

Application of Supercritical Carbon Dioxide in the Preparation of Biodegradable Polylactide Membranes

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ABSTRACT: The application of supercritical carbon dioxide (SCCO₂) has been attracting more and more attention, especially in the formation of polymer membranes. The membrane formation using SCCO₂ is analogous to conventional immersion precipitation process by using organic nonsolvent. Polylactide (PLA) membranes were prepared by phase separation with SCCO₂ as nonsolvent. Two kinds of solvents were used to study the effect of the solvent on the cross-section structure of the PLA membrane and the com-

patibility between the solvent and SCCO₂ was studied. The effect of the solvent and the preconditioning on the morphology of the PLA membrane was also investigated through scanning electron microscope, wide-angle X-ray diffraction, and polarizing microscopy. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2158–2163, 2004

Key words: supercritical carbon dioxide; polylactide; membrane; morphology; biopolymers; biodegradable; membrane

INTRODUCTION

It is well known that supercritical fluid has some distinctive properties which include gaslike viscosity and diffusivity, liquidlike density, and dissolvability, which makes it a tunable solvent.^{1–3} Supercritical fluid technology, referred to as Green Chemistry Technology, has been developed to form polymeric materials such as microspheres, porous fibers, porous foams, and porous membranes. Typical processes are a rapid expansion of supercritical solutions (RESS),^{4–6} a microcellular foaming process,^{7–9} and a precipitation with compressed fluid antisolvent (PCA).^{10–13} In the RESS process, supercritical solution is expanded through a nozzle to form microspheres or microfibers. In the microcellular foaming process, a pellet of polymer is saturated with supercritical carbon dioxide (SCCO₂) and nucleation is induced by supersaturation caused by a sudden depressurization. In the PCA process, a polymer solution is sprayed through a capillary into a vessel containing compressed or supercritical CO₂.

Most of the polymer membranes in use were prepared by the immersion precipitation process. The application of SCCO₂ has been attracting attention in the preparation of polymer membranes.^{14–16} Compared to the traditional immersion precipitation process, the advantages of this phase separation induced by SCCO₂ are as follows.^{14,17,18} First, CO₂ is inexpen-

sive, environmentally benign, nonflammable, and can be completely and easily removed from products. At the same time, the moderate critical conditions ($T_c = 31.1^\circ\text{C}$, $P_c = 73.8$ bar) of CO₂ allow CO₂ to be used within safe commercial and laboratory operation conditions. Another advantage is that the polymer membrane can be dried rapidly with SCCO₂, but without collapse of the structure due to the absence of a liquid-vapor interface. In addition, after the pressure is diminished, the solvent dissolved in the SCCO₂ can be removed from the gaseous CO₂. Furthermore, it is convenient to control the morphology of the products by altering the pressure.

Polylactide (PLA) is a kind of Green Material because of its biodegradability and biocompatibility. The use of PLA has been focusing on medicine and biology recently, such as PLA hollow fibers, PLA nanoparticles and porous PLA membranes used in the controlled delivery of drugs,^{19–21} and porous PLA films used to culture some cells.²²

Traditionally, PLA membranes were prepared by the immersion precipitation process with chloroform/methanol as the solvent/nonsolvent. In this article, PLA membranes were first prepared with SCCO₂, which replaced the conventional toxic nonsolvent methanol. Previous to this work, the compatibility between the solvent and SCCO₂ was studied. Moreover, we chose another solvent tetrahydrofuran (THF) to study the effect of different solvents on the cross-section structure of PLA membrane. The influence of the solvent and the preconditioning with SCCO₂ on the morphology of the PLA membrane was also investigated.

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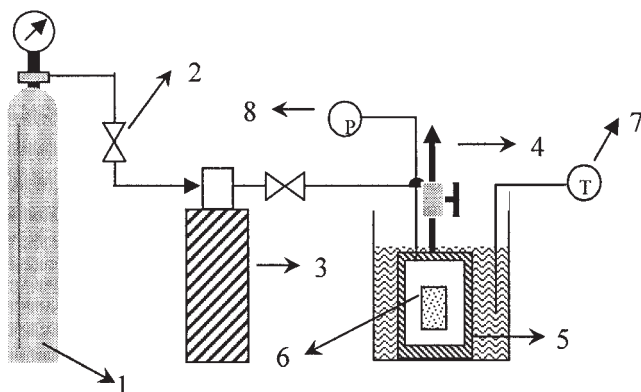


Figure 1 Apparatus description diagram: 1, gas cylinder; 2, valve; 3, syringe pump; 4, vent; 5, a pressure vessel with or without visual windows; 6, sample; 7, temperature circulator; 8, pressure gauge.

