

# Complex Interactions among Additive/Supercritical CO<sub>2</sub>/Polymer Ternary Systems and Factors Governing the Impregnation Efficiency

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**ABSTRACT:** Styrene and acrylic acid were impregnated into a series of polyamide products (nylon1212, nylon1010, nylon66, nylon6) using supercritical CO<sub>2</sub> as the additive-carrier and substrate-swelling agent. The impregnation efficiency of low molecular weight additives into substrates is attributed to complicated interactions among the system: (1) loading of additives in substrates, (2) dissolving of additives in CO<sub>2</sub> phase, (3) swelling and plasticizing of substrates by CO<sub>2</sub>. For the first time solubility parameter was introduced to discuss the impregnation efficiency. It was found that the

relative solubility of additive in the polymer substrate and CO<sub>2</sub> is a major factor governing the incorporated amount; yet swelling of the substrate and CO<sub>2</sub>-induced crystallization also contribute to the value. The study generalizes complex factors influencing the impregnation possibility of different systems. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 742–748, 2004

**Key words:** nylon; swelling

## INTRODUCTION

Recently, interests in supercritical fluid (SCF)-assisted impregnation and polymer modification have been growing rapidly. 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. CO<sub>2</sub> is non-flammable, nontoxic, and relatively inexpensive; its moderate critical conditions ( $T_c = 304.2$  K,  $P_c = 7.37$  MPa) make it a convenient fluid for experimentation. 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. Moreover, 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 sepa-

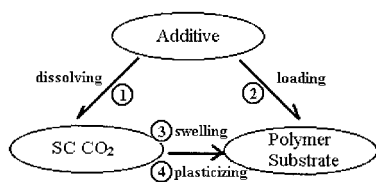
rated completely and easily from the substrate because CO<sub>2</sub> is gaseous at ambient conditions.

Phase behaviors of impregnation systems, especially the partitioning of a solute between CO<sub>2</sub> and a polymer substrate under supercritical conditions, have been studied by several researchers. Berens<sup>2</sup> and his colleagues reported kinetic and equilibrium data for the poly(vinyl chloride)/dimethyl phthalate/SC CO<sub>2</sub> system, as well as a number of other examples of CO<sub>2</sub>-assisted additive absorption. Kinetic study carried out by Shieh<sup>9</sup> and Sahle-Demessie<sup>10</sup> suggests that the major effect of CO<sub>2</sub> is not to improve the solubility of the additive but to accelerate the additive absorption by plasticizing the polymer. Kazarian<sup>11,12</sup> et al. reported the partitioning of deuterated methanol, deuterated propanol, 2-naphthol, naphthalene, and acridine between CO<sub>2</sub> and poly(cyanopropylmethylsiloxane) or poly(dimethylsiloxane) (PDMS). Johnston<sup>13,14</sup> and coworkers quantified the distribution of toluene between CO<sub>2</sub> and silicone rubbers as well as the partitioning of benzoic acid, phenanthrene, naphthalene, 2-naphthol, and pyrene between CO<sub>2</sub> and PDMS. More recently, Tomasko<sup>8</sup> et al. used confocal microscopy analysis to study supercritical fluid impregnation of polypropylene.

Furthermore, McCarthy<sup>15–23</sup> and coworkers have developed a new route to produce composite and foam materials using SC CO<sub>2</sub> impregnation. The method involves the swelling of polymer substrates by a SC CO<sub>2</sub> solution of monomer and appropriate thermal initiator. After SCF-assisted impregnation,

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**Figure 1** Interactions among the SC CO<sub>2</sub>-assisted impregnation system.

subsequent polymerization of incorporated monomer is carried out either with or without presence of SC CO<sub>2</sub>. Compared with traditional blending methods, this approach is more facile and versatile: blending can be performed at temperatures well below  $T_m$ , and blend composition is not limited by the solubility of the monomer in the matrix polymer.

The studies cited above confirm the advantages of a SCF to provide appropriate solvent power for the additive. The "pressure tuning" of this property ensures that the distribution coefficient of the additive strongly favors the polymer phase over the supercritical phase. Therefore, the supercritical solvent is much more efficient than most liquid solvents for impregnation because less additive remains in the solvent. This will have substantial implications for applications involving high-value or hazardous additives.

