

Structure and Properties of Tussah Silk Fibers Graft-Copolymerized with Methacrylamide and 2-Hydroxyethyl Methacrylate

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ABSTRACT: Tussah silk fibers were graft-copolymerized with methacrylamide (MAA) and 2-hydroxyethyl methacrylate (HEMA) in aqueous media, using a chemical redox system as an initiator. High weight gain values were obtained with both grafting agents (up to 175%). The extent of homopolymerization was negligible for the MAA grafting system over the entire range of monomer–silk ratios examined, while polymer deposition on the fiber surface occurred when the HEMA–silk ratio exceeded 0.5% (w/w). The moisture content of poly(MAA)-grafted silk fibers was enhanced by grafting. Breaking load, elongation at break, and energy decreased at low weight gain (0–20%) and then remained rather constant. The DSC curves of poly(MAA)-grafted silk showed a new endotherm at about 280°C, due to the melting of poly(MAA) chains. The loss modulus peak of poly(HEMA)-grafted silk fibers broadened and shifted to a lower temperature, showing a tendency to split into two peaks at high weight gain. On the other hand, grafting with poly(MAA) induced a noticeable upward shift of the loss peak. The TMA curves showed that grafting with poly(MAA) resulted in a higher extent of fiber contraction from room temperature to about 250°C. Moreover, the intensity of the final contraction step at about 350°C decreased with increasing weight gain and shifted to a lower temperature. The Raman spectra of grafted fibers were characterized by overlapping of the characteristic lines of both silk fibroin and polymer, the latter showing an intensity proportional to the amount of weight gain. Among the conformationally sensitive vibrational modes of tussah silk fibroin, the amide III range was significantly modified by grafting with both poly(MAA) and poly(HEMA). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1393–1403, 1998

Key words: tussah silk fibers; graft copolymerization; methacrylamine; 2-hydroxyethyl methacrylate

INTRODUCTION

During the past 3 decades there has been a considerable academic and technological interest in the

graft copolymerization of vinyl monomers onto silk fibers. Grafting has been originally introduced as an alternative to the traditional mineral weighting technique, a method used for decades to increase silk weight to compensate for the degumming loss. However, in recent years grafting has been regarded as a powerful method to improve some inferior silk properties, such as crease recovery, dimensional stability, rub resistance, photoyellowing, oil and water repellency, color fastness, etc.¹

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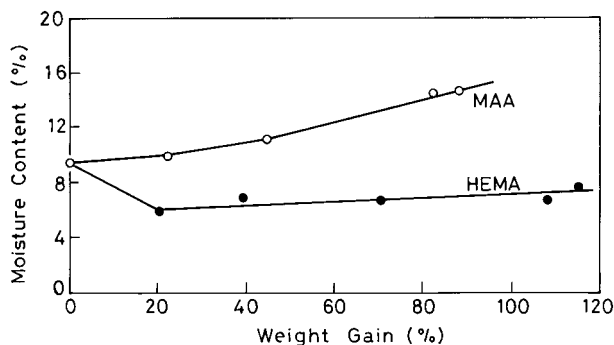


Figure 1 Relationship between moisture content and weight gain of poly(MAA) and poly(HEMA)-grafted silk fibers.

Extensive studies have been conducted on *Bombyx mori* silk fibers (mulberry silk).^{1,2} Various kinds of vinyl monomers have been used, and the properties of the resulting grafted fibers have been investigated. However, only a few grafting agents have been applied on industrial scale. Among them, styrene and methyl methacrylate were quite popular during the early 1970s, thanks to the fullness of handle and to the good crease recovery they conferred on silk. Methacrylamide (MAA) and 2-hydroxyethyl methacrylate (HEMA) are currently applied for silk grafting. Poly(MAA)-grafted silk fabrics maintain the typical silklike handle and drape. Significant improvements of comfort and easy-care behavior can also be achieved. MAA and HEMA can be applied onto silk alone or in a mixture grafting system.³

Besides mulberry silk, other protein filaments produced by various species of Lepidoptera have recently aroused a great interest for textile purposes. Among them, the silk produced by the species *Antheraea pernyi*, also known as tussah silk, is used by both clothing and furnishing industry to make various kinds of silk items that are particularly attractive for their intrinsic properties, such as appearance, handle, comfort, etc. However, compared to mulberry silk, the market share of tussah silk is still very limited. The application of chemical modification techniques may confer improved and/or new properties on tussah silk and give an impulse to develop new products and expand silk consumption. We have recently investigated the reaction of various kinds of epoxides with tussah silk, as well as the effect of the modifying agents on the chemical and physical structure of the fibers.^{4,5} Epoxide-treated tussah silk fibers maintained their intrinsic mechanical properties and showed improved crease recovery be-

havior. Regarding the grafting techniques, Kawahara et al.⁶ studied the changes in dyeing behavior, tensile properties, and the durability against laundering of tussah silk fibers grafted with MAA, and found that grafting conferred on tussah silk a higher resistance to abrasion.

