Studies on Some Physical Properties and Structural Characteristics of Methyl Methacrylate-Grafted Silk Fiber

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Synopsis

Structural characteristics and physical properties of methyl methacrylate-grafted silk fiber from *Bombyx mori* were studied by X-ray diffractometry, differential scanning calorimetry (DSC), thermogravimetry, and scanning electron microscopy. Methyl methacrylate (MMA)-grafted silk fiber with a grafting yield of more than 30% showed two endothermic peaks at 320°C and 390–410°C, which are attributed to the thermal decomposition of silk fibroin and MMA polymer filled in the fiber, respectively. These DSC results indicate that MMA-grafted silk fiber showed a poor compatibility in the relation between the silk fibroin molecules and MMA polymer. The weight of the MMA-grafted silk fiber decreased as observed at 160°C on the thermogravimetric thermograms due to the evaporation of water from the sample with increasing graft yield. The crystalline structure of MMA-grafted silk fiber remained unchanged regardless of MMA grafting. Taking into account the X-ray diffraction patterns and the increasing graft yield with reaction time, it is assumed that the graft chains of MMA polymer have penetrated into a weak aggregate region and not in the crystalline region of silk fibroin.

INTRODUCTION

Numerous investigations have been performed on the grafting of vinyl monomer onto fiber for improving fiber properties, including wrinkle recovery and heat-setting. It is anticipated that these experiments may enable expansion of the spectrum of utilization and increase the supply of fibers to meet the increasing demand in these materials. Methyl methacrylate (MMA) grafting onto silk fiber may also contribute significantly to improvement of the mechanical properties of the thread. Kobayashi et al.[1] observed that the wrinkle recovery of the MMA-grafted silk fiber increased when the graft yield was in the range of 30–60%. Recently Samal et al.[2,3] have proposed a suitable reaction sheme for MMA grafting onto silk fibers from *Bombyx mori*. The rate of grafting[4] was determined by varying the monomer concentration, and the physical properties of MMA-grafted silk fiber from *Antheraea pernyi* were studied.[5] Furthermore, qualitative and quantitative analysis of MMA-grafted silk was carried out by Ishiguro[6] and Hamanaka and Nagamine.[7] However, only limited information on the structural analysis of the effect of the grafting process is available.

This paper deals with the structural and thermal properties and morphological structure of MMA-grafted fibers by X-ray diffraction, differential scanning calorimetry (DSC), thermogravimetry, and scanning electron microscopy (SEM). It is considered that the experimental results obtained here

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may contribute to the promotion of fundamental studies on the grafting process and at the same time provide information for improvement of the current techniques of grafting.

EXPERIMENTAL

Materials

Raw silk fibers were obtained from reeling of cocoon threads of the domesticated mulberry silkworm, *Bombyx mori*. Silk thread (21 d size) was twisted together mechanically (750 t/m). Dried silk fibers were immersed in a solution of aqueous potassium persulfate (0.1%) as the initiator which contained MMA as the grafting agent emulsified by nonionic surfactant at temperature range of 75–80°C for 1-4 h. The graft mixture system was intermittently stirred. The material-to-liquor ratio of 1 : 100 was maintained. After the desired reaction time, silk fibers were taken out and washed thoroughly with water 3 or 4 times. The MMA monomer and its oligomer adhering to the silk fiber were removed by hot acetone. The washed and air-dried samples were dried in a forced draft oven at 100–105°C to achieve a constant weight, placed in a desiccator over silica-gel for 30 min, and weighed, the correction being made for the weight increase upon treatment with the MMA solution alone, thus the graft yield was obtained.

Measurements

The differential scanning calorimetry (DSC) measurements were performed on a Rigaku Denki instrument at a heating rate of 10°C/min. DSC range and sample weight were 2.5 mcal/s and 2 mg, respectively. The sample was put in a sealed open aluminum pan. The open aluminum cell was swept with N_2 gas during the course of the analysis.

The thermogravimetric analysis, (TGA) was performed using a Rigaku Denki thermal analyzer in a nitrogen atmosphere. X-ray diffraction pattern was recorded using a X-ray source with $C_u K_\alpha$ radiation (λ = 1.54Å).

