Structural Analysis of Methacrylamide-Grafted Silk Fibers

MASUHIRO TSUKADA,[1,*] GIULIANO FREDDI,[2] YOSIO ISHIGURO,[3] and HIDEKI SHIOZAKI[4]

[1]National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan; [2]Stazione Sperimentale per la Seta, Via G. Colombo 81, 20133 Milano, Italy; [3]Yokohama Center for Quality Control and Consumer Service, Kitanaka Dori, Nakaku, Yokohama, 231 Japan; [4]Textile Institute of Kanagawa, Aikawa-machi, Kanagawa 240-03, Japan

SYNOPSIS

The structural changes and the thermal behavior of silk fibers grafted with methacrylamide (MAA) were investigated as a function of the weight gain. The refractive index parallel to the fiber axis decreased with increasing weight gain, whereas that perpendicular remained almost unchanged. Accordingly, birefringence decreased with a steeper slope in the weight gain range 0–80%, suggesting a lower degree of average molecular orientation. Only small changes in the isotropic refractive index were detected, suggesting that the crystallinity of the fibers remained essentially unaffected by MAA grafting, as confirmed by the X-ray diffraction data. The molecular orientation in the crystalline regions remained unchanged in the weight gain range 0–60%, then sharply decreased. The strength and the initial tensile resistance of grafted silk fibers decreased both in the dry and wet states, while elongation at break increased in the dry state and remained almost constant in the wet state. The results of the thermal behavior, investigated by differential scanning calorimetry, thermomechanical and thermogravimetric analysis, and dynamic mechanical measurements, were consistent with an increased thermal stability conferred on silk fibers by MAA grafting. The cross-sectional area of MAA-grafted silk fibers increased. Moreover, ion-etched cross sections of the grafted silk fiber showed the presence of fibrils with a diameter larger than that of the untreated control. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

During the past two decades, there has been considerable academic and technological interest in the chemical modification of silk fibers. Though silk is highly appreciated for its outstanding properties, such as water absorption, heat retention, hand, luster, comfort, and brilliant color shades obtained by dyeing and printing, this fiber presents a few weak points, i.e., crease recovery, rub resistance, color fastness, wash and wear properties, and photoyellowing, which seriously limit its general use.

Among the chemical modification techniques, graft-copolymerization[1-6] of vinyl monomers onto silk fibers has been considered a powerful method to substantially improve some intrinsic fiber properties. A large number of vinyl monomers has been applied onto silk and their influences on the fiber properties have been extensively studied.[1-6] The use of methacrylamide (MAA)[7-8] as a grafting agent for silk fibers has recently become quite popular. The optimum reaction conditions,[7] as well as the influence of different parameters on the industrial process, have been extensively studied. Silk fibers are mainly treated in yarn form (hank or cone). At relatively high weight gain values, MAA grafting (known as organic weighting) can compete with the traditional mineral weighting (tin–phosphate–silicate method)[9] for the production of necktie silk yarn. However, MAA grafting is carried out not only to increase the weight of silk, but also to improve some inferior textile performances of silk fibers. The noticeable increase in moisture content even at relatively low graft yields plays a positive role in improving the comfort of silk fabrics without affecting their hand and luster. Due to the higher hydroscopicity of MAA-grafted silk fibers, no significant improvement of crease recovery can be obtained, whereas a certain resistance to oil staining (oil repellency) has been reported.[7] The dye affinity of

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 50, 1519–1527 (1993)
 CCC 0021-8995/93/091519-09

MAA-grafted silk fibers does not change when compared with ungrafted silk fibers, though the final shades obtained both with acid and reactive dyes are slightly different,[7] due to the reduced amount of dyestuff absorbed.

Though several papers dealing with the technological aspects of grafting silk fibers with MAA have been published, little attention has been paided so far to the physicochemical changes induced by the graft-copolymerization reaction. In this article, we report the fine structural changes, i.e., crystallinity and molecular orientation, as well as the thermal and the viscoelastic behavior of silk fibers with different amounts of weight gain. Moreover, the morphology of ion-etched cross sections of MAA-grafted silk fibers were examined in order to study at the microscopic level the attachment sites of the poly(MAA) chains.

EXPERIMENTAL

Materials

Raw silk fibers were obtained from reeling of cocoons threads collected from seven cocoons of the domesticated mulberry silkworm. Degummed silk fibers (ca. 5 g) were immersed in a solution of aqueous ammonium peroxodisulfate (0.1%) as the initiator that contained various amounts of MAA (2–40 g) at temperatures in the range of 75–85°C for 1–4 h. The pH of the grafting system was controlled at approximately 3.1 by adding a small amount of H_2SO_4 solution. After the desired reaction time, silk fibers were taken out and washed thoroughly with water three or four times. The unreacted MAA monomer and its oligomer physically adhered to the silk fibers were removed by rinse and washing with hot water. The washed and air-dried samples were dried in a forced draft oven at 100–105°C to achieve a constant weight, placed in a desiccator over silica gel for 30 min, and weighed. The MAA-grafted silk fibers with a weight gain of 5, 25, 59, 78, and 120% were thus obtained.