Polymeric substrates used in this study are a series of polyamides as nylon1212, 1010, 66, and 6, which are all widely applied as high-performance engineering plastics or synthetic fibers, and the study may benefit further application of SCF impregnation in material modification.

Phase behaviors of eight CO<sub>2</sub>/additive/nylon substrate ternary systems were studied under different supercritical conditions. The impregnation efficiency of low molecular weight additives into substrates is attributed to complicated interactions among the system, as shown in Figure 1: (1) dissolving of additives in CO<sub>2</sub> fluid phase; (2) loading of additives in substrates; (3) swelling and plasticization of substrates by CO<sub>2</sub>. Here, the concept solubility parameter  $\delta$  is used for discussion. It is found that compatibility of additive with substrate, relative solubility of the additive in polymer substrate and CO<sub>2</sub>, swollen degree of substrate by CO<sub>2</sub>, and induced crystallization of substrate all contribute to the final incorporated amount of small-molecule penetrants. We are, based on the study, aiming at finding a quantitative and relatively simple way to predict impregnation possibility of different systems.

## EXPERIMENTAL

### Materials

Nylon1212 was obtained from the Lab of Engineering Plastics at Zhengzhou University, in the form of trans-

parent light-yellow pellets. Nylon1010 (purchased from Xingda Synthetic Nylon Resin Plant, China), nylon66 (EPR27N, Mitsubishi, Japan), and nylon6 (1020C, Mitsubishi, Japan) were all industrial resin. After being dried in vacuum at 105°C for 48 h, all resin pellets were processed to  $0.9 \pm 0.02$  mm-thick sheets on the press vulcanizer (QLB-D, China). Physical properties of the substrates are given in Table I.

CO<sub>2</sub>, with a purity of 99.9%, was obtained from Zhengzhou Sanfa Gas Co. Styrene was purchased from Tianjin Dongda Chemical Co. and distilled under reduced pressure. Acrylic acid was purchased from the Tianjin Jinyu Chemical Plant and used as received.

Azobis(isobutyronitrile) (AIBN), supplied by Shanghai Sanpu Chemical Co. Ltd., was recrystallized twice from methanol.

### Procedures

Reactions were run in a 21.4-mL high-pressure stainless steel reactor. A high-pressure syringe pump (Beijing Satellite Manufacturing Factory, 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. In the experiments, the reactor was placed in a constant-temperature circulator consisting 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.

**TABLE I**  
Physical Properties of Nylon Substrates

Substrate	Melting range (°C)	$T_g$ (°C)	Density (g/cm <sup>3</sup> )	Solubility parameter <sup>a</sup> (cal <sup>1/2</sup> /cm <sup>3/2</sup> )
Nylon1212	182–184	54	1.013	9.66
Nylon1010	202–208	—	1.032	9.91
Nylon66	262–270	57	1.142	11.35
Nylon6	219–225	45	1.140	12.12

<sup>a</sup> Calculated with the molar attraction constant method.<sup>i)</sup> The classical formula as following was used:  $\delta = \Sigma F / V_0 = \Sigma F / (M_0 / \rho)$ ; where  $\Sigma F$  is the sum of the molar attraction constants of all groups or atoms in a repeating unit;  $V_0$  and  $M_0$  are the molar volume and the molar molecular weight of the repeating unit; and  $\rho$  is the density of the polymer. The molar attraction constants of some common groups<sup>ii)</sup> are given in Table II. <sup>i)</sup>Small, P. A. J. Appl. Chemistry 1953,3, 71. <sup>ii)</sup>Grulke, E. A. In Polymer Handbook; Brandrup, J.; Immergut, E. H.; Eds.; J. Wiley & Sons: New York, 1989, 3rd ed.

