

Morphology Evolution of Poly(vinylidene fluoride) Membranes during Supercritical CO₂ Assisted Phase Inversion*

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Abstract A supercritical carbon dioxide (ScCO₂) assisted phase inversion was developed to produce microporous poly(vinylidene fluoride) (PVDF) membranes whose morphology characteristics arise from both liquid-liquid demixing and solid-liquid demixing (crystallization). This result was confirmed by Fourier transform infrared spectroscopy (FTIR), from which both α and β crystals were found. As revealed by contact angle experiment, the PVDF membranes prepared *via* ScCO₂ assisted phase inversion were more hydrophobic compared with the control membrane produced *via* conventional immersion-precipitation technique. In particular, the sample with 15 wt% PVDF prepared at 45 °C and 13 MPa exhibited a contact angle of 142°, which was mainly caused by the multilevel micro- and nano- structure. The effects of polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP) and lithium chloride (LiCl) on the structures and crystal form were investigated. PVP promoted the formation of α phase crystal form, while PEG boosts the evolution of β phase. LiCl restrained the crystallization degree of PVDF membrane under ScCO₂.

Keywords: Poly(vinylidene fluoride); Supercritical carbon dioxide; Morphology; Hydrophobic; Micro-structure.

INTRODUCTION

Semi-crystalline polyvinylidene fluoride (PVDF) has been widely applied to produce ultrafiltration and microfiltration membranes with regard to its outstanding properties such as high mechanical strength, thermal stability, chemical resistance and high hydrophobicity^[1–8]. Porous polymeric membranes are mostly produced by non-solvent induced phase separation (NIPS) and thermally induced phase separation (TIPS)^[9]. In both processes, either organic solvents or diluents are needed and most of them are toxic or even carcinogenic. Besides, the reclamation of such solvents or diluents is also usually energy consuming^[10]. Moreover, the post treatment process is regarded as a time-consuming process with limited versatility to modulate pore size and membrane morphology^[11].

Therefore, an environmental benign supercritical carbon dioxide (ScCO₂) induced phase separation taking the place of non-solvent has been reported as a green technique^[2, 12–16]. Comparing with the traditional phase inversion process, ScCO₂ assisted phase separation technique possessed several unique advantages. First, the diverse porous structures of the produced membranes could be maintained perfectly without the collapse of the structure due to the absence of a liquid-vapor interface and the macrovoids or finger-like structure could also be avoided (which are usually taken place *via* immersion-precipitation technique). Second, the morphological

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structures of the membranes are accessible to be continuously modulated based on the mutual affinity between CO₂ and organic solvent by varying the temperature and/or pressure. Last, the dry porous membrane could be obtained in one single step without any further post treatment, and even the residual solvent will be extracted and reclaimed by ScCO₂.

Kim *et al.* produced polycarbonate membranes with high tearing stress and porosity through ScCO₂ assisted phase inversion^[17]. The phase inversion rate was defined and evaluated by the polyethylene glycol (PEG) removed by ScCO₂. It was found that the relationship between porosity and tearing stress was close and porosity should be increased in order to enhance tearing stress of polycarbonate membranes with porous structure.

Using ScCO₂ as a non-solvent, Matsuyama prepared porous cellulose acetate membranes and investigated the effect of the solvent on the membrane structure^[16]. The result showed that macrovoids could be avoided despite the organic solvents, although the phase separation occurred instantaneously after CO₂ was introduced. The membrane porosity and the average pore size near the center position increased, as the mutual affinity between the organic solvent and ScCO₂ decreased.

Cao produced microporous poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) membranes without macrovoids using ScCO₂ as the non-solvent^[2]. These membranes exhibited sponge-like pore structure. The average pore size increased with increasing CO₂ pressure and temperature, but decreased with increasing PVDF-HFP concentration. Huang revealed that morphologies of PVDF membranes were dependent on the polymer concentration in the casting dope. Addition of poly(methyl methacrylate) (PMMA) in the casting dope changed the membrane structure significantly. For instance, when PMMA concentration in the dope was above 4.5 wt%, the cell wall was composed of continuous matrix, comparatively, the cell wall was still composed of uniform spherulite particles in case of pure PVDF membrane^[14].

Different from above studies, the objective of this work is to investigate morphological evolution mainly regulated and controlled by additive polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP) and inorganic salt lithium chloride (LiCl), and besides, the influences of temperature, pressure and polymer concentration on membranes were also investigated in detail. The crystalline form and hydrophilicity were performed as well.

EXPERIMENTAL

Materials

PVDF (FR904) was supplied by Shanghai 3F New Material Co., Ltd. China. PVP ($M_n = 8000$) and LiCl were supplied by Shanghai Aladdin Chemistry Co., Ltd. China. They were dried at 80 °C in a vacuum oven for 24 h before use. PEG ($M_n = 600$) and analytical reagent *N,N*-dimethylformamide (DMF), which was used as the solvent for PVDF, were supplied by Sinopharm Chemical Reagent Co., Ltd. China. Carbon dioxide with a purity of 99% was supplied by Wanli Gas of Ningbo, China. All chemicals were used as received.

