Preparation of microporous poly(vinylidene fluoride) membranes via phase inversion in supercritical CO$_2$

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Abstract

Microporous poly(vinylidene fluoride) (PVDF) membranes were prepared from PVDF/N,N-dimethylacetamide (DMAC) solutions by using supercritical CO$_2$ phase inversion process. As revealed by scanning electron microscope (SEM) and differential scanning calorimeter (DSC), the PVDF membranes exhibit morphological characteristics resulting from both liquid–liquid phase separation and crystallization, i.e., cellular pores surrounded by interlinked PVDF particulate crystallites. This indicates that both types of phase separation processes take place in the supercritical CO$_2$ phase inversion process. The effects of pressure, temperature, and initial polymer concentration on the final membrane structures were investigated. We also investigated the effect of addition of poly(methyl methacrylate) (PMMA) in the casting dope on the PVDF membrane structure. The membrane structure changed significantly with the variation of PVDF/PMMA mass ratio in the casting dope as well as polymer concentration. It was found that the variation of temperature and pressure has a minor influence on the membrane structure.

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1. Introduction

Owing to its excellent chemical resistance and thermal stability, poly(vinylidene fluoride) (PVDF) is widely used as a ultrafiltration and microfiltration membrane material and is studied extensively [1–11]. Porous PVDF membranes are primarily prepared by wet phase inversion process from binary solutions containing PVDF and a high boiling point solvent, with or without additives like lithium chloride and poly(vinyl pyrrolidone) (PVP) [1–11]. In this process, a thin film of polymer solution is cast on an inert substrate and then immersed into a coagulant bath containing a non-solvent with respect to the polymer, rapid exchange of the solvent by non-solvent results in diffusion-induced phase separation and membrane formation. In general, large voids are formed when using water as the coagulant, while the voids become smaller or disappeared when using alcohol, a mixture of alcohol and water, or a mixture of water and solvent as the coagulant [1–11]. The formation of macropores is usually undesirable, because macropores may jeopardize the mechanical integrity of membrane and result in compaction or collapse of membranes when applied to high pressure processes [12]. Moreover, the wet phase inversion process involves the use of an organic solvent that must be expensively removed from the membrane by post-treatment. Since PVDF membrane is extensively used in biomedical fields [13], residual solvents are undesirable since they may contaminate the material and cause potential problems. In addition, long formation time is required to obtain dry membranes in this process.

As an alternative, supercritical CO$_2$ (SC CO$_2$) has recently been used as a non-solvent to induce phase separation of polymer solution for the purpose of obtaining dry membranes. Compared with the traditional wet phase inversion method, advantages of this phase separation process are as follows [14–24]. Firstly, dry membrane can be directly obtained without additional post-treatment, saving the time of membrane formation. Secondly, the solvent dissolved in SC CO$_2$ can be easily recovered in a separator located downstream of the membrane formation vessel by simply diminishing the pressure. Thirdly, CO$_2$ is
non-toxic, non-flammable, and cheap. In addition, membrane characteristics can be continuously modulated by varying the SC CO₂ property. This technique has been applied for the preparation of many polymer membranes, including Nylon 6 [14], polystyrene [15], cellulose acetate [16,17], polysulfone [18,19], poly(methyl methacrylate) [20,21], polylactide [22,23], poly(vinylidene fluoride-co-hexafluoropropylene) [24].

Previously, we used SC CO₂ as a foaming agent to foam PMMA microspheres and obtained PMMA microspheres possessing a non-porous skin and open cellular core structure [25]. In this work, SC CO₂ was used as a non-solvent to prepare microporous PVDF membrane from PVDF/DMAC solutions. The miscibility of CO₂ with DMAC has been measured at temperatures between 40 and 100 °C and pressures ranging from 16 to 180 bar [26]. To the contrary, CO₂ cannot dissolve PVDF even at 300 °C and 275 MPa [27]. Therefore, SC CO₂ plays a non-solvent role in the phase inversion process. The effects of polymer concentration, pressure, and temperature on the morphology and cell size of PVDF membrane were investigated. The effect of addition of a miscible polymer (PMMA) in the casting dope was studied as well. The variation of polymer concentration or the addition of a second polymer led to a significant change in the membrane morphology.

