

PVDF and HYFLON AD membranes: Ideal interfaces for contactor applications

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Abstract

Super-hydrophobic fluorinated membranes were tailored by combining traditional dry-wet phase inversion and wet chemical treatment techniques. PVDF and HYFLON AD 60X were selected as raw polymers for their chemical and mechanical resistance as well as hydrophobic and solvophobic properties. Membranes with modulated pore size, narrow distribution and high overall porosity were manufactured without using additional additives or modifiers. High resistance to liquid water entry pressure (LEP_w), high mass transfer and low surface free energy of the membrane surfaces were fully achieved. The combination of these two fluorinated polymers improved dramatically the mechanical resistance and the water repellence of the PVDF membranes. Well-controlled structure combined with aimed supra-molecular chemistry makes these porous layers ideal interfaces to be processed in membrane contactor devices.

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1. Introduction

It is well known, the membrane plays a key role in all separation processes, due to its capability to work as physical and selective support for the extraction of chemical species from one phase to the other one. Well-controlled structures combined with the process engineering can optimise efficiency and productivity of the separation [1,2].

Emerging membrane processes based on the contactor devices and equipped with well-controlled membranes are largely used in semiconductors [3], air and water purification [4,5], pharmaceuticals [6] and biotechnology [7,8]. The successful outcome of these all processes is strongly affected by the

morphological and chemical parameters of the membranes used, because they act as fixed interfaces between contacting media without dispersing one phase into another [9]. A membrane can usefully be processed in contactor devices, if it exhibits regular pore size and shape, uniform and mono-dispersive pore distribution as well as high overall porosity. In this way, higher interfacial area per unit volume can be assured and higher volumetric mass transfer rates can be achieved [10,11]. However, additional mass transfer resistance due to pores filled by the liquid phase can represent a drawback, especially in membrane gas–liquid contactors [12]. Since the mass transfer is the controlling parameter of the separation process, to maintain the membrane pores completely filled by the only gas phase (non-wetted) represents an important target [13]. Indeed, the viscous liquid inside the pores offers additional mass transfer resistance, affecting the process productivity over prolonged periods of operational time. Therefore, mutual membrane–liquid interactions have to be considered. With this respect, a good membrane performance can be achieved if structural parameters are combined with chemical and physical properties such as wetting tendency, chemical resistance and, if any, good mechanical resistance. Unfortunately, to merge all these aspects in only one membrane is not an easy task. Among the different approaches used for manufacturing

Abbreviations: FC40, commercial name of fluorinated solvent; PF, PVDF membranes (1–4 is for increasing pore size); PF-HYa, PVDF membranes treated by HYFLON solution at 0.1 wt.%; PF-HYb, PVDF membranes treated by HYFLON solution at 0.5 wt.%; PVDF, poly(vinylidene fluoride); HYFLON AD 60X, tetra-fluoroethylene (TFE)-2,2,4-trifluoro-5-tri-fluoromethoxy-1,3-dioxole (TIT); HFE-7100, metossi-nonafluoro-butane; IPA, propan-2-olo; NMP, N-methyl-2-pirolidinone

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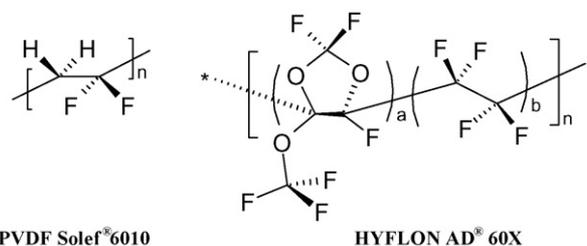
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systems, the phase separation appears to be one of the most flexible techniques. In the literature, the extent and sequence of the events of the phase separation that yields porous hydrophobic membranes are largely discussed [14–18]. Particular attention has been devoted to some parameters that control the polymer precipitation, such as the harshness of the coagulation bath [19], the composition of the casting solution [20], the precipitation temperature [21] and the solubility parameters of the solvent and no solvent used in the phase inversion process [15]. However, the manufacturing processes yielded often porous membranes that exhibited simultaneously only few of the characteristics necessary to make them ideal interfaces for membrane contactor applications. In addition, extensive studies have been carried out to improve the surface porosity of PVDF membranes by using pore forming additives in the casting solutions [22]. The use of pore formers such as poly(vinylpyrrolidone) (PVP) [23], calcium carbonate (CaCO_3) [24], lithium chloride (LiCl) [25] or tri-hydrated lithium perchlorate $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ [26] or ethylene glycol [27] allowed PVDF membranes with different morphologies to be manufactured. However, the films exhibited often macrovoids or cavities, affecting the mechanical stability of the membranes and skin with more or less open-end pores of the order of few nanometers [26], yielding significant changes in the effective porosity or in the resistance to liquid entry pressure of water (LEP_w) [25,27].

