Grafting Vinyl Monomers onto Silk (*Bombyx mori*) Using Different Initiators: Properties of Grafted Silk

MASUHIRO TSUKADA,[1] TAKAYUKI ARAI,[1] GIULIANO FREDDI,[2] TSUNEO IMAI,[1] NOBUTAMI KASAI[3]

[1] National Institute of Sericultural and Entomological Science, 1-2 Owashi, Tsukuba, Ibaraki 305-8634, Japan

[2] Stazione Sperimentale per la Seta, via Giuseppe Colombo 83, 20133 Milan, Italy

[3] Kobe Womens' University, Suma, Kobe 654, Japan

ABSTRACT: The graft–copolymerization of silk with methacrylamide (MAA), 2-hydroxyethyl methacrylate (HEMA), and methyl methacrylate (MMA) was studied using three different free-radical initiators: an inorganic peroxide [ammonium persulfate (APS)] and two azo compounds [2,2′-azobisisobutyronitrile (AIBN) and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (ADC)]. The rate and yield of grafting followed the order: APS > AIBN > ADC. The performance of AIBN was close to that of APS in terms of weight gain attained. The degree of yellowing of grafted silk varied as a function of the initiator–monomer system used. APS induced the highest degree of yellowing, regardless of which monomer was used, whereas silk grafted with the MAA/AIBN system displayed the lowest level of yellowing. Moisture regain of grafted silk changed as a function of the hydrophilic/hydrophobic character of the grafted polymer, regardless of the kind of initiator used. Accordingly, tensile properties showed a tendency to decrease with increasing weight gain of grafted silk, the extent of which was independent of the kind of monomer and initiator used. The different initiators did not induce any appreciable change in the fine structure of silk, as demonstrated by optical measurements. Uneven surface deposition of homopolymer was detected to variable extent with MMA and HEMA grafting, whereas the surface of MAA-grafted silk was completely free of any foreign deposit, independently of the initiator used. © 20012001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1401–1409, 2001

Key words: silk grafting; methacrylamide; 2-hydroxyethyl methacrylate; methyl methacrylate; ammonium persulfate; 2;2′-azobisisobutyronitrile; 2;2′-azobis(2-methyl-propionamidine) dihydrochloride

INTRODUCTION

Grafting is a well-established technique used to cause more or less extensive modification of properties and textile performance of silk, as well as other natural and synthetic fibers.[1,2] A great number of studies dealing with silk grafting, which appeared in the scientific literature during the last three decades, stimulated the development of industrial treatments currently performed on a routine basis for the production of specific textile articles (mainly kimonos, necktie yarns and fabrics, borders, embroidery). Grafting was originally introduced as an alternative to the traditional mineral weighting technique, to in-

crease silk weight and compensate for the loss resulting from degumming. However, in recent years grafting has been regarded as a powerful method for improving inferior textile performance of silk, such as crease recovery, dimensional stability, rub resistance, color fastness, and water and oil repellency.[1]

The range of vinyl monomers potentially useful for silk grafting is very wide. However, methacrylamide (MAA),[3–5] 2-hydroxyethyl methacrylate (HEMA),[6,7] and methyl methacrylate (MMA)[8–10] have been used to a greater extent on both laboratory and industrial scale. Advantages and drawbacks related to their application have been well elucidated. For example, it is well known that yellowing of silk may occur during grafting.[11,12] To overcome this drawback, suitable posttreatments are usually conducted, such as bleaching, although they entail additional costs in terms of time, energy, and chemical consumption. For this reason we were interested to undertake a study on the problem of silk yellowing associated with grafting. In a recent study[13] we reported the results of a systematic investigation on the role of different initiators [an inorganic peroxide: ammonium persulfate; and two azo compounds: 2,2′-azobisisobutyronitrile and 2,2′-azobis(2-methylpropionamidine) dihydrochloride] in inducing the yellowing of silk, as well as on the reaction conditions (initiator concentration, temperature, type of vinyl monomer), which are likely to enhance the degree of yellowing. The results emphasized the role of the initiator as the chemical agent mostly responsible for yellowing. In particular, the inorganic peroxide induced the highest degree of yellowing, whereas the azo compounds appeared safer from this point of view, enabling us to propose their use as free-radical initiators for the graft–copolymerization of vinyl monomers onto silk.

In this study, the most recent results on silk grafting with different initiator–monomer systems are reported. The rate and yield of grafting were studied as functions of monomer concentration, and the physical, mechanical, and morphological properties of grafted silk fibers were investigated. The results obtained seem highly promising for improving silk-grafting techniques at the industrial level.