In a recent study⁷ we reported the properties of mulberry silk grafted with MAA and HEMA by using the conventional chemical redox system as an initiator. High weight gains (until 300%) were obtained with both grafting agents. Although the extent of homopolymerization was negligible for the MAA grafting system, significant amounts of poly(HEMA) appeared on the fiber surface beyond 70% weight gain. In this work, tussah silk fibers were grafted with MAA and HEMA, and characterized for their physicochemical, thermal, and morphological properties. The changes induced by grafting in fiber fine structure were studied by Raman spectroscopy. This is an elective technique for the conformational analysis of polypeptides and proteins, thanks to the prominent amide I, III, and skeletal stretching modes, which can be correlated with conformational features of protein chains.⁸ The spectral features of grafted tussah silk fibers are discussed with reference to the detailed assignment of the conforma-

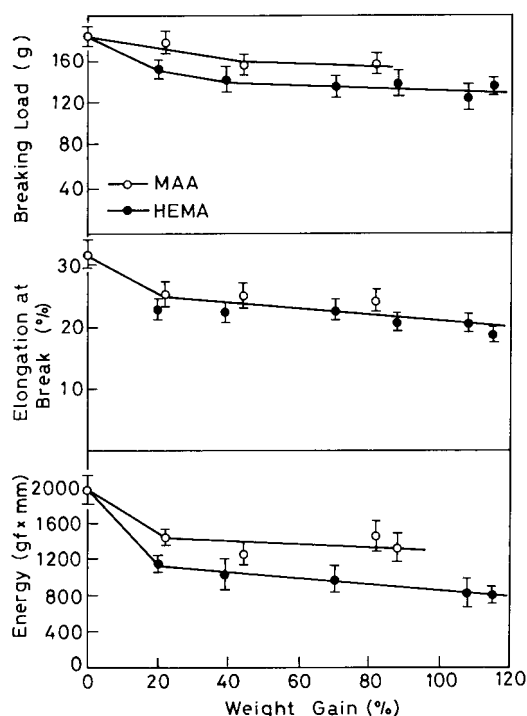


Figure 2 Breaking load, elongation at break, and energy of poly(MAA)- and poly(HEMA)-grafted silk fibers as a function of the weight gain.

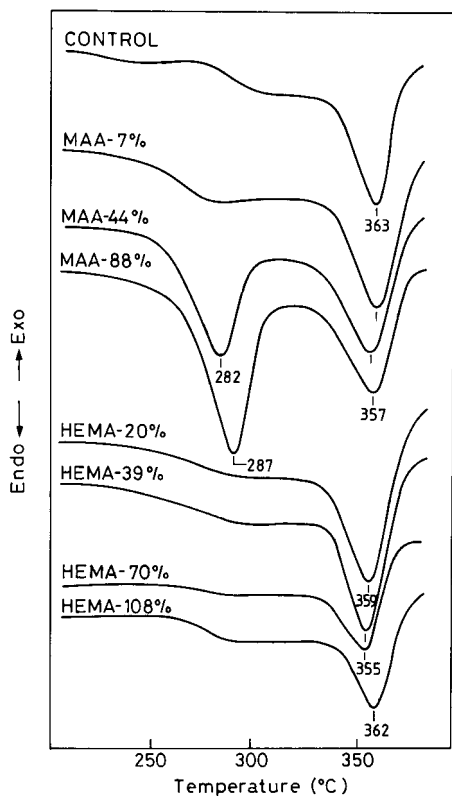


Figure 3 DSC curves of untreated, poly(MAA)- and poly(HEMA)-grafted silk fibers with increasing weight gain.

tion-dependent Raman bands of tussah silk fibroin films with α -helix and β -sheet conformation recently reported.⁹

EXPERIMENTAL

Materials

Tussah silk yarn, degummed with the conventional sodium carbonate–sodium silicate method, was used as a substrate for grafting. Reagent grade methacrylamide (MAA) and 2-hydroxyethyl methacrylate (HEMA), purchased from Wako Pure Chemicals, Ltd., were used without further purification.

Poly(MAA) and poly(HEMA)-grafted silk fibers were prepared as follows. Dried fibers (0.4 g) were immersed in a reaction system containing formic acid (0.4 and 0.8 mL for the MAA and HEMA grafting systems, respectively), grafting agent (from 0.1 to 1.0 g), and ammonium persulfate as initiator (monomer/initiator ratio: 100 : 1). The material-to-liquor ratio of 10 : 1 and 20 : 1

was maintained for the MAA and HEMA grafting systems, respectively. The temperature of the reaction system was raised to 80°C over 45 min and maintained constant for a further 60 min. At the end of the reaction the silk was extracted with acetone to remove unreacted monomers, washed with tap water, dried at room temperature, and placed in a desiccator before successive measurements.

Measurements

Moisture content was determined in standard conditions at 20°C and 65% relative humidity (RH).

Tensile properties were measured in standard conditions with a Tensilon UTM-II (Toyo Baldwin Co., Ltd.) tensile tester machine.

Differential scanning calorimetry (DSC) measurements were performed on a Rigaku Denki Co., Ltd. instrument (model DSC-10A) at a heating rate of 10°C/min. The open aluminium cell was swept with N₂ during the analysis.

Dynamic mechanical (DMA) properties were measured using a Toyoseiki Rheograph Solid-S. The frequency of oscillation was adjusted to 10 Hz. The temperature range studied was from –50 to 260°C. Samples were heated at 2°C/min. The sample length was 15 mm, with an initial tension of 30 gf.

