Grafting of Methyl Methacrylate onto *Antheraea pernyi* Silk Fiber with the Assistance of Supercritical CO$_2$

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ABSTRACT: Graft copolymerization of methyl methacrylate (MMA) onto *Antheraea pernyi* silk fibers, initiated by benzoyl peroxide in the supercritical CO$_2$ was investigated. The grafting degree was determined as a function of impregnating pressure, impregnating time, monomer concentration, initiator concentration, and reaction time. The structural properties of MMA-grafted fiber were characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. Grafted MMA was chemically bonded and/or physically adhered to the surfaces of the fibers. The grafted silk fibers exhibited two steps of weight loss according to the characteristic of each component as demonstrated by the thermogravimetric analysis. The water-retention values indicated that the hydrophobic nature of the fibers was improved. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1299–1305, 2006

Key words: supercritical CO$_2$; graft copolymerization; silk; methyl methacrylate

INTRODUCTION

Silk is a natural polymer composed of two main components, silk fibroin and silk sericin. Although both fibroin and sericin belong to protein consisted of 18 amino acids, their composition, microstructure, and biological functions are different. Usually sericin was removed from the cocoon in a process conventionally known as degumming. As a biopolymer and biomedical material, the applications of silk in surgical sutures, enzyme-immobilization, food additives, and cosmetic industries are increasing. But the main value of silk still embodies in textile industry. It is well known that the properties of silk such as dimensional stability, wash and wear, wrinkle recovery are inferior. Grafting is considered as an effective technique to improve fiber performance.[1,2] Numerous investigations have been carried out on the grafting of vinyl monomers to silk fiber.[3,4] Methyl methacrylate (MMA) is one of the most widely used monomers; thanks to the fullness of handle and to the good crease recovery it conferred on silk. The grafting reaction of MMA onto silk using liquid solvent method has been extensively studied.[5,6]

Recently, some studies are focused on modifying polymers with the aid of supercritical carbon dioxide (SC CO$_2$).[7–16] The advantages of using SC CO$_2$ are that it has high diffusivity, low viscosity, and absence of surface tension. Its solvent strength could be continuously tuned from gas-like to liquid-like by changing pressure or temperature. Moreover, it avoids using toxic and flammable solvent compared with the conventional method. Many works had taken advantage of the unique properties of SC CO$_2$ to physical[7,8] or chemical[17] modification of the polymers. In most of the grafting modifications, the matrices were always the synthetic polymer, such as poly (4-methyl-1-pentene)[12] or polypropylene.[18,19] To the best of our knowledge, there is no study about the modification of natural silk with supercritical fluid technology.

In this article, we present the results of the graft copolymerization of MMA onto *Antheraea pernyi* silk fiber, using SC CO$_2$ as solvent and swelling agent. *Antheraea pernyi* silk, a wild-type silk, has been used as textile materials as a variation to domestic silk (*Bombyx mori*). The grafting mechanism would be that the free-radical initiator BPO dissociates and subsequently abstracts hydrogen from the active -OH, -NH- groups in silk backbone to form macro-radicals, which then react with MMA to form the grafted silk fibers. The effects of varying impregnating time, impregnating pressure, monomer concentration, initiator con-

centration, and reaction time on the grafting were studied. The structure was determined by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and thermogravimetry (TG). The products were also further investigated of their water-retention capacity.

EXPERIMENTAL

Materials

Degummed *Antheraea pernyi* fibers were obtained from Key Laboratory of Molecular Engineering of Polymers of Education Ministry in Fudan University. Methyl Methacrylate (MMA) was produced by Tianjin Kemao Chemical Reagent Co. Ltd. (A. R. grade) and used without further purification. Benzoyl peroxide (BPO) purchased from Shanghai Sanpu Chemical Co. Ltd. was used after recrystallization in ethanol. Acetone, A. R. grade, was received from the Luoyang Chemical Reagent Plant. CO_2 with the purity of 99.9% was provided by the Zhengzhou Shuangyang Gas Co. and used as received.

