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Grafting of Silk Fibre with MMA, EMA and MAN for Improved Properties

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Abstract: Grafting copolymerization of silk fibre was carried out with methylmethacrylate (MMA), ethylmethacrylate (EMA) and methacrylonitrile (MAN) in aqueous media using $H_2O_2-Na_2S_2O_3$ as redox initiator. To make the graft copolymerization more efficient and economic, the optimum conditions for graft copolymerization were established. The optimum conditions e.g., monomer concentration, initiator concentration and time for MMA, EMA and MAN were 50.0, 0.2 and 90%, respectively and the temperature was 80°C for MMA and MAN and 90°C for EMA. The grafting percentages at optimum condition for MMA, EMA and MAN were 54.3, 34.94 and 19.87%, respectively. The loss in tenacity of non-modified silk fibre was higher (53.87%) than the modified silk (34-35%) after 300 h exposure in sunlight in open air. The modified fibre also showed better lustrous and softness than the non-modified silk.

Key words: Silk fibre, graft copolymerization, monomer, optimum conditions and tenacity

INTRODUCTION

Bangladesh has a rich historical past in silk manufacturing. In ancient time mulberry trees were cultivated in the high land of Bangladesh and by adopting various devices the silk was prepared and it was exported to other countries. Unfortunately, recently we are importing silk from India and China. This is because the quality of Indian and China silk are comparatively better than that of Bangladeshi Silk.

Since the beginning of the 1970's the efforts of both scientists and technologists have been focused on improving some textiles performance of silk by chemical modification techniques. Among the chemical modification techniques, graft co-polymerization has been suggested as a potentially effective means to enhance such properties as crease recovery, tensile strength and elongation, light resistance, wash and wear behaviour, without affecting handle and lustrous appearance of silk. A large number of vinyl monomers have been applied onto silk and they influence on the fibre properties (Joseph, 1976; Tsukada, 1993).

The graft copolymerization reaction of vinyl monomers onto silk fabrics may be activated by various methods, such as radiation and chemical or photochemical induced initiation. The use of chemical redox systems in aqueous media has played a major role for both scientific and technological purposes. The physico-chemical properties of grafted silk largely depend on the

chemical characteristics of the functional side groups carried by the vinyl monomer, as well as, on the extent of grafting and on the molecular weight at the chain polymerized inside the fibre (Tsukada, 1993; Hess, 1978; Encyclopedia of Textile, 1978).

The quality of Bangladeshi silk is poor than most of the other silk producing countries. In order to increase the demand of silk fibre and to speed the progress of silk industry, research on silk modification is an almost necessary in Bangladesh. By the chemical modification of silk it is expected to have the improved properties such as tolerability to the sunlight, atmospheric, adversities as well as the improved tenacity comparable to the rival synthetic fibres. It is also expected that the modified silk fabric which have the improved properties- must retain the comfortability.

In the present study, improved multi-voltine variety silk was chemically modification with methylmethacrylate (MMA), ethylmethacrylate (EMA) and methacrylonitrile (MAN) for improve its intrinsic properties (such as, tenacity, thermal resistant, resistant to sunlight (UV) etc.). In order to make the modification process more economic effort has been made to find out the optimum modification conditions depending on the concentration of monomer, concentration of initiator, modification time and temperature. To observe the effect of sunlight and effect of temperature on the degummed and modified degummed fibres, the tenacity of silk fibres has been measured.

MATERIALS AND METHODS

Improved multi-voltine variety of mulberry silk fibre was collected from Bangladesh Sericulture Research and Training Institute (BSR and TI), Rajshahi, Bangladesh. Methylmethacrylate (MMA), ethylmethacrylate (EMA) and methacrylonitrile (MAN) were freed from stabilizer by washing with 5% sodium hydroxide solution and water. These were then dried anhydrous sodium sulphate and distilled under reduced pressure in nitrogen before used (Mohanty *et al.*, 1983). All other chemicals e.g., Na₂CO₃, anhydrous Na₂SO₄, (NH₄)₂S₂O₈ etc. used were CP grade.

