Properties of Silk Fibers Modified with Diethylene Glycol Dimethacrylate

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ABSTRACT: A self-prepared novel bifunctional vinyl monomer diethylene glycol dimethacrylate (EGDMA-2) was graft copolymerized onto silk fibers initiated by potassium persulfate (KPS). The moisture regain and fiber fineness of grafted silk fibers increased linearly with graft yield. The enhancement of hygroscopicity can improve the comfort of silk fabrics. The grafting conditions caused a partial degradation of the tensile strength of silk fibers, as well as the whiteness. Elongation at break increased and initial modulus decreased, which indicated that the rigidity of silk fibers declined. Stress relaxation behavior shows that grafted silk fibers have better viscoelasticity than control silk fibers. Wrinkle recovery angle tests showed that grafted silk fabrics had better wrinkle resistance property. Laundering durability test showed that with increasing graft yield, the damage to the silk fibers during laundering decreased obviously. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 424–428, 2006

Key words: silk fibers; grafting; bifunctional vinyl monomer

INTRODUCTION

Silk fiber is a natural protein fiber and it is viewed as an environmentally favorable fiber, because it contains only natural amino acid units.[1] It has been known in China as the "queen of fibers" for over thousands of years for its luster, soft handle, wearing comfort, and esthetic appearance. However, silk fiber is facing some tough competition from the synthetic fibers that have many useful properties, such as durability, good shape retention, good crease recovery, and production economics. It must be constantly developed to improve the added value of silk fibers.

The chemical modification of silk fibers by means of grafting copolymerization techniques with vinyl monomers was the interest of the researchers during the past three decades.[2–11] Vinyl monomers are very effective in improving the functional properties of silk fibers, such as moisture regain, dye ability, handle, crease recovery, thermal and chemical resistance, etc.

Styrene (St) is the first hydrophobic vinyl monomer used onto silk fibers. St-grafted silk fibers have excellent crease recovery and appreciable bulkiness. But St is not an environmental-friendly compound.[3] Methacrylamide (MAA) is a widely used vinyl monomer for its lower cost, higher water solubility, and relatively lower toxicity than other vinyl monomers.[4,5] Other vinyl monomers such as methyl methacrylate (MMA)[6] and 2-hydroxyethyl methacrylate (HEMA)[7] have been extensively studied. Kato developed a new kind of bifunctional vinyl monomer polyethylene glycol dimethacrylate (PEGDMA) to graft silk fibers, which gained significant wet crease recovery.[8] Recently, vinyltrimethoxysilane monomer was successfully applied onto silk fibers to give silk fibers excellent wet crease recovery.[12,13]

Our work group successfully prepared a new bifunctional vinyl monomer diethylene glycol dimethacrylate (EGDMA-2). In a previous study, we reported the optimum technique of EGDMA-2 grafting onto silk fibers, using potassium persulfate (KPS) in alcohol aqueous solution.[10] We also investigated the characteristics of the grafted silk fibers of various graft yields, such as dyeing behavior, tensile properties, and solubility of silk fibers in NaOH solution.[11] In the present article, we further studied the structure and properties of silk fibers modified with EGDMA-2.

EXPERIMENTAL

Materials

Degummed silk fibers (21/22D) were kindly provided by Shanghai Silk Factory (Shanghai, China). Degummed silk fabrics (plain woven, 60 g/m^2) were kindly supplied by Soochow Silks and Satins Bleaching and Dyeing Factory (Soochow, Jiangsu Province, China). Bifunctional vinyl monomer diethylene glycol dimethacrylate (EGDMA-2) was prepared in our lab-

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oratory, and its purity was 96.8%. Other reagents were reagent grade commercial products.

Grafting procedure

Silk fibers were immersed in a reaction bath containing *x*% EGDMA-2 (on the weight of fibers [o.w.f.]), 1.85% potassium persulfate (KPS) (on the weight of monomer [o.w.m.]), 2 mL/L formic acid, y ml alcohol solution ($V_{alcohol}/V_{H2O}$ = 1:7). The material–liquor ratio was 1:30. The reaction system was heated from room temperature to 80°C in 40 min and maintained in vibrational water at the same temperature for 30 min. At the end of the reaction, silk fiber was washed with water (containing 0.5 g/L nonionic surfactant OP) at 60°C for 30 min, then rinsed with tap water and dried at 105°C for 2 h. Samples were placed in a desiccator over silica gel before measurements.

