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Preparation and Characterization of Dense Asymmetric co-polyimide P84/Multiwall Carbon Nanotube (MWCNT) Mixed Matrix Membranes for Desalination Application

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ABSTRACT

Polyimide (PI) membranes were prepared by non-solvent induced phase separation (NIPS) with different loading of MWCNT. 1, 5-Diamino-2-methylpentane (DAMP) was also used as crosslinker for purpose improving rejection properties of membranes. The morphology obtained is appropriate for high-pressure driven membrane process, like NF and RO, because the presence of a thin and dense skin layer allows to achieve higher flux, in comparison with symmetric dense membranes. Also the new prepared membrane shows a sponge like structure which guarantees a high mechanical resistance versus compacting phenomena under high pressure. The cross-linked membranes were characterized by higher rejection for NaCl and $MgCl_2$ than the not cross-linked membranes. This was due to positive charge of the crosslinked membranes which rejected the positive ions (having a lower mobility than the Cl^-) more efficiently than the not cross-linked membranes. The presence of MWCNT improved the rejection of all hybrid membranes as compared with corresponding polymeric membranes.

1. INTRODUCTION

CNTs have been entrapped in mixed matrix membranes (MMM) made of various polymeric materials by various techniques including: dispersion in the casting solution and successive phase separation, entrapping in the membrane pores using a polymer binder, in situ crosslinking of a polymer matrix around oriented CNTs (Ismail 2009). The resulting hybrid membranes offer, in many cases, a viable route to overcome some of the limitations of the traditional polymeric and inorganic membranes. Poly(vinyl alcohol) (PVA)/MWCNT membranes have been realized for pervaporation separation, obtaining significant improvement in Young's modulus and thermal stability, as compared to pure PVA membranes (Peng 2007). The entrapment of MWCNTs in polyethersulfone (PES) membranes reduced the fouling problems in water treatment (Celik 2011). MMM consisting of sulfonated carbon nanotubes (sCNTs) and sulfonated poly(ethersulfone ether ketone ketone) (SPESEKK) were also fabricated via the solution casting method (Zhou 2011). The proton conductivity of the SPESEKK membrane increased while the methanol permeability decreased as the sCNTs content increased. MWCNTs have been covalently linked to aromatic polyamide (PA) membranes by a polymer grafting process (Shawky 2011). Measurements of mechanical properties of this composite showed an increased membrane mechanical strength of the MMM. The addition of MWCNTs also improved the rejection of both salt and organic matter relative to the 10% PA polymeric membrane.

2. EXPERIMENTAL PROCEDURS

2.1. Procedure used for the Preparation of Polymeric PI Membranes

1) Solubilization of the PI in the DMF: THF (50:50 wt.%) solution under magnetically stirring at room temperature
2) Casting of the homogeneous solution obtained at 250 μm of thickness onto a glass plate
3) Solvent evaporation for 60 seconds
4) Immersion in the coagulation bath (water) for 24 hours
5) Storing in water until the use.

2.2. Procedure for the Preparation of Hybrid or Mixed Matrix PI Membranes

1) Dispersion of CNT in the DMF: THF (50:50 wt%).
2) Sonication for 1 hour.
3) Addition of PI in CNT dispersion and stirred magnetically for 24 hours.
4) Sonication of CNT/PI dispersion for 1 hour.
5) Casting of the dispersion obtained at 250 μm of thickness onto a glass plate.
6) Solvent evaporation for 60 seconds.
7) Immersion in the coagulation bath (water) for 24 hours.
8) Stored in water until the use.

2.3. Procedure for the Preparation of Cross-Linked PI Membranes with 1,5-Diamino-2-methylpentane (DAMP).

1) Immersion of the membrane in a 10 wt.% DAMP/Ethanol solution for 24 hours at 25±3°C.
2) Washing with fresh ethanol for 24 hours and then washing with water for additional 24hours, to wash out any residue of un-reacted cross linker.
3) Storing in water until their use.

3. RESULTS AND DISSCUSION

The morphology obtained of poly imide (PI) membrane is ideal for high-pressure driven membrane process, like NF and RO, because the presence of a thin and dense skin layer allows achieving higher flux, in comparison with symmetric dense membranes. Moreover, the sponge like structure guarantees a high mechanical resistance versus compacting phenomena under high pressure. Fig 1 shows SEM images of PI polymeric membrane (not cross-linked) characterized by a dense skin layer on the up-side and a sponge-like support layer. The presence of the volatile THF co-solvent (Boiling point 64-66 °C) in the casting solution allowed a partial solvent evaporation during the 60 seconds of exposure to air of the cast liquid film, with a consequent formation of the dense skin layer. Moreover, the initial solvent evaporation from the up-surface of the cast film in the dry-wet process increased the viscosity of the system in the upper layers with respect to the more internal layers, reducing the polymer chains mobility and macro-voids formation. In addition, the lower affinity THF/water respect the DMF/water affinity (solubility parameter of water 47.8; DMF: 24.9; THF: 19.5 J1/2 cm-3/213), reduced the rate of the phase separation process avoiding the formation of macro-voids.

