PREPARATION OF ZIF-8 LOADED PVA AND PES MIXED MATRIX MEMBRANES FOR DEHYDRATION OF ETHANOL SOLUTIONS

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ABSTRACT

PREPARATION OF ZIF-8 LOADED PVA AND PES MIXED MATRIX MEMBRANES FOR DEHYDRATION OF ETHANOL SOLUTIONS

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Solvent recovery is an important issue in chemical industry when low product cost is desired and also environmental concerns are considered. The conventional methods for solvent recovery are extractive distillation, adsorption, extraction and absorption. However, these methods require excessive amount of energy, cause product contamination due to additional components and need harsh conditions. Pervaporation separation is independent of the vapor-liquid equilibrium; therefore, it is a suitable technique especially for separation of azeotropic mixtures. Ethanol forms azeotrope with water and ethanol dehydration is one of the most popular usage area of pervaporation since high purity ethanol is required for use as biofuel and in pharmaceutical industry. For pervaporation applications, better performing membranes are desired in order to achieve high purity with faster separation.

In this study, asymmetric pure PES and PES/ZIF-8 membranes were prepared by non-solvent induced phase separation (NIPS) technique. Also dense pure PVA

membranes were prepared with solvent evaporation technique. They were cross-linked both thermally and chemically with glutaraldehyde solution. PVA/ZIF-8 MMMs were prepared with 5 wt. % ZIF-8 loading and cross-linked chemically. In order to examine the effect of particle size of ZIF-8 crystals on the pervaporation performances, MMMs were prepared with ZIF-8 crystals whose particle sizes were 17, 81, 190 and 340 nm. The pervaporation performance of all membranes were tested with ethanol-water (10/90 wt. %) mixture at 25°C

Asymmetric pure PES membranes prepared by wet-phase inversion technique and were annealed at three different temperature (40°C, 50°C and 70°C). The most selective membranes were the ones annealed at 50°C and had an average selectivity of 15.6 with an average flux of 71.5 g/m^{2}h. Besides, the flux of 5 wt. % ZIF-8 incorporated membranes was as twice as the flux through the pure PES membrane; however, a selectivity decrease of 75 % was observed.

Pure PVA membranes were prepared from 87-89 % degree of hydrolysis PVA and cross-linked by thermal treatment at different temperatures (90°C-160°C) for different times (1 hour and 48 hours). 1 hour thermal treatment caused an excessive decrease in normalized flux and a 20 % approximate increase in selectivity when compared to non-treated membranes. These membranes were also cross-linked chemically with GA solution having GA concentration of 0.5-3.0 wt. %. Membranes cross-linked with solution containing 0.5 wt. % GA had the highest selectivity (18.4, water/ethanol) with normalized flux value of 5800 µm g/m^{2}h, in average.

Pure PVA membranes also prepared from 98 % degree of hydrolysis PVA and were cross-linked chemically with GA solution having GA concentration of 0.5-1.5 wt. %. Membranes cross-linked with solution containing 0.5 wt. % GA had the highest selectivity and normalized flux with the average values of 77.2 and 1200 µm g/m^{2}h, respectively.

In order to observe the effect of particle size of ZIF-8 crystals on the performance of PVA membranes, the 5 % (w/w) ZIF-8 loaded PVA/ZIF-8 MMMs prepared using ZIF-8 with particle size of 17 nm, 81 nm, 190 nm and 340 nm. It was observed that, both normalized flux and selectivity of MMMs did not have a regular trend as

a function of particle size of ZIF-8 particles. The best performing MMMs were the ones filled with 190 nm ZIF-8 with an average normalize flux of 1300 µm g/m^{2}h and selectivity of 66, which was % 64 greater than the selectivity of pure PVA membranes.

Keywords: Pervaporation, Mixed matrix membranes, Zeolitic Imidazolate Framework-8 (ZIF-8), Ethanol dehydration

ÖZ

ZIF-8 İÇEREN PVA VE PES KARIŞIK MATRİSLİ MEMBRANLARIN ETANOL ÇÖZELTİLERİNİN SUSUZLAŞTIRILMASI İÇİN HAZIRLANMASI

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Çözücü geri kazanımı, kimyasal endüstrisinde üretim maliyetleri ve çevresel sorunsal dikkate alındığında önemli bir konu olmaktadır. Çözücü geri kazanımı için kullanılan başlıca konvansiyonel metotlar, özütlemeli damıtma, adsorpsiyon, özütleme ve absorpsiyondur. Ancak bu yöntemler fazla enerji tükettikleri gibi fazladan kimyasal kullanımından dolayı ürün kirliliğine sebep olmaktadır. Pervaporasyonun sıvı-buhar dengesinden etkilenmeyen bir ayırma yöntemi olması bu yöntemi özellikle eş-kaynar karışımların ayırılması için uygun kılmaktadır. Etanol su ile eş-kaynar bir karışım oluşturmaktadır. Etanolün ilaç endüstrisinde ve bio-yakıt amaçlı kullanımı için yüksek saflıkta olması gerekmektedir. Bu sebeple etanol susuzlaştırılması pervaporasyonun popüler bir kullanım alanıdır.

Bu çalışmada, asimetrik saf PES ve PES/ZIF-8 karışık matrisli membranlar çözücü olmayan madde içinde faz ayırımı yöntemi ile üretilmiştir. Ayrıca çözücü uçurma yöntemi ile yoğun saf PVA membranlar da üretilmiştir. PVA membranlar termal ve kimyasal olmak üzere iki şekilde çapraz bağlanmıştır. Kimyasal çapraz bağlama gluteraldehit (GA) çözeltisi ile yapılmıştır. PVA/ZIF-8 karışık matrisli membranlar ağırlıkça % 5 ZIF-8 dolgusu ile hazırlanmış ve GA ile çapraz bağlanmıştır. ZIF-8 parçacık boyutunun PVA/ZIF-8 karışık matrisli membranların pervaporasyon performansına etkisinin incelenmesi için, 17 nm, 81 nm, 190 nm ve 340 nm boyutlarında ZIF-8 sentezlenmiş ve PVA membranlara eklenmiştir. Pervaporasyon deneyleri ağırlıkça % 10 su içeren etanol-su karışımı ile 25° de yapılmıştır.

Asimetrik saf PES membranlar ıslak faz dönüşümü yöntemi ile hazırlanmış ve üç değişik sıcaklıkta tavlanmıştır (40°C, 50°C ve 70°C). En seçici membranların 50°C de tavlanan membranlar olduğu görülmüştür, ortalama seçiciliği 15,6 ve akısı 71,5 g/m^2.sa’tir. Bunun yanında % 5 ZIF-8 (81 nm parçacık boyutlu) içeren membranların akılarının saf PES membranın iki katı olduğu ancak seçicilikte % 75 kayıp olduğu gözlenmiştir. PES membranların daha kalın bir kabuk tabakalarını kalınlaştırmak için, saf PES membranlar pıhtılaştırmadan önce 5 dk. ve 60 dk.’lık çözücü uçurmaya maruz bırakılmıştır. Taramalı elektron mikroskobu görüntülerinde 60 dk. çözücü uçurmaya maruz kalan saf PES membranların kabuk tabakaları daha kalındır.

% 87-89 hidrolize PVA ile hazırlanan saf PVA membranlar değişik sıcaklıklarda (90°C, 100°C, 120°C, 140°C and 160°C) ve değişik sürelerde (1 saat ve 48 saat) termal olarak çapraz bağlanmıştır. Saf PVA membranların çapraz bağlamaları ayrıca GA derişimi % 0,5, 1,5 ve 3,0 olan çözeltiler ile de yapılmıştır. En yüksek seçicilik GA derişimi % 0,5 olan çözelti ile çapraz bağlanan membranlar ile elde edilmiştir (seçicilik 18,4, normalize akı 5800 µm g/m^{2}sa).

Saf PVA membranlar aynı zamanda hidroliz derecesi % 98 olan PVA ile de hazırlanmıştır. Çapraz bağlamaları GA derişimi % 0,5, 0,75 ve 1,5 olan çözeltiler ile yapılmıştır. En yüksek seçicilik GA derişimi % 0,5 olan çözelti ile çapraz bağlanan membranlar ile elde edilmiştir (seçicilik 77,2, normalize akı 1200 µm g/m^{2}sa)

ZIF-8 kristallerinin parçacık boyutunun PVA/ZIF-8 karışık matrisli membranların pervaporasyon performansına olan etkisini incelemek amacıyla parçacık boyutu 17 nm, 81 nm, 190 nm ve 340 nm olan ZIF-8 ile membranlar hazırlanmıştır. ZIF-8 içeriği ağırlıkça % 5’tir. Hem normalize flux hem de seçicilik ZIF-8’in parçacık boyutuna göre düzenli bir trend göstermemiştir. Ayırma performansı en iyi olan membranlar parçacık boyutu 190 nm olan ZIF-8 ile hazırlanan membranlardır. Bu membranların ortalama normalize akısı 1300 µm g/m^2sa ve seçiciliği 66’dır. Bu seçicilik değeri saf PVA membranlara göre % 64 daha fazladır.

Anahtar Kelimeler: Pervaporasyon, Karışık matrisli membranlar, Zeolitik Imidazolat Kafes-8 (ZIF-8), Etanol susuzlaştırılması

To the ones who

support me any time

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Symbols

A	Effective membrane area (cm^2)
J	Flux ($g/m^2.h$)
J_N	Normalized flux ($\mu m.g/m^2.h$)
M_w	Molecular weight (g/mol)
Q	Quantity of permeate collected (g)
t	Time (h)
T	Temperature (°C)
T_g	Glass transition temperature (°C)
W	Weight (g)
x	Mass fraction in feed
y	Mass fraction in permeate

Abbreviations

EtOH	Ethanol
DG	Degree of Swelling (%)
GA	Glutaraldehyde
IPA	Isopropanol
wt	Weight

Greek Letters

α	Selectivity
δ	Membrane thickness (µm)
Θ	Bragg Angle (^{o})

Subscripts

i	Component “i”
j	Component “j”
d	Dry
s	Swollen

CHAPTER 1

INTRODUCTION

Membrane is a thin film of natural or synthetic materials separating two phases which allows selective transportation between these phases. Membrane is permeable to a certain molecule, particle or component and with the help of a driving force it transfers this component from a mixture to the other side of the membrane and separation is achieved [1].

Membrane separation processes are easier to operate and use energy more efficiently when compared to the conventional separation techniques like adsorption, absorption and distillation [2–6]. Therefore during the past few decades these processes have started to be employed in industry more commonly. Pervaporation is a membrane separation technique that is used for separation of liquid mixtures and research on development of both hydrophilic and organophilic membranes for pervaporation has been going on intensively [1,5].

In pervaporation process feed solution, a liquid mixture, is in contact with the membrane and one or more of the components (permeate) removed from the feed and are taken from the permeate side in vapor phase [1]. Selective passing of molecules through membrane takes places due to their polarity, higher affinity and faster diffusivity. These molecules are instantly vaporized and removed from the membrane surface [7]. Component in the feed evaporates when passing through the membrane because lower partial pressure of the permeating component is provided then equilibrium vapor pressure. In this case, in order to create driving force for mass transfer either vacuum or inert carrier gas is used. In Figure 1.1 the schematic drawing of pervaporation can be seen [2,4,5].

Molecular transport during the pervaporation process is explained mostly with solution-diffusion mechanism. This mechanism states that, first permeant molecules are sorbed selectively by the membrane, then the molecules diffuse through the membrane and finally they are desorbed at the other interphase of the membrane [1,4,7–9].

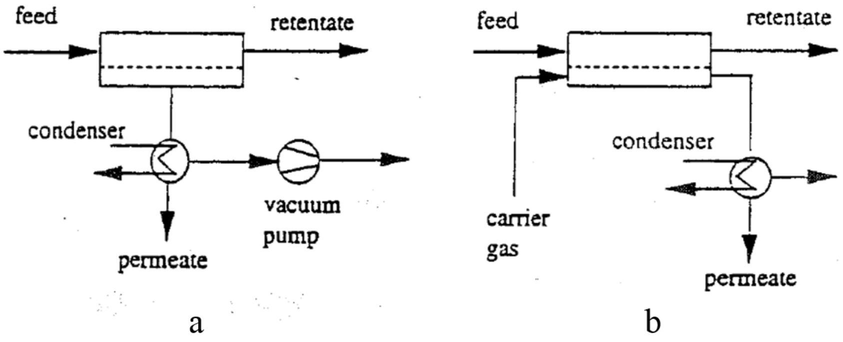


Figure 1.1 Schematic drawing of pervaporation process [1]

Performance of a pervaporation membrane is reported with two main parameters, flux and selectivity [8]. Flux is defined as total amount of material that permeated through the membrane per unit membrane area in unit time and calculated by the Equation 1.1,

$$J = \frac{Q}{A.t} \tag{1.1}$$

where Q is the mass of permeate (g), A is the active membrane area (m^2) and t (h) is the operating time [8,10].

Selectivity is related to the capability of the membrane to separate the desired components from the feed and calculated by the Equation 1.2,

$$\alpha_j^i = \frac{y_i/y_j}{x_i/x_j} \tag{1.2}$$

where x_i and x_j show the weight fractions of component i in the feed solution, y_i and y_j show the weight fractions of component i in the permeate [8,10].

For pervaporation applications, high selectivity and flux are desired since these indicate more selective process and faster separation. Both flux and selectivity are directly related to the membrane and component properties. Moreover, operation conditions such as temperature and feed composition may affect these parameters [11].

Pervaporation separation is independent of the vapor-liquid equilibrium; therefore, it is a suitable technique especially for separation of azeotropic and close-boiling mixtures [12,13]. Solvent recovery is an important issue in chemical industry when low product cost is desired and also environmental concerns are considered [8]. Ethanol forms azeotrope with water (4.4 wt. % water concentration) and ethanol dehydration is one of the most popular usage area of pervaporation since high purity is required for use as biofuel and pharmaceutical use. Therefore separation techniques for recovery and purification of these solvents should be developed in order to decrease the product cost and to be competitive in the market [8,14].

Pervaporation membranes can be categorized according to their materials; ceramic, polymeric and composite membranes [1,5]. Ceramic membranes are produced from silica, alumina and zeolites. These membranes are durable to high temperature and pressure, harsh chemicals. Also their fluxes and selectivities are quite high. On the other hand, their mechanical resistance is low, they are brittle and expensive [1,5,8,15]. Polymeric membranes are advantageous since their fabrication cost is relatively low also they are flexible and easy to process. However, they have limited resistance to chemicals and temperature also suffer from swelling [5,15]. Selectivity and permeability have tendency to be affected by swelling of polymeric membranes, while selectivity decreases higher flux is achieved [12,16].

Poly (vinyl alcohol) (PVA) is a commonly used polymer for pervaporation membranes with its hydrophilicity, good chemical stability, film forming ability, and low cost. However, since PVA is a water soluble polymer, the stability of PVA in aqueous solutions is limited which reduces the membrane performance especially in dehydration processes [17,18]. For preventing the PVA membranes suffer from swelling excessively, they are cross-linked either thermally or chemically. For ethanol dehydration purposes highest fluxes are obtained with PVA membranes cross-linked with carboxylic acid like glutaraldehyde. Selectivities of chemically cross-linked PVA membranes ranged from 70 to 380 and permeation rates from 30 to 1600 g/m^{2}h at 30–75 ◦C, according to the operating temperature, feed ethanol concentration and cross-linking agent. The major drawback of the PVA membranes is swelling which makes the membranes more permeable and causes a decrease in selectivity [4].

Mixed matrix membranes composed of two phases; a continuous phase which is polymer and a dispersed phase consists of inorganic materials [19,20]. By incorporation of inorganic fillers into polymeric membranes, combination of desired properties of ceramic and polymeric membranes can be possible [8,15]. For example, mechanical properties of membranes might enhance and swelling problem might reduce. Therefore, it is expected MMMs to have improved pervaporation performance [8]. However, there are still unsolved problems about the MMMs and most crucial one is incompatibility between inorganic fillers with the polymer phase. This problem cause non-selective voids and therefore, selectivity of mixed matrix membranes can be affected negatively [19,20].

Mixed matrix membranes for dehydration purposes prepared with variety of inorganic particles, zeolites, and carbon nanotubes are the most popular ones because they have been improved the pervaporation performance of polymeric membranes [21–24]. Nevertheless, it is examined that, lower interfacial area between polymer and filler due to incompatibility between polymer matrix and filler also large inorganic fillers prevent the enhancement of pervaporation performance [23,24].

Metal organic frameworks (MOFs) are inorganic-organic fillers which are consist of the functional groups that are the organic ligands and the metal ions or clusters. [15,25–27]. Zeolitic Imidazolate Frameworks (ZIFs), a sub-family of MOFs, are tetrahedral frameworks which link Zn clusters with imidazolate and this is a zeolite like structure [28]. ZIF-8 has a sodalite topology and is a really attractive filler because of uniform pore size, high thermal and chemical stability [28,29]. ZIF-8 crystal has been generally examined as filler material for MMMs used for gas separation purposes. Many researchers have worked on ZIF-8 as filler material with different polymer matrixes and reported that, enhanced permeabilities with some increase in selectivities [30–32]. Nevertheless, there are limited studies about the ZIFs as filler material in MMMs for pervaporation.

In this study, the main aim was to develop polymeric pervaporation membranes with high flux and selectivity. First of all, asymmetric membranes with non-solvent induced phase separation (NIPS) technique were prepared. Then both symmetric and asymmetric mixed matrix membranes (MMMs) were synthesized and the effect of ZIF-8 as a filler material was investigated. At first, asymmetric membranes were prepared using the polyethersulfone (PES) and membranes were annealed at three different temperature (40°C, 50°C and 70°C). Then, ZIF-8 particles were added in the proportion of 5 % of the polymer PES. After that polyvinyl alcohol (PVA), a more hydrophilic polymer than PES, with the degree of hydrolysis 87-89 % and 98 % used for membrane preparation. The dense PVA membranes synthesized with the solvent evaporation technique. Pure PVA membranes were cross-linked thermally and the effect of cross-linking time and temperature on the pervaporation performance were investigated. Other than the thermal cross-linking, PVA membranes were also cross-linked chemically and the cross-linking solution was containing glutaraldehyde (GA), sulfuric acid (H_2SO_4), water and acetone. The GA concentration was between 3.0 % and 0.5 % and the water concentration was between 0 % and 20 % by weight. After determination of suitable water and GA concentrations, ZIF-8 particles were added to 98 % hydrolyzed PVA membranes. Finally, in order to examine effect of particle size of ZIF-8 crystals on the pervaporation performances, MMMs were synthesized with ZIF-8 crystals whose particle sizes were between 17, 81, 190 and 340 nm. ZIF-8 crystals with different particle sizes were synthesized at room temperature from reaction mixtures with different methanol molar ratio method and recycling mother liquor methodology [29]. Synthesized ZIF-8 crystals were characterized by X-ray diffractometer and scanning electron microscopy (SEM). The pervaporation performance of all synthesized membranes were tested with ethanol-water (10/90 wt. %) mixture at 25°C.

CHAPTER 2

LITERATURE SURVEY

2.1 Polymeric Pervaporation Membranes

The pervaporation process through a polymeric membrane (Figure 2.1) generally explained by the solution-diffusion mechanism. According to solution-diffusion mechanism mass transfer through the non-porous polymeric membrane takes places in three steps; first, permeant is sorbed by the membrane surface, second, permeant diffuse through the membrane and third it desorbs from the other interphase of the membrane in vapor phase. [7,16]. This mechanism represented in Figure 2.2.

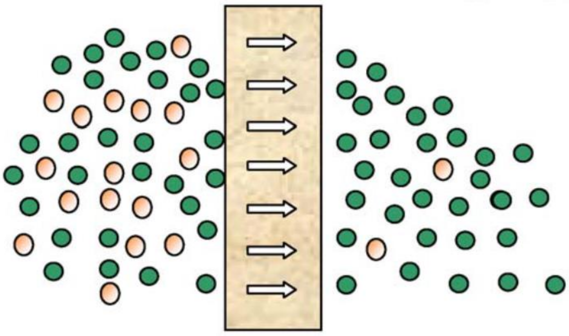


Figure 2.1 Pervaporation through a polymeric membrane [9]

Therefore, separation during pervaporation is dominated by the chemical properties of the membrane material, the physical structure of the membrane, and the permeant-permeant and permeant membrane interactions. Sorption step can affect diffusion and evaporation steps meaning that, better sorption of permeant might result in better separation performance.

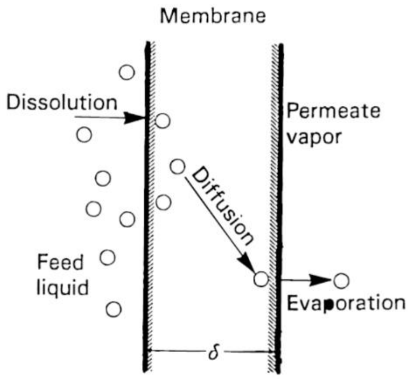


Figure 2.2 The solution-diffusion mechanism [7]

The performance of polymeric membranes reported with two main parameters, flux and selectivity [7–9,16]. Flux (J) is defined as total amount material that permeated through the membrane per unit membrane area in unit time and calculated by the Equation 2.1,

$$J = \frac{Q}{A.t} \tag{2.1}$$

where Q is the mass of permeate (g), A is the active membrane area (m^2) and t (h) is the operating time [8,10]. Permeation flux depends on effective thickness of the membranes [7]; therefore normalized flux (J_N), calculated as the mass flux times the membrane thickness, δ (μm) is used (Equation 2.2) [33],

$$J_N = \frac{Q.\delta}{A.t} \tag{2.2}$$

Selectivity is related to the capability of the membrane to separate the desired components from the feed and calculated by the Equation 2.3,

$$\alpha_j^i = \frac{{y_i}/{y_j}}{{x_i}/{x_j}} \tag{2.3}$$

where x_i and x_j show the weight fractions of component i in the feed solution, y_i and y_j show the weight fractions of component i in the permeate [8,10].

When polymeric membranes are considered, the classic solution-diffusion mechanism is convenient for non-swollen membranes. However, polymeric membranes usually swell especially when they are used in dehydration processes and the structure of the polymer changes. This behavior makes the mass transfer mechanism of polymeric membranes sophisticated [7,16].

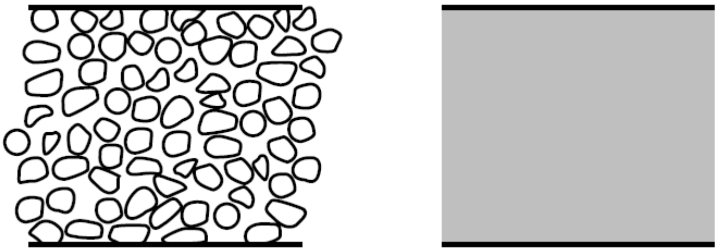
Polymeric membranes are considerably important for pervaporation processes because of their advantages such as being relatively low fabrication cost and easier processing. Besides in industry most of the membranes used in pervaporation are made up from polymers. On the other hand, polymeric membranes suffer from swelling and they are not stable at high temperatures [5,12,34].

Organic solvent dehydration is a highly common application area of the pervaporation separation. Many different polymeric materials have been used to produce membranes such as poly (vinyl alcohol), poly (vinylidene difluoride), poly (acrylic acid), polyurethane and naturally occurring cellulose for solvent dehydration. These materials have been popular since they have relatively good water perm-selectivity and permeation flux. However, swelling influences the performance of the polymeric membranes substantially during dehydration process. With the membrane swelling, the space between the polymer chains (free volume) are expanded which increases the membrane flux. However, membrane selectivity decreases since larger molecules can pass through the membrane in an easier way. It can be said that, the swelling degree of a polymeric membrane alter the overall membrane performance. Actually it is a kind of interchange that is seen in polymeric membranes in most cases, permeability varies inversely with selectivity [5,8,12,16].

For pervaporation, dense (non-porous) polymeric membranes are required for efficient separation. This morphology can be achieved with a dense membrane produced by solvent evaporation technique or with an asymmetric membrane having a dense skin layer produced by phase inversion technique. It can easily been inferred that membrane structure or morphology is a classification type for membranes.

There are mainly two types of polymeric membranes according to their structure; symmetric and asymmetric structured membranes. Symmetric membranes are subdivided as porous and non-porous (dense) structures and asymmetric membranes are subdivided as Loeb-Sourirajan anisotropic and thin-film composite anisotropic structures. The main structures of these membrane classes can be better understood by schematic representation of these classes (Figure 2.3) [1,2].

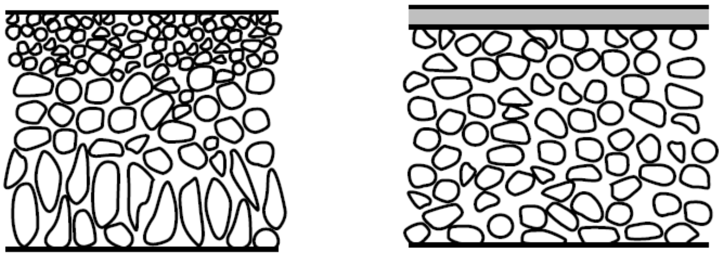
Symmetric Membranes



a) Microporous membrane

b) Non-porous dense membrane

Asymmetric Membranes



a) Loeb-Sourirajan anisotropic membrane

b) Thin-film composite membrane

Figure 2.3 Schematic representation of membrane structures [2]

2.1.1 Dense Pervaporation Membranes

Nonporous, dense pervaporation membranes comprise of a dense film through which permeant molecules are transported by diffusion under the driving force of a pressure gradient. Dense polymeric membranes are prepared by solvent evaporation technique. In this method a polymer is dissolved in a suitable solvent then an even film of a polymer solution is spread across a flat surface generally using a casting knife. After casting, solvent evaporates in an inert atmosphere and polymer solution leaves a thin, uniform film [1,2].

Poly (vinyl alcohol) (PVA) is an appropriate polymer for pervaporation membranes with hydrophilicity, good chemical stability, thermal resistance, film forming ability, and low cost. However, since PVA is a water soluble polymer, the stability of PVA in aqueous solutions is limited and this drops off the membrane performance by giving harm the integrity of the polymer [17,18,35]. Therefore, to prevent the PVA membranes suffer from swelling excessively, especially when used in dehydration processes, PVA should be cross-linked. PVA can be cross-linked either by heat treatment or by using a chemical cross-linking agent like glutaraldehyde, maleic acid, amic acid and tartaric acid [35,36]. In recent years, among the cross-linking agents, glutaraldehyde (GA) has gained increasing attention because GA do not need thermal treatment in order to drive the reaction [17].

Glutaraldehyde ($HCO–C_3H_6–CHO$) consists of two aldehyde groups (CHO), which can be attached to hydroxyl groups (OH) in PVA chains and make the PVA cross-linked. Figure 2.4 shows the reaction between PVA and GA [37].

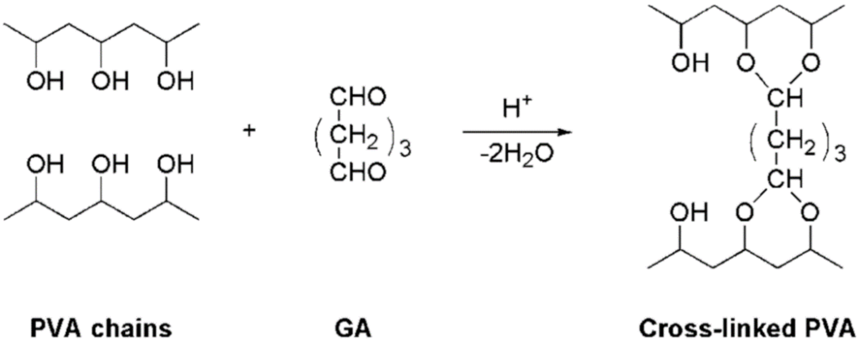


Figure 2.4 Cross-linking mechanism of PVA chains by GA [37]

PVA is synthesized via the saponification (alcoholysis) of poly (vinyl acetate) (PVAc) because vinyl alcohol monomer does not exist in the free state. The chemical structure of PVA is shown in Figure 2.5. The degree of saponification (hydrolysis) is the ratio of the number of hydroxyl groups to the sum of the number of hydroxyl and acetyl groups. Since hydroxyl groups are more hydrophilic than acetyl groups, PVA with higher degree of hydrolysis is more hydrophilic then PVA with lower degree of hydrolysis [38].

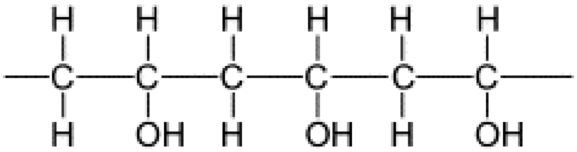


Figure 2.5 Chemical structure of PVA [39]

Heat treatment can allow the PVA membranes be cross-linked, also increases the crystallinity of the PVA. The schematic illustration of cross-linking of PVA chains by thermal inducing can be seen in Figure 2.6. The increase in crystallinity can takes place above the glass transition temperature (T_g). The glass transition of PVA is a function of degree of hydrolysis. The T_g of 98–99% hydrolyzed PVA is 85.8°C, whereas that of 87–89% hydrolyzed PVA is 58.8°C [38,40,41].

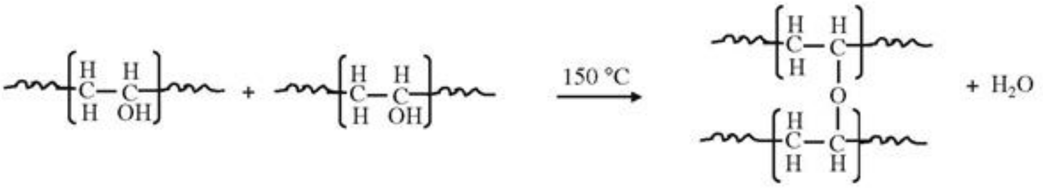


Figure 2.6 Cross-linking mechanism of PVA chains by thermal inducing [36]

In their research Zhang et al. [42] studied the effect of pre-treatment temperature during film formation on the surface structure of dense PVA membranes. The membranes were prepared from 2 wt. % PVA (98-99 % degree of hydrolysis, Mw~110,000) solution by using solvent evaporation technique. After casting the solution it was pre-treated at 30, 90, 110, and 140 °C for 150, 40, 25, 15 min, respectively. Then complete solvent evaporation was achieved in two steps; first at 25°C until fully solidification and second, at 40°C under vacuum for 24 h. The membranes were heat treated at 80°C for 1 h for water stability. The membranes were tested for dehydration of 90 wt. % ethanol-water solution with pervaporation technique. Increasing pre-treatment temperature yielded an improved selectivity whilst membrane flux remained nearly constant. They concluded that pervaporation performance was affected by surface structure of PVA membranes. Since the Differential Scanning Calorimetry (DSC) results have showed that membranes with pre-treated at different temperatures had almost same crystallinity degree. High pre-treatment temperature made the water evaporates in a faster way and caused a film surface covered with a CH_3 groups. This rapid change in surface structure made the PVA membrane more hydrophilic. On the contrary, at low pre-treatment temperatures, backbones of the PVA, CH_2 groups, covered the film surface and caused a more hydrophobic membrane surface.

Hyder et al. [9] prepared dense PVA membranes with 99.7 % degree of hydrolysis (M_w ~108,000). The PVA membranes were produced using solvent evaporation technique and PVA (5, 7 and 10 % by weight) was dissolved in deionized water. Cross-linking is achieved thermally or chemically. For thermal cross-linking PVA membranes were heated 125°C under vacuum for 30 min. For chemical cross-linking glutaraldehyde (GA) solution which contains 1.0 or 2.5 % glutaraldehyde (GA), 0.5 % sulfuric acid (H_2SO_4), % acetone, and balance deionized water by weight was used. The PVA membranes were kept in this solution for 30 min. Membranes were tested to dehydrate the ethanol–water solution and feed contained 10-70 % ethanol. They observed that 2.5 wt. % GA containing cross-link solution made the membranes less hydrophilic since more hydroxyl groups turned into acetyl groups. Also the structure of the membranes might result in more rigid structure which prevents the diffusion of water molecules. When thermal and chemical cross-linking were compared, it was seen that, thermally treated membranes had higher flux but lower selectivity in pervaporation experiments.

Praptowidodo used PVA membranes for dehydration of ethanol [39]. The cross-linking was achieved chemically with glutaraldehyde (GA) and the effect of cross-linking degree on swelling also pervaporation performance were examined. The reaction time of PVA membranes with GA was altered; therefore, degree of cross-linking was changed. The membranes were prepared using PVA with 98-99 % degree of hydrolysis (M_w ~ 40,000) with solvent evaporation technique. After drying, PVA membranes were cross-linked in GA solution with GA concentration of 0.025 and 0.1 wt. %. The membranes were cross-linked for 0.5, 1.0, 1.5 and 2.0

h. The pervaporation experiments were carried on with feed solution containing of 90 wt. % ethanol. It is clearly observed that increasing cross-linking time and GA concentration decreased the swelling degree of PVA membranes. Also the fluxes of more swollen membranes were higher, however, selectivity values were lower. The highest selectivity was determined as 108 with total flux of 0.249 kg/m^{2}h.