Measurements

The refractive indices were measured with the Beche's line method using a polarizing microscope and monochromatic light (Na light) at 20°C and 65% RH as previously described.[6]

X-ray diffraction patterns were obtained using an X-ray source with CuKα radiation (λ = 1.54 Å). The conditions for the X-ray measurements have been described in detail elsewhere.[10] Molecular orientation of the blend films was evaluated on the basis of the X-ray diffraction intensity curves according to the method described in the previous communication.[4]

The tensile properties of MAA-grafted silk fibers were measured with a Tensilon UTM-II (Toyo Baldwin Co.) both in the dry and wet states using the standard technique at 20°C and 65% RH at a gauge length of 50 mm and strain rate of 20 mm/min. The DSC measurement was carried out as described previously.[1-4]

Thermomechanical analyses (TMA) were carried out using a Rigaku Denki instrument at a heating rate of 10°C/min. TMA full scale was ±500 μm. The thermogravimetric analyses (TGA) were run in nitrogen atmosphere on a Rigaku Denki thermogravimetric thermoflex system, raised at 10°C/min to 400°C, according to the method reported in a previous paper.[11]

The dynamic storage (E') and loss moduli (E'') of the grafted silk fibers were measured at 10 Hz with a Toyoseiki Rheolograph Solid-S. The sample length was 15 mm. The initial tension was 30 gf.

The cross-sectional features of MAA-grafted silk fibers were examined under a JEOL JAX-333S scanning electron microscope after ion-etching treatment with JEOL JFC-1100 ion-spatter. Samples were ion-etched at 1.5 kV, 8 mA, for 15 min, and then gold-coated.

RESULTS AND DISCUSSION

Refractive Indices

The refractive indices have proved to be a useful source of information about the fine structural changes, i.e., crystallinity and molecular orientation, induced by grafting with vinyl monomers. Therefore, we investigated the changes in the optical properties of MAA-grafted silk fibers in relation to the weight gain. Figure 1 shows the refractive indices parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the fiber axis. The value significantly decreased with increasing weight gain, the slope of the curve being steeper in the weight gain range 0–80%. On the other hand, the value remained almost unchanged regardless of the increasing amount of MAA polymer grafted onto the fibrous substrate. These findings are in good agreement with those reported for silk fibers grafted with other vinyl monomers, such as methyl methacrylate (MMA)[2] and 2-hydroxyethyl methacrylate (HEMA).[1] This suggests that the grafting process preferentially affects the refractive index parallel to the fiber axis and that the high degree of order and orientation typical of the fibroin molecules in the

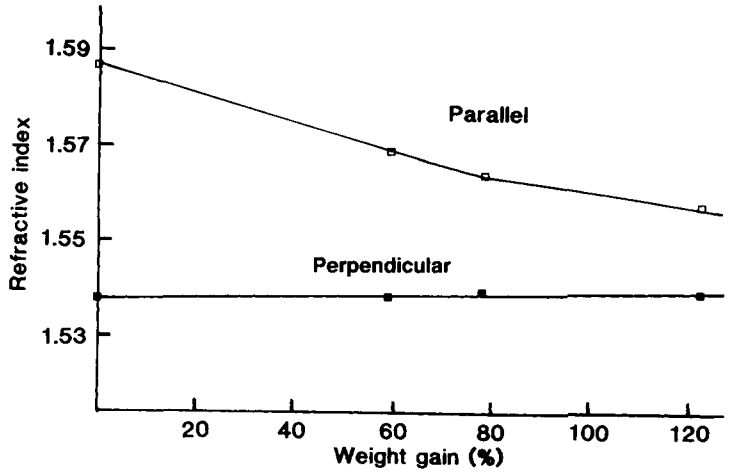

Figure 1 Refractive indices (□) parallel and (■) perpendicular to the fiber axis of the MAA-grafted silk fibers with different values of weight gain.

fiber is perturbed by the insertion of the unoriented grafted chains.

Figure 2 shows the changes in birefringence (Δn) and isotropic refractive index (n_{iso}) of MAA-grafted silk fibers. The birefringence decreased quite sharply in the weight gain range 0–80%, above which the Δn value remained almost unchanged. The first sharp drop of birefringence is in striking agreement with the steep decrease of the refractive index parallel to the fiber axis (see Fig. 1), suggesting that the grafting process induced a noticeable decrease of the average molecular orientation of silk fibers. The n_{iso} value showed a slight and linear decrease in the weight gain range examined. The behavior of the isotropic refractive index could be related to a lower degree of crystallinity of MAA-grafted silk fibers. However, from the X-ray diffraction data (see Fig. 3), it can be inferred that the crystalline structure was not directly affected by grafting with MAA. Therefore, we can attribute the decrease of the n_{iso} value to a lower fiber density, due to the loading of the amorphous poly(MAA) chains.

