

Grafting of Vinyl Monomers onto Silk Using Redox Systems. Yellowing of Silk

MASUHIRO TSUKADA,¹ TSUNEO IMAI,¹ GIULIANO FREDDI,² SUBASINI LENKA,³ NOBUTAMI KASAI⁴

¹ National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan

² Stazione Sperimentale per la Seta, via G. Colombo, 81, 20133 Milano, Italy

³ Ravenshaw College, Cuttack 753 003, Orissa, India

⁴ Kobe Womens' University, Suma, Kobe 654, Japan

Received 21 July 1997; accepted 24 November 1997

ABSTRACT: The aim of this study is to investigate the influence of temperature, initiator concentration, and vinyl monomer on silk yellowing during grafting. A series of silk fabrics was treated at four different temperatures (70, 75, 80, and 88°C), with different concentrations of initiator in the range 1–4% owf, with and without methacrylamide (MAA) or 2-hydroxyethyl methacrylate (HEMA). By treating silk with ammonium persulphate (APS), in the absence of a monomer, the degree of silk yellowing increased linearly with increasing both initiator concentration and treatment temperature, indicating that the initiator plays a specific role in enhancing silk yellowing through macro-radical formation. The graft copolymerization of MAA (with APS as the initiator) caused only slight changes in the intensity of silk yellowing compared to blank-treated fabrics. On the other hand, the use of HEMA resulted in a deeper yellowing of silk fabrics, especially in the 70–80°C temperature range, due to its higher reactivity and to the tendency to form a homopolymer, leaving unreacted macroradicals on silk fibroin backbone. Compared to APS, other initiators, such as 2,2'-azobis(isobutyronitrile) (AIBN) and 2-2'-azobis-(2-amidino propane) dihydrochloride (ADC), caused a significantly lower degree of silk yellowing when tested in the absence of a monomer. The yellowness of silk fabrics tended to increase by grafting with HEMA, while decreased by grafting with MAA. The use of variable amounts of monomer (25–150% owf) did not influence the degree of yellowing with ADC as the initiator. The results reported in this study show that the extent of yellowing induced on silk fabrics by grafting MAA and HEMA with APS as the initiator can be limited by a suitable selection of the processing parameters (initiator concentration, temperature). Moreover, the use of both AIBN and ADC appears promising, owing to their negligible effect on silk yellowing. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 239–246, 1998

Key words: silk redox systems; vinyl monomer grafting

INTRODUCTION

Modification of the properties of natural macromolecules, such as wool, silk, cellulose, through

graft copolymerization of vinyl monomers has attracted the interest of both scientists and technologists during the past 3 decades.^{1–5} Silk fibers exhibit many outstanding properties (handle, luster, dyeability, etc.) that distinguish them from other natural and synthetic fibers. However, some minor textile performances (crease recovery, thermal stability, wash and wear characteristics) need to be improved to expand silk consumption

Correspondence to: G. Freddi.

Contract grant sponsor: COE, Special Coordination Funds for Promoting Science & Technology, Japan.

Journal of Applied Polymer Science, Vol. 69, 239–246 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/020239-08

and meet consumer requirements. In recent years, grafting techniques have been regarded as a powerful tool to this purpose,⁵ although their application on an industrial scale is still confined to certain articles such as necktie yarn and fabric, borders, and embroidery.

Methacrylamide (MAA) and 2-hydroxyethyl methacrylate (HEMA) are currently applied for silk grafting, used either alone or in combination in the same grafting system. Compared to other vinyl monomers (styrene, methyl methacrylate), they have a softer impact on both silk fibers and processing plants. In fact, MAA-grafted silk fibers maintain a typical silk-like handle and drape, showing improved comfort and better easy-care properties. The graft copolymerization of MAA and HEMA onto silk fibers is usually carried out on degummed silk yarn in the hank or package form by means of spray-dyeing machines. Industrial grafting onto silk fabrics has also been reported.^{6,7} The fiber substrate is activated by the free radical initiation method, which involves the formation of free radical sites on the backbone of fibroin molecules. This can be achieved by both chemical and physical methods. The former, i.e., the use of chemical redox systems, have been extensively investigated at the scientific level,⁸⁻¹⁴ and still play the chief role for technological purposes, ammonium persulphate (APS) being widely used on an industrial scale for silk grafting.

