Effect of citrate-based non-toxic solvents on poly(vinylidene fluoride) membrane preparation via thermally induced phase separation

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A B S T R A C T

The replacement of commonly-used substances with non-toxic equivalents is attracting a great amount of attention in membrane preparation processes. In order to address this issue, we prepared poly(vinylidene fluoride) (PVDF) flat membranes via thermally-induced phase separation using non-toxic citrate-based solvents (Citroflex): acetyl tributyl citrate (ATBC); acetyl triethyl citrate (ATEC); and triethyl citrate (TEC). It was found that the three kinds of Citroflex showed the different solubility with PVDF: the solubility was improved in the following order of ATBC < ATEC < TEC. The prepared porous PVDF membranes were characterized in terms of their morphology observed by scanning electron microscopy, porosity, pore-size, contact angle, and tensile properties. The pore structures of the membranes were affected by the solvent’s affinity with PVDF, as well as by the gap between the casting knife and plate. This result was explained by taking into account the polymer / solvent phase separation behavior during the membrane formation. In the microfiltration test of pure water, the water permeability of the membranes widely changed depending on their pore structures. In conclusion, the prepared PVDF flat membranes exhibited the great potential for practical separation processes.

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1. Introduction

Membrane processes are currently used extensively in a number of areas of water treatment, thanks to their relatively low energy consumption, ease of operation, and lack of requirement for the addition of further chemicals to the process [1,2]. In particular, they represent one of the most attractive solutions to the problem of water shortage, which is an ongoing global issue because of population growth and economic expansion particularly in developing countries. Membrane processes are considered to be promising techniques for achieving a sustainable society; however the membrane preparation process itself remains problematic due to the use of substances that are hazardous to humans and environment.

Microfiltration (MF) is a liquid-phase pressure-driven membrane process that is widely applied to separate contaminants such as bacteria, algae, colloids, and macromolecules, from the feed water. Together with other pressure-driven membrane processes (e.g. ultrafiltration, nanofiltration, and reverse osmosis) and membrane distillation processes (especially coupled with crystallization), MF could become a useful tool in addressing the increasing worldwide demand for clean water [3,4]. The porous MF membranes play the role of a size exclusion barrier, through which only water and other substances smaller than the pore size can permeate from the feed side to the other side. The pore size of MF membranes tends to range from 0.05 to 10 μm [2], depending on the size of the contaminants to be separated. MF membranes are required to have not only suitable porous structures, but also sufficient mechanical strength and chemical resistance for long term stability and use.

Poly(vinylidene fluoride) (PVDF), a polymer with repeating units of (CF₂CH₂), is one of the most widely used polymers for membrane preparation, due to its outstanding chemical and physical stability [5–7]. PVDF is soluble at room temperature in polar aprotic solvents, and in addition, a range of chemicals can work as solvents at high temperatures [6]. PVDF membranes can therefore either be prepared via non-solvent induced phase separation (NIPS) or thermally induced phase separation (TIPS) methods [5,7]. In the NIPS process, the immersion of a polymer solution in a non-solvent causes the precipitation of a polymer-rich phase that turns into a membrane by exchange of a solvent with the non-solvent. In the TIPS process, the polymer solution is cooled from high temperature, and the polymer phase is expelled from the solvent to form a membrane due to the polymer/solvent

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immiscibility at low temperatures. Compared to the NIPS method, the TIPS method is capable of producing PVDF membranes with better mechanical strength, higher porosity and narrower pore-size distribution [7], which are appropriate properties for use in MF applications.

Traditionally, solvents such as dimethyl phthalate (DMP) [8,9], diethyl phthalate (DEP) [10], dibutyl phthalate (DBP) [11,12], and dioctyl phthalate (DOP) [12], have been used in the preparation of PVDF. However, these phthalate esters are extremely toxic and have a negative effect on human health [13]. As highlighted by Figoli et al. [14], one of the most urgent issues for membrane scientists is the discovery and development of less toxic alternatives to such solvents. However, this is not an easy task, and is complicated further by the fact that the structures of membranes prepared via the TIPS process are greatly influenced by the type of solvent used. Therefore, it is of paramount importance to select an appropriate solvent of low or non-toxicity, which is still capable of dissolving PVDF at high temperatures. In recent years, alternative solvents such as diphenyl ketone (DPK) [15] and diphenyl carbonate (DPC) [16] have been tested for PVDF membrane preparation via TIPS.

