Structural Characteristics of 2-Hydroxyethylmethacrylate (HEMA)/Methacrylamide (MAA)-Grafted Silk Fibers

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Synopsis

A series of 2-hydroxyethylmethacrylate (HEMA)/methacrylamide (MAA)-grafted silk fibers obtained in various comonomer compositions was prepared and their structural characteristics were studied by X-ray diffractometry, differential scanning calorimetry, and scanning electron microscopy. HEMA/MAA-grafted silk fibers with a graft yield of about 60% obtained in a HEMA/MAA mixture system containing 20% of HEMA and 80% of MAA on a weight basis showed endothermic peaks at 280 and 420°C (shoulder form), which are attributed to the thermal decomposition of the MAA and HEMA polymers, respectively, in addition to the thermal decomposition peak of the silk fibroin fiber which appeared at 323°C. These DSC results suggest that the HEMA/MAA-grafted silk fiber showed a low compatibility in the relation between the silk fibroin molecules and HEMA and/or MAA polymers. The crystalline structure of the HEMA/MAA-grafted silk fiber remained unchanged regardless of the HEMA/MAA grafting ratio even when the graft yield value reached 120%.

INTRODUCTION

As a fiber, silk is, from the textile point of view, reasonably resistant to acids, and is usually dyed with acid dyes or with direct dyes from a neutral salt solution. Silk has a high elastic modulus with a limited though useful extensibility but high strength both when dry and wet, mainly due to its peculiar microstructural characteristics such as crystallinity, strong hydrogen bonds between the C=O and NH groups of adjacent molecules, and amorphous regions showing a high crystalline order and composed of bulky side chains. However, the silk fiber displays a low light-resistance and low-wrinkle recovery which can be improved by modifying its properties. Among the various methods available for the modification of silk, graft copolymerization appears attractive. Considerable work on graft copolymerization of vinyl monomers onto silk has been published in the polymer literature.[1-4] As already discussed in a previous paper,[5] the MMA-grafted silk fiber showed a low compatibility in the relation between the silk fibroin molecules and MMA polymer based on the results of DSC analysis.

Among various kinds of vinyl monomer grafting agents, 2-hydroxyethylmethacrylate (HEMA) and methacrylamide (MAA) are the most popular and useful agents that enable to improve the characteristics of silk fibers. Therefore, the author considers that grafted silk fibers prepared in a HEMA/MAA

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mixture system could exhibit a chemical structure and mechanical properties suitable for textile use.

In the present paper, the author analyzes the structural characteristics and thermal properties of grafted silk obtained in a HEMA/MAA mixture system based on the results of differential scanning calorimetry, X-ray diffraction measurements, and electron microscopy studies.

EXPERIMENTAL

Materials

Raw silk fibers were obtained after reeling of cocoon threads of the commercial silkworm variety *Bombyx mori*. The composite threads made of the bave from several cocoons drawn off together were twisted mechanically (750 T/m). Dried silk fibers, used as the grafting substrate, were immersed in a HEMA/MAA mixture system with a different comonomer feed composition by using an aqueous solution of potassium persulfate (0.1%) as the initiator. In the case of a HEMA/MAA (60/40)-grafted silk fibroin, HEMA/MAA mixture system contains 60% of HEMA, and 40% of MAA on a weight basis. HEMA purchased from Wako Pure Chemical Industries Ltd. (lot no. PEL 1927) was purified by distillation to remove the hydroquinone monoethylether, stabilizer, and the middle fraction was stored in a refrigerator prior to use. MAA and potassium persulfate were reagent grade products purchased from Eastman Kodak Company (lot no. CDQ 1460) and Nakarai Chemicals Ltd. (lot no. V2T 9229), respectively. All the reactions for grafting were performed under a nitrogen atmosphere at temperatures in the range of 75–85°C for various periods of time to obtain different graft yields, and using a diluted sulphuric acid solution at pH 3.2. A material-to-liquor ratio of 1 : 100 was maintained. At the end of the reaction, oligomers formed by the polymerization of the comonomers were removed, according to the procedure described by Shiozaki and Tanaka.[6]

The graft yield was calculated from the increase in weight of the original silk fiber after grafting as follows:

$$\text{graft yield } (\%) = (W_2 - W_1)/W_1 \times 100$$

where W_1 and W_2 denote the weights of the original silk fiber and the grafted silk fiber, respectively.

Measurements

DSC measurement of the HEMA/MAA-grafted silk fibers was carried out in a Rigaku Denki differential calorimeter (DSC-10A) in a flowing nitrogen atmosphere. DSC range and sample weight were 2.5 mcal/s and 2 mg, respectively. The open aluminum cell was swept with nitrogen gas during the course of the analysis.