Grafting yield was calculated as follows:

Grafting yield (%) = $(w_2 - w_1)/w_1 \times 100$, where w_2 is the oven-dried weight of grafted silk fibers and w_1 is the oven-dried weight of the original silk fibers.

Measurements

Moisture regain

Moisture regain was measured according to GB/T 9995–1997(eqv ISO 2060: Determination of moisture content and moisture regain of textile-oven-drying method, 1994). The results are expressed as grams of moisture per 100 g of silk fibers.

Fiber fineness

Fiber fineness D (Denier) was equivalent to the weight in grams of 9000 m of continuous filament fiber. The result was the average of 10 measurements.

Whiteness index

Whiteness index was measured by WSD III whiteness instrument. The result was the average of eight measurements.

Mechanical properties

Tensile properties and elongation at break of single fibers were measured according to GB/T 3916–1997 (eqv ISO 2062: Textiles-yarns from packages-determination of single-end breaking force and elongation at break, 1993) on a YG003 Tester.

Stress relaxation

Single fibers were stretched in a YG003 Tensile Tester. The gauge length was fixed to 50 mm and the samples were tested at a speed of 10 mm/min up to an extension of 5.0% at 30°C, RH 65%. The strain was held constant after the required level was reached, and the decay in stress was recorded as a function of time for about 3 min.

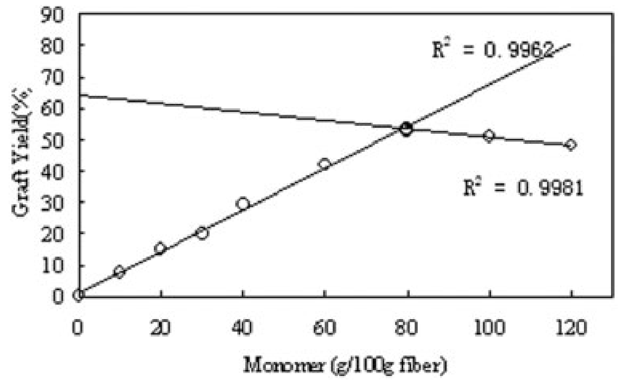

Figure 1 The graft yield of EGDMA-2 grafted silk fibers.

Crease recovery

Crease recovery angle was measured according to GB/T 3819–1997 (eqv ISO 2313: Textile fabrics determination of the recovery from creasing of a folded specimen by measuring the angle of recovery, 1972). The presented results are the sum of the recovery angles of the tested fabrics in the warp and filling (W + F) directions.

Laundry durability

Laundry durability was measured by strength retention ratio *R*. *R* is A_1/A_0, where A_1 and A_0 are the tensile strengths of unwashed and washed silk fibers, respectively. Laundry process was done according to GB/T 8629 A (eqv ISO 6330: Domestic washing and drying procedures for textile testing, 1984).

RESULTS AND DISCUSSION

Reactivity of EGDMA-2

Silk fibers were grafted with EGDMA-2, using KPS as an initiator. The KPS is water soluble, while EGDMA-2 is insoluble in water. Adding a small amount of alcohol can help it dissolve in water. In our previous study, we confirmed that EGDMA-2 was grafted onto the silk fibers by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and amino analysis.[14]

To explore the reactivity of EGDMA-2, we investigated the graft yield of different monomer concentration. The results were shown in Figure 1.

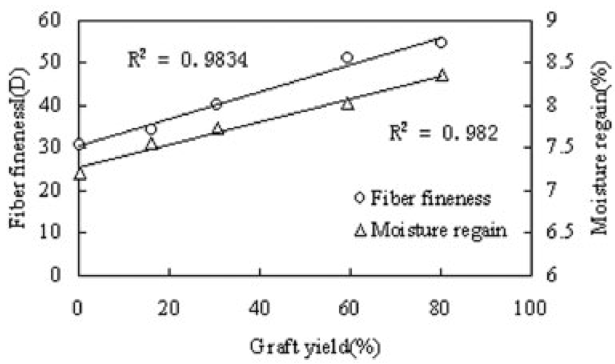

Figure 2 Fiber fineness and moisture regain of grafted and control silk fibers with EGDMA-2.

