

# Supercritical CO<sub>2</sub>-Assisted Synthesis of Poly(acrylic Acid)/*Antheraea pernyi* SF Blend

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**ABSTRACT:** Monomer acrylic acid (AA) and initiator azobis(isobutyronitrile) were carried into *Antheraea pernyi* silk fibroin (SF) fibers using supercritical CO<sub>2</sub> as a solvent and carrier, followed by free radical polymerization at a suitable temperature, resulting in PAA/SF blends. The binary system of CO<sub>2</sub>/AA and the ternary system of CO<sub>2</sub>/AA/AIBN systems were studied. Different impregnation conditions, such as time, pressure, and concentration of AA in the fluid phase on mass uptake, were studied. Fourier transform infrared spectroscopy and X-ray diffraction results confirmed

that PAA was indeed present in the silk and that there were intermolecular hydrogen bonds between PAA and SF. According to thermogravimetry and DTG, blending with PAA could enhance the thermal stability of SF slightly. The water retention values indicated that the hydrophilic nature of the fibers was improved. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 864–868, 2005

**Key words:** supercritical CO<sub>2</sub>; polymerization; silk fibroin; poly(acrylic acid); blend

## INTRODUCTION

There has been a great deal of interest in exploring and applying natural polymers due to their unique properties such as nontoxicity, biocompatibility, and biodegradability. Silk fibroin (SF), one of the typical natural protein polymers, is classified into domestic (*Bombyx mori*) and wild types (*Antheraea pernyi*, etc.). However, silk by itself suffers from some inferior performance, such as photoyellowing and wrinkle recovery. Many attempts have been made to improve their properties or add new functions by blending SF with other natural or synthetic polymers, such as poly(vinyl alcohol),<sup>1,2</sup> chitosan,<sup>3,4</sup> cellulose,<sup>5,6</sup> sodium polyglutamate,<sup>7</sup> and sodium alginate.<sup>8</sup> All such attempts are dependent on the solution blend method.

Supercritical (SC) fluids, especially CO<sub>2</sub>, due to their low viscosity, high diffusivity, zero surface tension, and strong solvent power for many organic com-

pounds, have been widely applied in polymer science to replace traditional organic solvents, including synthesis of different kinds of polymers,<sup>9,10</sup> preparation of fine particles,<sup>11,12</sup> production of foam materials,<sup>13,14</sup> and formation of porous flat membranes.<sup>15,16</sup> SC CO<sub>2</sub>-assisted polymer blend synthesis is a new and developing technology. Also, there is much research on preparing blends using SC CO<sub>2</sub> as a solvent and carrier, with the substrates varying from synthetic polymers to inorganic compounds such as molecular sieves and CNT. In this work, we synthesize PAA/*A. pernyi* SF fiber blends with the aid of SC CO<sub>2</sub>. This silk is one of the most important and commercially valuable. The effects of various factors on the blends were studied. The structure of blends was determined by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetry (TG). The products were also further evaluated for their water retention capacity.

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## EXPERIMENTAL

### Materials

Degummed *A. pernyi* SF fibers, supplied by Key Laboratory of Molecular Engineering of Polymers of Education Ministry in Fudan University, were dried in a vacuum oven at room temperature. Acrylic acid (AA) was purchased from Tianjin Fuchen Chemical Reagent Plant, A. R. grade, and was vacuum distilled. Azobis(isobutyronitrile) (AIBN), supplied by Shanghai

Sanpu Chemical Co. Ltd, was used after recrystallization from ethanol. Absolute ethanol, A. R. grade, was received from the Tianjin Kaitong Chemical Reagent Co. Ltd. CO<sub>2</sub>, with purity of 99.9%, was provided by the Zhengzhou Shuangyang Gas Co. and used as received.

### Volume expansion of monomer in compressed CO<sub>2</sub>

To determine the compatibility between the monomer and CO<sub>2</sub>, a suitable amount of AA and solution of AA–AIBN was loaded into a 50-mL optical stainless-steel reactor with a magnetic stirrer. The reactor was stabilized at 40°C in a water bath, which was controlled by a HAAKE C10 controller. The solution was swelled when CO<sub>2</sub> was successively charged into the reactor. The greater the swelling, the better is the compatibility between the monomer and compressed CO<sub>2</sub>. The volume expansion of the solution in compressed CO<sub>2</sub> is denoted ΔV%, which is given by Eq. (1),

