Grafting of Methyl Methacrylate onto Silk Fibers Initiated by Tri-*n*-Butylborane

MASUHIRO TSUKADA[1], TAKASHI YAMAMOTO[2], NOBUO NAKABAYASHI[2], HIROSHI ISHIKAWA[3], and GIULIANO FREDDI[4]

[1]National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan, [2]Institute for Medical and Dental Engineering, Tokyo Medical and Dental University, Surugadai, Kanda, Chiyodaku, Tokyo 101, Japan, [3]Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386, Japan and [4]Stazione Sperimentale Per La Seta, Via G. Colombo, Milano 20133, Italy

SYNOPSIS

Structural characteristics of the methyl methacrylate (MMA)-grafted silk fibers using tri-*n*-butylborane as an initiator were analyzed by infrared spectroscopy and differential scanning calorimetry (DSC), and their refractive index and tensile properties were measured. Graft polymerization was promoted by $FeCl_3$ pretreatment of the silk. The graft yield reached a maximum by the immersion in 4% $FeCl_3$ solution for 1 min at 25°C. The infrared spectrum of poly(MMA)-grafted silk fibers showed overlapped absorption bands of silk fibroin with the β structure and of the grafted MMA polymer. A grafted silk fiber with graft yield of more than 140% exhibited two endothermic peaks at 321°C and 396°C on the DSC curve, attributed to the thermal decomposition of silk fibroin and grafted poly(MMA) chain, respectively. Refractive index measurements suggested that the molecular orientation and the crystallinity of the silk fiber decreased with increasing graft yield. Electron photomicrographs showed that silk was coated by grafted PMMA. The tensile strength of the grafted silk decreased rapidly by the grafting even at a lower level.

INTRODUCTION

Chemical modification of the silk fiber to get a fiber of improved textile performance has been an important subject for scientists and technologists. Vinyl monomer grafting may also contribute significantly to the improvement of the functional properties of the thread. Of the several methods available, methyl methacrylate (MMA) promises to be an effective means of materially improving silk fiber and fabric properties. The experimental results supporting this view have been given. Kobayashi et al.[1] observed that the wrinkle recovery of the MMA-grafted silk fabric increased when the graft yield was in the range of 30–60%.

In general, vinyl monomer grafting onto silk was performed using salts such as potassium persulfate aqueous solution as the initiator at temperatures above 75°C for several hours. However, it is difficult to increase the add-on values by the conventional grafting technique. The grafting performed under these rigorous conditions sometimes produce injurious effects on mechanical and physiochemical properties of silk fibers. It is therefore preferable to modify silk through grafting under milder grafting conditions so not to destroy the basic properties of the parent fiber. Sugiyama and Murase[2] examined the grafting conditions of acrylamide onto silk fabric by ceric salts as the initiator and determined that the optimum pH of the treating bath for grafting the maximum of the add-on is about 1.8 at 30°C. Kojima et al. studied the graft copolymerization of MMA onto pepsin,[3] collagen,[4] cotton,[5] silk,[6] wool,[7] and other proteins[8] using alkylborane as the initiator at 35–40°C and determined the optimum conditions for the graft yield and efficiency of grafting by varying the grafting conditions, concentrations of tri-*n*-

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butylborane (TBB) and monomer, and reaction temperature.

For the iron pretreatment and its role in increasing graft yield, Hebeish et al.[9] examined Fe^{3+}–thiourea cocatalyst-induced copolymerization of MMA on wool and modified wool fibers. Yamamoto and Nakabayashi[10] recently investigated the effect of the pretreatment on the grafting of MMA onto silk fiber using TBB as an initiator. They elucidated the molecular weight of the grafted poly(MMA) chain separated from the grafted silk fibers with the GPC measurement. Tsukada[11] recently reported the morphological structure of the grafted silk fibers with MMA by ammonium persulfate as an initiator.

The purpose of the present paper is to report further studies on the physical properties of MMA-grafted silk fibers with a high graft yield using TBB and on their morphology.

