

Formation of Poly-Vinyl-Alcohol Structures by Supercritical CO₂

E. Reverchon, S. Cardea, C. Rapuano

Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, Via Ponte Don Melillo, Fisciano 84084, Italy

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ABSTRACT: Poly-vinyl-alcohol (PVA) porous structures have been prepared using a supercritical phase inversion process in which supercritical carbon dioxide (SC-CO₂) acts as the nonsolvent. First, we tested the versatility of the SC-CO₂ phase inversion process, forming PVA/dimethylsulfoxide (DMSO) solutions with polymer concentrations ranging from 1 to 35% (w/w) and changing the process parameters. We worked at temperatures from 35 to 55°C and pressures from 100 to 200 bar obtaining different membranes morphologies: dense films, membranes with coexisting morphologies, and microparticles. However, we did not produce symmetric or asymmetric porous membranes. To obtain this result, we used casting solutions

formed by adding acetone to DMSO with the aim of modifying the affinity between SC-CO₂ and the liquid solvent. In this series of experiments, we obtained asymmetric membranes with skin layer thicknesses lower than 10 μm. The results obtained in this work have been explained considering that the membranes formation mechanism is related to the kinetics of the process; i.e. the affinity between the solvent (mixture of solvents) and SC-CO₂. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3151–3160, 2007

Key words: poly-vinyl-alcohol; membranes; supercritical CO₂; phase inversion

INTRODUCTION

Poly-vinyl-alcohol (PVA) is an attractive material for producing membranes, because of its good chemical stability, thermal stability, biocompatibility, and biodegradability. Recently, it has been used in ultrafiltration and nanofiltration processes,^{1,2} in biomedical applications as drug release device³ or as catalytic support.^{4,5}

In general, depending on the manufacturing process, it is possible to obtain different morphologies: dense films, homogeneous microporous membranes, and asymmetric membranes, that can be useful for different separation processes, such as gas separation, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, etc. Today, the immersion-precipitation process is widely used in industry to synthesize polymeric porous structures. In this process the polymer solution is immersed into a coagulation bath filled with a nonsolvent: the solvent diffuses out the casting film while the coagulant (nonsolvent) diffuses into it. Therefore, the contact between the solvent and the nonsolvent causes the solid–liquid phase transition and polymer precipitation generating the porous structures.

Scientific literature contains some works on PVA membranes formation process.^{6–9} Young et al.⁶ pro-

posed the formation of PVA membranes starting from aqueous solutions and used a coagulation bath formed by Na₂SO₄ + KOH solution in H₂O. They obtained membranes with the typical asymmetric structure: formed by a dense thick layer and a porous sublayer. Subsequently, Chuang et al.⁷ studied the possibility of eliminating the skin layer adding a polymeric additive (dextran) in the starting solution. They observed that the structure of the skin layer strongly depended on the amount of additive in the casting solution; the addition of dextran induced the formation of pores in the top layer. Another attempt of avoiding skin layer formation was performed adding acetic acid in the casting solution.⁸ In this case, not only the surface morphology, but, also structure of the cross section was modified; indeed, the increase of the amount of acetic acid in the casting solution decreased the thickness of the skin layer and increased the overall porosity causing the formation of macrovoids. A mechanism describing the affinity between PVA solution and the coagulant medium was also proposed.

The results presented in scientific literature confirm the difficulty in producing PVA membranes and, especially, in controlling these membranes morphology (i.e., to control skin layer thicknesses and macrovoids formation). Moreover, the traditional immersion–precipitation process is characterized by long formation times and limited versatility; i.e., by a reduced possibility to modulate cell and pore size.

Correspondence to: E. Reverchon (ereverchon@unisa.it).

A new technique in which supercritical carbon dioxide (SC-CO₂) replaces the liquid nonsolvent has been proposed.^{10–18} SC-CO₂ can form and dry the membrane rapidly, the process does not require additional post-treatments and it is easy to recover the solvent. Kho et al.¹⁰ used compressed CO₂ for the formation of Nylon 6 membranes. The authors described the pore characteristics of the membranes by a competition between a liquid–liquid (L–L) demixing and solid–liquid (S–L) demixing. They concluded that the membrane pore structure was dominated by crystallization (S–L demixing), that is the thermodynamically favored demixing process.

Matsuyama et al.^{11,12} used a SC-CO₂ assisted phase inversion process to analyze the effect of several process parameters (temperature, pressure, and polymer concentration) on the pore size of polystyrene membranes¹¹ and the influence of the kind of solvent used in the formation of cellulose acetate membranes.¹²

Xu et al.,^{13,14} using a batch system, prepared polylactide (PLA) membranes and analyzed the effect of solvent used¹³ and of polymer concentration, depressurization rate, and nonsolvent composition¹⁴ on membranes cross section.

Using the SC-CO₂ assisted phase inversion method, Reverchon and Cardea studied the formation of cellulose acetate membranes from acetone,¹⁵ polysulfone membranes from *N*-methylpyrrolidone (NMP) and chloroform,¹⁶ poly-L-lactide (PLLA) membranes from chloroform,¹⁷ and Poly(methyl methacrylate) (PMMA) membranes from dimethylsulfoxide (DMSO), acetone, and tetrahydrofuran (THF).¹⁸ The overall result of these studies is that, changing the supercritical based process parameters, it is possible to modulate cell and pore size and to obtain various morphologies using the same liquid solvent: cellular structure, binodal structure, and microparticles. In some cases, it is also possible to modulate all membrane characteristics simply changing the nonsolvent power of SC-CO₂.

In the present study, we will evaluate the possibility to prepare and control the morphology of PVA membranes using the SC-CO₂ assisted phase inversion process, using DMSO and DMSO/acetone solutions. The effect of various process parameters on structure and morphology of membranes will be analyzed to verify the flexibility of the SC-CO₂ assisted process. An explanation of the results will be attempted, analyzing the mechanisms of membranes formation.

EXPERIMENTAL SECTION

Materials

PVA (average molecular weight 50,000), Dimethyl sulfoxide (DMSO), and acetone were bought from

Sigma-Aldrich (Milano, Italy); CO₂ (purity 99%) was purchased from S.O.N. (Società Ossigeno Napoli, Italy). All materials were processed as received.

