DEHYDRATION OF ETHANOL/WATER MIXTURES BY POLYMERIC MEMBRANE PERVAPORATION

INTRODUCTION

Membrane process is a technique that permits concentration and separation without the use of heat and has emerged as one of the fastest growing research areas today. Particles are separated on the basis of their molecular size and shape with the use of pressure and specially designed semi-permeable membranes. Membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient and the membrane thickness may vary from as small as hundred microns to several millimeters (Table 1).

A membrane separation system separates an influent stream into two effluent streams known as permeate and concentrate or retentate. The permeate is the portion of the fluid that has passed through the semi-permeable membrane, whereas the concentrate stream contains the constituents that have been rejected by the membrane (Figure 1). Generally, membrane technologies for kidney dialysis and water purification/treatment are relatively well developed and are approaching mature, while membrane technologies for gas/pervaporation and pharmaceutical/biomedical separations have received great attention from both industry and academic because they have many important and high value-added applications.

Table 1 Membrane separation processes, process driving forces and applications.

Process	Membrane Type and Pore Radius	Process Diving Force	Applications
Microfiltration	Symmetric microporous, 10^{-1}-10 μm	Hydrostatic pressure difference at approx. $\leq$5 bar	Sterile filtration, Clarification
Ultrafiltration	Asymmetric microporous, 10^{-2}-10^{-1} μm	Hydrostatic pressure difference at approx. $\leq$10 bar	Separation of macromolecular solutions
Nanofiltration	Thin-film membranes, 10^{-3}-10^{-2} μm	Hydrostatic pressure difference at approx $\leq$50 bar	Removal of hardness and desalting
Reverse Osmosis	Asymmetric skin-type, 10^{-4}-10^{-3} μm	Hydrostatic pressure difference at approx. $\leq$100 bar	Separation of salts and microsolutes from solutions
Electrodialysis	Cation and anion exchange membrane	Electrical potential gradient	Desalting of ionic solutions
Gas Separation	Asymmetric homogeneous polymer	Hydrostatic pressure ($\leq$80 bar) and concentration gradients	Separation of gas mixtures
Pervaporation	Asymmetric homogenous polymer (a non-porous membrane)	Vapor pressure gradient	Separation of azeotropic mixtures

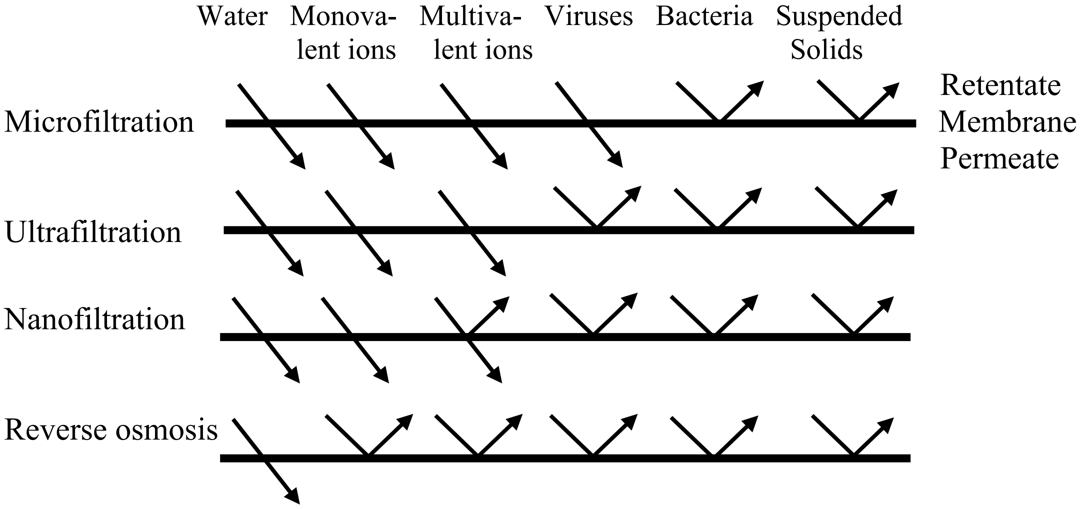


Figure 1 Membrane separation showing the retentate and permeate by pressure based separation processes.

Pervaporation is one of the membrane based processes that uses dense or composite membranes as the separation barrier for separating miscible liquids. It is attractive when it is difficult to apply distillation such as fractionation of azeotropic mixtures, close boiling point components and isomeric mixtures. In pervaporation, the liquid mixture to be separated (feed) is placed in contact with one side of membrane and the permeated is removed as a low-pressure vapor from other side, as shown in Figure 2. The permeate vapor condensed and collected or released as desired. The chemical potential gradient across the membrane is the driving force for the mass transport, which can be generated by applying either a vacuum pump or swept by a stream of gas (normally air) on the permeate side to maintain the permeate vapor pressure lower than the partial pressure of the feed liquid. Vacuum pervaporation is the most widely utilized mode of operation, while sweeping gas pervaporation is of interest if the permeated can be discharged without condensation.

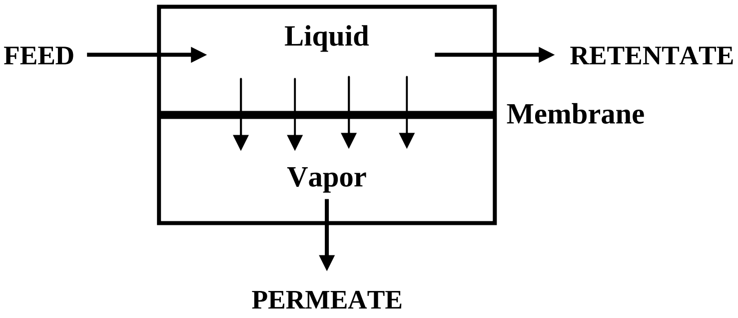


Figure 2 Schematic diagram of the pervaporation process.

Three different models have been suggested to explain the transport phenomena of pervaporation: non-equilibrium thermodynamics pore flow model and solution-diffusion model. The solution-diffusion model is the most widely accepted transport mechanism for dense pervaporation membranes. According to this model, pervaporation comprises three successive steps: sorption of solution from the liquid feed side to the membrane, diffusion of the absorbed components through the membrane and desorption of the diffused components from membrane to the vapor permeate side (Figure 3).

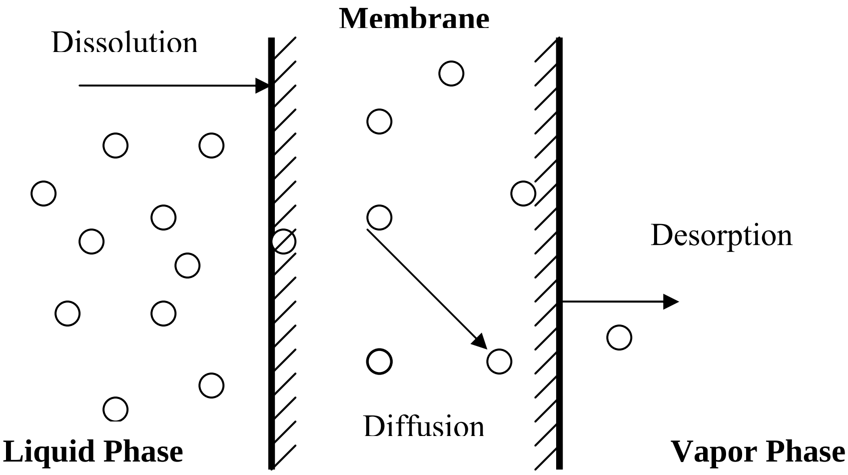


Figure 3 The solution-diffusion model for pervaporation.

Pervaporation performance of a membrane is affected by the following parameters: feed concentration, feed and permeate pressures, temperature and membrane thickness. Changing the composition of the feed solution results in the change of sorption behavior at the liquid-membrane interface and directly affects the concentration-dependent diffusion transport of the permeate. Generally, pervaporation process shows a highly concentration dependence compared to other membrane separation processes. As already mentioned, the driving force of mass transport in pervaporation is the difference in chemical potential across the membrane. Since the chemical potential is not strongly influenced by liquid pressure, the feed pressure (liquid state) shows relatively small effect on the pervaporation performance. The main contribution to the driving force is the permeate pressure so that the maximum driving force is achieved at zero permeate pressure. An increase in permeate pressure will diminish the driving force and the permeate rate. When the permeate pressure reaches the saturation pressure of the permeated, an abrupt decrease in permeation rate occurs. At the same time, the selectivity either increases or decreases depending on the relative volatilities of the component of the feed solution. Since the solubility and diffusivity of the permeate in membrane are generally dependent on the operating temperature, the pervaporation performance is also affected by temperature.

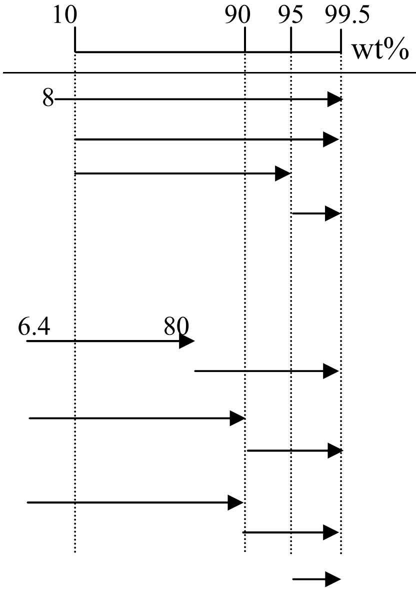
Typically, the permeation rate increases as temperature increases, while the selectivity declines. In addition, the permeation rate is inversely proportional to membrane thickness, but decreasing membrane thickness may reduce selectivity. As a rule, reducing the membrane thickness as much as possible, while still maintaining selectivity, is an important issue in preparing an effect pervaporation membrane.

However, the selectivity of a pervaporation process is determined by the membrane material itself. Due to the complicated nature of the pervaporation process, no well-established criteria are available to make an accurate selection of membrane materials for miscellaneous pervaporation purposes. Roughly speaking, for the dehydration of organic liquids, hydrophilic polymers such as poly(vinyl alcohol) and poly(acrylic acid) are suitable, while hydrophobic polymers such as poly(dimethylsiloxane) and polyethylene are more favorable for the removal of organic from water due to the preferential sorption and permeation of organic components.

Generally, diffusion of small molecules through a dense membrane is favored, and the solubility of a component in a polymeric membrane is governed by the chemical affinity between the permeant and the membrane. Therefore, when the difference in molecular size of two components to be separated in a mixture is large, the component of small molecular size may preferentially permeate through the membrane, even though the solubility of the component of large molecular size in the membrane may be great. For this reason, many polymers are preferentially permeable to water rather than organic components because water molecules are much smaller than organic molecules. An organic selective membrane must have very high solubility for organic molecules.

It was the rise of the oil and energy price that made pervaporation interesting because pervaporation could be used for the dehydration of azeotropic ethanol/water mixtures obtained by fermentation from renewable sources for production of pure ethanol as an alternative liquid fuel in the form of gasohol by mixing it with gasoline. It is simple and energy-effective ways in producing water-free alcohols that are difficult to separate by conventional techniques include low-pressure distillation, azeotropic distillation with pentane, benzene, and diethyl ether, and extractive distillation with gasoline or ethylene glycol (Table 2) (Maeda *et al.*, 1991).

Table 2 Energy requirements for dehydration of ethanol.



Energy needed (kcal/kg-EtOH)	Process
2480	Distillation
2310	Conventional “dual”
1520	distillation
790	Conventional distillation
	Conventional azeotropic
	distillation
1390	Distillation
340	Pervapoaration
Total	Distillation
1300	Pervapoaration
1220	Distillation
60	Pervapoaration
101	Pervapoaration

Almost all of petroleum fuels using in Thailand imports from abroad as crude oil or finished products. Research and development for using renewable energy to reduce using petroleum fuels in Thailand started since 1974 mainly to stabilize the price of agricultural crops, such as cassava and sugarcane, for production of ethanol as an alternative liquid fuel in the form of gasohol by mixing it with gasoline. It was found that using 10%vol of >95% to 99.5 % purity ethanol blending ratio gave minimum effect on the engine performance, and engine part failure. However, gasohol could not compete with gasoline price since the production cost of ethanol 99.5% purity is still higher without the subsidize from the government, even though the global oil price went up dramatically at present. The objective of this study is to use pervaporation for dehydration of azeotropic ethanol/water mixtures by varying the ethanol/water concentration, membrane type, membrane content, membrane preparation method, membrane thickness, additive type (non-solvent) and cross linking agent in the membrane in determination the flux and selectivity and hence the separation properties of the process. In the hope that it can promote ethanol blended gasoline utilization as an alternative energy in Thailand.

LITERATURE REVIEW

Pervaporation, a term derived from “permeate” and “evaporation”, was introduced by Kober in 1917 when he observed that water evaporated out of a tightly close collodion bag which was suspended in air. It may be defined one of the components can be preferentially removed from the mixture due to its higher affinity with, and/or quicker diffusivity in the membrane. As a result, both the more permeable species in the permeate and the less permeable species in the feed, can be concentrated. In order to ensure the continuous mass transport, very low absolute pressures, e.g., 133.3–400.0 Pa (1–3 mmHg), are usually maintained at the downstream side of the membrane, removing all the molecules migrating to the face, and thus rendering a concentration difference across the membrane. As a variant, the use of a sweeping gas in the downstream side of the membrane is also a feasible alternative for the generally used vacuum operation as the passage of liquid through a partial permeable membrane and subsequent evaporation of the liquid.

In 1956 Heisler published the first quantitative pervaporation study on the separation of ethanol and water mixtures by using a cellophane membrane. Membrane-based pervaporation (PV) is an energy-intensive method of separating liquid mixtures compared to the conventional distillation or cryogenic separations particularly involving azeotropic and closely boiling mixtures. Due to its high separation factor and flux rates, PV has been a well-established and commercially exploited method for the dehydration of alcohols. The success of PV depends mainly on the nature of the polymeric membrane chosen for a particular application in addition to its physical state, structure, chemically interacting groups, addition of filler particles, physicochemical properties of the feed mixture to be separated, feed component–component and component–membrane interactions (Hussain, 1996). However, the key to success in PV separation lies in the development of a suitable membrane material that offers high flux, good separation factor (selectivity) and long-term stability as well as the favorable mechanical strength to withstand the cyclic modes of PV operating conditions (Doyen, 1996). Thus, the success of any membrane depends upon the development of new polymeric materials that exhibit enhanced flux rates and selectivity in addition to strength and durability.

The possibility of ethanol/water separation by the use of pervaporation membranes was first applied by Binning in 1960. However, in spite of the intensive research conducted by his successors (Aptel *et al.*, 1976), this process has been left to more fundamental or laboratory scale work because of the poor separation characteristics of the membranes. Breakthrough was achieved in 1982 when GFT (Gesellschaft für Trenntechnik, German Company) first established the commercial base pervaporation in Brazil by the use crosslinked PVA (polyvinyl alcohol) composite membrane. Since then, numerous materials have been examined to achieve higher separation. At present, interest in the pervaporation process emerged and research in this field has found viable applications in the following three areas: (i) dehydration of organic solvents (e.g., alcohols, ethers, esters, acids); (ii) removal of dilute organic compounds from aqueous streams (e.g., removal of volatile organic compounds, recovery of aroma, and biofuels from fermentation broth); (iii) organic–organic mixtures separation (e.g., methyl *tert*-butyl ether (MTBE)/methanol, dimethyl carbonate (DMC)/methanol). Among them, dehydration of organic solvents is best developed. This resulted from the so-called synergic effect: water is both preferentially dissolved and transported in the hydrophilic membranes due to its much smaller molecular size. When pervaporation is used for removing organic compounds from water, the preferential transport of the organic species cannot be achieved in the organophilic membrane. As a result, the permselectivity of the pervaporation process is reduced, and less than the sorption selectivity. Theoretically speaking, pervaporation in these cases demonstrates no advantage over the adsorption technique. However, when the concentration of organic compounds in water is relatively high, pervaporation tends to be superior to the adsorption technology since pervaporation is a continuous process, it therefore suffers no limitation of the saturated adsorption capacity, which is however an intrinsic weakness of the adsorption process.

The production of ethanol is based either on fermentation or on synthesis methods. The synthesis method can be achieved by direct catalytic hydration according to the following reaction:

$$C_2H_2\,(g) + H_2O \longrightarrow C_2H_5OH \qquad \Delta H = -43.4\ kJ$$

Concentration of ethanol obtained from the fermentation process is usually 8 to 12 vol%. In order to recover and purify fermentation ethanol, distillation techniques are widely used. In this process at least three distillation columns are needed. To produce anhydrous ethanol, one more distillation column is needed because water/ethanol forms an azeotropic mixture at 95.57 wt%, 760 mmHg. Anhydrous ethanol for chemical or fuel use is usually obtained by azeotropic distillation by the use of benzene, ethyl ether, trichloroethylene, and cyclohexane. In case of the direct hydration process, the dilute crude ethanol is recovered through the purification section, in which it is freed from impurities by extractive distillation with water. Thus the synthetic ethanol is purified by distillation in a manner similar to ethanol made by fermentation.