EXPERIMENTAL

Materials

Raw silk fibers were obtained after reeling of cocoon threads of a commercial silkworm variety of *Bombyx mori*. The raw silk fibers were degummed in an aqueous solution of 0.4% soap solution for 2 h and washed with 0.05% aqueous sodium carbonate solution at 98°C followed by boiling water. The degummed silk fibers were purified by extraction with acetone in a Soxhlet apparatus for 24 h, followed by washing with methanol and drying under reduced pressure. MMA was purified in the usual manner: bp 44.5°C/95 mmHg (46°C/100 mmHg).[12] Stabilized TBB, which is very flammable originally, was supplied by Sunmedical Co. (Kyoto).[13]

Degummed silk fiber, 0.8 g, was immersed in 30 mL water at 25°C for 5 min and subsequently in different concentrations of $FeCl_3$ solution at 25°C for 1 min. To this were added 5 g MMA as the grafting agent and 0.4 mL TBB as an initiator at a temperature range of 35–37°C for 1 h. The reaction was stopped by pouring the mixture into 250 mL methanol. At end of the reaction, untreated MMA formed by the copolymerization in fiber was removed with acetone at 55°C for 48 h.

MMA-grafted silk fiber thus obtained was dried *in vacuo* to constant weight. The MMA-grafted silk prepared in the present study and the grafting conditions are listed in Table I.

The graft yield was calculated from the increase in weight of the original silk 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 and the grafted silk, respectively.

Infrared spectra were measured with a Japan Spectroscopic Co. spectrophotometer (IR-G) in the spectral region 4000–400 cm^{-1}. KBr pellets were prepared for the IR measurement.

The differential scanning calorimetry (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 2.5 mg, respectively. The measurements were carried out under an atmosphere of nitrogen.

The refractive indices parallel to the fiber axis, $n_{\parallel}$, and that perpendicular to the fiber axis, $n_{\perp}$, were measured with Beche's line method using a polarized microscope under monochromatic light (Na light) at 20°C and 65% RH, according to the procedure described in the previous communication.[14]

The surface of the grafted silk fibers was examined with a JEOL JAX-333S scanning electron microscope at 15 kV acceleration voltage after gold coating. Tensile strength at break was measured with an automatic Tensilon tensile tester (Toyo Baldwin, UTM-II) at 20°C and 65% RH.

RESULTS AND DISCUSSION

Effect of $FeCl_3$ Concentration on the Grafting

The effect of $FeCl_3$ concentration on the graft yield is summarized in Table I. The concentration ranged from 0 to 5% of the $FeCl_3$ solution. It was observed that the graft yield to original silk was about 40% when the sample was pretreated in water without $FeCl_3$. It is clear from Table I that the graft yield is greatly improved by $FeCl_3$ pretreatment, and it reached a maximum at a concentration of 4%. So the optimum concentration of $FeCl_3$ for grafting of MMA onto silk fiber initiated by TBB was found to be 4%. These findings suggest that the use of TBB as initiator coupled with an $FeCl_3$ pretreatment is particularly interesting in that it obtains very high grafting yields under reaction conditions (time, temperature) relatively mild for silk. As shown in Table I, the samples with different grafting percentages were obtained only by changing the pretreatment time in different kinds of concentrations of $FeCl_3$ solution without changing the MMA concentration and keeping the other reagents and reaction conditions unchanged.

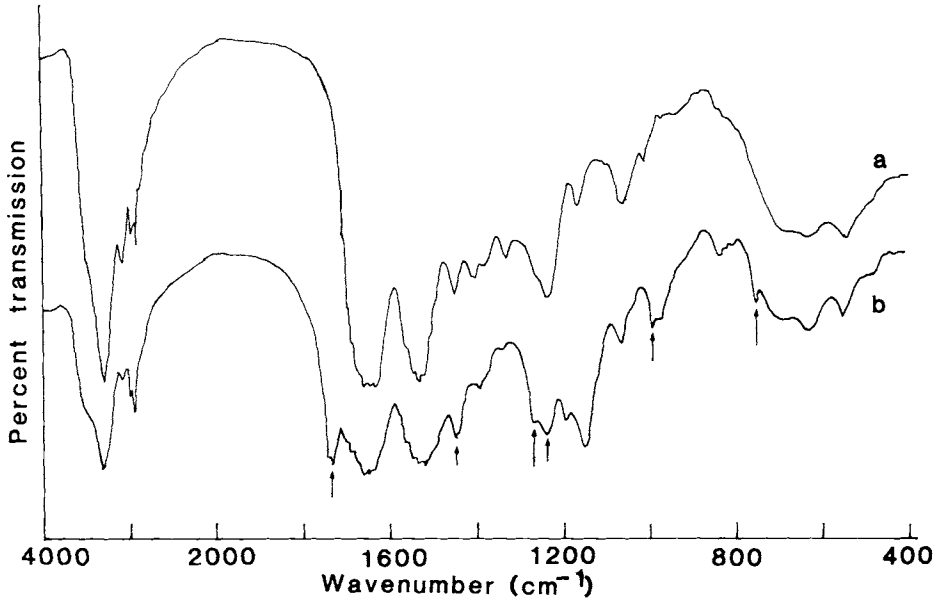

Figure 1 Infrared spectra of ungrafted (a) and MMA-grafted silk fiber (b). (↑) Absorption bands attributed to the MMA polymer.