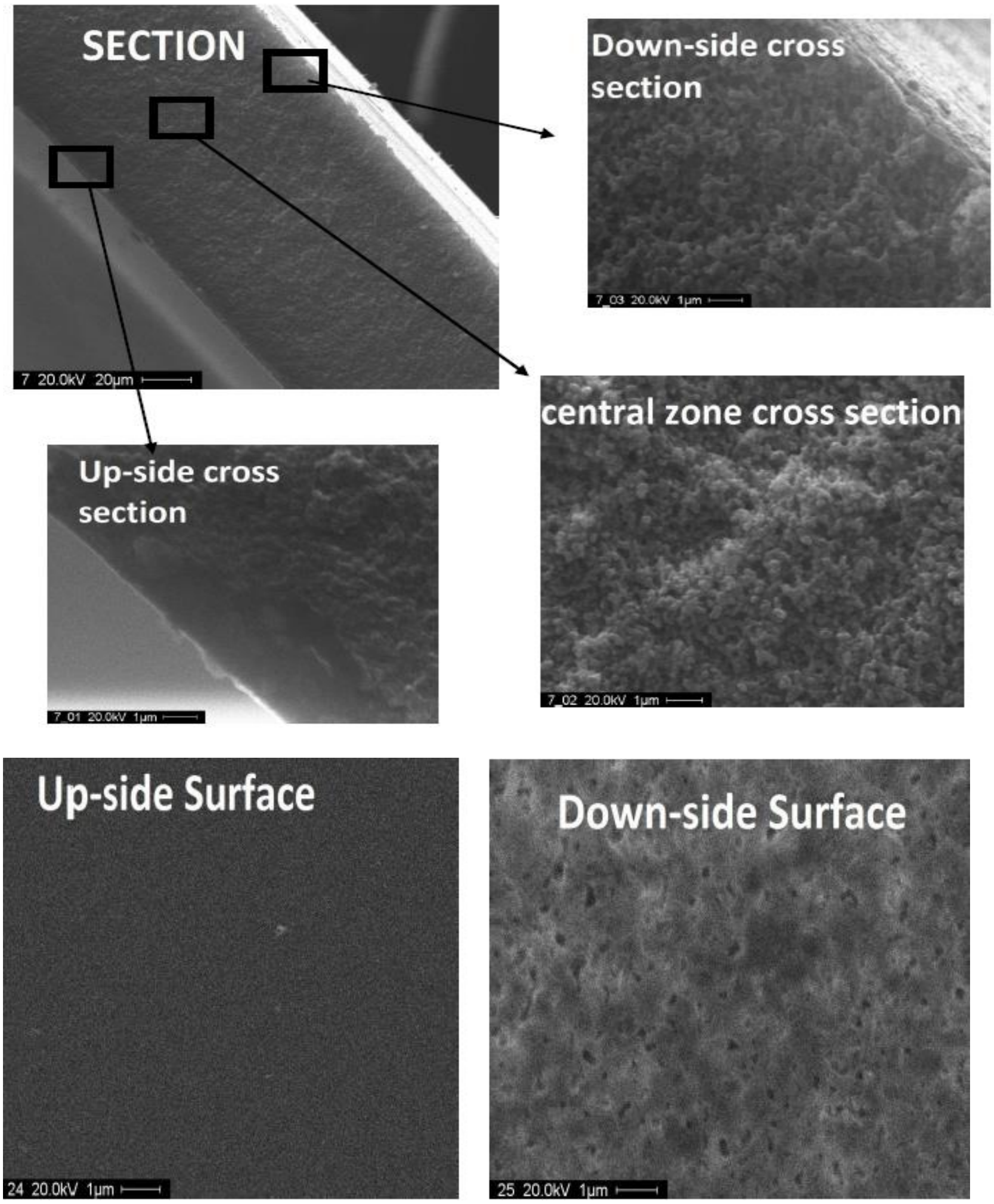

Fig 1. SEM images of the PI polymeric membrane not cross-linked

The morphology of the hybrid PI membranes containing the MWCNTs was similar to the polymeric samples (Fig 2). No aggregate of the MWCNTs were observed, confirming a good dispersion in the polymeric matrix, at least at the resolution level of the SEM technique.

