

Physical Properties of Silk Fibers Grafted with a Binary Mixture of Styrene and *n*-Butyl Methacrylate

MASUHIRO TSUKADA,^{1,*} GIULIANO FREDDI,² PATRIZIA MONTI,³ and ALESSANDRO BERTOLUZZA³

¹National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan, ²Stazione Sperimentale per la Seta, Via G. Colombo 81, 20133 Milano, Italy, and ³Dipartimento di Biochimica, Università di Bologna, Via Selmi, 2, 40126, Bologna, Italy

SYNOPSIS

The mechanical and physical properties, as well as the crystalline structure of silk fibers grafted with a binary mixture of styrene (St) and *n*-butyl methacrylate (BMA) were studied as a function of the weight gain. The size of the fibers increased linearly with the extent of grafting. The strength, the elongation at break, and the tensile modulus decreased with increasing weight gain, but the breaking load remained almost unchanged. The difference among the tensile properties measured in dry and wet states decreased beyond weight gain of 50% because of the hydrophobic properties of grafted silk fibers. The thermal behavior was determined by differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and thermogravimetric analysis (TGA) measurements. Silk fibers attained a higher thermal stability as the amount of loaded polymer increased. The thermally induced molecular movement of St/BMA-grafted silk fibers was enhanced as judged by shifting the onset and the position of the dynamic loss modulus (E'') peak to lower temperature when the weight gain increased. X-ray diffraction curves demonstrated that the crystalline structure of silk fibers remained unchanged regardless of the St/BMA grafting. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Since the beginning of the 1970s, grafting vinyl monomers onto silk fibers has been suggested as a potentially interesting method for improving some inferior properties of silk fibers.^{1–12} During the last two decades, several grafting techniques were developed and some of them were routinely applied to silk finishing, either for weighting purposes or for improving the textile performances^{10–17} of silk fabrics, such as crease recovery, wash and wear properties, antiphotoyellowing, water and oil staining resistance, etc.

Most of the methods applied for silk grafting makes use of a single monomer, which is induced to polymerize within the fibrous silk substrate by means of a redox system as the initiator. It follows,

therefore, that the final characteristics of the grafted material largely depend on the chemical properties of the vinyl monomer used. In fact, several monomers were tested according to their hydrophobic/hydrophilic behavior, as well as to the extent of the influence on the intrinsic outstanding appearance and feel of silk fabrics.

It is sometimes difficult to attain the desired degree of modification of the physico-chemical properties of silk fibers by using a single vinyl monomer. For example, styrene (St)¹⁸ and methyl methacrylate (MMA)³ were proved to confer to grafted silk fibers appreciable bulkiness and fullness of handle, as well as increased crease recovery⁹ and affinity toward disperse dyes.¹³ However, their use entailed some drawbacks, because of their strong hydrophobic properties, such as the hardness to touch and deterioration of silk fibers in the course of grafting, especially when high weight gains were required. On the other hand, more hydrophilic vinyl monomers, such as 2-hydroxyethyl methacrylate (HEMA),¹

* To whom correspondence should be addressed.

were effective in increasing the equilibrium regain and improving the comfort of silk fabrics, but the poor bulkiness of the grafted silk restrained them from application. Binary mixtures of vinyl monomers were thus suggested as a suitable means to avoid these negative consequences and to take advantage of the individual characteristics of each component of the grafting mixture. One of the authors⁴ has already reported the physical properties and structural characteristics of silk fibers grafted with a binary mixture⁴ of HEMA and methacrylamide (MAA). HEMA polymer, MAA polymer, and fibroin molecular chains showed a poor compatibility among them, as elucidated from the thermal behavior of grafted silk fibers with different amounts of each monomer in the grafting mixture.

This paper deals with the use of a binary mixture of St and *n*-butyl methacrylate (BMA) for grafting onto silk fibers. The former is no longer used alone for technological applications, because of the inferior characteristics as described. However, the effect of the full handle it confers to the silk at low/medium weight gain is still appreciated. BMA, on the other hand, has been reported to give silk fabrics good softness. The use of both of them could result in a final product with interesting textile characteristics.

In this paper we report the changes in the mechanical and physical properties, as well as in the crystalline structure of silk fibers grafted with the St/BMA binary mixture as a function of the weight gain.