TABLE II  
Molar Attraction Constant of Some Common Groups

Group	$F, 10^{-3}$ [(cal <sup>1/2</sup> cm <sup>3/2</sup> )/mol]	Group	$F, 10^{-3}$ [(cal <sup>1/2</sup> cm <sup>3/2</sup> )/mol]
—CH <sub>3</sub>	148.3	—COO—	326.58
—CH <sub>2</sub> —	131.5	>C=O	262.96
>CH—	85.99	—CH= (aromatic series)	117.12
—H (acidic dimer)	-50.47	—C= (aromatic series)	98.12
—NH—	368.37	>C=	84.51

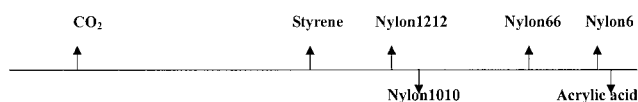
The initiator AIBN (0.3 mol %, based on additive) was dissolved in a certain amount of the additive (the concentration of additive was fixed at 30 wt %), and the solution was introduced to the bottom of the reactor. Then some glass wool was put in, upon which polymer samples were placed. The system was vacuumed, then filled with CO<sub>2</sub> to 5 MPa and the reactor was equilibrated in a 40 ± 0.1°C water bath and repressurized to the desired pressure. After 4 h 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 pressure from 8 to 20 MPa, the additives and nylon substrates. Twenty minutes after impregnation, the additive-impregnated samples were transferred to another identical reaction vessel. The vessel was then vacuumed and heated at a higher temperature (80°C for styrene and 62°C for acrylic acid) under the protection of N<sub>2</sub> for 4 h.

According to our previous study,<sup>24–26</sup> both CO<sub>2</sub> and additive are absorbed by substrates during the impregnation period, and the absorbed CO<sub>2</sub> is totally released during subsequent polymerization. So the mass gain of substrate after polymerization is equal to incorporated amount of the additive. Furthermore, the difference between the mass gain before and after polymerization can be regarded as absorbed amount of CO<sub>2</sub>.

## RESULTS AND DISCUSSION

Suppes and McHugh<sup>27</sup> have published the phase behavior of SC CO<sub>2</sub>/styrene system. DeSimone<sup>28</sup> et al. have determined solubility of acrylic acid in SC CO<sub>2</sub>. Based on their data, all experiments in this study were run under conditions at which additive and CO<sub>2</sub> are in a single phase. The additive concentration was held at 30 wt %.

In this study, we focus on various interactions among different ternary impregnation systems. To quantify these complicated effects, solubility parameter  $\delta$  is introduced. Solubility parameters of CO<sub>2</sub><sup>29</sup> (5.98 cal<sup>1/2</sup>cm<sup>3/2</sup>), styrene<sup>29</sup> (8.66 cal<sup>1/2</sup>cm<sup>3/2</sup>), acrylic acid<sup>30</sup> (12.19 cal<sup>1/2</sup>cm<sup>3/2</sup>), and nylon substrates (Table I) are shown in the following sketched axis.



Given our experimental results, it is found that many factors contribute to the final impregnation efficiency of different additives into different polymers.

### Compatibility of additive with substrate polymer

As shown in Figure 2, in the examined pressure range from 8 to 16 MPa, acrylic acid always has a higher impregnation amount than styrene. Based on the solubility sketch, it can be found that acrylic acid has a more similar  $\delta$  with nylon6 compared with styrene, so acrylic acid and nylon6 are highly physically compatible. As a result, acrylic acid is much easier to be impregnated into nylon6 than styrene.

### Relative solubility of additive in polymer substrate and in supercritical CO<sub>2</sub>

In Figure 3, incorporated amounts in the synthesized polystyrene/nylon1212 and poly(acrylic acid)/nylon1212 blends are given. It is found that the incorporated content of acrylic acid is higher than styrene. However, because  $|\delta_{\text{styrene}} - \delta_{\text{nylon1212}}| = 1$ , and

