Complex Interactions among Additive/Supercritical CO₂/Polymer Ternary Systems and Factors Governing the Impregnation Efficiency

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Styrene and acrylic acid were impregnated into a series of polyamide products (nylon1212, nylon1010, nylon66, nylon6) using supercritical CO_2 as additive-carrier and substrate-swelling agent. The impregnation efficiency of additives into substrates is attributed to complicated interactions among the system: (1) loading of additives in substrates, (2) dissolving of additives in CO_2 phase (3) swelling and plasticizing of substrates by CO_2. Solubility parameter was introduced to discuss the impregnation efficiency. It was found that the relative solubility of additive in the polymer substrate and CO_2 is a major factor governing the incorporated amount; yet swelling of the substrate and CO_2-induced crystallization also contribute to the value. The study generalizes complex factors influencing the impregnation possibility of different systems.

INTRODUCTION

Recently interests in supercritical fluid-assisted impregnation and polymer modification have been growing rapidly. The unique properties of SC CO_2 make it an ideal media for additive impregnation into polymers. Given this, phase behaviors of impregnation systems, especially the partitioning of a solute between CO_2 and polymer have been studied by several researchers. Berens[1] and his colleagues reported kinetic and equilibrium data for the poly(vinyl chloride)/dimethyl phthalate/SC CO_2 system. Kinetic study carried out by Shieh[2] and Sahle-Demessie[3] suggests that the major effect of CO_2 is not to improve the solubility of the additive but to accelerate the additive absorption by plasticizing the polymer. Kazarian[4, 5] et al reported the partitioning of deuterated methanol, deuterated propanol, 2-naphthol, naphthalene, and acridine between CO_2 and poly(cyanopropylmethylsiloxane) or poly(dimethylsiloxane) (PDMS). Johnston[6] and coworkers quantified the distribution of toluene between CO_2 and silicone rubbers as well as the partitioning of benzoic acid, phenanthrene, naphthalene, pyrene between CO_2 and PDMS. More recently, Tomasko[7] et al used confocal microscopy analysis to study supercritical fluid impregnation of polypropylene.

Polymeric substrates used in this study are a series of polyamides nylon1212, 1010, 66, and 6, which are all widely applied as high performance engineering plastics or synthetic fibers. The study may benefit further application of SCF impregnation in material modification. We are, based on the study, aiming at finding a quantitative and relatively simple way to predict impregnation possibility of different systems.
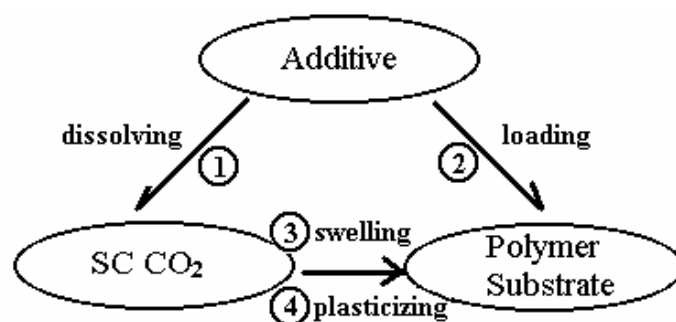
Figure 1. Interactions among the SC CO₂-assisted impregnation system.

MATERIALS AND METHODS

Nylon1212 was obtained from Lab of Engineering Plastics at Zhengzhou University. Nylon1010 (Xingda, China), nylon66 (EPR27N, Mitsubishi, Japan) and nylon6 (1020C, Mitsubishi, Japan) were all industrial resin. After being dried in vacuum at 105? for 48h, all resin pellets were processed to 0.9 ± 0.02mm-thick sheets. Physical properties of the substrates are given in Table 1.

Table 1. Physical properties of nylon substrates.

Substrate	Melting range (?)	T_g (?)	Density (g/cm^3)	Solubility parameter (cal$^{1/2}$/cm$^{3/2}$)
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

Reactions were run in a 21.4ml high-pressure stainless steel vessel. Similar apparatus and method described by McCarthy[8]. 0.3mol% (based on additive) initiator AIBN was dissolved in a certain amount of the additive (the concentration of additive was fixed at 30wt%). The solution was introduced to reactor, and samples were placed in. Then the system was vacuumed, filled with CO_2 to 5MPa, equilibrated in a 40 ± 0.1? water bath and repressurized to desired pressure. After 4 hours' treating, the reactor was depressurized. Samples were brought out and weighed. Later the additive-impregnated samples were transferred to another identical vessel for polymerization. According to our previous study[9, 10], both CO_2 and additive are absorbed by substrates during the impregnation period. And the absorbed CO_2 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_2.