EXPERIMENTAL

Materials

PLA (melt point: $\sim 120^\circ\text{C}$) was supplied by CSIRO CMIT in Australia in the form of semitransparent pellets. The solvents chloroform and THF of analytical grade were purchased from Tianjin Chemical Co. Methanol (analytical grade) was obtained from Louyang Chemical Plant. CO_2 with the purity of 99.9% was supplied by Zhengzhou Sanfa Gas Co. All reagents were used without any further purification.

Procedures

All the pressure vessels were stainless steel reactors. A high-pressure syringe pump (Beijing Satellite Manufacturing Factory, DB-80) used to charge CO_2 into the reactor was 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 an accuracy of ± 0.01 MPa was also connected to the reactor to observe the *in situ* pressure change of the system. During the experiments, the vessels were placed in the isothermal water bath that consisted of a temperature control module (Thermo Haake, C10) and a bath vessel (Thermo Haake, P5). The fluctuation of temperature of the bath was less than $\pm 0.1^\circ\text{C}$. The apparatus description diagram is shown in Figure 1.

Casting solution

PLA pellets were dried *in vacuo* at 353 K for 24 h and then placed in a desiccator prior to use. Casting solutions of 15 wt % PLA in chloroform and 15 wt % PLA in THF were prepared by magnetically stirring the

components for 24 h at an elevated temperature (308 K).

The compatibility between the solvent and SCCO_2 in the ternary system

To replace the toxic nonsolvent methanol with SCCO_2 and even change the solvent chloroform with THF, it is extremely necessary to study the compatibility between the solvent and SCCO_2 in the ternary system.

The PLA solution (15 wt %) was poured into the pressure vessel (50 mL) with visual windows. The vessel was put in the isothermal bath (308 K). After sealing the vessel, CO_2 was introduced into the reactor. Magnetic stirring of the solution was conducted to ensure complete dissolvability of the solvent in CO_2 . Then, different swelling of the solution in SCCO_2 was obtained at different pressures, which was indicated by volume expansion of the system. The larger the swelling of the solution in SCCO_2 , the stronger the compatibility between the solvent and SCCO_2 . The experimental results are shown in Figure 2. The volume expansion of the solution in SCCO_2 was denoted $\Delta V\%$, which was given as

$$\Delta V\% = [V(P,T) - V(P_0,T)]V(P_0,T) \times 100\%$$

where P_0 represents the atmospheric pressure, and T is the temperature of the system. From Figure 2, we could see that the compatibility of chloroform and THF with SCCO_2 were both satisfying (i.e., SCCO_2 could be used as nonsolvent for PLA solutions).

Membrane formation

A thin film from the casting solution was cast onto a clean glass slide by using a blade. The initial thickness of the film was $\sim 182 \mu\text{m}$. Then, the glass slide with the film was immediately transferred into a small pressure vessel (21.4 mL), and CO_2 was introduced into it. The reactor was placed in the isothermal bath (308 K). When the desired pressure (13 MPa) was reached, it was held for 1 h. Then, the vessel was depressurized slowly, which took 1 h. Thus, dry PLA membranes were obtained with different solvents, chloroform and THF.

Then, PLA membrane with preconditioning was also prepared. After casting a thin film from the solution of PLA/THF (15 wt %) onto a glass slide, we could ramp the CO_2 pressure to a certain level (7.9 MPa) below the desired pressure (13 MPa). The PLA membrane was preconditioned at 7.9 MPa for 20 min. Subsequently, the pressure of the system increased to the final magnitude (13 MPa), and the following procedures were the same as those discussed above.