The X-ray diffraction photographs were obtained using a Rigaku Denki automatic X-ray diffractometer (Ru-200) with Ni-filtered CuK_α radiation at room temperature. The voltage and current of the X-ray source were about 50 kV and 50 mA, respectively.

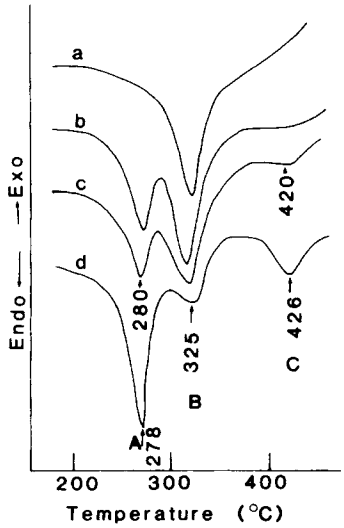

Fig. 1. DSC thermograms of silk fiber (a) and 2-hydroxyethylmethacrylate (HEMA)/methacrylamide (MAA)-grafted silk fibers (b–d). Grafted silk fibers: (b) HEMA/MAA (0/100), 59%; (c) HEMA/MAA (20/80), 61%*; (d) HEMA/MAA (20/80), 120%. *Grafted silk fiber with graft yield of 61% obtained in a HEMA/MAA mixture system containing 20% of HEMA and 80% of MAA on a weight basis at 75–85°C using potassium persulphate as the initiator.

The surface of the grafted silk fibers was examined, after gold coating, with a JEOL JAX-333S scanning electron microscope.

RESULTS AND DISCUSSION

Thermal Properties

DSC measurements were carried out for the purpose of analyzing the changes of the thermal properties of the silk fibers before and after grafting. Figures 1 and 2 show the DSC thermograms of grafted silk fibers. DSC thermogram of HEMA/MAA (0/100)-grafted silk fiber (b), i.e., MAA-grafted silk fiber, with a graft yield of 59% shows endothermic peaks at 280 and 323°C. The temperature at which the endothermic peak occurred (323°C) corresponds to the temperature for the thermal decomposition of the silk fibroin fiber with an oriented β' configuration.[7] HEMA/MAA (20/80) grafted silk fiber (c) with a graft yield of 61% showed a new minor endothermic peak (shoulder form) at 420°C, in addition to the major peaks at 280 and 323°C, although the intensity of the latter endothermic peak was low. HEMA/MAA (20/80)-grafted silk fiber (d) with a graft yield of 120% exhibited a distinct endothermic major peak at 278 and minor endothermic peak at 325°C. The amount of enthalpic change occurring at about 325°C decreased when the graft yield increased, while that appearing at 426°C increased. HEMA/MAA (100/0)-grafted silk fiber (g), i.e., HEMA-grafted silk fiber with a graft yield of 62%, showed an endothermic peak at 328°C and an additional minor endothermic peak at 425°C. Since the endothermic peak at about 325°C is attributed to the thermal decomposition of silk fibroin with an oriented β'

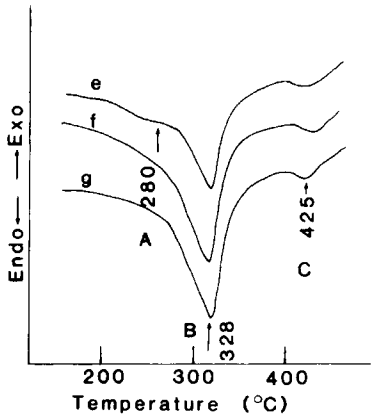

Fig. 2. DSC thermograms of HEMA/MAA grafted silk fibers. Grafted silk fibers: (e) HEMA/MAA (80/20), 61%; (f) HEMA/MAA (90/10), 61%; (g) HEMA/MAA (100/0), 62%.