Pervaporation application to ethanol dehydration

Application of membrane of membrane technology to ethanol purification as a complement to distillation has been extensively conducted mainly by reverse osmosis (RO) and pervaporation (PV) (Mehta, 1982 and Leeper, 1987). From the restriction of osmotic pressure, it is rather difficult to use only RO process to producing anhydrous ethanol. Through theoretical consideration (Lee, 1975) reported the use of RO with pressure smaller than 2,000 psi was calculated to be of limited use for the purification of water with small amounts of organics compounds. On contrary, since the driving force of pervaporation is considered to be the vapor pressure different between the feed and permeate sides, one can expect to no restriction of the operating pressure. Thus, the pervaporation process is now considered to be a useful and economical process to dehydrate organic solvents.

There exist two types of pervaporation membranes for water/ethanol mixture. One is water permselective and other is ethanol permselective membranes for low ethanol concentration region and to use water permselective membranes for high ethanol concentration feed so that one may eliminate the existing distillation columns. However, the competing ethanol permselective pervaporation membrane has not been developed yet. Thus, it might be impossible to use only pervaporation for ethanol purification. Instead, a combination process has been proposed. As mentioned, ethanol distillation consists of two parts, that is, normal distillation up to 95% ethanol and azeotropic distillation to 99.5%. This azeotropic distillation is a rather energy consuming process compared with the first part. A combination process has been considered in which the ethanol/water mixture is first concentrated to around the azeotropic mixture by the first distillation column and hereafter, pervaporation is applied.

Furthermore, pervaporation has another aspect in addition to the incentive coming from energy saving considerations. Benzene has been used as an azeotropic dehydrating agent in many plants, but some concern exists about carcinogenicity and toxicity. From this point, pervaporation is considered to be a suitable method to produce high purity for medical use.

Binning *et al.* (1958) was the first to report a process to separate azeotropic mixtures by using cellulose acetate membrane. In this patent หรือ report, the azeotropic mixture of ethanol with water (96.4 vol% of ethanol) is fed into the cellulose acetate membrane. After about 30% of the feed is removed, a non-permeated fraction consisting of 99.3 vol% ethanol is produced. The permeate fraction (88.5 vol% of ethanol) can be fractionated to produce a bottom fraction of water and overhead fraction of azeotropic mixture which is recycled to the pervaporation step. A similar process was also applied to the dehydration of ternary azeotropic mixture (isopropanol, ethanol, water). Pervaporative dehydration combined with distillation has been clearly demonstrated in this work.

Classification of dehydration membranes

New membrane materials have been sought by many investigators and some are now being put to practical use. Most of the works regarding dehydration have aimed at improving solubility selectivity by introducing hydrophilic groups into the polymer structure. That is, preferential partitioning of water can be expected, which leads to both high separation factors and high permeate rate. However, the introduction of hydrophilic groups sometimes swells the membrane significantly due to its plasticization action which results in poor selectivity. In order to adjust and control the hydrophilic and hydrophobic balance of the membrane, various techniques such as crosslinking, blending and copolymerization have been examined by many investigators.

Classification of published dehydration membrane is rather difficult because of their complexity. Generally, the dehydration membrane will be classified into the following three types according to Yamada (1986) shown in Table 3.

i) Hydrophilic commercial and synthesized membranes
ii) Introduction of hydrophilic group into the hydrophobic membranes
iii) Hydrophilic-hydrophobic block membranes

Typical examples for hydrophilic commercial and synthesized membranes are the various RO and ion-exchange membranes such as cellulose acetate were reported by Schissel (1984). For other membrane materials, Leeper (1986) described the characteristics in his review article. Nafion, which is a commercial ion-exchange membrane, was investigated by Ishikawa *et al.* (1980) and Cobasso *et al.* (1986). Poly(vinyl alcohol), poly(hydroxyl methylene), crosslinked poly(methyl acrylate), poly(vinyl aetate), N-methoxymethylated nylon-3, and silk fibroin are regarded as a membrane having nonionic hydrophilic group,i.e. –OH, -NHCO-, $-OCH_3$, $-OCOCH_3$. Nylon-3 was N-methoxymethylated by reacting paraformaldehyde/methanol in formic acid solution which examined by Hirotsu *et al.* (1989). While methoxymethylated Nylon-3 itself is soluble in water/ethanol mixture, the membrane war changed into an insoluble crosslinked membranes polymer during the heat treatment at 190°C.

Thermally crosslinked membranes applied to pervaporation tests exhibited a water permselective nature for the entire feed concentration.

Table 3 Classification of water-permselective PV membranes in water/ethanol pervaporation separation.

No.	Type	Examples
1	Hydrophilic commercial and synthesized membranes	- Non-ion groups: -OH, $-CONH_2$ - Cation Group: NH_4^+ - Anion groups: SO_3^- , COO^-
2	Introduction of hydrophilic group into the hydrophobic membranes	- Copolymerization - Blending - Plasma, electron beam and gamma ray initial graft polymer - Plasma polymerization onto hydrophobic substrate
3	Introduction of hydrophilic group into the hydrophobic membranes	Mosaic Membrane

Instead of nonionic groups, various polyelectrolyte membranes have been prepared, such as chitosan (Mochisuki *et al.*, 1988), poly(allyl ammonium) chloride (Hirotsu, 1987), and 4-vinylpyridine-acrylonitrile copolymerized (Yoshokawa *et al.*, 1987) are regarded as cationic polymer membranes. It was found that, ionically crosslinked chitosan yields high separation factor ($\alpha > 6,500$). Hirotsu (1987) reported composition membrane in which poly(allyl ammonium) chloride was encapsulated between ultrafiltration membranes made from Cuprophane or poly(vinyl alcohol). Compared to the Cupropane membrane, poly(allyl ammonium) chloride encapsulated membrane increases water permselectivity due to the lack of micropores and increase hydrophilicity. Similarly, anionic groups in various types of synthetic and natural polymers such as carboxylic acid and sulfonic acid, i.e., sulfonated polyethylene (PE), and anionic polysaccharides have been investigated by Mochozuki *et al.*(1986). As can be seen, anionic polysaccharides, carboxy methyl cellulose and alginic acid showed excellent properties.

In order to balance hydrophilicity with hydrophobicity and to achieve high selectivity, coplymerization and modification techniques have been widely examined. Nakagawa (1987) copolymerized hydrophilic N-vinyl pyrrolidone (PVP) and acrylic acid with hydrophobic methyl methacrylate (MMA) and ethyl methacrylate (EMA). Separation property of polyacrylonitrile (PAN) homopolymer has been reported by Mulder *et al.* (1983). It is widely known that PAN is used as a supporting material for GFT's pervaporation membrane. However, some anomalies have appeared in research of Spitzen *et al.* (1987) concerning the effect of PAN support, because PAN itself appeared to have a high separation factor depending on the membrane thickness.

Base on similar idea, the polymer blending technique has been studied to improved separation properties. A good article concerning polymer blending was published by Nguyen (1986). They selected the polymer blending system on the basis of the following criterion. First is the possibility of dissolving both polymers separately in the same solvent. Second is the mechanical resistance of thin films made from blend. They also arbitrarily classified the transport behavior of blending system into three categories. That is

- Blend in which the permeation is controlled by the transport properties of one of components, e.g. poly vinyl pyrrolidone (PVP)/PAN, PVP/PS(polystyrene).
- Blend in which permeation is governed by the transport through the modified structure of the main polymer, e.g. PAN/poly(ethylene glycol).
- Blend in which both polymers contribute significantly to permeation, e.g. cellulose nitrate – poly (methyl acrylate).

Modification of pervaporation membrane by the use of grafting techniques has been conducted by Aptel *et al.* (1976) and found that N-vinylppyrrolidone or 4-vinylpyridine grafted PTFE membrane exhibited only poor selectivity. Dimethyllaminoethylmethacrylate graft PE was examined by Kumata (1987) and styrene grafred PTFE was investigated by Tealdo *et al.* (1981) show similar results. Niemoller *et al.* (1988) examined monomers having anionic or cationic charge groups instead of nonionic monomers such as acrylic acid and 4-vinylpyridine. By the use of the electron beam initiation technique, these monomers are grafted onto various polymers. They observed that when the grafted 4-vinylpyridine or acrylic acid were converted to ionic from using CH_3I or alkali metal., excellent properties appeared. Through transmission electron microscope (TEM), it was proved that the grafting reaction uniformly proceeds in a membrane, and permeation rate increases with the saturated grafting yield. Especially, for acrylic acid grafted with poly(vinyl fluoride), PVF membrane, both separation factor and permeation rate increases with saturated grafting yield.

In contrast to grafting, the application of block polymers consisting 0f hydrophilic-hydrophobic microdomain is limited. Tanisugi *et al.* (1985) examined $(AB)_n$ type multiblock copolymers of bisphenol-A polycarbonate (PC) and polyoxyethylene (POE) with varying composition and block length. Most water-permselective membrane focused on separation based on solubility selectivity rather than mobility selectivity. Although the fluoroalkyl group which has a affinity toward ethanol are introduced, the separation performance of the fluoroalkyl acrylate-methyl styrene copolymer exhibits a water permselective nature having separation factor of more than 100 at higher ethanol concentration region (Toya *et al.*, 1985). This results were attributed to the mobility selectivity and it was suggested that there was another way to achieve high separation by the use of glassy and lower free volume polymers.

Aiming at the mobility selectivity, various glassy membrane such as polyacrylonitrile are examined by Mulder *et al.* (1983), polyimides by Kita *et al.* (1988) and poly(amideimide) by Torii (1987).

New developments

Recent research developments for pervaporation membrane process concerning types of polymer membranes, methods to prepared polymer membranes and various azeotropic mixtures were overviewed as followed:

In 1995, Sun *et al.* investigated the ionic crosslinking of the ferric ions and the carboxylic groups in the poly(vinyl alcohol-g-acrylic acid) (poly(VA-g-AA)) membranes to improve the size screening effect in the pervaporation of ethanol-water separation. In the grafting polymerization of acrylic acid monomer onto poly(vinyl alcohol) (PVA), ferric ions are remained in the polymer membranes as the Fenton's reagent(Fe^{2+}-H_2O_2) is used to initiate the reaction. Completely reversed trends in terms of the degree of swelling, the pervaporation selectivity, and the flux of permeates are obtained depending on that the ferric ions are present or absent in the membranes. The degree of swelling decreases, the pervaporation selectivity increases, and the flux decreases as the grafting percentage increases for the membranes containing ferric ions. The degree of swelling and the flux of permeates increase but the pervaporation selectivity is reduced as the grafting percentage increases for the membranes which were washed with acid to remove ferric ions.

The influence of the feed composition on ethanol dehydration by pervaporation is discussed by Altra *et al.* in 1999. The dehydration of ethanol-water mixture was carried out in a laboratory pervaporation unit with 110 cm^2 active surface by using different water permselective membranes (GFT-2000, CMC-CA-01, CMC-CE- 02). The experiments were performed at constant temperature (65 °C), flow rate (0.11 $m\ s^{-1}$), permeate side vacuum (30 mbar) and the initial concentration of the feed mixture (80 wt% ethanol). Comparing the separation behaviours of the membranes it was found that all the three types of membrane are suitable for ethanol dehydration by pervaporation and high concentration (99.64 wt%) ethanol product can be achieved.

Young *et al.* (2000) studied the effect of the nonsolvent absorption from the atmosphere into the casting solution on the membrane structure in the poly (ethylene-co-vinyl alcohol)–DMSO–water system was studied via scanning electron microscopy. If the casting solution was directly immersed into water bath, the membrane showed a typically asymmetric structure dominated by liquid–liquid demixing process. When the water vapor was used as a coagulant, the membrane showed another asymmetric structure: porous surface with cellular pores supported by a homogeneous particles-bonded sublayer. The particle structure was representative of crystallization-induced solid–liquid demixing from a homogeneous mixture. If the water absorption time was decreased, a progressive change in the membrane morphologies containing features from both liquid–liquid demixing and solid–liquid demixing phase separations could be observed.

For the purpose of separating aqueous alcohol solution mixtures by the use of the pervaporation technique, a composite membrane of polyacrylic acid (PAA) dip-coated asymmetric polycarbonate (PC) membrane was investigated by Lee *et al*. in 2000. To improve the interface peeling of the PAA/PC composite membrane, the PC membranes were surface-modified with residual air plasma in a tubular-type reactor. The effects of molecular weight of PAA, compositions of the coating solution and the plasma treatment time on the pervaporation performances were investigated. the PAA/PC composite membrane with plasma pretreatment effectively prevented interface peeling when compared with the PAA/PC composite membrane without plasma pretreatment. Optimal results were obtained with the PAA/PC composite membrane prepared from the PAA/ethylene glycol(EG)/aluminum nitrate=1/2/0.05 coating solution at the 5W/30s plasma treatment condition. The water concentration of the permeate approaches 100wt% and a 133g/m^{2}h permeation rate with a 90wt% feed ethanol concentration at 25^{o}C was obtained.

Poly ethylene-co-vinyl alcohol (PEVA) membranes were further investigated by Young *et al*. in 2001. Cells were cultured in smooth and particulate PEVA membranes for up to 7 days. Particulate membranes were prepared by using 1-octanol to precipitate PVAL solutions in DMSO. Such a membrane was microporous characterized by a packed bed of particles. Voids left between the aggregated particles formed a continuous and interconnected porous network. Crystallization of the PVAL polymer induced by 1-octanol is responsible for the formation of particulate morphology. The membrane structure and its relationship with cells were examined by scanning electron microscopy and the MTT assay. It was observed that the particulate membrane was more favorable for the neuron culture than the smooth membrane. Neurons seeded on the particulate membrane were able to regenerate with formation of an extensive neuritic network. Therefore, the particulate structure may spatially mediate cellular response that can promote neuronal cell attachment, differentiation and neuritic growth, indicating that the particulate structure should be useful as a new polymer scaffold for nerve repair.

In 2002, Wang *et al.* investigated a series of copoly(methacrylates) with pendant phosphate and carbamoylphosphonate groups were synthesized. The copolymer membranes were cross-linked by the chemical reaction of either ethylene glycol diglycidyl ether (EGDE) or toluene diisocyanate with hydroxyl or secondary amine groups in copolymer segments at 423 K. Pervaporation (PV) and sorption of aromatic/non-aromatic hydrocarbon mixtures for the membranes were investigated. The membranes were in rubbery state and preferentially permeable to aromatics. The membranes cross-linked with flexible EGDE residues and having diethyl phosphate and/or carbamoylphosphonate groups displayed higher PV performance to benzene/*n*-hexane mixtures with excellent durability. They had lower specific permeation flux and higher PV selectivity, compared with poly(ethylene oxide imide) segmented block copolymer membranes. The higher selectivity was due to a small, but positive contribution of diffusivity selectivity as well as reasonably high solubility selectivity. The lower specific permeation flux was due mainly to the lower diffusion coefficient. This diffusion behavior can be explained by dense polymer-chain packing due to the hydrogen bonding between carbonyl and hydroxyl groups of polymer side-chain as well as relatively high cross-linking density. Sorption isotherms of benzene/*n*-hexane mixtures could be represented by the Flory–Rehner model, but the model overpredicted the sorption amounts of hexane, leading to a little small predictions of solubility selectivity.

Zhang *et al.* (2002) examined pervaporation separation properties for the (MTBE)/C_5/methanol ternary system and three corresponding binary mixtures were measured with a cellulose acetate membrane. It was found that there are very high pervaporation properties for methanol, (the flux of methanol >430 g/m^2.h). However, the flux of methanol for methanol/ C_5/ MTBE is lower than 90 g/m^2.h. The methanol concentrations in permeate are similar for the two binary mixtures. From the result of ternary mixtures, the flux of methanol decreased from about 450 to 100 g/m^2.h, with an increase of MTBE concentration in the feed from 5 to 50 wt%, and there is a strong accompany effect between methanol and MTBE. Based on Fick’s law and the accompany effect, the models of pervaporation flux and quasi-phase equilibrium of permeate components for the ternary mixture were advanced. The calculated values agreed with the experiment results. The models will be useful for separation process design of the MTBE/ C_5/methanol ternary mixture.