EXPERIMENTAL

Materials

Silk fibers from *Bombyx mori* silkworm were used as grafting substrate after sericine removal by conventional alkaline degumming. Reagent-grade methacrylamide (MAA), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), ammonium persulfate (APS), 2,2′-azobisisobutyronitrile (AIBN), and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (ADC) were purchased from Wako Pure Chemicals (Tokyo, Japan), and used without further purification. The nonionic emulsifying agent Noigen HC was obtained from Daiichi Kogyo Seiyaku Co. (Japan). The chemical structures of the free-radical initiators are as follows:

$$(NH_4)_2S_2O_8$$
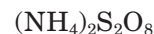
APS
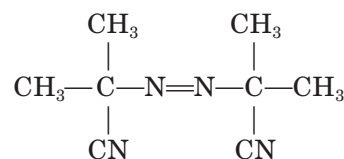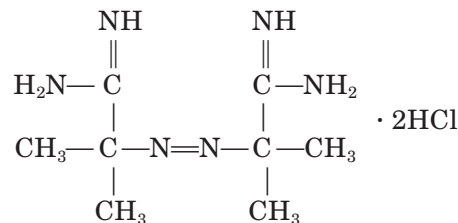
AIBN

ADC

Grafting was performed by immersing silk in the reaction system at pH 3 (adjusted with formic acid), containing 3% Noigen HC on the weight of fiber (owf), 2% owf initiator (APS, AIBN, or ADC), and the required amount of monomer (from 25 to 75% owf). The material-to-liquor ratio of 1 : 15 was maintained. The temperature was gradually raised from room temperature to the desired value (80°C) in 45 min and then maintained constant for the time required. At the end of the reaction, silk was soaked for 30 min at 80°C with distilled water containing 1 mL/L Noigen HC to remove the unreacted monomer, rinsed several times, and dried at room temperature.

Measurements

Weight gain and grafting efficiency were calculated on the basis of the weight of oven-dried silk

Table I Weight Gain (W.G.) and Grafting Efficiency of Silk Grafted with Different Vinyl Monomers (MMA, HEMA, and MAA: 75% owf) and Initiators (APS, AIBN, and ADC: 2% owf) for 2 h at 80°C

	APS		AIBN		ADC	
	W.G. (%)	Efficiency (%)	W.G. (%)	Efficiency (%)	W.G. (%)	Efficiency (%)
MMA	44.5	59.7	39.8	53.0	29.3	39.0
HEMA	60.2	80.3	59.0	78.6	49.8	66.4
MAA	47.3	63.1	36.0	48.1	25.2	33.6

owf, on the weight of fiber.

before and after the grafting procedure. A correction was made for the eventual weight loss occurring during the treatment in the reaction system, by comparison with a blank sample treated without monomer.

Color change of grafted silk was measured with a color difference meter–type CR-2000 spectrophotometer (Minolta Co., Japan) on the basis of the *L-a-b* system. The b^* parameter, denoting yellowing, was used as an index of the degree of silk yellowing. The higher the b^* value, the higher the yellowing of silk.

Moisture regain was determined on samples kept at 20°C and 65% relative humidity (R.H.) for 7 days and expressed as grams of moisture/100 g silk.

Tensile properties were measured with a Tensilon UTM-II (Toyo Boldwin Co., Japan), using the standard technique at 20°C and 65% R.H. at a gauge length of 100 mm and strain rate of 40 mm/min.

Refractive indices were measured using the Becke's line method, using a polarized microscope under monochromatic (Na) light at 20°C and 65% R.H. The measurement procedure was previously described in detail elsewhere.[14]

Surface morphology was examined with a Stereoscan 440 (LEO Electronic Microscopy Ltd., Cambridge, UK) scanning electron microscope, at 10 kV acceleration voltage, after gold coating.

RESULTS AND DISCUSSION

Kinetics of Silk Grafting with Different Initiators

The performance of the two azo initiators AIBN and ADC for silk grafting was studied by using the conventional aqueous reaction system containing MMA, HEMA, or MAA as the grafting agent. The inorganic peroxide APS, which is ex-

tensively used as a free-radical initiator for silk grafting on both laboratory and industrial scale,[1] was used as reference. Table I summarizes the results of weight gain and grafting efficiency of silk grafted with the three different initiators in the same experimental conditions (i.e., same initiator and monomer concentration, material-to-liquor ratio, time, and temperature). The weight gain and grafting efficiency followed the order APS > AIBN > ADC, irrespective of the kind of monomer used.

To investigate some kinetic aspects of the grafting process, the monomer concentration [*M*] was varied in the range 0.1–0.6*M*. This range covers the monomer-to-fiber ratios currently applied in industrial grafting of silk.[1] The rate of grafting (R_g) was calculated on the basis of the slope of the weight gain versus time curves at 2 h reaction time. The weight gain increased steadily with increasing the amount of monomer available in the reaction system. The plots of R_g versus [*M*] of the various initiator–monomer systems are shown in Figures 1 to 3. The rate of grafting displayed by the different grafting systems was in the order APS > AIBN > ADC. In all tests the best fit of the experimental results was obtained with a linear regression curve. The values of the correlation coefficients are given in the graphs and ranged from 0.973 to 1.

