Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.765365

51 (2013) 6003–6008
September

Taylor & Francis
Taylor & Francis Group

Characterization of polymeric membranes for membrane distillation using atomic force microscopy

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Received 20 November 2012; Accepted 5 January 2013

ABSTRACT

As membrane distillation (MD) is an under-developed separation process, specific membranes for MD applications are not yet commercially available. Therefore, microporous polymeric membranes made of hydrophobic materials fabricated for microfiltration purposes are usually used for MD applications. Characterization of such kind of membranes is important in order to achieve a better in-depth understanding of their performance and to fabricate specific membranes for MD process. One of the emerging characterization methods is atomic force microscopy (AFM) analysis. AFM is a newly developed high-resolution method that is useful for studying the surface topography of various types of membranes, and 3D images of the membrane surface can be obtained directly without special sample preparation. Consequently, a truer and clearer surface structure of a polymeric membrane can be observed. In this work, AFM method has been used for characterization of three hydrophobic membranes (polytetrafluoroethylene, polypropylene, and polyvinylidene fluoride) which are typically used for various MD applications. The membranes were characterized for their pore size, pore size distribution, surface roughness, and hydrophobicity. A sweeping gas membrane distillation apparatus was used for solute rejection evaluation of the applied membranes.

Keywords: Membrane distillation (MD); Hydrophobic membranes; Atomic force microscopy (AFM); Characterization

1. Introduction

Membrane distillation (MD) is a versatile membrane separation process [1–3] which is currently considered and used for various applications, i.e. desalination [4], food processing [5], water and wastewater treatment [6,7], and removal of volatile organic compounds [8]. It is a non-isothermal separation, based on the transport of volatile compound(s) (mostly water) in vapor phase through a microporous hydrophobic membrane, from the hot side (i.e. feed side) towards the cold side (i.e. permeate side) [9,10].

Most of applied membranes in MD are those commercially hydrophobic membranes fabricated for microfiltration purposes [11]. Therefore, characterization

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of such membranes could provide the knowledge for better understanding their behavior and performance. In this domain, atomic force microscopy (AFM) is a powerful tool for the characterization of polymeric membranes [12–15], leads to in-depth understanding of surface morphology and 3D view of membranes' topography [16,17] without any prior sample preparation as it is necessary in other microscopic methods such as scanning electron microscopy (SEM). Moreover, AFM provides a series of roughness parameters in nanometric scale [16].

In this work, three hydrophobic membranes were characterized by using AFM. Pore size, pore size distribution, and surface roughness were determined. SEM was used for observation of surface morphology. A sweeping gas membrane distillation (SGMD) apparatus was used for solute rejection measurements. Overall, this study is a short communication on the characterization of hydrophobic membranes for MD process using AFM method.

2. Materials and methods

Three commercial hydrophobic membranes with reported pore size of 0.22 μm made of polypropylene (PP), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE), supplied from Sepro (China), Membrane-Solutions (China), and Millipore (USA), respectively, were investigated. Table 1 shows the specifications of the membranes provided by the suppliers.

A multipurpose MD setup was designed, constructed, and used for the experiments. The effective area of the MD module was 0.0169 m^2. A diaphragm pump and an oil-free compressor were used for recirculation of hot feed and sweeping gas (SG) streams. A hot-water bath, equipped with five thermal sensors (Pt-100) and Autonics thermometer, was used for adjusting the hot and cold streams' temperature.

Applied membranes were characterized for pore size, pore size distribution, and surface roughness by using an AFM (DUALSCOPE 95-200E, DME, Denmark) and an SEM (VEGA, TESCAN, Czech Republic), and a contact angle measuring system (KRUSS G-10, Germany) was used for determining the surface energy.