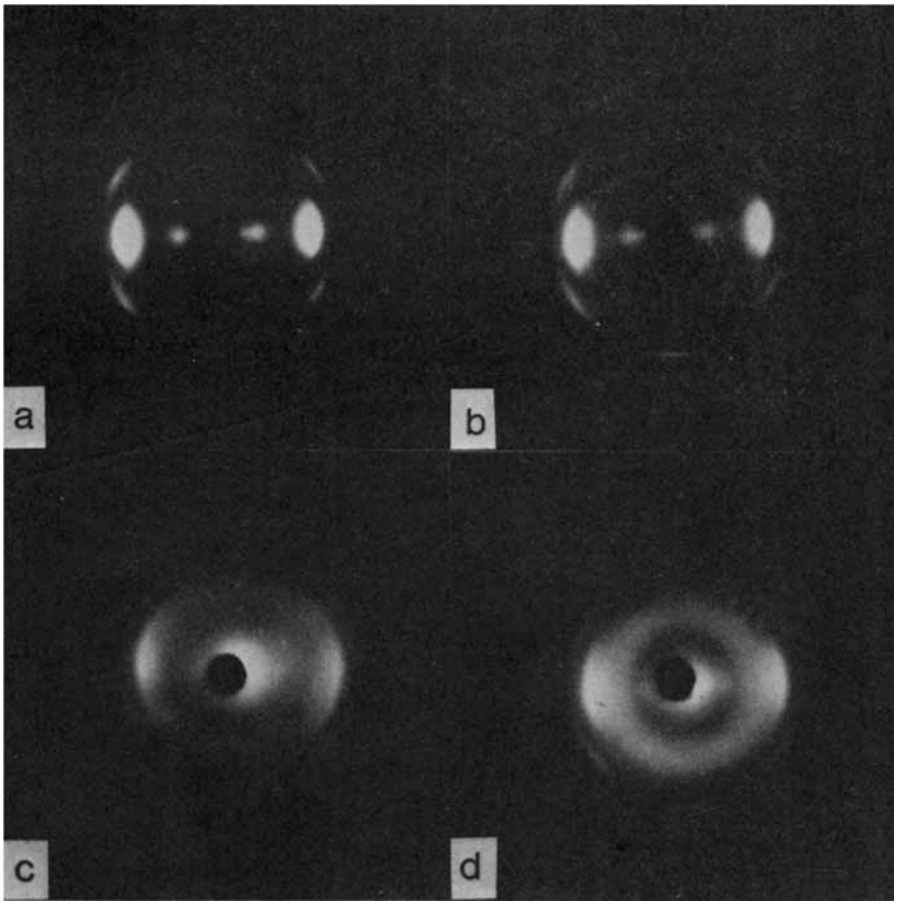

Fig. 3. X-ray diffraction patterns of silk fiber (a), HEMA/MAA grafted silk fibers (b–g), and HEMA polymer (h). Grafted silk fibers: (b) HEMA/MAA (0/100), 59%; (c) HEMA/MAA (20/80), 61%; (d) HEMA/MAA (20/80), 120%; (e) HEMA/MAA (80/20), 61%; (f) HEMA/MAA (90/10), 61%; (g) HEMA/MAA (100/0), 62%.

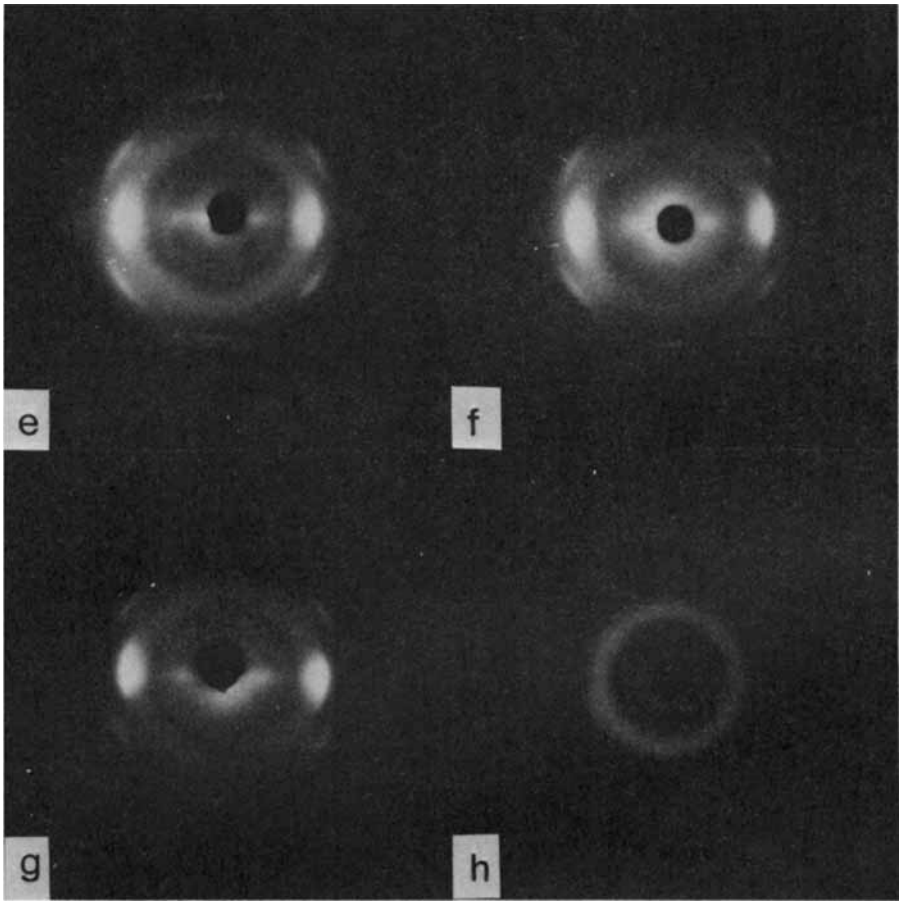

Fig. 3. (*Continued from the previous page.*)