Membranes preparation

Membranes are prepared in a laboratory apparatus (Fig. 1) equipped with a 316 stainless steel high-pressure vessel with an internal volume of 80 mL, in which SC-CO₂ contacts the polymer solution in a single pass. Membrane casting process is similar to the traditional procedure. Homogenous solutions of PVA are prepared by stirring the solution that is, then, placed in a membrane formation cell (steel caps with a diameter of 2 cm and height ranging between 200 and 400 μm) spreading it with a glass stick to control the thickness of the film. The cell is rapidly put inside the membrane preparation vessel to avoid the evaporation of the solvent. The vessel is, then, closed and filled from the bottom with SC-CO₂, up to the desired pressure using a high-pressure pump (Milton Roy-Milroyal B, Pont-Saint-Pierre, France). We operate in batch mode for 30 min; then, a micrometric valve is opened and the operation is performed in continuous mode; i.e., with a constant CO₂ flow rate of 1.5 kg/h. The phase-separated membrane is dried for 30 min. Pressure and temperature is holding constant during all the process. Then, the vessel is slowly depressurized for 10 min.

Membranes characterization

Scanning electron microscopy

PVA membranes are cryofractured using a microtome (Bio-optica S.p.A, Italy, Mod. Microm HM 550 OMVP); then, the sample is sputter coated with gold (at 30 mA for 180 s) and is analyzed by scanning electron microscope (SEM) (mod. LEO 420, Assing, Italy) to study cell and pore size and membrane structure.

Cell size analysis

Sigma Scan Pro 5.0 (Jandel scientific, San Rafael, Canada) and Origin 6 (Microcal, Northampton, USA) softwares are used to determine the average diameter of cells and pores and to calculate their distributions. We measured ~ 500 cells for each sample analyzed.

Using Origin software, we first represented a histogram with the percentage of the cells having a given diameter. Then, we performed a curve fitting to obtain the distribution curve.

Differential scanning calorimetry

Differential scanning calorimeter (DSC) traces of PVA membranes are obtained using a Mettler (mod. TC11,

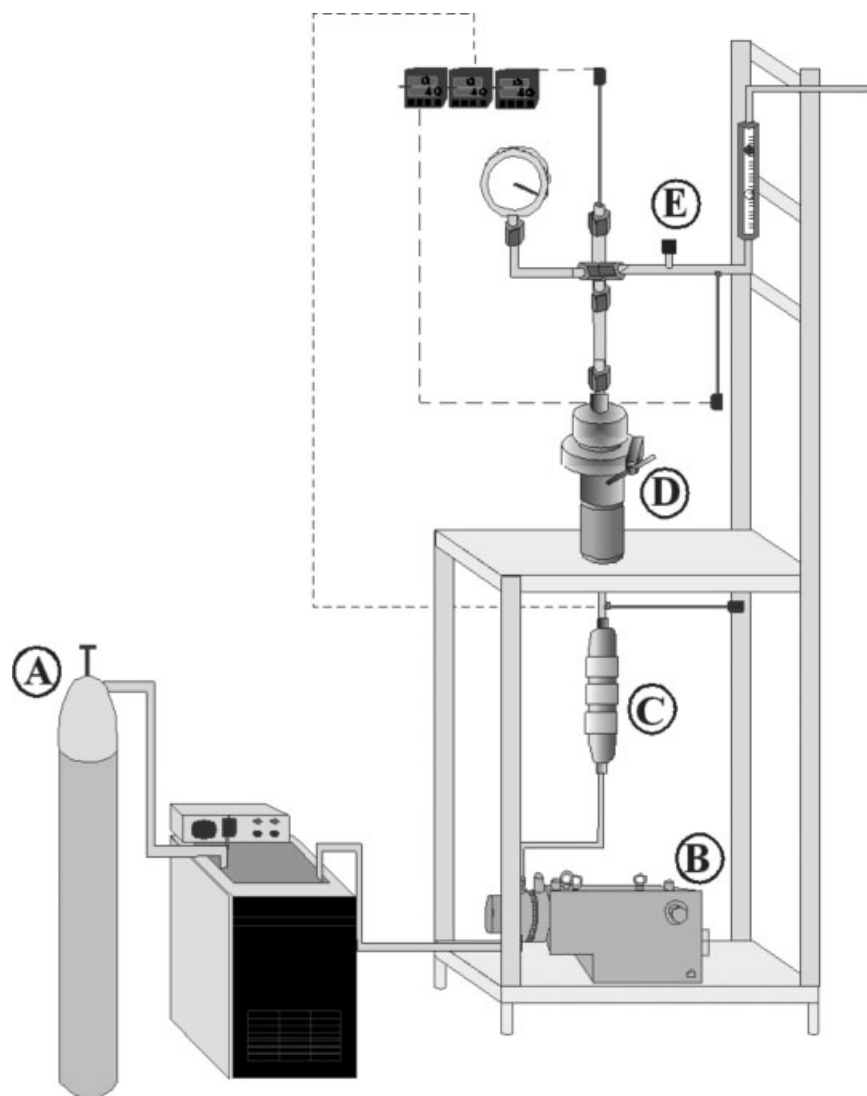


Figure 1 Schematic drawing of the process apparatus: (A) CO₂ tank; (B) high pressure pump for CO₂; (C) CO₂ pre-heater ($P_{\max} = 350$ bar, $T_{\max} = 300^{\circ}\text{C}$); (D) high pressure vessel ($P_{\max} = 350$ bar, $T_{\max} = 300^{\circ}\text{C}$); (E) micrometric valve.

Mettler Toledo, USA) DSC at a heating rate of $10^{\circ}\text{C}/\text{min}$ under a nitrogen atmosphere. The starting temperature of the analysis is 45°C , the ending temperature is 250°C and the nitrogen flow is 50 NL/min .

RESULTS AND DISCUSSION

In this work on PVA membranes, we focused our attention on their structure, characterized in terms of morphology and cells uniformity, size and distribution, and possible industrial applications. The operating conditions of the experiments performed are summarized in Table I.

Effect of polymer concentration

To evaluate the effect of polymer concentration, the experiments were performed at temperatures rang-

ing from 35 to 55°C and pressure from 100 to 200 bar, with PVA concentration in DMSO, ranging from 15 to 35% (w/w).

