PREPARATION OF A HYDROPHOBIC AND MICROPOROUS MEMBRANE FOR MEMBRANE DISTILLATION USING THE DRY-WET PHASE INVERSION TECHNIQUE

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1. INTRODUCTION

In recent years, membrane distillation (MD) has received increasing attention as a promising process for seawater desalination to augment fresh water supply in many areas around the world, including Vietnam [1-3]. Compared to other desalination processes, MD possesses several important attributes that make it an ideal candidate for seawater desalination applications at small-scale and in remote areas. The advantages of MD over other desalination processes include: (1) high rejection of dissolved salts and involatile contaminants, (2) low propensity to membrane fouling and scaling and therefore less feed water pre-treatment required, and (3) the ability to couple with renewable energy sources such as solar thermal energy and waste heat from other processes [4-6]. Given these advantages, MD has been explored for seawater desalination to provide potable water in many places such as on cruise ships and on remote islands [7, 8].

One integral component of the MD process is the hydrophobic microporous membrane [9-11]. In the seawater MD desalination process, this membrane acts as a physical barrier to separate a hot seawater stream from a cool fresh distillate stream. Due to its hydrophobic and microporous nature, the membrane prevents liquid water to penetrate through but allows water vapor to transfer across its pores from the hot seawater stream to the cool fresh distillate. As long as the membrane pores remain dry and a temperature difference is maintained between the two sides of the membrane, the MD process can achieve pure distillate directly from seawater without the need for boiling seawater as required in conventional thermal distillation methods. Given this working principle, the membrane and its characteristics play a vital role in determining the water flux and salt rejection of the MD process for the seawater desalination application [9-11].

Most of MD membranes are prepared from hydrophobic polymers using the phase inversion process [11-13]. The hydrophobic polymers used for the preparation of MD membranes include further polyethylene (PE), polypropylene (PP), polytetrafluoro ethylene (PTFE), and polyvinylidene difluoride (PVDF). Amongst these polymers, PVDF is the most widely reported polymer used for MD membrane preparation due to its excellent physio-chemical and thermal stability and the ease of processing [14-16]. During the phase inversion process to prepare MD membranes, a homogenous solution of two or more polymers is transformed to a solid state in which membrane rigid structure and pores are formed as a result of the phase inversion. There are several techniques to achieve phase inversion, but the dry-wet phase inversion (i.e. also called as the Loeb-Sourirajan) is the most commonly used technique for the preparation of PVDF-based MD membranes [16]. During the phase inversion to form the membrane, many factors can affect the characteristics of the prepared membrane. The most notable factors are polymer solution temperature and the ambient moisture.

This study aims to trial the preparation of hydrophobic microporous MD membranes from PVDF polymer using the dry-wet phase inversion technique. MD membranes were first prepared using the dry-wet phase inversion technique at different polymer solution temperature and ambient moisture. The prepared membranes were then characterized using various analytical methods to examine the effects of polymer solution temperature and ambient moisture on the membrane structural and morphological properties.

2. MATERIALS AND METHODS

2.1. Materials

Chemicals used to prepare MD membranes in this study included poly vinylidene fluoride (PVDF) (with molecular weight of ~400 kDa), tri-ethylene phosphate (TEP) (99.5%), 2-propanol (99.5%), and ethanol (95%). All chemicals were laboratory-grade and provided by Alfa Aesar. Deionized (DI) water was used to prepare the coagulation bath with 2-propanol (i.e. 40 ml of 2-propanol was mixed with 200 ml of DI water). Another chemical (n-butanol 99%) was used for the measurement of membrane porosity.

2.2. The preparation and characterization of the membrane

MD membranes were prepared using the dry-wet phase inversion technique [16]. Firstly, a 12 wt.% polymer solution was prepared by dissolving PVDF in TEP with magnetic agitation at 70°C prior to overnight cooling in a refrigerator. Then, the polymer solution was casted using a membrane casting machine (Fig. 1). The membrane casting machine was provided by Memcast (from The Netherlands), and it was able to regulate the casting temperature. The thickness of the casted membrane was controlled using a casting knife with different edge gaps. To regulate the moisture of the ambient air during the membrane casting process, the casting machine was put in an environmental chamber in which the air moisture was regulated using nitrogen gas flow. A glass plate was used as a base for membrane casting.