configuration,[7] it seems that the endothermic peaks observed at 280 and 425°C are due to the thermal decomposition of MAA, and HEMA polymer filled in the silk fiber, respectively. The intensity of the DSC endothermic peak of the HEMA/MAA-grafted silk fiber observed at 325°C decreased with increasing graft yield (c, d), possibly due to a decrease of the content of the silk fibroin fraction on a weight basis. In the present study, the temperature at which the silk fibroin decomposed remained unchanged regardless of the grafting. The results of the DSC analysis suggest that the HEMA/MAA-grafted silk fiber shows the thermal behavior of a blend of HEMA and MAA polymers. It is thus concluded that the HEMA/MAA-grafted silk fiber exhibits a low compatibility in the relation between the silk fibroin molecules and HEMA and/or MAA polymers.

Crystalline Structure

X-ray diffraction photographs of the grafted silk fibers are presented in Figure 3. These HEMA/MAA-grafted silk fibers showed diffraction patterns oriented toward the equator and corresponding to a spacing of 4.87, 4.28 Å,

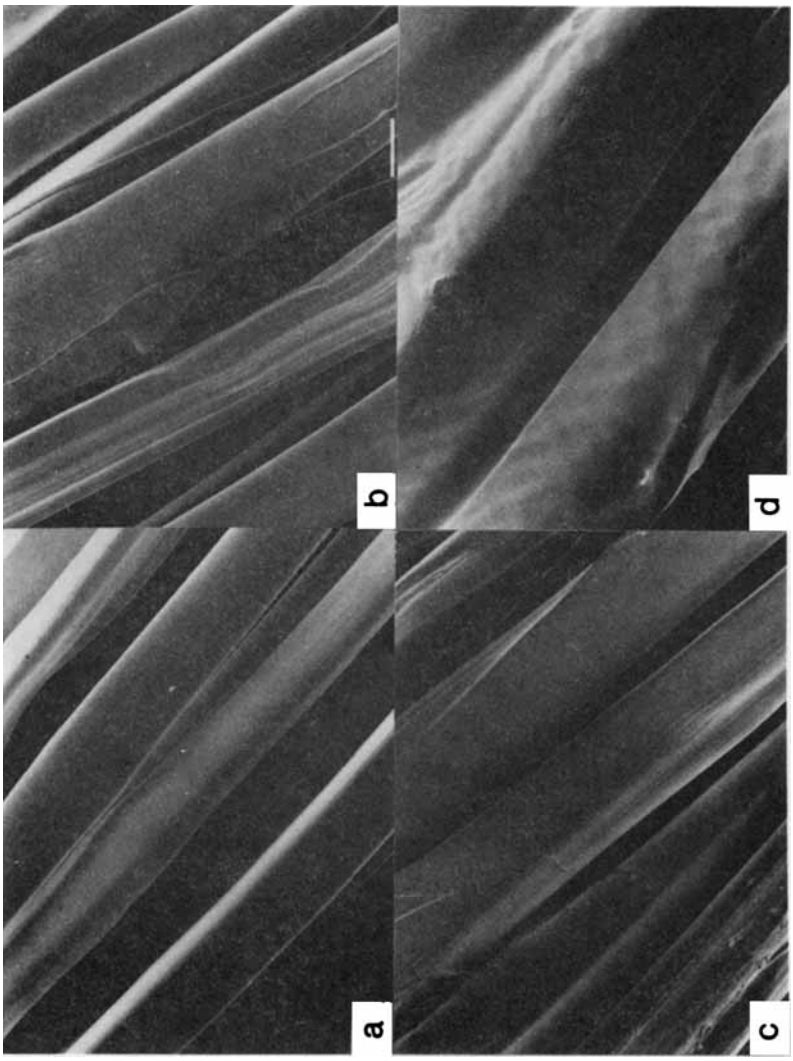

Fig. 4. Scanning electron micrographs of silk fibroin (a) and HEMA/MAA grafted silk fibers (b–h). Grafted silk fibers: (b) HEMA/MAA (0/100), 59%; (c) HEMA/MAA (20/80), 61%; (d) HEMA/MAA (20/80), 120%; (e) HEMA/MAA (60/40), 63%; (f) HEMA/MAA (80/20), 61%; (g) HEMA/MAA (90/10), 61%; (h) HEMA/MAA (100/0), 62%.

