

Modified Polydimethylsiloxane/Polystyrene Blended IPN Pervaporation Membrane for Ethanol/Water Separation

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ABSTRACT: In this article a modified polydimethylsiloxane (PDMS) blended polystyrene (PS) interpenetrating polymer network (IPN) membranes supported by Teflon (polytetrafluoroethylene) ultrafiltration membrane were prepared for the separation of ethanol in water by pervaporation application. The relationship between the surface characteristics of the surface-modified PDMS membranes and their permselectivity for aqueous ethanol solutions by pervaporation are discussed. The IPN supported membranes were prepared by sequential IPN technique. The IPN supported membrane were tested for the separation performance on 10 wt % ethanol in water and were characterized by evaluating their mechanical properties, swelling behavior, density, and degree of crosslinking. The results indicated that separation performance, mechanical properties, density, and the

percentage of swelling of IPN membranes were influenced by degree of crosslink density. Depending on the feed temperature, the supported membranes had separation factors between 2.03 and 6.00 and permeation rates between 81.66 and 144.03 g m⁻² h⁻¹. For the azeotropic water–ethanol mixture (10 wt % ethanol), the supported membrane had at 30°C a separation factor of 6.00 and a permeation rate of 85 g m⁻² h⁻¹. Compared to the PDMS supported membranes, the PDMS/PS IPN supported blend membrane ones had a higher selectivity but a somewhat lower permeability. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2666–2679, 2011

Key words: interpenetrating polymer network; polydimethylsiloxane; polystyrene; water–ethanol mixtures; pervaporation

INTRODUCTION

Separation of azeotropic mixtures, close boiling points mixtures or isomers and for the removal or recovery of trace substances by the use of pervaporation membrane separation process has been gaining greater interest in recent years. Since the pervaporation, technique is considered an energy saving process. Pervaporation is a separation technique based on a selective transport through a dense layer associated with an evaporation of the permeate. The efficiency of the pervaporation process depends mainly on the intrinsic properties of the polymers used to prepare the membrane. Therefore, designing membrane structure with a high permeation rate and separation factor is an important issue.¹

In recent years pervaporation separation, has emerged as relatively simple alternatives to greatly water/organic and organic/water separation applications.² Specifically there have been growing research interest in the application of pervaporation separation process with considerable innovative possibilities in the area of biotechnology. Particularly, the combination of bioreactor and pervaporation membrane has potential in the longer term as an alternative to conventional batch processes.^{2,3} However, a major difficulty limits pervaporation commercialization, namely, the deficiency of proper membrane materials for this application.⁴ After analyzing the fermentation–pervaporation processes of a commercial-scale fuel ethanol plant concluded that such a coupling system could be cost-competitive. If the performance of membranes was improved modestly so as to exhibit either the pervaporation total flux of 0.15 kg m⁻² h⁻¹ or selectivity of 10.3 for ethanol to water. By affinity, rubbery polymers are the most suitable material for hydrophobic/organophilic pervaporation separation; namely polybutadiene,⁵ terpolymer ethene-propene-diene (EPDM),⁶ poly(ether block amide) (PEBA),^{7,8} polyvinylidene fluoride,⁹ and the most frequent is polydimethylsiloxane.^{10–15}

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Polydimethylsiloxane (PDMS) is among the most interesting and promising membranes material for hydrophobic/organophilic separation that has been investigated extensively. This material has an alternating O—Si—O unit structure and has very good stability in operation particularly for the removal of volatile organic solvents (VOCs). The selectivity of supported PDMS for VOCs comparative to water is surprising.¹⁶ Other advantage of the PDMS membrane is high diffusivity of organic compounds in the membrane due to its low glass transition temperature, T_g .¹² Polymer which having low glass transition temperature shows rubbery nature and highly suitable for separation of organic compound. Though, PDMS has poor mechanical strength and film forming properties and it is thus challenging to prepare ultrathin membranes from this polymer.^{12,14,17,18} However, these properties have been enhanced by using the formation of interpenetrating polymer networks (IPN), crosslinked PDMS, block or graft PDMS with a polymer having excellent film-forming, and mechanical properties.^{19,20}

In this research, an attempt has been made to improve the mechanical strength, suppress swelling ability and also the selectivity or flux of the PDMS membrane toward ethanol separation in water by using interpenetrating polymer network method. Thus, in the present article, we report the preparation of PDMS-PS IPN membrane using fix amount of dicumyl peroxide (DCP) as the initiator for PS network and crosslinker for IPN system, supported on polytetrafluoroethylene (PTFE) ultrafiltration membranes. The membrane performance was characterized in the selective pervaporation of ethanol from ethanol–water mixtures. The IPN membrane can be utilized efficiently in biotechnology application especially in biomedical field where antiseptic recycling is one of the major concerns.

EXPERIMENTAL

Materials

The main material which is α,ω -dihydroxypolydimethylsiloxane (PDMS) with average molecular weight of 50,000 was generously donated by Wacker-Silicones, Germany. Reagent grade styrene monomer, tetraethylorthosilicate (TEOS), dibutyltin dilaurate, divinylbenzene (DVB), and sodium hydroxide (99.9%) were purchased from ζ -Aldrich Chemie GmbH, Germany. Dicumyl peroxide (DCP) was obtained from Aldrich Chemical Company, USA. Solvents used (ethanol, methanol, chloroform, and toluene), were of reagent grade purities and purchased from Merck Germany. The lists and the properties of the materials used in the experimental works are presented in Table I. Ultrafiltration mem-

branes made from polytetrafluoroethylene (PTFE) with an average molecular weight cut-off of more than 10,000 supplied from Donaldson Filtration (Asia Pacific), used as a support.

Material preparation

Purification of styrene monomer and divinylbenzene

Styrene monomer and divinylbenzene contain a certain amount of *tert*-butylcatecol as an inhibitor to prevent styrene monomer from polymerize and DVB from further reaction. The presence of *tert*-butylcatecol disturbs the process of styrene polymerization and crosslinking process. Thus, materials purification was undertaken prior to usage.

Styrene monomer was first prewashed with 10% aqueous sodium hydroxide (NaOH) repeatedly for three to four times to remove the inhibitor. Afterward, it was washed with distilled water, to remove the traces of NaOH and dried over molecular sieve 4A for a period of a week. It was then stored in a dark container (bottle) inside a refrigerator to prevent it from polymerize. The same process applied for divinylbenzene (DVB). Divinylbenzene has used as a crosslinking agent specifically for PS network.

Purification of dicumyl peroxide

Dicumyl peroxide (DCP) purchased from Aldrich was only 98% pure. It was important to use pure DCP for it acts as an initiator for PS polymerization as well as crosslinker for crosslinking process in the PDMS/PS IPN system. DCP was first dissolved in chloroform, and then recrystallized by adding methanol. After that, the crystallized DCP was put to dry in vacuum oven at 60°C for 24 h before use.

