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A more sustainable membrane preparation using triethyl phosphate as solvent

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Abstract: In this work, hydrophobic poly(vinylidene fluoride) membranes for potential membrane distillation applications, with pore sizes ranging from ~ 0.05 to ~ 0.30 µm, were prepared by employing triethyl phosphate (TEP) as a substitute to the hazardous, commonly used, toxic solvents. Membrane morphologies and properties were tailored based on the main parameters, such as the casting solution composition and the operational conditions, which affect the phase inversion process. Experimental results showed that exposure time to controlled humid air and temperature, as well as additive content in the dope solution, strongly influence the membrane formation. The use of TEP as an alternative solvent may contribute to the development of sustainable separation operations.

Keywords: green chemistry; membrane; PVDF; TEP.

1 Introduction

Poly(vinylidene fluoride) (PVDF, Figure 1) is one of the most attractive thermoplastic fluoropolymers for membrane preparation, due to its outstanding properties, such as high chemical and thermal resistance, excellent mechanical stability, and resistance to microorganism growth [1, 2]. Meanwhile, phase inversion is the most commonly used polymeric membrane preparation technique because of its high versatility and simplicity [3, 4]. However, it generally implies the use of highly hazardous compounds, which counteract the sustainable membrane separation development. In fact, PVDF membrane fabrication *via* phase inversion [4] commonly involves the use of solvents, such as DMF, DMA, and NMP. Although these diluents are considered superb solvents for the solubilization of both amorphous and semi-crystalline polymeric materials, according to Regulation (EC) N. 1272/2008, these are mutagenic and carcinogenic [3, 4]. DMF, as reported by the International Agency for Research on Cancer (IARC), is a possible carcinogen substance. In fact, many studies have been undertaken to demonstrate that liver disease can be related to DMF exposure [5]. Furthermore, it is also considered as a reproductive toxin that may cause damage to an unborn child [5]. DMA is rapidly absorbed by inhalation, and chronic exposure to this solvent causes severe liver damage in humans, which may even lead to an abnormal mental state [6]. Meanwhile, NMP is classified as a toxic compound that can potentially damage the reproductive system [7].

In this context, the use of less-toxic diluents for making PVDF membranes may open new perspectives for sustainable membrane fabrication [8, 9]. Herein, we present a method of PVDF flat sheet membrane production *via* NIPS coupled with VIPS, using TEP (Figure 2) as an alternative solvent. TEP does not possess high levels of toxicity, as confirmed by its Material Safety Data Sheet [9]. It is not mutagenic, teratogenic, or bioaccumulative; therefore; it does not pose severe risks to worker health. In in industrial applications, TEP is used for industrial applications as a flame retardant, a catalyst in the industrial acetic anidride synthesis, and a strengthening agent in the plastic industry [8]. Its high resistance to many organic and inorganic acids, its good thermal stability, and its toxicological profile, make this solvent an ideal substitute for traditional toxic diluents.

The experimental results of this study showed that TEP can be efficiently used for preparing hydrophobic porous membranes for potential uses in MD processes.

2 Materials and methods

Casting solution was prepared by mixing the correct amount of PVDF (Solef® 6010, ~ 322,000 g/mol) supplied by Solvay Specialty Polymers (Bollate, Italy) and TEP (Sigma-Aldrich) as a solvent. PVP (K17, BASF, Ludwigshafen, Germany; M.W. ~ 10,000 g/mol) and PEG (PEG-200, Sigma-Aldrich, Milan, Italy; M.W. ~ 200 g/mol) pore-former additives were added to the polymeric solution. The influence of these two hydrophilic agents on the resulting PVDF membrane structure has been reported in various publications [10, 11].

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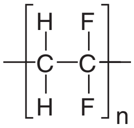

Figure 1: PVDF structural formula.

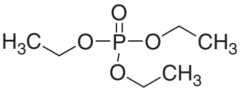

Figure 2: TEP structural formula.