RESULTS AND DISCUSSION

Suppes and McHugh[11] have published the phase behavior of SC CO_2/styrene system. DeSimone[12] et al have determined solubility of acrylic acid in SC CO_2. Based on their data, all experiments in this study were run under conditions at which additive and CO_2 are in a

single phase. Solubility parameters of CO_2 (5.98 cal$^{1/2}$cm$^{3/2}$), styrene (8.66 cal$^{1/2}$cm$^{3/2}$), acrylic acid (12.19 cal$^{1/2}$cm$^{3/2}$) and nylon substrates are shown in the following sketched axis.
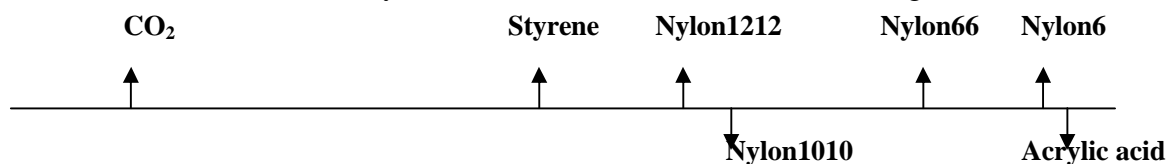
Solubility parameters of CO_2, additives, and different substrates.

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

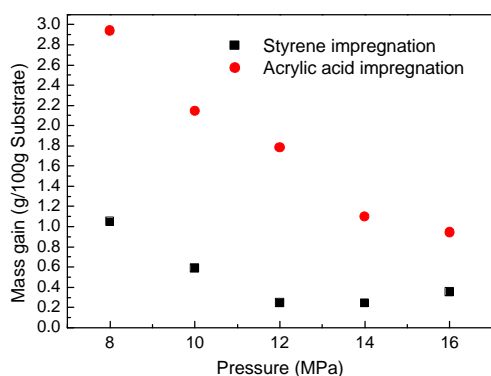**1. Compatibility of additive with substrate polymer.**

Figure 2. Impregnation of styrene and acrylic acid into nylon6.

Figure 3. Impregnation of styrene and acrylic acid into nylon1212.

As shown in Figure 2, in the examined pressure range from 8 to 16MPa, 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 d 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.
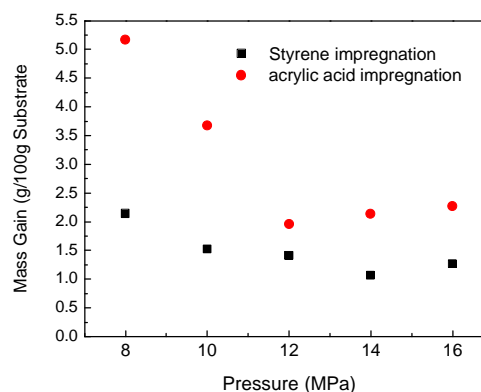
2. Relative solubility of additive in polymer substrate and in supercritical CO_2.

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, since $|d_{styrene} - d_{nylon1212}| = 1$ and $|d_{acrylic\ acid} - d_{nylon1212}| = 2.53$, 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. Here influence of the carrier SC CO_2 has to be considered.

Based on solubility parameters of the four different components: CO_2, styrene, acrylic acid and nylon1212, there is

$|d_{styrene} - d_{nylon1212}| = 1$ $|d_{styrene} - d_{CO_2}| = 2.68$

$|d_{acrylic\ acid} - d_{nylon1212}| = 2.53$ $|d_{acrylic\ acid} - d_{CO_2}| = 6.21$

$6.21 - 2.53 = 3.68 > 2.68 - 1 = 1.68$

Since $|d_{additive} - d_{nylon1212}|$ and $|d_{additive} - d_{CO_2}|$ stand for the solubility of additives in nylon1212 and in CO_2 respectively, their relative solubility in nylon1212 and in CO_2 can be represented by the difference between these two absolute values. Based on above calculation, it can be

found that the difference between $|d_{additive} - d_{CO_2}|$ and $|d_{additive} - d_{nylon1212}|$ in the acrylic acid-impregnation system is greater than in the styrene system, as shown following:

$$| |d_{acrylic\ acid} - d_{nylon1212}| - |d_{acrylic\ acid} - d_{CO2}| | > | |d_{styrene} - d_{nylon1212}| - |d_{styrene} - d_{CO2}| |$$

