

# Supercritical CO<sub>2</sub>-Assisted Synthesis of Poly(acrylic acid)/Nylon1212 Blend

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**ABSTRACT:** PAA/nylon1212 blend was prepared using supercritical CO<sub>2</sub> as substrate-swelling agent and monomer/initiator carrier. Both supercritical CO<sub>2</sub>/nylon1212 binary system and SC CO<sub>2</sub>/monomer/nylon1212 ternary system have been studied. Virgin nylon1212 and blends were characterized through differential scanning calorimetry

(DSC), infrared spectroscopy (IR), and scanning electron microscopy (SEM). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2040–2044, 2003

**Key words:** supercritical CO<sub>2</sub>; nylon1212; poly(acrylic acid); blend

## INTRODUCTION

Recently, people have shown more interest in supercritical fluid (SCF)-assisted polymer modification and blend synthesis. The high solubility, diffusivity, and plasticizing behavior of CO<sub>2</sub> in polymers make it a unique plasticizer to accelerate the impregnation of small molecules into polymer substrates. Although SC CO<sub>2</sub> is a weak solvent for most polymers, it is a desirable swelling agent for polymers and can dissolve many small molecules.<sup>1–4</sup> One of the most intriguing features of a SCF is that its density and solvent strength can be adjusted by changing the pressure and temperature of the system. As a result, the degree of swelling in polymers<sup>2,5,6</sup> as well as the partitioning of small molecules between the fluid phase and the substrate<sup>7,8</sup> can be manipulated simply. And maintaining conditions above the critical temperature avoids creation of vapor–liquid coexistence upon pressure releasing. This allows impregnation to proceed without substrate being distorted by capillary forces. In addition, the solvent can be separated completely and easily from the substrate.

So a new route to produce composite and foam materials has been developed by McCarthy<sup>9–16</sup> and coworkers. The method involves the swelling of the polymer substrate by a SC CO<sub>2</sub> solution of monomer and thermal initiator whose half-life is extremely long at the impregnation temperature. At higher temperature, with the initiator decomposing much faster, subsequent polymerization of the monomer is carried out and a composite system of the two polymers is yielded. Compared with traditional blending meth-

ods, this approach is more facile and versatile, and one of the most promising features is that blending can be performed at temperatures well below  $T_m$ . Moreover, the blend composition is not limited by the solubility of the monomer in the matrix polymer.

Nylon1212 is a new and high performance engineering plastic with relatively low water absorbability compared with other polyamide products. In this study, poly(acrylic acid)/nylon1212 blend was prepared and the purpose of the study is to explore better performance for the composite.

## EXPERIMENTAL

### Materials

Nylon1212 was obtained from the Lab of Engineering Plastics at Zhengzhou University, in the form of transparent light-yellow pellets. After being dried in vacuum at 116°C for 48 h, the pellets were processed to  $0.9 \pm 0.02$  mm-thick sheets on the press vulcanizer (Model QLB-D, made in China). A glass transition of 54°C and melting range of 182–184°C were determined by DSC with a heating rate of 10°C/min. The density was measured with volume–mass method at  $25 \pm 1^\circ\text{C}$  and found to be  $1.013 \text{ g/cm}^3$ .

CO<sub>2</sub> with purity of 99.9% was obtained from Zhengzhou Sanfa Gas Co. (Zhengzhou, China). Acrylic acid was purchased from Tianjin Jinyu Chemical Plant (Tianjin, China) and used as received. Azobis(isobutyronitrile) (AIBN) supplied by Shanghai Sanpu Chemical Co. Ltd. (Shanghai, China) was recrystallized twice from methanol.

