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Hydrothermal pretreatment: A simple method for dry substrate membrane regeneration

Yanni Liu, Zhi Wang*, Song Zhao, Xiaochang Cao, Nan Li, Jixiao Wang, Shichang Wang

Chemical Engineering Research Center, School of Chemical Engineering and Technology, Tianjin University, Yaguan Road, Jinnan District, Tianjin 300350, PR China
Tianjin Key Laboratory of Membrane Science and Desalination Technology, State Key Laboratory of Chemical Engineering, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Yaguan Road, Jinnan District, Tianjin 300350, PR China

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A B S T R A C T

Impacts of substrate membrane storage conditions, which might have special significance in the industry and laboratory research of composite membranes, are rarely reported. Herein, the polysulfone ultrafiltration membrane was chosen as a typical substrate membrane and differences between substrate membranes stored in wet and dry conditions were discussed. An easy-operational hydrothermal pretreatment method was therefore proposed to regenerate the dry substrate membranes. The substrate membranes were heated in deionized water, and the pore morphology was significantly improved after the pretreatment. Three types of additives were applied to improve the effects of pretreatment and the effects of the hydrothermal pretreatment turned to be stronger as the concentration of the additive increased. Membrane structure parameters were investigated and the dry support membranes pretreated with 3.0% or 6.0% molar fraction ethanol displayed approaching structure parameters with wet membranes pretreated with the same conditions, which means the dry substrate membranes were successfully regenerated. Poly(vinylamine)-polysulfone composite membranes were prepared with polysulfone substrates before and after pretreatment, and tested by using CO_2/N_2 (15/85 by volume) mixed gas. Composite membranes prepared with wet and dry polysulfone substrates pretreated with 3.0% molar fraction ethanol exhibited similar CO_2 permeance, which confirmed that the dry substrate membranes were effectively regenerated.

1. Introduction

Membranes are widely used in the environment and energy field [1–8]. Among all membranes, composite membrane has won great commercial success as its porous support and the selective layer can be separately optimized [9]. There are plenty of investigations on the selective layer these years, while less research about the porous support comparatively. Several investigators believe that the impacts of the substrate should no longer be negligible when the flux is high enough [9]. Early in 1998 and 1999, Beuscher and Gooding [10,11] reported the impacts of substrate on binary gas mixtures in volatile organic compounds separation. Trifunovic and Tragardh [12] then reported the influences of support layer structure on pervaporation procedure in 2005. They pointed out that increments of support porosity and pore size could facilitate the mass transfer of components in the support and decrease the pressure loss. Ghosh and Hoek [13] investigated the impacts of polysulfone (PSf) support morphology and chemistry on interfacial polymerization of composite membranes in 2009. They confirmed that PSf substrate with more, large, hydrophobic skin layer pores could improve the permeability of the composite membranes for osmosis application. Ramon et al. [14] theoretically investigated impacts of pore diameter and porosity of the substrate membrane on gas diffusivity in composite membranes in 2012. They concluded that the pore structure changes might result in changes on membrane performance. A series of poly(piperazine-amide)-poly(vinyl chloride) thin film composite membranes were prepared by Kong et al. [15] via interfacial polymerization in 2016. They investigated the effects of poly (vinyl chloride) substrate properties on the characteristics of the prepared nanofiltration membranes, and the results indicated that the increased substrate porosity may lead to an increased salt rejection rate of the composite membrane.

As most of the substrate membranes have been commercialized, the properties of the commercialized substrate membranes must be taken into account when fabricating composite membranes. Generally, substrate membranes are always stocked and transported in humid atmosphere to prevent water loss. However, if the substrate membranes are

* Corresponding author at: Chemical Engineering Research Center, School of Chemical Engineering and Technology, Tianjin University, Yaguan Road, Jinnan District, Tianjin 300350, PR China.
E-mail address: wangzhi@tju.edu.cn (Z. Wang).

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Table 1
Partial solubility parameter and Ra to PSf of materials mentioned in this article [19].

Material	δ_D	δ_P	δ_H	δ	Ra (PSf)
H_2O	15.5	16	42.3	47.8	35.9
Ethanol	16.6	8.8	17	25.3	10.7
Ethylenediamine	15.8	8.8	19.4	26.5	13.6
Imidazole	19.7	15.6	11.2	27.5	7.9
PSf	19.7	8.3	8.3	22.9	–

Table 2
Types and concentration of pretreatment additives.

Additive	Concentration (% molar fraction)				
Ethanol	0.3	0.6	1.5	3.0	6.0
Ethylenediamine	0.3	0.6	1.5		
Imidazole	0.3	0.6	1.5		

stocked in dry atmosphere with carelessness, which is not rare in lab or plant, performance degradation might occur. It has been proved by Fathizadeh et al. that thin film composite polyamide membrane fabricated over dry support layer had less water flux during water desalination process [16]. Overall, the performance of the dry membranes is much lower than the wet ones, thus the performance of the composite membranes fabricated with dry substrate membranes cannot be guaranteed. The dry substrate membranes not only influence the perm-selectivity of the composite membrane products in industrial applications, but also have remarkable influence on the repeatability of experimental data in laboratory research as we observed. Generally, the dry substrate membranes are treated like trash and thrown away, which results in a great waste and environmental pollution. In the meantime, we have not found any research about the regeneration of dry substrate membrane up to now. Hence, the main goal of our research is to find a simple method to regenerate the dry substrate membrane.

