Journal of Membrane Science 423–424 (2012) 11–19

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Synthesis and fabrication of nanostructured hydrophobic polyazole membranes for low-energy water recovery

Husnul Maab [1], Lijo Francis [1], Ahmad Al-saadi, Cyril Aubry, Noreddine Ghaffour, Gary Amy, Suzana P. Nunes *

Water Desalination and Reuse Center, King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal, Saudi Arabia

ARTICLE INFO

Article history:
Received 6 April 2012
Received in revised form
29 June 2012
Accepted 13 July 2012
Available online 20 August 2012

Keywords:
Polyoxadiazole
Polytriazole
Membranes
Membrane distillation

ABSTRACT

Aromatic fluorinated polyoxadiazoles (F-POD) and polytriazoles (F-PT) were synthesized and for the first time manufactured into porous membranes by phase inversion and by electrospinning. The phase inversion F-POD membranes had a mean flow pore size (MFP) of 51 nm, while for F-PT it was around 74 nm. The electrospun membranes had a much larger pore size, the MFP for F-POD membrane was around 1.7 μm and for F-PT it was 2.7 μm. The membranes were tested for desalination of Red Sea water using direct contact membrane distillation (DCMD). By combining the high polymer hydrophobicity and high porosity, apparent contact angles up to 162° were obtained, assuring the operation with practically no liquid water leakage under pressure up to 0.9 bar. Salt selectivity as high as 99.95% and water fluxes as high as 85 L m^{-2} h^{-1} were demonstrated, operating at 80 °C feed temperature and 22 °C permeate.

1. Introduction

Seawater desalination by reverse osmosis and thermal processes is widely used in Middle East countries. However, even in countries with oil abundance it is clear that the energy consumption still has to be substantially reduced. In remote regions with water scarcity the exploration and reuse of water from other sources have to be considered. The combination of more traditional desalination methods and less explored technologies like membrane distillation (MD) could be an effective option. MD can operate at low-grade thermal or solar heat to treat brackish water, non-condensable volatile organic compounds and/or, together with other separation and purification process, to produce fresh water. The principle of MD has been reviewed in detailed in different papers [1–3], but in summary saline or wastewater is kept in contact with a porous hydrophobic membrane and heated to a temperature below the water boiling point. In the direct contact membrane distillation, cold water circulates on the other side of the membrane. The partial vapor pressure difference aroused due to the temperature difference across the membrane is the driving force for water vapor transport. The operation at relatively low temperatures (30–80 °C) makes the process adequate to use low temperature heat sources, including waste or solar heat. When compared to RO or electrodialysis, the simplicity of the membrane is an advantage. Membranes for MD can be manufactured in one step with pores in the ultrafiltration or microfiltration range. They do not need the selectivity of an additional highly selective layer characteristic of thin-film composite membranes. On the other hand MD membranes need to be highly hydrophobic (large water–membrane contact angle or high liquid entry pressure (LEP)) to hinder the transport of liquid water as depicted in Fig. 1. To promote the water vapor transport through the membrane pores at acceptable rates, the porosity has to be as high as possible. Low pore tortuosity and low membrane thickness minimize the resistance to vapor transport. Materials with low thermal conductivity as well as thicker membranes help to keep high temperature differences between both sides of the membrane. High temperature stability is required to avoid any change during operation at temperatures close to 100 °C.

Most of the published work uses commercial porous hydrophobic membranes based on polypropylene (PP) (e.g. Celgard®, Accurel®) and polytetrafluoroethylene (PTFE) (e.g. Gore®) [2]. Typical pore diameters are 0.1–1 μm. Both PP and PTFE are hardly soluble in common solvents at lab temperature. Gore® and Celgard® membranes are available as flat sheets and their preparation usually involves extrusion, followed by stretching. These procedures lead to the formation of membranes with rather large pores and low porosity [4]. Thermally induced phase separation (TIPS) and extrusion with expandable/foaming gas are other methods used for PP membranes. Although PP and PTFE address the need for high hydrophobicity, their membranes cannot be manufactured by conventional phase inversion at lab

* Corresponding author. Tel.: +966 544700052.
E-mail address: Suzana.nunes@kaust.edu.sa (S.P. Nunes).
[1] Authors contributed equally to this research project.

0376-7388/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2012.07.009

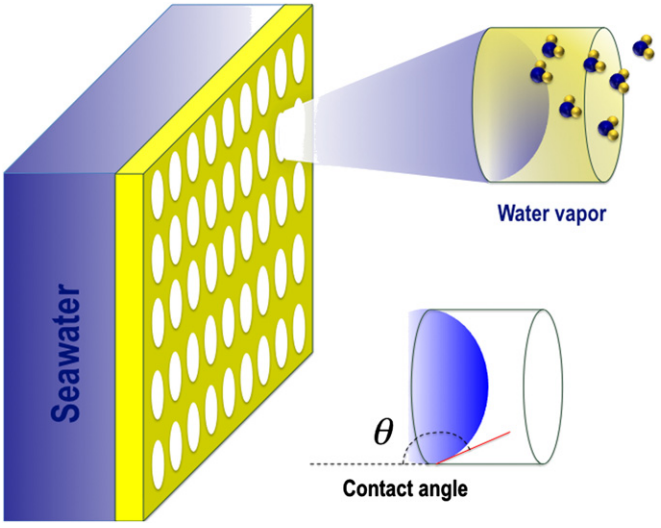

Fig. 1. Membrane distillation.

