Mechanical Property Studies of Poly(methyl methacrylate)-Grafted Viscose Fibers

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ABSTRACT: Graft copolymerization of methyl methacrylate (MMA) on viscose fibers (grade 1.5 × 51 mm; Nagda; grey staple; bright bleached) was studied under a photoactive condition with visible light using conventional Mohr's salt–potassium persulphate as the redox initiator. The mechanical properties of the grafted viscose fiber, such as tenacity, breaking extension, and initial modulus were studied. The effect of monomer–solvent combination on viscoelastic nature (elasticity work recovery and stress relaxation) of the grafted fibers have also been explained. The moisture regain characteristics of the grafted fibers were also studied. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2585–2591, 1998

Key words: graft copolymerization; viscose fiber; stress relaxation; tenacity; moisture regain

INTRODUCTION

Modification of viscose fiber properties through grafting has been the subject of many investigations in recent years. Grafting of vinyl monomer onto viscose fiber has improved various properties.[1–3] Various methods have been employed for graft copolymerization of vinyl monomers onto viscose fibers, such as high-energy radiation [1,4–6] and redox systems.[7–17] However, only limited information regarding the grafting of vinyl monomers onto viscose fibers under visible light is available in the literature. The present article reports the effect of grafting of MMA on viscose fibers under different conditions on tenacity, breaking extension, and initial modulus. The results of elasticity, work recovery, stress relaxation, and moisture regain characteristics of the grafted fibers are also reported in the present work.

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Journal of Applied Polymer Science, Vol. 69, 2585–2591 (1998)
 CCC 0021-8995/98/132585-07

EXPERIMENTAL

Materials

Processed viscose fiber was obtained by the courtesy of Jayasree Textiles, Rishra, West Bengal, India. Methyl methacrylate (MMA) was obtained from a local market and purified by standard procedures.[18] Mohr's salt (AR grade) obtained from Glaxo Laboratories, India, and potassium persulphate (AR Grade) from E. Merck, Germany, were used without further purification. All the solvents used were of analytical grade and were obtained from E. Merck, Germany (used without further purification). Photografting, homopolymer separation, and calculations for the percentage of grafting were done following general standard procedure.[19]

Measurements

Single fiber tests were carried out on samples selected randomly and conditioned at 25°C and 65% relative humidity (RH) using a Zwick Tensile Tester (Model 1445) for examining the mechanical

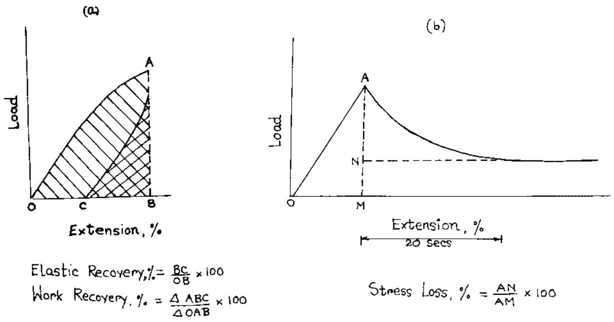

Figure 1 (a) Schematic diagram of elastic and work recovery. (b) Schematic diagram of stress relaxation.

characteristics of MMA-grafted viscose fibers under different conditions. The gauge length and rate of extension were 10 mm and 10 mm/min, respectively. The load–extension curves were obtained from the recorder chart. The breaking load, breaking extension, and force at 5% extension were obtained from the printer of the tensile tester. From these data, tenacity and initial modulus at 5% extension for single fibers were computed.

For elastic and work recovery, a single fiber was given one-extension cycling up to the maximum level of extension of 5% at a gauge length of 10 mm and a rate of extension of 6 mm/min. From the extension cycling curves obtained for 50 samples, the average elastic recovery and work recovery were computed as shown in Figure 1(a).

In case of studying stress relaxation, a single fiber was stretched at a speed of 6 mm/min up to an extension of 5% and kept at that extension level for a time period of 20 s. The relaxation in stress was recorded on the plotter graph. From the graphs, stress loss in 20 s was determined, as shown in Figure 1(b).

