

Weighting and Improvement of Silk Properties

A. M. Ramadan, S. Mosleh, S. M. Gawish

National Research Centre, Textile Division, Tahrir Street, Dokki, Cairo, Egypt

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Abstract: Silk was modified with the aim to increase the weight and improve the physical properties. A grafting chemical redox technique was adopted in this investigation by using ammonium persulfate (APS), copper sulfate as initiator and accelerator for the reaction, glycidyl methacrylate (GM), and acrylamide (AM), or their mixture. The optimum ASP and copper sulfate concentration needed to decrease the homopolymerization reaction was noted in the case of GM and AM. The percentage graft yield was found

to be highly affected by the various parameters studied, including the initiator, the monomer concentrations, the reaction time, and the temperature. The physical properties of the grafted silk fabric were done including crease recovery angles, abrasion resistance, and moisture regain. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1743–1747, 2004

Key words: silk modification; redox polymers; graft copolymers

INTRODUCTION

Modification of the proteinic fibers properties by graft copolymerization of vinyl monomers was the interest of both scientists and technologists during the past three decades.^{1–6} Grafting was introduced as an alternative technique to the traditional mineral method⁷ by using tin phosphate and silicate for increasing the silk weight to compensate for the loss resulting from the degumming process. Silk fibers have some good properties such as handle or luster that distinguish them from other fibers. However, some minor textile performances such as crease recovery, dimensional stability, rubbing resistance, photo-yellowing stability, oil and water repelling, and color fastness characteristics need to be improved by means of the grafting technique to increase the requirements and consumption of silk.

In recent years, grafting techniques were regarded to as a powerful tool for the above cited purposes,⁸ which can be achieved by both chemical and physical methods (electron beam irradiation). Chemical redox systems are extensively investigated^{9–13} and are still widely used on an industrial scale for silk grafting. Silk fibers are activated by the free-radical initiation method, which involves the formation of free-radical sites on the backbone of the fibroin molecules.

In the present article, silk was grafted by the chemical method with the aim of weighting and improving the physical properties. For this purpose, ammonium

persulfate was used as an initiator in the presence of acrylamide, glycidyl methacrylate (Fluka, Buchs, Switzerland), or a mixture of both monomers. The physical properties of the grafted silk were studied.

EXPERIMENTAL

Materials

Plain weave silk fabric (32/40) was degummed by using 1.5% (owf) of a nonionic surfactant solution at 50°C for 2 h. The fabric was thoroughly washed with warm water and then with cold water, and finally squeezed and air-dried.

Reagents

Acrylamide (AA), glycidyl methacrylate (GM), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS), copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), formic acid, and methylethylketone were analytical grade reagents and were used without purification.

POLYMERIZATION PROCEDURE

A graft copolymerization reaction was carried out. Silk fabric (1 g) was introduced into a stoppered Erlenmeyer flask containing 50 ml of the solution.

The previous solution consisted of water, monomer, copper sulfate, and ammonium persulfate. The acidity of the bath was adjusted to pH 3. The flask was stoppered and kept in a thermostated shaking water bath at the desired temperature during the polymerization reaction. After a desired time, the reaction mixture was then extracted several times with warm

Correspondence to: S. M. Gawish (samihagawish@yahoo.com).

water and then with methylethylketone, dried in an oven at 105°C for 2 h, and cooled to room temperature in a dessicator until a constant weight. The graft yield was calculated as

$$\% \text{ Graft yield } (G_0) = \frac{w - w_0}{w_0} \times 100$$

where w is the weight of grafted silk sample and w_0 is the weight of original silk fabric.

Crease recovery measurement

The dry crease recovery angle of silk was measured by using an iron recovery apparatus (Type FF-07 Metrepex) for 10 min crease period. The sum of creasing angles, the warp (W) and weft (F) directions, were measured.

Abrasion resistance measurement

Two hundred cycles were used for each fabric sample by using a Universal Textile Abrasion Tester (Custom type, ASTM D). The loss in weight and decrease in thickness were determined.