After casting the polymer solution on the glass plate at regulated polymer solution temperature and ambient moisture, the glass plate with the membrane formed on its surface was transferred to and immersed in the coagulation bath (the 16.7% solution of 2-propanol in DI water) in 5 minutes (i.e. the coagulation bath was also kept in the environmental chamber). Then the glass plate and the membrane were withdrawn from the environmental chamber and immersed in a DI water bath overnight to completely remove the residual of solvent. Subsequently, the glass plate and the membrane were dried in an oven at 60°C for 12 hours. After drying in the oven, the membrane was gently removed from the glass plate by partially spraying the membrane and the plate with the 30% ethanol in DI water solution. The membrane was air dried prior to its structural and morphological characterization analyses.

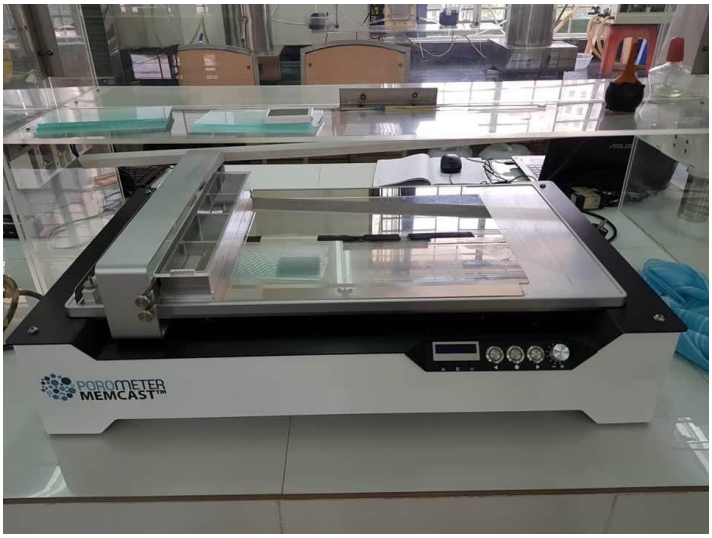

Figure 1. The photo of the MEMCAST membrane casting machine used for the preparation of the membrane in laboratory.

The structural and morphological properties of the prepared membranes were characterized using Fourier transform infrared spectroscopy (FT-IR), X-Ray diffraction (XRD), scanning electron microscope (SEM), and contact angle measurement (CAM). The FT-IR and contact angle measurement analyses were conducted using a Spectrum Two FT-IR Spectrometer and CAM 200, respectively, at the Faculty of Physio-Chemical Engineering of Le Quy Don Technical University, while the XRD and SEM analyses were conducted using the SIEMENS D-500 Bruker and SM-6510LV at Vietnam Academy of Science and Technology.

The porosity of the prepared membranes was determined using the gravimetric method. Briefly, a dried membrane coupon was weighted using an analytical balance and then totally submerged in n-butanol in a glass beaker for 2 hours. Then, the wetted membrane coupon was taken out of the beaker. The excessive n-butanol on the wetted membrane surfaces were removed using nylon fabrics. The wetted membrane was then quickly weighted using the analytical balance. The porosity of the membrane was calculated using the following equation [16]:

$$\varepsilon = \frac{{m_l}/{p_l}}{{m_l}/{p_l} + {m_p}/{p_p}} \; x \; 100\% \qquad (1)$$

where ε was the membrane porosity (%); m_l and m_p were the weight of the wetted and dry membrane coupon; and ρ_l and ρ_p were the density of n-butanol and PVDF.

3. RESULTS AND DISCUSSIONS

3.1. The formation of PVDF crystals during the dry-wet phase inversion

PVDF crystals exist in four different structures, including α, β, γ, and δ depending on their formation conditions. The XRD analyses of the membranes prepared in this study demonstrate the dominant structures of PVDF crystals formed during the dry-wet phase inversion process were α and β. In the XRD spectrum of the prepared MD membrane (Fig. 2), peaks (1 0 0) and (0 2 0) at the 2θ value of ~18.5° represent the α phase crystals (monoclinic, space group $P2_1/c$), while the peak (2 0 0) at the 2θ of 20.5° is for the β phase crystals (orthorhombic space group *Cm2m*). The FT-IT spectrum shown in Fig. 3 also confirms the formation of α and β-structure PVDF crystals during the preparation of the MD membrane using the dry-wet phase inversion technique. The peaks and vibration bands corresponding for α and β crystals presented in Fig. 3 match with those reported in the study by Gregorio et al. [17].