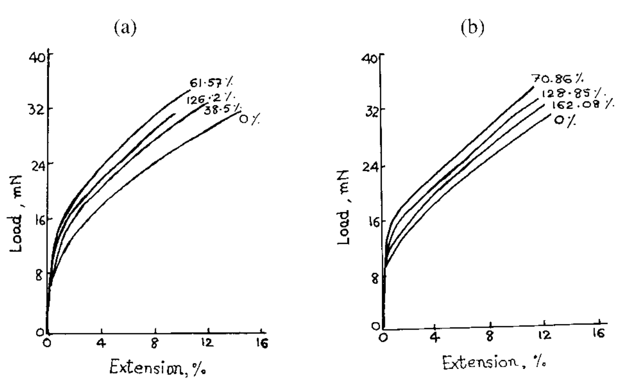

Figure 2 Typical load–extension curves for viscose fiber and MMA-grafted viscose fibers: (a) variation in monomer concentration; (b) variation in the time of polymerization.

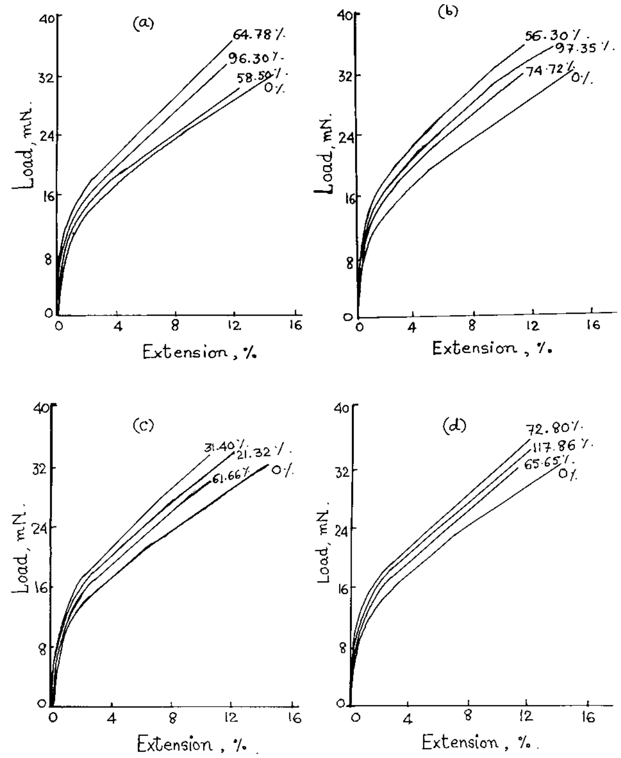

Figure 3 Typical load–extension curves for viscose fiber and MMA-grafted viscose fibers, where grafting has been done in different solvent media: (a) formic acid; (b) dioxane; (c) methanol; (d) tetrahydrofuran.

The moisture regain is defined as the weight of moisture present in a textile material and is expressed as a percentage of the oven dry weight. Thus,

$$\text{Moisture regain } (\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 denote the dry and conditioned weights, respectively.

Samples were kept in a vacuum desiccator containing phosphorus pentoxide for 6 to 8 weeks and then weighed. This process was repeated until the weight became constant. This was taken as dry weight, W_1. After drying, the samples were conditioned at 25°C and at relative humidities of 40% and 65% for 72 h and reweighed until the weight became constant. For obtaining different relative humidities, solutions of sulphuric acid of different concentrations were used.[20]

RESULTS AND DISCUSSIONS

The typical load–extension curves, shown in Figures 2 and 3 for viscose and MMA-grafted viscose

Table I Elastic and Work Recovery of MMA-Grafted Viscose Fibers

Sample Particulars	Swelling Agent	% Graft	Elastic Recovery (%)	Work Recovery (%)
Viscose fiber	—	0	55.8	22.5
Viscose-*g*-MMA	Water	65.95	61.0	32.1
	Methanol	61.66	56.3	22.8
	Dioxane	65.90	56.3	25.3
	Formic acid	64.78	67.4	33.3
	Tetrahydrofuran	65.66	61.9	35.2

fibers (where the percentage of grafting has been varied by varying the time of polymerization and the concentration of MMA and by using various solvent media) indicate that overall mechanical behavior up to rupture is not much affected by MMA polymers, even at high percentages of grafting but is affected by the type of solvent used (Table I).