A Rigaku Denki Co., Ltd. instrument (model CN-8361) was used for thermomechanical analysis (TMA). The heating rate was 10°C/min, and dry N₂ provided the inert atmosphere.

NIR-FT Raman spectra were obtained by means of a Perkin–Elmer 1700X spectrophotometer (500 scans), equipped with a Spectron Laser System Continuous Wave Raman module. An Nd/YAG Laser (1064 nm) was used as an exciting source.

The surface morphology of grafted silk fibers was examined by means of a Stereoscan 440 (Leica Cambridge) scanning electron microscope, at 10 keV acceleration voltage, after gold coating.

RESULTS AND DISCUSSION

Moisture Content and Tensile Properties

Poly(MAA)- and poly(HEMA)-grafted silk fibers of increasing weight gain were prepared by raising the monomer concentration in the reaction system, the other parameters (time, temperature, liquor ratio, monomer/initiator ratio) being con-

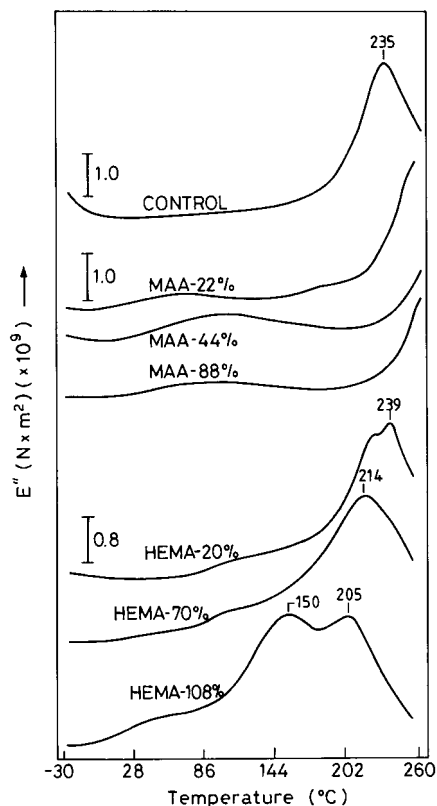


Figure 4 DMA curves of untreated, poly(MAA)- and poly(HEMA)-grafted silk fibers with increasing weight gain.

stant.⁷ Samples with weight gains up to about 100% were obtained and tested for their physicochemical and mechanical properties. As it is generally recognized, a 100% weight gain represents the upper limit of polymer loading for most textile applications of grafted silk fibers, because higher weight gains may entail some negative consequences on fiber properties.² However, it is interesting to note that the experimental conditions adopted permitted to raise the weight gain until about 175%. As previously reported for mulberry silk,⁷ the weight gain increased almost linearly with the amount of monomer in the reaction system. However, while poly(MAA) grew inside the fibers, poly(HEMA) exhibited a marked tendency to polymerize at the solution–fiber interface, especially at above 50% weight gain (monomer/silk ratio > 0.5 w/w), resulting in polymer deposition onto the fiber surface (see SEM observations).

The behavior of moisture content as a function of grafting is shown in Figure 1. Grafting with poly(MAA) resulted in a gradual increase of moisture content. The higher hygroscopicity attained by the grafted fibers should be regarded as a posi-

tive change in their properties, because it confers a softer handle and improves the comfort of fabrics. On the contrary, poly(HEMA) induced an initial steep decrease of moisture content, which remained below the value of the control sample over the entire weight gain range examined. This behavior might be attributed to the influence of the grafted polymer, which masked the active hydrophilic groups of silk and interfered with moisture absorption and retention.

The tensile properties of grafted silk fibers (i.e. breaking load, elongation at break, and energy) showed a fairly similar behavior, decreasing within an initial narrow range of weight gain (0–20%), thereafter remaining almost constant or decreasing very slowly (Fig. 2). It is interesting to note that the fibers grafted with poly(HEMA) exhibited values of breaking load and energy lower than those of poly(MAA)-grafted fibers (only the results of elongation at break fitted the same curve). The extent of polymer loading alone cannot be considered responsible for the above behavior, as demonstrated by the small changes in tensile properties observed at high weight gain. Grafting conditions (pH, temperature and time) must be regarded as responsible for the loss of fiber strength.⁷ The behavior of poly(HEMA)-grafted silk fibers, whose grafting system contained a higher amount of formic acid, is consistent with the conclusion that the acidity of the grafting medium, combined with the treatment temperature, resulted in fiber weakening by hydrolytic degradation. Finally, it is worth noting the less steep initial slope of the breaking load curve of poly(MAA)-grafted fibers. This feature may be related to the strengthening effect brought about by the loaded polymer, which filled the voids within the fiber and increased the cohesion between the fibroin chains, thus balancing the effect of chemical degradation. Similar results have been reported for mulberry silk.¹

Thermal Behavior

The study of the thermal properties is a useful tool for monitoring not only various kinds of polymer–fiber interactions, but also important processing and end-use performance of grafted silk fibers. Extensive studies on the graft copolymerization of vinyl monomers onto silk have shown that grafting may cause slight to drastic changes in the thermal behavior, the extent depending on various parameters, such as the kind of monomer, grafting conditions, weight gain, etc.¹