### Procedures

Reactions were run in a 21.4 mL high-pressure stainless steel reactor. A high-pressure syringe pump (Bei-

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jing Satellite Manufacturing Factory, Beijing, China; DB-80) was used to charge CO<sub>2</sub> into the reaction vessel and attached to the reactor via a coupling and high-pressure tubing. A pressure gauge consisting of a transducer (IC Sensors Co., Model 93) and an indicator (Beijing Tianchen Automatic Instrument Factory, XS/A-1) with the accuracy of  $\pm 0.05$  MPa was also connected to the reactor to observe the *in situ* pressure change of the system. In the experiments, the reactor was placed in a constant-temperature circulator, which consisted of a temperature control module (Thermo Haake, C10) and a bath vessel (Thermo Haake, P5). The fluctuation of temperature in the bath was less than  $\pm 0.1^\circ\text{C}$ . All sample sheets were weighed on a Shanghai 328A electrobalance with a sensitivity of 0.1 mg.

#### SC CO<sub>2</sub>/nylon1212 binary system study

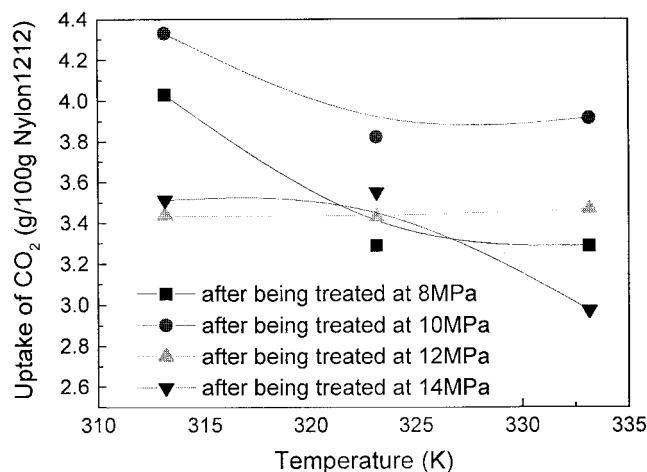
Nylon1212 sheets were sheared into  $1.2 \times 3.0$  cm samples with the thickness of  $0.9 \times 0.02$  mm. After being purged with CO<sub>2</sub> twice and equilibrated in the constant-temperature bath, the reactor was repressurized to the desired pressure. After 4 h treating, the reactor was depressurized and the samples were brought to an electronic balance immediately. Then the treated samples were placed in  $20^\circ\text{C}$ , clean and dry atmosphere for 72 h. Mass change was recorded regularly during the period.

#### Monomer/SC CO<sub>2</sub>/nylon1212 ternary system study and synthesis of blends

0.3 mol % (based on acrylic acid) initiator AIBN was dissolved in a certain amount of styrene, and the solution was introduced to the bottom of the reactor. Then some glass wool was put in, upon which nylon1212 samples were placed. So before charging CO<sub>2</sub> into the reactor, samples and monomer solution did not touch each other. After being filled with CO<sub>2</sub> to 5 MPa, the reactor was equilibrated in a  $40 \pm 0.1^\circ\text{C}$  water bath and repressurized to the desired pressure. After a period of treating, the reactor was depressurized. The samples were brought out, wiped by clean filter paper, and weighed. Variations of this procedure involved changing the impregnation time from 1 to 8 h and the pressure from 8 to 20 MPa. In 20 min after impregnation, the impregnated samples were transferred to another identical reaction vessel. The vessel was vacuumed and heated at  $62^\circ\text{C}$  under the protection of N<sub>2</sub> in the polymerization period of 4 h.

#### Characterization

Differential scanning calorimetry (DSC) measurements were conducted on a Netzsch 204 DSC under N<sub>2</sub> atmosphere with a heating rate of  $10^\circ\text{C min}^{-1}$  in the temperature range of  $30$ – $250^\circ\text{C}$ . IR spectroscopy,



**Figure 1** Uptake of CO<sub>2</sub> in nylon1212 as a function of temperature immediately after being treated in SC CO<sub>2</sub> for 4 h at different pressures.

experiments were performed using a Nicolet 460 FTIR under standard operating conditions. Sections of virgin nylon1212 and PAA/nylon1212 blend were observed through a JEOL JSM-5610LV scanning electron microscope (SEM). Each sample surface was coated with graphite and the accelerating voltage was between 5 and 15 kV.

