

Novel super-hydrophobic carbon nanotube-based nanomaterial for membrane distillation

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Abstract. Membrane distillation (MD) is a low-grade heat-based emerging technology found viable for seawater desalination. Membrane properties such as high hydrophobicity, mechanical strength, and thermal stability are crucial in assessing the compatibility of a membrane for use in this application. In this work, multiwall carbon nanotubes (MWCNTs) were modified with oleylamine (OI), which is an 18-carbon chain hydrocarbon. The attachment of oleylamine was confirmed via thermal gravimetric analysis (TGA). The modification resulted in an increase in the contact angle (CA) of MWCNTs from 104.0 ± 2.1 to $140.5 \pm 6.5^\circ$. Non-solvent Induced Phase Separation (NIPS) was then used to fabricate five polyvinylidene fluoride (PVDF) based composite membranes by varying nanomaterial concentration from 0 up to 15 wt% of the polymer. The incorporation of the nanomaterial in the membrane was confirmed via SEM, and fourier-transform infrared radiation. CA, porosity, liquid entry pressure (LEP), and tensile strength were utilized to investigate the membrane properties. A 5% and 15% increase in the CA and LEP, respectively, was observed. An increase in the tensile properties was also achieved, where the membrane consisting of 5.0 wt% nanomaterial exhibited maximum tensile stress of 34.0 MPa, compared to 23.6 MPa in the pristine PVDF. The developed nanomaterials were found to enhance the membrane properties and result in a stable overall flux of the MD system.

Keywords: Super-hydrophobic; carbon nanotubes; membrane distillation; chemical synthesis; desalination.

1. Introduction

Desalination is among the alternative freshwater resources of which demand for has increased because of global water scarcity. Membrane distillation (MD) is considered an emerging, state-of-the-art desalination technology (Zuo et al.). It utilizes low-grade heat to stimulate temperature difference across a porous membrane, allowing water vapor to penetrate the pores of the membrane and condensate on the permeate side. For successful, efficient, and continuous operation, tuning membrane features such as chemical, thermal, and mechanical stability, hydrophobicity, and porosity is vital (Hou et al.; Gryta and

Barancewicz). Lower surface wettability significantly enhances the operation of the MD process, hence a membrane with high hydrophobicity is required. Mixed matrix membranes are a common method of enhancing membrane properties (Lu et al.; Ardeshiri et al.). In this work, a new method of increasing the hydrophobicity of multiwall carbon nanotubes (MWCNT) is introduced. The new nanomaterial was embedded into a PVDF matrix to increase its hydrophobicity, and mechanical properties. The fabricated membranes were proven to have potential in the field of membrane distillation.

2. Materials and methods

Pristine MWCNT was first functionalized with carboxylic groups (MWCNT-COOH), via strong acid treatment at 70 °C for 2 h with H₂SO₄/HNO₃. The suspension was then washed and centrifuged to remove excess acid. The concentrated paste was freeze dried to obtain a dry powder.

To prepare MWCNT-oleylamine (MWCNT-OI), 1.0 g of MWCNT-COOH was added in an RB flask to 100 ml oleylamine and sonicated for 1 hr. The RB flask was then transferred to an oil bath, connected to a condenser and the temperature increased to 120 °C. To initiate the reaction catalytic amount of HCl was added and the reaction was continued for 4-6 hr. The solution was cooled to room temperature. Excess oleylamine was removed by repeated washing with hexane and centrifugation. Finally the concentrated product was transferred to a petri-dish and kept in fume hood for drying.

After the powder was dried, 5 dope solutions were prepared with mass percentages according to Table 1. The MWCNT-OI was sonicated in N-methyl (NMP) for 1 hr. The PVDF was then added, and the mixture was heated to 70 °C while stirring for 2 h. The mixture was left to stir overnight to ensure homogeneity. The mixture was then casted on a supported glass plate using a casting knife set at 200 μm. The membranes were then placed in a DI water coagulation bath at room temperature for 24 hours. The membranes were finally air dried, characterized, and tested

Table 1. Concentration of dope solutions used for nanocomposite membrane fabrication

	PVDF (%)	MWCNT-OI* (%)	NMP (%)
PVDF	10	0.0	90.00
C-1	10	2.5	89.75
C-2	10	5.0	89.50
C-3	10	7.5	89.25
C-4	10	15.0	88.50

*Percentage calculated with respect to the total mass of PVDF.