Membrane Preparation

The experimental apparatus used in our study was similar to that described by Matsuyama *et al.*^[18, 19]. Different amounts of PVDF with or without additive (PVP, PEG and LiCl) was dissolved in DMF at 60 °C and stirred at a constant speed for 24 h to achieve a homogenous casting solution, which was subsequently kept still overnight to remove air bubbles and then cast uniformly onto a clean polyimide film (diameter = 30 mm) using a casting knife with a knife gap of 200 μm. Afterwards the polyimide film was rapidly transferred into a high pressure vessel which was preheated to the settled temperature. This process was finished within 1.5 min for the sake of solvent evaporation. The vessel was immediately filled with CO₂ until the required pressure which was attained using a high-pressure pump as soon as the sealing was accomplished. The vessel was held for 1 h at the desired temperature and pressure, and thereafter, the system was performed in a continuous mode for another 1 h so as to ensure complete drying of the membrane. Finally the vessel was slowly depressurized for about 1 h to collect the white and opaque membrane. Preparation conditions of all PVDF membranes are listed in Table 1.

Table 1. Preparation conditions of all PVDF membranes

Membrane sample	Temperature (°C)	Pressure (MPa)	PVDF (content wt%)	PEG (content wt%)	PVP (content wt%)	LiCl (content wt%)
M1	40	13	15	—	—	—
M2	45	13	15	—	—	—
M3	50	13	15	—	—	—
M4	45	18	15	—	—	—
M5	45	8	15	—	—	—
M6	45	8	18	—	—	—
M7	45	8	20	—	—	—
M8	45	8	16	2	—	—
M9	45	8	16	—	2	—2
M10	45	8	16	—	—	—

Membrane Characterization

Morphological structures of the prepared PVDF membranes were examined by a scanning electron microscope (SEM, S-4800, Hitachi, Japan) with an accelerating voltage of 4.0 kV and 7 μ A. The cross-section of the membranes was fractured in liquid nitrogen. Both surface and cross-section of the samples were gold sputtered for 2 min before observation.

An atomic force microscope (AFM, Veeco Dimension 3100V, US) was also used to further study the surface topography of the membranes. All membranes were fixed on the magnetic disk and then attached to a magnetic sample holder, finally located on top of the scanner tube. The laser beam of the AFM was focused on the pre-selected spot of the surface prior to the engagement of the cantilever. AFM images were carried out in the tapping mode with silicone tip cantilevers having a force constant of 20 mN/cm, and an arithmetic mean of the surface roughness (R_a) was calculated from the roughness profile determined by AFM.

The melt temperature and crystallinity of the formed membranes were determined by a differential scanning calorimeter (DSC, Pyris Diamond, Perkin Elmer, US) equipped with a cooling apparatus under a nitrogen atmosphere at a heating rate of 10 K/min over the range of 30–250 °C. The flow rate of nitrogen gas is 15 mL/min. In each measurement, approximately 7.0 mg sample was sealed in an aluminum pan and placed in the heating chamber together with an empty pan which was used as a reference. Melting temperature (T_m) and heat of fusion (ΔH_f) were determined from the melting endotherms. Crystallinity of membrane was calculated by dividing the measured ΔH_f by the value of perfect PVDF crystal ($\Delta H_0 = 105$ J/g) reported in the literature^[20].

The hydrophilicity of the formed membranes was evaluated by water contact angle measurements using a contact angle meter (OCA20, Dataphysics, Germany). During the measurement, 2 μ L deionized water was dropped onto the top surfaces of the membranes using a micro-syringe automatically, the images were captured by a digital camera. Each membrane was measured at least 5 times at different surface locations, and the mean value was calculated.

The crystal form was detected by Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet 6700, US) over a range of 4000–400 cm^{-1} .

RESULTS AND DISCUSSION

Formation Mechanism of PVDF Membranes by ScCO_2 Assisted Phase Inversion

In our study, the casting solution was spread uniformly on a polyimide film, and the polyimide film was transferred to a high pressure vessel which was preheated to the settled temperature immediately. During this course, some amounts of organic solvent were evaporated inescapably and a polymer concentration gradient took place, and as a result, usually a dense top surface and a porous bottom surface were formed. Then the vessel was filled with CO_2 to the required pressure and thus generated the exchange between organic solvent and CO_2 . CO_2 could be considered as non-solvent because it was unable to dissolve PVDF even at 300 °C and 275 MPa^[21]. In this process, both liquid-liquid demixing and crystallization contributed to the formation of diverse microporous structure^[22], which will be fully discussed later on. In general, the liquid-liquid demixing process leads to

cellular pores whereas the crystallization engenders interlinked crystalline particles. Macrovoids and finger-like pores can usually be eliminated in ScCO₂ assisted phase inversion, which is different from conventional immersion precipitation using water as non-solvent^[23]. As shown in Table 1, various experiments were carried out to access the effects of temperature, pressure and polymer composition on the morphology and crystal form of the membranes.

Morphology Evolution of PVDF Membrane by ScCO₂ Assisted Phase Inversion

The effect of temperature on the morphology of PVDF membranes

Figure 1 shows the morphology evolution of the membranes prepared at different temperatures. From the cross section part, none finger-like pores or macrovoids are found in all cases. M1 demonstrated bi-continuous interconnected pores about 2 μm in the cross section, and both top and bottom surfaces are quite dense, which were caused by liquid-liquid demixing by nucleation and growth of the droplets of a polymer lean phase^[24]. It is worth mentioning that M2 prepared at 45 °C exhibited complete interlinked PVDF crystalline particles in both cross section and membrane surfaces mainly generated by crystallization, and skin layer was totally eliminated, which is entirely different from the reported result^[14]. They only obtained 1 μm cellular pores in PVDF membranes, just like what obtained in our case of M3. Liquid-liquid phase separation took place first to form the cellular pores around 4 μm , and crystallization coarsening happened thereafter to form the crystalline particle structure on the cellular pore walls. The evaporation of the solvent caused the polymer concentration gradient and therefore a dense top surface and a porous bottom surface were formed in M3. Actually, all three membranes had experienced crystallization during the phase separation. DSC results in Table 2 show that M1, M2 and M3 obtained crystallinity of 34%, 34% and 44%.

