Studies of Mechanical and Moisture Regain Properties of Methyl Methacrylate Grafted Silk Fibers

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ABSTRACT: The mechanical properties such as the tenacity, breaking extension, initial modulus, elastic and work recovery, and stress relaxation behavior of methyl methacrylate (MMA) grafted silk fibers prepared under different conditions were measured and explained in terms of the relative dominance of the stress concentration, reduction in the interchain cohesion, and fiber matrix stiffening at different grafting percentages. The moisture regain characteristics of fibers grafted in the presence of different solvents were also studied and compared. The grafting of MMA on silk was found to improve the recovery properties significantly without affecting the stress relaxation behavior. The moisture regain studies indicate that moisture regain is reduced with increasing length of the grafted poly(MMA) chains. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 969–974, 2002; DOI 10.1002/app.10202

Key words: grafting; tenacity; stress relaxation; moisture regain; elastic and work recovery

INTRODUCTION

The modification of silk fiber properties through graft copolymerization has evoked considerable interest in recent years. Various authors[1–10] have studied and reported the mechanical and moisture regain characteristics of grafted fibers. However, only limited information regarding those above studies by using grafted fibers prepared under different conditions (e.g., variations in time, monomer concentration, type of solvent, etc.) is available. The results are reported for the mechanical and moisture regain properties of methyl methacrylate (MMA) grafted silk fibers prepared under different experimental conditions using a titanium(III) chloride–potassium persulfate redox initiator under visible light in a limited aqueous medium.

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EXPERIMENTAL

Materials

Mulberry silk fibers were collected from Birbhum, West Bengal. Potassium persulfate (AR grade) and titanium(III) chloride (15% solution in 10% HCl) were from E. Merck and were used directly.

Scouring of Silk

Scouring was done by boiling raw silk fiber in an aqueous solution containing 0.4% sodium lauryl sulfate for 2 h. The fiber was then washed with a 0.05% sodium carbonate solution and then with cold distilled water until it was alkali free. The scoured silk was dried at room temperature in a current of dust-free air.

Purification of MMA

The MMA was freed from the inhibitor by repeated washing with a 4% aqueous NaOH solution, followed by washing with distilled water. The inhibitor-free monomer was then dried over fused calcium chloride and distilled under reduced pressure, and the middle fraction was collected. It was stored in a dark colored bottle in a refrigerator at a temperature of 5°C.

Moisture Regain Determination

Samples were at first put into a vacuum desiccator containing phosphorus pentoxide for 6–8 weeks and then weighed. This process was repeated, if necessary, until the weight became constant. This was termed the dry weight. The samples were then conditioned at 25°C and corresponding relative humidity for 72 h and reweighed until the weight became constant. This weight was termed the conditioned weight. Thus,

$$\% \text{ moisture regain} = \frac{\text{conditioned weighted} - \text{dry weight}}{\text{dry weight}} \times 100$$

Measurements

Mechanical Properties

Tenacity, Breaking Extension, and Initial Modulus. Single fiber tests were carried out on samples selected randomly and conditioned at 25°C and 65% relative humidity using a Zwick tensile tester (model 1445). The gauge length and rate of extension were kept at 10 mm and 10 mm/min, respectively. Typically, 50 specimens were tested. The load extension curves of the fibers were obtained from the recorder chart. The breaking load, breaking extension, and force at 5% extension were obtained from the tensile tester. From these data the tenacity and initial modulus at 5% extension for single fibers were computed.

Elastic and Work Recovery. Single fibers were given one extension of cycling up to a maximum level of extension of 3.5% at a gauge length and rate of extension of 10 mm and 6 mm/min, respectively. From the extension cycling curve obtained for 50 samples, the average elastic and work recovery were computed.

Stress Relaxation. Single fibers were stretched at a speed of 6 mm/min up to an extension of 3.5% and kept at that extension level for 20 s. The relaxation in stress was recorded on a chart recorder. The stress loss in 20 s was determined from the graph.

Moisture Regain Properties. For measuring the percentage of moisture regain at different relative humidities, solutions of sulfuric acid were used.

RESULTS AND DISCUSSION

The typical load extension curves shown in Figures 1 and 2 indicate that the overall mechanical behavior up to rupture is not much affected by the MMA polymers, even at a high level of grafting onto the main polypeptide chain backbone of the silk fiber.