Yellowing of silk may occur during grafting.^{6,15} To overcome this drawback, suitable aftertreatments are usually conducted, such as bleaching. However, this aspect of silk grafting, whose importance in terms of time, energy, and chemical consumption at the industrial level cannot be underestimated, has not been extensively studied yet. Some of the authors¹⁵ have recently reported experimental evidences on a specific effect of the initiator (APS) on silk yellowing. In this work, the yellowing of silk has been systematically investigated by studying the effect of various parameters, such as temperature and APS concentration, during the graft copolymerization of MAA and HEMA onto silk. Moreover, the influence on silk yellowing of other initiators, such as 2,2'-azobis(isobutyronitrile) (AIBN) and 2-2'-azobis(2-amidino propane) dihydrochloride (ADC), which can be used for initiating the graft copolymerization of vinyl monomers, has been evaluated. The results obtained seem highly promising for improving silk grafting at the technological level.

EXPERIMENTAL

Materials

Habutae silk fabric (plain weave, ca. 60 g/m²) was used as grafting substrate. Reagent grade MAA and HEMA, purchased from Wako Pure Chemicals Ind., Ltd., were used without further purification. The nonionic emulsifying agent Noigen HC was obtained from Daiichi Kogyo Seiyaku Co.

Silk grafting was performed as follows. The fabric was immersed in the reaction system at pH 3 (adjusted with formic acid), containing 3% Noigen HC on the weight of fabric (owf), and the required amounts of initiator and monomer. The material-to-liquor ratio of 1 : 30 was maintained. The temperature was gradually raised to the desired value (70–88°C) in 45 min and then maintained constant for 1 h. At the end of the reaction, silk fabric was soaked for 30 min at 80°C with water containing 1 mL/L Noigen HC, then rinsed with water to remove the unreacted monomer and dried at 105°C for 2 h. Samples were placed in a desiccator over silica gel before measurements.

Measurements

The color change of silk fabric was measured with a Colour Difference Meter Type CR-2000 (Minolta Co.) spectrophotometer on the basis of the L,a,b system. The b* parameter, denoting yellowness, was used as an index of the degree of silk yellowing. The higher the b* value, the higher the yellowness of silk.

RESULTS AND DISCUSSION

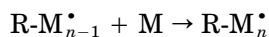
Mechanism of Grafting and Silk Yellowing

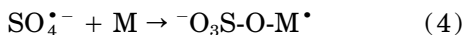
On the basis of a large number of studies conducted on silk grafting,⁸⁻¹³ the following reaction scheme can be suggested as a possible mechanism for the initiation, propagation, and termination of the graft copolymerization of vinyl monomers onto silk by using APS as the initiator:



⋮

⋮





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 homopolymerization of monomer, reactions 2 and 3 show the steps for graft copolymerization. The free radicals formed by the initiator interact with reactive sites on 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.¹⁶ and Enomoto and Suzuki¹⁷ emphasized the role of glycine residues, i.e., the $-\text{NH}$ moieties of the peptide bond, as the site for grafting on silk. The silk macroradical can react with the monomer, leading to the propagation of a grafted polymer chain. Homopolymer can be formed as well, by interaction of the initiating free radicals with the monomer. The coexistence of both grafted chains and homopolymer within the silk fiber matrix cannot be excluded. With regard to the steps that are likely to promote the yellowing of silk, step 2 is thought to play an important role because the extent of silk yellowing should depend on the amount of macroradicals formed.