2. Experimental section

2.1. Materials

PVDF (FR904, powder) was supplied by Shanghai 3F New Material Co. Ltd., China. PMMA, also in powder form, was purchased from Soken Chemical & Engineering Co. Ltd., Japan. They were dried at 60 °C in a vacuum oven for 24 h and placed in a desiccator prior to use. Reagent-grade N,N-dimethylacetamide (DMAC) was used as the solvent for PVDF. Carbon dioxide (>99.5% pure) was from Loutang Special Gases of Shanghai. All materials were used as received.

2.2. Membrane preparation

Details of our supercritical CO₂ experimental setup was described previously [25]. Porous membranes were prepared as follows. PVDF and/or PMMA polymer powder were pre-weighed and poured into DMAC contained in a 50 ml beaker. The mixture was capped and stirred until a homogenous casting solution was formed. After standing overnight to remove air bubbles, the polymer dope solution was spread uniformly on a glass plate to form a laminate (ca. 250 μm). Then the glass plate was rapidly put inside the high pressure vessel that was pre-heated to the desired temperature. After sealing, the vessel was immediately filled with CO₂ to the desired pressure using a high pressure pump. The system was held for 1 h at a fixed temperature. At the end of this period, a continuous mode with a CO₂ flow rate of 30 g/min was applied to dry the phase-separated membrane for another 1 h. The vessel was then slowly depressurized for 1 h. Once the depressurization process was finished, the resulting white and opaque membrane was collected from the vessel.

2.3. Membrane characterization

Structures of the membranes in the top, bottom, and cross-section views were examined by scanning electron microscope (SEM) (JEOL JSM-6360LV). The cross-section of membrane was obtained by fracturing the membrane in liquid nitrogen. All samples were sputter-coated with about a 15 nm layer of gold. Average cell size was determined from the SEM images of the membrane cross-section by using Image-Pro Plus 4.0 software (Media Cybernetics). The average distance of two orthogonal cell dimensions was taken as the cell diameter [28]. Approximately 150 cells were measured for each membrane analyzed. OriginPro 7.0 software (OriginLab Corp., Northampton, MA, USA) was used to calculate the cell size distribution.

Porosity (p) of PVDF membrane was determined by a procedure similar to that described previously by Xu and co-workers [24]. For PVDF/PMMA membrane, its porosity was calculated from the density of membrane (ρm) and the density of dense PVDF/PMMA film (ρb): p = 1 − ρm/ρb. The dense PVDF/PMMA film was formed from homogeneous PVDF/PMMA solution in DMAC by drying the casting film at 60 °C under vacuum for 24 h.

The melting endotherms of polymer powder and the formed membranes were determined by differential scanning calorimeter (DSC) (Mettler TA822e) under a nitrogen atmosphere at a heating rate of 10 °C/min over the range of 40–250 °C. The flow rate of nitrogen gas is 50 ml/min. An appropriate amount of membrane sample (typically 5 mg) was sealed in an aluminum pan and placed in the heating chamber together with an empty pan used as the reference. Melting temperature (Tm) and heat of fusion (ΔHf) were determined from the melting endotherms. Crystallinity of membrane was calculated by dividing the measured ΔHf by the value for perfect PVDF crystal (ΔHf = 105 J/g) reported in the literature [29].

3. Results and discussion

In the traditional wet phase inversion process, a homogeneous polymer solution is immersed in a non-solvent bath to induce phase separation; liquid–liquid demixing plays a central role in this process [30]. Although water is generally used as a non-solvent, SC CO₂ can also be used to induce phase separation since many polymers are insoluble in it [31]. The process of using SC CO₂ to induce phase separation is as follows [16]. After a thin film was cast onto a glass plate, the glass plate was immediately transferred to and sealed in a pressure vessel. During this procedure, some amounts of organic solvent were evaporated and the polymer concentration gradient was formed. Then, supercritical CO₂ was introduced and the inflow of CO₂ to the polymer solution and the outflow of the organic solution occur, inducing the phase separation. During the sweeping of CO₂ through the vessel, organic solvent in the membrane solution was extracted to the supercritical CO₂ phase. After depressurization, a dry porous membrane was obtained.

