Wetting Behaviour of Superhydrophobic Membranes Coated with Nanoparticles in Membrane Distillation

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The field of membrane distillation (MD) is currently enjoying a great deal of interest and its possible fields of application are being explored. However, penetration of liquid feed in membrane pores (wetting phenomenon) has caused in the lack of overall attention in the MD processes. Even though commercial polymeric membranes (e.g., polyvinylidene fluoride (PVDF), polypropylene (PP), and polytetrafluoroethylene) show intrinsic hydrophobicity, the pore wetting may still take place for treatment of solutions with surface tensions lower than water. Depositing nanoparticles (nPs) on membrane surface to form a microstructure on top of macrostructure (physical property rather than a chemical property of surface) as it is in natural superhydrophobic surfaces such as lotus leaf can increase water repelling effect of membranes.

In this paper, membrane pore wetting behavior is investigated by depositing/grafting SiO_2 nanoparticles on the surface of commercially available polypropylene membrane. Dip coating method is used to deposit nPs for increasing the membrane surface roughness, water contact angle and consequently reducing membrane wettability. The effect of experiment parameters on the superhydrophobicity and permeability of nano-coating membranes are examined herein to explore the optimum preparing conditions. Atomic force microscope (AFM) and contact angle goniometry measurements are applied to study the influences of surface coating on the surface structure and performance of the original and coated membranes.

Moreover, membrane distillation tests are performed for modified and virgin flat sheet PP membranes. By comparing the performance of the original and modified membranes in direct contact membrane distillation experiments in the presence of a surfactant (sodium dodecyl sulphate, SDS), the influence of coating on membrane pore wetting and contamination degree of permeate with a surfactant is shown.

1. Introduction

Membrane distillation (MD) is a thermally driven process in which unlike the other membrane technologies, volatile component of a mixture in the form of vapor travels through a porous hydrophobic membrane. In MD, mass transfer is caused via a difference in transmembrane vapor pressure induced by temperature gradient on both sides of the membrane. Since the mass transfer through the membrane takes place in the vapor phase, membrane liquid wetting resistibility is of a high importance (Molina et al. 2015). Even though commonly used polymeric membranes show intrinsic hydrophobicity, increasing membrane liquid repelling property can lead to more MD industrial practices where low surface tension solutions need to be treated (Franken et al. 1987).

One way to increase membrane wetting resistance is to increase the membrane surface roughness (Razmjoua et al. 2012). By increasing surface roughness, the contact angle between the membrane and liquid increases, which consequently can lead to a property known as lotus leaf effect (Dorrer et al. 2009). In order to increase membrane surface roughness, membrane macrostructures can be coated by nanoparticles.

In this paper, we increased the membrane hydrophobicity via coating the commercial polypropylene with prepared SiO_2 sol nanoparticles. Coated membranes were post-treated via temperature and UV irradiation. Then, these modified membranes were characterized via contact angle measurements and atomic force microscopy. Finally, membrane distillation tests were performed to compare the salt rejection and permeate flux in both modified and original membranes in the presence of sequential addition of sodium dodecyl sulfate.

2. Experimental

2.1 Materials
Commercial polypropylene (PP) flat sheet membranes (MEMBRANE, ACCUREL®, nominal pore size: 0.2 µm) as virgin membrane was used. Tetraethyl orthosilicate (reagent grade) as SiO_2 precursors, absolute isopropanol as solvents, sodium dodecyl sulphate as a surfactant, hydrochloric acid (33%), sodium chloride (NaCl) were purchased from Sigma–Aldrich and were used as received.

2.2 Nanoparticle coating solution preparation
To form a stable sol for coating purpose, SiO_2 precursor sol was prepared by mixing absolute isopropanol with TEOS, HCl and deionized water at room temperature with vigorous stirring for 2h. The final molar ratio of each component in the solution was TEOS: H_2O: HCl: isopropanol = 1:4.52:0.02:42.57.