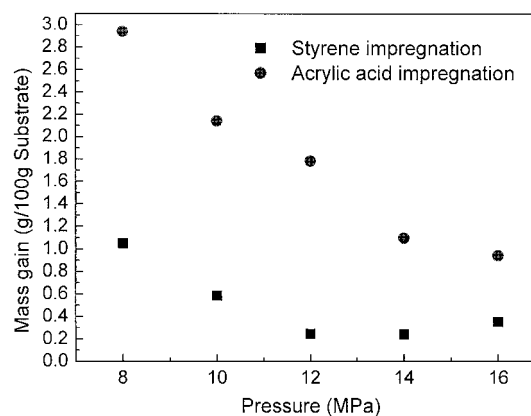
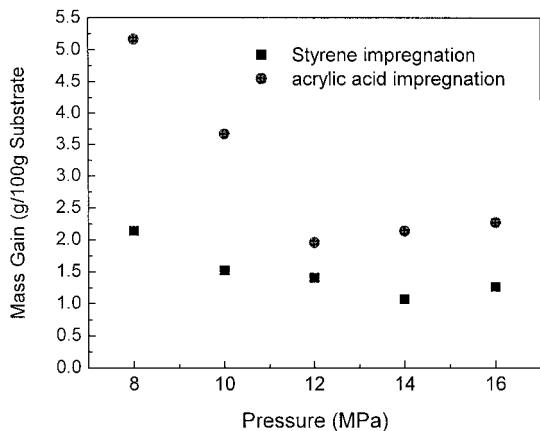


Figure 2 Impregnation of styrene and acrylic acid into nylon6 (after polymerization).



**Figure 3** Impregnation of styrene and acrylic acid into nylon1212 (after polymerization).

$|\delta_{\text{acrylic acid}} - \delta_{\text{nylon1212}}| = 2.53$ , the solvent interaction between styrene and nylon1212 is better than that between acrylic acid and nylon1212. According to the compatibility conclusion drawn above, styrene should have a higher impregnation amount than acrylic acid. So there must be something else governing the impregnation efficiency rather than compatibility of penetrant with substrate. Here, influence of the carrier SC CO<sub>2</sub> has to be considered.

For the four different components: CO<sub>2</sub>, styrene, acrylic acid, and nylon1212, their solubility parameters are 5.98, 8.66, 12.19, and 9.66 cal<sup>1/2</sup>cm<sup>3/2</sup>, respectively. So  $|\delta_{\text{styrene}} - \delta_{\text{nylon1212}}| = 1$ ;  $|\delta_{\text{styrene}} - \delta_{\text{CO}_2}| = 2.68$ ;  $|\delta_{\text{acrylic acid}} - \delta_{\text{nylon1212}}| = 2.53$ ;  $|\delta_{\text{acrylic acid}} - \delta_{\text{CO}_2}| = 6.21$ ;  $6.21 - 2.53 = 3.68 > 2.68 - 1 = 1.68$ .

Because  $|\delta_{\text{additive}} - \delta_{\text{nylon1212}}|$  and  $|\delta_{\text{additive}} - \delta_{\text{CO}_2}|$  stand for the solubility of additives in nylon1212 and in CO<sub>2</sub>, respectively, their relative solubility in nylon1212 and in CO<sub>2</sub> can be represented by the difference between these two absolute values. Based on above calculation, it can be found that the difference between  $|\delta_{\text{additive}} - \delta_{\text{CO}_2}|$  and  $|\delta_{\text{additive}} - \delta_{\text{nylon1212}}|$  in the acrylic acid-impregnation system is greater than in the styrene system, as shown in the following:

$$\begin{aligned}
 & \left| |\delta_{\text{acrylic acid}} - \delta_{\text{nylon1212}}| - |\delta_{\text{acrylic acid}} - \delta_{\text{CO}_2}| \right| \\
 & > \left| |\delta_{\text{styrene}} - \delta_{\text{nylon1212}}| - |\delta_{\text{styrene}} - \delta_{\text{CO}_2}| \right|
 \end{aligned}$$

Acrylic acid's relative solubility in nylon1212 and in CO<sub>2</sub> is greater than styrene's, that is, compared to styrene impregnation system, it is easier for acrylic acid to load in nylon1212 than to dissolve in SC CO<sub>2</sub>, and the incorporated amounts of acrylic acid are higher than styrene at all examined impregnation pressures. So it can be concluded that solubility of additive acrylic acid or styrene in the carrier SC CO<sub>2</sub> is very important. But at the following impregnation process, the partitioning of additive in nylon1212 and

SC CO<sub>2</sub> is more important, and this process is determined by relative solubility of the additive in nylon1212 and CO<sub>2</sub>. In fact, Berens<sup>3</sup> et al. have given similar experimental result in relevant work. Here, we use solubility parameters to quantify it.