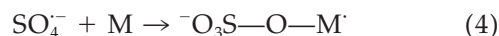
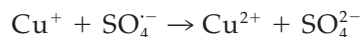
RESULTS AND DISCUSSION

Grafting mechanism

On the basis of studies conducted on silk grafting,⁸⁻¹³ the following reaction scheme is suggested as a possible mechanism for the initiation, propagation, and

termination of the graft copolymerization of vinyl monomers onto silk, using APS as the initiator.

The presence of Cu^{2+} has an accelerating effect on the decomposition of APS:



where >RH , R^{\cdot} , and M represent silk, primary silk macroradical, and monomer, respectively. Reaction (1) describes the primary radical formation; reaction (4) shows the initiation of monomer homopolymerization, and reactions (2) and (3) demonstrate the different steps of the graft copolymerization. The free radicals formed by the initiator interact with the reactive sites on the silk fibroin backbone, forming a macroradical. Carboxyl, amine, and hydroxyl side groups of various amino acid residues are likely to form radicals. Arai et al.¹⁴ and Enomoto and Suzuki¹⁵ emphasized the role of the glycine residues (i.e., the $-\text{NH}$ moieties of the peptide bond) as a site for grafting silk. The silk macroradicals can react with the monomer, leading to the propagation of a grafted polymer chain.

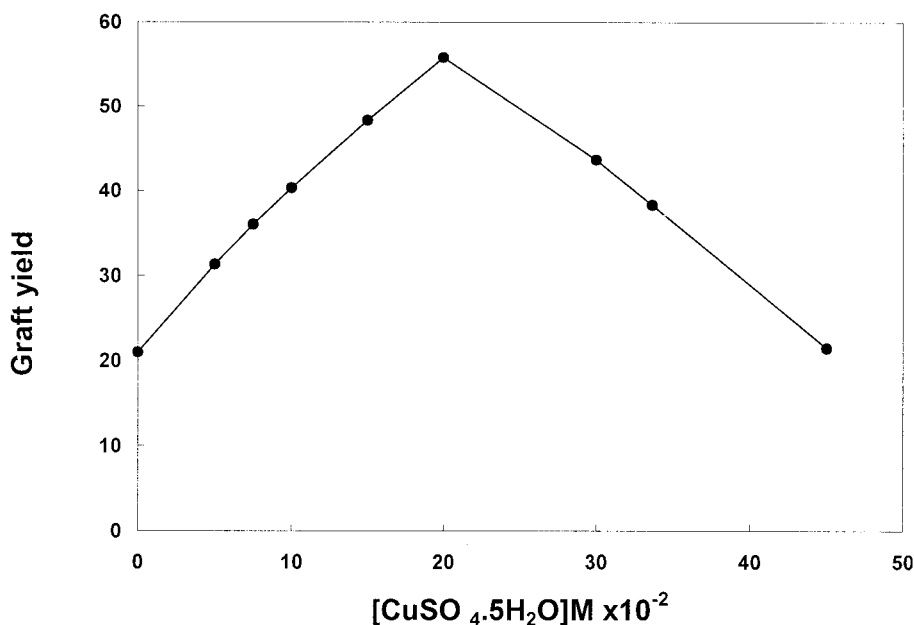


Figure 1 Effect of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentrations on the graft yield of glycidylmethacrylate onto silk fabric. (GM) 0.146M; (APS) $1.76 \times 10^{-3}\text{M}$; temperature, 85°C; reaction time, 60 min; liquor ratio, 1 : 50.

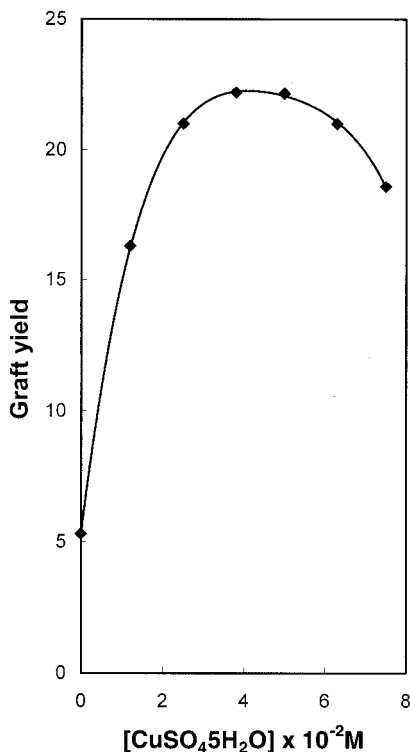


Figure 2 Effect of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentration on the graft yield of acrylamide onto silk fabric. (AM) 0.422M; (APS) $2.6 \times 10^{-3}\text{M}$; temperature, 85°C; reaction time, 60 min; liquor ratio, 1 : 50.

