Structural Analysis of Methyl Methacrylate-Grafted Silk Fibers

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SYNOPSIS

The structural changes of silk fibers grafted with methyl methacrylate (MMA) were investigated in relation to the weight gain. Both the refractive indices, parallel and perpendicular to the fiber axis, decreased with increasing weight gain, although the former showed a steep drop in the weight gain range of 0–30%. Accordingly, birefringence and the isotropic refractive index also decreased, suggesting a lower degree of molecular orientation and crystallinity of MMA-grafted silk fibers. However, X-ray diffraction curves demonstrated that the crystalline structure remained unchanged, regardless of MMA grafting, implying that the MMA polymer attached preferentially within the amorphous regions of the fiber. Tensile strength and elongation at break of the grafted silk fibers, measured in dry and wet states, gradually decreased over the weight gain range examined. MMA-grafted silk fibers in wet state exhibited comparatively lower values of strength and elongation, though the hydrophobicity, induced by the grafted polymer, resulted in an attenuation of the differences, especially at high weight gains. TMA analysis demonstrated that the onset temperature of the final extension shifted to a higher value, in the weight gain range 30–50%. Dynamic mechanical measurements showed that the thermally induced molecular movement of MMA-grafted silk increased, as illustrated by the trend of both dynamic storage and loss modulus curves. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The weighting of silk fibers with mineral compounds, first developed in France,[1] is an effective technique to increase silk weight and to give silk fibers and fabrics special properties, such as excellent handle, bulkiness, and lustrous appearance.[2] The tin–phosphate–silicate method[3] contributed to the increase in thermal stability[3] and, at low weight gain amounts, sensibly improved the flame resistance of the treated fabrics.[4] The dyeability properties of the silk fiber remained unchanged, regardless of the weighting treatment.[5]

The graft-copolymerization of silk fibers with vinyl monomers[6–10] is considered to be a powerful method, either for weighting purposes or for producing substantial modification of the physical, mechanical, and morphological properties of the fibers. These techniques were first developed in Japan, where they are widely used for industrial applications.

The physicochemical properties of grafted silk fibers largely depend on the chemical characteristics of the vinyl monomer used, as well as on the extent of grafting and on the reaction conditions. In the early stages of the development of the grafting techniques, hydrophobic vinyl monomers, such as styrene (St)[11] and methyl methacrylate (MMA),[6] were used. Kobayashi et al.[11] observed that the crease recovery, one of the most important functional properties of textiles, was greatly improved by St grafting, especially in the weight gain range of 30–60%. However, the extensive application of these monomers entailed some negative consequences, due to the strong hydrophobic properties of the grafting polymer chains loaded inside the silk fibers and to the hard handle and stiffness of treated silk fabrics.

Among the vinyl monomers, methyl methacrylate

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(MMA) was one of the most widely studied and still represents an attractive model for the investigation of the physicochemical and structural changes induced by grafting. In a previous article, the authors[6] reported the thermal behavior of MMA-grafted silk fibers by differential scanning calorimetry and by thermomechanical analysis. Compatibility between silk fibroin molecules and poly-MMA chains attached inside the fibers is poor.[6]

The study of the changes in the physical properties, induced by grafting MMA onto silk fibers, are interesting from the standpoint of exploiting the modified fibers for textile and nontextile applications.

The balance between the hydrophilic and hydrophobic behavior of grafted silk fibers largely depends on the nature of the vinyl monomer used, and can result in significant changes of equilibrium regain, dyeability, and mechanical properties. Among these factors, the amount of water absorbed by the fibers is important to determine the functional performances of the textile material. It is, therefore, of primary interest to compare the tensile properties in the standard state, as well as in the wet state.

This article documents the study of the optical properties, the crystalline structure, and the mechanical and thermal behaviors of MMA-grafted silk fibers. Birefringence and isotropic refractive index measurements, X-ray diffraction curves, thermomechanical (TMA), and viscoelastic analysis were carried out on the MMA-grafted silk fibers with different amounts of weight gain. It is expected that this information will improve our understanding of the effect of grafting parameters on the characteristics of grafted silk fibers, as well as provide new tools for evaluating and exploiting the resulting fibrous copolymer.