The system was left at an ambient temperature for 2 h to form PDMS network before it has been subjected to heat treatment at 80°C for 4 h in an oven to complete the crosslinking process. The crosslinked membrane was then left to dry in an ambient air for 24 h before used in pervaporation.¹⁶

Preparation of crosslinked PDMS supported membranes

A preweight of PDMS was mixed with 16 wt % percentage of tetraethylorthosilicate (TEOS) which act as crosslinking agent and 2 wt % of dibutyltin dilaurate (DD) which act as catalyst in the reaction before been dissolved in fixed volume of toluene to produce PDMS network solution.¹⁶ The solution has stirred until it became sufficiently viscous (about 30 min). Then, it poured on the surface of PTFE membrane inside a stainless steel plate by an area of 15 cm \times 15 cm with 3-cm height. Aluminum foil with small holes has used to cover the stainless steel plate

TABLE I
Design of Experiment for PDMS/PS IPN Supported Membrane Solution Composition

Membrane	PS (wt %) ^a in IPN	PDMS network ^a			PS network			DCP (wt %) in PS network
		PDMS (g)	TEOS (g) ^a	DD (g) ^a	S (g) ^a	DVB (g) ^a	DCP (g) ^a	
PDMS	0%	28.0	5.460	0.686	0	0	0	0%
90/10	10%	25.2	4.914	0.617	2.8	0.283	0.063	2%
70/30	30%	19.6	3.822	0.480	8.4	0.848	0.189	2%
50/50	50%	14.0	2.730	0.343	14.0	1.414	0.315	2%
30/70	70%	8.4	1.638	0.206	19.6	1.980	0.441	2%

^a PDMS = polydimethylsiloxane, PS = polystyrene, S = styrene monomer, TEOS = tetraethylorthosilicate, DVB = divinylbenzene, DCP = dicumyl peroxide, DD = dibutyltin dilaurate, IPN = interpenetrating polymer network.

preventing rapid evaporation. Fixed volume of 100 mL total membrane solution was used for every membranes fabricated to control the membrane range thickness over the PTFE membrane support surface area.

Preparation of PDMS/PS IPN supported membranes

The compositions of casting solutions used to prepare PDMS/PS IPN layers are summarized in Table I. Mixed solutions of PDMS, Styrene monomer, crosslinking agent as well as initiator were stirred for 30 min until it became sufficiently viscous. The solution then poured on the surface of PTFE membrane. To prevent the evaporation of styrene and DVB, the system was covered with a glass dish. The system left at an ambient temperature for 2 h for the preliminary formation of PDMS network as the reaction for PDMS networks start at room temperature. It was then, introduced into an oven at 80°C for 6 h to complete the crosslinking of PDMS and for the polymerization of styrene monomer to begin. The system again introduced into the oven at 100°C to complete the polymerization and crosslinking of polystyrene network. All the supported membrane would then be subjected to drying in ambient temperature for 24 h before used in pervaporation.²¹

MEMBRANE CHARACTERIZATION

Fourier transform infrared (FTIR) spectroscopy

The infrared absorption through Fourier Transform Infrared (FTIR) spectroscopy technique was employed, to identify the presence of styrene and siloxanes groups in the polymer samples. In the present study, FTIR spectra obtained from Nicolet (Magna-IR 560) spectrometer equipped with attenuated total reflection having a Ge spherical crystal. The spectra measured in transmittance mode over a wave number range of 4000–400 cm⁻¹.

Field emission scanning electron microscope (FESEM)

The morphology of the PDMS/PS IPN supported membranes was determined by Carls Zeiss Supra 35 variable pressure field emission scanning electron microscope (FESEM). Membranes samples for the VPFESEM were prepared by freeze-fractured in liquid nitrogen and mounted on the aluminum stub. The specimens were coated with thin layer of gold to improve macroscopic image. The membranes were examined to determine if there were any defects in term of existing visible holes or flaws in the membrane through the surface and cross section SEM micrograph. Besides that, SEM micrographs were also used to show the existing layer inside the membrane.

Tensile testing

Tensile strength-elongation tests of PDMS/PS supported membrane were performed according to the standard method (ASTM D638-58T) using a Lloyd universal testing machine (model Lloyds EZ50, Lloyds Instruments, Fareham, UK). The test specimens were cut into strips 9.53-mm long and 3.18-mm wide (fixed value on specimen mold), and the thickness of each strip (~ 400 μm) was measured with digital vernier calipers. First, the membranes specimens were cut into dumbbell shape. The dumb bell shaped specimens were cut into different directions of grains of each IPN membrane sheets, so as overall tensile property can be studied. Each end of the membrane specimens were taped with masking tape to prevent it from being torn when it was placed in the grips of the testing instrument. Once membrane specimen was properly place in the testing instrument, the grips were tightened evenly and firmly to prevent slippage of the specimen during test. The crosshead speed of the instrument was fixed to 10 mm min⁻¹ at room temperature. The minimum number of specimens needed for each sample was five and average value was taken for the respective data.

Determination of IPN membrane density

Density of the membranes were determined using digital electronic balance with a precision $\pm 1.5 \times 10^{-5}$ g (model AT-201, Mettler Toledo, Switzerland). Prior to measurement the membranes, samples were first weighed in air, then were immersed in distilled water and the weights in distilled water were determined. Density of the specimens had calculated using the following equation:

$$\rho_s = \frac{A_d}{A_d - B_w} \times \rho_0 \quad (1)$$

where ρ_s is density of the solid specimen (membranes), A_d is weight of the solid specimen in air; B_w is weight of solid specimen in distilled water, and ρ_0 is density of distilled water at given temperature.

Density and degree of crosslinking

Crosslink density can be determined by the two methods, modulus, and swelling measurements. Values of network-chain segment concentrations, n obtained can be used to calculate Young's Modulus, E using the relationship in eq. (2):

$$E = 3nRT \quad (2)$$

where E is the Young Modulus, n is the number of effective crosslink per unit volume, R being the gas constant, and T is the temperature. The modulus will give a direct measurement of stiffness, which is directly proportional to the crosslink density.

Network-chain segment concentration, n , mol per cm^3 was calculated by using Flory-Rehner's equation for crosslinked polymers.²²

$$n = - \frac{[\ln(1 - v_2) + v_2 + \chi_{12} v_2^2]}{V_1 [v_2^{1/3} - v_2/2]} \quad (3)$$

where, v_2 is the volume fraction of polymer in the swollen areas, V_1 is the molar volume of solvent; toluene taken as $106.8 \text{ cm}^3 \text{ mol}^{-1}$, and χ_{12} is Flory-Huggins polymer-polymer interaction parameter.²³

Degree of swelling (q) can be related to the volume fraction of polymer in the gel v_2 , by the following equation.

$$v_2 = - \frac{w_1/\rho_1}{w_1/\rho_1 + w_2/\rho_2} \quad (4)$$

where w_1 is the weight of polymer in grams, ρ_1 is the density of polymer, g cm^{-3} , w_2 is the weight of solvent in a swollen sample in grams, ρ_2 is the density of solvent, g cm^{-3} . The Flory-Huggins χ_{12} parameter has been one of the most widely used

quantities, characterizing a variety of polymer-solvent and polymer-polymer interactions. It is a unitless number. While the original theory proposed that χ_1 be concentration independent, many polymer-solvent systems exhibit increases of χ_1 with polymer concentration.²³ The polymer-solvent interaction parameter χ_{12} for the system was calculated by using the following equation,²²

$$\chi_{12} = \beta + \frac{V_1(\delta_1 - \delta_2)^2}{RT} \quad (5)$$

while β , sometimes called the lattice constant of entropic origin,

$$\chi_{12} = \frac{V_1(\delta_1 - \delta_2)^2}{RT} \quad (6)$$

where V_1 is the molar volume of the solvent, δ_1 and δ_2 are the solubility parameters of the solvent and polymer, R is the universal gas constant, and T the absolute temperature. However, for a polymer-polymer system as in IPN, the following calculations were assumed for the interaction between PDMS-toluene and PS-toluene:

$$\chi_{12} = \frac{V_1(\delta_{\text{tol}} - \delta_{\text{PDMS}})^2}{RT}; \chi_{12} = \frac{V_1(\delta_{\text{tol}} - \delta_{\text{PS}})^2}{RT} \quad (7)$$

The χ_{12} parameter, also called Flory's χ_{12} parameter or Flory-Huggins χ_{12} parameter, and χ_{12} is also called χ_{blend} blend is a dimensionless interaction parameter defined as,^{22,24}

$$\chi_{12} = \sum_{ij} c_{ij} \chi_{i,j} \quad (8)$$

where the coefficients c_{ij} are functions of the copolymer compositions, with $0 \leq c_{ij} \leq 1$.