Homopolymers can be formed by interaction of the initiating free radicals with the monomer.

Effect of cupric ions concentration

The effect of copper sulfate concentration on the percentage graft yield of GM onto silk fabric is shown in

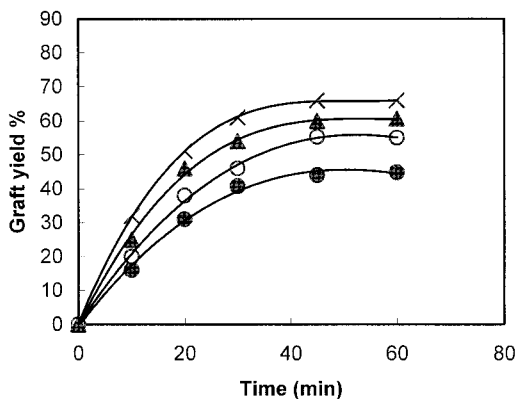


Figure 3 Rate of the percentage graft yield using of glycidylmethacrylate onto silk in the presence of ammonium persulfate as follows: (x) $10^{-3} \times 0.21\text{M}$, (▲) $10^{-3} \times 0.44\text{M}$, (●) $10^{-3} \times 0.88\text{M}$, (○) $10^{-3} \times 1.76\text{M}$; CuSO_4 concentration; $20 \times 10^{-2}\text{mM}$; (GMA) 0.146M; temperature, 70°C; pH = 3; liquor ratio, 1 : 50.

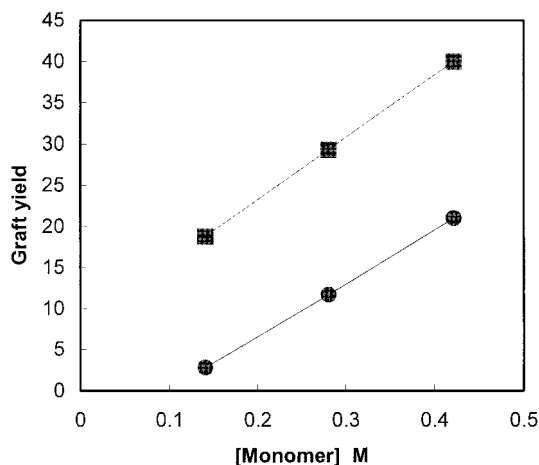


Figure 4 Effect of AM and AM/GM mixture concentrations on the percentage graft yield of silk fabric. (●), [AM] 0.141M, 0.281M, 0.422M; (■), mixture [AM](0.141M or 0.281M or 0.422M)/[GM](0.037M); ammonium persulfate concentration, $2.6 \times 10^{-3}\text{M}$; CuSO_4 concentration, $4 \times 10^{-2}\text{mM}$; pH 3; temperature, 85°C; reaction time, 60 min; liquor ratio, 1 : 50.

Figure 1. It was observed that the presence of the cupric ion played a significant role in increasing the grafting reaction. An increase in the graft yield was achieved when Cu^{2+} ion concentration was increased gradually and reached 55% at 0.2M. By further increasing Cu^{2+} concentration, the graft yield was decreased and reached 27% at 0.45M Cu^{2+} . The increase in the graft yield produced in the presence of Cu^{2+} ion is referred to as an accelerating effect of this ion on the decomposition of APS.