3. Results and discussion

MD process is a thermal-driven separation in which only vapor should be passed through the membranes' pores. One of the major drawbacks of the MD process is pore-wetting when the process liquid penetrates into the pores. Therefore, the membrane pore size is a critical parameter in order to prevent the pore-wetting phenomenon. In another word, the pore size should be as small as possible (in the range of 0.1–1 μm). Moreover, the pore size distribution should be as narrow as possible too. It is worth quoting that the membranes of the size of 0.22 μm are usually investigated as the best choice for various MD applications [19,20]. Based on various fabrication methods [11], pore size and pore size distribution could be different for various membranes. For instance, the PTFE membranes are usually prepared via film-stretching method, while PVDF membranes and PP membranes are usually fabricated via solution-casting and melt-spinning methods, respectively. It is worth noting that the fabrication method can directly affect the pore size and pore size distribution as well as the surface topography. Fig. 1 shows the SEM images of the investigated membranes in this study. As it could be observed, the surface topography and morphology of these membranes are completely different and the membranes have non-circular pore structure. The pore size and pore size distribution of these membranes were characterized using AFM method (Fig. 1). The ability to determine the size and the distribution of pores by AFM can obviously be enhanced when a good image is produced. Further information on this matter could be found in the literature [12,14,15]. Table 1 presents the reported and characterized values for the applied membranes. Fig. 2 shows the pore size distribution of these membranes. It could be observed that the reported pore size for all the membranes was at 0.22 μm, while the measured values were at 0.311, 0.282, and 0.278 μm for PVDF, PP, and PTFE membranes, respectively.

Another important property of the MD membranes is hydrophobicity. When a droplet of water is placed on a membrane surface and if the surface tension of

Table 1
The reported and the characterized specifications of applied membranes

Membrane	Reported			Characterized		
	Pore size (μm)	Thickness (μm)	Porosity (%)	Pore size (μm)	Roughness (nm)	CA (°)
PVDF	0.22	184	80	0.311	11.9	98.7 ± 0.5
PP	0.2	200	75	0.282	51.7	113.5 ± 0.5
PTFE	0.22	175	70	0.278	68.9	132.2 ± 0.5

CA: Contact angle (°).