The alcohol/water separation of polyelectrolyte multilayer membranes of high charge density prepared upon electrostatic layer-by-layer (LBL) adsorption of cationic and anionic polyelectrolytes is described by Toutianoush (2002). Polyvinylamine (PVA) was used as the cationic polyelectrolyte, and polyvinylsulfonate (PVSu), polyvinylsulfate (PVS) and polyacrylate (PAA) were used as anionic polyelectrolytes; the separation was studied under pervaporation conditions. At low water content in the feed (<20 wt.%), the strongly hydrophilic PVA/PVSu membrane is best suited for separation, while at higher water content the less hydrophilic PVA/PAA membrane exhibits the best separation. Membranes prepared at pH 1.7 with no salt present in the polyelectrolyte solution exhibit a substantially worse separation capability than membranes prepared at pH 1.7 in the presence of NaCl, or at pH 6.8 in the absence of salt. Use of PAA of low molecular weight (m.w. 5000) leads to membranes of much lower total flux than use of PAA of molecular weight 250,000.

Malladi *et al*. (2006) prepared poly(vinyl alcohol)–titanium dioxide (PVA–TiO_2) mixed matrix membranes by incorporating nano-sized titanium dioxide (21 nm) and titanium dioxide surface modified with polyaniline (PANI) into PVA and crosslinked with glutaraldehyde. Suitability of these membranes to dehydrate isopropanol by pervaporation (PV) has been demonstrated. However, swelling results of the crosslinked (unfilled) PVA membranes are higher than all the mixed matrix membranes. The addition of filler particles has decreased the extent of swelling and the flux properties, giving an increase in selectivity.

Guo *et al*. (2006) used co-hydrolysis and co-condensation to prepared polymer membrane of γ-glycidyloxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS) in poly(vinyl alcohol) (PVA) aqueous solution. The effect of the relative molar content of GPTMS on the physicochemical properties of membranes, such as morphology, thermal, mechanical and swelling properties, as well as pervaporation performance for dehydration of ethylene glycol (EG) aqueous solution were investigated. GPTMS exhibited the highest permselectivity of 714 with a permeation flux of 60 g/m^2 h at 70^{o}C for 80 wt.% EG aqueous solution.

Multilayer mixed matrix membranes (MMMMs) consisting of a selective mixed matrix membrane (MMM) top layer, a porous poly(acrylonitrile-co-methyl acrylate) [poly(AN-co-MA)] intermediate layer and a polyphenylene sulfide (PPS) nonwoven fabrics substrate were developed by Guan in 2006. The selective MMM layer was formed by incorporating KA zeolite in poly(vinyl alcohol) (PVA) matrix followed by the cross-linking reaction of PVA with fumaric acid. The fumaric acid induced cross-linking reactions were confirmed by Fourier-transformation infrared (FTIR), and their effects on PVA thermal stability and glass transition temperature were characterized by thermolgravimetric analysis (TGA) and differential scanning calorimetry (DSC). The separation performance of the newly developed MMMMs was investigated in terms of permeance and selectivity (as well as flux and separation factor) with respect to zeolite content, feed temperature and composition for the ethanol-water separation by pervaporation. It is found that the separation performance of the MMMM is superior to that of multilayer homogenous membranes (MHM) containing no zeolite. For example, the MMMM with 20 wt.% KA zeolite loading exhibits a much higher selectivity than that of MHM (1279 versus 511) at 60 °C if the feed is a mixture of 80/20 (wt.%) ethanol/water. In addition, the activation energy of the water permeation is significantly reduced from 16.22 to 10.12kJ/mol after adding of KA zeolite into the PVA matrix, indicating that water molecules require a much less energy to transport through the MMMM because the presence of hydrophilic channels in the framework of zeolite. The excellent pervaporation performance of the MMMM is also resulted from the good contact between zeolite-incorporated and polymer matrix cross-linked by fumaric acid.

In 2006, ε-caprolactam (CPL) aqueous solution dehydration process, pervaporation separation of caprolactam–water system was investigated by Zhang *et al*. using PVA crosslinked membranes. An in depth study of sorption, swelling, pervaporation performances of caprolactam–water mixtures and crosslinked membrane had been conducted. The experimental data demonstrated that the PVA crosslinked with glutaraldehyde showed excellent dehydration performances. The novel separation technique is feasible for application to the dehydration of CPL–water mixtures.

In 2006, A series of soluble polyimides derived from 3,3′,4,4′-benzhydrol tetracarboxylic dianhydride (BHTDA) with various diamines such as 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (BATB), 1,4-bis(4-aminophenoxy)-2,5-di-*tert*-butylbenzene (BADTB), and 2,2′-dimethyl-4,4′- bis(4-aminophenoxy)biphenyl (DBAPB) were investigated for pervaporation separation of ethanol/water mixtures by Li *et al.* Diamine structure effect on the pervaporation of 90 wt% aqueous ethanol solution through the BHTDA-based polyimide membranes was studied. The separation factor ranked in the following order: BHTDA-DBAPB > BHTDA-BATB > BHTDA-BADTB. The increase in molecular volume for the substituted group in the polymer backbone increased the permeation rate. As the feed ethanol concentration increased, the permeation rate increased, while the water concentration in the permeate decreased for all polyimide membranes. The optimum pervaporation performance was obtained by the BHTDA-DBAPB membrane with a 90 wt% aqueous ethanol solution, giving a separation factor of 141, permeation rate of 255 g m^{-2} h^{-1} and 36 000 pervaporation separation index (PSI) value.

Guo *et al.* (2007) examined dehydration of ethylene glycol (EG) aqueous solution by pervaporation by study the surface of the crosslinked poly(vinyl alcohol) membrane using glutaraldehyde as crosslinking reagent. The membrane showed desirable thermal stability, mechanical stability and pervaporation performance (for 80 wt% EG aqueous solution at 70°C, the permeation flux and separation factor are 211 g m^{-2} h^{-1} and 933 respectively. The remarkable dependence of water and EG concentration in permeate side as well as their activity coefficients within the membrane on feed concentration indicate that a strong coupling effect exists between water and EG, which effectively inhibits the permeation of EG and thus considerably enhances the separation selectivity of membrane. With feed temperature increasing, the permeation flux increases but separation factor decreases significantly due to the difference of activation energies between water and EG. With feed flow rate increasing, both the permeation flux and separation factor increase correspondingly.

MATERIALS AND METHODS

Materials

1. Chemicals

The following chemicals were obtained from commercial sources and used directly without further purification unless noted:

1.1 Poly(vinyl alcohol), PVA (87-89% hydrolyzed, average M_W 85,000-146,000, Aldrich), $-[\mathrm{CH_2CH(OH)}]_{87-89}-[\mathrm{CH_2CH(O_2CCH_3)}]_{11-13}-$

1.2 Poly(vinyl alcohol-*co*-ethylene), PVAE (ethylene content 32 mole%, may contain <0.7% polymerized vinyl acetate, Aldrich),

$-[\mathrm{CH_2CH_2}]_{32}-[\mathrm{CH_2CH(OH)}]_{67.3}-[\mathrm{CH_2CH(O_2CCH_3)}]_{0.7}-$

1.3 Polysulfone, PSF (average M_n 22,000, Aldrich)

$-[\mathrm{C_6H_4\text{-}4\text{-}C(CH_3)_2C_6H_4\text{-}4\text{-}OC_6H_4\text{-}4\text{-}SO_2C_6H_4\text{-}4\text{-}O}]_n-$

1.4 Acetic acid (glacial, 99.7%, Lab Scan)

1.5 Acetone (99+%, Merck)

1.6 Ethanol (anhydrous 99.9%, Merck)

1.7 Deionized water used for all the experiments was produced by a water purifier ELGASTAT optima 60 model.

1.8 Dimethyl sulfoxide, DMSO (Analytical reagent grade, Aldrich)

1.9 Hydranal®-Composite 5 (one component reagent for volumetric Karl Fischer titration, Aldrich)

1.10 2-Methoxyethanol, ME ($CH_3OCH_2CH_2OH$, A.C.S grade, Aldrich)

1.11 N-Methyl-2-pyrrolidone, NMP (Analytical reagent grade, Fluka)

1.12 Sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10\ H_2O$, A.C.S grade, Merck)

2. Instrument

The water concentration in both feed and permeate was analyzed by Karl Fischer method on METROHM TITRINO model 701 KF as shown in Figure 4. The permeate sample was weight by a Presica120A balance.

The Water Determination Test (Karl Fischer Method) is designed to determine water content in substances, utilizing the quantitative reaction of water with iodine and sulfur dioxide in the presence of a lower alcohol such as methanol and an organic base such as pyridine, as shown in the following formula:

$$H_2O+I_2+SO_2 + 3\ C_5H_5N \rightarrow 2(C_5H_5N{+}H)I^- + C_5H_5N\cdot SO_3$$

$$C_5H_5N\cdot SO_3 + CH_3OH \rightarrow (C_5H_5N{+}H)O^-SO_2\cdot OCH_3$$

2.1 Standardization

At first 30 ml. methanol was pump into the provided glassware and automatic titration by hydranal-Composite 5 was obtained to get rid of water content in methanol, then 10 ml deionized water was injected into the same glassware for calculating the content of water from concentration of hydranal-Composite 5 used the software of Metrohm Titration.

2.2 Sample test

Prepare 1.0 g. of sample by suck with syringe and inject to glassware. Start to titrate sample with hydranal-Composite 5 then wt% of water in sample was calculated.

2.3 Calculation

$$\text{Water (wt\%)} \quad = \quad \frac{(\text{KFR volume - blank}) \times \text{titer} \times \text{factor}}{\text{Sample size} \times \text{divisor}}$$

Factor and divisor are used for the conversion of the result to different unites which the unit of the result can be selected with the <unit> key.

In this work we investigate water content in wt%, used sample unit in gram which factor is 0.1 and divisor is 1. Blank was determined with an excessive solvent volume, the result can be converted to the amount used subsequently with the aid of the factor. Titer was calculated from equation below:

$$\text{Titer} = \frac{\text{Sample size} \times \text{factor}}{\text{KFR volume}}$$

The factor is used to enter the water content of the standard this work used sample size in g. the factor is 1,000.

Figure 4 Metrohm Titrino model 701 KF for determination of water concentration by Karl Fischer method.

Methods

1. Membrane Preparation

Dense flat sheet membranes with various weight ratios of polymers as summarized in Table 4, They were produced by casting and subsequent solvent evaporation or phase inversion (Figure 5) as followed:

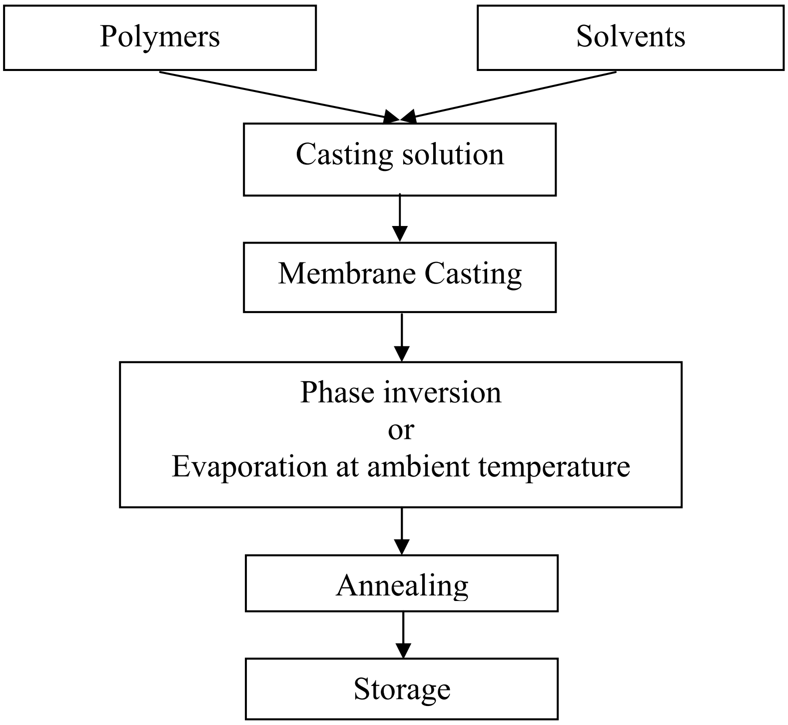


Figure 5 Schematic of general procedure for production of membranes by the phase inversion process.

1.1 Casting solution

1.1.1 Polysulfone (PSF) membrane preparation

Polysulfone casting solutions were prepared by dissolving 5.0, 7.5 and 10.0 wt% of PSF in a water miscible solvent, N-methyl-2-pyrrolidone (NMP), with or without 2-methoxyethanol (ME) with stirring the solution at room temperature for 12 hrs or until the mixture was completely homogeneous.

1.1.2 Poly(vinyl alcohol-*co*-ethylene), PVAE, membrane preparation

Poly(vinyl alcohol-*co*-ethylene) casting solutions were prepared by dissolving 7.5, 10.0 and 12.5 wt.% of PVAE in a water miscible solvent, dimethyl sulfoxide, DMSO with stirring the solution at room temperature for 12 hrs or until the mixture was completely homogeneous.

1.1.3 Poly (vinyl alcohol), PVA, membrane preparation

Poly (vinyl alcohol) casting solutions were prepared by dissolving 7.5, 10.0 and 12.5 wt% of PVA in deionized water with stirring the solution at 90°C for 1 hour or until the mixture was completely homogeneous.

1.1.4 Poly(vinyl alcohol-*co*-ethylene), PVAE, and polysulfone, PSF blended membrane preparation

Poly(vinyl alcohol-*co*-ethylene), PVAE, and polysulfone, PSF blended casting solutions were prepared by dissolving 7.5, 10.0 and 12.5 wt% of PVAE and 2.5 wt% of PSF in DMSO with stirring the solution at room temperature for 12 hrs or until the mixture was completely homogeneous.

1.2 Membrane casting

The prepared casting solutions were poured on a glass plate at room temperature when PSF or PVAE was used but at 90°C when PVA was used. Membrane casting was accomplished with a glass rod and the required thickness was controlled with the aid of an appropriate spacers provided on both ends of the glass plate (Figure 6). Then, casted membrane was either immersed into a deionized water bath in which the solvent was removed by miscible with the deionized water and a gel was formed (Figure 7), or evaporated the solvent under ambient temperature (30^{o}C) in a fume hood for 24 hours (Figure 8). The membrane was cut into required sizes and dried by keeping the membrane in desiccators at room temperature for 24 hours or kept in vacuum oven at 40 °C for 24 hours.

Figure 6 Membrane casting.

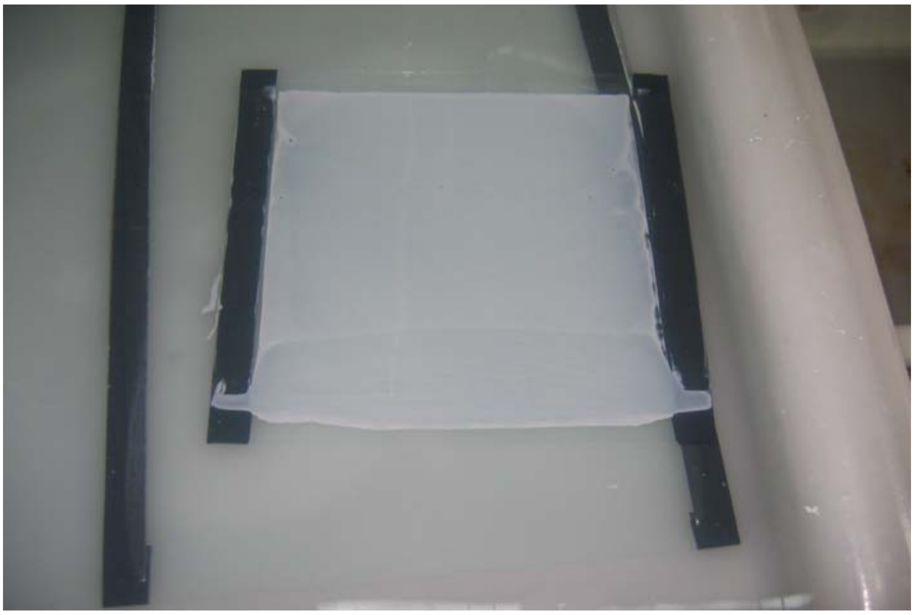


Figure 7 Membrane formation by phase inversion method.

Figure 8 Membrane formation by evaporation.

1.3 Crosslinking

The PVA membrane film was hydrophilic and absorbed water quickly, assuming a swollen film state. Swelling of the membrane film was not desirable since it would disrupt the membrane integrity and lower the separation efficiency. Thus, the dried PVA membranes prepared were further crosslinked to decrease the hydrophilicity of the membranes. The dried PVA membranes were thermally crosslinked by heating the film in a vacuum oven at 90^{o}C for 30 minutes or immersed in sodium tetraborate decahydrate solution for 6 and 10 hours and then kept the membrane in desiccators at room temperature for 24 hours or kept in vacuum oven at 40 °C for 24 hours.

Table 4 Composition of casting solutions and membrane formation conditions.