The kinetics of the graft–copolymerization of vinyl monomers onto silk has been extensively investigated by Nayak and coworkers.[15–18] The accumulated data support the free-radical reaction mechanism in which the kinetic chain reaction consists of at least three basic steps: (1) initiation, involving the formation of silk and/or monomer radicals; (2) propagation, implying a series of identical reactions repeated many times, leading to growth of polymer chains; and (3) termination, which ends the kinetic chain reaction.
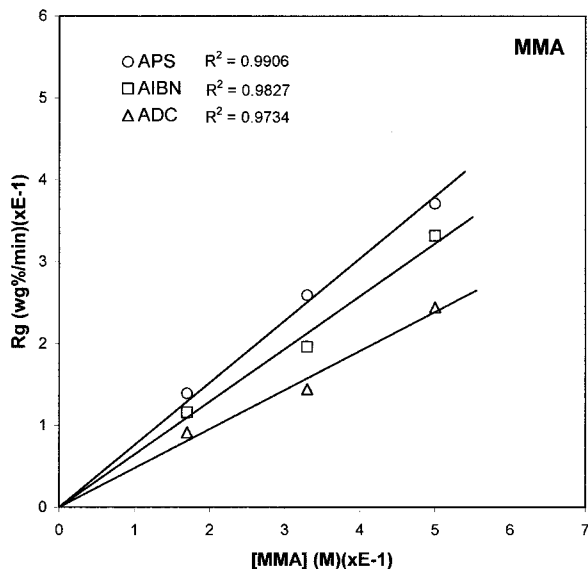
Figure 1   Rate of grafting versus monomer concentration of MMA silk grafting with different initiators.

Assuming the steady-state hypothesis, a rate equation was derived in which the rate of grafting is directly proportional to the monomer concentration. The linearity of the relation between R_g and $[M]$ observed in our tests is in good agreement with the established reaction mechanism. In particular, the results of MMA (Fig. 1) are consistent with a typical first-order kinetics, because the lines pass through the origin, regardless of which initiator was used. Likewise, the
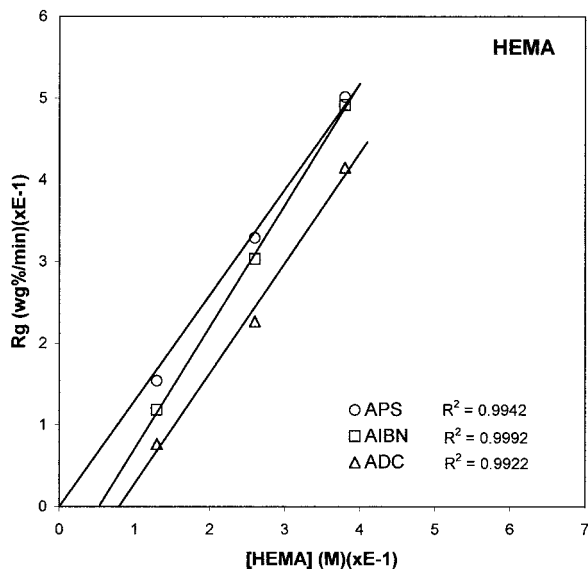

Figure 2   Rate of grafting versus monomer concentration of HEMA silk grafting with different initiators.
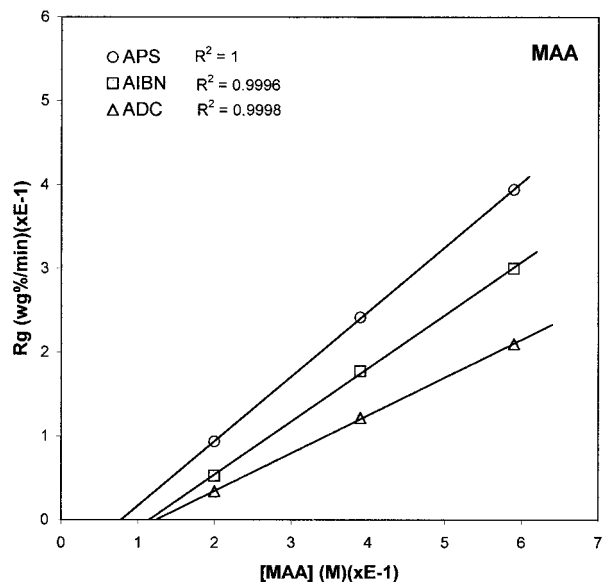

Figure 3   Rate of grafting versus monomer concentration of MAA silk grafting with different initiators.

results of grafting HEMA with APS as the initiator showed the same trend (Fig. 2). However, in the other grafting systems, that is, HEMA with AIBN or ADC (Fig. 2), and MAA with APS, AIBN, or ADC (Fig. 3), the lines did not intersect the origin of the axes, but showed slight deviations from the expected trend. If the origin of the axes is included in the computation, the best fit of the data points is given by a regression curve of the type $y = ax^n$, with $1 < n < 2$. These findings seem to indicate that, in some cases, the grafting reaction did not follow a pure first-order kinetics. Further studies directed to elucidate these aspects of the reaction mechanism are in progress.

