fibroin molecules was accelerated by the presence of the poly-MAN chains attached to the amorphous regions of silk fibroin fibers. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Silk fibers are valued for the outstanding characteristics that have been exploited for the production of precious textile goods. However, silk possesses some inferior textile performances, such as photoyellowing, wash and wear (W & W), abrasion resistance, and crease proofing properties, which could be improved by graft-copolymerization and/or chemical modification techniques. Among the chemical modifying agents, epoxides have proved to be of particular interest and were recently used in industrial applications.<sup>1,2</sup> By reacting with epoxides, silk fabrics showed improved and outstanding dyeability with acid dyes, as well as excellent resilience and color fastness to washing.<sup>3</sup> The reactivity of mono- and bifunctional epoxides towards silk fibers

has been extensively studied.<sup>1,2</sup> It has been pointed out that the side chains of basic and acidic amino acid residues, as well as tyrosine, showed reactivity towards various kinds of epoxides.<sup>2</sup>

The use of aliphatic<sup>4</sup> (succinic, glutaric) and aromatic<sup>5</sup> (phthalic, *o*-sulfobenzoic) dibasic acid anhydrides has been an effective chemical modification for improving crease recovery and reducing photoyellowing of silk fabrics without affecting the tensile properties. Moreover, the acylation with dibasic acid anhydrides appeared particularly attractive, because a slight chemical modification resulted in a significant change of the dyeing properties of silk and other animal protein fibers.<sup>6,7</sup> We studied the physical properties and the thermal behavior of silk fibers, modified by acylation, and found that dibasic acid anhydrides were reactive mainly towards basic amino acid residues.<sup>8</sup>

Several vinyl monomers, such as methyl methacrylate (MMA),<sup>9</sup> methacrylamide (MAA),<sup>10</sup> 2-hydroxy-ethyl methacrylate (HEMA),<sup>11</sup> ethoxy-

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ethyl metacrylate (ETMA),<sup>12</sup> methacrylonitrile (MAN),<sup>13</sup> and styrene (St)<sup>14</sup> have been used as grafting agents, and some of them were successfully applied on the industrial scale for silk processing, that is, silk grafted with MAA. The physical and mechanical properties, as well as the structural characteristics, of silk fibers, grafted with different vinyl monomers, have been reported. Silk fibers, copolymerized with HEMA/MAA at low graft yield, showed a noticeable increase of moisture content,<sup>15</sup> which played a positive role in improving the comfort of silk fabrics without affecting the handling and luster. Silk fiber, containing ETMA polymer, exhibited an increased uptake of acid dye, as well as good transfer printability.<sup>12</sup> Styrene grafted silk fibers, due to their high hydrophobic properties, showed affinity for disperse dyes and were used for heat-transfer printing.<sup>14</sup> Wrinkle recovery of MMA-grafted silk fabric increased when the weight gain was in the range 30–60%.<sup>14</sup>

We reported some physical and thermal properties of MAN grafted silk fibers.<sup>13</sup> We found that the moisture absorption slightly decreased from 10% to about 7%, as the weight gain increased from 10% to 60%. The tensile strength and elongation remained almost unchanged, while the alkali solubility appreciably decreased. The strong interaction between poly-MAN chains and silk fibroin molecules was elucidated by the increase of decomposition temperature measured by DSC. Moreover, from both DSC and TMA analyses, we observed the increased thermal stability of MAN-grafted silk fibers. SEM photographs showed that the surface of silk fibers after grafting was as smooth as the untreated sample, in contrast with the results reported for MMA-grafted fibers.<sup>9</sup>

The aim of this work is to study the weight gain increase as a function of reaction time and to collect further information on the physical characteristics of grafted silk fibers. We also examined the location of the MAN polymer inside silk fibers on the basis of X-ray diffraction analysis and refractive index measurements. Dynamic viscoelastic measurements were conducted in order to detect the changes in thermal behavior of silk fibers following MAN grafting.