RESULTS AND DISCUSSION

Add-on of Methyl Methacrylate

The effect of reaction time was investigated. Results are shown in Figure 1. The reaction between silk fibroin and methyl methacrylate was carried out at 75–80°C with the use of potassium persulfate as the initiator. The add-on under these conditions varied with reaction time and reached about 80% for 3.5 h. It appears that these results partly give evidence in support of the proceeding of silk/MMA grafting.

Thermal Properties

Figure 2 shows the DSC thermograms of MMA-grafted silk fiber for the purpose of elucidating the thermal properties of the silk fiber before and after MMA grafting. Ungrafted silk fiber [Fig. 2(a)] showed a single endothermic peak at around 323°C which was attributed to the thermal decomposition of

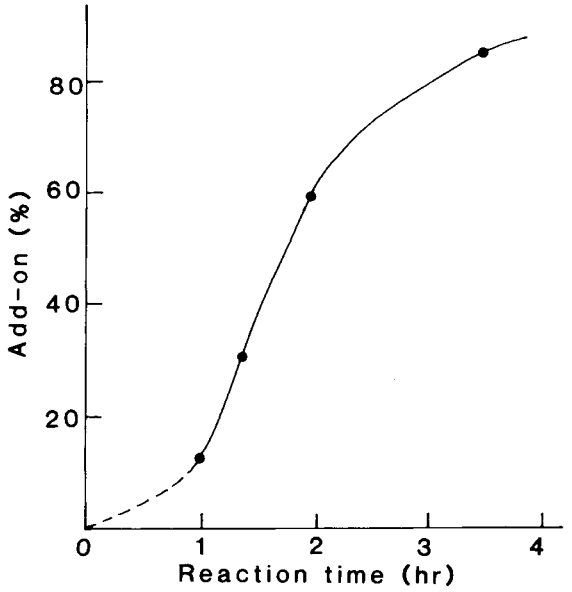

Fig. 1. Effect of reaction time on the add-on of methyl methacrylate (MMA). Dried and purified silk fibers were immersed in a solution of aqueous potassium perfulfate (0.1%) as the initiator which contained MMA as the grafting agent emulsified by nonionic surfactant at temperature in the range of 75–80°C.

silk fibroin with oriented β' configuration.[8] DSC thermograms of MMA-grafted silk fiber [Fig. 2(b)] with a graft yield of 12% was similar to that of ungrafted silk fiber. Silk fiber [Fig. 2(d-e)] with a graft yield of more than 30% exhibited two endothermic peaks at around 326°C (major peak) and at 390–410°C (minor peak), respectively. The position of the endothermic peak which appeared at about 320°C remained unchanged regardless of the MMA grafting. MMA-grafted silk fiber [Fig. 2(d)] has an inflection as to the endothermic peak at about 380°C. Whereas, the enthalpic change corresponding to the endothermic peak observed in the range of 380–410°C in the MMA-grafted silk fiber increased appreciably when the graft yield exceeded 59%. The endothermic peak at around 390°C became clearly single peaked when the graft yield reach 85%. Based on the above DSC results, it is assumed that the endothermic peak at 390°C, which was observed on the DSC thermograms for the specimen [Fig. 1(d,e)] is related to the presence of the MMA polymer filled in the silk fiber. DSC thermograms of commercial MMA polymer with a polymerization degree of more than 1000 was compared with the DSC results of Figure 2. The base line of the DSC thermograms of the commercial MMA polymer shifted toward the exothermic reaction at above 200°C. DSC thermograms of commercial MMA polymer [Fig. 2(f)] exhibited very sharp endothermic peak (major peak) at 382°C and an additional minor peak at about 412°C. However, no trace of endothermic and/or endothermic peak appeared on the DSC thermograms of commercial MMA polymer.[10] Judging from the abrupt decrease in the sample weight revealed by thermogravimetric measurement of MMA polymer (detailed data will be published elsewhere), it is estimated that the commercial MMA polymer decomposes at

