

Reductions in Rate of Yellowing Following Irradiation of Poly[*N*(*n*-butoxymethyl) methacrylamide]-grafted Silk Fibers

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SYNOPSIS

The physical properties, including changes in the yellowness index, following UV irradiation of *Bombyx mori* silk fibers loaded with poly[*N*(*n*-butoxymethyl) methacrylamide], poly(BMA), are examined in relation to the amount of held polymer. The percentage weight gain by the silk fibers observed after 45 min at 80°C increased with increasing initial amounts of BMA monomer in the reaction system. Differential scanning calorimetry (DSC) observations suggest that the thermal decomposition behavior of the heated silk fiber was little affected, with but an apparent small shift of the endothermic decomposition temperature range to higher temperatures. The tensile properties of the treated silk fibers remained effectively unchanged, independent of the polymer weight gains. There was, however, a marked effect of the poly(BMA) weight gains onto silk in maintaining the whiteness and reducing the rate of yellowing following irradiation of treated habutae silk fabrics. These observations suggest that the rate of photoyellowing of silk fabrics can be retarded by the presence of the poly(BMA) in the fabric. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Considerable interest has been shown for the improvement of the inferior textile features of silk such as photoyellowing and wash and wear properties. Among these less desirable characteristics, the photoyellowing of silk fabrics on exposure to sunlight greatly depreciates their textile value. A considerable effort has been expended to find practical ways for reducing the influence of sunlight on silk. Chemical treatments^{1,2} to retard the photoyellowing of animal protein fibers have been the subject of many investigations. The application of a polymer graft using vinyl monomers³⁻⁸ or of chemical modification techniques using epoxides⁹⁻¹¹ on silk fibers and keratin yarns have been the subject of several investigations.

It has been demonstrated that epoxide treatments have promise as effective means of materially improving silk fibers because these modifications significantly retard their photoyellowing. However, the magnitude of the protective effects achieved by the epoxide treatments are still inadequate for their commercial implementation. At present no commercially satisfactory method has been found to adequately reduce the photoyellowing of silks.

One of the authors has demonstrated that when the grafting monomer that possessed a high hydrophobic character was employed, a high level of weight gain and grafting efficiency resulted (Shiozaki, in preparation). It was thus of great interest to examine alkoxyethyl derivatives of methacrylamide with a higher hydrophobicity as the grafting monomer in order to increase the weight gains and grafting efficiencies compared with the use of the hydroxymethyl derivatives. We looked therefore for a source of an appropriate monomer such as *N*(*n*-butoxymethyl) methacrylamide (BMA) from a chemical company.

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Previous studies in this series have described changes in physical properties of grafted silk and chemically modified silk and the achievement of material improvement in silk properties. The grafting to and loading of silk with vinyl polymers, e.g., poly(methacrylamide)-grafted silk fibers, resulted in significant decrease in their yellowing following subsequent UV irradiation. One possible solution against the yellowness problem would be to incorporate special substituents, such as alkoxyethyl groups, in the side chain of the poly(methacrylamide) grafted and loaded into silk fibers and fabrics.

In this study the term "grafting" follows the description previously used.³⁻⁸ The adjective is here employed to describe that held material following *in situ* polymerizations within the fiber and subsequent monomer/oligomer extraction. It is recognized that this polymer load within the fiber will contain not only chemically bound (true graft) material but also that which is only physically held within the fiber structure. No attempt has been made to identify the relative proportions of these two components.

This article examines ways to reduce by the polymer weighting technique, the photoyellowing of silks following UV irradiation. A study was undertaken to provide technical information to reduce the rate of sunlight photoyellowing with a grafting technique using the monomer *N*(*n*-butoxymethyl)-methacrylamide (BMA), which possesses an alkoxyethyl group bound to the amide nitrogen.