From the values of n , the molecular weight between crosslink \bar{M}_c is determined as follows:

$$n = \rho/M_c \quad (9)$$

$$M_c = \rho/n \quad (10)$$

where n is network-chain segment concentration, ρ is density of the IPN polymer, and M_c is molecular weight between crosslinks.

Subsequently, values of E , Young's modulus can be determined using values of n found from eq. (3). Network-chain segment concentrations, n also can be determined via the relationship in eq. (3). Thus, two values of M_c can be determined using relationship stated above i.e., via swelling methods and mechanical testing. The crosslink density then calculated by the following equation:

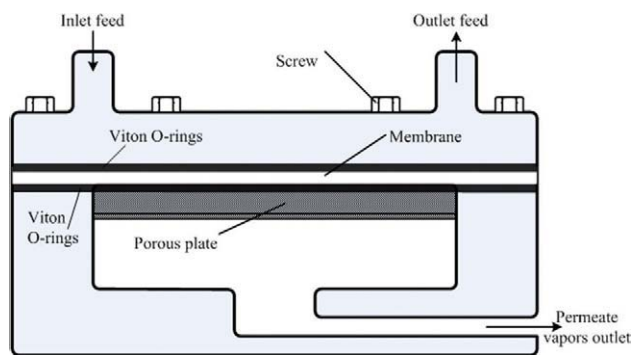


Figure 1 Schematic diagram of the pervaporation cell. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\rho_{C_x} = \rho/2M_c \quad (11)$$

where ρ_{C_x} is crosslink density, ρ is density of the IPN polymer, and M_c is molecular weight between crosslinks.

Determination of membrane swelling behavior

A known weight of the each samples, $1 \times 1 \text{ cm}^2$ was placed in a stopper bottle of a freshly distilled toluene, chloroform, ethanol and water for a period of 7 days. The samples were re-weighted every day until a constant weight had been achieved indicating that equilibrium swelling has taken place. The equilibrium swelling of the sample obtained using the expression:

$$\% \text{ Swelling} = \frac{W_s - W_d}{W_d} \times 100 \quad (12)$$

where W_s is weight (g) of wet membrane, W_d weight (g) of dry membrane

MEMBRANE EVALUATION

Membrane performance test—Pervaporation

Pervaporation cell and apparatus specially designed and ordered for laboratory membrane testing by Solteq Company. Pervaporation cell used consisted of two detachable 316 stainless steel parts as showed in Figure 1. The upper part was equipped with inlet and outlet of the feed mixtures. A porous stainless steel plate with pore size $\sim 50 \mu\text{m}$ and 1 mm thickness fixed in the lower part of the cell supported the membrane. The lower and upper parts of the cell set in proper alignment and sealed tightly with two Viton O-rings. The effective area for membrane permeation was 63.62 cm^2 . The feed tank has made from hardened stainless steel and had a maximum solution capacity of $\sim 5 \text{ L}$.

Figure 2 shows the schematic representation of the pervaporation apparatus. The feed mixture enters the cell through the inlet opening and leaves the cell through the outlet opening on the opposite site. The feed mixture then circulated through the cell by a circulation pump, which controlled by using control valve. The operation of this unit was in batch mode since the feed was continuously recycled back to the feed tank and the vapor permeated through the membrane was removed from the lower part of the cell, which was kept under vacuum pressure and condensed in a cold trap that was immerse in the liquid nitrogen.

Downstream pressure was controlled directly by adjusting the control panels, which connected to the pressure probe in the membrane outlet cell. The system directly attached with vacuum pump to control its operation. Vacuum pump will stop operating once desired pressure achieved and start to operate again when the pressure fall *vice versa*. Similarly, the feed temperature has controlled by using the same method with the temperature probe inside the feed tank. The feed tank used jacketed heating system to increase the temperature of the feed. If compared to direct heating system where heat is supplied directly, jacketed heating system is much safer. Once the feed achieved desired temperature, jacketed heating system will stopped *vice versa*.

Pervaporation system was run for at least 1 h for startup process until the permeation flow reached steady state. Permeate sample can only be collected after permeation flow reached steady state. Permeate sample was removed from the system and left to warm up to ambient temperature before being weighed and analyzed for the composition. The composition of permeate was analyzed using

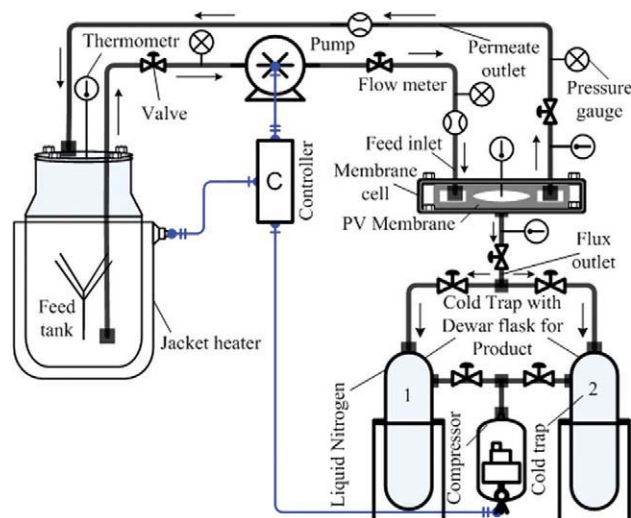


Figure 2 Schematic representation of the Pervaporation experimental setup. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

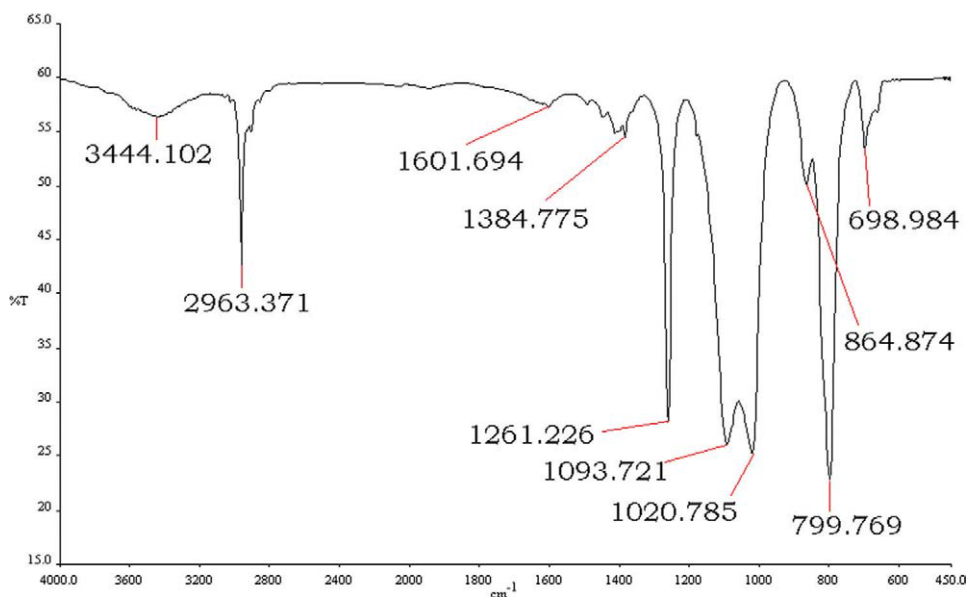


Figure 3 FTIR spectra of 70/30 (PDMS/PS) IPN supported membrane with 2% of DCP content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

refractive index and compared with the prepared standard curve for pure ethanol. Composition of the feed mixture in the feed tank has also measured, to verify consistency of the mixture. However, it is safe to assume that the feed composition remains constant during the duration of the experiment due to the fact that, weight of permeate collected was less than 1% of the total feed weight placed into the tank.