2.3 Coating of nPs onto membranes
The membranes were dip coated in the SiO_2 coating solution with coating withdrawal rate of 1 mm/s and 10 s retention time. The coated membranes were dried at oven at 120 °C for 2 h. After the heat treatment, membranes were gently rinsed with deionized water and irradiated by UV light with UVA and UVC intensities of 67 and 500 W/m^2 for 3 h to decompose any organic residuals.

3. Membrane characterization

3.1 Atomic force microscopy
Atomic force microscopy (AFM) images were used to examine the membrane amplitude roughness parameters. AFM images were taken by MFP-3D Stand Alone Asylum Research device using Olympus AC240-TS cantilever. Non-contact mode in air of AFM images (5x5 µm) were analysed and membrane mean roughness (R_a) and root mean square of Z data (R_q) were calculated as follows (Chibowski et al. 2008):

$$R_a = \frac{1}{n}\sum_{i=1}^{n}|z_i| \tag{1}$$

$$R_q = \sqrt{\frac{1}{n}\sum_{i=1}^{n}z_i{}^2} \tag{2}$$

The roughness parameters are calculated from n ordered equally spaced points where z_i is the vertical distance from a calculated mean line to the ith data point.

3.2 Contact angle measurement
Contact angle measurement was used to evaluate the hydrophobicity of original and modified membranes. The contact angles of the membrane samples were measured by contact angle goniometer (DataPhysics OCA - Series) using sessile drop method through Laplace-Young fitting mode. Droplets of water and 0.3 mM sodium dodecyl sulphate solution with a dosing volume of 3 µl and dosing rate of 1 µl/s were placed on membrane samples using a syringe and the contact angles were taken by a high-speed camera.

4. Membrane performance in a membrane distillation cell

The performance of the membranes in a horizontal counter-current configuration of a direct contact membrane distillation cell with the contact area of 0.01 m^2 was measured (Figure 1). Feed and permeate inlet temperatures were adjusted to 60 °C and 20 °C. The feed inlet and outlet temperature difference was approximately 5 °C while for permeate this difference was 10 °C. The average bulk feed and bulk permeate temperature difference was 35 °C to attain a high driving force. The experiments for original and coated membranes started with deionized water as feed and permeate. Then, NaCl was added to the feed side to make a solution of 1.0 M NaCl while keeping the all other variables constant. The experiments continued by sequential addition of 0.1 mM sodium dodecyl sulphate (SDS) to decrease gradually the surface tension of the solution.
In all the experiments, a higher feed cross flow rate than permeate was applied. Generally, a higher feed cross flow rate than permeate cross flow rate creates a higher hydraulic pressure for feed side which then, when pore wetting happens, can lead to membrane pore wetting identification (Lin et al. 2014).
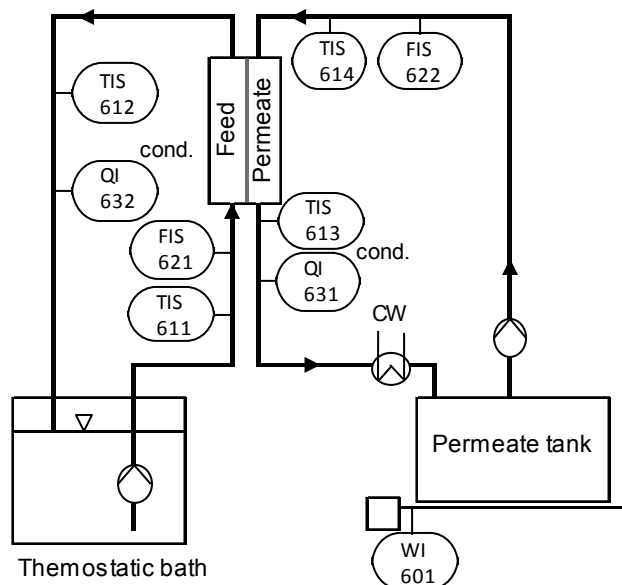
Figure 1: Schematic diagram of the lab-scale DCMD setup.