EXPERIMENTAL

Materials

Raw silk fibers were obtained after reeling of cocoon threads of the commercial silkworm variety of *Bombyx mori*. The composite threads, made of the bave from several cocoons drawn together, were twisted mechanically (S-twist, 640T/m; Z-twist, 720T/m). These raw-silk yarns were degummed in an aqueous solution containing 0.4% soap and 0.1% Na₂CO₃ for 2 h at 98–100°C and then washed with 0.05% sodium carbonate solution followed by boiling water.

The *N*(*n*-butoxymethyl)methacrylamide (BMA) [Eq. (1)] was



kindly presented by Mitsubishi Rayon Co., Ltd., and

was used without further purification. The emulsifying agent (Newkalgen 1515-2H, Takemoto Yushi Co. Ltd.), which contained a nonionic emulsifying agent (polyoxyethylenonyl phenylether) and an anionic emulsifying agent (sodium dodecylbenzenesulfonate), was mixed at 10% on the weight of silk fabric; 2.2% ammonium persulfate on the weight of BMA monomer was added as the initiator. Poly(BMA)-grafted silk fibers with weight gains of 10.7, 16.6, 32.3, and 57.5% were thus prepared in the grafting system containing different amounts of BMA [15–75% over weight fiber (o.w.f.)]. The poly(BMA)-grafted habutae silk fabrics (plain weave, ca. 60 g/m²) with gains in weight of 6.7, 16.8, 18.3, and 33.9% were also prepared in the same manner as the silk yarns, and used for the photoyellowing experiments. A material-to-liquor ratio of 1 : 15 was maintained in all systems. The graft polymerization reaction was started at 40°C and gradually raised to 80°C over 15 min and then was maintained at this temperature for 45 min. At the end of the reaction, the treated silk was soaked at 80°C for 30 min in a solution containing 1 mL/L of an ether-type nonionic detergent (Noigen HC, Daiichi Kogyo Seiyaku Co.) and then thoroughly rinsed with water to remove any unreacted BMA and oligomers. The preparation conditions for the grafted silks with the observed polymer gains are tabulated in Table I.

Measurements

Equilibrium regains of the treated silks were calculated on the basis of moisture uptake by the fiber after 2 weeks conditioning at 20°C, 65% RH. The polymer weight gains were measured according to the method described in previous studies.³⁻⁸

Heat flux differential scanning calorimetry (DSC) measurements were performed on a Rigaku Denki instrument (DSC-10A). Cut fibers (2 mg) were compressed in sealed aluminum pans and heated at 10°C/min in a nitrogen atmosphere (flow rate 200 mL/min but with no attempt made to dry). A heat flux sensitivity of 10.5 mJ/s 10 mV analog signal output was employed.

Thermomechanical analysis (TMA) curves were obtained on a Rigaku Denki instrument at a heating rate of 10°C/min on 15 mm lengths with a 1 gf applied load in a nitrogen flow of 200 mL/min. The TMA sensitivity range was ±500 μm/mV analogue signal which was recorded as a 1% length change per cm.

The dynamic moduli E' and E'' were measured at 10 Hz with a Toyoseiki Rheograph Solid-S. The

Table I Poly(BMA)-grafted Silk Samples Used in This Work and Their Initial Tensile Moduli (Rate of Strain as 40%/Min)^a

Sample	Amount of BMA [% (o.w.f.)]	Add-on (%)	Efficiency ^b (%)	Tensile Modulus ^c (g/d)
<i>Silk Fiber</i>				
Control	0	0	—	90
D-1	20	10.7	53.5	96
D-2	30	16.6	55.3	78
D-3	50	32.3	64.6	70
D-4	75	57.5	76.7	50
<i>Habutae (silk plain weave)</i>				
Control	0	0	—	
H-1	15	6.7	44.7	
H-2	35	16.8	48.0	
H-3	40	18.3	45.8	
H-4	60	33.9	56.5	

^a BMA-grafted silk fibers were prepared in the grafting system containing different amounts of BMA monomer according to the procedure described in the experimental section.

^b Grafting efficiency (%).

