

Supercritical CO₂ Assisted Processing of Polystyrene/Nylon 1212 Blends and CO₂-Induced Epitaxy on Nylon 1212

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ABSTRACT: Polystyrene/nylon 1212 blends were prepared with supercritical CO₂ as the substrate swelling agent and monomer/initiator carrier. Original nylon 1212 and blends were characterized with differential scanning calorimetry (DSC), polarizing microscopy, wide-angle X-ray diffraction, and scanning electron microscopy (SEM). A novel phenomenon, CO₂-induced epitaxy, was discovered, and its mechanism was deduced. Thermal analysis performed with

DSC indicated that the polystyrene/nylon 1212 blends had thermal stability superior to that of virgin nylon 1212. The DSC and SEM measurements indicated that incorporated polystyrene could notably improve the mechanical performance of nylon 1212. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2023–2029, 2004

Key words: nylon; polystyrene; blends

INTRODUCTION

Recently, interest in supercritical fluid (SCF) assisted polymer modification and blend synthesis has been growing rapidly. The high solubility, diffusivity, and plasticizing behavior of CO₂ in polymers make it a unique plasticizer for accelerating the impregnation of small molecules into polymer substrates. CO₂ is non-flammable, nontoxic, and relatively inexpensive; its moderate critical conditions ($T_c = 304.2$ K and $P_c = 7.37$ MPa) make it a convenient fluid for experimentation. Although supercritical (SC) CO₂ is a weak solvent for most polymers, it is a desirable swelling agent for polymers and can dissolve many small molecules.^{1–4} One of the most intriguing features of an SCF is that its density and solvent strength can be adjusted through changes in the pressure and temperature of the system. As a result, the degree of swelling in polymers,^{2,5,6} as well as the partitioning of small molecules between the fluid phase and the substrate,^{7,8} can be manipulated simply. Moreover, maintaining conditions above the critical temperature avoids the creation of vapor–liquid coexistence upon the release of pressure. This allows impregnation to proceed without the substrate being distorted by capillary

forces. In addition, the solvent can be separated completely and easily from the substrate because CO₂ is gaseous under ambient conditions.

On the basis of these factors, a new route for producing composite and foam materials has been developed by McCarthy^{9–16} and coworkers. This method involves the swelling of the polymer substrate by an SC CO₂ solution of the monomer and thermal initiator, the half-life of which is extremely long at the impregnation temperature. At a higher temperature, the initiator decomposes much more quickly; the subsequent polymerization of the monomer is carried out, and a composite system of the two polymers is yielded. In comparison with traditional blending methods, this approach is more facile and versatile, and one of its most promising features is that blending can be performed at temperatures well below the melting temperature (T_m). Furthermore, the blend composition is not limited by the solubility of the monomer in the matrix polymer.

The partitioning of a solute between CO₂ and a polymer substrate under SC conditions has been studied by several researchers. Berens et al.² reported kinetic and equilibrium data for a poly(vinyl chloride)/dimethyl phthalate/SC CO₂ system, as well as a number of other examples of CO₂-assisted additive absorption. Kinetic studies carried out by Shieh et al.¹⁷ and Sahle-Demessie et al.¹⁸ suggest that the major effect of CO₂ is not to improve the solubility of the additive but to accelerate the additive absorption by plasticizing the polymer. Kazarian and coworkers^{19,20} reported the partitioning of deuterated methanol, deu-

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terated propanol, 2-naphthol, naphthalene, and acridine between CO₂ and poly(cyanopropylmethylsiloxane) or poly(dimethylsiloxane) (PDMS). Johnston and coworkers^{21,22} quantified the distribution of toluene between CO₂ and silicone rubbers as well as the partitioning of benzoic acid, phenanthrene, naphthalene, 2-naphthol, and pyrene between CO₂ and PDMS. More recently, Tomasko⁸ et al. used confocal microscopy analysis to study the SCF impregnation of polypropylene. Their study further demonstrated the principle of the impregnation process and investigated different factors contributing to the final distribution of the modifiers.