Throughout the experiment, feed mixture has fixed to 10 wt % of ethanol in water. Low concentration of ethanol was used, as the purpose of this experiment was to allow only ethanol to permeate through the membrane while retaining water in feed stream to achieve high separation process. Each type of membranes was tested with a fixed composition of feed mixture at four different temperatures namely 30, 40, 50, and 60°C. The upstream pressure of the pervaporator was at atmospheric pressure, while the downstream pressure had maintained at 0.07 bars with vacuum pump. The flow rate of the feed mixture circulating system had fixed at 3.5 L min⁻¹. Every permeate sample collected was run at least three times before data for the permeation flux and separation factor can be obtained to validate repeatability. The permeation flux of the membrane was calculated with the eq. (13) where membrane area, A (m²) = 6.36×10^{-3} m². The permeation rate (J) at steady state calculated using the expression¹⁷:

$$Jt = \frac{w}{A\Delta t} \quad (13)$$

where w is the total amount of permeate at steady state during the experimental permeation time (t)

Δt , and A is the effective membrane surface area. The permselectivity of the membrane expressed via the separation factor (α) defined as¹⁷:

$$\alpha_{ij} = \frac{Y_i/Y_j}{X_i/X_j} \quad (14)$$

Subscript Y_i and Y_j are the weight fraction of component i and j in the permeate respectively, whereas X_i and X_j are the feed phase weight fraction of component i and j . Component i is more preferentially permeating component in i and j mixture.

RESULTS AND DISCUSSION

Infrared study using Fourier transform infrared spectroscopy (FTIR)

To identify the presence of Polydimethylsiloxane (PDMS) and polystyrene (PS) group in PDMS/PS IPN supported membranes, Fourier Transform Infrared (FTIR) spectroscopy used in the present study. A sample spectrum of IPN membrane is used to verify the presence of PDMS and PS group in the system as the rest of the spectrum shows similar absorption peak wavelength with different intensity.

Figure 3 shows the FTIR spectra of an IPN supported membrane by a composition of 70/30 (PDMS/PS) with 2% DCP. The absorption peak at 2963 cm⁻¹ can be assigned to the symmetric stretching vibration of the CH₃ groups of the PDMS. The absorption peaks due to the Si-CH₃ bonds in the PDMS are located at 799.769 and 1261.226 cm⁻¹.²⁵ While the absorption peak at 1384.775 cm⁻¹ can be assigned to the aromatic skeletal vibration of PS and

TABLE II
Values of Network Chain Segment Concentration (n), Molecular Weight (M_c), Density (ρ), and Crosslink Density (ρ_{Cx}) Obtained from Swelling Test and Tensile Strength Test for 2% DCP PDMS/PS IPN Supported Membrane with Various Composition of PS

Membrane composition	Density; ρ (g cm^{-3})	Network-chain segment concentration (mol cm^{-3})		Molecular weight (g gmol^{-1})		Crosslink density (gmol cm^{-3})	
		$n_{\text{swell}} \times 10^{-4}$	n_{tensile}	$M_{c(\text{swell})} \times 10^{-3}$	$M_{c(\text{tensile})}$	$\rho_{Cx(\text{swell})} \times 10^{-4}$	$\rho_{Cx(\text{tensile})}$
PDMS	0.999	3.7	16.4	2.7	0.06	1.8	8.2
90–10, 2% DCP	0.997	4.8	28.4	2.1	0.03	2.4	14.2
70–30, 2% DCP	1.004	5.0	34.4	2.0	0.03	2.5	17.2
50–50, 2% DCP	1.033	4.0	23.4	2.6	0.04	1.8	11.7
30–70, 2% DCP	1.040	6.0	58.2	3.0	0.02	3.0	30.1

the peak at 698.984 cm^{-1} to the aromatic C–H out of plane deformation vibration. These characteristic absorptions showed that PS was incorporated and presence in PDMS matrix during IPN synthesis.

Density study on PDMS/PS IPN supported membranes

Table II shows the density, (g cm^{-3}) versus PDMS/PS supported membrane composition with preset DCP amount, 2 wt %. An increase in the value of density was observed for all IPN membrane samples compared to PDMS crosslinked sample. Density for each IPN membranes increased with the increased amount of PS in the membrane composition for 2 wt % DCP content. These phenomena of increasing IPN density is a result of interpenetration between two networks filling the relatively loose and amorphous molecular structure and the formation of a more compact structure.²² The effect of increasing density observed in this PDMS/PS IPN supported membrane with respect to PS composition was attributed to the increase number of crosslink because of interpenetrating forming a more compact structure whereby the rigid PS phase reinforces the more elastic PDMS matrix.

Tensile strength study on blended IPN PDMS/PS IPN supported membranes

The tensile strength is the measure of the stress needed to break the material.²⁶ Through the tensile strength test analysis, it found that the tensile strength increases tremendously with the increase of PS in the mixture of PDMS/PS IPN supported membrane composition regardless of PS content in IPN. The relationship between PS composition in the system and tensile strength of the PDMS/PS IPN membrane is shown in Figure 4.

The tensile strengths of PDMS/PS IPN supported membranes increase following the increase of PS content in the system. Rigid PS phase reinforce and interpenetrate with the more elastic and rubbery

PDMS matrix transforming it into tight and dense network thus increasing its strength towards creep and flow as reported by Mathew et al.²⁷ Compared to PDMS, the stress-strain curves of PDMS/PS IPN membrane reveal a larger tensile strength and strain %. From Figure 4, it was shown that supported IPN membranes which contains 70 wt % PS dominate the highest level of tensile strength (3.4 MPa). While 30 wt % PS shows highest strain is (382%), indicating superior flexibility as well as strength of the PDMS membrane. It is attributed that PDMS membranes which contains higher amount of PS shows a durable yielding polymer. However, low amounts of PS shows elastomeric and high initial moduli with low yielding point, particularly the 30 wt % of PS showing significant elongation in PDMS/PS IPN network. This major different may be because of DCP which showing good crosslinker for IPN system. Figure 4 also illustrates IPN compositions with 10 wt % PS content have the lowest tensile strength and strain. The phenomenon was may be due to PS content which is beyond the acceptable limit in the system thus reduces the compatibilities of both components. Another reason probably due to the degradation and chain scission from the excess amount of PS in PDMS/PS blend matrices become soft and lose

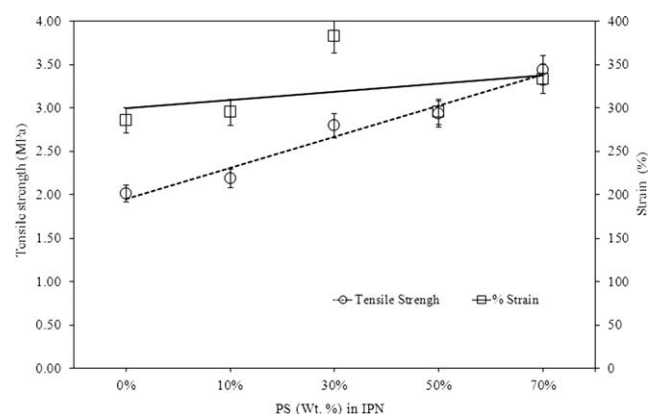


Figure 4 Tensile strength for various composition of PS (wt %) in IPN for PDMS/PS IPN supported membrane.