^c 1 g/d = 1.22×10^3 kgf/cm².

temperature range studied was from room temperature to 260°C and samples were heated at 2°C min. The sample length was 15 mm with an initial tension of 30 gf.

Tensile strengths and elongations at break were measured on single silk fibers at 20°C and 65% RH with an automatic Tensilon Tester (Tohyo Baldwin Co. Ltd.). The rate of strain was 20 mm/min on a sample length of 50 mm. Each recorded value was the average of 25 results.

Poly(BMA)-grafted habutae silks were irradiated using a carbon arc source with a Phadoemeter (FAL-AU H) from Suga Test Instrument Co., Ltd. (major wavelength emitted and intensity of illumination was 385 nm, 490 W/m², respectively). The yellowness index was measured on a color computer (SM-3) of Suga Test Instrument Co., Ltd. and whiteness (W) was calculated in the following manner:

$$W(L^*, a^*, b^*) = 100 - \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}}$$

$$L^* = 116 (Y/100)^{1/3} - 16$$

$$a^* = 500 [(X/98.05)^{1/3} - (Y/100)^{1/3}]$$

$$b^* = 200 [(Y/100)^{1/3} - (Z/118.10)^{1/3}]$$

where L^* , a^* , and b^* denote, respectively, the lightness, blueness, and yellowness evaluated by a Suga Test Instrument AUD-SCH-2U colorimeter.

RESULTS AND DISCUSSION

Effect of Initial BMA Concentration on Polymer Add-on

The graft polymerizations of the BMA monomer onto silk fibers were effected at 80°C for 45 min, according to the procedure described in the experimental part, with a reaction system containing as initiator 2.2% (with respect to monomer) ammonium persulfate and different amounts of BMA [15–75% (o.w.f.)]. As shown in Table I, the weight gain of the prepared grafted silk increased steadily with increasing initial BMA amount.

Equilibrium Regain

Changes in the equilibrium regain of the grafted silk specimens were measured in relation to the levels of polymer add-on (Fig. 1). The equilibrium regains changed little over the polymer add-on range of 0–32%, but then they increased dramatically with further increases in weight gain. The increase in the regain of the grafted silk fibers observed at higher levels of weight gain (above 32%) was attributed to the hydrophilic properties of the poly(BMA), which had been inserted in the silk matrix. The equilibrium regain did not differ essentially between the grafted silk fibers and the habutae silks grafted with poly(BMA).

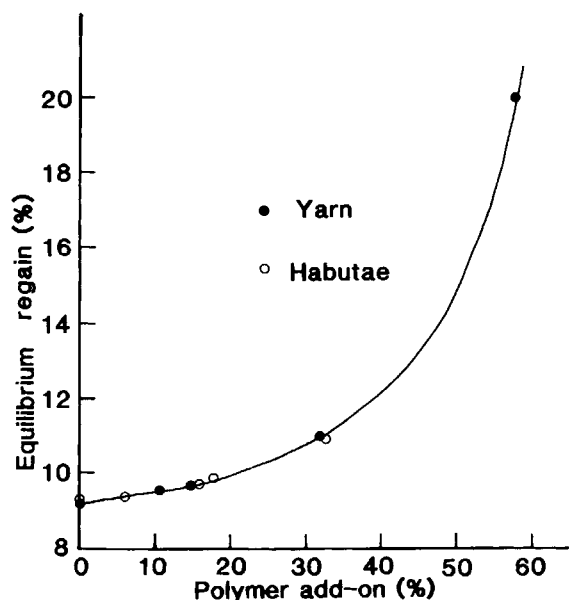


Figure 1 Equilibrium regains of the *N*(*n*-butoxy-methyl) methacrylamide (BMA)-grafted silk fibers as a function of polymer add-on. Sample: ● silk yarn, ○ silk plain weaven.