Porous morphology of the formed membranes may result from the CO₂-assisted foaming during depressurization, due to the possible plasticization of polymers by CO₂ [32,33]. Several
experiments were performed to ensure that such processes did not significantly influence the membrane structure in our studies. After a homogeneous PVDF solution in DMAC was cast on the glass plate, the film was dried at 60 °C under vacuum condition for 24 h to evaporate the solvent. The formed transparent and dense film was exposed to high pressure CO2 (10 or 20 MPa, and 45 or 65 °C) for 2 h, and then slowly depressurized over 1 h. No samples exhibited any evidence of foaming as a result of the CO2 exposure and slow depressurization.

It has long been recognized that the morphology of the obtained phase inversion membranes is governed by the simultaneous thermodynamic and kinetic events leading to precipitation [30]. For a crystallizable polymer, precipitation may take place by means of liquid–liquid phase separation, crystallization or combination of both to yield sophisticated morphologies [6–11,34,35]. In general, liquid–liquid demixing results in a cellular structure with cells that are formed from the nucleated polymer lean phase [30], whereas crystallization forms interlinked crystalline elements [6–11]. The sequence of these two precipitation events dictates the final morphology of the membrane. By changing the composition and/or temperature of the dope, the coagulant or both, it is possible to allow one of these two precipitation events to dominate the phase separation and thereby control the final membrane morphology [6–11,34,35].

When supercritical CO2 is used as a non-solvent, its density (antisolvent strength) can be tuned by controlling the pressure and/or temperature, thus introducing the pressure of antisolvent phase as an additional variable by which to influence the demixing process and control the membrane morphology [14]. Interpretation of the formed membrane morphology is usually based on structural features observed for traditional phase inversion membranes [14–24]. As shown in Table 1, various experiments were carried out to assess the effects of polymer concentration, pressure, temperature, and addition of a miscible polymer (PMMA) on the morphology and cell size of the membranes.

### 3.1. Effect of polymer concentration

The effect of polymer concentration on membrane structure was examined at 45 °C and 10 MPa. Fig. 1 shows the top surface structure of PVDF membranes measured by SEM. As the polymer concentration increases, the top surface changes from an array of particulate (skinless) surface to a dense one. Owing to the evaporation of solvent before the introduction of CO2 and the dissolution of solvent in the supercritical CO2 phase, the polymer concentration at the top surface became higher [15]. In this case, the polymer solution at the top surface may be in a state of ‘incipient precipitation’ with respect to crystallization. Thus, crystallization occurs exclusively in the top gel layer before there is any chance of liquid–liquid phase separation after immersion [6–11], as confirmed in Fig. 1. For 10 wt.% solution (Fig. 1a), the surface is skinless and composed of rather uniform spherical particles that interlock into an irregular porous structure. The crystal elements appear as truncated, flattened crystal particles. Similar surface structure has also been observed in the membrane prepared by immersing a 20 wt.% PVDF/NMP dope in 70 wt.% NMP aqueous solution [7].

A continuous top surface was observed in the membrane from solutions with over 15 wt.% of PVDF (Fig. 1b and c), showing a skin layer formed at the top surface (also shown in Fig. 3b and c). This implies that during the precipitation, crystallization instead of liquid–liquid phase separation occurs underneath the top surface. Once the crystalline nuclei were formed, they grew radially following the habits of spherulites until their fronts impinged each other to form the spherulite structure with linear grain boundaries [34]. Their sizes become smaller and density becomes higher with the increase of polymer concentration, due to the larger degree of supersaturation with respect to crystallization [10].

Fig. 2 shows an example of bottom surface morphology. It has a truncated cellular structure formed by liquid–liquid demixing. Unlike the membrane interior (shown in Fig. 3), the cells are independent and have neither regular shape nor uniform size. They are surrounded by interlocked particulate crystallites. These particles are flattened since they are grown against the smooth glass plate [7,34].