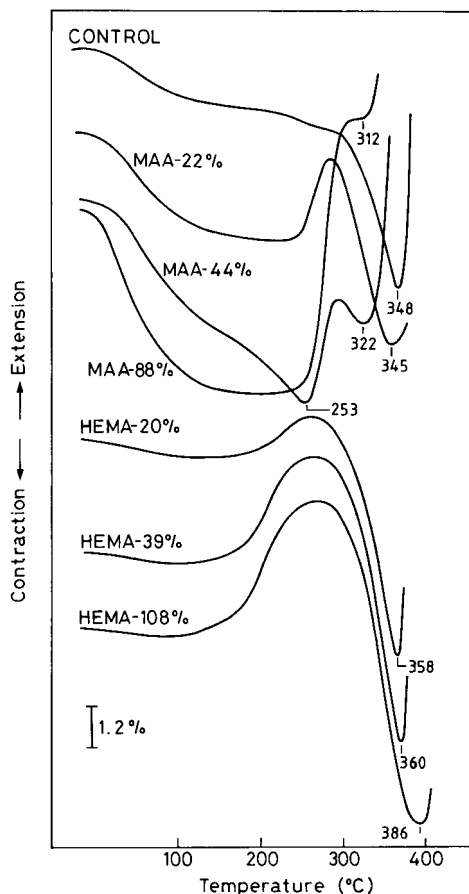


Figure 5 TMA curves of untreated, poly(MAA)-, and poly(HEMA)-grafted silk fibers with increasing weight gain.

Figure 3 shows the DSC curves of untreated and grafted silk fibers with increasing weight gain. The control sample displayed an intense endothermic peak at 363°C, attributed to the thermal decomposition of tussah silk fibroin with oriented β -sheet structure,¹⁰ preceded by two weak and broad endothermic deflections starting beyond 220 and 280°C, respectively. The latter may be related to various thermally induced physical and chemical changes, involving both the occurrence of inter- and intramolecular rearrangements and the beginning of thermal degradation (amino acid side-chain group and peptide bond cleavage, formation of peptide fragments, and degradation products).¹¹ In fact, thermogravimetry measurements (curve not shown) showed that the onset of extensive weight loss was located in a temperature range coinciding with the above DSC endotherms. Following grafting with poly(MAA), a new endothermic peak appeared at about 280–290°C, in addition to the decomposition endo-

therm of silk fibroin. Its intensity was roughly proportional to the amount of weight gain, suggesting that the peak may be attributed to specific thermal transitions of poly(MAA) chains (melting). The DSC profiles of the fibers grafted with poly(HEMA) did not display additional peaks, the most significant changes pertaining the prominent decomposition peak of silk fibroin, which markedly broadened at high weight gain (>70%). The above DSC patterns are in good agreement with the results reported for mulberry silk grafted with the same vinyl monomers.^{12,13} On increasing the weight gain, the decomposition peak of silk fibroin in the grafted samples showed a tendency to move downwards. However, these changes were too small to be considered indicative of a selective modification of the thermal behavior of

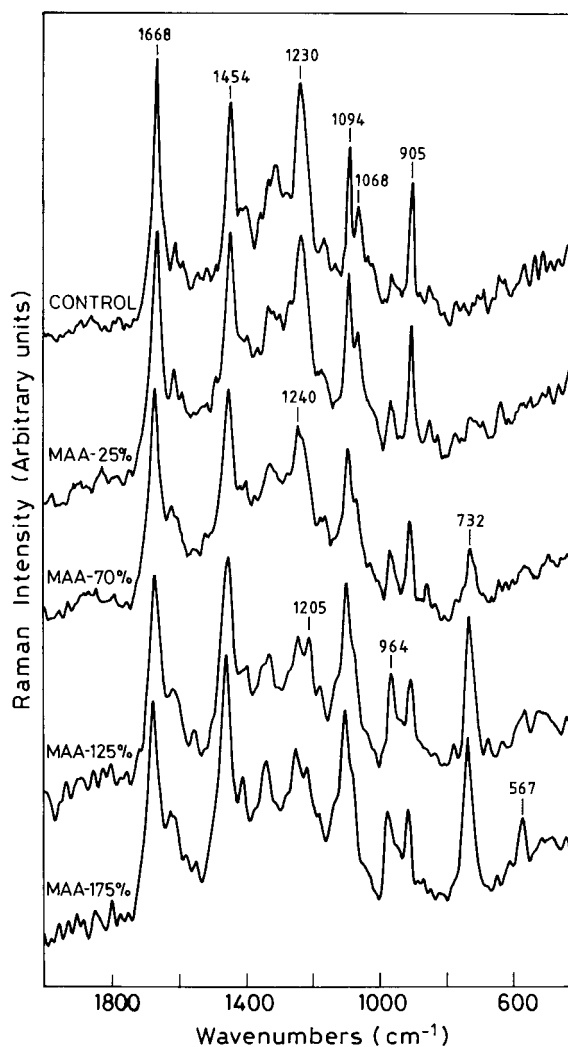


Figure 6 Raman spectra of untreated and poly(MAA)-grafted silk fibers with increasing weight gain.