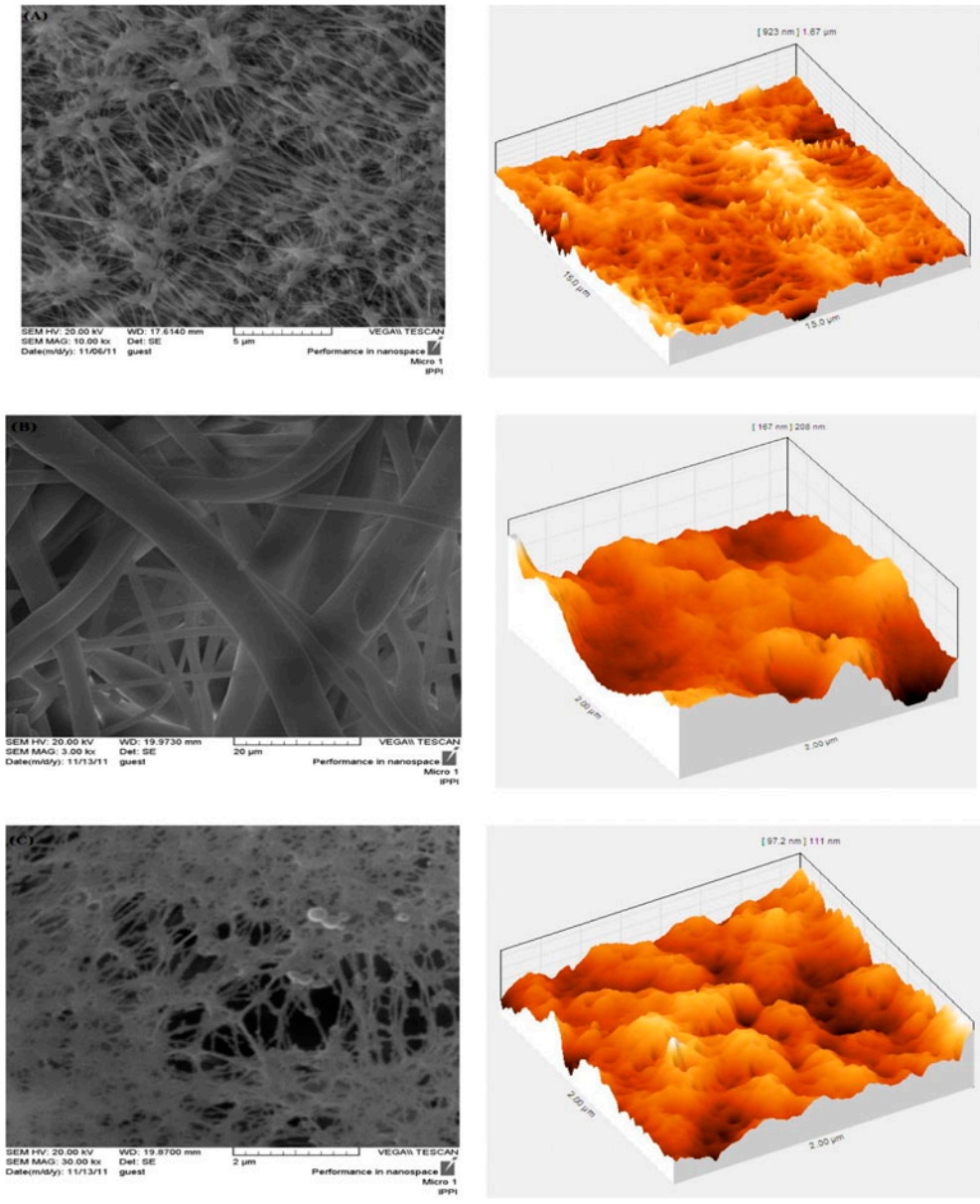

Fig. 1. SEM (left) and AFM (right) images of (A) PTFE, (B) PP, and (C) PVDF membranes with 0.22 μm reported pore size.

Table 2
Surface energy of common materials for MD membranes

Membrane material	Surface energy (10^{-3} N/m)
PVDF	~30.3
PP	~30.0
PTFE	~19.1

water is larger than that of the polymer, it makes a large contact angle between the water droplet and the membrane surface. Therefore, hydrophobic membranes are difficult to wet with water droplets and the contact angle of the water droplets and the membrane surface is higher than 90°. Hydrophobicity is affected by two major parameters, the polymer intrinsic hydrophobicity and surface roughness. The intrinsic hydrophobicity of PTFE, PP, and PVDF membranes was measured using the surface contact angle of their flat sheets. The obtained values were at 120.7°, 103.2°, and 90.5° for PTFE, PP, and PVDF sheets, respectively. This means that all the investigated polymers were hydrophobic in nature. Table 2 presents the surface energy of the studied membranes. The

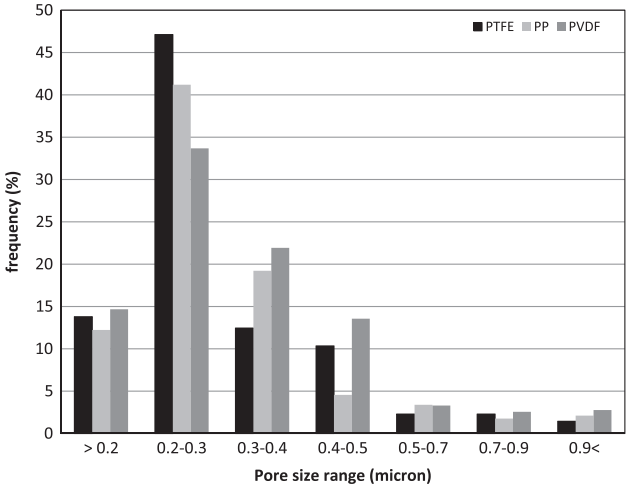

Fig. 2. Pore size distribution of applied membranes analyzed by AFM method. (PTFE, PP, and PVDF with 0.22 μm reported pore size).

obtained values for water contact angle of the polymeric sheets were found lower than those of the microporous membranes (Table 1). This could be explained by the well-known Cassie–Baxter theory. According to the Cassie–Baxter theory, when a water droplet is placed on a membrane surface, it can be held up by the trapped air in the membrane's pores. It means that the air trapped in the membrane's pores, placed under the water droplet, affects the hydrophobicity of the membrane surface, because the water–air contact angle is considered to be at 180°. Moreover, higher surface roughness leads to increased hydrophobicity.

One of the other practical surface's parameters which can be directly measured using AFM is the surface roughness. AFM analysis provides about 15 different roughness parameters which could be used for topographical studies as well as surface energy measurements. Table 3 presents the most important roughness parameters and their definitions. The

Table 3
Typical roughness parameters and their definitions that can directly obtained by the use of AFM method

