Fabrication and characterization of tubular ceramic-supported maleic acid / poly (vinyl alcohol) composite membranes for dehydration of ethanol by pervaporation

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Abstract: Maleic acid (MA) was used as a cross-linking agent for fabrication of MA/poly(vinyl alcohol) (PVA) flat sheet and tubular ceramic-supported MA/PVA membranes by solvent evaporation and dip-coating methods, respectively. The effect of MA concentrations (0-40 wt% MA with respect to PVA) on pervaporation (PV) performance of MA crosslinked PVA (MA/PVA) flat sheet membranes for dehydration of 80 wt% ethanol solution was investigated. The characterizations of MA/PVA flat sheet membranes were performed by X-ray diffraction spectrum, Fourier-transform infrared spectroscopy, differential scanning calorimetry, swelling rate, and contact angle measurement. The characterization and PV experimental results showed that MA concentration of 20 wt% was suitable for cross-linking PVA membrane. Number of interior coating times of MA/PVA layer on the ceramic tube was studied by PV experiments. The results indicated that 4 time coated tubular composite membrane presented high flux and good selectivity of 0.064 kg/m^{2}h and 30.2, respectively for dehydration of 80 wt% ethanol solution at 50 ^{o}C and vacuum pressure of 100 kPa. In addition, the structure of tubular ceramic-supported 20 wt% MA/PVA composite membrane was taken by scanning electron microscopy (SEM). The SEM image revealed that the average thickness of thin MA/PVA active layer was less than 50 μm coated on inside of the ceramic tube.

Keywords: Tubular, Ceramic-supported, Maleic Acid, Poly (vinyl alcohol), Composite Membrane, Dehydration, Ethanol, Pervaporation.

Introduction:

Pervaporation (PV) is a membrane separation process in which the feed is a liquid mixture under atmospheric pressure and the permeate is vapor phase under vacuum or sweep gas, as shown in Figure 1. PV is combination of permeation and evaporation across a semipermeable membrane, which involving liquid-vapor phase change to achieve separation. In PV, the driving force for the mass transfer is chemical potential gradient between the two sides of the membrane [1].

In dehydration of ethanol solution, a hydrophilic membrane which selectivity is for water removal. Poly(vinyl alcohol) (PVA) is a good membrane for PV dehydration of ethanol-water mixture because of its good properties such as hydrophilic, well-forming, low cost, and compatibility with water. However,

PVA membrane has low efficiency due to swelling in water and instability at high temperature operation [1-2]. There are many methods to improve the properties of PVA membranes. Among them, chemical cross-linking agent is widely used because it has advantages like simple process, low energy consuming, variety of cross-linking agents. The cross-linked bonds are produced by removing H$_2$O from the connection of –OH groups of PVA chains and –COOH, CHO groups of cross-linking agents. The bonds make the membrane with thermal stability and life time increase, whereas swelling rate decrease with the increasing of cross-linking agent concentration.
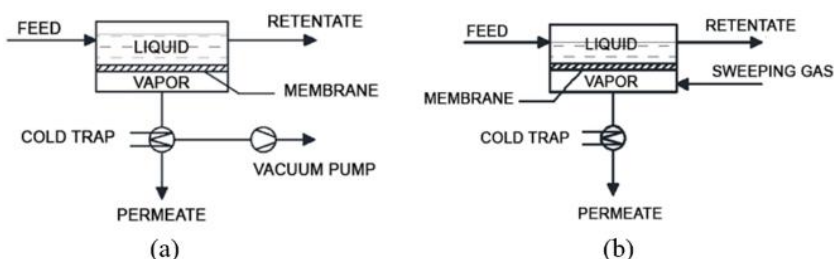

Figure 1: Working principle of pervaporation using: (a) vacuum pump and (b) sweep gas

In addition, these led to a decrease in hydrophilicity and water compatibility of cross-linked membranes. Previous studies had revealed that maleic acid (MA) is used as a cross-linking agent for PVA. The MA cross-linked PVA membranes present a good PV performance for dehydration of ethanol solution due to only two carboxylic groups of MA making less intramolecular cross-linking [3-4].

On the other hand, in industry, tubular membrane modules are suitable for dehydration of ethanol because they provide good mechanical stability and package-able into high surface area. The tubular ceramic supports are popular for fabrication of thin-film composite membranes [5-7].