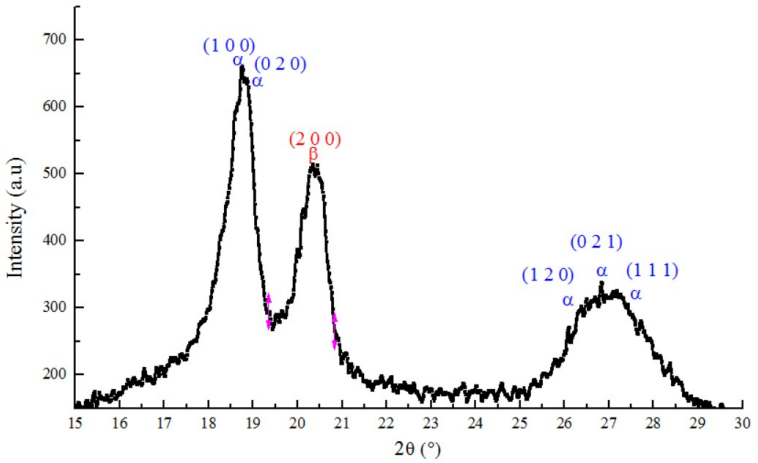

Figure 2. The XRD spectrum of the MD membrane prepared using the dry-wet phase inversion technique. The XRD analysis was conducted using the SIEMENS D-500 Bruker at Vietnam Academy of Science and Technology.

The structural analyses of the MD membrane prepared in this study are consistent with the results reported in the study by Buonomenna et al. [14] in which a PVDF-based MD membrane was also prepared using the dry-wet phase inversion technique but with two different coagulation solutions including dimethyl acetammide (DMA)/water and DMA/alcohol. The PVDF-based MD membrane reported in the study [14] also existed in crystal structures of α and β, despite the varying ratio between these two crystal structures when the casting conditions changed. The formation of α and β crystals during the preparation of the MD membranes prepared in this study might be also subjected to the phase inversion conditions, particularly the polymer solution temperature and the ambient moisture. This will be elucidated in the next sections.

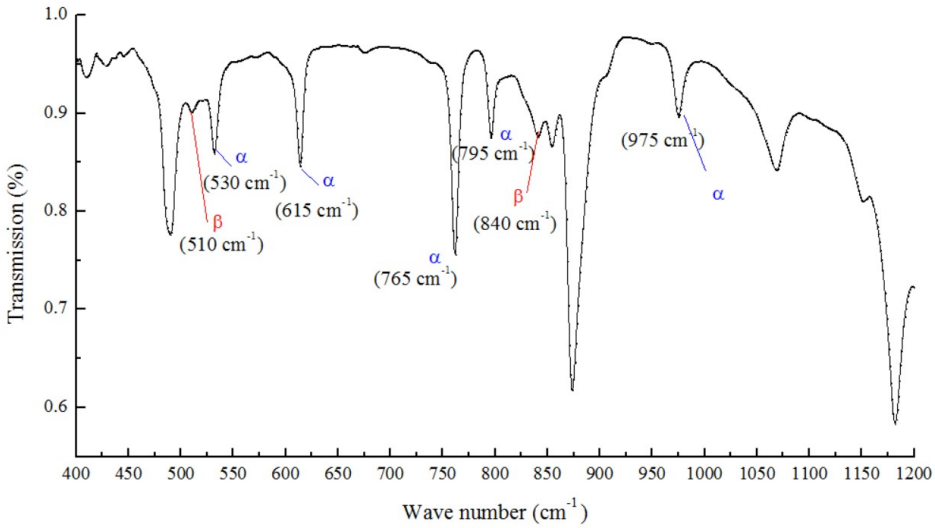

Figure 3. The FT-IR spectrum of the MD membrane prepared using the dry-wet phase inversion technique. The FT-IR analysis was conducted using the Spectrum Two FT-IR Spectrometer at the Faculty of Physio-Chemical Engineering of Le Quy Don Technical University

3.2. Effects of the preparation conditions on the crystal structures and porosity of the PVDF membrane

Factors that can affect the formation of PVDF crystals during the MD membrane preparation using the dry-wet phase inversion technique include polymer solution composition and temperature, ambient moisture, coagulation conditions (e.g. coagulation mixture composition and coagulation time), and thermal post-treatment of the membrane after the coagulation step. Previous studies have investigated the effects of polymer solution and coagulation compositions and the coagulation duration and thermal post-treatment on the structural properties of the PVDF-based MD membranes [14-16]. Therefore, this study only aims to examine the effects of polymer solution temperature and ambient moisture on the crystal structures and porosity of the PVDF-based MD membranes prepared using the dry-wet phase inversion technique.