TENACITY

As shown in Figure 4, it is observed that fiber tenacity decreases continuously with the percentage of grafting, and the decreasing trend becomes more rapid when the percentage of grafting is increased by an increasing monomer concentration than when it is increased by an increasing polymerization time. This indicates that with more and more monomer molecules available in the solvent, grafting occurs more heterogeneously within the fiber matrix, creating a higher number of stress concentration sites, thus lowering its load-bearing capacity. The reduction in fiber tenacity with an increasing percentage of grafting (Fig. 5) has been found to be more or less of the same order when different solvents have been used for varying the grafting percentage. This may be explained by the fact that fiber strength is deter-

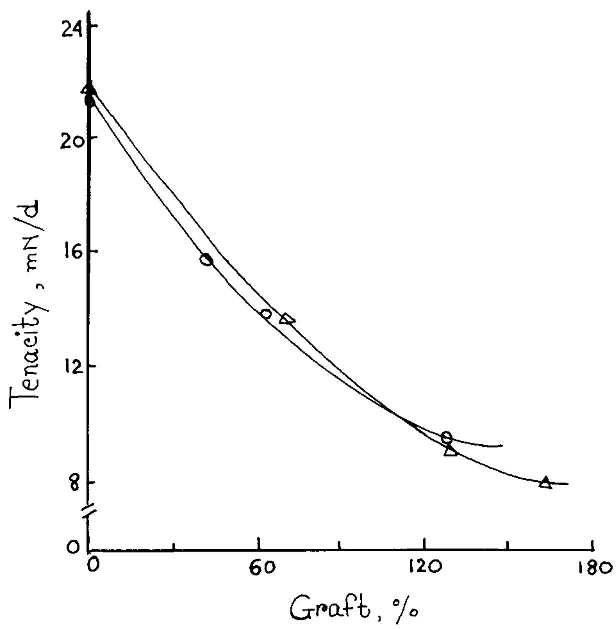

Figure 4 Tenacity versus the percentage of grafting curves for MMA-grafted viscose fibers: (△) variation in the time of polymerization; (○) variation in the monomer concentration.

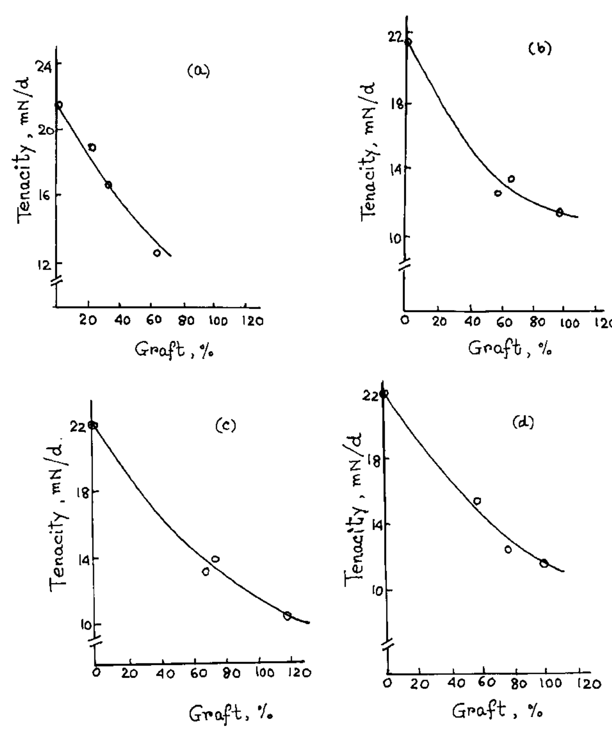

Figure 5 Tenacity versus the percentage of grafting curves for MMA-grafted viscose fibers prepared under different solvents: (a) methanol; (b) formic acid; (c) tetrahydrofuran; (d) dioxane.