temperature due to solubility restrictions. Other more soluble polymers need to be considered for manufacturing membranes by phase inversion. Taking this in consideration, the membranes for MD fabricated by other groups worldwide are in great part based on poly (vinylidene fluoride) (PVDF) [2,5–7] and modified polyethersulfone (PES) or polyetherimide (PEI) [8]. The first reported MD membranes were based on modified cellulose acetate (CA) [9]. All of these polymers can be manufactured into membranes from casting solutions both as flat sheet and hollow fiber with high porosity using conventional machines. However all the mentioned polymers are much less hydrophobic than PTFE, leading to partial surface wetting. Membrane modification has been proposed by different groups, starting with radiation grafting of polystyrene on CA membrane [9] and addition of fluorinated "surface modifying macromolecules" [8] to PES casting solutions, which migrate to the air/polymer interface during casting. PVDF still has a higher surface energy (30.3 mN/m) than PTFE (18.5 mN/m) and the introduction of self-synthesized fluorinated silica particles to PVDF hollow fibers during spinning has been reported in an attempt to improve hydrophobicity [6], leading to permeation flux as high as 83 $L\,m^{-2}\,h^{-1}$.

Among other novel membranes are ceramic membranes [10] modified with perfluoroalkylsilanes [11], membranes with carbon nanotubes [12,13] and super hydrophobic glasses [14]. Beside the flat sheet and hollow fiber membranes prepared by phase inversion, new methods of manufacture like electrospinning have been recently proposed [15] as a possibility to increase porosity and vapor flux. Electrospinning requires polymer solutions with optimized viscosity for the membrane manufacture. While the focus on membrane distillation has increased in the last years, not much attention has been given to the synthesis of new materials, particularly tailored for application in this technology. We believe that, for the full optimization of MD systems, innovations in all different steps are needed, starting from design and synthesis of polymers, which would be the best suitable for MD, and going further to choose the most effective membrane manufacture and testing under different operational conditions.

High hydrophobicity, low heat transfer, high thermal stability, and high dimension stability at operation temperature and maximum porosity are the important targeted properties for membrane materials and membranes. We chose a class of materials widely explored in our group for other membrane applications: polyoxadiazoles and polytriazoles [16–21]. They are known for their high temperature stability and their synthesis has been optimized to supply high molecular weight polymers with the best film-forming characteristics for membranes. While poly (phenylene oxadiazole) [22] is hardly soluble, enabling film casting only from strongly acid solution, the substitution of the phenylene group by diphenyl ether or diphenyl hexafluoroisopropylidene increases the solubility in dimethylformamide and dimethylacetamide, facilitating membrane casting by phase inversion and electrospinning. Particularly when fluorinated groups, like diphenyl hexafluoroisopropylidene, are chosen for polyoxadiazole or polytriazole synthesis, highly hydrophobic products are expected.

A new class of fluorinated polytriazole has been synthesized for the first time in this study. Polytriazole or polyoxadizole membranes have not yet been considered for MD process. A series of aromatic polyoxadiazole and polytriazole polymers (fluorinated and non-fluorinated) have been synthesized and manufactured into porous membranes by phase inversion and electrospinning. Synthesized polymers and fabricated membranes were characterized and tested in the MD process for the desalination of seawater. Their performance in membrane distillation operation was evaluated with very promising perspectives.

2. Experimental

2.1. Materials

4,4′-(Hexafluoroisopropylidene)bis(benzoic acid) (CAS 1171-47-7) (HFA) (99% Aldrich), hydrazine sulphate (HS) (CAS 10034-93-2) (98% Aldrich), N-methyl pyrrolidone (NMP) (99% Aldrich), N, N-dimethylformamide (DMF), polyphosphoric acid (PPA) (ca 84% as phosphorous pentaoxide, Alfa Aesar), tetrahydrofurane (THF), gamma butyrolactone, isopropanol and aniline from Sigma Aldrich were used as received. PVDF was purchased from Alfa Aesar.

2.2. Synthesis of polyoxadiazole and polytriazole

The synthesis of polyoxadiazole and polytriazole was based on a procedure reported by our group before for related polymers [16–18]. For the synthesis of polyoxadiazole, first polyphosphoric acid (PPA) was added to a 250 mL three necked flask and was heated at temperature to 100 °C for 1 h under mechanical stirring along with the passage of dry N_2 gas to ensure the removal of water contents. Hydrazine sulphate (HS) was added to the PPA and in the meantime the temperature was raised to 160 °C and the reaction mixture was vigorously stirred to get a homogeneous solution till it dissolved completely. Once the desired temperature was attained, then HFA was added and the reaction constitutes were stirred for about 3 h under dry N_2 purge. The molar dilution ratio of (PPA/HS) and molar monomer ratio of (HS/HFA) was kept as 10 and 1.2, respectively. The final viscous polymer solution was poured into cold 1 M NaOH solution under constant stirring for 1 h. The precipitated polymer was transferred into de-ionized water and was stirred overnight at 80 °C. Finally it was dried in vacuum oven at 100 °C for 24 h.

For the preparation of polytriazole, aniline was added to the system 1 h after the addition of HFA at high temperature (180 °C). The final product is a dark blue colored polymer, the hydrophobic fluorinated polytriazole. Scheme 1 represents the synthesis routes for fluorinated (a) polyoxadiazole and (b) polytriazole used in this study.

2.3. Preparation of porous membranes by phase inversion

18 wt% (w/w) polymer solutions in NMP were prepared at 80 °C with constant stirring for 24 h. The polymer solution was cast with doctor blade on a glass plate (100 μm thick solution) or on a polyester non-woven support and immersed in water for 1 h.