Citric acid esters, commercially known as “Citroflex”, represent a non-toxic family of plasticizers used in food contact polymer applications. The toxicological safety of Citroflex is demonstrated by satisfactory results in numerous long-term tests conducted in animals [17], and therefore Citroflex is expected to be an environmentally-friendly reagent for use in a range of chemical processes. To date, there have been few reports regarding the TIPS membrane preparation employing Citroflex as a solvent. The citroflex used in these studies are tributyl citrate (TBC), acetyl tributyl citrate (ATBC), and triethyl citrate (TEC). Liu et al. reported the preparation of flat PVDF membranes using a ternary system comprising the polymer, TBC as the solvent, and di-(2-ethylhexyl) phthalate (DEHP) as the non-solvent. They examined the effect of the PVDF/TBC/DEHP composition on the structures and properties of the resulting PVDF membranes [18]. Cui et al. prepared both flat and hollow fiber PVDF membranes using ATBC, and reported that the membrane structures were significantly affected by the experimental conditions, including the polymer concentration, quenching temperatures, air gap, and bore fluid temperature [19]. Hassankiadeh et al. also reported the preparation of PVDF hollow fiber membranes using ATBC, and examined the effect of polymer molecular weight on the membrane structures [20]. Besides PVDF, Mullette et al. also successfully prepared both poly(ethylene chlorotrifluoroethylene) (ECTFE) flat and hollow fiber membranes using TEC [21]. These previous studies clearly demonstrate that Citroflex appears to be an extremely useful solvent for application in the TIPS membrane preparation process.

Therefore, in the study reported herein, in addition to the use of the previously reported ATBC [19,20], we employed for the first time two additional Citroflex solvents, namely acetyl triethyl citrate (ATEC) and TEC, for the preparation of flat PVDF membranes via TIPS. The effect of the different solvents, together with that of the gap between the casting knife and plate, on the structures and properties of the resulting PVDF membranes was investigated. As mentioned in Section 3.1, the solubility for PVDF of the used Citroflex (ATBC, ATEC, and TEC) is closely similar but clearly different from each other. Accordingly, the selection of these three Citroflex allowed us to in detail examine how the polymer/solvent affinity influenced the membrane formation during the TIPS process.

2. Experimental

2.1. Materials

PVDF (Solef 1015, purity: 100%) was kindly provided by Solvay Specialty Polymers (Bollate, Italy). ATBC (purity: 99%), ATEC (purity: 99%), TEC (purity: 99%), kerosene (purity: 100%) and ethanol (purity: 99.8%) were purchased from Sigma-Aldrich. The chemical formulae, properties and safety data information of the Citroflex solvents used in this study are shown in Table 1. Liquid nitrogen was purchased from Pyrosgeno (Cosenza, Italy). Deionized water was obtained from a water purification system (Zeneer RO 180), and was used for the water permeability test.

2.2. Sol–gel transition temperature

PVDF solubility in ATBC, ATEC, and TEC was evaluated by monitoring the sol–gel transition of solutions with variation of the PVDF polymer concentration. A vessel containing the PVDF/solvent solution was heated in an oil bath at 200 °C for 2 h to give a homogeneous solution. Then, the temperature of the oil bath was dropped to the planned value in the range of 100–170 °C, causing the solution in the vessel to be gradually cooled and reach the equilibrium state after 3 h. The vessel was removed from the oil bath, and tilted for observation of the state of the PVDF/solvent mixture at this temperature. If the mixture was homogeneous and can smoothly flow (at higher temperature), it was recorded as a “solution”. If the mixture was viscous and partially solidified (at
lower temperature), it was recorded as a "gel". In this way, the following procedures were repeatedly conducted: heating of the vessel to 200 °C again to revert the mixture to a homogeneous solution; cooling of the vessel to another temperature; and record of the mixture state (solution or gel). The sol–gel transition temperature was defined as the lowest temperature at which the PVDF/solvent mixture was a smooth-flowing liquid.

2.3. Preparation of PVDF flat membranes

The PVDF polymer and Citroflex (ATBC or ATEC or TEC) were mixed in a closed vessel, and heated at 190 °C in an oil bath. The polymer concentration was 16 wt% in all cases (When the polymer concentration was more than 16 wt%, the solution became too viscous, thereby failing to prepare the homogeneous membrane). The resulting solutions were stirred for 3 h at 190 °C until complete dissolution of the polymers was achieved. After the stirring was stopped, the solution was kept exposed to the air for 2 h to degas. The flat PVDF membranes were prepared by using the casting knife containing a narrow rectangular opening at the bottom and a smooth glass support plate set below the casting knife. The polymer solution poured into the casting knife at 190 °C passed through the opening, and then was accumulated on the plate at 30 °C. Just after that, the glass plate started moving at the fixed velocity of 22 cm/min, spreading the polymer solution onto the glass plate. The gap between the casting knife and the glass plate for membrane casting was varied between 200 and 400 μm, allowing the thickness of the final membrane to be varied. After being kept under the ambient atmospheric condition for 2 h, the nascent membrane with a glass plate was immersed in an ethanol bath (purity: 99.8%) for 24 h to extract solvents from the membrane. Finally, the membrane was dried in an oven at 40 °C for 24 h. The membrane side exposed to air during the casting is referred to as the “top side” surface, whereas the side contact with the glass plate is referred to as the “bottom side” surface. The membranes prepared using ATBC, ATEC and TEC are referred to as the “PVDF/ATBC membrane”, “PVDF/ATEC membrane” and “PVDF/TEC membrane”, respectively.

