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Supercritical CO_2-assisted synthesis of poly(acrylic acid)/nylon6 and polystyrene/nylon6 blends

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Abstract

Poly(acrylic acid)/nylon6 and polystyrene/nylon6 blends were prepared using supercritical CO_2 as substrate-swelling agent and monomer/initiator carrier. Both supercritical CO_2/nylon6 binary system and SC CO_2/monomer/nylon6 ternary system were studied. Virgin nylon6 and synthesized blends were characterized through differential scanning calorimetry, infrared spectroscopy, and polarizing microscopy. Supercritical CO_2-induced crystallization was found in modified nylon6.

Keywords: Supercritical CO_2; Nylon6; Poly(acrylic acid)

1. Introduction

Recently, people have more interest in supercritical fluid (SCF)-assisted polymer modification and blend synthesis. The high solubility, diffusivity, and plasticizing behavior of CO_2 in polymers make it a unique plasticizer to accelerate the impregnation of small molecules into polymer substrates. Although, SC CO_2 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 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 [2,5,6] as well as the partitioning of small molecules between the fluid phase and the substrate [7,8] 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 [9–16] and coworkers. The method involves the swelling of the polymer substrate by a SC CO_2 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 methods, 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.

Nylon6 is a kind of semi-crystalline thermoplastic and its decomposition temperature is higher than 300 °C, so it is convenient for fabrication. Besides it has high pliability, excellent self-lubricating ability, and fine weather resisting property. So, it is widely used as high performance synthetic fiber and engineering plastic. In this study, poly(acrylic acid)/nylon6 and polystyrene/nylon6 blends were prepared at temperatures well below T_m. The synthesized blends were found to have higher crystallinity, thermal stability and better performance.

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2. Experimental section

2.1. Materials

Nylon6 (1020C, Mitsubishi, Japan) in the form of transparent pellets were dried in vacuum at 140 °C for 48 h and then processed to 0.9 ± 0.02 mm-thick sheets on the press vulcanizer (Model QLB-D, made in China). A glass transition of 45 °C and melting range of 219–225 °C were determined by differential scanning calorimetry (DSC) with a heating rate of 10 °C/min. The density was measured with volume-mass method at 25 ± 1 °C and found to be 1.140 g/cm^3.

CO_2 with purity of 99.9% was obtained from Zhengzhou Sanfa Gas Co. Acrylic acid was purchased from Tianjin Jinyu Chemical Plant and used as received. Styrene was purchased from Tianjin Dongda Chemical Co. and distilled under reduced pressure. Azobis (isobutyronitrile) (AIBN) supplied by Shanghai Sanpu Chemical Co. Ltd. was recrystallized twice from methanol.

2.2. 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_2 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 ±0.01 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 ±0.1 °C. All sample sheets were weighed on a Shanghai 328A electrobalance with a sensitivity of 0.1 mg.

2.2.1. SC CO_2/nylon6 binary system study

Nylon6 sheets were sheared into 1.2 × 3.0 cm samples with the thickness of 0.9 ± 0.02 mm. After being purged with CO_2 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 25 °C, clean and dry atmosphere for 72 h. Mass change was recorded regularly during the period.

2.2.2. Monomer/SC CO_2/nylon6 ternary system study and synthesis of blends

In a certain amount of monomer, 0.3 mol% (based on monomer) initiator AIBN was dissolved, and the solution was introduced to the bottom of the reactor. Then some glass wool was put in, upon which nylon6 samples were placed. So before charging CO_2 into the reactor, samples and monomer solution did not touch each other. Having been purged and filled with CO_2 to 5 MPa, the reactor was equilibrated in a 40 ± 0.1 °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 pressure from 8 to 20 MPa. Twenty minutes after impregnation, the impregnated samples were transferred to another identical reaction vessel. The vessel was vacuumed and heated at 80 °C (styrene) or 62 °C (acrylic acid) under the protection of N_2 in the polymerization period of 4 h.