$$\Delta V\% = [V(P,T) - V(P_0,T)]/V(P_0,T) \times 100\%, \quad (1)$$

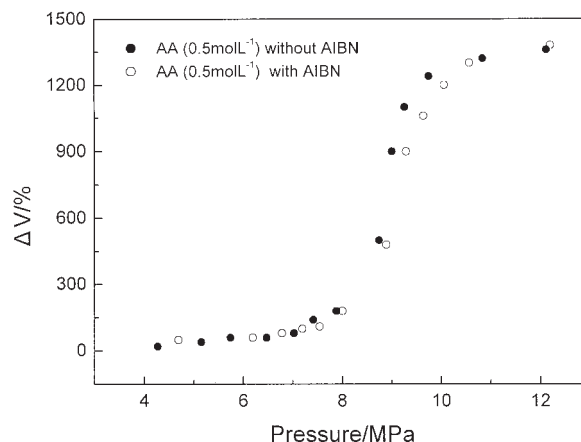
where  $P_0$  is the atmospheric pressure and  $T$  is the temperature of the system.

### Blends synthesis

The procedures consisted of two steps: an impregnating process and a polymerization reaction. In a typical experiment, suitable amounts of SF fibers and AA–AIBN (0.3 mol % based on AA) 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<sub>2</sub> was charged by a syringe pump (DB-80, Beijing Satellite Manufacturing Factory) until the desired pressure was reached. During this process, some of AA–AIBN infused into the fibers. After a desired impregnating time, the fluid in the system was released. The impregnated fibers were transferred into another stainless-steel vessel and the air in the vessel was replaced by N<sub>2</sub>. The polymerization was carried out at 70°C for 6 h. Then the sample was taken out, washed with absolute ethanol for 24 h to remove the unreacted monomer and homopolymer, which adhered to the surface of SF fibers, and afterward dried under vacuum at 35°C for 24 h.

### Characterization

FTIR spectra were recorded on a Nicolet FTIR-460 spectrometer by the transmission method. The fibers were crushed and then examined in KBr discs. XRD measurements were performed using a Rigaku D/MAX-IIIIB diffractometer (Japan), using CuKα radi-



**Figure 1** Volume expansion of AA in CO<sub>2</sub> as a function of pressure with and without AIBN at 40°C.

ation with a wavelength of 1.54 Å. The scanning speed was 4°/min and the measurement range was  $2\theta = 3\sim 50^\circ$  under 35 kV and 30 mA. Thermogravimetric analysis was run under a flow of nitrogen gas at a scanning speed of 10°C/min from 30 to 700°C using a Netzsch TG-209. The water absorbencies of the original SF fiber and the blends were determined by immersing the fibers in distilled water for 2 h. After that, the fibers were taken out and excess water was removed by putting two filter papers inside under gentle pressure. The fibers were weighed. The weight of a sample was recorded as WET and samples were then dried in an oven at  $65 \pm 2^\circ\text{C}$ : The dry weight was recorded as DRY.<sup>17</sup> The water absorbency was expressed as the water retention value (WRV) and was calculated as

$$\text{WRV}(\text{g/g}) = (\text{WET} - \text{DRY})/\text{DRY} \quad (2)$$

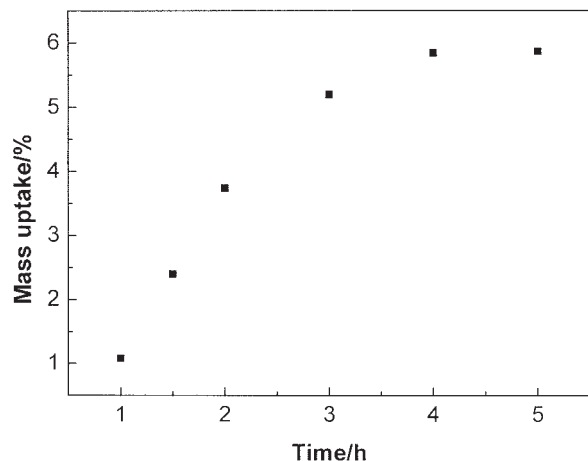
## RESULTS AND DISCUSSION

### Compatibility between monomer and CO<sub>2</sub>

The volume expansion of the solution is related to the solubility of CO<sub>2</sub> in it. The curves make a distinct turn when the pressure reaches the critical point of CO<sub>2</sub>, as shown in Figure 1. This indicates that SC CO<sub>2</sub> and AA have good compatibility when the experimental pressures are higher than 9 MPa. It is also shown that 0.3 mol % AIBN has little impact on the compatibility.