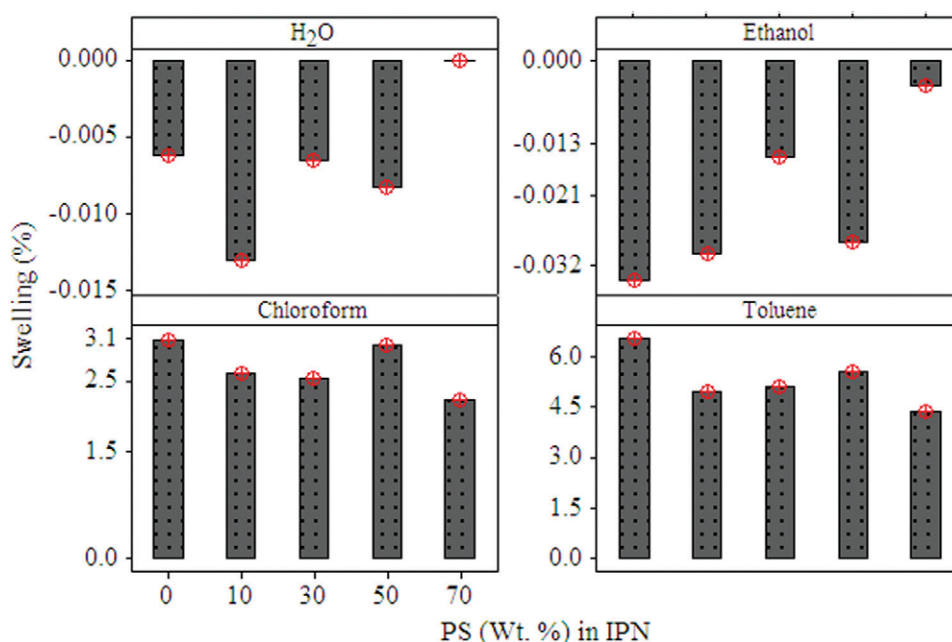


Figure 5 Percentage of swelling in various solvents for IPN supported membranes base on PDMS/PS composition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

its strength, resulting in a decrease of tensile strength.

Blended PDMS/PS IPN swelling ratio and percentage of swelling

Figure 5 shows the relationship between percentages of swelling with the composition of PDMS/PS IPN supported membranes in various solvents (H₂O, toluene, ethanol, and chloroform). In an IPN consisting of both hydrophobic polymers, the swelling capability of the PDMS/PS blend in water is a result of the hydrophobic nature of both polymers. Results show that the difference between degree of swelling of PDMS membrane with and without PS in both solvents is small due to the high polarity of water and ethanol. The percentage of weight reduction in two solvents of PDMS membranes might be due to two different polarities of two materials, i.e., membrane surface which contains nonpolar behavior and continuously opposing to polar solvents molecules. Since the membrane surface contains hydrophobic and are nonpolar in nature, it keeps opposing to two polar solvents continuously in nonequilibrium form. This was due to the interpenetration between both molecules into the PDMS/PS matrix which leads to compact and dense membrane structure thus suppress swelling. However, nearly all of the IPNs showed swelling in toluene and chloroform and reached to equilibrium swelling due same polarity of membrane and solvents surface. It was shown that the PDMS/PS IPN supported membranes have lower value of swelling compared to crosslinked

PDMS supported membrane in toluene and chloroform. The higher degree of swelling of PDMS membranes into chloroform may be attributed to molecular size of toluene and chloroform. It can be said that increasing molecular size of chloroform is smaller than toluene causes PDMS membrane to swell more. The effects of swelling due to PS content were similar to the density effects of the same membranes compositions but in an opposite direction. The results thus, consistent with the theory which stated that, increase of crosslinking in the IPN will result in increase of density and suppress swelling.²⁸

Network chain segment concentration, n , and value of crosslink density on blended PDMS/PS IPN supported membranes

Applying Flory-Rehner equation for crosslinked polymers, eq. (3), the values of n have calculated both for crosslinked PDMS and PDMS/PS IPN supported membranes samples from their equilibrium swelling results. The polymer-solvent interaction parameter χ_{12} for the system calculated using eq. (5) where the following values were used:¹⁷

$V_1 = 106.29 \text{ cm}^3 \text{ mol}^{-1}$, $\delta_{\text{Toluene}} = 8.9 \text{ (cal cm}^{-3}\text{)}^{1/2}$, $\delta_{\text{PDMS}} = 7.5 \text{ (cal cm}^{-3}\text{)}^{1/2}$, $R = 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$, and $T = 300.15 \text{ K}^\circ$.

The interaction between PS and toluene then taken as using eq. (5), where the following values were used¹⁷:

$V_1 = 106.29 \text{ cm}^3 \text{ mol}^{-1}$, $\delta_{\text{Toluene}} = 8.9 \text{ (cal cm}^{-3}\text{)}^{1/2}$, $\delta_{\text{PS}} = 9.1 \text{ (cal cm}^{-3}\text{)}^{1/2}$, $R = 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$, $T = 300.15 \text{ K}^\circ$.

Subsequently the interaction parameter χ_{12} was calculated using eq. (8):

This value of χ_{12} was then substituted into the Flory-Rehner eq. (3) to give values of network chain segment concentration, n which is tabulated in Table II; where n_{Tensile} represented the values calculated using tensile strength result, and n_{swell} represented the values calculated from their equilibrium swelling behavior.

The values of n were also determined from the relationship of $E = 3nRT$, thus giving the experimental value of n using tensile strength tests. To comparing the two values of n (n_{swell} and n_{tensile}) calculated using both methods is tabulate in Table II. The values calculated from the tensile strength results were more than four to nine times higher, compared to swelling test. This indicates that, in spite of the PDMS, the density of PDMS/PS varies with increasing the amount of PS in IPN system except 10 wt % PS of PDMS/PS membrane. It was observed that the increment of PDMS/PS density is directly influence on molecular weight, and degree of crosslinking of the IPN network which is true for most IPN.²⁸

From Table II, it has shown that, higher degrees of network chain segment concentration, n were obtained when the PS is increased inside the membrane composition. Both of the value for network chain segment concentration, n obtained by tensile test and swelling test showing similar trend with a different ratio. All of the IPN supported membranes showed increase in network chain segment concentration, n compared with crosslinked PDMS supported membrane. The effect of PS contents (30–70 wt %) in each respective IPN supported membranes composition showed increase in value of network chain segment concentration. It was shown that for the composition of PS of 70 wt % content in the system gave the highest value for network chain segment concentration, n_{swell} and n_{tensile} is 6.0×10^{-4} and 58.2 mol cm^{-3} . Increasing PS content over DCP 2 wt %, eventually privileged the value for network chain segment concentration, n and lowered the molecular weight of PDMS/PS IPN's membrane except 50 wt % of PS. Thus, increment in PS composition within IPN supported membrane highly influence the tensile strength and swelling resistant where as a rigid polymer, PS reinforce tensile strength and swelling resistant not only by crosslinking but also physical entanglement between molecules which leads to higher degree of network chain segment concentration, n .

Table II also represents the crosslink density of each respective membranes composition using both value of n_{swell} and n_{tensile} . It was clear that the trend of crosslink density were similar to network chain segment concentration, n . As the value of network chain segment concentration was used to calculate crosslink density as well as molecular weight between crosslink or chain molecular weight, M_c .

Experimental result shows that the trend for molecular weight between crosslink, M_c were opposite with the trend of crosslink density for the respective membranes. Molecular weight between crosslink, M_c shows lower value compared to crosslink density for the respective membranes which indicated distance between crosslink networks is small, indicative of compact chain structure. On a molecular level, a shorter chain/length between crosslink networks with a high degree of crosslink density obtained both from chemical crosslink and physical entanglement leads to dense and close membrane structure. Dense membrane structure with close network between crosslink leads to suppress swelling in the membrane and lowered flux for separation. On contrary, the effects of dense membrane although resulted in lower flux for separation usually will produce higher membrane selectivity depends on the affinity of the membrane. The following SEM micrograph in the next subchapter will prove the findings of dense microstructure on the IPN supported membrane.

Morphologies of the membranes

Field Emission Scanning Electron Microscope (FESEM) was used to study the morphology of the supported crosslinked PDMS membrane and PDMS/PS IPN supported membranes with the magnification level of 5000 \times for surface and 500 \times for cross-sectional area. The structures of the respective membranes depend heavily on the percentage of PS in the membrane mixture as well as DCP content towards degree of crosslinking density.

