

Physical Properties of 2-Hydroxyethyl Methacrylate-Grafted Silk Fibers

MASUHIRO TSUKADA,^{1,*} GUILIANO FREDDI,² PATRIZIA MONTI,³ ALESSANDRO BERTOLUZZA,³ and HIDEKI SHIOZAKI⁴

¹National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan; ²Stazione Sperimentale per la Seta, via G. Colombo 81, 20133 Milano, Italy; ³Dipartimento di Biochimica, Università di Bologna, Via Selmi, 2, 40126, Bologna, Italy; ⁴Textile Institute of Kanagawa, Aikawa-machi, Kanagawa 243-03, Japan

SYNOPSIS

This paper deals with the physical properties of silk fibers grafted with 2-hydroxyethyl methacrylate (HEMA). Both tensile strength and elongation measured in the dry and wet states gradually decreased with increasing weight gain. The initial modulus of the grafted silk fibers in the dry state sharply increased in the weight gain range of 0–16%, then decreased to a lower value than the reference untreated sample. The refractive indices parallel and perpendicular to the fiber axis decreased, though the former showed a steeper slope. Accordingly, birefringence and isotropic refractive index also decreased, suggesting a lower degree of crystallinity and molecular orientation of grafted silk fibers. DSC, TMA, and TGA curves of the HEMA-grafted silk fibers indicated an increased higher thermal stability of silk fibers due to the HEMA grafting. The dynamic mechanical measurements showed that the thermally induced molecular movement of both amorphous and crystalline domains of silk fibers was enhanced by HEMA grafting. X-ray diffraction curves, however, implied that the crystalline structure of the silk fibroin remained unchanged regardless of HEMA polymerization. The introduction of HEMA polymer in silk fibers was evidenced by the infrared spectra, exhibiting the absorption bands characteristic of either the grafted HEMA polymer and the fibroin molecules with ordered β structure. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, many attempts have been made to modify silk fibers by graft-copolymerization techniques and/or chemical modification to improve crease recovery, thermal stability, dyeability, and wash-and-wear properties. A variety of grafting monomers, including vinyl monomers with different functional groups at the side chains,^{1–8} and modifying agents, such as epoxides^{9–12} and dibasic acid anhydrides,¹³ have been applied with varying degrees of success.

Among the vinyl monomers, styrene (St)¹⁴ and methyl methacrylate (MMA)² were widely used at

in first stages of the industrial application of the grafting techniques in Japan. These monomers conferred appreciable bulkiness and fullness of handle on grafted silk fabrics, as well as better crease recovery and affinity toward disperse dyes. However, their use entailed some drawbacks, due to the strong hydrophobic properties, to the hardness of handle and to the deterioration of silk fibers in the course of grafting, especially when high weight gains were required.

To overcome these difficulties, attempts have been made to select proper grafting monomers that would increase the equilibrium regain of grafted silk fibers. Methacrylamide (MAA)¹ and 2-hydroxyethyl methacrylate (HEMA)¹⁵ were then applied with appreciable results, due to their good hydrophilic properties. The former is, at present, the most widely used vinyl monomer, not only for weighting purposes but also for improving some deteriorated textile

* To whom correspondence should be addressed.

functional performances of silk fibers. In fact, the noticeable increase in equilibrium regain, even at comparatively low weight gain, plays a positive role in improving the comfort of silk fabrics, without affecting their handling and luster.

The use of HEMA as the conventional silk grafting monomer was partly restrained because of the hard handle and stiffness of the silk fabrics with high weight gain. However, this monomer still is of considerable interest not only for industrial application, but also for fundamental studies on the relation between the grafted polymer chains attached within the fiber matrix and silk fibroin molecules.

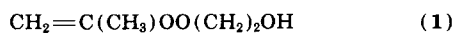
This paper deals with the physical properties of HEMA-grafted silk fibers with different amounts of weight gain. The changes in tensile and optical properties, thermal behavior, and fine structure will be discussed to ascertain the effect of grafting on the textile functional performances of silk fibers.

EXPERIMENTAL

Materials

Raw silk fibers were obtained after reeling of cocoon threads of the commercial silkworm variety of *Bombyx mori*. The composite threads, made of the bave from several cocoons drawn together, were twisted mechanically (Z-twist, 640T/m; S-twist, 720T/m). The raw silk fibers were degummed in an aqueous solution containing a 0.4% soap solution for 2 h at 98–100°C and washed with a 0.05% sodium carbonate solution followed by boiling water.

Reagent-grade 2-hydroxyethyl methacrylate (HEMA) (1), purchased



from Wako Pure Chemicals was used without further purification. Degummed silk fiber was immersed in a mixture of 2% ammonium persulfate on the weight of the HEMA monomer containing different values (10–100%) of the HEMA monomer on the basis of the fiber weight. A material-to-liquor ratio of 1 : 15 was maintained. The reaction bath was brought to 75–80°C for different values of reaction time (1–1.5 h) to obtain the HEMA-grafted silk fibers with different amounts of weight gain. At the end of the reaction, the treated silk was soaked in a solution containing 1 g/L nonionic detergent at 75°C for 30 min and rinsed with water thoroughly.