Infrared Spectra

Infrared spectra of the untreated and MMA-grafted silk fiber are shown in Figure 1. Infrared spectra of the grafted silk fiber with a graft yield of 36% showed absorption bands at 1630 cm^{-1} (amide I) and 1530 cm^{-1} (amide II) assigned to the β structure of the silk fibroin[15] and additional bands at 1730, 1489, 1452, 1448, 1272, 1245, 1082, 994, and 750 cm^{-1}, characteristic of the spectra of syndiotactic MMA polymer.[16] Additionally, the infrared spectra of MMA-grafted silk fiber showed overlapped absorption bands of silk fiber with the β structure and of the grafted MMA polymer filled in the silk fiber.

Table I List of Methyl Methacrylate (MMA)-Grafted Silk Fibers Prepared and the Grafting Conditions[a]

Expt	Pretreatment[a,b]	Graft Yield (%)
1	None	0 (untreated)
2	None	36
3	1% $FeCl_3$	140
4	2% $FeCl_3$	301
5	5% $FeCl_3$	514
6	4% $FeCl_3$	720

[a] Grafting conditions: MMA, 5 g; silk fiber, 25 g; TBB, 0.4 g; 35–37°C; 1 h.

[b] Pretreatment: Degummed silk fibers were immersed in water at 25°C for 5 min and then in $FeCl_3$ solution of different kinds of concentration for 1 min for experiment numbers 3–6.

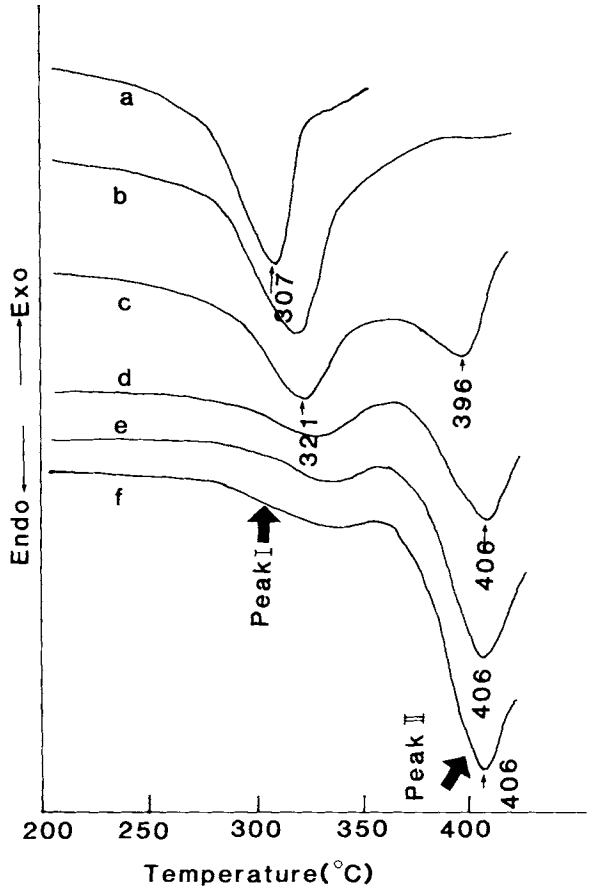

Figure 2 Effect of graft yield on DSC curves of MMA-grafted silk fibers. Graft yield (%): (a) 0; (b) 36; (c) 140; (d) 301; (e) 514; (f) 729. For peaks I and II, see text.