When nylon1010 was used as a substrate polymer the same results can be found, as is shown in Figure 4. In this system,

$$|\delta_{\text{styrene}} - \delta_{\text{nylon1010}}| = 1.25 \quad |\delta_{\text{styrene}} - \delta_{\text{CO}_2}| = 2.68$$

$$|\delta_{\text{acrylic acid}} - \delta_{\text{nylon1010}}| = 2.28 \quad |\delta_{\text{acrylic acid}} - \delta_{\text{CO}_2}| = 6.21$$

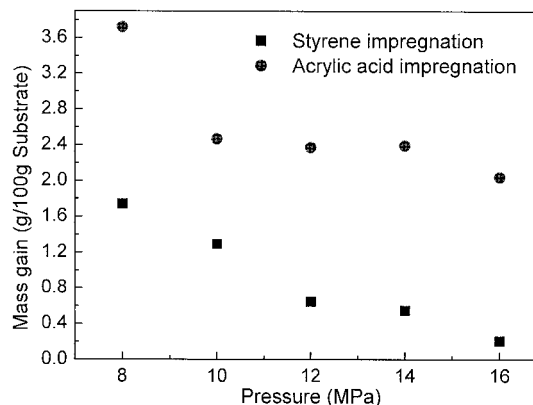
$$6.21 - 2.28 = 3.93 > 2.68 - 1.25 = 1.43$$

That means acrylic acid's relative solubility in nylon1010 and in CO<sub>2</sub> is also greater than styrene's.

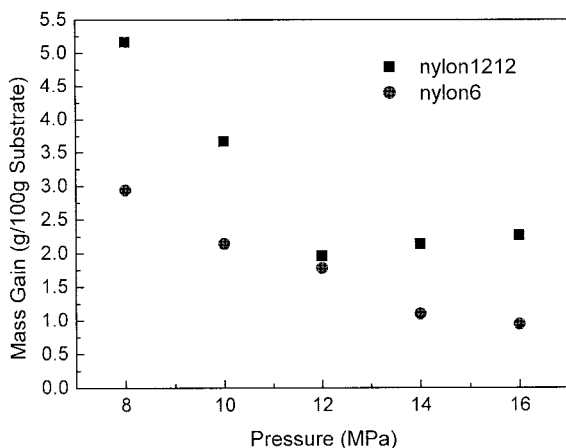
Based on what has been discussed above, it is concluded that rather than compatibility of additives with substrates, the relative solubility of additives in polymer substrate and in CO<sub>2</sub> is a key factor governing the overall efficiency of SC CO<sub>2</sub>-assisted impregnation.

Effect of swollen degree of polymer substrates by SC CO<sub>2</sub>

Figure 5 shows the incorporated amounts of acrylic acid in nylon1212 and nylon6 after impregnation at different pressures. It can be seen that in the experimental pressure range from 8 to 16 MPa, acrylic acid always has higher loading efficiency in nylon1212 than in nylon6. From the sketched solubility axis we can see that nylon6 has a very similar  $\delta$  with acrylic acid. Considering the effect of compatibility of additive with substrate polymer, it should be easier to incorporate acrylic acid into nylon6 than nylon1212. Yet this does not concord with truth as shown in Figure 5. Then how about the relative solubility? In these two systems,