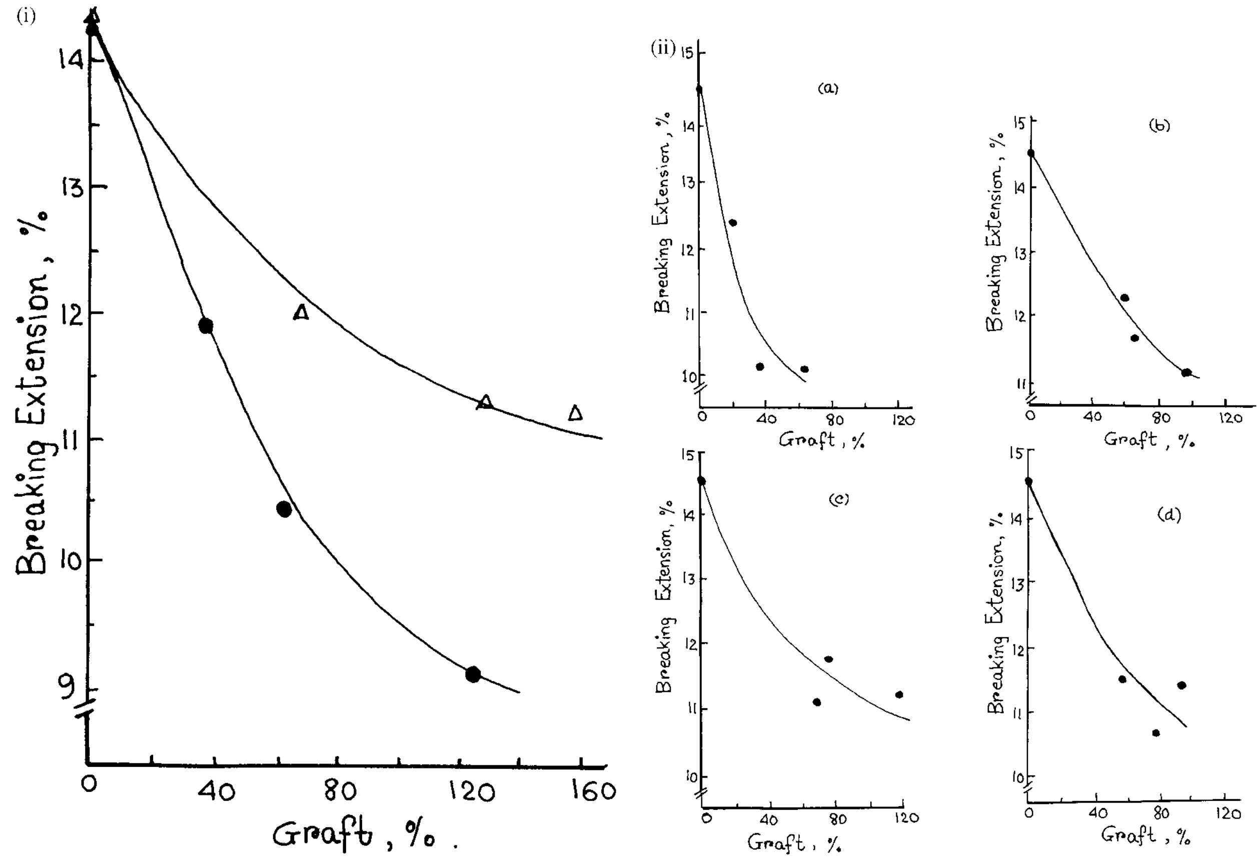

Figure 6 (i) Breaking extension versus the percentage of grafting curves for MMA-grafted viscose fibers: (△) variation in time of polymerization; (●) variation in monomer concentration. (ii) Breaking extension versus the percentage of grafting of MMA-grafted viscose fibers prepared under different solvents: (a) methanol; (b) formic acid; (c) tetrahydrofuran; (d) dioxane.

mined mostly by the degree of stress concentration rather than by the effect of dispersion of the monomers in different solvents.

BREAKING EXTENSION

Figure 6 shows the extension at break of viscose fibers grafted with MMA under different conditions. With the increase in the percentage of grafting, the breaking extensions follow a decreasing trend. This may be attributed to the occurrence of more stress concentration points at a high grafting percentage, which leads to early rupture.

INITIAL MODULUS

The initial modulus value initially increases and then decreases with an increasing graft percentage as shown in Figure 7. The rise may be attributed to the stiffening of the disordered region due to the deposition of MMA polymer, and the latter decreasing trend may be due to the gradual reduction in interchain cohesion, augmenting slippage of chain ends, as a higher amount of graft polymer gets deposited inside the fiber matrix.

EFFECT OF MONOMER–SOLVENT COMBINATION ON THE VISCOELASTIC NATURE OF GRAFTED FIBER

In order to study this effect, fibers with approximately the same add-on percentage of polymer, but grafted using different solvents or swelling agents, have been considered for testing. The stress relaxation and recovery properties have been studied with fibers having around 65% grafted MMA.