The gummy substance (sericin) of raw silk was removed by degumming process in alkaline soap bath. The soap solution of strength 3.5 g L⁻¹ was prepared and its pH was adjusted to 10.0-10.5 by adding 1 g L⁻¹ of soda ash (pH change was observed directly with pH meter). For each gm of silk fabric 30 mL of liquor was taken and degumming was conducted at temperature 95-100°C for 1 h. During the operation the pH of the bath falls and then silk fabric was transferred into 2nd bath and heated for 45 min at the same temperature. After degumming the silk fabric was washed well with hot distilled water for 3-4 times (Sheikh *et al.*, 1994).

Tenacity (breaking strength) of silk fibre was measured by using the tensile strength tester (Torsee's Schopper type-OS-100). At first the denier of silk fibre was determined by the following equation (Krishnaswami *et al.*, 1974).

$$\text{Denier} = \frac{\text{Weight of sample in g}}{\text{Length of the sample in meter}} \times 9,000$$

Silk fibres were cut into equal pieces of length 30 cm and weighed (about 0.25 g) and the denier of the samples was measured. One twist per 2 cm was given along the length of the sample and placed between the jaws of the tensile tester and maintains the length of each specimen 10 cm. After starting the machine the breaking load was gradually increased and at a particular point the specimen was broken down. The breaking load was shown at the point of break on the scale of the machine in kg. In each experiment tenacity for 10 specimens was taken and the mean of 10 readings gave the tenacity of the fabric. The tenacity of the fibre was measured by the following equation (International Standard ISO 5081-1977-E).

$$\text{Tenacity} = \frac{\text{Average breaking load in g}}{\text{Denier}} \text{ (g/denier)}$$

The graft copolymerization of silk fibre was carried out in a 100 mL stoppered Erlenmeyer flask. Polymerization was done with 30-80% monomer and 0.1-0.5% H₂O₂- Na₂O₃S₂ redox initiator based on the weight of fibre at 60-100°C for 60-180 min in the fibre liquor ration of 1:30. At the end of the reaction period, the grafted silk fibre was thoroughly wash with hot water followed by cold methanol to remove the loosely adhered polymer (Tsukada, 1993; Hiroshi, 1986; Lee *et al.*, 1985).

Percent grafting and grafting efficiency were calculated by taking the weight of dried fibre before and after grafting with monomers. A correction was made for the eventual weight loss occurred during the treatment in the reaction system by using a blank sample treated without monomer. Following formulas were adopted to calculate the percentage grafting (Sikder *et al.*, 1995).

$$\text{Grafting (\%)} = \frac{B-A}{A} \times 100$$

Where,

A, the weight of degummed silk fibre before modification; B, the weight of the grafted silk fibre; C, the weight of total monomer used.

This study was carried out at the Polymer and Textile Research Laboratory in the Department of Applied Chemistry and Chemical Technology, University of Rajshahi, Bangladesh.

RESULTS AND DISCUSSION

Degummed silk fibre was chemically modified by MMA, EMA and MAN monomers to observe their effect on the inherent properties of silk fibre. In the modification process it was seen that the grafting was depended on the monomer concentration, initiator concentration, modification time and temperature. The percent grafting increases with the increase of monomer concentration up to 50% for MMA, EMA and MAN monomers and the corresponding percent grafting are 54.29, 23.40 and 19.87%, respectively (Fig. 1). Beyond this concentration the percent grafting started to decrease. The graft percentage increases with increase of monomer concentration may be explained that, when silk is immersed into the solution of vinyl monomer in presence of the redox initiator, the silk fibre is attacked by the redox initiator and the free radical is formed on the silk fibroin backbone. Carboxyl (-COOH), amine (-NH₂) and hydroxyl (-OH) side groups of acidic, basic and hydroxyl amino acid residues are the main reactive sites of silk fibre. These reactive sites interact with vinyl monomer thus