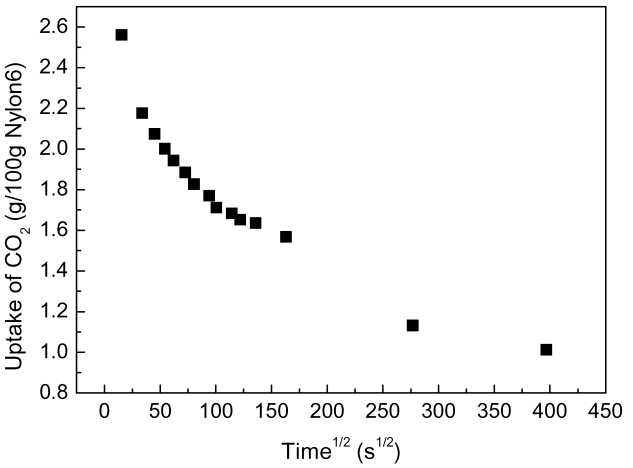


Fig. 1. Uptake of CO_2 in nylon6 as a function of the square root of desorption time after being treated in SC CO_2 for 4 h at 40 °C and 12 MPa.

2.3. Characterization

DSC measurements were conducted on a Netzsch 204 DSC under N_2 atmosphere with a heating rate of 10 °C/min

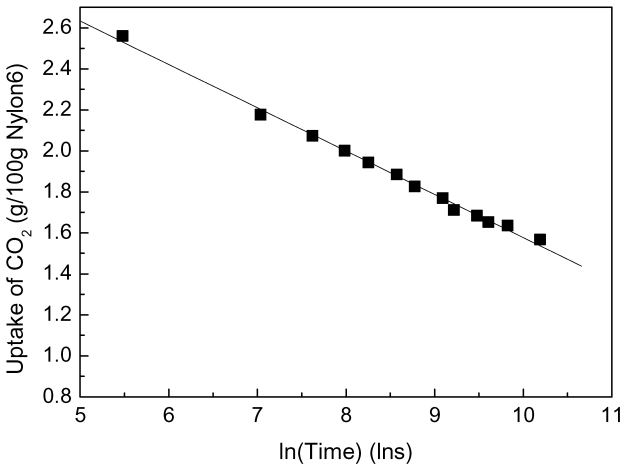


Fig. 2. Uptake of CO_2 in nylon6 as a function of the natural logarithm of desorption time after being treated in SC CO_2 for 4 h at 40 °C and 12 MPa.

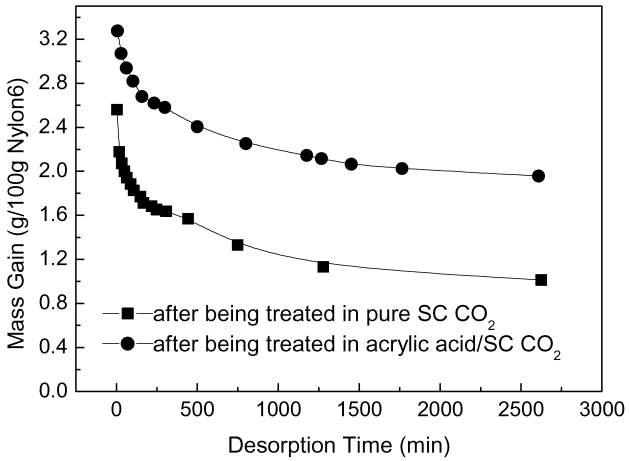


Fig. 3. Mass gain of nylon6 as a function of desorption time after being treated in SC CO_2 and 30 wt% acrylic acid/SC CO_2 for 4 h at 40 °C and 12 MPa.

in the temperature range of 30–350 °C. Infrared spectroscopy (IR) spectroscopy experiments were performed using a Nicolet 460 FTIR under standard operating conditions. Samples were observed through a micropolariscope (Leica, DM LP), and photos were taken with a Leica MPS30 camera. Wide-angle X-ray diffraction measurements were carried out on an X-ray diffraction unit (RIGAKU, D/MAX-3B) with a Nifiltered Cu K_α beam and a step length of 0.02 deg.

3. Results and discussion

3.1. Sorption and desorption kinetics of CO_2 in nylon6

The sorption and desorption kinetics of CO_2/nylon6 system was measured using a method similar to that described by Berens and Huvard [2,3]. Through these measurements, average mass gain was calculated, and the results were plotted versus the square root of desorption

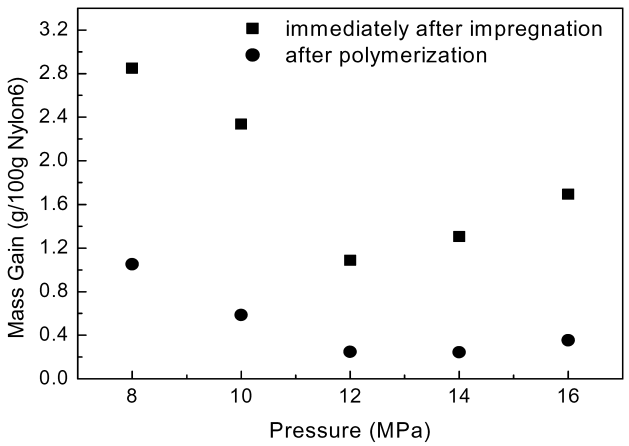


Fig. 4. Mass gain of nylon6 as a function of impregnation pressure (impregnation in 30 wt% styrene/SC CO_2 for 4 h at 40 °C, polymerization at 80 °C for 4 h).