**Figure 4** Impregnation of styrene and acrylic acid into nylon1010 (after polymerization).



**Figure 5** Acrylic impregnation into nylon1212 and nylon6 (after polymerization).

$$|\delta_{\text{acrylic acid}} - \delta_{\text{CO}_2}| = 6.21$$

$$|\delta_{\text{acrylic acid}} - \delta_{\text{nylon1212}}| = 1$$

$$|\delta_{\text{acrylic acid}} - \delta_{\text{nylon6}}| = 0.07$$

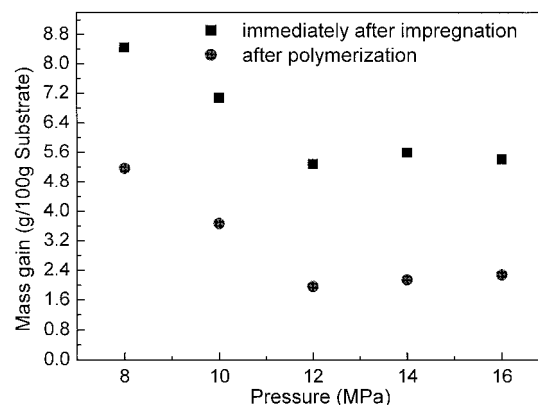
$$6.21 - 0.07 = 6.14 > 6.21 - 1 = 5.21$$

The above calculation shows that acrylic acid's relative solubility in nylon6 and in  $\text{CO}_2$  is a bit higher than that in nylon1212 and in  $\text{CO}_2$ . Given the conclusion we have drawn in the second part, it should have better impregnation efficiency in nylon6 than in nylon1212. So the influence of additive's relative solubility still cannot explain the experimental result.

Here we have to consider the interaction between  $\text{CO}_2$  and the substrate as shown in Figure 1: swelling and plasticizing effects existing between SC  $\text{CO}_2$  and polymer substrates. From the sketched solubility axis we can see that  $\delta$  of nylon6 ( $11.35 \text{ cal}^{1/2}\text{cm}^{3/2}$ ) is much bigger than that of nylon1212 ( $9.66 \text{ cal}^{1/2}\text{cm}^{3/2}$ ), so solvent interaction between nylon1212 and  $\text{CO}_2$  ( $\delta = 5.98 \text{ cal}^{1/2}\text{cm}^{3/2}$ ) is stronger than that between nylon6 and  $\text{CO}_2$ . As a result, the swollen degree of nylon1212 by SC  $\text{CO}_2$  should be better than that of nylon6. In fact, this has been demonstrated by experimental results given in Figures 6 and 7. The figures show the amounts of  $\text{CO}_2$  absorption (difference of substrate's mass gain immediately after impregnation and after polymerization, see above) in nylon1212 and nylon6, respectively. It can be clearly seen that  $\text{CO}_2$  has higher solubility in nylon1212 than in nylon6 at all pressures. Thus, it is concluded that effect of swelling of substrate also contributes to impregnation efficiency of additives.

#### Plasticization of substrates by SC $\text{CO}_2$

As shown in Figure 1, besides the solvent swelling effect, supercritical  $\text{CO}_2$  has another effect on the poly-

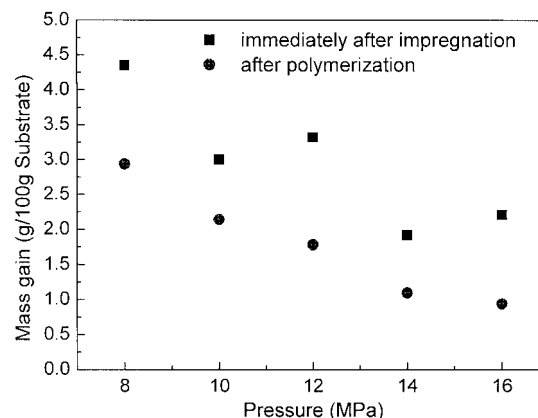


**Figure 6** Mass gain of nylon1212 after being incorporated with acrylic acid.

mer substrates: plasticization and induced crystallization.<sup>31-34</sup> In general, swelling makes polymers' volume expand, which contributes to higher absorption of additive in polymers. The plasticizing effect of SC  $\text{CO}_2$  increases chain mobility of the polymer, decreases  $T_g$ , and then induces crystallization in the amorphous regions.<sup>35,36</sup> The increased crystallinity of the substrate may counteract additive loading on the polymer. Figure 8 shows the incorporated amounts of acrylic acid in nylon66 and nylon6 after impregnation at different pressures. It can be seen that when the pressure is lower than 11.5 MPa, acrylic acid has a higher loading efficiency in nylon6 than in nylon66; however, when the pressure is higher than 12 MPa, impregnation into nylon66 has a better efficiency than in nylon6. Because