Ethanol (Sigma Aldrich, Milan, Italy) was used as coagulation medium. The dope solution was stirred constantly at 100°C until a homogeneous solution was obtained. Then, the solution was cast onto a glass plate using a manual casting knife (Elcometer 3700 Doctor Blade Film Applicator with Reservoir, Elcometer Instrument GmbH, Aalen, Germany) with a 350-μm gap. The nascent membranes were either mmediately immersed in the coagulation bath composed of ethanol (NIPS) or exposed for 5 min to controlled relative humidity (RH, 65%) and temperature (25°C) in a climatic chamber (DeltaE srl, Rende (CS), Italy) before passing them in the ethanol bath (NIPS coupled with VIPS). The formed membranes were then washed with hot water (60°C) for three consecutive times to well remove the solvent and additives residues. The membranes were finally heated in an oven at 45°C for 24 h before their characterization.

Table 1 presents the list of the prepared membranes. As can be seen, the membranes were characterized in terms of morphology (by SEM), pore size, pure water permeability (PWP), thickness, mechanical strength, porosity, and contact angle.

2.1 SEM

SEM pictures of the membranes were registered by using a Zeiss-EVO Ma10 instrument (Oberkochen, Germany).

2.2 Thickness

Membrane thickness was measured by using a digital micrometer (Carl Mahr, Göttingen, Germany) with a precision of ± 0.001 mm.

Table 1: List of the prepared membranes.

Membrane code	PVDF (wt%)	PEG (wt%)	PVP (wt%)	TEP (wt%)	Exposure to RH% (min)
M1	15	10	5	70	0
M2	15	10	5	70	5
M3	15	15	5	65	0
M4	15	15	5	65	5
M5	15	20	5	60	0
M6	15	20	5	60	5

2.3 Porosity

Membrane porosity, defined as the pore volume divided by the total volume of the flat sheet membranes, was calculated using the following correlation [12]:

$$\text{Porosity }(\%) = \frac{(w_w - w_d)/\rho_w}{(w_w - w_d)/\rho_w + (w_d/\rho_p)} \times 100,$$

where w_w is the weight of the wet membrane, w_d is the weight of the dry membrane, ρ_w is the kerosene density, and ρ_p is the polymer density.

2.4 Contact angle

Membrane contact angle measurements were performed by using an optical tensiometer (CAM100 Instrument, Nordtest srl, GI, Serravalle Scrivia (AL) Italy) *via* the drop method. A drop of bi-distilled water was deposited on a membrane using a micropipette.

2.5 Mechanical strength

Strains at break and Young's modulus were measured using the Zwic/Roell test unit (Z2.5, Zwick/Roell, Ulm, Germany). For each membrane, five samples were analyzed.

2.6 Pore size

Pore size was evaluated by the liquid-gas displacement process using a capillary flow porometer (CFP-1500 AEXL, PMI Porous Materials Inc., Ithaca, NY, USA). Membranes were kept in Porewick® (Sigma-Aldrich, Milan, Italy, superficial tension 16 dyne/cm) for 24 h so that they were fully wetted. Nitrogen was gradually allowed to flow into the membrane by increasing its pressure during this time. Gas pressure and permeation flow rates across the dry membrane were registered, facilitatinh the calculation of the final pore size distribution.

2.7 Pure water permeability

PWP was measured at 25°C by using a laboratory cross-flow cell. Pure water was pumped through the membrane (area of 0.0008 m^2) by means of a gear pump (Tuthill Pump Co., Alsip, USA). PWP was evaluated by collecting the permeate in the unit time and applying the equation

$$\text{PWP} = Q/A\,t\,p,$$

where Q is the permeate volume in liters, A is the membrane area (expressed in m^2), t is the time (expressed in hours), and p is the pressure (expressed in bar).