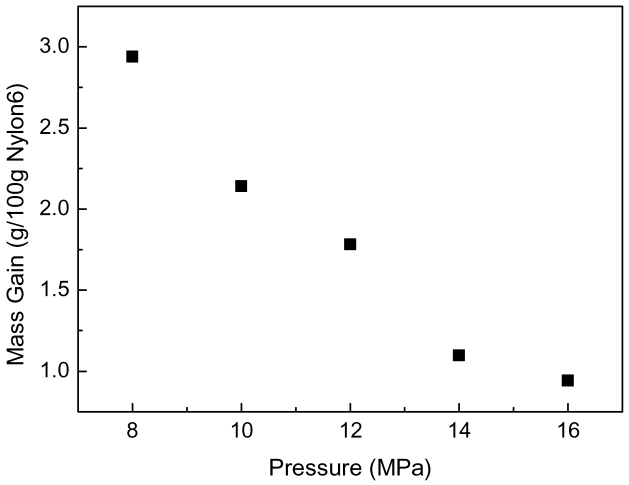


Fig. 5. Mass gain of nylon6 as a function of impregnation pressure (impregnation in 30 wt% acrylic acid/SC CO_2 for 4 h at 40 °C, polymerization at 62 °C for 4 h).

time. In Fig. 1 we can see that in the initial stage of desorption period, the plots appear linear versus the square root of time, and this conforms to Fickian's Diffusion Kinetics. However when desorption time is longer to be more than 5 h, Fickian's theory does not fit with the plots perfectly. Then we plotted the same data versus the natural logarithm of desorption time, as shown in Fig. 2. It can be seen that the mass change shows a linear dependence on the logarithm of time in a long desorption period of around 24 h. And this linear dependence is found to be accordant with Elovich's equation of desorption rate:

$$R_d = -d\theta/dt = ke^{\alpha\theta} \quad (1)$$

where R_d stands for rate of desorption, θ is the percentage of coverage, k and α are constants varying with different conditions. Through a series of integration and derivation, the equation is transformed into:

$$\theta = K + b\ln(t + t_0) \quad (2)$$

where K, b and t_0 are all constants. As absorption ratio Q is in direct proportion to θ, Eq. (2) can be followed by:

$$Q = K' + b'\ln(t + t_0) \quad (3)$$

In our experiment t_0 is near to zero infinitively, so the uptake of CO_2 (Q) shows a linear dependence on ln t.

In addition to uptake of CO_2 by the substrate, uptake of

Table 1
Absorbed amounts of CO_2 and styrene in nylon6

Pressure (MPa)	Absorbed amount of CO_2 (%)	Absorbed amount of styrene (%)
8	1.80	1.05
10	1.75	0.59
12	0.84	0.24
14	1.06	0.24
16	1.34	0.35

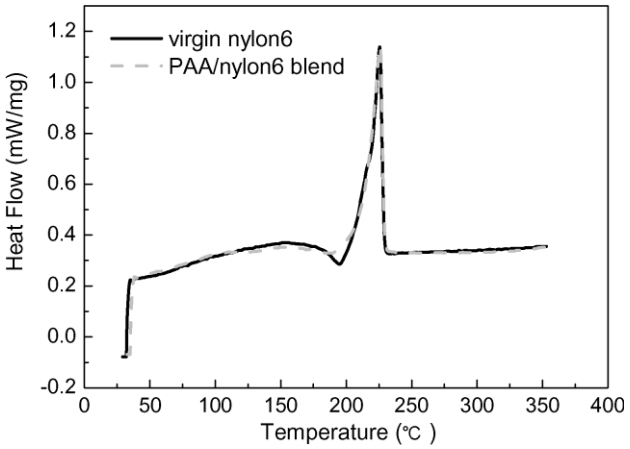


Fig. 6. DSC results of virgin nylon6 (a) and PAA/nylon6 (2:100) blend (b). The heating rate is 10 °C/min and temperature-scanning range is 30–350 °C.

acrylic acid by nylon6 at same condition was also determined. The results are given in Fig. 3. It is found that when samples were weighed immediately after being treated, the difference of mass gain between them was 0.81 g/100 g nylon6. After 3000 min, the difference was 0.89 g/100 g nylon6, almost unchanged. This demonstrates that with releasing CO_2, mass loss of the incorporated acrylic acid is small and an absolute majority remained in the substrate.

