Physical Properties and Dyeability of Silk Fibers Modified with Ethoxyethylmethacrylate Polymer

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SYNOPSIS

The structural characteristics, physical properties, and dyeing behavior of *Bombyx mori* silk fibers containing ethoxyethylmethacrylate (ETMA) polymer are reported in relation to the add-on. The add-on value increased with the reaction time and attained a maximum after 60 min at 80°C. The surface of silk fibers with an add-on value of 40% showed the presence of several irregular granules, consisting of ETMA oligomers. The infrared spectrum of the silk fibers containing the ETMA polymer showed overlapped absorption bands due to the molecular conformation of untreated silk and ETMA polymer, giving evidence that the ETMA polymerization occurred inside the fiber matrix. The DSC results suggested that the thermal decomposition behavior of the silk fiber remained almost unchanged, except that the decomposition temperature shifted slightly to higher temperature. The tensile properties of the silk fiber remained unchanged regardless of the ETMA polymerization. The rate and extent of acid dye uptake was greatly increased by the polymerization of ETMA into the silk fibers as well as the transfer printing properties.

INTRODUCTION

In recent years many attempts have been made to improve silk fiber properties by graft copolymerization and/or chemical modification techniques. With the wide variety of vinyl monomers, epoxides,[1,2] and other modifying agents available, these techniques promise to be a powerful method for producing substantial modification of fiber properties as well as improving their textile performances. Among the vinyl monomers, methyl methacrylate (MMA),[3] methacrylamide (MAA),[4] 2-hydroxyethyl methacrylate (HEMA),[5] methacrylonitrile (MAN),[6] and styrene (St) have been extensively studied, and some of them are successfully applied on the industrial scale for silk processing. The physical and mechanical properties as well as the structural characteristics of silk fibers graft-copolymerized with MMA,[3] MAA,[4] HEMA/MAA,[7] and MAN[6] have been recently reported. Kobayashi et al.[8] observed that the wrinkle recovery of MMA-grafted silk fibers increased when the graft yield was in the range of 30–60%. Silk fibers copolymerized with MAA[9] and HEMA at low graft yield show a noticeable increase of moisture content which plays a positive role in improving the comfort of silk fabrics, without affecting their handling and luster. Shiozaki and Tanaka[1,2] extensively studied the reactivity of epoxides toward silk fibroin and indicated that silk fibers modified by epoxide treatment show improved properties as concerns crease resistance, W & W characteristics, and color fastness to washing.[10] The chemical modification of silk with dibasic acid anhydrides,[11] i.e., succinic and glutaric anhydrides, has been recently reported to be effective in increasing the crease resistance and reducing the photoyellowing of silk fabrics without affecting the tensile properties.

The physical and chemical properties of silk fibers either grafted or chemically modified depend not

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only on the extent of grafting and/or weight gain, but also on the characteristics of the functional group carried by the monomer, which becomes an integral part of the silk fiber. Moreover, the degree of polymerization of the grafted chains might bring about additional effects on the properties of the copolymerized silk fibers, due to the iterative repetition of the chemical function of the monomer side chain. According to the kind of monomer used for grafting or modification, silk fibers undergo from slight to drastic changes in their dyeing behavior, i.e., rate of dyeing and uptake of acid dyes. Styrene-grafted silk fibers, due to their hydrophobic properties, show affinity for disperse dyes[12] and have been suggested to be suitable for transfer printing. However, the use of styrene monomer for silk grafting entails some negative consequences due to its strong hydrophobic properties, to the hard hand it confers to silk fabrics, and to the problems of air pollution during application in industrial plants. To overcome these drawbacks, new vinyl monomers selected according to the properties of the functional group carried by their side chain should be studied. Matsumura and Shiozaki[13] have reported the optimum conditions for the polymerization of ethoxyethylmethacrylate (ETMA) on silk fibers initiated by ammonium persulfate and some transfer printing characteristics of the grafted silk fabrics. However, no detailed information is available on the physical properties of silk fibers containing ETMA polymer and on the rate of absorption of acid dyes during the dye process.