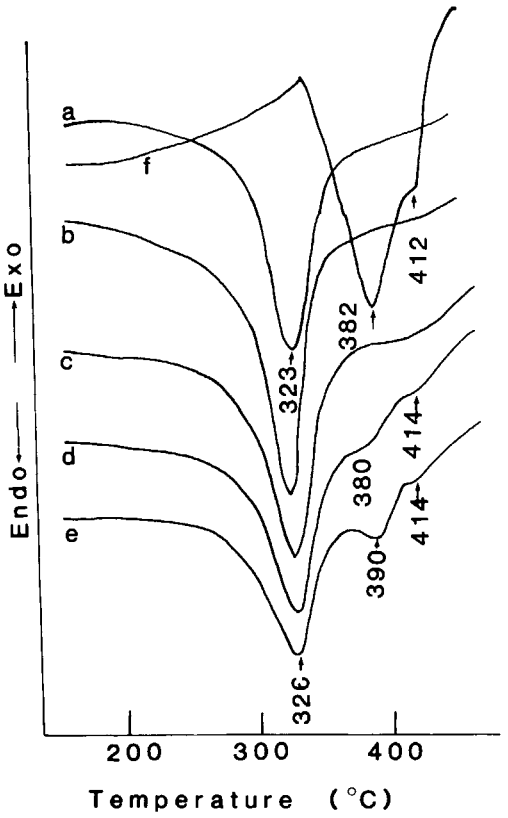

Fig. 2. DSC thermograms of methyl methacrylate (MMA)-grafted silk fiber (a-e) and commercial MMA polymer (f). Graft yield (%); a : 0, b : 12, c : 30, d : 59, e : 85.

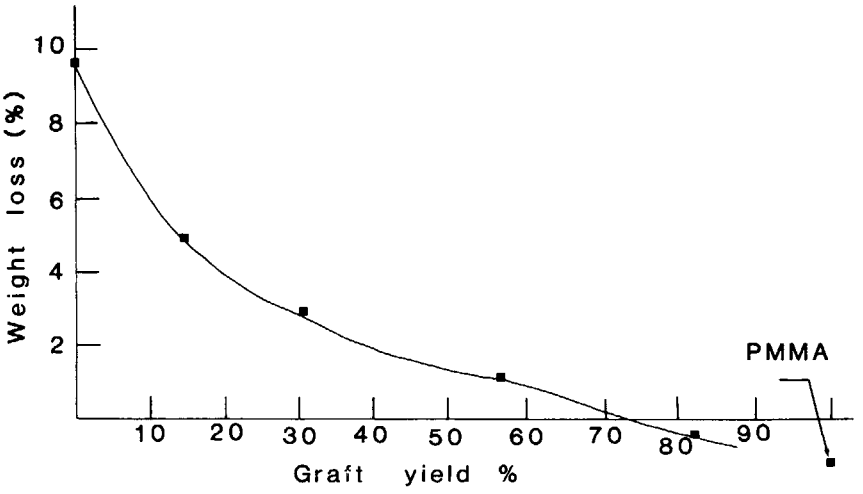

Fig. 3. Weight loss (%) recorded on the thermogravimetric curve at the temperature of 160°C of methyl methacrylate (MMA)-grafted silk fiber and commercial MMA polymer (↓).

about 382°C. The position of the peak (382°C) of MMA polymer corresponds to the endothermic peak which appeared on the DSC thermograms of the MMA-grafted silk fiber [Fig. 2(e)].

As stated above, the DSC results suggest that the double endothermic peaks exhibited on the DSC thermograms of MMA-grafted silk fiber were due to the thermal decomposition of silk fibroin and the MMA polymer filled in