Svang-Ariyaskul et al. [37] produced PVA and chitosan (CS) blended pervaporation membranes for dehydration of isopropanol. The effect of CS content of the blended membranes on the pervaporation performance was examined. At the same time, pure PVA membranes were also produced from 99 % hydrolyzed PVA (M_w ~133,000) with solvent evaporation technique. The polymer solution contained 10 % PVA and after solvent evaporation membranes were thermally treated at 150 °C for 1 h. Then membranes were immersed in cross-linking solution containing 1.5 wt. % glutaraldehyde (GA), 0.5 wt. % sulfuric acid, 48 wt. % of acetone and balance deionized water for 25 min. The pervaporation performance of the membranes were tested at 30°C with feed water content of 10 wt. % and total flux and selectivity were reported as 200 g/m^{2}h and 490, respectively. Also the swelling degree of pure PVA membrane was reported as nearly 100 % in pure water.

In their study Yeom at al. [43] focused on pervaporation performance of a homologous series of alcohol aqueous solutions using glutaraldehyde (GA) cross-linked PVA membranes. Alcohol solutions that investigated in this study were methanol, ethanol, 1-propanol, and 1-butanol. The membranes were casted form 10 wt. % PVA solution and the degree of hydrolysis of PVA was 99 % with average molecular weight of 50,000. The cross-linking reaction mixture was composed of 10 vol. % of GA and 0.05 vol % of HCl and balance acetone. The membranes were immersed in this solution at 40°C for 48 h. They first determined the swelling ratios of the PVA membranes in alcohol solutions and found that swelling ratios were consistent with alcohol solubility parameters. Namely, the swelling ratios were, 1-butanol, 1-propanol, ethanol and methanol in increasing order. Then permeation rates and selectivities were measured with feed solutions containing water between 30.0 – 2.0 wt. %. It is found that, the total flux increased while selectivity decreased with more water content as expected. When the alcohol content of the feed was higher than 92 %, the total fluxes were in the order of swelling ratios. However, below 92 % alcohol content, the total fluxes changed inversely with swelling ratios. That means, the fluxes were decreasing in the order of, 1-butanol, 1-propanol, ethanol and methanol. The total flux and selectivity for 10 wt. % water-ethanol feed at 30°C were approximately 90 g/m^{2}h and 60, respectively.

2.1.2 Asymmetric Pervaporation Membranes

Asymmetric membranes are composed of layers with different porosity, pore size, membrane composition from the top to the bottom surface of the membrane. Generally, asymmetric membranes have a thin, selective “skin layer” and below it a thicker, highly permeable layer in order to make the membrane stronger [2].

An asymmetric structured membrane can be produced by dry or wet phase inversion techniques like, precipitation from the vapor phase, precipitation by controlled evaporation, thermal precipitation, and immersion precipitation. Among these technique immersion precipitation, also known as non-solvent induced phase separation (NIPS) is a widely used one since several kinds of membrane morphologies can be achieved [44].

In NIPS method, simply, a polymer solution (polymer and solvent) is cast on a suitable support as a thin film and immersed in a non-solvent bath. The solvent diffuses into the non-solvent (coagulation bath), meanwhile non-solvent diffuses into the polymer film. Finally polymer solution becomes solid and produces an asymmetric membrane. Schematic representation of bath-film interface during phase inversion. Throughout this process, polymer solution is precipitated into two phases: a solid, polymer-rich phase that forms the matrix of the membrane and a liquid, polymer-poor phase that forms the membrane pores [1,2,44].

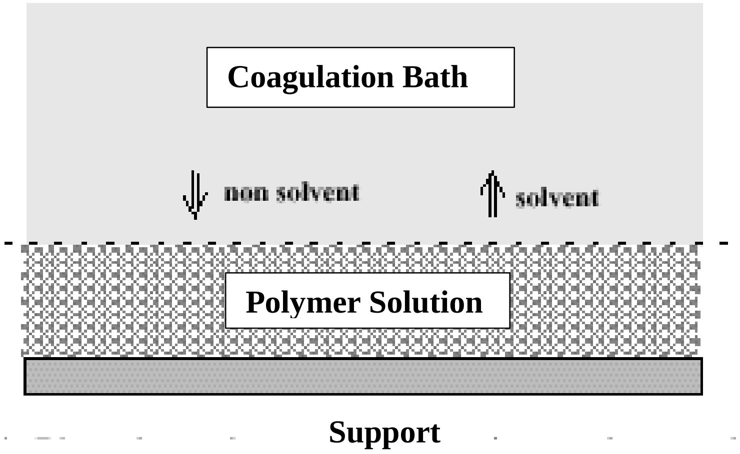


Figure 2.7 Schematic representation of NIPS [1]

The skin layer thickness of the asymmetric membranes produced by NIPS method is affected by coagulation rate. In general when the polymer solution coagulates fast asymmetric membranes having a thin microporous skin layer is arisen, when it coagulates slow, membranes have thicker skin layer [45].

In dry-wet phase inversion technique, before immersion in coagulation bath, the casted polymer film is subjected to an evaporation step. During evaporation, solvent and/or non-solvent in the polymer solution moved away partially and outer part of the membrane is formed. The bulk structure on the other hand, is formed during solvent-non-solvent exchange in coagulation step [1,46]. The dry-wet phase inversion process and comparison with wet phase inversion are illustrated in Figure 2.8.

It is possible to produce asymmetric membranes having very thin skin layer with NIPS method; however, defects or pinholes can occur on the skin surface easily because of incomplete coalescence of polymer molecules in the skin layer. Hence, dry-wet phase inversion might be employed to prevent this problem [1].

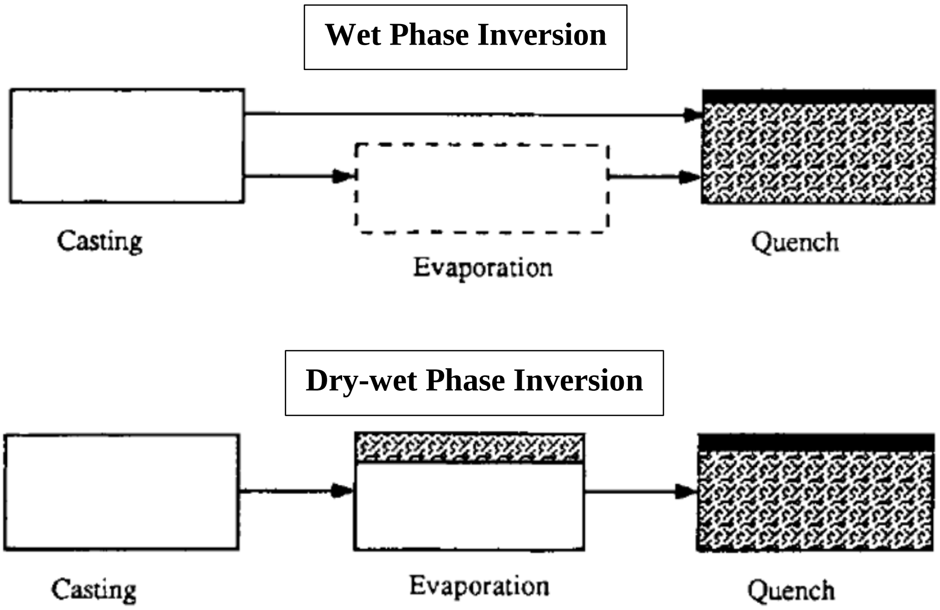


Figure 2.8 Phase Inversion Processes [46]

Although asymmetric membranes produced by phase inversion techniques are extensively used in ultrafiltration, microfiltration and reverse osmosis processes, the usage of them in pervaporation purposes is not very common.

Permeation flux and selectivity are the two most important success criterions for pervaporation membranes. In the literature studies on development of pervaporation membranes with high flux and selectivity are going on intensively. However the key factor for taking full performance from a membrane material is minimizing the effective membrane thickness. A structure with a thin selective layer thereby a higher flux without much decrease in selectivity can be achieved with asymmetric membranes [47].

Jiang and co-workers [48] produced asymmetric composite membranes from PVA polyvinyl alcohol (PVA) and polyethersulfone (PES) polymer blend with wet phase inversion technique. They aimed to enrich membrane surface with more hydrophilic PVA by surface segregation. The PVA rich surface was cross-linked with glutaraldehyde (GA). The membrane performances of membranes for ethanol dehydration were considered by using different PVA content and annealing temperature. Besides, the effect non-solvent type on membrane morphology was studied. Membranes contained 5 different amount of PVA, 0 %, 5.56 %, 8.33 %, 11.11 % and 16.67 % by weight, were produced. It is observed that membranes consisted of a PES rich porous support layer and a PVA rich dense selective layer. Ethanol, isopropanol (IPA) and butanol were preferred as non-solvent. When coagulation bath was IPA or butanol, membranes had sponge-like porous top layer and finger like porous support layer, whereas when coagulation bath was ethanol the support layer was finger-like and skin layer was porous. Only the performances of membranes that coagulated in IPA were measured since finger-like pores have relatively small mass transfer resistance. Pervaporation experiments were carried at 25°C with feed water content of 10 wt. %. The selectivity values enhanced with increasing PVA content; however selectivity remained unchanged after 5.6 wt. % PVA content. Membranes containing more PVA also had higher permeation fluxes. The flux and selectivity of the membrane with 16.67 % PVA were reported as 297.6 $g/m^2.h$ and 86.1, respectively.

Huang et al. [47] examined the asymmetric polyetherimide (PEI) membranes produced by dry-wet phase inversion method in terms of, polymer concentration, solvent evaporation temperature and time. The pervaporation performances of the membranes tested for isopropanol (IPA) dehydration. Membranes were casted from a solution composed of PEI (polymer), N,N-Dimethylacetamide (solvent) and $LiNO_3$ (additive). Increasing PEI content of casting solution caused an enhancement in selectivity values while it caused a decrease in molar fluxes. These changes were less significant with PEI concentrations above 25 wt. %. In this study, solvent evaporation temperature was ascended from 32°C to 100°C, a minimum value was observed in molar flux and a maximum value in selectivity. When the temperature increased further a maximum flux was observed at 120°C; however, decreasing trend of selectivity continued. The solvent evaporation time also affected the pervaporation performance. When the evaporation time went up an increase in separation factor and a decrease in permeation flux were seen. Furthermore, increase of drying time from 0 to 2 min caused a tremendous decline (2.0 mol/m^2h from 96.6 mol/m^2h) and selectivity increased 23 times. After that point the change in pervaporation performance was mild.

Hong et al. [35] investigated the effects of PVA molecular weight, PVA concentration and glutaraldehyde (GA) content of cross-linking solution of asymmetric poly (vinyl alcohol) (PVA) membranes for isopropanol (IPA) dehydration. PVA (99 % hydrolized) with molecular weights 89 000–98 000 and 124 000–186 000 were used. For membrane production phase inversion technique was applied, before immersing in coagulation bath, which was containing 16 % Na_2SO_4, 2 % NaOH by weight and balance water, solvent evaporation at room temperature was applied for 10 min. For cross-linking an aqueous solution of Na_2SO_4 (45 g/l), H_2SO_4 (5 g/l) and GA with changing concentrations (10, 17.2, 25 g/l). Low molecular weight PVA (LPVA) membranes had higher fluxes then high molecular weight ones (HPVA) and the selectivities of HPVA membranes were substantially higher with HPVA membranes when IPA concentration was higher than 75 wt.%. Cross-link solution having higher amount of GA made the membranes more selective to water; however, reduced their flux. High PVA concentration caused a thicker skin layer, hence while fluxes were decreasing, selectivities were increasing with increasing PVA concentration.

2.2 Mixed Matrix Membranes

Polymeric membranes are extensively used in pervaporation processes, especially for dehydration purposes because polymeric membranes are easy to fabricate and relatively cheap. Moreover, commercially available pervaporation membranes used in industry are generally polymeric type. Nonetheless, polymeric membranes suffer from swelling and permeability alter inversely with selectivity in general sense. Hence, the selectivity of membranes having high permeabilities do not reach the desired values. Also they have limited resistance to chemicals and temperature [1,3,5,12]. Therefore, to cope with these problems new type of organic-inorganic composite membranes called mixed matrix membranes (MMMs) have been developed in recent years and researches have been going on extensively.

Mixed matrix membranes composed of two phases; a continuous phase which is polymer and a dispersed phase consists of inorganic materials, figure 2.9 shows the schematic of a MMM [2,8,19].

In order to implement the pervaporation separation in industry, it is really important to develop high flux, high selectivity and defect-free membranes. These MMMs are expected to combine the thermal, chemical and mechanical stability, also good separation performance of inorganic fillers with the low cost and ease of manufacture of polymeric membranes. [2,5]

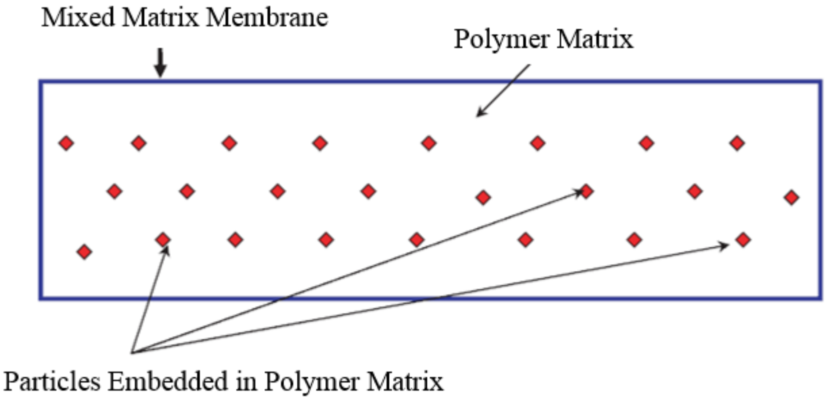


Figure 2.9 Schematic of a mixed matrix membrane (MMM) [30]

Many types of particle can be used as filler materials in MMMs, such as zeolites, mesoporous molecular sieves, carbon nanotubes and silicas. In general, for MMMs employed in dehydration processes, zeolite crystals are preferred because of high water sorption capacity. The incorporation of different kind s of zeolites, silicalite-1, ZSM-5, T, NaA or NaX in polymer phase increased the flux, selectivity or both of them [22,49,50]. However, there are still some challenges about preparing MMMs. The most critical of them is incompatibility between inorganic fillers and polymers which causes non-selective voids on polymer-filler interface. Thus, a decrease in selectivity of the membrane occurs. Besides, most organic fillers can provide only a slight increase in permeation flux of the polymeric membranes. There are mainly two reasons behind this. First, chain rigidification in polymer chains might causes partial pore blockage. Second, the small interface between polymer and filler due to bigger size of fillers [23,24,49].

In order to cope with the mentioned problems, fillers which can be more compatible with polymer matrix namely, metal organic frameworks (MOFs) are proposed.

Since they have both organic and inorganic parts, their interaction with polymers might better [23,49].

2.1.1 Filler Materials for Mixed Matrix Membranes for Pervaporation

Zeolites are widely used as filler material in MMMs for dehydration processes due to its molecular sieving effect and hydrophilic nature.

In their study Gao et al [51] intended to enhance the pervaporation performance of PVA membranes by incorporation of KA, NaA, CaA, and NaX zeolites. The cross-linking of PVA membranes were achieved by heat treatment at 160-200°C. The membranes were tested for dehydration of methanol, ethanol, isopropyl alcohol, and tert-butanol. Type A zeolites made the transport of water molecules easier since they have smaller size then ethanol and higher molecular weight alcohols. Also the flux of membranes filled with KA raised with increasing loading amount without any change in selectivity for ethanol-water system. Total flux increased to 1212 g/m^2h from 776 g/m^2h and selectivity remained as 20. After the loading of 11 wt. % flux continued to rise; however, selectivity decreased nearly 40 %.

Another study which was related to Poly(acrylonitrile) PAN based MMMs filled with 3 different zeolites, 3A, 4A and 13X conducted by Okumuş et al [50]. PAN was selected as polymer base because of its high selectivity and low flux for dehydration of ethanol. The zeolites were added into PAN solution after heat treatment at 300°C. It seen with SEM images that, the prepared MMMs had three apparent layers, a polymer layer without zeolite, zeolite-filled polymer layer and skin layer. MMMs containing zeolite 13X had better selectivity then membranes with 3A and 4A and nearly same fluxes at a zeolite content of around 32 wt. %. This results explained with preventing the transport of water due to smaller pore sizes of 3A and 4A. The increasing loading of 13X enhanced the permeation flux enhanced 6 times on average, with a decrease in selectivity until 30 wt. % loading. With zeolite content of 30-35 wt. % flux increased 10 times causing a moderate decrease in selectivity. After the loading of 35 wt. %, there was a tremendous rise in selectivity with almost no selectivity because of loosen structures of MMMs.

Jones et al [52] examined a different filler material for separation of ethanol-water mixture, namely, single-walled aluminosilicate nanotube (aluminosilicate SWNT). The dense MMMs were produced using PVA as continuous phase and SWNT powder was added with volume fractions of 0.1, 0.2, 0.2 and 0.4. Membranes were cross-linked in a solution composed of 50 mL of water, 50 mL of acetone, 0.5 g sulfuric acid, and 1.25 g of glutaraldehyde for 30 min. SEM images and EDX analysis showed that the SWNT were distributed uniformly in PVA until the loading of 30 vol. %, after that point the start of bundle formation was observed. A considerable enhancement was observed in the total flux with the addition of MWNTs. Besides, MMMs comprising 10 and 20 vol. % SWNT had selectivity 40 % greater than neat PVA membrane with little differences in total flux. Addition of more than 30 vol. % of SWNT, the total flux increased 200 %; however, selectivity reduced excessively. The reduction selectivity was explained with microstructural alteration of the PVA matrix with incorporation of SWNTs. The idea supported by the crystallinity of the PVA matrix, it was dropped and that meat, the mobility of PVA chains increased with the presence of SWNTs in the matrix

In their research Adoor et al [53] preferred phosphotungstic acid (PTA) as nano-filler in order to enhance the pervaporation performance of sodium alginate (NaAlg) membranes. PTA is a heteropolyacid and their water solubility make them suitable filler for dehydration processes. MMMs were prepared with PTA nano-filler (260-280 nm) content of 0 %, 3 % 5 %, 7 % and 10 % by weight and used for ethanol dehydration. The selectivity values increased with increasing loading amount. The development in both flux and selectivity for 3 wt. % PTA loading were significant, 2 times greater for flux, 10 times greater for selectivity. After 3 wt. % loading amount selectivity continued to go up, whilst the fluxes were remained nearly constant. The increase in selectivity was correlated to overcoming of swelling problem by filling of the free volume of PVA by PTA particles. Flux enhancement was attributed to easier diffusion and transport of water molecules with the help of PTA.

Flynn et al. [54] examined mesoporous silica having particle size of 1.8-2.0 as a filler material for PVA based MMM. The effect of particle loading on the membrane performance for ethanol dehydration was studied in detail. The PVA-silica MMMs were casted on asymmetric poly (acrylonitrile) PAN membrane as support. The prepared membranes were cross-linked thermally. MMMs are produced with mesoporous silica content of 5 %, 10 % and 15 % by weight. It was seen in the SEM images that until loading amount of 15 wt. % the particle were well distributed. When the loading amount was 15 wt. % agglomerations were clearly observed and particles segregated to the membrane surface. Integration of 5 wt. % silica created a small increase in selectivity over the pure PVA membrane, with almost no alteration in flux. At a 10 wt. % loading, there was a significant increase in selectivity to 42, approximately, 2 times greater that of the 5 wt. % loading. At a loading of 15 wt. %, there is a tremendous decline in selectivity to 10 and this value was even smaller than the selectivity of pure PVA membrane. This behavior was result of particle agglomeration. It was seen in the SEM images that until loading amount of 15 wt. % the particle were well distributed. When the loading amount was 15 wt. % agglomerations were clearly observed and particles segregated to the membrane surface.

All the inorganic fillers mentioned in this section have the general problem that is, even the high flux is achieved, selectivity values decreases with high loading amounts. The main reasons behind this is particle agglomeration and incompatibly of inorganic fillers with organic structured polymers. A new kind of inorganic filler material called metal organic frameworks (MOFs) are attracted the researchers attention.

Metal Organic Frameworks are a newer class of hybrid materials consist of a metal ion in the middle and organic ligands that encircle it. The metal ions function as connectors and the organic ligands function as linkers. There are strong bonds between connectors and linkers, with the aid of these bonds, one, two or three-dimensional porous frameworks are formed. The structures of MOFs are enlarged also their surface area and pore volumes are extremely high. Unlike zeolitic fillers, MOFs have high surface areas, and high flexibility due to their crystal structures and chemical composition. These properties of MOFs makes the bonding of functional groups in selected linkers possible. By this way both pore size and chemical properties of MOFs can be changed. Also since they have organic ligands, MOFs are expected to have better compatibility with polymers with respect to other inorganic fillers [23,28,55,56]

Due to its attractive properties, MOFs have been widely studies in recent years as filler material for MMMs for gas separation processes [15,20,28,30]. Also different MOF types, for example, $Cu_3(BTC)_2$, MIL-47, MIL-53 and NH_2-MIL-53 are incorporated in polymeric membranes for nanofiltration purposes and enhancement in both flux and rejections are reported [57].

2.2.2. Metal Organic Framework-Mixed Matrix Membranes for Pervaporation

Zeolitic Imidazolate Frameworks (ZIFs), a sub-family of MOFs, are tetrahedral frameworks which link Zn(II) or Co clusters with five membered imidazolate (Im) ring. This structure makes these crystalline porous materials zeolite like. The Im links functionalized to produce neutral framework, also, boosts the creation of tunable nano-sized pores [28,58,59].

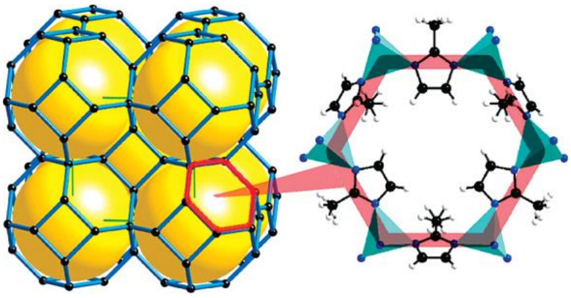


Figure 2.10 Sodalite topology of ZIF-8 (left) and its narrow six-membered-ring opening (right) [59]

The framework of ZIF-8 is sodalite (SOD) topology that its structure of is given in Figure 2.10. ZIF-8 is really attractive filler because of uniform pore size, high thermal and chemical stability [28,29]. ZIF-8 crystal has been generally examined as filler material for MMMs used for gas separation purposes. Many researchers have worked on ZIF-8 as filler material with different polymer matrixes and reported that, enhanced permeabilities with some increase in selectivities [30–32].

ZIF-8 might be also a suitable filler for MMMs pervaporation application [23]. It has an aperture size of 3.4°A and large cavity size of 11.6°A [58] which are appropriate for separation alcohols and water. However, although ZIF-8 has a hydrophobic nature and may favor alcohol sorption it might ease the diffusion of water due to its small aperture size [23,28]. Therefore, there are limited studies about the ZIF-8 as filler material in MMMs for pervaporation since its behavior is unclear.

Yang et al. [60] produced ZIF-8-PMPS (poly methylphenylsiloxane) MMMs and accomplished to incorporate high amount of ZIF-8 homogenously by using a hierarchically ordered stainless-steel-mesh (HOSSM) with a technique called "Plugging Filling". The membranes were developed in order to recover furfural from its water mixture containing 1 wt. % furfural. Membranes showed perfect stability during long pervaporation experiments (at 80 °C). Particle size of ZIF-8 synthesized during the research was about 60 nm according to SEM images. The selectivity and flux of the membranes prepared with solution-blending technique were increased with increasing ZIF-8 loading since ZIF-8 might create an alternative path for furfural. Loading higher than 16.7 wt. % caused a decrease in selectivity due to particle agglomeration which was observable by SEM images. Employment of plugging-filling technique allowed the high ZIF-8 loading with better dispersion; hence, a considerably high flux and selectivity were achieved with the MMM having 41.3 wt. % ZIF-8, which were reported as 0.90 kg/m^{2}h and 53.3, respectively.

Unlike the research conducted by Yang et al. [60], Chung and coworkers [23] examined ZIF-8 as a filler material in PBI based MMMs for ethanol dehydration process. The effect of inclusion amount of ZIF-8 in Polybenzimidazole (PBI)-ZIF-8 MMMs on pervaporation performances of different alcohol solutions (ethanol, isopropanol and n-butanol) was investigated. The ZIF-8, amounts were 33.7 % and 58.7 % by weight. The particle sizes of ZIF-8 crystals determined by dynamic light scattering (DSL) as smaller than 50 nm, mostly. For isopropanol (IPA) and buthanol dehydration, addition of ZIF-8 nano-crystals to PBI enhanced the membrane flux with small loss in selectivity. Especially, MMM loaded with 33.7 % ZIF-8 provided an increase in flux more than 4 times. When ethanol dehydration was considered, there was an appreciable rise in selectivity and small a reduction in flux with 33.7 wt. % ZIF-8 loading. This enhancement was explained with suppression of the swelling of the membrane caused by ethanol since ZIF-8 rigidified the PBI structure. Higher amount of ZIF-8 (58.7 wt. %) made the membrane much more (nearly 8 times greater than pure PBI) permeable, however less selective. In general, n-butanol solution had highest and ethanol had lowest selectivity.

Tung at al. [61] preferred ZIF-7 to improve the pervaporation performance of ethanol-water mixture of chitosan (CS). MMMs containing 2.5 %, 3.5 %, 4 %, 5 % and 6 % ZIF-7 by weight were prepared and glutaraldehyde (GA) was added as cross-linking agent. The particle size of ZIF-7 was indicated as 1-2 µm by TEM images. It was observed that with more doping content higher selectivity was achieved. Whereas, total flux through the membranes, whereas, increased up to 4 wt. % doping then it dropped more than 50 %. Because of chain rigidification caused by ZIF-7 nano-crystals, large ethanol molecules could not pass through CS matrix but smaller water molecules could pass; therefore, increase in selectivity and decrease in flux were observed. The best loading was reported as 5 wt. % having selectivity as 2812 and flux as 322 g/m^2.h.

In another study, Amirilargani [62] synthesized ZIF-8 nano-crystals and produced PVA-ZIF-8 MMMs for isopropanol (IPA) dehydration. The poly(vinyl alcohol) (PVA) used in this study had MW of 130,000 with degree of hydrolysis 98 %. In-situ cross-linking was achieved by adding glutaraldehyde (GA) and HCl (as catalyst) in polymer solution. The mass ration of ZIF-8 was changing as 1, 2.5, 5.0, 7.5 and 10.0 %. The FESEM images of ZIF-8 particles indicated that particles were not in distinct morphology and their particle sizes were smaller than 60 nm. Since swelling is an important property that gives idea about the transfer of molecules during pervaporation, degree of swelling (DS) of the membranes were determined. Incorporation of ZIF-8 decreased the DS and the possible reasons behind this were stated as, chain rigidification, hydrophobic nature of ZIF-8 and agglomeration of particles due to high doping. The doping of 1.0 and 2.5 wt. % ZIF-8 subjected to dramatic decrease in selectivity whilst 2.5 fold increase in total flux. It was stated that, interfacial voids between ZIF-8 and polymer matrix and sorption of IPA molecules by ZIF-8 might be responsible for increasing flux. Further particle doping led to a substantial rise in total flux and decline in selectivity which were explained by free volume expansion by particle agglomeration. The flux and selectivity of the MMM with loading of 5 wt. % were declared as, 868 g/m^{2}h and 132, respectively.

In their research Coronas et al. [49] examined the effect of two filler material, ZIF-8 and mesoporous silica (MCM-41) on pervaporation performance of polyimide (Matrimid 5218) based MMMs for ethanol dehydration. ZIF-8 and MCM-41 were selected since they had different hydrophilicity and particle size. The particle size of ZIF-8 was reported as 0.17 µm and two different sizes of MCM-41, 3.1µm (MSM-1) and 0.53 µm (MSM-2) were used. The MMMs were prepared with filler loading of 12 wt. %. When the pervaporation results were investigated, it is seen that, ZIF-8 incorporation caused a slight rise in total flux (0.24 to 0.26 kg/m^2/h) and selectivity increased to 300 from 260. The rise in flux was attributed to the gaps between particles due to agglomeration. The highest flux was achieved with MSS-2 as 0.44 kg/m^2/h since hydrophilic meseopores eased the adsorption and diffusion of water molecules, while selectivity was nearly same as pure PI membrane. MMMs filled with MSS-1 had the lowest selectivity (190) and its flux was 0.31 kg/m^2/h, slightly higher than the pure PI. The smaller particles provided a bigger polymer-filler interface, therefore improved the water selectivity.

CHAPTER 3

EXPERIMENTAL

3.1 ZIF-8 Synthesis

Zeolitic imidazolate frameworks (ZIFs) consist of cationic transition metals which are linked by anionic imidazolate ligands, in ZIF-8 transition metal is Zinc [58]. For ZIF-8 synthesis, zinc nitrate hexahydrate ($ZnNO_3.6H_2O$, 98% pure) used as zinc source and was purchased from Acros Organics. As ligand source, 2-methylimidazole (Hmim, $C_4H_6N_2$, 99% pure) was used and purchased from Sigma-Aldrich. Methanol (MeOH, 98 % pure) was used as solvent and purchased from Sigma-Aldrich.

A ligand solution which included 5.28 g of 2-methyl imidazolate (Hmim) and 90.4 g of methanol and another solution composed of 2.4 g zinc nitrate hexahydrate and 90.4 g methanol were prepared. These two solutions were mixed rapidly in order to obtain synthesis solution with a molar composition of $ZnNO_3.6H_2O$:7.9Hmim:695.1MeOH. This synthesis lasted 1 hour at room temperature with the aid of 300 rpm stirring. Then the solid ZIF-8 crystals separated from the synthesis solution by centrifuging at 6000 rpm for 5 min. In order to purify the obtained crystals, they were washed with methanol 2 times. ZIF-8 particles were dried at 80^oC overnight [29,63]. Finally, ZIF-8 crystals with average particle size of 81 nm were obtained. ZIF-8 crystals with average particle sizes of 190 nm and 340 nm were also synthesized from solution with MeOH/Zn^{+2} molar ratios of 347.5 and 86.9, respectively [63].

ZIF-8 crystals having average particle size of 17 nm were synthesized by recycling the mother liquor which remained after the separation of ZIF-8 crystals synthesized from solution with MeOH/Zn^{+2} of 695.1. This production technique was developed in our laboratory by Keser et al. [64]. In this technique, first the mother liquor was aged one day and its pH was increased to 9.0 by adding NaOH, 0.36 g NaOH was used for 100 g mother liquor. After one hour stirring (300 rpm) ZIF-8 crystals separated from the solution by centrifuging [29,63]. The amounts of chemicals for the ZIF-8 synthesis are given in Appendix A.

3.2 Membrane Preparation Techniques

In this study, pure polymeric and mixed matrix membranes (MMMs) prepared from two different polymers, PES and PVA. Pure PES and PES/ZIF-8 MMM were prepared with non-solvent induced phase separation (NIPS) technique while pure PVA and PVA/ZIF-8 MMMs were prepared with solvent evaporation technique.

3.2.1 Non-Solvent Induced Phase Separation (NIPS) Technique

Using NIPS technique asymmetric PES membranes were produced. Membranes produced from Polyethersulfone (PES) having an average molecular weight of 53,000. A commercial Radel A-100 grade PES was supplied from Solvay. The glass transition temperature (T_g) of PES is 220°C [1]. The structure of repeating unit of PES is shown in Figure.3.1.

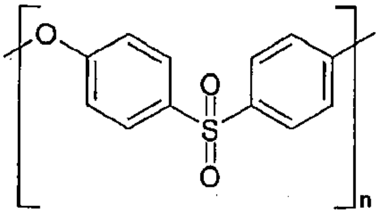


Figure 3.1 The repeating unit of PES [1]

Dimethylformamide (DMF), chemical formula of C_3H_3ON, used as solvent, was purchased from Lab-Scan Analytical Sciences. As non-solvent ethanol (99% pure) was used and purchased from Merck.

In this study, two types of membranes were prepared by NIPS technique, pure PES and PES/ZIF-8 membranes. In the preparation of all membranes, the concentration of PES in DMF was kept constant as 20 % (wt/vol). In PES/ZIF-8 membranes, the ZIF-8 concentration was 5 wt. % of the total PES. The average particle size of ZIF-8 crystals were 81 nm.

In order to prepare pure PES membranes, PES, dried overnight at 80^{o}C, was added into 15 ml DMF gradually. Before the polymer addition steps dissolved gas removed with 10 min ultrasonication. The final solution was stirred overnight at 300 rpm.

For PES/ZIF-8 membrane, first ZIF-8 crystals (after drying at 80°C overnight) were put in the DMF, ultrasonicated for 30 min for uniform distribution and stirred overnight at 300 rpm. Secondly, 15 w % of the total amount of PES was mixed with the solution and stirred overnight. Then, the remaining PES was added into the solution step by step. Before the polymer addition steps 30 min ultrasonication was applied.

Both PES-DMF solutions and PES-ZIF-8-DMF solutions were cast on a glass plate at room temperature with Automatic Film Applicator with the help of a casting knife of 500 µm. After casting membrane film was immersed in coagulation bath and waited until the casted film left the glass plate. Ethanol (1 liter) at room temperature (20-25 °C) put in a container and was used as coagulation bath. Finally membranes were annealed at different temperatures (room temperature, 40, 50 and 70°C) under vacuum for 3 days to investigate the effect of annealing temperature on the pervaporation performance. Different from the pure PES membranes PES/ZIF-8 MMMs were annealed only at 50°C.

Other than the wet phase inversion, dry-wet phase inversion technique was also applied to produce asymmetric pure PES membranes. For this purpose after blade casting, membrane film dried for 5 min and 60 min under vacuum, approximately 0.1 bar, at 30°C in an oven. In order to minimize the effect of humidity on membrane formation, zeolite 3A beads were placed in oven. Then coagulation was achieved under the same conditions with wet-phase inversion technique. Finally, membranes were annealed at 50°C under vacuum for 3 days.