This paper deals with the characterization of the silk fibers containing the ETMA polymer. The physical, mechanical, and thermal properties, the dyeing behavior with acid dyes, and the transfer printing of silk fibers modified with ETMA are discussed in the light of the characteristics of the polymer inserted in the fiber substrate.

EXPERIMENTAL

Materials

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

Reagent grade ethoxyethylmethacrylate (ETMA) (1) (purity 99.6%; specific gravity 0.967) purchased

$$CH_2{=}C(CH_3)\overset{\overset{O}{\|}}{C}O(CH_2)_2OC_2H_5 \qquad (1)$$

from Mitsubishi Rayon Co., Ltd. was used without further purification. Degummed silk fiber was immersed in a mixture of 1 g/L nonion emulsifying agent (polyoxyethylenealkylphenylether), 1 g/L anion emulsifying agent (sodium dodecylbenzenesulfonate), 2% ammonium persulfate on the weight of ETMA monomer, 2 mL/L formic acid and 30% ETMA (owf), or 40% ETMA (owf) in another experiment (material to liquor ratio 1 : 15); the reaction bath was brought to the required temperatures (60, 70, and 80°C) for different periods of time. At the end of the reaction the treated silk was soaked in a solution containing 1 g/L nonionic detergent and 0.5 g/L sodium hydrosulfite at 75°C for 30 min, and rinsed with water thoroughly. Unreacted ETMA not utilized in the polymerization and ETMA oligomers were removed with acetone at 55°C for 1 h.

The add-on was calculated from the increase in weight of the control silk after ETMA polymerization as follows:

$$\text{Add-on (\%)} = (W_2 - W_1)/W_1 \times 100$$

where W_1 and W_2 denote the weights of the original silk and the silk containing ETMA polymer, respectively.

ETMA polymer was separated from the silk fiber containing ETMA polymer with an add-on of 40% at 98°C for 20 min in a mixture system containing 10 parts (w) of water, 10 parts (w) of sodium hypochlorite solution (active chlorine content, 2.5%) and 0.3 g NaOH (material to liquor ratio 1 : 50). The residue thus obtained was washed with water and dried *in vacuo*.

Styrene-grafted silk fabrics with different graft yields were prepared according to the procedure already reported.[12]

Measurements

Infrared absorption was obtained by the KBr disk method using a Japanese Spectroscopic Co., Ltd. infrared spectrophotometer IR-G.

DSC measurements were performed on a Rigaku Denki instrument (DSC-10A) at a heating rate of 10°C/min. The DSC range and sample weight were 2.5 mcal/s and 2 mg, respectively. The open alu-

minum cell was swept with N_2 gas during the course of the analysis.

The surface of the silk fibers containing ETMA polymer were examined, after gold coating, with a JEOL JAX-333S scanning electron microscope at acceleration voltage of 15 kV.

Fiber strength and elongation at break were measured on a single thread with an automatic tensilon tester (Tohyo Baldwin Co. Ltd.) at 20°C and 65% RH. Each value is the average of 25 results.

Dyestuff absorption of the silk containing ETMA polymer was evaluated by measuring transmission of the dye bath, using a dye-o-meter (STD-3P) of Suga Test Instrument Co., Ltd. with a red filter (λ = 742 nm). About 2.5 g of silk yarns were sealed in the pyrex tube (15 × 100 mm) containing the dye bath with 1.2% (owf) of dye (C.I. Acid Orange 51). The dyeing was started at 40°C. The dyeing temperature was gradually increased from 40 to 100°C over 30 min and was maintained at the same temperature for 45 min.

Silk fabrics containing different amounts of ETMA polymer were subjected to transfer printing with paper containing 2% C.I. Disperse Blue 3 at 203°C for 30 s. Silk fabrics grafted with styrene and artificial fiber fabric (polyester) were transfer-printed using Naomoto Kogyo 2R Nao printer in the same conditions as reference samples. The dye absorption was measured with a Hitachi color analyzer 607 and expressed in term of K/S values.