The above results concerning the optical properties of MAA-grafted silk fibers confirm those already reported for silk fiber graft-copolymerization with other vinyl monomer.[12] A common feature of the grafting process, whichever vinyl monomer used, is a significant drop of birefringence, especially in the low-to-medium weight gain range, associated with a slight decrease of the isotropic refractive index. Also, the extent of the fine structural changes registered by measuring the refractive indices may vary according to the kind of monomer used, the grafting conditions adopted, the weight gain at-

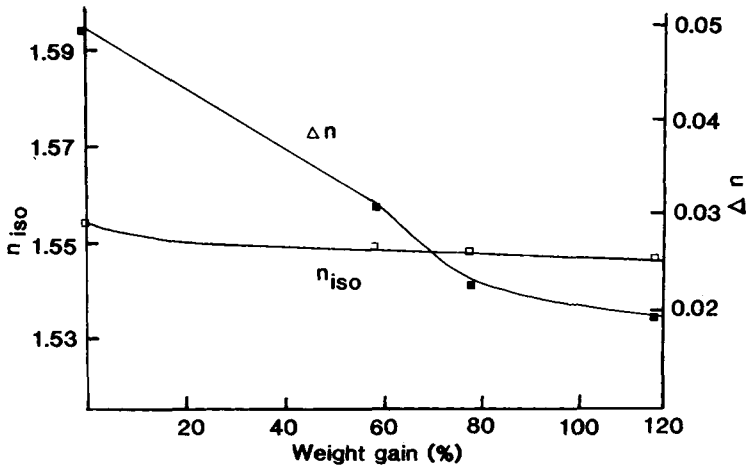

Figure 2 Isotropic refractive index (n_{iso}) and birefringence (Δn) of the MAA-grafted silk fibers with different amounts of weight gain.

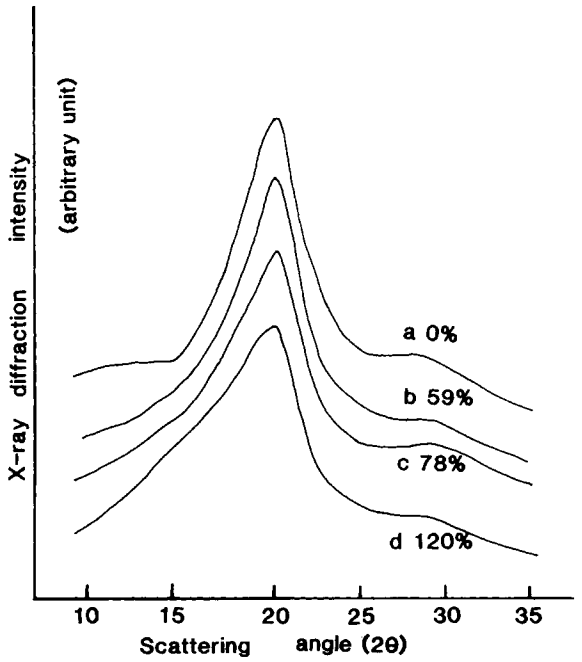

Figure 3 X-ray diffraction intensity curves of the MAA-grafted silk fibers with different amounts of weight gain. Weight gain (%): (a) 0; (b) 59; (c) 78; (d) 120.

tained, the molecular weight of the grafted chains, etc.

X-ray Diffraction Curves

The X-ray diffraction intensity curves of MAA-grafted silk fibers with different amounts of weight gain were measured to ascertain whether fine structural changes in the crystalline regions were induced by the grafting process (Fig. 3). The untreated control sample (a) exhibited a major X-ray diffraction peak at 20.5°, corresponding to the specific crystalline spacing of 4.39 Å, which is characteristic of silk fibers with a highly oriented β structure. MAA-grafted silk fibers with 59, 78, and 120% weight gain (curves b, c, and d, respectively) showed diffraction curves essentially similar to the untreated sample in regard to the position and intensity of the major diffraction peak at 20.5°, which remained almost unchanged. An additional minor diffraction peak appeared in the lower scattering region, below 20.0°, of MAA-grafted silk fibers. This peak, quite broad and in shoulder form, is clearly visible from the curve of the sample with the highest weight gain (d). The presence of the minor and broad diffraction peak can be attributed to the contribution of the MAA polymer attached within the fibrous substrate.

The above results are consistent with those reported from silk fibers grafted with other vinyl monomers,[2-4] demonstrating that the crystalline structure with oriented β crystals remained essentially unaffected by the graft-copolymerization reaction that occurred inside the silk fibers.