EXPERIMENTAL

Materials

Dried silk fibers were immersed in a solution of aqueous potassium persulfate (0.1%) as the initiator that contained St and BMA as the grafting agents emulsified by nonionic surfactant at a temperature range of 78–80°C for different periods of reaction time to obtain grafted silk fibers with various weight gains. The silk yarns were immersed in a binary mixtures of St and BMA (50% St and 50% BMA on a weight basis) by using a aqueous solution of potassium persulfate (0.1%). The material-to-liquor ratio of 1 : 25 was maintained. The St and BMA monomers and oligomers adhering to the silk fibers and contained within the silk fibers were removed by hot acetone. The sample was dried and weight gain was calculated in the same manner of a previous paper.⁵

Measurements

The tensile strength and elongation at break of the St/BMA-grafted silk fibers were measured with a Tensilon UTM-II (Toyo Baldwin Co.) using standard techniques under standard conditions (20°C, 65% RH) and under wet conditions at a gauge length of 30 mm, strain rate of 101 mm/min, and chart speed of 200 mm/min.

The differential scanning calorimetry (DSC) measurements were carried out under nitrogen as described in a previous paper.⁶

Thermogravimetric analysis (TGA) were run under nitrogen on a Rigaku Denki instrument TGA thermogravimetric system, programmed under isothermal conditions, raised at 10°C/min to 400°C. Sample weight and TGA full scale were both 5 mg.

Thermomechanical analysis (TMA) was obtained on a Rigaku Denki instrument at a heating rate of 10°C/min. TMA full scale and initial force applied to the silk fibers were $\pm 500 \mu\text{m}$ and 1 gf, respectively.

The dynamic moduli E'' were measured at 10 Hz with a Toyoseiki Rheograph Solid-S. The temperature range studied was from room temperature to 270°C and samples were heated at 2°C/min. The sample length was 15 mm. The initial tension was 30 gf.

X-ray diffraction patterns were obtained using an x-ray source with $C_{\mu}K_{\alpha}$ radiation ($\lambda = 1.54 \text{ \AA}$). The conditions for the x-ray measurements have been described in detail elsewhere.⁸

The surface of the treated silk fibers was examined, after gold coating, with a JEOL JAX-333S scanning electron microscope (SEM) at 15 kV acceleration voltage.

RESULTS AND DISCUSSION

Tensile Properties

Figure 1 shows the tensile strength and elongation at break of St/BMA-grafted silk fibers measured both in dry and wet states as a function of the amount of weight gain. The size of silk fibers linearly increased following the loading of the polymer chains within silk fibers. As already observed for other vinyl monomers used for silk grafting, the strength (g/d) decreased with increased weight gain. However, the breaking load (g) measured in dry state remained almost constant at about 160–170 g, regardless of the St/BMA grafting in the weight gain range examined. These data of the tensile measurements

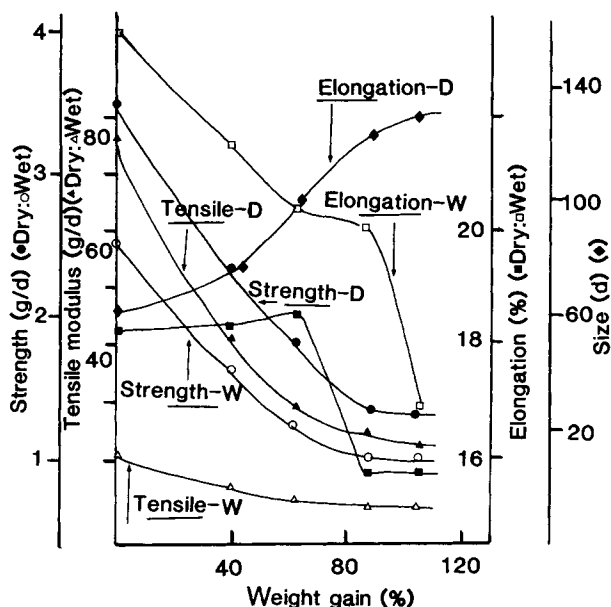


Figure 1 Tensile strength, elongation, and tensile modulus of the St/BMA-grafted silk fibers in dry (D) and wet (W) states with different amounts of weight gain. For example, Elong-D represents the elongation of the grafted silk fiber measured in the dry state.

imply that the decrease of strength should be mainly attributed to the increase of cross sectional area of silk filaments that occurred by grafting.

