Characterization of Methacrylonitrile-Grafted Silk Fibers

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Synopsis

The structure and physical properties of silk fibroin fibers graft-polymerized with methacrylonitrile (MAN) were analyzed in relation to the weight gain on the basis of the results of tensile properties as well as of thermal analysis and X-ray diffractometry. The solubility of the specimen in NaOH solution and the moisture absorption decreased slightly with the duration of the MAN treatment. However, the polymerizing treatment with MAN did not affect significantly the tensile properties, i.e., strength and elongation at break of the original fibers. The position of the endothermic peak attributed to the thermal decomposition of the silk fibroin shifted to higher temperatures when the weight gain exceeded 25%, and a constant value at 328°C was obtained above a weight gain of 40%. Wide-range X-ray diffraction diagram of silk fibers with a weight gain of 10% showed diffraction maxima at the equator corresponding to the molecule oriented crystal structure of the silk fiber, in addition to the spots on a series of hyperbolic arcs arranged symmetrically at about the equator, which are associated with the crystalline form of the MAN polymer copolymerized in the specimen. Crystalline structure of the silk fiber remained unchanged essentially regardless of MAN treatment.

INTRODUCTION

Silk possesses many outstanding attributes such as dyeability, moisture absorption, and excellent fabric hand, in striking contrast with the synthetic fibers and fabrics. However, silk characteristics including photoyellowing, wrinkle recovery, rub resistance, and color fastness should be further improved. Chemical modification of silk by graft copolymerization has been developed to alleviate such shortcomings.[1,2]

One of the authors analyzed the structural and thermal properties of methyl-methacrylate-grafted silk fibers in relation to the compatibility between the silk fibroin molecules and methyl methacrylate polymer copolymerized in the fibrous specimen. In addition, in a preceeding paper, we[4] reported that the chemical modification of silk with dibasic acid anhydrides, i.e., succinic and glutaric anhydrides, was effective in increasing the crease proofing and reducing the photoyellowing of the silk fabric without affecting the tensile properties.

Shiozaki and Tanaka,[5] who extensively studied the reactivity of the epoxide toward silk fibroin indicated that the epoxide treatments applied to silk contribute significantly to the increase in fabric hand properties such as crease proofing, wash and wear characteristics, and color fastness to washing.

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Negishi and Arai[6] studied the graft copolymerization of acrylonitrile by the application of a vapor-phase method to the silk fabric preimmersed in an aqueous solution of ammonium persulfate, and they analyzed the mechanism and reactivity of the reaction. However, only limited information on the characteristics of methacrylonitrile grafted silk is available.

In this paper the effect of methacrylonitrile (MAN) grafting onto silk on the structure and characteristics of the grafted silk has been studied under various weight gains conditions based on the results of tensile properties, as well as of scanning electron microscopy, DSC measurements, thermomechanical analysis, and X-ray diffractometry. These studies may provide an important basis for and valuable information about the improvement of the current techniques of chemical modification.

EXPERIMENTAL

Materials

Degummed silk fibers were set in the box of a package-type tester containing 2.5% (o.w.f.) sodium persulfate, 2 mL/L formic acid (85%), 12% nonionic surfactant, and various amounts of methacrylonitrile (15–70%, o.w.f). The material-to-liquor ratio of 1 : 20 was maintained. The mixture system was heated at room temperature to 80°C for 20 min, and then maintained at the same temperature for 40 min.

At the end of the reaction, the samples were washed with water. They were extracted with a 1 g/L sodium hydrosulfate solution containing 1 mL/L nonionic surfactant (Noigen EC, Daiichikogyo Seiyaku Co.) at 70°C for 20 min to remove the unreacted MAN, and washed in tap water. The washed and air-dried silk fibers were dried in a forced draft at 100–105°C for 2 h, placed in desiccator over silicagel for 30 min, and weighted. The weight gain of silk fibers treated with MAN was calculated based on the oven-dried weights of the sample before and after the treatment, a correction being made for the weight loss in the treatment with mixture system in the absence of MAN. Thus silk fibers with a weight gain of 10, 25, 32.5, 40, and 60% were prepared. Before the tests were performed, the samples were conditioned at 20°C and 65% RH.