Nylon 1212 is a new high-performance engineering plastic with relatively low water absorbability in comparison with other polyamide products. In this study, polystyrene (PS)/nylon 1212 blends were prepared, and the phase behavior of the SCF swelling system was examined.

EXPERIMENTAL

Materials

Nylon 1212 was obtained from the Laboratory of Engineering Plastics at Zhengzhou University in the form of transparent, light-yellow pellets. After being dried *in vacuo* at 116°C for 48 h, the pellets were processed into 0.9 ± 0.02-mm-thick sheets on a press vulcanizer (model QLB-D, Beijing, China). A glass transition of 54°C and a melting range of 182–184°C were determined with differential scanning calorimetry (DSC) at a heating rate of 10°C/min. The density was measured with a volume–mass method at 25 ± 1°C and was found to be 1.013 g/cm³.

CO₂ with a purity of 99.9% was obtained from Zhengzhou Sanfa Gas Co. (China). Styrene was purchased from Tianjin Dongda Chemical Co. (China) and was distilled under reduced pressure. Azobisisobutyronitrile (AIBN), supplied by Shanghai Sanpu Chemical Co., Ltd. (China), was recrystallized twice from methanol.

Procedures

The reactions were run in a 21.4-mL high-pressure stainless steel reactor. A high-pressure syringe pump (DB-80, Beijing Satellite Manufacturing Factory, China) was used to charge CO₂ into the reaction vessel and was attached to the reactor via a coupling and high-pressure tubing. A pressure gauge, consisting of a transducer (model 93, IC Sensors Co., China) and an indicator (model XS/A-1, Beijing Tianchen Automatic Instrument Factory, China), with an accuracy of ±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 (C10, Thermo Haake, Germany) and a bath vessel (P5, Thermo Haake). The fluctuation of the temperature in the bath was less than ±0.1°C.

SC CO₂/nylon 1212 binary system study

Nylon 1212 sheets were sheared into 1.2 cm × 3.0 cm samples with a thickness of 0.9 ± 0.02 mm. Two samples were placed in the high-pressure reactor and were separated with the assistance of glass wool inside. After being purged with CO₂ twice and equilibrated in the constant-temperature bath, the reactor was repressurized to the desired pressure. After 4 h of treatment, the reactor was depressurized, giving off CO₂, and the samples were brought to an electronic balance immediately. Then, the treated samples were kept in a clean and dry atmosphere for 72 h at 20°C. The mass change was recorded regularly during the period.

Monomer/SC CO₂/nylon 1212 ternary system study and blend synthesis

The initiator AIBN (0.3 mol % based on styrene) was dissolved in a certain amount of styrene, and the solution was added to the bottom of the reactor. Then, some glass wool was added, and on it nylon 1212 samples were placed. Before CO₂ was charged into the reactor, the samples did not touch each other. After being filled with CO₂ to 5 MPa, the reactor was equilibrated in a 40 ± 0.1°C water bath and was repressurized to the desired pressure. After treatment, the reactor was depressurized. The samples were taken out, wiped with clean filter paper, and weighed. The variations of this procedure involved changing the impregnation time from 4 to 24 h, the styrene concentration from 15 to 55 wt %, and the pressure from 8 to 20 MPa. After 20 min, the styrene-impregnated samples were transferred to another identical reaction vessel. The vessel was then vacuumed and heated at 80°C under the protection of N₂ for 4 h.