The preparation steps of pure PES membranes by wet-phase inversion and dry-wet phase inversion techniques, also PES/ZIF-8 MMMs by wet-phase inversion technique are summarized in a flowchart illustrated in Figure 3.3.

3.2.2 Solvent Evaporation Technique

Using solvent evaporation technique dense PVA membranes were produced. Two types of poly (vinyl alcohol) (PVA) having 87-89 % and 98 % degree of hydrolysis were used. Their average molecular weights were very close to each other, 130,000 and 125,000, respectively. All the PVA types were purchased from Sigma-Aldrich with a commercial name of *Mowiol*®. Ultra-pure (UP) water was used as solvent and it has approximate electrical conductivity of $5.5*10^{-6}$ S/m.

Chemical cross-linking of PVA were achieved with glutaraldehyde (GA) solution consisting of GA, sulfuric acid (H_2SO_4), acetone and water. GA has a chemical formula of $C_5H_8O_2$ and its structural formula is given in Figure.3.3. GA (25 wt. % in H_2O) and sulfuric acid (95-98 % pure) were purchased from, Sigma-Aldrich and

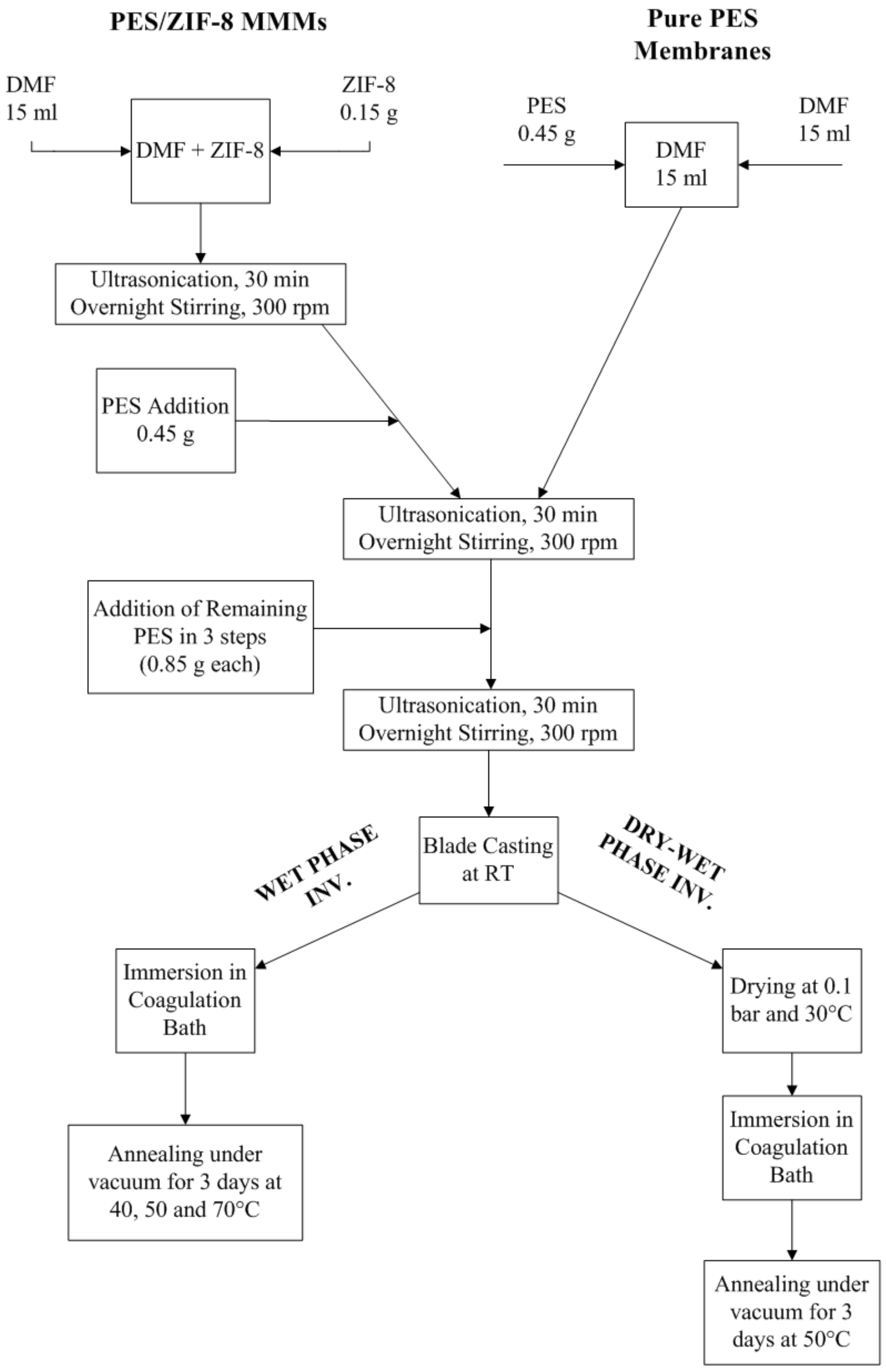


Figure 3.2 Preparation steps of asymmetric pure PES and PES/ZIF-8 MMMs

Merck, respectively. Technical acetone (99.5 % pure) were purchased from Birpa Chemicals.

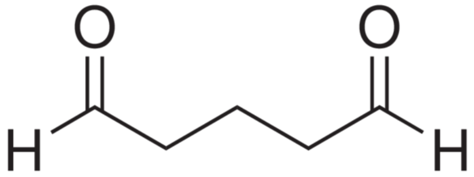


Figure 3.3 Chemical structure of GA [39]

In this study, two types of dense membranes were prepared by solvent evaporation technique, pure PVA and PVA/ZIF-8 membranes. Pure PVA membranes were prepared from both 87-89 % and 98 % hydrolyzed PVA. In order to cross-link the pure PVA membranes either thermal or chemical cross-linking method was applied. PVA/ZIF-8 MMMs prepared from PVA having 98 % degree of hydrolysis and these membranes cross-linked chemically. All the pure PVA and ZIF-8/PVA MMMs prepared in this work were stated in Table 3.1 with the PVA and ZIF-8 content of polymer solutions and cross-linking type.

Table 3.1 Properties of pure PVA and PVA/ZIF-8 MMMs

	Hydrolysis degree of PVA, %	**PVA content, wt. %**	**ZIF-8 content wt. %**	**Cross-linking type**
PVA87-T	87-89	10	0	Thermal
PVA87-GA	87-89	10	0	Chemical
PVA(10)98-GA	98	10	0	Chemical
MMM- PVA(10)98-GA	98	10	5	Chemical
PVA(5)98-GA	98	5	0	Chemical
MMM- PVA(5)98-GA	98	5	5	Chemical

The preparation methodology of the membranes stated in Table 3.1 are as follows;

Pure PVA (87-89 % degree of hydrolysis), 5.0 g PVA was added into 45.0 g UP water at room temperature in two step and stirred overnight at 300 rpm. Afterwards, polymer solution was degassed under vacuum until getting a homogenous solution without any bubble.

Pure PVA (98 % degree of hydrolysis), PVA was added into UP water at 90°C in two step and a condenser was used to recycle back the evaporated water. Vigorous stirring was applied for 4 hours. The prepared solution was waited to cool down to room temperature and was degassed under vacuum until getting a homogenous solution without any bubble.

PVA/ZIF-8 (PVA, 98 % degree of hydrolysis), first ZIF-8 particles were put into the UP water and stirred overnight at 300 rpm. After application of 20 min ultrasonication, solution heated to 90°C, during heating evaporated water refluxed with the help of a condenser. Then PVA was added in two step into the solution which was stirring vigorously and stirred for 4 hours. The prepared solution was waited to cool down to room temperature and filtered with stainless steel sieve with 325 mesh. The filtered solution exposed to 30 min ultrasonication and stirred overnight at 200 rpm. The amount of ZIF-8 crystals in MMMs was 5 wt. % of total polymer

Both PVA-water solutions and PVA-ZIF-8-water solutions were casted on a glass plate at room temperature using Automatic Film Applicator with the help of a casting knife of 800 µm. After casting, polymer film heated at 40°C in an oven for 24 hours at ambient pressure in order to evaporate the solvent. The membranes were peeled from glass plate carefully and cross-linked either thermally or chemically. The preparation steps of pure PVA membranes and PVA/ZIF-8 MMMs are summarized in a flowchart illustrated in Figure 3.4.

For thermal cross-linking; first membrane films were cut in circle shape having a diameter a little bigger from the membrane module, approximately 12 cm. Then they were heated in oven at different temperatures and for different times under 1 bar N_2 atmosphere. The temperatures and period of the thermal crosslinking are given in table 3.2.

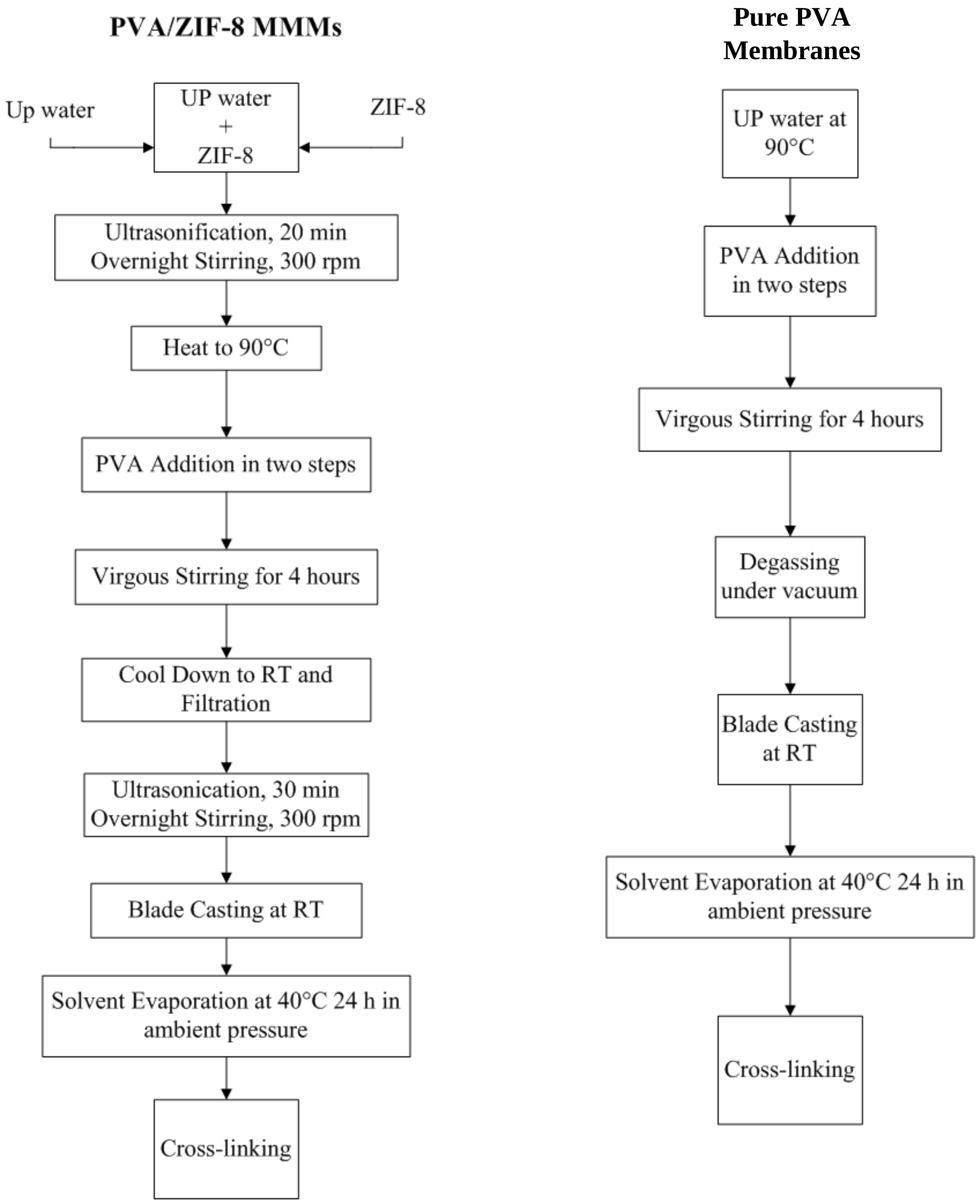


Figure 3.4 Preparation steps of dense pure PVA (98 % degree of hydrolysis) and PVA/ZIF-8 MMMs

Table 3.2 Temperatures and periods of thermal crosslinking

Temperature, °C	**Period, hour**
90	0.5 and 1.0
100	1.0
120	1.0 and 48
140	1.0 and 48
160	48

For chemical crosslinking, 8 different crosslinking solution were used. Crosslinking solution consisted of glutaraldehyde (GA), sulfuric acid (H_2SO_4), acetone and deionize (DI) water. The crosslink solutions used and their content can be seen in Table 3.3.

Table 3.3 Composition of the cross-link solutions

	GA, %	**H_2SO_4, %**	**Acetone, %**	**Water, %**
Solution 1	1.5	0.5	98.0	0.0
Solution 2	1.5	0.5	93.0	5.0
Solution 3	1.5	0.5	88.0	10.0
Solution 4	1.5	0.5	83.0	15.0
Solution 5	1.5	0.5	78.0	20.0
Solution 6	3.0	0.5	76.5	20.0
Solution 7	0.75	0.50	78.75	20.00
Solution 8	0.5	0.5	79.0	20.0

By using crosslink solutions having different compositions effect of GA content on the pervaporation performance of pure PVA (both 87-89 % and 98 % hydrolyzed) membranes were investigated. Only pure PVA membranes produced from 87-89 % hydrolyzed PVA were cross-linked with GA solution having different water content and they were not tested for pervaporation; however, their swelling properties were observed.

Before the chemical crosslinking, membranes were cut in circle shape having a diameter a little bigger from the membrane module, approximately 12 cm. They were weighed and immersed in 40 ml crosslinking solution bath. After 3 hours membranes were taken out from the solution. Excess water on the membrane surface was gently dried with a paper towel and weighed again. Then membranes were dried at 90°C for 1 hour at 1 bar N_2 atmosphere. Membranes were weighed in order to determine swelling ratios.

All the pure PVA and PVA/ZIF-8 MMMs were soaked in 30 ml feed solution at room temperature one night before the pervaporation experiment (in order to reach the equilibrium) and their swelling degree were determined. Swelling degree of the membranes were calculated by the Equation 3.1.

$$Degree\ of\ swelling\ (\%\ DS) = \frac{W_s - W_d}{W_d}\ x\ 100 \tag{3.1}$$

where W_s and W_d are the weights of the swollen and the dried membranes, respectively.

3.3 Material Characterization

3.3.1 ZIF-8 Characterization

X-ray diffraction (XRD) patterns of synthesized ZIF-8 crystals were obtained by Philips model PW 1840 X-Ray diffractometer by using Cu-Kα radiation source at a 30 kV voltage and 24 mA current. Angle of diffraction (Bragg angle, 2θ) was changed between 5° to 40° with a scan rate of 0.05 °/s. XRD patterns of the synthesized ZIF-8 crystals were compared to simulated peak positions of ZIF-8 [64]. In order to determine the relative crystallinity, area under the curve of peaks for (011), (002), (112), (022), (013), (222), (114) and (134) planes were used. The ZIF-8 synthesized by Keser et al. (ZIF-8.6) was assigned as reference with 100 % crystallinity [29]. The diffraction peaks of all the ZIF-8 crystals used for MMM preparation and their calculated crystallinities were given in Appendix B.

The morphologies and the particle sizes of crystals were determined by scanning electron microscopy (SEM) at a magnification range of 50,000-200,000x by QUANTA 400F Field Emission device. Average particle sizes were determined using 18-20 crystals on SEM images. Then, average particle sizes of ZIF-8 crystals given in Table.4.2 were calculated by using these data. The average particle size calculations and the full size SEM images of ZIF-8 particles used for average particle size calculations were given in Appendix C.

3.3.2 Membrane Characterization

Morphologies of asymmetric pure PES, PES/ZIF-8 MMMs, pure PVA and PVA/ZIF-8 MMMs were examined by using FEI QUANTA 400F series scanning electron microscopy (SEM). The images taken from the cross-sections of PVA/ZIF-8 MMMs were used in order to better observe the distribution of ZIF-8 particles. The SEM analysis was carried out at a magnification range of 1,000-50,000x. Samples were coated with Au-Pd. Acceleration voltage was 20.0 kV for ZIF-8 and PES based membranes and 5.0 kV for PVA based membranes.

3.4 Pervaporation Experiments

3.4.1 Chemicals

The feed solution was prepared from ethanol and deionized water. Ethanol was obtained from Merck with an analytical grade of 99.5 % purity. The feed solution composed of 10 wt. % water and balance ethanol.

3.4.2 Pervaporation Set-up and Procedure

The prepared membranes were tested in pervaporation system for dehydration of ethanol. The pervaporation set-up is illustrated in Figure 3.5.

Pervaporation set-up consists mainly of, membrane module, cold traps and a vacuum pump. Feed solution was recirculated between the feed tank and the membrane module by a centrifugal pump (IWAKI, 72010-25). Tubing was Masterflex® silicon tubing with a diameter of 3.1 mm. In order to set the temperature of feed solution, feed tank was placed in a circulatory water bath (Polyscience Model 912). Feed tank was open to atmosphere. Vacuum, driving force for transport though membrane, was applied at the permeate side using rotary vane pump (Edwards, RV5). The pressure of the permeate side was measured by Edwards Pirani Gauge and controlled with Edwards Active Digital Controller (ADC) with an accuracy of 15 %.

The membrane module has circular shape and made from stainless steel. Figure 3.6 illustrated this membrane module. Its diameter is 90 mm; therefore, active membrane area is 0.00635 m^2. The membrane was placed on a perforated plate and a silicon O-ring was employed for sealing.

Permeate side of the pervaporation system consisted of glass pipes in order to observe condensation problem due to any reason. Two parallel permeate lines are connected to the membrane module and by this way continuous operation could be achieved. They are connected to each other by a 3-way valve, which are switched manually to take one line under vacuum at a time. Permeate passed through the open line; meanwhile, other line was open to atmosphere to take the collected permeate without any interruptions.

A safety trap were employed before the vacuum trap to protect the vacuum pump from any leakage. Permeate were collected in glass traps in a condensed form with the help cold traps which were dewar flasks filled with liquid nitrogen.

During the pervaporation experiments, Samples were taken from the permeate side for every 3 hours and pervaporation experiments were carried out for 9 hours. Experiments were conducted with 2 kg feed amount; hence feed concentration was assumed during experiments.

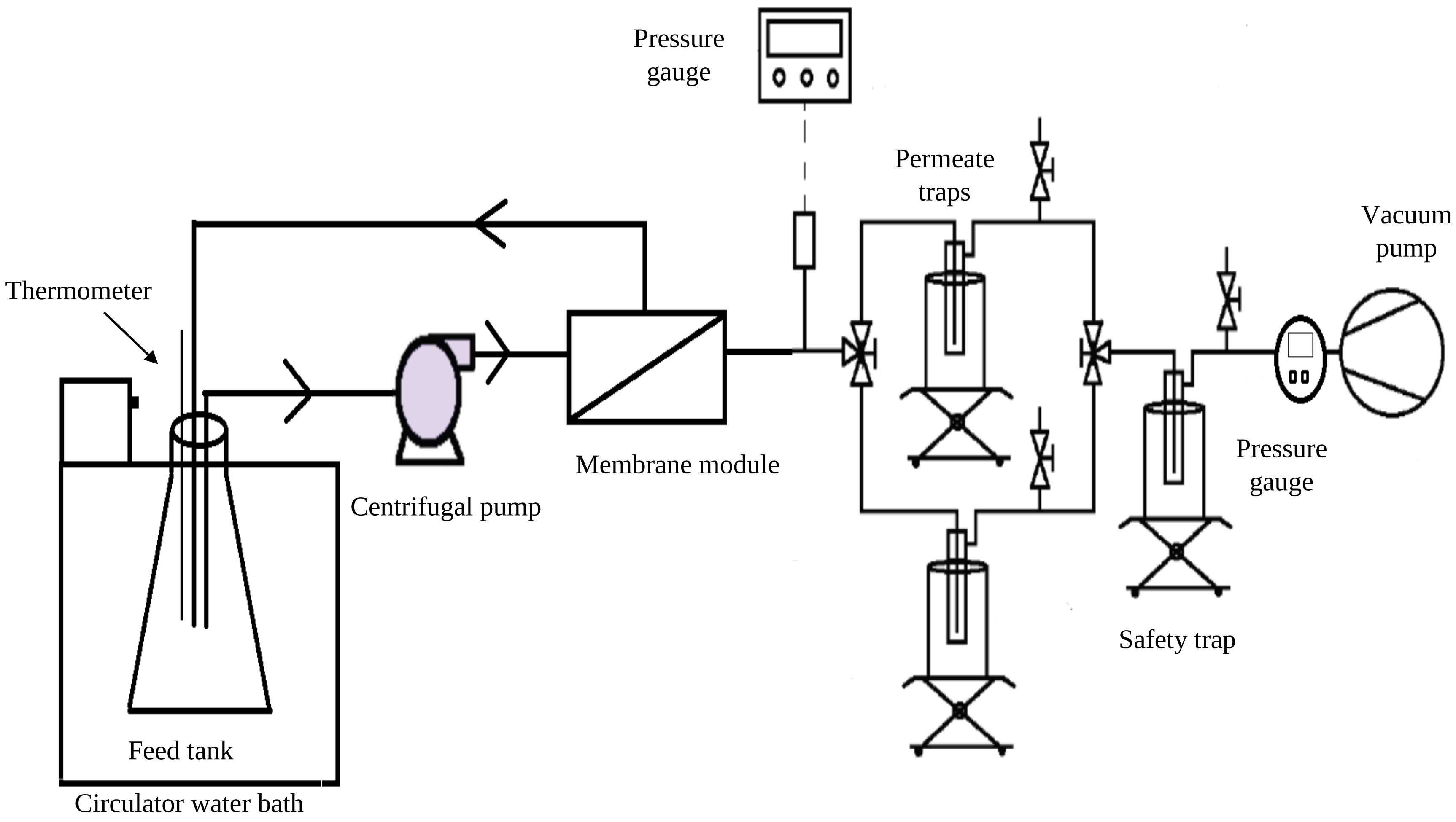


Figure 3.5 Pervaporation set-up

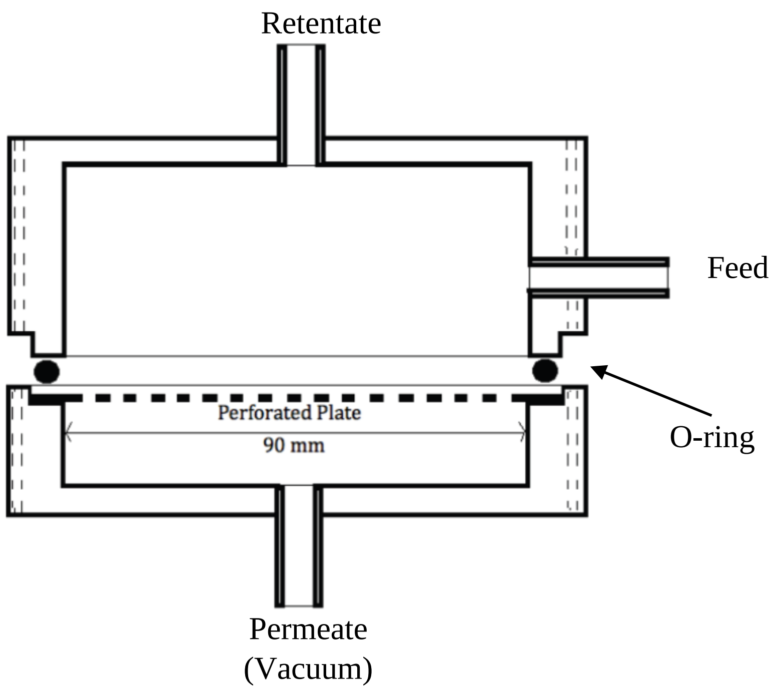


Figure 3.6 Schematic representation of membrane module

All the pervaporation experiments were conducted under same conditions and these conditions are given in Table 3.4.

Table 3.4 Pervaporation experiment conditions

Feed Temperature	25°C
Permeate Side Pressure	3 torr, approx.
Feed Flow Rate	1.5 l/min
Feed Water Content	10 wt. %
Feed Amount	2 Kg

3.4.3 Ethanol-Water Analysis

The water content of the feed solution and permeate were determined using KEM Karl Fischer Moisture Titrator (MKS-520). For Karl Fischer (KF) analysis, Hydranal® Karl Fischer titrant-2 was used as titrating agent and Hydranal® solvent were used as working medium and they were obtained from Fluka Chemicals.

During the analysis, typically 0.03- 0.08 g sample taken from permeate was used to determine the water content. Firstly, sample was taken into the syringe and weighed, then injected into the titration medium. After the injection it was weighted again and recorded to the KF device. The automatic titration started and KF determined the end point using the signal collected by the potentiometer. Upon finishing the titration, it calculated and gave the result using initial and final weight of the syringe and the amount of reagent used during the analysis.

Each sample was analyzed minimum twice in order to lessen the tolerance of the analysis. Before starting the pervaporation experiments, water content of the feed solution also determined by KF.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Preparation of Asymmetric Membranes by NIPS Method

Pervaporation performance of a membrane is strongly affected by the membrane morphology. Asymmetric membranes generally have a thin selective layer and below it a thicker highly permeable layer. Since asymmetric membranes have thin skin layer, their fluxes might be high. Wet-phase inversion and dry-wet phase inversion are two widely used techniques to prepare an asymmetric membrane [1-2].

4.1.1. Preparation of Asymmetric Pure PES Membranes by Wet-Phase Inversion

Annealing at elevated temperatures can alter the membrane structure by inducing an increase in packing density and reduction in free volume; hence, selectivities increase while total fluxes decrease [65–67]. Therefore, in this part of the research asymmetric PES membranes were prepared and annealed at different temperatures, below the T_g of PES.

In present study asymmetric PES membranes were obtained by wet-phase inversion technique and phase separation was achieved by means of a non-solvent (NIPS method). Membranes were prepared from PES-DMF solutions with a PES content of 20 % (wt/vol) and ethanol was used as the non-solvent. Following the blade casting, membrane films were immersed into coagulation bath, filled with ethanol, at room temperature for phase inversion. Membranes were then annealed at selected temperatures (20-70°C) under vacuum for 3 days.

Membranes were tested to separate ethanol-water mixture with water concentration of 10 wt. % by pervaporation at 25°C. The feed was 2 kg and experiments lasted for 9 hours; hence, feed concentration was assumed constant throughout the experiments. A sample calculation for constant feed assumption can be seen in Appendix D.

Figure 4.1 shows the results of pervaporation tests for all membranes and Table 4.1 summarizes the effect of annealing temperature on pervaporation performance of asymmetric pure PES membranes. Higher annealing temperatures resulted in more selective and less permeable membranes. Nevertheless, high standard deviations and large area shown on Figure 4.1 indicate low reproducibility. Membranes prepared without annealing and annealed at 40°C exhibit similar separation performance. Apparently annealing at 40°C has a weak effect on chain packing of PES. With an increase of annealing temperature to 50°C membranes with higher selectivities were obtained. The most selective membranes had an average selectivity of 15.6 with an average flux of 71.5 g/m^{2}h. Increase of annealing temperature to 70°C engendered a 42 % increase in flux and a 24 % reduction in selectivity when compared to membranes annealed at 50°C. Increasing flux with a decrease in selectivity is a typical membrane behavior for pervaporation processes. Similar conclusion were also withdrawn in the literature; fluxes reduced while selectivities enhance with increasing annealing temperature due to the denser packing of polymer chains and reduced free volume at higher annealing temperature [48,65,68,69]. Pervaporation Separation Indexes (PSI) in Table 4.1 indicated that, membranes annealed at different temperatures had similar pervaporation performance.

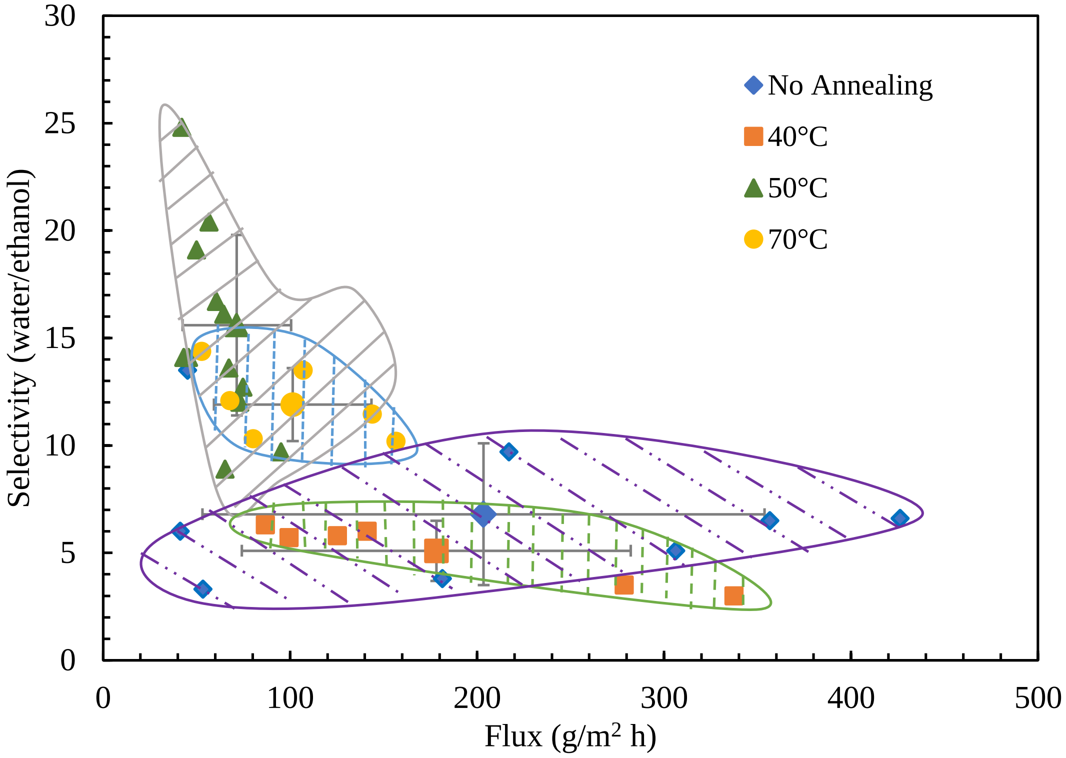


Figure 4.1 All selectivity and flux values of asymmetric PES membranes annealed at different temperatures and their average values

Table 4.1 Effect of annealing temperature on pervaporation performance of asymmetric pure PES membranes

Annealing Temp, °C	**Flux (J), $g/m^2.h$**	**Permeate water content, %**	**Selectivity (α), water/ethanol**	**PSI, (J.α)**
70	101.4 ± 42.1	55.1 ± 3.8	12.0 ± 1.7	1216
50	71.5 ± 29.0	60.7 ± 7.0	15.6 ± 4.2	1115
40	178.2 ± 104.0	35.3 ± 6.9	5.1 ± 1.4	908
No Annealing	203.5 ± 150.3	41.2 ± 10.2	6.8 ± 3.3	1384

Figure 4.2 illustrates the cross-sectional SEM images of asymmetric pure PES membranes annealed at 70°C, 50°C and non-annealed one. All membranes has support layers with sponge like structure. The thicknesses of skin layer of membranes annealed at 70°C and 50°C are approximately 2.4 µm and 2.6 µm. The

thickness of skin layer of the membrane annealed at 70°C is more uniform than the one annealed at 50°C. The non-annealed membrane had a skin layer of approximately 400 nm, which is much thinner than the annealed membranes. The morphology of skin layer strongly influences the membrane performance. Membranes with thinner skin layers has higher fluxes; nevertheless, non-uniform skin layers, which may have defects, may cause lower selectivities.