3 Results and discussion

The morphologies of the prepared membranes were analyzed by SEM. Figures 3 and 4 present the cross-section

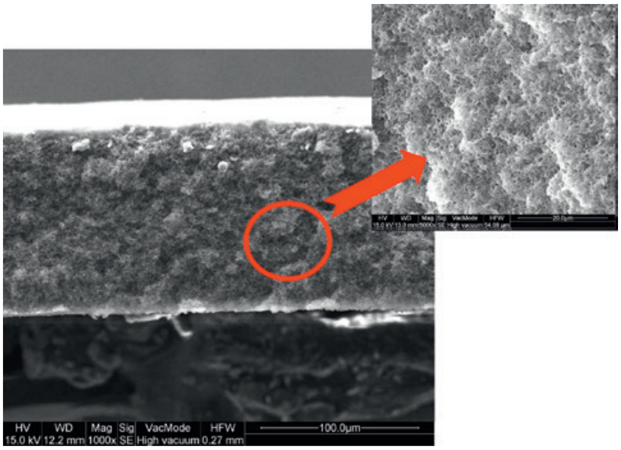

Figure 3: Cross-section of the membranes prepared with the dope solution composed of 15 wt% PVDF, 5 wt% PVP, 10 wt% PEG, and 70 wt% TEP.
Samples were obtained by direct immersion in ethanol bath (NIPS process). Mag. 1000 × in the inserted enlarged view of the cross-section mag. 5000 ×.

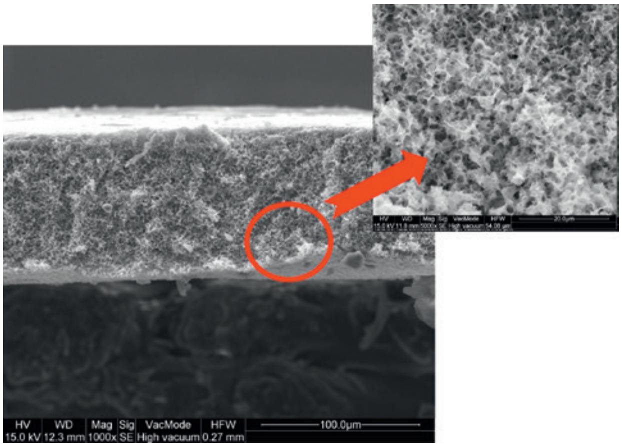

Figure 4: Cross-section of the membrane prepared with the dope solution composed of 15 wt% PVDF, 5 wt% PVP, 10 wt% PEG, and 70 wt% TEP.
Samples were obtained by exposure to humidity for 5 min followed by immersion in ethanol bath (NIPS-VIPS process). Mag. 1000 × in the inserted enlarged view of the cross-section mag. 5000 ×.

images of the membranes. The membranes were prepared with the casting solution containing 10 wt% of PEG; these were then immediately immersed in the coagulation bath (membrane M1 in Table 1, NIPS) or exposed for 5 min to humidity before subjecting them to polymer precipitation in ethanol (membrane M2 in Table 1, NIPS-VIPS).

Both membranes M1 and M2 (Table 1) present a symmetric, porous, and sponge-like matrix; moreover, between them, the membrane obtained *via* NIPS-VIPS procedure (M2 in Figure 4) presented a more open structure, which reflects the result of the pore size analysis (Figure 5). The presence of ethanol in the coagulation bath may reduce the membrane formation rate during the phase inversion. In fact, nascent PVDF films coagulated in water, instead of ethanol, during the NIPS process show finger-like morphologies and dense skin layers on the top surface, indicating that water possesses stronger coagulation ability than ethanol [13–17]. The TEP-weakened precipitation ability slows down the phase separation rate, leading to porous spongy membranes. Similar results were obtained when ethanol was used as the precipitation medium, and when DMF, DMA, and NMP were used as solvents [14, 18–20]. These findings indicate that TEP could efficiently replace the traditional, hazardous solvents. The use of safer materials [8, 9, 21, 22], together with the sustainability related to the membrane processes [1, 23, 24], can provide a strong chemical support to the growth of the sustainable industrial chemistry.

Meanwhile, membranes obtained by direct immersion in the ethanol bath present smaller pore sizes compared with those of the membranes derived from the NIPS-VIPS procedure (exposure to humid air for 5 min, followed by coagulation in ethanol). In particular, the NIPS process generated membranes with pore sizes in the range of ultrafiltration (~ 0.05 µm), whereas membranes with larger pore dimensions (~ 0.2 µm – 0.3 µm) were successfully produced *via* the NIPS-VIPS procedure. In the latter case, the increasing PEG concentration in the dope solution from 10 wt% to 20 wt% promoted the increase in pore size (Figure 5). It should be noted that the membrane obtained with a 20 wt% of PEG in the casting solution *via* NIPS was too fragile for the characterization tests.