## EXPERIMENTAL

### Materials

Degummed silk fibers were immersed in a reaction bath containing 2.5% (o.w.f.) sodium persulfate as initiator, 2 mL/L formic acid (85%), 12% nonionic

surfactant (Noigen EC, Daiichikogyo Seiyaku Co.), and various amounts of methacrylonitrile (15–70% o.w.f.). The material-to-liquor ratio of 1 : 20 was maintained. The reaction system was heated to 80°C in 20 min and was maintained at the same temperature for the time required. At the end of the reaction, the samples were washed with water and then were extracted with 1 g/L sodium hydrosulfate solution, containing nonionic surfactant at 70°C for 20 min to remove unreacted MAN. The fibers were washed with tap water, were air-dried at 100–105°C for 2 h, and were placed in a desiccator over silica gel before weighing. The weight gain of silk fibers grafted with MAN was calculated on the basis of the oven-dried weights before and after reaction, a correction being made for the weight loss during the treatment with the mixture system without MAN. Before testing, samples were conditioned at 20°C and 65% R.H.

### Measurements

The tensile properties of grafted silk fibers were measured with a Tensilon UTM-II (Toyo Baldwin Co.), using the standard technique at 20°C and 65% R.H. at a gauge length of 100 mm and strain rate of 40 mm/min.

X-ray diffraction curves were recorded using an X-ray source with  $C_{\alpha}K_{\alpha}$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The conditions for X-ray measurements have been described in detail elsewhere.<sup>16</sup>

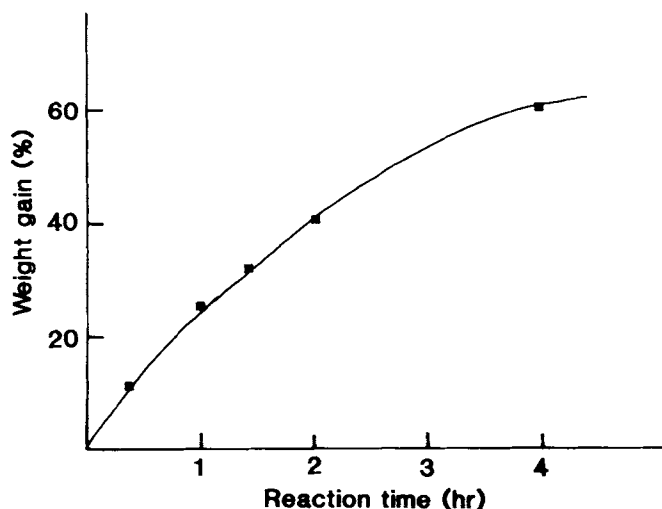
Refractive indices were measured with the Becke's line method, using a polarized microscope under monochromatic light (Na light) at 20°C and 65% R.H. The conditions for measurement have been described in detail elsewhere.<sup>17</sup>

The dynamic mechanical properties were measured using a Toyoseiki Rheograph Solid-S. The frequency of oscillation was adjusted to 10 Hz. The temperature range studied was from 25°C to 250°C, and the samples were heated at a heating rate of 2°C/min.

## RESULTS AND DISCUSSION

### Weight Gain by MAN Grafting

The graft-copolymerization reaction of MAN onto silk fibers was carried out at 80°C for different periods of time. The relationship between weight gain and reaction time is shown in Figure 1. The weight gain increased steadily during the first 60 min, then the rate of weight gain slowly decreased until an



**Figure 1** Effect of reaction time on weight gain of silk fibers grafted with methacrylonitrile (MAN) at 80°C, using sodium persulfate as the initiator.

equilibrium value of about 60% was attained after 4 h.

It is of interest to compare the amount of weight gain as a function of the reaction time in the course of silk fiber grafting using MAN and other vinyl monomers. The MMA-grafted silk showed a weight gain of about 80% at the reaction time of 3.5–4 h under the same grafting conditions as those used for grafting silk with MAN. These experimental results suggest that kinetics of silk grafting with MAN was not significantly different from that reported for methyl methacrylate (MMA).<sup>9</sup>

### Mechanical Properties

The initial tensile resistance, corresponding to the measured Young's modulus, was evaluated from the slope of the stress–strain curves of the MAN-grafted silk fibers. The initial tensile resistance, and the size of grafted silk fibers, are listed in Table I. Compared with the untreated control, the initial tensile resistance value of grafted silk fibers slightly decreased from 83 g/d to about 72 g/d and remained almost constant as the weight gain reached 40%. Then, a further increase of weight gain to 60% led to a remarkable fall of tensile resistance (50.4 g/d). These results suggest that MAN-grafted silk fibers became softer and less resistant to the initial load applied. Moreover, we reported that both strength and elongation of MAN grafted silk fibers slightly decreased as the weight gain increased.<sup>13</sup> These experimental results showed that the mechanical properties of silk fibers could be adjusted by varying the amount of MAN polymer attached inside the fibers.