In the experiments performed at 35°C and 100 bar, we obtained membranes with a dense top thick layer, with a cellular internal structure (Fig. 2), and with a porous bottom surface. Increasing the percentage of polymer from 15 to 35% , a decrease of cell size can be qualitatively observed in Figure 3; whereas, the dense layer does not show appreciable changes. We measured cells size of these membranes using the procedures described in the membrane characterization paragraph and reported the results in Figure 4. This diagram confirms the qualitative observations performed: increasing the PVA percentage in the casting solution, the diameter of the cells decreases. The mean diameter varies from about 0.4 μm at 35% w/w to 2 μm at 15% w/w. The same

TABLE I
Summary of the Results on PVA Structures Formation

Solvent	<i>T</i> (°C)	<i>P</i> (bar)	CO ₂ density (Kg/m ³)	Polymer concentration (w/w) (%)	Morphology
DMSO	35	100	710	15	Dense + cellular
				25	Dense + cellular
				35	Dense + cellular
	45	100	497	15	Dense + cellular
				25	Dense + cellular
				35	Dense + cellular
	55	100	329	1	Cellular
				15	Dense
				25	Dense
	35	150	815	35	Dense
				15	Dense + cellular
				25	Dense + cellular
	45	150	741	35	Dense + cellular
				1	Bicontinuous
				15	Dense + cellular
	55	150	652	25	Dense + cellular
				35	Dense + cellular
				15	Dense + cellular
	35	200	866	25	Dense + cellular
				35	Dense + cellular
				1	Particles
	45	200	803	15	Dense + cellular
				25	Dense + cellular
				35	Dense + cellular
55	200	754	15	Dense + cellular	
			25	Dense + cellular	
			35	Dense + cellular	
DMSO/acetone w/w (65/20)	35	200	866	15	Skin + cellular
DMSO/acetone w/w (70/15)	55	100	329	15	Dense + cellular
DMSO/acetone w/w (80/5)	35	200	866	15	Skin + cellular

trend was observed at all the other experimental conditions indicated at the beginning of this chapter.

In the traditional phase inversion method, the modifications in the composition of the polymer–solvent–nonsolvent system are produced by mass transfer of the nonsolvent into the cast solution and of the solvent into the coagulation bath. They can be schematically reported in a ternary phase diagram indicating “composition paths,”^{19–21} as in Figure 5, where a qualitative ternary phase diagram is presented. It consists of a liquid–liquid (L-L) demixing gap, divided into a region of spinodal demixing, two regions of nucleation and growth located between the binodal and the spinodal curve and a gelation region are schematically reported. The arrows numbered from 1 to 4 report the different composition paths that can occur during membranes formation:

1. The concentration of the polymer in the ternary system increases because the outflow of the sol-

vent from the solution is faster than the inflow of the nonsolvent; the phase inversion does not occur and the polymer molecules solidifies by gelation or crystallization into a dense structure.

2. The ternary polymer solution becomes metastable; nucleation and growth of droplets of the polymer-lean phase occurs with further solidification of the polymer-rich phase, leading to a cellular structure;
3. The ternary polymer solution becomes unstable; spinodal phase separation with the subsequent solidification of the polymer-rich phase takes place, leading to the formation of a bicontinuous structure;
4. In this case nucleation and growth of droplets of the polymer-rich phase is obtained, followed by solidification of the polymer-rich phase; a beads-like (particulate) structure is obtained.

Translating these considerations to the phase inversion process assisted by supercritical CO₂, the

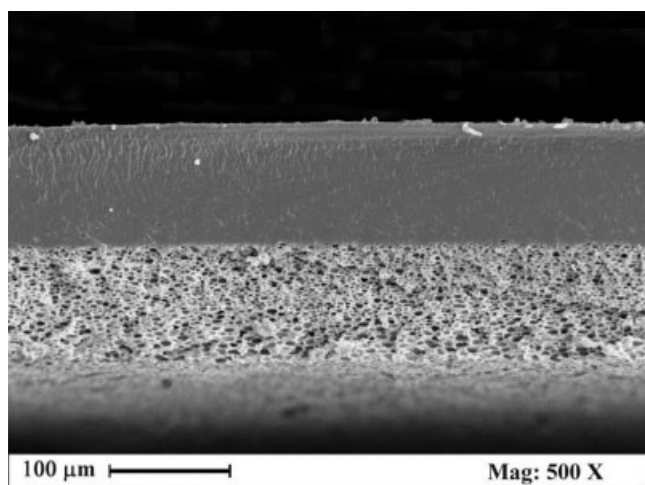


Figure 2 Complete cross section of the PVA membrane obtained at $P = 100$ bar, $T = 35^\circ\text{C}$ and 15% w/w in DMSO.

simultaneous presence of dense and cellular structure observed in the case of PVA membranes indicates that the competition between two different mass transport mechanisms occurs during the membrane formation process: the accumulation of polymer due to the outflow of the solvent (that causes the dense layer formation) and the L-L phase separation in the upper demixing gap (that leads to cellular structure). This result can be schematically represented considering the process in two consecutive steps. In a first step, the solvent outflows from the solution before the SC-CO₂ can cause the phase separation and the dense layer is generated. Subsequently, the outflow of the solvent is stopped by the dense layer formation, and SC-CO₂ diffuses inside the remaining solution causing the L-L phase separation that leads to cellular structure formation.

The effect of polymer concentration on cell size, can be related to the increase of the polymer concentration in the starting solution: the overall system viscosity increases, as a consequence, the polymer lean phase growth is arrested in a shorter time and smaller cells are generated (as it is possible to observe in Fig. 4).

Summarizing, PVA membranes produced until now in this study are characterized by two different coexisting morphologies: dense and cellular structure. From an industrial point of view, these membranes could be useful for specific separation processes such as gas separation. Indeed, the double-morphology structure assures both high flexibility (because of cellular sublayer) and a selective barrier to gas transport (because of dense layer).

However, other applications require the use of dense films (pervaporation processes; i.e. separation of azeotropic mixtures), or of porous membranes; i.e., membranes characterized by thin dense skin ($< 10 \mu\text{m}$) or by porous skin, that could be useful

for microfiltration, nanofiltration, ultrafiltration, and reverse osmosis processes.