Characterization

DSC measurements were conducted with a Netzsch 204 differential scanning calorimeter (Germany) under an atmosphere of N₂ at a heating rate of 10°C/min from 30 to 250°C. Thin samples were observed through a micropolariscope (DM LP, Leica, Germany), and photographs were taken with a Leica MPS30 camera. Sections of nylon 1212 and PS/nylon 1212 blends were observed with a JEOL JSM-5610LV scanning electron microscope (USA). Each sample surface was coated with graphite, and the accelerating voltage was between 5 and 15 kV. Wide-angle X-ray diffraction (WAXD) measurements were carried out on an X-ray diffraction unit (D/MAX-3B, Rigaku Co., Japan) with

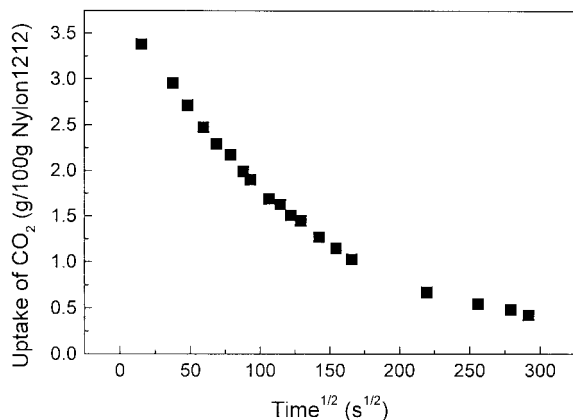


Figure 1 Uptake of CO₂ in nylon 1212 as a function of the square root of the desorption time after treatment in SC CO₂ for 4 h at 40°C and 12 MPa.

a nickel-filtered Cu K α beam and a step length of 0.02°.

RESULTS AND DISCUSSION

Desorption kinetics

The sorption and desorption kinetics of the CO₂/nylon 1212 system were measured with a method similar to that described by Berens and coworkers.^{2,3} With these measurements, the average mass gain was calculated, and the results were plotted versus the square root of the desorption time. In Figure 1, we can see that in the initial stage of the desorption period, the plots appear to be linear versus the square root of time, and this conforms to Fickian diffusion kinetics. However, when the desorption time is longer than 7 h, the Fickian theory does not fit the plots perfectly. We plotted the same data versus the natural logarithm of the desorption time, as shown in Figure 2. The mass

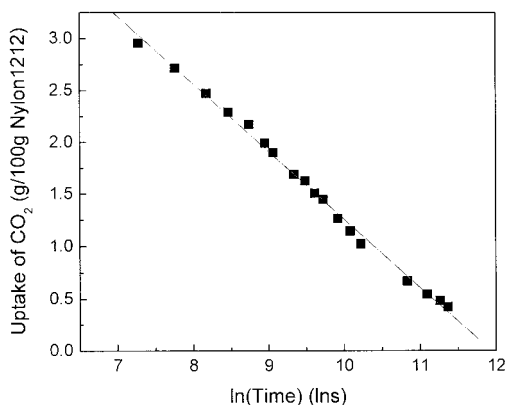


Figure 2 Uptake of CO₂ in nylon 1212 as a function of the natural logarithm of the desorption time after treatment in SC CO₂ for 4 h at 40°C and 12 MPa.

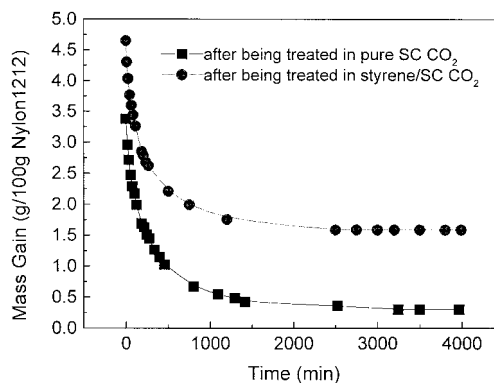


Figure 3 Mass gain of nylon 1212 after treatment in SC CO₂ and 30 wt % styrene/SC CO₂ for 4 h at 40°C and 12 MPa.

change shows a linear dependence on the logarithm of time in the entire desorption period of approximately 24 h. This linear dependence agrees with Elovich’s equation of the desorption rate:

$$R_d = -d\theta/dt = ke^{a\theta} \tag{1}$$

where R_d is the rate of desorption, θ is the percentage of coverage, and k and α are constants varying under different conditions. Through a series of integrations and derivations, the equation can be transformed as follows:

$$\theta = K + b\ln(t + t_0) \tag{2}$$

where K , b , and t_0 are constants. As the absorption ratio (Q) is in direct proportion to θ , eq. (2) can be rewritten as follows:

$$Q = K' + b'\ln(t + t_0) \tag{3}$$

In our experiments, t_0 tended to zero infinitely, and so the uptake of CO₂ (Q) shows a linear dependence on $\ln t$.