Molecular Orientation

Figure 4 shows the curve obtained by plotting the molecular orientation values as a function of the increasing amounts of weight gain. The curve is characterized by an initial plateau in the weight gain range 0–60%, followed by a steep drop registered as the weight gain increased further on. These results imply that silk fibers can be grafted up to a weight gain of about 55–60% without any negative consequence on the fine structure of the crystalline regions, in fair agreement with the results reported in a previous paper on methacrylonitrile (MAN)-grafted silk fibers.[4] It is interesting to note that the most noticeable decrease of the Δn value (see Fig. 2) was registered just within the above weight gain limits. This behavior can be attributed to the fact that for low-to-medium amounts of grafted polymer the amorphous regions of the fiber play the major role, due to their accessibility and to the room available between the fibroin molecules, which can be easily filled by the growing polymer chains.

The decrease of molecular orientation in the crystalline region observed above 60% weight gain

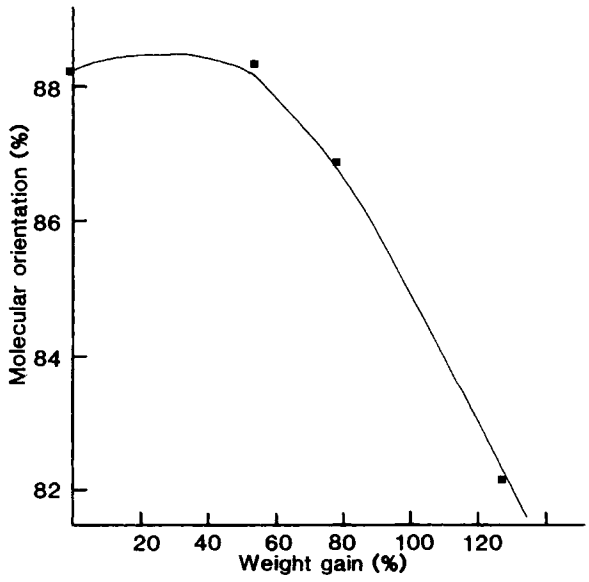

Figure 4 Molecular orientation evaluated from the X-ray diffraction curves of the MAA-grafted silk fibers as a function of the weight gain.

suggests that a certain degree of disorder has affected also the most ordered and tightly packed domains of silk fiber. However, on the basis of the above X-ray diffraction results, we attribute the lower degree of molecular orientation to the disordering of the silk fibroin molecules in the laterally ordered regions,[10] which connect, as an intermediate phase, the β crystals to the amorphous regions.

The above findings, combined with those obtained from the measurement of the refractive indices, emphasize that the fine structural changes induced by grafting occur as a sequence of events, which are strictly dependent on the amount of weight gain attained.

Tensile Properties

The tensile properties, i.e., strength, elongation at break, and tensile modulus, are important characteristics that determine the functional performances of textile materials. We measured the tensile properties of MAA-grafted silk fibers both in the dry and wet states as a function of the weight gain (Table I). The tensile strength of grafted silk fibers gradually decreased either in the dry or wet state as the weight gain increased up to 127%. However, it is interesting to note that the original breaking load of the untreated control fiber (200 g) remained almost unchanged regardless of the MAA grafting, suggesting that the intrinsic mechanical properties of silk are not directly affected by the grafting process and that the decrease in strength should be attributed mainly to the increase in cross-sectional area of the silk filament. The elongation at break measured in dry state increased with the weight gain, mainly because of the enhanced hydroscopicity of MAA-grafted silk fibers, which exhibit a higher moisture regain than that of the untreated ones. As expected, the percentage of elongation is larger in the wet state and the differences between the untreated control sample and those grafted with MAA becomes smaller. The initial tensile resistance, corresponding to the measure of the Young's modulus, was determined from the slope of the stress–stain curve. Both dry and wet state values decreased almost linearly as the weight gain increased, confirming the lower degree of stiffness of MAA-grafted silk fibers, perhaps due to the plasticizing effect of the grafted polymer.

DSC Curves

Figure 5 shows the DSC curves of MAA-grafted silk fibers with different amounts of weight gain. The untreated control sample (a) showed a single endothermic peak at about 319°C, attributed to the thermal decomposition of silk fibroin with oriented β configuration.[13] MAA-grafted silk fibers (b–d) exhibited a new endothermic peak at around 280°C, in addition to the above endotherm, which slightly shifted to higher temperature (324°C). The intensity of the former became higher with increasing weight gain, and the latter accordingly decreased. The position of the new endothermic peak slightly shifted to higher temperature, from 282 to 288°C for the 59 and 78% grafted samples, respectively, and then remained essentially unchanged from a further increase of weight gain up to 120%. The endothermic transition registered in the lower temperature range below 300°C can be attributed to the thermal decomposition of the MAA polymer attached within the silk fiber matrix.