### X-ray Diffraction Curves

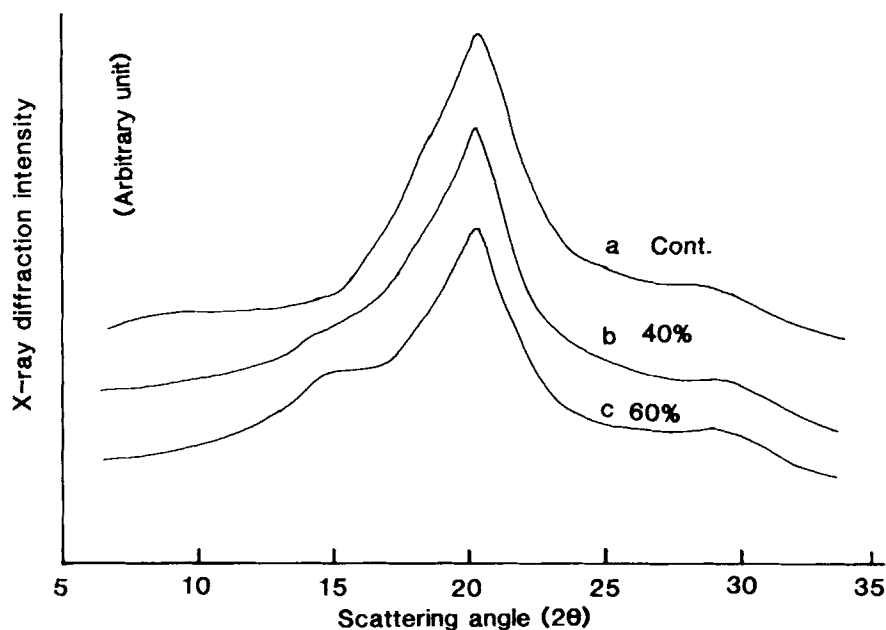
Figure 2 shows the X-ray diffraction curves of MAN-grafted silk fibers with different amounts of weight gain. The control silk fibers [Fig. 2(a)] exhibited a major X-ray diffraction peak at 20.5 deg, corresponding to the specific crystalline spacing of 4.39 Å for silk fibers with high molecular orientation. The position and intensity of the main X-ray diffraction peak at 20.5 deg did not change significantly, regardless of MAN grafting [Fig. 2(b,c)]. These results imply that the crystalline structure of silk fibers remained almost unchanged, even after MAN grafting. A minor diffraction peak at 14.3 deg appeared as the weight gain increased up to 60% [Fig. 2(c)], suggesting that this diffraction was probably due to the MAN polymer grafted into silk fibers.

**Table I** Size and Tensile Modulus of the MAN-grafted Silk Fibers as a Function of the Different Values of Weight Gain

Weight Gain (%)	Size (Denier <sup>a</sup> )	Tensile Modulus (g/d) <sup>b</sup>
0	31	83.1
10	33	71.5
25	40	72.8
32.5	41.5	71.6
40	44	72.9
60	53.5	50.4

<sup>a</sup> Denier (d) is a measure of the size of the silk fiber, evaluated according to the equation:  $d = 9000 \times W/L$ , where W and L denote, respectively, the weight (g) and length (m) of a silk fiber.

<sup>b</sup>  $1 \text{ g/d} = 1.22 \times 10^3 \text{ kgf/cm}^2$ .



**Figure 2** X-ray diffraction intensity curves of untreated control (a) and MAN-grafted silk fibers (b,c) with different amounts of weight gain. Weight gain: (b) 40%, (c) 60%.

The above results are consistent with those reported for silk grafted with MAN<sup>13</sup> and other vinyl monomers, such as MMA<sup>9</sup> and MAA,<sup>10</sup> demonstrating that the crystalline structure of silk fibers with oriented  $\beta$  crystals was not affected by the graft-copolymerization reaction taking place inside the fibers. The grafted polymer is supposed to attach to the amorphous regions of silk fibers.