RESULTS AND DISCUSSION

Effect of Reaction Time on Add-on

Polymerization of ETMA monomer on silk fibers was carried out for different periods of time at three temperatures (60, 70, and 80°C) in a reaction system containing 2 mL/L formic acid, 0.6% (owf) ammonium persulfate, and 30% ETMA (owf). The relationship between add-on and reaction time is shown in Figure 1. In all the cases examined, the add-on value has been found to increase steadily with the reaction time and attain an equilibrium value within 60 min. These findings suggest that the ETMA polymer was introduced into silk fibers in the course of polymerization reaction and that the rate and extent of reaction are not affected by the temperature in the range from 60 to 70°C. Raising the temperature up to 80°C causes a noticeable increase of the maximum add-on value. Thus, under the present reaction conditions, the optimum add-on is obtained at 80°C for 60 min.

Surface Characteristics

Properties of silk fiber, such as handling, luster, and rubbing behavior, can be greatly influenced by the polymerization of vinyl monomers and for this reason it is interesting to investigate the surface mor-

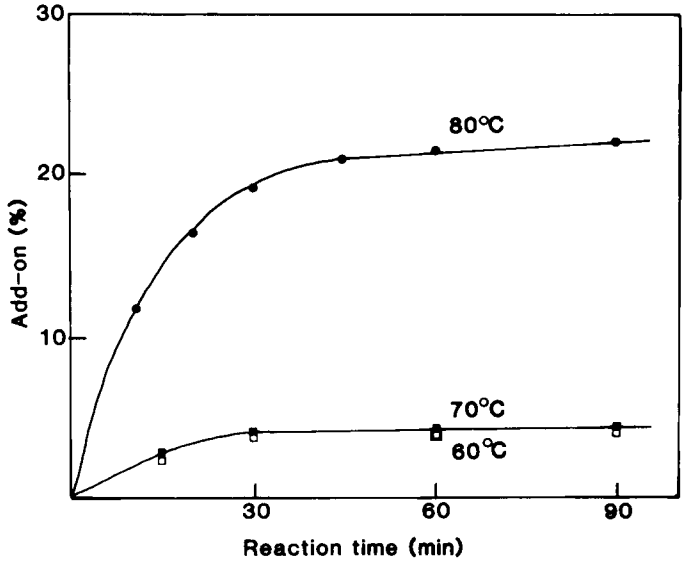

Figure 1 Add-on of the silk fibers following ETMA polymerization for different periods of time, at three different temperatures: 60, 70, and 80°C. ETMA concentration: 30% (owf).

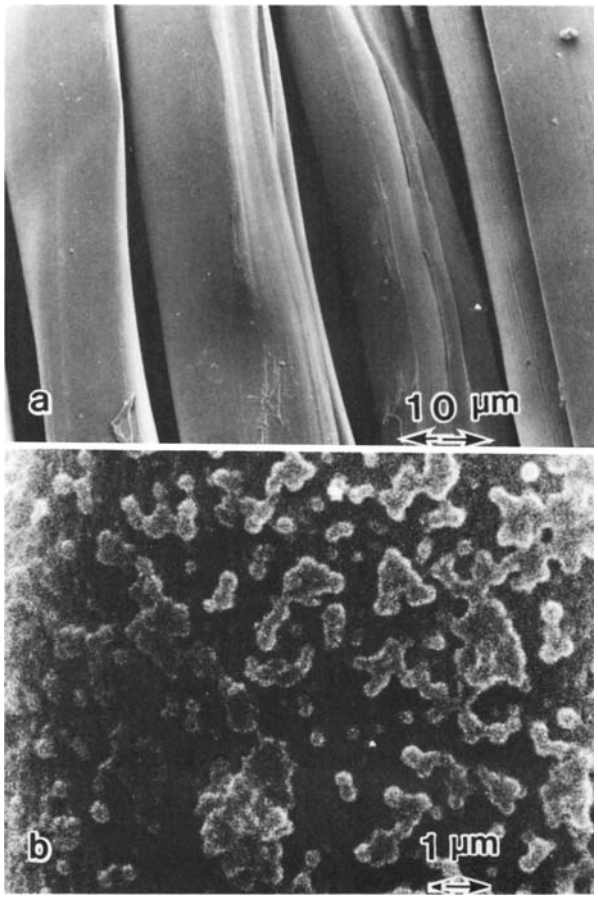

Figure 2 Scanning electron micrographs of control silk (a) and silk fiber containing ETMA polymer with an add-on of 40% (b).