Polysulfone ultrafiltration membrane was chosen as a typical substrate membrane in our investigations. Polysulfone membrane is a kind of commonly used substrate membrane due to the low price, process easiness, and stability against thermal, mechanical, chemical and bacterial attack characteristics of the material. Differences in pore morphology between wet and dry substrate membranes were discussed in this work and then an easy-operational hydrothermal pretreatment method was applied to regenerate the improperly stocked dry substrate membranes. As the surface morphology like porosity, pore area, pore length and pore equivalent diameter of the polymer membrane can be changed when exposed to water in a long period [17], the main principle of the pretreatment method is facilitating the swelling of the substrate polymer so that the collapsed pores in dry substrate membranes can be re-enlarged. According to thermodynamics theory, when temperature of the system rises, the absolute value of the negative mixing Gibbs free energy tends to be larger, which means the extent of mixing or swelling is larger. In this case, the dry substrate membrane can be regenerated in a short time by a hydrothermal method where a higher temperature is employed.

Three different types of pretreating additives including ethanol, ethylenediamine and imidazole were applied to get better pretreatment results since they might have better swelling capacity to PSf than water. Solubility parameter was applied to describe the swelling effects. In accordance with Hansen's description in 2007 [18], solubility parameter could be measured by total cohesive energy E, which is the sum of three major individual energies that make it up

$$E = E_D + E_P + E_H \tag{1}$$

where E_D, E_P and E_H represent for dispersion cohesive energy, polar cohesive energy and hydrogen bonding cohesive energy, respectively. Thus, the square of Hildebrand (or total) solubility parameter δ is given by

$$E/V = E_D/V + E_P/V + E_H/V \tag{2}$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{3}$$

An equation which depicted the solubility parameter "distance", Ra, was developed by Skaarup in 1967 [19]. The equation depicts the difference in solubility parameter between two materials based on their respective partial solubility parameter components:

$$(\mathrm{Ra})^2 = 4(\delta_{D2}-\delta_{D1})^2 + (\delta_{P2}-\delta_{P1})^2 + (\delta_{H2}-\delta_{H1})^2 \tag{4}$$

The greater Ra is, the lower affinity of two materials have. The partial solubility parameter and Ra to PSf of materials mentioned in this article are listed in Table 1.

As listed in Table 1, all of the three additives have smaller Ra value than pure water, which means, all of the additives have better affinity with PSf than pure water. Ethanol (EtOH) is a commonly used nonsolvent during PSf fabrication via phase inversion method. As ethanol is a weak nonsolvent to PSf, the hydroxyl group in ethanol has Van der Waals forces with the ether oxygen group and sulfur oxygen group in the PSf polymer chain, which is beneficial for the swelling process. Moreover, ethanol is a cheap and readily available chemical, which means it is capable of being applied in industrial substrate membrane pretreatment. Ethylenediamine (EDA) is applied in fabricating high-performance membranes in our former works [20,21]. We chose ethylenediamine as the second additive because the amino group can interact with the ether oxygen group and sulfur oxygen group in the PSf polymer chain as well. Herein, we proposed another type of chemical, imidazole (Im), as the third additive. The imidazole group is a proton donor as well as a proton accepter, which means, it may have Lewis

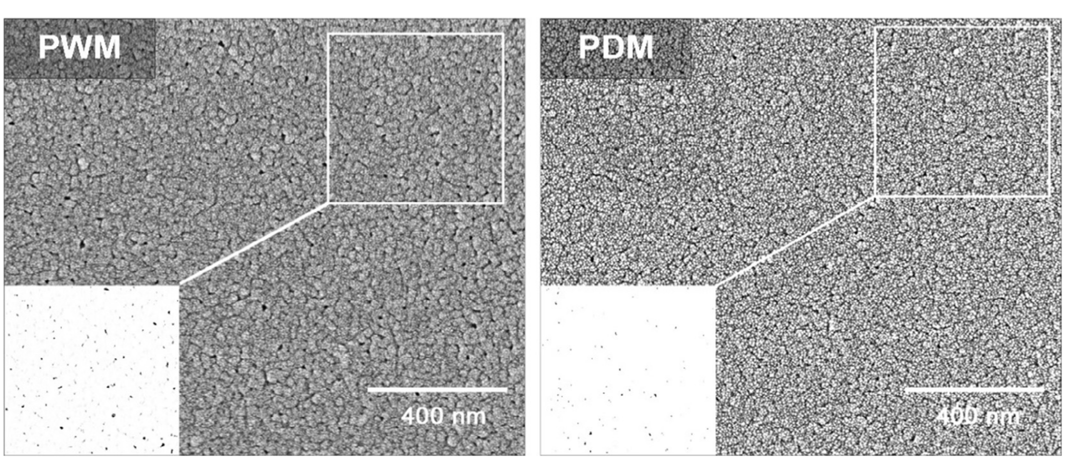

Fig. 1. Surface SEM images of the pristine wet membrane (PWM) and the pristine dry membrane (PDM).