Grafting

The procedures consisted of two steps: impregnating process and grafting polymerization reaction. In a typical experiment, suitable amount of silk fibers and MMA–BPO solution were loaded in a stainless steel vessel of 21.4 mL. The vessel was placed into a constant temperature water bath. After the system had reached thermal equilibrium, CO_2 was charged into the vessel by a syringe pump (DB-80, Beijing Satellite Manufacturing Factory) until the desired pressure was obtained. After a desired impregnating time, the fluid in the system was released. The impregnated fibers were transferred into another stainless steel vessel and air in the vessel was replaced by N_2. The polymerization was carried out at 80°C for 6 h. The unreacted MMA monomer and its oligomers adhering to the silk fiber were removed by acetone in Soxhlet's apparatus. The washed samples were dried under vacuum at 50°C for 12 h.
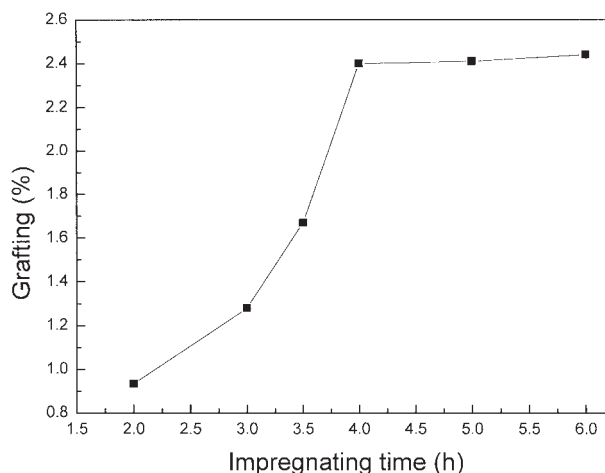
The percent of grafting was calculated by using the following relation:

$$\% \; Grafting = \frac{W_t - W_0}{W_0} \times 100 \qquad (1)$$

where W_0 and W_t denote the weight of the untreated silk and the grafted silk after washing, respectively.

Characterization

FTIR spectra were recorded on a NICOLET FTIR-460 spectrometer (USA) by the method of transmission.

Figure 1   Grafting of silk as function of impregnating time at 40°C and 14 MPa. The concentration of MMA with 0.6 mol % BPO is 1.25 mol/L.

The fibers were crushed and then examined in KBr discs. The surface of grafted silk fibers was examined before and after acetone extraction with a JEOL JSM-5600LV scanning electron microscope (Japan) at 15 kV acceleration voltage after gold coating.

Thermogravimetric analysis was run under the flow of nitrogen gas at a scanning speed of 10°C/min from 30 to 700°C using NETZSCH TG-209 (Germany).

The water absorbency of the untreated fiber and the grafted silk fibers were determined by immersing them in distilled water for 3 h. After that, the fibers were taken out and excess water was removed by putting them inside two filter papers under gentle pressure. The fibers were weighed. This weight of the samples was recorded as WET and the samples were then dried in an oven at (65 ± 2)°C. The dry weight was recorded as DRY.[20] The water absorbency was expressed as the water-retention value (WRV) and was calculated as follows:

$$WRV \; (g/g) \; = \; (WET - DRY)/DRY \qquad (2)$$

RESULTS AND DISCUSSION

Effect of impregnating time

Figure 1 shows the dependence of grafting on impregnating time. It can be seen that at the beginning, from 2 to 4 h, the graft percentage increases abruptly with time. Then it became steady with impregnating time above 4 h and nearly leveled off. So in the following study, the impregnating time of 4 h was chosen.

Effect of impregnating pressure

The effect of impregnating pressure was investigated over the range of 10–16 MPa and the results are shown
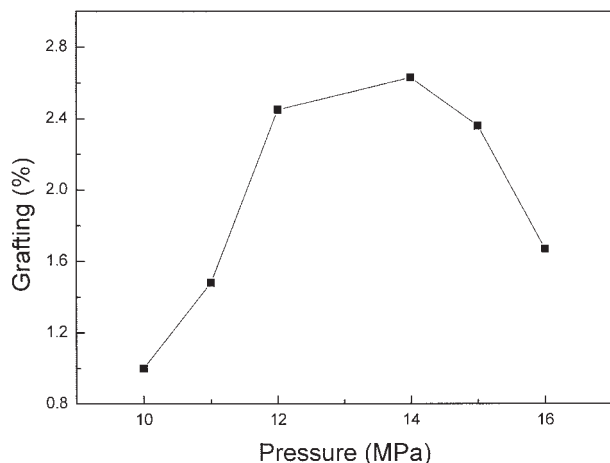
Figure 2 Grafting of silk as function of impregnating pressure at 40°C for 4 h. The concentration of MMA with 0.6 mol % BPO is 1.25 mol/L.