In addition to the uptake of CO₂ by the substrate, the uptake of styrene by nylon 1212 under the same conditions was determined. The results are given in Figure 3. In the presence of styrene, the desorption kinetics of CO₂ are similar to those without styrene’s influence. Moreover, when samples were weighed immediately after being treated, the difference in the mass gain between them was 1.28 g/100 g of nylon 1212. After 4000 min, the difference was 1.29 g/100 g of nylon 1212 (i.e., almost unchanged). This demonstrates that with the release of CO₂, the mass loss of incorporated styrene is negligible, and all the styrene remains in the substrate.

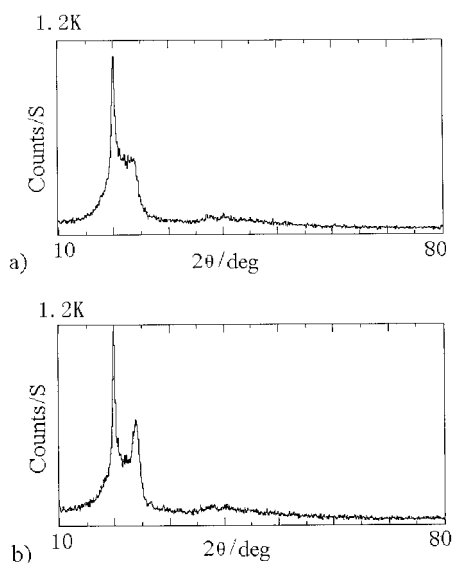


Figure 4 Results of WAXD measurements of (a) virgin nylon 1212 and (b) SC CO₂ treated nylon 1212.

Effect of CO₂ on the nylon 1212 aggregation structure

It is well known that the crystallization of some amorphous and semicrystalline polymers can be induced by solvents as well as heat and strain. The interaction between the polymer and the solvent reduces the effective glass-transition temperature (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.^{23,24} Chiou et al.,²⁵ Johnston and coworkers,^{26,27} and Mizoguchi et al.²⁸ all discovered that SC CO₂ can induce crystallization in polymers. In our study, the WAXD method was used to determine possible changes in the nylon 1212 aggregation structure after CO₂ absorption. The results are shown in Figure 4: with CO₂ sorption in the nylon 1212 substrate, there appears an apparent crystalline peak at 23.89°, besides the former one at 20.01°. This demonstrates that the aggregation structure and the partitioning between the crystalline and amorphous regions of nylon 1212 have changed, and it also indicates that absorbed CO₂ has a plasticizing action on the polymer.

For further evidence, we observed untreated and CO₂-treated nylon 1212 samples through a polarizing microscope. The photographs are given in Figure 5. There were some arborescent and bacillary structures on the surfaces of CO₂-treated samples. To further investigate this phenomenon, we carried out measurements with scanning electron microscopy (SEM), and similar structures on the nylon 1212 sample surface were found, as shown in Figure 6. When the enlargement factor was changed to 500× to achieve a wider

field of vision, we found that the distribution of these structures on the polymer surface was highly uniform. On the basis of these results, we can conclude that the epitaxy or crystalline overgrowth described by Wittmann and coworkers^{29–31} took place on the sample surface.