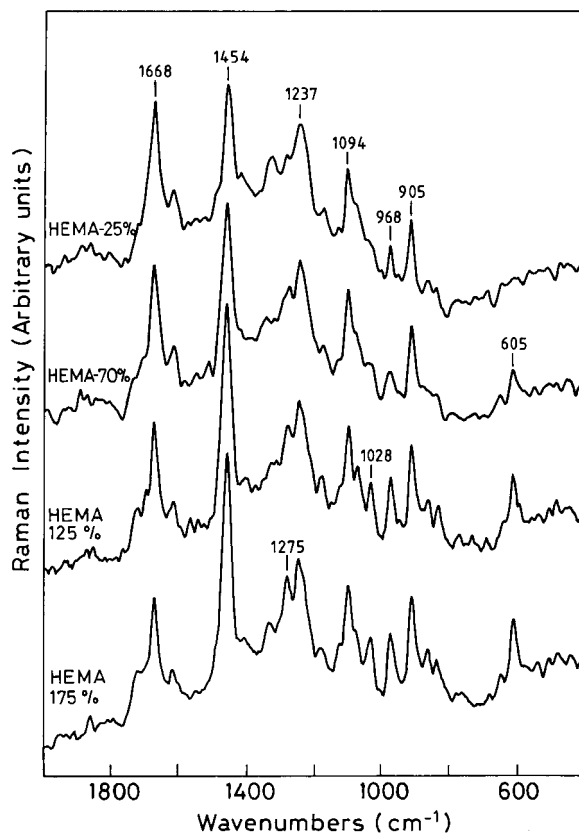


Figure 7 Raman spectra of poly(HEMA)-grafted silk fibers with increasing weight gain.

the fibers induced by grafting. They were probably caused by local interactions between the degradation products of both the polymer and the fibers during burning in the DSC crucible. It is noteworthy that the presence of separated thermal transitions in the DSC pattern of grafted silk fibers may be considered indicative of a poor compatibility between silk fibroin and the grafted polymer chains.

To further investigate the thermal behavior of grafted silk fibers, the temperature dependence of the dynamic loss modulus (E'') was studied as a function of the weight gain (Fig. 4). The control sample showed an intense E'' peak at 235°C, whose onset coincided with the T_g of tussah silk fibroin.¹⁴ The large changes in modulus evidenced by the loss peak have been attributed to the thermally induced molecular motion of the fibroin chains in the crystalline regions.¹⁰ Poly(MAA)- and poly(HEMA)-grafted silk fibers exhibited a markedly different viscoelastic response. The former displayed weak and broad secondary transitions below T_g , followed by the E'' peak, whose onset and maximum markedly shifted upwards

with increasing weight gain. On the other hand, the main feature of the latter was a significant broadening and shifting to lower temperature of the loss peak, which showed a tendency to split into two separated transitions at high weight gain (108%). These results are consistent with those reported for mulberry silk.^{12,13} The viscoelastic properties of silk may be significantly influenced by grafting, the changes being closely dependent on the kind of monomer used, as well as on the weight gain attained. The tendency to induce broadening and shifting to lower temperature of the dynamic loss modulus peak is shared by HEMA and other vinyl monomers.¹ The poly-(HEMA) chains immersed in the amorphous fiber matrix are thought to enhance the mobility of the fibroin chains not only in the amorphous, but also in the crystalline regions, as shown by the downward shift of the loss peak. The sample with 108% weight gain, showing the loss peak splitting into two components at 150 and 205°C, probably behaved as a compositelike material, owing to the extensive polymer deposition on the fiber surface (see SEM results). The upward shift of the loss peak should be considered a peculiar feature of the poly(MAA) grafting system. The same kind of viscoelastic response has been reported for mulberry silk grafted with poly(MAA).¹² This behavior might be attributed to a reduction of chain mobility selectively induced by the poly(MAA) chains, which filled the voids within the fiber and established various kinds of interactions that resulted in a substantial restriction of the interatomic vibrations of the chain segments forming the β -crystals. Due to the industrial relevance of the poly(MAA) grafting system, the nature of the above polymer-fiber interactions are worthy of further studies.

The thermomechanical behavior of untreated tussah silk (Fig. 5) was characterized by a first slight contraction step from room temperature until about 100°C, essentially due to the release of moisture. It was followed by a plateau, extending over a wide temperature range, during which the fiber underwent only a very slight contraction. A sharp contraction peak appeared at above 300°C, with a peak temperature of 348°C, preceding the final abrupt extension due to the beginning of fibroin backbone thermal degradation (see DSC curves). The samples grafted with poly(MAA) exhibited a steeper contraction in the low temperature range. The higher the weight gain, the more intense the contraction, in good agreement with the behav-