Fig. 3 shows the cross-sectional structures of PVDF membranes. With increasing polymer concentration, the membrane cross-sectional structure varies significantly. In the case of the 10 wt.% solution, the cross-section consists of many cells enclosed in a polymer mat. The cells are irregular and distorted from a perfect sphere. The cell size increases gradually from the top surface toward the bottom surface. Such a porous morphology indicates liquid–liquid demixing as the dominant mechanism of membrane formation [30]. Crystallization-associated morphology (e.g. crystalline particles) was not observed on the walls of the cells, suggesting that

### Table 1

Experimental conditions and typical properties of the formed membranes

<table>
<thead>
<tr>
<th>Membrane sample</th>
<th>PVDF (concentration wt.%)</th>
<th>PMMA (concentration wt.%)</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>Average cell size (μm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.0</td>
<td>–</td>
<td>10</td>
<td>45</td>
<td>7.0</td>
<td>88.1</td>
</tr>
<tr>
<td>B</td>
<td>15.0</td>
<td>–</td>
<td>10</td>
<td>45</td>
<td>6.2</td>
<td>79.6</td>
</tr>
<tr>
<td>C</td>
<td>20.0</td>
<td>–</td>
<td>10</td>
<td>45</td>
<td>8.8</td>
<td>64.4</td>
</tr>
<tr>
<td>D</td>
<td>15.0</td>
<td>–</td>
<td>20</td>
<td>45</td>
<td>7.2</td>
<td>81.5</td>
</tr>
<tr>
<td>E</td>
<td>15.0</td>
<td>–</td>
<td>10</td>
<td>65</td>
<td>6.4</td>
<td>77.3</td>
</tr>
<tr>
<td>F</td>
<td>13.5</td>
<td>1.5</td>
<td>10</td>
<td>45</td>
<td>5.5</td>
<td>57.4</td>
</tr>
<tr>
<td>G</td>
<td>10.5</td>
<td>4.5</td>
<td>10</td>
<td>45</td>
<td>7.1</td>
<td>71.6</td>
</tr>
<tr>
<td>H</td>
<td>7.5</td>
<td>7.5</td>
<td>10</td>
<td>45</td>
<td>5.2</td>
<td>67.2</td>
</tr>
</tbody>
</table>
liquid–liquid demixing has taken place much earlier than crystallization [34] and rapidly fixed the cellular structure before the initiation of crystallization in the gel layer surrounding the formed liquid micelles. During the polymer gelation near the cell wall, solvent and non-solvent were rejected into the liquid micelles, causing the cells to be distorted from a perfect sphere [34]. In the traditional phase inversion process, this type of sequential phase separation was often observed in the membrane forming systems containing a crystalline polymer [6–9,34,35].

At a concentration of 15 wt.%, the membrane cross-section exhibits an asymmetric structure, consisting of a dense skin and a cellular bulk. The cells in this membrane are nearly spherical and their size increases gradually from the top surface toward the bottom surface. These morphological features are often observed in amorphous membranes and result from the liquid–liquid phase demixing [30]. Although this kind of morphology suggests the liquid–liquid demixing is dominant over the precipitation, crystallization occurs during the late stage of the precipitation process. This can be clearly seen from the cell walls that are composed of a layer of particulate crystallites with identical size. Once liquid–liquid demixing completely established the bulk porous structure, crystallization could take effect only on the gel phase that surrounds the cellular pores [9]. Evidence of crystallization during the precipitation is also confirmed by DSC analysis, as shown in Fig. 4 and Table 2 (discussed later). Since the cell wall is composed of particulate crystallites, the cells are interconnected (termed as open cell in the literature [7,10]).

At a concentration of 20 wt.%, the membrane cross-section also exhibits an asymmetric structure, consisting of a denser
skin and a cellular bulk. The cells in this membrane are almost perfect spheres. Unlike that observed in Fig. 3b, the cells in the membrane are more isolated. Their density is very low, suggesting that liquid micelles are not extensively formed during the nucleation stage of membrane formation [10]. The cell wall is composed of a relatively loosely packed agglomerate of particulate crystallites in identical size. Thus, the cells are actually interconnected. The crystallite particles surrounding the cells suggest that crystallization occurs rapidly following the liquid–liquid demixing and locks the cellular structure. It is also possible that liquid–liquid demixing and crystallization occur simultaneously. In both cases, the morphologies exhibit features of both liquid–liquid phase separation and crystallization [8]. For the dope containing 20% PVDF, an intense competition between
Table 2
Melting temperature and crystallinity of PVDF and PMMA/PVDF membranes