In this study, the effects MA cross-linking agent concentration on PV performance of the flat sheet PVA membranes and thickness of MA/PVA layer on PV performance of tubular ceramic-supported membranes for the dehydration of 80 wt% ethanol solution are investigated. Simultaneously, these membranes were characterized by X-ray diffraction spectrum (XRD), Fourier-transform infrared spectro-scopy (FTIR), differential scanning calorimetry (DSC), swelling rate, contact angle measurement, and scanning electron microscopy (SEM).

Materials and Methods:
PVA (molecular weight and the degree of saponifi-cation were 80,000 and > 98 %, respectively) and MA (99 wt%) were purchased from Xilong Chemical, China. Ethanol (96 vol%) was purchased from ViNa Chemsol, Vietnam. Ceramic tubes (length: 300 mm, diameter: 15 mm, thickness: 2 mm) were fabricated by Faculty of Materials Technology, HCMUT. All chemicals were used without any further purification.

Preparation of MA cross-linked PVA (MA/PVA) flat membranes
The MA/PVA membranes were fabricated by solution-casting method as follows: 3g PVA was dissolved in 120 mL water at 80 $^{\circ}$C. MA was put gradually into the PVA solution with MA concentration of 0, 10, 20, 30, and 40 wt% (respect to the weight of PVA). The MA-PVA mixture was concentrated and cooled to room temperature. 20 mL of MA-PVA mixture was poured onto a petri disk with a filter paper inside to form a membrane and dried at room temperature for 24-48 h. Finally, the membrane was dried at 120 $^{\circ}$C for 3 h.

Preparation of tubular composite membranes
The tubular MA/PVA composite membranes with the suitable concentration of cross-linker were prepared by dip-coating method as follows: ceramic tubes were dried at 100 $^{\circ}$C for 30 mins. MA-PVA solution with the suitable concentration of cross-linking agent was prepared same as described above. The inside of ceramic tube was dip-coated with MA-PVA solution for 10 minutes and dried at 100 $^{\circ}$C while rotating the

mandrel to assure uniform coverage by the thin layer. The process was repeated to obtain the desired number of coating time. Finally, the tubular composite membrane was dried at 120 $^{\circ}$C for 3 h.

Pervaporation experiments
PV system diagram as shown in Figure 2. At first, MA/PVA flat sheet membranes were put into the module as shown in Figure 3a. 2 L of 80 wt% ethanol solution was put into the feed tank. The flow rate was fixed at 60 L/h. The vacuum pressure on the permeate side was 100 kPa. The heating coil was turned on to heat the solution up to 50 $^{\circ}$C. All experiments were carried out during 2 h for finding out the optimal cross-linking agent concentration. The PV experiments with the tubular ceramic-supported MA/PVA composite membrane module (Figure 3b) were conducted at the same conditions with the flat sheet membrane to determine the reasonable MA/PVA layer thickness or number of coating times.
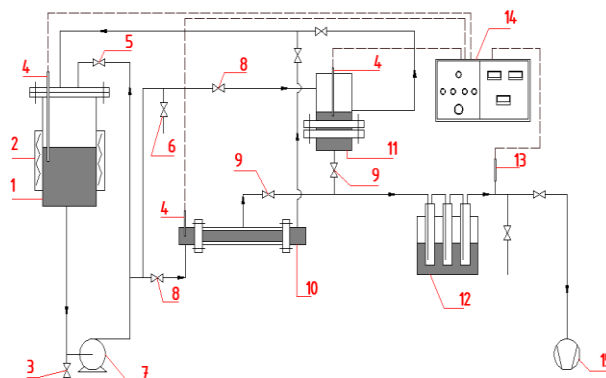

Figure 2: Schematic diagram of combined flat and tubular membrane modules PV system

1. Feed tank
2. Heating coil
3. Drain valve
4. Thermometer
5. Recirculation valve
6. Sample valve
7. Centrifugal pump
8. Flow rate control valve
9. Permeate valve
10. Single tubular membrane module
11. Flat sheet membrane module
12. Cold trap
13. Vacuum gauge
14. Process control panel
15. Vacuum pump

The PV performance of the membranes was evaluated through permeate flux (J), separation factor (α), and PSI (PV separation index) as follows [8].

$$J = \frac{1}{A}\frac{\Delta W}{\Delta t} \quad (1)$$

$$\alpha = \frac{y_{H_2O}/y_{C_2H_5OH}}{x_{H_2O}/x_{C_2H_5OH}} \quad (2)$$

$$PSI = J(\alpha - 1) \quad (3)$$

where: ΔW (kg) is the mass of permeate, Δt (h) is time, A (m^2) is the effective membrane area, and x, y are the mass fraction of either water or ethanol in the feed and permeate, respectively.