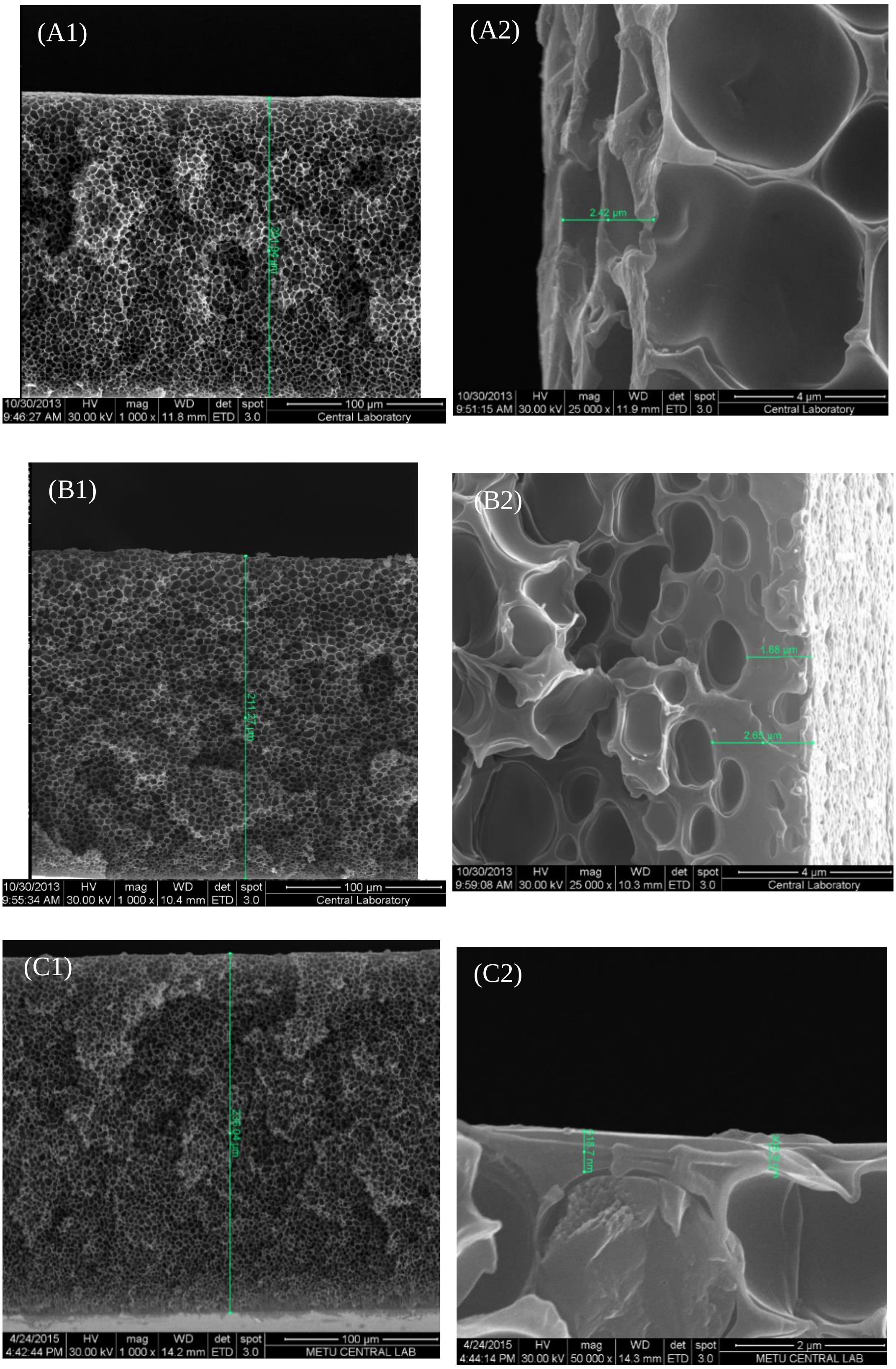


Figure 4.2 Cross-sectional SEM images of asymmetric pure PES membranes according to annealing temperature (A) 70°C (B) 50°C (C) non-annealed

4.1.2. Preparation of Asymmetric PES/ZIF-8 MMMs by Wet-Phase Inversion

In order to enhance the pervaporation performance of asymmetric PES membranes, MMMs containing 5 wt. % ZIF-8 were prepared by wet-phase inversion. They were annealed at 50°C and tested to separate ethanol-water mixtures with water concentration of 10 wt. % by pervaporation.

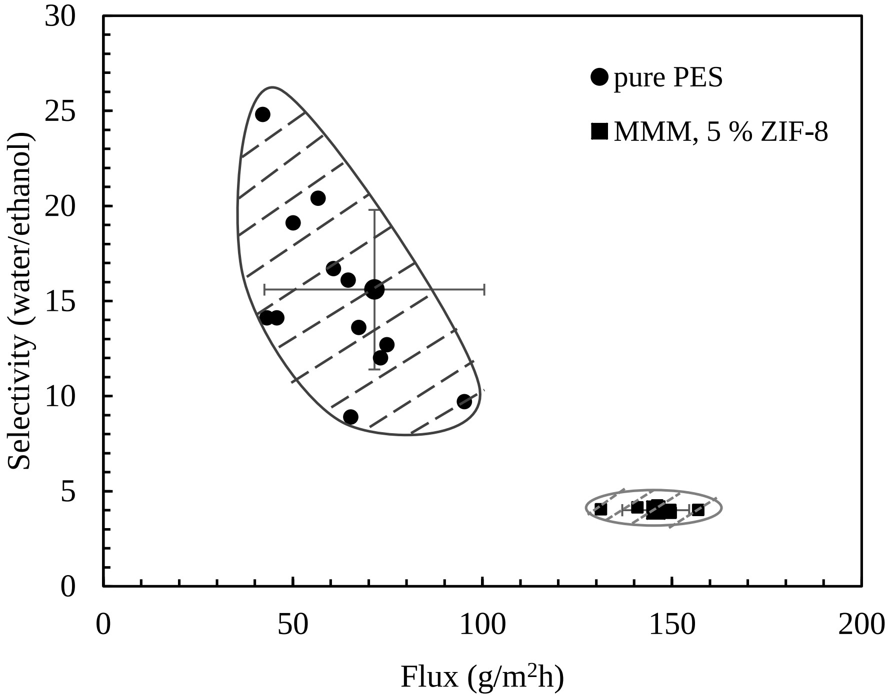


Figure 4.3 Effect of ZIF-8 addition on pervaporation performance of asymmetric pure PES membranes

The flux through ZIF-8 incorporated membranes was as twice as the flux through the pure PES membrane (Figure 4.3); however, PES/ZIF-8 membranes had substantially lower selectivity. Interfacial voids between ZIF-8 particles and PES matrix are likely to result in large fluxes with low selectivities. A similar trend has observed in the literature [23,61,62].

4.1.3. Preparation of Asymmetric Pure PES Membranes by Dry-Wet Phase Inversion

Asymmetric membranes can be produced by dry-wet phase inversion technique [1]. In dry-wet phase inversion, the casted polymer film is subjected to evaporation before immersing into the coagulation bath. Partial evaporation of solvent concentrates the polymer at the solution-air interface and ends up with an asymmetric membrane with a thicker skin layer [70]. In this part of study, polymer films were exposed to 5 min and 60 min evaporation at 30°C 0.1 bar air atmosphere after casting. Then the membrane films were immersed into ethanol bath at ambient temperature.

Figure 4.4 exhibits the selectivity and flux data of asymmetric pure PES membranes prepared by dry-wet inversion. The figure also compares pervaporation performance of membranes prepared by dry-wet and wet phase inversion techniques. Zones were specified for pervaporation performance according to duration of solvent evaporation. The flux and selectivity zone of wet-phase inversion membranes nearly enclosed the zone of the membranes exposed to solvent evaporation for 5 min., indicating that 5 min. solvent evaporation did not alter the skin layer thickness effectively. DMF (solvent) has a boiling point of 153°C; therefore, evaporation for 5 min is probably short for evaporation of DMF for formation of a selective skin layer. Besides when the solvent evaporation period was extended to 60 min, a decline in flux was observed without any change in selectivity. Moreover, the flux and selectivity of PES membranes prepared by the dry-wet phase inversion showed that these membranes were more reproducible than the membranes prepared by the dry-wet phase inversion.

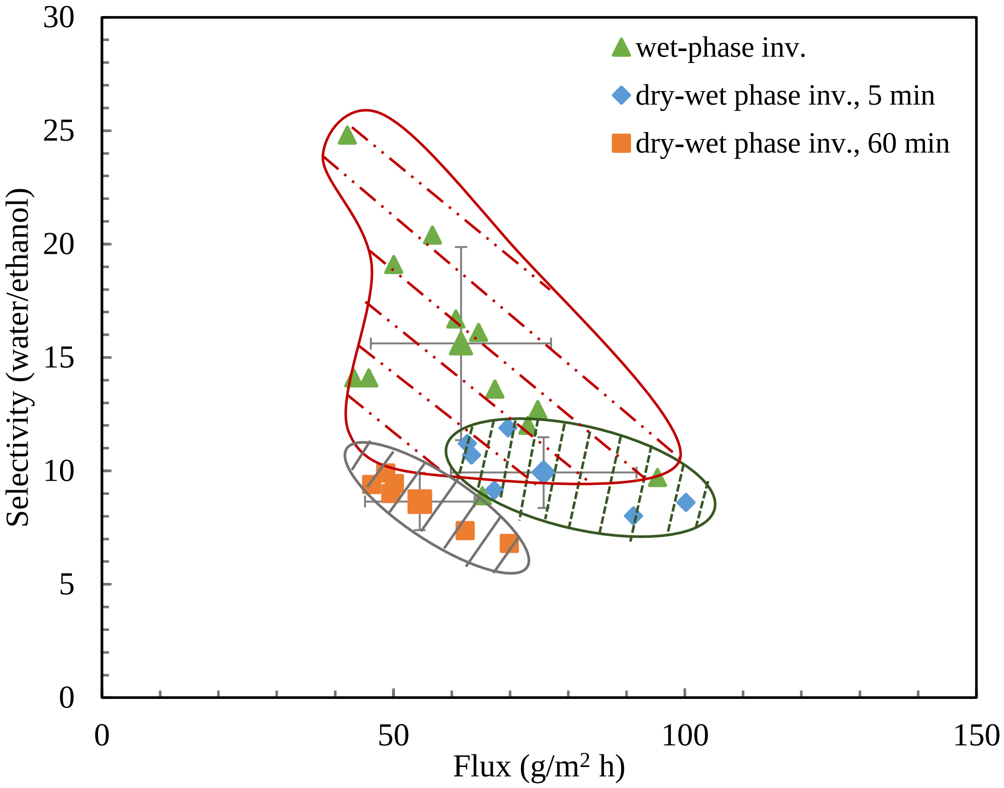


Figure 4.4 All selectivity and flux values of asymmetric PES membranes annealed at different temperatures and their average values

Table 4.2 summarizes the pervaporation performance of asymmetric pure PES membranes according to evaporation time. Longer evaporation time resulted in a decrease in membrane flux and slight decrease in selectivity. In the literature similar influences of drying time was observed. Huang et al. [47] investigated the pervaporation performance of asymmetric PEI membranes for IPA dehydration and the flux decreased tremendously while selectivity increased with the application of 2 min drying. Longer than 2 min drying caused only small changes.

Standard deviation for membranes prepared by dry-wet phase inversion are lower than membranes prepared by wet phase inversion indicating a more reproducible membranes.

Table 4.2 Effect of annealing temperature on pervaporation performance of asymmetric pure PES membranes

Drying Time, min	Annealing Temp, °C	Flux (J), $g/m^2.h$	Selectivity (α) water/ethanol
0	50	71.5 ± 29.0	15.6 ± 14.2
5	50	75.8 ± 14.5	10.0 ± 1.4
60	50	54.5 ± 8.6	8.6 ± 1.5

Figure 4.5 illustrates the cross-sectional SEM images of asymmetric pure PES membranes prepared by wet-phase inversion and dry-wet phase inversion techniques. All membranes has the support layers with sponge like structure which is mainly resulted from wet-phase inversion. Thickness of skin layer of the membrane exposed to 5 min solvent evaporation was almost the same as that of the membrane prepared with wet-phase inversion. On the other hand the skin layer of the membrane exposed to 60 min. solvent evaporation was thicker than the membrane prepared by 5 min solvent evaporation, thus thicker skin layer was the probable reason for decreased flux.

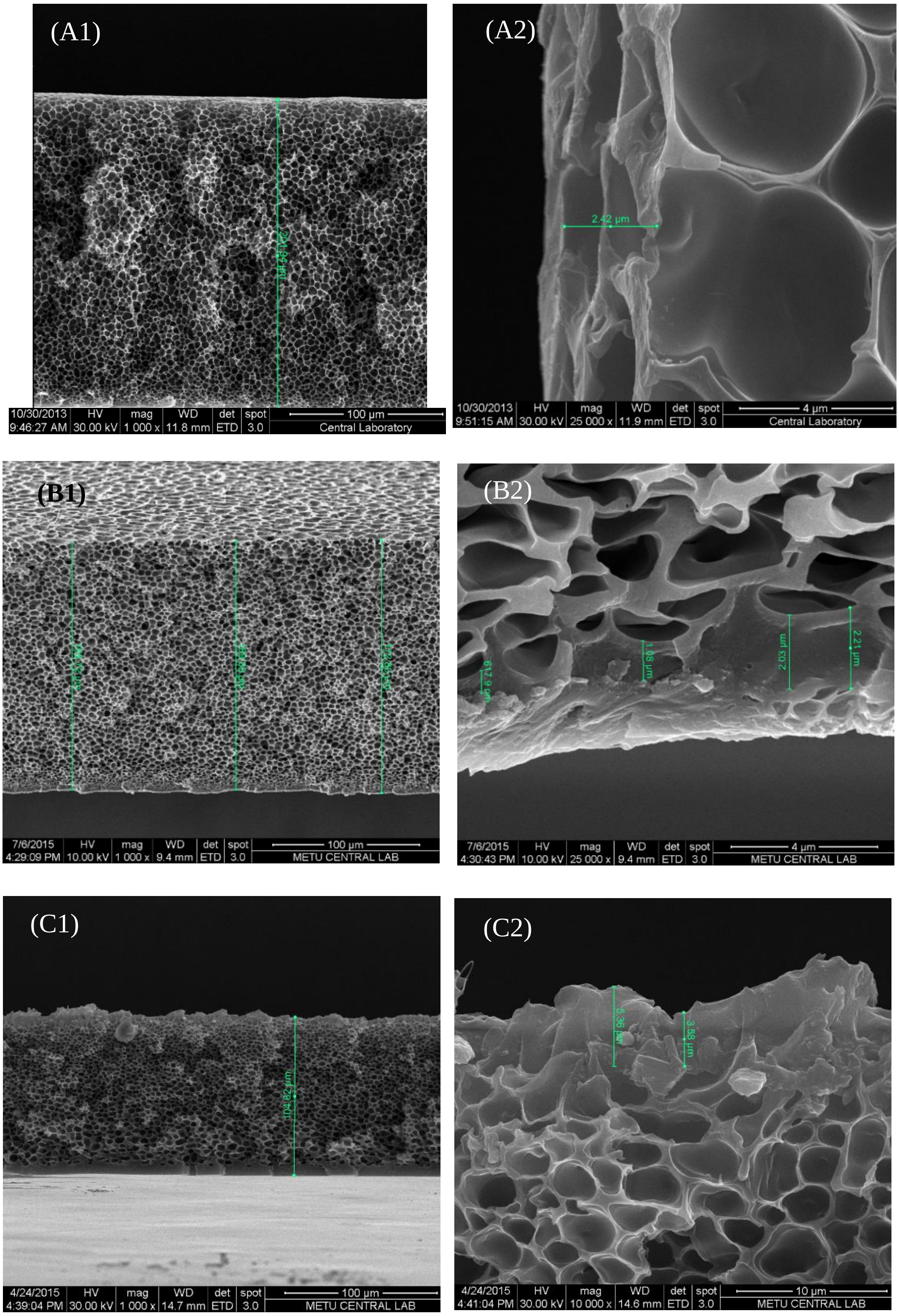


Figure 4.5 Cross-sectional SEM images of asymmetric pure PES according to solvent evaporation periods (A) wet-phase inversion, no solvent evaporation step (B) 5 min solvent evaporation (C) 60 min solvent evaporation

4.2.Preparation of Dense PVA Membranes

Poly (vinyl alcohol) (PVA), which is a water soluble polymer, is suitable for preparation of pervaporation membranes for dehydration processes due to its hydrophilicity. However, PVA membranes suffer from swelling, which is the increase in free volume of polymer due to absorption of a solvent, and swelling leads to membranes with very low selectivity. Therefore, in order to prevent swelling problem PVA should be cross-linked and PVA can be cross-linked either by heat treatment or by using a chemical cross-linking agent [5,34–36].

4.2.1. Preparation of Pure PVA Membranes by Thermal Cross-linking

Thermal cross-linking is one of the easiest way to achieve effective cross-linking of poly (vinyl alcohol) (PVA) [5,34–36]. In this part of the study pure PVA membranes were cross-linked thermally.

Pure PVA membranes were prepared by solvent evaporation technique from PVA with 87-89 % degree of hydrolysis. Membranes were casted from PVA-water solution with a PVA content of 10 wt. %. After blade casting, solvent evaporation was carried out at 40°C for 24 hours at ambient pressure. Cross-linking temperature and time were changed between 90°C and 160°C, and between 1 and 48 hours, respectively. Swelling degrees of these membranes in feed solution (used in pervaporation tests) were determined and membranes were tested to separate ethanol-water mixture with water concentration of 10 wt. % by pervaporation. Pervaporation experiments were carried out at 25°C. The feed amount was 2 kg and experiments lasted 9 hour; hence, feed concentration was assumed constant throughout the experiments.

Figure 4.6 and 4.7 present the effect of thermal cross-linking temperature and thermal treatment time on pervaporation performance of pure PVA membranes, respectively. Table 4.3 summarizes the effect of cross-linking temperature and period on the pervaporation performance of pure PVA membranes. Normalized fluxes (J_N) were calculated to compare the membrane performances since membrane thicknesses were not same. It was observed that, thermal treatment affected especially the normalized fluxes of the membranes. Short period of thermal cross-linking (1 hour) at all temperatures caused a decrease in normalized flux and without a significant change in selectivities in comparison to non-treated membranes. Membranes cross-linked thermally for a longer period (48 hours) had more than two fold higher selectivities than membranes cross-linked thermally for short period (1 hour). Percentage swelling also reduced by half by extending thermal cross-linking to 48 hours.

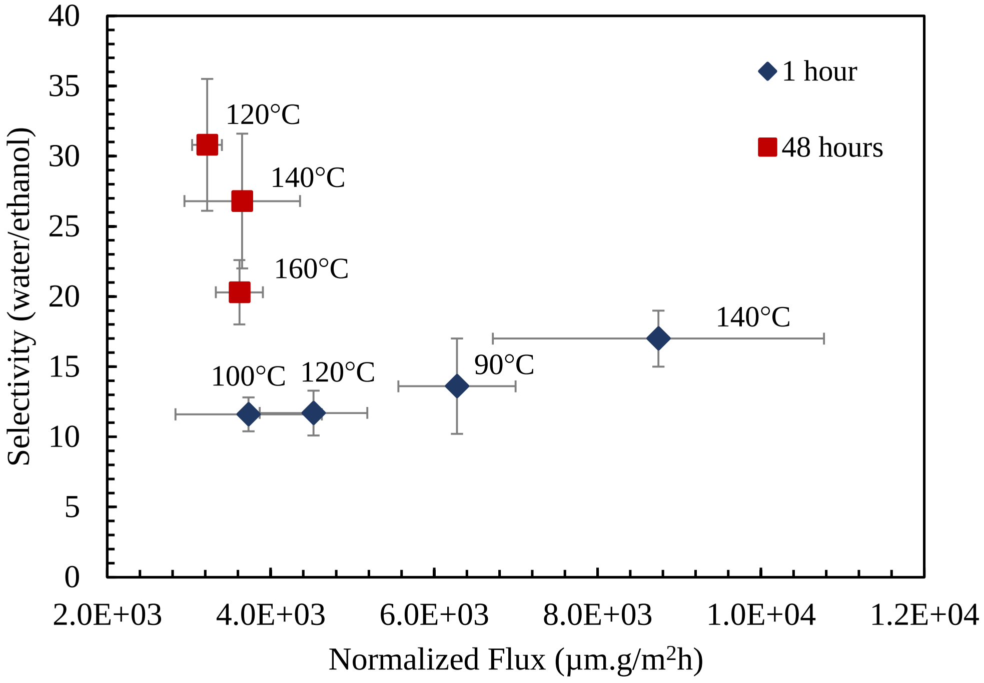


Figure 4.6 Effect of thermal cross-linking temperature on pervaporation performance of pure PVA membrane.

Table 4.3 Effect of thermal cross-linking temperature and period on pervaporation performance of pure PVA[a] membranes

Thermal Cross-linking Temp, °C	**Thermal Cross-linking Period, h**	**Flux (J), g/m^2.h**	**Normalized Flux (J_M), μm.g/m^2.h**	**Selectivity (α), water/ethanol**	**PSI (J.α)**	**Swelling Degree, %**	**Membrane Thickness, μm**
No treatment	-	184.0 ± 95.4	$15.0*10^3 \pm 7.6*10^3$	10.0 ± 3.3	1840	104.0 ± 14.8	80.0 ± 0
90	0.5	76.1 ± 14.5	$4.9*10^3 \pm 0.9*10^3$	9.7 ± 0.6	738	80.8 ± 8.8	61.4 ± 11.4
90	1.0	104.6 ± 14.3	$6.3*10^3 \pm 0.7*10^3$	13.6 ± 3.4	1423	88.5 ± 11.4	65.0 ± 13.5
100	1.0	70.7 ± 7.5	$4.4*10^3 \pm 0.5*10^3$	11.6 ± 1.2	822	58.0 ± 7.4	62.5 ± 2.5
120	1.0	91.6 ±18.5	$4.5*10^3 \pm 0.7*10^3$	11.7 ± 1.6	1072	63.0 ± 8.7	50.0 ± 4.1
140	1.0	133.6 ± 24.5	$8.7*10^3 \pm 2.0*10^3$	17.0 ± 2.0	2271	62.8 ± 10.3	65.0 ± 14.7
120	48	44.0 ± 8.7	$3.2*10^3 \pm 0.2*10^3$	30.8 ± 4.7	1355	33.0 ± 2.8	75.0 ± 14.0
140	48	46.6 ± 8.0	$3.7*10^3 \pm 0.7*10^3$	26.8 ±4.8	1249	37.6 ± 1.5	78.3 ± 7.6
160	48	45.2 ± 3.6	$3.6*10^3 \pm 0.3*10^3$	20.3 ± 2.3	917	30.0	80

[a] PVA with 87-89 % degree of hydrolysis and MW 130,000

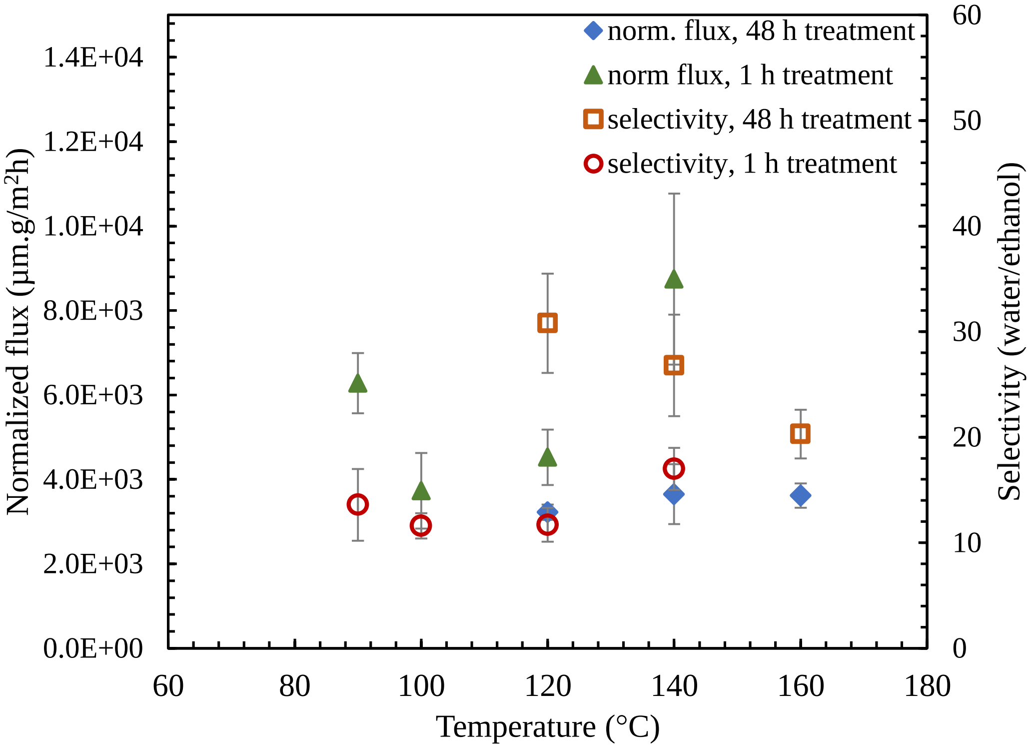


Figure 4.7 Effect of thermal cross-linking period on pervaporation performance of pure PVA membranes

In the literature, the effect of thermal treatment time and temperature on the pervaporative ethanol dehydration performance of approximately 99 % hydrolyzed PVA membranes before solvent evaporation were investigated [42]. Pure PVA membranes treated at 30, 90, 110, and 140 °C for 150, 40, 25, 15 min, respectively. Increasing treatment temperature yielded an improved selectivity while membrane flux remained nearly constant. Also swelling and crystallinity of the membranes were almost constant. It is inferred that, surface structure of PVA membranes changed with thermal treatment temperature and selectivity improved. In this study, however, increasing temperature for 1 hour thermal treatment caused the PVA membranes less permeable.

The cross-linking of PVA membranes by thermal treatment may take place in two possible ways. One possibility is that, cross-link occurs top to bottom of the membrane. Therefore, short thermal cross-linking period might cause the formation of cross-linked and non-cross-linked layers across the membrane thickness. This type of cross-linking a decrease was expected in normalized flux with increasing temperature since higher temperature may result in more cross-linked membranes. Also when the thermal treatment time at 90°C lengthened to 1 hour from 30 min normalized flux increased instead of decreasing. The other possibility is that, the cross-linking initiates at random points along the cross-section. In this case, there could be spots having different degree of cross-linking in the membrane. If cross-linking is not completed, it is expected that membrane consists of randomly boasted cross-linked spots without interconnection. This kind of a membrane morphology may not yield an improvement in flux and selectivity. Moreover, both selectivity and the flux of the membranes cross-linked thermally at 140°C were the highest among 1 hour treated membranes, indicating the removal of residual solvent.

The thermally cross-linked PVA membranes were prepared from PVA with 87-89 % degree of hydrolysis; that indicates 11-13 % of the membranes was poly (vinyl) acetate (PVAc). The T_g of the PVAc is 28°C [1] which is close to the room temperature and the operating temperature of pervaporation experiments. Therefore, PVAc were annealed under ambient condition which might have affected the membrane selectivity.

Figure 4.8 compares the pervaporation performances of pure PES membranes prepared by dry-wet phase inversion technique with 60 min. solvent evaporation time and pure PVA membranes prepared from PVA with 87 % degree of hydrolysis which were thermally treated at 140°C for 60 min. It is obvious that pervaporation performance of PVA membranes were much better than PES membranes. Therefore, PVA was selected as base polymer for the rest of this study.

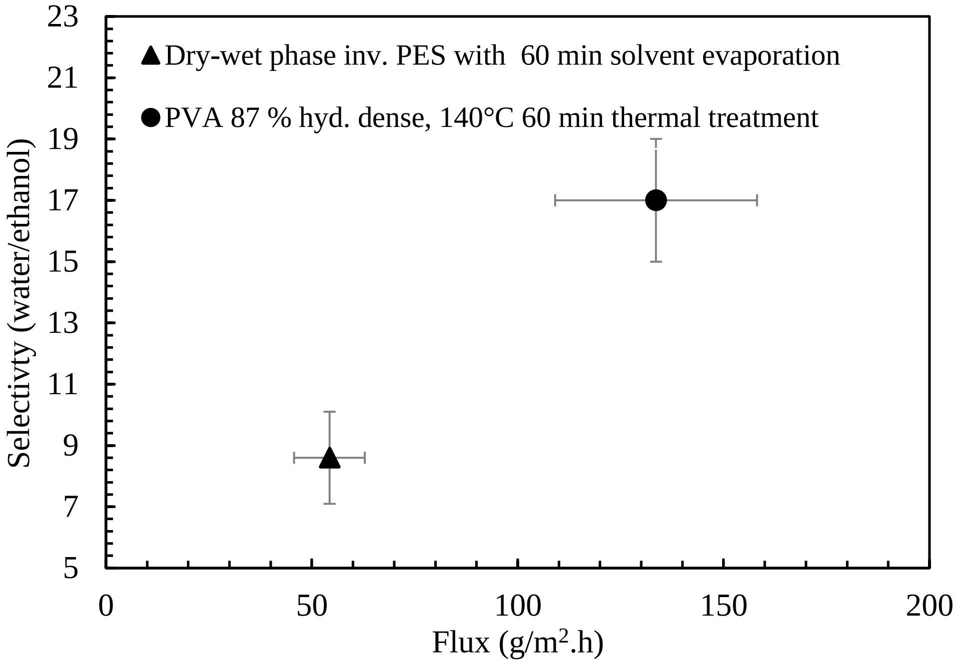


Figure 4.8 Pervaporation performances of dry-wet phase inv. pure PES membranes and 87 % hyd. dense pure PVA membranes heat treated at 140°C 60 min

4.2.2. Preparation of Pure PVA Membranes by Chemical Cross-linking

Poly (vinyl alcohol) (PVA) can be cross-linked by using a chemical cross-linking agent. Glutaraldehyde (GA) is one of the most widely used cross-linking agents [35,36,71,72]. It ($HCO–C_3H_6–CHO$) consists of two aldehyde groups (CHO), which can be attached to hydroxyl groups (OH) in PVA chains with the aid of an acid catalyst and cross-links PVA chains [17,18,35,37].

In this part, pure PVA membranes prepared by solvent evaporation technique and preparation conditions were the same as the thermally treated pure PVA membranes. Membranes were cross-linked chemically by immersing into a solution of GA, H_2SO_4, acetone and water for 3 hours. The cross-linked membranes were then dried at 90°C for 1 hour at 1 bar N_2 atmosphere. Swelling degrees of these membranes, both in cross-link solution and in pure water, were determined since swelling indicated the degree of cross-linking. The cross-linking solutions and their composition are listed in Table 4.4. Secondly, the water content of the cross-link solution held constant at the 20 wt. % and effect of GA content on the pervaporation performance of the pure PVA membranes were investigated. Pervaporation test conditions were same with the thermally treated pure PVA membranes.

Table 4.4 Compositions of cross-linking solution having different water content, for swelling tests

	Solution 1	**Solution 2**	**Solution 3**	**Solution 4**	**Solution 5**
GA, %	1.5	1.5	1.5	1.5	1.5
H_2SO_4, %	0.5	0.5	0.5	0.5	0.5
Acetone, %	98.0	93.0	88.0	83.0	78.0
Water, %	-	5.0	10.0	15.0	20.0

Figure 4.9 presents the degrees of swelling of the pure PVA membranes in cross-linking solution. Degree of swelling during cross-linking was minimum when cross-linking solution contained no water. With the addition of 5 wt. % water into cross-linking solution, a slight increase was observed in degree of swelling during cross-linking and further addition of water caused almost no change in degree of swelling. PVA is a water soluble polymer; therefore, PVA swells more during the cross-linking process if cross-linking solution contains water. With enhanced swelling of PVA during cross-linking, GA diffuses better and reacts with PVA more effectively. Membranes with higher degree of cross-linking are expected to have more rigid structure; therefore, low degree of swelling in pure water is expected.

Figure 4.10 shows the degree of swelling of pure PVA membranes (cross-linked) in pure water. It is observed that membranes cross-linked with solution without water swelled excessively in pure water with average degree of swelling 709.9 %. Also high standard deviation value of swelling indicated a reproducibility problem. Addition of 5 wt. % water in cross-link solution reduced the swelling degree in pure water more than seven-fold. Increasing water content of cross-linking solution caused almost no change in degree of swelling in pure water. This observation was consistent with the preceding discussion.

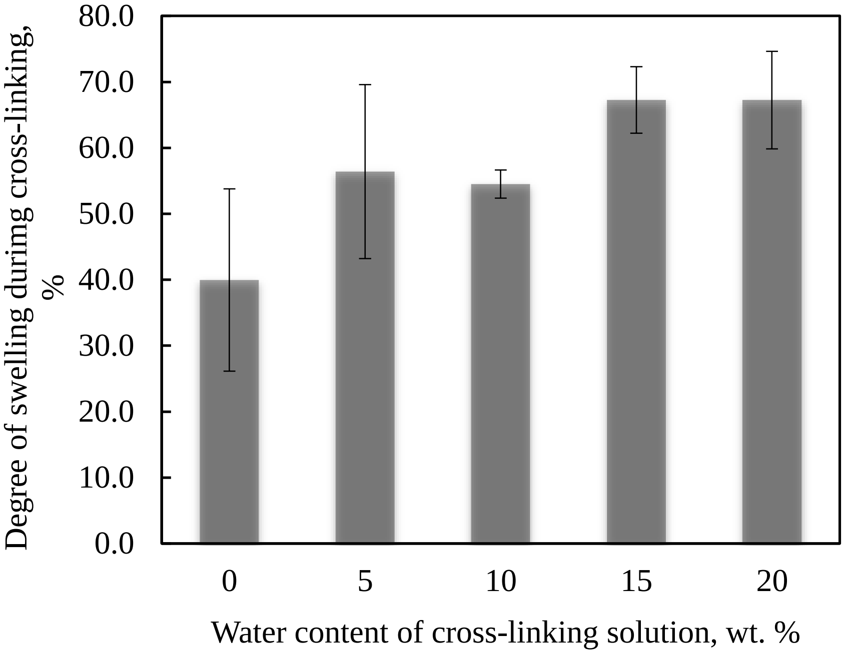


Figure 4.9 Degree of swelling of pure PVA membranes during cross-linking according to water content of cross-linking solution

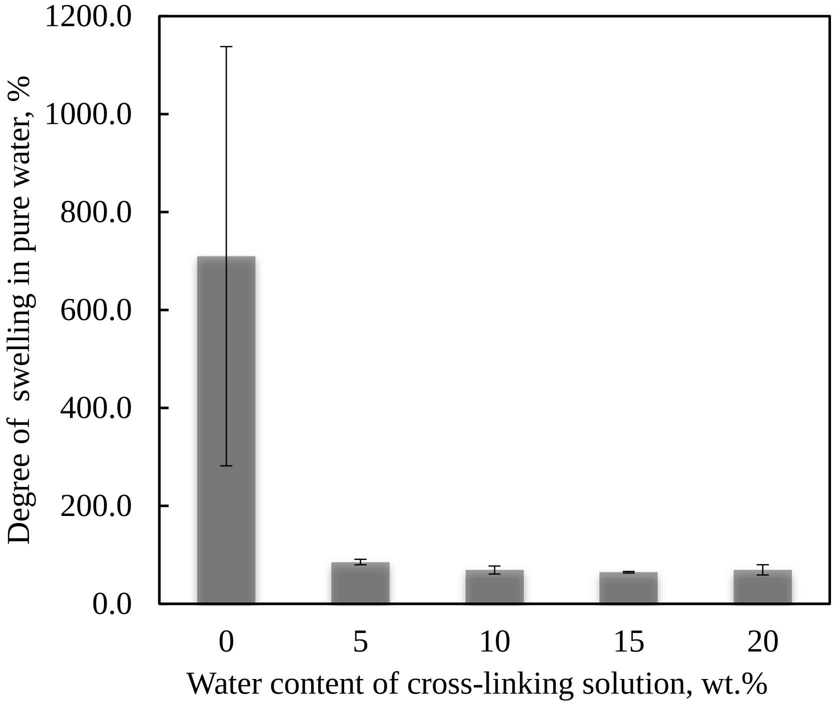


Figure 4.10 Degree of swelling of pure PVA membranes (cross-linked) in pure water according to water content of cross-linking solution

Figure 4.11 compares the pervaporation performances of pure PVA membranes cross-linked with solutions containing 0 and 20 wt. % water. The selectivity of pure PVA membranes raised from 7.5 to 12.0 and normalized flux decreased from 12000 µm g/m^2.h to 8500 µm g/m^2.h with the addition of water into the cross-linking solution.