3. Results and Discussion

Figure 1 displays thermal gravimetric analysis (TGA) graphs used to characterize the pristine and modified MWCNT obtained via TGA 4000, Perkin Elmer. MWCNT before functionalization shows high thermal stability, with initial degradation around 500°C and complete degradation around 680°C. In the case of MWCNT-COOH, the first degradation step is below 120°C due to adsorbed water, indicating the hydrophilicity of the material after oxidation. The second step degradation initiates at around 120 to 280°C due to the removal of the less thermally stable -COOH groups from MWCNT-COOH. Above 300°C, the degradation is similar to MWCNT, indicating the high thermal stability up to 500°C. However, in case of MWCNT-OI, there was no weight loss until 200°C, which suggests little adsorbed water due to the disappearance of the -COOH. The initial degradation step initiates at around 200 to 300°C due to the removal of unreacted COOH. The second thermal degradation step from 300°C to 450°C is due to the decomposition of oleylamine groups. This indicates the successful amination reaction between COOH and amine group in MWCNT-COOH. Above 450°C, the material shows similar degradation to the pristine MWCNT.

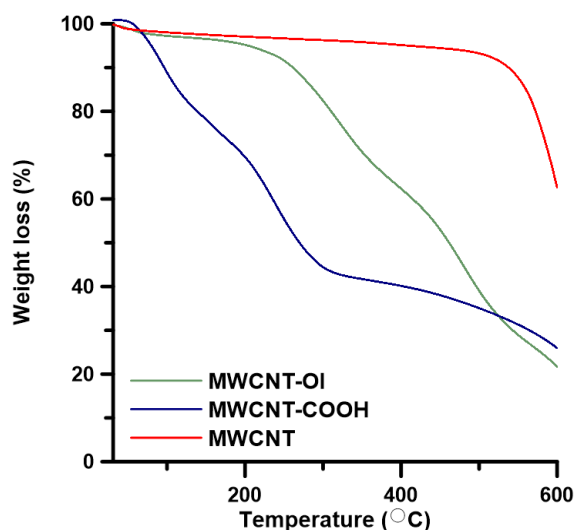


Figure 1. TGA analysis of pristine and modified MWCNT.

Table 2 shows further proves the successful two-step modification of the MWCNT. MWCNT-COOH have a contact angle of 0° (measured via Krüss GmbH' Drop Shape Analyzer), due to the strong hydrogen bonds between -COOH and the water molecule, resulting in a super-hydrophilic surface. Upon completing the final step in the synthesis, the contact angle of the MWCNT increased from 104.0±2.1 to 140.5 ± 6.5°, making the MWCNT super-hydrophobic (Figure 2).

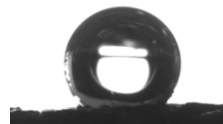


Figure 2. Contact angle image of MWCNT-OI.

Table 2. Contact angle comparison of pristine and modified MWCNT based materials

	Contact angle (°)
MWCNT	104.0±2.1
MWCNT-COOH	0
MWCNT-OI	140.5±6.5

Table 3 displays the properties of the fabricated nanocomposite membranes. The contact angle of the composite membranes is found to increase with increasing nanocomposite concentration. This is expected due to the high hydrophobicity of the material, and as a result of the 18-carbon chain in the oleylamine. However, at the highest concentrations, there is a sharp decline. This can be due to the formation of defects and a non-homogenous membrane formed due to the high nanocomposite loading. The hydrophobicity of the material limits its complete dissolution in the dope solution.

Table 3. Contact angle, porosity, and liquid entry pressure of nanocomposite membranes.