2.4. Characterization of PVDF membranes

2.4.1. FT-IR Analysis

The crystalline phase of PVDF membranes was studied by Fourier-transform infrared (FT-IR) spectroscopy. Spectral data were recorded on a Nicolet™/IST™ 10 FT-IR ATR spectrometer over the range of 400–1000 cm⁻¹ with a resolution of 2 cm⁻¹.

2.4.2. Crystallinity

The thermal properties of the PVDF membranes were examined by differential scanning calorimetry (DSC) using a Rigaku Thermo plus DSC 8230 under N₂. Thermograms of the heat flow vs. temperature of the specimens (around 5 mg) were obtained in the range of 100–200 °C at a heating rate of 5 °C/min. The heat of the fusion of the specimens, H₀, was calculated from the peak area of the thermograms. The degree of crystallinity, X_c, was calculated by:

\[ X_c = 100 \times \frac{H_c}{H_{100}} \]  

where \( H_{100} \) is the heat of fusion for the 100% crystalline PVDF sample (104.7 J/g) [23].

2.4.3. SEM morphology

The morphology of the top-side and bottom-side of the prepared membranes was observed using a scanning electron microscope (SEM) (Carl Zeiss Microscopy EVO Ma 10). The cross-section morphology of the membranes was also observed using an SEM (JSM-5600, JEOL). Cross-section samples were prepared by freeze fracture in liquid nitrogen. Before analysis by SEM, all samples were sputter-coated with a thin gold film to improve the imaging resolution and to avoid electrical charging during the SEM observation.

2.4.4. Porosity

The overall porosity of the membrane defined as the volumetric ratio of the voids to the entire membrane was determined by the gravimetric method as described elsewhere [24–26]. The membrane weight in a dry state, \( M_d \), was measured, and then the membrane was immersed in kerosene for 24 h. After the excess kerosene was wiped off from the surface by a tissue paper, the membrane weight in a fully-wet state, \( M_w \), was measured. The porosity was calculated by

\[ \text{Porosity} = \frac{M_w - M_d}{\rho_k} \times 100, \]

where \( \rho_k \) is the density of crystalline PVDF (1.92 g/cm³) [23], \( \rho_p \) is the density of amorphous PVDF (1.68 g/cm³) [23], and \( \rho_k \) is the density of kerosene (0.82 g/cm³). The \( \rho_p \) is the value for α-phase crystals, because all membranes had α-phase crystals as mentioned in Section 3.2.1.

2.4.5. Pore size

The pore size of the membranes was determined by using a PMI Capillary Flow Porometer (CFP 1500 AXEL, Porous Materials Inc., USA) as described elsewhere [25,26]. Membrane samples were immersed in a Porewick solution (its surface tension is 16 dyne/cm) for 24 h to achieve full wetting, and were placed in the sealed chamber. Nitrogen gas (with increasing pressure over time) was supplied to one side of the sample in order to record the gas pressure and gas flow rate through the sample. The so-called “bubble point” corresponds to the pressure at which the first gas flow is detected. After the bubble point, the gas pressure increased until all pores were empty and the sample was considered to be dry. Gas pressure and flow rate for the dry samples were also recorded. This “wet-up/dry-up” mode was selected using the CapWIN software. Information relating to pore size and pore size distribution was determined based on Laplace’s equation as follows:

\[ d_p = 4 \sigma \cos \theta / P, \]

where \( d_p \) is the pore diameter, \( \sigma \) is the surface tension of the liquid, \( \theta \) is the contact angle of the liquid (assumed to be 0 in the case of full wetting), and \( P \) is the external pressure.

2.4.6. Static contact angle

The static contact angle of water is defined as the angle between the membrane surface and the tangent line at the contact point of the water droplet on the membrane surface. The contact angles at room temperature were measured using an optical contact angle meter (CAM100, KSV Instruments) as described elsewhere [27]. A water droplet of 5 μL was placed on the top- or bottom-side surface of the membrane sample. The measurements were repeated in quintuplicate for each membrane, and the average value was reported.

2.4.7. Tensile properties

The mechanical properties of the membranes were measured using a ZWICK/ROELL Z 2.5 test unit at room temperature. Rectangular samples (1 × 5 cm²) were extended at a constant
elastomer, and the average value was reported. The measurements were repeated in quintuplicate for each membrane, and the average value was reported.