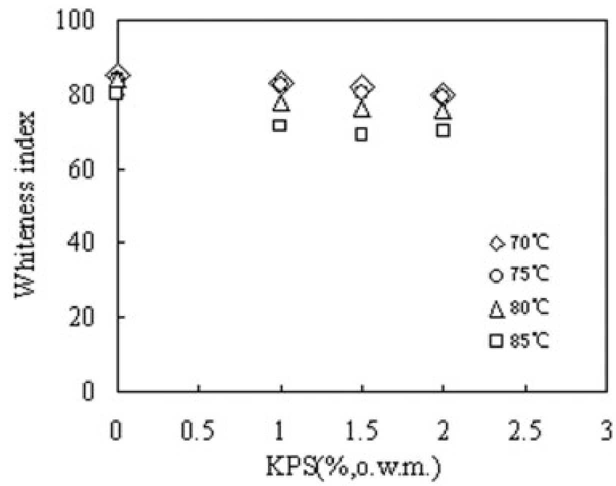

Figure 3 Whiteness index of silk fibers versus the concentrations of KPS at different temperatures (EGDMA-2 is 80% o.w.f.).

From Figure 1, it is clear that the graft yield exhibits a sharp increase with the increase of the concentration of EGDMA-2 at low monomer concentration (below 80% o.w.f.)(R^2 = 0.9962). But the graft yield decreased linearly (R^2 = 0.9981) when the concentration of EGDMA-2 is higher than 80%, which attributed to the probable absorption of monomer onto silk fibers impedes diffusion of the initiator inside the fibers. And another reason is that homopolymerization of the monomer prevails over polymerization between EGDMA-2 and silk fibers.

Moisture regain and fiber fineness

Figure 2 showed a marked increase of moisture regain and fiber fineness with the increase of the graft yield. The values of moisture regain increased almost linearly (R^2 = 0.982). These results confirm that EGDMA-2 grafting can enhance the moisture absorption of silk fibers effectively, which can improve the comfort of silk fabrics largely.

EGDMA-2 grafting has noticeable effects on the transverse dimension of silk fibers, As shown in Figure 2, the fiber fineness of grafted silk fibers increased linearly with the increase of graft yield (R^2 = 0.9834). Our previous study through SEM analysis also confirmed this effect.[14] Generally, these increases of fiber fineness (or size) will influence the functional properties of silk fibers to some extent, such as tensile properties, touch, luster, dye ability, etc.[15]

Whiteness index

Yellowing of silk fibers always occurs during grafting,[16,17] which is mainly attributed to initiators.[15] To explore the influence of KPS, silk fibers were treated with different amounts of KPS at different temperatures. The result is shown in Figure 3.

The whiteness index of grafted silk fibers decreased linearly with the increase of reaction temperature. At a certain temperature, whiteness index decreased with the increase of the concentration of KPS up to 1.5%; while KPS% is above 1.5%, the whiteness index of silk fibers had little decrease, which may be due to the free radical initiation mechanism of KPS used for EGDMA-2 grafting onto silk fibers.[18,19]

Tensile properties

The evaluation of the grafted silk fibers' tensile properties is vital to minimize the adverse effects on the tensile properties caused by grafting and to establish guidelines to decide grafting limits. The results of the tensile measurements are listed in Table I. The tensile strength of grafted silk fibers was a little lower compared with that of the control sample and declined with the increase of the graft yield. Tensile strength

TABLE I
Tensile Properties of Grafted Silk Fibers with Different Graft Yields

Graft yield (%)	Tensile strength (CN/dtex)	Elongation at break (%)	Initial modulus (CN/dtex)
0 (Control sample)	2.9 ± 0.1	20.2 ± 0.5	55.9 ± 0.7
15.8	2.8 ± 0.1	22.0 ± 0.8	44.1 ± 0.9
30.5	2.3 ± 0.2	24.9 ± 0.4	41.3 ± 0.9
42.0	2.0 ± 0.2	26.3 ± 0.7	37.2 ± 0.5

CN is centinewton.

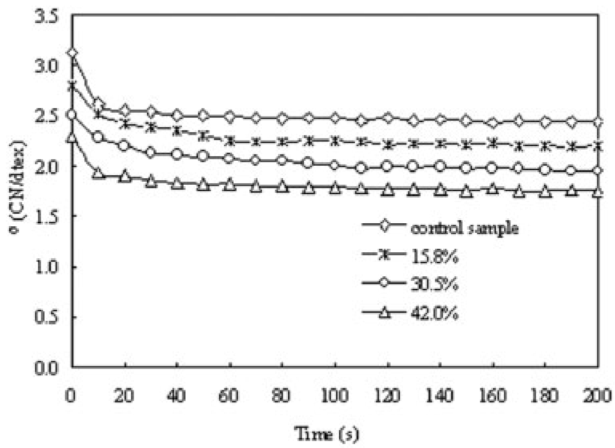

Figure 4 Stress relaxation of silk fibers with different graft yields.