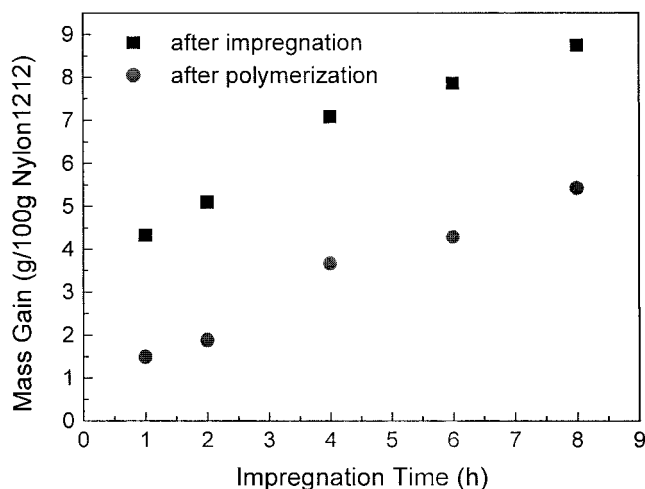
## RESULTS AND DISCUSSION

### Sorption of CO<sub>2</sub> in nylon1212

In CO<sub>2</sub>/nylon1212 binary system study, CO<sub>2</sub> absorption under different conditions was measured. It has been found that uptake of CO<sub>2</sub> is a function of pressure and temperature. In Figure 1 it can be seen that at low pressures (8–10 MPa), mass gain decreases with the increase of treating temperature and the decreased amount is more notable in low temperature region than in relatively high temperature region. At high pressures ( $\sim 14$  MPa), CO<sub>2</sub> absorption also decreases with temperature, the decreased amount, however, is more notable at high temperatures than at low temperatures. It is because that when experimental pressure was constant, the concentration of CO<sub>2</sub> in the reaction system decreased with temperature and so the uptake of CO<sub>2</sub> in the substrate decreased with temperature. It is true for the lower pressures 8, 10 MPa, and higher pressure of 14 MPa. For the pressure of 12 MPa, the mass gain of CO<sub>2</sub> was nearly constant with the change of temperature. So under this condition, temperature is not the only factor affecting the CO<sub>2</sub> uptake.

### Effects of impregnation conditions on blend synthesis

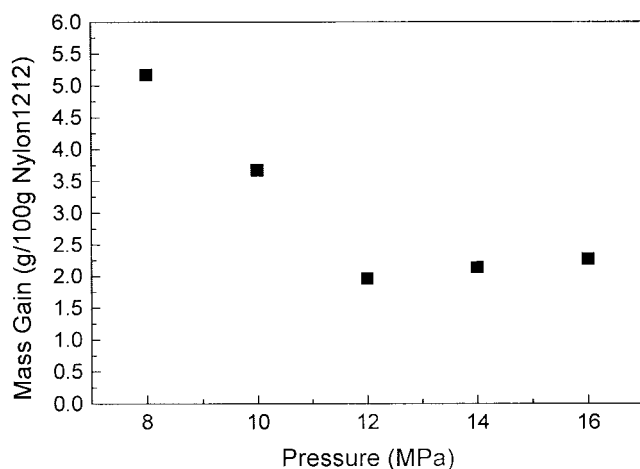
DeSimone et al.<sup>17</sup> have published the phase behavior of SC CO<sub>2</sub>/acrylic acid system. Based on the data, all experiments in this study were run under the condi-