2.4.8. Water flux

Water permeation experiments were conducted at room temperature using a stainless steel dead-end filtration cell (Model HP4750, supplied from Sterlitech Co.) with an effective permeation area of 20.4 cm². The membrane sample was submerged in purified water for 24 h by putting it under a metallic stick to ensure complete wetting prior to measurement. The membrane was placed at the bottom of the cell, and the reservoir (300 mL) behind the membrane was filled with purified water. Transmembrane water flux was driven by applying pressure with nitrogen gas. The gas pressure was varied in the order of 1.0, 0.7 and 0.4 bar. Permeated water was collected, and its mass was recorded on a balance at the desired time intervals. Water flux, \( J_w \), was calculated using the following equation:

\[
J_w = \frac{W}{\rho_w A t},
\]

where \( W \) is the weight of permeated water (g), \( \rho_w \) is the density of water (1 g/cm³), \( A \) is the permeation area (20.4 cm²), and \( t \) is the permeation time (s).

3. Results and discussion

3.1. Phase diagrams of PVDF/citroflex systems

Several number of previous studies [15,16,18] have focused on the phase diagrams of PVDF solutions with relation to the cloud point temperature, at which a transparent polymer solution becomes more viscous and turbid. Cloudiness can occur in a solution of PVDF concentration, the sol becomes turbid until they begin to form gels at the sol–gel transition temperature, at which a transparent polymer solution becomes more viscous and turbid. Cloudiness can occur in a solution of PVDF concentration, the sol

\[
\delta_o, \delta_a, \text{and} \delta_v \text{values for PVDF and the three Citroflex solvents. Although the chosen Citroflex solvents have similar molecular structures, their Hansen parameters show a degree of variation. For example, TEC shows the highest } \delta_v \text{ of 12 as it contains polar hydroxyl groups (–OH). The } R_s \text{ between PVDF and Citroflex was calculated by Eq. (5), and also shown in Table 2. It can be seen that the } R_s \text{ value decreased in the order of ATBC > ATEC > TEC, and it could therefore be predicted that the solubility of PVDF in each solvent was enhanced in the order of ATBC > ATEC > TEC, which agrees with the miscibility trend expected from the sol–gel transition temperature. Based on these results, it was worth examining how the structure and properties of the membranes were affected by the solvents with such different miscibility values.}

3.2. Membrane morphology studies

3.2.1. Crystal structure

As reported in literature [31], PVDF possesses at least four different crystalline phases, named \( \alpha, \beta, \gamma \) and \( \delta \). Among these, the two most common polymorphs are the \( \alpha \) (trans-gauche, TGTG) and \( \beta \) (all-trans, TTGT) phases. The \( \alpha \) phase is a kinetically stable non-polar crystalline form with a monolithic lattice structure, whereas the \( \beta \) phase is a thermodynamically favored polar form with an orthorhombic lattice structure [32]. The type of PVDF crystalline phase depends on the temperature of the solution before casting. The \( \alpha \) phase usually forms at high temperature (> 110 °C), while the \( \beta \) phase is formed exclusively at lower temperature (< 70 °C) [33].

Fig. 2 shows the FT-IR spectra of the PVDF/ATBC, PVDF/ATEC and PVDF/TEC membranes prepared in this study. For all membranes, characteristic peaks were observed at 409, 532, 764, 795, and 972 cm⁻¹, which are indicative of the \( \alpha \)-phase of PVDF [19]. Accordingly, it was found that all the three kinds of Citroflex, i.e., ATBC, ATEC, and TEC, induced the formation of \( \alpha \)-phase PVDF.

Fig. 3 shows the DSC thermograms of the prepared PVDF membranes. The endothermic peak temperature, \( H_m \) and \( X_c \), are

\begin{table}
\centering
\caption{Hansen solubility parameters of PVDF and citroflex.}
\begin{tabular}{|l|lll|}
\hline
Polymer or solvent & \( \delta_o \) (MPa¹/²) & \( \delta_p \) (MPa¹/²) & \( \delta_v \) (MPa¹/²) & \( R_s \) (MPa¹/²) \\
\hline
PVDF & 17.2 \text{a} & 12.3 \text{a} & 9.2 \text{a} & - \\
ATBC & 15.4 \text{b} & 4.1 \text{b} & 6.2 \text{b} & 9.6 \\
ATEC & 16.6 \text{b} & 3.5 \text{b} & 8.6 \text{b} & 9.1 \\
TEC & 16.5 \text{b} & 4.9 \text{b} & 12 \text{b} & 8.2 \\
\hline
\end{tabular}
\end{table}

\textit{Note:}

\text{a} Ref. [29],

\text{b} Ref. [30].

