Physical Properties of Silk Fibers Grafted with Vinyltrimethoxysilane

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ABSTRACT: Silk fibers from *Bombyx mori* silkworms were grafted using a novel grafting monomer, vinyltrimethoxysilane (VTMSi), with various grafting initiators. The effects of these grafting initiators were evaluated. It was possible to successfully copolymerize VTMSi within the silk fiber matrix without disturbing the fine structure of the fiber matrix, which was shown by FTIR analysis and refractive index measurements. The physical properties of VTMSi grafted silk were analyzed and compared to fibers grafted with conventional monomers such as methyl methacrylate, methacrylamide, and 2-hydroxyethyl methacrylate. No trend in the tensile strength and elongation at break was observed when grafting silk fibers with VTMSi. Crease recovery in the wet state improved significantly, suggesting that this new grafting technique is important for the production of washable silk fabrics. The thermal stability of VTMSi grafted silk fibers was improved as shown by the shift of the endothermic peak for the thermal decomposition toward higher temperatures. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1764–1770, 2001

Key words: *Bombyx mori* silk; grafting; vinyltrimethoxysilane; thermal stability; crease recovery

INTRODUCTION

Grafting of silk fibers with vinyl monomers is considered a powerful method to substantially improve a number of intrinsic fiber properties.[1] Many vinyl monomers have been applied to silk fibers and their influences on fiber properties have been studied extensively.[2–4] Grafting silk fibers with vinyl monomers improves the handle and comfort of silk. However, the physical properties may change significantly when the fiber weight gain exceeds values beyond 40–50%.[1,5]

The grafting of vinyl monomers onto silk is currently confined to the textile field. However, the use of silk for nontextile applications has recently become attractive, because of its excellent biocompatibility with human tissues[6] and interesting biochemical properties. By modifying the biophysical properties of silk proteins using novel grafting and chemical modification techniques, new materials could be specifically tailored to an application in the biomedical field. In this context,

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grafting of silk fibers may therefore become a powerful method to produce new proteins with multifunctional properties.

The most popular vinyl mononers currently used in the textile industry are methacrylamide[2] (MAA) and 2-hydroxyethyl methacrylate[3] (HEMA). Active research to find vinyl monomers besides MAA as grafting monomers that prevent fiber deterioration, regardless of the grafting process, is a necessity to further improve and modify fiber properties. The vinyl monomer used in this study, vinyltrimethoxysilane (VTMSi), is an organosilicon compound that has not been used previously as a grafting agent for silk. Compounds containing silicon–oxygen bonds occupy a position of special importance in textile processing (finishing). Commercial finishing products with antistatic, antisoil, and anticrease properties often contain polysiloxanes [usually poly(dimethylsiloxane)] as the active ingredient. These products are nonionic in character and are applied from an emulsion. The presence of siloxane bonds in the molecule impart various interesting properties, such as improved thermal stability and resistance to oxidation, retention of physical properties over a wider temperature range, water repellency, and surface active properties, due to the high flexibility of the Si—O bond. Moreover, organosilicon compounds are characterized by low toxicity.

This study focuses on grafting silk fibers with the novel VTMSi monomer. The influence of various grafting initiators on the grafting efficiency is investigated. Then the physical, mechanical, thermal, and functional (crease recovery) properties of the grafted silk fibers are evaluated as a function of the grafting weight gain. This new vinyl monomer is expected to confer onto the silk excellent thermostability and other properties not inherent to the native silk protein, thus opening the way to use silk in novel nontextile applications.

EXPERIMENTAL

Materials

The grafting initiators 2,2′-azobisisobutyronitrile (AIBN; cat. no. 019-04932), 2,2′-azobis(2-amidino propane) dihydrochloride (ADC; cat. no. 017-11062), and ammonium persulfate (APS; cat. no. 011-08912) and the grafting monomers methyl methacrylate (MMA; cat. no. 139-02726), MAA (cat. no. 138-08232), and HEMA (cat. no. 086-04385) were purchased from Wako Pure Chemical Ind., Ltd. The VTMSi [$CH_2{=}CHSi(OCH_3)_3$; cat. no. 44,022-1] was purchased from Sigma Aldrich Japan.