Effect of Grafting Percentage on Tensile Characteristics

Tenacity

Table I shows the effect of the grafting percentage on the tenacity of the fibers. It is observed that with the increase in the grafting percentage the tenacity of the fibers follows a regular decreasing trend. The decrease in the tenacity becomes more rapid when the grafting percentage is increased by the increasing monomer concentration, compared to that by increasing the time of reaction. This indicates that with the availability of increasing numbers of monomer molecules, the grafting occurs more heterogeneously within the fiber matrix, creating a greater number of sites of stress concentration, which causes a reduction in the fiber load-bearing capacity.

With increasing grafting percentage the decrease in the fiber tenacity was found to be of more or less the same order with the different solvents used for grafting. This is due to the fact that the solvents used here are not true solvents for fiber and MMA but help in swelling. Hence, the solvents do not have much of an affect on the fiber orientation before and after have grafting. Whenever the grafting reaction is conducted in their presence, the tenacity remains almost unchanged because it is a function of the fiber orientation.[11]

Breaking Extension

The change in the breaking extension with the increase in the percentage of grafting of MMA

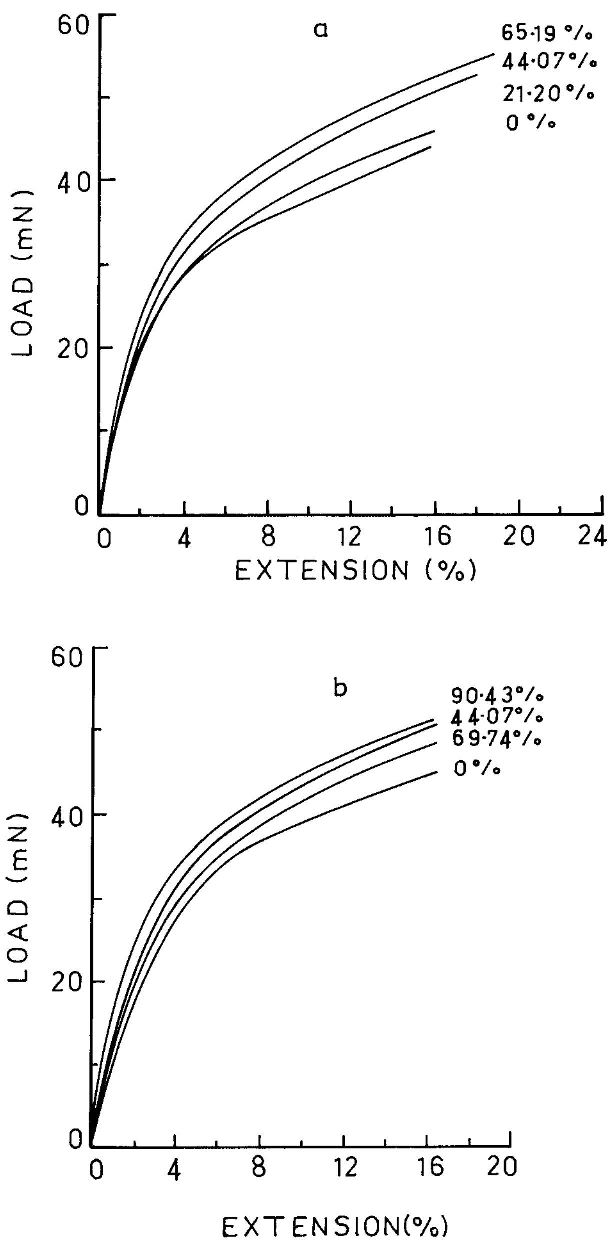

Figure 1 Load-extension curves for silk fibers and MMA-*g*-silk fibers with variation in (a) time of polymerization and (b) monomer concentration.

grafted fibers prepared under different conditions are shown in Table I. With the increase in the percentage of grafting, the breaking extension increases first and then decreases. This may be explained in the following way.

As grafting takes place in the amorphous region, it restricts chain mobility as the percentage of grafting increases, thus causing a decline in the breaking extension value. However, at a lower percentage of grafting the short polymer chains may be regarded as interchain plasticizers, which induces polymer chain slippage, thus leading to an increase in the breaking extension.

Table I shows the initial modulus of MMA grafted fibers. It is observed that the initial modulus first decreases and then increases with the increase in the percentage of grafting. The initial deposition of polymer helps the crystalline region to shear more, causing a reduction in the modulus at first; but later, due to a substantial increase in polymer deposition, the fiber matrix as a whole becomes stiff, resulting in an increase in the modulus.