Figure 3 Effect of the concentration of MMA with 0.3 mol % BPO on grafting at 40°C and 14 MPa for 4 h.

in Figure 2. The original concentration of MMA was 1.25 mol/L and the impregnating time was 4 h. The grafting percentage increases with increasing impregnating pressure and then decreases after 14 MPa. So there exists a maximum point in the range of our study, and this is due to the competition effect of the swelling of SC CO_2 on the silk, which is helpful for the impregnation of monomer onto the silk; and the solubility of monomer of MMA in SC CO_2, which is not helpful for the monomer impregnation. When the pressure is relatively low from 10 to 14 MPa, the swelling effect is prominent, and when pressure is higher than 14 MPa, the later effect of solubility of monomer in SC CO_2 is decisive; thus, more monomers are dissolved in the fluid phase, which is not favorable in increasing the mass uptake of matrix silk. The competition of these two opposite factors reaches the balance at 14 MPa.

Effect of monomer concentration

Figure 3 illustrates the influence of monomer concentration on the grafting of MMA on silk fibers. The impregnating process was conducted at 14 MPa and 40°C for 4 h. The initiator concentration was maintained at 0.3 mol % based on the monomer; therefore the overall initiator concentration in the fluid phase varied with MMA concentration. It indicates that the grafting initially increases sharply and then passes the maximum point. There exists competition between graft copolymerization and homopolymerization. The increasing trend in the grafting may be ascribed to the possibility that increasing monomer concentration favors the adsorption of the monomer on the silk, while the decreasing trend is probably due to the faster rate of combination of macro-radicals MMA among themselves versus their combination with silk. As a result,
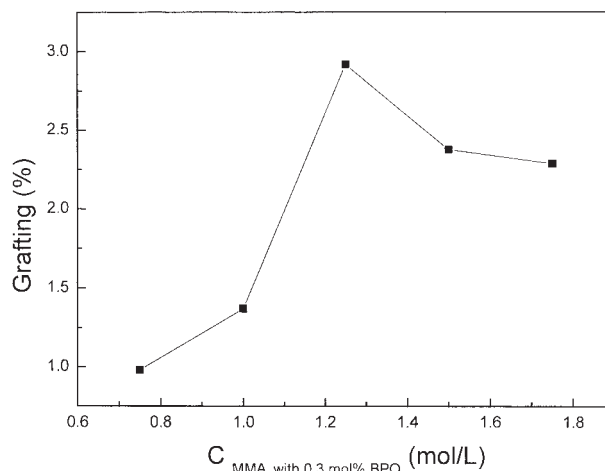
the extent of homopolymerization increases and the grafting decreases.

Effect of initiator concentration

By varying the BPO concentration, the grafting percentage is found to increase progressively with the increase of the initiator concentration up to 0.45 mol % and decreases thereafter (Fig. 4). This is a typical behavior observed in grafting processes occurring via chain transfer mechanism.[21,22] As the concentration of BPO increases, a large number of silk macro-radicals will be formed through the interaction of free radicals with the groups present in the silk main chain that initiate grafting, thereby the grafting percentage increases. However, the higher concentration of initiator will result in the production of more free radicals, more PMMA macro-radicals, as well as more ho-
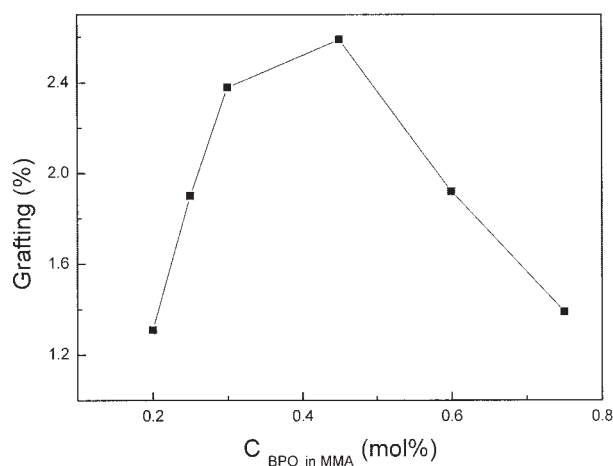
Figure 4 Effect of initiator concentration on grafting at 40°C and 14 MPa for 4 h.
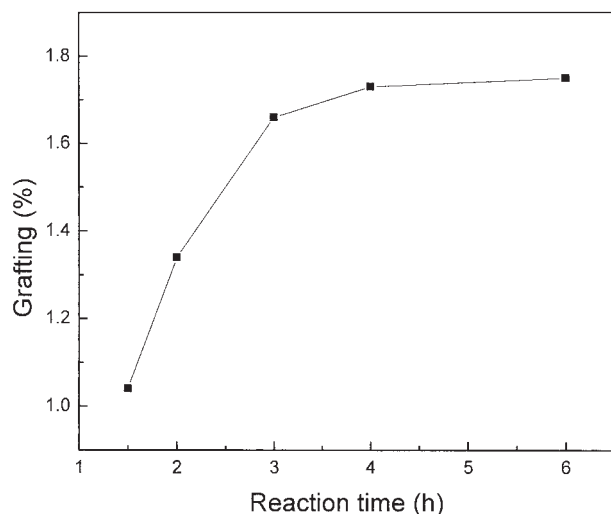
Figure 5 Effect of reaction time on grafting.

