

# APPLICATION OF SUPERCRITICAL CARBON DIOXIDE IN THE PREPARATION OF BIODEGRADABLE POLYLACTIDE MEMBRANES

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## 1. INTRODUCTION

It is well known that supercritical fluid has some distinctive properties like gaslike viscosity and diffusivity, liquidlike density and dissolvability. Small changes in temperature and pressure could cause dramatic changes in the density, viscosity and dielectric properties of the fluid, which makes it a tunable solvent [1]. Supercritical fluid technology referred as “Green Chemistry Technology” has been developed to form polymeric materials such as microspheres, porous fibers, and porous membranes. Typical processes are a rapid expansion of supercritical solutions (RESS) [2,3], a microcellular foaming process [4,5] and a precipitation with compressed fluid anti-solvent (PCA) [6-8].

Most of the polymer membranes in use were prepared by the immersion precipitation process. And the application of SCCO<sub>2</sub> has been attracting attentions in the preparation of polymer membranes [9-11]. The advantages are as follows [9,12,13]. First, CO<sub>2</sub> is inexpensive, environmentally benign, nonflammable, and can be completely and easily removed from products. At the same time, the moderate critical conditions ( $T_c=31.1\text{ ?}$ ,  $P_c=73.8\text{ bar}$ ) of CO<sub>2</sub> allow CO<sub>2</sub> to be used within safe commercial and laboratory operation conditions. Another advantage is that the polymer membrane can be dried rapidly with SCCO<sub>2</sub>, but without collapse of the structure. Furthermore, after the pressure is diminished, the solvent dissolved in the SCCO<sub>2</sub> can be removed from the gaseous CO<sub>2</sub>. In addition, it is convenient to control the morphology of the products by altering the pressure.

Poly lactide (PLA) is a kind of “Green Materials” because of its biodegradability and biocompatibility. Recently, the use of poly lactide has been focusing on medicine and biology. Traditionally, PLA membranes were prepared by the immersion precipitation process with chloroform/methanol as the solvent/nonsolvent. In this paper, PLA membranes were first prepared with SCCO<sub>2</sub> which replaced the conventional toxic nonsolvent methanol. Moreover, we chose another solvent tetrahydrofuran (THF) to replace the traditional toxic solvent chloroform.

## 2. MATERIALS AND METHODS

### 2.1 Materials

PLA (melt point:  $\sim 120\text{ ?}$ ) in the form of semi-transparent pellets was supplied by CSIRO CMIT in Australia. The solvents chloroform and THF of analytical grade were purchased from Tianjin Chemical Co. Methanol (analytical grade) was obtained from Louyang Chemical Plant. CO<sub>2</sub> with the purity of 99.9% was supplied by Zhengzhou Sanfa Gas Co. All reagents were used without any further purification.

## 2.2 Methods

### 2.2.1 Casting solution

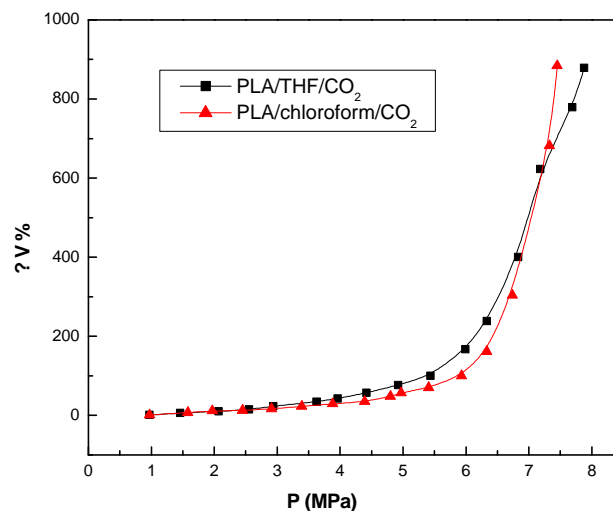
PLA pellets were dried in vacuum at 80 °C for 24 h and then placed in a desiccator prior to use. Casting solutions of 15wt% PLA in chloroform and 15wt% PLA in THF were prepared by magnetically stirring the components for about 24h at an elevated temperature (313 K).