The effect of copper sulfate concentration on the percentage graft yield of AM on silk fabric is shown in Figure 2. The graft yield increased gradually with

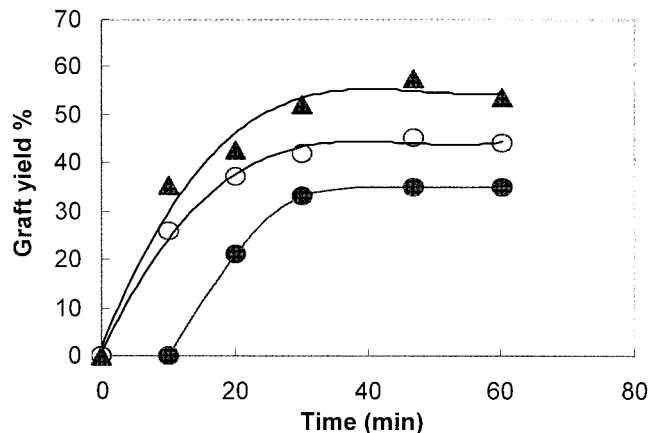


Figure 5 Effect of temperature on the percentage graft yield rate of GM onto silk fabric. (APS) $3.5 \times 10^{-3}\text{M}$; CuSO_4 $20 \times 10^{-2}\text{mM}$; pH 3; temperature (●) 50°C, (○) 70°C, (▲) 85°C; liquor ratio, 1 : 50.

increasing Cu^{+2} ion concentration and reached 22% at $4 \times 10^{-2} \text{M}$ Cu^{2+} and by further increasing its concentration, the percentage graft yield decreased gradually to reach 18.5% at $7.5 \times 10^{-2} \text{M}$.

Effect of initiator

The effect of the APS concentration as an initiator on the percentage graft yield rate at 70°C is shown in Figure 3. It was observed that the increase of APS concentrations caused a decrease in the graft yield. Also, it was clear that at $0.21 \times 10^{-3} \text{M}$ APS, the graft yield rate reached 70% in 45 min and at $1.76 \times 10^{-3} \text{M}$ APS, the graft yield decreased and reached 45% in 45 min.

Effect of monomers concentrations and their mixture

The effect of acrylamide/glycidylmethacrylate mixture on the graft yield of silk fabric is shown in Figure 4. It can be observed that the percentage graft yield increases by increasing the concentration of acrylamide. It was observed at 0.141M AM that the graft yield reached about 3%. When a mixture of the same concentration of AM and 0.037M GM was used, the graft yield increased and reached 19%. In the same manner, the increase in AM concentration to 0.422M caused an increase in the graft yield to 22%. A mixture of the same concentration of AM and 0.037M of GM increased the percentage graft yield to 40%. The increase in graft yield is due to the increase of the monomer concentration. In the case of the mixture, this may be due to the introduction of epoxide group¹⁶ in the backbone of silk fabric in an acidic medium¹⁷ of pH 3 and the change of the epoxide group to hydroxy group, causing a high increase of graft yield.

Effect of temperature on the percentage graft yield rate of silk

The effect of temperature on the percentage graft yield of GM was presented in Figure 5. The graft copoly-

TABLE I
Effect of Percentage Graft Yield of GM, AM, and Mixture of GM/AM on the Percentage Moisture Regain of Silk Fabric

Monomers	Graft yield (%)	Moisture regain (%)
Silk	None	10.5
GM	35.8	6.48
GM	58.7	5.79
AM	15	10.21
AM	22	10.48
Mixture		
AM/GM	34	9.4
AM/GM	53	10.36

TABLE II
Crease Recovery Angles of Grafted Silk Using AM and GM

Graft yield (%)	Crease recovery angles (mean of warp and weft directions)	
AM	9	323
AM	19	338
GM	12.4	296
GM	22.2	300
Silk	None	287

merization reaction of GM was done for three temperatures varying between 50 and 85°C . It was observed that at 50°C the graft yield was quite low and the induction period was 10 min. Upon raising the reaction temperature to 70 and 85°C , the percentage graft yield was increased and the grafting reaction proceeded without any induction period. The enhancement in the grafting yield by raising temperature is due to the monomer diffusion and adsorption from the solution phase to fabric. Finally, the adsorption of GM onto the silk fabric resulted in increasing the silk weight. This fact could be attributed to reaction of the epoxide groups with the reactive macroradical sites of silk fibrin backbone, which resulted in the change of the chemical and physical properties of silk. Also, as the temperature increases, it may increase the radical sites onto the silk fabric, which reacts with the monomer, leading to the propagation of the grafted polymer chain.