As demonstrated in Fig. 4, elevating the polymer solution temperature resulted in increases in the porosity of the MD membranes using the dry-wet phase inversion technique. The porosity of the MD membranes increased from 70.5% to nearly 76% when the polymer solution temperature was elevated from 15°C to 60°C, regardless either α or β crystals were formed during the phase inversion of PVDF. The increased membrane porosity at elevated polymer solution temperature might be attributed to the reduced viscosity of the polymer solution but increased mass transfer of solvent (i.e. TEP) from the polymer solution to the coagulation bath. The

more polymer solvent transferred to the coagulation bath, the more voids were formed during the dry-wet phase inversion, and hence the more porous MD membrane was created. The porosity is a vital structural property of MD membranes as it determines several important membrane characteristics such as water permeability, thermal conductivity, and mechanical strength [9, 18]. It is noteworthy that the porosity of the prepared MD membranes reported in this study was measured and then calculated using the equation (1) which involved the density of PVDF. As β PVDF crystal has higher density than α one (i.e. 1.97 versus 1.92), the calculated porosity of the β-PVDF membrane was slightly higher than that of α-PVDF membrane (Fig. 4).

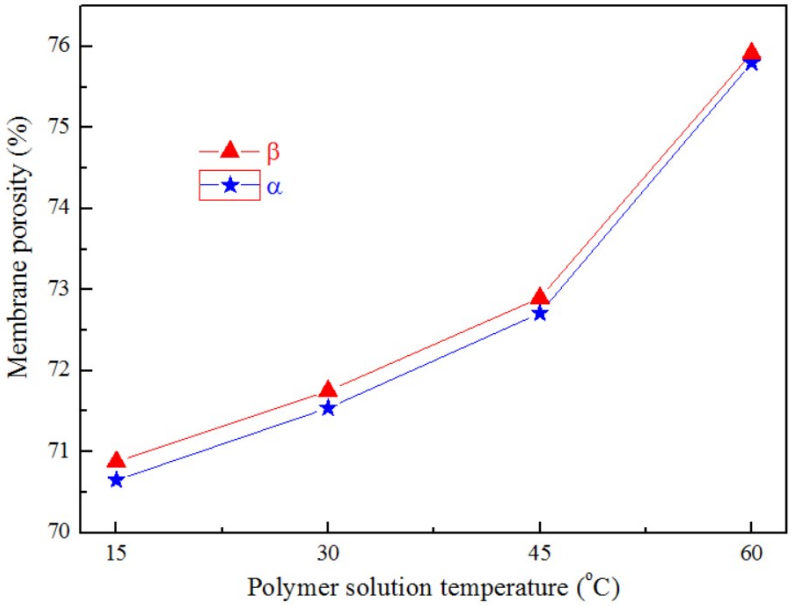

Figure 4. The effects of the polymer solution temperature on the porosity of the prepared MD membranes using the dry-wet phase inversion at ambient moisture of 30%

The XRD analyses of the prepared MD membranes reveal that elevating the polymer solution temperature favored the formation of α crystals over the β crystals. In the XRD spectra shown in Figure 5, the middle peaks represent the overlap spectra of α and β crystals. On the spectra of M15 (the membrane prepared at the polymer solution temperature of 15°C), the middle peak approached closer to the line of 20.5°, which is the 2θ value for β crystals), whereas the middle peak of the M45 moved towards the 18.5° corresponding to the α crystals. This means that more β crystals were formed in the M15 than in the M45. In other words, more β crystals and less α crystals were formed during the phase inversion at lower polymer solution temperature. This trend was confirmed by the FT-IR analyses of the M15 and M45 membranes shown in Figure 6.