The tensile strength of grafted silk fibers in the wet state was lower than the corresponding values obtained in the dry state (about -30%), caused by the swelling effect of absorbed water. However, the difference between the two sets of values decreased as the amount of weight gain increased (Fig. 1). These findings are in agreement with the results recently reported for MMA-grafted silk fibers¹⁹ and are greatly attributed to the influence of the different rate and extent of hydration of the grafted polymer compared with the silk fibroin matrix.

The elongation at break of grafted silk fibers measured in dry state remained almost unchanged in the weight gain range of 0-60% and then showed a sharp drop beyond 60%. The weight gain determined in the wet state decreased at a constant rate over the weight gain range examined. The elongation in the wet state was also slightly larger than that in the dry state for St/MBA-grafted silk fibers.

The tensile modulus, calculated from the initial slope of the strength/elongation curve, decreases both in the dry and wet states. Following the grafting with the St/BMA mixture, the silk fibers became softer and less resistant to the initial load applied,

perhaps because of the plasticizing effect of the grafted polymer. As observed for the behavior of the strength values, the larger the weight gain was, the lower the difference between the wet and dry tensile moduli.

DSC Curves

Figure 2 shows the DSC curves of St/BMA-grafted silk fibers with different amounts of weight gain. Although not demonstrated at present, the untreated control showed a prominent single endothermic peak at about 318°C,¹⁴ attributed to the thermal decomposition of silk fibroin with oriented β' configuration.¹⁶ The position of this peak shifted slightly to higher temperature with increasing weight gain [Fig. 2(b-d)]. Similar findings were reported for silk fibers grafted with other vinyl monomers.¹⁴

A new endothermic peak at 410-420°C appeared in the DSC curves of St/BMA-grafted silk fibers. The intensity of this peak was roughly proportional to the amount of loaded polymer. It has been reported¹⁸ that the polystyrene residue removed from St-grafted silk fibers exhibited a prominent endothermic peak at about 430°C. It could be therefore speculated that the new endotherm appearing

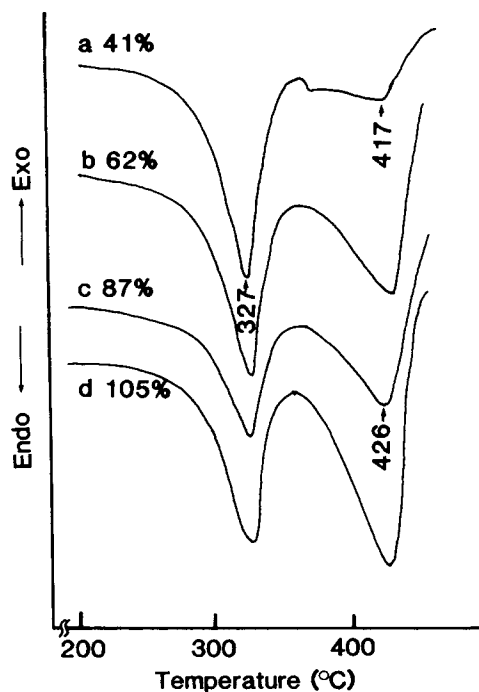


Figure 2 DSC curves of the St/BMA-grafted silk fibers with different amounts of weight gain. Weight gain (%): (a) 41; (b) 62; (c) 87; (d) 105.

at high temperature in St/BMA-grafted silk fibers can be related to the thermal behavior of the St and/or St/BMA polymer attached within the silk fibroin matrix following the graft-copolymerization reaction.

The appearance of additional thermal transitions in the DSC curves of silk fibers grafted with St/BMA, as well as other vinyl monomers¹⁴ has been interpreted as evidence of the poor compatibility existing at the molecular level between silk fibroin and the grafted polymer chains.

TMA Curves

The change in the expansion and contraction properties induced in the course of the heating process of St/BMA-grafted silk fibers were evaluated by TMA measurements. Figure 3 shows the TMA curves of the untreated control [Fig. 3(a)] and of fibers with weight gain of 41% [Fig. 3(b)], and 62% [Fig. 3(c)].

The untreated control sample [Fig. 3(a)] heated at a rate of 10°C/min exhibited a slight contraction in the temperature range 25–120°C, when the maximum shrinkage value of 0.7% was attained. Then the sample gradually began to extend; the major extension step appeared at above 300°C.