Degummed silk fibers from *Bombyx mori* silkworms or Habutae silk fabric (plain woven, about 60 g/m^2) were immersed in a reaction bath containing 2% (on weight of fibers [o.w.f.]) initiator, 2 mL/L formic acid (85%), 12% nonionic surfactant (Noigen EC, Daiichikogyo Seiyaku Co.), and various amounts of vinyl monomer. A material–liquor ratio of 1:15 was maintained for the course of the reaction. The reaction system was heated from room temperature to 83°C in 45 min and was maintained at this temperature. At the end of the reaction, the samples were washed with water and then were extracted twice with 1.7 g/L sodium hydrosulfate solution, which contained nonionic surfactant, at 80–83°C for 20 min to remove any unreacted monomer. The fibers were then washed 3 times with hot water, air dried at 100–105°C for 2 h, and placed in a desiccator over silica gel before weighing.

The weight gain was calculated on the basis of the oven-dried weights before and after the grafting procedure. A correction was made for the fiber weight loss in the reaction system that occurred during the treatment by a comparison with a blank sample treated without monomer.

Analytical Measurements

Tensile Properties

The tensile properties of the modified silk fibers were measured with a Tensilon UTM-II (Toyo Boldwin Co.) using the standard technique at 20°C and 65% relative humidity (RH) at a gauge length of 100 mm and a strain rate of 40 mm/min.

Crease Recovery

The crease recovery of silk fabrics in the dry and wet states was evaluated from measurements based upon the method described in JIS standard L1079. A sample measuring 1.5 $\times$ 4 cm was pleated and subjected to 500-g pressure for 5 min. Samples were taken out from the holder and allowed to stand for 5 min. The crease recovery was examined using a crease recovery measuring instrument. The crease recovery was also measured for the wet state according to the following procedure. After immersing the sample in water at 20°C for 2 h, the excess water was removed from the sample by wiping it with cellulose filter paper and the crease recovery test was conducted as described above.

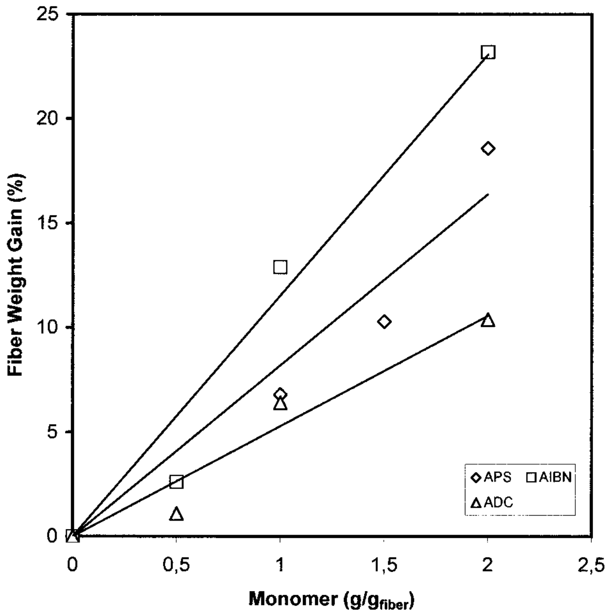

Figure 1 The weight gain of VMTSi grafted silk fibers using the grafting initiators ammonium persulfate (APS), 2,2′-azobisisobutyronitrile (AIBN), and 2,2′-azobis(2-amidino propane) dihydrochloride (ADC).

Differential Scanning Calorimetry (DSC)

The DSC measurements were performed on a Rigaku Denki Co., Ltd. DSC-10A instrument. The DSC range and heating rate were 10.5 mJ/s/10 mA and 10°C/min, respectively. The sample was compressed in sealed aluminium pans under an N_2 atmosphere at a flow rate of 200 mL/min. The open aluminium cell was swept with N_2 gas during the analysis.