Visual assessment of the transparent cell proved the existence of transmembrane pressure difference in which the membrane was pushed toward the permeate spacer. In this case, when pore wetting occurs the hydraulic pressure difference converts membrane distillation to microfiltration in which the liquid feed moves toward permeate side leading to the rise of water flux and lessening in salt rejection.

To calculate the water vapour flux, the weight of permeate solution was divided to the time span and membrane contact area. To evaluate membrane pore wetting and salt rejection calculation, the electrical conductivity of the permeate was measured. The salt rejection was calculated as follows:

$$R = \left(1 - \frac{C_{b,p}}{C_{b,f}} \right) * 100 \tag{3}$$

where $c_{b,p}$ is the solute concentration in the permeate (mol/L) and $c_{b,f}$ is the solute concentration in the bulk feed (mol/L).

5. Results and discussion

5.1 Membrane surface roughness

AFM images were used to examine the membrane amplitude roughness parameters. Scan rates for images with sizes of 60x60 µm and 5x5 µm were 0.25 Hz and 0.75 Hz, respectively. The effect of nanoparticle coating on the structure of the membranes is presented in figure 2. As can be seen in figure 2, the deposition of nanoparticles on original membrane pore structures (left) changed the membrane porosity and aggregation of nanoparticles on wall pores led to higher membrane roughness. The mean values of roughness parameters for original and coated membranes which are reported in table 1 confirm this observation. In general, the roughness parameters of original membranes became higher when they were coated with nanoparticles. These observations are also reported by other authors (Singh et al. 1998).

Table 1: Roughness parameters for original and coated membranes

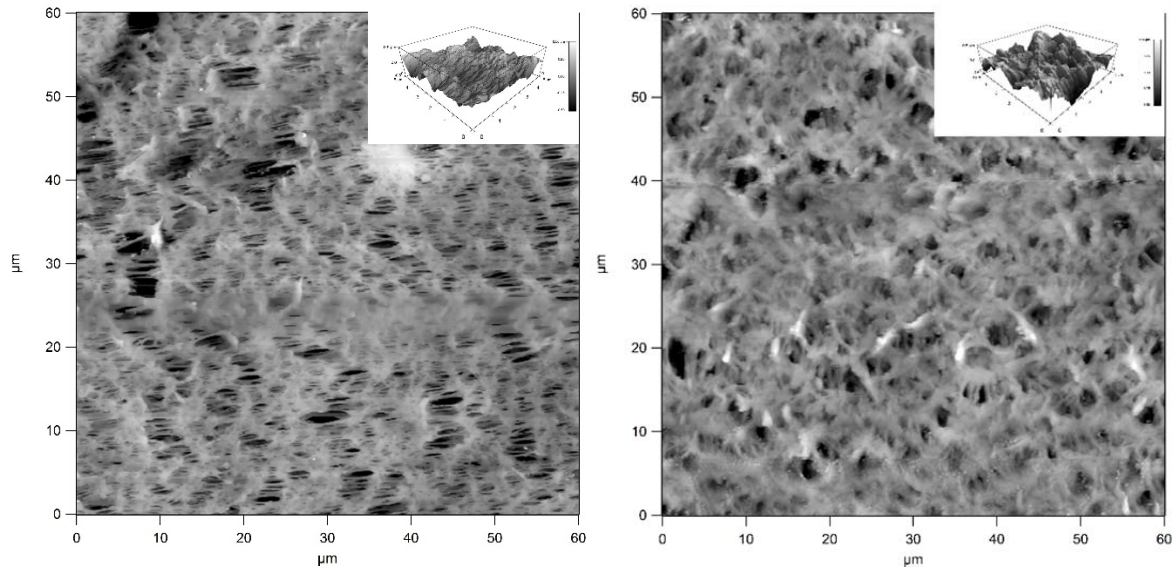| Membrane	Roughness parameters		
		R_a (nm)	R_q (nm)
PP original		87	108
PP SiO$_2$ modified		126	160

Figure 2: AFM images of original (left) and modified membranes (right). Depositing SiO₂ nanoparticles on the macrostructure of original membrane increased the membrane roughness.