Considering both normalized flux and selectivity, the pure PVA membranes cross-linked with cross-link solution containing 20 wt. % water were used for further swelling and pervaporation tests.

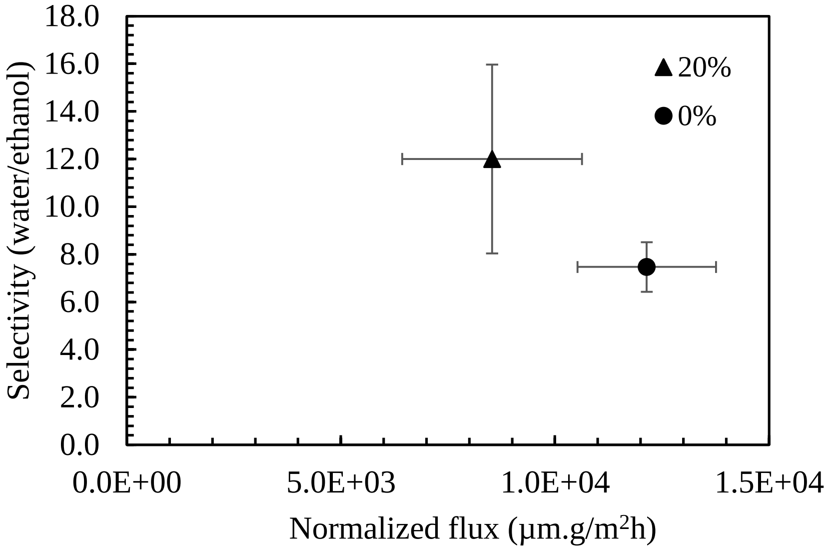


Figure 4.11 Pervaporation performances of pure PVA membranes cross-linked with solution containing 0 wt. % and 20 wt. % water

The effect of GA content of cross-linking solution on the pervaporation performance of the pure PVA membranes was investigated. Table 4.5 shows the composition of cross-linking solution.

Table 4.5 Composition of cross-link solution having different GA content, for pervaporation tests

	Solution 1	**Solution 2**	**Solution 3**
GA, %	0.5	1.5	3.0
H_2SO_4, %	0.5	0.5	0.5
Acetone, %	79.0	78.0	76.5
Water, %	20.0	20.0	20.0

Effect of GA content of cross-link solution on the pervaporation performances of pure PVA membranes is demonstrated in Figure 4.12. Table 4.6 summarizes the effect of GA content of cross-linking solution on pervaporation performance and swelling degree. With increasing GA content of cross-linking solution, normalized flux and selectivity values passed through a maximum and minimum, respectively, with a large deviation from average. This indicates that partial cross-linking, as PVA membranes prepared without cross-linking were almost dissolved in feed solution, which was 10 wt. % water and balance ethanol, was accomplished. The partial cross-linking can be the reason of low reproducibility. No significant change was observed in the membrane swelling with extending the cross-linking period. This was attributed to the nature of PVA used so PVA with higher degree of hydrolysis was than investigated.

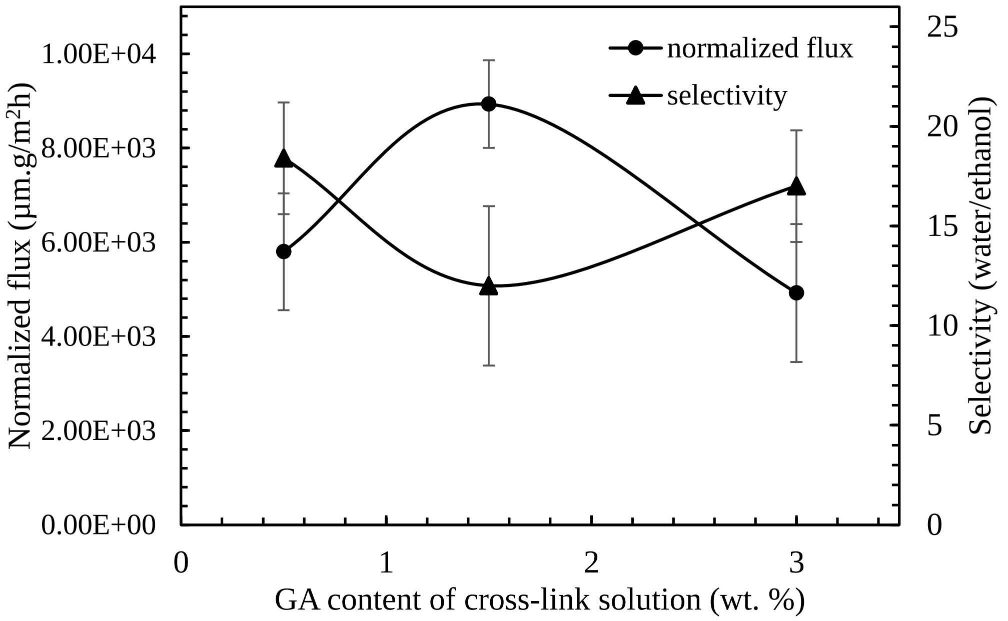


Figure 4.12 Effect of GA content of cross-link solution on the pervaporation performances of pure PVA (87 % hyd.) membranes

Table 4.6 Effect of GA content of cross-link solution on the pervaporation performances and swelling degree of pure PVA (87 % hyd.) membranes

GA Content of Cross-link Solution, wt. %	**Flux (J), g/m^2.h**	**Selectivity (α), water/ethanol**	**PSI, (J.α)**	**Swelling Degree in Feed, %**
3.0	105.9 ± 33.8	17.0 ± 2.8	1800	75.8 ± 8.4
1.5	146.6 ± 35.2	12.0 ± 4.0	1759	90.5 ± 19.2
0.5	113.2 ± 19.4	18.4 ± 2.8	2083	80.0 ± 9.8

The general relationship between degree of swelling and membrane performance seen in literature was similar. Pure PVA membranes having higher degree of swelling have higher fluxes, conversely membrane selectivity decreases with increasing degree of swelling. This situation is explained with increase of free volume of PVA chains which eases the diffusion of ethanol and water molecules across the membrane. Therefore, selectivity decreases while flux increases [9,39].

Besides, Chen et al. [9] investigated the effect of GA content of the cross-linking solution on the ethanol dehydration performance of approximately 99 % hydrolyzed PVA membranes. Two GA concentrations 1 wt. % and 2.5 wt. % were tested. It was observed that, fluxes decreased with increasing GA content when the feed solution contained less than 50 wt. % water and selectivites enhanced slightly. The fluxes remained constant and selectivities increased slightly with increasing GA content when feed solution contained 30 wt. % water.

PVA is synthesized via the alcoholysis of poly (vinyl acetate) (PVAc). The degree of hydrolysis of PVA indicates the ratio of the number of hydroxyl groups to the sum of the number of hydroxyl and acetyl groups. Since hydroxyl groups are more hydrophilic than acetyl groups, PVA with higher degree of hydrolysis is more hydrophilic than PVA with lower degree of hydrolysis [38]. Therefore, PVA membranes prepared from PVA with higher degree of hydrolysis are more selective than those prepared from lower degree of hydrolysis and their flux values are lower.

In order to have more effective membranes for ethanol dehydration, pure PVA membranes prepared from PVA with 98 % degree of hydrolysis by solvent evaporation technique. Solvent evaporation conditions were the same as the thermally treated pure PVA membranes. Membranes were cross-linked chemically with three different GA concentrations (Table 4.7). Pervaporation test conditions were the same as the thermally treated pure PVA membranes.

Table 4.7 Composition of cross-link solution having different GA content

	Solution 1	**Solution 2**	**Solution 3**
GA, %	0.5	0.75	1.5
H_2SO_4, %	0.5	0.50	0.5
Acetone, %	79.0	78.75	78.0
Water, %	20.0	20.00	20.0

Effect of GA content of cross-linking solution on the pervaporation performances of pure PVA (98 % hyd.) membranes can be seen in Figure 4.13. Membranes cross-linked with solution containing 0.5 wt. % GA had the highest selectivity and normalized flux with the average values of 77.2 and 12000 µm g/m^{2}h, respectively. Increase of GA content to 0.75 wt. % caused a 60 % decrease in normalized flux and a 50 % decrease in selectivity, approximately. When the membranes cross-linked with solution containing 1.5 wt. % GA a slight enhancement in selectivity was observed in comparison to the membranes cross-linked with 0.75 wt. % GA containing solution.

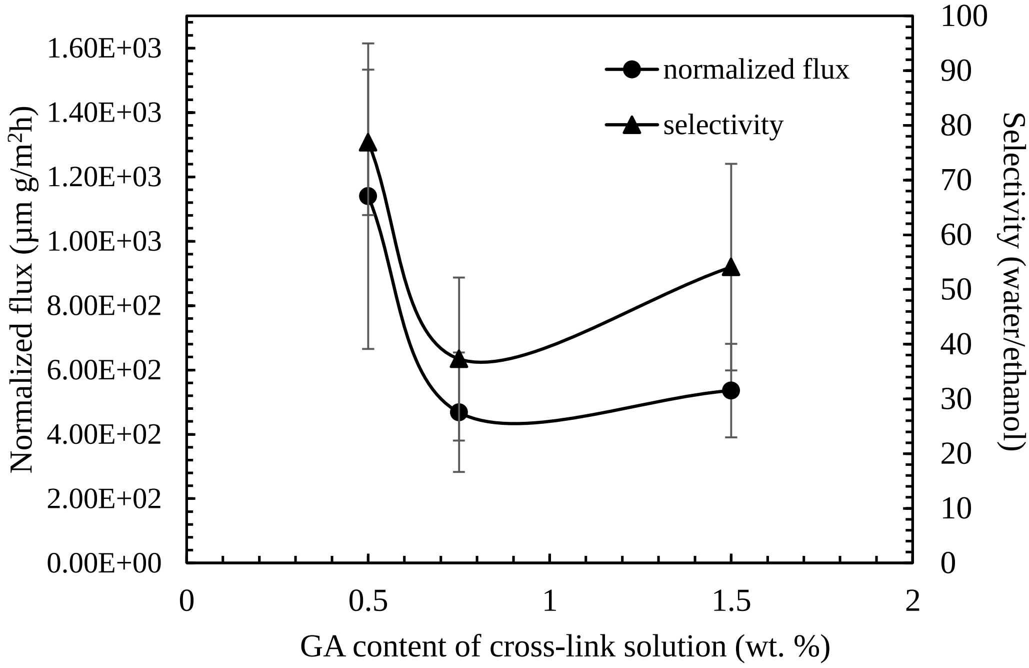


Figure 4.13 Effect of GA concentration of cross-link solution on pervaporation performance of pure PVA (98 % hyd.) membranes

Table 4.8 presents the average flux and selectivity values. The normalized fluxes of theses membranes remained constant when standard deviations were taken into consideration.

Table 4.8 Effect of GA content of cross-link solution on the pervaporation performances and swelling degree of pure PVA (98 % hyd.) membranes

GA Content of Cross-link Solution, wt. %	Flux (J), $g/m^2.h$	Selectivity (α), water/ethanol	PSI, (J.α)	Swelling Degree in Feed, %	Membrane Thickness, μm
0.5	18.2 ± 5.7	77.2 ± 14.0	1405	41.0 ± 4.6	61.6 ± 8.5
0.75	5.6 ± 2.4	37.3 ± 14.9	209	40.1 ± 2.0	85.0 ± 5.0
1.5	9.4 ± 2.9	54.1 ± 19.0	508	31.4 ± 3.0	57.5 ± 2.5

Generally increasing GA concentration in cross-link solution led to less swollen membranes by water [9,35,39]. In the literature, cross-linking reaction alters the polymer structure and makes the polymer network more rigid and less hydrophilic; therefore, degree of swelling generally decreases. A similar effect of GA concentration on degree of swelling was observed in the present study. Membranes cross-linked in solutions with 0.5 % and 0.75 % GA had degree of swelling nearly 40 % but it decreased to 31 % by substantial increase of GA concentration to 1.5 %.

Another common observation in the literature is that; pure PVA membranes with higher degree of swelling have higher fluxes and lower selectivities than those with lower degree of swelling [9,39,73]. This is explained again with increase in free volume of PVA chains, which eases the diffusion of ethanol and water molecules across the membrane. Hence, the lower the GA content of cross-linking solution, the higher the degree of swelling of membrane and lower fluxes are expected. However, Chen et al. [9] observed that fluxes decreased with increasing GA content when the feed solution contained less than 50 wt. % water and selectivites enhanced slightly. The fluxes remained constant and selectivities increased slightly with increasing GA content when feed solution contained 30 wt. % water. That introduces water content of feed solution as an additional parameter affecting membrane performance.

In this study; however, increase of GA concentration of cross-link solution to 1.5 wt. % from 0.5 wt. % caused a decrease in both normalized flux and selectivity. The degree of swelling also decreased. Since the surface of the membranes cross-linked more, the diffusion of cross-linked solution through the membrane might have hindered and caused membranes with less cross-linked interior layer. Therefore, while more cross-linked surface might have led to a decreased normalized flux, less cross-linked interior might have led to decreased selectivity.

Practically PVA is a water soluble polymer. The solubility of PVA in water depends on the degree of hydrolysis. Fully hydrolyzed (98-99 %) PVA is soluble only in hot to boiling water whereas partially hydrolyzed (87-89 %) ones are soluble at room temperature [74]. Pure PVA membranes and PVA/ZIF-8 MMMs were prepared from 98 % hydrolyzed PVA and the polymer solution which contained 10 wt. % PVA. Therefore, there could be undissolved PVA in the polymer solution which may affect the membrane performance. The amount of undissolved PVA can be different in each polymer solution which ended up with reproducibility problem.

In order to alleviate mentioned reproducibility problem, pure PVA membranes prepared from a polymer solution with 5 wt. % PVA instead of 10 wt. %. It was expected that, the decrease of PVA concentration to 5 wt. %, from 10 wt. % could help to form more homogenous polymer solution since it had less undissolved PVA. Therefore it was thought that to prepare more reproducible membranes could be possible.

Effect of PVA concentration of polymer solution on the reproducibility of pure PVA membranes is exhibited in Figure 4.14. Selectivities and normalize fluxes of 3 different membranes prepared from 10 wt. % PVA solution and 5 different membranes prepared from 5 wt. % PVA solution were measured. For each membrane 3 measurements were taken. The reproducibility of pure PVA membranes enhanced by decreasing the PVA concentration of polymer solution to 5 wt. % from 10 wt. %.

The normalized flux of pure PVA membrane risen to 1430 µm g/m^{2}h from 1190 µm g/m^{2}h while selectivity dropped to 40.1 from 77.2 with the decreasing the PVA concentration of polymer solution to 5 wt. % from 10 wt. % as seen in Figure 4.14.

This change in membrane performance indicated that the membrane structure become looser that eased the transport of both ethanol and water molecules through the membrane.

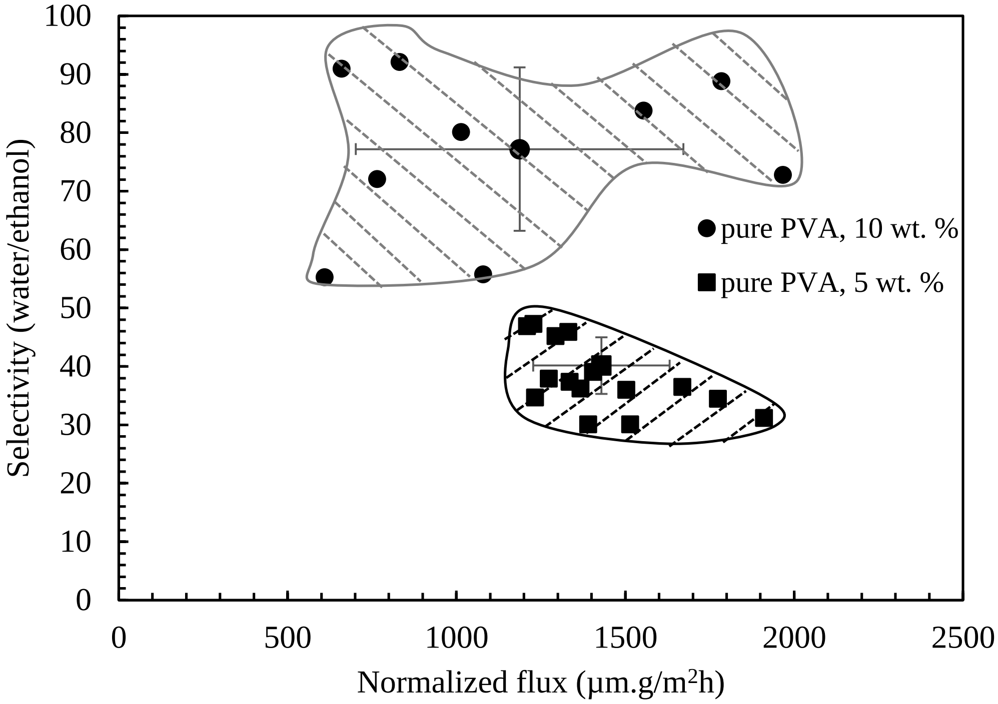


Figure 4.14 Effect of PVA concentration of polymer solution on the reproducibility of pure PVA membranes

Figure 4.15 shows the swelling degrees of pure PVA membranes both prepared from 5 wt. % and 10 wt. % polymer solution. Decreasing the PVA concentration of membrane casting solution to 5 wt. % from 10 wt. % caused almost no change in degree of swelling in feed solution. Figure 4.16 illustrates the final thicknesses of PVA membranes prepared from 5 wt. % and 10 wt. % polymer solution. Final membrane thickness decreased nearly 25 % by decreasing the polymer solution concentration to 5 wt. % from 10 wt. %. Membranes were casted at same conditions but thinner membranes were obtained. Decrease in membrane thickness might be a sign of looser membrane structure which may also explain the increase in normalized flux increase and decline in selectivity.

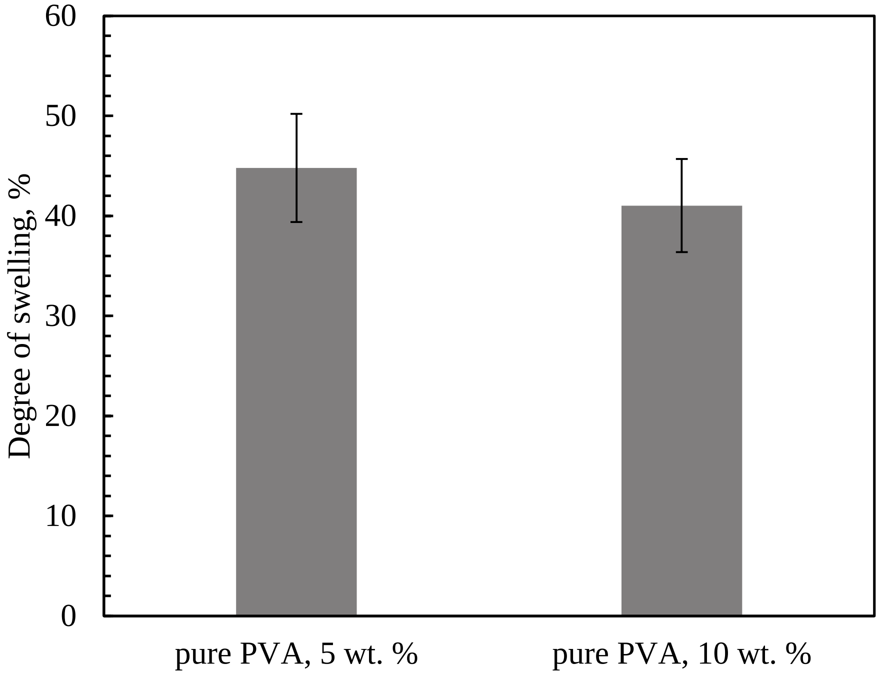


Figure 4.15 Effect of PVA concentration of the polymer solution on the degree of swelling (in feed solution) of pure PVA membranes

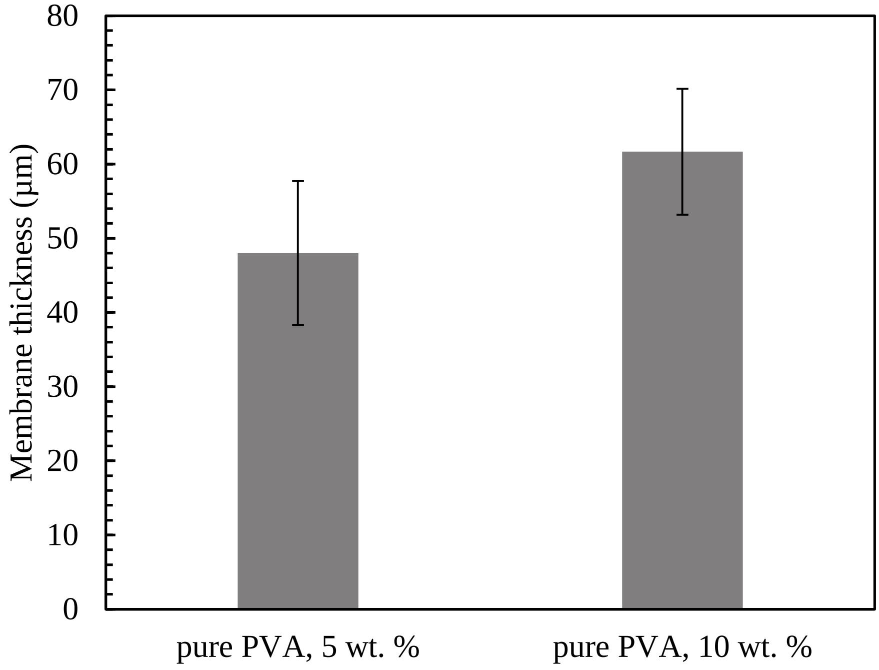


Figure 4.16 Effect of PVA concentration of the polymer solution on the final thickness of pure PVA membranes

4.2.3. Preparation of PVA/ZIF-8 MMMs for Pervaporation

4.2.3.1. ZIF-8 Synthesis

In this part of study, ZIF-8 crystals were synthesized in order to investigate the effects of ZIF-8 addition on the pervaporation performances of the PVA based MMMs. Different molar compositions of the solution, $ZnNO_3.6H_2O$/Hmim/MeOH, were used to synthesize ZIF-8 with particle sizes of 81, 190 and 340 nm. ZIF-8 particles with particle sizes of 17 nm were synthesized by using the recycled mother liquor synthesis methodology [63-64].

XRD measurements were conducted for synthesized ZIF-8 crystals for phase identification. XRD patterns of ZIF-8 crystals were given in Figure 4.17. The peak positions of synthesized ZIF-8s were in agreement with the peak positions of ZIF-8 by Keser at al. [64] and whose synthesis procedure was followed in this study. The crystallinities of ZIF-8 crystals were determined by the area under the peaks. The particle size of 60 nm ZIF-8 sample of Keser study was used as reference ZIF-8 that assumed 100% crystallinity for this calculation [64]. The areas between baseline and peaks were determined from raw X-ray diffraction pattern data by using Jade Software (version 2.1). The area values of the peaks of (011), (002), (112), (022), (013), (222), (114) and (134) planes were used for calculation of the total area values of the samples. The ratio of the total area values of the sample to the total area of the reference sample gives the information of the crystallinity of the sample. Crystallinities and average particle sizes of synthesized ZIF-8 particles based on SEM images with synthesis molar ratios were given in Table 4.9. The SEM images used for determination of particle sizes of ZIF-8 particles can be seen in Figure 4.18.

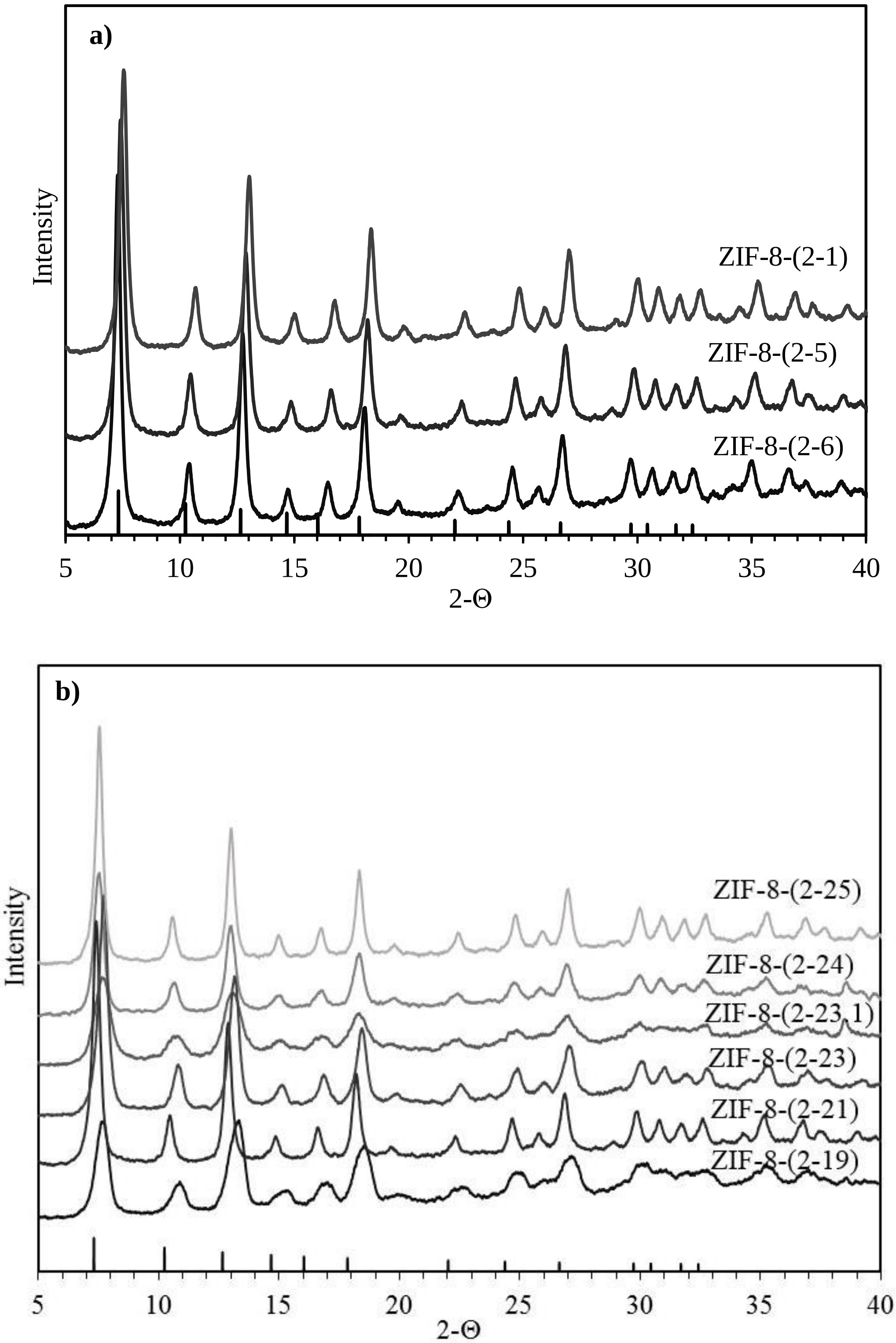


Figure 4.17 XRD patterns of ZIF-8 particles used for preparation of a) MMM-PVA(10)98-GA b) MMM-PVA(5)98-GA

Table 4.9. Crystallinities and average particle sizes of ZIF-8 based on SEM images with synthesis molar ratios

Sample Code	**Sample No**	**MeOH to $ZnNO_3.6H_2O$ Molar Ratio**	**Particle size by SEM images**	**Crystallinity, %**
ZIF-8-(2)	ZIF-8-(2-1)	695.1	81	93.2
ZIF-8-(2)	ZIF-8-(2-5)	695.1	81	90.0
ZIF-8-(2)	ZIF-8-(2-6)	695.1	81	96.9
ZIF-8-(2)	ZIF-8-(2-19)	695.1	81	75.4
ZIF-8-(2)	ZIF-8-(2-21)	695.1	81	86.2
ZIF-8-(2)	ZIF-8-(2-23)	695.1	81	96.8
ZIF-8-(1)	ZIF-8-(2-23.1)	1130	17	62.5
ZIF-8-(4)	ZIF-8-(4-24)	86.9	340	65.3
ZIF-8-(4)	ZIF-8-(4-25)	86.9	340	86.3

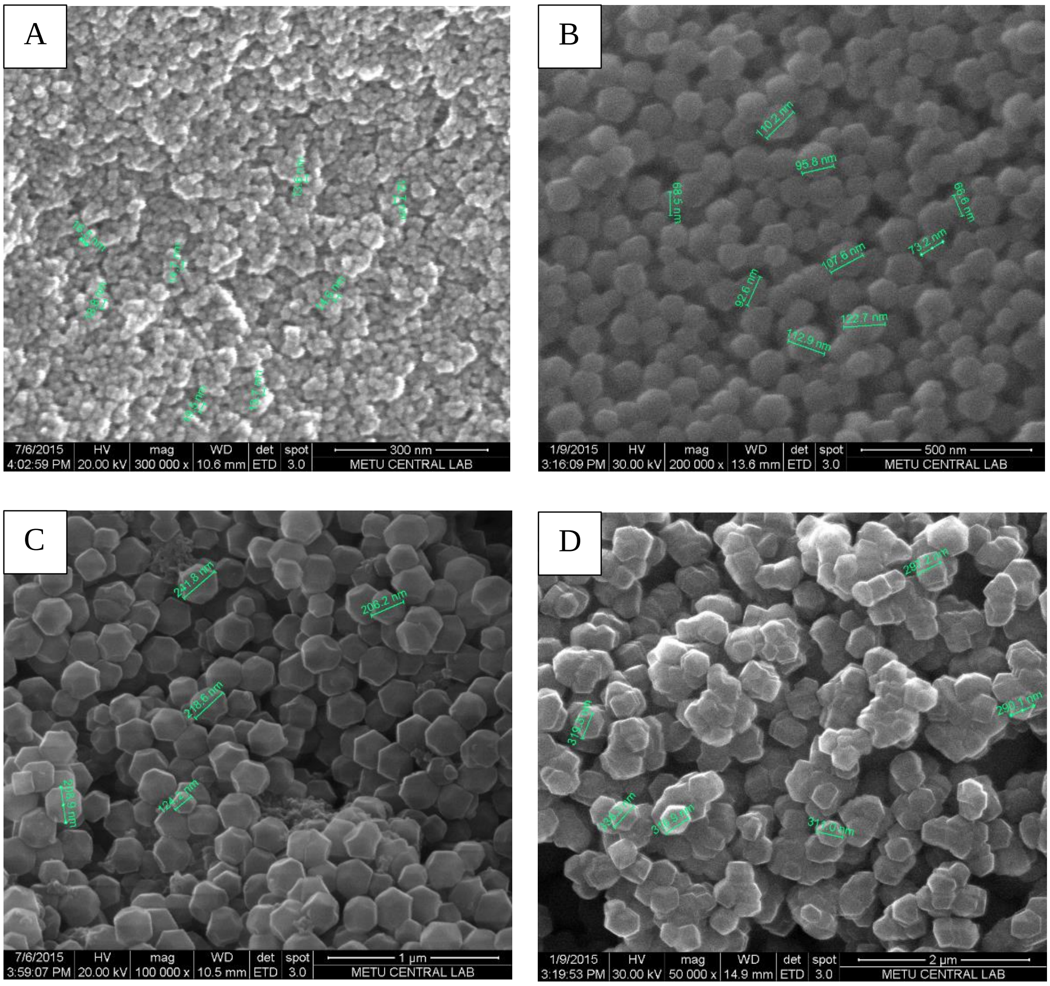


Figure 4.18 SEM images of ZIF-8 crystals A) 17 nm, B) 81 nm, C) 190 nm, D) 340 nm

4.2.3.2. Preparation of PVA/ZIF-8 MMMs by Chemical Cross-linking

In order to enhance the pervaporation performance of pure PVA membranes, MMMs containing 5 wt. % ZIF-8 were prepared using PVA with 98 % degree of hydrolysis. ZIF-8 particles were added into polymer solution directly after separating from the synthesis medium or after drying at 80°C overnight. The XRD patterns of dried ZIF-8 crystals used for MMM preparation and their calculated crystallinities were given in Appendix B.