The results obtained show that the rate and yield of grafting are influenced by the kind of initiator used, and confirm the superior performance of APS, regardless of the monomer used. Although ADC displayed the lowest performance in terms of both rate and yield of grafting, AIBN may compete with the peroxide as a suitable candidate for silk grafting in consideration of the fairly high weight gains attained. The subsequent results on physical and morphological properties of grafted silk will contribute additional information on the possibility of introducing AIBN in the number of initiators useful for silk grafting.

Degree of Yellowing

In a previous study[13] silk yellowing was systematically investigated as a function of grafting tem-
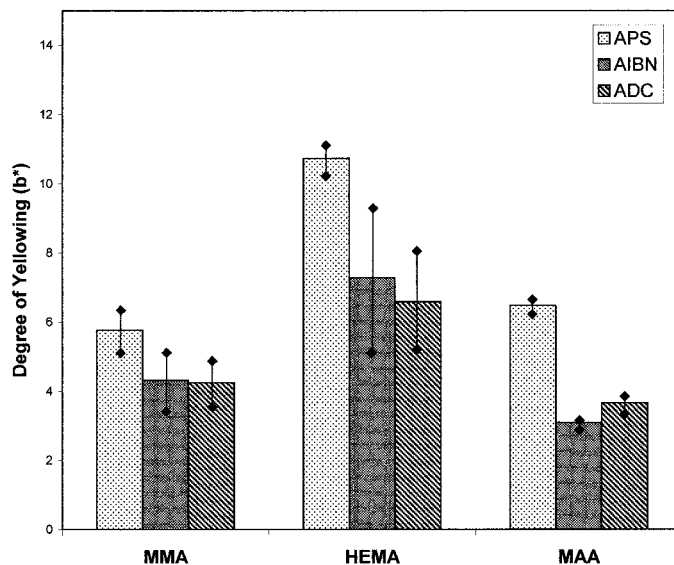
Figure 4 Degree of yellowing of silk grafted with MMA, HEMA, and MAA with different initiators.

perature, initiator concentration, and kind of monomer used. It was elucidated that the initiator is mainly responsible for yellowing as a result of its ability to interact with potentially reactive sites of the fibrous substrate through formation of silk macroradicals. As expected, the effect is temperature and concentration dependent, that is, the higher temperature and initiator concentration, the higher the degree of yellowing. The grafted polymer may either reduce or enhance the yellowing effect brought about by the initiator, depending on the kind of vinyl monomer used and grafting temperature.

The degree of yellowing of the silk samples prepared in this study was determined spectrophotometrically and expressed by means of the parameter b^*. Figure 4 shows the results obtained. The height of the bars represents the average values of b^*, whereas the error bars show the variability associated with each set of measurements. Because samples within each group had different weight gains (from 10 to 50–60%), the observed variability must be mainly associated with this parameter. It was generally low, except for silk grafted with HEMA/AIBN or ADC (the higher the weight gain, the higher the degree of yellowing).

The results obtained are substantially consistent with the previous results,[13] indicating that the degree of yellowing is both monomer and initiator dependent. Silk grafted with HEMA exhibited the highest values of b^*, regardless of which

initiator was used. Comparing the effect of the different initiators, APS induced the highest levels of yellowing. The difference in the degree of yellowing between the samples grafted with APS and those grafted with AIBN or ADC was statistically significant, regardless of which monomer was used, as indicated by the results of the t test $(t_{(\text{APS versus AIBN; APS versus ADC})} \gg t_{5;95\%})$. Silk grafted with the MAA/AIBN grafting system displayed the lowest degree of yellowing. This result is of particular interest because MAA is the most popular vinyl monomer used in industrial grafting of silk. The replacement of the conventional initiator (usually an inorganic peroxide such as APS) with a new one possessing comparable grafting efficiency but lower yellowing power, such as the azo compound AIBN, might significantly contribute to improve the process.

Moisture Regain

Figure 5 shows the plot of moisture content as a function of weight gain of silk fibers grafted with different initiator–monomer systems. Silk grafted with the same monomer followed the same trend, irrespective of the initiator used. With increasing the weight gain, the moisture content of MAA-grafted silk increased linearly, that of MMA-grafted silk decreased, whereas HEMA-grafted silk did not change with respect to the control sample.