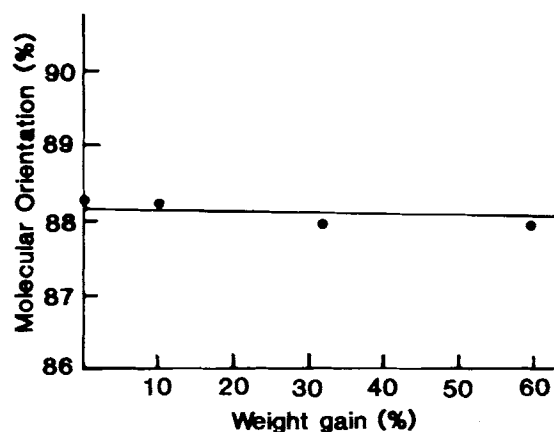
### Molecular Orientation

In order to investigate further the physical structure of MAN-grafted silk fibers and to elucidate precisely the mechanism of grafting, we evaluated the molecular orientation of the fibers, either on the basis of crystallinity data or by measuring the optical properties.

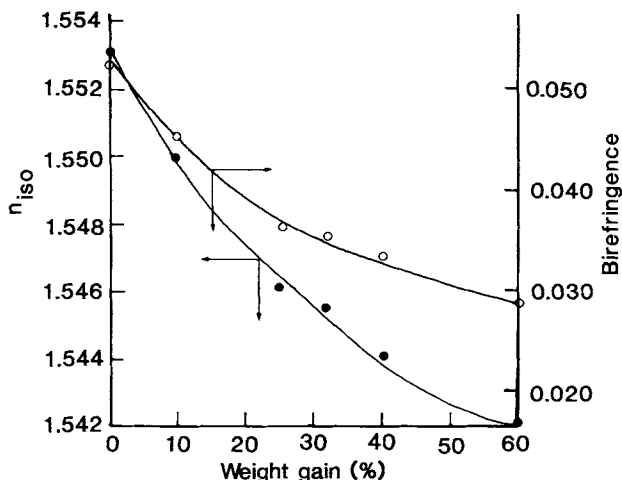
Figure 3 shows the molecular orientation of grafted silk fibers, evaluated from the X-ray diffraction data as a function of the weight gain. The trend of the curve clearly showed that the molecular orientation of the crystalline regions did not change, regardless of weight gain increase. These findings confirm that neither the size nor the arrangement of the crystalline regions of silk fibers were directly affected by the copolymerization reaction within the weight gain range examined.

Figure 4 shows the curves obtained by plotting birefringence ( $\Delta n$ ) and isotropic refractive index ( $n_{150}$ ) values as a function of weight gain. Both  $\Delta n$

and  $n_{150}$  values significantly decreased as the weight gain increased. Since birefringence and the isotropic refractive index are two optical parameters, related to the degree of order and orientation of the molecules in a fibrous polymer, these results showed that the average molecular orientation of MAN-grafted silk fibers decreased by the graft-copolymerization reaction. On the basis of the above crystalline data, we could elucidate, and therefore conclude, that most of the physical changes took place in the amorphous



**Figure 3** Molecular orientation of the MAN-grafted silk fibers evaluated by X-ray diffraction intensity curves. Molecular orientation thus obtained corresponds to the crystalline regions of the fibers.



**Figure 4** Birefringence ( $\Delta n$ ) and isotropic refractive index ( $n_{iso}$ ) of MAN-grafted silk fibers as a function of weight gain.

regions of silk fibers, where vinyl monomers easily penetrated and bound to reactive sites and where the MAN polymer chains could grow, filling the room available between the fibroin molecules. In this respect, it is worth mentioning, therefore, the role of the amorphous regions in determining the reactivity of silk fibers towards modifying agents.

### Dynamic Mechanical Behavior

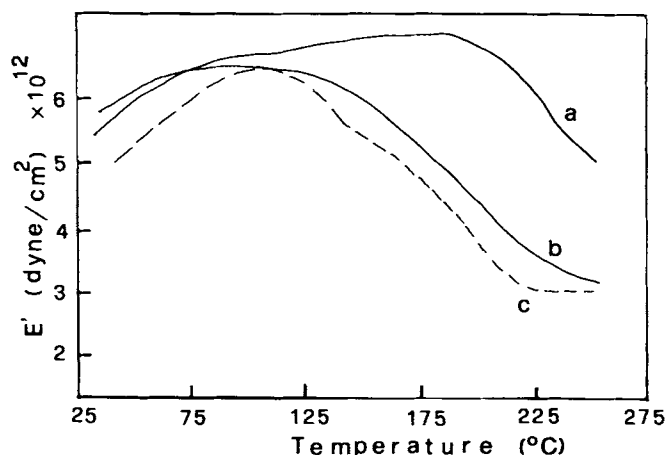
Figure 5 shows the temperature dependence of the dynamic storage modulus ( $E'$ ) of MAN-grafted silk fibers with different amounts of weight gain, measured in the range of 25–250°C. The  $E'$  value of the control sample [Fig. 5(a)] slightly increased from room temperature to about 175°C. The thermal