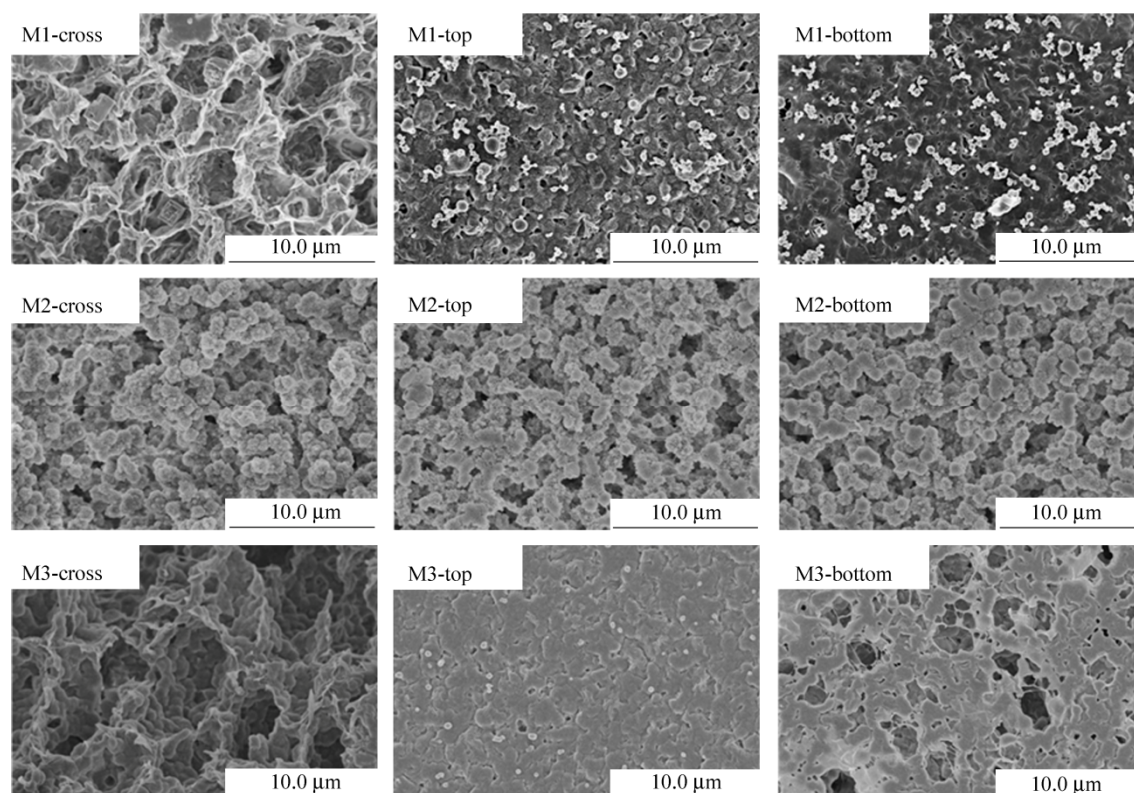


Fig. 1 SEM images of PVDF membranes M1, M2 and M3 prepared at 40, 45 and 50 °C respectively

Table 2. Melting temperature and crystallinity of the membranes

Membrane sample	T_m (°C)	ΔH_f (PVDF) (J/g)	Crystallinity (%)
M1	164.53	36.06	34
M2	166.17	35.83	34
M3	164.19	45.93	44
M4	165.01	40.81	39
M5	164.51	38.62	37
M6	164.61	39.03	37
M7	164.72	41.09	39
M8	166.37	42.22	40
M9	160.51	34.28	33
M10	— ^a	24.78	24
PVDF powder	160.23	38.46	37

^a No defined melting temperature of M10 is measured

The effect of pressure on the morphology of PVDF membranes

Figures 1 and 2 show the morphology of M4, M2 and M5 prepared at 18, 13 and 8 MPa respectively. It can be seen that the pore size in cross section decreased with increasing the pressure from 8 MPa to 18 MPa. The pressure variation is closely related to the solubility power of ScCO_2 . As pressure increased, the affinity of ScCO_2 to the organic solvent was enhanced, the liquid-liquid demixing was accelerated, which resulted in the formation of smaller bi-continuous pores due to the nucleation of polymer lean phase^[11, 25]. For M5, the mean size of cellular pores surrounded by interlocked particulate crystallites in cross-section is around 6–10 μm ; whereas for M4, the mean size of bi-continuous pores decreased around 1 μm . It is obvious that M4 prepared at higher pressure demonstrated a more porous surfaces and higher connectivity than other samples (M2 and M5) prepared at lower pressures, which was also attributed to the competition between liquid-liquid demixing and crystallization. The diffusion of ScCO_2 to solvent and extraction of solvent by ScCO_2 determined the variation of polymer concentration gradient at the interface and regulated the pathway evolution in the ternary diagram, and mainly controlled kinetics of phase inversion.