<table>
<thead>
<tr>
<th>Membrane sample</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (membrane) (J/g)</th>
<th>$\Delta H_f$ (PVDF) (J/g)</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>165.1</td>
<td>54.52</td>
<td>54.52</td>
<td>0.52</td>
</tr>
<tr>
<td>B</td>
<td>165.3</td>
<td>65.68</td>
<td>65.68</td>
<td>0.63</td>
</tr>
<tr>
<td>C</td>
<td>165.6</td>
<td>75.61</td>
<td>75.61</td>
<td>0.72</td>
</tr>
<tr>
<td>D</td>
<td>164.9</td>
<td>71.96</td>
<td>71.96</td>
<td>0.69</td>
</tr>
<tr>
<td>E</td>
<td>164.4</td>
<td>63.66</td>
<td>63.66</td>
<td>0.61</td>
</tr>
<tr>
<td>F</td>
<td>164.2</td>
<td>62.75</td>
<td>69.72</td>
<td>0.66</td>
</tr>
<tr>
<td>G</td>
<td>162.7</td>
<td>35.18</td>
<td>50.23</td>
<td>0.48</td>
</tr>
<tr>
<td>H</td>
<td>157.2</td>
<td>15.60</td>
<td>31.20</td>
<td>0.30</td>
</tr>
<tr>
<td>Original PVDF</td>
<td>159.6</td>
<td>39.64</td>
<td>39.64</td>
<td>0.38</td>
</tr>
</tbody>
</table>

crystallization and liquid–liquid demixing may occur, producing a membrane with cellular structure from liquid–liquid phase separation and crystallite wall.

Evidence of crystallization during the precipitation was confirmed by DSC analysis, as shown in Fig. 4 and Table 2. Compared to the original PVDF powder, both the crystallinity and melting point of the membranes are higher and they increase with increasing the polymer content in dope. This implies that the CO$_2$-induced crystallization [36] may occur in the course of membrane formation and the level of PVDF crystal perfection in the membrane is higher than that in the original PVDF powder [9].

In the literature [14,17–20], a hypothetical ternary diagram was frequently used for qualitative interpretation of the simultaneous thermodynamic and kinetic events that lead to precipitation in the SC CO$_2$-induced phase inversion process. Fig. 5 demonstrates a hypothetical ternary diagram for the PVDF/DMAC/SC CO$_2$ system. Representative mass transport pathways at different initial polymer casting concentrations were indicated in the diagram. At PVDF concentration of 15 wt.% and lower, the process driven by SC CO$_2$ is very fast. Therefore, after introducing the SC CO$_2$ into membrane formation cell, the exchange of solvent with SC CO$_2$ is rapid, leading to entry of the membrane solution into the binodal rapidly and liquid–liquid demixing as the dominant mechanism of membrane formation. However, as the polymer concentration increases up to 20 wt.%, the solution viscosity is also increased, leading to the delay of mutual diffusion between solvent and non-solvent. Therefore, a phase separation delay is induced. Because of the delay in liquid–liquid demixing and possible supersaturation of the membrane solution with respect to crystallization, nucleation and growth of polymer crystallites became competitive relative to liquid–liquid demixing. This leads to the formation of mixed morphology presented in Fig. 3c.

Fig. 6 shows the cell size distribution of the membranes produced from different PVDF concentrations. By increasing the
PVDF percentage from 10% to 20% (w/w), the cell diameter first decreases but then increases. At a concentration of 15% (w/w), the formed membrane has a sharper and more symmetrical cell size distribution than the samples prepared from other concentrations. The average cell size and porosity of the membranes generated at different PVDF concentrations are shown in Table 1. The data show that as the polymer concentration increases from 10 to 20 wt.%, the mean cell diameter decreases from 7.0 to 6.2 μm and then increases to 8.8 μm; the porosity decreases from 88.1% to 64.4%. At lower polymer concentration (thus lower solution viscosity), the coarsening of the polymer lean droplets [15] leads to a decrease in average cell size from 7.0 to 6.2 μm with increasing the polymer concentration from 10 to 15 wt.%. However, for the 20 wt.% solution, as mentioned