The weight gain was calculated from the increase in weight of the control silk after HEMA polymerization as follows:

$$\text{Weight gain (\%)} = (W_2 - W_1)/W_1 \times 100$$

where W_1 and W_2 denote the weights of the original silk and the silk containing HEMA polymer, respectively.

Measurements

Fiber strength and elongation at break were measured on a single thread with an automatic tensile tester (Tohyo Baldwin Co.) both in standard conditions (20°C, and 65% R.H.) and in water. Each value is the average of 25 results.

The refractive indices were measured with the Beche's line method using a polarized microscope under monochromatic light (Na light) at 20°C and 65% R.H., according to the procedure described in a previous paper.¹²

DSC measurements were performed on a Rigaku Denki instrument (DSC-10A) at a heating rate of 10°C/min. The DSC range and sample weight were 2.5 mcal/s and 2 mg, respectively. The open aluminum cell was swept with N₂ gas during the course of the analysis.

Thermomechanical properties of the grafted silk fibers were examined using a Rigaku Denki Model CN-8361 apparatus. The heating rate was 10°C/min, and sweep dry N₂ gas provided the inert atmosphere. The measuring conditions were the same as reported in a previous paper.⁸

Thermogravimetric analyses (TGA) were run under nitrogen on a Rigaku Denki instrument programmed under isothermal conditions, raised at 10°C/min to 400°C.

Spectral transmittance curves of grafted silk fibers were obtained with a Perkin-Elmer 1670 × spectrophotometer. The disks for the spectroanalysis were made of potassium bromide (30 mg) and the sample (3 mg).

The X-ray diffraction intensity curves were obtained at a scanning rate of 1 degree/min, a time constant of 2 s, and a counterrange of 800. The voltage and current of the X-ray source were 30 kV and 20 mA, respectively.

The surface of the HEMA-grafted silk fibers were examined, after gold coating, with a JEOL JAX-333S scanning electron microscope at acceleration voltage of 15 kV.

RESULTS AND DISCUSSION

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. The tensile properties of HEMA-grafted silk fibers were measured in both the dry and wet states in relation to the weight gain (Table I).

The strength value (3.1 g/d) of the untreated control measured in the dry state gradually decreased to 1.6 g/d when the weight gain attained 66%. However, the original breaking load of untreated silk (150–160 g) remained almost unchanged regardless of the HEMA grafting. These data suggest that the graft-copolymerization reaction only indirectly influenced the mechanical properties of silk, essentially by increasing the cross-sectional area of the fibers. This means that the increase in the size of the single filament may be attributed to the amounts of the loaded HEMA polymer within the silk fiber without affecting their intrinsic tenacity.

The strength measured in the wet state showed a similar trend, decreasing at a rate and extent almost comparable to those observed in the dry state. The high hydrophilic properties of the HEMA monomer did not affect the behavior of grafted silk fibers in water, as was ascertained with hydrophobic vinyl monomers, such as styrene¹⁴ and methyl methacrylate.²

The elongation at break of the untreated control in the wet state was significantly higher than that in dry state (+37%). The elongation values of

HEMA-grafted silk fibers decreased in both the dry and wet states. However, the decrease in elongation of the grafted silk fibers in the dry state was gradual and linear in the range of weight gain studied. The elongation in the wet state decreased clearly at small weight gain (14%) and then remained almost unchanged. The HEMA grafting significantly reduced the difference between the elongation values determined in the dry and wet states. This effect was primarily due to the lower elongation exhibited in the wet state by grafted silk fibers, as though the extensibility of the fibroin chains subjected to the applied load was reduced in some way by the HEMA grafting.

The tensile modulus in the dry state, which is a measure of the initial tensile resistance of the fibers to the load applied, sharply increased at low weight gain (+32%, compared with the untreated control sample) and then decreased for HEMA-grafted silk fibers with higher weight gain values. No traces of this initial stiffness induced by HEMA grafting were found when the tensile modulus was measured in the wet state. In fact, the values were found to decrease almost linearly with the weight gain.

Refractive Indices

In an attempt to ascertain if the changes in the tensile properties of HEMA-grafted silk fibers were due to the modification of the fiber's fine structure, i.e., molecular orientation and crystallinity, we studied the optical properties in relation to the weight gain.

Figure 1 shows the experimental results of the refractive indices parallel (n_{\parallel}) and perpendicular (n_{\perp}) to the fiber axis. Both n_{\parallel} and n_{\perp} values linearly decreased in the weight gain range of 0–66%, though the former exhibited a steeper negative slope. These findings are in good agreement with the literature¹⁶ on the MMA-grafted silk fibers, suggesting that grafting affected the molecular orientation of fibroin chains and preferentially decreased the degree of order of the molecules aligned along the fiber axis.

Figure 2 shows the results of birefringence (Δn) and isotropic refractive index (n_{iso}) of HEMA-grafted silk fibers with different amounts of weight gain. The n_{iso} value decreased linearly over the weight gain range of 0–20%. Above 20%, the Δn values linearly related to the weight gain increase. Since birefringence and the isotropic refractive index are a measure¹² of the average molecular orientation and crystallinity of silk fibers, respectively, it was elucidated that the grafting process induced some changes in the fine structure of silk fibers.