### 5.2 Membrane wetting property

It was found that modified membranes have higher static sessile drop water contact angle than original membranes (Table 2). For the 1.0 M NaCl solution with 0.3 mM SDS concentration, the contact angle for original membrane decreased by almost 20%, whereas the contact angle for the modified membrane remained constant (Figure 3).

Table 2: Contact angle for original and modified membranes

Membrane	Pore size (μm)	Contact angle (°)	
		Water	0.3 mM SDS
PP original	0.2	139	110
PP SiO₂ modified	0.2	154	154

5.3 Membrane distillation tests

The membrane distillation experiments were started using deionized water as feed and distillate with the temperature of 60 °C and 20 °C. Then in the next step, the experiments were proceeded by adding NaCl to the feed to reach the concentration of 1.0 M (electrical conductivity: ~79 mS/cm). Finally, sodium dodecyl sulphate (SDS) was added gradually to the feed to decrease the surface tension of the feed solution.
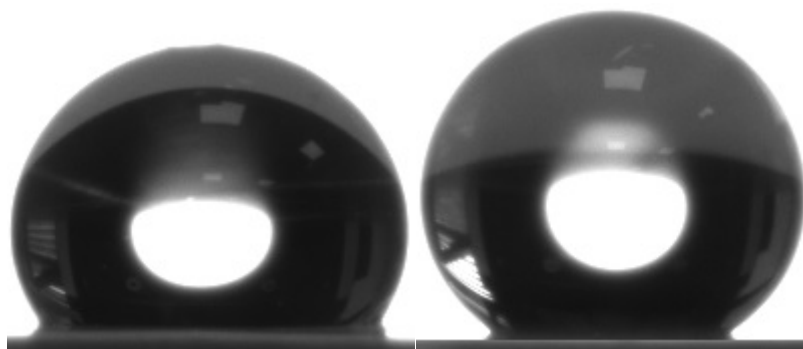
Original   *Modified*

Figure 3: Contact angle of original and modified membranes for 0.3 mM SDS solution. The instant contact angle of original membrane reduced to 110° while the contact angle of coated membrane remained constant in 154°.
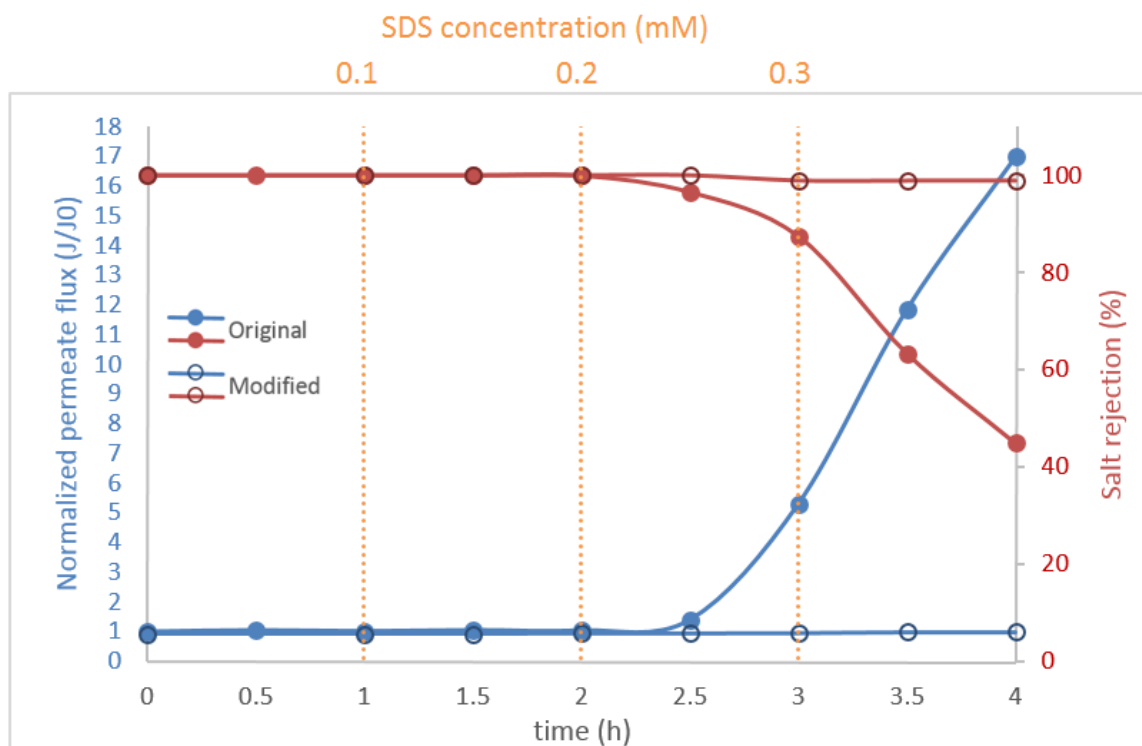
Figure 4: The permeate flux and salt rejection in DCMD experiments for original and modified membranes. The permeate fluxes are normalized by initial permeate fluxes. The orange round dots represent the SDS concentration in the solution. The concentrations of SDS after each stepwise addition are written on top of the figure. The temperature of feed and permeate were 60 °C and 20 °C, respectively.