Acrylic acid's relative solubility in nylon1212 and in CO_2 is greater than styrene's, i.e. compared to styrene impregnation system, it is easier for acrylic acid to load in nylon1212 than to dissolve in SC CO_2. So it can be concluded that although solubility of additive acrylic acid or styrene in the carrier SC CO_2 is very important, in the following impregnation process, the partitioning of additive in nylon1212 and SC CO_2 is more important and this process is determined by relative solubility of the additive in nylon1212 and CO_2.
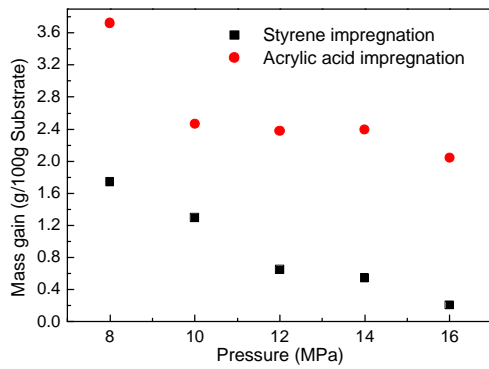

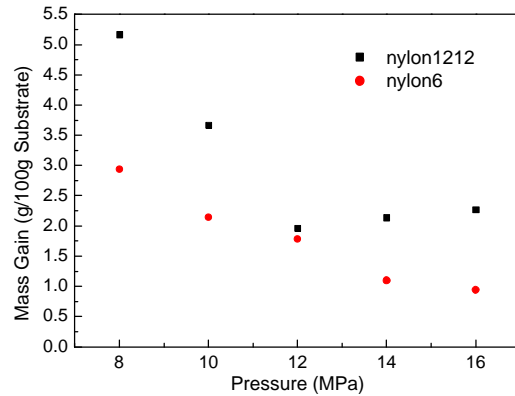**Figure 4. Impregnation of styrene and acrylic acid into nylon1010.**

Figure 5. Acrylic impregnation into nylon1212 and nylon6.

When nylon1010 was used as substrate, same results can be found as shown in Figure 4.

3. Effect of swollen degree of polymer substrates by SC CO_2.

Figure 5 shows the incorporated amounts of acrylic acid in nylon1212 and nylon6 after impregnation at different pressures. It can be seen that 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 d 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,

$|d_{acrylic\ acid} - d_{CO2}| = 6.21$ $|d_{acrylic\ acid} - d_{nylon1212}| = 1$

$|d_{acrylic\ acid} - d_{nylon6}| = 0.07$ $6.21 - 0.07 = 6.14 > 6.21 - 1 = 5.21$

Above calculation shows that acrylic acid's relative solubility in nylon6 and in CO_2 is a bit higher than that in nylon1212 and in 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 CO_2 and the substrate. As shown in Figure 1: swelling and plasticizing effects exist between SC CO_2 and polymer substrates. From the sketched solubility axis we can see that d of nylon6 (11.35 $cal^{1/2}cm^{3/2}$) is much bigger than that of nylon1212 (9.66 $cal^{1/2}cm^{3/2}$), so solvation between nylon1212 and CO_2 (d = 5.98 $cal^{1/2}cm^{3/2}$) is stronger than that between nylon6 and CO_2. As a result, the swollen degree of nylon1212 by SC CO_2 should be better than that of nylon6. In fact, this has been

demonstrated by experimental results given in Figure 6 and Figure 7. The figures show the amounts of 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 seen clearly that CO_2 has higher solubility in nylon1212 than in nylon6 at all pressures. Thus it is concluded that effect of substrate swelling also contributes to impregnation efficiency of additives.
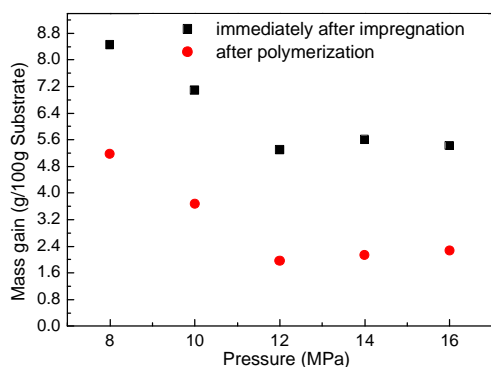