Royer³² reported that the occurrence of epitaxy is based on the structural resemblance between the substrate and the overgrown matter; that is, it depends on certain geometric matching between the two:

$$\Delta = 100\% \times (d - d_0)/d_0 \quad (4)$$

where d and d_0 are the partitioning parameters of the overgrown matter and the substrate, respectively, and Δ is the ratio of mismatch. When nylon 1212 was treated in CO₂ above T_c and P_c , a certain number of macromolecules were dissolved in or were highly swollen by the SCF.³³ These dissociated molecules

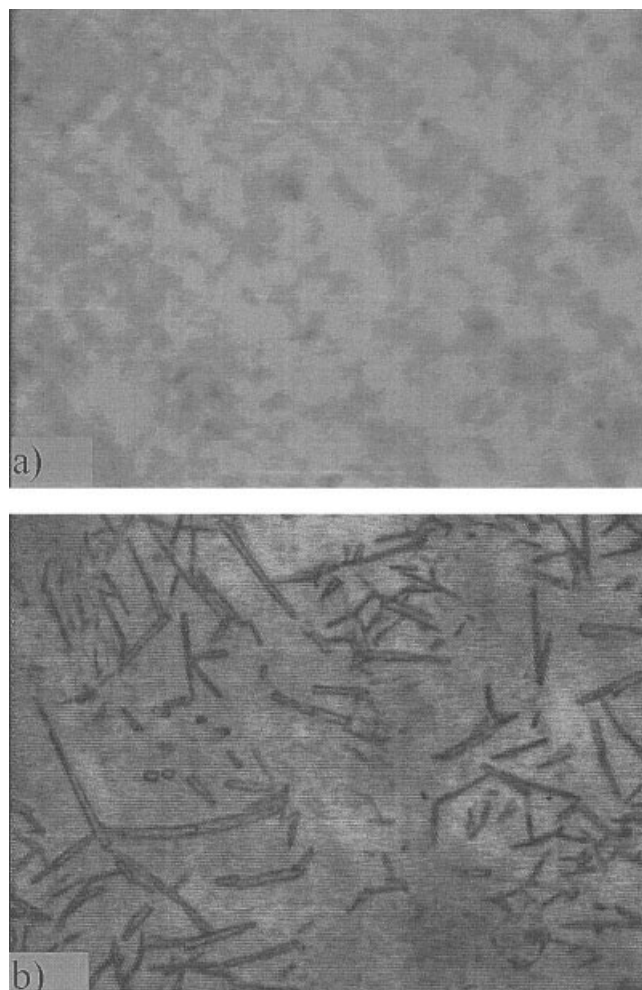


Figure 5 Micropolariscopy photographs (100 × 0.9 × 10) of (a) virgin nylon 1212 and (b) SC CO₂ treated nylon 1212.