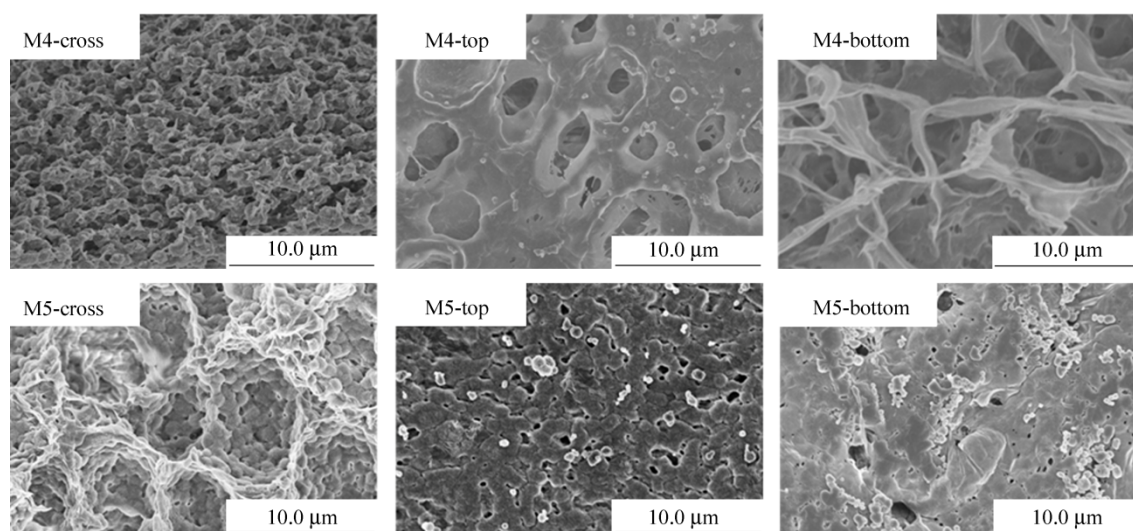


Fig. 2 SEM images of PVDF membranes M4 and M5 prepared at 18 MPa and 8 MPa respectively

The thickness of membrane prepared during ScCO_2 induced process and traditional NIPS method was investigated taking M0, M4 and M5 as examples, see in Fig. 3. M0 obtained a thickness around 90 μm , whereas membranes produced during ScCO_2 induced process owned a widely varied thickness at different operating conditions. At high pressure, the solubility power of ScCO_2 is strong, thus the solidification of membrane can be

finished in a short time and pores lack enough time to grow, relatively small pores are obtained, leading M4 a decreased thickness ($\sim 40\ \mu\text{m}$). Compared with initial liquid membrane ($200\ \mu\text{m}$), the thickness nearly shrinks to one fifth. In the case of low pressure (8 MPa), weaker solubility power of ScCO_2 leading to a low exchange rate between non-solvent and solvent. Thus, pores of M5 get longer time to expand and larger thickness about $130\ \mu\text{m}$ observed. The result once again reveals that membrane morphology can be modified by ScCO_2 easily.

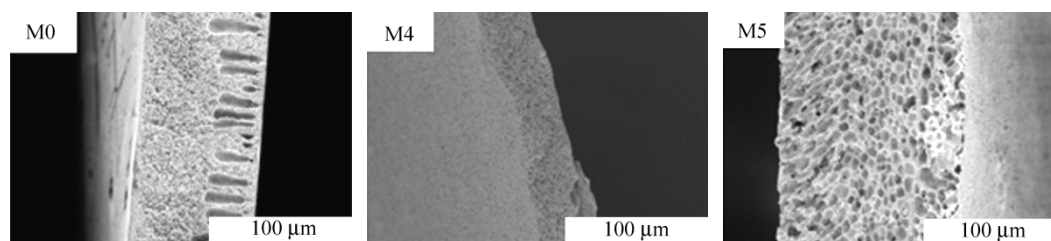


Fig. 3 SEM images of whole cross-section for M0, M4 and M5 (M0 is a control sample prepared *via* immersion-precipitation technique: 15 wt% PVDF in DMF, and $45\ ^\circ\text{C}$ H_2O as coagulation bath.)

The effect of additives on the morphology of PVDF membranes

The morphology of M6, and M7 prepared from 18 wt% and 20 wt% PVDF concentrations at $45\ ^\circ\text{C}$ and 8 MPa is shown in Fig. 4. The mean pore size decreases qualitatively with the increase of the polymer concentration, when PVDF concentration is 18 wt%, the mean pore size is about $5\ \mu\text{m}$, whereas it decreases to almost $1\ \mu\text{m}$ with 20 wt% concentration. At meantime the cells become more irregular and distorted from perfect spheres. At lower concentrations, it is easier for ScCO_2 to diffuse into the lower viscous solution to trigger the liquid-liquid demixing and form the larger cellular pores and high connectivity. However, for M7, the phase separation was delayed due to the higher viscous solution and therefore favored the formation of smaller crystalline structure pores. The increase of crystallinity and melting temperature as shown in Table 2 supported the occurrence of crystallization.