3.2. Effects of impregnation condition on blend synthesis

DeSimone et al. [17] have published the phase behavior of SC CO_2/acrylic acid system. Suppes and McHugh [18] have determined solubility of styrene in SC CO_2. Based on the data, all experiments in this study were run under the conditions that monomer and CO_2 were in a single phase.

For pressure effect on blend synthesis, it is found that the dependence of incorporated monomer with pressure is different with different monomer/SC CO_2/nylon6 systems. For styrene/SC CO_2/nylon6, it can be observed that the amount of incorporated styrene first decreases with pressure till 12 MPa, then increases with pressure and this is shown in Fig. 4. But for acrylic acid/SC CO_2/nylon6, in Fig. 5, it is otherwise that the incorporated acrylic acid always decreases with pressure increase.

According to previous and our studies, usually there are three factors effecting the additive impregnation when SCF is used as the swelling agent. They are (1) the solubility of additive in SC CO_2, (2) the compatibility of additive with polymer substrate and (3) the swelling or plasticizing effect of CO_2 on polymer substrate. How to identify which factor is decisive? It can be justified with the solubility parameter sketch. The solubility parameter of styrene is much closer to CO_2's, so its solubility in SC CO_2 can become a decisive factor on the impregnation. The experimental result of the adsorbed CO_2 and the impregnated styrene at different pressure is shown in Table 1 and it can be found that there exists dependence of absorbed styrene amount on CO_2. For acrylic acid/SC CO_2/nylon6 system, from the sketch it can be seen that the solubility parameter of acrylic acid is much closer to nylon6, so the compatibility of acrylic acid with nylon6 is pretty better and unlike the styrene/SC CO2/nylon6 system, the impregnated acrylic acid is not influenced by adsorbed CO_2 in the substrate. But there are more complex interactions as the swelling and plasticizing effect of CO_2 on substrate and the solubility of acrylic acid in SC CO_2, etc. which may have influence on the end incorporation of acrylic acid.

Table 2
Heat of fusion of PAA/nylon6 blends calculated with DSC results

PAA: nylon6	Impregnation condition	Heat of fusion (J/g)
1.10/100	40 °C, 14 MPa, 4 h	49.70
1.78/100	40 °C, 12 MPa, 4 h	46.04
2.14/100	40 °C, 10 MPa, 4 h	44.53

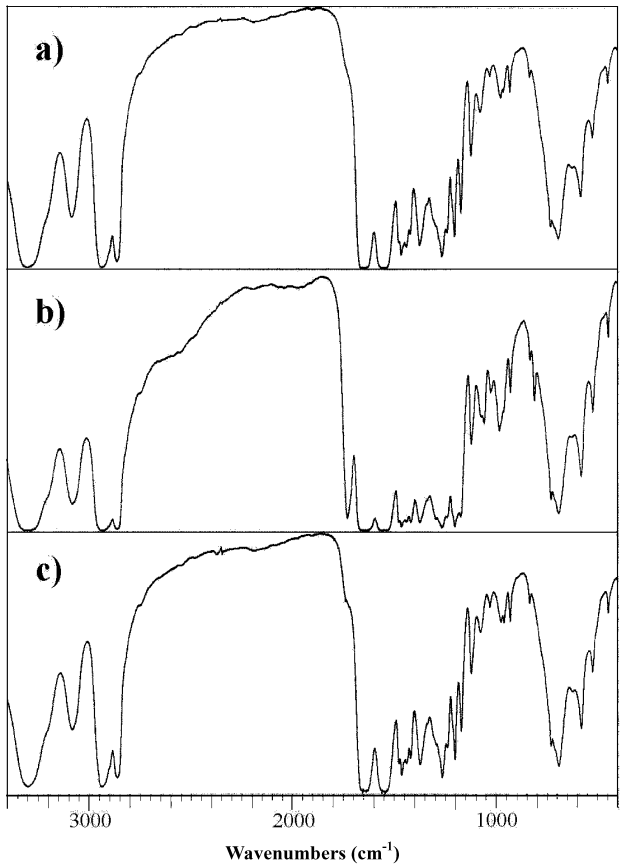
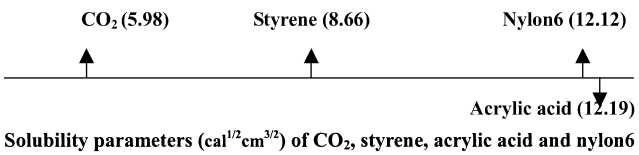


Fig. 7. IR spectra of virgin nylon6 (a), PAA/nylon6 blend (b), and the same blend extracted with water followed by drying in vacuum (c).