Effect of APS

Silk fabrics treated with APS in the absence of monomer displayed a linear increase of the b^*

value with increasing the concentration of initiator in the reaction system (Fig. 1). The four series of b^* values obtained by exposing silk at different temperatures and APS concentrations fitted straight lines with values of the correlation coefficient ranging from 0.96 to 0.99. The finding that APS concentration and degree of silk yellowness are a correlated variable is in good agreement with the results previously reported by some of the authors,¹⁵ and can be primarily attributed to the formation of an increasing number of macroradicals on the silk fibroin backbone.

The influence of temperature on silk yellowing is worth noting. With increasing the temperature, the curves shifted towards higher b^* values. Various factors can be considered responsible for this effect, such as a greater activation energy, an increase in solubility of the initiator, a higher diffusion rate from solution to the more swollen fiber phase, and a higher accessibility of the potentially reactive sites in the fiber matrix. Their cooperative action probably resulted in an increase of silk macroradical formation, according to step 2 of the reaction, thereby enhancing silk yellowing.

Effect of MAA and HEMA (APS Grafting System)

The addition of the grafting agent resulted in slight to drastic changes in the yellowing behavior of silk. The b^* values of silk fabrics grafted with 60% owf MAA or HEMA at four different tempera-

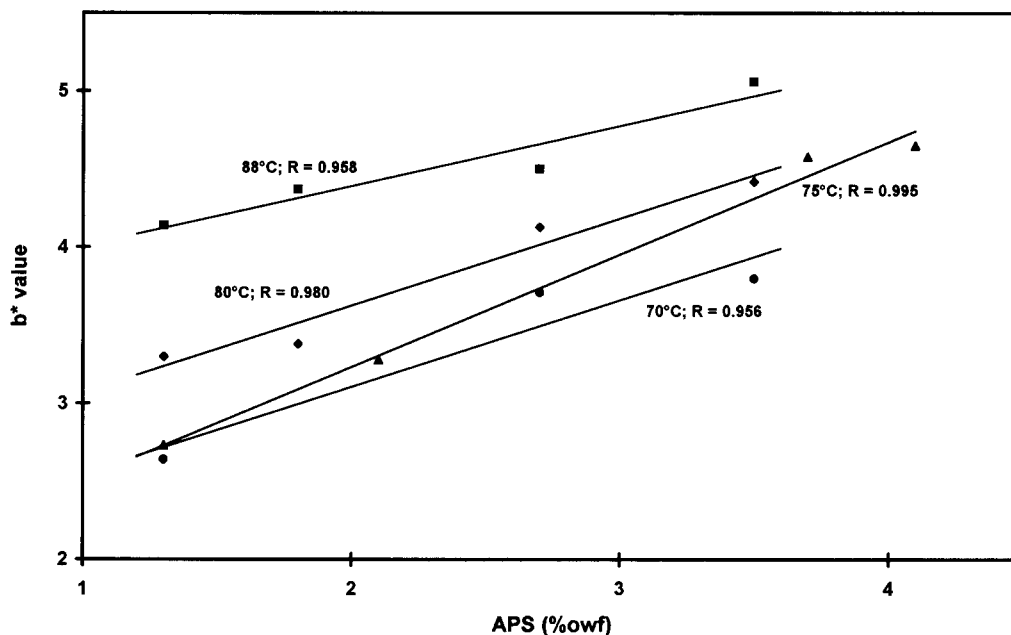


Figure 1 b^* vs. APS concentration of blank-treated silk fabrics at 70, 75, 80, and 88°C.