The effect of PEG, PVP and LiCl on membrane morphology was studied in detail. PEG or PVP is an effective additive to manipulate the morphology and property of PVDF membrane in traditional phase inversion process. As shown in Fig. 4, both cross-sections of M8 and M9 are composed of similar uniform and regular cellular pores sized at $6\ \mu\text{m}$. Less porous top surfaces and more porous bottom surfaces are produced *via* ScCO_2 assisted phase inversion. To be specific, abundant micropores less than $1\ \mu\text{m}$ are distributed on the cellular pore walls in the cross section for M9 doped with PVP, which is absent for M8 doped with PEG. Nano fibrils are formed in the pores of bottom surface of M9. The influences of additives on the membrane formation can be summarized as follows: first, the addition of PVP or PEG reduced the thermodynamic miscibility of the casting solution, and indicated the enhancement of liquid-liquid demixing; besides, the addition of PVP or PEG increased the diffusion and solubility of ScCO_2 due to its better affinity, however, the increase of solution viscosity induced by the additive depressed the diffusion of ScCO_2 in the opposite way, therefore, delayed liquid-liquid demixing^[26]. In case of M9, the liquid-liquid demixing mainly dominated the porous cellular structure. While in case of M8, both liquid-liquid demixing and crystallization mutually promoted the combination of cellular pores and crystalline particle structures on the pore walls. M9 showed lower crystallinity 33% and melting temperature $160.51\ ^\circ\text{C}$ than 40% and $166.37\ ^\circ\text{C}$ of M8. The effect of inorganic salt LiCl on the membrane morphology was further investigated. The cross-section, top and bottom surfaces of M10 doped with LiCl are similar to those of M8. However, LiCl greatly reduced the thermodynamic stability of the system and enhanced the solubility of ScCO_2 in the dope solution, promoting the instantaneous demixing in the phase inversion process, and smaller pores around $4\ \mu\text{m}$ were formed. Thus there is not enough time for crystallization to develop, which is in great agreement with the low crystallinity of 24% as listed in Table 2.

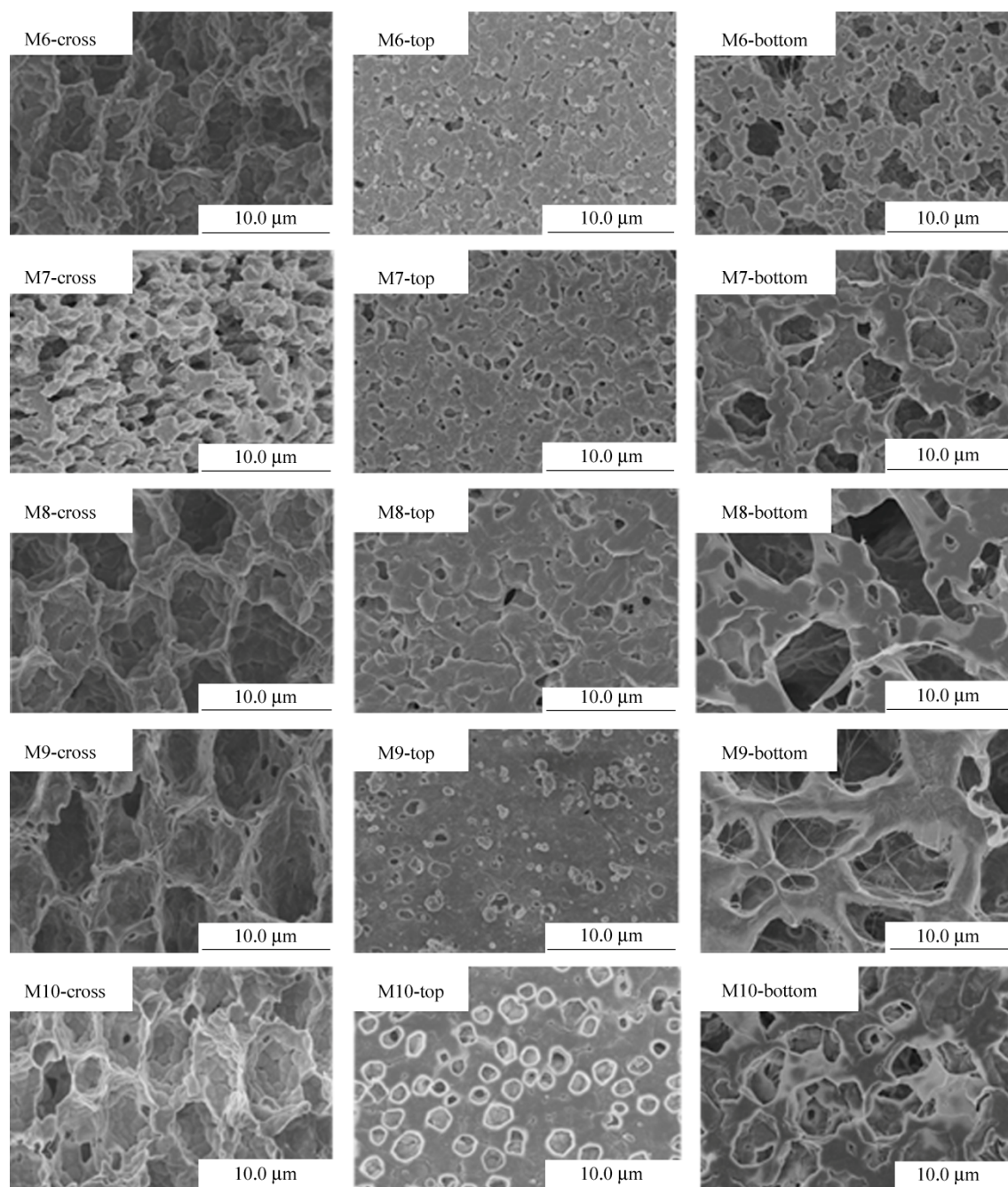


Fig. 4 SEM images of PVDF membranes M6, M7 prepared from 18 wt% and 20 wt% PVDF and membranes M8, M9 and M10 doped by PEG, PVP and LiCl, respectively