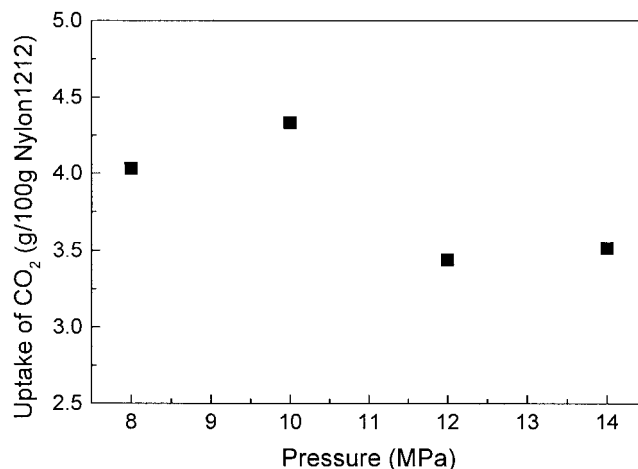
**Figure 2** Mass gain of nylon1212 as a function of impregnation time after being treated in 30 wt % acrylic acid/SC CO<sub>2</sub> at 40°C and 10 MPa and polymerization at 62°C for 4 h.

tions that monomer and CO<sub>2</sub> were in a single phase. First a series of experiments were carried out to determine the effect of impregnation time on nylon1212 substrate. The concentration of acrylic acid was fixed at 30 wt % and the SC CO<sub>2</sub>-assisted impregnation were carried at 40°C and 10 MPa. Two groups of experimental data were given: one is after impregnation and before polymerization and the other is after polymerization. The results are given in Figure 2. It is found that in the considered time range, the plots of mass uptake versus impregnation time are nearly in linear increasing trend.

As for the effect of pressure, from Figure 3 it can be seen that the amount of impregnated acrylic acid first decreases with pressure till 12 MPa, then increases slightly with pressure. There are a lot of factors contributing to the amount of impregnated monomer such as the diffusion rate of CO<sub>2</sub>, the amount of CO<sub>2</sub> in



**Figure 3** Mass gain of nylon1212 as a function of impregnation pressure (impregnation in 30 wt % monomer/SC CO<sub>2</sub> for 4 h at 40°C, polymerization for 4 h).



**Figure 4** Uptake of CO<sub>2</sub> in nylon1212 as a function of pressure after being treated in SC CO<sub>2</sub> for 4 h at 40°C.

the substrate, and the partition of acrylic acid between CO<sub>2</sub> and substrate, etc. In order to make sure the accurate factors, impregnation of pure CO<sub>2</sub> was studied and the experimental results are shown in Figure 4. It can be seen that except for 8 MPa, there exist the same inclination of CO<sub>2</sub> impregnation with pressure. So it can be deduced that in the range of pressure, there exist cooperation effect between CO<sub>2</sub> and acrylic acid. But at 8 MPa, there exist competition between CO<sub>2</sub> and acrylic acid because lower impregnation of CO<sub>2</sub> induced higher impregnation of acrylic acid. And the detail mechanism needs to be further studied.