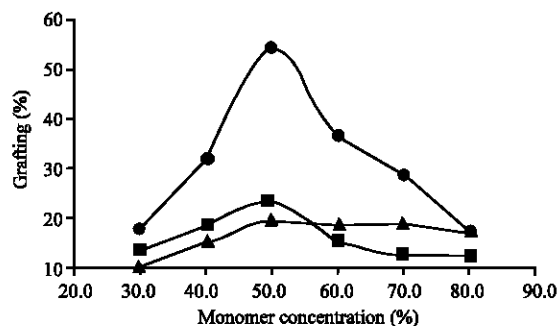


Fig. 1: Effect of monomer concentration on percent grafting of MMA, EMA and MAN monomers onto degummed silk fiber (Initiator, 02%; time, 90min.; 80°C; fiber-liquor ratio, 1:50). ●, MMA; ■, EMA; ▲, MAN

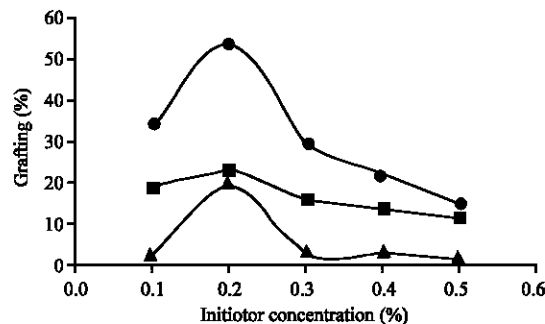
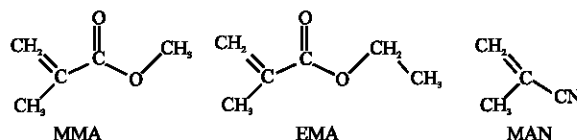


Fig. 2: Effect of initiator ($H_2O_2-Na_2O_3S_2$) concentration on percent grafting of MMA, EMA and MAN monomers onto degummed silk fiber (monomer, 50%; time, 90.; temp., 80°C; fiber-liquor ratio, 1:50). ●, MMA; ■, EMA; ▲, MAN

grafting is occurred (Tsukada, 1993). The monomer concentration decreases throughout the course of reaction as the number of high polymer molecules increases (Odian, 1970). The decrease in percent grafting may be due to the homopolymerization of monomer at high concentration. Another cause may be that during grafting the reactive sites of silk are blocked and after equilibrium no more monomers will be attached on to the silk fibre (Odian, 1970). The used monomers are not the same (Fig. 1). Grafting percentage occurred in order of MMA>EMA>MAN. This is due to the different chemical features and the presence of double bonds in vinyl monomer molecule bestows poly-functionality of them (Gowariker *et al.*, 1996). These bonds react as reactive sites which are grafted with silk fibres. The behaviour of monomers in copolymerization reaction is especially useful for studying the effect of chemical structure on reactivity. The relative thermodynamic feasibility of any one monomer varies depending on the substituents present in the monomer. Substituents increase the reactivity of a monomer towards radical attack in the general order. The order of monomer reactivities corresponds to the order of increased resonance stabilization. From the chemical structure, it is seen that MMA has two double bonds at same side, EMA has two double bonds at opposite side and MAN has only one double bond. Another reason is that the presence of other substituents as methyl group (-CH₃) may react with silk fibroin. MMA and EMA contain two methyl groups and MAN contains only one methyl group. So, it can be said that there are four reactive sites of MMA, three reactive sites (due to the opposite of double bonds) and two reactive sites of MAN. The presence of more in number of these reactive sites in the monomer will give greater graft-copolymerization (grafting) (Odian, 1970).