### 2.2.2 The compatibility between the solvent and SCCO<sub>2</sub> in the ternary system

In order to replace the toxic nonsolvent methanol with SCCO<sub>2</sub> and even change the solvent chloroform with THF, it is very necessary to study the compatibility between the solvent and SCCO<sub>2</sub> in the ternary system. The PLA solution (15wt%) was placed into the visual-window pressure vessel (50 ml). The vessel was put in the isothermal bath (308 K). Then CO<sub>2</sub> was introduced into the system with Magnetic stirring. Then different volume expansion of the solution in CO<sub>2</sub> was obtained at different pressures. The larger swelling of the solution in SCCO<sub>2</sub>, the stronger compatibility between the solvent and SCCO<sub>2</sub>. The volume expansion of the solution in SCCO<sub>2</sub> was denoted as  $\Delta V\%$ .

$$\Delta V\% = [V(P, T) - V(P_0, T)] / V(P_0, T) \times 100\% \quad (1)$$

where  $P_0$  represents the atmospheric pressure,  $T$  is the temperature of the system. The experimental results were shown in **Figure 1**. From **Figure 1**, we could see that the compatibility of PLA/chloroform and PLA/THF with SCCO<sub>2</sub> were both pretty well, i.e., SCCO<sub>2</sub> could be used as effective nonsolvent for PLA solutions.



**Figure 1** Volume expansion of PLA solution in CO<sub>2</sub> as a function of pressure

### 2.2.3 Membrane formation

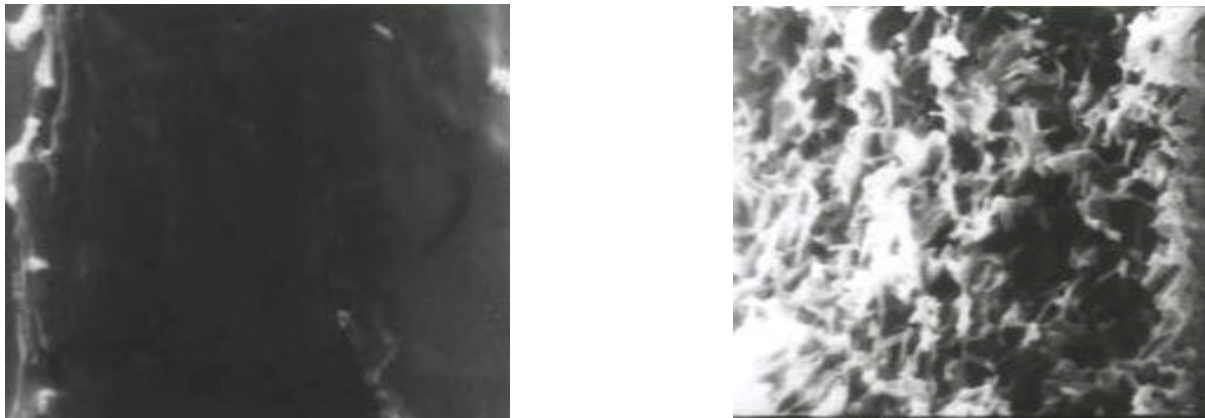
A thin film from the casting solution was cast onto a glass slide using a blade. The initial thickness of the film was 182 μm. Then the glass slide with the film was immediately transferred into a small pressure vessel (21.4 ml), and CO<sub>2</sub> was introduced into it. The reactor was placed in the isothermal bath (308 K). When the desired pressure (13 MPa) was reached, it was held for 1 hour. Then the vessel was depressurized slowly, which lasted 1 hour. Thus dry PLA membranes were obtained with different solvent chloroform and THF.

Then, PLA membrane with preconditioning was also prepared. After casting a thin film onto a glass slide from the solution of PLA/THF (15wt%), we could increase the CO<sub>2</sub> pressure to a certain level (7.9 MPa) below the desired pressure (13 MPa). And 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 with those discussed above.