Moisture Regain

The moisture regain was determined on dried samples kept in standard conditions at 20°C and 65% RH for 7 days and expressed as grams of moisture/100 g of silk fiber.

FTIR

IR spectra were recorded with a Perkin–Elmer 1700 FTIR spectrophotometer under dried air in the spectral region of 2000–400 cm^{-1}.

Refractive Indices

Refractive indices were measured using the Becke's line method with a polarized microscope under monochromatic (Na) light at 20°C and 65% RH. The measurement procedure is described in detail elsewhere.[2]

RESULTS AND DISCUSSION

Grafting of Silk Fibers with VTMSi

The amount and type of initiator are very important factors in controlling the extent of fiber grafting.[1] Because VTMSi is a new grafting monomer, it was important to investigate the performance of different grafting initiators in the reaction system. Figure 1 shows the weight gain of the silk fibers after grafting with VTMSi using various grafting initiators.

The initiators were APS, AIBN, and ADC. AIBN and APS showed a higher grafting efficiency compared with ADC. APS is used extensively as an initiator for grafting reactions on both the laboratory and industrial scales and many related basic information studies on APS and its reaction mechanisms are available. The use of AIBN and ADC for silk grafting was recently reported by Tsukada et al.[7]; they showed that these initiators were effective in inducing a lower degree of fiber yellowing than APS, although the grafting efficiency was lower.

Mechanical Properties

The evaluation of the fiber's tensile properties obtained in the grafting process is important to

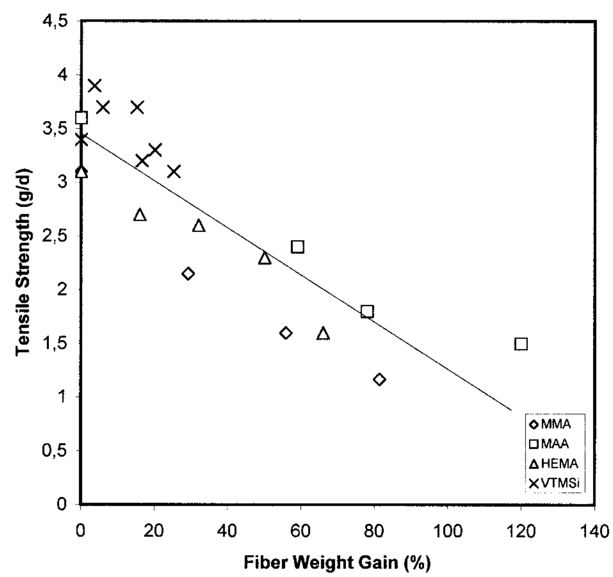

Figure 2 The tensile strength of silk fibers grafted with various vinyl monomers as a function of weight gain. The data for MMA, MAA, and HEMA are cited from the literature.[1]

Table I Tensile Strength of Silk Fibers Grafted with VTMSi Using Different Grafting Initiators

APS		AIBN		ADC	
Weight Gain (%)	Strength (g/d)	Weight Gain (%)	Strength (g/d)	Weight Gain (%)	Strength (g/d)
Control	3.4 ± 0.19	Control	3.9 ± 0.22	Control	3.9 ± 0.23
3.6	3.9 ± 0.18	2.4	3.5 ± 0.21	1.0	3.8 ± 0.21
5.9	3.7 ± 0.42	11.7	3.7 ± 0.18	6.2	3.5 ± 0.19
15.2	3.7 ± 0.24	12.9	3.4 ± 0.15	6.5	3.8 ± 0.16
16.6	3.2 ± 0.11	23.3	2.9 ± 0.20	10.2	3.6 ± 0.17
20.1	3.3 ± 0.12	=	=	=	=
25.2	3.1 ± 0.15	=	=	=	=

minimize the detrimental effects grafting has on the tensile properties and to establish guidelines to decide grafting limits. Figure 2 shows the tensile strength of silk fibers grafted with various vinyl monomers as a function of the weight gain.