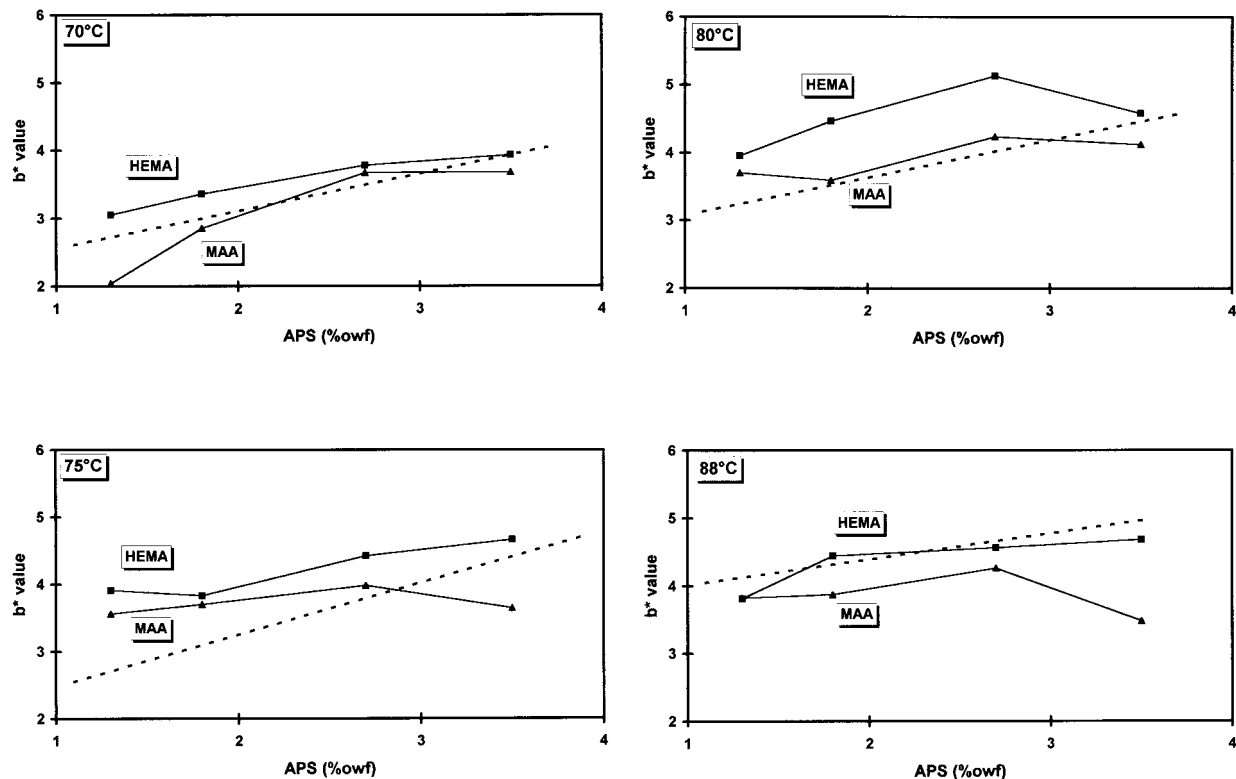


Figure 2 b^* vs. APS concentration of silk fabrics grafted with 60% owf MAA and HEMA at 70 (a), 75 (b), 80 (c), and 88°C (d). Dotted lines show the corresponding blank-treated fabrics (see Fig. 1).

tures were plotted as a function of the initiator concentration [Fig. 2(a)–(d)]. The dotted lines show the behavior of blank-treated fabrics at each temperature. It can be observed that the degree of silk yellowing increased with increasing APS concentration in the range 1–3% owf, thereafter tending to attain a constant value or decreasing slightly. In the presence of a monomer, pathways 3 and 4 occurred, leading to the formation of both the graft copolymer and homopolymer. At high APS concentration, step 4 probably took place at a higher extent. The amount of silk macroradicals formed remained constant or decreased slightly, thereby the degree of silk yellowing became steady.

HEMA-grafted silk fabrics displayed b^* values systematically higher than those of the corresponding samples grafted with MAA. This behavior might be attributed to the lower grafting efficiency of HEMA compared to MMA.⁵ In fact, it has been shown that by graft copolymerizing HEMA and MAA onto silk in the same conditions of time, temperature, monomer, and initiator concentration, the former usually showed a higher tendency to homopolymer formation.⁵ The greater

amount of unreacted silk macroradicals might have contributed to enhance silk yellowing.