(A) (B)

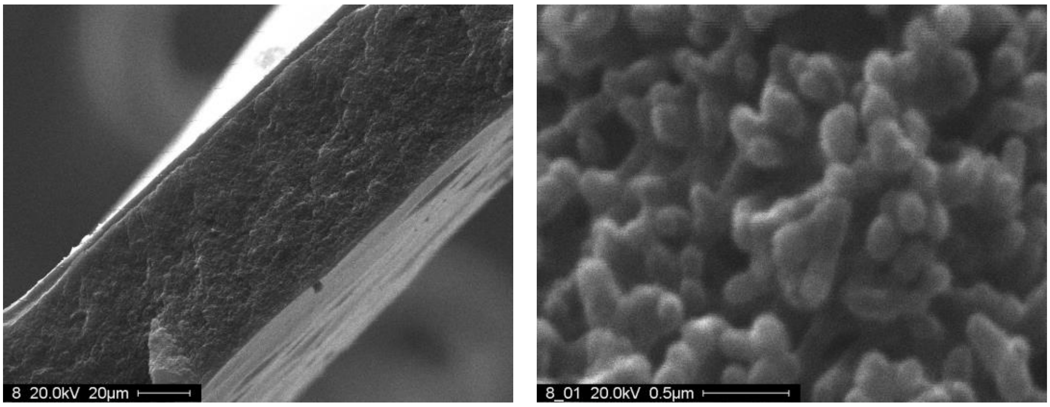

Fig. 2. Cross-section (A) and particular of the cross-section (B) of the hybrid PI membrane containing MWCNTs.

Water flux measurements were performed in a dead-end mode with a SterlitechTM HP4750 stirred cell, pressurized by nitrogen and operating at 25±3°C. The active membrane area was 14.6 cm^2. The transmembrane pressure (TMP) applied was 20 bar. Permeate sample were collected over the time in order to determine the flux (J) as reported in the eq 1.

$$J = \frac{V_p}{t \cdot A} \qquad (1)$$

Where V_p (L) is the permeate volume; t (h) is the time and A (m^2) is the active membrane area.

In the single salt rejection test 100 mL of NaCl (0.5 M) was used as feed; 50 ml of permeate were collected under TMP of 20 bar. The concentration of the salts solution employed were similar to those present in seawater. The concentration of the solute in the feed, retentate and permeate was analysed by a conductimeter. During the experiment, the feed solution was stirred using a magnetic stirrer at high speed to prevent concentration polarization. The membrane rejection (R) was calculated using the eq. 2.

$$R\ (\%) = \left(1 - \frac{C_p}{C_r}\right) \times 100 \qquad (2)$$

Where C_p and C_r represent feed and permeate concentrations, respectively. In all rejections, a mass balance (Eq. 3) was used to check any loss during the experiment.

$$\text{Mass balance (\%)} = \left(\frac{V_p \cdot C_p + V_r \cdot C_r}{V_f \cdot C_f} \right) \times 100 \qquad (3)$$

Where C_f, C_p and C_r represent concentrations of feed, permeate and retentate and V_f, V_p and V_r are volumes of feed, permeate and retentate, respectively.

The results of the NaCl rejection test are reported in Table 1 for the not cross-linked membranes as well as for the cross-linked membranes. Cross-linked membranes with 1, 5-Diamino-2-methylpentane (DAMP) has great impact on improving transport properties of membranes (Table 1). These results were due to the positive charge of the cross-linked membranes which rejected the Na+ cation (ions with a lower mobility than Cl-) more efficiently than the not cross-linked membrane with having a negative charge. Moreover, the presence of the MWCNT increased the rejection of all the hybrid samples respect to the corresponding polymeric samples, but, in the case of the cross-linked membranes containing 0.5 wt% of MWCNTs, also the fluxes were improved together with a relevant increase of the rejection.

Table 1. Experimental conditions and transport properties of hybrid PI membranes.

Exp. No.	Membrane composition	Flux [l/hr*m^2]	Rejection %
1	PI, 5.5 g THF, 11.2g DMF, 11.2 g	3.5	32.0
2	PI, 5 g THF, 13 g DMF, 13 g CNTs, 0.05 g, 0.16 % Cross-linked by DAMP	12.5	61.3
3	PI, 3 g THF, 6 g DMF, 6 g CNTs, 0.075 g, 0.5 % Cross-linked by DAMP	51.5	56
4	PI, 5 g THF, 10 g DMF, 10 g CNTs, 0.125 g, 0.5 %	6.5	35
5	PI, 5.0 g DMF, 11.2 g THF, 11.2 g CNTs, 0.1 g, 0.37 %	3.5	10.0

NaCl, 1800 ppm concentration, membrane thickness 250 um.

4. CONCLUSIONS

1) Mixed matrix membranes (MMM) containing different percentages (from 0.1 to 0.5 wt. %) of MWCNTs were prepared using three different PI polymers.
2) Poly imide (PI) membrane is ideal for high-pressure driven membrane process, like NF and RO, because the presence of a thin and dense skin layer allows achieving higher flux, in comparison with symmetric dense membranes. Moreover, the sponge like structure guarantees a high mechanical resistance versus compacting phenomena under high pressure
3) The dense asymmetric PI membranes, cross linked with DAMP, given better performance than the un-cross linked PI membranes in the rejection of salts (NaCl), because of charge effect (Donnan exclusion). The cross-linked PI membrane containing 0.5 wt. % MWCNTs was individuated as the most promising among the PI-based membranes prepared.

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