Effect of SC-CO₂ density

In this series of experiments, we processed PVA-DMSO solutions with polymer concentrations rang-

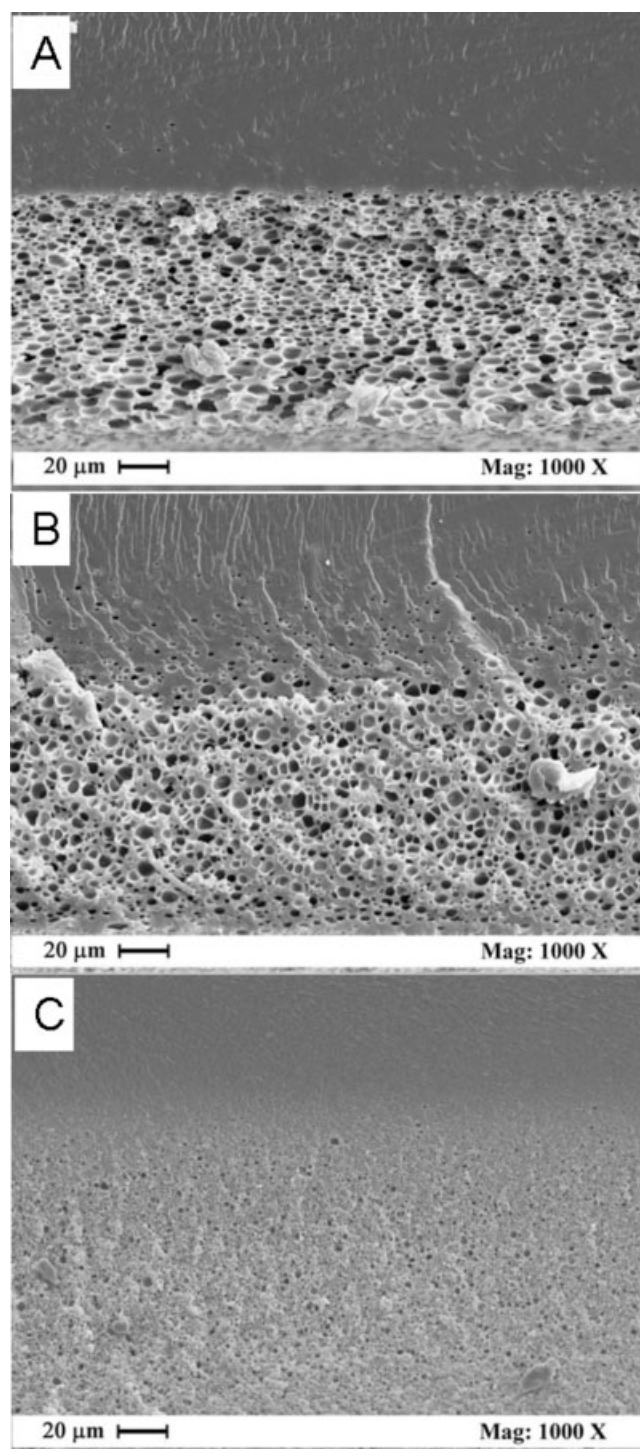


Figure 3 Effect of the polymer concentration on membrane sections at $P = 100$ bar, $T = 35^\circ\text{C}$ and (A) 15% w/w, (B) 25% w/w, (C) 35% w/w, in DMSO.

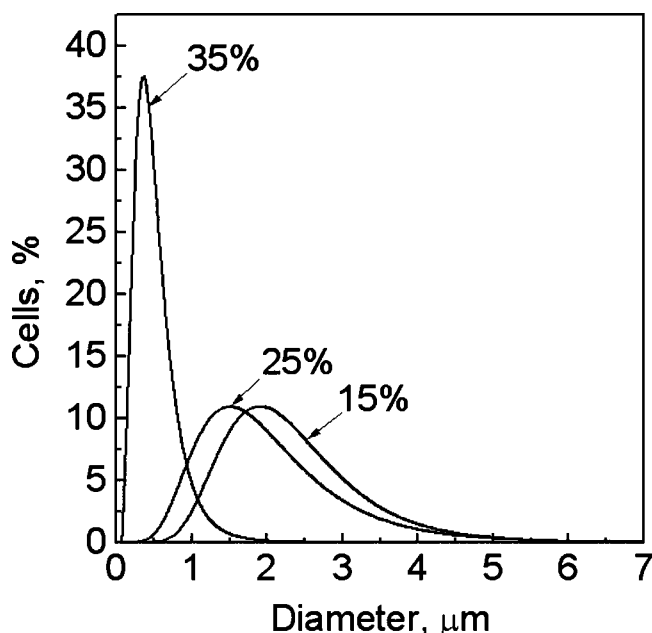


Figure 4 Cell size distribution at different polymer concentrations obtained operating at 35°C and 100 bar.

ing from 15 to 35% (w/w) and analyzed the effect of SC-CO₂ on membranes structure and cell size, operating at 100 bar 55°C (329 kg/m³), 150 bar 45°C (741 kg/m³), and 200 bar 35°C (866 kg/m³). Observing SEM images in Figure 6, it is clear that membranes morphology changes by increasing the nonsolvent density (i.e. SC-CO₂ solvent power): operating at 25% w/w and at 100 bar, 55°C a dense film structure is obtained [Fig. 6(A)]; but, operating at 150 bar 45°C and 200 bar 35°C at the same concentration, structures formed by a dense thick layer and cellular sublayer are obtained [Fig. 6(B)].

These experiments confirm that, changing SC-CO₂ solvent power, it is possible to modify substantially the PVA membrane formation mechanism. Considering again a qualitative phase diagram for the system PVA/DMSO/SC-CO₂ reported in Figure 7, it is possible to hypothesize that, when the process is slower (i.e. at lower SC-CO₂ solvent power), the outflow of the solvent from the solution is favored and the trajectory of the pathway moves towards the pure polymer vertex and does not "enter" in the miscibility gap (Path 1), leading to a direct accumulation of polymer [i.e. dense structure formation—Fig. 6(A)]. When the process is faster (i.e. at higher SC-CO₂ solvent power) the outflow of the solvent from the solution is limited and the trajectory of the pathways "enters" in the upper demixing gap (between spinodal and binodal curves) (Path 2) producing a cellular structure in the sublayer [morphology in Fig. 6(B)].