The St/BMA-grafted silk fibers showed a lower degree of contraction from room temperature to

about 120°C, which could be attributed to the reduced amount of water absorbed by the fibers, mainly because of the strong hydrophobic properties of the St/BMA polymer. The fibers started to extend at a rate and extent lower than the untreated control beyond 150°C. Moreover, the final extension appeared at a temperature that was 10–20°C higher than the reference. These data reveal that the St/BMA grafting onto silk fiber result in an increase in thermomechanical stability. In this way an increase in thermomechanical stability of silk fiber can be deduced, in good agreement with DSC data (Fig. 2).

TGA Curves

The thermal stabilities of the grafted silk fibers were examined by measurement of their decompositions in flowing nitrogen. Figure 4 shows the results of the thermogravimetric analysis of St/BMA-grafted silk fibers with different weight gains. As the amount of loaded polymer increased, the behavior of the grafted fibers deviated from that of the untreated control sample in the direction of an increased retention of weight. Though the trend of the curve corresponding to the sample with a weight increase of 40% almost coincided with that of the reference sample, those of the other two samples (87 and 105%, respectively) showed a higher thermal sta-

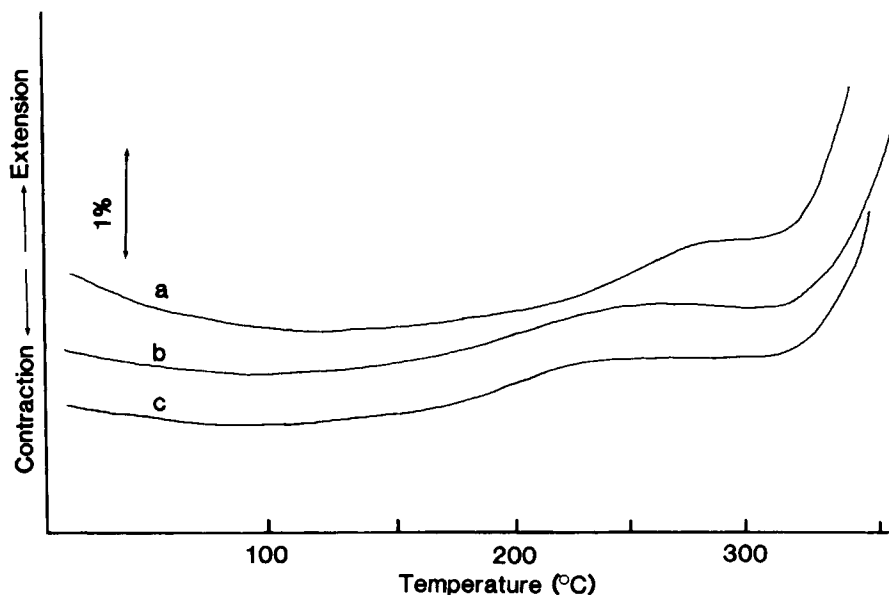


Figure 3 TMA curves of the St/BMA-grafted silk fibers. Weight gain (%): (a) 0; (b) 41; (c) 105.

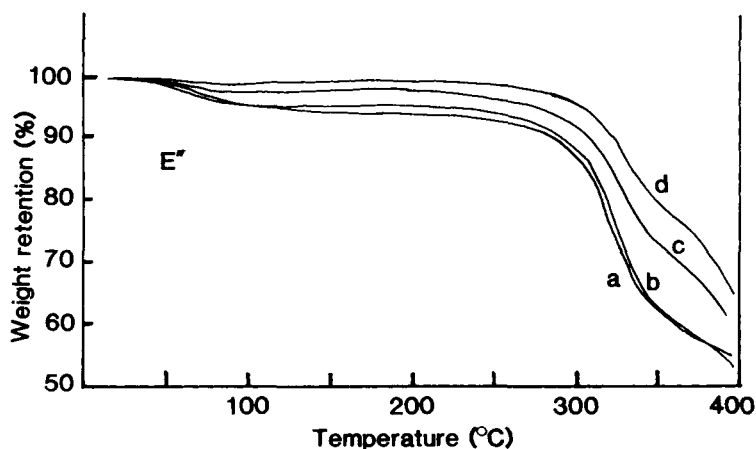


Figure 4 Thermogravimetric curves of the grafted silk fibers. Weight gain (%): (a) 0; (b) 41; (c) 87; (d) 105.

bility. As expected, the first step of weight loss above 50°C , essentially caused by the evaporation of water, showed a relevant decrease, attributed to the lower moisture regain of grafted silk fibers. Moreover, the onset temperature of the second step of weight loss at about 300°C shifted to higher temperature, as shown by the behavior of the TMA curves of the 87 and 105% samples, whose percentage of residual mass retention in the range of $350\text{--}400^{\circ}\text{C}$ was higher than that of the corresponding untreated control.