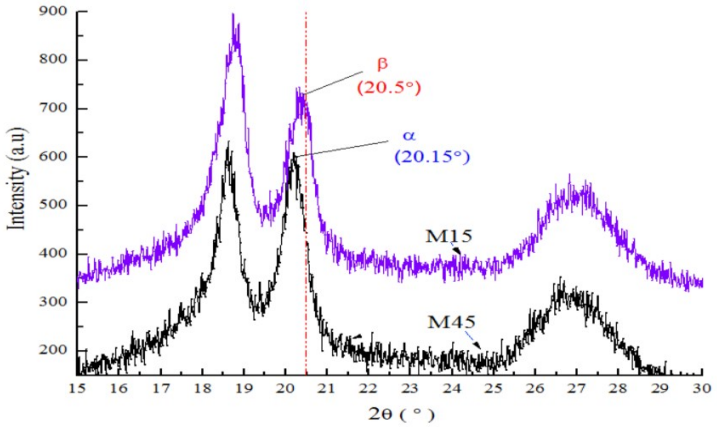

Figure 5. The XRD spectra of two MD membranes prepared at polymer solution temperature of 15°C (M15) and of 45°C (M45), and ambient moisture of 30%

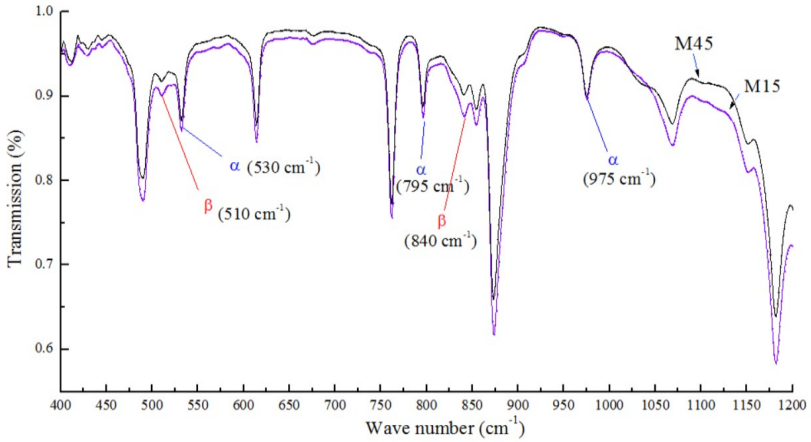

Figure 6. The FT-IR spectra of membranes prepared using the dry-wet phase inversion technique at polymer solution temperature of 15° (M15) and of 45°C (M45), and ambient moisture of 30%

Unlike polymer solution temperature, ambient moisture negatively affected the porosity of the prepared MD membranes. The membrane prepared at the phase inversion ambient moisture of 30% had porosity of 74.5%, which was much higher than the porosity of the membrane prepared at the ambient moisture of 55%. The decreased porosity of the prepared membrane at higher phase inversion ambient moisture might be because of the rapid crystallization of the PVDF crystals at high ambient moisture. Due to the high affinity of the TEP solvent, moisture (water vapor) was absorbed to the polymer solution during the casting of the membrane on the glass plate. As a non-solvent, water facilitated the crystallization of the PVDF, and hence accelerated the formation of crystal nuclei over the growth of formed crystals, resulting in the formation of more small crystals. The PVDF-based MD membrane with smaller crystals had lower porosity than that with larger crystals. This will be manifested later by analyzing the microscope and SEM images of the prepared MD membranes.

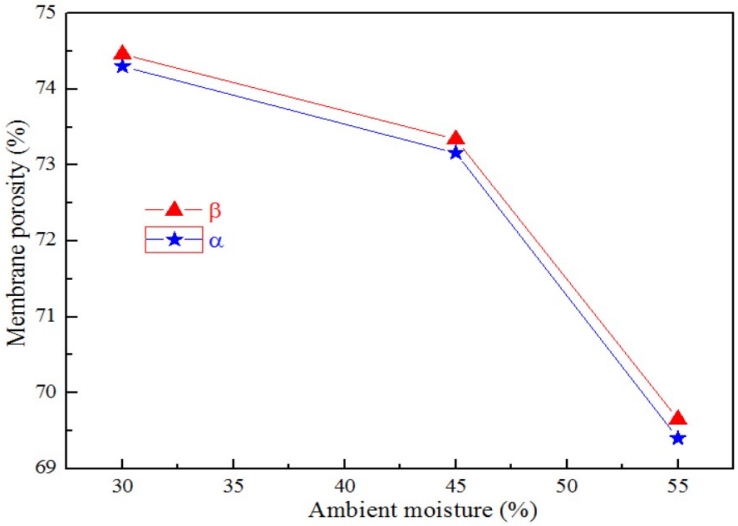

Figure 7. Effect of the ambient moisture during the phase inversion on the porosity of the prepared membrane (polymer solution temperature of 30°C)