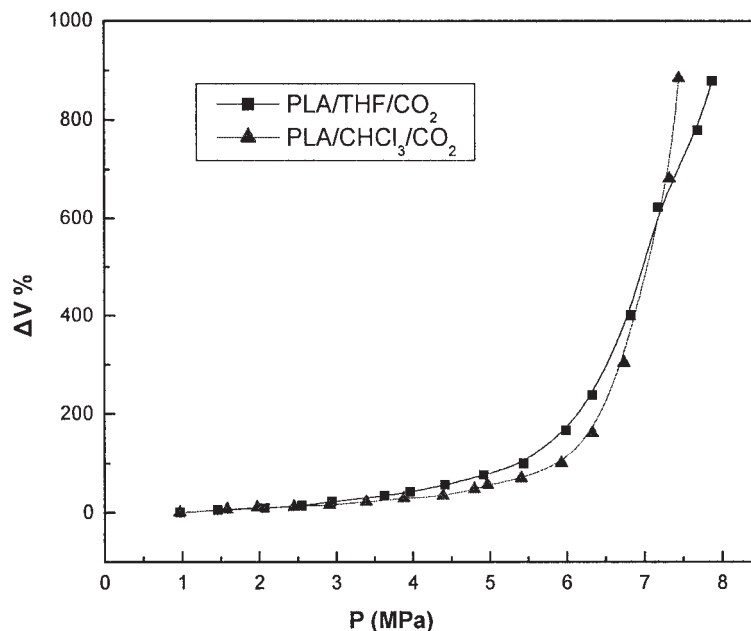


Figure 2 The volume expansion ($\Delta V\%$) of polymer solution in CO_2 at different pressures.

Membrane characterization

SEM observation

The PLA membranes were prepared for SEM analysis by first fracturing them in liquid nitrogen. Then, the fractured samples were stabilized vertically on aluminum stubs by using a particular adhesive and sputter coating an $\sim 100 \text{ \AA}$ layer of gold. A scanning electron microscope (SEM; AMRAY-1000B) at an accelerating voltage of 20 kV was used to examine the structure of PLA membranes.

Wide-angle X-ray diffraction (WAXD)

WAXD measurements were conducted to examine the crystallinity of the membranes. The apparatus was made up of an X-ray diffraction unit (RIGAKU Co., D/MAX-3B) with a Ni-filtered $\text{CuK}\alpha$ beam and a step length of 0.02° .

Polarizing microscope

The morphology of the crystalline of PLA membranes was studied by Polarizing microscope (Leica, DMLP). The photos were taken with a camera (Leica, MPS30).

RESULTS AND DISCUSSION

The effect of solvent on the cross-section structure of PLA membranes

When SCCO_2 was used as the nonsolvent, the effect of solvent on the cross-section structure of PLA membranes was studied, which are shown in Figures 3 and

4. As shown in Figure 3, PLA membrane prepared with SCCO_2 as nonsolvent for the PLA/chloroform binary system was dense and nonporous. In contrast, when SCCO_2 was used as nonsolvent for PLA/THF binary system, a porous membrane was obtained (Fig. 4). It was apparent that PLA membranes with different cross-section structure could be obtained with different solvents.

According to Figure 2, it can be seen that in the range of CO_2 pressure from 1 to 7 MPa, there was not much difference between the swelling of PLA/chloroform and PLA/THF with SCCO_2 . When the pressure reached ~ 7 MPa, the swelling of the system of PLA/chloroform was larger than that of PLA/THF system [i.e., at our experimental pressure of 13 MPa (>7 MPa), the compatibility between chloroform and su-

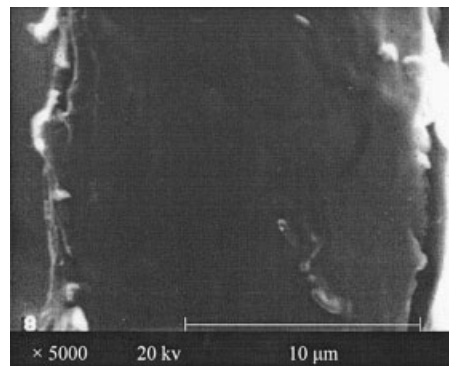


Figure 3 SEM photographs of the cross-section structure of PLA membranes: solvent: chloroform; polymer concentration: 15 wt %; CO_2 pressure: 13 MPa; temperature: 308 K.