Thermal Behavior

In DSC the endothermic peak temperature was not an accurate description for the transition temperature. A more reliable description for the thermally induced transition would have been the onset temperature of the recorded endothermal or exothermal peak. However, variations in those characteristics, which determine the net heat flow into the sample system, make the reliable and reproducible recognition of this temperature difficult.¹² When the sample size, its form, the applied heating rate, and the character of the induced transition were effectively constant, the temperature difference between T_{peak} and T_{onset} for an observed curve can then be reasonably assumed as also constant. Positive statements are therefore possible concerning shifts in transition location based on observations of the peak temperatures. It was in this context that the peak temperatures were employed in this presentation.

Figure 2 shows the DSC curves of poly(BMA)-grafted silk fibers. Untreated silk fibers (a) showed a single endothermic peak at about 314°C, which has been attributed to the thermal decomposition of silk fibroin with an oriented β' configuration.¹³ The position of this endothermic peak shifted slightly to higher temperatures as the polymer

weight gain increased. In the DSC curves there appeared a broad endothermic peak at about 236°C, for those samples where the polymer weight gain was above 16.6%. The size of this peak increased and its position shifted to higher temperatures with further increases in weight gain. It can be speculated that this endothermic peak is associated with the thermal decomposition of the poly(BMA) present in the silk matrix.

The dynamic viscoelastic properties of the poly(BMA)-grafted silk fibers were assessed in relation to the weight gain. The dynamic storage modulus (E') curves of the grafted silk are presented in Figure 3. In air, the control silk fiber exhibited a decreasing E' value, beginning at around 185°C, which was followed by a more drastic decrease at temperatures above 213°C. The E' curves of the silk showed that the onset temperature for this decrease in E' shifted to lower temperatures with increasing polymer weight gains by the fiber. This suggested that thermally induced molecular movement of the poly(BMA)-grafted silk fiber occurred even at 185°C. This interpretation would be consistent with the loaded silks exhibiting a slightly lower thermal stability than the control silk fibers.

Figure 4 shows the dynamic loss modulus (E'')

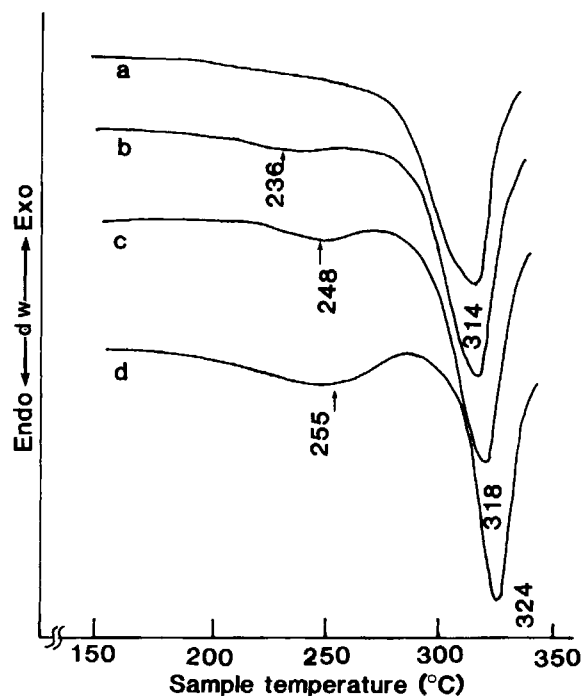


Figure 2 DSC curves of poly(BMA)-grafted silk fibers with various polymer weight gains. Add-on (%): (a) 0, (b) 16.6, (c) 32.3, (d) 57.5