The Hydrophilicity Property of the Membranes

The water contact angle measurements were performed on the top surface to evaluate the hydrophilicity/hydrophobicity of the membranes, the results are shown in Fig. 5. It is interesting that the membranes produced *via* ScCO₂ assisted phase inversion have much higher contact angle than control membrane M0 (80°) produced by conventional immersion-precipitation technique. The hydrophilicity of membranes prepared at different supercritical conditions (varied temperature, pressure and composition) is also changeable. The high roughness of the membranes should be accounted for the high contact angle. As shown in

Fig. 6, R_a of M2 is 485 nm, whereas, R_a of M3, M4 is only 247 and 168 nm comparatively. The contact angle of M3, M4 is 30°, 50° lower than that of M2 as a result. With regard to M5, M6 and M7, the contact angle varies likewise, which is in accordance with the roughness variation trend. M5 has the largest roughness 287 nm and resulted in the higher contact angle than M6 and M7. For membranes doped by additives, the contact angle increased with increasing the roughness as well.

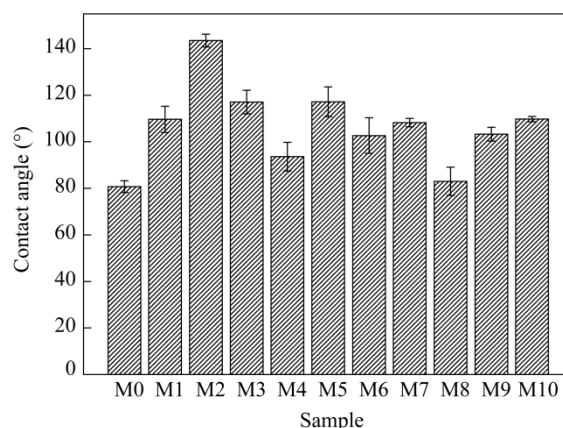


Fig. 5 Contact angle of membranes prepared at different conditions

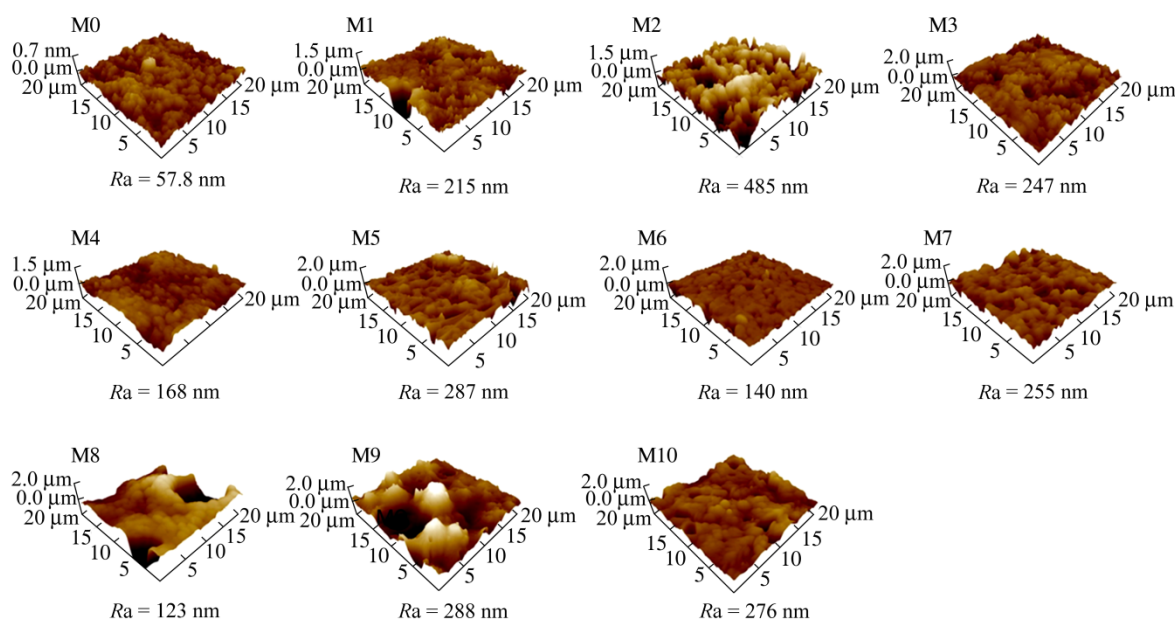


Fig. 6 AFM images of all membranes

Identification of Membrane Crystalline Behavior by FTIR

Identification of the crystalline behavior of PVDF based membranes was carried out by FTIR spectroscopy. It is known that PVDF crystallizes in four different polymorphs (α , β , γ and δ)^[27, 28]. Gregorio and Cestari reported on the FTIR absorption band characteristics of α phase (531, 612, 766, 795, 855 and 976 cm⁻¹), β phase (470, 511 and 840 cm⁻¹) and γ phase (430 cm⁻¹)^[29]. One crystalline phase could be converted to another one by the appropriate thermal, mechanical or electric treatments^[30]. Usually α and β phases, belonging to monoclinic and orthorhombic crystalline system respectively, are reported and identified. The nonpolar α phase, most readily obtained from the melt, has a trans-gauche conformation (TG⁺TG⁻). The polar β phase, with improved pyro and piezoelectric properties, has an all trans planar zigzag conformation (TTT)^[31]. In our study, we focused on these