![Fig. 7. Effects of pressure and temperature on cross-section structures. Polymer concentration, 15 wt.%: (a) 10 MPa, 45 °C; (b) 20 MPa, 45 °C; (c) 10 MPa, 65 °C. The images in the right column are enlargements of the corresponding images in the left column. T, top surface and B, bottom surface.](image-url)
above, liquid–liquid demixing and crystallization may occur simultaneously. In this case, the formation of nuclei of the polymer lean phase may be inhibited when PVDF crystal nuclei are formed extensively in a fixed volume of membrane, resulting in a lower nucleation density of the polymer lean phase. On the other hand, higher polymer concentration leads to a slower exchange rate between solvent and non-solvent and a slower rate of liquid–liquid demixing. Also, the fixation of membrane structure will be delayed. This means that there is enough time for the polymer lean phase formed by the phase separation to grow, thus leading to a larger cell size. On the other hand, the skin layer becomes denser at higher polymer concentration, indicating the increase in volume fraction of polymer and the decrease of membrane porosity. Xu and co-workers [24] previously reported similar results for PVDF–HFP membranes formed by SC CO₂-induced phase separation.

3.2. Effects of pressure and temperature

Fig. 7 shows the effects of pressure and temperature on cross-sectional structures of the PVDF membranes. Fig. 7a has been shown previously in Fig. 3b and is shown here again for comparison. Since the top and bottom surfaces of membranes formed at different pressures and temperatures are similar to those shown in Figs. 1b and 2, respectively, they were not shown here again. The effect of pressure was examined at 45 °C at polymer concentration of 15 wt.%. Fig. 7a and b shows the cross-sections of membranes produced at 10 and 20 MPa, respectively. It can be seen that both membranes exhibit an asymmetric structure, consisting of a dense skin and a cellular bulk. Such morphology indicates liquid–liquid demixing as the dominant mechanism of membrane formation at different pressures. Crystallization also occurs during the late stage of the precipitation process, as clearly seen in Fig. 8a and b. The crystallinity of membranes increases with increasing the pressure. This implies again that the CO₂-induced crystallization [36] may occur in the course of membrane formation.

As shown in Fig. 9 and Table 1, both the cell size and the porosity slightly increase with pressure increase, the average cell diameter increases from 6.2 to 7.5 μm with increasing the pressure from 10 to 20 MPa. Similar pressure dependence of cell size has been previously reported by Matsuyama et al. for polystyrene membranes [15] and by Cao et al. for PVDF–HFP membranes [24]. These authors attributed this to the decrease of solution viscosity caused by the CO₂ incorporation. As a consequence, the coarsening of the polymer lean phase (droplet) formed by the phase separation may occur in the solution with low viscosity. Thus, larger cells were formed at high pressure, leading to an increase of the membrane porosity.

The effect of temperature on membrane structure was studied at 10 MPa and at polymer concentration of 15 wt.%. Fig. 7a and c shows that the membranes produced at 45 and 65 °C possess similar structure. The cell size distributions and the porosity at different temperatures are shown in Fig. 9 and Table 1, respectively. The cell diameters of both membranes are almost the same, but the membrane formed at higher temperature has a lower porosity. Close examination shows that the membrane formed at 65 °C has a denser top layer, and the asymmetry becomes more pronounced. With increasing the temperature, the evaporation and dissolution of the solvent into the supercritical CO₂ phase are enhanced, thereby resulting in higher polymer concentration near the top surface and sharper concentration gradient over the cross-section [15]. On the other hand, CO₂ density decreases at higher temperature, leading to a slower exchange rate between non-solvent and solvent [20]. These two factors lead to a thicker skin and more pronounced asymmetry of the formed membrane as well as lower porosity, in agreement with the previous reports on the membranes of polystyrene [15], cellulose acetate [17], PMMA [20,21], and PVDF–HFP [24].