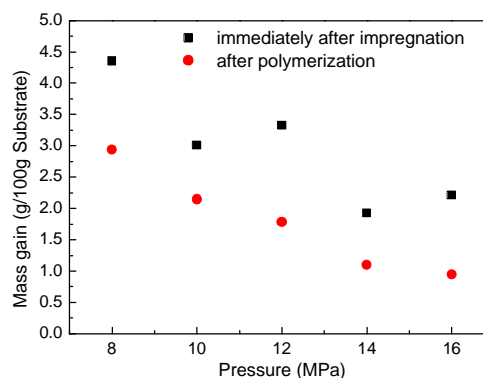**Figure 6. Mass gain of nylon1212 after being incorporated with acrylic acid.**

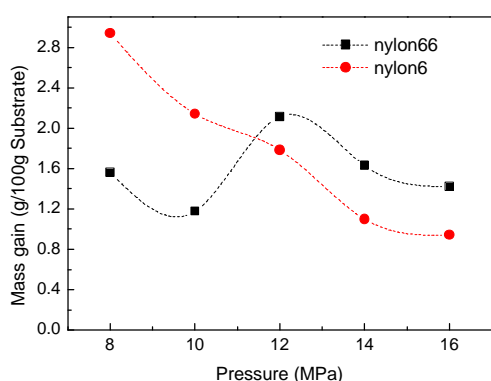**Figure 7. Mass gain of nylon6 after being incorporated with acrylic acid.**

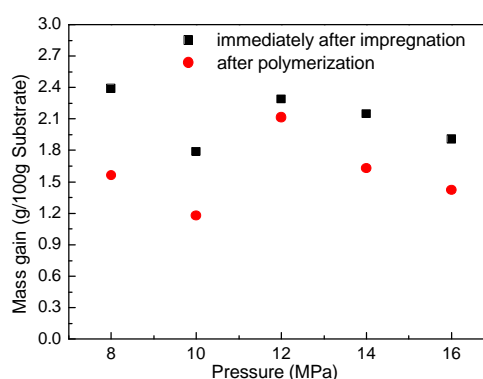**Figure 8. Acrylic acid impregnation into nylon66 and nylon6.**

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

4. Plasticization of substrates by SC CO_2.

As shown in Figure 1, besides the solvent swelling effect, supercritical CO_2 has another effect on the polymer substrates: plasticization and induced crystallization[13-15]. In general, swelling makes polymers' volume expand, which contributes to higher absorption of additive. Plasticizing effect of SC CO_2 increases chain mobility, decreases T_g and then induces crystallization in the amorphous regions[16, 17]. The increased crystallinity of the substrate may counteract additive loading. Figure 8 shows the incorporated amounts of acrylic acid in nylon66 and nylon6. It can be seen that when the pressure is lower than 11.5MPa, acrylic acid has a higher loading efficiency in nylon6; however, when the pressure is higher than 12MPa, it is reverse. Since

$|d_{acrylic\ acid} - d_{CO_2}| = 6.21$ $\qquad$ $|d_{acrylic\ acid} - d_{nylon66}| = 0.84$

$|d_{acrylic\ acid} - d_{nylon6}| = 0.07$ $\qquad$ $6.21 - 0.07 = 6.14 > 6.21 - 0.84 = 5.37,$

acrylic acid has a higher relative solubility in nylon6 and CO_2 than in nylon66 and in CO_2. In

addition, nylon6's solubility parameter is adjacent to acrylic acid's. So both compatibility and relative solubility comparisons indicate better impregnation efficiency in nylon6. From Figure 8, it is true in the low-pressure range ($T_c \sim 11.5MPa$); yet it is not in high-pressure region. Here is an explanation for it. Figure 7 and Figure 9 show the amounts of absorbed CO_2 in nylon6 and nylon66 respectively. It can be found that when impregnation pressure increased to 12MPa, CO_2 absorption in nylon6 increased dramatically while absorption in nylon66 decreased dramatically. Increase of CO_2 solubility in nylon6 led to better plasticization and remarkable crystallization of the amorphous regions, which counteracted acrylic acid's loading into the substrate. Similarly, decrease in CO_2 absorption led to poor plasticization of nylon66 and it made the incorporated amounts of additive in nylon66 substrate increase.

CONCLUSION

CO_2/styrene/nylon ternary systems and CO_2/acrylic acid/nylon systems were studied under different conditions. Interactions among all the components were discussed and it was found that all these actions contribute to impregnation efficiency: when 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_2 should be considered; when impregnation efficiency of same additive in different substrates was studied, in addition to factor (1) and (2), the swelling and plasticizing effect of SC CO_2 on the substrate have to be considered, which may be the decisive factor governing the impregnation efficiency.

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