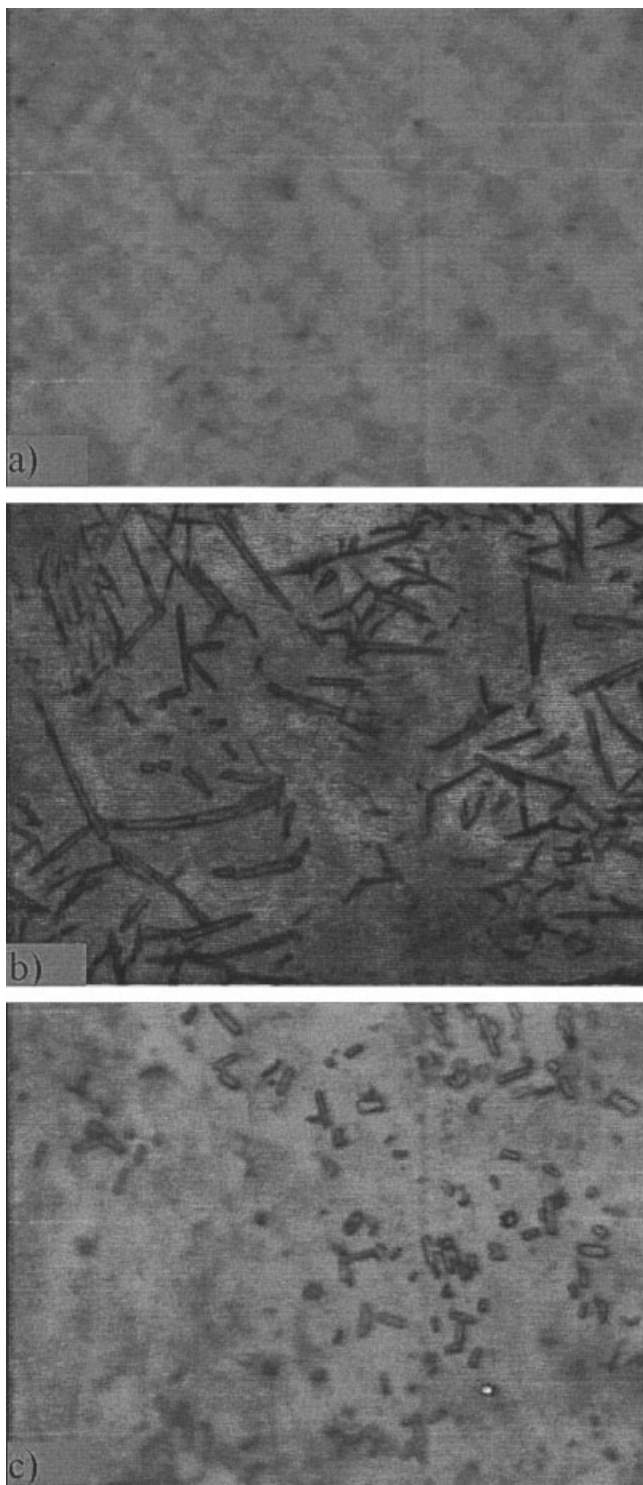
### Blends characterization

To determine the properties and internal structure of PAA/nylon1212 blend, a series of characterization measurements were carried out. DSC was performed to measure the thermal properties of the blends. As mentioned in the Experimental section, the virgin nylon1212 has been dried in vacuum at 116°C for 48 h. The temperature of maximum crystalline growth velocity ( $T_{max} = 116^\circ\text{C}$ ) calculated with the following empirical formula:

$$T_{max}(\text{K}) = 0.63T_m(\text{K}) + 0.37T_g(\text{K}) - 18.5$$

So nylon1212 samples have achieved maximum crystallinity before DSC measurements.

It is well known that crystallization of some amorphous and semicrystalline polymers can be induced by solvent as well as by heat and strain. The interaction between polymer and the solvent reduces the effective  $T_g$  and, if the reduction of  $T_g$  is large enough to put the system in the crystallization temperature region, the polymer chains rearrange themselves into a lower free energy state.<sup>18,19</sup> Chiou,<sup>20</sup> Johnston,<sup>21,22</sup> and K. Mizoguchi et al.<sup>23</sup> have all discovered that supercritical CO<sub>2</sub> has inducing crystallization effect on