Crosslinked PDMS supported membranes

Micrograph images for cross-sectional and surface areas of supported crosslinked PDMS membranes are shown in Figure 6(a,b). These SEM micrograph images were used as comparison to the IPN supported membranes with multiple compositions. The micrograph of the supported crosslink PDMS membrane showed the membranes structure was uniform and no pores were visible even at higher level of magnification (5000 \times). This showed that the supported crosslinked PDMS membrane was dense membrane. The thickness of the supported layer and PDMS film were obtained from the micrograph images of scanning electron microscope and was 34.39 μm .

Comparison of PDMS/PS IPN blend supported membranes with different composition of PS and preset amount of dicumyl peroxide (DCP)

The cross-sectional structures at 500 \times magnification of the PDMS/PS IPN supported membranes

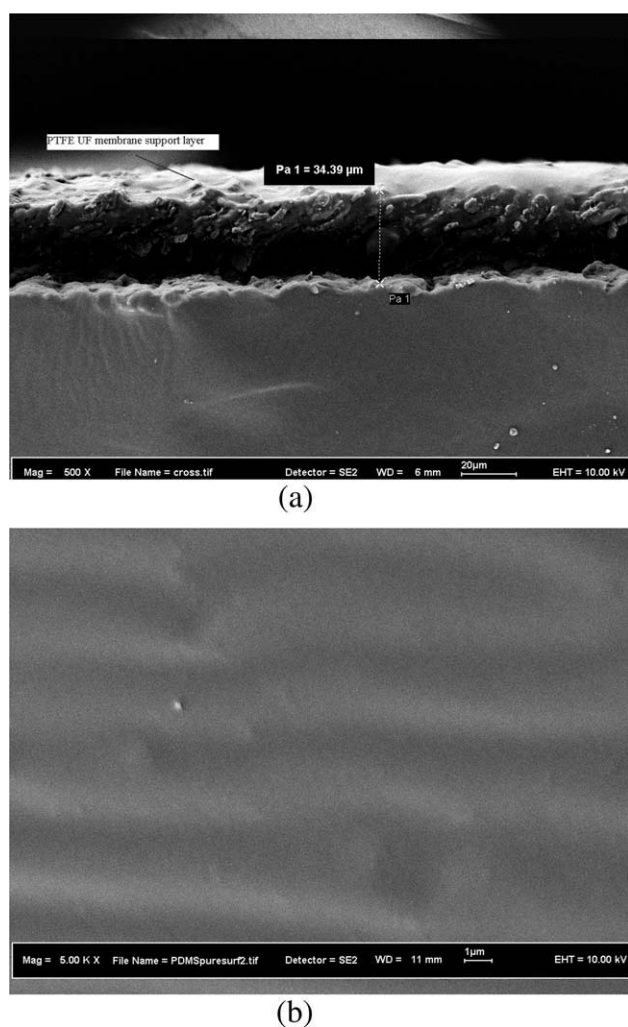


Figure 6 Micrograph image for crosslink PDMS supported membrane; (a) Cross-sectional area; (b) Surface area.

produced from the various amount of PS with fix amount 2 wt % of DCP are shown in Figure 7(a–d). Prior research had shown that the casting solution characteristics and formulations at the presence of catalysts (DCP and DD) have direct influences on IPNs pervaporation membrane formation and structure.^{12,17,29} Figure 7(a–d) shows a small increase in smoothness of the structures due to different molecules that interpenetrates in each others network which leads to high degree of crosslink density compared to crosslink PDMS in Figure 6. However, the effect was minimal as PDMS dominate the structure due to high PDMS percentage in the composition. It was proven that 2% DCP usage in IPN membrane composition of 90/10 (PDMS/PS) and 70/30 leads to the smooth structure as compared to Figure 6(a). However, Figure 7(c–d) shows distinguished difference in smoothness for each of the respective categorical IPN supported membrane structure especially in cross-sectional area when the PS content increases.

In addition Figure 7(a–d) shows that the structures of the supported membranes were smooth until reaching 50 wt % of PS composition in the IPN system. The IPN supported membrane structure was then shows a minimal effect of roughness when the PS concentration reached 70 wt % of PS in the IPN supported membrane composition. It suspected that the increase amount of PS in the IPN supported membrane composition was having the attribute toward the roughness structure when exceeding 50–70 wt %. It was suspected that when the content of PS dominate the IPN supported membrane composition, large domain of PS formed which in turn stops or agitate the continuity phase of PDMS matrix thus showing an effects of minimal roughness on the IPN supported membrane structure as well as texture. Sperling³⁰ stated that; for a polymer blend, even if the two polymer components are well mixed with each other, they are often phase separated to some extend. Then, the two components tend to form two mutually continuous phases in which the first-formed network is predominant. However, in this case the morphology of the PDMS/PS membranes structures suggest that microphase-separated structures consisting of PS domain and continuous PDMS phase has taken place the same as been reported by Miyata et al.³¹

Micrograph image of surface area for PDMS-PS IPN supported membrane is presented in Figure 8(a–d). It was found that the morphological structure corresponding well with the degree of crosslink density with respect to the IPN support membrane composition. The morphological structure of the respective membranes was in agreement with generally accepted theory, which stated that higher crosslinking density leads to fine microphase structure. The findings with regards to correlation of IPN microphase structure with crosslink density were supported by Kim et al.,³² stated that crosslink density is the controlling factor in determining the morphology of IPN system thus higher degree of crosslink density will results in finer structure.

MEMBRANES PERFORMANCE STUDY ON PERVAPORATION SYSTEM

In this experiment, attempt to separate ethanol in water has been made and selectivity as well as flux for the crosslinked PDMS and various composition of PDMS/PS IPN supported membrane been recorded and analyzed. Parameter such as temperature against flux and selectivity of respective membranes has taken into account. Feed concentration was set to a constant of 10 wt % ethanol in water and has been monitored for consistency. The effective surface area of the resulting membranes in contact with the feed mixture was 63.62 cm².