The increase in weight retention of the St/BMA-grafted silk fibers were generally in good agreement with the thermal observations recorded by DSC (Fig. 2) and TMA (Fig. 3).

Dynamic Mechanical Behavior

The temperature dependence of the dynamic loss modulus (E'') as a function of the increasing weight gain of silk fibers grafted with St/BMA mixture is shown in Figure 5. The E'' curve of the untreated control [Fig. 5(a)] was characterized by a prominent peak at about 230°C , whose onset temperature was located at around $180\text{--}485^{\circ}\text{C}$. It was elucidated that the E'' peak is attributed to thermal movement of the ordered crystalline regions, because the spacing [$d_{(200)}$] or [$d_{(002)}$] corresponding to the intersheet distance was found to gradually expand beyond 180°C .¹⁷

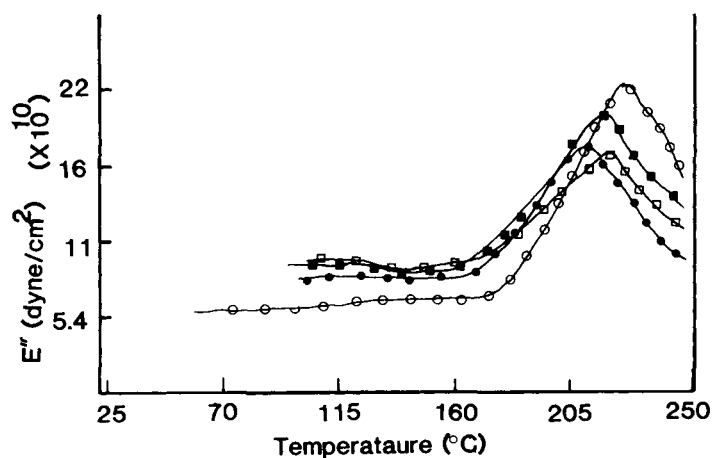


Figure 5 Dynamic loss modulus (E'') of the St/BMA-grafted silk fibers. Weight gain (%): (○) 0; (■) 41; (□) 62; (●) 105.

The loss modulus peak of St/BMA-grafted silk fibers [Fig. 5(b-d)] shifted to lower temperature as the weight gain increased up to 150°C. Moreover, the E'' peak became broader and its onset temperature moved down to about 160°C, about 20°C lower than the untreated control sample.

These viscoelastic changes suggest that the molecular motion of the fibroin chains, induced by thermal treatment, was enhanced by grafting silk fibers with the St/BMA vinyl monomer mixture. The observation that the crystalline regions were also affected by St/BMA grafting led us to envisage the possibility that the polymer chains penetrated within both the amorphous and the laterally ordered regions of the fibers, thus exerting their influence on the thermal behavior of crystalline elements.

X-Ray Diffraction Curves

The x-ray diffraction intensity curves of St/BMA-grafted silk fibers with different amounts of weight gain were examined in order to ascertain if changes in the fine structure were induced by grafting (Fig. 6). The untreated control sample [Fig. 6(a)] exhibited a major x-ray diffraction peak at 20.5° corresponding to the crystalline spacing of 4.39 Å, which

is characteristic of silk fibers with high molecular orientation. The position and intensity of the main x-ray diffraction peak did not change regardless of St/BMA grafting as shown by the curves of the samples with weight gain of 62% [Fig. 6(b)] and 105% [Fig. 6(c)].

These accumulated data are consistent with those reported for silk fibers grafted with other vinyl monomers, demonstrating that the crystalline structure with oriented β' crystals was not affected by the graft-copolymerization reaction occurring inside the fiber. Moreover, they confirmed the results of the tensile properties (Fig. 1), which showed that the breaking load remained almost unchanged after grafting.