Compared to the blank-treated fabrics, those grafted with HEMA at 70, 75, and 80°C showed deeper yellowing [Fig. 2(a)–(c)], suggesting that the vinyl monomer had an additive effect in determining the final degree of yellowness. The contribution of HEMA to the yellowing of silk became almost negligible at 88°C [Fig. 2(d)], when the b^* values overlapped those of the reference sample. Probably this temperature was more favorable for graft copolymerization, according to step 3 of the reaction.

Depending on treatment temperature and APS concentration, the b^* values of MAA-grafted silk fabrics fell sometimes above, sometimes below those of the blank-treated samples [Fig. 2(a)–(d)]. An interesting feature was that at 88°C [Fig. 2(d)] the degree of yellowing was even lower than that of the corresponding blank-treated fabrics, in the entire range of APS concentration examined. In these conditions, the formation of silk–MAA macroradicals, followed by chain propagation and formation of the graft copolymer, was probably favored by a higher diffusion rate of the

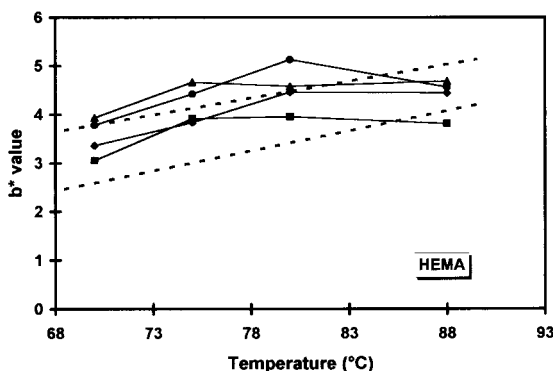
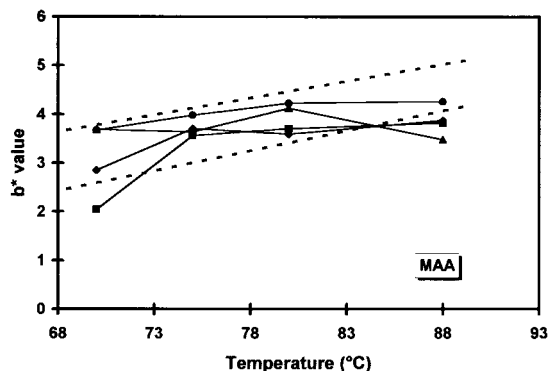


Figure 3 b^* vs. grafting temperature of silk fabrics grafted with 60% owf MAA (a) and HEMA (b) at different APS concentrations (1.3–3.5% owf). Dotted lines show the fabrics blank-treated with 1.3 and 3.5% owf APS (lower and upper line, respectively).

monomer within the fibers, accompanied by a higher reactivity of both initiator and monomer. This conclusion is in good agreement with the well-known high efficiency of the MAA grafting system.⁵

By plotting the values of b^* of MAA- and HEMA-grafted silk fabrics as a function of the treatment temperature (Fig. 3), it can be observed that the former gathered inside or below the “yellowing area” defined by the blank samples treated with 1.3 and 3.5% APS (lower and upper dotted line, respectively). On the other hand, the latter tended to fall close to the upper limit or above the “yellowing area”, especially at 75 and 80°C. Provided that the initiator is the most important factor driving yellowing of silk during grafting, these results demonstrate that HEMA can be ascribed of a positive contribution to this phenomenon, as discussed above, while the influence of MAA is almost negligible. From the accumulated results we can therefore conclude that an accurate selection of the grafting conditions,

i.e., temperature, monomer/initiator ratio, may bring to an effective reduction of silk yellowing during grafting. This aim can be easily achieved with MAA in a wide range of grafting conditions. On the other hand, it appears more difficult to reduce this undesired effect with HEMA, although a temperature of 88°C and an initiator concentration in the range 1–3% owf seem to permit a partial limitation of the final degree of silk yellowing.