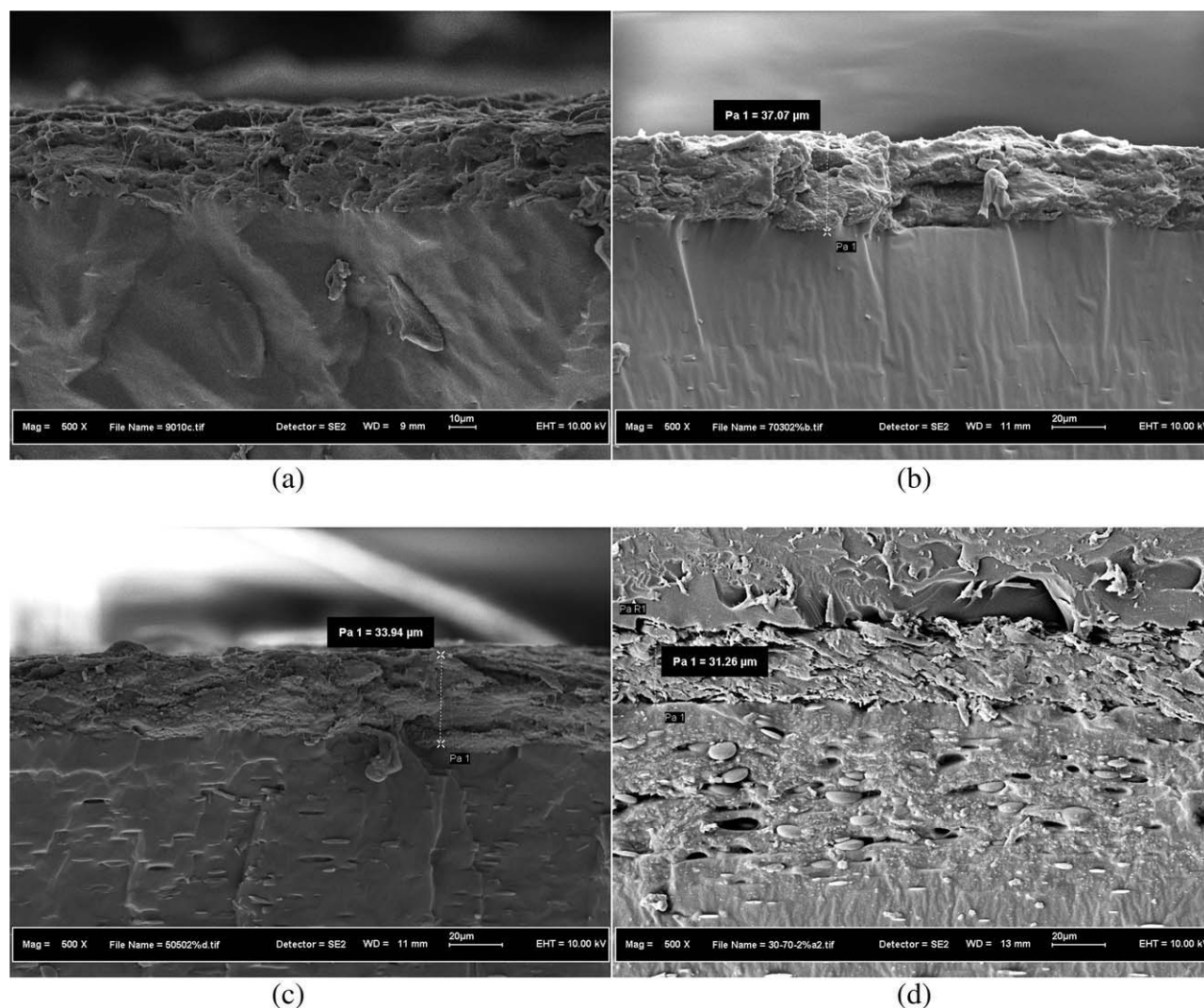


Figure 7 Micrograph image of cross-sectional area for 2% DCP PDMS/PS IPN supported membrane with various composition of PS; (a) 90/10; (b) 70/30, (c) 50/50, (d) 30/70.

Influence of PS content on blended IPN supported membrane performance

Figure 9 shows the permeation rate and separation factor versus the PS content for $\text{H}_2\text{O}/\text{EtOH}$ solution at temperature 30°C . Results revealed that the permeation rate and selectivity for $\text{H}_2\text{O}/\text{EtOH}$ solution is significantly affected by PS contents (wt %) added to blended IPN supported membrane. It was observed that PDMS membrane without PS exhibits highest permeation rate of $179.39 \text{ g m}^{-2} \text{ h}^{-1}$ and lowest separation factor of 0.55 compared to blend membranes. This indicates that the PDMS membranes have ethanol permselectivity. Miyata et al.²⁹ has also reported the similar results. Addition of PS contents in the blended IPN supported membrane reduces permeation rate and increases selectivity linearly. However, blended IPN supported membrane containing 50–70 wt % PS show an excellent increase in the selectivity with low permeation rate as com-

pared to PDMS membrane. Apparently, the results indicated that the hydrophobicity of the membrane increases with increasing amount of PS content. Liang and Ruckenstein¹⁷ has also reported similar results and this conclusion is in agreement with the observed effects of crosslink density on minimum swelling (Fig. 5) in $\text{H}_2\text{O}/\text{EtOH}$ mixture.

Influence of feed temperature and PS content on blended IPN supported membrane performance

The effect of the temperature on the permeation rate and separation factor for an ethanol–water mixture containing 10 wt % EtOH is presented in Figures 10 and 11, respectively. It can be seen that higher flux and lower selectivity rate are obtained at higher operating temperature of PDMS membrane without PS. However, it was observed that the PDMS membranes composition contains 0% PS, 10, 30, and 50 wt % PS

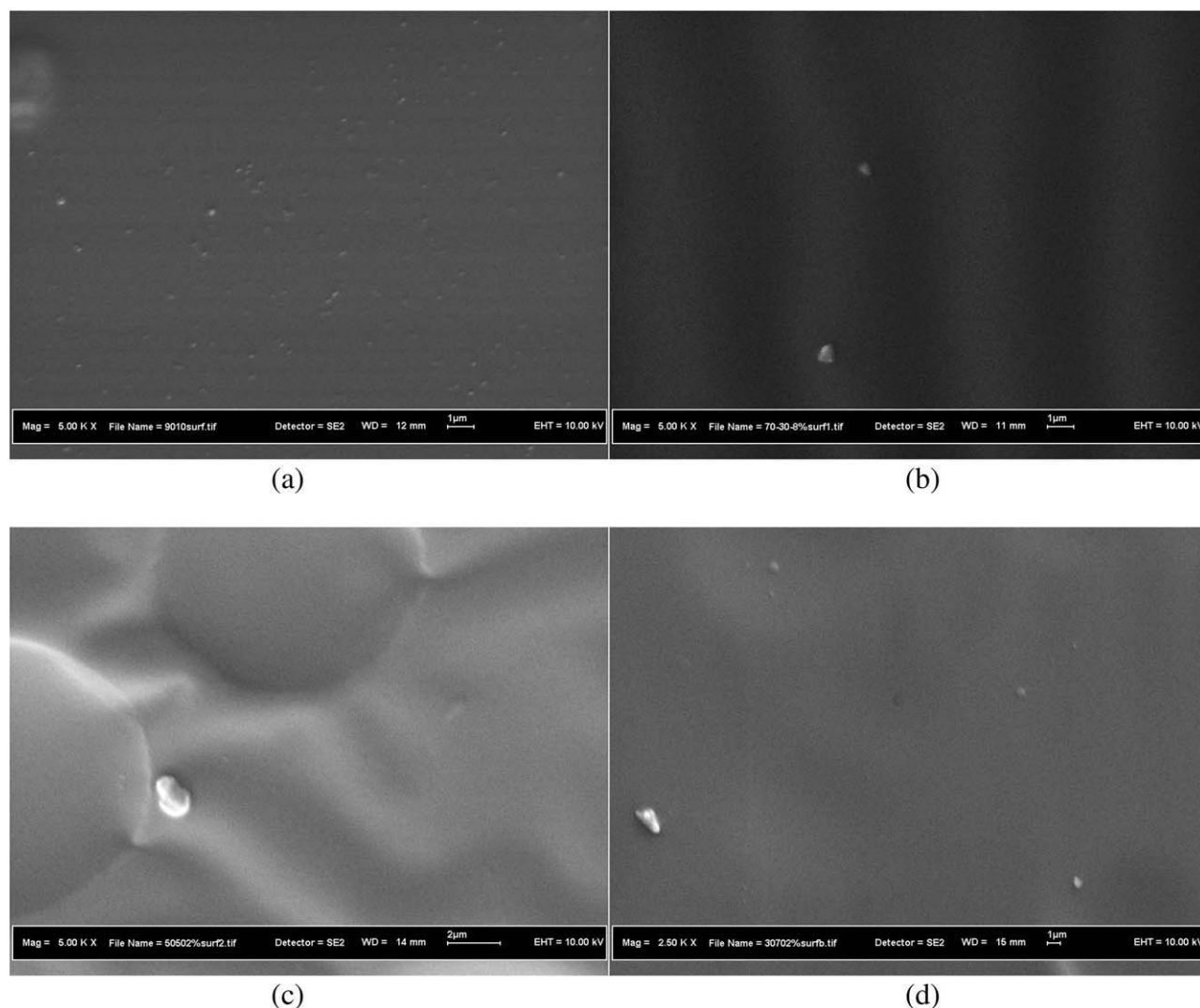


Figure 8 Micrograph image of surface area for 2% DCP PDMS/PS IPN supported membrane with various composition of PS; (a) 90/10; (b) 70/30, (c) 50/50, (d) 30/70.