phology by scanning electron microscopy. Figure 2 shows the SEM micrographs of the surface of silk fibers before and after ETMA polymerization. The surface of the control silk (a) is smooth, showing a typical appearance of *Bombyx mori* silk fibers. The fibers containing ETMA polymer with an add-on of 40% (b) revealed the presence of several irregular granules which apparently were not chemically bonded to the fiber surface, since they were removed easily by extraction with hot acetone. The same result was observed for the MMA-grafted silk fibers obtained by using potassium persulfate as initiator.[14] The granules were identified as MMA oligomers, on the basis of gel permeation chromatography measurements, with an average molecular weight of about 1000 D.[14] They begin to appear on the fiber surface only after a certain graft yield has been attained, usually 40–50%, and are easily removed by acetone extraction.

Infrared Spectra

Figure 3 shows the IR spectra of silk fibers containing ETMA polymer, together with those of the control silk and of the ETMA polymer separated from silk. The IR spectra of silk fibers containing ETMA polymer (b,c) show minor absorption bands (shoulder form) at 1730, 1120, and 1030 cm^{-1}, whose intensity increases as the add-on value increases, in addition to the absorption bands at 1630 cm^{-1} (amide I) and 1530 cm^{-1} (amide II) due to the β-structure of silk fibroin.[15] The absorption band at 1730 cm^{-1} is attributed to the ester group and those at 1120 and 1030 cm^{-1} are probably assigned to the $—CH_2—CH_2—$ bonds of the side chains of the ETMA polymer. The spectrum of the ETMA polymer separated from silk fibers (d) by treatment with NaClO/NaOH mixture system shows clear absorption bands at 1730, 1120, and 1030 cm^{-1}. The IR spectra of silk fibers containing ETMA polymer show absorption bands characteristic either of silk with β molecular conformation[15] or ETMA polymer overlapping in the spectral region from 4000 to 400 cm^{-1}, suggesting that the polymerization or copolymerization of the ETMA occurred in the fiber matrix. However, detailed study will be needed to elucidate whether ETMA polymer is chemically grafted or just trapped into the amorphous regions of silk fiber.

Thermal Properties

Figure 4 shows the DSC curves of silk fibers containing ETMA polymer. Untreated silk fibers (a) showed a single endothermic peak at around 318°C, which is attributed to the thermal decomposition of silk fibroin with oriented β' configuration.[16] The position of the endothermic peak appearing at about 320°C slightly shifted to higher temperature as the add-on increased (b,c). The ETMA polymer separated from silk fibers (d) exhibited a minor and broad endothermic peak at about 300–340°C, in addition to the clear endothermic peak at 392°C, which can probably be attributed to the decomposition of the ETMA polymer.

Tensile Properties

The strength and elongation at break of the silk fibers containing ETMA polymer with different add-on values are given in Table I. The strength and elongation at break of the silk fibers remained un-