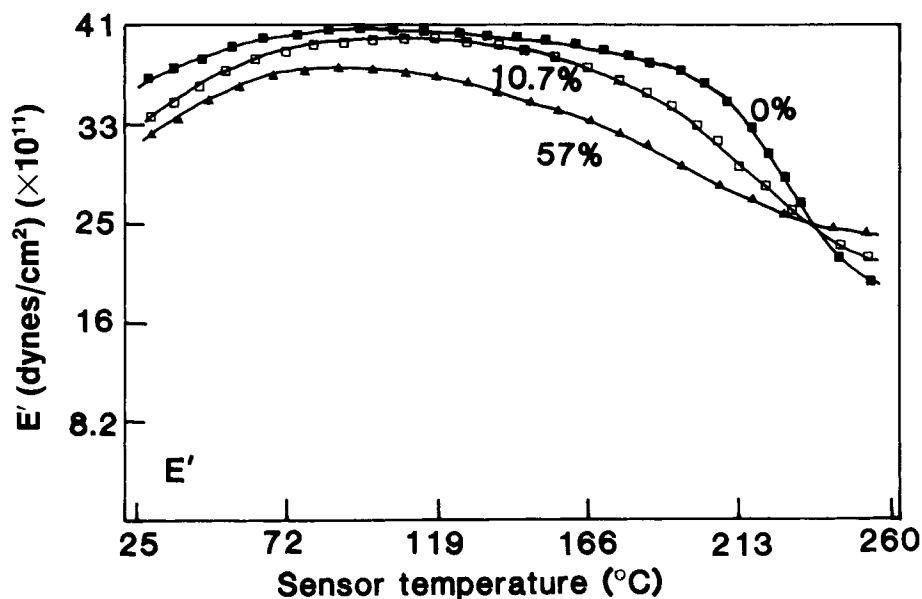


Figure 3 Dynamic storage (E') modulus of poly(BMA)-grafted silk fibers with different add-on values. Add-on (%): ■ 0, □ 10.7, △ 57.5.

curves of the grafted silk fibers. The E'' curves show a major peak at about 200–220°C. The untreated control sample showed the E'' peak maximum at around 223°C. The peak temperature of the loss modulus E'' shifted to lower values, and the peak was also widened by the poly(BMA) grafting. The extent of broadening of the E'' peak became signif-

icant when the polymer add-on was increased above 10%. The loss peak shifted linearly to lower temperatures with increasing polymer. This observation suggested that the molecular motions within the crystalline regions were influenced by the thermal motions of the poly(BMA) molecules grafted onto the silk fiber matrix. The dynamic viscoelastic be-

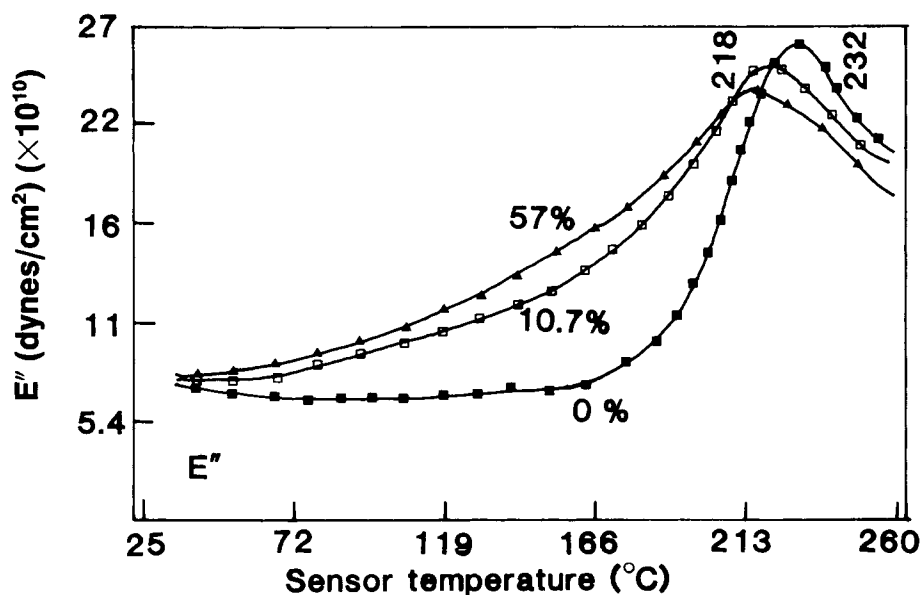


Figure 4 Dynamic loss modulus (E'') of the poly(BMA)-grafted silk fibers with different add-on values. Add-on (%): ■ 0, □ 10.7, △ 57.5.

haviors of the grafted silks indicate that the interatomic vibration within the chain segments of the ordered regions becomes more facile with increasing levels of polymer loading. These results imply that the BMA polymer was not only present in the amorphous regions but was also located within the fringed fibril volumes at the ends of each individual ordered element aligned along the filament axis.