Measurements

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

The moisture absorption of the silk fiber was calculated from the increase in weight of the original silk fiber after the conditioning at 20°C and 65% RH for 2 weeks as follows:

$$\text{moisture absorption (\%)} = W_1/(W_2 + W_3) \times 100$$

where W_1, W_2, and W_3 denote the weights of the amount of absorbed water, silk fiber and poly-MAN, respectively.

The alkali solubility of the silk fiber was evaluated based on the oven-dried weights of the sample before and after the treatment in 0.5*N* NaOH solution at 65°C for 60 min.

Each fibrous specimen was placed in a vacuum evaporator and coated with gold. Observations were made with a JEOL JXA-733S scanning electron microscope operating at 15 kV accelerating voltage.

The differential scanning calorimetry (DSC) measurements were performed on a Rigaku Denki instrument, thermoflex DSC-10A, according to the method described in a previous paper.[7]

A Rigaku Denki Model CN-8361 apparatus for thermomechanical analysis (TMA) was used to detect the onset of the contraction and extension. The heating rate was 10°C/min and sweep dry N_2 gas provided the inert atmosphere.

X-ray diffraction pattern was recorded using an X-ray source with C_uK_α radiation (λ = 1.54 Å). The conditions for the X-ray measurements have been described in detail elsewhere.[7]

RESULTS AND DISCUSSION

Size and the Moisture Absorption

Yarn size and moisture absorption are important factors in the textile hand. The changes in yarn size and moisture absorption in relation to the weight gain were analyzed (Fig. 1). The experiments revealed that the yarn size is linearly related to the weight gain. The increase of the rate of yarn size induced by the MAN treatment was the same as or slightly higher than that for methacrylamide-grafted silk fiber.[8] On the other hand, the moisture absorption decreased slightly to 7.2% for the MAN-treated silk fiber with a weight gain of 60%, indicating a decrease in the moisture absorption by the MAN treatment, in contrast to the grafted silk fibers with methacrylamide[8] or 2-hydroxyethyl methacrylate.[9] However, it appears that the MAN treatment does not remove the original absorption characteristics of the parent fiber,

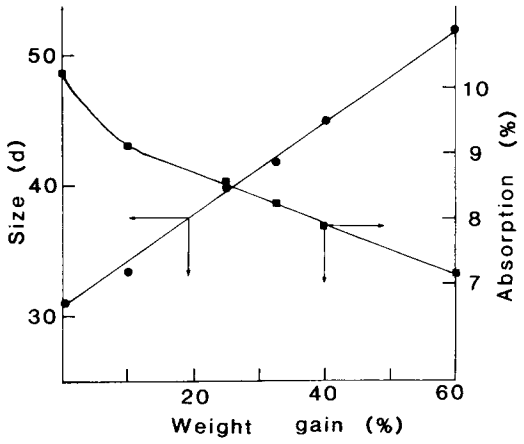

Fig. 1. Changes in yarn size and moisture absorption of silk fibers treated with methacrylonitrile in relation to weight gain: (●), size; (■), moisture absorption.

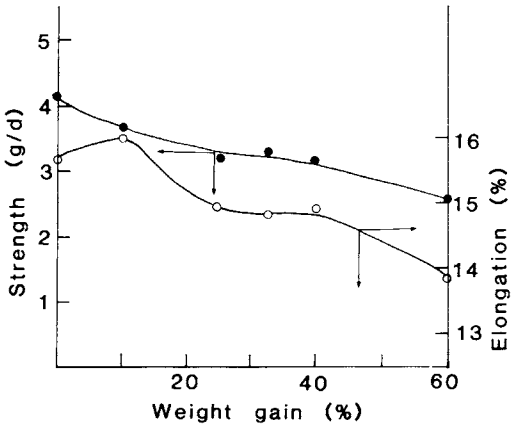

Fig. 2. Changes in strength and elongation at break of silk fibers treated with methacrylonitrile in relation to weight gain: (●), strength; (○), elongation.

because the decrease in the amount of moisture absorption was very low with a value of 3% in the weight gain range of 0–60%. In addition, in the silk fibers treated with succinic anhydride[4] or epoxide,[10] the change in the moisture absorption was similar to that observed in the MAN-treated silk fibers.