3.3. Blends characterization

3.3.1. DSC

To determine the properties and internal structure of PS/nylon6, PAA/nylon6 blends, a series of characterization measurements were carried out. DSC was performed to measure the thermal properties of the blends. As mentioned in Section 2, virgin nylon6 was dried in vacuum at 140 °C for 48 h. The temperature of maximum crystalline growth velocity (T_{max}), calculated with the following empirical formula is 140 °C.

$$T_{max}(K) = 0.63T_m(K) + 0.37T_g(K) - 18.5 \quad (4)$$

So nylon6 samples have achieved maximum crystallinity before DSC measurements. From Fig. 6 it is found that the thermal stability of nylon6 has been improved remarkably by incorporation of poly(acrylic acid), as shown by the disappearance of the original exothermic peak. It means the SC CO_2-assisted impregnation of PAA into nylon6 can notably improve its service performance and it is identified this method is efficient and environment-harmless for nylon6's modification.

In another series of DSC measurements, the fusion peak areas of blends containing different PAA contents were calculated. The results were given in Table 2, which shows that the heat of fusion decreases with increase of PAA content. For polymers, the heat of fusion is in direct proportion to crystallinity; it indicates that the overall crystallinity of the blend decreases with PAA content. So the method supplies a quite convenient way to control the crystallinity by changing PAA content in the blend.

3.3.2. IR

Fig. 8 shows FTIR spectra of virgin nylon6, a PAA/nylon6 (3:100) blend, and the same blend sample extracted by water. From Fig. 7(b), it can be seen that a spectral feature of PAA whose C=O stretching appeared at 1727 cm^{-1} and it clearly demonstrates the existence of poly(acrylic acid) in the nylon6 matrix. Although, for nylon6, 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 ~1640 cm^{-1} instead of 1700–1750 cm^{-1}.

PAA is a water-soluble polymer, so the blend sample was extracted with water at 25 °C for 2 h and then dried at 60 °C for 12 h. In Fig. 7(c), it can be seen the disappearance of the 1727 cm^{-1} wave number and this indicates that almost all of the incorporated poly(acrylic acid) has been removed.