mopolymer. Hence when the concentration of initiator reaches to some degree, the grafting percentage will decrease.

Effect of reaction time

The effect of the reaction time on the grafting degree was investigated for reactions carried out for 1–6 h. The results are presented in Figure 5. The grafting degree initially increases with reaction time and reaches a plateau after 4 h. After a certain reaction time, the initiator will be consumed up and all the monomer will be polymerized, thus no further change in grafting degree was observed with increasing reaction time.

Ir analysis

FTIR spectroscopy is useful in structural analysis of silk.[23,24] Figure 6 shows the infrared spectra of the untreated and MMA-grafted *Antheraea pernyi* silk fibers. The untreated silk (Fig. 6(a)) shows characteristic absorption bands at 1660 cm^{-1}(amide I),1515 cm^{-1} (amide II), and 1238 cm^{-1} (amide III), which are assigned to β-sheet structure. Because of the overlap of amide I of silk fibroin and C=O of poly(MMA), the band at 1650–750 cm^{-1} broadened as shown in Figure 6(b) and it shows clear absorbance at 1727 cm^{-1}, which is attributed to the carbonyl group of the side chain of the MMA polymer present in the silk fiber. In Figure 7, it is observed that the band of hydrogen-bonded *N*-H stretching vibration at 3269 cm^{-1} (Fig. 7(a)) is shifted to 3283 cm^{-1} (Fig. 7(b)). This may be due to weakening of hydrogen bonding between adjacent silk chains. The result is in accordance with Saikia's research using conventional method.[25] All
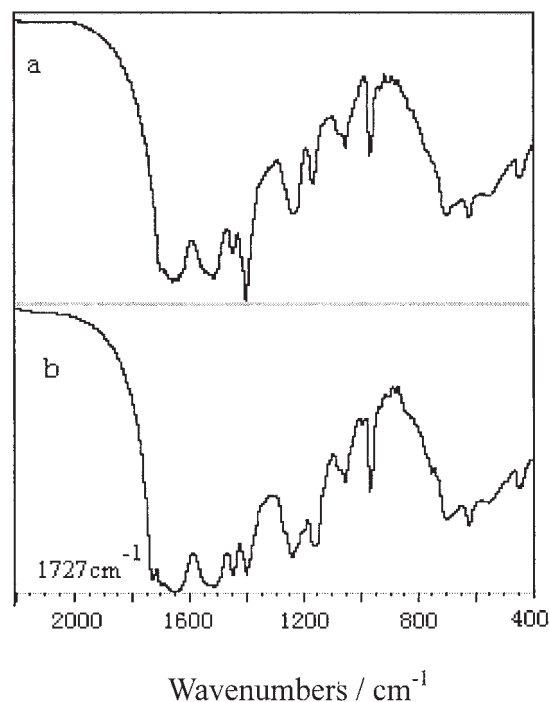

Figure 6 FTIR spectra in 400–2200 cm^{-1} of (a) untreated and (b) MMA-grafted silk fibers at grafted level of 2.38%.

these indicate the evidence that the MMA has grafted onto the silk fiber backbone.