### 3. RESULT AND DISCUSSION

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

The SEM of PLA membranes prepared with different solvent was shown in **Figure 2**. As shown in **Figure 2**, PLA membrane prepared from PLA/chloroform/SCCO<sub>2</sub> ternary system was dense and nonporous. In contrary, for the solution of PLA/THF, porous membrane was obtained. It was apparent that different cross-section structure could be obtained with different solvent.



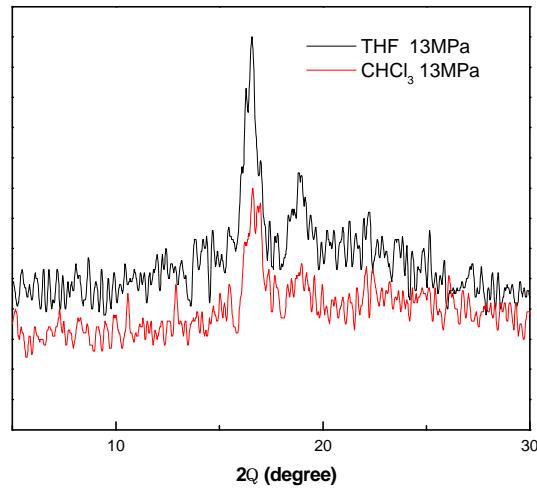
**Figure 2** SEM micrograph of the cross-section structure of PLA membranes: left: PLA/chloroform; right: PLA/THF (polymer concentration: 15wt%; CO<sub>2</sub> pressure: 13 MPa; temperature: 308 K)

According to **Figure 1**, when CO<sub>2</sub> pressure was in the range of 1 MPa to 7 MPa, there was no much difference between the swelling of PLA/chloroform and PLA/THF with SCCO<sub>2</sub>. But after the pressure reached approximately 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 PLA/chloroform and SCCO<sub>2</sub> was better than that between PLA/THF and SCCO<sub>2</sub>.

When CO<sub>2</sub> was introduced into the system of PLA/chloroform, the solvent strength of chloroform decreased greatly because of the better compatibility of chloroform with SCCO<sub>2</sub> at the experimental pressure (13 MPa). And 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/SCCO<sub>2</sub>, the polymer lean phase and polymer rich phase formed because of the exchange of THF and CO<sub>2</sub>. Then the polymer rich phase nuclei and grew, and the porous structure was obtained due to Liquid-Liquid phase separation.

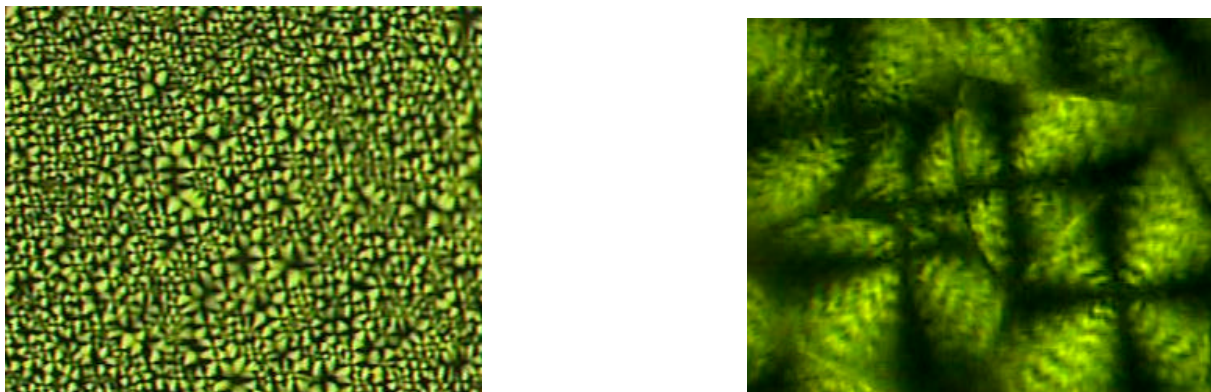
#### 3.2 The effect of solvent on the crystalline morphology of PLA membranes

The WAXD results of PLA membranes were shown in **Figure 3**. From **Figure 3**, we could see that the PLA membranes prepared with different solvent were both crystalline. This indicated that crystallization occurred after the phase separation of the systems.