Effect of AIBN and ADC

The use of AIBN and ADC for the graft copolymerization of vinyl monomers onto silk has not been reported yet. To study the effect of these two initiators on silk yellowing, silk fabrics were blank treated at different initiator concentrations and temperatures. Figure 4 shows the behavior of the b^* values as a function of initiator concentration at 88°C (the curve of APS at the same temperature was included as a reference). It is interesting to note that, even at 88°C, the extent of silk yellowing with both AIBN and ADC was significantly lower than that induced by APS. The curves of AIBN and ADC run almost parallel in the range of concentration examined, with only a slight positive slope, suggesting that the influence of the amount of initiator was negligible.

These results might reflect a lower ability of both AIBN and ADC to form silk macroradicals, attributable either to a lower activation energy, or to a lower solubility and diffusion of the initiator from the solution to the fiber phase.

Effect of MAA and HEMA (AIBN and ADC Grafting Systems)

By adding the grafting agent (60% owf) to the AIBN and ADC reaction systems, at 80°C, the degree of silk yellowing displayed the behavior shown in Figure 5. HEMA-grafted silk fabrics showed b^* values systematically higher than MAA-grafted and blank-treated fabrics, whatever the kind of initiator and concentration. Grafting with MAA generally resulted in a very low degree of silk yellowing, even lower than that of the blank-treated samples. These results are in good agreement with those obtained with APS, confirming that HEMA had an additive effect in enhancing silk yellowing, while the use of MAA partly limited this negative consequence of the grafting process.

In our tests, AIBN tended to cause a deeper yellowing of silk than ADC. Although the differ-

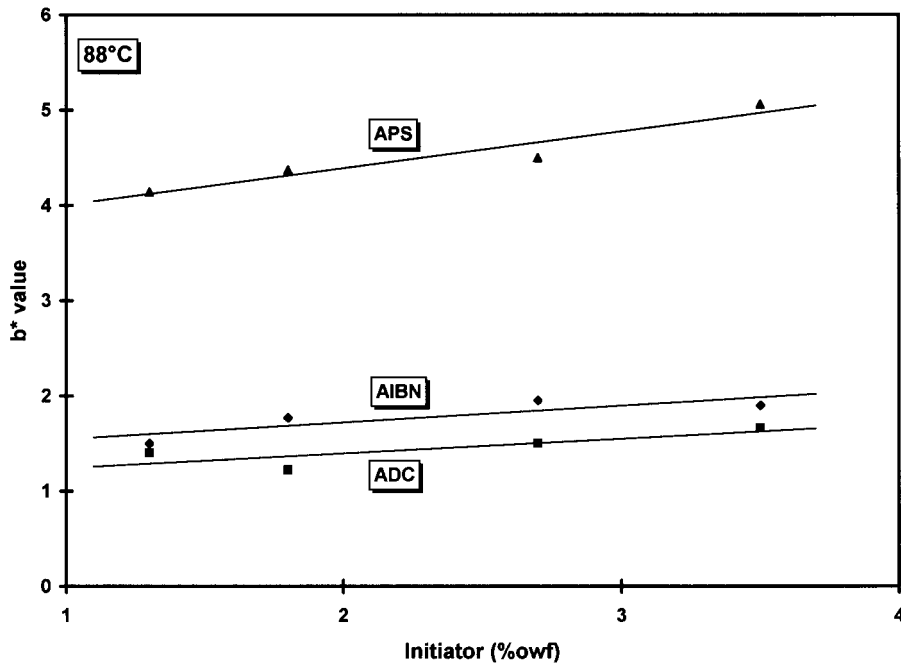


Figure 4 b^* vs. initiator concentration of silk fabrics blank-treated with AIBN, ADC, and APS at 88°C.

ences were rather small, requiring additional analytical confirmation, the latter might be considered a more suitable candidate for substituting APS as the initiator for grafting silk with vinyl

monomers. We, therefore, assayed the effect of different monomer concentrations (from 25 to 150% owf) on the yellowing of silk, by keeping temperature and ADC concentration constant