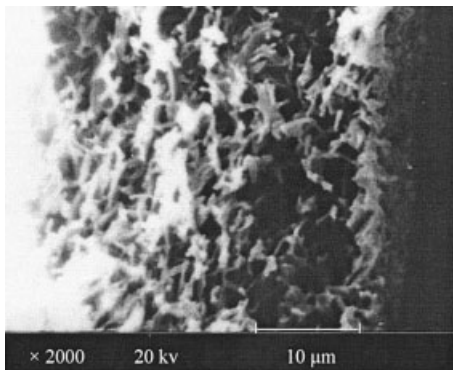


Figure 4 SEM photographs of the cross-section structure of PLA membranes: solvent: THF; polymer concentration: 15 wt %; CO₂ pressure: 13 MPa; temperature: 308 K.

percritical CO₂ was better than that between THF and supercritical CO₂ in respective ternary system].

When CO₂ was introduced into the system of PLA/chloroform, the solvent strength of chloroform decreased greatly because of the better compatibility of chloroform with supercritical CO₂ at the experimental pressure (13 MPa). In the process of membrane formation, Liquid-Liquid demixing could not take place before the phase transition and dense membrane was obtained.

For the ternary system of PLA/THF/SCCO₂, the compatibility between SCCO₂ and THF was not very strong. Therefore, the polymer-lean phase and polymer-rich phase formed because of the exchange of THF and CO₂. Then, the polymer-rich phase nuclei grew, and the porous structure was obtained due to Liquid-Liquid phase separation.

The effect of solvent on the crystalline morphology of PLA membranes

The WAXD results of PLA membranes from PLA/chloroform and PLA/THF are shown in Figure 5. From Figure 5, we could see that the PLA membranes prepared with different solvents were both crystalline. This indicated that crystallization occurred after the phase separation of the systems.

The membrane prepared from PLA/chloroform was transparent and crystalline. Small spherulites were observed through a polarizing microscope, which was shown in Figure 6. Spherulites were not observed, however, in the membrane prepared from PLA/THF, and rodlike crystallines were found from the SEM micrograph (Fig. 4).

As discussed above, after CO₂ was introduced into PLA/chloroform, the solvent strength of chloroform decreased because of the strong compatibility between SCCO₂ and it. Then, the solution became supersaturated and there would be some segments in the polymer chains arraying regularly to form many bundles

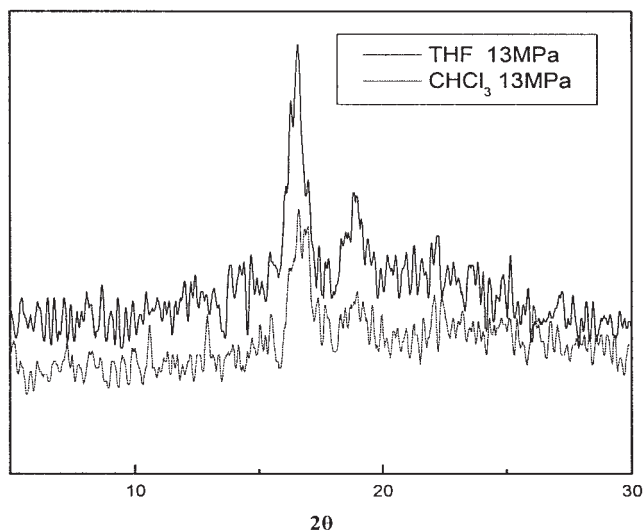


Figure 5 The results of WAXD measurements of PLA membranes prepared with different solvents: solvent: chloroform (CHCl₃) and THF; polymer concentration: 15 wt %; CO₂ pressure: 13 MPa; temperature: 308 K.

of crystalline. Then, the well-distributed nuclei formed in the system from those bundles and these nuclei grew and small spherulites were obtained. This was why the membrane prepared from PLA/chloroform was transparent.