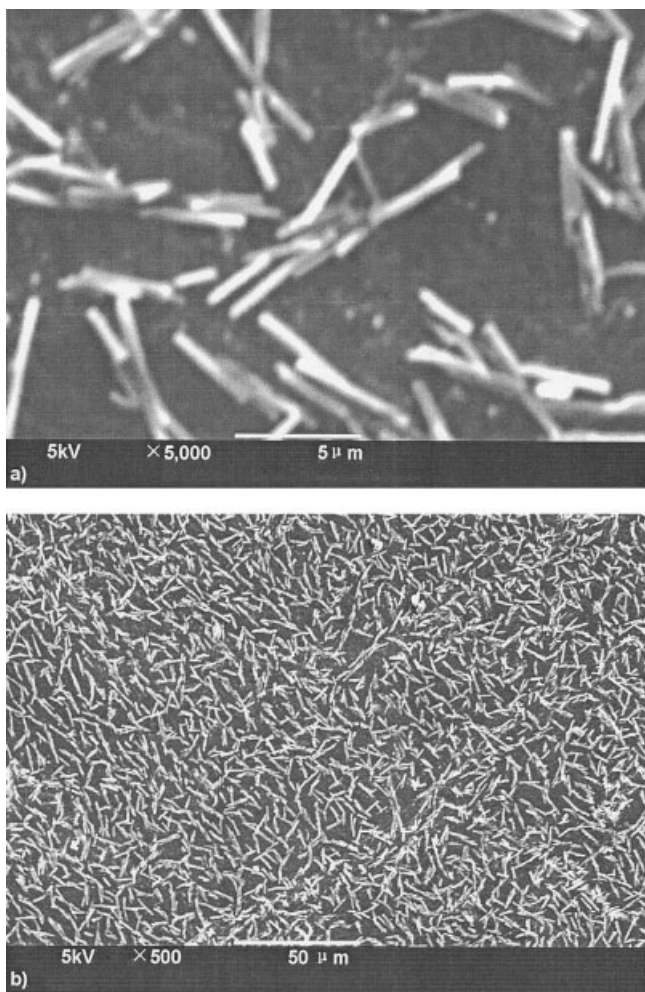


Figure 6 SEM photographs of SC CO₂ treated nylon 1212.

acted as overgrown matter in the crystallization process. In addition, on the basis of the Bragg equation, it is known from the WAXD data that the *d*-spacing values of the surface crystalline structure were

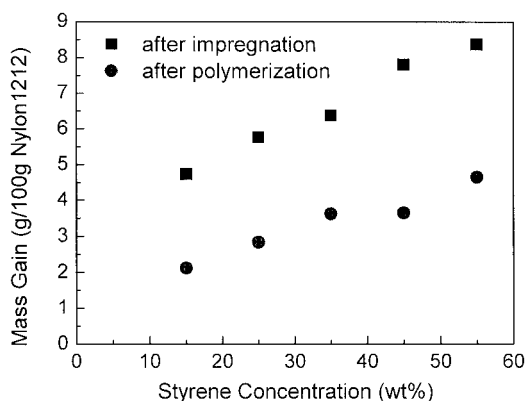


Figure 7 Mass gain of nylon 1212 as a function of the styrene concentration (impregnation for 24 h at 40°C and 14 MPa and polymerization at 80°C for 4 h).

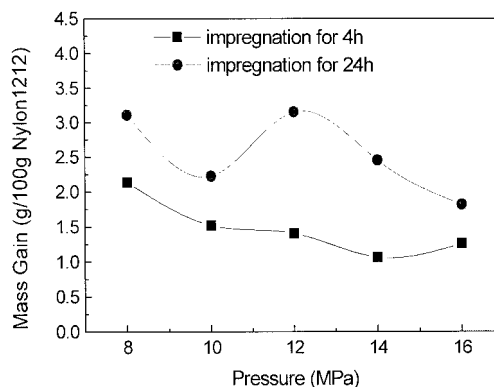


Figure 8 Mass gain of nylon 1212 as a function of pressure after impregnation in 30 wt % styrene/SC CO₂ for different times at 40°C and polymerization for 4 h at 80°C.

changed by the SC CO₂ treatment. Therefore, it is reasonable that this CO₂-induced change caused a certain effect on the substrate's geometric dimension and the partitioning parameters between dissociated nylon 1212 and substrate nylon 1212. Then, Δ of the system changed, followed by epitaxy and crystal formation on the polymer surface.

Effects of the reaction conditions on the blend synthesis

Suppes and McHugh³⁴ reported the phase behavior of an SC CO₂/styrene system. On the basis of their data,