**Figure 3** Wide-angle X-ray diffraction results of PLA membranes: polymer concentration: 15wt%; CO<sub>2</sub> pressure: 13 MPa; temperature: 308 K.

The membrane prepared from PLA/chloroform was transparent and crystalline. Small spherulites were observed through polarizing microscope, which was shown in **Figure 4**. But spherulites were not observed in the membrane prepared from PLA/THF, and rod-like crystalline were found from the SEM micrograph (**Figure 2**).



**Figure 4** Micropolariscopy photographs (left: ×50; right: ×500) of membrane prepared from PLA/chloroform: polymer concentration: 15wt%; CO<sub>2</sub> pressure: 13 MPa; temperature: 308 K.

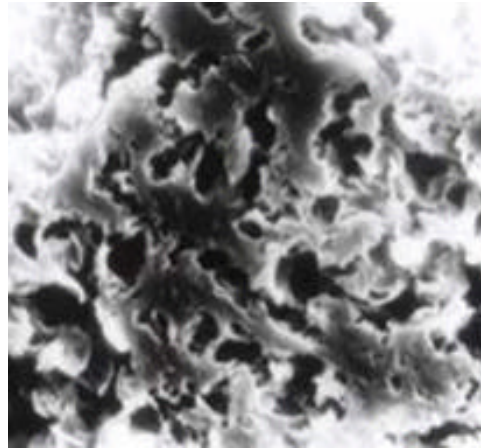
As discussed above, after CO<sub>2</sub> was introduced into the system of PLA/chloroform, the solvent strength of chloroform decreased. Then the solution became supersaturated and there would be some segments in the polymer chains arraying regularly to form many bundles of crystalline. Then the well-distributed nuclei formed in the system from those bundles and these nuclei grew and small spherulites were obtained finally. This was why the membrane prepared from PLA/chloroform was transparent. However, when CO<sub>2</sub> 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 non-solvent and that of solvent with solute might play additional important role in the formation and even the growth of the nuclei, which needs to be studied further.

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

It is well known that crystallization of some amorphous and semi-crystalline 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 [14,15]. Chiou [16], Johnston [17] and K. Mizoguchi [18] et al. have all discovered that  $SCCO_2$  has inducing crystallization effect on polymers.



**Figure 5** SEM micrograph of the cross-section structure of PLA membrane with preconditioning: solvent: THF; preconditioning pressure: 7.9 MPa; time: 20 min; final pressure: 13 MPa; time: 1 hour; temperature: 308K.

As shown in **Figure 5**, leafy structure was obtained in the membrane prepared from PLA/THF with preconditioning at 7.9 MPa for 20 min. This was completely different with the rod-like structure found in the PLA membrane without preconditioning. After the preconditioning, the membrane had precipitated due to the phase separation and phase transitions. So the following pressurization should be a post-treatment to the membrane and it involved the modification on the membrane. The absorbed  $CO_2$  had plasticization effect on the polymer and this contributed to the decrease of  $T_g$ . Then the segments and other parts in the polymer chains could move more easily and actively. So the polymer chains rearrange themselves into a lower free energy state, i.e., previous structure was damaged and leafy structure formed.

## 4. CONCLUSION

When supercritical carbon dioxide was used as nonsolvent, PLA membranes prepared with different solvent were studied by SEM, WAXD and polarizing microscope. It was found that the solvent had a profound effect on the cross-section structure of PLA membranes. The solvent and the preconditioning had some effect on the crystalline morphology of PLA

membranes with SCCO<sub>2</sub> as nonsolvent. Small spherulites were found in the membrane prepared from PLA/chloroform, but rod-like crystalline formed in the membrane prepared from PLA/THF. The rod-like morphology was changed into leafy structure for the PLA membrane with preconditioning. Therefore, compared to the traditional membrane formation, SCCO<sub>2</sub> can be used as convenient driving force to prepare membranes with different morphology.

## ACKNOWLEDGEMENTS

We are grateful for the financial support from the Ministry of Education of China.

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