The pore size data may be related to the different solvent/non-solvent exchange rates during phase

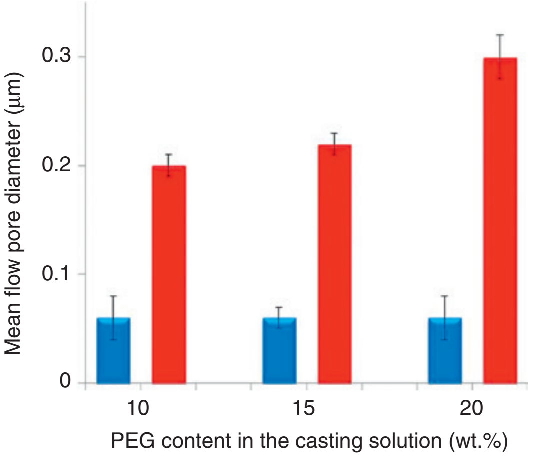

Figure 5: Pore size of the prepared PVDF membranes.
In blue: membranes prepared via the NIPS process. In red: membranes prepared via the NIPS-VIPS process.

inversion. The immediate immersion of the nascent film in the coagulation bath *via* NIPS procedure seems to promote rapid demixing, thus favoring the fast polymer precipitation, even when PEG content increased from 10 wt% to 20 wt%. By contrast, exposure to humid air may delay the coagulation process in the polymer matrix, thus leading to a slower membrane formation. The PWPs of the fabricated PVDF membranes are illustrated in Figure 6.

The experimental results show that the membranes prepared by direct coagulation in the ethanol bath lead to a very low PWP, which is strictly associated to their porosity and pore size. For these membranes, PWP reached a value of ~ 50 l/m²hbar for the sample produced with the lowest PEG content in the dope solution (M1 in Table 1). The value is even lower (~ 0.1 l/m²hbar) for M3, which has been prepared with higher PEG content in the casting solution (15 wt%). The membrane obtained with 20 wt% of PEG in the dope solution is too brittle and breakable to be characterized by PWP tests. This may be due to the high PEG content, which may have conferred high porosity to the final membrane.

Meanwhile, by coupling NIPS with VIPS, the PWP drastically changed. Exposure to humidity for 5 min prior to their passage in the precipitation medium resulted in membranes with higher PWP as follows: ~ 1800, ~ 500, and ~ 150 l/m²hbar for samples prepared with 10 wt%, 15 wt% and 20 wt% of PEG, respectively, (M2, M4, and M6, respectively, in Table 1). The PWP may be influenced by the thickness, porosity, and hydrophilicity (Table 2) as well as the pore size (Figure 5) of the membranes. The casting solution containing 10 wt.% PEG shows the lowest thickness (M2 in Table 1), which could be related to the higher phase inversion rate, compared with those of the two other investigated cases (15 wt% and 20 wt%).