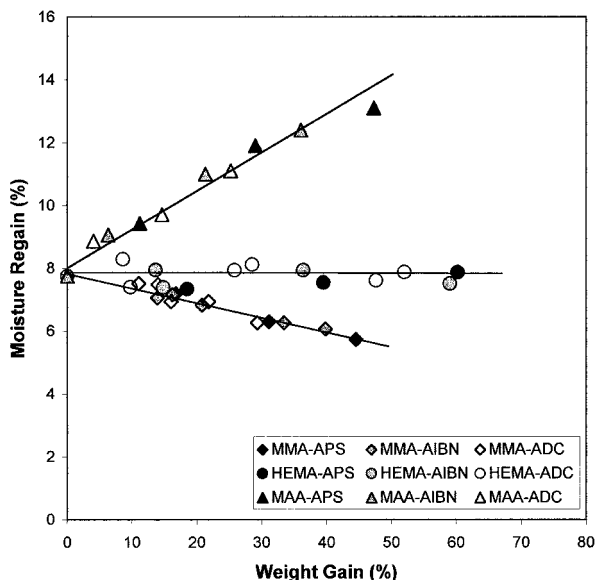The ability of grafted silk to absorb and bind water is closely related to the hydrophobic/hydro-

Figure 5 Moisture regain versus weight gain of silk grafted with MMA, HEMA, and MAA with different initiators.

Figure 6 Tensile strength versus weight gain of silk grafted with MMA, HEMA, and MAA with different initiators.

philic balance of the silk/polymer combination. Although the grafted polymer is thought to form separate domains within the silk matrix, filling the void space available in the amorphous regions and limiting chemical and physical interactions with silk fibroin chains to boundary contacts, its relative contribution to the total amount of absorbed water may become significant, especially at medium-to-high weight gain. Poly(MAA) is hydrophilic in nature and enhances moisture absorption, as demonstrated by the positive slope of the curve. On the other hand, the hydrophobicity of poly(MMA) induces a steady decrease of moisture content, whereas the intermediate properties of poly(HEMA) do not significantly influence the balance of absorbed moisture.

Tensile Properties

Intrinsic tensile properties of silk are influenced by grafting as a result of various physicochemical and morphological changes.[1] The former refer to selective cleavage of covalent bonds and other weak interactions sensitive to grafting temperature, pH, chemicals, and so forth. The latter mainly consist in the increase in fiber size, induced by filling silk with an almost inert material, from the viewpoint of mechanical performance.

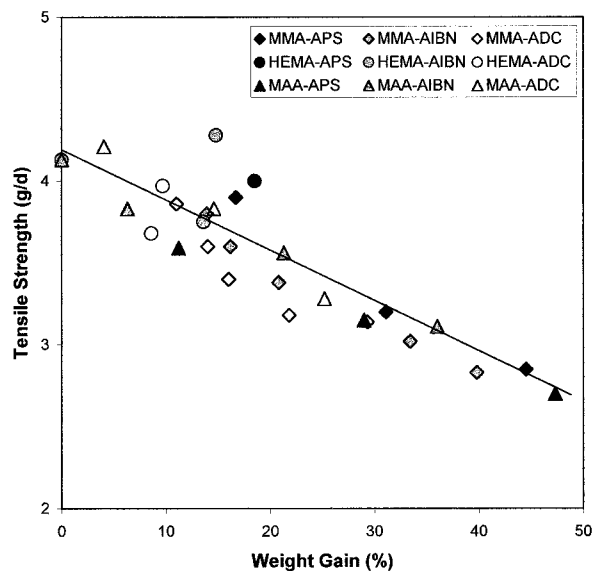Tensile strength, elongation at break, and energy of MMA-, HEMA-, and MAA-grafted silk fi-

bers decreased with increasing weight gain (Figs. 6-8). It is interesting to note that the values of tensile strength fit the same regression curve, regardless of monomer and initiator used. The same trend was observed for elongation at break and energy, although the experimental data showed a slightly wider scattering.
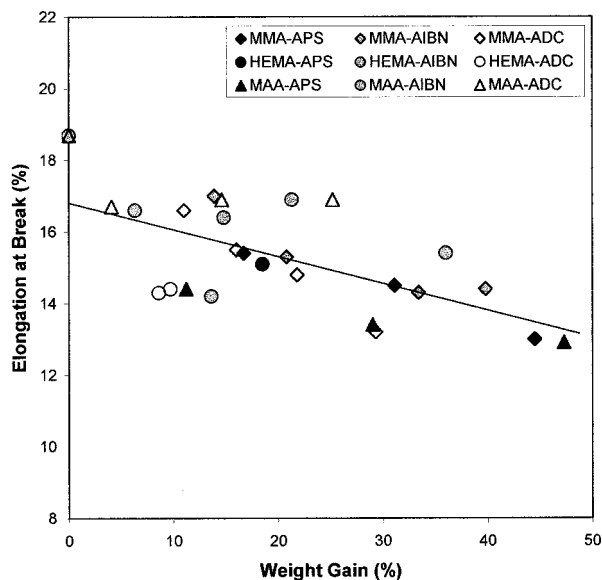