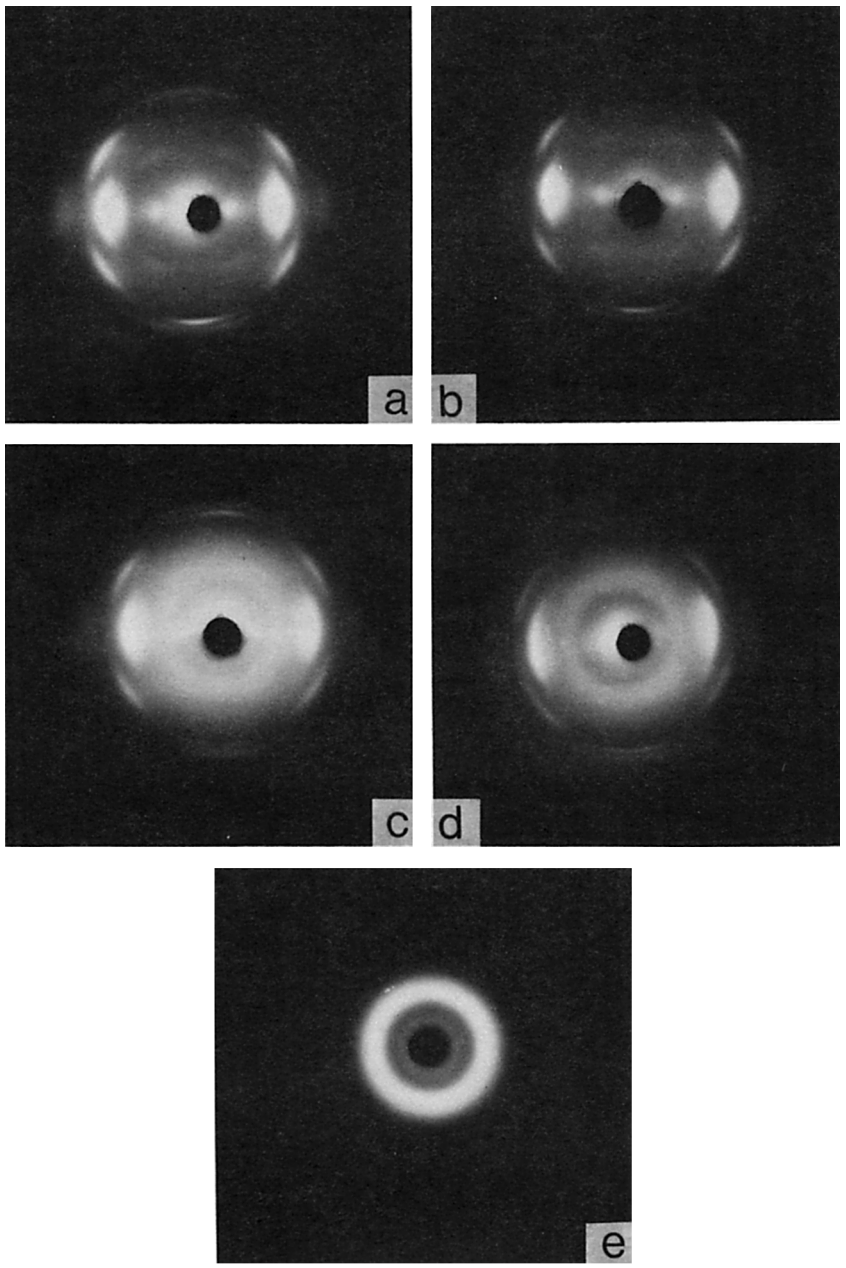

Fig. 4. X-ray diffraction patterns of methyl methacrylate (MMA)-grafted silk (a-d) and MMA polymer (e). Graft yield (%); a : 0, b : 12, c : 30, d : 59.

the fiber, when the graft yield exceeded 30%. This could be attributed to the poor compatibility in thermal properties in the relation between the silk fibroin molecules and MMA polymer.

Figure 3 illustrates the weight decrease of MMA-grafted silk fiber which was recorded in the thermogravimetric thermograms at 160°C. The weight loss observed at 160°C decreased with increasing graft yield. However, MMA-grafted silk fiber with a graft yield of 85% showed a weight increase of 0.5%. The commercial MMA polymer also showed an increase in weight of about