In the literature [15,17–22,24], many studies revealed that membrane characteristics could be continuously modulated by varying the SC CO₂ property. However, our results show that both CO₂ pressure and temperature have a minor influence on the structure of PVDF membranes. The reason may be as follows [14]. Due to the constraints of our experimental apparatus, pressurization and heating are gradual and not instantaneous. Therefore, the membranes were actually subjected to a gradual change in the antisolvent strength as the final conditions were
Fig. 10. SEM micrographs of the membranes prepared from dopes containing different PMMA/PVDF ratios. Dope: 15 wt.% polymer (PMMA + PVDF) in DMAC; pressure, 10 MPa; temperature, 45 °C: (a) 0/10 (w/w); (b) 1/9 (w/w); (c) 3/7 (w/w); (d) 5/5 (w/w). T, top surface and B, bottom surface.
approached, leading to the reduction of the full impact of that change on the membrane structure.

3.3. Effect of the addition of PMMA

PMMA and PVDF are miscible polymers and they can form a homogeneous blend [37–39]. Many studies imply that, in the traditional phase inversion process, the incorporation of PMMA in the casting dope is an effective method to manipulate the morphology of the formed PVDF membrane and thereby to modify the membrane property [29,40,41]. A significant change in membrane morphology was often found with the addition of a second polymer into the casting dope. In order to confirm whether this is true in the SC CO2 assisted phase inversion process, we investigated the effect of PMMA content in the dope on the membrane structure. The casting dope was prepared by dissolution of polymer (PMMA and/or PVDF) in DMAC to form a solution containing 15 wt.% polymer. Fig. 10 shows morphologies of the membranes prepared from the dopes with different PMMA/PVDF mass ratios. All the membranes possess the so-called asymmetric morphology that is characterized by a skin layer and a porous bulk. This morphology results from liquid–liquid demixing by nucleation and growth of droplets of the polymer lean phase. With increasing the PMMA content in the dope, the cell shape is distorted from spherical and the cell wall structure changes significantly. For pure PVDF membrane, the cell wall is composed of uniform spherulite particles. When the PMMA concentration in the dope is above 4.5 wt.%, the cell wall is composed of continuous matrix. For the membrane generated at 1.5 wt.% PMMA, they are intermediate between these two cases, i.e., the cell wall is composed of continuous matrix in which many spherulite particles are embedded. Fig. 11 shows the cell size distributions of the membranes prepared from the dopes with different PMMA/PVDF mass ratios. As the PMMA content in the dope increases, the cell size becomes less uniform, in good agreement with the qualitative observations shown Fig. 10. In addition, for the membrane produced from the solution containing 4.5 wt.% PMMA, both the cell size and the porosity are larger than those of the membranes formed at other PMMA concentrations.

Although PVDF content in the casting dope decreased with the increase of PMMA content, crystallization still occurs in the late stage of the phase inversion process. This is evident from the DSC thermograms of the membranes prepared from the casting dopes in different PMMA/PVDF mass ratios, as shown in Fig. 12. The crystallinity data calculated based on the heat of fusion of perfect PVDF crystal ($\Delta H_0 = 105$ J/g) are summarized in Table 2. The melting point ($T_m$) of PVDF crystal decreases with increasing PMMA content in the dope. As shown in Table 2, the crystallinity of PVDF in the membrane decreases significantly with increasing PMMA content. With the addition of PMMA to 7.5 wt.% in the casting dope (membrane H), the crystallinity decreases to 30%, indicating the inhibition of crystallization. Such a dramatic decrease in crystallinity is related to the good miscibility between PMMA and PVDF [29]. Similar observation was also reported by Walker et al., who treated a miscible perdeuterated PMMA/PVDF (55/45) blend plaque at 13.8 MPa of CO2 and 180°C and subsequently cooled to ambient temperature under CO2 pressure [42]. We also found that when PMMA content is below 4.5 wt.%, the crystallinity of PVDF in all the membranes is higher than that of original PVDF powder, indicating the occurrence of CO2-induced crystallization.

4. Conclusion

Microporous PVDF membranes possessing structures reflecting both liquid–liquid demixing and crystallization were prepared from PVDF solutions by using the SC CO2 assisted phase inversion process in which supercritical CO2 acted as a non-solvent. Morphologies of the formed membranes were found to be dependent on the polymer concentration in the casting dope. Addition of PMMA in the casting dope changed the membrane structure significantly. It was also found that by increasing the pressure from 10 to 20 MPa, the average cell size slightly increased from 6.2 to 7.5 μm, whereas the temperature over the investigated range had little influence on the membrane structure.
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