The strength of grafted silk fibers decreased with increasing weight gains. Compared to grafting monomers such as MMA, MAA, and HEMA, the change in strength for VTMSi grafted silk fibers was within the instrumental error of the measurement. No systematic trend could be observed because of the narrow weight gain range explored.

Table I shows the tensile strength of silk fibers grafted with VTMSi with different kinds of initiators.

The tensile strength values were almost the same for the silk fibers grafted with different kinds of initiators, suggesting that the changes of the tensile strength canno ticity on silk. On the other hand, silk grafted with MMA and HEMA became slightly stiffer at high weight gains, mainly because of the more hydrophobic character of the monomers. No trend was observed for VTMSi grafted silk fibers. Moreover, the use of different kinds of grafting initiators seemed inconsequential with regard to the fiber performance (Table III).

Crease Recovery

The crease recovery behavior is one of the weak points of silk fabrics that should be improved in order to meet the increasing requirements for better textile performances. Table IV shows the results of crease recovery tests of the grafted silk fabrics in dry and wet states.

Grafting with VTMSi had no detectable effect on the crease recovery measured in the dry state while that in the wet state showed a tendency to increase beyond 10% weight gain. Because the poor wash and wear properties of silk fabrics are

Table II Elongation at Break of Silk Fibers Grafted with VTMSi Using Various Vinyl Monomers

MMA		MAA		HEMA		VTMSi	
Weight Gain (%)	Elongation at Break (%)	Weight Gain (%)	Elongation at Break (%)	Weight Gain (%)	Elongation at Break (%)	Weight Gain (%)	Elongation at Break (%)
Control	21.7 ± 0.8	Control	21.3 ± 0.7	Control	21.0 ± 0.9	Control	16.0 ± 0.8
29.2	16.1 ± 0.7	59	20.3 ± 0.9	16	16.6 ± 0.8	3.6	18.0 ± 0.7
55.8	13.8 ± 0.6	78	24.7 ± 0.7	32	17.7 ± 0.7	5.9	14.3 ± 0.6
81.3	12.4 ± 0.8	120	24.7 ± 0.8	50	16.5 ± 0.9	15.2	15.7 ± 0.7
=	=	=	=	66	12.5 ± 0.5	16.6	15.3 ± 0.8
=	=	=	=	=	=	20.1	14.6 ± 0.9
=	=	=	=	=	=	25.5	16.1 ± 0.7

The data for MMA, MAA, and HEMA are from the literature.[1]

Table III Elongation at Break of Silk Fibers Grafted with VTMSi Using Different Grafting Initiators

APS		AIBN		ADC	
Weight Gain (%)	Elongation at Break (%)	Weight Gain (%)	Elongation at Break (%)	Weight Gain (%)	Elongation at Break (%)
Control	16.0 ± 0.9	Control	16.8 ± 1.4	Control	18.5 ± 1.1
3.6	18.0 ± 1.3	2.4 ± 1.3	16.1 ± 1.2	1.0	17.5 ± 1.3
5.9	14.3 ± 1.2	11.7 ± 1.4	15.1 ± 1.1	6.2	17.0 ± 1.0
15.2	15.7 ± 1.1	12.9 ± 1.1	16.8 ± 0.9	6.5	18.3 ± 0.9
16.6	15.3 ± 0.9	23.3 ± 0.9	17.2 ± 0.9	10.2	18.2 ± 1.2
20.1	14.6 ± 0.7	=	=	=	=
25.5	16.1 ± 1.1	=	=	=	=

closely related to the low value of crease recovery, particulary in the wet state, grafting with VTMSi might become an interesting, novel technique for the production of washable silk fabrics with improved crease recovery properties.

Thermal Stability

Figure 3 shows the DSC curves of silk fibers untreated and grafted with VTMSi.