A confirmation of the influence of SC-CO₂ solvent power on the kinetics of the process has been

obtained by DSC analysis. In Figure 8, the fusion peaks of the membranes obtained at 200 bar, 35°C and 25% w/w and at 100 bar, 55°C and 25% w/w are shown. The endothermic peaks at about 100°C are related to the evaporation of water absorbed by the membranes (PVA is very hydrophilic). The endothermic peaks located at about 190°C are related to the fusion temperature of membranes. From the integration of these peaks we calculated the heats of fusion:

$$\Delta H_{200 \text{ bar } 35^\circ\text{C}} = 24.3 \text{ J/g}$$

$$\Delta H_{100 \text{ bar } 55^\circ\text{C}} = 41.4 \text{ J/g}$$

This information suggests that membranes obtained at 200 bar and 35°C present a lower degree of crystallinity than membranes obtained at 100 bar 55°C. This data confirms that, operating at higher SC-CO₂ solvent power, the process is faster and the crystallization is limited.

To gain further information on the influence of SC-CO₂ solvent power on the morphologies of PVA structures, other experiments have been performed in the extreme case of 1% w/w PVA-DMSO solutions. We again tested various sets of process parameters from 100 bar 55°C (329 kg/m³) to 200 bar 35°C (866 kg/m³). As shown in Figure 9, in this case structures morphology changes completely by increasing SC-CO₂ density: at 100 bar 55°C, a mem-

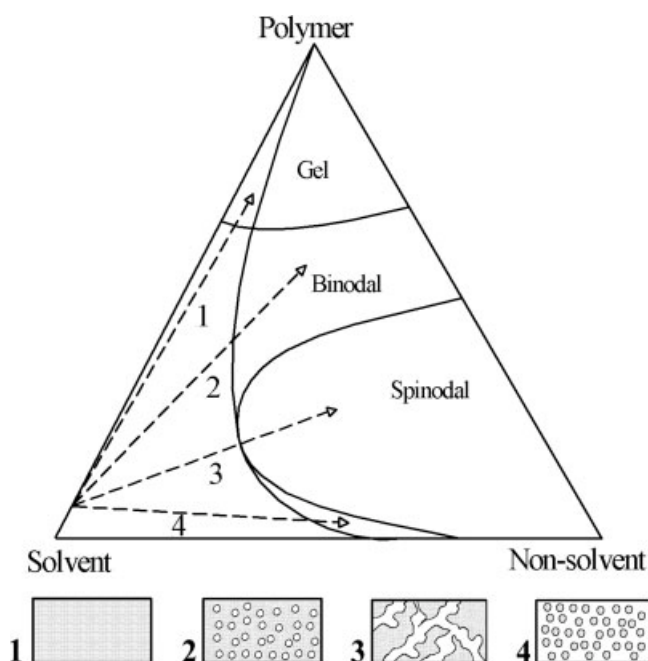


Figure 5 Ternary phase diagram of a generic polymer/solvent/nonsolvent system with various composition paths indicated by arrows and numbers; the typical membrane structures related to the composition paths are also reported.

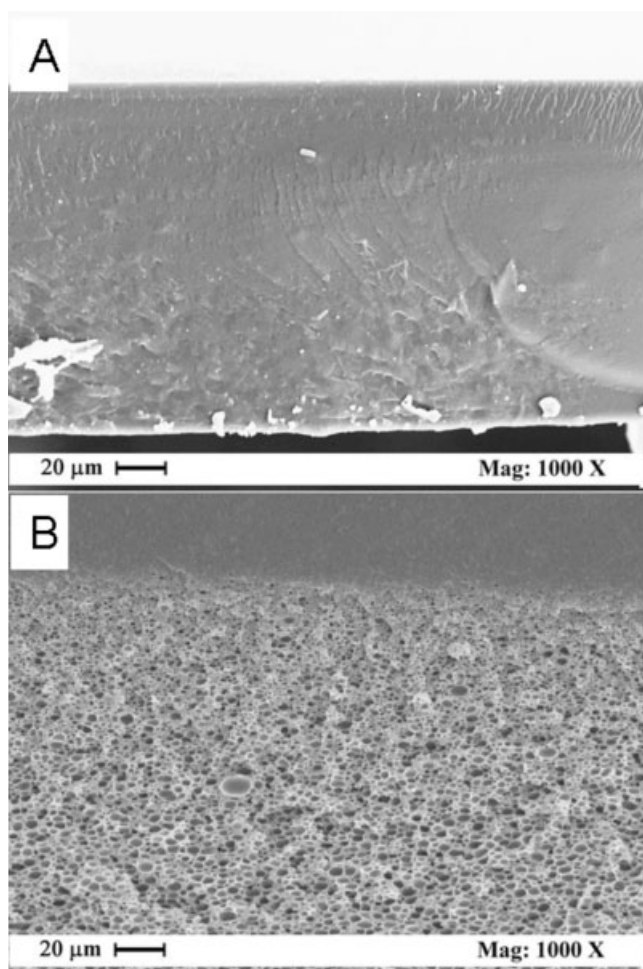


Figure 6 Effect of supercritical CO₂ density on PVA membranes morphology at 25% w/w in DMSO, operating at: (A) 100 bar, 55°C (329 kg/m³); (B) 200 bar, 35°C (866 kg/m³).

brane with a cellular structure is obtained [Fig. 9(A)]; at 150 bar 45°C, the structure becomes bicontinuous [Fig. 9(B)] and is formed by filaments and crosslinked microparticles; at 200 bar 35°C, a membrane is not formed but well-defined spherical submicroparticles are generated with a diameter ranging between 0.2 and 0.7 µm [Fig. 9(C)].

Again, it is possible to explain these results representing the various composition paths on the qualitative ternary phase diagram, reported in Figure 10. When the pressure is high (200 bar) and the temperature is low (35°C), the outflow of the solvent from the solution is limited and the trajectory of the pathways moves towards the pure antisolvent vertex leading to microparticles formation (Path 1) [Fig. 9(C)]; decreasing pressure (150 bar) and increasing temperature (45°C), the process becomes slower and the pathway “enters” in the central region of demixing gap (part of the solvent is lost by outflowing) leading to bicontinuous structures (Path 2) [Fig. 9(B)].