Effect of Monomer–Solvent Combination on Viscoelastic Nature of Grafted Fiber

To study this effect, fibers were considered with approximately the same percentage of grafting of polymer but grafted in the presence of different solvents. Recovery properties and stress relaxation were studied with fibers having around 40% grafted MMA. Considering the swelling and miscibility with MMA, it may be assumed that acetic acid will help in greater dispersion of grafted polymer, followed by dimethylformamide (DMF) and alcohol. Such differences in the location of grafted polymer in the fiber matrix are expected to influence the tensile behavior of the fiber to a varying degree.

Elastic and Work Recovery

The elastic and work recovery results are shown in Table II. The grafted fibers show better elastic and work recovery than ungrafted fibers. This may be explained in terms of the rise in the internal viscosity by stiff MMA polymer deposition, which results in higher storage of energy in the fiber during its deformation and thereby results in higher elasticity. In this respect, acetic acid was found to be better than alcohol because it helps in better dispersion of polymer within the fiber matrix.

Stress Relaxation

The results for stress relaxation are shown in Table II. The effect of grafting in stress relaxation behavior was found to be negligible in all cases. This indicates only little plasticization was achieved due to deposition of poly(MMA) (PMMA) in the fiber when deformed to 3.5% extension.

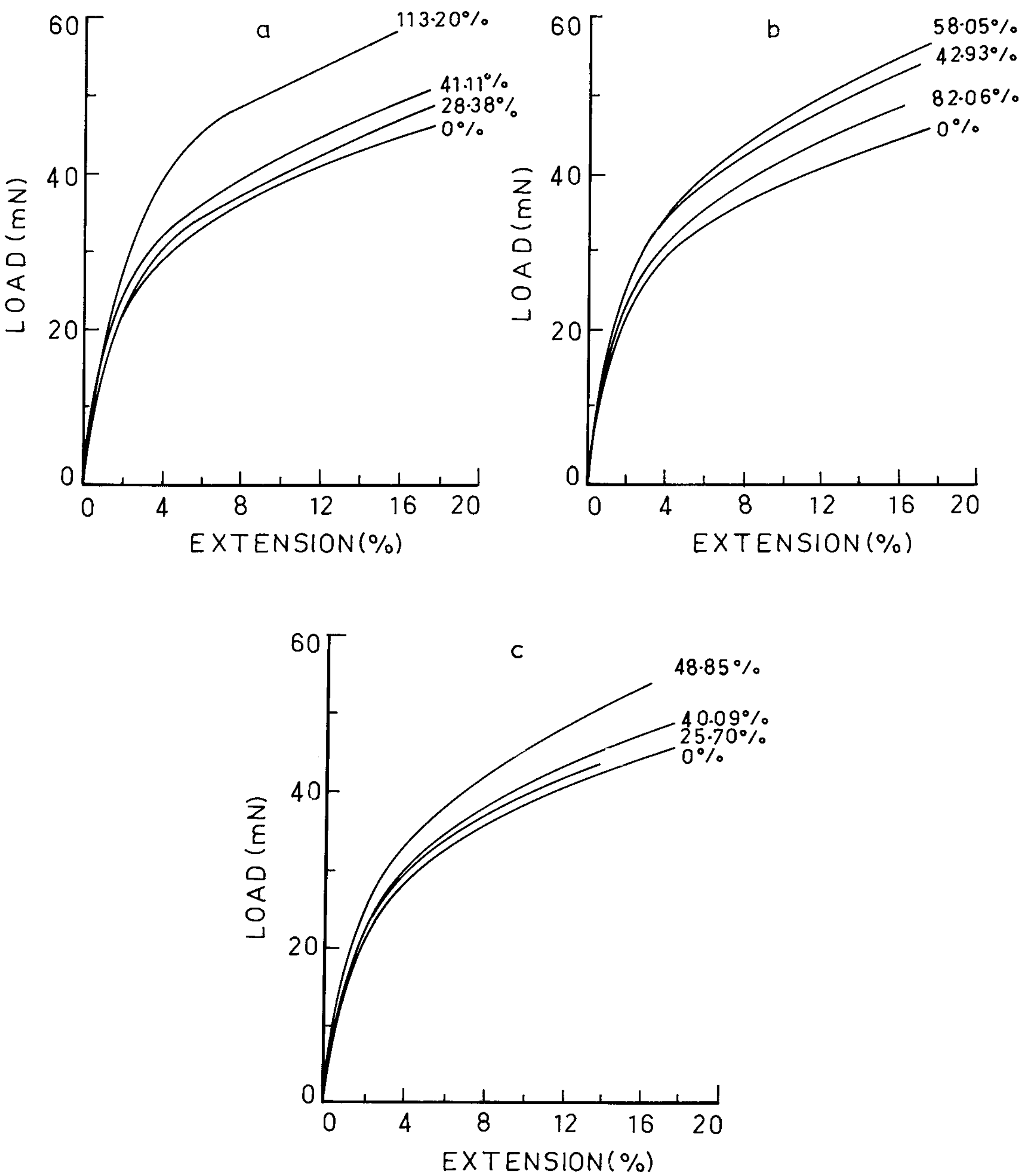

Figure 2 Load-extension curves for silk fibers and MMA-*g*-silk fibers prepared in the presence of (a) acetic acid, (b) methanol, and (c) dimethyl formamide solvents.

Effect of Grafting Percentage on Moisture Regain Properties

Figures 3 and 4 show the moisture regain (%) of silk fibers grafted with MMA under different conditions at different relative humidities. It is observed that the moisture regain decreases with the increase in the percentage of grafting. This may be attributed to the fact that the addition of more and more hydrophobic PMMA chains on the fiber surface lowers the absorption of moisture from the atmosphere. The moisture regain values of MMA grafted silk fibers prepared in the presence of different solvents and with approximately the same level of percentage of grafting are examined and compared to that of ungrafted fiber in Table III. The dependency on solvent is also presented in Table III. The moisture regain value decreases in the order control > methanol > water > DMF > acetic acid. This may be understood by considering the swelling power of solvent to