The FT-IR analysis of the prepared MD membranes also reveals that at higher ambient moisture, α crystals tended to be formed more than β ones (Fig. 8). The FT-IR spectrum of the membrane prepared at the ambient moisture of 30% (M30) was always below the spectrum of the membrane prepared at the ambient moisture of 55% (M55), indicating that more α crystals were formed at higher ambient moisture, whereas low ambient moisture was favorable for the formation of β crystals. Crystal structures of the PVDF-based MD membranes not only affected their porosity but also determined their morphological properties. The next section will provide more details about this.

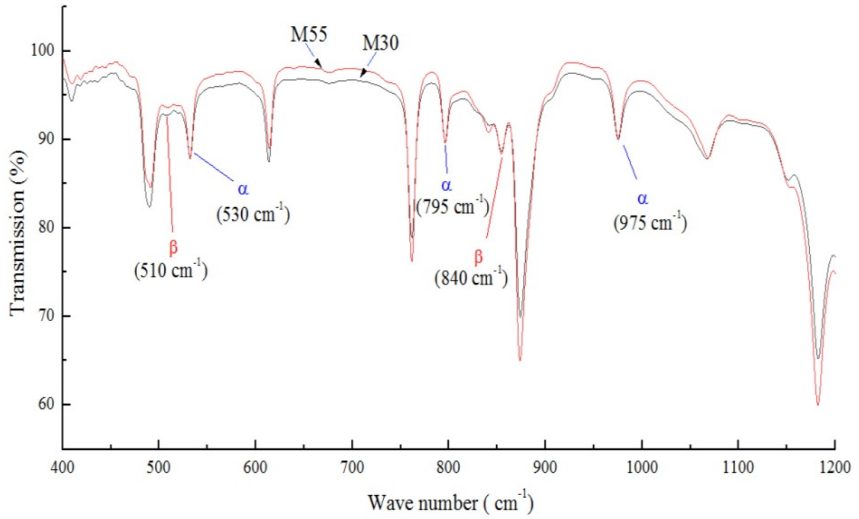

Figure 8. The FT-IR spectra of membranes prepared at ambient moisture of 30% (M30) and of 55% (M55) (polymer solution temperature of 30°C)

3.3. The morphological properties of the prepared MD membranes

Surface analyses of the prepared MD membranes underpin the profound effects of polymer solution temperature and ambient moisture on the morphology of the membranes. When conducting the dry-wet phase inversion at higher polymer solution temperature and ambient moisture, PVDF-based membranes with more α crystals were formed; therefore, MD membranes prepared at these conditions appeared to have particulate morphology (i.e. corresponding to the particle α crystals) (Fig. 9 A&B). On the other hand, reducing the polymer solution temperature and ambient moisture promoted the formation of β-PVDF membranes and hence they exhibited more cellular structure (Fig. 9 C&D). The PVDF-based MD membranes with cellular structure possess higher mechanical strength than the particulate-structure membranes with the similar membrane porosity. Thus, the results reported here highlight the need to conduct the dry-wet phase inversion step at low polymer solution and ambient moisture to obtain PVDF-based MD membranes with better mechanical strength.

The SEM analyses also confirm that microporous MD membranes were achieved after the preparation process using the dry-wet phase inversion technique. The obtained membranes were porous with pore sizes in the μm range for both particulate and cellular structure (Fig. 9 B&D).