Membrane code	Amount of PSF (wt%)	Amount of PVAE (wt%)	Amount of PVA (wt%)	Amount of solvent (wt%)	Casting temp (^oC)	Casting process	Drying (h)	Amount of Cross linking agent or non-solvent (%w/w)	Immersing time (h)
PSF-1	5.0	-	-	NMP, 95.0	30^oC	phase inversion[1]	Vacuum, 40^oC, 24h	-	-
PSF-2	7.5	-	-	NMP, 92.5	30^oC	phase inversion	Vacuum, 40^oC, 24h	-	-
PSF-3	10.0	-	-	NMP, 90.0	30^oC	phase inversion	Vacuum, 40^oC, 24h	-	-
PSF-4	5.0	-	-	NMP, 95.0	30^oC	phase inversion	In desiccators 30^oC, 24h	-	-
PSF-5	7.5	-	-	NMP, 92.5	30^oC	phase inversion	In desiccators, 30^oC, 24h	-	-
PSF-6	10.0	-	-	NMP, 90.0	30^oC	phase inversion	In desiccators, 30^oC, 24h	-	-

Table 4 (Continued)

Membrane code	Amount of PSF (wt%)	Amount of PVAE (wt%)	Amount of PVA (wt%)	Amount of solvent (wt%)	Casting temp (^oC)	Casting process	Drying (h)	Amount of Cross linking agent or non-solvent (%w/w)	Immersing time (h)
PSF-7	5.0	-	-	NMP, 95.0	30^{o}C	phase inversion	Vacuum, 40^{o}C, 24h	ME, 2%	-
PSF-8	7.5	-	-	NMP, 92.5	30^{o}C	phase inversion	Vacuum, 40^{o}C, 24h	ME, 2%	-
PSF-9	10.0	-	-	NMP, 90.0	30^{o}C	phase inversion	Vacuum, 40^{o}C, 24h	ME, 2%	-
PVAE-1	-	7.5	-	DMSO, 92.5	30^{o}C	phase inversion	Vacuum, 40^{o}C, 24h	-	-
PVAE-2	-	10.0	-	DMSO,90.0	30^{o}C	phase inversion	Vacuum, 40^{o}C, 24h	-	-
PVAE-3	-	12.5	-	DMSO, 87.5	30^{o}C	phase inversion	Vacuum, 40^{o}C, 24h	-	-

Table 4 (Continued)

Membrane code	Amount of PSF (wt%)	Amount of PVAE (wt%)	Amount of PVA (wt%)	Amount of solvent (wt%)	Casting temp (°C)	Casting process	Drying (h)	Amount of Cross linking agent or non-solvent (%w/w)	Immersing time (h)
PVAE-4	-	7.5	-	DMSO, 92.5	30°C	phase inversion	In desiccators 30°C, 24h	-	-
PVAE-5	-	10.0	-	DMSO,90.0	30°C	phase inversion	In desiccators, 30°C, 24h	-	-
PVAE-6	-	12.5	-	DMSO, 87.5	30°C	phase inversion	In desiccators, 30°C, 24h	-	-
PVA-1	-	-	7.5	Deionized water, 92.5	90°C	Evaporated at ambient temp.	Vacuum, 40°C, 24h	-	-
PVA-2	-	-	10.0	Deionized water, 90.0	90°C	Evaporated at ambient temp.	Vacuum, 40°C, 24h	-	-

Table 4 (Continued)

Membrane code	Amount of PSF (wt%)	Amount of PVAE (wt%)	Amount of PVA (wt%)	Amount of solvent (wt%)	Casting temp (^{o}C)	Casting process	Drying (h)	Amount of Cross linking agent or non-solvent (%w/w)	Immersing time (h)
PVA-3	-	-	12.5	Deionized water, 87.5	90^{o}C	Evaporated at ambient temp.	Vacuum, 40^{o}C, 24h	-	-
PVA-4	-	-	7.5	Deionized water, 92.5	90^{o}C	Evaporated at ambient temp.	In desiccators 30^{o}C, 24h	-	-
PVA-5	-	-	10.0	Deionized water, 90.0	90^{o}C	Evaporated at ambient temp.	In desiccators, 30^{o}C, 24h	-	-
PVA-6	-	-	12.5	Deionized water, 87.5	90^{o}C	Evaporated at ambient temp.	In desiccators, 30^{o}C, 24h	-	-

Table 4 (Continued)

Membrane code	Amount of PSF (wt%)	Amount of PVAE (wt%)	Amount of PVA (wt%)	Amount of solvent (wt%)	Casting temp (^{o}C)	Casting process	Drying (h)	Amount of Cross linking agent or non-solvent (%w/w)	Immersing time (h)
PVAE-PSF-1	2.5	7.5	-	DMSO, 90.0	30^{o}C	phase inversion	Vacuum, 40^{o}C, 24h	-	-
PVAE-PSF -2	2.5	10.0	-	DMSO, 87.5	30^{o}C	phase inversion	Vacuum, 40^{o}C, 24h	-	-
PVAE-PSF -3	2.5	12.5	-	DMSO, 85.0	30^{o}C	phase inversion	Vacuum, 40^{o}C, 24h	-	-
PVAE-PSF -4	2.5	7.5	-	DMSO, 90.0	30^{o}C	phase inversion	In desiccators, 30^{o}C, 24h	-	-
PVAE-PSF -5	2.5	10.0	-	DMSO, 87.5	30^{o}C	phase inversion	In desiccators, 30^{o}C, 24h	-	-
PVAE-PSF -6	2.5	12.5	-	DMSO, 85.0	30^{o}C	phase inversion	In desiccators, 30^{o}C, 24h	-	-

Table 4 (Continued)

Membrane code	Amount of PSF (wt%)	Amount of PVAE (wt%)	Amount of PVA (wt%)	Amount of solvent (wt%)	Casting temp (°C)	Casting process	Drying (h)	Amount of Cross linking agent or non-solvent (%w/w)	Immersing time (h)
X-PVA-1[2]	-	-	7.5	Deionized water, 90.0	90°C	Evaporated at ambient temp.	Vacuum, 40°C, 24h	$Na_2B_2O_7$, 2.5	6
X-PVA-2[2]	-	-	10.0	Deionized water, 87.5	90°C	Evaporated at ambient temp.	Vacuum, 40°C, 24h	$Na_2B_2O_7$, 2.5	6
X-PVA-3[2]	-	-	12.5	Deionized water, 85.0	90°C	Evaporated at ambient temp.	Vacuum, 40°C, 24h	$Na_2B_2O_7$, 2.5	6
X-PVA-4[2]	-	-	7.5	Deionized water, 90.0	90°C	Evaporated at ambient temp.	In desiccators, 30°C, 24h	$Na_2B_2O_7$, 2.5	6

Table 4 (Continued)

Membrane code	Amount of PSF (wt%)	Amount of PVAE (wt%)	Amount of PVA (wt%)	Amount of solvent (wt%)	Casting temp (°C)	Casting process	Drying (h)	Amount of Cross linking agent or non-solvent (%w/w)	Immersing time (h)
X-PVA-5[2]	-	-	10.0	Deionized water, 87.5	90°C	Evaporated at ambient temp.	In desiccators, 30°C, 24h	$Na_2B_2O_7$, 2.5	6
X-PVA-6[2]	-	-	12.5	Deionized water, 85.0	90°C	Evaporated at ambient temp.	In desiccators, 30°C, 24h	$Na_2B_2O_7$, 2.5	6
X-PVA-7[2]	-	-	7.5	Deionized water, 90.0	90°C	Evaporated at ambient temp.	In desiccators, 30°C, 24h	$Na_2B_2O_7$, 2.5	10
X-PVA-8[2]	-	-	10.0	Deionized water, 87.5	90°C	Evaporated at ambient temp.	In desiccators, 30°C, 24h	$Na_2B_2O_7$, 2.5	10

Table 4 (Continued)

Membrane code	Amount of PSF (wt%)	Amount of PVAE (wt%)	Amount of PVA (wt%)	Amount of solvent (wt%)	Casting temp (^{o}C)	Casting process	Drying (h)	Amount of Cross linking agent or non-solvent (%w/w)	Immersing time (h)
X-PVA-9[2]	-	-	12.5	Deionized water, 85.0	90^{o}C	Evaporated at ambient temp.	In desiccators, 30^{o}C, 24h	$Na_2B_2O_7$, 2.5	10

[1]phase inversion by immersed into deionized water bath; [2]crosslinked PVA

2. Pervaporation Process

Ethanol/water binary mixture contains 3-10 wt% water was used as feed. The pervaporation experiments were conducted in a laboratory scale unit supplied by Nitto Denko Corporation as shown in Figure 9. The flat sheet membranes were put into a stainless steel test cell with an inner diameter of 7.5 cm and the estimated surface area is 4.42 cm^2. A 200 g of prepared ethanol/water binary mixture was fed into the test cell and maintained at a constant temperature of 30°C. The flow rate was set at 30 ml/min according to the unit specifications. On the permeate side, a vacuum of around 133 Pa (1 mmHg) was applied and the permeates were condensed by a cold trap with liquid nitrogen to ensure all the permeates were fully collected. Both the permeate and feed sides were sampled in a fixed interval (normally hour) and the components of the permeate and feed samples were analyzed to determine the separation factor.

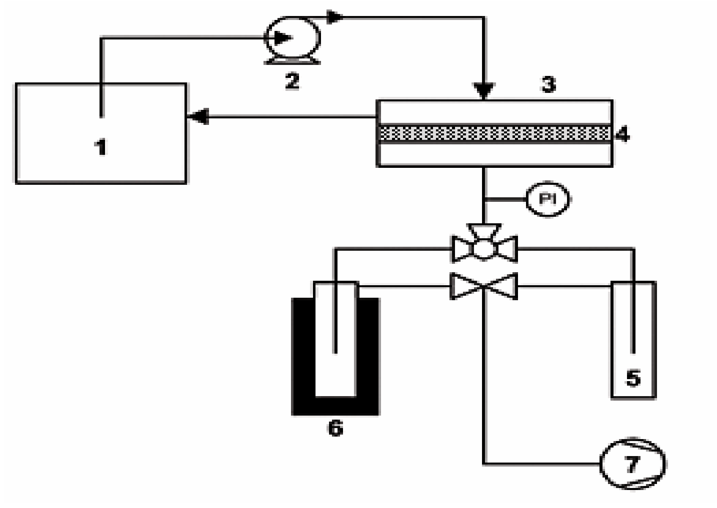


Figure 9 Schematic diagram of the test cell set up used in this study. 1.feed tank, 2.pump, 3.membrane module, 4.membrane, 5.cold trap, 6.liquid nitrogen and 7.vacuum pump.

3. Analysis

The membrane performance was determined by the water permeate flux and the selectivity or separation factor which were calculated as followed:

3.1 The water permeate flux

The flux was determined by weighing the permeate sample mass then divided by the product of sample time and the membrane area.

$$J = \frac{Q}{A\Delta t}$$

where J = flux in kg/m^2 h

Q = quantity of the permeate kg

A = effective membrane area in m^2

and Δt = time interval to collect the permeate in h

3.2 The selectivity or the separation factor of water to ethanol

The selectivity or separation factor (α) is defined by the following equation:

$$\alpha = \frac{y_w / y_a}{x_w / x_a}$$

where α = selectivity or separation factor

y = weight fraction of component in permeate

x = weight fraction of component in feed subscripts “w” and “a” = water and alcohol in the ethanol/water mixture

RESULTS AND DISCUSSION

Polymer concentrations in the casting solution were studied as shown in Table 5. It was found that the suitable concentration for casting the membrane of polysulfone, PSF; poly(vinyl alcohol), PVA; and poly(vinyl alcohol-*co*-ethylene), PVAE, are in the range of 5.0-10.0wt%, 7.5-12.5wt% and 7.5-12.5wt% respectively.

Casting solutions from PSF, PVAE and PVAE-PSF blended were obtained by dissolving the polymer at room temperature (30°C) in a polar aprotic solvent (water miscible solvent) such as NMP or DMSO with or without pore making agent such as 2-methoxyethanol, and membranes were obtained by phase inversion process into deionized water which eluted the solvent along with the pore making agent, then subsequently dried under vacuum at 40°C or were kept in desiccators for 24 hours. On the other hand, PVA could not dissolve in deionized water at room temperature, casting solvents were obtained at 90°C and the membranes were obtained by evaporation off the deionized water at ambient temperature for 24 hours and were kept in desiccators for 24 hours. Membranes from PVA were further crosslinked to decrease the hydrophilicity of the membranes by immersed into sodium tetraborate solution for 6 and 10 hours. All membranes obtained are flat sheet type having thickness varied from 28 μm to 30.5 μm which are unavoidable in membrane casting, however, the thickness obtained are not dependent on the casting process as reported in Table 6. This thickness range are considered insignificantly different, although, the thickness of membranes obtained from PVAE (30 μm) was slightly thicker than the thickness of membranes obtained from PSF, PVA (28 μm) and PVAE-PSF (29μm). Hence, effects of the membrane thickness on the membrane performances were omitted in this study.

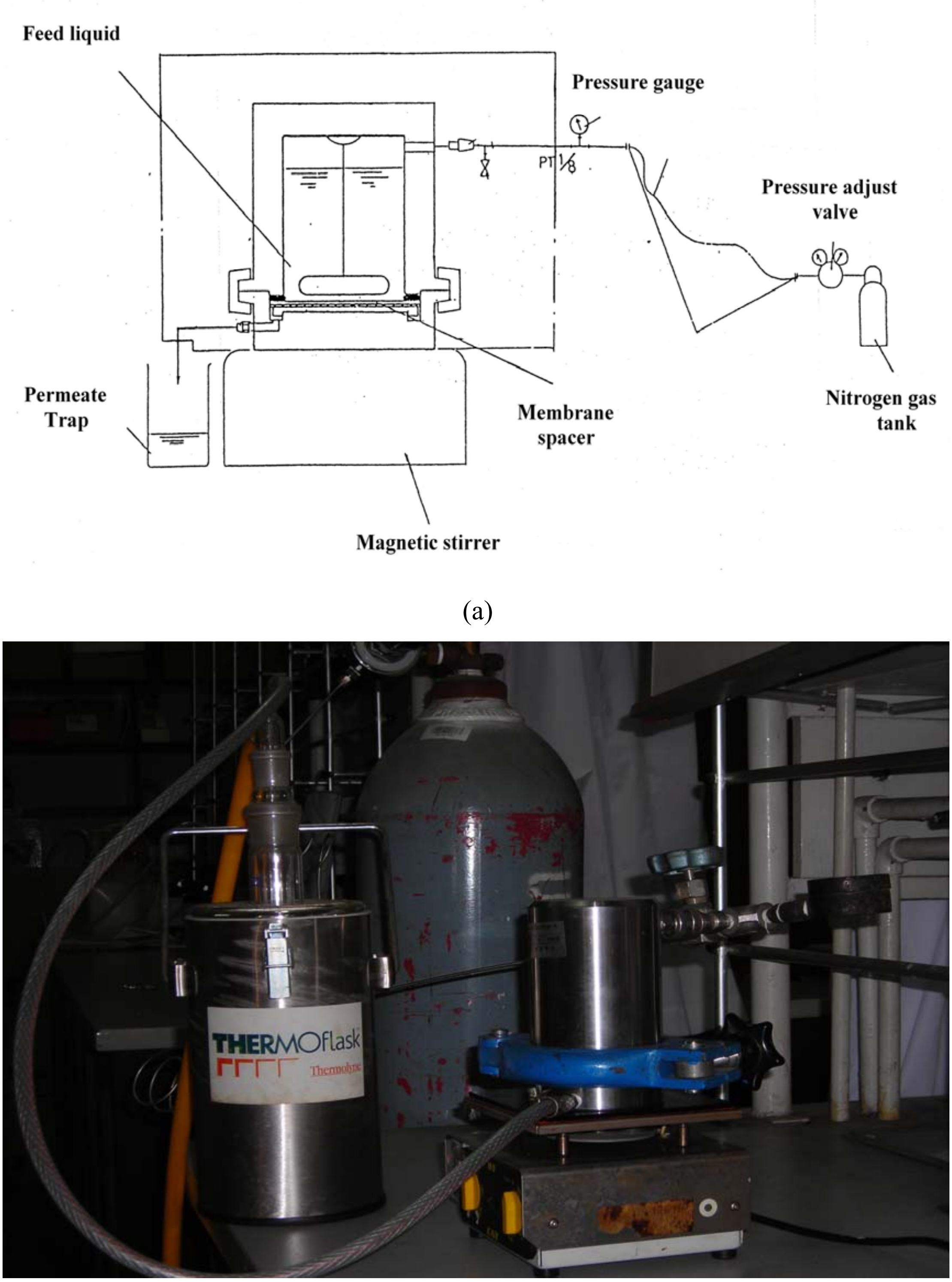
Dehydration of azeotropic water/ethanol (W:E) mixtures with wt% ratio from 3.0:97.0, 5.0:95.0 and 10.0:90.0 by pervaporation membrane separation through all flat sheet membranes obtained were investigated as shown in Figure 10.