EXPERIMENTAL

Materials

Raw silk fibers were obtained from the reeling of cocoon threads, collected from seven cocoons of the domesticated mulberry silkworm. Dried silk fibers were immersed in a solution of aqueous potassium persulfate (0.1%) as the initiator, which contained methyl methacrylate (MMA) that was emulsified by nonionic surfactant at temperatures in the range 75–85°C for 1–4 h. After the desired reaction time, silk fibers were taken out and were washed thoroughly in water 3 or 4 times. The unreacted MMA monomer and its oligomer, that were physically adhered to the silk fibers, were removed by hot acetone. The washed and air-dried samples were dried in a forced draft oven at 100–105°C to achieve a constant weight, were placed in a desiccator over silicagel for 30 min, and were weighed. The MMA-grafted silk fibers, with weight gain of 12, 30, 35, 59, and 82%, were thus obtained.

Measurements

The refractive indices were measured with the Beche's line method, using a polarized microscope under the monochromatic light (Na light), at 20°C and 65% RH, as previously described.[12]

X-ray diffraction patterns were obtained using an X-ray source with CuK_α radiation ($\lambda = 1.54$ Å). The conditions for the X-ray measurements have been described in detail elsewhere.[13]

The tensile properties of MMA-grafted silk fibers were measured with a Tensilon UTM-II (Toyo Baldwin Co.), using the standard technique at 20°C and 65% RH at a gauge length of 50 mm and strain rate of 20 mm/min.

Thermomechanical analysis (TMA) were carried out using a Rigaku Denki instrument at a heating rate of 10°C/min. TMA, full scale, was ±500 μm.

The dynamic storage (E') and loss modulli (E'') of the grafted silk fibers were measured at 10 Hz with a Toyoseiki Rheolograph Solid-S.[13] The sample length was 15 mm. The initial tension was 30 *gf*.

RESULTS AND DISCUSSION

Refractive Indices

The changes in the optical properties of MMA-grafted silk fibers were investigated in relation to the weight gain. Figure 1 shows the behavior of refractive indices that were parallel ($n\parallel$), and perpendicular ($n\perp$) to the fiber axis. Both $n\parallel$ and $n\perp$ values decreased as the weight gain increased, though the former exhibited a steeper negative slope, especially in the weight gain range 0–30%. The refractive index, perpendicular to the fiber axis, showed only a slight decrease in the range 0–60%, and then seemed to reach an equilibrium value, because a further increase in weight gain does not induce a significant change in its value.

Tsukada et al.[14] studied the molecular weight of poly-MMA chains that were separated from MMA-grafted silk fibers, prepared using potassium persulfate as the initiator, and concluded that the molar ratio between silk fibroin and the grafted polymer

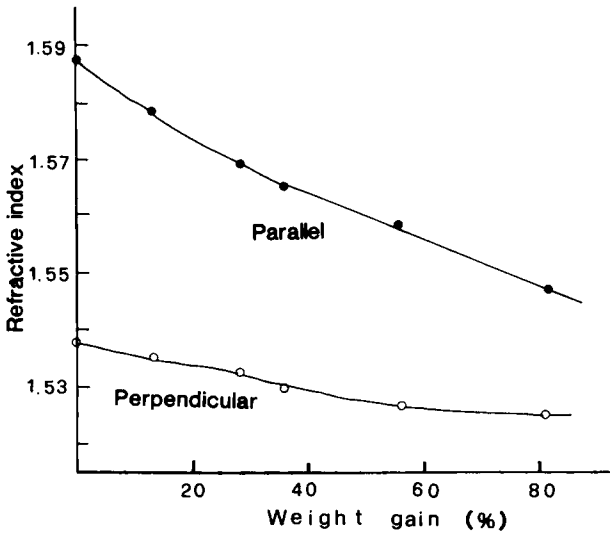

Figure 1 Refractive indices parallel (●) and perpendicular (○) to the fiber axis of the MMA-grafted silk fibers with different values of weight gain.

chains reached a constant value at a weight gain of about 30%. These findings were attributed to the (mechanism of silk fiber grafting) kinetics of the graft-copolymerization reaction. In fact, during the first stages of silk grafting, the increasing number of newly initiated poly-MMA chains greatly contributes to raise the weight gain, while the growth of the polymer chains, already grafted to the silk fibroin backbone, plays the major role in enhancing the graft yield beyond the weight gain of about 30%.[14]

The most noticeable decrease of the refractive indices was observed during the first stage of the graft copolymerization reaction, when the kinetics of the process were mainly controlled by the activation of reactive sites on the fibroin backbone chains, followed by the initiation of new polymerization. Moreover, the refractive index, parallel to the fiber axis, was more influenced by the newly grown polymer chains in the fibrous substrate.