Table I Tensile Strength, Elongation at Break, and Tensile Modulus of the HEMA-grafted Silk Fibers with Different Amounts of Weight Gain in the Dry (20°C, 65% R.H.) and in Wet States

Sample	Strength (g/d)		Elongation (%)		Modulus ^a (g/d)	
	Dry	Wet	Dry	Wet	Dry	Wet
Control	3.1	2.9	21.0	28.8	38.0	18.0
HEMA (16%) ^b	2.7	1.5	16.6	16.0	50.0	13.7
HEMA (32%)	2.6	1.3	17.7	14.6	45.6	12.2
HEMA (50%)	2.3	1.3	16.5	17.7	43.4	10.1
HEMA (66%)	1.6	1.0	12.5	17.4	31.9	7.5

^a Tensile modulus.

^b HEMA (16%) represents the HEMA-grafted silk fiber with weight gain of 16%.

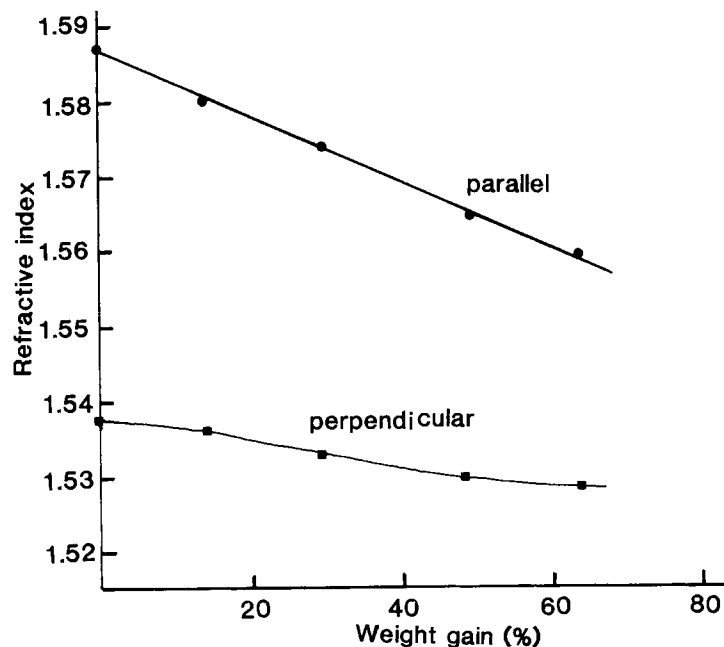


Figure 1 The refractive index (●) parallel and (■) perpendicular to the HEMA-grafted silk fibers with different amounts of weight gain. Silk fibers were grafted at 75–80°C for different periods of time in a mixture of 2% ammonium persulfate on the weight of HEMA monomer containing different amounts of HEMA monomer (16–66%) on the basis of the silk fiber weight.

The sharp decrease of birefringence in the low weight gain range is a common feature observed for silk fibers grafted with different vinyl monomers (MMA,² MAN,⁴ etc.). One of the authors^{5,6} demonstrated recently that the increase in weight gain

from 0% to about 30% is closely related to the initiation of new polymer chains attaching and growing onto newly activated reactive sites, whereas the lengthening of the chains already grafted greatly contributed to enhance the weight gain above 30%.

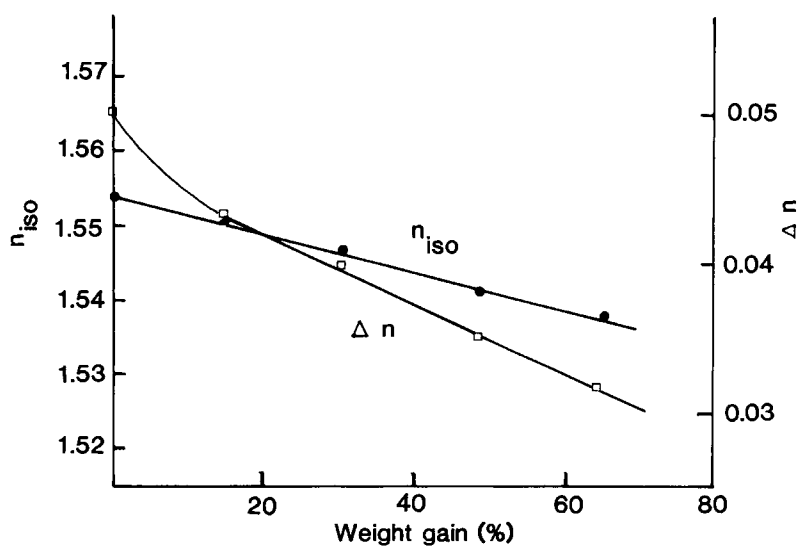


Figure 2 The relationship between (●) the isotropic refractive index and (●) the birefringence of the HEMA-grafted silk fibers and weight gain.

From the above findings, it was therefore elucidated that the chemical reactions taking place during the first stages of the grafting process played the major role in decreasing the birefringence of silk fibers.