As can be seen in figure 4, the permeate flux for virgin membrane increased drastically while the salt rejection was reduced significantly. On the other hand, coated membranes resisted against the pore wetting with ~100% salt rejection and no noticeable effect on the water vapor flux was found as the concentration of SDS increased sequentially.

6. Conclusions

Polypropylene membrane macroscale structures were coated with SiO_2 nanoparticles. Original and coated membranes were characterized by atomic force microscopy and contact angle goniometer to measure membrane roughness parameters and contact angles. It was found that depositing nanoparticles on membrane macrostructure increased membrane roughness from 126 nm to 160 nm (and accordingly the water contact angle from 139° to 154°), leading to increasing liquid repelling property of the coated membranes. Moreover, the results of the membrane distillation experiments confirmed the higher wetting resistibility of coated membranes against low surface tension solutions. Membrane distillation tests were performed with 1.0 M sodium chloride solution while sodium dodecyl sulphate was stepwise added to the feed. While adding SDS in the feed solution changed the original hydrophobic membranes to act as microfiltration membrane with low salt rejection, coated membranes resisted to the pore wetting with ~100% salt rejection.

Reference

Chibowski E., Terpilowski K., 2008, Surface Free energy of sulfur- yellow and orange samples solidified against glass surface, Journal of Colloid and Interface Science, 319, 505-513, DOI: 10.1016/j.jcis.2007.10.059

Dorrer C., Rühe J., 2009, Some thoughts on superhydrophobic wetting, Soft Matter, 5, 51-61, DOI: 10.1039/B811945G

Franken, A.C.M., Nolten, J.A.M., Mulder, M.H.V., Bargeman, D., Smolders, C.A., 1987, Wetting criteria for the applicability of membrane distillation, Journal of Membrane Science, 33, 315-328.

Khayet M., Matsuura T., 2011, Membrane Distillation Principles and Applications. Elsevier, Amsterdam, the Netherlands

Lin S., Nejati S., Boo C., Hu Y., Osuji C. O., Elimelech M., 2014, Omniphobic membrane for robust membrane distillation, Environmental Science & Technology Letters, 1, 443-447, DOI: 10.1021/ez500267p

Molina C. T., Bouallou C., 2015, Carbon dioxide absorption by ammonia intensified with membrane contactors, Chemical Engineering Transactions, 45, 253-258, DOI: 10.3303/CET1545043

Razmjoua A., Arifin E., Donga G., Mansouri J., Chen V., 2012, Superhydrophobic modification of TiO2 nanocomposite PVDF membranes for applications in membrane distillation, Journal of Membrane Science, 415-416, 850-863, DOI: 10.1016/j.memsci.2012.06.004

Singh S., Khulbe K.C., Matsuura T., Ramamurthy P., 1998, Membrane characterization by solute transport and atomic force microscopy. Journal of Membrane Science, 142, 111-127, DOI: 10.1016/S0376-7388(97)00329-3