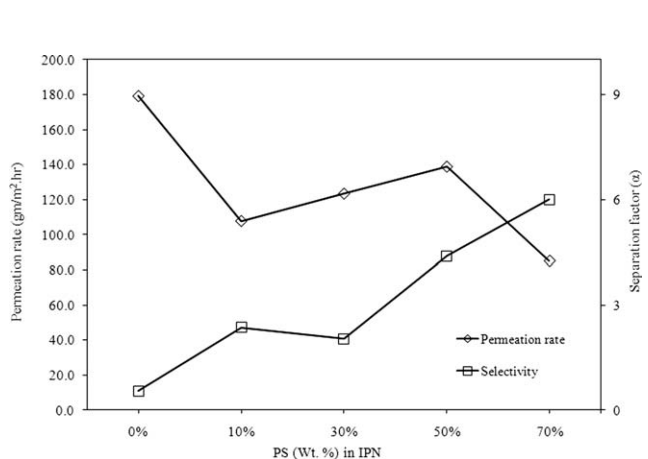


Figure 9 Permeation rate and separation factor versus the PS content for H₂O/EtOH solution at temperature 30°C, “0%” shows PDMS.

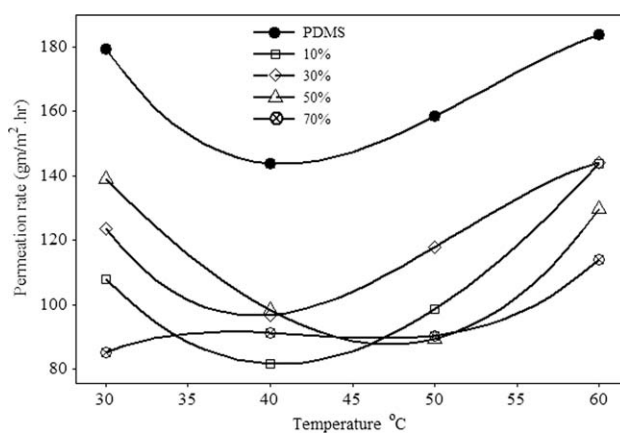


Figure 10 Flux comparison with temperature of various composition of PS for PDMS/PS IPN supported membranes with preset amount of DCP and crosslinked PDMS supported membrane.

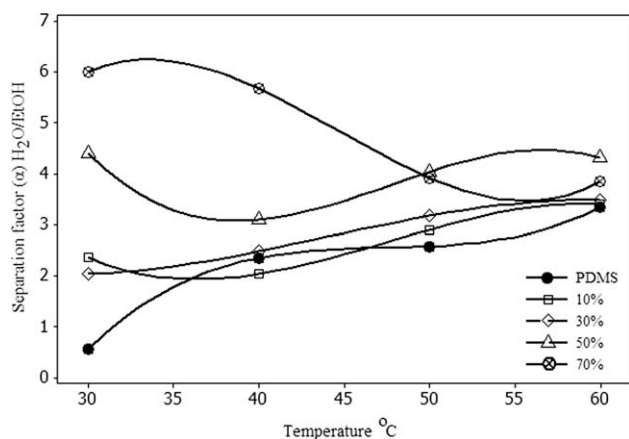


Figure 11 Flux comparison with temperature of various composition of PS for PDMS/PS IPN supported membranes with preset amount of DCP and crosslinked PDMS supported membrane.

showing similar variance trend in flux and separation factor at temperatures 40–60°C. Results are revealed that the permeation rate of all membranes increases with increasing temperature (40–60°C) because the mobility of the permeating molecules has enhanced both by the temperature and by the higher mobility of the polymer segments.¹⁷ Besides that, with increasing temperature it has suspected that vibration between dense and close chain molecular structure of crosslinked polymer increase thus enables permeant molecules to permeate through which in turn increase flux as well.

Though, the PDMS membranes contains 70 wt % PS shows different and significant trend compared to all other membrane. The selectivity of the respective supported membrane shows declining trend across the temperature gradient. Parallel with the supported membrane composition of 50/50 wt % (PDMS/PS) IPN, the result agrees with findings reported by Miyata et al.,¹² which stated that PS membrane is water-permselective in spite of the hydrophobicity of PS. As the PS composition in the respective membrane was greater compared with the previous membrane which employed 50% PS composition, the declining value shows steeper trend (refer Fig. 10). It was because of the temperature increases; simultaneously it increases the interaction between water-permselective natures of PS with feed solution thus lowering the membrane selectivity. One of the reasons for the behavior was due to increase amount of PS in the PDMS network. Work done by Uragami¹³ stated that PS membrane shows water-permselective in spite of the hydrophobic nature of PS. Therefore, increasing the composition of PS in the PDMS network will increase total membrane degree of water-permselectivity, thus lower the value of selectivity at higher temperature during separation. The higher content of polystyrene in PDMS/PS IPN supported

membrane will results in increase of selectivity in term of ethanol–water separation. On contrary with selectivity, flux for the composition of 50 wt % shows increasing value with temperature. Nevertheless overall results revealed that supported membrane composition of 50/50 wt.% and 30/70wt% (PDMS/PS) shows overall good trend in selectivity compared to PDMS, 90/10 and 70/30 wt %.

CONCLUSIONS

The conclusions that extract from the present study are:

1. In general, the incorporation of rigid phase or glassy type polymer such as PS has improved the properties of PDMS membrane. It can conclude that an effective polymer blend using interpenetrating polymer network technique, with the combination of PS and PDMS have successfully synthesized.
2. PS has proven to reinforce the physical properties of PDMS supported membrane. From their tensile testing as well as swelling testing, it has confirmed that PDMS/PS IPN supported membrane showed an increase in the tensile strength and at the same time suppresses swelling effect towards toluene.
3. The highest value for flux and selectivity for the pervaporation process to separate 10 wt % ethanol in water using IPN supported membrane in this study was 85 and 6 g m⁻² h⁻¹, respectively. These values were achieved using membrane composition of 30/70 wt % PDMS/PS with 2% DCP having approximate average total thickness off 600 μm with pervaporation feed temperature of 30°C and operating system vacuum pressure of under 0.07 bars. The highest total flux and selectivity has in practice reached the requirement of the membranes for the use in cost-competitive fermentation–pervaporation processes, assuming that thermodynamic effects of other component in fermentation broth on activity coefficients and coupling effects will not severely affect pervaporation performance.
4. Generally, it can be conclude that higher degree of crosslink density in the respective membrane resulted in increase of selectivity with reasonably lower flux.

LIST OF SYMBOLS

A	Membrane surface area (m ⁻²)
A_d	Weight of the solid specimen in air (g)
B_w	Weight of solid specimen in distilled water
ρ_s	Density of the solid specimen (g cm ⁻³)
ρ_o	Density of distilled water (g cm ⁻³)

E	Young's modulus (MPa)
n	Number of effective crosslink per unit volume ($\text{kg mol}^{-1} \text{m}^{-3}$)
R	Gas constant
T	Absolute temperature ($^{\circ}\text{C}$)
n_{swell}	Network-chain segment concentration (mol cm^{-3})
n_{tensile}	Network-chain segment concentration (mol cm^{-3})
v_2	Volume fraction of polymer in the swollen areas
V_1	Molar volume of solvent ($\text{cm}^3 \text{mol}^{-1}$)
X_{12}	Flory-Huggins polymer-polymer interaction parameter
δ_1	Solubility parameters of solvent
δ_2	Solubility parameters of polymer
M_c	Molecular weight (g gmol^{-1})
ρC_x	Crosslink density (gmol cm^{-3})
W_s	Weight of wet membrane (g)
W_d	Weight of dry membrane (g)
w	The total amount of permeate at steady state (cm^{-3})
α	Separation factor
Y_i, Y_j	Weight fraction of component i and j in the permeate
X_i, X_j	Feed phase weight fraction of component i and j
v_1	Volume fraction of solvent
v_2	Volume fraction of polymer
δ_s	Solubility parameters of the solvent and polymer
ρ	Density of polymer
Δt	Permeation time
σ	Tensile stress
ε	Tensile strain
η	Number of effective crosslink per unit volume or network chain segment concentration

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