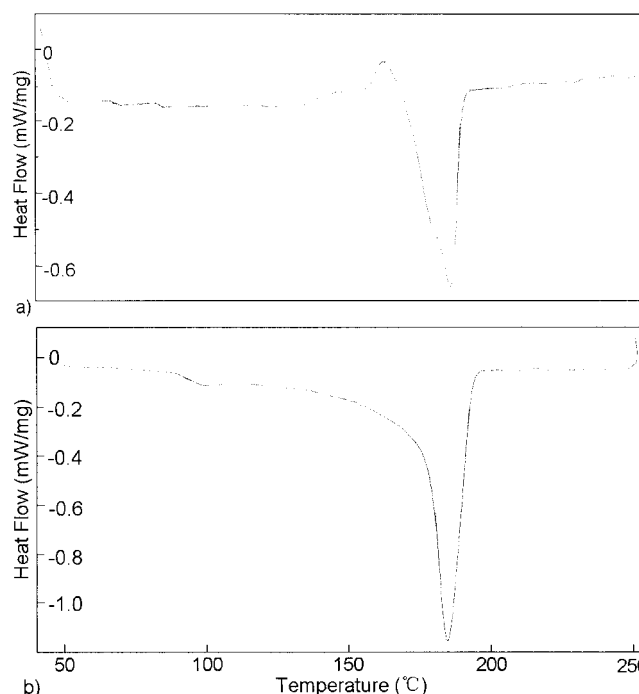


Figure 9 DSC results for (a) virgin nylon 1212 and (b) a PS/nylon 1212 (2/100) blend. The heating rate was 10°C/min, and the temperature scanning range was 30–250°C.

all experiments in this study were run under conditions at which the monomer and CO₂ were in a single phase.

Effect of the monomer concentration

To study the effect of the monomer concentration on the impregnation of the monomer and blend composition, we fixed the impregnation time, temperature, and pressure at 24 h, 40°C, and 14 MPa, respectively. The initiator concentration was maintained at 0.3 mol % (based on the monomer). Figure 7 shows that both before and after polymerization, the mass gain in the nylon 1212 substrate increased as the styrene concentration increased in the experimental range. Although an approximately linear increasing trend appears in the mass uptake with the monomer concentration, we do not think it is a general regularity. This is because in the styrene/CO₂/nylon 1212 system, both the absorption kinetics and the solvent quality of the fluid phase varied with the styrene concentration. The difference contributed to the equilibrium partitioning among CO₂, styrene, and the substrate.

Effects of the pressure and time

The effects of pressure on the mass gain were not identical when the impregnation times were different. Figure 8 shows that, except for the highly compressible region of CO₂ at 40°C (<10 MPa), the plots formed an olive-shaped region in the pressure range of 10–16 MPa. This means that, under high or low pressures, the time effect on the PS uptake was considerably less than under medium pressures. The periods for achieving absorption equilibrium were different under different pressures and at different temperatures.¹¹ It is thought that in this system, equilibrium uptake was reached when the impregnation time was 24 h. Therefore, the maximum incorporated PS content can be explained: at low pressures, CO₂ was too poor a solvent to swell the nylon 1212 substrate sufficiently to permit the rapid infusion of styrene. At high pressures, CO₂ readily swelled nylon 1212; it was also a much better solvent for styrene, and the partitioning of styrene in the fluid phase was enhanced. At intermediate pressures, however, this competition achieved a balance, and the maximum uptake was observed. However, as equilibrium uptake was not reached in 4 h of impregnation, the diffusion rate of CO₂ was the dominant factor governing PS incorporation. As the diffusion coefficient decreased with an increase in pressure, the PS uptake in the substrate also decreased accordingly.

Blend characterization

To determine the properties and internal structure of PS/nylon 1212 blends, we performed a series of char-

TABLE I
Heat of Fusion of PS/Nylon 1212 Blends Calculated with DSC Results

PS/nylon 1212	Impregnation conditions	Heat of fusion (J/g)
2.228/100	40°C, 10 MPa, 24 h	96.92
2.454/100	40°C, 14 MPa, 24 h	71.91
3.154/100	40°C, 12 MPa, 24 h	34.02

acterization measurements. DSC was used to measure the thermal properties of the blends. As mentioned in the Experimental section, virgin nylon 1212 was dried *in vacuo* at 116°C for 48 h. 116°C is the temperature of the maximum crystalline growth velocity (T_{\max}), which was calculated with the following empirical formula:

$$T_{\max}(\text{K}) = 0.63T_m(\text{K}) + 0.37T_g(\text{K}) - 18.5 \quad (5)$$

Therefore, the nylon 1212 samples achieved maximum crystallinity before the DSC measurements. Figure 9 shows that the thermal stability of virgin nylon 1212 was improved remarkably by the incorporation of PS, as shown by the disappearance of the original exothermic peak. This means that the SC CO₂ assisted impregnation of PS into nylon 1212 could notably improve its service performance.