Thermomechanical analysis (TMA) curves of the grafted silk fibers were also obtained to observe the contractions and extension of the fiber in the course of the heating process (Fig. 5). The control fibers demonstrated similar thermal behaviors to those previously described. The poly(BMA)-grafted silk fiber with small weight gains (less than 16%) showed a close similarity to the control fibers. TMA curves of the more heavily loaded grafted silk fibers, with weight gains up to 32%, exhibited a broad and increasing contraction with temperatures up to 316°C.

Tensile Properties

The tensile strengths, elongations at break, and initial moduli of the poly(BMA)-grafted silk fibers with different values of polymer weight gain are reported in Figure 6 and Table I. The tensile strength of the grafted silk fibers was observed to remain un-

changed at a constant value of 4.4–4.5 g/d ($1 \text{ g/d} = 1.22 \times 10^3 \text{ kgf/cm}^2$) when the polymer add-on was 10% or below. Above this value, the strengths of the fiber decreased sharply over a narrow weight gain range (10–17%) and then decreased more gradually with further weight gains. Any weight gain caused an initial steep decrease in the elongation at break. This decrease continued more gradually with polymer add-on values beyond an initial 10%. It is of interest to note that the breaking load of single grafted silk fibers is about 144–150 gf, a value that remained effectively unchanged regardless of the poly(BMA) add-on. The identified decreases in the tensile strength can be explained in terms of the swelling of the filaments on loading with poly(BMA) beyond the first 10% by weight add-on with the consequential increased cross-sectional area.

Poly(BMA) grafting onto silk would thus minimize the risk of adversely affecting the tensile properties if the weight gain was kept below 16%.

The initial tensile modulus of the grafted silk fiber with poly(BMA) was evaluated from the initial gradient of the strength–elongation curves and expressed in term of grams per denier. The initial tensile modulus of the silk fibers remained almost unchanged in the weight gain range of 0–10% but then decreased gradually with further polymer weight gains.

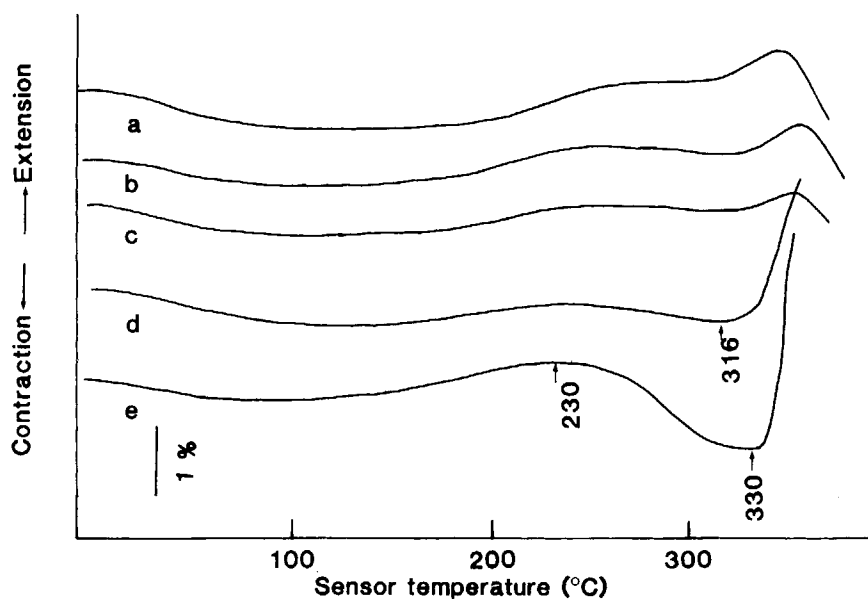


Figure 5 TMA of the poly(BMA)-grafted silk fibers with different weight gain values. Add-on (%): (a) 0, (b) 10.7, (c) 16.6, (d) 32.3, (e) 57.5.