### Effect of impregnating time

Impregnating time was varied from 1 and 5 h at 40°C and 12 MPa. The original concentration of AA was 0.5 mol/L. Figure 2 shows the dependence of mass uptake on impregnating time. It can be seen that mass uptake increases steadily with impregnating time and levels off in 3 h. SF is a partly crystalline polymer,

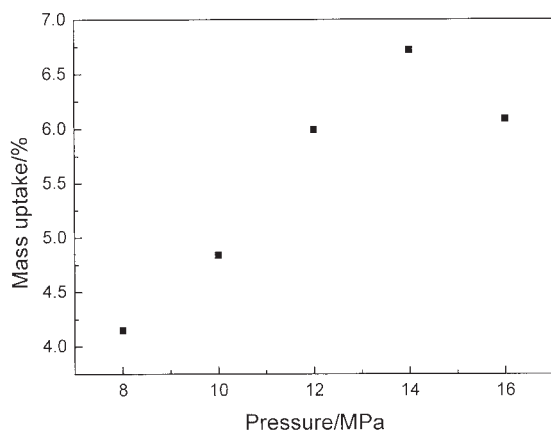


**Figure 2** Mass uptake of silk as a function of impregnating time at 40°C and 12 MPa (AA concentration = 0.5 mol/L).

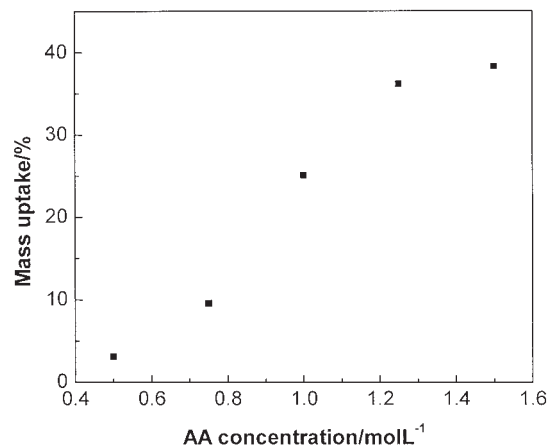
containing crystalline, amorphous, and quasicrystalline regions. The amorphous region, due to its loose structure, is favorable for various kinds of molecules to permeate and disperse. In addition, the supercritical solution has good diffusion ability; thus, equilibrium absorption can be reached after a period of impregnating time.

#### Effect of impregnating pressure

A series of experiments was performed with various impregnating pressures in the range 8 to 16 MPa. The original concentration of AA was 0.5 mol/L and the impregnating time was 4 h. Figure 3 shows the effect of impregnating pressure on the mass uptake of SF. The mass uptake increases with increasing impregnating pressure up to 14 MPa and then decreases from 14 to 16 MPa. Increasing pressure of CO<sub>2</sub> is better to swell SF; however, CO<sub>2</sub> is also a much better solvent for AA at high pressures; thus, more monomers are dissolved



**Figure 3** Mass uptake of silk as a function of impregnating pressure at 40°C for 4 h.



**Figure 4** Mass uptake of silk as a function of AA concentration at 40°C and 12 MPa.

in the fluid phase, which is not favorable to increasing the mass uptake. The competition of these two opposite factors reaches a balance at 14 MPa. Similar pressure effects have also been observed by Watkins and McCarthy<sup>18</sup> and by Li and Han.<sup>19</sup>

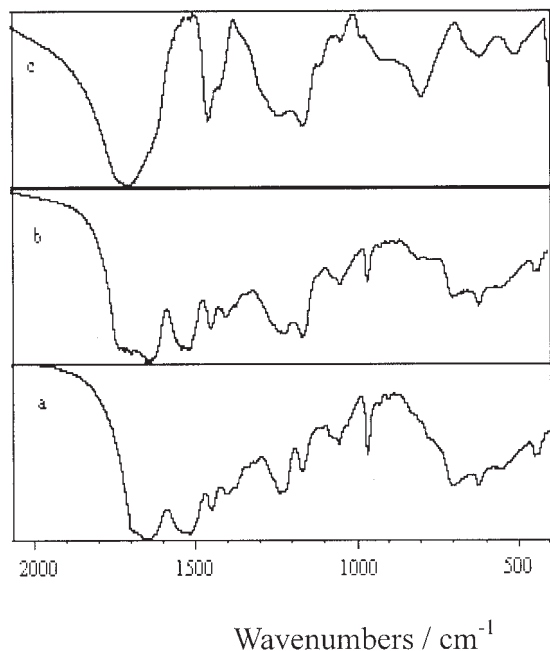
#### Effect of monomer concentration

The effect of monomer concentration on mass uptake was also studied. The impregnating process was conducted at 12 MPa and 40°C for 4 h. The initiator concentration was maintained at 0.3 mol %, based on monomer; the overall initiator concentration in the fluid phase therefore varied with AA concentration. Figure 4 illustrates the effect of AA concentration on mass gain, which indicates that the mass uptake increases significantly with AA concentration in the experimental range and then tends to stabilize after 1.25 mol/L.