Figure 7 Elongation at break versus weight gain of silk grafted with MMA, HEMA, and MAA with different initiators.
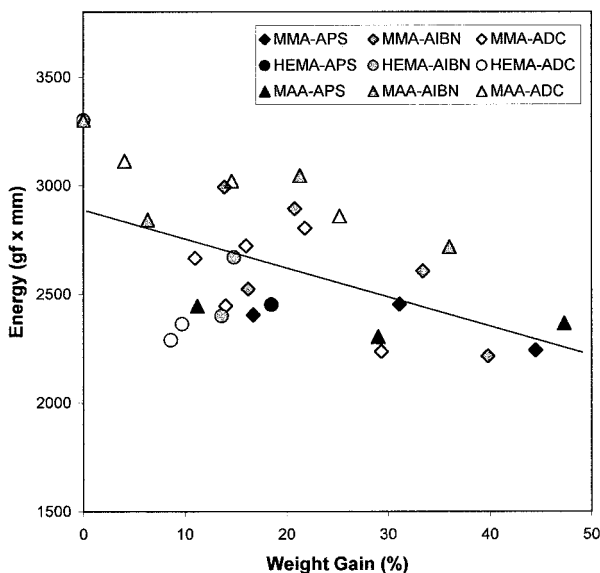
Figure 8 Energy versus weight gain of silk grafted with MMA, HEMA, and MAA with different initiators.

Grafting resulted in a general loss of tensile performance of silk, in good agreement with previously reported results.[1] The intrinsic physicochemical characteristics of the grafted polymer are known to exert only a marginal effect on the tensile properties of grafted silk. On the basis of the present results we may infer that the effect of the initiator must be considered negligible as well. The drastic changes in fiber morphology, that is, increase of fiber cross-sectional area, as well as other factors, such as disordering of chain arrangement, steric hindrance, increase in fiber density as a consequence of polymer loading, and the presence of newly established boundary interactions between silk fibroin chains and grafted polymer, must be considered mainly responsible for the observed drop of fiber strength, extensibility, and toughness induced by grafting.

Optical Properties

Optical measurements, that is, birefringence (Δn) and isotropic refractive index (n_{ISO}), were used to detect fine structural changes eventually induced by treating silk with the different initiators, in the absence of monomer. The results are listed in Table II. No significant changes were observed in values of either Δn or n_{ISO} with respect to the control sample. We may therefore conclude that the different initiators did not induce any change in the fine structure of silk in the conditions adopted for grafting.

Table II   Birefringence (Δn) and Isotropic Refractive Index (n_{ISO}) of Silk Treated with Different Initiators at 80°C for 2 h Without Grafting Agent

Initiator	Δn	n_{ISO}
Control	0.050	1.553
APS	0.048	1.554
AIBN	0.049	1.552
ADC	0.050	1.553

Surface Morphology of Grafted Silk Fibers

The appeal of silk consists primarily in its smooth and shiny surface, whose modification may seriously impair the quality of silk articles. One drawback in grafting is the surface deposition of homopolymer that may occur during the reaction. For this reason it was thought to be beneficial to analyze the surface morphology of the silk samples grafted in this study, to give an exhaustive description of the process performance.

The surface of MAA-grafted silk fibers (Fig. 9) was as smooth as that of untreated silk, irrespective of the initiator used and weight gain attained. The use of MMA as the grafting agent led to morphological differences among the samples (Fig. 10). Silk grafted with the MMA/APS system with 45% weight gain exhibited only slight traces of surface deposition of a very thin and uneven layer of foreign material attributable to poly(MMA). The deposit became more frequent and thicker on the surface of silk fibers grafted with AIBN and ADC as the initiators, especially at above 25% weight
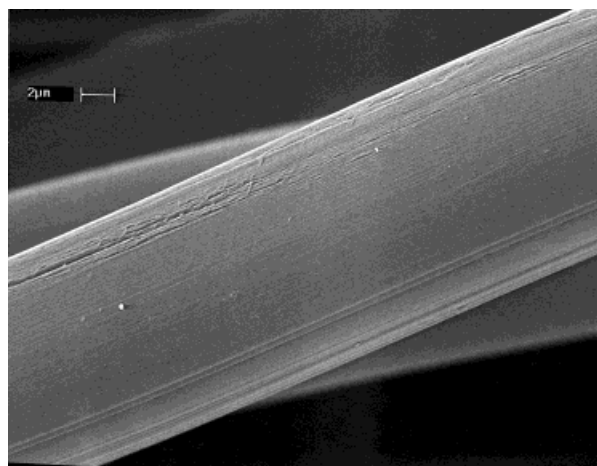