The presence of an additional thermal transition in the DSC curve of silk fibers grafted with MAA, as well as with other vinyl monomers,[1-4] confirms the poor compatibility existing at the molecular level between the fibroin molecules and the loaded polymer chains, whichever are the physicochemical

Table I Tensile Strength, Elongation at Break, and Tensile Modulus of the MAA-grafted Silk Fibers Both in the Dry and Wet States

	Strength		Elongation (%)		Modulus (g/d)	
Sample	Dry	Wet	Dry	Wet	Dry	Wet
Control	200 (3.6)	164 g[a] (3.1 g/d)[b]	21.3	28.6	54.1	18.2
59% MAA[c]	193 (2.4)	126 (1.5)	20.3	23.2	41.6	9.0
78% MAA	219 (1.8)	157 (1.2)	24.7	28.6	30.7	5.9
120% MAA	200 (1.5)	128 (1.0)	24.4	29.1	25.7	4.4

[a] Tensile strength of single MAA-grafted silk fiber.
[b] Tensile strength per fiber size (corresponding to the cross-sectional area). 1 g/d = 1.22×10^3 kgf/cm^2.
[c] MAA-grafted silk fiber with weight grain of 59%.

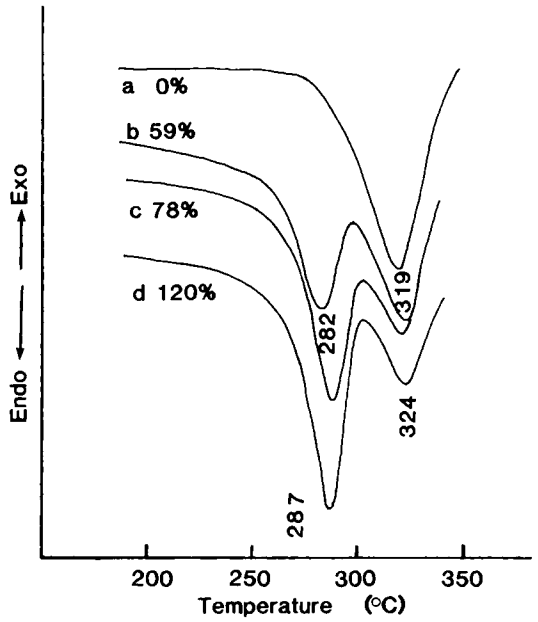

Figure 5 DSC curves of the MAA-grafted silk fibers with different amounts of weight gain. Weight gain (%): (a) 0; (b) 59; (c) 78; (d) 120.

properties of the latter, at least from the point of view of the DSC measurements.

TMA Curves

The resistance of the fibers to shrinkage and/or elongation in the course of heating is an important property related to the behavior of textile goods during use and maintenance. We therefore measured the changes in expansion and contraction properties of MAA-grafted silk fibers with different amounts of weight gain by thermomechanical analysis (Fig. 6). The TMA curve of the untreated control sample (a), heated at a rate of 10°C/min, exhibited a slight contraction of about 0.2% over the temperature range 25–130°C, mainly due to evaporation of water. Then, the fiber began to extend beyond 180°C and the major extension appeared from 280°C upward. The MAA-grafted silk fibers (b–d) showed a prominent contraction in the temperature range 25–180°C, which can be attributed to the hydrophilic properties of the grafted poly-MAA chains, resulting in a comparatively larger moisture content.

Moreover, the onset temperature of the final abrupt extension sensibly shifted to higher temperature as the weight gain increased. An interesting feature of MAA-grafted silk fibers is the equilibrium step between contraction and extension, registered by the TMA curve as a plateau in the temperature range 180–300°C. At the same temperature, the control sample has already started its final extension, coinciding with the minimal resistance to the load applied and with the beginning of thermal degradation phenomena. This effect should be attributed to the thermal behavior of the MAA polymer attached within the fiber matrix, which conferred on grafted silk fibers a higher stability in the course of heating. Additionally, the higher the weight gain (d), the larger was the thermal stability in the high temperature range. These results are in fair agreement with those already reported for silk fibers

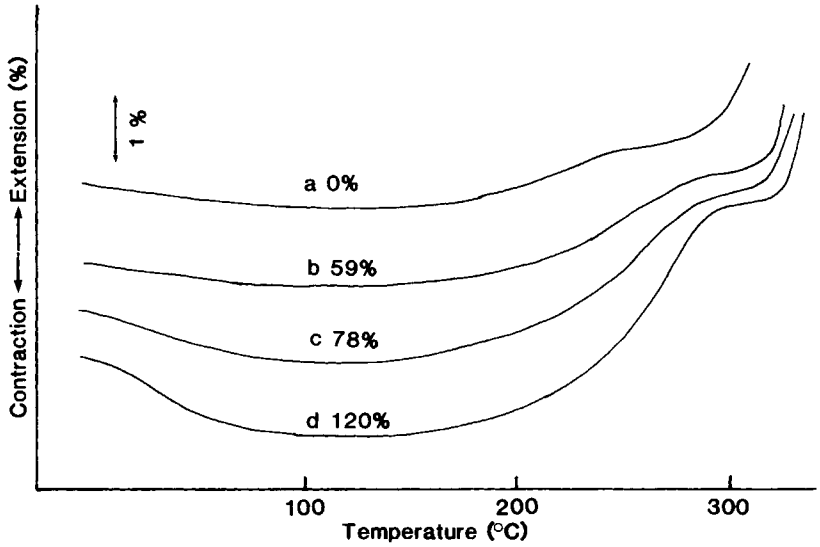

Figure 6 Thermomechanical analysis (TMA) curves of the MAA-grafted silk fibers with different amounts of weight gain. Weight gain (%): (a) 0; (b) 59; (c) 78; (d) 120.