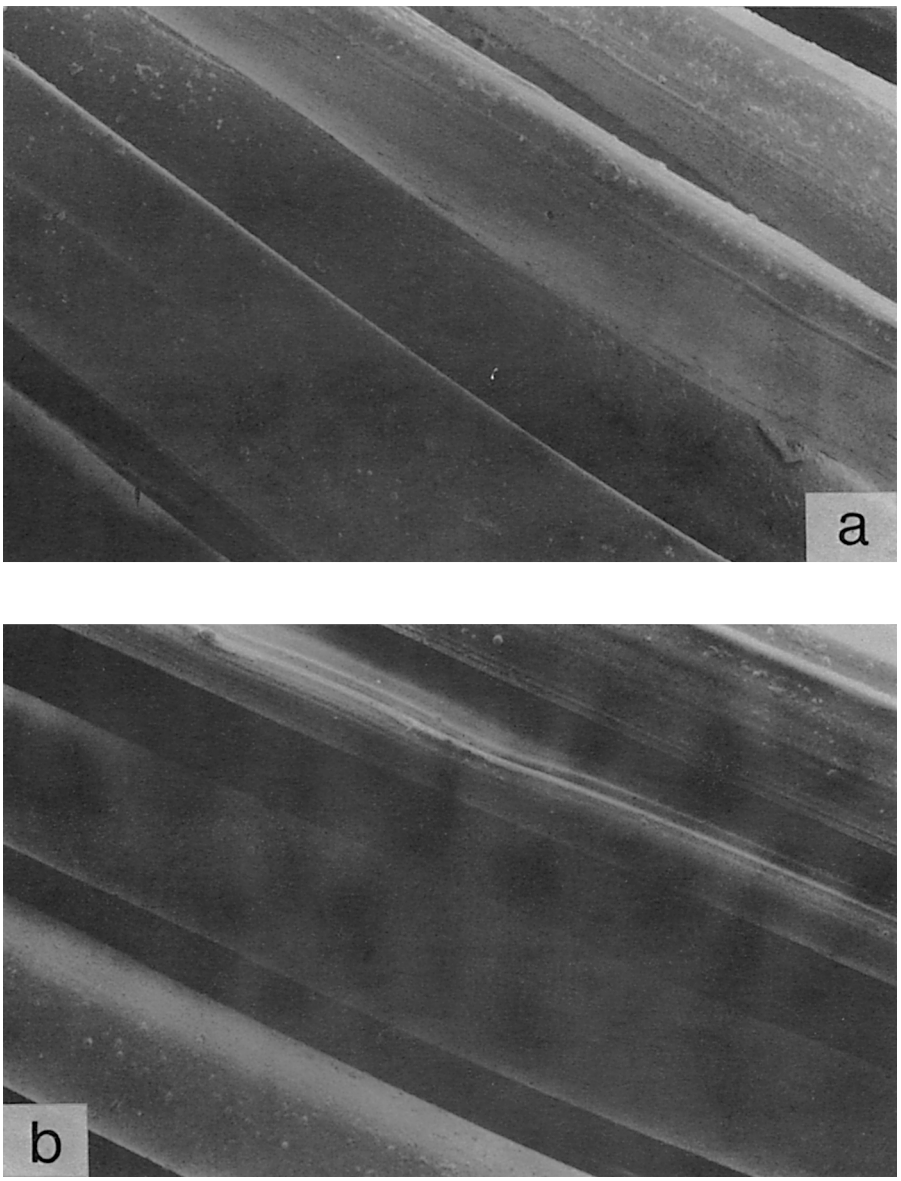

Fig. 5. Scanning electron micrographs of Methyl methacrylate-grafted silk fibers. Graft yield (%), a : 0, b : 30, c : 59, d : 85.

1%. Since the decrease in the sample weight at about 160°C is attributed to the evaporation of water from the specimen, the data presented above suggest that the weight of sorbed water of the MMA-grafted silk fiber decreased with increasing graft yield due to the nature of the hydrophobic side chains of the MMA polymer filled in the fiber.

Crystalline Structure

In order to define the crystalline structure of the MMA-grafted silk fiber before and after grafting, X-ray diffraction patterns were analyzed as shown