Figure 2 shows the changes in birefringence (Δn) and isotropic refractive index (n_{iso}) of MMA-grafted silk fibers as a function of the weight gain. The n_{iso} value, which is related to the crystallinity of the fibers,[12] linearly decreased from 1.555 down to 1.530 when the weight gain attained 80%. The birefringence decreased sharply in the weight gain range 0–30%, and the slope of the curve then attained a constant value. The first sharp drop of the Δn value should be related to the behavior of the refractive index parallel to the fiber axis (see Fig. 1).

The accumulated data suggest that some structural changes in the fine structure of silk fibers were induced in the course of grafting. Birefringence is an optical parameter that is related to the average molecular orientation of the fibers. Two factors contribute to the determination of the Δn value; namely, the orientation of both the amorphous and crystalline regions. In a previous article[14] on metacrylonitrile (MAN)-grafted silk fibers, it was shown that the decrease of molecular orientation was mainly due to the structural changes that occurred in the amorphous regions, while the crystalline regions were almost unaffected in the weight gain range below 82%. Due to the similarity of the grafting mechanism and kinetics between the MAN[14] and MMA vinyl monomes, the molecular orientation in the amorphous regions is considered to decrease preferentially following the graft copolymerization reaction for silk fibers.

X-ray Diffraction Curves

Figure 3 shows the X-ray diffraction intensity curves of MMA-grafted silk fibers with different amounts of weight gain. 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 high molecular orientation. The position of the main X-ray diffraction peak did not change, regardless of MMA grafting (b, c).

The above results are consistent with those reported for silk fibers grafted with other vinyl monomers,[14] demonstrating that the crystalline structure with oriented β crystals was not affected by the graft-copolymerization reaction that occurred inside the fiber.

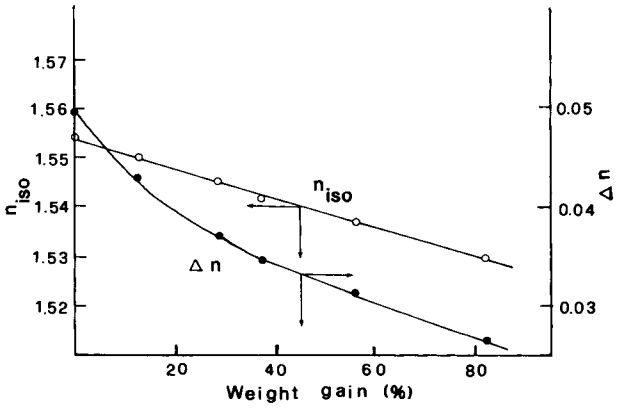

Figure 2 Isotropic refractive index and birefringence of the MMA-grafted silk fibers with different amounts of weight gain.

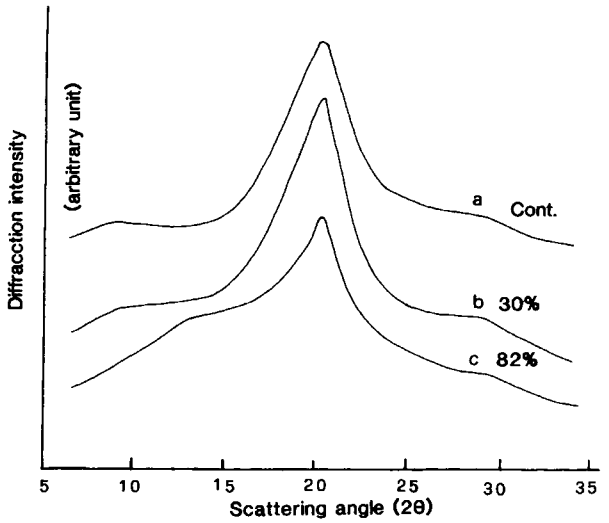

Figure 3 X-ray diffraction intensity curves of the grafted silk fibers with different amounts of weight gain. Weight gain (%): (a) 0, (b) 39, and (c) 82.