movement of fibroin molecules, due to the weakening of the intermolecular interactions, subsequently became evident, and the  $E'$  curve steadily decreased. The glass transition temperature of silk fibroin was 175°C,<sup>18</sup> which corresponded to the decrease of the  $E'$  value. Below the glass transition temperature, silk fibroin fibers showed high thermal stability, while above 175–180°C they became softer, and behaved as a rubber-like material.

The dynamic storage modulus curves of MAN-grafted silk fibers, with weight gains of 32.5% [Fig. 5(b)] and 60% [Fig. 5(c)], showed a significant shift to lower temperature of the position at which the  $E'$  value began to decrease. These thermal behaviors indicated a lower degree of thermal inertness of grafted silk fibers, as compared with the untreated ones. The two-step decrease of the  $E'$  value, exhibited by the fiber sample with 60% add-on, is worth mentioning. The first drop of storage modulus, starting at about 110°C, should be attributed to the poly-MAN chains, and corresponds to their glass transition temperature, while the second step, appearing as a shoulder on the  $E'$  curve, should be mainly due to the silk fibroin chains.

The viscoelastic properties of MAN-grafted silk fibers were significantly affected by the copolymerization reaction. The poly-MAN molecules, inserted into the amorphous regions, weakened the interactions between the fibroin chains and induced an apparent decrease of the glass transition temperature, as evaluated from the increased molecular motion registered at relatively low temperature, starting from about 120–130°C. Similar features were also observed on epoxide-treated tussah silk fibers.

The above dynamic viscoelastic results are consistent with those previously reported for MAN-



**Figure 5** Dynamic storage modulus ( $E'$ ) of untreated control (a) and MAN-grafted silk fibers (b,c) with different amounts of weight gain. Weight gain: (b) 32.5%, (c) 60%.

grafted silk fibers by thermomechanical analysis. In fact, as the weight gain increased from 10% to 60%, the extent of extension increased in the range of 25–200°C and the onset temperature of extension shifted to lower temperature, down to about 100°C.

## REFERENCES

1. H. Shiozaki and Y. Tanaka, *Makromol. Chem.*, **143**, 25 (1971).
2. Y. Tanaka and H. Shiozaki, *Makromol. Chem.*, **129**, 12 (1969).
3. H. Shiozaki, Japanese Patent 2677742 (1986).
4. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **37**, 2637 (1989).
5. M. Tsukada, Y. Gotoh, G. Freddi, and H. Shiozaki, *J. Appl. Polym. Sci.*, to appear.
6. M. Tsukada, *J. Appl. Polym. Sci.*, **37**, 2637 (1989).
7. M. Tsukada, H. Shiozaki, and A. Konda, *J. Appl. Polym. Sci.*, **41**, 1213 (1990).
8. M. Tsukada, Y. Gotoh, G. Freddi, H. Shiozaki, and H. Ishikawa, *J. Appl. Polym. Sci.*, to appear.
9. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 965 (1988).
10. A. Bianchi Svilokos, M. R. Massafra, and S. Beretta, *La Seta*, **46**, 4 (1983).
11. M. Tsukada, *J. Seric. Sci. Jpn.*, **56**, 157 (1987).
12. M. Tsukada, J. S. Crighton, and H. Shiozaki, *J. Appl. Polym. Sci.*, to appear.
13. M. Tsukada, *J. Appl. Polym. Sci.*, **39**, 1289 (1990).
14. S. Kobayashi, M. Sugiyama, and H. Yoshida, *Rep. Tokyo Met. Text. Res. Inst.*, **15**, 137 (1979).
15. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 2133 (1988).
16. Tsukada, *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 1227 (1986).
17. M. Tsukada, M. Nagura, H. Ishikawa, and H. Shiozaki, *J. Appl. Polym. Sci.*, **43**, 643 (1991).
18. J. Magoshi, Y. Magoshi, S. Nakamura, N. Kasai, and M. Kakudo, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 1675 (1977).

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