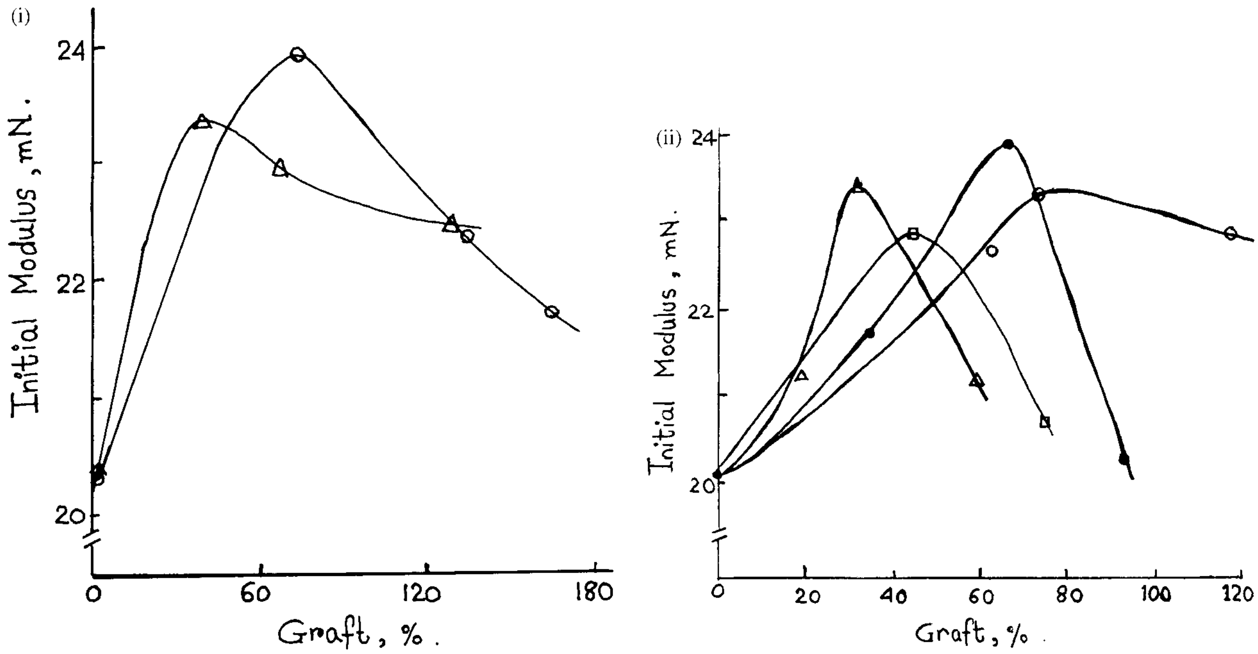

Figure 7 (i) Initial modulus versus percentage curves for MMA-grafted viscose fibers: (○) variation in time of polymerization; (△) variation in monomer concentration. (ii) Initial modulus versus graft percentage curves for MMA-grafted viscose fibers prepared using different solvents: (○) tetrahydrofuran; (△) methanol; (●) formic acid; (□) dioxane.

ELASTIC AND WORK RECOVERY VALUES

The elastic and work recovery values of MMA-grafted viscose fibers are presented in Table I. The grafted fibers show improvement in elastic and work recovery as compared to ungrafted fibers. This may be explained by the fact that the expected increase in internal viscosity due to deposition of stiff MMA polymer is offset by the reduction in interchain interactions.

STRESS RELAXATION

The stress relaxation values using different solvents are shown in Table II. The grafted fibers show slightly higher stress loss percentages compared to ungrafted fiber. This may be attributed to the counterbalancing of reduction in intercellulose chain interaction by the increase in rigid PMMA–PMMA and PMMA–cellulose chain interactions. Stress relaxation is found to be maximum in the case of viscose fiber grafted in the presence of dioxane, compared to the other solvents, as dioxane provides better dispersion of polymer in the fiber matrix.