Structure of MMA, EMA and MAN

Figure 2 shows that the percent grafting by silk increases with the increase of initiator concentration (0.1-0.2%) and then the grafting percent decreases with the further increase of initiator concentration. This is because the redox initiator generates macro-radicals on the fibre backbone as well as activates monomers in the reaction system; the increasing concentration of the initiator gave the higher percent grafting. But at maximum concentration of initiator, the activated monomer concentration increase to high which brought out homopolymerization and faster rate of termination of the growing chain resulting decreased grafting yield (Mohanty *et al.*, 1983; Samal *et al.*, 1986; Hebeish *et al.*, 1971). The maximum percent grafting was 54.29, 23.40 and 19.47% obtained at 0.2% initiator for MMA, EMA and MAN, respectively.

Figure 3 shows percent grafting increased with the increase of reaction time up to 90 min and then started to decrease. In this span of time the activated monomer combines with active sites on the fibre matrix. After 90 min monomers find no more reactive sites on the fibre backbone and so, become homopolymerized. Hence, at longer reaction time, the percent grafting due to partial dissolution of grafted fibre (Monthly *et al.*, 1986; Mishra *et al.*, 1987).

Figure 4 shows the percentage grafting increases initially with the rise of temperature (80-90°C) and then falls with further increase of temperature. The increasing

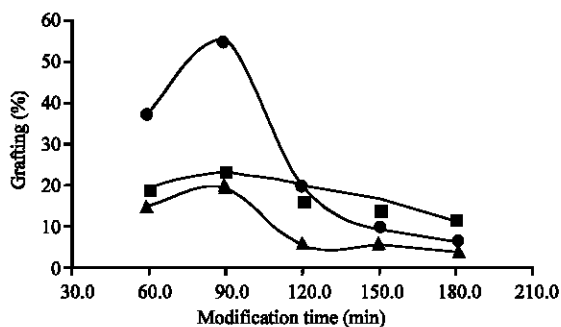


Fig. 3: Effect of modification time on percent grafting of MMA, EMA and MAN monomers onto degummed silk fiber (monomer, 50%; initiator, 0.2%; temp., 80°C; fiber-liquor ratio, 1:50). ●, MMA; ■, EMA; ▲, MAN

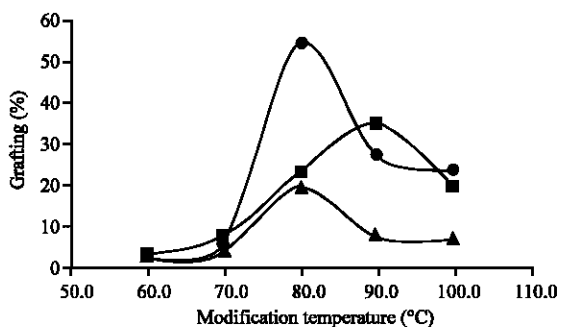


Fig. 4: Effect of modification temperature on percent grafting of MMA, EMA and MAN monomers onto degummed silk fiber (monomer, 50%; initiator, 0.2%; time, 90 min; fiber- liquor ratio, 1:50). ●, MMA; ■, EMA; ▲, MAN

trend of grafting was due to the increase in the rate of production of active free radicals which increased the number of grafting sites at higher rate. The increase in temperature increased the rate of diffusion of monomer onto the silk fibroin backbone also contributed for higher grafting (El-Rafie *et al.*, 1994). At ceiling temperature the propagation and depropagation rate is equal where the net rate of polymer production is zero. Vinyl monomer undergoes termination by both coupling and disproportionation. The extent of disproportionation increases with increasing temperature. It is also proved that the number average degree of polymerization decreases rapidly with increasing temperature (Odian, 1970). The maximum grafting percentages of MMA and MAN at 80°C and EMA at 90°C are 54.3, 19.87 and 34.94%, respectively (Table 1).