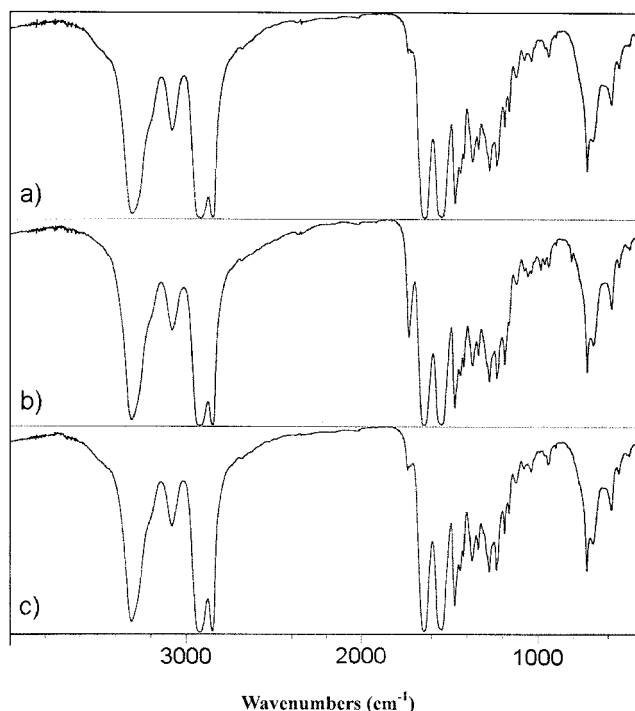
**Figure 5** Micropolariscopy photograph ( $\times 100 \times 0.9 \times 10$ ) of virgin nylon1212 (a), SC CO<sub>2</sub>-treated nylon1212 (b), and PAA/nylon1212 blend (c).

polymers. In our study, a novel phenomenon, SC CO<sub>2</sub>-induced epitaxial crystallization was found on the surface of nylon1212 samples. In the micropolariscopy photographs it can be seen that with SC CO<sub>2</sub> treatment, some arborescent or bacillary structures formed on the surface of nylon1212, as shown in Figure 5(b).

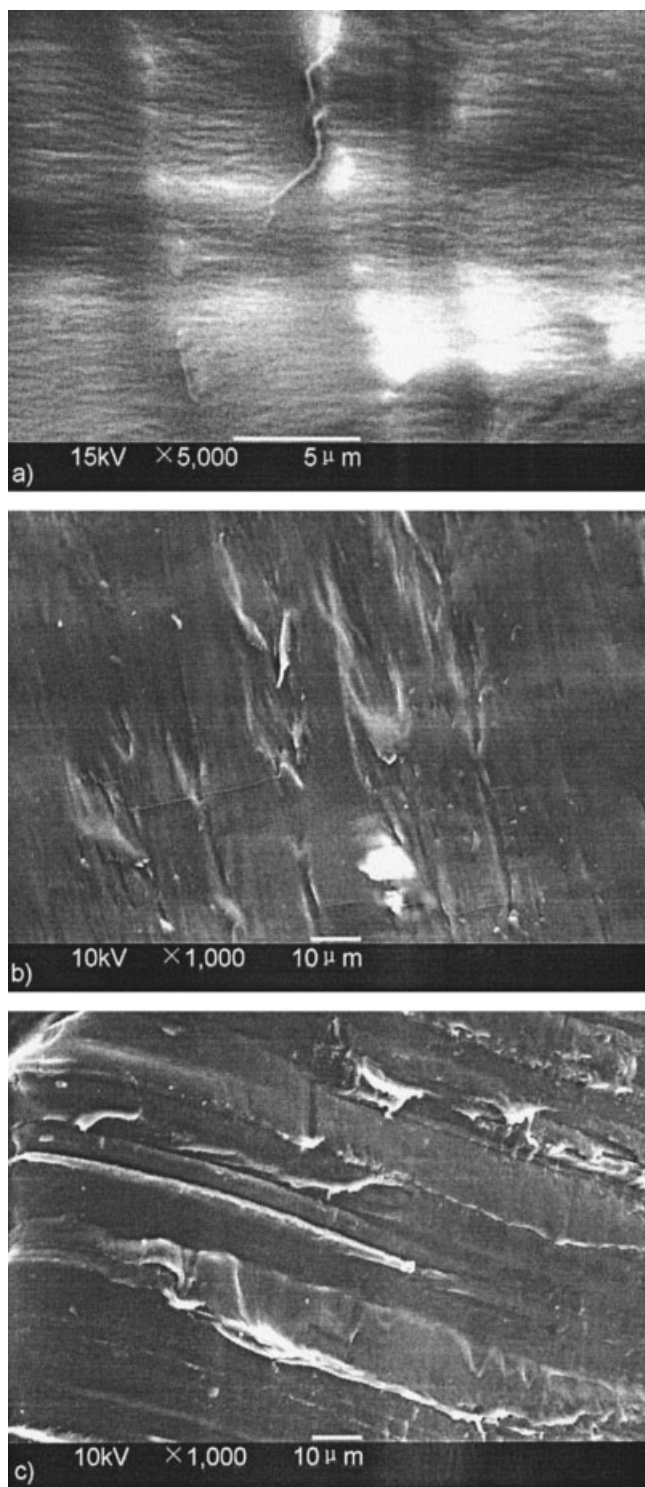
Study of the phenomenon has been discussed in our previous study.<sup>24</sup> In subsequent experiment effect of incorporated poly(acrylic acid) on nylon1212's aggregation structure was studied. Figure 5(c) is the micropolariscopy photograph of PAA/nylon1212 blend. It can be seen that original arborescent or bacillary structures were partially destroyed by incorporation of poly(acrylic acid). Only some crystal of small-dimension remained and the distribution uniformity dropped considerably. Without doubt, the impregnated PAA changed nylon1212's crystallizing environment and dimensions of the crystal patterns.