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Characterization
XRD patterns were obtained by D8-ADVANCE with a voltage of 40 kV and electric current of 40 mA, K_α =1.54184 Å. The sweeping speed is 0.01 $^\circ$/0.2s. FTIR spectra were analyzed in the range of wavenumber from 4000 to 500 cm^{-1} during 64 scans on Alpha–E Brucker (Bruker Optik GmbH, Ettlingen, Germany) spectrometer. DSC was performed with Mettler Tolado, heating step 10 ^{o}C/min, amplitudes of 0-250 ^{o}C. SEM images were taken by JSM 7401F-ICT-VAST, the sample is scatter by natural force to find the natural thickness of the membrane.

Contact angles of membranes with water were measured using SCA20. Swelling degree was carried out by dipping the membranes in pure water for 1 day then calculating the swelling rate: $SR = \frac{W_m - D_m}{D_m} 100\%$ (4).

where: W_m (g) is the wet mass of the membrane, D_m (g) is the dry mass of the membrane. All measurements were carried out under the following conditions: 25 ^{o}C and relative humidity of 30%.
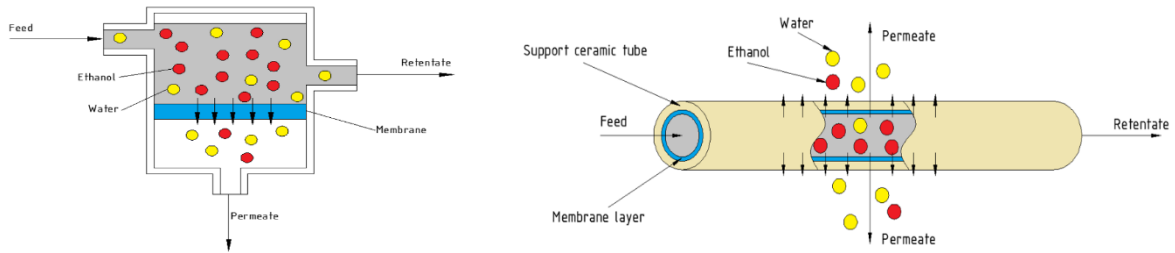

Figure 3: Pervaporation (a) flat sheet and (b) tubular composite membrane modules

Results and Discussion:
Effect of cross-linking agent concentration on PV performance of MA/PVA flat membranes:
Figure 4a shows that when concentration of MA was less than 20 wt%, the separation factor increased while the permeate flux increased and then decreased. However, the separation factor decreased while the permeate flux increased at the MA concentrations were higher than 20 wt%. Figure 4b presents that the PSI was highest at 20 wt% of MA.
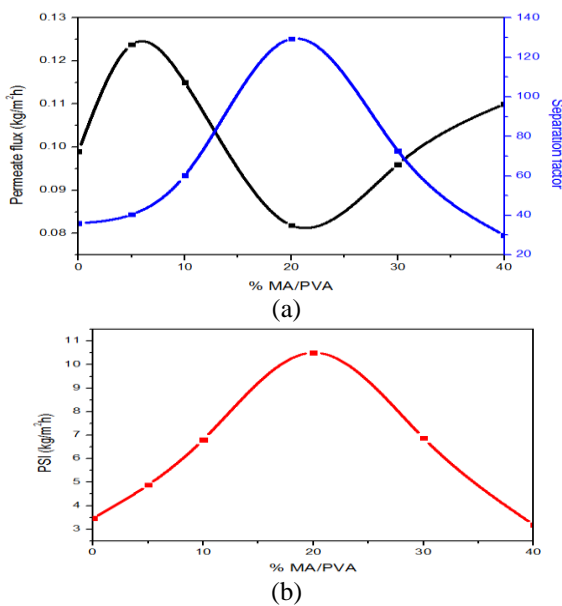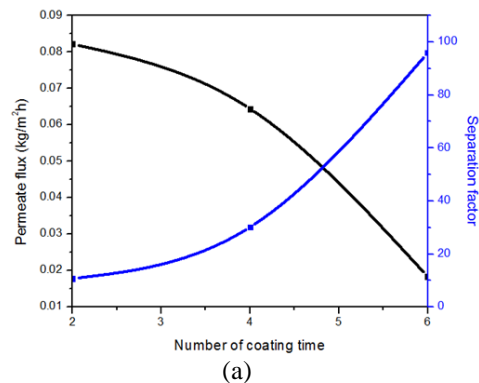
These can be explained that at lower cross-linking concentrations (< 20 wt%), the crystallinity of PVA membrane was not completely disrupted but the membranes became less hydrophilic; thus, the membranes showed a decrease in permeability. At higher cross-linking concentrations (> 20 wt%), greater cross-linking degrees more completely disrupt PVA crystallinity as well as change the structure of the membrane, which resulted in higher permeability.
Therefore, 20 wt% of MA is suitable concentration for cross-linking PVA membranes. This result is consistent with previous study [9].