Tensile Properties

Figure 2 shows the relationship between the tensile strength, elongation, and weight gain of the silk fiber treated with MAN. The tensile strength decreased slightly with the increase in the weight gain. The value of the elongation remained unchanged in the low weight gain range between 0 and 10% and decreased in the weight gain range between 10 and 25%. The elongation remained temporarily at a constant value of 15% in the region where the weight gain exceeded 25%. Thereafter, the value of the elongation of the silk fiber decreased again gradually above a weight gain of 40%. The tensile elasticity refers to the tensile modulus of elasticity taken as the slope of a linear portion of the strength–elongation curve of silk fibers. The tensile elasticity of the untreated silk fiber was 80 g/d. Its value decreased when the weight gain increased and remained constant at 73 g/d, suggesting that the silk fibers became soft and elastic due to the MAN treatment.

Alkali Solubility

The alkali solubility of the silk fibroin fiber treated with MAN was studied in relation to the weight gain (Fig. 3). The solubility of the untreated silk fiber in a 0.5*N* NaOH solution was 36%. When the weight gain increased, the solubility decreased, as shown in Figure 3, suggesting that the MAN treatment of silk is characterized by a high alkaline stability.

Morphological Structure

Scanning electron micrographs (SEM) of the silk fibroin fibers treated with MAN for different values of weight gain (Fig. 4) revealed that there were no

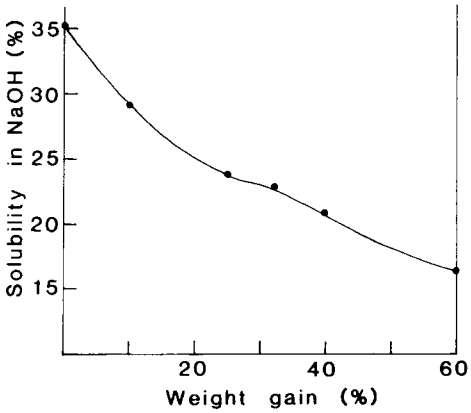

Fig. 3. Solubility of silk fibers treated with methacrylonitrile in 0.5*N* NaOH solution at 65°C for 60 min.

traces of peeling and fibrillation damage in the silk fibers. The surface of the specimen was smooth, showing the typical features of untreated silk fiber regardless of the MAN treatment in the weight gain range studied. These results are in sharp contrast with the SEM studies of methyl methacrylate-grafted silk fibers,[3] demonstrating the presence of granules adhering to the surface of the silk fiber when the weight gain exceeded 85%.

Thermal Properties

Figure 5 shows the DSC thermograms of silk fibroin fibers treated with MAN. Untreated silk fiber (a) showed a single and broad endothermic peak at around 314°C, which was attributed to the thermal decomposition of silk fibroin with oriented β' conformation of silk fibroin.[11] The position of the endothermic peak which appeared at about 314°C remained unchanged regardless of the MAN treatment in the weight gain range of 0–25%. On the other hand, the position of the endothermic peak shifted to higher temperatures when the weight gain exceeded 25%. However, the fact that the peak remained at a constant value of 328°C above a weight gain of 40% may be ascribed to the strong interaction between the silk fibroin and poly-MAN molecules. It is interesting to note that the DSC thermograms of the silk fiber treated with MAN did not show any evidence of baseline shift attributed to the glass transition (110°C)[12] of the MAN polymer, which will be described in detail elsewhere.

Thermomechanical Analysis

The influence of the MAN treatment on the thermal stability of the silk fibroin was investigated in relation to the weight gain (Fig. 6) based on thermomechanical analysis (TMA) measurements. The untreated silk fibroin exhibited a slight contraction of 0.3% in the temperature range of 25–200°C, which may be due to the evaporation of the humidity absorbed by the specimen. Silk fibroin showed temporarily a slight extension at above 190°C, and thereafter the extension remained at a constant value at 260°C. Silk