PES/ZIF-8 MMMs were prepared by solvent evaporation technique from a polymer solution 10 wt. % and the ZIF-8 concentration was 5 wt. % of the total PVA amount. Solvent evaporation conditions were the same as the thermally treated pure PVA membranes. MMMs were cross-linked with solution containing 0.5 wt. % GA since pure PVA membranes cross-linked with this solution had the highest normalized flux and selectivity. Pervaporation test conditions were the same as the thermally treated pure PVA membranes.

Effect of ZIF-8 (81 nm particle size) addition on the pervaporation performance of PVA based membranes and the effect of ZIF-8 condition on the pervaporation performance of MMMs are illustrated in Figure 4.19. ZIF-8 addition led to an enhancement in normalized flux and a decrease in selectivity. Dried ZIF-8 addition caused a 60 % approximate increase in normalized flux and a 60 % approximate decrease in selectivity comparing to pure PVA membranes. As synthesized ZIF-8 addition resulted in 140 % approximate increase in normalized flux and a tremendous decrease in selectivity, nearly 95 %, comparing to pure PVA membranes. Standard deviations from the average values indicated a reproducibility problem and this problem were significant with the pure PVA and PVA/ZIF-8 (dried) membranes.

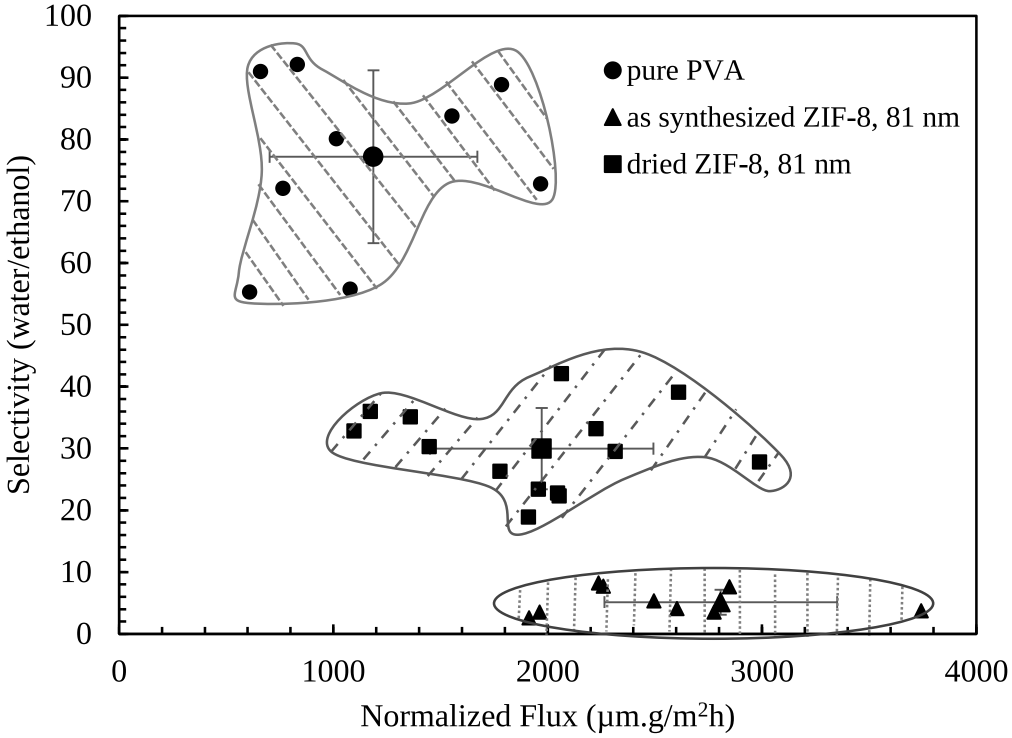


Figure 4.19 Effect of ZIF-8 (81 nm particle size) addition on the pervaporation performance of PVA based membranes

In the literature, it is stated that ZIF-8 loading is an important parameter for pervaporation performance of MMMs. Generally, fluxes of the ZIF-8 filled polymeric membranes enhanced significantly with a loss in selectivity when compared to pristine membranes. This behavior can be attributed to the interfacial voids between ZIF-8 and polymer matrix and particle agglomeration [62]. Besides hydrophobic nature of ZIF-8 particles may lead to higher fluxes but relatively lower selectivities [23,62]. On the other hand, Chung et al. prepared PBI based MMMs with high ZIF-8 loading (33.7 wt. %) and observed that, there was an appreciable rise in selectivity and small a decline in flux when compared to pure PBI membranes [23].

By using the ZIF-8 particles directly after separating from the synthesis medium (as synthesized), it was aimed to provide better dispersion of ZIF-8 into the PVA matrix. It was thought that, since as synthesized ZIF-8 contained small amount of methanol which was the medium of ZIF-8 synthesized reaction; it might have helped to dispersed better in polymer solution. However, membranes prepared with dry ZIF-8 particles had better pervaporation performance than the ones prepared with as-synthesized ZIF-8 particles.

The cross-sectional SEM images of PVA/ZIF-8 (81 nm) MMMs with 5 wt. % ZIF-8 loading, containing dried and as synthesized ZIF-8 are illustrated in Figure 4.20. No significant difference is observed in ZIF-8 distribution of membranes prepared with as-synthesized and dried ZIF-8 (Figure 4.20-A1 and B1). Figure 4.20-A2 and B2 focuses the probable agglomerated areas of the membranes prepared with as-synthesized and dried ZIF-8, respectively. It could be said that dried ZIF-8 particles were distributed slightly better than as-synthesized ones in PVA matrix.

As-synthesized ZIF-8 used for membrane preparation after separating from the synthesize medium which is methanol. Therefore, ZIF-8 added into the membrane casting solution might contain small amount of methanol. Methanol is a non-solvent for PVA, this situation might affect the dispersion of ZIF-8 particle in PVA matrix. Also ZIF-8 particles have a hydrophobic nature and water was used as solvent for preparation of PVA/ZIF-8 MMMs. Therefore, as-synthesized ZIF-8 particles might tend to stay together instead of dispersed in water.

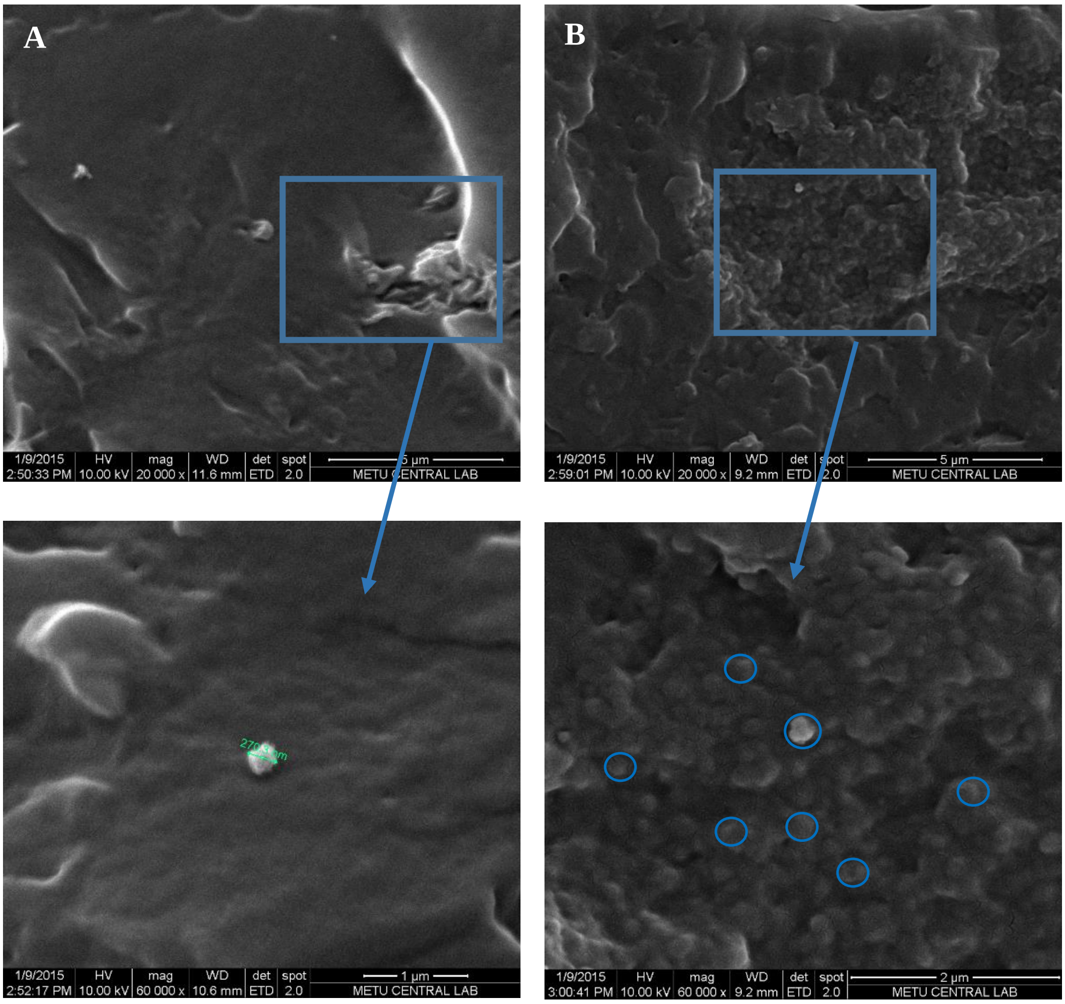


Figure 4.20 Cross-sectional SEM images of PVA/ZIF-8 (81 nm) MMMs with 5 wt. % ZIF-8 loading, containing (A) as synthesized ZIF-8 (B) dried ZIF-8

4.2.3.3. Effect of Particle Size of ZIF-8 on the Pervaporation Performances of PVA/ZIF-8 MMMs

It was observed that with the addition of ZIF-8 particles into the pure PVA membranes selectivity decreased while normalized flux increased. PVA/ZIF-8 MMMs were also prepared from ZIF-8 particles with average particle sizes of 17 nm, 81 nm, 190 nm and 340 nm. The XRD patterns of dried ZIF-8 crystals used for MMM preparation and their calculated crystallinities were given in Appendix B. MMMs were prepared by solvent evaporation technique from a polymer solution 5 wt. % and the ZIF-8 concentration was 5 wt. % of the total PVA amount. ZIF-8 particles were used after overnight drying at 80°C. Solvent evaporation conditions were same with the thermally treated pure PVA membranes. MMMs were cross-linked with solution containing 0.5 wt. % GA. Pervaporation experiment were carried out at the same conditions with the thermally treated pure PVA membranes.

Table 4.10 gives the pervaporation performances of PVA/ZIF-8 MMMs loaded with ZIF-8 particles having different particle sizes. ZIF-8 addition into the pure PVA membranes caused decline in selectivity decline and increase in normalize flux. However, no direct correlation was observed between particle sizes of ZIF-8 and membrane pervaporation performance.

MMMs filled with 190 nm ZIF-8 had the highest selectivity which was % 64 greater than the selectivity of pure PVA membranes. Both normalized flux and selectivity of MMMs filled with ZIF-8 with average particle size of 17 nm had the highest standard deviation values.

Table 4.10 Pervaporation performances of PVA/ZIF-8 MMMs loaded with ZIF-8 particles having different particle sizes

Average Particle Size of ZIF-8, nm	**Flux (J) g/m^2.h**	**Normalized Flux (J$_N$) µm. g/m^2.h**	**Permeate water content, wt. %**	**Selectivity (α), water/ethanol**	**PSI (J.α)**	**Swelling Degree in Feed, %**	**Membrane Thickness, µm**
Pure PVA	31.7 ± 10.6	$1.3*10^3 \pm 0.2*10^3$	81.5 ± 1.8	40.1 ± 4.8	1271	44.8 ± 5.4	47.0 ± 8.1
17	57.7 ± 40.3	$2.3*10^3 \pm 1.1*10^3$	68.9 ± 15.0	24.9 ± 12.7	1437	51.5 ± 11.5	44.6 ± 11.2
81	80.7 ± 25.4	$3.5*10^3 \pm 0.9*10^3$	61.6 ± 6.2	15.5 ± 2.2	1251	52.9 ± 10.3	42.0 ± 6.0
190	27.8 ± 5.0	$1.3*10^3 \pm 0.3*10^3$	86.6 ± 4.3	65.9 ± 20.7	1832	40.9 ± 4.7	47.5 ± 6.1
340	48.1 ± 11.4	$2.2*10^3 \pm 0.3*10^3$	71.7 ± 3.7	23.3 ± 3.8	1120	50.1 ± 3.3	46.0 ± 5.8

All the data taken during the pervaporation experiments with PVA/ZIF-8(17 nm) membranes were shown in Figure 4.21. Selectivities and normalize fluxes of 12 different membranes prepared and for each membrane 2-3 measurements were taken. Group 1 includes 7 membranes while group 2 and group 3 includes 2 and 3 membranes, respectively.

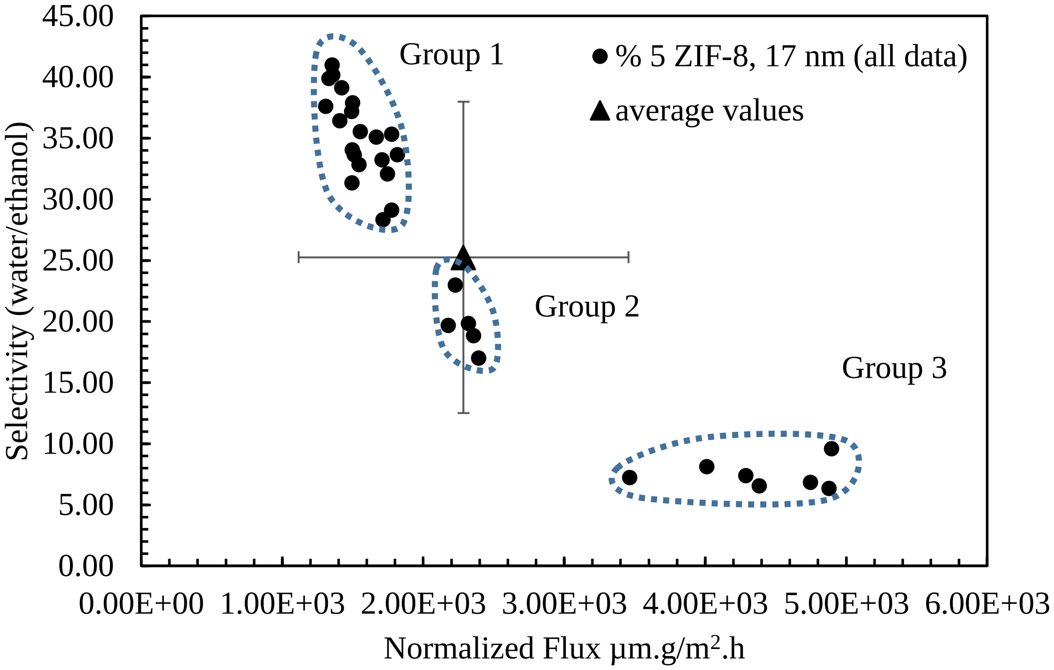


Figure 4.21 All the pervaporation data of PVA/ZIF-8(17 nm) MMMs

Membrane selectivities and normalized fluxes are accumulated in three groups. In the first group, the membranes had a selectivity of approximately 35 and normalized flux of 1800 µm.g/m^{2}h. In the second group the selectivity was about 20 and normalized flux was about 2200 µm.g/m^{2}h. The third group exhibited the worst performance so that selectivity was as low as 10 and flux was above 3600 µm.g/m^{2}h. Although the membranes were prepared using similar condition, there is a great variety in pervaporation performances. One possible explanation is non-uniform distribution of ZIF-8 in membrane matrix. Also random cross-linking of PVA caused by ZIF-8 particles and particle distribution might be reason of variety in pervaporation performances. ZIF-8 particle dispersion might be better for membranes having higher selectivity and lower normalized flux (group 1) while

ZIF-8 particles in the membranes having lower selectivity but higher normalized flux (group 3) might agglomerate more than others.

Figure 4.22 illustrates the cross-sectional SEM images of PVA/ZIF-8(17 nm) MMMs having higher flux but lower selectivity (group 3) and lower flux but higher selectivity (group 1). No significant difference is observed in ZIF-8 distribution of membranes (Figure 4.22-A1 and A2). Figure 4.22-A2 and B2 focuses the probable ZIF-8 agglomerated areas of the membranes. Almost no difference is seen in the structures of membrane matrix due to agglomeration.

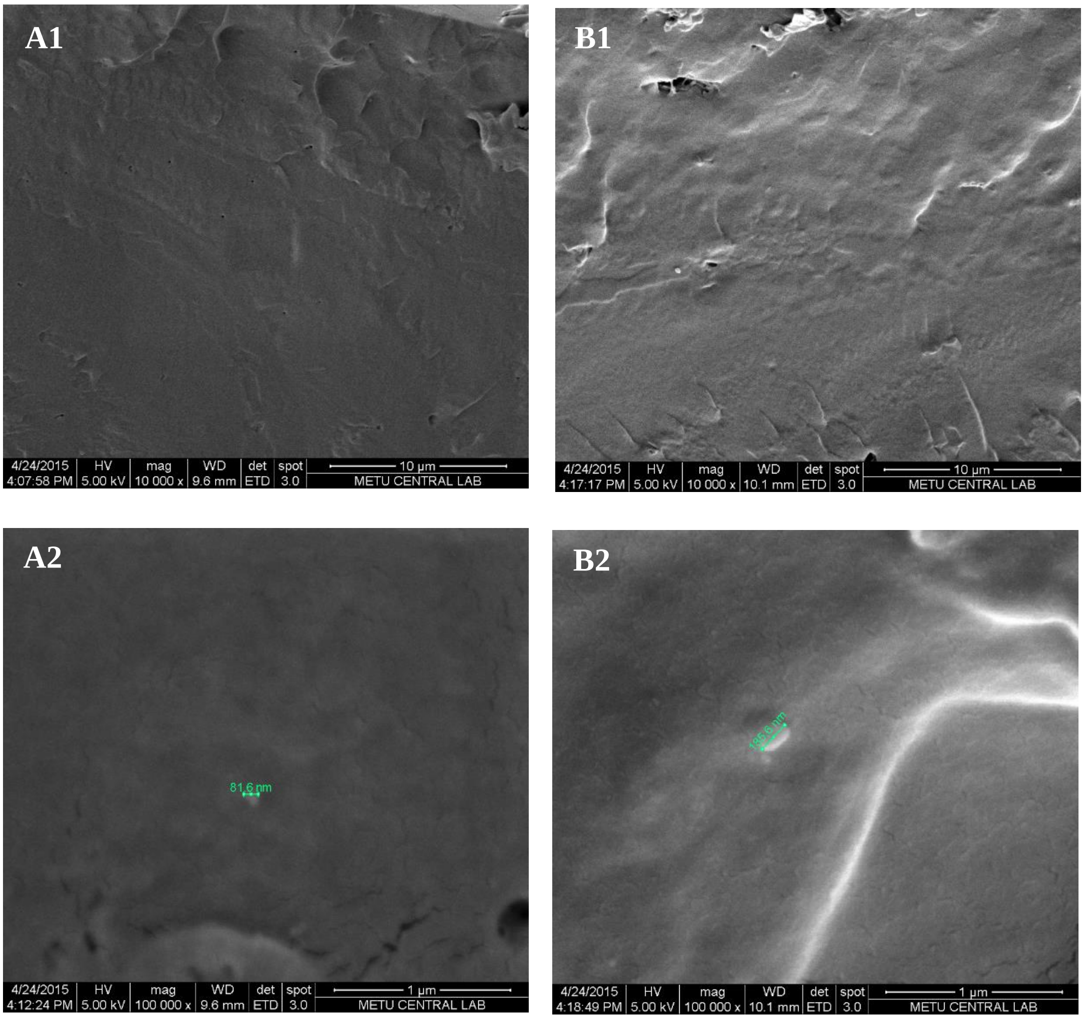


Figure 4.22 Cross-sectional SEM images of PVA/ZIF-8(17 nm) having a) higher flux and lower selectivity b) lower flux and higher selectivity

Figure 4.23 illustrates the swelling degrees of PVA/ZIF-8 MMMs in feed solution according to particle size of ZIF-8 crystals. No significant change is observed in degree of swelling with changing particle size of ZIF-8 particles. However, with a small difference the least swollen membranes are the ones filled with ZIF-8 with particle size of 190 nm and this result is compatible with pervaporation performances of these membranes.

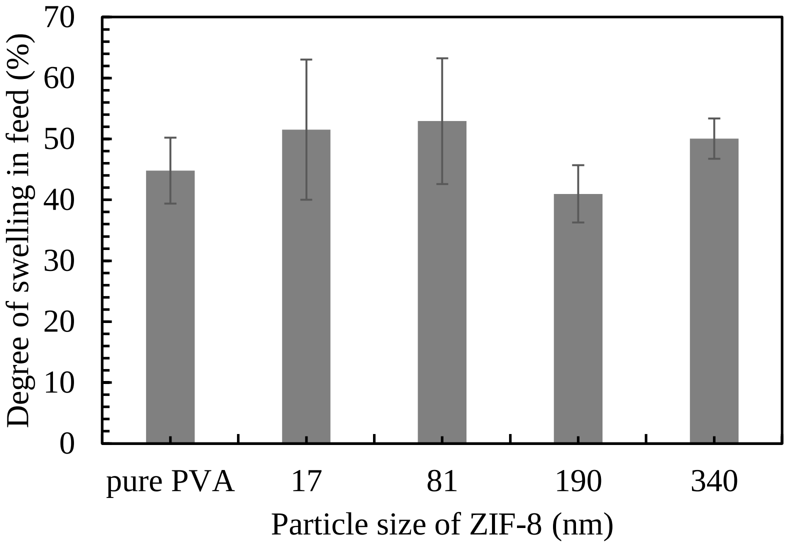


Figure 4.23 Swelling degree of PVA/ZIF-8 in feed solution according to particles size of ZIF-8 crystals

In order to better observe the effect of particle size of ZIF-8 crystals on the pervaporation performance, normalized flux and selectivity of each MMM and pure PVA membrane were shown in Figure 4.24. MMMs filled with 340 nm ZIF-8 particles had better normalized flux than pure PVA membranes with a selectivity loss and they had better selectivity than MMMs filled with 81 nm ZIF-8 with a lower normalized flux. This situation could be related to fact that there were higher numbers of particles when smaller particle size of ZIF-8 was used in the MMM. Moreover, the normalized flux of MMMs filled with 81 nm ZIF-8 particles were varying without much change in selectivity.

In general manner, both normalized flux and selectivity of MMMs did not have a regular trend according to particle size of ZIF-8. One possible explanation is heterogeneity of MMM in the level of polymer chains.

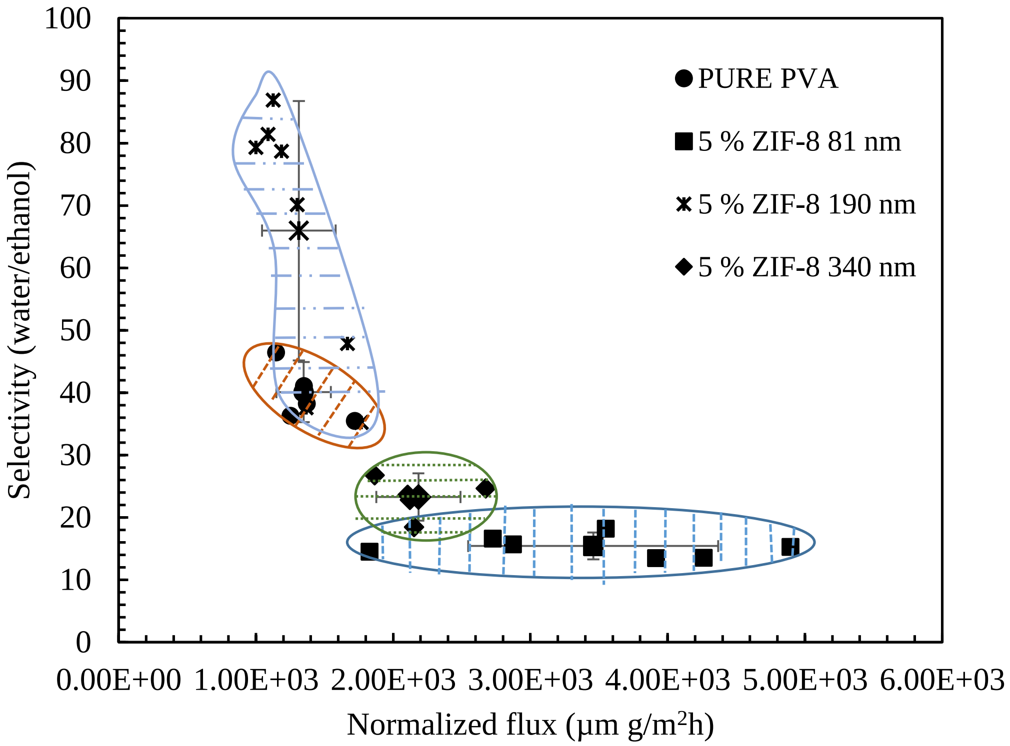


Figure 4.24 Pervaporation data of each PVA/ZIF-8 MMM according to particle size of ZIF-8 and the average values

In order to understand the reason of normalize flux variation of 81 nm ZIF-8 loaded MMMs, cross-sectional SEM images of MMMs having lowest and highest normalized flux were investigated. Figure 4.25 illustrates the cross-sectional SEM images of stated MMMs. Figures 4.25-A1 and B1 had not a distinct difference both ZIF-8 particle distribution and PVA-ZIF-8 adhesion point of view. However, in both SEM images distribution of ZIF-8 particles into the PVA matrix was not actually uniform and could not alter the structure of PVA matrix significantly. In Figures 4.25-A2 and B2 the agglomerated areas are seen for both membranes. There is no significant difference in ZIF-8 agglomeration. The normalize flux variation of 81 nm ZIF-8 loaded MMMs might be caused by agglomerated particles located in a few points in the membrane. The number of points of agglomerated particles and particle distribution due to agglomeration could be different for each membrane

Therefore, other parts of the membrane might have the properties similar to pure PVA membranes.

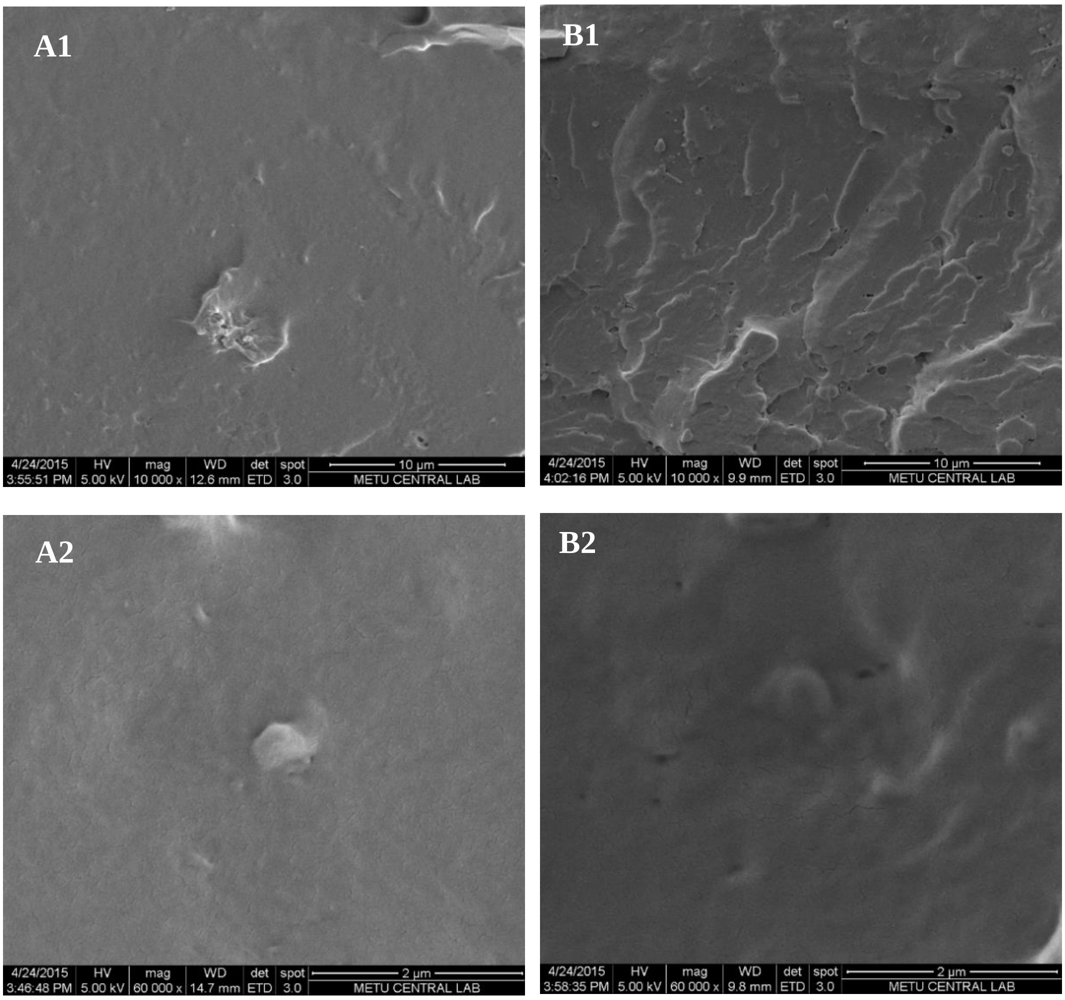


Figure 4.25 Cross-sectional SEM images of PVA/ZIF-8(81 nm) having a) lowest normalized flux b) highest normalized flux

SEM images of the cross-sectional views of PVA/ZIF-8 MMM with 5 % loading MMMs according to particle size of ZIF-8s were shown in Figure 4.26. ZIF-8 particles, in MMM filled with 17 nm ZIF-8 are hardly seen in membrane matrix (A). This can be the indication of particle agglomeration. The particle distribution in PVA matrix is better observed in MMM filled with 81 nm ZIF-8 (B). However, particle agglomeration is still observed. ZIF-8 particles in MMM filled with 190 nm ZIF-8 (C) is hardly observed. It could be said that the structure of membrane did not change with the addition of 190 nm ZIF-8. It was already seen that the pervaporation performance of this membrane was the closest to pure PVA. When the SEM image of MMM filled with 340 nm ZIF-8 (D) was observed, it is seen that the ZIF-8 particles are placed mostly in the part of the membrane which might have caused the membrane to behave like a two layered membrane.

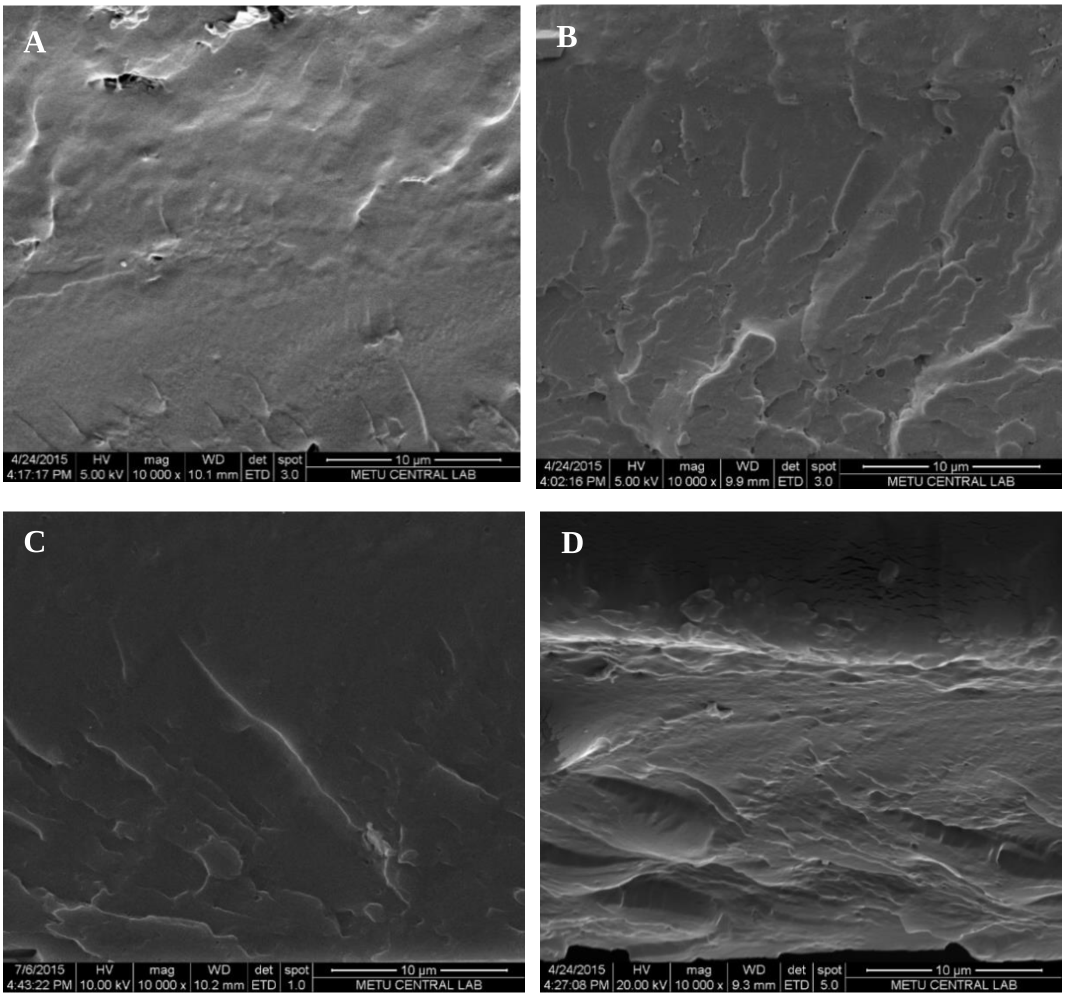


Figure 4.26 Cross-sectional SEM images of PVA/ZIF-8 MMM with 5 % loading with respect to increasing particle size of ZIF-8 A) 17 nm B) 81 nm C) 190 nm D) 340 nm

CHAPTER 5

CONCLUSION

In this study, asymmetric pure PES and PES/ZIF-8 membranes were prepared. Pure PES membranes prepared with both wet and dry-wet phase inversion while PES/ZIF-8 MMM were prepared with wet phase inversion technique. Moreover, dense pure PVA membranes were prepared with solvent evaporation technique using PVA with degree of hydrolysis 87-89 % and 98 %. Pure PVA membranes were cross-linked thermally and the effect of cross-linking time and temperature on the pervaporation performance were investigated. Pure PVA membranes were also cross-linked chemically with a solution containing glutaraldehyde (GA). Finally, ZIF-8 particles were added to 98 % hydrolyzed PVA membranes and cross-linked chemically. In order to examine the effect of particle size of ZIF-8 crystals on the pervaporation performances, MMMs were prepared with ZIF-8 crystals whose particle sizes were 17, 81, 190 and 340 nm. The pervaporation performance of all synthesized membranes were tested with ethanol-water (10/90 wt. %) mixture at 25°C.