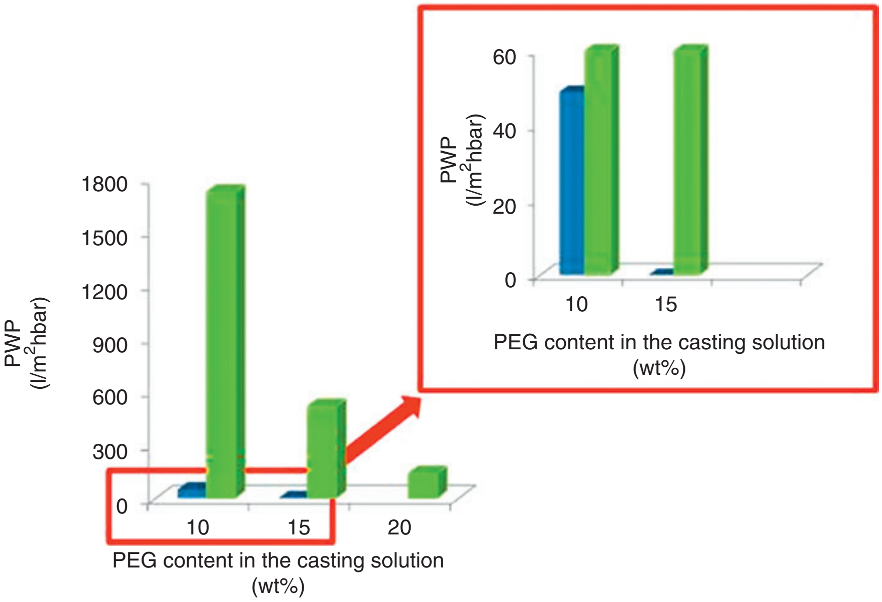

Figure 6: PWP of the prepared membranes.
In blue: membranes prepared via the NIPS process. In green: membranes prepared via the NIPS-VIPS process.

Table 2: Thickness, mechanical resistance, porosity, and contact angles of the fabricated membranes.

Membrane code	Thickness (mm)	Mechanical strength Young's modulus (N/mm²)	Break (%)	Porosity (%)	Contact angle °
M1	0.111±0.003	84.0±1.6	2.6±0.5	84.2±1.1	95.0±0.9
M2	0.091±0.002	21.0±0.9	17.1±1.5	85.9±1.3	86.6±0.8
M3	0.125±0.001	139.5±3.2	3.6±0.4	78.5±1.5	118.2±0.6
M4	0.124±0.004	73.7±5.5	11.3±1.4	80.5±1.4	110.0±0.1
M5[a]	–	–	–	–	–
M6	0.120±0.003	84.0±1.6	16.6±0.5	85.5±0.8	100.4±0.8

[a] Membrane was too fragile to be characterized.

This, in turn, may be due to a lower solution viscosity [21]. This membrane showed the highest PWP and porosity as well as the lowest contact angle. At the same time, this membrane presented a certain degree of breakability, as demonstrated by the Young's Modulus and the percentage of break reported in Table 2.

M4 membrane (~ 0.2 µm in pore size), cast from the solution containing 15 wt% of PEG, resulted in the production of more hydrophobic samples with good mechanical properties and higher thickness compared with M2 (~ 0.090 vs. 0.125 mm for M2 and M4, respectively), although the PWP is lower (Figure 6). In addition, the M6 membrane (~ 0.3 µm), despite the low PWP (~ 150 l/m^{2}hbar), is a potential candidate for MD processes, showing a contact angle of ~ 100° as well as adequate thickness and mechanical features.

4 Conclusions

Porous, hydrophobic PVDF membranes for potential applications in MD processes were successfully prepared by using TEP as an alternative and less toxic solvent. The experimental results showed that membranes with different morphologies and levels of performance could be obtained by changing the PEG content in the dope solution and the exposure time to controlled humidity and temperature. In this study, membranes with promising properties for potential MD applications were prepared by combining NIPS with VIPS techniques. In particular, PVDF membranes with a contact angle of ~ 100°C and pore sizes in the range 0.2 µm–0.3 µm were successfully produced by exposing the forming film to humidity for 5 min before their complete formation in the coagulation ethanol bath. However, further investigations are needed to improve the membrane preparation procedure, such as developing methods for the physical and chemical treatments of the coagulation bath, which should allow the recovery and reuse of TEP.

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Bionotes

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Tiziana Marino received her PhD in Chemical Engineering and Materials from the University of Calabria in collaboration with the Universitat Politecnica de Valencia, Spain, in 2012. She is currently a post-doc at the Institute on Membrane Technology of the Italian National Research Council (ITM-CNR). Her research mainly focuses on green chemistry and separation processes, with particular interest in polymeric flat sheet membrane preparation by using alternative sustainable solvents for water treatments.

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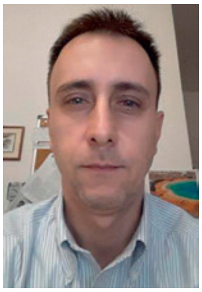
Serenella Blefari graduated in Pharmaceutical Chemistry and Technology from the University of Calabria in 2015. Her master's thesis focused on preparation of novel polymeric flat sheet membranes by using alternative solvents, and was carried out at the Institute on Membrane Technology of the Italian National Research Council (ITM-CNR).



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