Membrane	Contact angle (°)	Porosity (%)	LEP (bar)
PVDF	90.5±1.2	46.3±1.7	2.9±0.1
C-1	92.8±1.1	40.3±1.7	3.2±0.1
C-2	94.0±1.3	42.7±5.1	3.2±0.3
C-3	94.9±0.9	43.5±0.6	3.3±0.4
C-4	87.5±0.5	48.7±3.4	3.4±0.4

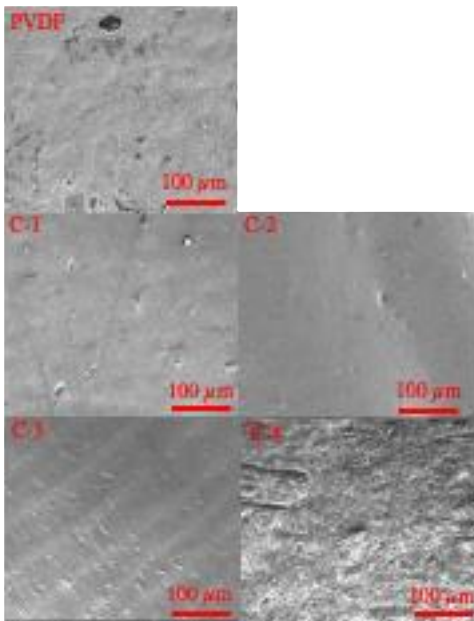


Figure 3. SEM images of prepared nanocomposite membranes

Figure 3 displays the SEM images of the fabricated nanocomposite membranes. The SEM images show a homogenous surface, with less macro-void formation as the loading of the nanocomposite increases. The non-homogeneity is seen at C-4, resulting in a slightly defected membrane. The liquid entry pressure (LEP), measured via Convergence Liquid Entry Pressure Tester, was also found to increase with increasing nanomaterial loading. This can also be as a direct effect of the increase in the contact angle, requiring a higher pressure for wetting. The porosity of the material, measured from the dry and wet weight of a membrane coupon, was also found to increase. The contact angle, liquid entry pressure, and porosity show that C-3 can potentially enhance the operation of an MD system. This was confirmed via a 240 min study, in which Figure 4 shows a stable flux and rejection of C-3 compared to the pristine PVDF membrane. Addition of the nanomaterial was also found to increase the membrane's tensile stress, but at higher loading the membranes become more brittle. This is because excess amount of nanomaterial limits the elasticity of the polymer.

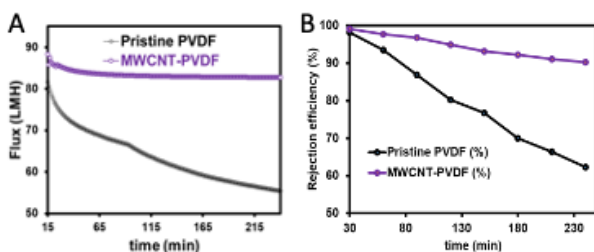


Figure 4. A: Flux of PVDF versus C3, B: Rejection of PVDF versus C3

4. Conclusions

Among the alternative water resources to survive with water scarcity comes desalination. Membrane distillation is an emerging desalination technology that utilizes low grade heat. In this work, a novel MWCNT based material is fabricated to increase the hydrophobicity of a commercially used polymer, i.e., PVDF. MWCNT was functionalized with OI to maximize their hydrophobicity, allowing for a more hydrophobic membrane. The composite material resulted in an up to 36.5° increase in the contact angle of pristine PVDF, and a 15% increase in the LEP. These combined, along with the increase in the porosity resulted in enhanced membrane properties to fit MD. The flux and salt rejection of the best performing membrane as a result were found to be more stable during membrane operation compared to the pristine PVDF membrane.

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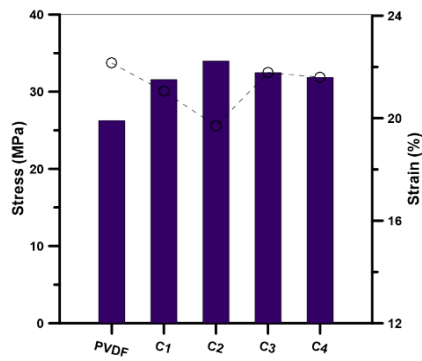


Figure 5. Mechanical properties of all composite membranes.