In another series of DSC measurements, the fusion peak areas of blends containing different PS contents were calculated. The results are given in Table I, which shows that the heat of fusion decreased considerably as the PS content increased. For the polymers, the heat of fusion was proportional to the crystallinity; it indicated that the overall crystallinity of the blend decreased as the PS content increased.

SEM photographs of nylon 1212 and a PS/nylon 1212 blend are shown in Figure 10. For the blend, the surface was no longer even and homogeneous like that of pure nylon 1212. Many PS microspheres were formed and impregnated in the near surface region, and their diameters were 3–5 μm. As for the cross section of the blend, there appeared some tubelike structure that could contribute to the increase in the tenacity and intensity of the material.

CONCLUSIONS

This study shows that SC CO₂ can penetrate a nylon 1212 substrate and act as a carrier for the monomer in an impregnation process. PS/nylon 1212 blends can be prepared by the infusion of styrene into and radical polymerization within solid nylon 1212 with SC CO₂ as a carrier. Moreover, characterization has shown that the prepared PS/nylon 1212 blend has much better thermal stability than the original nylon 1212. A

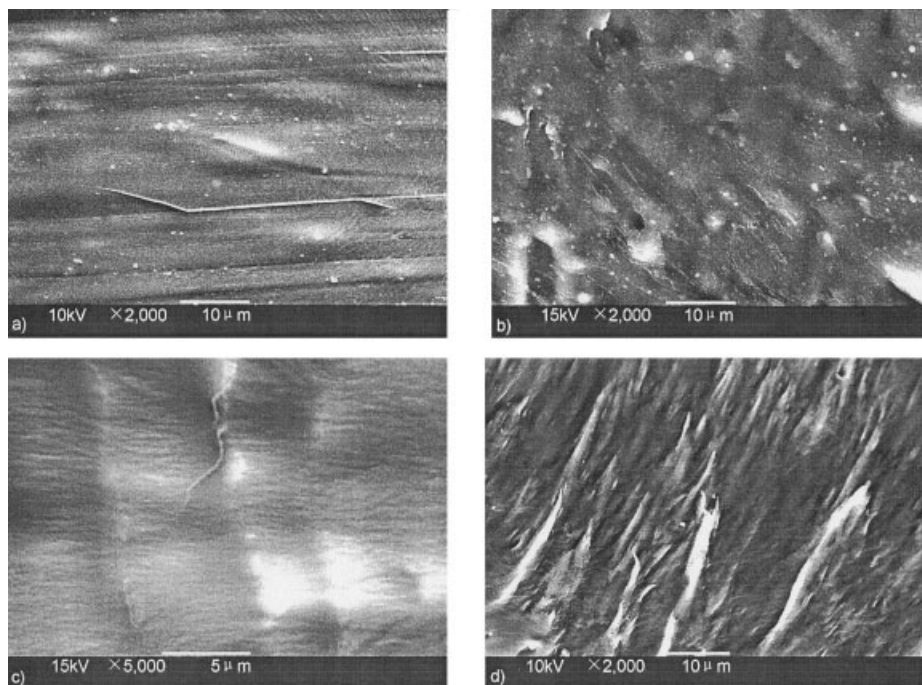


Figure 10 SEM photographs of virgin nylon 1212 and a PS/nylon 1212 blend: (a) the surface of virgin nylon 1212, (b) the surface of the PS/nylon 1212 blend, (c) the cross section of virgin nylon 1212, and (d) the cross section of the PS/nylon 1212 (3/100) blend (impregnated for 24 h at 40°C and 14 MPa and polymerized for 4 h at 80°C).

novel phenomenon of CO₂-induced epitaxy has been discovered.

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