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig1.png}
\caption{Sol–gel transition temperature of PVDF solutions with (●) ATBC, (△) ATEC, and (◆) TEC.}
\end{figure}
listed in Table 3. For all solvent cases, the peak temperature and \( X_c \) increased as the gap between the casting knife and plate became wider. This means that the size of each crystal and the total amount of crystalline regions increased with the gap widening.

### 3.2.2. SEM morphology

The SEM analyses of the membranes prepared under a range of conditions are shown in Figs 4–6. The first comparison was made for the membranes prepared at the knife / plate gap of 400 \( \mu m \) (Fig. 4(c), Fig. 5(c), and Fig. 6(c)) to examine the effect of solvents on the morphology. For the PVDF/ATEC and PVDF/TEC membranes, it can be seen that spherulites are formed at both the top and bottom sides of the membranes, indicating the occurrence of the solid–liquid (S–L) phase separation. During the casting process, the polymer solution on the glass plate was cooled to 30 \( ^\circ \)C, which is significantly lower than the crystallization temperature of PVDF. The polymer chains aggregated each other to form a primary nucleus, to which further polymer chains moved by thermal diffusion to initiate crystallization. These polymer aggregations grew over time to become spherulites, composed of lamellar stacks of alternating crystalline and amorphous layers radiating from the nucleic center. On the other hand, in the case of PVDF/ATBC membranes, only fibrillar structures were observed instead of spherulites, suggesting that the system underwent an L–L phase separation and subsequent crystallization [34]. Cui et al. also observed that this L–L phase separation took place in PVDF / ATBC systems at PVDF concentration lower than 24 wt% [19]. According to the TIPS mechanism [35], S–L phase separation occurs if the compatibility between the polymer and the solvent is high, whereas L–L phase separation occurs if this compatibility is low. Since ATBC has lower affinity with PVDF compared to ATEC and TEC, as shown by the sol–gel transition temperature (Section 3.1), it should cause L–L phase separation in the solution system.

For the PVDF/ATEC membranes prepared at the knife/plate gap of 400 \( \mu m \), it can be seen that the top-side and bottom-side surfaces are porous and considerably dense, respectively. The observed asymmetric structure can be explained by taking into account the difference in the cooling speed of the polymeric solution during the casting process. The bottom side of the nascent membrane was in direct contact with the glass plate at 30 \( ^\circ \)C and underwent fast cooling. Polymer chains were thought to be immediately phase separated from solvent molecules to gather with each other. Additional polymer chains that happened to approach the bottom side by thermal diffusion presumably lost the molecular mobility due to low temperature, and then began to be aggregated together, excluding solvent molecules. Such a fast phase transformation is expected to lead to the formation of fibrillar structures.
separation behavior should increase the local polymer concentration to make the bottom surface dense. Solvent molecules rejected from the polymer phase were forced to vertically ascend to the upper regions. In contrast to the bottom side, the cooling speed of the top side was quite slow, since it was exposed to the air, whose thermal conductivity was far lower than that of the glass plate. Consequently, it is expected that solvent molecules were accumulated in the top side to decrease the local polymer concentration, thereby producing the porous top surface. A similar morphology of a porous top surface and dense bottom surface has been previously reported in studies on the preparation of ECTFE membranes via the TIPS process [36,37].

It is seen from Fig. 4a–c that the top side surface of the PVDF/ATBC membranes became less porous as the knife/plate gap was reduced. As mentioned above, the formation of the porous top surface was related to the slower cooling speed in comparison with the bottom side. When the membrane was thinner, the cooling speed of the top side was faster and closer to that of the bottom side due to the enhanced transmembrane thermal conduction. In other words, the thinner membrane was more homogeneously cooled in whole, producing the less porous top surface. At the narrowest gap of 200 μm, the top side and bottom side surfaces looked alike each other, which may be caused by the almost same cooling speed at the both sides.

Unlike the PVDF/ATBC membranes, the PVDF/ATEC and PVDF/TEC ones prepared at the knife/plate gap of 400 μm did not have the dense skin surface at the bottom side (Figs. 5c and 6c). This result can be related to the fact that ATEC and TEC were better solvents for PVDF than ATBC, as mentioned in Section 3.1. In both the ATEC and TEC cases, even in the fast-cooled bottom side,
polymer chains may keep their molecular mobility at a certain degree because of the high polymer/solvent miscibility. As a consequence, the phase separation throughout the membrane probably occurred at the similar speed, making the both top- and bottom-side surfaces porous. The avoidance of formation of the dense skin layer is an advantage when using ATEC and TEC as solvents. When the gap was narrowed from 400 to 200 μm, the spherulites looked less prominent, and their size tended to be smaller (seen in the cross section images of Figs. 5 and 6). The gap narrowing quickened the cooling of the whole membrane and gave a polymer solution shorter time for phase separation to form spherulites. This result was in consistent with the DSC data in Table 3 (i.e., the membranes prepared at the narrower gap showed the lower $X_c$). It was noted that the PVDF/TEC membrane prepared at 200-μm gap seemed to have almost no spherulites (especially in the bottom side). This membrane with the lowest thickness of only 90 μm (see Table 4) was cooled at the fastest speed, and so the phase separation would be significantly restricted.