Morphological structure

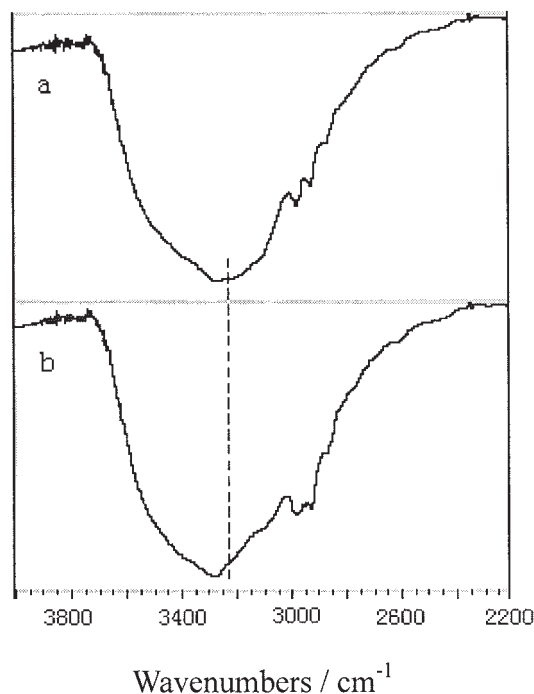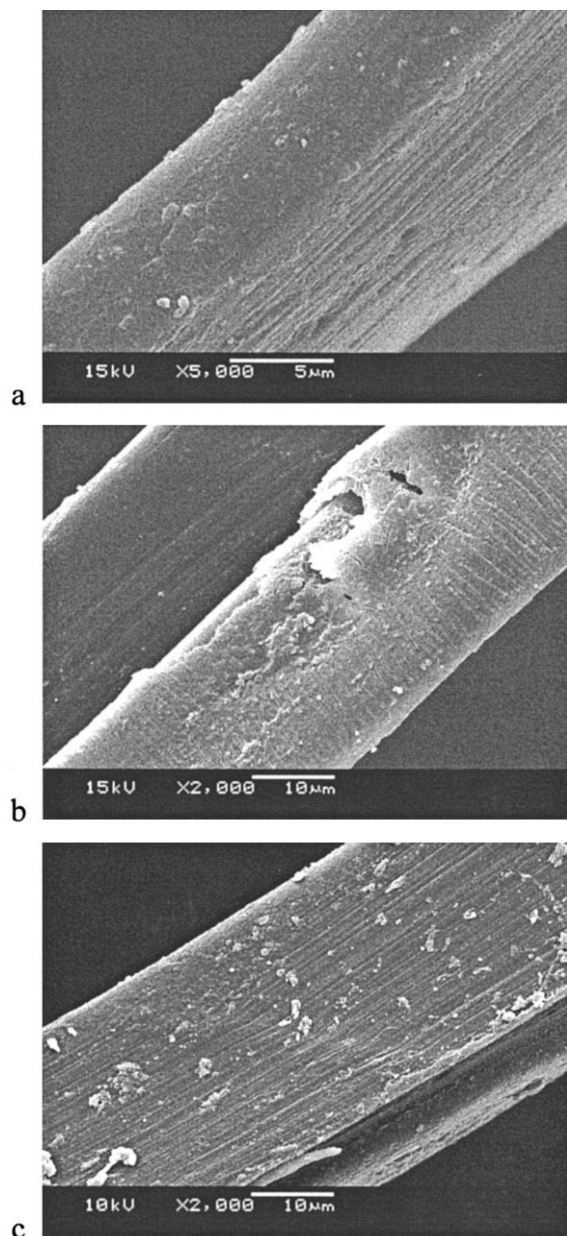The surface characteristics of untreated and grafted silk fibers were investigated using SEM. All the sam-