Figure 9 SEM micrograph of silk fiber grafted with the MAA/APS grafting system with 47.3% weight gain.
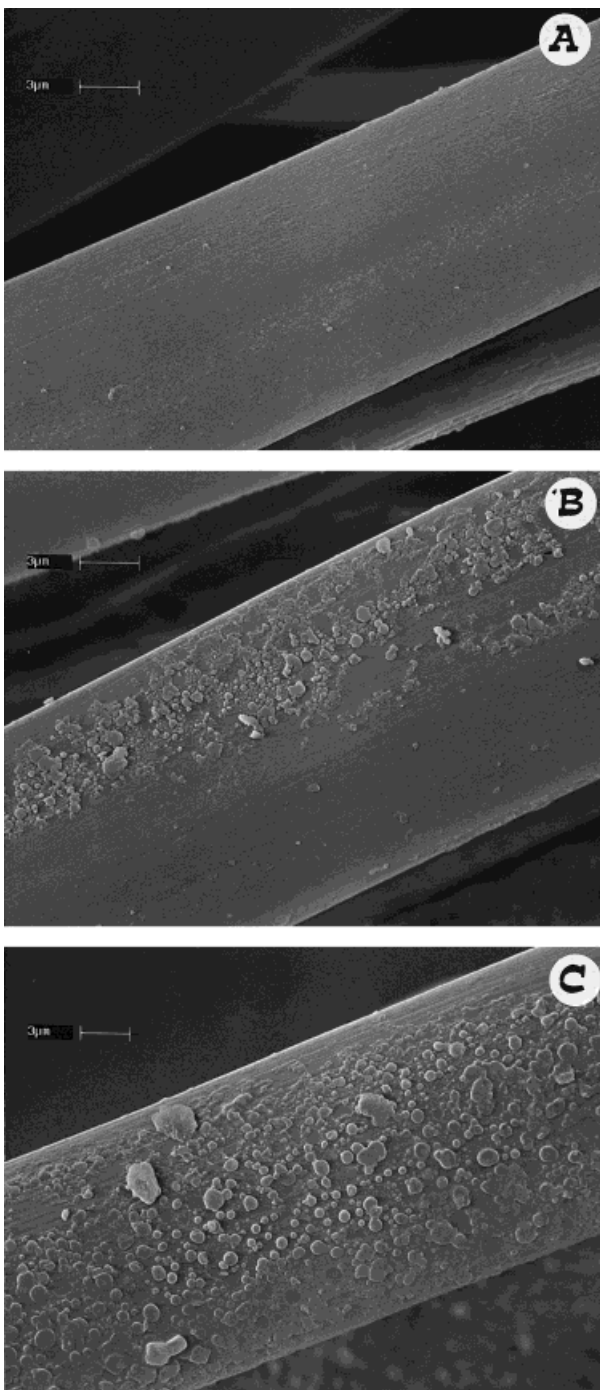
Figure 10   SEM micrographs of MMA-grafted silk fibers. (A) MMA/APS, 44.5% weight gain; (B) MMA/AIBN, 38.9% weight gain; (C) MMA/ADC, 29.3% weight gain.

gain, assuming a characteristic beadlike shape. In the case of HEMA-grafted silk, only very slight traces of surface homopolymer deposits were found up to 30% weight gain, independently of the

initiator used. With a further increase of weight gain, the amount of deposited poly(HEMA) became higher and higher, leading to extensive surface covering and sticking together of fibers (Fig. 11).

The above-reported morphological observations, combined with the results noted earlier, confirm the potentiality of the MAA/AIBN grafting system, which appears consistent with industrial requirements with respect to amount weight gain, reduction of yellowing, and absence of surface homopolymerization.

CONCLUSIONS

The two azo compounds AIBN and ADC, used as initiators for grafting vinyl monomers onto silk, proved to be effective in sustaining the reaction, that is, in causing a detectable weight increase of silk as a result of both graft–copolymer and/or homopolymer deposition into the fiber matrix. In particular, AIBN made possible the achievement of appreciable weight gain values, although slightly lower than those by APS, but still attractive from the viewpoint of an industrial grafting process.