3.3. Membrane properties

3.3.1. Pore structure

Table 4 shows the thickness, porosity, mean pore size, and contact angle of the prepared PVDF membranes. For all the cases, the thickness was significantly lower than the knife/plate gap due to evaporation of solvent from the nascent membrane cast on the plate. The pore size obviously increased in the following order of solvent: ATBC < ATEC < TEC. For example, at the gap of 400 μm, the pore sizes were 0.93 μm (ATBC), 2.98 μm (ATEC) and 7.24 μm (TEC), respectively. This pore size trend is in consistent with the
order of the PVDF/solvent miscibility shown in Fig. 1, and can be explained based on the TIPS mechanism [38,39]. For the TEC case, as discussed in Section 3.2, a high PVDF/TEC miscibility resulted in remarkable S–L phase separation. Simultaneously with the spherulite formation, TEC molecules gathered to form solvent-rich regions that turned into large pores after solvent extraction. For the ATEC case, a lower PVDF/ATEC miscibility resulted in a more viscous solution, retarding the molecular mobility of polymer and solvents. The formation of spherulites and solvent-rich regions was a little restricted, thereby producing smaller pores, as well as smaller spherulites. Moreover, for the ATBC case, the TIPS mechanism shifted to the L–L phase separation due to the lowest PVDF/ATBC miscibility. ATBC molecules had less time to aggregate with each other, leading to formation of very small pores. This pore-size trend is in agreement with the work of Su et al. [11], who prepared PVDF membranes via TIPS using four types of solvents: γ-butyrolactone (γ-BL); propylene carbonate (PC); DBP; and dibutyl sebacate (KD). The membrane pore size was reduced by changing the solvents from γ-BL and PC (higher miscibility with PVDF) to DBP and KD (lower miscibility with PVDF). In contrast to their qualitative discussion based on only SEM observation, we quantitatively reported the effect of solvent on the pore size, leading to a better understanding of pore formation via TIPS.

At the knife/plate gap of 400 μm, the PVDF/ATBC membrane showed the porosity of 65.9%, while the PVDF/ATEC and PVDF/TEC membranes showed the higher porosity of 76.0% and 75.5%, respectively. During the casting process, groups of solvent molecules can reach the top side surface and be expelled to the outside of the membrane. Accordingly, the porosity corresponds to the total amount of the remaining solvents inside the membrane. Since
ATBC had the lowest miscibility with PVDF. ATBC were relatively easily expelled to the outside (low porosity). On the other hand, ATEC and TEC with higher miscibility likely remained inside the membrane (high porosity). When the knife/plate gap was wider, an increase in both porosity and pore size was observed, especially for the ATEC and TEC cases. The enlargement in the knife/plate gap presumably caused the two effects. The first effect is that solvents were unable to easily reach the top side surface owing to the greater distance to move. The amount of solvents remaining inside the membrane increased, leading to an increase in porosity. The second effect is that the cooling speed throughout the membrane was slow due to low vertical thermal conduction. The polymer/solvent phase separation took place over a longer period of time, resulting in an increase in pore size. To the best of our knowledge, our study reported in detail for the first time that the pore structure was significantly influenced by the knife/plate gap in the TIPS membrane preparation.

3.3.2. Contact angle

The measured contact angle of a sessile droplet, $\theta_m$, is related to the roughness of the surface by the following equation [40]:

$$\cos \theta_m = r \cos \theta_y,$$

(6)

where $r$ is the ratio of the actual to projected surface area ($r = 1$ for a smooth surface and $r > 1$ for a rough surface), and $\theta_y$ is the Young contact angle, which is equal to $\theta_y$ if $r = 1$. From Eq. (6), we can determine that the greater the roughness of the surface, the higher the measured contact angle is. This relationship is useful for analyzing the contact angle data.

As shown in Table 4, the contact angle measured on the top side surface was higher than that on the bottom side surface for all membranes. This suggests that the top side surface was somewhat more porous and rough than the bottom side surface as shown in Figs. 4–6. The PVDF/ATBC membranes showed the lowest contact angle of 82–98° at the bottom side surface, which is in agreement with the dense and flat surface observed by SEM (see Fig. 4). The reason for formation of porous top and dense bottom sides is due to the different cooling speed of the two polymeric film surfaces after casting, as discussed in Section 3.2.