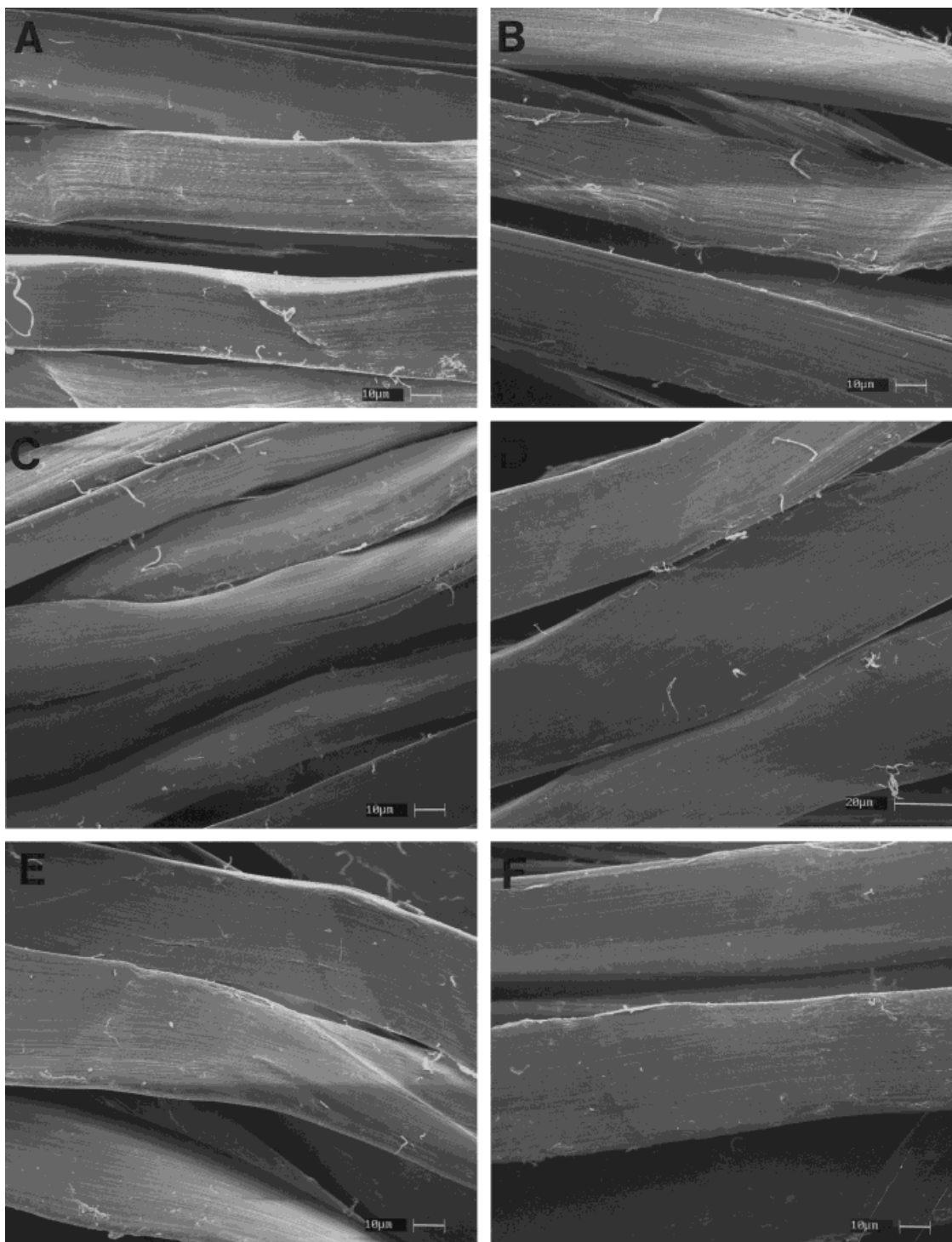


Figure 8 SEM photographs of untreated (A) and poly(MAA)-grafted silk fibers with increasing weight gain: (B) 25%, (C) 50%, (D) 70%, (E) 125%, and (F) 175%.

ior of moisture content (see Fig. 1). A common feature of the grafted samples was the presence of a sharp extension phase in the range 250–300° C. This event coincided with the DSC endo-

therm attributed to poly(MAA) melting. Accordingly, the intensity of the extension increased with increasing the weight gain. The contraction peak at above 300° C gradually be-

