

# DEVELOPMENT OF NATURAL RUBBER MEMBRANES FOR SEPARATION OF METHYL TERT-BUTHYL ETHER AND METHANOL

Nur Azrini Ramlee<sup>a\*</sup>, Ghazali Mohd Nawawi<sup>b</sup> and Khairulzaman Dahlan<sup>a</sup>

<sup>a</sup>University Technology Malaysia,  
81310 SKUDAI JOHOR

<sup>b</sup>Malaysian Nuclear Agency Bangi,  
43000 KAJANG, SELANGOR

\*Email: [nurazrini@nuclearmalaysia.gov.my](mailto:nurazrini@nuclearmalaysia.gov.my)



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## ABSTRACT

*As a new commercial process, membrane separation raises significant expectations in the process plant of the future and therefore this research was being initiated to develop and characterize pervaporation membrane based on natural rubber (NR). Natural rubber SMR-L grade which was supplied by Malaysia Rubber Research Institute (MRRI) was used for the development of the membranes via interpenetrating polymer network (IPN) techniques. Polystyrene (PS) was used to modify the natural rubber to further improve their mechanical and chemical properties. The membranes were prepared with various blend ratios of natural rubber, polystyrene and divinyl benzene as crosslinker with constant 1% of dicumyl peroxide as the initiator. The developed membranes were then characterized to study the functional group presence, membranes morphology, crosslink density, tear strength, adsorption of the membranes and pervaporation separation of methyl-tert-buthyl-ether (MTBE) and methanol. Pervaporation process was conducted by using varies of MTBE concentration 10, 30, 50 and 70wt% and at differ operation temperature, 25°C and 55°C. Separation performance of IPN NR/PS membranes were based on the presented permeation flux and separation factor. Examination through Fourier Transform Infrared Spectroscopy (FTIR), determined crosslink density and tear strength, 6 series of IPN NR/PS membranes were successfully developed using natural rubber. Observation from Scanning Electron Microscopy (SEM) showed that the membranes were dense and appropriated for the pervaporation process application. From the pervaporation of MTBE and methanol, IPN NR/PS membranes of series D<sub>4</sub>N<sub>30</sub> shown low permeation flux of MTBE but high separation factor while D<sub>2</sub>N<sub>70</sub> membranes was vice versa for both temperature of 25°C and 55°C.*

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Keywords: Natural rubber, Polystyrene, IPN Crosslinking, Pervaporation, Membranes separation

## INTRODUCTION

Membrane and membrane processes have been widely used in different industries since 50 years ago. The growth of membrane utilization for separation is mainly because the mass separation can be performed at ambient temperature, thus the constituents to be separated are not exposed to thermal stress or chemical alteration. Such membranes technologies are microfiltration, ultrafiltration, pervaporation, reverse osmosis and dialysis or electrodialyses. The first major effort in commercializing pervaporation was undertaken by Bining in the 1950's and new membrane separation process was discovered potentially for various applications (Kujawski, 2000). There are three current separations of pervaporation; dehydration of organic solvents (removal water from organics), removal of organic compounds from aqueous solution (organic removal from water) and the separation of organic mixtures. Therefore, pervaporation is suited for mixtures with azeotrope and/or small differences in boiling characteristics specifically for MTBE and methanol separation. On the contrary, pervaporation and vapor permeation process, no industry scale application for both processes are being practiced and they offer the possibility of totally new developments of membrane and modules.

Therefore this research was initiated to develop a new pervaporation membrane from natural rubber (NR) by using interpenetrating polymer network (IPN) technology. As to modify the natural rubber, polystyrene (PS) was used to improve the chemical and physical properties of natural rubber. IPN natural rubber/polystyrene membranes that had been developed were used for the separation of methyl tert-butyl ether (MTBE)/methanol (MeOH) mixtures. Performance of membrane in pervaporation separation of MTBE/MeOH been analyzed in terms of permeation flux and separation factor. During the separation process, effect of IPN membranes composition blend ratio, concentration and temperature of pervaporation feed were investigated on the separation performances of the membrane. The characterization of the IPN natural rubber/polystyrene membrane been developed were based on its morphology, presence of functional group, crosslink density, tear strength of the membranes and adsorption study.