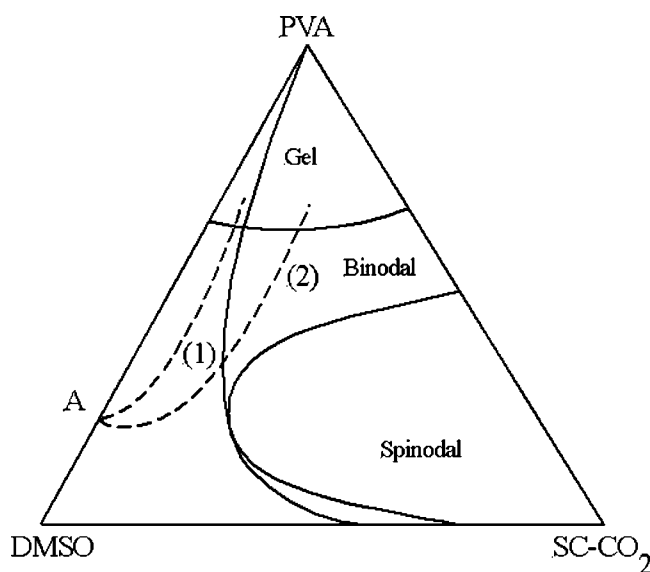


Figure 7 Qualitative ternary diagram with different formation pathways depending on process conditions: (1) 100 bar, 55°C, (2) 200 bar, 35°C.

Further, decreasing pressure (100 bar) and increasing temperature (55°C), the outflow of the solvent increases and the pathway “enters” inside the upper demixing gap (between spinodal and binodal curves) leading to a cellular structure (Path 3) [Fig. 9(A)].

All these results confirm the versatility of the process and the possibility to obtain different morphologies, varying the process parameters, and, in particular, dense films. On the contrary, it has not

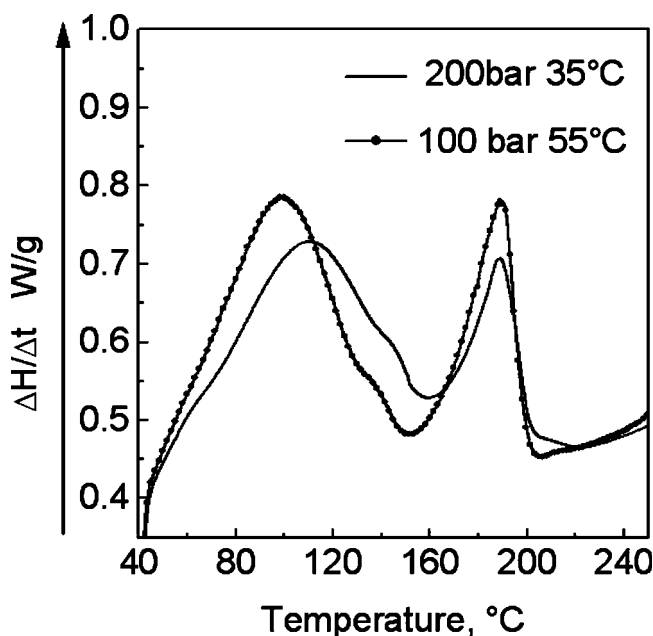


Figure 8 DSC analysis performed on PVA membranes obtained at different process conditions: 200 bar 35°C and 100 bar 55°C (25% w/w).

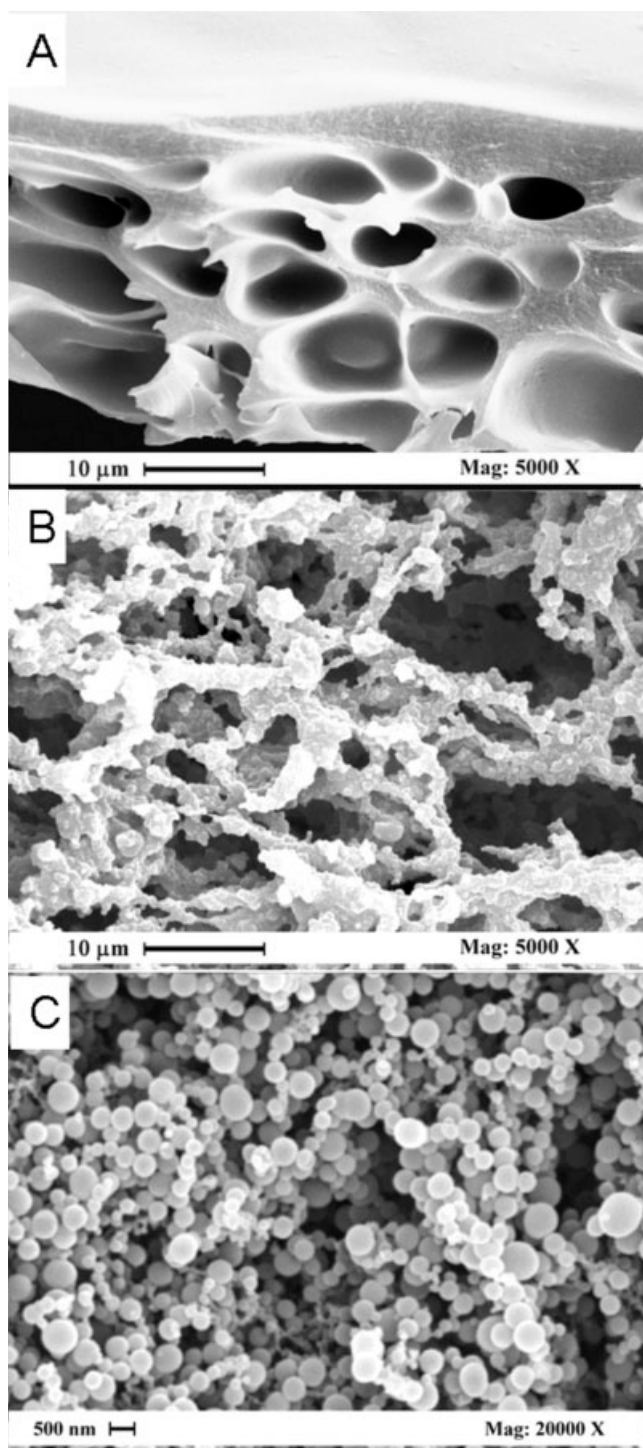


Figure 9 Effect of supercritical CO_2 density on membrane morphology and cell size at 1% w/w in DMSO, operating at: (A) 100 bar, 55°C (329 kg/m^3); (B) 150 bar, 45°C (741 kg/m^3); (C) 200 bar, 35°C (866 kg/m^3).

been possible to produce asymmetric porous membranes (membranes with skin layer thinner than 10 μm and a porous sublayer) or symmetric porous membranes (membranes without the skin layer), probably because the demixing process rate has not

been sufficiently fast to limit the dense layer formation.