Mechanical Properties

The tensile properties of MMA-grafted silk fibers were measured as a function of the weight gain both in dry and wet states. Figures 4 and 5 show the behavior of the tensile strength and of the elongation at break of the MMA-grafted silk fibers, respectively. The comparison of both tensile properties, measured in wet and dry states, is considered particularly interesting because it permits the elucidation of the effect of increasing hydrophobicity induced by MMA-grafting on the mechanical properties of silk fibers.

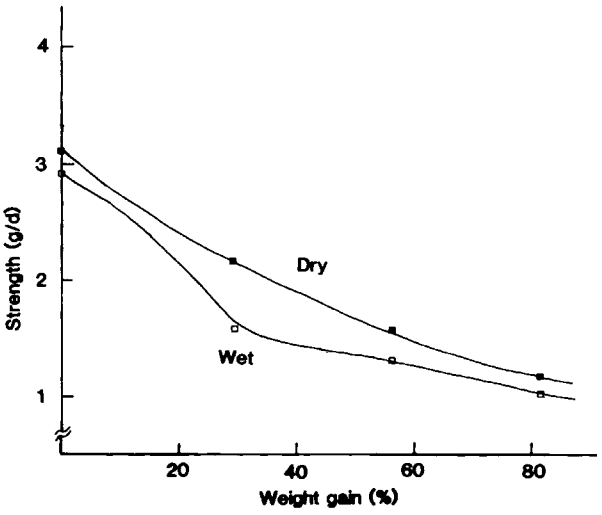

Figure 4 Tensile strength of the MMA-grafted silk fibers with different amounts of weight gain in dry (■) and wet states (□).

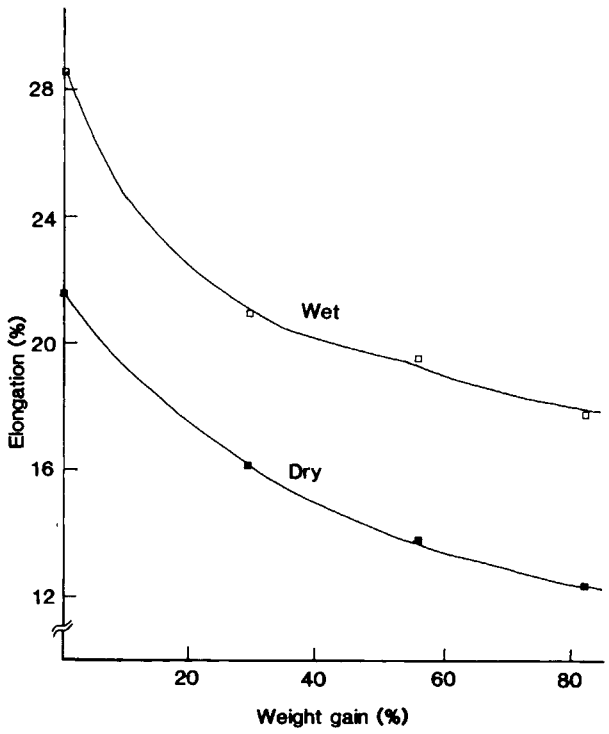

Figure 5 Elongation at break of the MMA-grafted silk fibers with differing amounts of weight gain in dry (■) and wet states (□).

The tensile strength of grafted silk fibers that were measured in dry state decreased gradually over the weight gain range 0–80% (Fig. 4). The same samples, examined in a wet state, showed a different behavior. The decrease of strength, with an increasing amount of grafted MMA polymer, was characterized by two distinct steps. The former step showed a steeper slope than the latter. The boundary point between the two kinds of regions for the mechanical behavior can be located at about 30% weight gain. This value roughly corresponds to the inflection point observed on the refractive index parallel to the fiber axis, which is the weight gain curve (Fig. 1).