Effect of coating times on PV performance of tubular composite membranes:
The effect of number of coating times on PV of tubular ceramic-supported 20 wt% MA/PVA composite membranes as shown in Figure 5.

(a)

(b)

Figure 4: Effect of MA concentration on PV performance of MA/PVA flat sheet membranes: (a) Permeate flux and Separation factor; (b) PSI
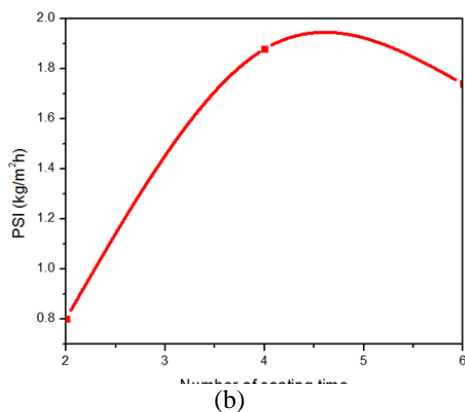

(a)

(b)

Figure 5: Effect of coating time on PV performance of tubular ceramic-supported 20 wt% MA/PVA composite membranes: (a) Permeate flux and separation factor; (b) PSI

It shows that the separation factor increased, permeate flux decreased, and PSI increased and then slowly decreased with increasing number of coating times. This is due to the increase coating times resulted in the thicker membrane. In addition, the PV performance indicates that 4 times of dip-coating was reasonable to fabricate the tubular composite membranes. The 4 times coated tubular composite membrane exhibited the acceptable PV performance with a permeate flux of 0.064 kg/m^2h and a separation factor of 30.2. These values are in good agreement with earlier report [9].

Membrane characteristics:

XRD analysis

XRD patterns of pristine PVA and 20 wt% MA cross-linked PVA flat sheet membranes as shown in Figure 6. It can be seen that the peak at $2\theta=19.6$ is the characteristic peak of PVA polymer [10]. In addition, the intensity of this peak was reduced when the degree of cross-linking increased, that made the membrane crystallinity decreased. The decrease in crystallinity leads to increase permeability because crystallinity prevents water molecules entering the membrane structure [10]. The XRD patterns demonstrate that the crystalline regions of polymer network were broken, which explain for the increase in the permeate flux of MA cross-linked PVA membrane compared with pristine PVA. This result is consistent with the PV experimental data as shown above in Figure 4.

FTIR analysis:

FTIR spectra of pristine PVA and 20 wt% MA cross-linked PVA flat sheet membranes as shown in Figure 7. It can be seen that the broad band appeared at 3250-3500 cm^{-1} is attributed to O–H stretching [10-11]. The spectrum of 20 wt% MA/PVA membrane presents the OH peak became larger corresponding to the –OH stretching vibration of the adsorbed water. In addition, the OH peak also is assigned to stretching of free hydroxyl groups of carboxylic acid

due to MA didn't completely react with PVA to form cross-linking bonds. Besides, the band at 1750 cm^{-1} is due to the stretching vibration of C=O and the bands in the range of 900-1200 cm^{-1} are stretching vibrations of C-O [11-13]. These peaks appear in the spectrum of 20 wt% MA/PVA membrane, which confirm that cross-links were formed between PVA and MA.
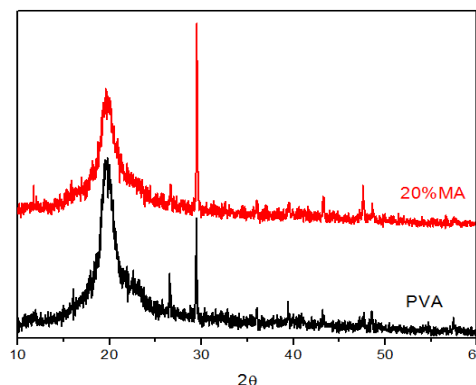