The decrease in the isotropic refractive index should imply a lower crystallinity of HEMA-grafted silk fibers. However, this observation does not entail that the crystalline regions of silk fibers were directly affected by grafting, as will be demonstrated by the X-ray diffraction data (see Fig. 9). These results should therefore be related to the loading of amorphous poly(HEMA) chains within the fiber matrix and with a general decrease of fiber density.

DSC Curves

Figure 3 shows the DSC curves of HEMA-grafted silk fibers with different amounts of weight gain. The untreated control (a) showed a major single endothermic peak at about 315°C, attributed to the thermal decomposition of silk fibroin with oriented β configuration.¹⁷ The peak broadened and its position shifted to higher temperature (340°C) with increasing weight gain (b–d). Similar findings were observed for silk fibers grafted with other vinyl monomers. A minor and broad endothermic peak appeared in the temperature range 395–420°C, whose intensity increased when the weight gain increased.

The thermal behavior of the HEMA polymer, synthesized in this work, was also examined (e). Poly(HEMA) exhibited two relevant endotherms: a major endotherm at 314°C and the minor endotherm at 418°C. The position of the major endotherm of control silk fibroin (a) and HEMA polymer (e) is almost the same. The temperature of the major endotherm of the HEMA-grafted silk fiber (c, d) shifted slightly to a higher temperature than that of the peak position for the control silk (a) and the HEMA polymer (e), suggesting the presence of a strong interaction between fibroin molecules and HEMA molecules attached within the silk fiber.

On the basis of these results, we elucidated that the endothermic transition registered in the high-temperature range (400°C) should be attributed to the poly(HEMA) chains loaded within the silk fibers. Moreover, the broadening of the endothermic transition at 340°C should also be related to the presence of the HEMA polymer chains.

The appearance of additional thermal transitions in the DSC curves of silk fibers grafted with HEMA, as well as other vinyl monomers, gives evidence of the poor compatibility existing at the molecular level between silk fibroin and the grafted polymer chains.

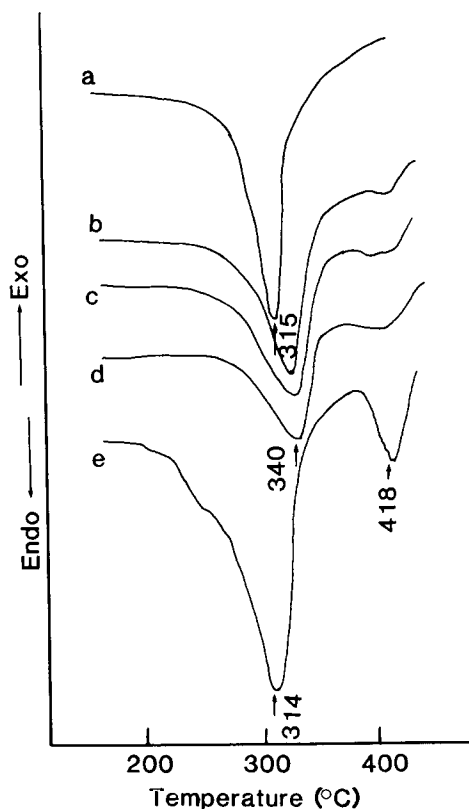


Figure 3 DSC curves of (a–d) HEMA-grafted silk fibers with different amounts of weight gain and (e) the HEMA polymer. Weight gain (%): (a) 0; (b) 32; (c) 50; (d) 90.

TMA Curves

The stability of the fiber length, i.e., the resistance to shrinkage and/or elongation, is a very important property related to the functional performances of textile fibers and to their maintenance, for instance, during washing and drying. The changes in the expansion and contraction properties of HEMA-grafted silk fibers, induced in the course of the heating process, were evaluated by thermomechanical analysis.

Figure 4 shows the TMA curves of untreated (a) and HEMA-grafted silk fibers (b–e) with different weight gains ranging from 16 to 66%. Both the untreated and grafted fibers, heated at a rate of 10°C/min, exhibited a slight contraction in the temperature range 25–120°C, which should be related mainly to the evaporation of water. HEMA-grafted silk fibers exhibited a slightly higher degree of contraction, because the presence of poly(HEMA) chains with high hydrophilic properties resulted in a comparatively higher moisture content.

Above 150°C, all the samples started to extend slightly. The onset temperature of the final abrupt