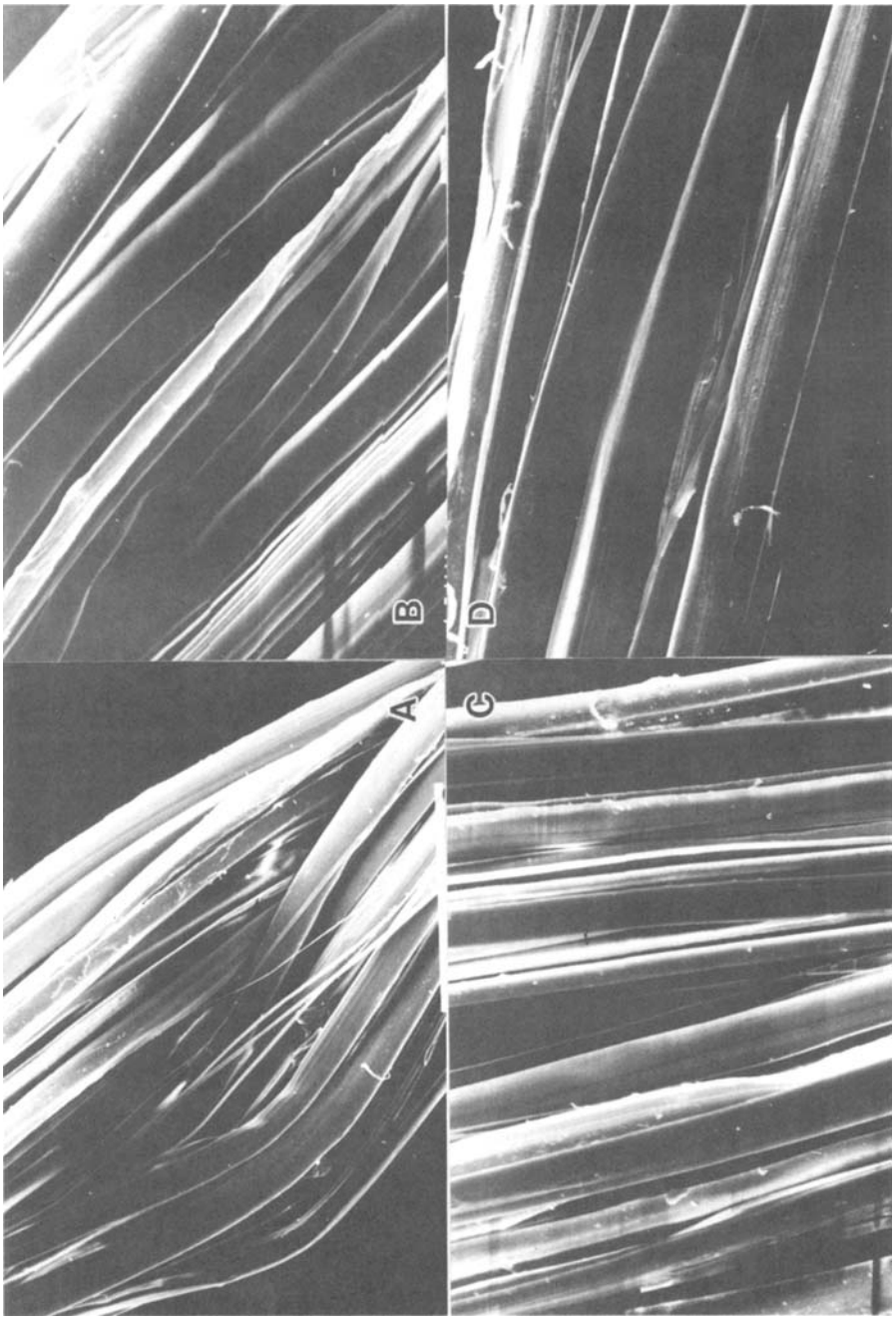

Fig. 4. Scanning electron micrographs of silk fibers treated with methacrylonitrile in relation to weight gain (%): (A), 0; (B), 10; (C), 32.5; (D), 60.