In a previous study,¹⁷ we evaluated the affinity between SC-CO_2 and various organic solvents, finding that acetone presents the highest affinity for SC-CO_2 . As a consequence, we decided to use acetone as an additive in the casting solution with the aim of enhancing the demixing process rate and to reduce, consequently, the dense layer formation.

Effect of acetone in DMSO

In this series of experiments, we evaluated the effect of the presence of acetone in the starting DMSO based solution. We tested solutions with different DMSO/acetone ratios maintaining the polymer concentration constant (at 15% w/w). In Figure 11(A,B), SEM images of PVA membranes obtained at the same operative conditions (200 bar and 35°C) starting from a PVA-DMSO solution (15/85 w/w) and a PVA-DMSO-acetone solution (15/65/20 w/w) are reported. The membrane shown in Figure 11(A) is similar to those presented before and is characterized by two different regions: a dense layer of about 100 μm and a cellular sublayer. On the contrary, observing the membrane obtained starting from DMSO-acetone solutions [Fig. 11(B)], the cellular structure is dominant and the dense layer is strongly reduced (< 10 μm), as it is well shown at a higher magnification in Figure 12; i.e. an asymmetric porous membrane has been generated.

This result confirm the effect of acetone addition on the kinetics of phase separation process. As discussed earlier, the affinity between SC-CO_2 and

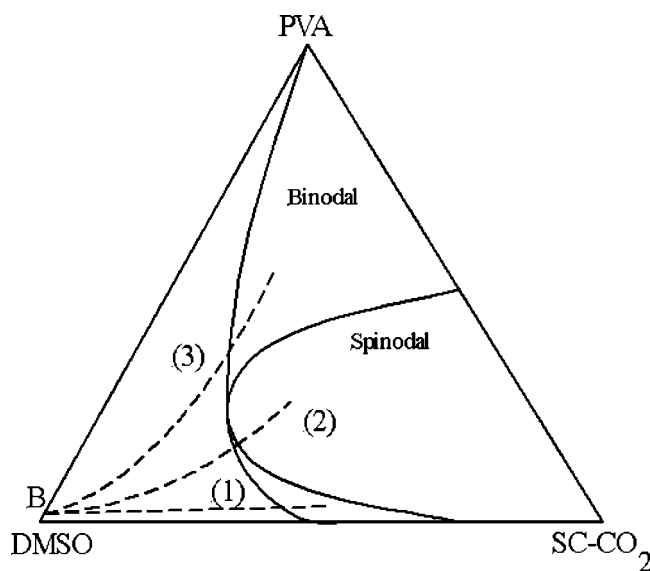


Figure 10 Qualitative ternary diagram with different formation pathways depending on process conditions: (1) 200 bar 35°C, (2) 150 bar 45°C, (3) 100 bar 55°C.

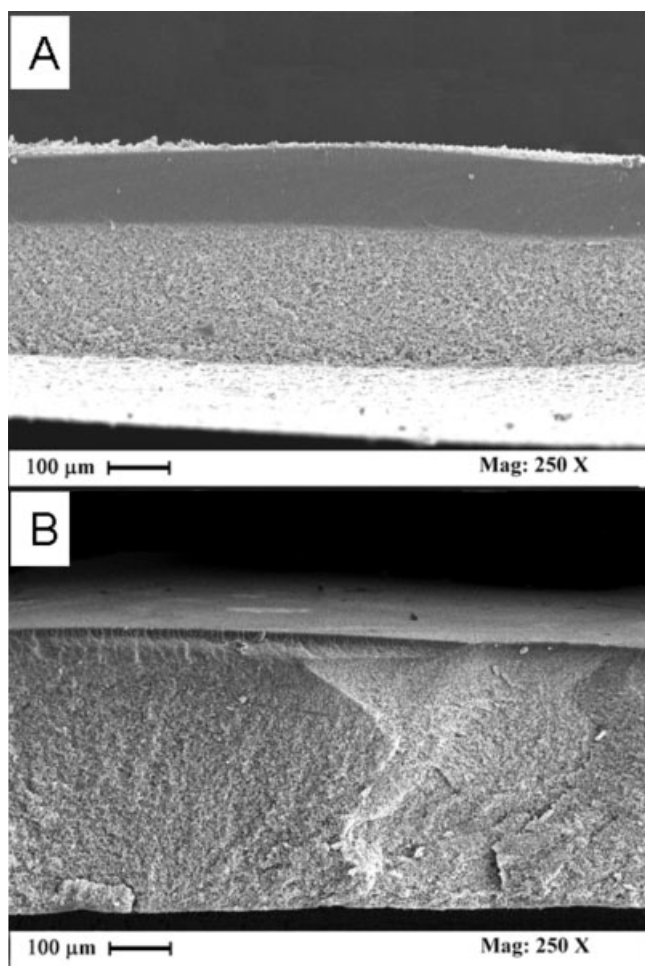


Figure 11 Comparison between PVA membranes morphology and cell size obtained at 200 bar and 35°C starting from: (A) PVA-DMSO solution (15/85 w/w) and (B) PVA-DMSO-acetone solution (15/65/20 w/w). In the second case a very thin nonporous top layer has been obtained.

acetone is higher than between SC-CO₂ and DMSO; as a consequence, when we add acetone in the starting solution, phase separation process is faster, limiting the outflow of the solvent, and as a consequence, the skin layer formation.