loss may be due to the addition of formic acid. The grafting solutions containing formic acid might cause the hydrolysis of some sensitive peptide bonds.[20] Initial modulus also decreased with increasing graft yield, which indicated that grafted silk fibers were softer than control sample and the rigidity of grafted silk fibers decreased with the increase of the graft yield. While elongation at break of grafted silk fibers were higher than that of control sample and increased with the increase of graft yield, which should be mainly attributed to the changes of the inner orientation of silk fibers caused by grafting process. Grafted silk fibers had lower average orientation than that of control sample, the polymer grown during the grafting process filled the space available within the fiber matrix, which disturbed the arrangement of the fibroin chains in the amorphous regions and partially hindered their mobility when subjected to tension, which can be confirmed by the decline of specific birefringence of grafted silk fibers.[11]

Stress relaxation

Stress relaxation studies can provide a route to study time dependence shown by fibers and thus gain an understanding of their viscoelastic behavior. The stress relaxation characteristics of silk fibers with different graft yields are shown in Figure 4.

It can be seen clearly from Figure 4, that the grafted silk fibers showed lower initial (time is zero) stress than control sample during stress relaxation. And the initial stress for relaxation decreased with increasing graft yield. The stress was seen to relax at a rapid rate in the beginning and, with increasing time, the rate of stress relaxation gradually decreased. By the time the experiment was terminated, the stress had become almost constant. The stress relaxation of grafted silk fibers is significantly greater than that of control sample. Given that stress relaxation is a characteristic of viscoelastic materials, it may be concluded that grafted silk fibers have better viscoelasticity than control silk fibers. These differences shown by the silk fibers in their viscoelastic behavior would be related to the difference in their structures. After being grafted with EGDMA-2, silk fibers have lower degree of molecular orientation compared to that of control silk fibers.[11]

TABLE II
Wrinkle Recovery Angles of Control and Grafted Silk Fibers with Different Graft Yields

Graft yield (%)	Wrinkle recovery angles (WRA) (W+F) (degrees)	
	Dry state	Wet state
0 (Control sample)	242.5	197.3
6.2	279.1	235.8
15.9	285.6	245.1
30.0	311.4	275.6

Wrinkle recovery

The crease recovery behavior is one of the weak points of silk fabrics that should be improved. Table II shows the results of dry and wet wrinkle recovery angles of control and grafted fabrics.

It can be seen that the recovery angles increased with increasing graft yield, and the wet recovery angles increased obviously. As we all know, poor wash and wear properties of silk fabrics are related to their poor crease recovery, particularly in the wet state. After being grafted with EGDMA-2, silk fabrics have better wash and wear properties.

Laundry durability

Table III shows the strength retention ratio of control and grafted silk fibers after 10 times washing. It can be seen from Table III that the strength retention ratio of control sample is 0.75, which is much lower than that of grafted silk fibers. After 10 times laundering, silk fibers with higher grafted yield has higher retention ratio, which means that the EGDMA-2 grafting pro-

TABLE III
Retention Ratio of Grafted Silk Fibers after 10 Times Laundering

Graft yield (%)	*R*
0	0.75
12.5	0.89
22.5	0.91
32.9	0.93

cess reduced the damage to the silk fibers during laundering.

Silk fibers contain many fibrils that are bound together by hydrogen bonding. When exposed to wetness, the hydrogen bonding is easily damaged and the fibers are easily torn into fibrils, and therefore their laundering durability decreases. After being grafted with EGDMA-2, the surface of silk fibers generated a film of network structure caused by crosslinking among EGDMA-2 polymer chains. This network structure can reduce the damage to the silk fibers during laundering.[10]

CONCLUSIONS

The self-prepared bifunctional vinyl monomer EGDMA-2 was effective for silk fibers' modification. The hygroscopicity and fineness of silk fibers increased after being grafted with EGDMA-2. Tensile strength and whiteness decreased a little, which could be negligible. Stress relaxation behavior shows that grafted silk fibers have better viscoelasticity than control silk fibers. Crease recovery angles in dry state and especially wet state increased evidently, which indicated that the wash and wear properties of silk fabrics were largely improved. Grafting with EGDMA-2 also improved the laundry durability of silk fibers.

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