two polymorphs and deal with them from a qualitative point of view. The FTIR spectra of membranes with 15 wt% PVDF prepared at different supercritical conditions is shown in Fig. 7. Varying temperature, no significant changes can be found. M1, M2 and M3 obtained a crystal form combined with α and β phases. When the processing temperature is low (40 °C), the membrane (M1) has more α phase for the signals of 796 and 976 cm^{-1} appeared. It is accepted that at low temperature, an increased density of CO_2 is obtained, in this case a favored liquid-liquid demixing is performed which leads to α type of crystal^[31, 32]. Compared with the membranes prepared at 13 MPa, α signals of M4 and M5 weakened, only a faint peak at 612 cm^{-1} reflects the α phase. With regard to these two membranes, β phase is dominant for the strong signal of 840 cm^{-1} . As directed by Young *et al.*^[33], for PVDF and DMF system, on the basis of phase diagram, the kinetic factor played an important role in the membrane formation. At low pressure (8 MPa), the exchange between solvent and non-solvent was slow, thus a delayed phase separation was favored and more β phase gained. Nevertheless, when the pressure was too high (18 MPa), a plenty of ScCO_2 diffused into the membrane acted as nucleator, in this case M4 obtained a fast initial crystallization and β phase formed.

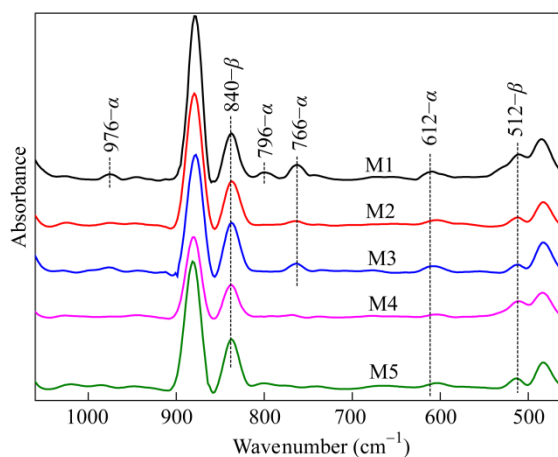


Fig. 7 FTIR spectra of membranes M1, M2, M3, M4 and M5 with 15 wt% PVDF

In Fig. 8 the effect of casting solution concentration on the crystal form is revealed. All the membranes show a mixture of two crystalline phases, α and β . Compared to 15 wt% and 18 wt% polymer concentration, α phase seems to disappear at 20 wt% concentration as a result from 612, 766 and 976 cm^{-1} bands, small and broad. However, peak at 840 cm^{-1} stands for β phase is still visibly sharper. As mentioned above, during the phase separation, the kinetic factor plays an important role on the type of crystal. Therefore, with 20 wt% high concentration casting solution, the diffusional mass transfer of solvent and non-solvent is slower than the one with 15 wt% and 18 wt%, thus the nucleation process of crystallization takes places prior to the liquid-liquid demixing. In this case, less α phase is formed.

The effect of the additive on the crystal structure was investigated as well, and the result is shown in Fig. 9. This method exploits the fact that after adding PVP (M9), β characteristic peak at 840 cm^{-1} can't be observed, whereas peaks at 532, 612, 762, 795 and 976 cm^{-1} , typical of α phase, are of very high intensity. In contrast, the former signal (840 cm^{-1}) exists apparently when PEG or LiCl was added (M8 or M10). In the FTIR spectra of these membranes, the peaks represent α phase is tiny compared with β phase. All information draw a conclusion that PVP promotes the liquid-liquid demixing which is responsible for α phase, nevertheless, PEG and LiCl favored a delay phase separation which boosts β phase.

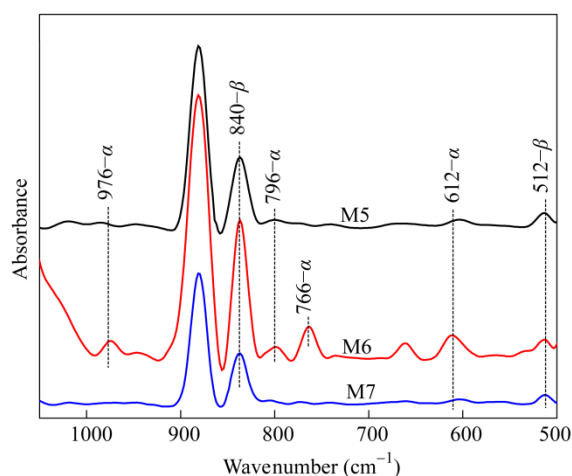


Fig. 8 FTIR spectra of membranes M5, M6 and M7 prepared at 45 °C and 8 MPa

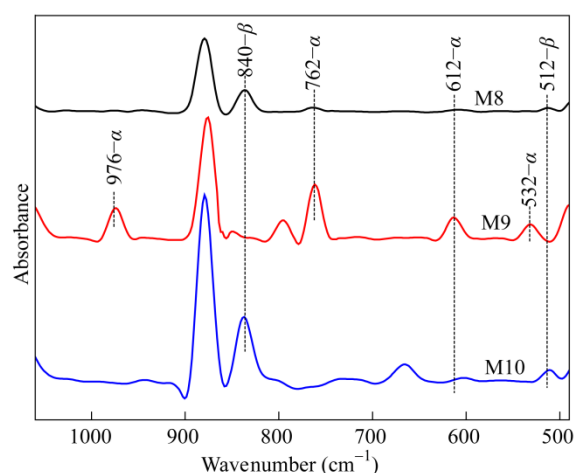


Fig. 9 FTIR spectra of membranes M8, M9 and M10 prepared at 45 °C and 8 MPa

CONCLUSIONS

PVDF membranes with various morphologies have been produced by ScCO₂ assisted phase inversion. The competition between liquid-liquid demixing and crystallization mainly dominated the evolution of the morphology. The additive, temperature and pressure influenced the affinity of ScCO₂ and solvent, and therefore determined the kinetics of phase inversion. M2 membrane prepared at 45 °C, 13 MPa with 15 wt% PVDF content exhibited a contact angle of 142° ascribed to the high roughness. The crystal behavior was mainly influenced by the polymer concentration and additives. PEG and LiCl favored the formation of β phase, while PVP promoted α phase.