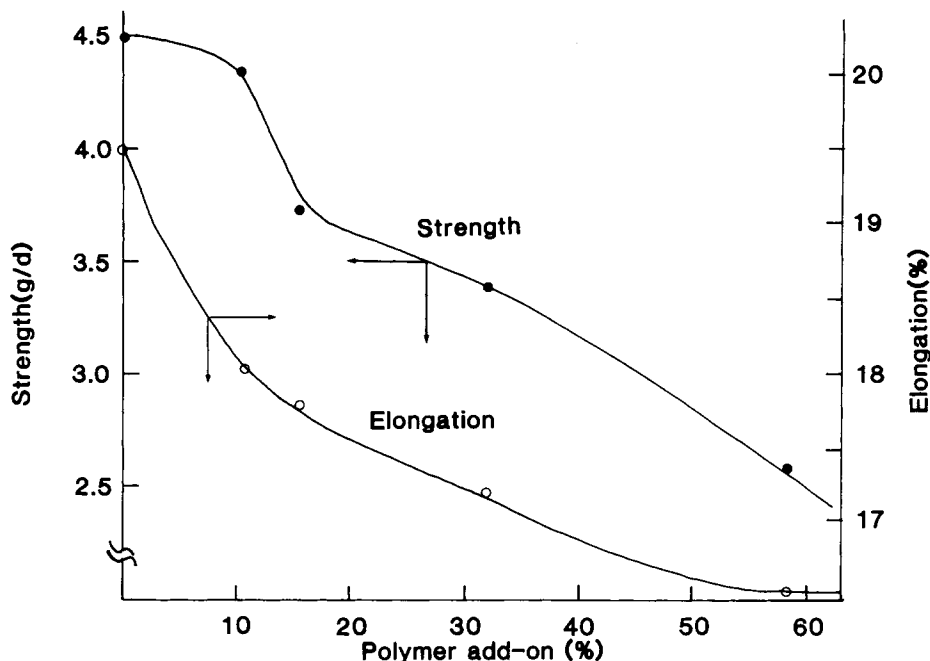


Figure 6 Tensile strengths (●) and elongation at break (○) at the poly(BMA)-grafted silk fibers as a function of the add-on values. (1 g/d = 1.22×10^3 kgf/cm²).

Yellowing Following Irradiation

Figure 7 shows the changes in whiteness due to carbon arc irradiation for the poly(BMA)-grafted habutae silk fabrics with different add-on values. The whiteness values exhibited a gradual decrease fol-

lowing irradiation for the exposure times here studied, as a consequence of the photoyellowing of the silk fabrics. We would like to draw particular attention to these results, which demonstrate that with increasing polymer weight gain the rate of loss of whiteness was greatly decreased. The changes in the