Surface Characteristics

The surface characteristics of the grafted silk fibers were investigated by SEM analysis. Figure 7 shows the SEM micrographs of St/BMA-grafted silk fibers. No significant differences were detected between the untreated control, although not presented, and the grafted silk with weight gain of 41%. On the other hand, when the weight gain increased to 105%, the SEM micrograph of the silk fiber with high

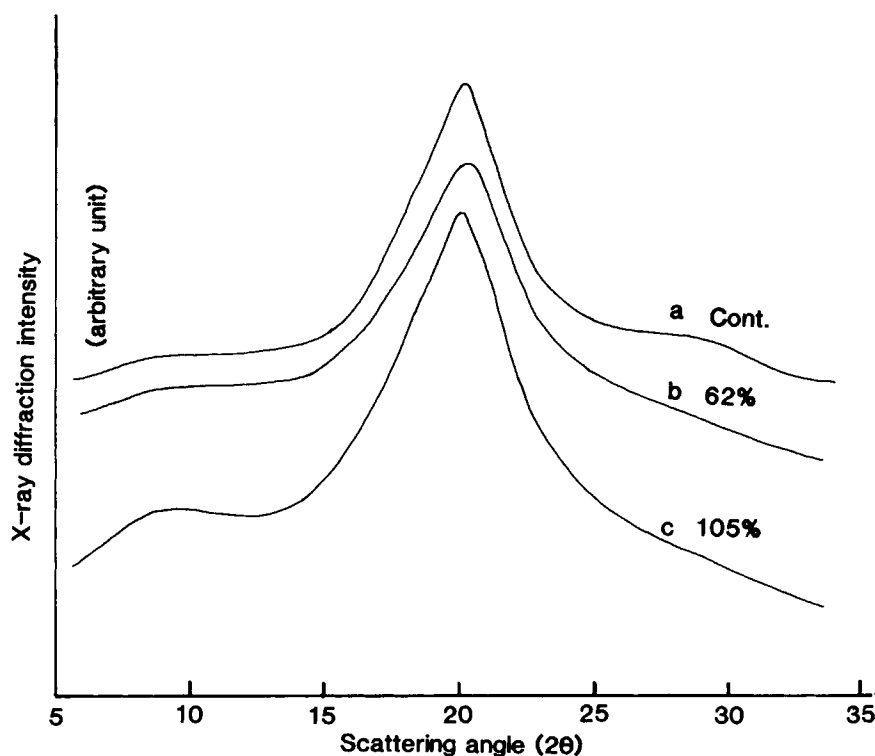


Figure 6 X-ray diffraction intensity curves of the St/BMA-grafted silk fibers. Weight gain (%): (a) 0; (b) 62; (c) 105.