The major endothermic peak, corresponding to the decomposition temperature of silk with an oriented β-sheet structure,[8] was observed to be 318°C for untreated silk. For VTMSi grafted silk fibers with 21.4% weight gain the decomposition endotherm was slightly broadened and the peak temperature shifted toward higher temperatures (327°C), suggesting a positive effect of VTMSi grafting in enhancing the thermal stability of silk. The protection of silk from thermal degradation exerted by the poly(VTMSi) chains copolymerized within the fiber matrix may be related to both the intrinsic thermal properties of the grafted polymer and boundary interactions between the latter and the adjacent fibroin chains.

Table IV Dry and Wet Crease Recovery of VTMSi Grafted Silk Fibers with Different Weight Gains

	Crease Recovery (%)	
Weight Gain (%)	Dry[a]	Wet[a]
Control	79.5	69.0
6.9	81.0	73.7
11.3	76.5	81.7
15.8	76.9	78.3

[a] The average of three measurements.

Moisture Regain

Water content is an important physical parameter that, together with other factors, can significantly influence the functional behavior of silks (i.e., comfort, crease recovery, etc.). Changes in moisture regain induced on silks by treatment with different grafting initiators and different grafting procedures were studied as a function of weight gain.

The moisture regain of the untreated control silk fiber fell in the range of 7.5–8%. Figure 4 shows that the moisture regain of the VTMSi grafted silk fiber decreased when increasing the

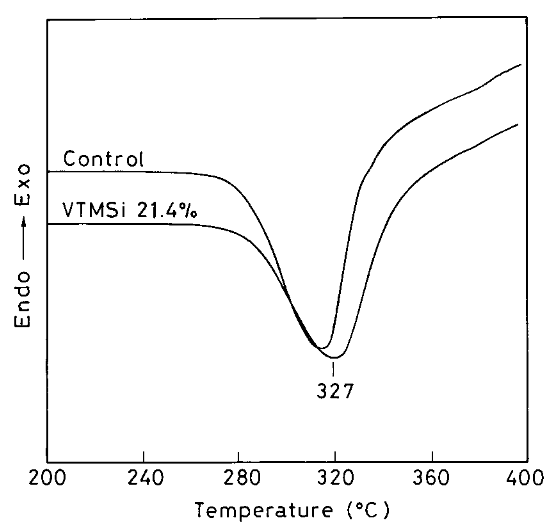

Figure 3 DSC curves of control and VTMSi grafted silk fibers with 21.4% weight gain.

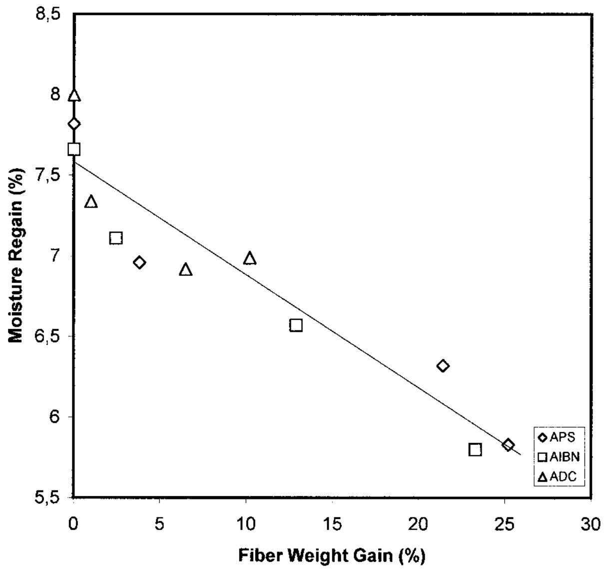

Figure 4 The moisture regain versus the weight gain of VTMSi grafted silk fibers using various grafting initiators.

amounts of VTMSi polymer. This behavior can be attributed to the growth of hydrophobic hydrocarbon/siloxane chains caused by the polymerization of VTMSi. The use of different initiators for VTMSi grafting seemed to have no influence whatsoever on the grafted fiber performance in this regard.