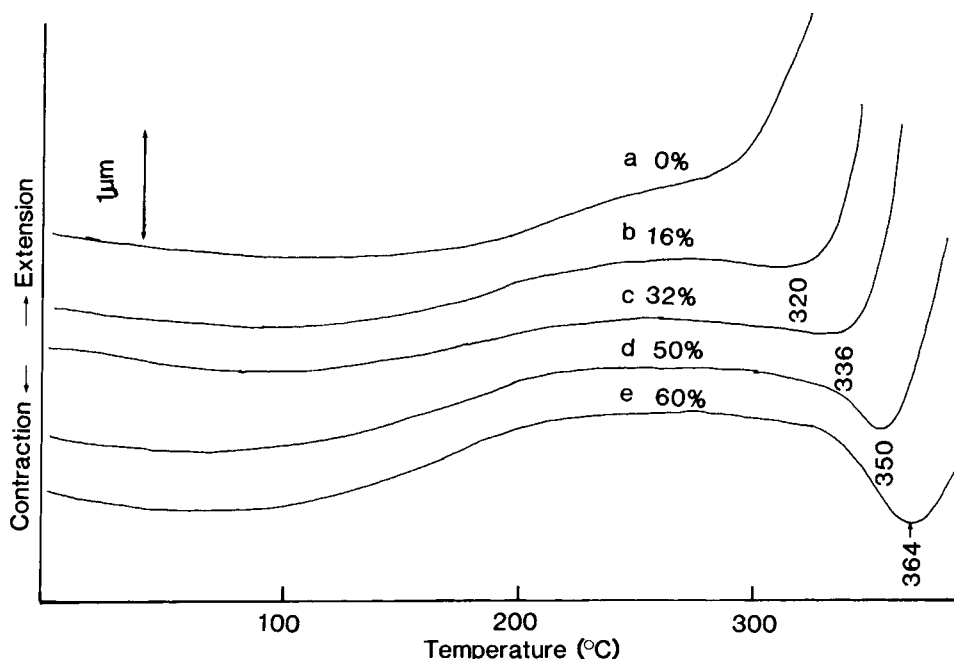


Figure 4 Thermomechanical analysis (TMA) curves of the HEMA-grafted silk fibers with different amounts of weight gain. Weight gain (%): (a) 0; (b) 16; (c) 32; (d) 50; (e) 60.

extension was located at about 280°C for the untreated fibers. HEMA-grafted silk fibers, however, showed a different behavior. A minor and broad contraction peak started to appear at about 320°C, at 16% weight gain. As the amount of poly(HEMA) grafted increased, the peak shifted to higher temperature and became more intense. This effect should be related to the thermal behavior of the polymer chains attached within silk fibers and resulted in an increased thermal stability of grafted

silk fibers, because the temperature of the final extension induced by thermal treatment under the applied load shifted to higher values.

TGA Curves

Figure 5 shows the TGA curves of HEMA-grafted silk fibers with different amounts of weight gain. Both untreated (●) and grafted silk fibers (○, ■) showed a first step of weight loss at above 50°C,

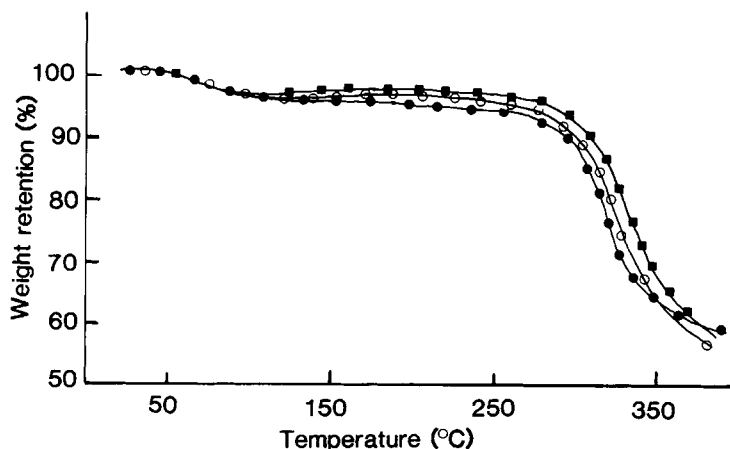


Figure 5 Thermogravimetric (TGA) curves of the HEMA-grafted silk fibers with different values of weight gain. Weight gain (%): (●) 0; (○) 16; (■) 66.

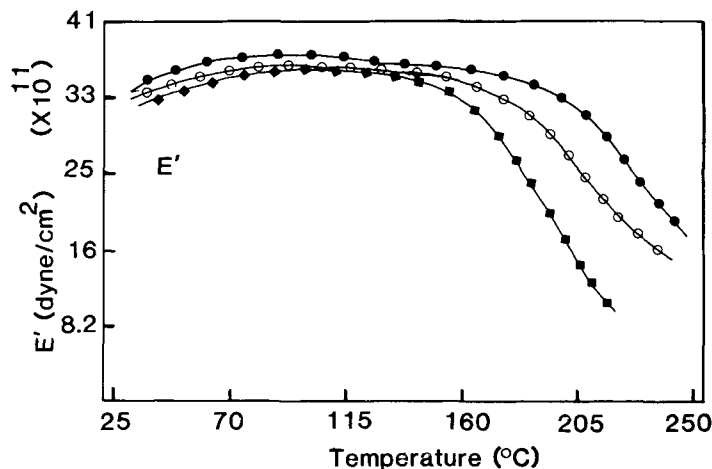


Figure 6 Dynamic storage modulus (E') of the HEMA-grafted silk fibers with different amounts of weight gain. Weight gain (%): (●) 0; (○) 32; (■) 66.

whose intensity was almost similar for all the samples examined. These thermal behaviors correspond to the evaporation of water.