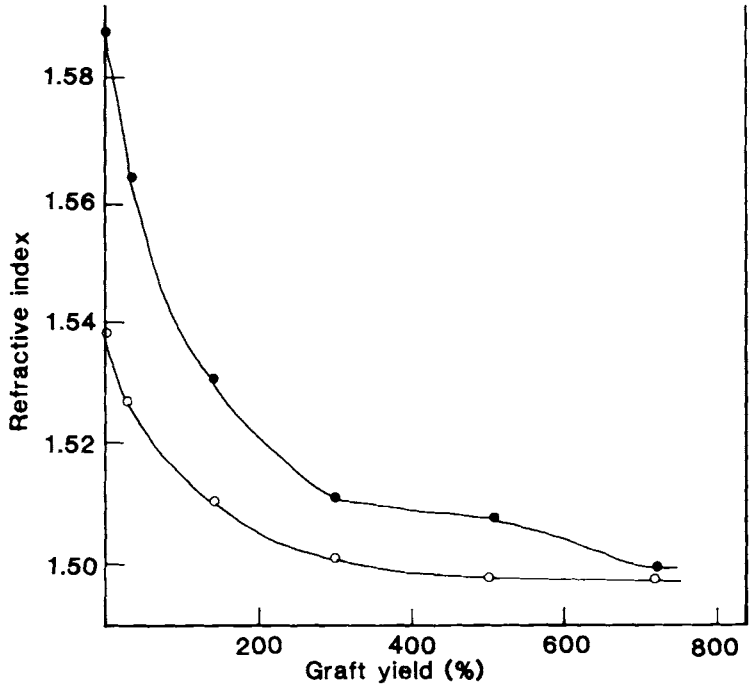

Figure 3 Effect of graft yield on refractive index: (●) parallel to fiber axis ($n_{\parallel}$); (○) perpendicular to fiber axis ($n_{\perp}$).

Thermal Behavior

The thermal behavior of MMA-grafted silk fibers was examined through DSC curves (Fig. 2). A single endothermic peak at 307°C was clearly observed for the untreated silk fiber (a), which was attributed to the thermal decomposition of the silk fiber with an oriented β' configuration.[17] The endothermic peak of the MMA-chain-grafted silk fiber with a low graft yield (36%) shifted slightly to higher temperature

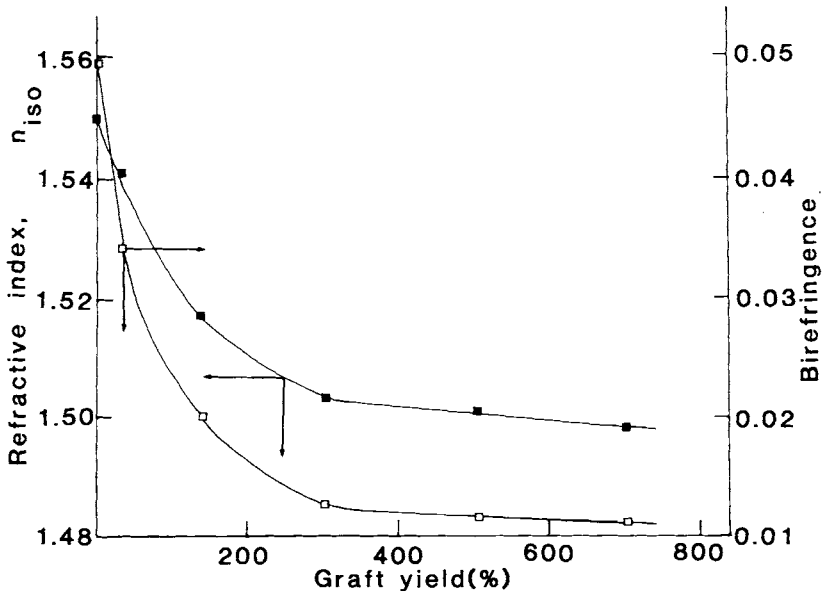

Figure 4 Isotropic refractive index (n_{iso}) and the birefringence (Δn) of the silk fibers with different graft yields.