#### Characterization

##### IR studies

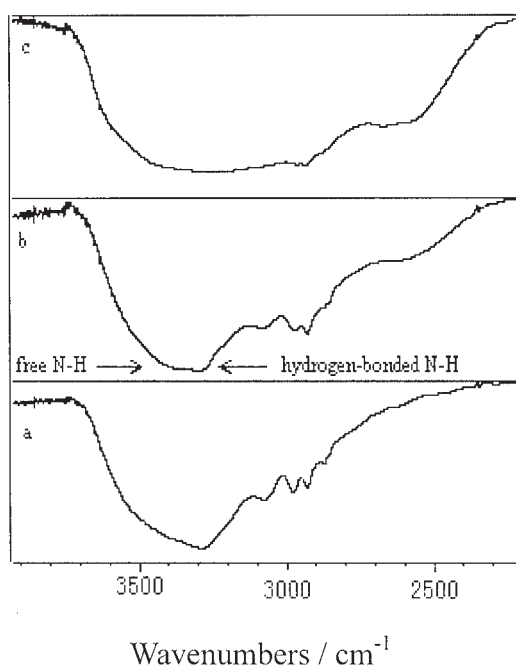
FTIR spectroscopy is useful in structural analysis of SF.<sup>20,21</sup> The IR spectra in the 500–2000 cm<sup>-1</sup> range of original *A. pernyi* SF, PAA/SF, and pure PAA are shown in Figure 5. *A. pernyi* SF (Fig. 5a) shows strong absorption bands at 1571 (amide II), 1238, (amide III), 965, (amide IV) and 698 cm<sup>-1</sup> (amide V), all assigned to  $\beta$ -sheet conformation; and 1647 (amide I) and 622 cm<sup>-1</sup> (amide V), attributed to the  $\alpha$ -helix conformation. On the other hand, the PAA (Fig. 5c) showed absorption bands at 1701 cm<sup>-1</sup>, attributed to the C=O stretching. The absorption bands at 1238 and 1164 cm<sup>-1</sup> are assigned to the C-O stretching. In the blend (Fig. 5b), due to the overlap of amide I of SF and C=O of PAA, the band at 1640–1735 cm<sup>-1</sup> broadened. The relative intensity of two bands at 1160–1240 cm<sup>-1</sup>



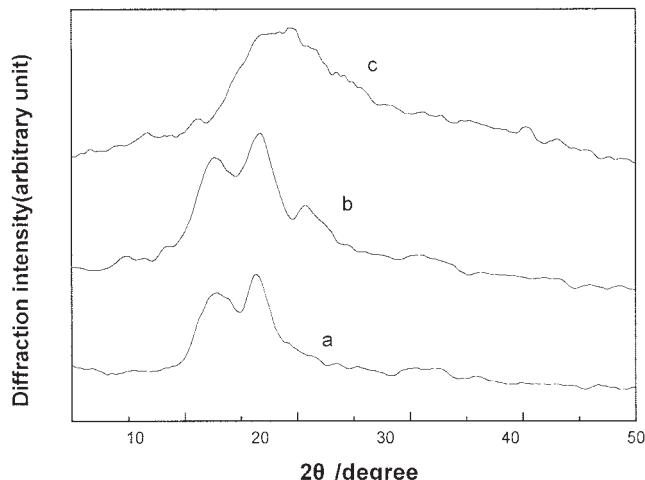
**Figure 5** FTIR spectra in 500–2000  $\text{cm}^{-1}$  of (a) original SF, (b) PAA/SF, and (c) pure PAA.

shows a distinct change compared to the same range in pure PAA.