As the temperature increased, the behavior of the fibers grafted with HEMA appeared quite different, in that they exhibited a slightly higher weight retention, compared with the untreated silk. The onset temperature of the second step of weight loss, corresponding to the starting of thermal decomposition, shifted to higher temperature, as shown by the TMA curves (b) and (e) of the samples with 16 and 66% weight gain, respectively.

The increase of weight retention exhibited by the HEMA-grafted silk fibers confirmed the above DSC and TMA observations of an increased thermal stability by the fibers after grafting.

Dynamic Mechanical Properties

To further investigate the thermal behavior of HEMA-grafted silk fibers, we studied the temperature dependence of the dynamic storage (E') and loss (E'') moduli as a function of the increasing weight gain. The E' and E'' curves are shown in Figures 6 and 7, respectively.

The dynamic storage modulus of the untreated control [Fig. 6(a)] slightly increased from room temperature to about 180°C, beyond which value it exhibited a sharp decrease. It has been reported that the glass transition temperature of silk fibers is located around 175°C, which value roughly corresponds to the position of the E' drop. Silk fibers possess a remarkable thermal stability below their

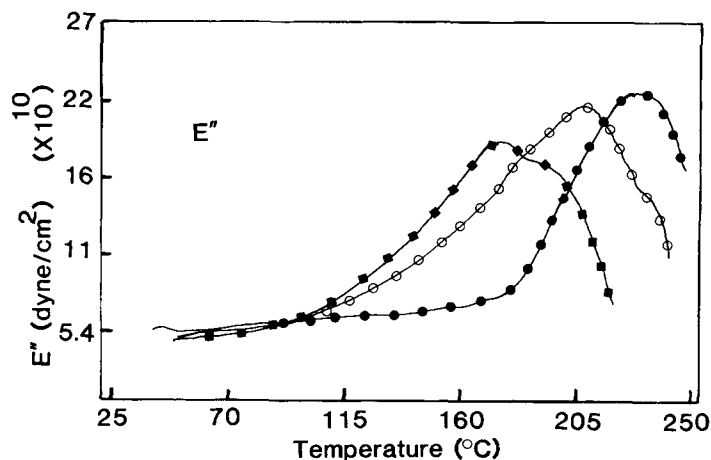


Figure 7 Dynamic loss modulus (E'') of the HEMA-grafted silk fibers with different amounts of weight gain. Weight gain (%): (●) 0; (○) 32; (■) 66.

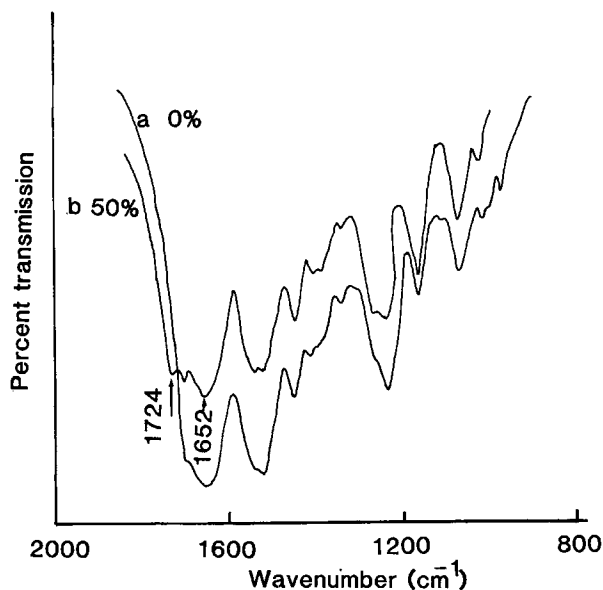


Figure 8 FTIR spectra of (a) the untreated control and (b) the HEMA-grafted silk fiber with weight gain of 50%.

glass transition temperature,¹⁸ but above it, they become soft and behave like a rubberlike material.

The E' value of silk fibers with 32 and 66% weight gain [(○) and (■), respectively] started to decrease at a temperature significantly lower than that of the untreated fibers. This viscoelastic behavior suggests

that the HEMA polymer attached within the fibers reduced the threshold value, leading to the rubberlike behavior, which resulted in a noticeable decrease of the glass transition temperature. The same effect was observed for silk fibers grafted with other vinyl monomers, such as methyl methacrylate (MMA),² methacrylonitrile (MAN),⁴ and *N*-(*n*-butoxy-methyl)methacrylamide (BMA),⁸ as well as with epoxides.^{1,2,10-12}

The loss modulus curves of the untreated control (●) and HEMA-grafted silk fibers (○, ■) are shown in Figure 7. The control sample exhibited a major E'' peak at about 230°C, whose onset temperature was located at about 180°C. This prominent E'' peak was attributed to the thermal movements of the ordered crystalline regions, because the spacing [$d_{(200)}$] corresponding to the intersheet distance¹⁹ of the β structure was observed to gradually expand at above 180°C.

The loss modulus peak of HEMA-grafted silk fibers shifted to lower temperature and became broader as the weight gain increased up to 66%. Its onset temperature shifted down to about 100°C, a value noticeably lower than that of the untreated control sample.