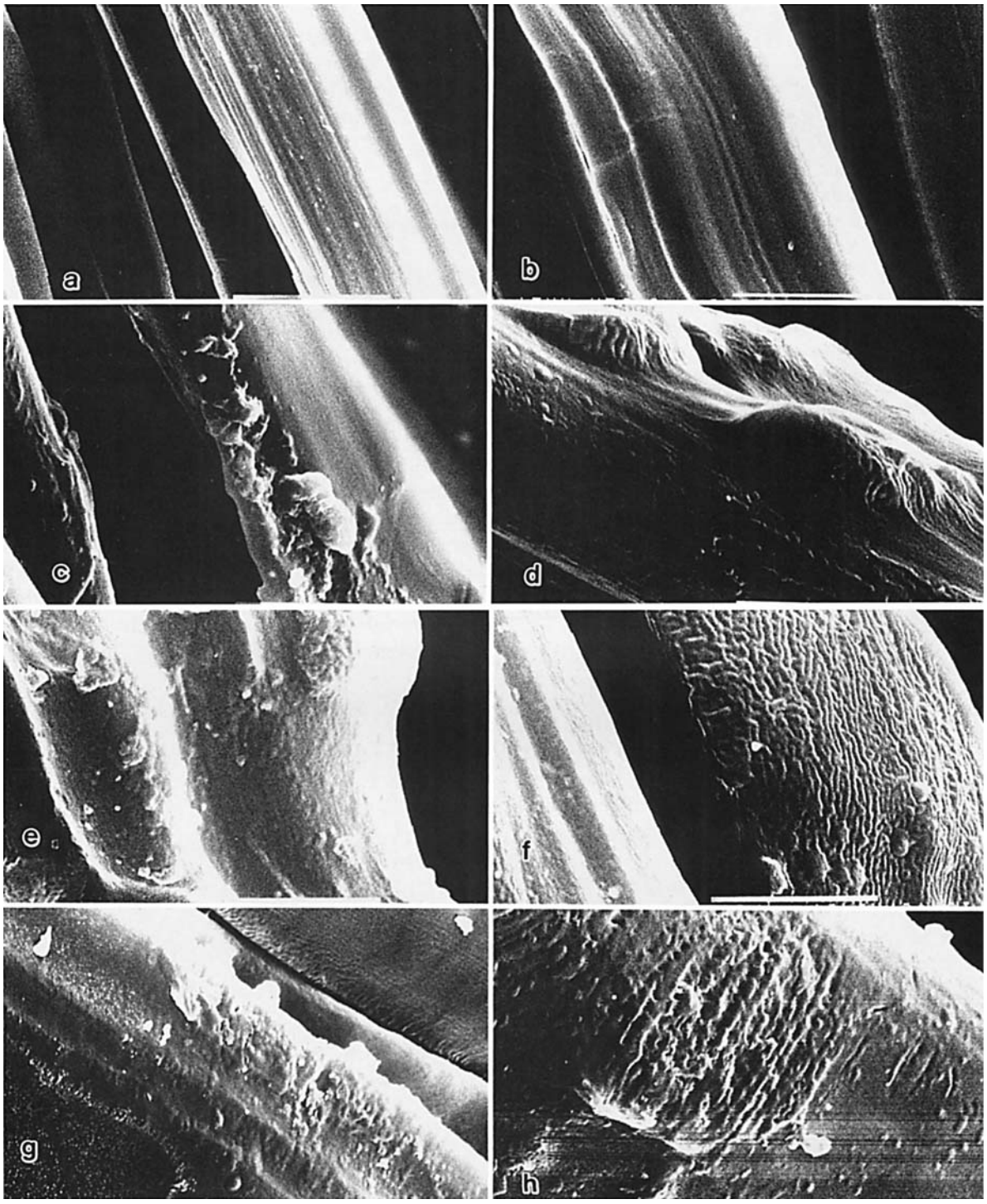

Figure 5 Scanning electron micrographs of MMA-grafted silk fibers. Graft yield (%): (a) 0; (b) 36; (c, d) 140; (e, f) 301; (g, h) 729.

(318°C). From Figure 2 it is observed that the grafted silk fiber with a high graft yield (above 140%) exhibited two endothermic peaks at 321°C (peak I) and 396°C (peak II). The temperature of endothermic peak I shifted to higher temperature and the endotherm intensity decreased reversely as the graft yield increased. The peak temperature of endotherm peak II of the grafted silk fiber with a

high graft yield (301%) stayed unchanged regardless of MMA grafting, while the endotherm was sharpened and intense.

In a previous paper,[11] one of the authors showed that commercial MMA polymer with molecular weight of ca. 100,000 showed a very sharp endothermic peak (major peak) at 382°C and an additional minor peak at about 412°C attributed to the thermal decomposition of the MMA polymer. Thus, it is elucidated that the peak II that appeared on the DSC curves of the MMA-grafted silk fiber with a graft yield of 140% is due to the thermal decomposition of the poly(MMA) chain with high molecular weight. There is additional evidence that the mean molecular weight of the grafted MMA chain is comparative high. It is evident on the basis of the GPC measurements that the average molecular weight of the grafted poly(MMA) chain, after hydrolysis of the silk peptide chain and separated from the MMA-grafted silk fiber initiated by TBB with a graft yield of 40%, is 340,000.[10]

Refractive Indices

Figure 3 shows the refractive indices, $n_{\parallel}$ and $n_{\perp}$, of the MMA-grafted silk fibers with different values of graft yield. The value of $n_{\parallel}$ *and* $n_{\perp}$ of the grafted silk fiber decreased gradually with increase of the graft yield above 140% and tends to saturate to constant value at above graft yield of 300%. On the other hand, increase of the graft yield causes, at first, a steep decrease of n value.