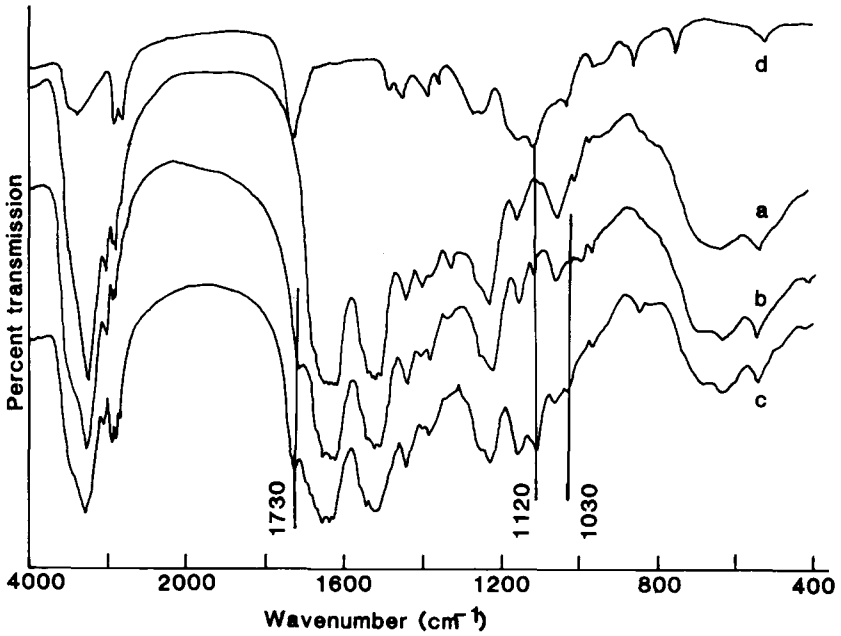

Figure 3 Infrared spectra of control silk (a), silk fiber containing different amounts of ETMA polymer (b, c), and ETMA polymer separated from the silk fiber containing ETMA polymer with an add-on of 40% (d). Add-on (%): (b) 15; (c) 40.

changed regardless of the ETMA polymerization, as reported also for silk fibers modified with epoxides and dibasic acid anhydrides.[11]

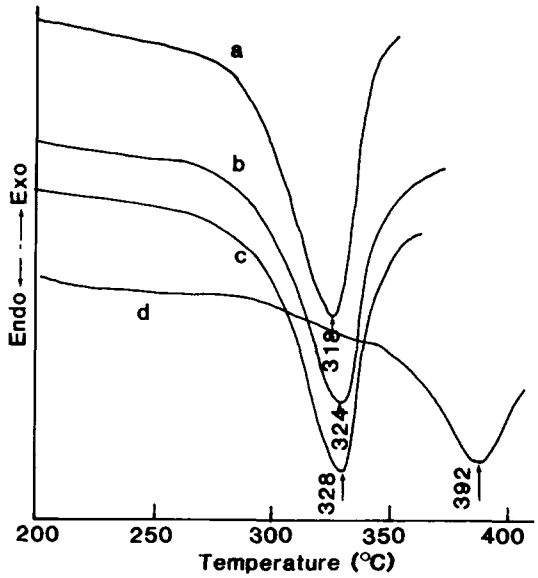

Figure 4 DSC curves of control silk (a), silk fiber containing different amounts of ETMA polymer (b, c), and the ETMA polymer separated from silk fiber containing ETMA polymer with an add-on of 40% (d). Add-on (%): (b) 15; (c) 40.

Dyeing Behavior

Figure 5 shows the results obtained by measuring the uptake of Acid Orange 51 acid dye in silk fibers containing ETMA polymer with different add-on values. The silk fibers containing ETMA polymer show a rather steep rise of dye uptake at the beginning of the dyeing cycle and attain exhaustion levels significantly higher than that of the untreated sample. It is interesting to note that the dye uptake attained by the untreated silk sample at the end of the dyeing cycle approximately corresponds to the amount of dye absorbed by the silk fibers containing ETMA polymer after only 30 min since the beginning of dyeing. Moreover, the extent of dye-bath exhaustion increases as the add-on value increases from 17.5 to 30%.

Table I Tensile Properties of Silk Fibers Containing Different Amounts of ETMA Polymer

Add-on (%)	Strength (g)	Elongation (%)
5	992	23.2
15	994	22.9
30	967	22.0
40	973	21.8
Control	960	23.0

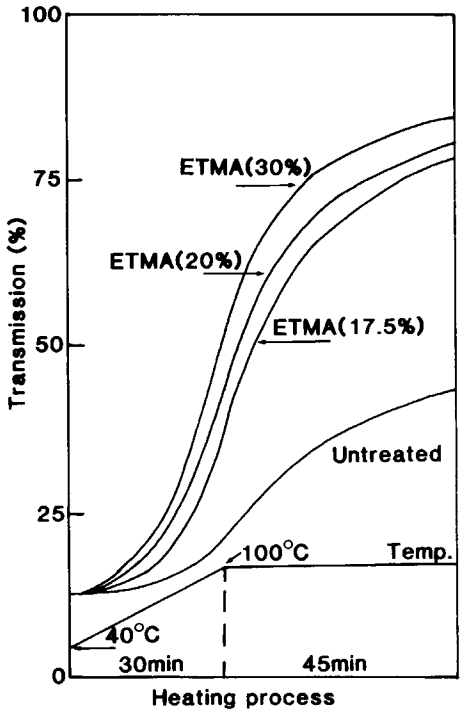

Figure 5 Percent transmission of the dye bath measured by dye-o-meter in the course of the heating process using red filter (λ = 742 nm) for the untreated fiber and the silk fibers containing different amounts of ETMA polymer.