Table 5 Effect of polymer concentration in the casting solution on the resulting membranes.

%wt of casting solution		Characteristics of membranes
Polymer	Solvent	
PSF, 5.0	NMP, 95.0	Satisfactory
PSF, 7.5	NMP, 92.5	Satisfactory
PSF, 10.0	NMP, 90.0	Satisfactory
PSF, 12.5	NMP, 87.5	Too thick
PVA, 5.0	Deionized water, 95.0	Imperfect
PVA, 7.5	Deionized water, 92.5	Satisfactory
PVA, 10.0	Deionized water, 90.0	Satisfactory
PVA, 12.5	Deionized water, 87.5	Satisfactory
PVAE, 5.0	DMSO, 95.0	Imperfect
PVAE, 7.5	DMSO, 92.5	Satisfactory
PVAE, 10.0	DMSO, 90.0	Satisfactory
PVAE, 12.5	DMSO, 87.5	Satisfactory

Table 6 The thickness of the prepared membranes.

Membrane code	Thickness (μm)	Membrane code	Thickness (μm)
PSF-1	28.0	PVA-1	28.1
PSF-2	28.2	PVA-2	28.3
PSF-3	28.3	PVA-3	28.4
PSF-4	28.1	PVA-4	28.0
PSF-5	28.2	PVA-5	28.2
PSF-6	28.4	PVA-6	28.4
PSF-ME-1	28.1	PVAE -1	30.3
PSF-ME-2	28.4	PVAE -2	30.5
PSF-ME-3	28.5	PVAE -3	30.5
X-PVA-1	28.2	PVAE -4	30.3
X-PVA-2	28.4	PVAE -5	30.4
X-PVA-3	28.4	PVAE -6	30.5
X-PVA-4	28.3	PVAE -PSF-1	29.3
X-PVA-5	28.4	PVAE -PSF-2	29.4
X-PVA-6	28.5	PVAE -PSF-3	29.4
X-PVA-7	28.2	PVAE -PSF-4	29.2
X-PVA-8	28.2	PVAE -PSF-5	29.4
X-PVA-9	28.3	PVAE-PSF-6	29.5



(a)

(b)

Figure 10 Membrane module (a),set up for pervaporation membrane process (b), prepared polymeric membrane (c), for dehydration of water of ethanol water azeotropic mixture in this study.

(c)

Figure 10 Membrane module (a),set up for pervaporation membrane process (b), prepared polymeric membrane (c), for dehydration of water of ethanol water azeotropic mixture in this study. (Continued)

The effect of membrane performances were monitored by measuring water concentration in the retentate and permeate by Karl Fischer method. It was found that the water permeate flux decrease but the selectivity increase with an increase in time because of permeate being continuously removed during the experiment, followed by a relatively steady state flux as shown in Figure 11. Results of pervaporation separation of membrane performances as expressed in term of the steady state flux and selectivity are shown in Table 7.

Generally, the component with the smallest weight fraction in the mixture could preferentially be transported across the membrane. In this study, water component in the feed composition was smaller (3-10 wt%). Thus, the efficiency of pervaporation depends to a great extent on the polymeric materials used for casting membranes. Water always shows preferential permeation for membrane made from hydrophilic polymers. This hydrophilicity is caused by groups present in the polymer chain that are able to interact with water molecules, e.g., by hydrogen bonding or dipole-dipole interaction. On the other hand, water repellent hydrophobic polymers possess no groups that show affinity for water due to the fact that there are no strong interaction forces to take place, thus permeation and separation can only take place based on differences in size and shape.

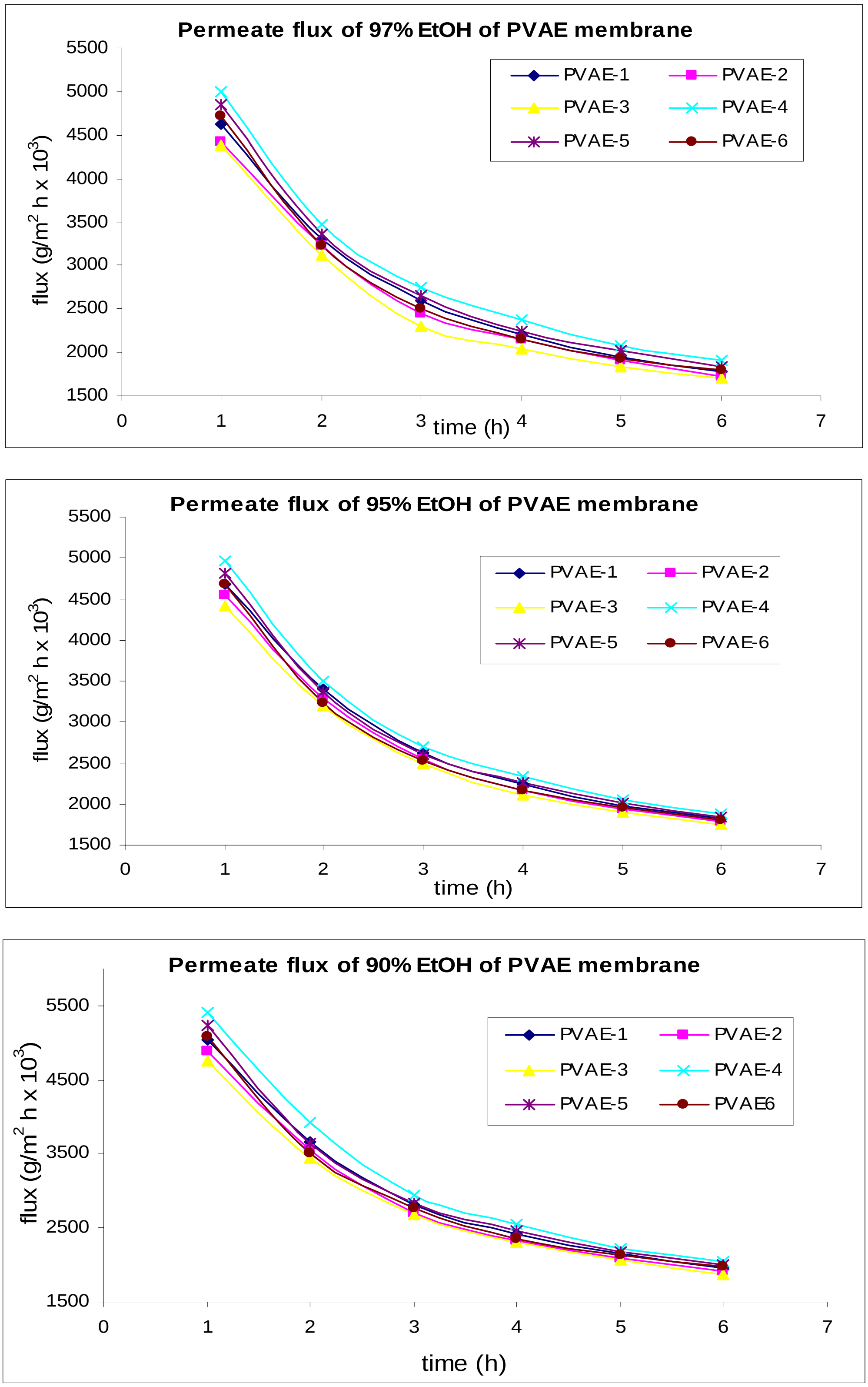
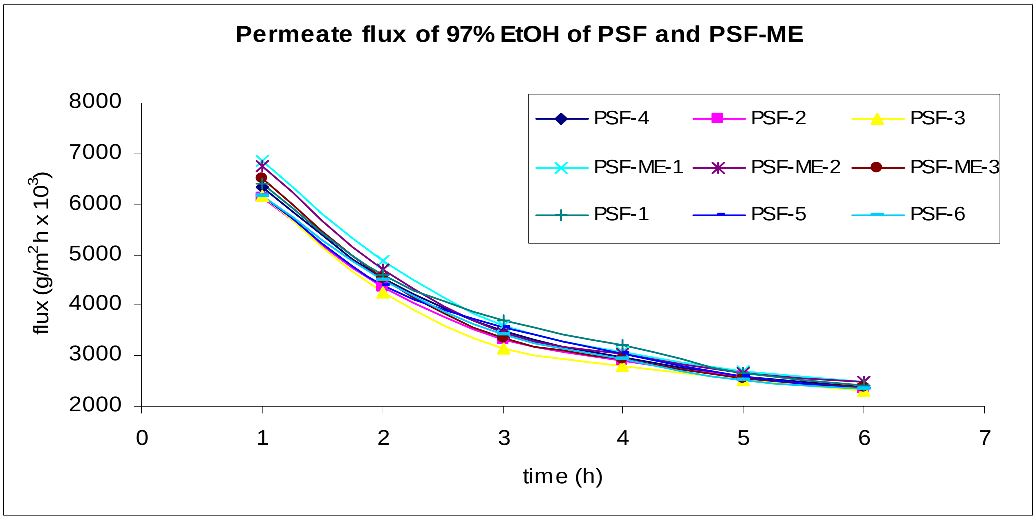
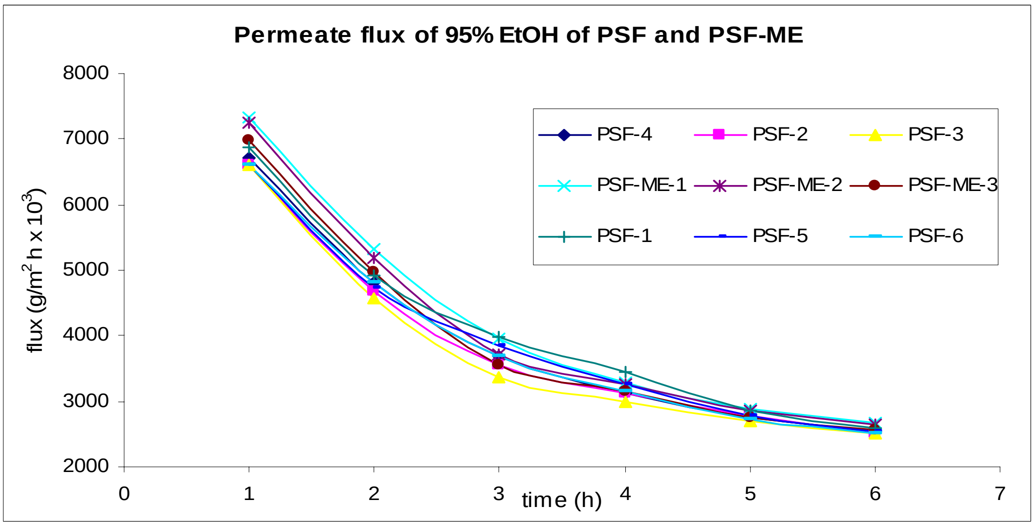


Figure 11 Water permeate flux as a function of time of the prepared polymeric membranes.


Permeate flux of 97% EtOH of PSF and PSF-ME


Permeate flux of 95% EtOH of PSF and PSF-ME

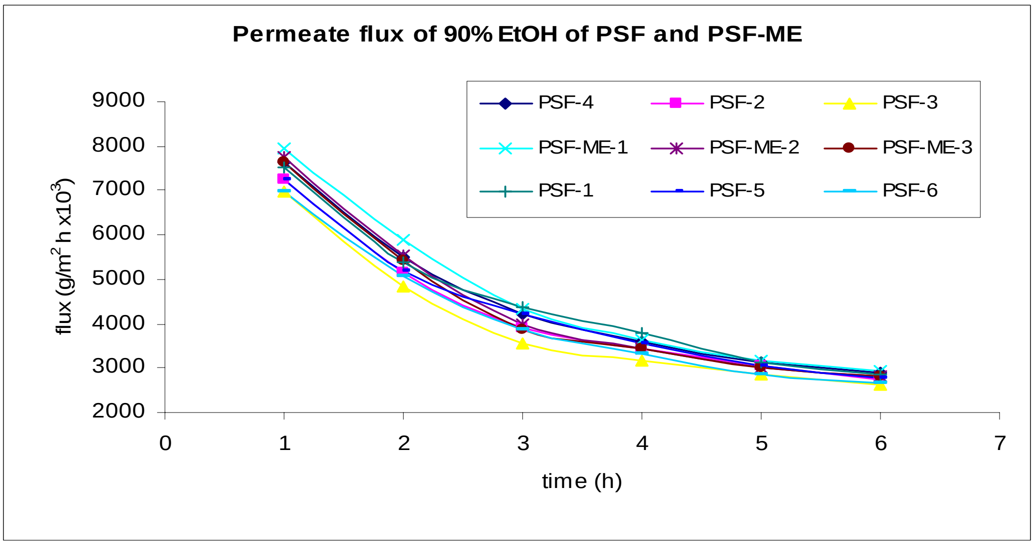
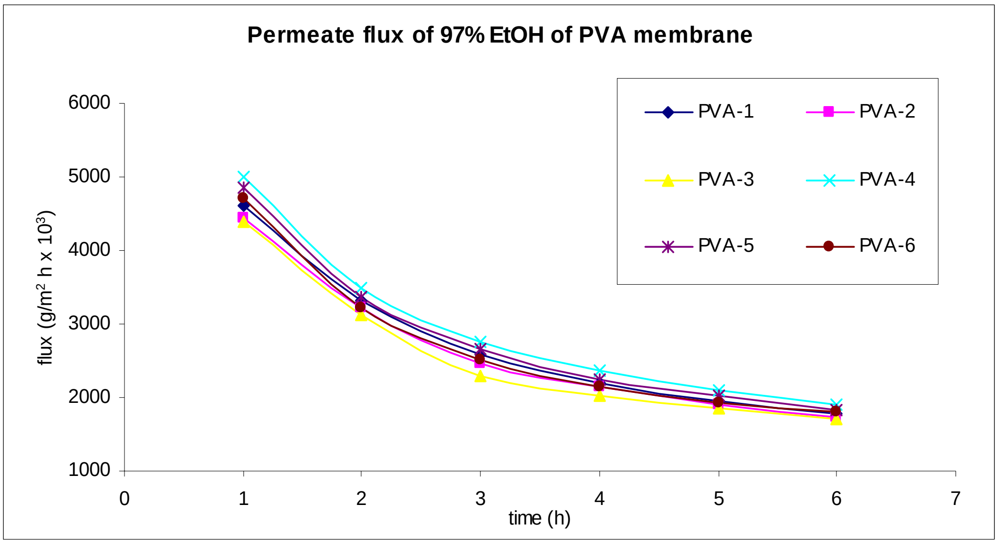
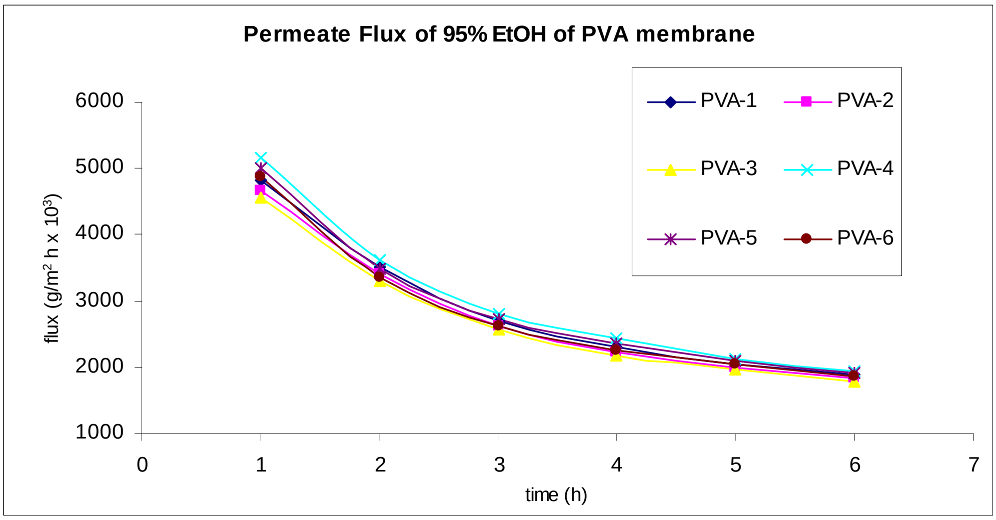
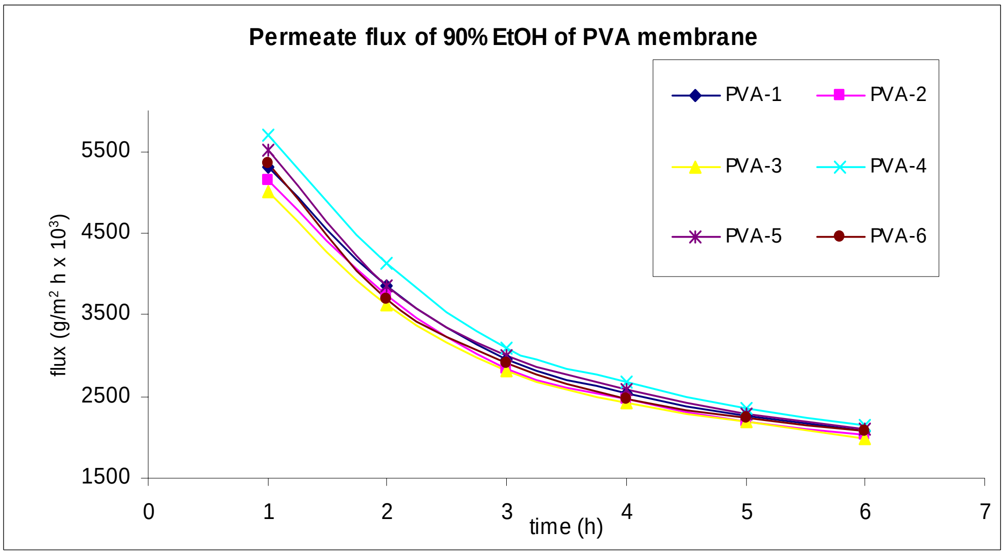