Table I Tensile Characteristics of MMA Grafted Silk Fibers

Conditions	Grafting (%)	Tenacity (mN/d)	Breaking Extension (%)	Initial Modulus (mN)
Time variation	0	34.50	14.80	35.63
	21.20	27.00	16.25	31.75
	44.07	25.75	17.90	34.95
	65.19	24.75	17.60	37.25
Monomer concn variation	44.07	25.75	17.90	34.95
	69.74	21.50	16.63	35.44
	90.43	19.75	15.31	38.05
Solvent variation				
Dimethylformamide	25.70	22.87	15.10	32.13
	40.09	24.00	17.63	32.40
	48.85	24.25	16.50	36.63
Methanol	42.93	27.00	16.90	35.20
	58.05	26.75	18.25	37.81
	82.06	19.25	16.00	38.80
Acetic acid	28.38	26.50	16.63	33.13
	41.11	25.50	17.25	33.75
	113.20	19.50	16.80	40.75

silk, PMMA, and the miscibility of the solvent with MMA. The swelling power of the solvent follows the same order as that of the moisture regain. Acetic acid, a solvent for both MMA and PMMA, causes high propagation rates and very fast termination rates, resulting in very short PMMA chains that are likely to admix with silk chains, causing the moisture regain to drop more compared to others. On the other hand, methanol, being a weak swelling agent for silk and a non-solvent for PMMA, produced long, consolidated, and tightly coiled PMMA chains, because of very slow propagation and termination rates. These PMMA chains are much more domainlike compared to those of chains produced in an environment likely to favor rapid termination, thereby affecting the moisture regain less. The length of pendent chains produced in the presence of water and DMF are in between those of chains produced from methanol and acetic acid. Of these, the chains produced in the DMF are somewhat shorter because of the high propagation rate compared to those of water.

CONCLUSION

The results obtained from elastic and work recovery and from stress relaxation studies indicate that grafting of MMA on silk improves the recovery properties significantly without affecting the stress relaxation behavior. Moisture regain studies indicate that the shorter the length of grafted PMMA chains, the lower the moisture regain. The

Table II Elastic Work Recovery and Stress Relaxation of MMA Grafted Silk Fibers

Sample Particulars	Solvents	Grafting (%)	Elastic Recovery (%)	Work Recovery (%)	Stress Loss (%)
Silk fiber		0	53.73	28.58	20.52
Silk-*g*-MMA	Water	44.07	62.07	43.18	20.00
	Methanol	42.93	71.43	46.22	23.72
	Dimethylformamide	40.09	75.00	47.92	22.24
	Acetic acid	41.11	75.00	47.01	21.82

The data are the averages of 50 samples.