Figure 6 gives the spectra in range of 2000–4000  $\text{cm}^{-1}$ . For SF, the band at 3288  $\text{cm}^{-1}$  is due to the hydrogen-bonded N-H stretching vibration.<sup>22</sup> As to PAA, the wide and strong band at 3000–3500  $\text{cm}^{-1}$  is



**Figure 6** FTIR spectra in 2000–4000  $\text{cm}^{-1}$  of (a) original SF, (b) PAA/SF, and (c) pure PAA.



**Figure 7** X-ray diffraction patterns of (a) SF, (b) PAA/SF, and (c) PAA.

attributed to the hydrogen-bonded O-H stretching vibration in PAA dimers, which is character of carboxylic acid.<sup>23</sup> After PAA is blended with SF, the strength of the absorption band at 3400  $\text{cm}^{-1}$  is enhanced. This implies that parts of the hydrogen bonds, in which the amide groups of SF are involved, were broken by the addition of PAA and that free amide groups and/or new hydrogen bonds were formed. A broad distribution of local -CO-NH- environments of SF in the blend, i.e., the formation of various kinds of hydrogen bonds differing in length and strength, may account for band broadening in the N-H stretching region. This indicates that a partial molecular mixing occurred and molecular interactions, mainly based on hydrogen bonding, were established between SF and PAA chains. These results are in accordance with other research.<sup>24,25</sup>

#### XRD studies

To confirm the above interpretation, X-ray diffraction curves of SF, PAA/SF, and PAA are displayed in Figure 7. SF shows two major diffraction peaks at 16.68 and 19.78° with a Bragg spacing  $d = 5.32$  and 4.48 Å, which shows that the conformation in the pure SF was  $\beta$  crystal (silk II) and  $\alpha$  crystal (silk I) coexisting. The curve of PAA does not show any characteristic crystalline peak, indicating that PAA is amorphous. Upon blending, there are three diffraction peaks at 16.36, 20.12, and 23.64°, corresponding to 5.42, 4.41, and 3.75 Å spacing, which are characteristics of a  $\beta$ -sheet crystalline structure.<sup>26</sup> This suggests that interpolymer hydrogen-bonding between SF and PAA is introduced; moreover,  $\alpha$ -helix crystal transits to  $\beta$ -sheet form.

#### Thermal behavior

Thermogravimetric analysis was also performed. A. pernyi SF fiber underwent three main thermal decom-

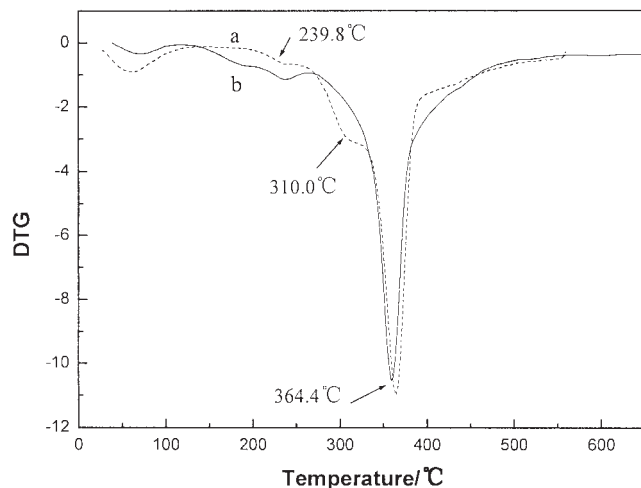


Figure 8 DTG curves of (a) SF and (b) PAA/SF blend.

position stages: the first step, slight thermal decomposition of SF molecules, occurs from 220 to 280°C; the second, abrupt decomposition step from 280 to 320°C, and the third, from 320 to 400°C, are attributed to the disintegration of intermolecular interaction and the partial breakage of the molecular structure. The differential weight loss (DTG) curves (see Fig. 8) provide clear evidence for the three degradation steps. The maximum degradation temperatures of the three steps in SF were 239.8, 310.0, and 364.4°C, in agreement with literature data.<sup>27</sup> In the blend, the second decomposition peak disappeared.

## WRV

It should be pointed out that grafting can take place in SF because it contains many active groups like -OH, -NH<sub>2</sub>, and -COOH. Thus, graft copolymerization of AA onto the silk fibers using AIBN as initiator was possible. The WRV data of the blends were higher than that of the single SF, as shown in Table I. This indicates that some AA chains were grafted onto the SF; thereby, the hydrophilic nature of the fibers was increased.

TABLE I  
WRV of SF and the Blend

Samples	Mass uptake of PAA on SF (%)	WRV (g/g)
SF	0	0.58
PAA/SF	5.8	0.66
	7.0	0.79

## CONCLUSIONS

According to the literature, this is the first work using SF as a matrix to blend with PAA in supercritical CO<sub>2</sub>. PAA content can be controlled by adjusting the impregnating time and impregnating pressure or by manipulating the concentration of AA in the supercritical fluid. Based on the results of FTIR and XRD, the PAA indeed existed in SF. Furthermore, SF and PAA have intermolecular hydrogen bond interaction, which led to the conformation transition of SF, and the addition of PAA slightly improved the thermal stability of SF. The water retention values indicated that the hydrophilic nature of the fibers was improved.

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