Permeate flux of 90% EtOH of PSF and PSF-ME

Figure 11 (Continued)







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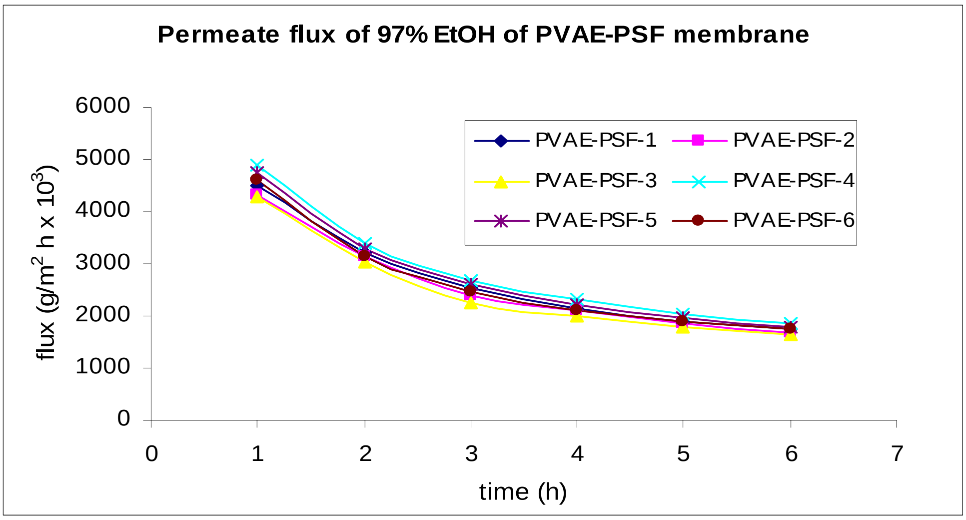
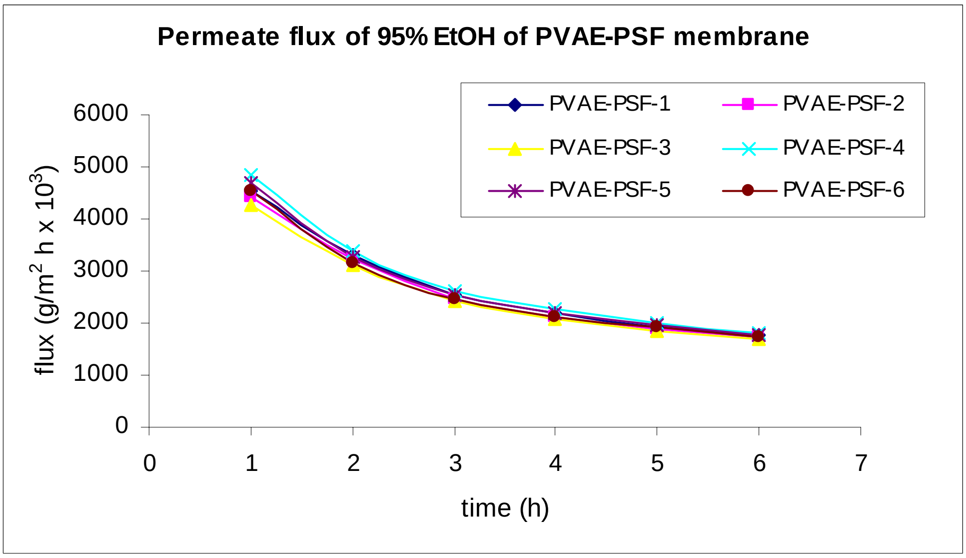




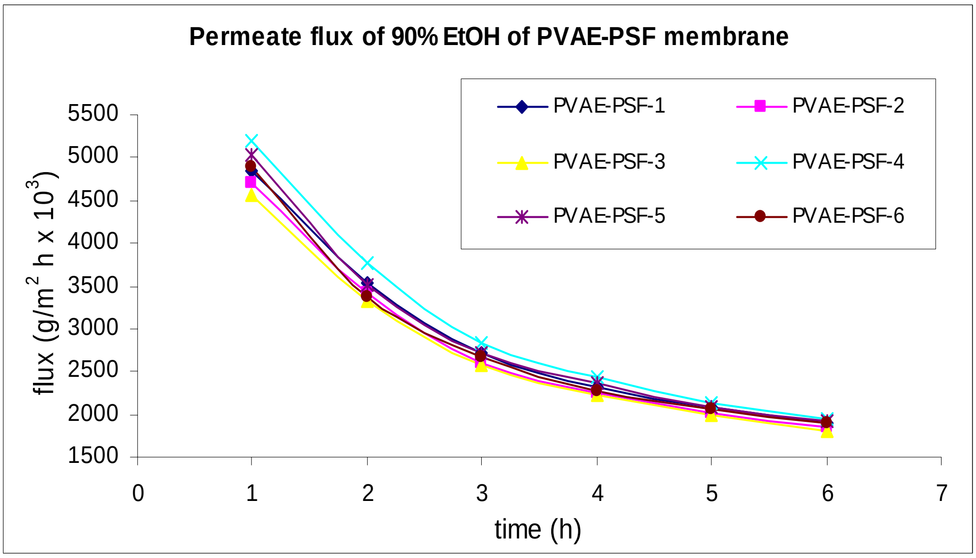
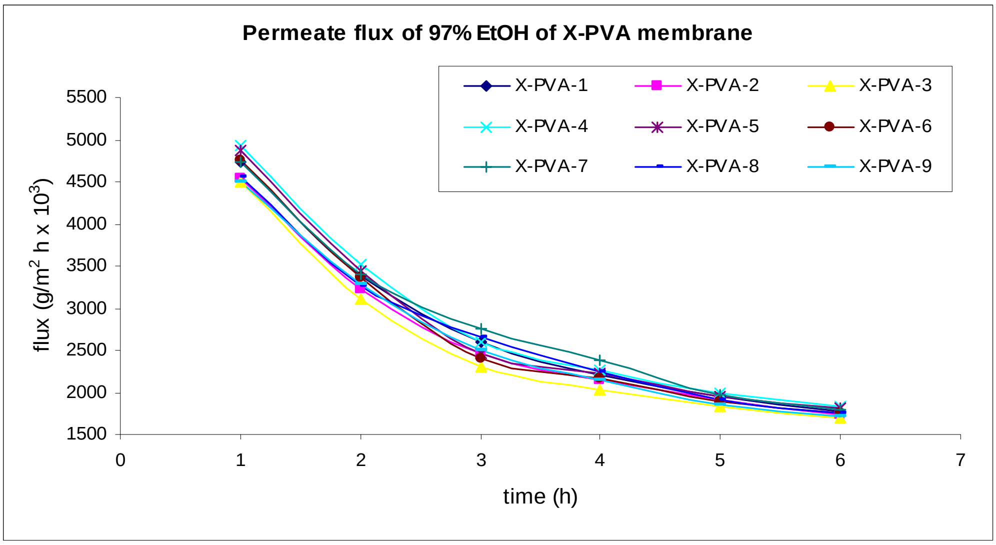
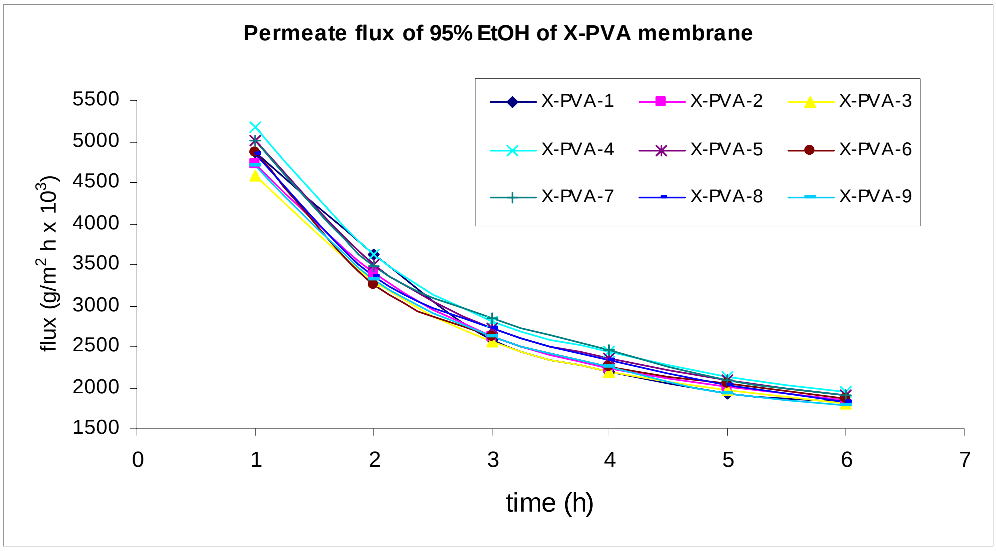


Figure 11 (Continued)





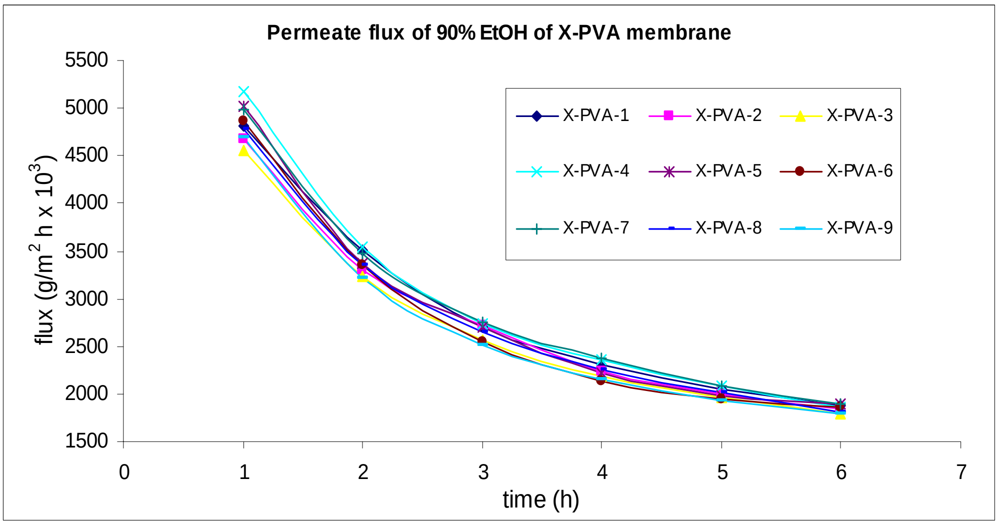


Figure 11 (Continued)

Table 7 Water permeate flux and selectivity for water dehydration pervaporation having the feed composition of water/ethanol (W:E)= 3.0:97.0, 5.0:95.0 and 10.0:90.0 from prepared polymeric membranes.

Polymer code (wt%)	(W:E) in feed (wt%)	(W:E) in retentate (wt%)	Water in permeate (wt%)	Flux (*J*) (kg/m^2 h)	Selectivity (α)
PSF-1	3 : 97	2.41:97.59	6.87	1.174	2.38
(5.0%)	5 : 95	3.45:96.55	10.64	1.225	2.26
	10 : 90	6.20:93.80	17.10	1.293	1.86
PSF-2	3 : 97	2.08:97.92	8.80	1.137	3.12
(7.5%)	5 : 95	3.11:96.89	12.71	1.177	2.77
	10 : 90	5.50:94.50	19.15	1.243	2.13
PSF-3	3 : 97	1.67:98.33	10.96	1.102	3.98
(10.0%)	5 : 95	2.62:97.38	14.74	1.157	3.29
	10 : 90	5.20:94.80	20.98	1.211	2.39
PSF-4	3 : 97	2.47:97.53	6.90	1.180	2.40
(5.0%)	5 : 95	3.51: 96.49	10.74	1.232	2.29
	10 : 90	6.26:93.74	17.13	1.301	1.86
PSF-5	3 : 97	2.12:97.88	8.85	1.145	3.14
(7.5%)	5 : 95	3.16:96.84	12.74	1.195	2.78
	10 : 90	5.56:94.44	19.18	1.251	2.14
PSF-6	3 : 97	1.70:98.30	10.99	1.111	4.00
(10.0%)	5 : 95	2.67:97.33	14.78	1.165	3.30
	10 : 90	5.25:94.75	21.04	1.219	2.40
PSF-ME-1	3 : 97	2.95:97.05	7.41	1.201	2.59
(5.0%)	5 : 95	3.98:96.02	11.04	1.255	2.36
	10 : 90	6.71:93.29	16.33	1.331	1.76
PSF-ME-2	3 : 97	2.60:97.40	8.52	1.174	3. 01
(7.5%)	5 : 95	3.61:96.39	12.89	1.227	2.81
	10 : 90	5.98:94.02	18.35	1.282	2.02

Table 7 (Continued)

Polymer code (wt%)	(W:E) in feed (wt%)	(W:E) in retentate (wt%)	Water in permeate (wt%)	Flux (*J*) (kg/m^2 h)	Selectivity (α)
PSF-ME-3 (10.0%)	3 : 97	2.19:97.81	10.08	1.131	3.63
	5 : 95	3.19:96.81	14.96	1.197	3.34
	10 : 90	5.86:94.14	20.21	1.251	2.28
PVAE-1 (7.5%)	3 : 97	1.04:98.96	11.04	1.040	4.02
	5 : 95	2.16:97.84	16.00	1.090	3.62
	10 : 90	4.55:95.45	20.29	1.140	2.29
PVAE-2 (10.0%)	3 : 97	0.47:99.53	14.11	0.983	5.32
	5 : 95	1.61:98.39	18.91	1.039	4.43
	10 : 90	4.03:95.97	21.34	1.084	2.44
PVAE-3 (12.5%)	3 : 97	0.14:99.86	15.90	0.962	6.12
	5 : 95	1.23:98.77	20.93	1.015	5.03
	10 : 90	3.72:96.28	22.76	1.072	2.65
PVAE-4 (7.5%)	3 : 97	1.27:98.73	10.93	1.051	3.97
	5 : 95	2.33:97.67	15.89	1.106	3.59
	10 : 90	4.79:95.21	20.17	1.165	2.28
PVAE-5 (10.0%)	3 : 97	0.64:99.36	14.00	1.006	5.27
	5 : 95	1.91:98.09	18.79	1.050	4.40
	10 : 90	4.37:95.63	21.22	1.115	2.43
PVAE-6 (12.5%)	3 : 97	0.39:99.61	15.79	0.971	6.07
	5 : 95	1.58:98.42	20.81	1.028	5.00
	10 : 90	4.07:95.93	22.64	1.082	2.64
PVAE- PSF-1 (7.5:2.5%)	3 : 97	1.46:98.54	9.14	1.063	3.26
	5 : 95	2.57:97.43	14.11	1.116	3.12
	10 : 90	5.06:94.94	19.43	1.175	2.17

Table 7 (Continued)