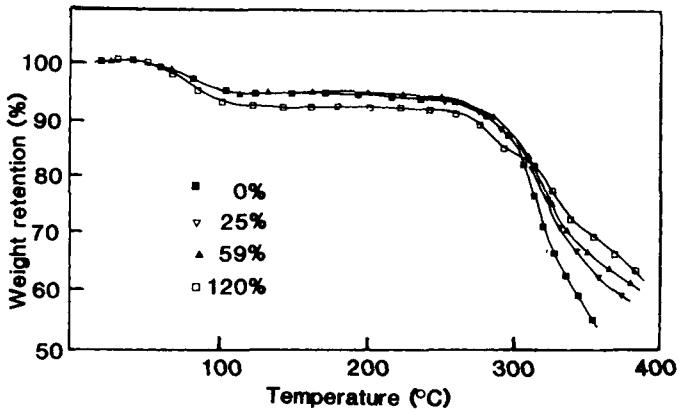

Figure 7 Thermogravimetric analysis (TGA) curves of the MAA-grafted silk fibers. Weight gain (%): (a) 0; (b) 25; (c) 59; (d) 120.

grafted with other vinyl monomers, such as MMA[2] and HEMA.[1]

TGA Curves

Figure 7 shows the thermogravimetric analysis of MAA-grafted silk fibers with different weight gains. The curve of the untreated control sample (a) displayed two inflection points, the first at about 50°C, corresponding to the loss of moisture regain and the second at 280°C, steeper and more prominent than the former, which coincides with the beginning of the thermal degradation of the fibers, as confirmed by the above discussed DSC and TMA data. The behavior of MAA-grafted silk fibers with 25% (b) and 59% (c) weight gain was roughly similar to that of the untreated sample over the temperature range 25–300°C. They exhibited rather higher weight retention values than the control sample at 350°C, as shown by the less steep drop of the TGA curves. The sample with a weight gain of 120% (d), besides confirming the above feature of a larger weight retention value at 350°C, showed two distinct steps of weight loss in the high temperature range, one at 280°C, similar to that of the other samples, and the other at about 320°C. The latter can be attributed to the MAA polymer grafted within the fibroin matrix.

The above findings are in good agreement with the TMA data and confirm the tendency of an increased thermal stability conferred on silk fibers by grafting with MAA.

Dynamic Mechanical Properties

To further investigate the thermal behavior of MAA-grafted silk fibers, we studied their viscoelastic properties by measuring the temperature dependence of the dynamic storage (E') and loss (E'') moduli. The E' and E'' curves of MAA-grafted silk fibers with different amounts of weight gain are shown in Figures 8 and 9, respectively. The viscoelastic behavior of untreated silk fibers has been already elucidated in previous articles.[14-15] The dynamic storage modulus of silk fibers grafted with MAA remained almost unchanged in the temperature range 25–180°C, regardless of the amount of weight gain. Above 180°C, the E' value decreased with a rate inversely proportional to the weight gain.

In fact, as the amount of MAA polymer loaded increased, the onset temperature of the E' drops slightly, shifting to higher values, and the slope of the curve decreased. It has been reported that the inflection point of the E' curve at around 170–180°C corresponds to the glass transition temperature[14,15] of untreated silk fibers. It can therefore be inferred that the grafted poly(MAA) chains interacted with

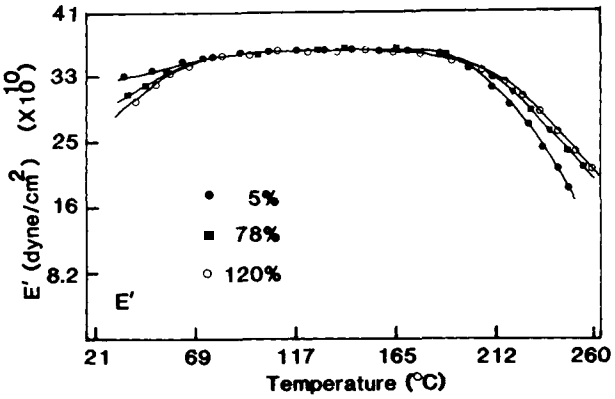

Figure 8 Dynamic storage modulus (E') of the MAA-grafted silk fibers with different amounts of weight gain. Weight gain (%): (a) 5; (b) 78; (c) 120.