The above viscoelastic behaviors imply that the HEMA polymer chains attached within the silk fibroin matrix influenced the thermally induced mo-

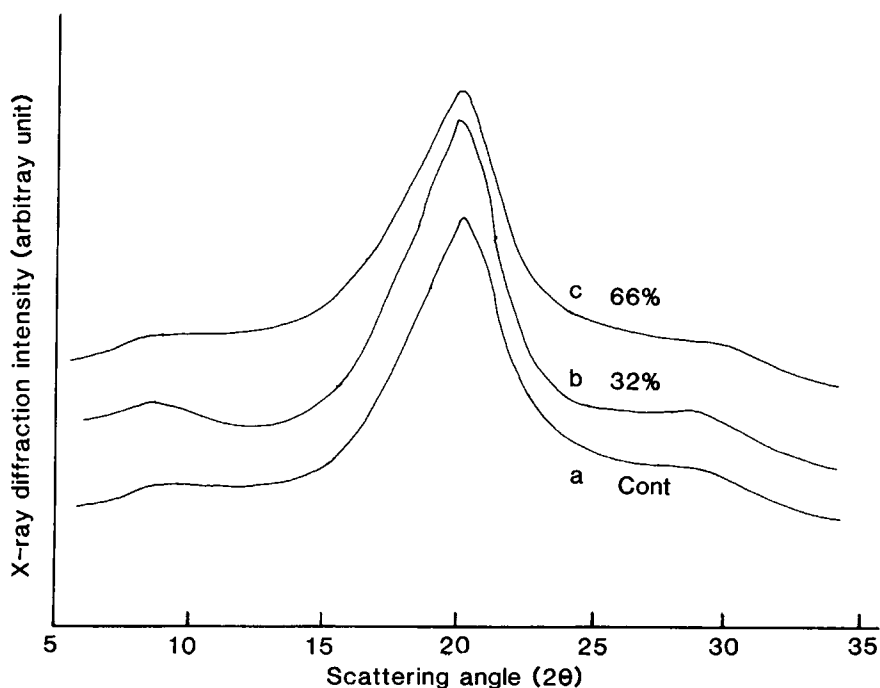


Figure 9 X-ray diffraction intensity curves of (b) the HEMA-grafted silk fibers with different values of weight gain. Weight gain (%): (a) 0; (b) 32; (c) 66.

lecular movement not only in the amorphous but also in the crystalline regions of silk fibers. These results suggest that the poly(HEMA) chains were located also within the ordered fringed fibril domains at the end of each crystalline segment aligned along the fiber axis.

Infrared Spectra

Figure 8 shows the infrared spectra of the untreated (a) and HEMA-grafted silk fibers (b) with a weight gain of 50%. The spectrum of the grafted silk fibers exhibited the minor and prominent absorption

bands (shoulder form) of 1724 and 1701 cm^{-1} and 1200 and 1030 cm^{-1} , in addition to the absorption bands at 1652 and 1635 cm^{-1} attributed to the β structure of silk fibroin.²⁰

The absorption band at 1724 cm^{-1} , not present in the IR spectrum of the untreated silk fiber, was attributed to the ester group of the side chains of the HEMA polymer attached within the silk fibers. The infrared spectrum of the grafted silk fibers showed absorption bands characteristic either of silk fibroin with the β conformation²⁰ or HEMA polymer overlapping in the spectral region from 2000 to 400 cm^{-1} , suggesting that the graft-copolymerization of the HEMA occurred within the fiber matrix.