Figure 6: XRD patterns of PVA and 20 wt% MA/PVA flat sheet membranes
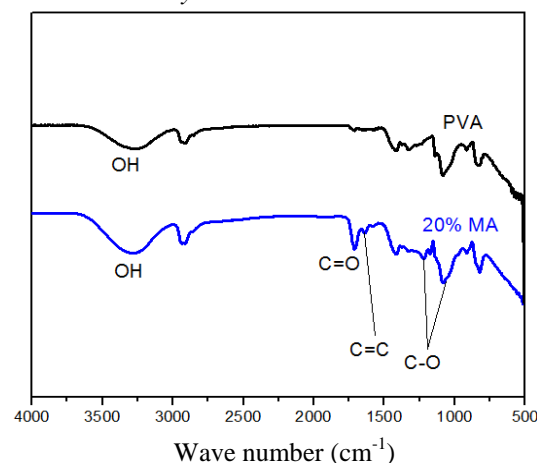
Thermal stability:

Figure 7: FTIR spectra of PVA and 20 wt% MA/PVA flat sheet membranes

Figure 8 shows that the glass transition temperature (Tg) increased when the presence of cross-linking agent in the membrane. Accordingly, Tg of pristine PVA is 91 ^oC while 20% MA/PVA is 112 ^oC, these results are in good agreement with other published report [2]. For a cross-linked polymer, Tg depends on the cross-linking density as well as on the chemical structure of the cross-linking agent by restricting the thermal motion of PVA molecular chains. Besides, the pristine PVA shows a melting point of 214 ^oC, however the MA/PVA does not display a sharp melting point. Additionally, the endothermic peaks of PVA and MA/PVA membranes at 153 ^oC and 156 ^oC, respectively, which can be expected to cause dehydration of water point. The DSC results reveal that the thermal stability of PVA was improved by cross-linking with MA.
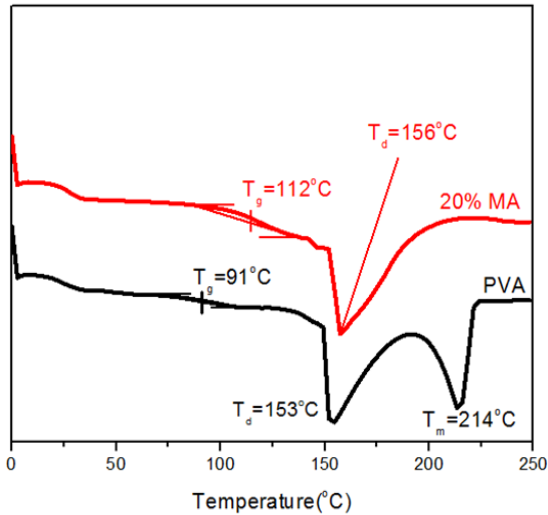
*Figure 8: DSC curves of PVA and
20 wt% MA/PVA flat sheet membranes*

Swelling rate:

Figure 9 shows swelling rate of MA cross-linked PVA membranes. The swelling rate decreased with increasing MA concentration. In other words, when concentration of cross-linker was higher than 30 wt%, the swelling rate remained unchanged. This means that the PVA matrix was full of cross-linking and no longer swells. The 20 wt% MA cross-linked PVA membrane shows the swelling rate of 75%.
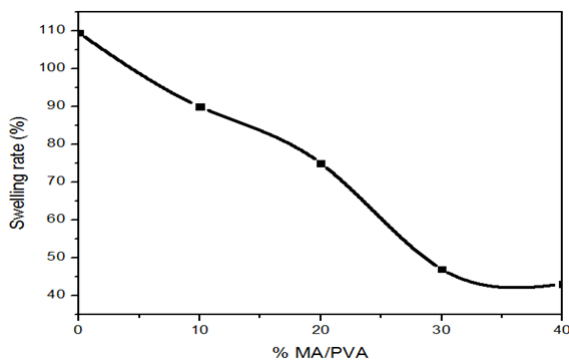