Figure 7 FTIR spectra in 2200–4000 cm^{-1} of (a) untreated and (b) MMA-grafted silk fibers at grafted level of 2.38%.
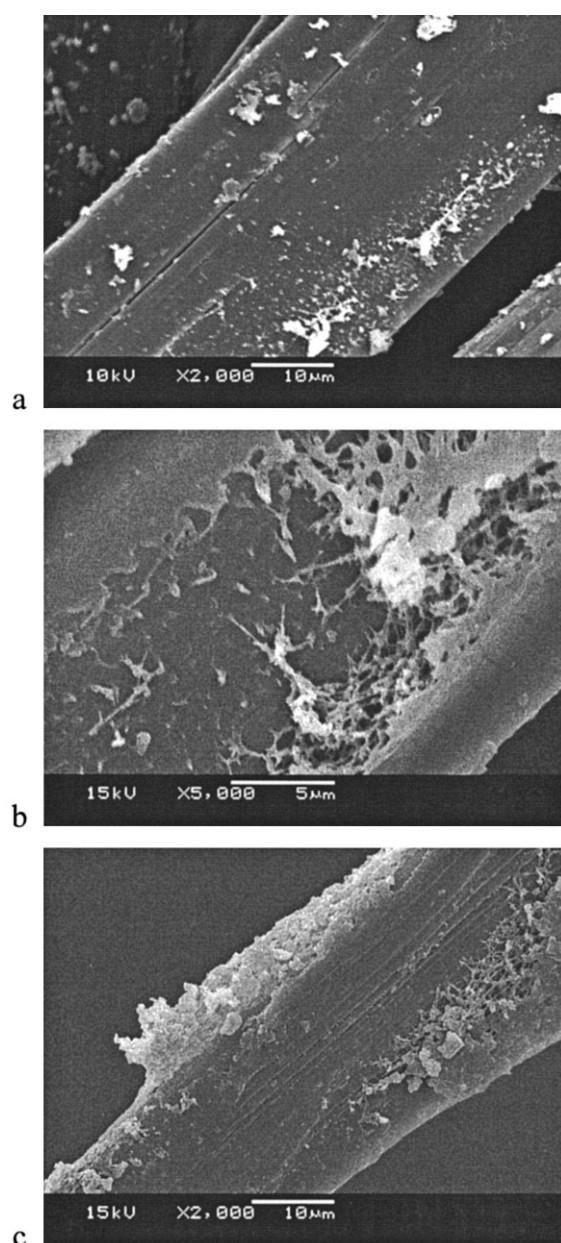

Figure 8 Scanning electron micrographs of silk fibers. (a) Untreated silk, (b) treated silk in SC CO_2 without washing, and (c) treated silk and after extraction with acetone.

ples show the typical feature of *Antheraea pernyi* silk with longitudinal fringes in the surface. The silk fiber treated in supercritical CO_2 without washing shows the presence of a "PMMA cloth" coated on the smooth surface of the silk (Fig. 8(b)) and this indicates the homopolymerization of MMA in our system. Although "PMMA cloth" was removed after acetone extraction (Fig. 8(c)), there were still some deposition, which chemically bonded or physically adhered to the surfaces of the fibers, allowing the surfaces of the *Antheraea pernyi* silk to look more rough.

It is interesting to note that graft polymerization of MMA onto the silk fiber using SC CO_2 as solvent and

swelling agent produced some peculiar effect to the silk. Figure 9(a) shows that the silk presents distinct lengthwise cracks, and this may be attributed to the low viscosity and zero surface tension of SC CO_2, allowed for well penetrating into the silk. This provides a quite promising method to obtain expanded silk. In Figure 9(b) and 9(c), network structures covered on the surface of the silk were seen. What led to this morphology? It is quite likely that a little amount of monomer casually had bulk polymerization during the impregnating process. When the system was rapidly depressurized to atmospheric pressure, CO_2 was released from the silk and this could destroy the thin layer of homopolymer to form this structure.

Figure 9 Scanning electron micrographs of MMA-grafted silk fibers.