## MATERIALS AND METHODS

### Preparation of Interpenetrating Polymer Networks (IPN)

Sequential Interpenetrating Polymer Networks (IPN) technique has been applied to prepare the natural rubber/polystyrene membranes. For this technique, the components of the second network were swollen crosslinked/polymerized inside the previous crosslinked polymer network I. Natural rubber membranes have higher flux in comparison to other non-rubber polymers but the poor selectivity of these membranes limits its applications. The reason behind this is associated with its poor crosslinking. In this study, the sequential IPN steps were crosslinking of natural rubber and polymerization/crosslinking of polystyrene.

### Crosslinking of Natural Rubber

The natural rubber which was supplied by Rubber Research Institute (RRI) was masticated in a two roll mixing mill at room temperature. Dicumyl peroxide (4phr) was added into natural rubber and mixed thoroughly for 15 min. The mix was then cured at 160°C in a hydraulic press to get the crosslinked membranes.

### Polymerization and Crosslinking of Polystyrene

Series of interpenetrating polymer network membranes were prepared using DCP as initiator. The cured natural rubber (NR) membranes were weighted and kept immersed in inhibitor free styrene monomer containing initiator and 2 and 4% of divinyl benzene (DVB) as the crosslinker for polystyrene (PS) phase. The membranes were swollen for 30 min. The swollen samples were kept at 4°C for few hours to achieve equilibrium distribution of styrene monomer in the matrix. The swollen network sheets were heated at 80°C for 6 hours and 100°C for 2 hours, respectively to complete the polymerization and crosslinking reaction.

Table 1 indicates the series of IPN networks. The IPN were coded based on composition and crosslinker content. The crosslinker system was denoted by D and the blend composition is denoted as N<sub>30</sub>, N<sub>50</sub> and N<sub>70</sub>, where the subscripts indicate the weight percentage of rubber. The amount of 1% dicumyl peroxide was added to initiate the crosslinking process. The divinyl benzene content was varied in order to have varying level of crosslinking.

Table 1 : Series of Interpenetrating Polymer Networks

Sample Code	NR/PS Ratio	DVB content (%)
D <sub>2</sub> N <sub>30</sub> , D <sub>2</sub> N <sub>50</sub> , D <sub>2</sub> N <sub>70</sub>	30/70, 50/50, 70/30	2
D <sub>4</sub> N <sub>30</sub> , D <sub>4</sub> N <sub>50</sub> , D <sub>4</sub> N <sub>70</sub>	30/70, 50/50, 70/30	4

## Characterization of the Interpenetrating Polymer Networks

### Membrane Morphological

The structural morphologies of the membrane been developed were examined using a PHILIPS XL-40 Scanning Electron Microscope (SEM). The specimen surface was sputter-coated with gold prior to macroscopic observation before examining under the microscope. The membranes were observed from surface layer view and cross-section view of the membrane structures.

### Presence of Functional Groups

Fourier Transformation Infra Red (FTIR) Spectrometer by Perkin Elmer was used to study the presence of functional groups in the IPN membranes. A thin film membrane was placed on the sample holder and scanned by the spectrometer. The spectra of each sample were studied to confirm the functional groups presence.

### Tear Strength

The tear strength of membranes was measured using tensile testing machine at a crosshead speed of 50 mm/min. The measurements were done according to ASTM D-624 at room temperature. This test was done to investigate the crosslink performance physically.