*Figure 9: Swelling rate of MA/PVA flat sheet
membranes*

Contact angle:

The results of contact angle measurement of pristine PVA and 20 wt% MA/PVA flat sheet membranes as shown in Figure 10. PVA membrane has a low contact angle of 54°, which is consistent with its hydrophilic properties. 20 wt% MA/PVA membrane has a high contact angle of 81° indicating that the surface of this membrane became more hydrophobic. This can be explained that when MA was incorporated with PVA, the crosslinking among PVA and MA led to the consumption of –OH group, thus the hydrophobicity of membrane increased [14].
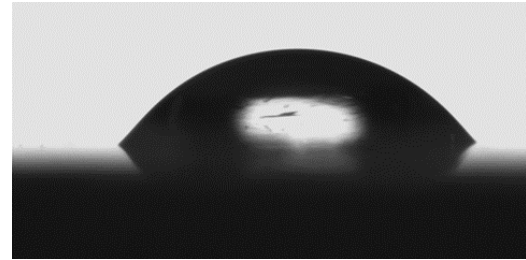
(a) PVA (54°)
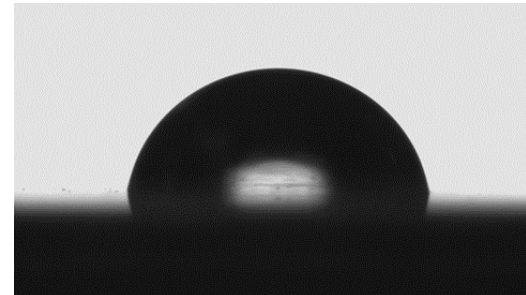
(b) 20 wt% MA/PVA (81°)

*Figure 10: Water contact angle of: (a) PVA
and (b) 20 wt% PVA/MA membranes*

Morphology:

Figure 11 shows SEM image of 4-time coated tubular ceramic-supported 20 wt% MA/PVA membrane. It can be seen that the cross-section of 20 wt% MA/PVA layer was coated on the inside of ceramic tube with an average thickness in the range of 37.5-48.5 µm. This optimum thickness of the MA/PVA separation layer coated on ceramic-supported provided the good PV performance of the tubular composite membrane for dehydration of 80 wt% ethanol solution as shown in Figure 5.
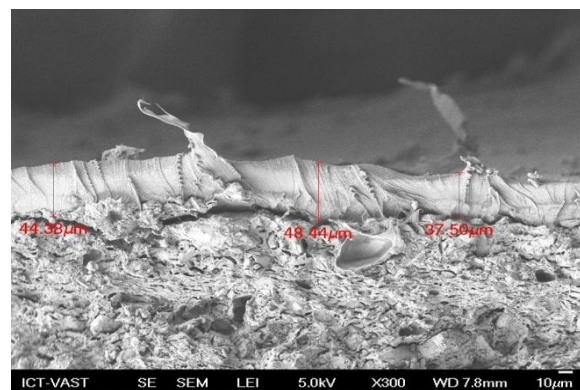

*Figure 11: SEM image of 4-time coated tubular
ceramic-supported 20 wt% MA/PVA membrane*

Conclusions:

MA cross-linked PVA flat sheet and tubular composite membranes were fabricated and characterized. PV experiments for dehydration of 80 wt% ethanol solution were studied at operating conditions at feed temperature 50 ^{o}C, flow rate 60 L/h, and permeate vacuum pressure 100 kPa. PV performance of the MA/PVA flat sheet membrane

indicates that MA concentration of 20 wt% was suitable for cross-linking PVA membrane. PV experimental results and SEM image reveal that 4 times was reasonable for coating 20 wt% MA/PVA separation layer with a thickness of 37.5-48.5 μm on the inside of ceramic tube. This tubular composite membrane exhibited a good PV performance with a permeate flux of 0.064 kg/m^{2}h and a separation factor of 30.2. The XRD, FTIR, DSC, swelling rate, and contact angle analyses confirm that by cross-linking using MA the crystallinity was reduced but the membrane became less hydrophilic and more thermal stable.

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