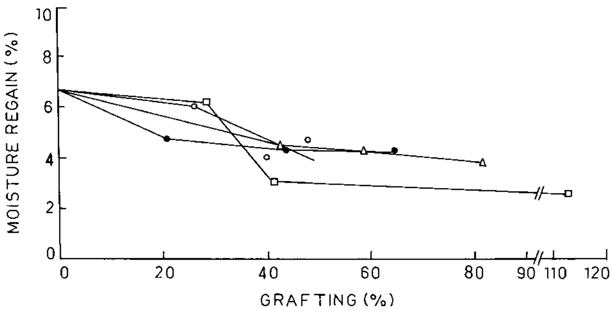

Figure 3 The moisture regain and grafting percentage curves at 40% relative humidity for MMA-*g*-silk fibers prepared in the presence of (●) water, (○) dimethyl formamide, (△) methanol, and (□) acetic acid.

probable reason for this is that, when the percentage of grafting is almost the same, the shorter length of the side chain indicates higher depletion of OH groups, which causes reduction in the moisture absorption.

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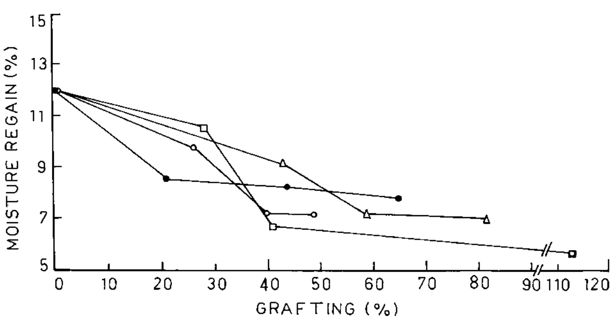

Figure 4 The moisture regain and grafting percentage curves at 65% relative humidity for MMA-*g*-silk fibers prepared in the presence of (●) water, (○) dimethyl formamide, (△) methanol, and (□) acetic acid.

Table III Moisture Regain (%) of MMA Grafted Silk Fibers

		Moisture Regain (%)	
Sample Description	Swelling Agent	at 40% RH	at 65% RH
Ungrafted		6.70	12.05
42.93% graft	Methanol	4.51	9.02
44.07% graft	Water	4.28	8.21
40.09% graft	Dimethyl-formamide	3.99	7.12
41.11% graft	Acetic acid	3.00	6.60

The data are the averages of 50 samples.

REFERENCES

1. Usmanon, Kh. U.; Yullchibacv, A. A.; Valiev, V.; Saidaliev, T.; Muratov, A. Vysokomol Soed Ser A 1978, 20, 1214.
2. Tsukada, M.; Aoki, A. Nippon Sanshigaku Zasshi 1985, 54, 354.
3. Tsukada, M.; Shiozaki, H. J Appl Polym Sci 1990, 39, 1289.
4. Tsukada, M.; Yamaguchi, Y. Nippon Sanshigaku Zasshi 1987, 56, 157.
5. Chiaki, M.; Tokunaga, T.; Nakazato, A. Gyomu Hokoku-Gunma-Ken Seni Kogyo Shikenj, 1978 (Publ. 1979), 24-6 Chin Abstr 106, 198361, 1987.
6. Tokunaga, T.; Senshokuto Kako 1986, 2947; Chin. Abstr 106, 19836f, 1987.
7. Mohanty, N.; Torasia, S. N.; Mohanta, M. C.; Roat, D. K.; Das, H. K. J Macromol Sci Chem A 1983, 20, 409.
8. Ishill, S.; Hirata, A. Seni Seihin Shohi Kagaku 1985, 26, 176; Chin Abstr 103, 55355, 1985.
9. Tsukada, M.; Yamaguchi, Y. J Ser Sci Jpn 1987, 56, 157.
10. Tsukada, M. J Ser Sci Jpn 1984, 53, 380.
11. Maji, T. K.; Banerjee, A. N. J Appl Polym Sci 1999, 73, 2187.
12. Skinle, J. H. Textile Testing: Physical, Chemical and Microscopical; Chemical Publishing Co., Inc.: New York, 1940; 246.