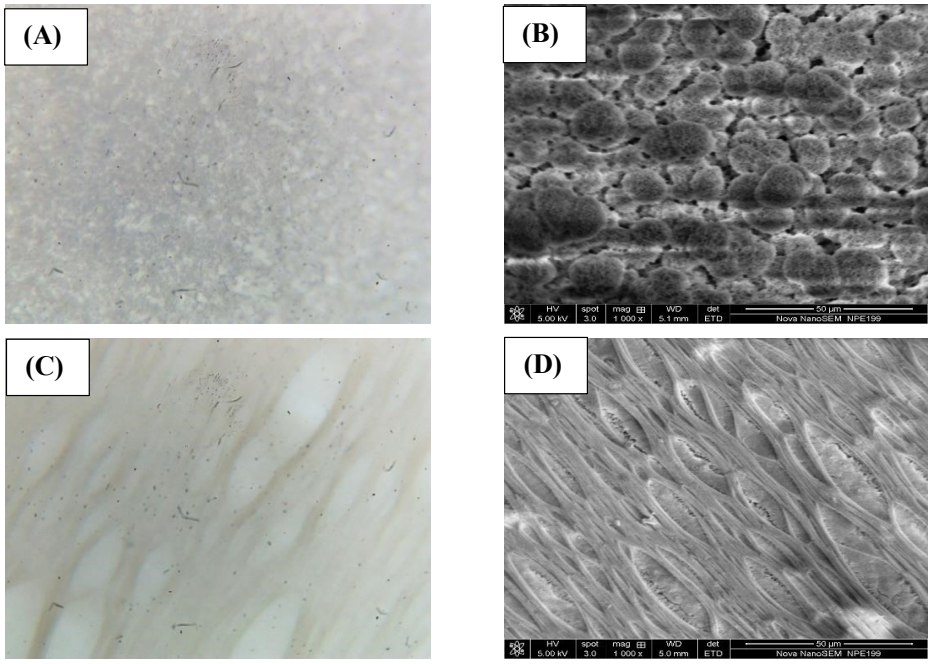

Figure 9. Microscope and SEM images of the MD membranes prepared at different polymer solution temperature and ambient moisture: (A) & (B) polymer solution temperature = 45°C, ambient moisture 55%; and (C) & (D) polymer solution temperature = 15°C, ambient moisture 30%

The contact angle measurements of the PVDF-based MD membranes prepared in this study confirm their hydrophobicity. The membrane-water contact angle of the M30 membrane was slightly lower than that of the M55 membrane (i.e. 121° versus 125°), but both were far higher than 90°, which is the benchmark water contact angle for MD membranes used for desalination purposes. Therefore, the MD membranes prepared using the dry-wet phase inversion technique in this study are suitable for seawater desalination applications. However, further studies are required to examine the thermal and mechanical stability of these membranes and their performance in MD systems under real conditions.

4. CONCLUSIONS

In this study, PVDF-based hydrophobic microporous MD membranes were successfully prepared using the dry-wet phase inversion technique. The structural and morphological analyses of the prepared MD membranes demonstrate profound effects of the polymer solution temperature and ambient moisture on the forms of PVDF crystals and the membrane porosity. The PVDF-based prepared MD membranes existed in crystal forms of α and β, and reducing polymer solution temperature and ambient moisture promoted the formation of β-PVDF crystals. The MD membranes prepared at low polymer solution temperature and ambient moisture tended to have more β crystals and exhibited cellular structure, while the particulate α-PVDF membranes were obtained at high polymer solution temperature and ambient moisture.

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SUMMARY

PREPARATION OF A HYDROPHOBIC AND MICROPOROUS MEMBRANE FOR MEMBRANE DISTILLATION USING THE DRY-WET PHASE INVERSION TECHNIQUE

In recent years, membrane distillation (MD) has been increasingly explored for seawater desalination to augment fresh water supply around the world and in Vietnam. In a MD system, the hydrophobic microporous membrane plays a vital role, profoundly affecting the water flux and salt rejection of the system. In this study, poly vinylidene difluoride (PVDF)-based hydrophobic microporous MD membranes were prepared using the dry-wet phase inversion technique to investigate the effects of the preparation conditions on the membrane structure and surface morphology. The experimental results show that by using the dry-wet phase inversion technique, the prepared PVDF membranes existed in crystal forms of a and b, and the casting polymer solution temperature and the ambient moisture exhibited profound effects on the formation of crystals and the membrane porosity. Indeed, reducing the polymer solution temperature and the ambient moisture favoured the formation of the b crystals and the resultant cellular membranes. Finally, morphological analyses (e.g. microscope, scanning electro microscope (SEM), and contact angle measurement) proved that the prepared MD membranes using the dry-wet phase inversion technique were hydrophobic and microporous, having a liquid-membrane surface contact angle of 121°-125° and membrane pores with μm sizes.

Keywords: *Membrane distillation, seawater desalination, membrane preparation, phase inversion, membrane characterization, chưng cất màng, khử mặn nước biển, chế tạo màng, đảo pha, đặc trưng màng lọc.*

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