### Measurement of Crosslink Density by Chemical Method

The crosslink density value of each developed crosslinked membrane was determined by swelling method. Small pieces with area 2.4 cm<sup>2</sup> of different dried crosslinked membranes were weighted and the adsorbed in pure toluene for 120h when equilibrium sorption was attained as evidenced by no further increment of weight between two readings of sample weights at different times. The crosslink density values ( $\nu$ ) were determined by swelling method equation;

$$\nu = \frac{1}{2} M_c \quad (1)$$

where  $M_c$  is the molecular weight between crosslink. In this case the equation simplifies to the original Flory-Rehner equation;

$$M_c = \frac{-\rho_p \nu_n \phi^{1/3}}{[\ln(1-\phi) + \phi + \chi \phi^2]} \quad (2)$$

where,  $\nu_n$  is molar volume of the solvent,  $\rho_p$  is density of the polymer,  $\chi$  is interaction parameter,  $\phi$  is volume fraction of the swollen sample and the volume fraction of polymer  $\phi$  in the swollen sample was calculated using the equation;

$$\phi = \frac{W_1/\rho_1}{(W_1/\rho_1) + (W_2/\rho_2)} \quad (3)$$

where,  $W_1$  is weight of polymer,  $W_2$  is weight of solvent,  $\rho_1$  is density of polymer,  $\rho_2$  is density of solvent and  $\chi$  is an changeable parameter, a fraction of polymer-solvent interaction and considered to be made up to components, one entropic and the other energetic in origin. Value  $\chi$  is given by the equation;

$$\chi = \beta + \frac{V_s}{RT} (\delta_s - \delta_p)^2 \quad (4)$$

where,  $\beta$  is lattice constant,  $V_s$  is molar volume of the solvent,  $\delta_s$  is solubility parameter of the solvent,  $\delta_p$  is solubility parameter of the polymer, R is gas constant and T is absolute temperature.

### Adsorption Study

Samples were cut 1.5x1.0 cm each. The initial weight of the samples was determined by weighing on a highly sensitive electronic balance having an accuracy of 0.00001g. The samples were kept immersed separately in different composition of MTBE-methanol mixtures at room temperature. The swollen samples were taken out at fixed time intervals, wiped free of adhering solvents and weighed immediately on the electronic balance. The process was continued until equilibrium swelling which was indicated by the constancy in weight. The swelling ratio (S) was determined as;

$$S = \frac{W_s - W_d}{W_d} \quad (5)$$

where  $W_d$  and  $W_s$  are the weight of dry and swollen membranes, respectively.

Table 2 : Solution mixtures for membranes series

Membrane	Solution Mixtures of MTBE/Methanol (wt %)			
D <sub>2</sub> N <sub>30</sub> D <sub>2</sub> N <sub>50</sub> D <sub>2</sub> N <sub>70</sub>	30/70	50/50	70/30	100 wt% MTBE
D <sub>4</sub> N <sub>30</sub> D <sub>4</sub> N <sub>50</sub> D <sub>4</sub> N <sub>70</sub>				

### Performances of Pervaporation Separation MTBE/MeOH

There are several factors affecting the performances of pervaporation separation MTBE/MeOH. This is including the effect of natural rubber and polystyrene composition blend ratio, concentration and temperature of pervaporation feed. Efficiency of pervaporation separation process depends on the flux and separation factor. The amount of permeates through the membranes will affect these performance. In general, MTBE material is more selective to NR/PS composition and will be permeate. However, high concentration of MTBE will affect the selective diffusivity of the membrane during the separation process. Therefore, in this research the effect of NR/PS composition on pervaporation separation performance was studied.

During pervaporation separation of MTBE/MeOH, process temperature will affect permeation rates of permeates through the membrane, according to Arrhenius equation. The pervaporation separation of MTBE/MeOH were carried out at different temperature ranging from 25 to 55°C with pressure maintained at 2-3mbar. Best operating condition for the separation processes were investigated based on the measured separation factor and permeability of membrane. The permselective properties of pervaporation membranes were determined by solubility and diffusivity of the permeating components in the membrane. Since generally, both sorption and diffusion phenomena are dependent on the concentration of the liquid mixture, the permeation characteristic of membranes are usually strongly influenced by the feed concentration. Consequently, performance of pervaporation separation was studied based on different percentage of MTBE and MeOH which was 10% MTBE+90% MeOH, 30% MTBE+70% MeOH, 50% MTBE+50% MeOH and 70% MTBE+30% MeOH.