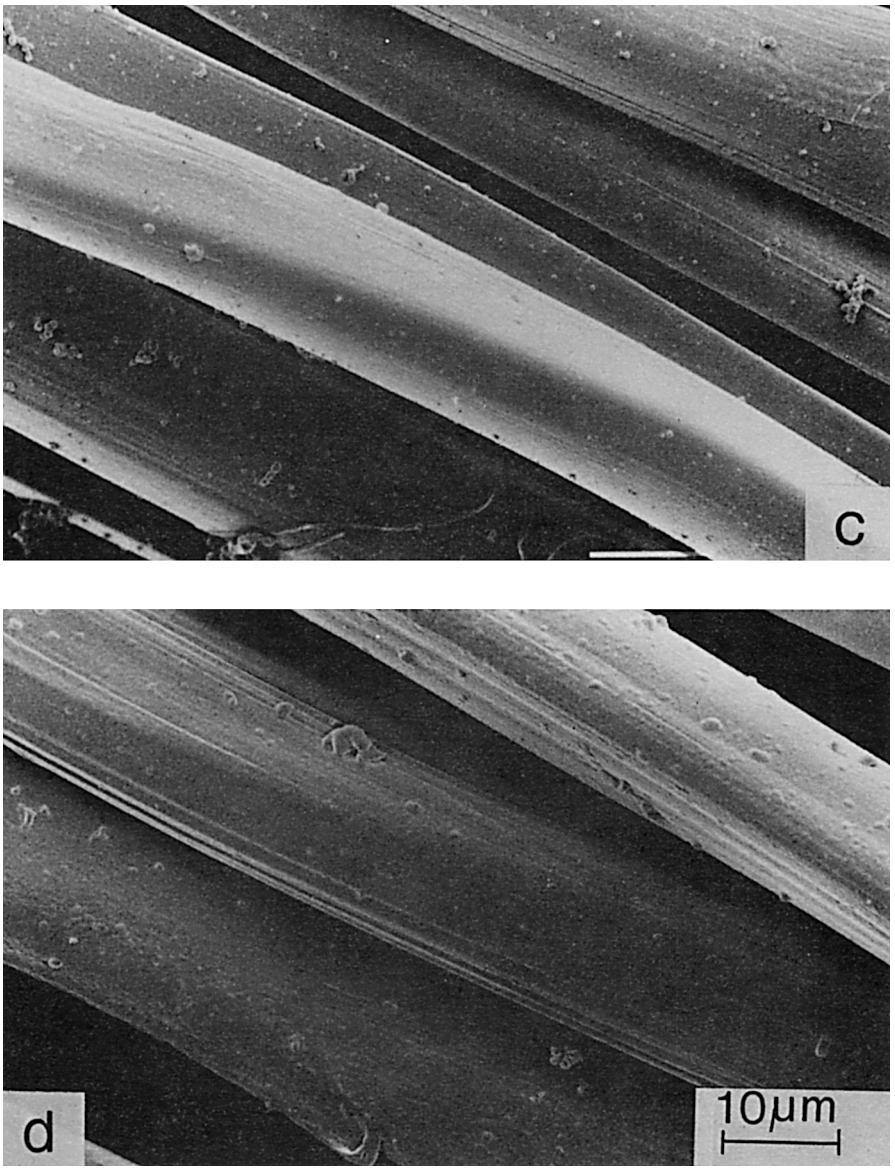

Fig. 5. (*Continued from the previous page.*)

in Figure 4. MMA-grafted silk fibers showed diffraction patterns oriented toward the equator and corresponding to the spacing of 4.87Å and 4.28Å, which is characteristic of the oriented β' configuration.[9] The diffraction patterns corresponding to the spacing of 3.47Å (II_0) and 3.30Å (II_1) which are attributed to the well oriented molecular crystalline form appeared in a meridian direction. MMA-grafted silk fiber with a graft yield of 59% showed halo diffraction pattern corresponding to the spacing of 6–7Å attributed to the MMA polymer which is amorphous in nature, in addition to the diffraction patterns associated with the oriented β' configuration.[9] It should be stated that the X-ray diffraction data presented above suggest that the crystalline structure of the MMA-grafted silk fiber remained unchanged even after MMA grafting. It is thus reasonable to assume that the MMA monomer as well as the initiator was immersed into the amorphous region and not in the crystalline region, and the graft chains of MMA polymer have penetrated into a weak aggreate region of silk fibroin.

Morphological Structure

The morphological structure of MMA-grafted silk fiber was investigated by scanning electron microscopy. Figure 5 shows the scanning electron micrographs of the surface of the MMA-grafted silk fibers. The surface of the specimen was smooth, showing the typical feature of ungrafted silk fiber when the graft yield was below 30%. Scanning electron micrographs revealed the presence of granules which appeared chemically bonded and/or physically adhered to the surface of the MMA-grafted silk fiber when the graft yield exceeded 85%.

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