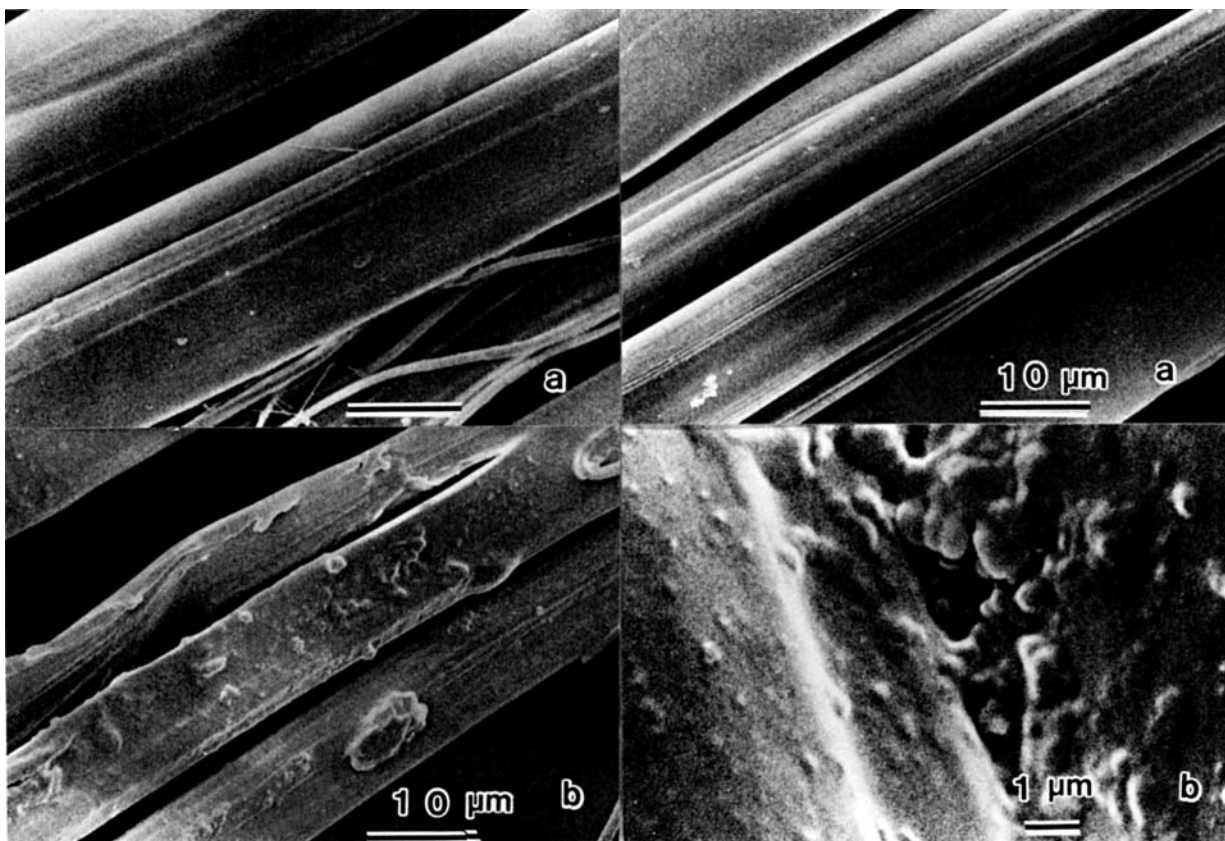


Figure 7 SEM micrographs of the St/BMA-grafted silk fibers with weight gain of (a) 41% and (b) 105%.

weight gain showed the attachment of St, BMA, and/or St/BMA oligomers on the surface of the silk fibers.

REFERENCES

1. M. Tsukada, *J. Seric. Sci. Jpn.*, **53**, 380 (1984).
2. M. Tsukada, *J. Seric. Sci. Jpn.*, **56**, 157 (1987).
3. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 965 (1988).
4. M. Tsukada, *J. Appl. Polym. Sci.*, **35**, 2133 (1988).
5. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **39**, 1289 (1990).
6. M. Tsukada, T. Yamamoto, N. Nakabayashi, and G. Freddi, *J. Appl. Polym. Sci.*, **43**, 2115 (1991).
7. M. Tsukada, Y. Gotoh, G. Freddi, K. Yamamoto, and N. Nakabayashi, *J. Appl. Polym. Sci.*, **44**, 2197 (1992).
8. M. Tsukada, G. Freddi, H. Shiozaki, and N. Pusch, to appear.
9. S. Kobayashi, M. Sugiyama, and H. Yoshida, Rep. Tokyo Metropolitan Textile Res. Institute, **15**, 137 (1979).
10. S. Samal and G. Sahu, *J. Macromol. Sci. Chem.*, **A21**, 725 (1984).
11. S. Samal, G. Sahu, and P. L. Nayak, *J. Appl. Polym. Sci.*, **29**, 3283 (1984).
12. N. Mohanty, B. Pradha, M. C. Mohanta, and H. K. Das, *J. Macromol. Sci. Chem.*, **A19**, 1189 (1983).
13. T. Kako, A. Katayama, and N. Kuroki, *J. Seric. Sci. Jpn.*, **46**, 103 (1977).
14. M. Tsukada, G. Freddi, M. Matumura, H. Shiozaki, and N. Kasai, *J. Appl. Polym. Sci.*, **44**, 799 (1992).
15. M. Tsukada, H. Shiozaki, J. S. Crighton, and N. Kasai, to appear.
16. H. Ishikawa, M. Tsukada, I. Doizume, A. Konda, and K. Hirabayashi, *Sen-i Gakkaishi*, **28**, 91 (1972).
17. M. Nagura, M. Urushidani, H. Shinohara, and H. Ishikawa, *Kobunshi Ronbunshu*, **34**, 389 (1977).
18. M. Tsukada and Y. Ishiguro, *J. Seric. Sci. Jpn.*, **53**, 310 (1984).
19. M. Tsukada, N. Kasai, and G. Freddi, *J. Appl. Polym. Sci.*, to appear.

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