Figure 6 shows FTIR spectra of virgin nylon1212, a PAA/nylon1212 (3:100) blend, and the same blend sample extracted by water. From Figure 6(b), it can be seen that a spectral feature of PAA which is C=O stretching appeared at  $1,730\text{ cm}^{-1}$  and it clearly demonstrates the existence of poly(acrylic acid) in the nylon1212 matrix. Although for nylon1212, there also exists a C=O stretching absorption. As the carbonyl is one part of the principal molecular chain, its stretching motion is limited. In addition, affected by the imidogen, the stretching absorption of C=O in polyamide is at  $\sim 1,640\text{ cm}^{-1}$  instead of  $1,700\text{--}1,750\text{ cm}^{-1}$ .

PAA is a water-soluble polymer, so the blend sample was extracted with water at  $25^\circ\text{C}$  for 2 h and then dried at  $55^\circ\text{C}$  for 2 h. In Figure 6(c), it can be seen that the disappearance of the  $1,730\text{ cm}^{-1}$  wave number occurs and this indicates that almost all of the incorporated poly(acrylic acid) has been removed.



**Figure 6** IR spectra of virgin nylon1212 (a), PAA/nylon1212 blend (b), and the same blend extracted with water followed by drying in vacuum (c).



**Figure 7** SEM photographs of cross-sections of virgin nylon1212 and PAA/nylon1212 blends. (a) virgin nylon1212; (b) impregnated for 4 h at 40°C and 10 MPa, polymerized for 4 h at 62°C; (c) impregnated for 8 h at 40°C and 10 MPa, polymerized for 4 h at 62°C.

Cross-sections of nylon1212 and PAA/nylon1212 blends are observed through SEM and the photos are given in Figure 7. It can be found that in the PAA/nylon1212 blend, the cross-section is no longer even as before and there appear some ribbon-like structures.

Further from Figure 7(b,c), it can be seen that the impregnation time has notable influence on the morphology of PAA/nylon1212 blend. With the increase of the time, the ribbon phenomenon became more notable.

## CONCLUSIONS

The study shows that SC CO<sub>2</sub> can penetrate into nylon1212 substrate and act as a carrier for the monomer in an impregnation process. Poly(acrylic acid)/nylon1212 blend was prepared by infusion of acrylic acid into and radical polymerization within solid nylon1212. And the concentration of incorporated polymers can be controlled by adjusting reaction conditions such as the impregnation time and pressure. CO<sub>2</sub>-induced epitaxial crystallization was found on the surface of nylon1212 samples and the arborescent or bacillary structure was partially destroyed by incorporation of poly(acrylic acid). For the PAA/nylon1212 blend, the impregnation time has notable effect on the cross section.

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