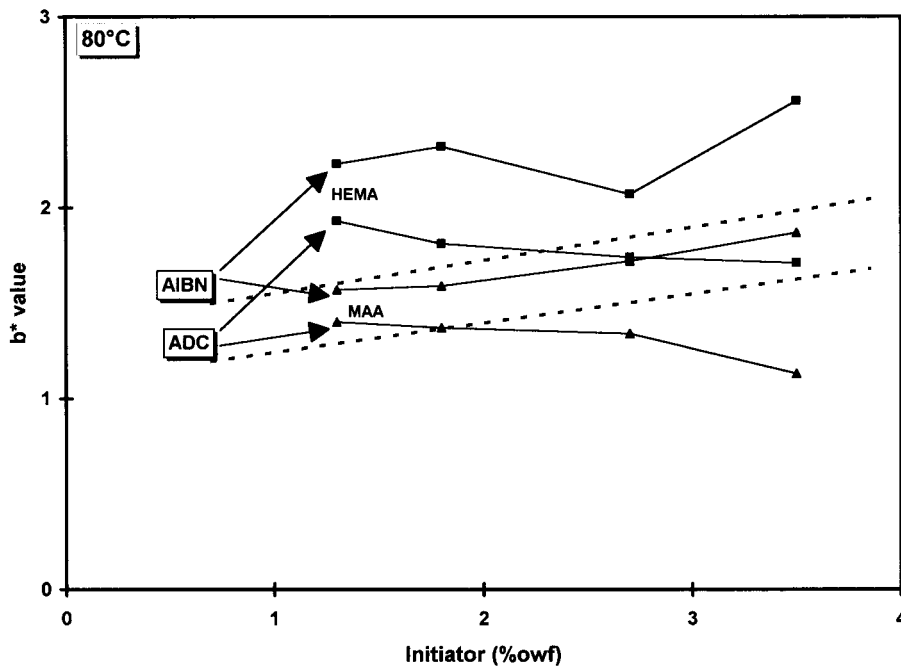


Figure 5 b^* vs. initiator concentration of MAA- and HEMA-grafted silk fabrics, by using AIBN and ADC as the initiator, at 80°C. Dotted lines show the fabrics blank-treated with AIBN and ADC (upper and lower line, respectively).

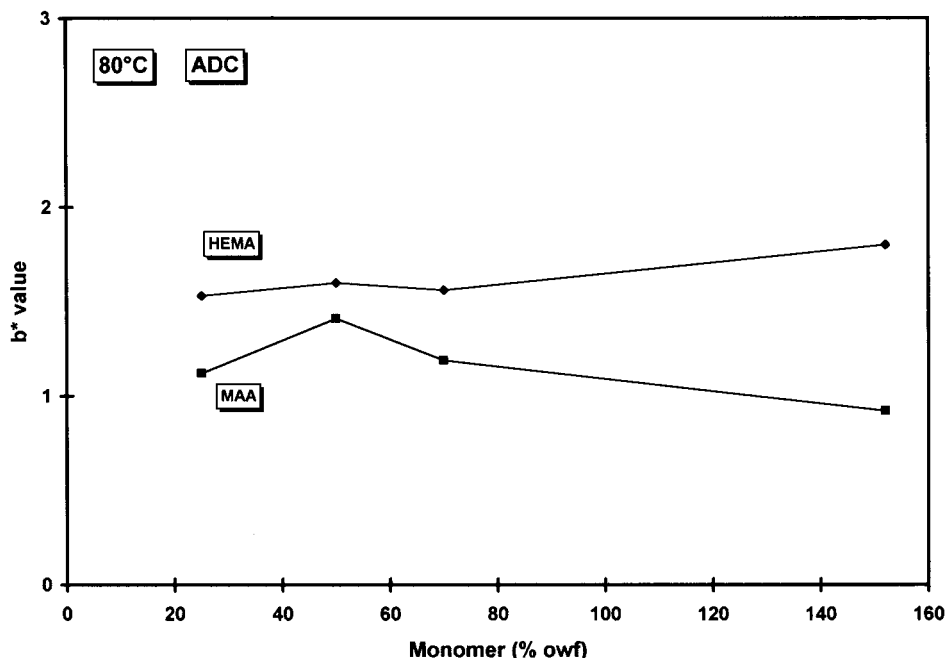


Figure 6 b^* vs. monomer concentration of silk fabrics grafted with MAA and HEMA at 80°C by using 3.5% owf ADC as the initiator.