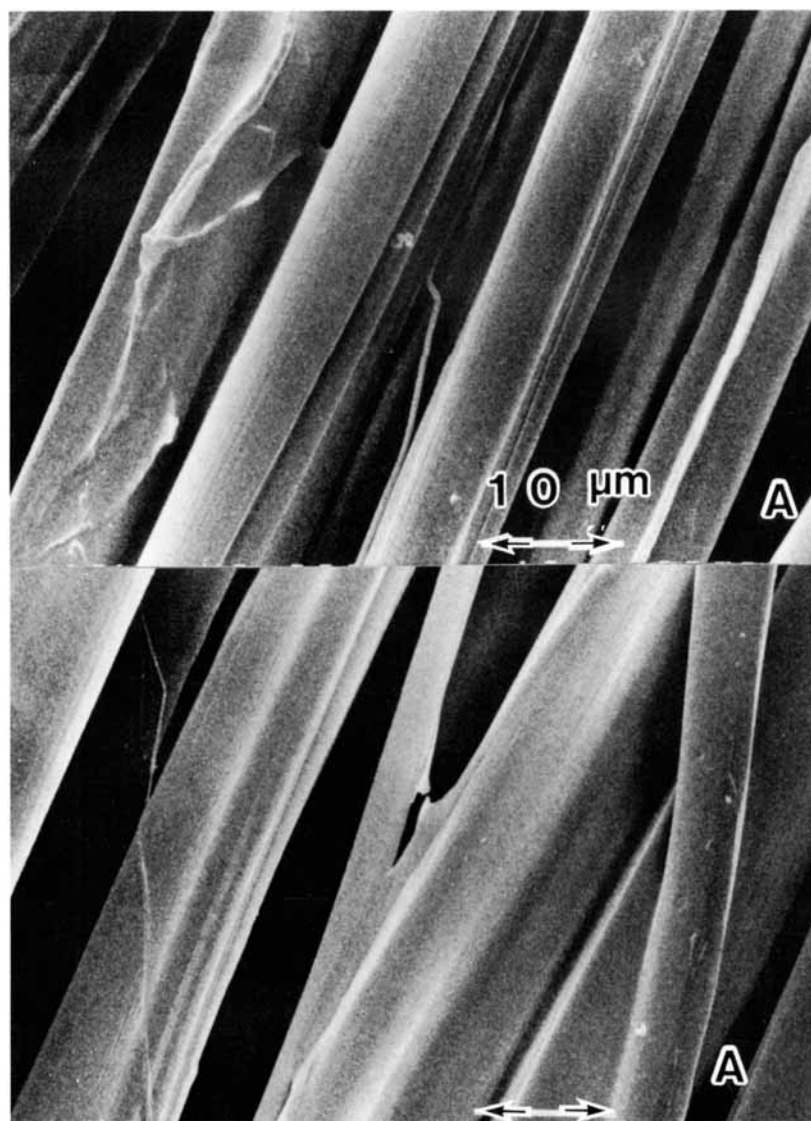


Figure 10 Scanning electron micrographs of the HEMA-grafted silk fibers with weight gain of 32%.

X-ray Diffraction Curves

The X-ray diffraction intensity curves of HEMA-grafted silk fibers with different amounts of weight gain were examined to ascertain if changes in the fine structure were induced by grafting (Fig. 9). The untreated control (a) exhibited a major X-ray diffraction peak at 20.5 degrees, corresponding to the crystalline spacing of 4.39 Å, which is characteristic of silk fibers with highly ordered β structure. The position and intensity of the major X-ray diffraction peak did not change regardless of HEMA grafting, as shown by the curves of the samples with 32 and 66% weight gain [(b) and (c), respectively].

The above findings are consistent with those reported for silk fibers grafted with other vinyl monomers¹⁶ and imply that the crystalline structure with oriented β crystals was not directly modified by the graft-copolymerization reaction that occurred within the silk fiber.

Surface Characteristics

The abrasion-resistance and the rubbing behavior of the textile fabric depend largely on the state of the surface of the fibers. It is of interest to observe, therefore, the surface morphology of the HEMA-grafted silk fibers by scanning electron microscopy. Figure 10 shows the SEM micrographs of HEMA-grafted silk fiber with a weight gain of 32%. The surface of the grafted silk fiber is smooth, showing the typical appearance of *Bombyx mori* silk fibers.

REFERENCES

1. A. Bianchi Svilkos, M. R. Massafra, and S. Beretta, *La Seta*, **46**, 4 (1983).
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, T. Yamamoto, N. Nakabayashi, H. Ishikawa, and G. Freddi, *J. Appl. Polym. Sci.*, **43**, 2115 (1991).
6. M. Tsukada, Y. Goto, G. Freddi, T. Yamamoto, and N. Nakabayashi, *J. Appl. Polym. Sci.*, **44**, 2197 (1992).
7. M. Tsukada, G. Freddi, M. Matsumura, H. Shiozaki, and N. Kasai, *J. Appl. Polym. Sci.*, **44**, 799 (1992).
8. M. Tsukada, H. Shiozaki, J. S. Crighton, and N. Kasai, *J. Appl. Polym. Sci.*, to appear.
9. H. Shiozaki and Y. Tanaka, *Makromol. Chem.*, **143**, 25 (1971).
10. Y. Tanaka and H. Shiozaki, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 2741 (1979).
11. M. Tsukada, Y. Goto, G. Freddi, M. Matsumura, H. Shiozaki, and H. Ishikawa, *J. Appl. Polym. Sci.*, **44**, 2203 (1992).
12. M. Tsukada, M. Nagura, H. Ishikawa, and H. Shiozaki, *J. Appl. Polym. Sci.*, **43**, 643 (1991).
13. M. Tsukada and H. Shiozaki, *J. Appl. Polym. Sci.*, **37**, 2637 (1989).
14. S. Kobayashi, M. Sugiyama, and H. Yoshida, *Rep. Tokyo Metropolitan Textile Res. Instit.*, **15**, 137 (1979).
15. M. Tsukada, *J. Serc. Sci. Jpn.*, **53**, 380 (1984).
16. M. Tsukada, N. Kasai, and G. Freddi, to appear.
17. H. Ishikawa, M. Tsukada, I. Doizume, A. Konda, and K. Hirabayashi, *Sen-i Gakkaishi*, **28**, 91 (1972).
18. J. Magoshi, and S. Nakamura, *J. Polym. Sci. Phys. Ed.*, **17**, 1675 (1977).
19. M. Nagura, A. Shinohara, M. Urushidani, and H. Ishikawa, *Kobunshi Ronbunshu*, **35**, 81 (1978).
20. T. Miyazawa, and E. R. Blout, *J. Am. Chem. Soc.*, **83**, 712 (1961).

Received November 30, 1992

Accepted December 30, 1992