Thermal behavior

Figure 10 shows the thermal curves (TG and DTG) for untreated and grafted silk fibers. Untreated silk fiber (see Fig. 10(a)) shows a distinct decomposition peak at
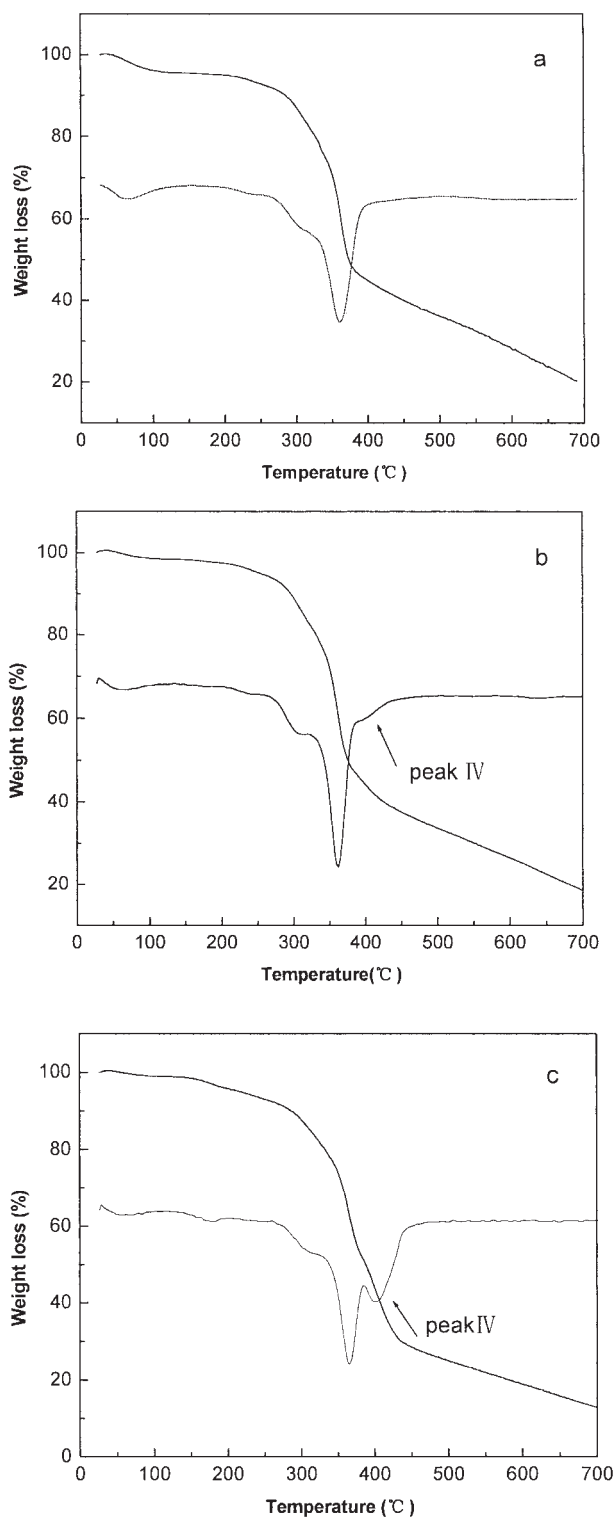
TABLE I
WRV of Untreated and Grafted Silk Fibers

Samples	Grafting (%)	WRV (g/g)
Untreated	0	0.964
Grafted	1.49	0.905
	1.91	0.811
	2.29	0.778

362°C, which is attributed to the thermal decomposition of silk fibroin with oriented β-sheet structure.[26,27] On grafting with MMA, a new degradation peak appears at about 410°C. The intensity of this peak increases with the increasing grafting of silk fiber. Tsukada[28] have shown that commercial PMMA with molecular weight of ~100,000 has 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. So it is indicated that the peak IV that appeared on the DTG curve of the MMA-grafted silk fibers corresponds to the thermal decomposition of the grafted poly(MMA) chain. In addition, with the increase of grafting degree, the poor compatibility in the thermal properties can be shown between the silk fibroin molecules and MMA polymer.

WRV

The WRV data are shown in Table I. The values of the WRV are in decreasing order with increasing grafting, thereby the hydrophobic nature of the fibers increase because of the MMA polymer filled in the fibers.

CONCLUSIONS

The results reported in this work indicated that MMA could be successfully grafted onto the *Antheraea pernyi* silk using supercritical CO_2 as a solvent and swelling agent. The grafting degree can be tuned by altering the impregnating time, impregnating pressure, monomer concentration, initiator concentration, and reaction time. According to the FTIR and SEM results, MMA was either chemically bonded or physically adhered to the silk fiber. The thermal stability of the silk did not change noticeably. The water-retention values (WRVs) indicated that the hydrophobic nature of the fibers was improved with the increase of PMMA amount. The experimental results obtained here may contribute to the improvement of the current technique of grafting of some polymer with silk.

Figure 10 TG and DTG curves of (a) untreated and grafted fibers at grafted level of (b) 1.34% and (c) 2.38%.

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