Figure 5 shows the relationship between the elongation at break of the grafted silk fibers and the weight gain. The two curves ran parallel to each other. As expected, the percent elongations measured in a wet state were significantly higher than the corresponding ones obtained in a dry state.

Both strength and elongation at break of MMA-grafted silk fibers decreased as the weight gain increased. This should be primarily attributed to the plasticizing effect of the amorphous poly-MMA chains loaded within the amorphous regions of silk fibers, which limit the movement of the fibroin molecules.

The differences in tensile strength, observed between the dry and wet states, became smaller when the weight gain increased beyond 30–40%. As previously reported,[14] the increase of weight gain above these values is mainly controlled by the poly-MMA chains. Strongly hydrophobic domains are formed and grow within the amorphous network of the fibroin chains, with the effect that they hamper the complete hydration and swelling of the accessible amorphous regions of silk fibers, which are mainly responsible for the decrease of strength in the wet state.

The behavior of the tensile strength in a wet state below 30% weight gain should be related to the fact that the molecular weight and, therefore, the hydrophobicity of the poly-MMA chains is still too low.

TMA

In order to evaluate the expansion and contraction properties in the course of the heating process, TMA of silk fibers, grafted with MMA having different weight gains, were carried out (Fig. 6). The untreated control sample (a) showed a slight contraction of about 0.2% over the temperature range 25–130°C and began then to extend beyond 180°C. The major extension appeared from 280°C upwards. The MMA-grafted silk fibers (b–e) showed a similar behavior in the temperature range 25–250°C, regardless of the amount of polymer loaded. However, the onset temperature of the final large extension shifted to higher temperature as the weight gain increased to about 60% (d), beyond which value it seemed to attain an equilibrium state. A further increase in grafted polymer up to 80% did not affect the TMA curve of the fibers (e).

These findings suggest that grafting with MMA had a noticeable effect on the thermomechanical behavior of silk fibers, making the fibers more stable against the load applied, especially in the temperature range of around 300°C. This effect was highest when the weight gain ranged from 30% to 50%.

Dynamic Mechanical Properties

Figures 7 and 8 show the temperature dependance of the dynamic storage (E') and loss (E'') modulus curves, respectively, of silk fibers that were grafted with MMA as a function of the weight gain. The E' value of untreated control silk fibers (a) increased slightly with increasing temperature between 30 and about 180°C, beyond which the value decreased gradually and then more quickly from 200°C upwards. The glass transition temperature of silk fibers is located at around 175°C. Below this temperature, the fibers are thermally stable, but above it they became soft and behaved as a rubber-like material, as confirmed by the E' curve.

In MMA-grafted silk fibers, (b–d) shifted significantly to lower temperature. This effect was roughly proportional to the amount of MMA polymer grafted

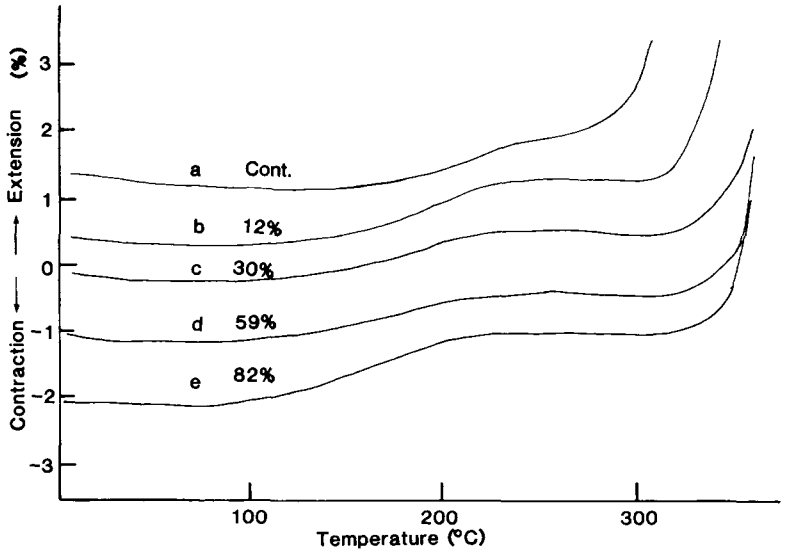

Figure 6 Thermomechanical analysis (TMA) curves of the MMA-grafted silk fibers with differing amounts of weight gain. Weight gain (%): (a) 0, (b) 12, (c) 30, (d) 59, and (e) 82.

within the fiber. However, no significant differences were found in the temperature range 25–150°C among the MMA-grafted silk fibers as a function of differing amounts of weight gain.