Asymmetric pure PES membranes and PES/ZIF-8 MMM were prepared by wet-phase inversion and dry-wet phase inversion techniques. However, reproducible membranes could not be obtained.

Pure PVA membranes prepared from 87-89 % degree of hydrolysis PVA by solvent evaporation technique. Membranes were prepared from PVA-water solution with a

PVA content of 10 wt. % and cross-linked thermally at different temperatures (90°C-160°C) for different times (1 hour and 48 hours). Short (1 hour) cross-linking periods caused an excessive decrease in normalized flux and a 20 % approximate increase in selectivity when compared to non-treated membranes. Membranes cross-linked thermally for longer time (48 hours) had more than two times greater selectivities than membranes cross-linked for short time (1 hour).

Pure PVA membranes prepared from 87-89 % degree of hydrolysis PVA cross-linked chemically with GA solution with GA concentration of 0.5-3.0 wt. %. With increasing GA concentration the flux and selectivity of 87-89 % hydrolyzed PVA membranes passed through a maximum and minimum. The best performing pure PVA (98 % hydrolyzed) membranes were the ones cross-linked with 0.5 wt. % GA containing solution.

Pure PVA membranes prepared from 10 wt. % PVA solution had some reproducibility problems. More reproducible pure PVA membranes were prepared by decreasing the PVA concentration of polymer solution to 5 wt. % from 10 wt. %.

The 5 % (w/w) ZIF-8 loaded PVA/ZIF-8 MMMs prepared using both dried and as-synthesized ZIF-8 particles with average particle size of 81 nm. PVA/ZIF-8 MMM prepared with dried ZIF-8 were more selective but less permeable than prepared with as-synthesized ZIF-8.

Both normalized flux and selectivity of MMMs did not have a regular trend according to particle size of ZIF-8 particles. The best performing MMMs were the ones filled with 190 nm ZIF-8 with an average normalize flux of 1300 µm g/m^{2}h and selectivity of 66, which was % 64 greater than the selectivity of pure PVA membranes.

REFERENCES

[1] M. Mulder, Basic Principles of Membrane Technology, 2nd ed., Kluwer Academic Publishers, Netherlands, 1998.

[2] R.W. Baker, Membrane Technology and Applications, 2nd ed., John Wiley & Sons, Ltd, USA, 2004. doi:10.1002/0470020393.

[3] T.C. Bowen, R.D. Noble, J.L. Falconer, Fundamentals and applications of pervaporation through zeolite membranes, J. Memb. Sci. 245 (2004) 1–33. doi:10.1016/j.memsci.2004.06.059.

[4] B. Bolto, M. Hoang, Z. Xie, A review of membrane selection for the dehydration of aqueous ethanol by pervaporation, Chem. Eng. Process. Process Intensif. 50 (2011) 227–235. doi:10.1016/j.cep.2011.01.003.

[5] S.L. Wee, C.T. Tye, S. Bhatia, Membrane separation process-Pervaporation through zeolite membrane, Sep. Purif. Technol. 63 (2008) 500–516. doi:10.1016/j.seppur.2008.07.010.

[6] E. A. Fouad, X. Feng, Use of pervaporation to separate butanol from dilute aqueous solutions: Effects of operating conditions and concentration polarization, J. Memb. Sci. 323 (2008) 428–435. doi:10.1016/j.memsci.2008.06.054.

[7] X. Feng, R.Y.M. Huang, Liquid Separation by Membrane Pervaporation: A Review, Ind. Eng. Chem. Res. 36 (1997) 1048–1066. doi:10.1021/ie960189g.

[8] P.D. Chapman, T. Oliveira, A.G. Livingston, K. Li, Membranes for the dehydration of solvents by pervaporation, J. Memb. Sci. 318 (2008) 5–37. doi:10.1016/j.memsci.2008.02.061.

[9] M.N. Hyder, R.Y.M. Huang, P. Chen, Correlation of physicochemical characteristics with pervaporation performance of poly(vinyl alcohol) membranes, J. Memb. Sci. 283 (2006) 281–290. doi:10.1016/j.memsci.2006.06.045.

[10] P. Peng, B. Shi, Y. Lan, A Review of Membrane Materials for Ethanol Recovery by Pervaporation, Sep. Sci. Technol. 46 (2010) 234–246. doi:10.1080/01496395.2010.504681.

[11] R.W. Baker, J.G. Wijmans, Y. Huang, Permeability, permeance and selectivity: A preferred way of reporting pervaporation performance data, J. Memb. Sci. 348 (2010) 346–352. doi:10.1016/j.memsci.2009.11.022.

[12] V. V. Namboodiri, L.M. Vane, High permeability membranes for the dehydration of low water content ethanol by pervaporation, J. Memb. Sci. 306 (2007) 209–215. doi:10.1016/j.memsci.2007.08.050.

[13] B. Smitha, D. Suhanya, S. Sridhar, M. Ramakrishna, Separation of organic-organic mixtures by pervaporation - A review, J. Memb. Sci. 241 (2004) 1–21. doi:10.1016/j.memsci.2004.03.042.

[14] A.C. Duque Salazar, M.Á. Gómez García, J. Fontalvo, M. Jedrzejczyk, J.M. Rynkowski, I. Dobrosz-Gómez, Ethanol dehydration by pervaporation using microporous silica membranes, Desalin. Water Treat. (2012) 1–9. doi:10.1080/19443994.2012.728053.

[15] H.B. Tanh Jeazet, C. Staudt, C. Janiak, Metal–organic frameworks in mixed-matrix membranes for gas separation, Dalt. Trans. 41 (2012). doi:10.1039/c2dt31550e.

[16] P. Shao, R.Y.M. Huang, Polymeric membrane pervaporation, J. Memb. Sci. 287 (2007) 162–179. doi:10.1016/j.memsci.2006.10.043.

[17] C. Guo, L. Zhou, J. Lv, Effects of expandable graphite and modified ammonium polyphosphate on the flame-retardant and mechanical properties of wood flour-polypropylene composites, Polym. Polym. Compos. 21 (2013) 449–456. doi:10.1002/app.

[18] B. Bolto, T. Tran, M. Hoang, Z. Xie, Crosslinked poly(vinyl alcohol) membranes, Prog. Polym. Sci. 34 (2009) 969–981. doi:10.1016/j.progpolymsci.2009.05.003.

[19] T.S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, Prog. Polym. Sci. 32 (2007) 483–507. doi:10.1016/j.progpolymsci.2007.01.008.

[20] P.S. Goh, A. F. Ismail, S.M. Sanip, B.C. Ng, M. Aziz, Recent advances of inorganic fillers in mixed matrix membrane for gas separation, Sep. Purif. Technol. 81 (2011) 243–264. doi:10.1016/j.seppur.2011.07.042.

[21] S.G. Adoor, L.S. Manjeshwar, S.D. Bhat, T.M. Aminabhavi, Aluminum-rich zeolite beta incorporated sodium alginate mixed matrix membranes for

pervaporation dehydration and esterification of ethanol and acetic acid, J. Memb. Sci. 318 (2008) 233–246. doi:10.1016/j.memsci.2008.02.043.

[22] S. Mosleh, T. Khosravi, O. Bakhtiari, T. Mohammadi, Zeolite filled polyimide membranes for dehydration of isopropanol through pervaporation process, Chem. Eng. Res. Des. 90 (2012) 433–441. doi:10.1016/j.cherd.2011.07.021.

[23] G.M. Shi, T. Yang, T.S. Chung, Polybenzimidazole (PBI)/zeolitic imidazolate frameworks (ZIF-8) mixed matrix membranes for pervaporation dehydration of alcohols, J. Memb. Sci. 415-416 (2012) 577–586. doi:10.1016/j.memsci.2012.05.052.

[24] L.Y. Jiang, Y. Wang, T.S. Chung, X.Y. Qiao, J.Y. Lai, Polyimides membranes for pervaporation and biofuels separation, Prog. Polym. Sci. 34 (2009) 1135–1160. doi:10.1016/j.progpolymsci.2009.06.001.

[25] J.L.C. Rowsell, O.M. Yaghi, Metal-organic frameworks: A new class of porous materials, Microporous Mesoporous Mater. 73 (2004) 3–14. doi:10.1016/j.micromeso.2004.03.034.

[26] S. Liu, G. Liu, X. Zhao, W. Jin, Hydrophobic-ZIF-71 filled PEBA mixed matrix membranes for recovery of biobutanol via pervaporation, J. Memb. Sci. 446 (2013) 181–188. doi:10.1016/j.memsci.2013.06.025.

[27] X.L. Liu, Y.S. Li, G.Q. Zhu, Y.J. Ban, L.Y. Xu, W.S. Yang, An organophilic pervaporation membrane derived from metal-organic framework nanoparticles for efficient recovery of bio-alcohols, Angew. Chemie - Int. Ed. 50 (2011) 10636–10639. doi:10.1002/anie.201104383.

[28] K.S. Park, Z. Ni, A.P. Côté, J.Y. Choi, R. Huang, F.J. Uribe-Romo, et al., Exceptional chemical and thermal stability of zeolitic imidazolate frameworks., Proc. Natl. Acad. Sci. U. S. A. 103 (2006) 10186–10191. doi:10.1073/pnas.0602439103.

[29] N. Keser Demir, B. Topuz, L. Yilmaz, H. Kalipcilar, Synthesis of ZIF-8 from recycled mother liquors, Microporous Mesoporous Mater. 198 (2014) 291–300. doi:10.1016/j.micromeso.2014.07.052.

[30] M.J.C. Ordoñez, K.J. Balkus, J.P. Ferraris, I.H. Musselman, Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes, J. Memb. Sci. 361 (2010) 28–37. doi:10.1016/j.memsci.2010.06.017.

[31] K. Díaz, M. López-González, L.F. Del Castillo, E. Riande, Effect of zeolitic imidazolate frameworks on the gas transport performance of ZIF8-poly(1,4-phenylene ether-ether-sulfone) hybrid membranes, J. Memb. Sci. 383 (2011) 206–213. doi:10.1016/j.memsci.2011.08.042.

[32] Q. Song, S.K. Nataraj, M. V. Roussenova, J.C. Tan, D.J. Hughes, W. Li, et al., Zeolitic imidazolate framework (ZIF-8) based polymer nanocomposite membranes for gas separation, Energy Environ. Sci. 5 (2012) 8359. doi:10.1039/c2ee21996d.

[33] S. Jessie Lue, S.H. Peng, Polyurethane (PU) membrane preparation with and without hydroxypropyl-β-cyclodextrin and their pervaporation characteristics, J. Memb. Sci. 222 (2003) 203–217. doi:10.1016/S0376-7388(03)00291-6.

[34] H.M. Van Veen, Y.C. Van Delft, C.W.R. Engelen, P.P. a C. Pex, Dewatering of organics by pervaporation with silica membranes, Sep. Purif. Technol. 22-23 (2001) 361–366. doi:10.1016/S1383-5866(00)00119-2.

[35] J. Yu, C.H. Lee, W.H. Hong, Performances of crosslinked asymmetric poly(vinyl alcohol) membranes for isopropanol dehydration by pervaporation, Chem. Eng. Process. 41 (2002) 693–698. doi:10.1016/S0255-2701(01)00186-6.

[36] B. Villagra Di Carlo, A.C. Habert, Plasma-treated polyethersulfone coated with crosslinked poly(vinyl alcohol): Composite membranes for pervaporation dehydration of ethanol, J. Mater. Sci. 48 (2013) 1457–1464. doi:10.1007/s10853-012-6899-8.

[37] A. Svang-Ariyaskul, R.Y.M. Huang, P.L. Douglas, R. Pal, X. Feng, P. Chen, et al., Blended chitosan and polyvinyl alcohol membranes for the pervaporation dehydration of isopropanol, J. Memb. Sci. 280 (2006) 815–823. doi:10.1016/j.memsci.2006.03.001.

[38] Y. Ueda, T. Tanaka, A. Iizuka, Y. Sakai, T. Kojima, S. Satokawa, et al., Membrane separation of ethanol from mixtures of gasoline and bioethanol with heat-treated PVA membranes, Ind. Eng. Chem. Res. 50 (2011) 1023–1027. doi:10.1021/ie1014662.

[39] V.S. Praptowidodo, Influence of swelling on water transport through PVA-based membrane, J. Mol. Struct. 739 (2005) 207–212. doi:10.1016/j.molstruc.2004.04.035.

[40] M. Krumova, Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol), Polymer (Guildf). 41 (2000) 9265–9272. doi:10.1016/S0032-3861(00)00287-1.

[41] A. Hasimi, A. Stavropoulou, K.G. Papadokostaki, M. Sanopoulou, Transport of water in polyvinyl alcohol films: Effect of thermal treatment and chemical crosslinking, Eur. Polym. J. 44 (2008) 4098–4107. doi:10.1016/j.eurpolymj.2008.09.011.

[42] W. Zhang, Z. Zhang, X. Wang, Investigation on surface molecular conformations and pervaporation performance of the poly(vinyl alcohol) (PVA) membrane, J. Colloid Interface Sci. 333 (2009) 346–353. doi:10.1016/j.jcis.2009.01.058.

[43] C.K. Yeom, S.H. Lee, J.M. Lee, Pervaporative permeations of homologous series of alcohol aqueous mixtures through a hydrophilic membrane, J. Appl. Polym. Sci. 79 (2001) 703–713. doi:10.1002/1097-4628(20010124)79:4<703::AID-APP150>3.0.CO;2-O.

[44] G.R. Guillen, Y. Pan, M. Li, E.M. V Hoek, Preparation and characterization of membranes formed by nonsolvent induced phase separation: A review, Ind. Eng. Chem. Res. 50 (2011) 3798–3817. doi:10.1021/ie101928r.

[45] J.C. Jansen, M.G. Buonomenna, A. Figoli, E. Drioli, Asymmetric membranes of modified poly(ether ether ketone) with an ultra-thin skin for gas and vapour separations, J. Memb. Sci. 272 (2006) 188–197. doi:10.1016/j.memsci.2005.07.036.

[46] I. Pinnau, W.J. Koros, Structures and gas separation properties of asymmetric polysulfone membranes made by dry, wet, and dry/wet phase inversion, J. Appl. Polym. Sci. 43 (1991) 1491–1502. doi:10.1002/app.1991.070430811.

[47] X. Feng, R.Y.M. Huang, Preparation and performance of asymmetric polyetherimide membranes for isopropanol dehydration by pervaporation, J. Memb. Sci. 109 (1996) 165–172. doi:10.1016/0376-7388(95)00198-0.

[48] H. Wu, X. Li, M. Nie, B. Li, Z. Jiang, Integral PVA-PES composite membranes by surface segregation method for pervaporation dehydration of ethanol, Chinese J. Chem. Eng. 19 (2011) 855–862. doi:10.1016/S1004-9541(11)60065-7.

[49] A. Kudasheva, S. Sorribas, B. Zornoza, C. Téllez, J. Coronas, Pervaporation of water/ethanol mixtures through polyimide based mixed matrix membranes containing ZIF-8, ordered mesoporous silica and ZIF-8-silica core-shell spheres, J. Chem. Technol. Biotechnol. (2014). doi:10.1002/jctb.4352.

[50] E. Okumuş, T. Gürkan, L. Yilmaz, Effect of fabrication and process parameters on the morphology and performance of a PAN-based zeolite-filled pervaporation membrane, J. Memb. Sci. 223 (2003) 23–38. doi:10.1016/S0376-7388(03)00287-4.

[51] Z. Gao, Y. Yue, W. Li, Application of zeolite-filled pervaporation membrane, Zeolites. 16 (1996) 70–74. doi:10.1016/0144-2449(95)00094-1.

[52] D. Kang, H.M. Tong, J. Zang, R.P. Choudhury, D.S. Sholl, H.W. Beckham, et al., Single-Walled Aluminosilicate Nanotube/Poly(vinyl alcohol) Nanocomposite Membranes, (2012).

[53] S.G. Adoor, V. Rajineekanth, M.N. Nadagouda, K. Chowdoji Rao, D.D. Dionysiou, T.M. Aminabhavi, Exploration of nanocomposite membranes composed of phosphotungstic acid in sodium alginate for separation of aqueous-organic mixtures by pervaporation, Sep. Purif. Technol. 113 (2013) 64–74. doi:10.1016/j.seppur.2013.03.051.

[54] E.J. Flynn, D. A. Keane, P.M. Tabari, M. a. Morris, Pervaporation performance enhancement through the incorporation of mesoporous silica spheres into PVA membranes, Sep. Purif. Technol. 118 (2013) 73–80. doi:10.1016/j.seppur.2013.06.034.

[55] H.C. Zhou, J.R. Long, O.M. Yaghi, Introduction to metal-organic frameworks, Chem. Rev. 112 (2012) 673–674. doi:10.1021/cr300014x.

[56] B. Zornoza, C. Tellez, J. Coronas, J. Gascon, F. Kapteijn, Metal organic framework based mixed matrix membranes: An increasingly important field of research with a large application potential, Microporous Mesoporous Mater. 166 (2013) 67–78. doi:10.1016/j.micromeso.2012.03.012.

[57] S. Basu, M. Maes, A. Cano-Odena, L. Alaerts, D.E. De Vos, I.F.J. Vankelecom, Solvent resistant nanofiltration (SRNF) membranes based on metal-organic frameworks, J. Memb. Sci. 344 (2009) 190–198. doi:10.1016/j.memsci.2009.07.051.

[58] S.R. Venna, J.B. Jasinski, M. A. Carreon, Structural evolution of zeolitic imidazolate framework-8, J. Am. Chem. Soc. 132 (2010) 18030–18033. doi:10.1021/ja109268m.

[59] H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, Zeolitic Imidazolate Framework Molecular Sieving Membrane Titania Support, (2010) 907359. doi:10.1021/cm902032y.

[60] X. Liu, H. Jin, Y. Li, H. Bux, Z. Hu, Y. Ban, et al., Metal-organic framework ZIF-8 nanocomposite membrane for efficient recovery of furfural via pervaporation and vapor permeation, J. Memb. Sci. 428 (2013) 498–506. doi:10.1016/j.memsci.2012.10.028.

[61] C.H. Kang, Y.F. Lin, Y.S. Huang, K.L. Tung, K.S. Chang, J.T. Chen, et al., Synthesis of ZIF-7/chitosan mixed-matrix membranes with improved separation performance of water/ethanol mixtures, J. Memb. Sci. 438 (2013) 105–111. doi:10.1016/j.memsci.2013.03.028.

[62] M. Amirilargani, B. Sadatnia, Poly(vinyl alcohol)/zeolitic imidazolate frameworks (ZIF-8) mixed matrix membranes for pervaporation dehydration

of isopropanol, J. Memb. Sci. 469 (2014) 1–10. doi:10.1016/j.memsci.2014.06.034.

[63] I. Ayas, Effect of the Particle Size of Zif-8 on the Separation Performance of ZIF-8/PNA/PES Membranes, METU, 2014.

[64] N. Keser, Production and Performance Evaluation of ZIF-8 Based Binary and Ternary Mixed Matrix Gas Separation Membranes, METU, 2012.

[65] H. A. Tsai, Y.S. Ciou, C.C. Hu, K.R. Lee, D.G. Yu, J.Y. Lai, Heat-treatment effect on the morphology and pervaporation performances of asymmetric PAN hollow fiber membranes, J. Memb. Sci. 255 (2005) 33–47. doi:10.1016/j.memsci.2004.09.052.

[66] F. Zhou, W.J. Koros, Study of thermal annealing on Matrimid?? fiber performance in pervaporation of acetic acid and water mixtures, Polymer (Guildf). 47 (2006) 280–288. doi:10.1016/j.polymer.2005.11.017.

[67] T.S. Chung, W.F. Guo, Y. Liu, Enhanced Matrimid membranes for pervaporation by homogenous blends with polybenzimidazole (PBI), J. Memb. Sci. 271 (2006) 221–231. doi:10.1016/j.memsci.2005.07.042.

[68] H. Yanagishita, C. Maejima, D. Kitamoto, T. Nakane, Preparation of asymmetric polyimide membrane for water/ethanol separation in pervaporation by the phase inversion process, J. Memb. Sci. 86 (1994) 231–240. doi:10.1016/0376-7388(93)E0147-C.

[69] H. Wu, X. Li, C. Zhao, X. Shen, Z. Jiang, X. Wang, Chitosan / Sulfonated Polyethersulfone − Polyethersulfone (CS / SPES- PES) Composite Membranes for Pervaporative Dehydration of Ethanol, (2013).

[70] L. Gao, B. Tang, P. Wu, An experimental investigation of evaporation time and the relative humidity on a novel positively charged ultrafiltration membrane via dry-wet phase inversion, J. Memb. Sci. 326 (2009) 168–177. doi:10.1016/j.memsci.2008.09.048.

[71] Z. Huang, H.M. Guan, W.L. Tan, X.Y. Qiao, S. Kulprathipanja, Pervaporation study of aqueous ethanol solution through zeolite-incorporated multilayer poly(vinyl alcohol) membranes: Effect of zeolites, J. Memb. Sci. 276 (2006) 260–271. doi:10.1016/j.apcatb.2005.10.011.

[72] M.C. Burshe, S.B. Sawant, J.B. Joshi, V.G. Pangarkar, Sorption and permeation of binary water-alcohol systems through PVA membranes crosslinked with multifunctional crosslinking agents, Sep. Purif. Technol. 12 (1997) 145–156. doi:10.1016/S1383-5866(97)00042-7.

[73] C.H. Lee, W.H. Hong, Influence of different degrees of hydrolysis of poly (vinyl alcohol) membrane on transport properties in pervaporation of IPA / water mixture, J. Memb. Sci. 135 (1997) 187–193.

[74] L.W. Chan, J.S. Hao, P.W.S. Heng, Evaluation of Permeability and Mechanical Properties of Composite Polyvinyl Alcohol Films., Chem. Pharm. Bull. (Tokyo). 47 (1999) 1412–1416. doi:10.1248/cpb.47.1412.

APPENDIX A

AMOUNTS OF CHEMICALS USED FOR ZIF-8 SYNTHESIS

Table A.1 Weight of chemicals used for synthesized of ZIF-8 with different average particle size

Average Particle Size based on SEM, (nm)	**$Zn(NO_3)_2.6H_2O$, (g)**	**Hmim, (g)**	**MeOH, (g)**	**NaOH, (g)**	**Mother Liquor, (g)**
17	-	-	-	13	356.6
81	4.8	10.6	361.6	-	-
190	4.8	10.6	179.4	-	-
340	4.8	10.6	44.9	-	-

APPENDIX B

XRD PATTERNS AND CRYSTALLINITIES OF ZIF-8 PARTICLES USED FOR MMM PREPARETION

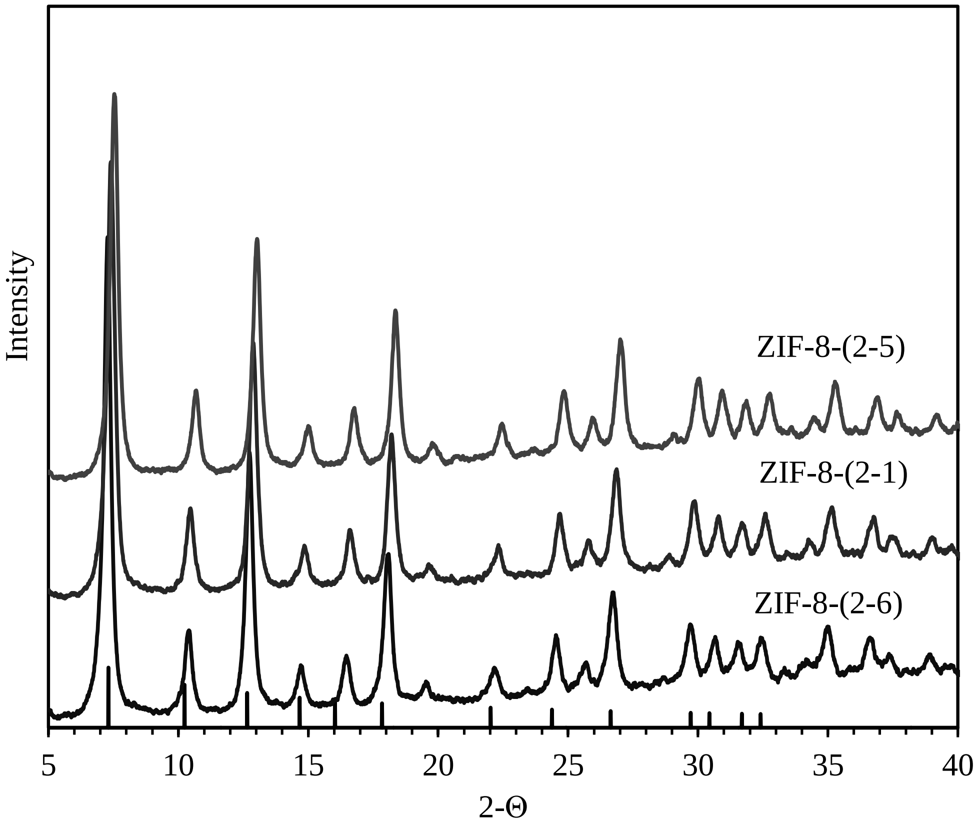


Figure B.1 XRD patterns of ZIF-8 particles (81 nm) used for preparation of MMM- PVA(10)98-GA

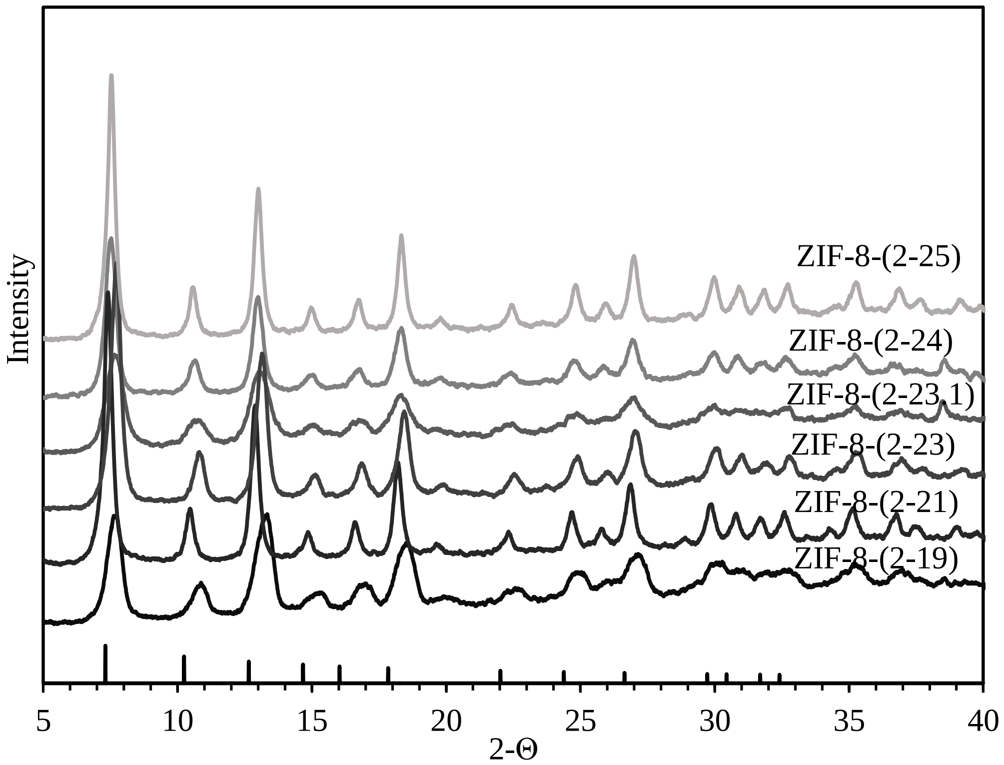


Figure B.2 XRD patterns of ZIF-8 particles used for preparation of MMM-PVA(5)98-GA

Table B.1 Crystallinities and particle sizes of ZIF-8 crystals used for MMM preparation with their synthesis molar ratios

Sample Code	**Sample No**	**MeOH to $ZnNO_3.6H_2O$ Molar Ratio**	**Particle size by SEM images**	**Crystallinity, %**
ZIF-8-(2)	ZIF-8-(2-1)	695.1	81	93.2
ZIF-8-(2)	ZIF-8-(2-5)	695.1	81	90.0
ZIF-8-(2)	ZIF-8-(2-6)	695.1	81	96.9
ZIF-8-(2)	ZIF-8-(2-19)	695.1	81	75.4
ZIF-8-(2)	ZIF-8-(2-21)	695.1	81	86.2
ZIF-8-(2)	ZIF-8-(2-23)	695.1	81	96.8
ZIF-8-(1)	ZIF-8-(2-23.1)	1130	17	62.5
ZIF-8-(4)	ZIF-8-(4-24)	86.9	340	65.3
ZIF-8-(4)	ZIF-8-(4-25)	86.9	340	86.3

APPENDIX C

DETERMINATION OF AVERAGE PARTICLE SIZES OF ZIF-8 BY USING SEM IMAGES

The particle sizes were determined by measuring the length of 20 particles for each sample from the SEM images. The particles full size SEM images were given in Figure C.1. The Image-J Software was used for measuring the particles sizes and particle sizes of crystals were given in Table C.1.

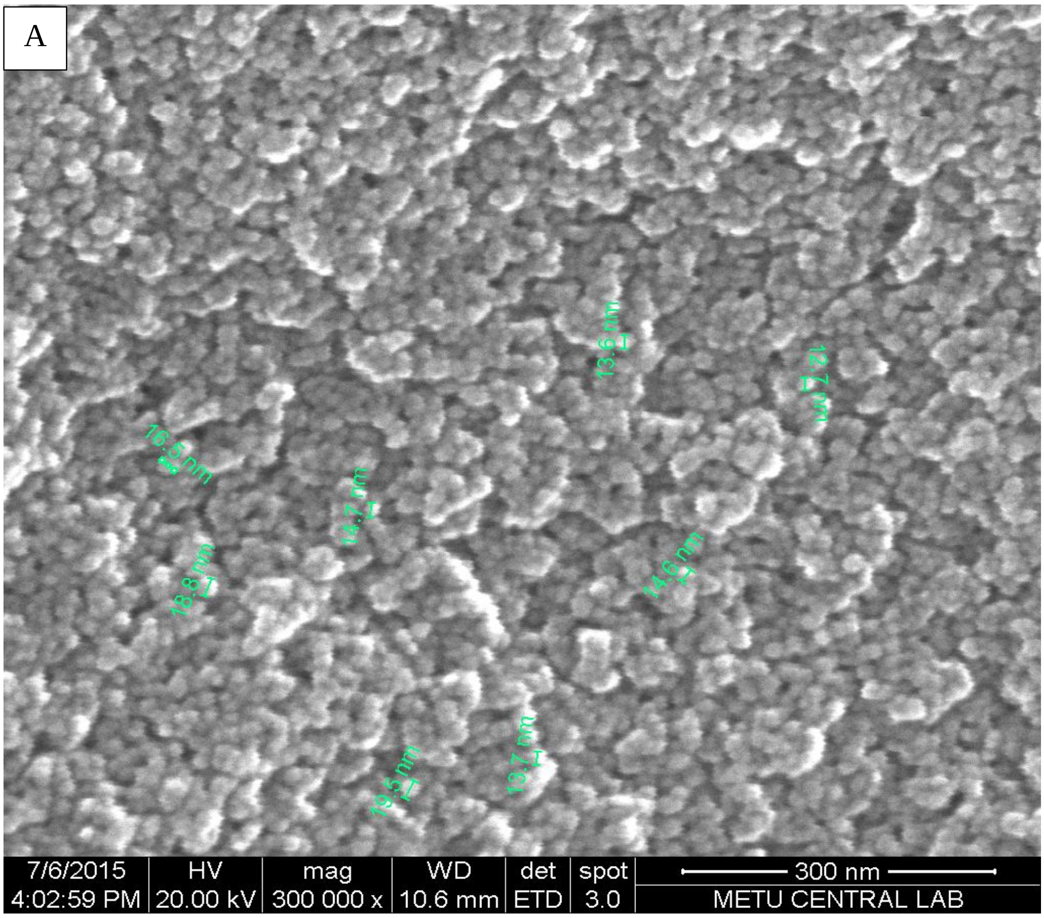


Figure C.1 SEM images of ZIF-8 crystals A) 17 nm, B) 81 nm, C) 190 nm, D) 340 nm (cont.)