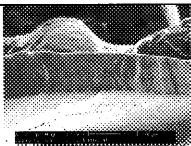
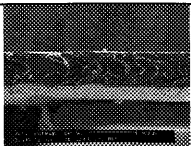
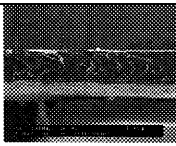
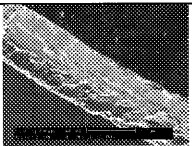
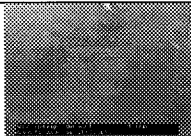
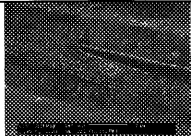
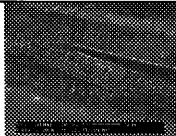
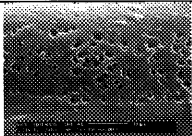
## RESULTS & DISCUSSION

SEM was carried out to characterize the IPN natural rubber/polystyrene membranes in terms of its morphology. The membranes were observed from the surface layer view and cross-section view of the membrane structures. Figure in table 3 shows the surface layer and cross-section SEM of samples pure natural rubber, D<sub>2</sub>N<sub>30</sub> and D<sub>4</sub>N<sub>30</sub> respectively.

It is observed at a very high level of magnification that the surface layer morphology of the membranes became rougher from pure natural rubber to D<sub>4</sub>N<sub>30</sub> when the crosslinker level increased. This is most probably caused by the

crosslinking formation of polystyrene phase. The crosslinking method applied has formed full-IPN membrane. As in full-IPN, the increasing of crosslinker level will increase the number of crosslinkers. Since natural rubber and polystyrene phases are crosslinked, both the phases are co-continuous in all the full IPNs (Thomas and Mathew, 2001).

Table 3 : Comparison of natural rubber & IPN membranes morphology

Micrograph	Natural Rubber	IPN NR/PS Membranes	IPN NR/PS Membrane D2N30	IPN NR/PS Membrane D4N30
Cross-section layer Magnification: 50x				
Surface layer Magnification: 2000x				

For the cross section SEM, the absence of pores is observed at 50x magnification level indicating the dense structure of the IPN natural rubber/polystyrene membranes at different blending ratio. Thus, the prepared membranes are suitable for pervaporation separation process since the process needs dense structure membrane. Dense structure membrane is used in pervaporation process because pervaporation separates liquid-liquid phase mixture. The dense membrane can separate permeants of similar size if their concentration in the membrane material differs significantly (Baker, 2004).

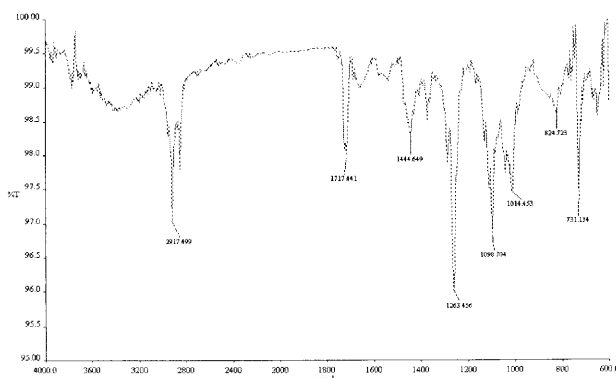


Fig. 1 : FTIR spectra of sample N<sub>50</sub> with 2% DVB

Table 4 : FTIR spectra of sample N<sub>30</sub>, N<sub>50</sub> and N<sub>70</sub>

Sample	C=C aromatic Stretching Absorption Peak (cm <sup>-1</sup> )
D <sub>2</sub> N <sub>30</sub>	1659.0 and 1449.5
D <sub>2</sub> N <sub>50</sub>	1717.4 and 1444.6
D <sub>2</sub> N <sub>70</sub>	1656.5 and 1499.9

Presence of functional groups in the IPN membranes was illustrated via FTIR spectra as shown in Fig. 1. Fig. 1 shows the FTIR spectra of sample N<sub>50</sub> with 2% DVB respectively and Table 5 tabulates the FTIR spectra of C=C aromatic stretching absorption peak of each sample with different in level of wt% Polystyrene. This is due to the presence of polystyrene phase in the blends.