3.3.3. Polarizing microscopy

It is well known that crystallization of some amorphous

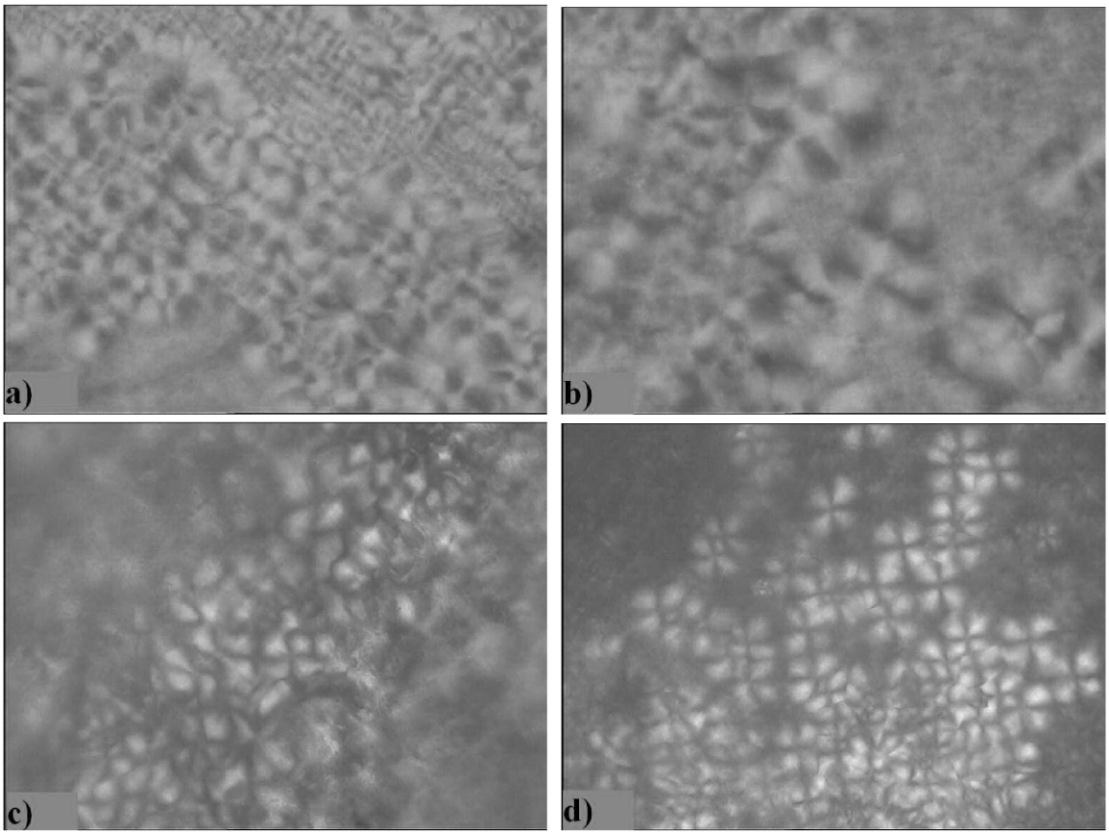


Fig. 8. Micropolariscopy photograph (× 100 × 5) of virgin nylon6 (a), SC CO_2-treated nylon6 (b), PAA/nylon6 blend (Impregnation condition: 40 °C, 12 MPa, 4 h) (c) and PS/nylon6 blend (Impregnation condition: 40 °C, 12 MPa, 4 h) (d).

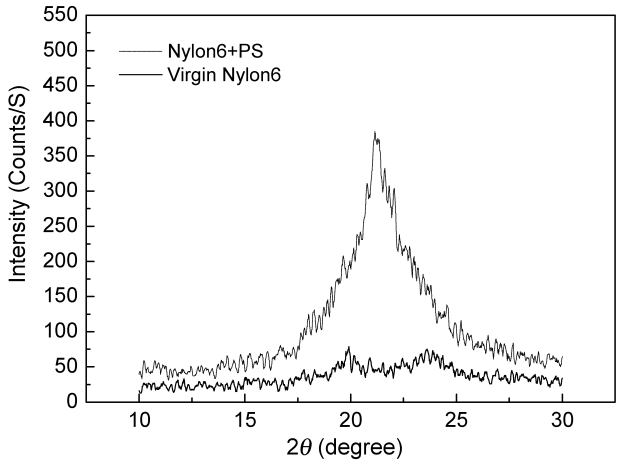


Fig. 9. X-ray diffraction results of original nylon6 and PS/nylon6 blend (impregnation in 30 wt% styrene/SC CO_2, 12 MPa for 4 h at 40 °C, polymerization at 80 °C for 4 h).

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 [19,20]. Chiou [21], Johnston [22,23] and K. Mizoguchi [24] et al. have all discovered that supercritical CO_2 has inducing crystallization effect on polymers. Moreover, in our previous study [25], some forms of CO_2-induced crystallization have been found and reported. Here induced crystallization is also found in CO_2-treated nylon6 and blends, as shown in Fig. 8. It can be seen that through CO_2 treatment, the average size of nylon6 spherocrystal increased notably, though the crystal had not grown sufficiently to achieve high crystallinity. For the crystalline structure of synthesized blends, spherocrystal can be clearly seen to grow further. In PS/nylon6 blend, radiating spherocrystal formed and overall crystallinity increased remarkably. This should be attributed to the annealing effect during polymerization at high temperature. As styrene was polymerized at a higher temperature (80 °C) than acrylic acid (62 °C), spherocrystal in PS/nylon6 blend grew more sufficiently and the radial structure was more integrated. The increased crystallinity of the PS/nylon6 compared to the original sample was also indicated by the experimental results of XRD shown in Fig. 9.

4. Conclusions

Poly(acrylic acid)/nylon6 and polystyrene/nylon6 blends can be prepared by infusion of acrylic acid or styrene into and radical polymerization within solid nylon6 using supercritical CO_2 as a carrier. The content of incorporated polymers can be controlled by adjusting the reaction conditions. Moreover, characterization shows that the prepared PAA/nylon6 blend has much better thermal stability than original nylon6. CO_2-induced crystallization was found in CO_2-treated nylon6 and blend samples.

Acknowledgements

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