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Novel PVDF-HFP flat sheet membranes prepared by triethyl phosphate (TEP) solvent for direct contact membrane distillation

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ABSTRACT

Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) flat sheet membranes were prepared for aqueous membrane distillation (MD) applications using triethyl phosphate (TEP) as less-toxic solvent *via* phase inversion. PVDF-HFP concentrations of 10, 12 and 15 wt.% were investigated and it was observed that different polymer concentrations led to membranes with different surface structure and performance; the use of different coagulation bath compositions played a key role in the membrane fabrication and affected the performance in membrane distillation. The results showed that the permeation decreased sharply when the polymer concentration increased from 12 to 15 wt.%. By adding isopropanol as non-solvent to coagulation medium led to interesting results in terms of permeation. However, the use of lithium chloride to the casting solution had also a positive impact on membrane characteristics in price of retrograde membrane mechanical properties. Particularly interesting was the membrane produced from solution containing the 12 wt.% polymer and coagulated in the isopropanol–water mixture, which gave a DCMD permeation of 16.1 kg h^{-1} m^{-2} at feed temperature of 60 °C, and a salt rejection of 99.3%.

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1. Introduction

The growth of modern applications by using artificial membranes needs prominent properties of polymers. Polymeric materials need to have high resistance to acids, bases, oxidants or reductants, high pressures and high temperatures, as well as suitable chemical properties in order to enhance the permeation flux with suitable solute separation factor of the membranes for the foreseen applications [1,2].

PVDF-HFP is a copolymer which attracted attention as a possible material for membrane applications [3–6]. In comparison with poly(vinylidene fluoride) (PVDF), PVDF-HFP have lower crystallinity due to the incorporation of the hexafluoropropene comonomer (HFP) into the main backbone which significantly enhances the amorphous phase content. It is also believed that the presence of HFP groups resulting in an increase of the fluorine content and leads to PVDF-HFP with better hydrophobic chains [3–6]. Therefore, for many applications where the hydrophobicity of membrane material is decisive, PVDF-HFP is a potential candidate [7]. Hence, it is believed that the PVDF-HFP is a good candidate to be used for MD applications. Few works has been done using PVDF-HFP copolymer for producing membranes. Among them, Garcia-Payo et al [7] prepared PVDF-HFP copolymer hollow fiber membranes for MD using dry/wet spinning technique at different copolymer concentrations. They found that there is no significant change of the thickness of all hollow fibers. They showed that at low copolymer concentration, finger-like structure was detected in cross-section membrane. While at high copolymer content, a sponge like structure was observed. They foreseeable that permeate flux of MD process would decline with increasing the copolymer composition. Khayet et al. [8] made PVDF-HFP hollow fiber membranes using different polymer concentrations *via* phase inversion method for direct contact membrane distillation (DCMD). They used a fractional factorial design and a steepest ascent method for possible fabrication of hollow fiber membranes.

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The optimized hollow fiber membranes revealed the highest performance index and the greatest global desirability.

Bottino et al. [9] studied the influence of the type of solvent on the final membrane structure and performance. The obtained results highlighted as the solvent/non-solvent mutual diffusivity plays a relevant role in evaluating the morphology of the membrane.

The 5th principle of Green Chemistry encourages the use of safer solvents and auxiliaries [10]. This comprises any materials that do not directly influence the molecular structure of the reaction product(s) but are still required for the process to occur. Solvents are the most common example of auxiliary compounds for membrane preparation *via* phase inversion. In fact, they are needed for dissolving the selected polymer and their chemical–physical properties strongly influence the membrane formation and, consequently, its performance. Among the most widely used solvents, *N*,*N*-dimethyl formamide (DMF), *N*,*N*-dimethyl acetamide (DMAc) and *N*-methyl pyrrolidone (NMP), represent an excellent choice for dissolving PVDF-HFP. However, they are classified as highly nephrotoxic and developmental harmful [11]. Consequently their use should be avoided whenever possible. Taking into account its low toxicity for human health and worker safety, TEP was proposed as promising solvent for replacing the traditional, highly toxic ones. Although it cannot be defined “green”, it represents a valid choice towards the improvement of membrane preparation in terms of worker safety. Table 1 shows a comparison between the hazard and precautionary phrases of DMF, DMA, NMP and TEP, evidencing as the selected diluent is not classified as carcinogenic, mutagenic and teratogenic, like the traditional used solvents. Its complete miscibility with water and alcohols such as isopropanol, as well as its high boiling point, make it a favorable alternative for dissolving the selected polymer by using water/alcohols as coagulation bath. When TEP was used as solvent, a porous membrane was obtained.