Polymer code (wt%)	(W:E) in feed (wt%)	(W:E) in retentate (wt%)	Water in permeate (wt%)	Flux (*J*) (kg/m^2 h)	Selectivity (α)
PVAE-PSF-2 (10.0:2.5%)	3 : 97	0.96:99.04	12.03	1.016	4.43
	5 : 95	2.02:97.98	16.97	1.058	3.89
	10 : 90	4.53:95.47	21.48	1.125	2.46
PVAE-PSF-3 (12.5-2.5%)	3 : 97	0.58:99.42	13.66	0.981	5.12
	5 : 95	1.63:98.37	18.90	1.037	4.43
	10 : 90	4.26:95.74	22.36	1.092	2.59
PVAE-PSF-4 (7.5:2.5%)	3 : 97	1.78:98.22	9.01	1.077	3.20
	5 : 95	2.83:97.17	13.98	1.129	3.09
	10 : 90	5.76:94.24	19.39	1.190	2.17
PVAE-PSF-5 (10.0:2.5%)	3 : 97	1.10:98.90	11.90	1.029	4.37
	5 : 95	2.46:97.54	16.84	1.072	3.85
	10 : 90	4.87:95.13	21.34	1.138	2.44
PVAE-PSF-6 (12.5:2.5%)	3 : 97	0.89:99.11	13.54	0.993	5.07
	5 : 95	2.18:97.82	18.76	1.050	4.39
	10 : 90	4.57:95.43	22.31	1.107	2.59
PVA-1 (7.5%)	3 : 97	1.53:98.47	9.05	1.094	3.22
	5 : 95	2.64:97.36	14.01	1.145	3.10
	10 : 90	5.14:94.86	19.51	1.213	2.18
PVA-2 (10.0%)	3 : 97	1.05:98.95	11.93	1.057	4.38
	5 : 95	2.11:97.89	16.86	1.097	3.86
	10 : 90	4.61:95.39	21.46	1.163	2.46
PVA-3 (12.5%)	3 : 97	0.65:99.35	13.54	1.022	5.07
	5 : 95	1.72:98.28	18.80	1.077	4.40
	10 : 90	4.33:95.67	22.44	1.131	2.61

Table 7 (Continued)

Polymer code (wt%)	(W:E) in feed (wt%)	(W:E) in retentate (wt%)	Water in permeate (wt%)	Flux (J) (kg/m^2 h)	Selectivity (α)
PVA-3	3 : 97	0.65:99.35	13.54	1.022	5.07
(12.5%)	5 : 95	1.72:98.28	18.80	1.077	4.40
	10 : 90	4.33:95.67	22.44	1.131	2.61
PVA-4	3 : 97	1.74:98.26	8.92	1.117	3.17
(7.5%)	5 : 95	2.80:97.20	13.86	1.172	3.06
	10 : 90	5.72:94.28	19.18	1.228	2.14
PVA-5	3 : 97	1.08:98.92	11.80	1.073	4.33
(10.0%)	5 : 95	2.37:97.63	16.75	1.113	3.83
	10 : 90	4.84:95.16	21.22	1.178	2.43
PVA-6	3 : 97	0.87:99.13	13.43	1.036	5.02
(12.5%)	5 : 95	2.02:97.98	18.64	1.090	4.36
	10 : 90	4.51:95.49	22.31	1.149	2.59
X-PVA-1	3 : 97	1.81:98.19	8.85	1.126	3.14
(7.5%)	5 : 95	2.87:97.13	13.82	1.175	3.05
	10 : 90	5.56:94.44	18.51	1.246	2.05
X-PVA-2	3 : 97	1.49:98.51	11.13	1.088	4.05
(10.0%)	5 : 95	2.48:97.52	16.06	1.127	3.64
	10 : 90	4.91:95.09	20.56	1.205	2.33
X-PVA-3	3 : 97	1.02:98.98	12.76	1.052	4.73
(12.5%)	5 : 95	1.99:98.01	18.19	1.109	4.23
	10 : 90	4.53:95.47	21.30	1.158	2.44
X-PVA-4	3 : 97	1.90:98.10	8.61	1.133	3.05
(7.5%)	5 : 95	2.99:97.01	13.24	1.204	2.90
	10 : 90	5.98:94.02	18.33	1.252	2.02

Table 7 (Continued)

Polymer code (wt%)	(W:E) in feed (wt%)	(W:E) in retentate (wt%)	Water in permeate (wt%)	Flux (*J*) (kg/m^2 h)	Selectivity (α)
X-PVA-5	3 : 97	1.61:98.39	10.99	1.100	4.00
(10.0%)	5 : 95	2.60:97.40	15.92	1.134	3.60
	10 : 90	4.99:95.01	20.85	1.209	2.37
X-PVA-6	3 : 97	1.18:98.82	12.63	1.059	4.68
(12.5%)	5 : 95	2.11:97.89	17.79	1.116	4.11
	10 : 90	4.67:95.33	21.49	1.162	2.47
X-PVA-7	3 : 97	1.86:98.14	8.79	1.126	3.12
(7.5%)	5 : 95	2.97:97.03	13.74	1.175	3.03
	10 : 90	5.63:94.37	18.43	1.246	2.04
X-PVA-8	3 : 97	1.57:98.43	11.06	1.097	4.02
(10.0%)	5 : 95	2.54:97.46	15.98	1.176	3.62
	10 : 90	4.99:95.01	20.50	1.213	2.32
X-PVA-9	3 : 97	1.11:98.89	12.69	1.062	4.70
(12.5%)	5 : 95	2.05:97.95	18.12	1.118	4.21
	10 : 90	4.60:95.40	21.22	1.166	2.43

The effects of polymeric materials on cast membranes in pervaporation of water/ethanol azeotropic mixtures were evaluated. Results confirmed that water content in the retentate decreases more in hydrophilic poly(vinyl alcohol), PVA, than in hydrophobic poly(sulfone), PSF (Figure 12) because membrane with lower hydrophilicity generally shows smaller water fluxes. In order to obtain a good membrane for the dehydration of water in water/ethanol mixture, an optimum hydrophilicity is required. The effect of hydrophilic content on cast membranes in pervaporation of water/ethanol azeotropic mixtures was evaluated by using a copolymer containing both hydrophilic and hydrophobic poly(vinyl alcohol-*co*-ethylene), PVAE, with ethylene content = 32 mol%. Results showed that water content in the retentate of PVAE decrease more than when hydrophilic homopolymer of PVA and hydrophobic homopolymer of PSF were used (Figure 13), although, hydrophilicity of PVAE copolymers is lower than the hydrophilicity of PVA homopolymer. The reason may be due to the decrease of the degree of swelling in PVAE, since PVA membranes were hydrophilic and thus absorbed water quickly. It is known that both water flux and selectivity decrease as the degree of swelling increase. The same results were obtained when blending hydrophilic and hydrophobic copolymer of PVAE with hydrophobic PSF at various composition with wt% ranging from 7.5:2.5, 10.0:2.5 and 12.5:2.5. Water content in the retentate of PVAE-PSF blends decreases less than when hydrophilic hydrophobic polymer of PVAE but decreases more than hydrophilic homopolymer of PVA and hydrophobic homopolymer of PSF (Figure 14). The essential difference of blending compared with copolymer is that the two polymers are covalently bonded in copolymer, which gives the membranes more mechanically stability than blending.

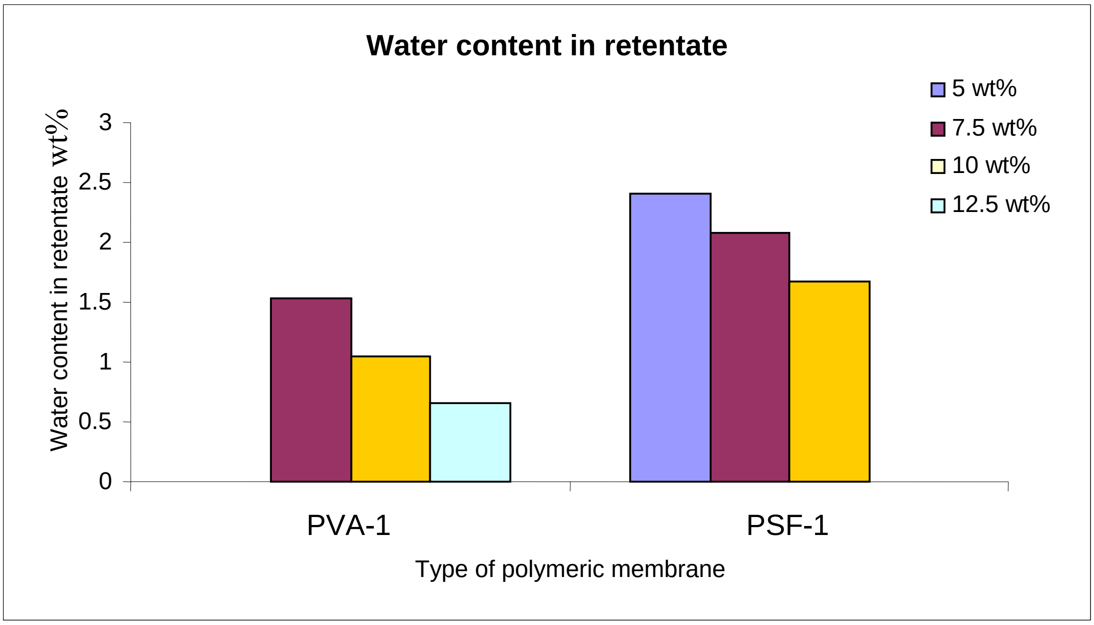


Figure 12 Water content in the retentate of hydrophilic poly(vinyl alcohol), PVA, and in hydrophobic poly(sulfone), PSF.

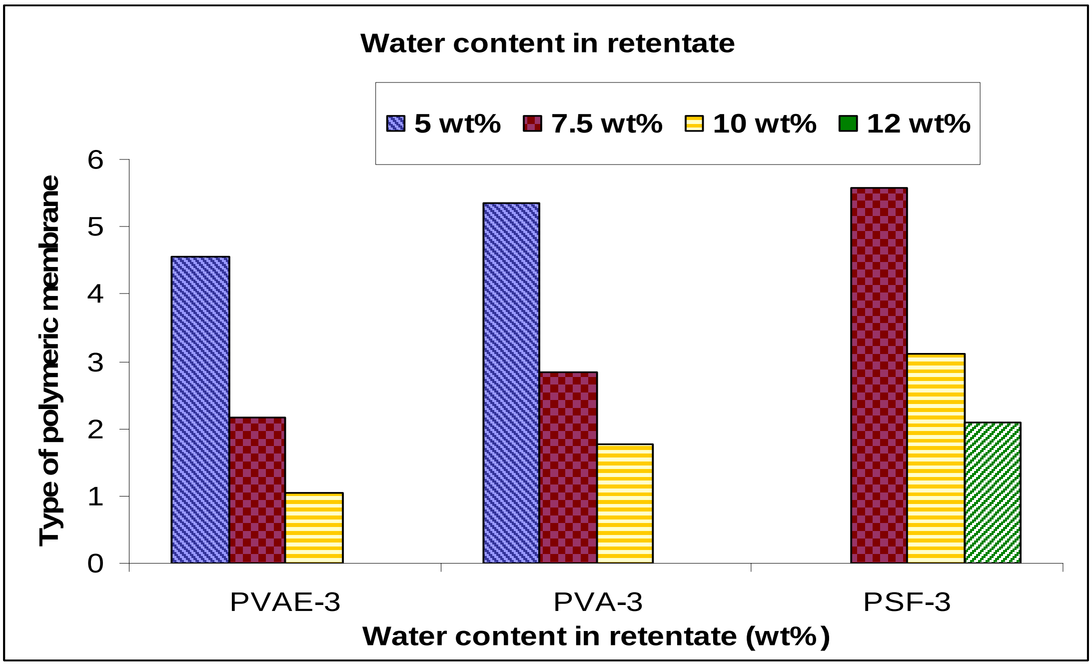


Figure 13 Water content in the retentate of PVAE, PVA and PSF.

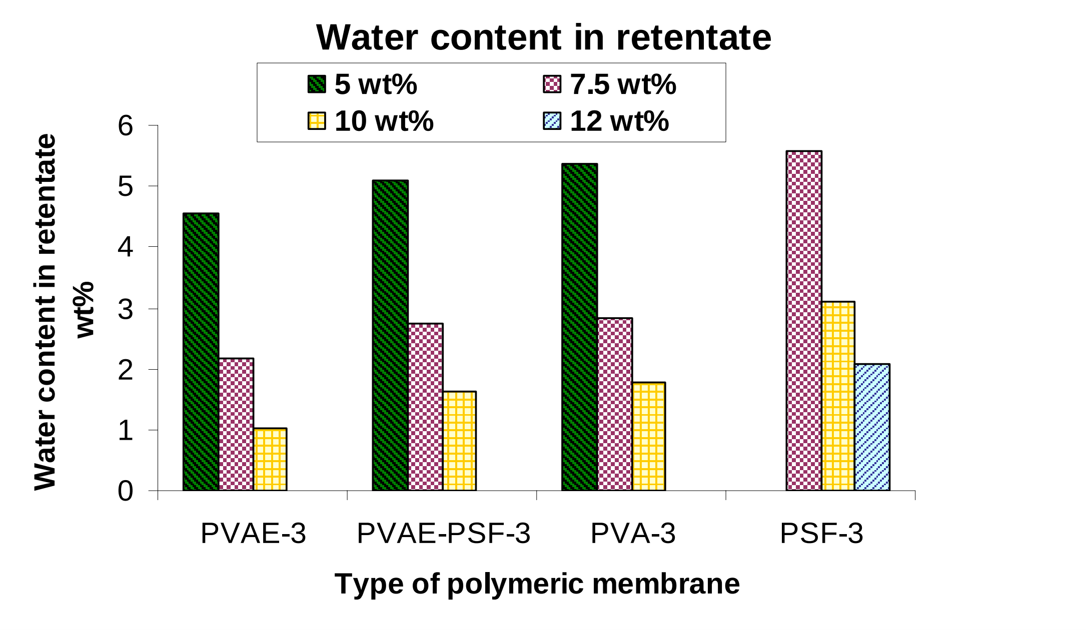


Figure 14 Water content in the retentate of PSF, PVAE, PVAE-PSF and PVA.

The effects of cross-linking of PVA were further investigated to study the degree of swelling on cast membranes in pervaporation of water/ethanol azeotropic mixtures. The reason for crosslinking is to decrease the degree of swelling in order to maintain selectivity. PVAs with high hydrophilicity show high degree of swelling with water when not crosslinked. Generally, water flux and selectivity decrease with increasing degree of swelling because the solubility as well as the diffusion of the ethanol in water/ethanol mixtures both increase. Water fluxes normally decrease with crosslinking content because cross-linking lower the hydrophilic content, however, selectivity normally increases with crosslinking content because cross-linking prevent the swelling and only water can permeate across the membrane. This is in agreement with the results obtained in this study as shown in Figure 15.

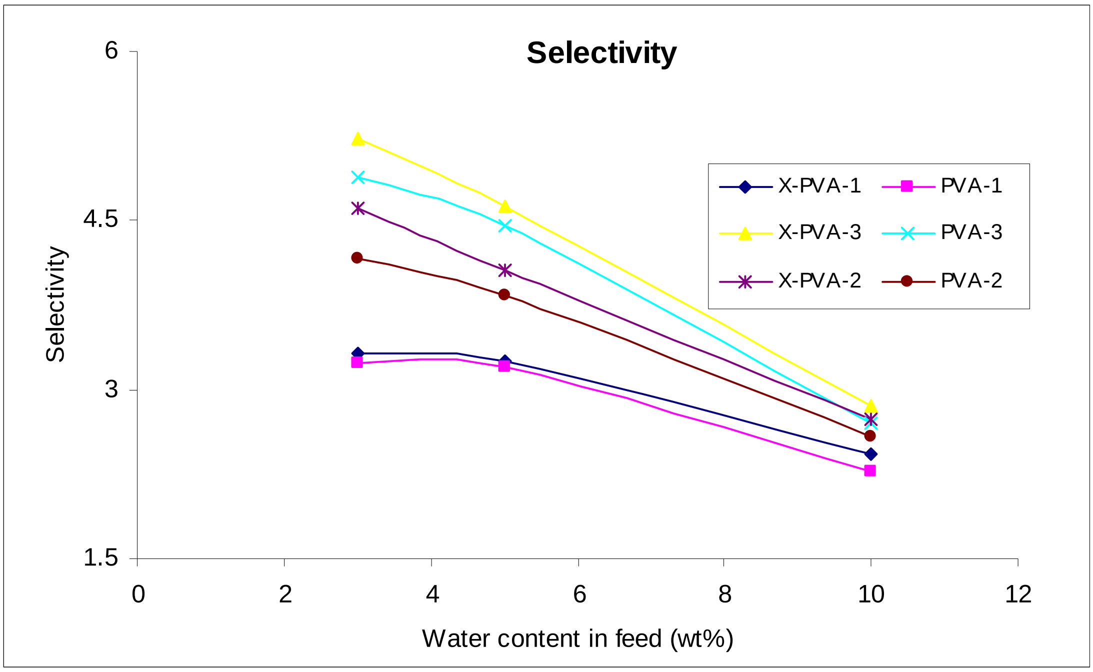


Figure 15 Selectivity of cross-linked PVA and non-crosslinked PVA membranes.

Membrane performance also depends on the polymeric concentration of the casting solution. The higher the casting solution coneent, the denser the membrane obtained. As a consequent, the smaller water permeate flux was observed as can be seen from the water content in the retentate decreases with increasing the concentration of polymeric materials in casting solution (10.0>7.5>5.0 wt% in PSF, 12.5>10.0>7.5 wt% for PVA, X-PVA and PVAE and 12.5:2.5>10.0:2.5> 7.5:2.5 wt% for PVAE:PSF) as shown in Figure 16.