The viscoelastic behavior suggests that the MMA grafting had the primary effect of lowering the glass transition temperature of silk fibers by increasing the thermally induced molecular movement of the fibroin chains. The same effect was found for silk fibers grafted with other vinyl monomers, such as methacrylonitrile (MAN)[8] and *N*(*n*-butoxymethyl) methacrylamide (BMA),[16] as well as with epoxides.

Figure 8 shows the loss modulus curves of untreated control (a) and MMA-grafted silk fibers with differing amounts of weight gain (b–d). The control sample exhibited a major *E″* peak at about 230°C, which was attributed to the thermal movements in the crystalline regions, because the spacing [$d_{(200)}$], corresponding to the intersheet distance of the β structure, was observed to expand gradually at the temperature above 180°C.[15]

The *E″* curves of MMA-grafted silk fibers showed a shift to a lower temperature of the loss modulus peak, which also caused a change in its shape, making it broader and broader as the weight gain increased above 60%.

The viscoelastic properties strongly suggest that the MMA polymer chains, grafted within the silk fibroin matrix, influence the thermally induced molecular movement in both amorphous and crystalline domains of the silk fibers. This implies that not only the amorphous regions were directly affected by the MMA grafting, but also the crystalline regions were affected; namely, a part of the fringed fibril volumes, at the end of each individual ordered element aligned along the filament axis, were involved and were

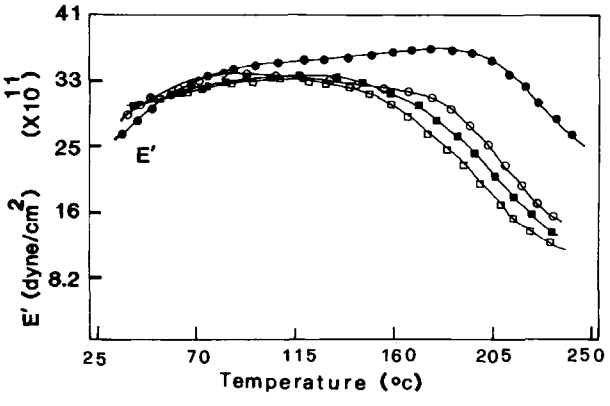

Figure 7 Dynamic storage modulus (*E′*) of the MMA-grafted silk fibers with differing amounts of weight gain. Weight gain (%): (●) 0, (○) 12, (■) 59, (□) 82.

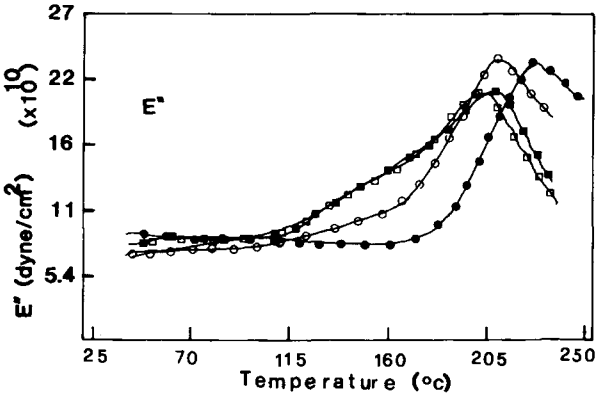

Figure 8 Dynamic loss modulus (*E″*) of the MMA-grafted silk fibers with differing amounts of weight gain. Weight gain (%): (●) 0, (○) 12, (■) 59, (□) 82.

partly penetrated by the growing poly-MMA chains, especially as the weight gain exceeded a certain limit. However, X-ray diffraction results showed that the β crystals were not modified by the graft copolymerization reaction of MMA onto silk fibers.

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