3.3.3. Tensile properties

Table 5 shows the tensile properties of the prepared membranes. One notable point is that the Emod of the PVDF/ATBC membranes are 2-times or more higher than that of the other two membranes. This can be explained by taking into account that the PVDF/ATBC membranes had the smallest pore sizes amongst all the prepared membranes.

The tensile strength and elongation at breaking point did not strongly depend on the identity of the solvent used in the membrane preparation process, but decreased as the thickness of the membranes increased. This is consistent with the result that the porosity and mean pore size increased with the membrane thickness (see Table 4). For the thick membrane, highly porous structures would make the samples more fragile, reducing the tensile strength and elongation at breaking point.

3.4. Water flux

For all the membranes, the amount of permeated water increased proportionally with time at every water supply pressure, indicating the continuous porous structure to transport water through the membrane. As shown in Fig. 7, the $J_w$ of the membranes was linearly raised with increasing the water supply pressure. This means that the pore structure is stable and unchanged regardless of the pressure, which should be due to enough mechanical strength of the membranes suggested in Section 3.3.3. If the membranes had had poorer mechanical property, high pressure would have caused the collapse of the porous structures to merge plural inside pores into larger ones. If so, the $J_w$ would have been abnormally high at the high pressure, deviating from the linear relationship (this is not the case with our membranes). The data plots shown in Fig. 7 were fit to a straight line using the least squares regression method. The water permeability of the membrane, $P_w$, corresponding to the slope of the line, is listed in Table 6.

In order to fairly compare the water flux for all the membranes, the effect of the thickness should be obviated. Then, the thickness-normalized water permeability, $P_w \rho_w$, was calculated by multiplying the $P_w$ with the membrane thickness, and listed in Table 6.

Based on the Hagen–Poiseuille flow, the $P_w \rho_w$ through a material is expressed as follows:

$$P_w \rho_w = \frac{\varepsilon \rho_w^2}{8 \eta \tau},$$

(7)

where $\varepsilon$ is the porosity of the material, $\rho_w$ is the pore radius, $\eta$ is the dynamic viscosity of water, and $\tau$ is the tortuosity of the water transport pathways. The $\tau$ value represents the degree of geometrical complexity of the water transport pathways, which are not perfectly straight but curved and branched. The $\tau$ is defined as $L/\text{material thickness}$, where $L$ is the actual average length traveled by water from the feed side to the permeate side. As expressed in Eq. (7), the $P_w \rho_w$ is determined by the three factors, $\varepsilon$, $\rho_w$, and $\tau$.

As shown in Table 6, the thicker membranes (prepared at a wider knife/plate gap) enhanced the $P_w \rho_w$. This could be because

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Properties of prepared PVDF membranes.</th>
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<tbody>
<tr>
<td>Solvent</td>
<td>Knife/plate gap (μm)</td>
</tr>
<tr>
<td>ATBC</td>
<td>200</td>
</tr>
<tr>
<td>ATBC</td>
<td>300</td>
</tr>
<tr>
<td>ATBC</td>
<td>400</td>
</tr>
<tr>
<td>ATEC</td>
<td>200</td>
</tr>
<tr>
<td>ATEC</td>
<td>300</td>
</tr>
<tr>
<td>ATEC</td>
<td>400</td>
</tr>
<tr>
<td>TEC</td>
<td>200</td>
</tr>
<tr>
<td>TEC</td>
<td>300</td>
</tr>
<tr>
<td>TEC</td>
<td>400</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Tensile properties of PVDF membranes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Knife/plate gap (μm)</td>
</tr>
<tr>
<td>ATBC</td>
<td>200</td>
</tr>
<tr>
<td>ATBC</td>
<td>300</td>
</tr>
<tr>
<td>ATBC</td>
<td>400</td>
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<tr>
<td>ATEC</td>
<td>200</td>
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<td>ATEC</td>
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<td>ATEC</td>
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<tr>
<td>TEC</td>
<td>200</td>
</tr>
<tr>
<td>TEC</td>
<td>300</td>
</tr>
<tr>
<td>TEC</td>
<td>400</td>
</tr>
</tbody>
</table>
the porosity and pore size increased with the membrane thickness, as already reported in Table 4. The results from these measurements were then compared with literature data reported by Cui et al. [19], who performed the water flux test of the PVDF/ATBC membranes prepared at a knife/plate gap of 400 μm. At a polymer concentration of 15 wt%, the \( J_w \) was reported to be 1550 L/m² h (at 0.82 μm), 2410 L/m² h (at 1.0 bar), and 1720 L/m² h (at 1.5 bar), respectively. Since the thickness was 186 μm, the \( P_w^1 \) of Cui’s membrane was calculated to be 0.59 L/m² h/bar. This value is somewhat lower than the \( P_w^1 \) for our PVDF/ATBC membrane, due to the smaller pore size of Cui’s membrane.