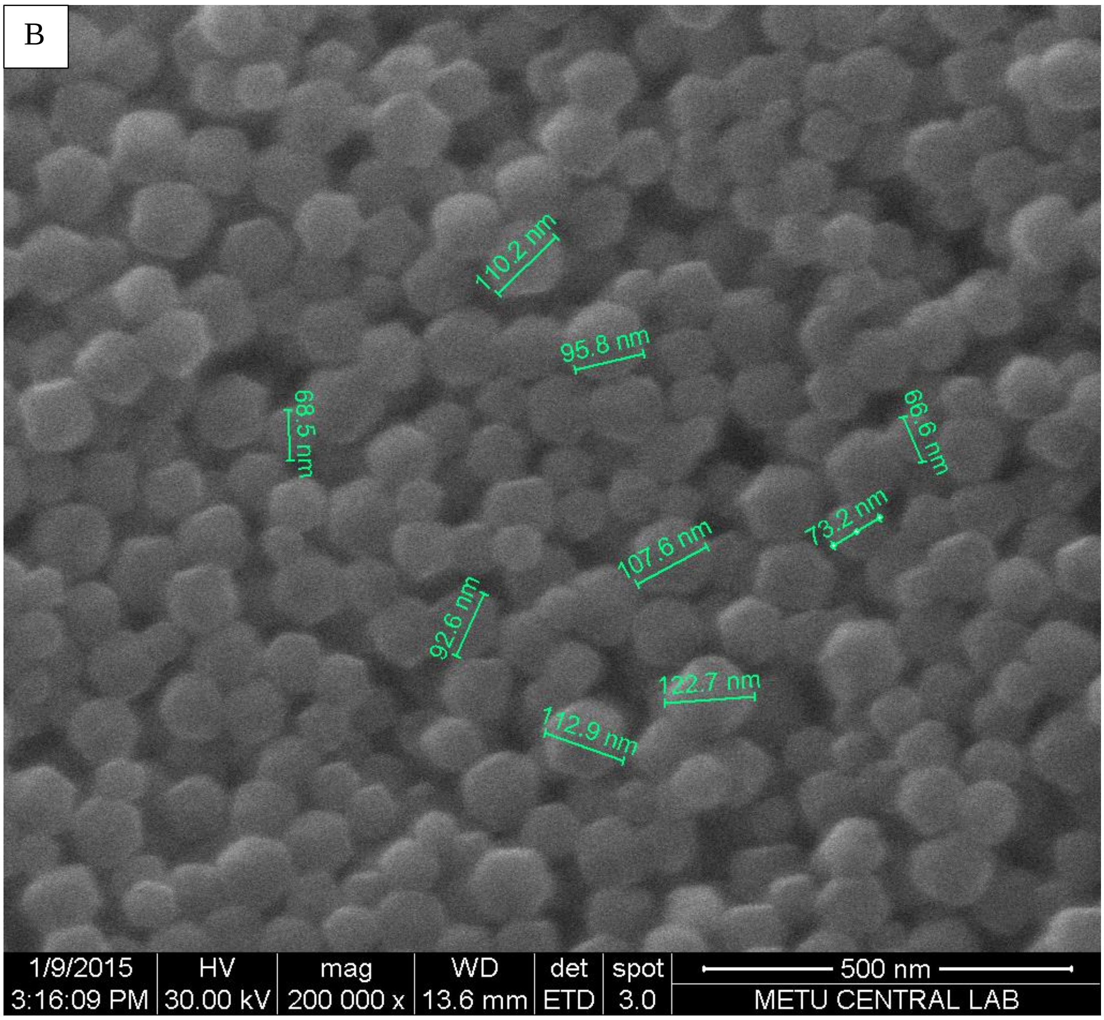


Figure C.1 SEM images of ZIF-8 crystals A) 17 nm, B) 81 nm, C) 190 nm, D) 340 nm (cont.)

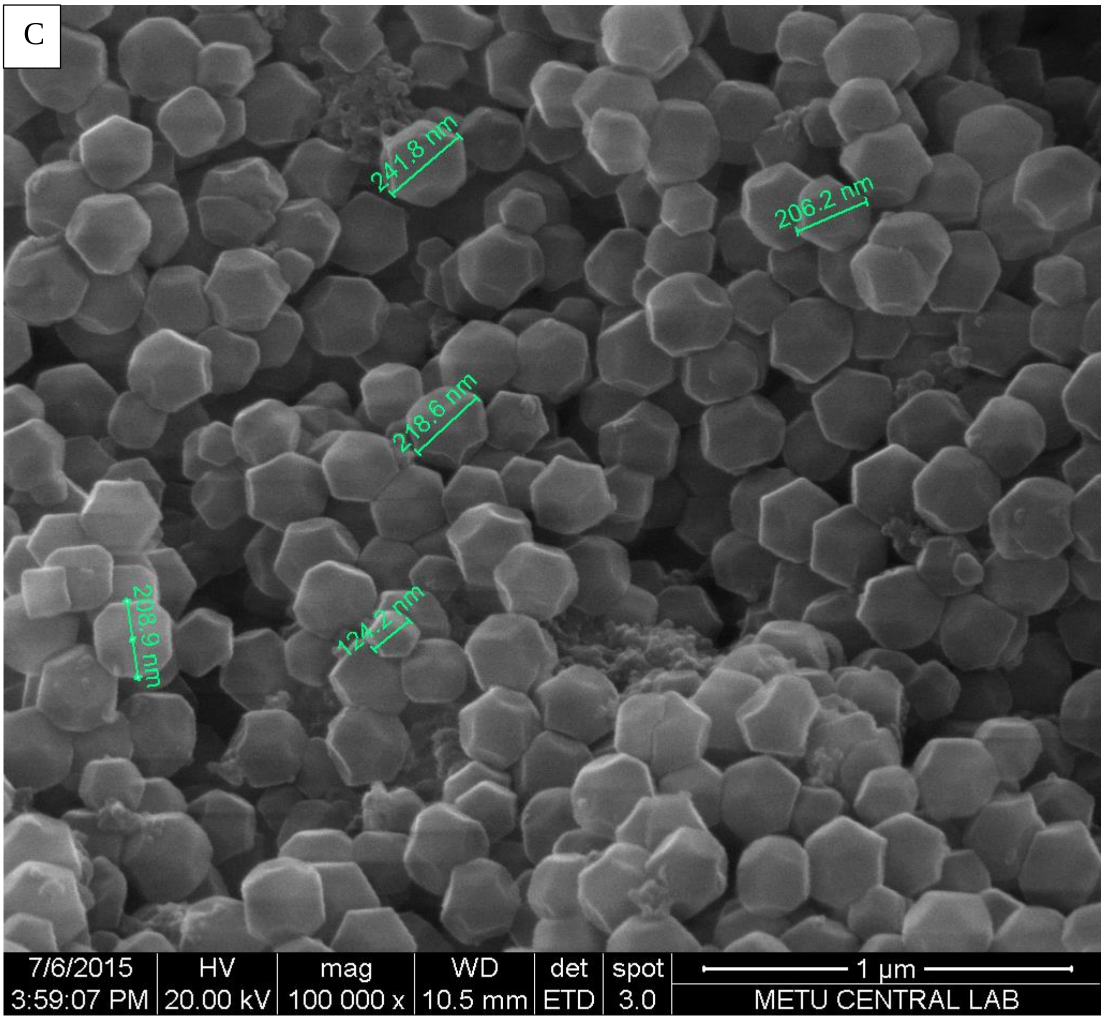


Figure C.1 SEM images of ZIF-8 crystals A) 17 nm, B) 81 nm, C) 190 nm, D) 340 nm (cont.)

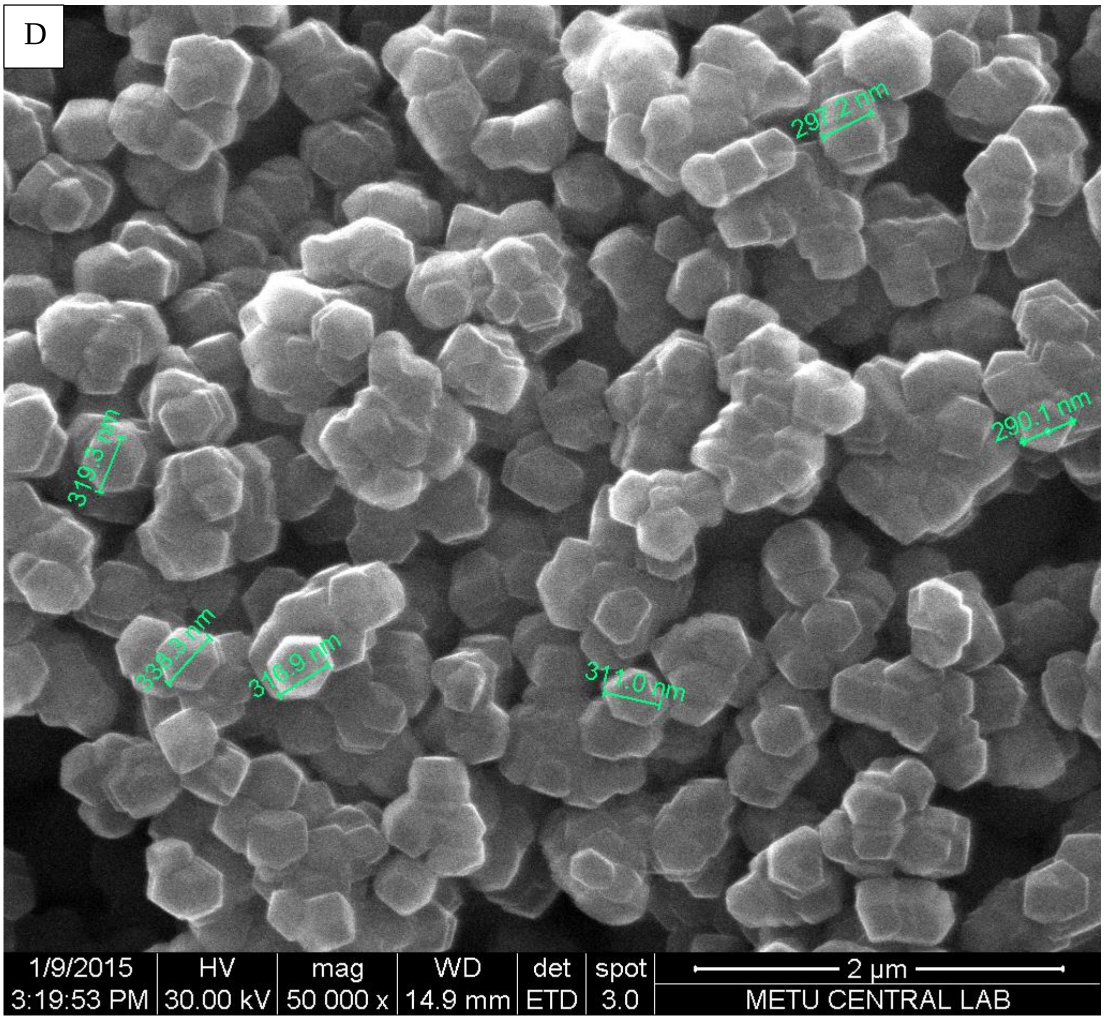


Figure C.1 SEM images of ZIF-8 crystals A) 17 nm, B) 81 nm, C) 190 nm, D) 340 nm (cont.)

Table C.1 Particle sizes of each crystals and average particle sizes of ZIF-8 samples

	ZIF-8-(1)	**ZIF-8-(2)**	**ZIF-8-(3)**	**ZIF-8-(4)**
	15.0	63.7	201.6	328.8
	25.8	69.2	234.7	326.6
	22.3	71.2	213.2	360.8
	12.3	91.5	124.6	375.1
	18.6	73.3	217.2	325.3
	14.2	88.7	192.7	369.1
	21.2	81.3	215.5	395.2
	13.3	72.7	195.3	324.5
	22.2	79.2	181.8	307.6
	19.4	89.4	216.2	307.2
	15.0	72.6	213.7	395.9
	17.8	75.3	226.6	284.2
	14.4	81.1	177.1	387.8
	16.1	88.2	190.9	302.6
	17.2	92.5	203.0	315.1
	15.0	71.4	133.8	369.9
	12.6	81.3	181.0	343.3
	19.1	90.9	146.8	318.3
	18.0	91.4	169.2	354.4
	14.3	91.7	184.8	291.9
Average	17.3±3.6	80.8±9.0	190.0±29.0	339.2±33.8

APPENDIX D

FEED COMPOSITION CHANGE THROUGHOUT PERVAPORATION EXPERIMENTS CALCULATION

Calculation for the pervaporation result given in Table 4.1 for "Annealing Temperature 70°C"

Flux (J) = 101.4 g/m^2.h

Permeate water content = 55.1 %

Feed water content at the beginning = 10 %

Total feed amount = 2.0 kg

Membrane area = 0.00635 m^2

For 3 hours operation;

$$\left(101.4\,\frac{\mathrm{g}}{m^2}.\mathrm{h}\right) * (3\ \mathrm{h}) * (0.00635\ m^2) = 1.93\ g\ permeate$$

$$(1.93\ g) * (0.551) = 1.06\ g\ water\ in\ permeate$$

$$New\ water\ content\ of\ feed = \frac{(2000) * (0.1) - 1.1}{2000 - 1.9} = 0.0996$$

$$= 9.96\ \%\ water\ in\ feed$$

APPENDIX E

PERVAPORATION EXPERIMENT RESULTS

Table E.1 Pervaporation experiment data of asymmetric PES membranes by wet-phase inversion

Membrane	Annealing Temp. °C	Flux (g/m2.h)	Selectivity	Permeate water content %
PES-5-1	70	52.8	14.4	61.5
		144.1	11.5	56.0
		107.0	13.5	60.0
PES-5-2	70	156.7	10.2	53.1
		67.8	12.1	57.3
		80.4	10.3	53.4
PES-3-2	50	60.7	16.7	65.0
		50.1	19.1	68.0
		130	16.7	65.0
PES-6-1	50	71.5	14.3	47.4
		67.4	13.6	60.3
		64.6	16.1	64.2
PES -6-2	50	95.3	9.7	51.9
		74.8	12.7	58.5
		73.1	12.0	57.0
PES -7-1	50	65.3	8.9	49.8
		43.2	14.1	61.1
		42.1	24.8	73.4
PES -7-1	50	132.4	13.0	59.0
		56.7	20.4	69.4
		45.8	14.1	61.1
PES -8-1	40	337.4	3.0	25.0
		86.9	6.3	41.0
		141.3	6.0	40.0

Table E.1 Pervaporation experiment data of asymmetric PES membranes by wet-phase inversion (cont.)

PES -8-2	40	278.8	3.5	28.0
		125.4	5.8	39.3
		99.6	5.7	38.8
PES -4-1	No annealing	181.5	3.8	30.0
		53.5	3.3	27.0
PES -4-2	No annealing	45.3	13.5	60.0
		217.2	9.7	52.0
		41.4	6.0	40.0
PES -4-3	No annealing	426.4	6.6	42.5
		356.6	6.5	42.0
		306.3	5.1	36.1

Table E.2 Pervaporation experiment data of asymmetric PES/ZIF-8 MMM by wet-phase inversion

Membrane	ZIF-8 (81nm) Loading, wt.%	Annealing Temp. °C	Flux (g/m2.h)	Selectivity	Permeate water content, %
PES/ZIF-8-11-1	5.0	50	157.0	4.0	31.0
			149.6	4.0	31.0
			149.7	3.9	30.0
PES/ZIF-8-14-1	5.0	50	146.2	4.2	32.0
			131.3	4.0	31.0
			140.9	4.1	31.5

Table E.3 Pervaporation experiment data of asymmetric PES membranes by dry-wet phase inversion

Membrane	Solvent Evaporation Time, min	Annealing Temp. °C	Flux (g/m2.h)	Selectivity	Permeate water content, %
PES-8-1	5	50	100.2	8.6	49.0
			69.7	11.9	57.0
			62.7	11.2	55.8
PES-9-1	5	50	91.2	8.01	47.1
			67.3	9.15	50.4
			63.4	10.7	54.3
PES-12-1	60	50	62.3	7.5	45.0
			50.2	9.4	51.2
			48.7	9.9	52.4
PES-13-1	60	50	69.9	6.8	42.4
			49.6	9.0	50.9
			46.3	9.4	51.0

Table E.4 Pervaporation experiment data of pure PVA (87 % hyd.) by thermal cross-linking (PVA87-T) (cont.)

Membrane	Cross-linking Temp. °C	Cross-linking Period, h	Flux ($g/m^2.h$)	Normalized Flux ($\mu m.g/m^2.h$)	Selectivity	Permeate water content %
PVA87-T-1-1	90	0.5	65.8	5593	10.1	53.0
			61.6	5236	9.9	52.2
			60.5	5142	10.0	52.6
PVA87-T-2-1	90	0.5	92.8	5568	9.3	50.9
			83.2	4992	8.8	49.3
			82.6	4956	10.2	53.0
PVA87-T-3-1	90	0.5	110.4	6624	2.4	21.3
			81.6	4896	3.1	25.8
			73.1	4386	3.4	27.1
PVA87-T-38-1	90	1.0	124.3	8079	13.2	59.5
			87.4	5681	22.5	71.4
			105.1	6831	14.3	61.4
PVA87-T-39-1	90	1.0	90.1	5856	12.4	58.0
			86.8	5642	14.1	61.0
			86.5	5622	15.0	62.5

Table E.4 Pervaporation experiment data of pure PVA (87 % hyd.) by thermal cross-linking (PVA87-T) (cont.)

PVA87-T-39-2	90	1.0	117.6	6468	14.0	60.9
			110.8	6094	11.7	56.6
			109.3	6011	11.5	56.2
PVA87-T-39-3	90	1.0	104.0	5720	13.2	59.5
			118.9	6539	10.6	54.0
			113.7	6253	10.2	53.1
PVA87-T-40-1	100	1.0	71.2	4272	11.5	56.2
			66.3	3978	12.2	57.6
			69.1	4146	11.7	56.6
PVA87-T-40-2	100	1.0	84	5460	9.6	51.7
			66.6	4329	12.1	57.4
			66.6	4329	12.8	58.8
PVA87-T-41-1	120	1.0	71.9	3954	12.8	58.8
			69.4	3817	13.3	59.7
			67.6	3718	14.4	61.6
PVA87-T-41-2	120	1.0	104.4	5220	9.9	52.4
			100.1	5005	11.9	57.0
			96.6	4830	11.9	56.9
PVA87-T-41-3	120	1.0	123.7	5566	9.4	51.2
			96.9	4360	11.0	55.0
			94.5	4252	10.7	54.2
PVA87-T-17-1	140	1.0	133.0	6650	20.1	69.1
			163.5	8175	20.1	69.1
			163.8	8190	20.9	69.9
PVA87-T-17-2	140	1.0	118.7	6528	16.8	65.1
			121.9	6704	17.6	66.2
			113.3	6231	15.2	62.7
PVA87-T-18-1	140	1.0	173.4	13005	15.1	62.7
			147.3	11047	17.7	66.3
			129.2	9690	17.3	65.8
PVA87-T-18-2	140	1.0	117.4	9392	16.3	64.4
			112.4	8992	15.1	62.6
			103.1	8248	15.1	62.6
PVA87-T-30-1	No Cross-link	-	371.3	29704	8.3	48.0
			119.4	9552	14.5	61.8
			112.0	8960	14.0	60.9
PVA87-T-35-1	No Cross-link	-	179.0	14320	7.5	45.6
			166.2	13296	8.0	47.1
			156.3	12504	7.6	45.9
PVA87-T-15-1	120	48	37.5	3187	29.6	76.7
			35.2	2992	34.5	79.3
			35.6	3026	35.3	79.7

Table E.4 Pervaporation experiment data of pure PVA (87 % hyd.) by thermal cross-linking (PVA87-T) (cont.)

PVA87-T-15-2	120	48	52.4	3406	25.5	73.9
			52.4	3406	34.9	79.5
			50.9	3308	25.2	73.7
PVA87-T-08-1	140	48	57.7	33.3	78.7	4904
			48.8	33.6	78.9	4148
			51.4	30.8	77.1	4369
PVA87-T-11-1	140	48	54.1	21.0	70.0	3787
			50.8	27.4	75.3	3556
			46.5	26.3	74.5	3255
PVA87-T-11-2	140	48	37.8	21.6	70.6	3024
			37.1	23.0	71.9	2968
			35.6	24.2	72.9	2848
PVA87-T-16-1	160	48	48.7	17.9	64.6	3896
			41.5	21.0	70.0	3320
			45.4	22.4	71.3	3632

Table E.5 Pervaporation experiment data of pure PVA (87 % hyd.) by chemical cross-linking (PVA87-GA) (cont.)

Membrane	GA content of cross-link solution, %	Flux (g/m^2.h)	Normalized Flux (µm.g/m^2.h)	Selectivity	Permeate water content %
PVA-87-GA-18-1	3.0	158.8	7146	13.6	60.2
		149.9	6745	13.7	60.4
		147.7	6646	15.0	62.5
PVA-87-GA-23-1	3.0	90.9	4545	15.1	62.7
		95.2	4760	18.3	67
		92.4	4620	16.2	64.3
PVA-87-GA-25-1	3.0	73.6	3312	21.3	70.3
		68.4	3078	19.7	68.6
		76.6	3447	20.5	69.5
PVA-87-GA-05-1	1.5	142.7	8562	18.1	66.8
		150.1	9006	21.1	71.9
		144.6	8676	18.4	67.2
PVA-87-GA-07-1	1.5	117.7	8239	11.3	55.8
		113.9	7973	12.1	57.4
		119.3	8351	11.7	56.5

Table E.5 Pervaporation experiment data of pure PVA (87 % hyd.) by chemical cross-linking (PVA87-GA) (cont.)

PVA-87-GA-07-2	1.5	144.7	8682	11.4	55.8
		140.6	8436	16.6	64.8
		147.7	8862	16.7	65.0
PVA-87-GA-09-1	1.5	188.9	10389	8.6	48.9
		166.1	9135	7.8	46.6
		211.8	11649	7.3	44.7
PVA-87-GA-10-1	1.5	192.0	9600	8.2	47.7
		202.8	10140	9.0	50.0
		202.1	10105	9.5	51.4
PVA-87-GA-12-1	1.5	146.0	8760	7.8	46.6
		129.1	7746	7.5	45.5
		132.7	7962	7.6	45.8
PVA-87-GA-15-1	1.5	99.6	8964	10.7	54.3
		93.7	8433	11.6	56.3
		91.6	8244	13.3	59.7
PVA-87-GA-20-1	0.5	87.5	5250	11.8	56.7
		102.0	6120	22.7	71.6
		94.3	5658	20.7	69.7
PVA-87-GA-22-1	0.5	144.8	7964	17.7	66.3
		137.4	7557	17.7	66.3
		138.9	7639	17.8	66.4
PVA-87-GA-24-1	0.5	123.8	5571	20.0	69.0
		124.3	5593	18.9	67.7
		116.3	5233	15.7	63.5
PVA-87-GA-24-2	0.5	96.3	4333	19.3	68.2
		99.9	4495	22.0	71.0
		93.1	4189	16.9	65.3

Table E.6 Pervaporation experiment data of pure PVA (98 % hyd.) by chemical cross-linking [PVA(10)98-GA]

Membrane	GA content of cross-link solution, %	Flux (g/m^2.h)	Normalized Flux (µm.g/m^2.h)	Selectivity	Permeate water content %
PVA-98-GA-14-1	1.5	8.4	504	50.2	84.8
		6.7	402	80.1	89.9
		6.8	408	61.8	87.3
PVA-98-GA-16-1	1.5	15.2	836	17.9	66.1
		10.2	561	51.0	85.0
		9.2	506	63.6	87.6
PVA-98-GA-17-1	0.75	10.3	824	30.6	77.3
		4.0	320	21.3	70.3
		4.4	352	30.3	77.1
PVA-98-GA-16-2	0.75	7.8	702	37.4	80.5
		5.3	477	39.6	81.5
		4.1	369	64.8	87.8
PVA-98-GA-21-1	0.5	15.3	765	72.1	88.9
		12.2	610	55.3	86.0
		13.2	660	91.0	91.0
PVA-98-GA-26-1	0.5	16.6	1079	55.7	86.1
		15.6	1014	80.1	89.9
		12.8	832	92.1	91.1
PVA-98-GA-27-2	0.5	28.1	1967	72.8	89.0
		25.5	1785	88.8	90.8
		22.2	1554	83.8	90.3

Table E.7 Pervaporation experiment data of PVA/ZIF-8(81 nm) MMM [MMM-PVA(10)98-GA] according to ZIF-8 condition

Membrane	ZIF-8 condition	Flux (g/m^2.h)	Normalized Flux (µm.g/m^2.h)	Selectivity	Permeate water content %
MMM-PVA98-GA-28-1	81 nm dried	42.7	2989	27.8	75.6
		37.3	2611	39.1	81.3
		36.4	2548	64.2	87.7
MMM-PVA98-GA-29-1	81 nm dried	29.4	1911	18.9	67.7
		31.5	2047	22.8	71.7
		31.6	2054	22.3	71.2
MMM-PVA98-GA-45-1	81 nm dried	16.0	1360	22.3	71.2
		12.9	1096	35.1	79.6
		13.8	1173	32.8	78.5
MMM-PVA98-GA-43-1	81 nm dried	26.1	1957	36.0	80.0
		19.3	1447	23.4	72.2
		23.7	1777	30.3	77.1
MMM-PVA98-GA-50-1	81 nm dried	38.6	2316	26.3	74.5
		34.4	2064	29.5	76.6
		37.1	2226	42.1	82.4
MMM-PVA98-GA-38-1	81 nm As-synthesized	51.8	2849	7.6	45.8
		41.1	2260	7.7	46.0
		40.7	2238	8.2	47.6
MMM-PVA98-GA-31-1	81 nm As-synthesized	62.4	3744	3.7	29.2
		43.4	2604	4.1	31.2
		41.6	2496	5.3	36.9
MMM-PVA98-GA-32-1	81 nm As-synthesized	192.8	10604	3.5	28.2
		134.3	7386	2.6	22.7
		128.1	7045	3.5	28.1

Table E.8 Pervaporation experiment data of pure PVA (98 % hyd.) by chemical cross-linking [PVA(5)98-GA]

Membrane	Flux (g/m^2.h)	Normalized Flux (µm.g/m^2.h)	Selectivity	Permeate water content %
PVA98-GA-51-1	30.4	1370	36.2	80.1
	29.6	1330	45.9	83.6
PVA98-GA-51-2	50.7	1770	34.4	79.3
	47.7	16700	36.5	80.2
PVA98-GA-53-1	28.1	1410	39.1	81.3
	26.7	1340	37.4	80.6
PVA98-GA-55-1	27.4	1230	34.7	79.4
	28.3	1270	37.9	80.8
PVA98-GA-56-1	19.9	1190	45.2	83.4
	18.9	1130	47.3	84.0
	18.6	1120	46.9	83.9

Table E.9 Pervaporation experiment data of PVA/ZIF-8 MMM [MMM-PVA(5)98-GA] according to particle size (cont.)

Membrane	Average particle size of ZIF-8	Flux (g/m^2.h)	Normalized Flux (µm.g/m^2.h)	Selectivity	Permeate water content %
MMM-PVA98-GA-52-1	81 nm	85.8	4290	13.7	60.3
		84.6	4230	12.8	58.8
		85.4	4270	14.2	61.2
MMM-PVA98-GA-52-2	81 nm	111.0	3890	13.2	59.5
		112.7	3940	13.8	60.6
MMM-PVA98-GA-54-1	81 nm	94.2	3770	14.7	62.1
		87.4	3500	17.9	66.6
		84.6	3380	22.0	71.0
MMM-PVA98-GA-57-2	81 nm	44.7	1790	15.0	62.5
		46.7	1870	14.0	60.8
MMM-PVA98-GA-59-1	81 nm	127.1	5080	15.3	63.1
		117.7	4710	15.2	62.8

Table E.9 Pervaporation experiment data of PVA/ZIF-8(81 nm) MMM [MMM-PVA(5)98-GA] according to particle size (cont.)

MMM-PVA98-GA-59-2	81 nm	49.7	2730	15.6	63.4
		49.4	2720	17.7	66.3
MMM-PVA98-GA-60-1	81 nm	64.1	2880	14.3	61.4
		62.1	2790	16.3	64.5
		65.4	2940	16.5	64.7
MMM-PVA98-GA-58-1	17 nm	40.5	2230	23.0	71.9
		39.6	2180	19.7	68.6
MMM-PVA98-GA-58-2	17 nm	43.7	1750	32.1	78.1
		37.5	1500	37.9	80.8
		37.3	1490	37.2	80.5
MMM-PVA98-GA-62-1	17 nm	37.4	1500	31.4	77.7
		38.6	1540	32.9	78.5
MMM-PVA98-GA-62-2	17 nm	29.6	1780	29.1	76.4
		28.6	1720	28.3	75.9
		30.3	1820	33.6	78.9
MMM-PVA98-GA-64-1	17 nm	100.3	4010	8.1	47.5
		122.4	4900	9.6	51.6
MMM-PVA98-GA-64-2	17 nm	79.8	2390	17.0	65.4
		78.6	2360	18.9	67.7
		77.4	2320	19.8	68.8
MMM-PVA98-GA-70-1	17 nm	158.2	4750	6.8	43.3
		146.1	4380	6.6	42.2
		162.6	4880	6.4	41.4
MMM-PVA98-GA-69-1	17 nm	86.6	3460	7.2	44.6
		107.2	4290	7.4	45.1
MMM-PVA98-GA-71-1	17 nm	31.3	1410	36.5	80.2
		29.1	1310	37.6	80.7
		31.6	1420	39.1	81.3
MMM-PVA98-GA-72-1	17 nm	22.2	1550	35.5	79.8
		21.4	1500	34.1	79.1
		21.6	1510	33.6	78.9
MMM-PVA98-GA-73-1	17 nm	44.4	1780	35.3	79.7
		42.7	1710	33.5	78.7
		41.7	1670	35.1	79.6

Table E.9 Pervaporation experiment data of PVA/ZIF-8(81 nm) MMM [MMM-PVA(5)98-GA] according to particle size (cont.)

MMM-PVA98-GA-74-1	17 nm	29.6	1330	39.9	81.6
		30.2	1360	40.1	81.7
		30.1	1350	41.0	82.0
MMM-PVA98-GA-75-1	191 nm	29.8	1490	36.2	80.1
		26.4	1320	39.6	81.5
		25.8	1290	36.9	80.4
MMM-PVA98-GA-76-1	191 nm	36.4	1820	34.1	79.1
		33.6	1680	35.6	79.8
		36.1	1805	36.0	80.0
MMM-PVA98-GA-77-1	191 nm	33.8	1690	45.9	83.6
		31.8	1590	52.6	85.4
		34.4	1720	45.2	83.4
MMM-PVA98-GA-79-1	191 nm	29.8	1341	56.2	86.2
		26.6	1197	77.5	89.6
		30.4	1368	76.7	89.5
MMM-PVA98-GA-80-1	191 nm	22.8	1368	80.1	89.9
		18.2	1092	79.2	89.8
		18.4	1104	76.7	89.5
MMM-PVA98-GA-81-1	191 nm	29.7	1188	75.1	89.3
		27.2	1088	89.9	90.9
		27.5	1100	95.7	91.4
MMM-PVA98-GA-82-1	191 nm	22.6	1017	53.5	85.6
		22.4	1008	88.8	90.8
		21.7	977	95.7	91.4
MMM-PVA98-GA-83-1	191 nm	25.7	1028	80.1	89.9
		27.7	1108	85.7	90.5
		28.3	1132	78.4	89.7
MMM-PVA98-GA-61-1	340 nm	57.4	2296	16.64	64.9
		52.7	2108	17.16	65.6
		51.3	2052	21.61	70.6
MMM-PVA98-GA-63-1	340 nm	73.2	2928	24.33	73
		62.3	2492	24.21	72.9
		65.2	2608	25.48	73.9
MMM-PVA98-GA-66-1	340 nm	54.1	2435	16.71	65
		42.3	1904	25.35	73.8
		45	2025	26.43	74.6

Table E.9 Pervaporation experiment data of PVA/ZIF-8(81 nm) MMM [MMM-PVA(5)98-GA] according to particle size (cont.)

MMM-PVA98-GA-67-1	340 nm	37.6	1880	27.00	75
		37.4	1870	26.43	74.6
		36.9	1845	26.86	74.9
MMM-PVA98-GA-68-1	340 nm	41.5	2283	19.13	68
		37.1	2041	25.62	74
		36.3	1997	26.16	74.4