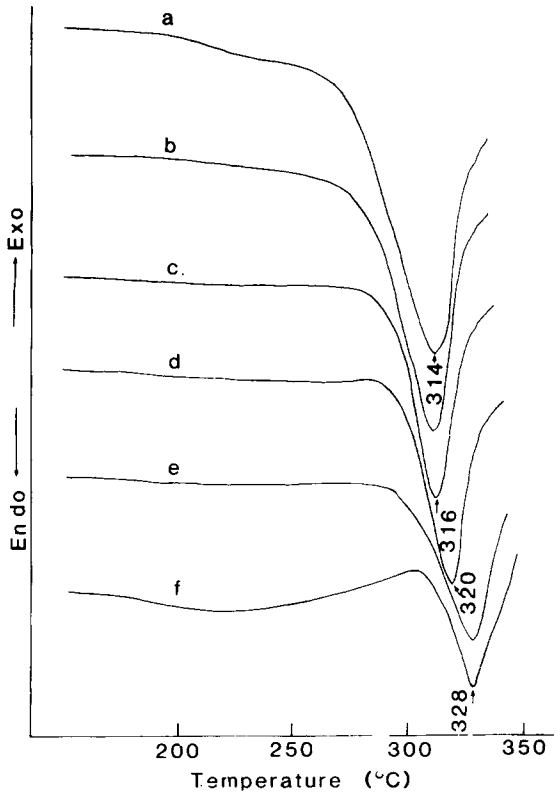

Fig. 5. DSC thermograms of silk fibers treated with methacrylonitrile in relation to weight gain (%): (a), 0; (b), 10; (c), 25; (d), 32.5; (e), 40; (f), 60.

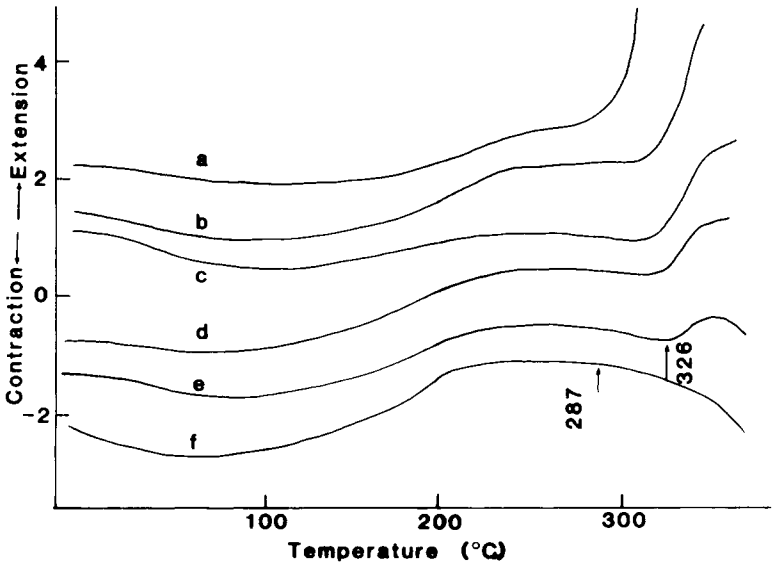

Fig. 6. TMA curves of silk fibers treated with methacrylonitrile in relation to weight gain (%): (a), 0; (b), 10; (c), 25; (d), 32.5; (e), 40; (f), 60.

fibroin then showed a distinct extension at above 260°C, which was due to the effect of the weight applied to the specimen, resulting in the thermal decomposition of the silk fibroin molecules. It can be noted that the starting point of the extension shifted slightly to higher temperatures and the amount of extension decreases when the weight gain increased. Silk fibroin with a weight gain of 60% did not show any evidence of extension, and then was only a slight contraction above 280°C, which should be attributed to the enthalpy elasticity induced by the thermal movement of the amorphous region of the fibrous specimen.

Crystalline Structure

In order to evaluate the changes in the crystalline structure of the silk fiber induced by the MAN treatment, X-ray diffraction patterns were analyzed (Fig. 7). Untreated silk fiber showed moderately sharp reflections oriented toward the equator and corresponding to the spacings of 4.86 and 4.27 Å,