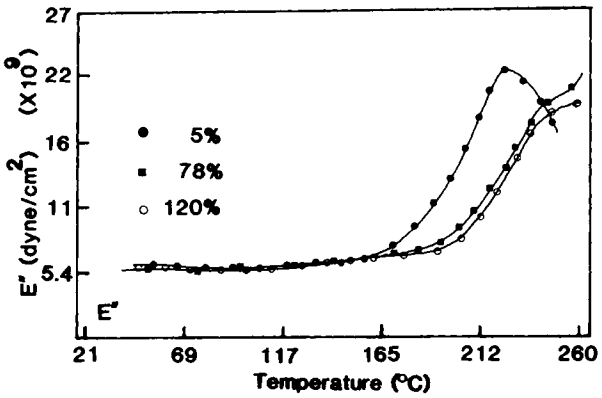

Figure 9 Dynamic loss modulus (E'') of the MAA-grafted silk fibers with different amounts of weight gain. Weight gain (%): (a) 5; (b) 78; (c) 120.

the fibroin molecules in the amorphous regions and slightly moved upward the threshold of their sensitivity to the thermally induced molecular movement, which leads to the rubberlike behavior.

The dynamic loss modulus curves shown in Figure 9 elucidated that at low weight gain (5%) the viscoelastic behavior of MAA-grafted silk fibers just resembles that of the untreated fibers (data not shown), with a major E'' peak at about 225°C, which has been attributed to the thermal movement of the fibroin molecules in the ordered crystalline regions. At high weight gain values, such as 78 and 120%, the beginning of loss modulus increase significantly shifted to higher temperature. Accordingly, the E'' peak appears as a shoulder of the loss modulus curve, still increasing at 260°C. The marked changes in the loss modulus curves of MAA-grafted silk fibers with large amounts of weight gain strongly suggests that the poly(MAA) chains attached within the silk fibers restricted the segmental motion of the fibroin molecules even in the crystalline and laterally ordered regions,[10] interfering with the rate of breaking and reforming of the intra- and intermolecular hydrogen bonds.

These findings suggest that the viscoelastic behavior of silk fibers is significantly influenced by the MAA grafting and that the mutual interaction between the MAA chains and the fibroin molecules is strong enough to affect the thermally induced molecular motion not only in the amorphous but also in the laterally ordered regions, i.e., in the fringed fibril volumes located at the end of each crystalline region, which was partly penetrated by the growing poly(MAA) chains.

In previous articles we reported the dynamic mechanical behavior of silk fibers grafted with other vinyl monomers, such as MMA, MAN,[4] N(n-butoxymethyl)methacrylamide (n-BMA),[14,15] as well as modified with epoxides.[6] It is interesting to note that, while the general effect of the above grafting and modifying agents was that of decreasing the glass transition temperature and enhancing the molecular motion of the fibroin molecules, the poly(MAA) grafted chains conferred on silk fibers a higher thermal stability than did the untreated sample.

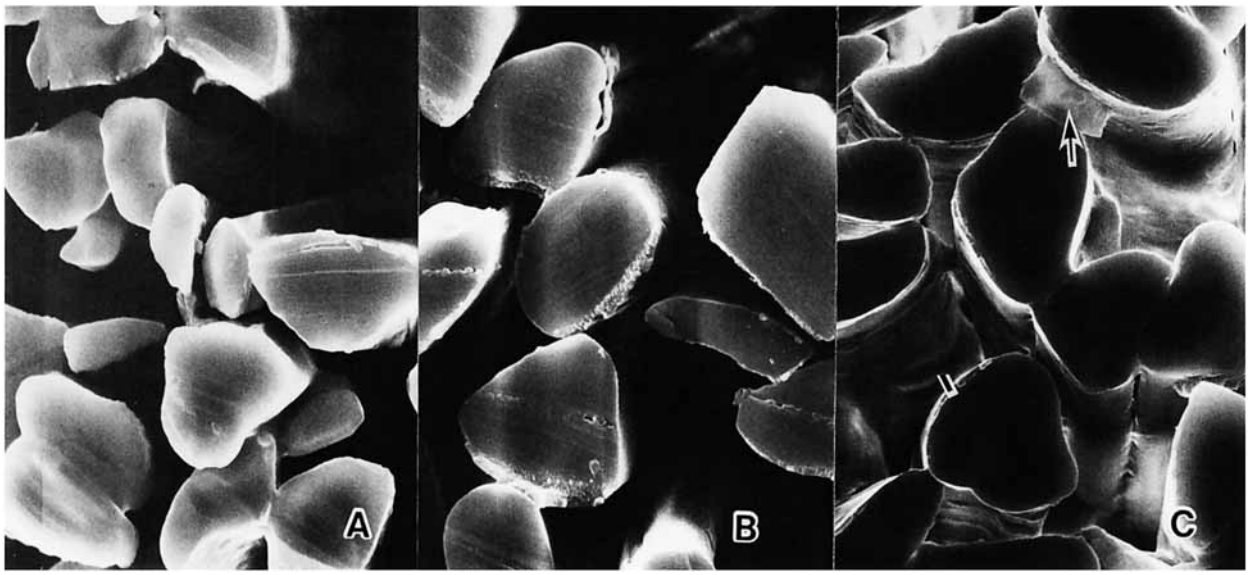

Figure 10 SEM photographs of the grafted silk fibers with different amounts of weight gain. Weight grain (%): (A) 0; (B) 25; (C) 59.