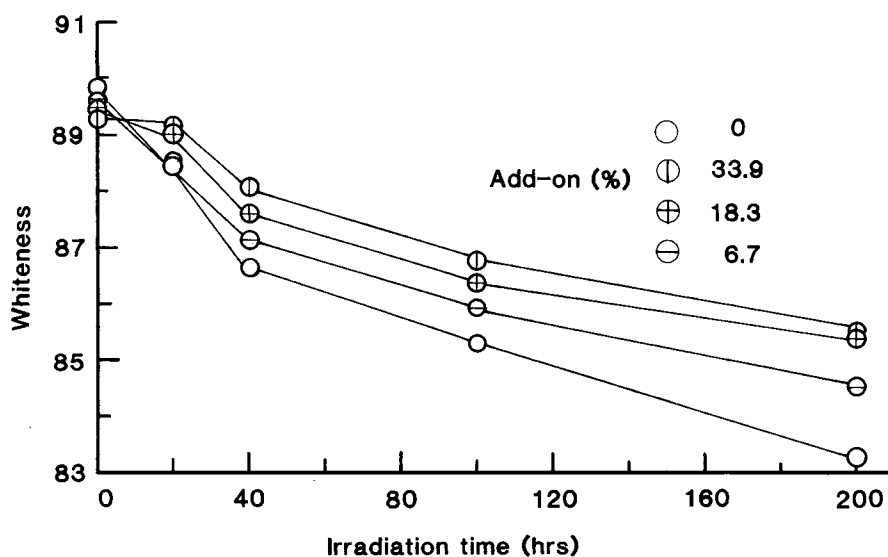


Figure 7 The whiteness of the poly(BMA)-grafted silk fabrics with different add-on values following carbon arc irradiation as a function of the irradiation time. (Major wavelength and intensity of illumination was 385 nm and 490 W/m², respectively.)

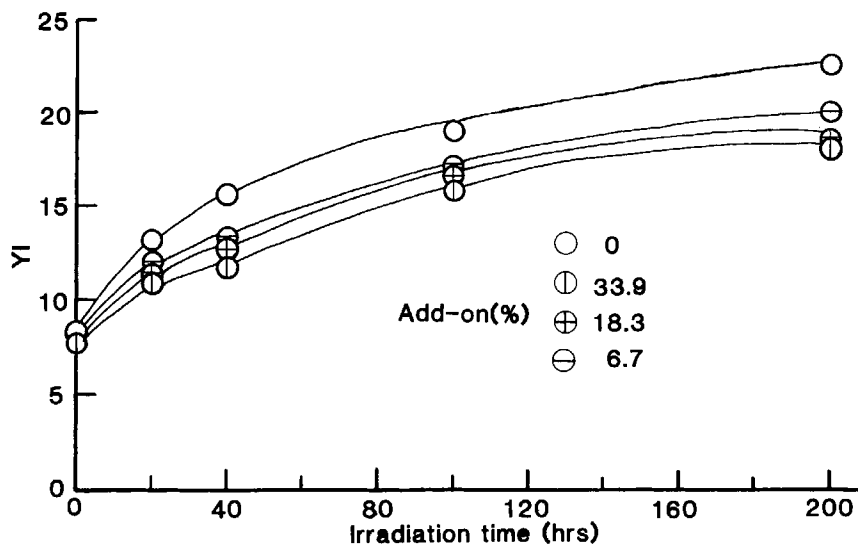


Figure 8 Yellowness index of the poly(BMA)-grafted silk fibers due to the carbon arc irradiation as a function of the irradiation time. (Illumination as in Fig. 7)

rate of increasing yellowness index of the silk fabric due to irradiation are presented in Figure 8. The yellowness index value of the control ungrafted habutae silk increased considerably during the irradiation, while the comparable rates of increase in the yellowness index were lower for the silk fabrics with grafted poly(BMA). It was concluded that the poly(BMA) weight gain has a marked influence on sustaining whiteness and in reducing the rate of increase in the yellowness index of irradiated silk fibers/fabrics.

The results here reported demonstrate that the production of poly(BMA) within silks is effective for reducing their photoyellowing. Further investigations are necessary in order to elucidate both the mechanisms of grafting and, in particular, the mechanisms by which poly(BMA) grafting can be so effective for decreasing the rate of photoyellowing. The above results draw attention to the particular BMA monomer, which has an alkoxy group in the side chain. In other experimental results (Shiozaki, in preparation), with polymerizations onto silk using vinyl monomers such as the *N*(alkoxymethyl) methacrylamides with methoxy, ethoxy- and *n*-prooxy groups, we have found these are also effective in reducing the rate of photoyellowing of UV-irradiated silk fabrics. We can thus identify that vinyl monomers with alkoxy groups in their structure appear to provide a potentially powerful approach for the development of practical techniques for producing new property-modified silks for applications beyond their traditional elite areas.

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