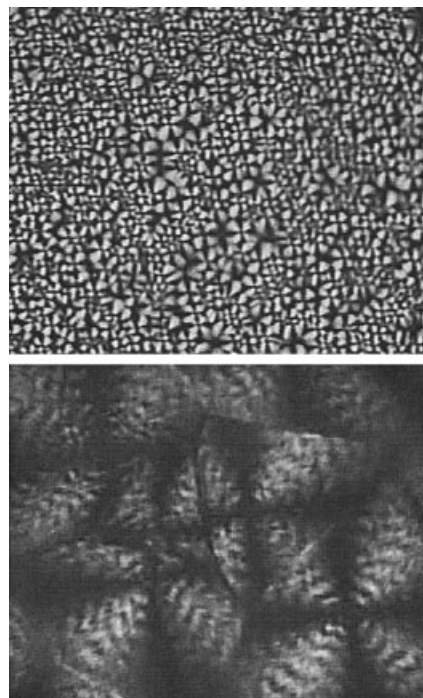


Figure 6 Micropolariscopy photographs of PLA membranes: top: ×50; bottom: ×500; solvent: chloroform; polymer concentration: 15 wt %; CO₂ pressure: 13 MPa; temperature: 308 K.

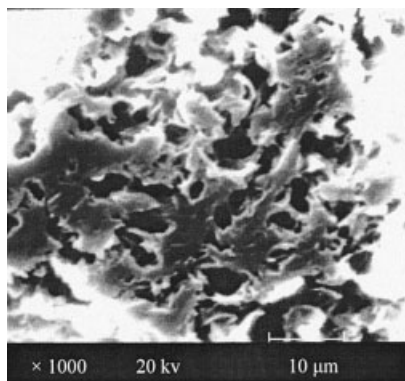


Figure 7 SEM photographs of the cross section structure of PLA membranes prepared with preconditioning: solvent: THF; preconditioning pressure: 7.9 MPa; pressure-keeping: 20 min; final pressure: 13 MPa; pressure-keeping: 1 h; temperature: 308 K.

However, when CO₂ was introduced into the PLA/THF, the polymer-lean phase and polymer-rich phase could be formed. The nuclei could not form uniformly in the polymer-rich phase. It was difficult to grow into well-distributed spherulites and rod-like crystalline formed.

In addition, the complex interaction of solvent with nonsolvent and that of solvent with solute might play an additional important role in the formation and even the growth of the nuclei; this needs to be further studied.

The effect of preconditioning on the crystalline morphology of the PLA membranes

It is well known that crystallization of some amorphous and semicrystalline polymers can be induced by solvent as well as heat and strain. The interaction between polymer and the solvent reduces the T_g effectively, and if the reduction of T_g is large enough to put the system in the crystallization region, the polymer chains rearrange themselves into a lower free-energy state.^{23–25} Chiou et al.,²⁶ Johnston et al.,^{27,28} and Mizoguchi et al.²⁹ have all discovered that SCCO₂ has an inducing crystallization effect on polymers.

As shown in Figure 7, a leafy structure was obtained in the membrane prepared from PLA/THF with preconditioning at 7.9 MPa for about 20 min. This was completely different with the rodlike structure found in the PLA membrane without preconditioning. During the preconditioning process, the membrane had precipitated because of the phase separation and the subsequent phase transitions. So, the following pressurization should be a posttreatment to the membrane and it involved the modification on the membrane.

In this process, the absorbed CO₂ had a plasticization effect on the polymer and this contributed to the decrease of T_g . With the decrease of T_g , the free volume of polymer chains increased. The segments and other parts in the polymer chains could move more easily and actively. This could cause the polymer chains to rearrange themselves into a lower free energy state (i.e., the previous structure was damaged and a leafy structure formed).

CONCLUSION

When supercritical carbon dioxide was used as nonsolvent, PLA membranes prepared with different solvents were studied by SEM, WAXD, and polarizing microscopy. It was found that the solvent had a profound effect on the cross-section structure of the membranes. When chloroform was used as solvent, the PLA membrane was dense and nonporous. However, porous PLA membrane was obtained with THF as solvent. The solvent and the preconditioning had some effect on the crystalline morphology of the membranes. Small spherulites were found in the membrane prepared from PLA/chloroform, and rodlike crystallines were found in the membrane prepared from PLA/THF. The rodlike morphology was changed into leafy structure for the PLA membrane with preconditioning. Therefore, compared to the traditional membrane formation, SCCO₂ can be used as a convenient driving force to prepare membranes with different morphologies.

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