FTIR

Figure 5 shows the FTIR spectrum of VTMSi grafted silk fibers. It is evident that the FTIR spectrum of grafted silk with a weight gain of 21.4% is almost identical to the control silk, except in the wave number range of 1200–1000 cm^{-1}, where the intensity of the IR absorption increased significantly because of the contribution of the strong siloxane bands (Si—O stretching).

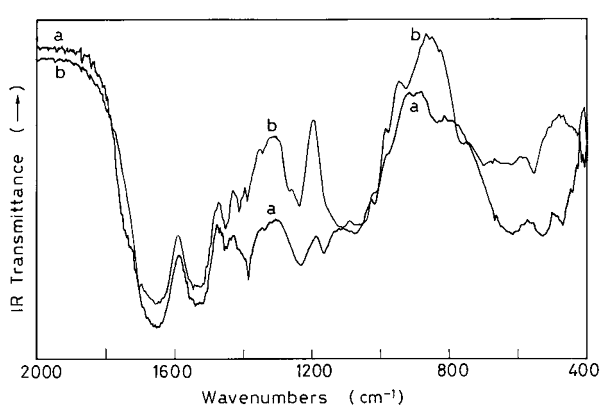

Figure 5 FTIR spectra of control (spectrum a) and VTMSi grafted silk fibers with 21.4% weight gain (spectrum b).

Hence, the above FTIR spectra of the VTMSi grafted silk fiber indicated the successful copolymerization of VTMSi within the silk fiber matrix.

Table V Birefringence (Δn) and Isotropic Refractive Index (n_{ISO}) of VTMSi Grafted Silk Fibers with Different Weight Gains

Weight Gain (%)	Δn	n_{ISO}
Control	0.050	1.552
3.9	0.054	1.552
11.7	0.051	1.548
25.5	0.042	1.544

Refractive Indices

The changes induced in the fine structure of silk fibers by grafting with VTMSi were determined on the basis of the optical properties by measuring the birefringence (Δn) and the isotropic refractive index (n_{iso}) of silk untreated and grafted with VTMSi as a function of weight gain (Table V).

Although the birefringence values were slightly increased at a weight gain of 5%, the isotropic refractive index did not show any significant changes in the weight gain below 5% compared to the untreated sample. However, both values decreased with further increasing weight gain. Because the birefringence and isotropic refractive indices are measures of the average molecular orientation and crystallinity, respectively, it can be concluded that the average molecular orientation and the crystallinity of silk fibers grafted with VTMSi tended to decrease after grafting, which was due to the disordering of the fine structure induced by the growing poly(VTMSi) chains.

CONCLUSIONS

In this study techniques for grafting silk fibers with a novel grafting monomer (VTMSi) were developed. As is evident from the FTIR data, the grafting with VTMSi yielded the desired result of incorporating the VTMSi into the fiber structure. The silk fibers could be grafted with VTMSi using various grafting initiators such as AIBN and ADC and also commonly used intitiators such as APS. VTMSi grafted silk fibers showed interesting changes in their physical properties. The crease recovery in the wet state improved for grafted fabrics, which was due to the slightly hydrophobic character imparted on silk by the grafted poly-(VTMSi). Accordingly, the moisture regain of grafted fibers decreased. The thermal stability improved compared to the untreated fibers, which was attributable to the protection of the fiber by the thermally stable VTMSi that was present as copolymerized poly(VTMSi) at higher weight gains. Additionally, the more dense structure of grafted silk fibers, resulting from filling the interfibrillar voids with poly(VTMSi) copolymers, and the intermolecular interactions occurring at the boundary between the grafted polymer and adjacent fibroin chains should account for the increased thermal stability of the grafted silk. The tensile properties (i.e., tensile strength and elongation at break) of VTMSi grafted silk fibers were almost identical to fibers grafted with other grafting monomers.

Finally, the importance of these results should be emphasized in view of both the developing of a new category of silk-based textiles with excellent wear and maintenance performance (easy care, wash and wear, etc.) and the manufacturing of new silk-based biomaterials with increased bulk and surface hydrophobicity for various kinds of devices.[6]

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