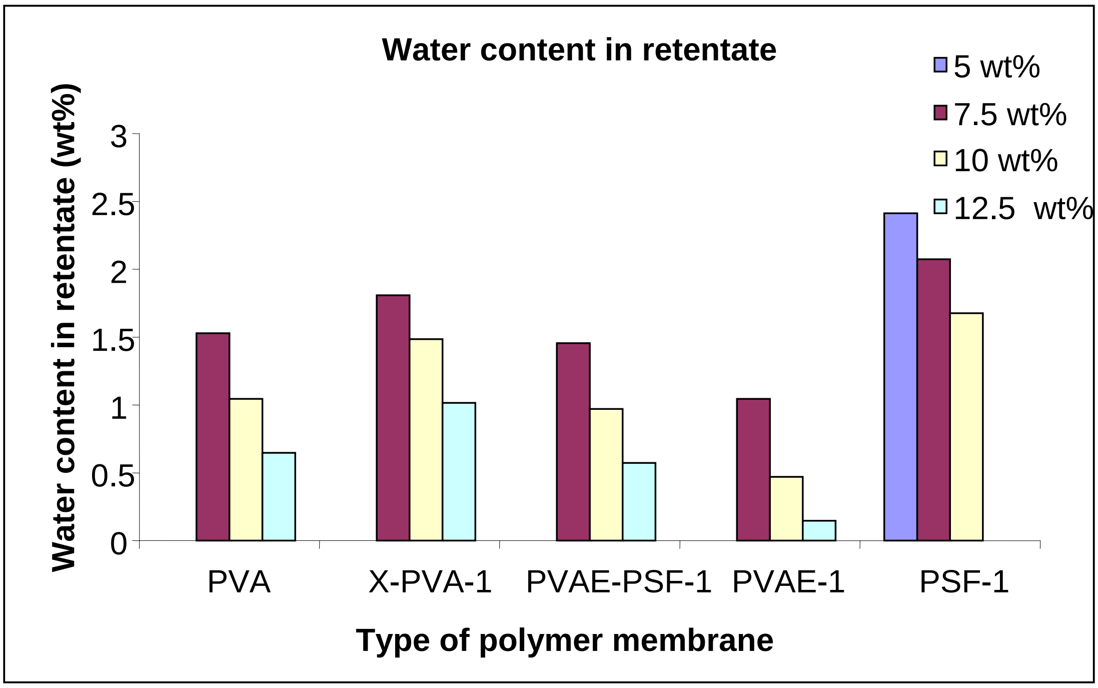


Figure 16 Water content in the retentate in PVA, X-PVA, PVAE-PSF, PVAE and PSF.

The effect of feed composition in wt% of water: ethanol ranging from 3.0:97.0, 5.0:95:0 and 10.0:90.0 wt% on the water permeate flux and selectivity was also studied. The relationship between the water permeates flux and selectivity with the composition of feed mixture is shown in Figure 17. The flux increases with increasing water concentration in the feed. These phenomena can be explained by the interaction between the polymer molecules and permeate. PVA is hydrophilic membrane, which normally has a relative high polarity groups that have a strong interaction with water by hydrogen bonding. As the water concentration is higher, more water molecules interact with membrane molecules and this causes the membranes to become more swollen. Therefore, the permeate molecules are able to pass through the membrane more easily and the permeate flux increase.

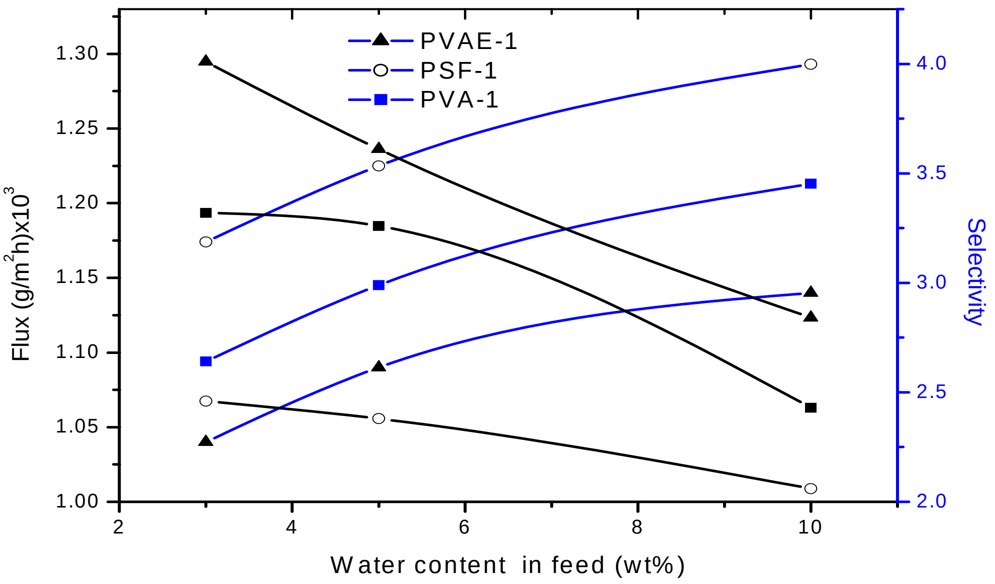


Figure 17 The relationship between water permeate flux and selectivity with the composition of feed mixture.

Finally, the morphology of the membrane is studied. The well known phase-inversion process, which is widely used for producing asymmetric membranes, in fact turns out to be unsuitable for production of pervaporation membranes. Dense nonporous structures were needed for pervaporation which can be obtained by evaporation of polymer solutions which had previously been thoroughly degasified and caste to produce a smooth dense, devoid of porosity, and mechanically resistant membrane. There is a difference in transport mechanism even the pervaporation membranes produced from the same polymeric material and the same morphology. This difference is mainly caused by large difference in affinity between the permeating molecules and the polymeric membrane. In the case of an open microporous membrane only a small driving force is needed to obtain a relatively high flux because the membrane resistance is low, however, in the case of dense nonporous membrane the resistance is much higher. For the pervaporation the main driving force is caused by the activity gradient of the components in the membranes. Anyway, the morphology of the pervaporation membranes was compared from the water permeate flux and selectivity of membranes obtained by phase inversion but subsequently annealed under vacuum at 40°C or dried in desiccators at room temperature for 24 hrs from PSF and PSF+2-methoxyethanol (PSF+ME) as pore making agent to produce dense, nonporous and microporous membranes respectively. No significant difference in water permeates flux and selectivities were found between PSF and PSF-ME as shown in Figure 18.

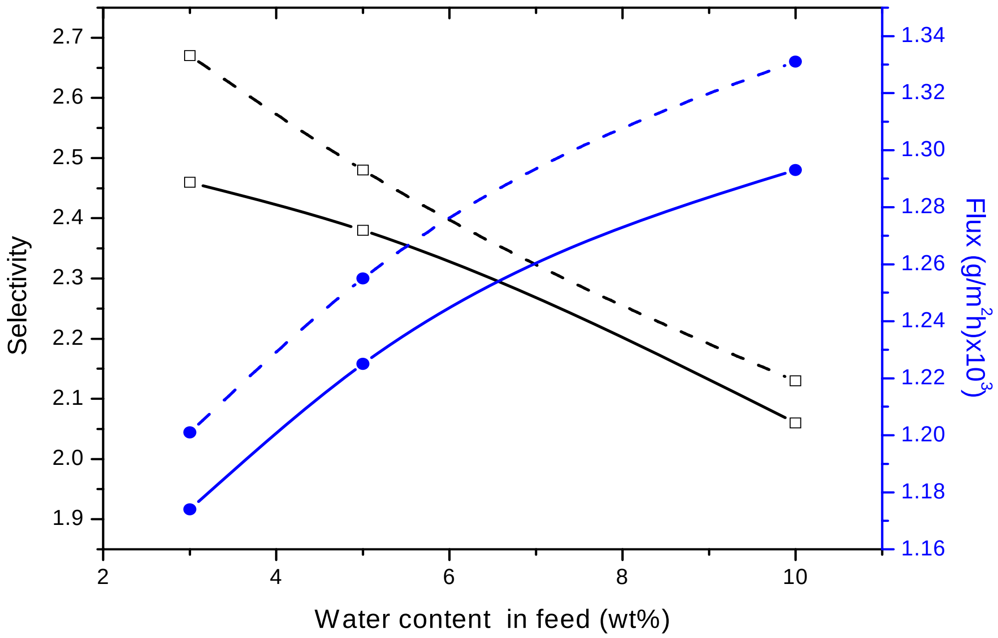


Figure 18 Water permeate flux and selectivity of PSF (---) and PSF-ME (-).

In pervaporation membrane process it is desirable to have a polymer with combine characteristics of high permeate flux and good selectivity. It can be concluded that the order of the polymeric materials effect on cast membranes and polymeric concentration of casting solution, and water/ethanol feed compositions, in pervaporation of water/ethanol azeotropic mixture in term of water permeation flux and selectivity in this study according to the hydrophilic content. It can be concluded that the order of the polymeric materials effect on cast membranes, polymeric concentration of casting solution, and water/ethanol feed compositions, in pervaporation of water/ethanol azeotropic mixture in term of water permeation flux and selectivity in this study according to the hydrophilic content are as followed: PVAL > PVAL-PSF > PVA > X-PVA > PSF > PSF-ME in Figure 19

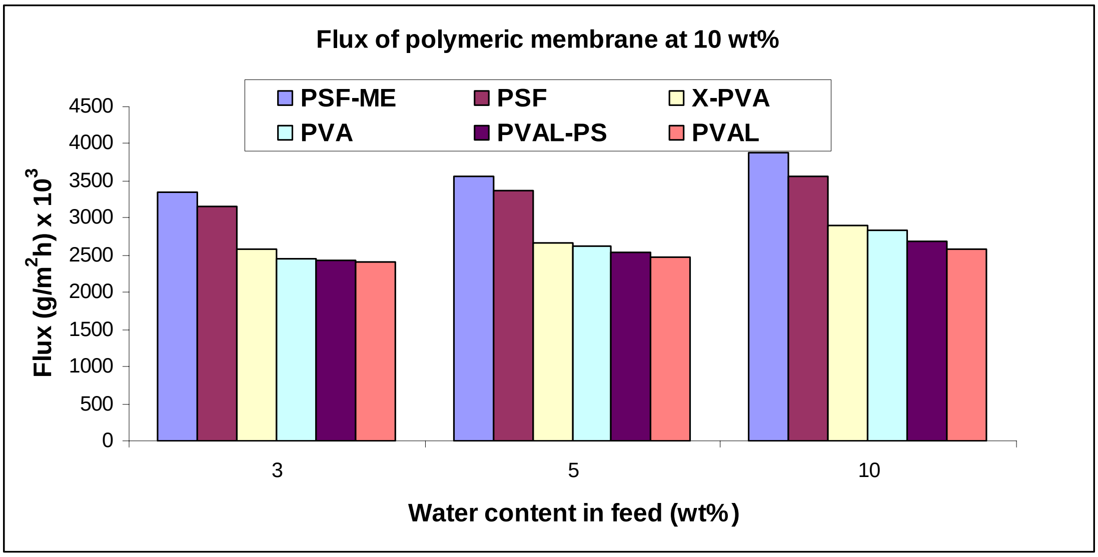


Figure 19 Permeate flux of prepared polymeric membranes at 10 wt% polymer concentrations.

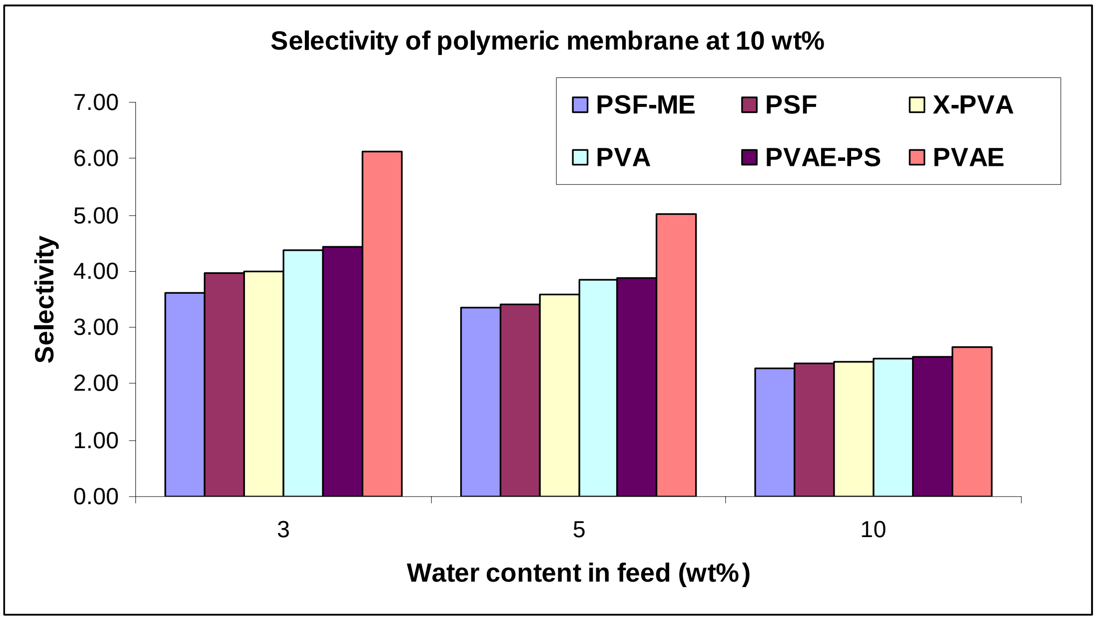


Figure 20 Selectivity of prepared polymeric membranes at 10 wt% polymer concentrations.

CONCLUSION

Suitable concentration for casting the membranes in this study are as followed: hydrophobic polysulfone, PSF; hydrophilic poly(vinyl alcohol), PVA and crosslinked poly(vinyl alcohol), X-PVA; copolymer of hydrophilic and hydrophobic poly(vinyl alcohol-*co*-ethylene), PVAE; and hydrophilic and hydrophobic blended poly(vinyl alcohol-*co*-ethylene) and polysulfone, PVAE:PSF are in the range of 5.0-10.0, 7.5-12.5 and 7.5-12.5, 7.5:2.5-12.5:2.5 wt% respectively. Membranes produced from PSF, PVAE, PVAE; PSF blend were obtained by phase inversion process, while membranes produced from PVA were obtained by evaporation at ambient temperature. Membranes produced from PVA were further crosslinked to decrease the hydrophilicity of the membranes by immersed into sodium tetraborate solution for 6 and 10 hours. All membranes obtained are flat sheet type having thickness varied from 28 μm to 30.5 μm.

The effects of polymeric materials, hydrophilicity of polymeric materials, polymer concentration of casting solution and feed composition in pervaporation of water/ethanol azeotropic mixtures in term of steady state water permeate flux and selectivity were investigated. It was found that the water permeate flux decreases but the selectivity increases with increasing time. Water concentration in the retentate decreases more in hydrophilic PVA than in hydrophobic PSF polymeric membranes because hydrophilicity is caused by –OH groups presenting in the PVA chain that are able to interact with water molecules, e.g., by hydrogen bonding or dipole-dipole interaction. When membranes produced from copolymer combined of hydrophilic and hydrophobic, PVAE were used, water concentration in the retentate decreases much more than hydrophilic PVA because homopolymer PVA showed higher degree of swelling with water. The effects of cross-linking of PVA with sodium tetraborate were further investigated to study the degree of swelling on cast membranes and it was confirmed that water concentration in the retentate decreases more than PVA because cross-linking prevent the swelling and only water can permeate across the membrane. For feed composition in wt% of water: ethanol, it was found that the flux increases with increasing water concentration in the feed. But selectivity decrease with increasing of water content in feed. Finally, the morphology of the membrane is studied. the morphology of the pervaporation membranes was compared from the water permeate flux and selectivity of membranes obtained by phase inversion but subsequently annealed under vacuum at 40^oC or dried in desiccators at room temperature for 24 hrs from PSF and PSF+2-methoxyethanol (PSF+ME) as pore making agent to produce dense, nonporous and microporous membranes respectively. No significant difference in water permeates flux and selectivity were found between PSF and PSF-ME because the main driving force in pervaporation is caused by the activity gradient of the components in the membranes.

It can be concluded that the order of the polymeric materials effect on cast membranes, polymeric concentration of casting solution, and water/ethanol feed compositions, in pervaporation of water/ethanol azeotropic mixture in term of water permeation flux and selectivity in this study according to the hydrophilic content are as followed: PVAL > PVAL-PSF > PVA > X-PVA > PSF > PSF-ME.

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