MOISTURE REGAIN CHARACTERISTICS

The effect of grafting on moisture regain are shown in Figure 8(a, b) at 40 and 65% RH, respec-

Table II Stress Relaxation in MMA-Grafted Viscose Fibers

Sample Particulars	Swelling Agent Used	% Graft	Stress Loss (%)
Viscose fiber	—	0	27.20
Viscose-*g*-MMA	Water	65.95	28.10
	Methanol	61.66	28.30
	Dioxane	65.90	29.40
	Formic acid	64.78	25.00
	Tetrahydrofuran	65.66	28.40

Table III Moisture Regain (%) Value of MMA-Grafted Viscose Rayons

Sample Description	Swelling Agent	Moisture Regain at 40% RH	Moisture Regain at 65% RH
Ungrafted	—	10.36	15.35
61.66% graft	Methanol	6.29	10.06
65.66% graft	Tetrahydrofuran	5.39	9.88
65.90% graft	Dioxane	5.74	9.92
64.78% graft	Formic acid	4.63	7.17

tively. In all cases, moisture regain follows a declining trend as the percentage of grafting rises. This is due to the addition of the hydrophobic natured PMMA chains on the fiber surface. To study the effect of different swelling agents on the moisture regain properties, grafted fibers using the different swelling agents and having about the same percentage of grafting were chosen and examined at 40 and 60% RH and compared to ungrafted fiber. The results are shown in Table III. The data indicate that the percentage of moisture regain of the different grafted fibers at both relative humidities are lower compared to the ungrafted fiber. Also, the graft copolymer prepared in the presence of methanol has slightly higher moisture regain compared to the graft copolymers prepared in the presence of other solvents. This may be possibly due to the fact that methanol, which is neither a solvent nor a swelling agent for PMMA, causes very slow termination rates, resulting in long, consolidated, tightly coiled PMMA chains, which are much more domain-like than PMMA produced in an environment likely to favor rapid termination and short chain formation. On the other hand, short chains of approximately the same level of grafting are more likely to admix with the viscose fiber, resulting in a drop in the moisture regain.

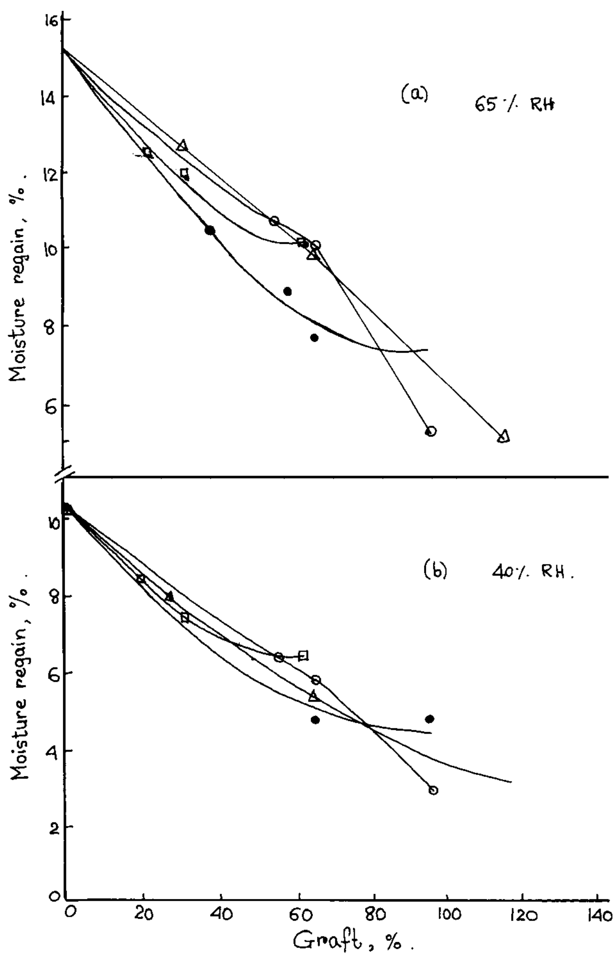

Figure 8 Moisture regain versus graft percentage at 40 and 65% relative humidities for MMA-grafted viscose fibers prepared under different solvents: (●) formic acid; (○) dioxane; (□) methanol; (△) tetrahydrofuran.

CONCLUSION

Tenacity and extension at break of the MMA-grafted viscose fibers are lower than the ungrafted ones and decreases with an increasing grafting percentage. The initial modulus, though it first increases, follows a declining trend with a rise in the percentage of grafting. The grafted fibers, however, exhibit an improvement in elastic and work recovery characteristics and higher stress loss percentages compared to ungrafted fibers. The moisture regain value is higher in the case of the ungrafted fiber.

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