We also measured cells size of these membranes using the procedures described in the membrane characterization paragraph and reported the results in Figure 13. Cells size distributions put in evidence that when acetone is present in the casting solution, the cell size decreases. This result is related to the mechanism of cells formation. It consists of the nucleation of the polymer lean phase inside the polymer rich phase; as a consequence, it is possible to make a parallelism between this process and the crystallization from a solution. In the case of crystallization, there is a competition between the rate of nucleation and the rate of crystal growth. The parameter that determines which is the controlling mechanism is the supersaturation of the solute in the solution. When

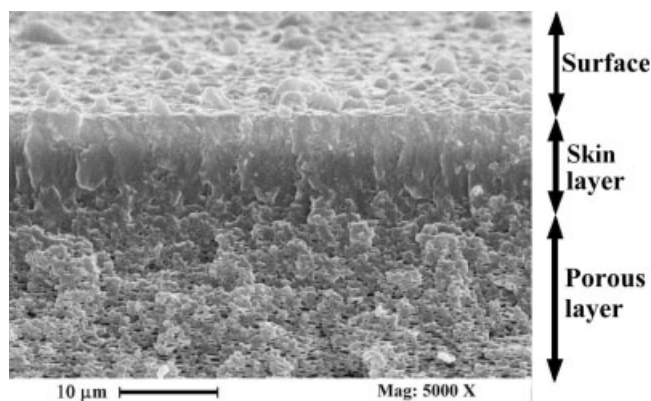


Figure 12 Enlargement of Figure 11(B) representing the skin layer of membranes obtained using PVA-DMSO-acetone (15/65/20) solution at 200 bar and 35°C.

the supersaturation is high, the crystals nucleation process is faster: numerous nuclei are formed and the solute concentration decrease rapidly, i.e. nuclei growth is limited. On the contrary, when the supersaturation is low, few nuclei are formed but their growth is favored. In the first case many small crystals are formed, in the second case, few larger crystals are formed. Considering the SC-CO₂ driven phase separation process, the key parameter is the amount of SC-CO₂ that solubilizes inside the solution during the process. Indeed, it determines the amount of nuclei of polymer lean phase formed. When the solution contains acetone, SC-CO₂ solubilizes rapidly in the casting solution leading to the formation of

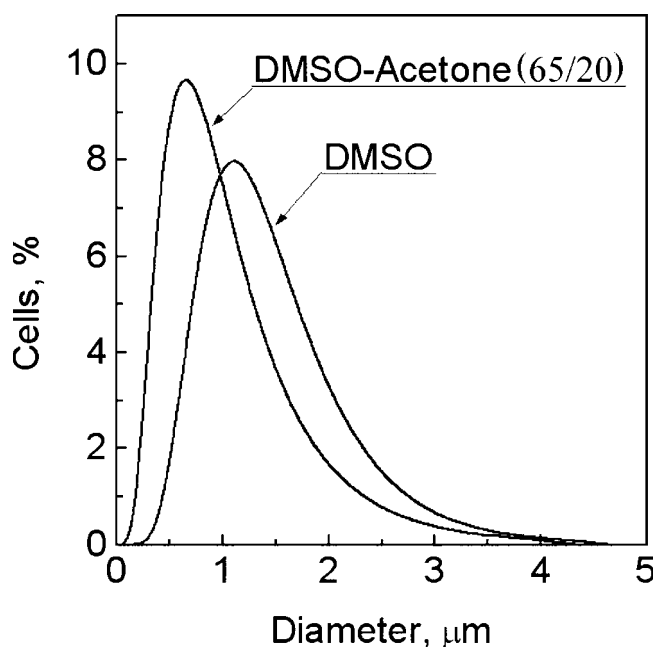


Figure 13 Comparison between cell size distributions obtained operating at 15% w/w polymer, 35°C and 200 bar and starting from different liquid solutions.

numerous nuclei, i.e., smaller cells are formed. On the contrary, when no acetone is present, few nuclei are formed and their growth is favored, i.e. larger cells are generated.

CONCLUSIONS

PVA membranes have been successfully produced using the SC-CO₂ assisted phase inversion method. The results obtained confirmed the versatility of the process; indeed, changing the process conditions, it has been possible to modulate cell size and membranes morphology (from dense films to microparticles). We also obtained porous membranes adding acetone to the starting solution.

References

- Zhang, W.; He, G.; Gao, P.; Chen, G. *Sep Purif Technol* 2003, 30, 27.
- Amanda, A.; Kulprathipanja, A.; Toennesen, M.; Mallapragada, S. *J Membr Sci* 2000, 176, 87.
- Mallapragada, S.; Peppas, A.; Colombo, P. *J Biomed Mater Res* 1997, 36, 125.
- Liu, Q.; Chen, H.; Jia, P. *J Membr Sci* 1999, 159, 233.
- Liu, Q. L.; Li, Q. B. *J Membr Sci* 2002, 202, 89.
- Young, T. H.; Yao, N. K.; Chang, R. F.; Chen, L. W. *Biomaterials* 1996, 17, 2139.
- Chuang, W. Y.; Young, T. H.; Chiu, W. Y.; Lin, C. Y. *Polymer* 2000, 41, 5633.
- Chuang, W. Y.; Young, T. H.; Chiu, W. Y. *J Membr Sci* 2000, 172, 241.
- Yu, J.; Lee, C. H.; Hong, W. H. *Chem Eng Process* 2002, 41, 693.
- Kho, Y. W.; Kalika, D. S.; Knutson, B. L. *Polymer* 2001, 42, 6119.
- Matsuyama, H.; Yamamoto, A.; Yano, H.; Maki, T.; Teramoto, M.; Mishima, K.; Matsuyama, K. *J Membr Sci* 2001, 194, 157.
- Matsuyama, H.; Yamamoto, A.; Yano, H.; Maki, T.; Teramoto, M.; Mishima, K.; Matsuyama, K. *J Membr Sci* 2002, 204, 81.
- Xu, Q.; Pang, M.; Peng, Q.; Li, J.; Jiang, Y. *J Appl Polym Sci* 2004, 94, 2158.
- Xu, Q.; Pang, M.; Peng, Q.; Li, J.; Jiang, Y.; Wang, H.; Zhu, M. *J Appl Polym Sci* 2005, 98, 831.
- Reverchon, E.; Cardea, S. *J Membr Sci* 2004, 240, 187.
- Reverchon, E.; Cardea, S. *J Supercrit Fluids* 2005, 35, 140.
- Reverchon, E.; Cardea, S. *Int J Artif Organs* 2005, 28, 538.
- Reverchon, E.; Schiavo Rappo, E.; Cardea, S. *Polym Eng Sci* 2006, 46, 188.
- Stropnik, C.; Germic, L.; Zerial, B. *J Appl Polym Sci* 1996, 61, 1821.
- Stropnik, C.; Musil, V.; Brumen, M. *Polymer* 2000, 41, 9227.
- Stropnik, C.; Kaiser, V. *Desalination* 2002, 145, 1.