The apparent deviation from the first-order reaction rate observed for some monomer–initiator systems may depend on various factors. Grafting is a very complex reaction system in which various kinetic and thermodynamic parameters related to chemistry and reactivity features of monomer, initiator, solvent, fibrous substrate,
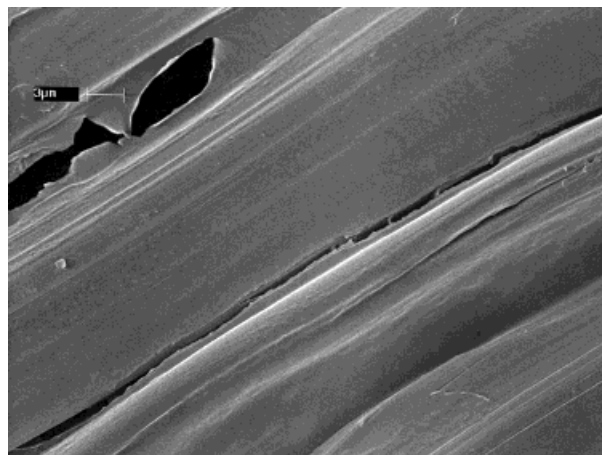

Figure 11   SEM micrograph of silk fibers grafted with the HEMA/APS grafting system with 60.2% weight gain.

and so forth, are known to play a key role in determining the outcome of the process. The univocal attribution of the observed behavior to a specific factor is out of the scope of the present work and requires further studies. Referring to the initiators, the mineral peroxide and the azo compounds used, although different in chemical structure, possess almost the same activation energy (about 30 kcal/mol) and, in principle, should exhibit the same efficiency during the initial step of free-radical formation. Other factors related to radical–monomer and radical–substrate interactions, as well as solubility of the monomer in the reaction system, rate of diffusion, and affinity for the fibrous substrate must be considered. Studies dealing with the evaluation of these aspects are in progress and will be reported in future studies.

With reference to silk yellowing induced by grafting it is clearly evident that AIBN gives the best performance, especially with MAA as the monomer, because the level of yellowing was almost half of that induced by APS in the same reaction conditions and with comparable weight gain. The accumulated results confirm the MAA/AIBN grafting system as a suitable candidate for replacing the conventional MAA/APS system.

The physical, mechanical, and morphological properties of grafted silk did not show any specific relation with the kind of initiator used, although other aspects of the grafting process, such as the kind of vinyl monomer and weight gain attained, were demonstrably more important. These findings give further support to the possibility of innovating the grafting technique by the introduction of free-radical initiators not yet considered for the graft–copolymerization of vinyl monomers onto silk.

REFERENCES

1. Freddi, G.; Tsukada, M. Polymeric Materials Encyclopedia; Salamone, J.C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 10, p. 7734.
2. Nayak, P. L.; Lenka, S. in Proceedings of the International Meeting on Grafting Processes onto Polymeric Fibres and Surfaces: Scientific and Technological Aspects; Bellobono, I., Ed.; Milano University, Italy, 1990; pp. 85, 243.
3. Tsukada, M.; Freddi, G.; Ishiguro, Y.; Shiozaki, H. J Appl Polym Sci 1993, 50, 1519.
4. Bianchi Svilokos, A.; Massafra, M. R.; Beretta S. La Seta 1986, 44, 4.
5. Schindler, W.; Dietel, A. Melliand Textilberichte 1993, 74, 81.
6. Tsukada, M. J Appl Polym Sci 1988, 35, 2133.
7. Tsukada, M.; Freddi, G.; Monti, P.; Bertoluzza, A.; Shiozaki, H. J Appl Polym Sci 1993, 49, 1835.
8. Nayak, P. L.; Lenka, S.; Pati, N. C. Angew Makromol Chem 1979, 75, 29.
9. Tsukada, M.; Kasai, N.; Freddi, G. J Appl Polym Sci 1993, 50, 885.
10. Tsukada, M.; Yamamoto, T.; Nakabayashi, N.; Ishikawa, H.; Freddi, G. J Appl Polym Sci 1991, 43 2115.
11. Czerny, A. R.; Ubler, A. M.; Schindler, W. Melliand Textilberichte 1990, 71, 211.
12. Freddi, G.; Massafra, M. R.; Beretta, S.; Shibata, S.; Gotoh, Y.; Yasui, H.; Tsukada, M. J Appl Polym Sci 1996, 60, 1867.
13. Tsukada, M.; Imai, T.; Freddi, G.; Lenka, S.; Kasai, N. J Appl Polym Sci 1998, 69, 239.
14. Tsukada, M.; Nagura, M.; Ishikawa, H.; Shiozaki, H. J Appl Polym Sci 1988, 43, 643.
15. Nayak, P. L.; Lenka, S.; Mishra, M. K. J Polym Sci Polym Chem Ed 1980, 18, 2247.
16. Misra, S.; Nayak, P. L.; Sahu, G. J Appl Polym Sci 1982, 27, 1903.
17. Samal, S.; Sahu, G.; Nayak, P. L. J Appl Polym Sci 1984, 29, 3283.
18. Samal, S.; Sahu, G.; Lenka, S.; Nayak, P. L. J Appl Polym Sci 1987, 33,1853.