Another particular aspect to be considered is related to the effects of the pore forming additive on the final membrane surface properties. Although the most part of pore formers are soluble in water, their removal away from the polymer matrix is not easy to get completely. The surface free energy of the membrane results consequently affected and the PVDF matrix loses its intrinsic hydrophobic character as a function of the enrichment in the hydrophilic domains dispersed onto the membrane surface [28]. The use of hydrophilic pore former represents, therefore, a critical factor, especially if highly hydrophobic membrane surfaces are required. Additionally, high waterproofness should be gained by combining low surface free energy with high LEP_w . This target is achieved as specific topography and chemistry properties merge in the same layer. With this regard, many efforts have been done in order to improve the surface properties of the membranes without modifying the bulk characteristics [24,29]. Plasma, grafting or blending techniques have been usefully used [30–32], but in all cases the approach required additional steps or somewhat more complicate procedures.

In this work novel super-hydrophobic membranes tailored by combining two simple and no cost-effective techniques are discussed according to all requirements in contactor technology. Two fluorinated polymers such as poly(vinylidene fluoride) [PVDF] and tetra-fluoroethylene (TFE) and 2,2,4-trifluoro-5-tri-fluoromethoxy-1,3-dioxole (TIT) [HYFLON AD 60X] were selected for their intrinsic hydrophobic character (Scheme 1).

PVDF membranes (PF1–4) were tailored by dry-wet phase inversion technique, resulting in super-hydrophobic porous films with modulated pore size, which covered a range from 0.2 to 3.5 μm , and overall porosity higher than 70%. Despite the large pore size, all membranes exhibited high resistance to



PVDF Solef® 6010

HYFLON AD® 60X

Scheme 1. Chemical structure of PVDF and HYFLON AD 60X ($a=0.6$; $b=0.4$).

water liquid entry pressure (LEP_w 0.4–2.5 bar), keeping high gas transport properties. After treatment by HYFLON AD 60X solutions, the membranes (PF-HY) resulted in enhanced mechanical resistance and water repellence. An assessment of the full performance allowed indicating these membranes as ideal interfaces to process in contactor devices.

2. Experimental

2.1. Materials

PVDF (Solef® 6010, Solvay Solexis: water adsorption $< 0.04\%$ at 23°C after 24 h; $d_p = 1.78 \text{ kg/m}^3$) and HYFLON® AD 60X with 60 mol% in TTD content, were supplied by Solvay Solexis. The metossi-nonafluoro-butane (HFE-7100) and Fluorinert (FC40) were purchased from 3M Novoc. *N*-Methyl-2-pyrrolidinone (NMP, Riedel de Haëm: max 0.05% in water, $d = 1.03 \text{ kg/m}^3$) and propan-2-olo (IPA, WWR PROLABO: $d = 0.78 \text{ kg/m}^3$) were used as solvent and non solvent, respectively. The probe liquids used to perform contact angle measurements were ultra-pure water (filtered by USF ELGA plant), glycerol (Fluka AG, 88%), di-iodomethane (Aldrich, 99%), ethanol (Carlo Erba, 99.8%). Ethanol/water solutions (10/90, 20/80, 30/70, 40/60, v/v) were used for both contact angle and swelling measurements, respectively. All materials were used as received.

2.2. Membrane preparation

The membranes were prepared by dry-wet phase inversion according to the procedure detailed in [17,33]. Homogenous dopes of PVDF at 20 wt.% in NMP were thermally treated at $30\text{--}60^\circ\text{C}$ and uniformly cast on glass plate by using a casting knife regulated on 250 μm (Elcometer Instruments Inc.). The casting solutions were coagulated for 5 min in a bath containing IPA in order to promote solid–liquid demixing and then washed in ultra-pure water. The films were air-dried at room temperature and, then, annealed at 65°C for 4 h.

Fluorinated composite membranes were also prepared by treating any samples of PVDF membranes (PF1–4) with solutions of HYFLON AD 60X in HFE-7100 at 0.1 and 0.5 wt.% in polymer, respectively. For each PF sample, three specimens of membrane were cut and dipped into the HYFLON solutions for 5 min. Then, the membranes were dried and treated at 30°C for 24 h.

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