Feng et al. [13] prepared PVDF-HFP flat sheet membranes for DCMD. They found that high value of pore radius of membranes occurred when ethanol or *n*-butyric acid composition increased in the solidification bath. Also they found that PVDF-HFP membranes presented a stronger hydrophobic nature than PVDF membranes.

Recently, Nejati et al. [14] proposed TEP as less toxic solvent for PVDF homopolymer membrane preparation, obtaining samples with an asymmetric structure (a dense skin layer and highly porous bottom side) suitable for MD applications.

The aim of this research is to discuss a detailed investigation on the production of PVDF-HFP membranes for aqueous membrane distillation application using TEP as alternative, less toxic, solvent. The influence of lithium chloride as pore former agent and different coagulation bath composition, some of which including isopropanol, was studied. Although both the lithium salt and the alcohol used are not safe for human health [15,16] and further investigations are needed to make the entire membrane preparation procedure completely sustainable and harmless, minimizing the toxic effects related to the use of the solvent, represents a first step for the human health protection [17]. Different parameters affecting membrane production including polymer concentration, membrane coagulation medium type and the presence of lithium chloride (LiCl), are studied. The PVDF-HFP membranes were characterized by means of scanning electron microscopy (SEM), capillary flow porometer (PMI), thickness, void volume fraction, mechanical properties and contact angle measurements.

2. Experimental

2.1. Materials

PVDF-HFP copolymer (Solef® 21510) was kindly supplied by Solvay Specialty Polymers (Bollate (MI), Italy) and used to prepare the dope solutions. This copolymer possesses a significantly lower melting temperature (130–136 °C) and lower heat of fusion (20–24 J/g) than the corresponding homopolimer with the same molecular weight [18]. Triethyl phosphate (TEP) (Sigma–Aldrich, USA) was used as solvent to dissolve the polymer dope solution.

Table 1
Classification according to Regulation (EC) No 1272/2008 [12] of DMF, DMA, NMP and TEP used as solvents for preparing.

Solvent	Classification according to regulation (EC) no 1272/2008	
	Hazard statements	Precautionary statements
DMF	H226 flammable liquid and vapour H312 + H332 harmful in contact with skin or if inhaled H319 causes serious eye irritation. H360D may damage the unborn child Germ cell mutagenicity: mouse, lymphocyte Mutation in mammalian somatic cells	P201 obtain special instructions before use P280 Wear protective gloves/protective clothing P305 + P351 + P338 if in eyes rinse cautiously with water for several minutes Remove contact lenses, if present and easy to do. Continue rinsing P308 + P313 IF exposed or concerned: get medical advice/attention
DMA	H312 + H332 harmful in contact with skin or if inhaled H319 causes serious eye irritation H360D may damage the unborn child May cause congenital malformation in the fetus. presumed human reproductive toxicant overexposure may cause reproductive disorder(s) based on tests with laboratory animals	P201 obtain special instructions before use P280 Wear protective gloves/protective clothing P305 + P351 + P338 if in eyes rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing P308 + P313 if exposed or concerned: get medical advice/attention
NMP	H315 causes skin irritation H319 causes serious eye irritation H335 may cause respiratory irritation H360D may damage the unborn child Damage to fetus possible	P201 obtain special instructions before use P261 Avoid breathing vapors P305 + P351 + P338 if in eyes rinse cautiously with water for several minutes Remove contact lenses, if present and easy to do. Continue rinsing P308 + P313 if exposed or concerned: get medical advice/attention
TEP	H302 harmful if swallowed H319 causes serious eye irritation Other hazards: this substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic, or very persistent and very bioaccumulative at LEVELS OF 0.1% or higher	P305 + P351 + P338 if in eyes: rinse cautiously with water for several minutes Remove contact lenses, if present and easy to do. Continue rinsing

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