REFERENCES

- Shih, C.H., Gryte, C.C. and Cheng, L.P., *J. Appl. Polym. Sci.*, 2005, 96(3): 944
- Cao, J.H., Zhu, B.K., Ji, G.L. and Xu, Y.Y., *J. Membr. Sci.*, 2005, 266(1–2): 102
- Huang, S., Wu, G. and Chen, S., *J. Supercrit. Fluids*, 2007, 40(2): 323
- Buonomenna, M.G., Macchi, P., Davoli, M. and Drioli, E., *Eur. Polym. J.*, 2007, 43(4): 1557
- Abed, M.R.M., Kumbharkar, S.C., Groth, A.M. and Li, K., *J. Membr. Sci.*, 2012, 407: 145
- Cha, B.J. and Yang, J.M., *J. Membr. Sci.*, 2007, 291(1–2): 191
- Chang, H.H., Yao, L.C., Lin, D.J. and Cheng, L.P., *Sep. Purif. Technol.*, 2010, 72(2): 156
- Liu, F., Hashim, N.A., Liu, Y., Abed, M.R.M. and Li, K., *J. Membr. Sci.*, 2011, 375(1–2): 1
- Cho, I.S., Kim, J.H. and Kim, S.S., *Korean Polym. J.*, 1997, 5(3): 191
- Cui, Z., Hassankiadeh, N.T., Lee, S.Y., Lee, J.M. and Woo, K.T., *J. Membr. Sci.*, 2013, 444: 223
- Reverchon, E. and Cardea, S., *Ind. Eng. Chem. Res.*, 2006, 45(26): 8939
- Stephan, A.M., Renganathan, N.G., Gopukumar, S. and Dale, T., *Mater. Chem. Phys.*, 2004, 85(1): 6
- Reverchon, E., Rappo, E.S. and Cardea, S., *Polym. Eng. Sci.*, 2006, 46(2): 188
- Huang, S., Wu, G. and Chen, S., *J. Membr. Sci.*, 2007, 293(1–2): 100
- Li, Z., Tang, H., Liu, X., Xia, Y. and Jiang, J., *J. Membr. Sci.*, 2008, 312(1–2): 115
- Matsuyama, H., Yamamoto, A., Yano, H., Maki, T., Teramoto, M. and Mishima, K., *J. Membr. Sci.*, 2002, 204(1–2): 81
- Kim, M.S. and Lee, S.J., *J. Supercrit. Fluids*, 2004, 31(2): 217
- Krause, B., Mettinkhof, R., van der Vegt, N.F.A. and Wessling, M., *Macromolecules*, 2001, 34: 874
- Krause, B., Sijbesma, H.J.P., Munuklu, P., van der Vegt, N.F.A. and Wessling, M., *Macromolecules*, 2001, 34(25): 8792

- 20 Lin, D.J., Chang, C.L., Lee, C.K. and Cheng, L.P., *Eur. Polym. J.*, 2006, 42(10): 2407
- 21 Rindfleisch, F., DiNoia, T.P. and McHugh, M.A., *J. Phys. Chem.*, 1996, 100(38): 15581
- 22 vandeWitte, P., Dijkstra, P.J., vandenBerg, J.W.A. and Feijen, J., *J. Membr. Sci.*, 1996, 117(1–2): 1
- 23 Tao, M.M., Liu, F., Ma, B.R. and Xue, L.X., *Desalination*, 2013, 316: 137
- 24 Reverchon, E. and Cardea, S., *J. Membr. Sci.*, 2004, 240(1–2): 187
- 25 Duarte, A.R.C., Mano, J.F. and Reis, R.L., *J. Supercrit. Fluids*, 2009, 49(2): 279
- 26 Fontananova, E., Jansen, J.C., Cristiano, A., Curcio, E. and Drioli, E., *Desalination*, 2006, 192(1–3): 190
- 27 Hirschinger, J., Schaefer, D., Spiess, H.W. and Lovinger, A.J., *Macromolecules*, 1991, 24(9): 2428
- 28 Lovinger, A.J., *Macromolecules*, 1982, 15(1): 40
- 29 Gregorio, R. and Cestari, M., *J. Polym. Sci., Part B: Polym. Phys.*, 1994, 32(5): 859
- 30 Wang, J.J., Li, H.H., Liu, J.C., Duan, Y.X., Jiang, S.D. and Yan, S.K., *J. Am. Chem. Soc.*, 2003, 125(6): 1496
- 31 Gregorio Jr, R. and Borges, D.S., *Polymer*, 2008, 49(18): 4009
- 32 Chinaglia, D.L., Gregorio, R., Jr., Stefanello, J.C., Pisani, Altafim, R.A., Wirges, W. and Wang, F., J., *Appl. Polym. Sci.*, 2010, 116(2): 785
- 33 Young, T.H., Lin, D.J., Gau, J.J., Chuang, W.Y. and Cheng, L.P., *Polymer*, 1999, 40(18): 5011