These results draw our attention to the peculiar characteristics of silk fibers containing the ETMA polymer. Unlike most of the other vinyl monomers so far used for silk grafting, the ETMA monomer, after reaction in the fiber substrate, enhances the affinity of silk fibers for acid dyes (Fig. 5), increasing the rate of dyeing as well as the dye uptake and the dye-bath exhaustion. A similar effect, even if not so important, has been observed by studying the dyeing behaviour of silk fiber modified with some epoxides, such as ethylene glycol diglycidyl ether (EGDGE), one of the most widely used for silk processing on industrial scale.

The transfer printing properties of silk fibers containing ETMA polymer have been studied in comparison with styrene-grafted silk fibers. The results are reported in Figure 6. Both ETMA and styrene-modified silk fibers show an increase of disperse dye absorption as the add-on value increases. It is interesting to observe that the initial slope of the curve is noticeably higher for silk fibers containing ETMA polymer than for styrene-grafted silk fibers. As a consequence, in order to attain a K/S value similar to that of polyester printed with the same technique, silk fibers containing ETMA polymer require an add-on value, which is almost a half of that required by styrene-grafted silk fibers.

The results reported in this paper give evidence of the enhanced dyeability characteristics of silk fibers containing ETMA polymer. Further investigations should be carried out in order to elucidate the mechanism of dyeing and the similarities and/or differences among ETMA, epoxides, and styrene as concerns the affinity for acid and disperse dyes, respectively. The reaction mechanism of ETMA monomer and silk fibroin molecules has not been

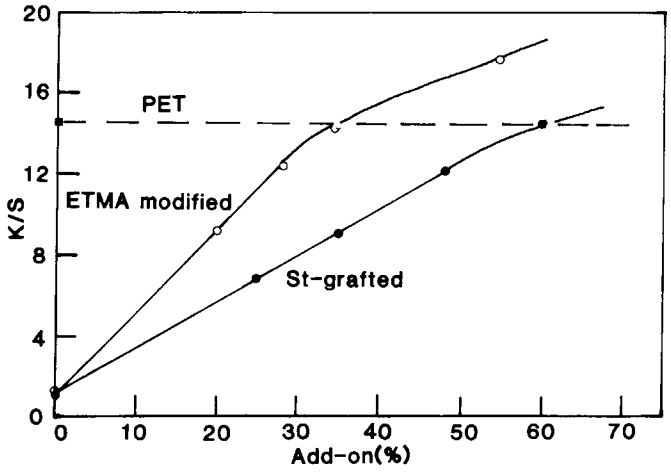

Figure 6 Relationship between K/S and add-on values of modified silk fabrics in comparison with polyester fabric after transfer printing: (○) silk fabrics containing ETMA polymer with different add-on values; (●) silk fabrics grafted with styrene with different graft yields; (■) polyester fabric.

elucidated yet. ETMA monomer is supposed to polymerize inside the fiber. This fact should entail some modifications of the morphology of the amorphous region of the fiber due to the steric interaction between the ETMA polymer chains and the fibroin molecules. These structural effects due to the ETMA polymer chains inserted into the silk matrix should be taken into consideration for a proper evaluation of the dyeing behavior of silk fibers modified with ETMA.

Finally, we would like to emphasize the interest of the experimental results concerning the dyeing behavior with acid dyes for the improvement of current dyeing techniques. They seem to offer new opportunities for the dyeing of silk yarns and fabrics in "mild" conditions, reducing temperature and/or treatment time. This would minimize the risk of affecting the physical properties and damaging the surface of silk fibers, which are very sensitive to prolonged treatments at high temperature, as happens during dyeing processes.

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