Furthermore, at the same knife/plate gap, the \( P_w^1 \) depended on the type of solvent used. With a gap of 300 μm, the \( P_w^1 \) was 1.03 L/m² h/bar (ATBC), 1.14 L/m² h/bar (ATEC) and 1.29 L/m² h/bar (TEC), respectively. Since these three membranes have similar porosity (56.1–58.9%), the increase in \( P_w^1 \) was mainly caused by the enlargement of the pore size: ATBC (0.82 μm) < ATEC (2.88 μm) < TEC (4.29 μm). However, it is noteworthy that the \( P_w^1 \) of the PVDF/ATBC and PVDF/ATEC membranes did not differ to a great extent even though the latter membrane had about 3.5-times larger pores than the former one. According to Eq. (7), the \( P_w^1 \) increases 3.5 times. Contrary to this estimation, the \( P_w^1 \) of the PVDF/ATEC membrane was only 1.1-times higher than that of the PVDF/ATBC one. This result could be justified by considering the following two factors that relatively increased the \( P_w^1 \) of the PVDF/ATBC membranes. The first factor is the \( \tau \), the geometrical complexity of water transport pathways. Recall that ATBC induced L–L phase separation, while ATEC and TEC induced S–L phase separation. L–L phase separation was assumed to produce the bicontinuous porous structures [15,16,18] for smooth water transportation. This result was confirmed by considering the following two factors that relatively increased the \( P_w^1 \) of the PVDF/ATBC membranes. The first factor is the \( \tau \), the geometrical complexity of water transport pathways. Recall that ATBC induced L–L phase separation, while ATEC and TEC induced S–L phase separation. L–L phase separation was assumed to produce the bicontinuous porous structures [15,16,18] for smooth water transportation. This result was confirmed by considering the following two factors that relatively increased the \( P_w^1 \) of the PVDF/ATBC membranes.

### Table 6

<table>
<thead>
<tr>
<th>Solvent</th>
<th>knife/plate gap (μm)</th>
<th>( P_w^1 ) (L/m² h bar)</th>
<th>( P_w^j ) (L/m² h bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATBC</td>
<td>200</td>
<td>9.20 ± 0.28</td>
<td>0.89 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>8.87 ± 0.27</td>
<td>1.03 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>8.23 ± 0.25</td>
<td>1.13 ± 0.03</td>
</tr>
<tr>
<td>ATEC</td>
<td>200</td>
<td>10.54 ± 0.32</td>
<td>0.99 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>10.20 ± 0.31</td>
<td>1.14 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>10.29 ± 0.31</td>
<td>1.53 ± 0.05</td>
</tr>
<tr>
<td>TEC</td>
<td>200</td>
<td>9.77 ± 0.29</td>
<td>0.88 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>10.29 ± 0.31</td>
<td>1.29 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>9.95 ± 0.30</td>
<td>1.56 ± 0.05</td>
</tr>
</tbody>
</table>

### Fig. 7

Fig. 7. \( J_w \) of the PVDF membranes prepared from (a) PVDF/ATBC, (b) PVDF/ATEC, and (c) PVDF/TEC systems.

### 4. Conclusions

In this study, we successfully prepared flat PVDF membranes via TIPS using three non-toxic Citroflex solvents, namely ATBC, ATEC, and TEC. From the results obtained during these studies we could conclude the following:

- Sol–gel transition temperature measurements revealed that the three solvents had different miscibility with PVDF, which increased in the order of ATBC < ATEC < TEC. This miscibility trend coincides with that predicted by Hansen solubility parameter theory.
- SEM analysis showed that the formation of spherulites was observed in the PVDF/ATEC and PVDF/TEC membranes, indicating S–L phase separation during the casting process. In contrast, the PVDF/ATBC membranes formed only fibrillar structures, indicating L–L phase separation.
Pore size of the membranes increased in the solvent order of ATBC < ATEC < TEC. Both pore size and porosity increased with a wider knife/plate gap. The dependence of the pore structures on the solvent and knife/plate gap was explained by taking into account the phase separation behavior during the membrane casting.

For all the membranes prepared in this study, the $P_W$ also varied with both the solvent type and the knife/plate gap. The result of $P_W$ can be explained by taking into account the porosity, pore size, and the tortuosity of water transport pathways.

This work therefore demonstrates how a detailed analysis of membrane preparation using non-toxic solvents can lead to interesting and useful results, which proves the feasibility of the replacement of more toxic solvents in the membrane preparation. Finally, the application of the produced membranes into microfiltration has also the aim of increasing the sustainability and reducing the environmental impact of human activities.

References