Moisture regain

Silk has a relatively high moisture regain¹⁸ of 11%. Grafting of silk with AM does not change appreciably the moisture regain of silk (10.2–10.48%) (Table I), which is attributed to the similarity of AM and silk amino acids in their chemical structures. On the other hand, the grafting of GM onto silk decreases the moisture regain to 6.48% for 35.8% GM graft, which may be due to a deposition of GM graft mainly on the silk surface, thus decreasing absorption of moisture from the ambient atmosphere.

TABLE III
Abrasion Resistance of Grafted Silk by GM and AM and Their Mixture

Graft yield (%)	Weight loss (%)	Thickness weight loss (%)
Silk	none	7.32
GM	35.8	4.82
GM	58.7	6.25
AM	15	3.7

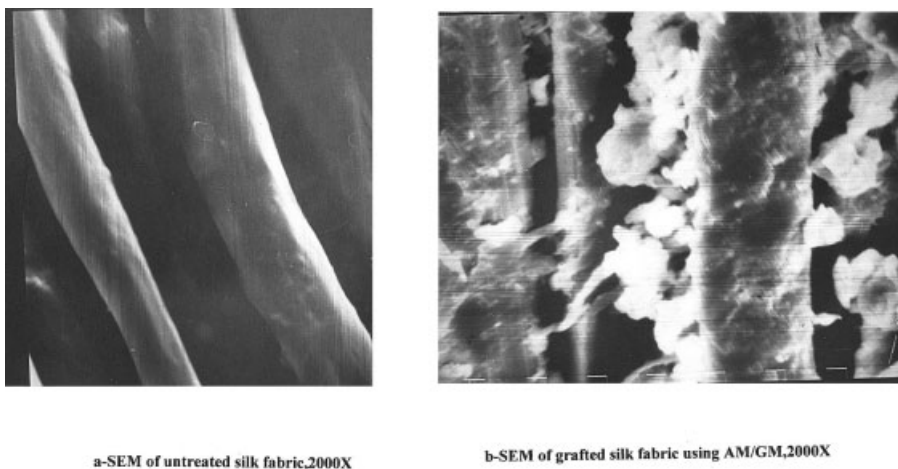


Figure 6 (a) SEM of untreated silk fabric, $\times 2000$; (b) SEM of grafted silk fabric using AM/GM, $\times 2000$.

Crease recovery angle

The crease recovery angle of silk (Table II) was improved as was stated by other authors⁷ by using the grafting technique in the presence of both AA and GM monomers. The crease recovery angle of the untreated silk is 287. The grafting of silk by AA improves the recovery angle to 323 for 9% AM graft and 338 for 19% AM graft.

In the case of GM, the recovery angle was 296 for 12.4% GM graft and 300 for 22.2% GM graft, as shown in Table II.

Abrasion resistance

The silk grafting by AM decreases its abrasion weight loss to 4.76% and the thickness to 3.7 compared to 5.39% weight loss and 7.32% thickness weight loss for the untreated silk. Thus, grafting of AM improves the abrasion resistance of grafted silk (Table III). In the case of grafted silk by GM, the loss in weight is approximately similar to the untreated silk, but there is a decrease in the thickness weight loss to 4.82% for 35.8% graft GM and 6.25% for 58.7% graft GM. The grafting of silk by GM improves the abrasion resistance of the thickness only.

SEM observations

SEM micrographs were done on a JEOL JSM/T 20 instrument. The samples were placed on an aluminum holder and covered with gold.

The SEM micrographs of ungrafted and grafted silk fabrics are shown in Figure 6 (a, b). The ungrafted silk fabric revealed a highly clean and smooth surface. Whereas in the case of grafted silk fabric, using AM/GM, the grafting showed the creation of a large amount of side chains compared to the original ungrafted sample.

CONCLUSION

A redox technique was adopted to graft silk fabric using AM/GM, with the aim to increase the weight and to improve silk properties.

In this study, APS was used as an initiator, and Cu^{2+} was used to increase grafting rate. The presence of Cu^{2+} caused an accelerating effect on the decomposition of APS. Physical properties of silk were improved by grafting, including the crease recovery angle, moisture regain, and abrasion resistance. SEM observations revealed a morphological change of grafted silk fabric by using a mixture of AM/GM compared to the untreated one.

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