(80°C and 3.5% owf, respectively). The results obtained (Fig. 6) show that the amount of monomer did not affect the b^* values of grafted silk fabrics, the curves of MAA and HEMA running almost parallel to each other and to the x axis. Once again, it is worth noting that the latter was displaced at higher b^* values.

CONCLUSIONS

The results reported in this study confirm that the silk yellowing during grafting was mainly caused by the initiator used, i.e., by its ability to interact with potentially reactive groups on silk fibroin backbone and form silk macroradicals. The extent of yellowing induced by the different initiators tested in the absence of the grafting agent was in the following order: APS \gg AIBN $>$ ADC. APS was more sensitive to temperature than AIBN and ADC.

HEMA was effective in enhancing silk yellowing, whatever the kind of initiator, concentration, and temperature, while the effect of MAA was almost negligible. Indeed, the latter often resulted in a lower degree of silk yellowing. It has been shown that a suitable choice of the processing parameters (initiator concentration, temperature) may lead to a considerable decrease in

the extent of yellowing of MAA-grafted silk fabrics.

The use of AIBN and ADC as the initiator for the graft copolymerization of vinyl monomers onto silk appeared promising with respect to their lower contribution to the phenomenon of silk yellowing. However, their effectiveness in promoting an efficient grafting of silk in the range of weight gains required by the present industrial applications (40–60%) is still questionable and should be assayed by means of additional tests on both laboratory scale and pilot plants.

This work was supported by the COE (Center of Excellence), Special Coordination Funds for promoting Science and Technology, of the Science and Technology Agency, Japan.

REFERENCES

1. I. C. Watt, *J. Macromol. Sci. Rev., Macromol. Chem.*, **C5**, 176 (1970).
2. K. Arai, in *Block and Graft Copolymerization*, Vol. 1, R. Ceresa, Ed., John Wiley and Sons, London, 1973, p. 193.
3. P. L. Nayak, *J. Macromol. Sci. Rev., Macromol. Chem.*, **C14**, 192 (1976).

4. S. Lenka, *J. Macromol. Sci. Rev., Macromol. Chem. Phys.*, **C22**, 303 (1982).
5. G. Freddi and M. Tsukada, in *Polymeric Materials Encyclopedia*, Vol. 10, J. C. Salamone, Ed., CRC Press, Boca Raton, FL, 1996, p. 7734.
6. A. R. Czerny, A. M. Ubler, and W. Schindler, *Melliand Textilberichte*, **71**, 211 (1990).
7. W. Schindler and A. Dietel, *Melliand Textilberichte*, **74**, 81 (1993).
8. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **68**, 117 (1978).
9. P. L. Nayak, S. Lenka, and N. C. Pati, *J. Appl. Polym. Sci.*, **23**, 1345 (1979).
10. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2247 (1980).
11. S. Lenka, P. L. Nayak, and M. K. Mishra, *Angew. Makromol. Chem.*, **84**, 183 (1980).
12. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **85**, 29 (1980).
13. N. C. Pati, S. Lenka, and P. L. Nayak, *J. Macromol. Sci. Chem.*, **A16**, 487 (1981).
14. T. K. Maji and A. N. Banerjee, *J. Appl. Polym. Sci.*, **62**, 595 (1996).
15. G. Freddi, M. R. Massafra, S. Beretta, S. Shibata, Y. Gotoh, H. Yasui, and M. Tsukada, *J. Appl. Polym. Sci.*, **60**, 1867 (1996).
16. K. Arai, M. Negishi, S. Komine, and K. Takeda, *J. Appl. Polym. Symp.*, **18**, 545 (1971).
17. M. Enomoto and T. Suzuki, *Acta Sericol. (Tokyo)*, **47**, 104 (1963).