Parameter	Definition
Arithmetic average height ($\bar{z}$)	General description of height variations $\bar{z}(N,M) = \frac{1}{N}\sum_{x=1}^{N} z(x,y)(2D)$ $\bar{z}(N,M) = \frac{1}{MN}\sum_{x=1}^{N}\sum_{y=1}^{M} z(x,y)(3D)$
Average roughness (R_a)	Gives the deviation in height. Different profiles can give the same R_a $R_a(N,M) = \frac{1}{N}\sum_{x=1}^{N}(z(x,y) - \bar{z}(N,M))(2D)$ $R_a(N,M) = \frac{1}{NM}\sum_{x=1}^{N}\sum_{y=1}^{M}(z(x,y) - \bar{z}(N,M))(3D)$
Root-mean-square roughness (R_q)	Represents the standard deviation of surface heights $R_q(N,M) = \sqrt{\frac{1}{N}\sum_{x=1}^{N}(z(x,y) - \bar{z}(N,M))^2}(2D)$ $R_q(N,M) = \sqrt{\frac{1}{NM}\sum_{x=1}^{N}\sum_{y=1}^{M}(z(x,y) - \bar{z}(N,M))^2}(3D)$
Maximum profile peak height (R_p)	Height of the highest peak above the mean line in the profile $R_p = \max(z_i - \bar{z});\ 1\langle i\langle N$
Maximum profile valley depth (R_v)	Depth of the deepest valley below the mean line in the profile $R_v = \left\lvert\min(z_i - \bar{z})\right\rvert;\ 1\langle i\langle N$
Total roughness (R_t)	$R_t = R_p + R_v$

average roughness parameters of the applied membranes are presented in Table 1. As observed, among the membranes studied, the PTFE membrane was the roughest one. The contact angle was the highest for PTFE and was the lowest for PVDF membranes, respectively. In another word, both the higher roughness and the air trapped in the pores led to higher hydrophobicity of the PTFE membrane. These results are in agreement with those of the previous studies where they concluded that PTFE membranes were the most suitable choice for various MD applications [4,8,11,18–20].

Fig. 3 shows the solute rejection for three applied membranes during concentrating of glucose syrup experiment using SGMD at constant operating conditions of 65˚C feed temperature, 600 mL/min feed flow rate, 50 kg/m^3 feed concentration, and 0.453 Nm^3/h SG flow rate. As demonstrated, both PTFE and PP membranes showed high solute rejection, 99.9% (complete solute rejection) and 99%, respectively; while about 96% rejection was measured for PVDF membrane. This could be explained by the results obtained through membranes' characterisation.

Although the reported pore size for the applied membranes in this work was identical (0.22 μm), the other specifications (both reported and characterized) were different. For example, the thickness of the PTFE membrane was 175 μm, while the thickness of the PP membrane was about 200 μm. Another example was the surface hydrophobicity. The contact angle for the PTFE and PP membranes was measured at 132.2˚ and 113.5˚ respectively, while this value for the PVDF membrane was at 98.7˚. Moreover, as it could be seen in the SEM image (Fig. 1), the PP membrane structure contained randomly fabricated fibers. This is due to the melt-spinning fabrication method used for PP membranes. This randomly inter-connected pore structure significantly increases the solute rejection [21].

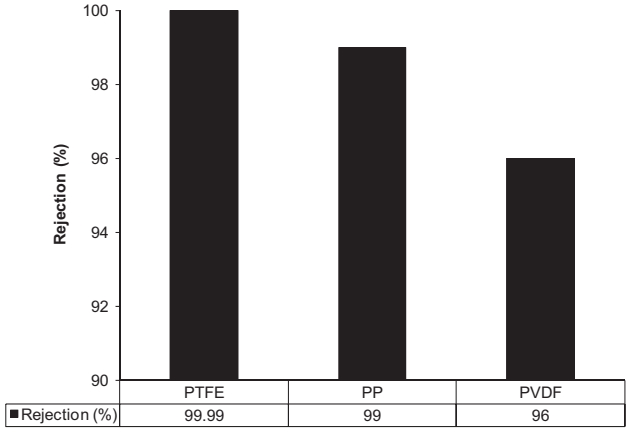

Fig. 3. Glucose rejection values of the applied membranes. (T_h = 65˚C, Q_h = 600 mL/min, C_i = 50 kg/m^3, and Q_s = 0.453 Nm^3/h).

4. Conclusion

Pore size, pore size distribution, and hydrophobicity of membranes are the most important specifications, especially in case of MD process, and significantly influence their performance. Based on the obtained results, the reported and measured specifications of the applied membranes, e.g. pore sizes, were different. Therefore, the reported specifications by manufacturers are not completely trustable, and it would be better if the membrane(s) is characterized for pore size, pore size distribution, hydrophobicity, and other specifications prior to any experiments. AFM is proven to be a powerful and high-resolution method for studying the surface topography of various types of membranes. Based on the results obtained in this study, AFM is strongly recommended for analyzing and characterizing the membranes for MD process applications, either those commercial or those synthesized.

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