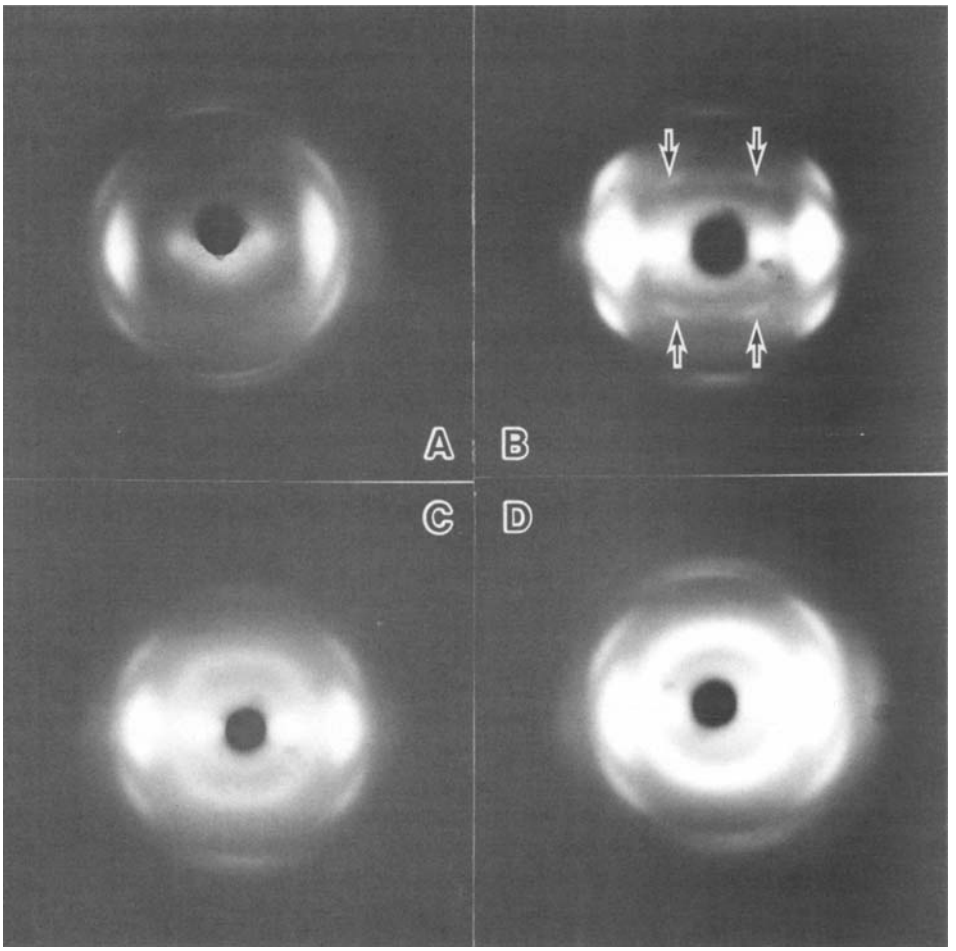

Fig. 7. X-ray diffraction patterns of silk fibers treated with methacrylonitrile in relation to weight gain (%): (A), 0; (B), 10; (C), 32.5; (D), 60. Arrows: see the text.

which are characteristic of the oriented β' conformation.[13] The X-ray diffraction pattern of the silk fiber with a weight gain of 10% is characterized by the occurrence of spots (Fig. 7 arrow), corresponding to the oriented structure whose spacing is 6 Å, on a series of hyperbolic arcs (layer line) arranged symmetrically at about the equator in addition to the diffraction patterns associated with the oriented β' configuration. Based on X-ray diffraction studies of the polyacrylonitrile fiber,[14,15] the packing repeat unit of the acrylonitrile polymer in relation to the chain direction is more regular compared with that in relation to the normal direction. These results suggest that the MAN polymer copolymerized in the silk fiber assumes an oriented molecular crystalline form in the weight gain range of 0–10% and two phase systems consisting of more and less ordered regions.[14,15] In contrast, the conformation of the poly-MAN crystal is considered to assume a randomly coiled form for the MAN copolymer produced in the silk fibroin with a weight gain above 32.5%. This assumption is based on the observation that the silk fibroin with a weight gain of above 32.5% showed a broad diffuse diffraction pattern corresponding to the spacing of 6 Å attributed to the MAN copolymer in the amorphous form in addition to the above diffraction patterns associated with the oriented β' conformation. However, it should be noted that the crystalline structure of the silk fiber remained unchanged essentially regardless of MAN treatment.

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