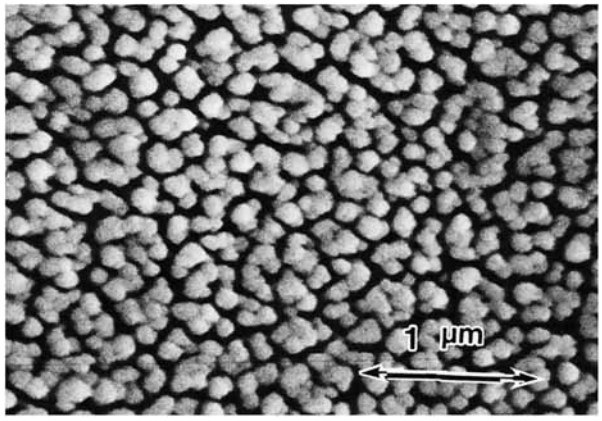

Figure 11 Cross-sectional features of the grafted silk fibers with weight grain of 25%.

Cross-sectional Characteristics

The cross sections of MAA-grafted silk fibers with different amounts of weight gain were examined by scanning electron microscopy (SEM). Figure 10 shows that the cross-sectional area of silk fibers with 25 and 59% weight gain is significantly larger than that of the untreated control sample (0%). Moreover, a thin layer of MAA polymer seems to coat the external surface of the fibers (see arrow) when the weight gain exceeds a certain limit. The cross section of MAA-grafted silk fiber was also examined by SEM after ion etching. Figure 11 represents the SEM photograph of the cross section of MAA-grafted silk fiber with a weight gain of 25%. Many fibril structures were irregularly round in shape and their diameters were found to be in the range of 0.2–0.4 μm. It is supposed that they are formed by a large number of microfibrils having a diameter of 100–150 Å. The diameter of the fibril increased following grafting with MAA, suggesting that the MAA polymer chains inserted not only in the room available within the fibrils, but also within the intermicrofibrillar space, which is noncrystalline in nature.

REFERENCES

1. M. Tsukada, *J. Seric. Sci. Jpn.*, **53,** 380 (1984).
2. M. Tsukada, *J. Appl. Polym. Sci.*, **35,** 965 (1988).
3. M. Tsukada, *J. Appl. Polym. Sci.*, **35,** 2133 (1988).
4. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **39,** 1289 (1990).
5. M. Tsukada, G. Freddi, M. Matsumura, H. Shiozaki, and N. Kasai, *J. Appl. Polym. Sci.*, **44,** 799 (1992).
6. M. Tsukada, Y. Gotoh, G. Freddi, M. Matsumura, H. Shiozaki, and H. Ishikawa, *J. Appl. Polym. Sci.*, **44,** 2203 (1992).
7. A. Bianch Svilokos, M. R. Massafra, and S. Beretta, *La Seta,* **44,** 4 (1986).
8. W. Schindler, G. Laubert, and A. R. Czerny, *Melliand Textilberichte,* **72,** 1031 (1991).
9. I. Sakaguchi, K. Hirabayashi, Y. Kakegawa, M. Mitsui, and M. Tsukada, *J. Seric. Sci. Jpn.*, **40,** 192 (1971).
10. M. Tsukada, G. Freddi, M. Nagura, H. Ishikawa, and N. Kasai, *J. Appl. Polym. Sci.*, **46,** 1945 (1992).
11. M. Tsukada, G. Freddi, and H. Shiozaki, *J. Appl. Polym. Sci.*, **45,** 1719 (1992).
12. M. Tsukada, K. Yamamoto, N. Nakabayashi, H. Ishikawa, and G. Freddi, *J. Appl. Polym. Sci.*, **43,** 2115 (1991).
13. H. Ishikawa, M. Tsukada, T. Doizume, and K. Hirabayashi, *Sen-i Gakkaishi,* **28,** 91 (1972).
14. M. Tsukada, H. Shiozaki, J. S. Crighton, and N. Kasai, *J. Appl. Polym. Sci.*, **48,** 113 (1993).
15. M. Tsukada, H. Shiozaki, and J. S. Crighton, *J. Appl. Polym. Sci.*, **48,** 1409 (1993).

Received February 1, 1993
Accepted April 2, 1993