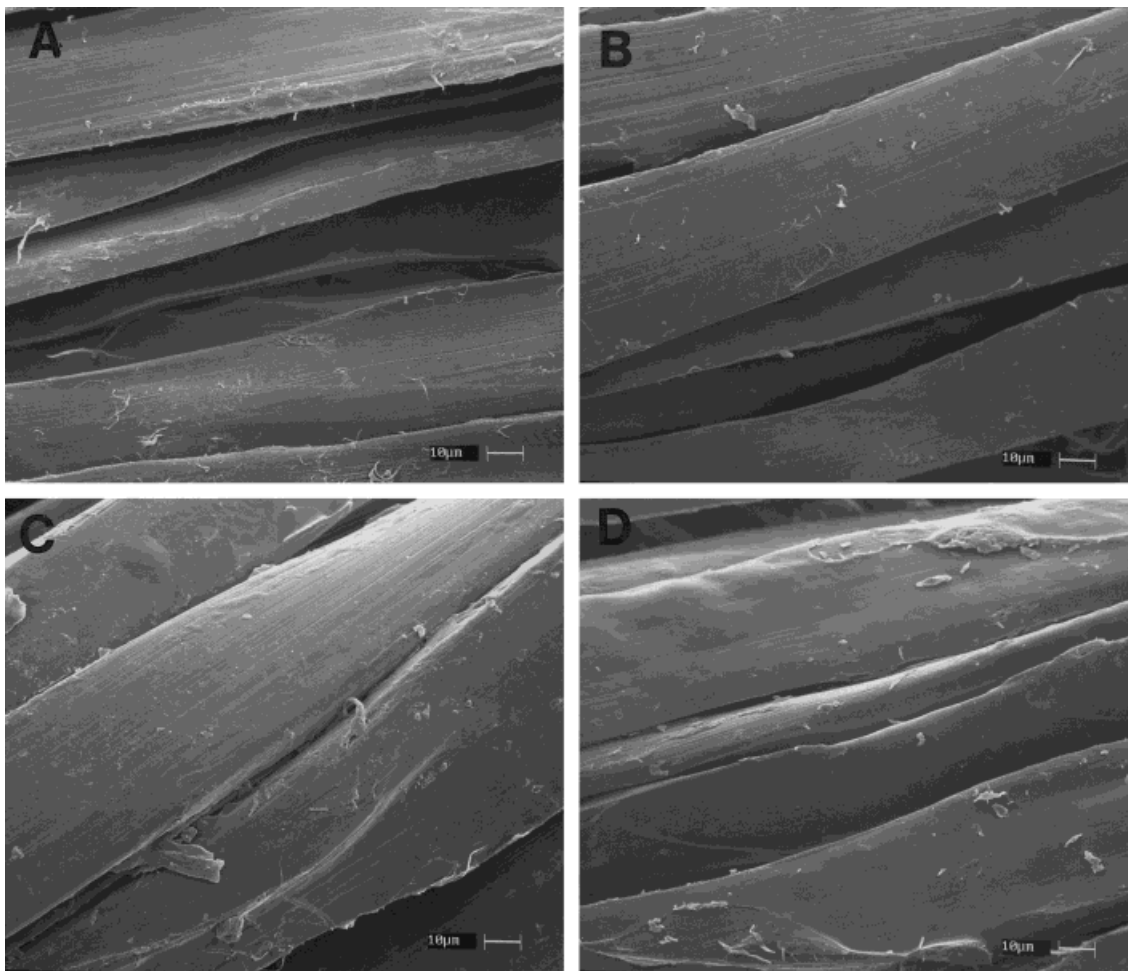


Figure 9 SEM photographs of poly(HEMA)-grafted silk fibers with increasing weight gain: (A) 25%, (B) 50%, (C) 70%, and (D) 125%.

came weaker and shifted to lower temperature. This behavior can be explained taking into account both the microscopic texture of tussah silk fibers and the location of the grafted polymer within the fiber matrix. Microscopic observations of cocoon filament cross sections have shown the presence of several vacuolar droplets of different shape and size (from 0.2 to 1.3 μm).¹⁵ The presence of these voids may allow the thermally excited fibroin chains to shrink at a very high extent, resulting in a strong fiber contraction. Filling up the internal voids with the grafted polymer had the effect of limiting the ability of the fibers to contract, as evidenced by the TMA results. Poly(HEMA)-grafted silk fibers exhibited a rather different behavior, the main feature differentiating them from the control sample being the occurrence of fiber extension at above 200°C. The extent of extension was

roughly proportional to the amount of weight gain and preceded the final contraction peak, whose intensity remained almost unchanged, though its position slightly shifted upwards. The onset of the above extension step coincided with the changes in loss modulus observed in the DMA curves, suggesting that these transitions probably reflected the thermal behavior of the grafted poly(HEMA) chains.

Raman Spectra

The Raman spectra of poly(MAA)- and poly(HEMA)-grafted silk fibers, measured in the spectral region 2000–400 cm^{-1} , are shown in Figures 6 and 7, respectively. Samples with weight gain exceeding 100% were included to study in detail the effect of grafting on fiber structure and conformation. We refer to the data published in a

previous article for the spectral features of poly(MAA) and poly(HEMA) homopolymers.⁷

Untreated tussah silk (Fig. 6) showed characteristic vibrations in the amide and skeletal ranges. The bands at 1668 (amide I), 1230 (amide III), 1094 and 1068 cm^{-1} were due to vibration of parts of the fibroin chains containing polypeptide sequences (prevalently L-alanine residues) with β -sheet molecular conformation.⁹ In addition, other strong lines appeared at 1454 (amide II) and 905 cm^{-1} , whose position and intensity are thought to be independent from the influence of chain conformation.^{8,9} The most characteristic spectral features of silk fibers grafted with poly(MAA) and poly(HEMA) consisted in the appearance of new bands, as well as in the change in intensity of the existing bands. Poly(MAA)-grafted silk fibers with increasing weight gain (Fig. 6) showed new bands at 567, 732, 964, and 1330 cm^{-1} attributable to specific vibrational modes of poly(MAA).⁷ The higher the weight gain, the stronger the intensity. Overlapping of silk and poly(MAA) lines was observed in the amide I and II ranges. The former broadened at higher weight gain, while the latter markedly grew, due to the contribution of the aliphatic portions of the grafted polymer chains. Moreover, a gradual loss of resolution affected the couple of bands at 1094 and 1068 cm^{-1} . Regarding the Raman spectra of poly(HEMA)-grafted silk fibers (Fig. 7), new bands appeared at 605, 968, 1028, 1275, and 1720 cm^{-1} , in addition to the characteristic vibrational modes of silk fibroin. The intensity of the bands at 905, 968, and 1454 cm^{-1} increased with increasing the weight gain. Especially the amide II band at 1454 cm^{-1} exhibited a sharp increase in intensity, due to the strong contribution of the methylene bending vibration of poly(HEMA) chains.⁷