The isotropic refractive index (n_{iso}) and the birefringence (Δn) of the MMA-grafted silk fiber initiated by TBB are shown in Figure 4. The values of n_{iso} and the refractive indices of the MMA-grafted silk fiber decreased with increasing graft yield values. The decreased amount of the refractive index was greater than that of the n_{iso} value. A significant decrease in the birefringence of the silk fiber was observed from 0.05 for untreated silk fiber down to 0.01 for MMA-grafted silk fiber with a graft yield of 300%, suggesting that the structural changes were induced in the course of the grafting. Because the birefringence and n_{iso} value are closely related to the molecular orientation and the crystallinity, respectively, these findings suggest that the molecular orientation and the crystallinity of the silk fiber decreased with increasing graft yield.

The results of the refractive index and birefringence measurements are interpreted as an indication of decreasing molecular orientation and crystallinity of the silk fiber. The diminution of crystallinity should be interpreted mainly as a decrease in the degree of order of the fiber (as a result of the insertion of a totally amorphous polymer into it), not as a modification of the crystalline regions of the silk fiber.

Morphological Structure

The morphological structure of MMA-grafted silk fibers initiated by TBB were investigated by scanning electron microscopy. Figure 5 shows the scanning electron micrographs of MMA-grafted silk fibers. There were noticeable changes after MMA grafting, especially on the surface of the grafted silk fibers [Fig. 5(b)] with a high graft yield. The surface of the MMA-grafted silk fiber with a low graft yield (36%) was smooth, showing the typical features of the control silk fiber [Fig. 5(a)]. However, electron photomicrographs illustrate a coating of the MMA-grafted silk fibers [Fig. 5(c–h)] with grafted MMA polymer. Chemical bonds and/or physical adhesion were observed on the surface of the MMA-grafted silk fibers with a high graft yield [Fig. 5(c–h)].

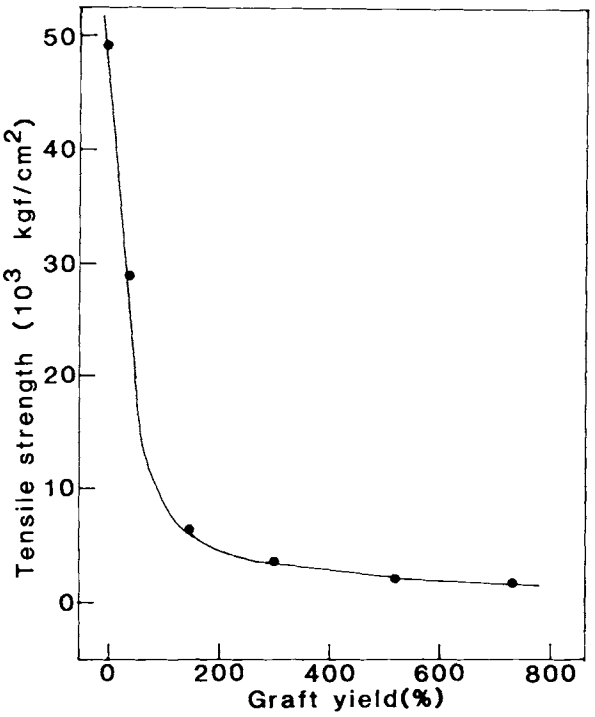

Figure 6 Effect of graft yield on tensile strength of the MMA-grafted silk fibers in relation to the graft yield.

Tensile Properties

Figure 6 shows the tensile strength of the MMA-grafted silk fibers in relation to the graft yield. The untreated sample has the highest strength. When graft yield was higher, the strength of the sample decreased rapidly in a short initial stage and tended to saturate to constant value in the 500–729% graft yield range. Because it is known that tensile strength is closely related to crystallinity and molecular orientation of the silk fibers, the results of the tensile properties (Fig. 6) of the MMA-grafted silk fibers are consistent with those of the refractive index measurements (Figs. 3 and 4). The variation of the tensile strength values as a function of grafting percentage is in fair agreement with the data concerning refractive indices and provides a clear understanding of the physical and structural features of the samples of silk examined.

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