$$|\delta_{\text{acrylic acid}} - \delta_{\text{CO}_2}| = 6.21$$

$$|\delta_{\text{acrylic acid}} - \delta_{\text{nylon66}}| = 0.84$$



**Figure 7** Mass gain of nylon6 after being incorporated with acrylic acid.

$$|\delta_{\text{acrylic acid}} - \delta_{\text{nylon6}}| = 0.07$$

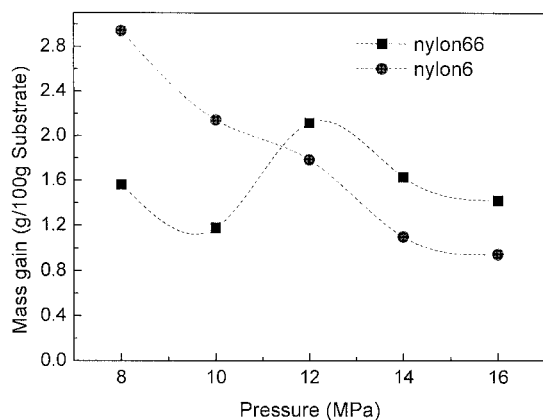
$$6.21 - 0.07 = 6.14 > 6.21 - 0.84 = 5.37,$$

acrylic acid has a higher relative solubility in nylon6 and CO<sub>2</sub> than in nylon66 and in CO<sub>2</sub>. In addition, nylon6's solubility parameter is adjacent to that of acrylic acid. So both compatibility and relative solubility comparisons indicate better impregnation efficiency in nylon6. From Figure 8 we know that it is true in the low-pressure range ( $T_c \sim 11.5$  MPa); yet it does not concord with truth in high-pressure region. Here is an explanation for it. Figures 7 and 9 show the amounts of absorbed CO<sub>2</sub> in nylon6 and nylon66, respectively. It can be found that when impregnation pressure increased to 12 MPa, CO<sub>2</sub> absorption in nylon6 increased dramatically while absorption in nylon66 decreased dramatically. Increase of CO<sub>2</sub> solubility in nylon6 led to better plasticization and remarkable crystallization of the amorphous regions, which counteracted acrylic acid's loading into the substrate. Similarly, a decrease in CO<sub>2</sub> absorption led to poor plasticization of nylon66 and thus caused considerable a decrease of CO<sub>2</sub>-induced crystallization; consequently, it made the incorporated amounts of additive in nylon66 substrate increase.

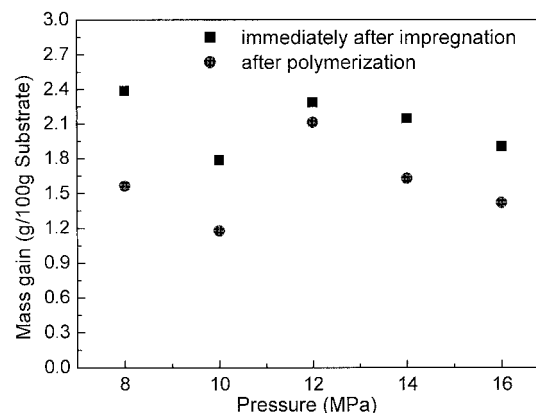
## CONCLUSIONS

SC CO<sub>2</sub>/styrene/different nylon ternary systems and SC CO<sub>2</sub>/acrylic acid/different nylon ternary systems were studied under different supercritical conditions. Interactions among all the components were discussed, and it was found that all these actions contribute to impregnation efficiency.

When the impregnation efficiency of different additives on the same substrate was studied, (1) the compatibility of additive with substrate, (2) the relative solubility of additive in substrate and SC CO<sub>2</sub> should



**Figure 8** Acrylic acid impregnation into nylon66 and nylon6 (after polymerization).



**Figure 9** Mass gain of nylon66 after being incorporated with acrylic acid.

be considered; when the impregnation efficiency of one additive in different substrates was studied, in addition to factors (1) and (2), the swelling and plasticizing effect of SC CO<sub>2</sub> on the substrate have to be considered, which may be the decisive effect on the impregnation efficiency of additive.

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