The spectral features of grafted silk fibers show that the position and intensity of amide I and other skeletal stretching modes characteristic of β -sheet tussah silk fibroin remained essentially unchanged, suggesting that grafting with both poly(MAA) and poly(HEMA) did not affect the crystalline structure of the fibers. Only the amide III range showed interesting features that are worthy of some comment. Studies on β -sheet tussah silk fibroin films⁹ have shown that amide III consists of two lines appearing at about 1230 and 1240 cm^{-1} . On the basis of vibrational analysis, both components of the amide III vibrational mode have been assigned to the β -sheet conformation,¹⁶ though a contribution

of the disordered fiber domains at higher wavenumbers (about 1243 cm^{-1}) cannot be excluded.¹⁷ The control sample (Fig. 6) was characterized by a higher intensity of the line at 1230 cm^{-1} . On increasing the weight gain, the intensity of the line at 1240 cm^{-1} increased in both poly(MAA)- and poly(HEMA)-grafted silk fibers. The absence of strong Raman lines attributable to the grafted polymer in this spectral range may lead to the conclusion that the vibrational modes of silk fibroin were modified by the presence of the polymer chains immersed in the fiber matrix. The higher intensity of the amide III component at 1240 cm^{-1} can be interpreted as an increase of the degree of disorder of grafted silk fibers. This conclusion agrees fairly well with the results of Kawahara et al.,¹⁸ who reported that polymer deposition inside tussah silk fibers caused a significant decrease of both the degree of crystallinity and orientation, probably due to swelling of the noncrystalline regions and preferential degradation of the smaller size crystallites.

Finally, it is interesting to note that the Raman spectra of grafted silk fibers displayed strong and well-resolved lines characteristic of the grafted polymer. Their intensity can be directly related to the weight gain, indicating the possibility of using them not only as markers for the identification of the grafting agent used for silk weighting, but also as a reference for calculating the amount of grafted polymer. Additionally, the values obtained by ratioing the intensity of selected bands, such as amide I and II, were found to be linearly related to the amount of weight gain. Though these aspects are still under study, the preliminary results are quite promising in view of the application of Raman spectroscopy as a routine analytical tool for both qualitative and quantitative characterization of grafted industrial samples, with an accuracy even higher than that so far obtained by using infrared spectroscopy.¹⁹

Surface Characteristics

The surface morphology of grafted silk fibers was studied by means of scanning electron microscopy. Figure 8 shows the SEM images of untreated and poly(MAA)-grafted silk fibers. The control sample was characterized by the typical ribbonlike shape and longitudinal striation. Following grafting, the fibers showed a tendency to swell as a consequence of the internal polymer deposition. No traces of foreign material adhering

to the fiber surface were found, suggesting that the extent of homopolymerization was negligible. The MAA grafting proceeded with high efficiency, the formation of graft copolymer being favored under the reaction conditions adopted. These results are consistent with those reported for mulberry silk.⁷

The morphology of poly(HEMA)-grafted silk fibers (Fig. 9) showed significant changes as a function of the weight gain. At low weight gain (<50%), the fiber surface was similar to that of the untreated sample, while at higher weight gain (>70%) a thin polymeric film partly covered the fibers. As the weight gain increased further, the film became thicker and thicker. As a consequence, these samples exhibited a harsh handle, while those without polymer deposits maintained a soft handle, likewise the fibers grafted with poly(MAA). The homopolymer strongly adhered to the fiber surface and was resistant to the conventional aftertreatments. The behavior of the HEMA grafting system can be attributed to the higher reactivity of the monomer. When the monomer–silk ratio exceeded 0.5 (w/w), the homopolymerization competed with grafting, leading to polymer deposition on the fiber surface.

CONCLUSIONS

The results reported in this study showed that MAA can be successfully applied as grafting agent for the organic weighting of tussah silk fibers. This grafting system was characterized by a high efficiency, combined with a reduced level of homopolymerization. This is a prerequisite for the textile application of the grafting techniques, because the original handle and appearance of silk are retained. The weight gain was raised until 175% without any appreciable degradation of the intrinsic fiber properties. It is interesting to note that this weight gain value is much larger than that currently used on industrial scale for silk grafting. On the other hand, the HEMA grafting system showed some negative aspects that may limit its application in the textile field. However, these results might become a starting point for the development of new textile-based composite biomaterials.²⁰ In fact, silk fibers may confer the desired mechanical properties on the composite, while the polymer covering the fiber surface may represent an optimum interface between the material and the

biological environment. Studies on this subject are in progress.

Finally, we would like to point out the positive contribution of Raman spectroscopy to the study of chemically modified natural fibers. This technique is a powerful tool for studying proteins at a molecular level, because it provides information on the peptide backbone structure and conformation, owing to the strong response of the amide I, III, and skeletal stretching ranges. The changes observed in the amide III vibrational mode may give a new impulse to the study of the interactions between the grafted polymer and the fibroin chains in the fiber. Moreover, the appearance of new Raman lines in the spectra of grafted silk fibers can be used for analytical purposes, such as the qualitative identification of the grafting agent and the quantitative determination of the amount of grafted polymer.

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