Table 1: Effective optimum conditions of grafting and grafting percentage

Parameters					
Monomer used	Monomer conc. (%)	Initiator conc. (%)	Modification time (min)	Modification temp. (°C)	Grafting (%)
MMA	50	0.2	90	80	54.30
EMA	50	0.2	90	90	19.87
MAN	50	0.2	90	80	34.94

Table 2: Loss in tenacity of degummed and modified silk fibre on exposure to sunlight in air

Exposure period (h)	Loss in tenacity (%)			
	Degummed silk	Modified with		
		MMA	EMA	MAN
50	12.90	7.94	8.15	8.07
100	22.58	12.82	13.15	13.01
150	27.41	17.94	18.42	18.11
200	32.35	23.58	24.21	23.86
250	41.29	28.97	29.73	29.50
300	53.87	33.10	35.50	35.25

Physico-chemical properties of modified and unmodified fibre

Effect of sunlight (UV) on the strength (tenacity) of silk fibre:

Table 2 shows that the loss in tenacity of degummed (unmodified) and MMA, EMA and MAN modified silk fibres are 53.87, 34.10, 35.00 and 35.95% respectively on exposure to sunlight in air at 300 h. The loss in tenacity increases with the progress of exposure time under the sun. This is because silk is composed of amino acid to form a polypeptide chain. The glycidyl radicals formed in silk fibroin by the irradiation immediately react with atmospheric oxygen and change to peroxy radicals, i.e., photooxidative degradation occurs (Setoyama and Kouchi, 1982). From the Table 2 it is also observed that the loss in tenacity of unmodified silk (~54%) much more higher than that of modified silk (~33%) at the same period of exposure and the loss in tenacity of modified fibre is not the same. This happens, probably, due to the presence of vinyl monomers which are grafted on to the silk fibre. Grafting is considered a powerful method to substantially improve some intrinsic properties. Grafting has been suggested as a potentially effective means to enhance such properties as light resistance (Tsukada, 1993). Roy *et al.* (1968) showed from X-ray work that the fibre become more rigid on grafting resisting the penetration of moisture into the active core area of the fibre which ultimately reduced the action of UV light towards atmospheric oxidation. As a result, the loss in tenacity decreased with the increase of polymer loaded onto the silk fibre.

Effect of sunlight (UV) on the yellowing of silk fibre:

Table 3 shows that the yellowing of unmodified and modified fibres are more or less similar. Yellowing of silk

Table 3: Colourfastness of degummed and modified silk fibre on exposure to sunlight in air

Exposure period (h)	Fastness grade and colour			
	Degummed silk	Modified with		
		MMA	EMA	MAN
00	5 (White)	5 (White)	5 (White)	5 (White)
50	4-5 (Slightly yellowish)	4-5 (Slightly yellowish)	4-5 (Slightly yellowish)	4-5 (Slightly yellowish)
100	4-5 (Slightly yellowish)	4-5 (Slightly yellowish)	4-5 (Slightly yellowish)	4-5 (Slightly yellowish)
150	4 (Slightly yellowish)	4-5 (Slightly yellowish)	4-5 (Slightly yellowish)	4-5 (Slightly yellowish)
200	3-4 (Slightly yellowish)	4 (Slightly yellowish)	4 (Slightly yellowish)	4 (Slightly yellowish)
250	3 (Slightly yellowish)	4 (Slightly yellowish)	4 (Slightly yellowish)	4 (Slightly yellowish)
300	3 (Slightly yellowish)	4 (Slightly yellowish)	3-4 (Slightly yellowish)	3-4 (Slightly yellowish)

fibre occur due to the formation of glycidyl radicals in silk fibroin by the irradiation which react with atmosphere oxygen and change to peroxy radicals (Setoyama and Kouchi, 1982). As the grafted silk fibre shows less affinity towards moisture can somehow protect the yellowing trend of the fibre. Polymer loaded in case of MMA fibre was more, so good result was found as compared to others modified fibres.

CONCLUSIONS

The properties of silk fibre can be improved by chemical modification with vinyl monomers (MMA, EMA and MAN). This modification can bring out some physico-chemical changes in fibre structure that sustain its textile properties (degradation and colour fastness, strength etc.) for comparatively longer period of time.

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