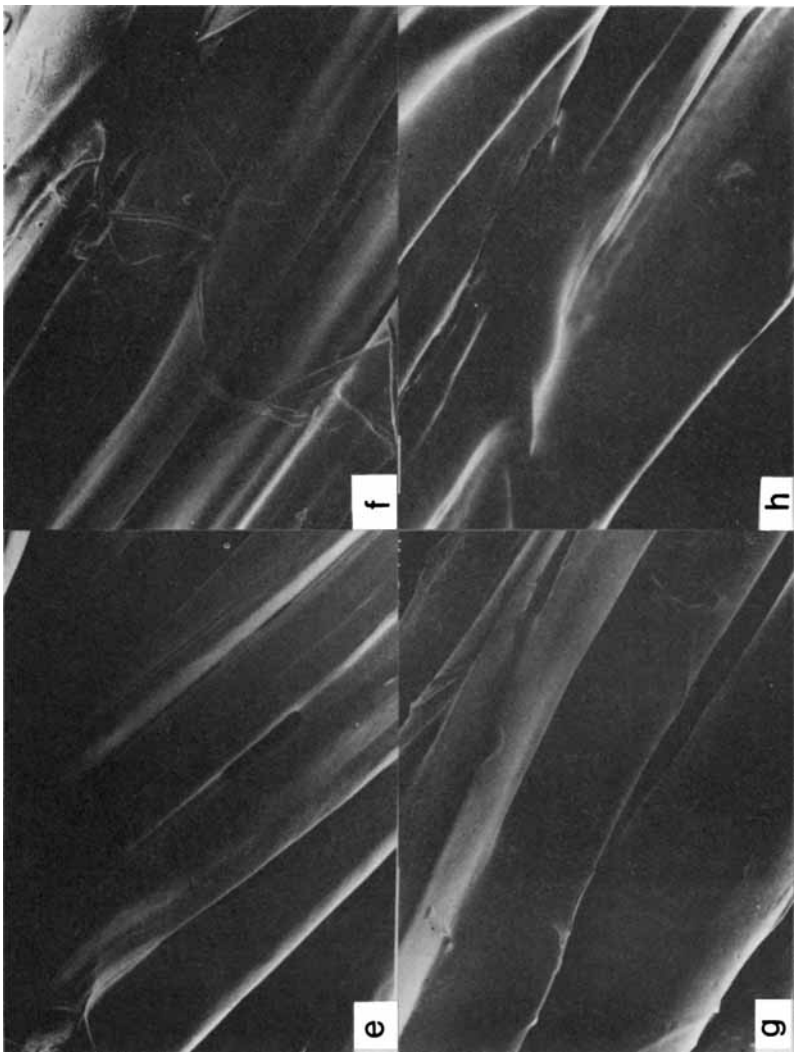

Fig. 4. *(Continued from the previous page.)*

which is characteristic of the oriented β' configuration.[8] When the HEMA composition and graft yield increased, the HEMA/MAA-grafted silk fiber (d) showed a diffraction ring with a spacing of about 8 Å attributed to the HEMA polymer (h), which is amorphous in nature, in addition to the above diffraction patterns. The X-ray diffraction pattern of the HEMA/MAA-grafted silk fiber was similar to that of the ungrafted silk fiber (a) even when the graft yield increased up to 120%. These results indicate that the crystalline structure of the grafted silk fiber remained unchanged even after grafting and that the crystalline structure of silk fibroin is independent of the structure of the grafted polymers.

Fiber Morphology

Figure 4 shows the surface of the HEMA/MAA-grafted silk fiber with different graft yields. The surface of the HEMA/MAA-grafted silk fiber (b, c) appeared to be as smooth as that of the ungrafted silk fiber (a), except for the HEMA/MAA (20/80)-grafted silk fiber (d) with a graft yield of 120%, HEMA/MAA (100/0) grafted silk fiber (h) with a graft yield of 62%, and HEMA/MAA grafted silk fibers (e–g). It thus appears that the chemical bonds and/or physical adhesion to the surface of the grafted silk fibers are likely to occur in the HEMA oligomers and HEMA polymers when the graft yield increases. Compared to the methyl methacrylate (MMA)-grafted silk fibers described in a previous paper,[5] very similar structural characteristics were observed for the HEMA/MAA-grafted silk fibers.

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