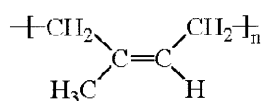


Fig. 2 : Natural rubber molecule structures

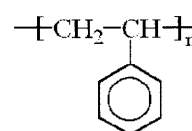


Fig. 3: Polystyrene Molecule Structure

Polystyrene does have the C=C aromatic structure as shown in Fig. 3. In comparison of natural rubber molecules structure shown in Fig. 2, it is proven that the FTIR absorption bands indicate that polystyrene presence in the full-IPN membranes for sample with 2% and 4% DVB.

Tear strength is a measure of the resistance to failure of a material when it is subjected to continue stretching (Setua et al, 2005). The effect of blend ratio and crosslink level on tear strength of the membranes is shown in Fig. 4. Based on the experimental data, the uncrosslink sample has the resistance value of 2.6 N/mm. Meanwhile the tear resistance values of these samples with 2% and 4% DVB were in the range of 3.5 to 6.1 N/mm. The result indicated that crosslinking had improved the strength of membranes. Crosslinking of rubber makes it less permeable with high selectivity and strength (Ray and Ray, 2006).

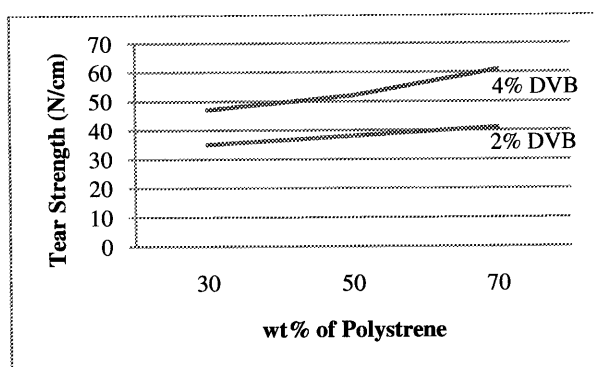


Fig. 4 : Effect of blend ratio and crosslinker level on tear strength

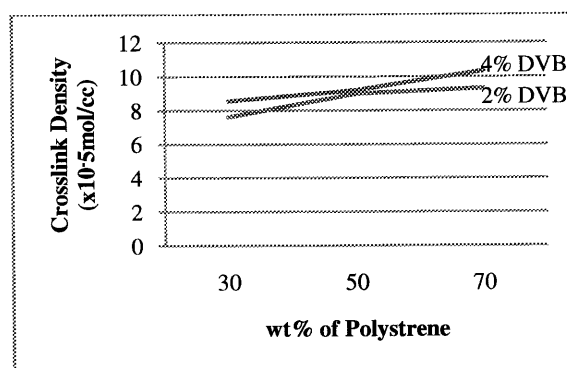


Fig. 5 : Effect of blend ratio and crosslinker level on crosslink density

On the other hand, the 4% DVB level was observed to have higher tear strength than 2% DVB level. This indicates the tear strength increases in the order of increasing crosslinking level. Furthermore, the addition of DVB level has improved the tear strength value around 34.29 to 48.78%. When the DVB level increased, the crosslinking in the PS phase increased making the material more rigid. Overall the observation indicated that the sample D<sub>4</sub>N<sub>30</sub> has the maximum tear strength value due to high degree of crosslinking while sample D<sub>2</sub>N<sub>70</sub> has the minimum tear strength value due to low degree of crosslinking. Tear strength plot trending was similar to the crosslink density plot trending. It is suggested the crosslink density was related to the tear strength of the membranes. By increasing the PS content, the number of crosslinking unit area increased (Thomas et. al, 2001). Moreover, as the DVB level increased, the crosslinking of PS phase also increased (Thomas et. al, 2002). These factors have led to the increasing of crosslink density and furthermore the tear of the membranes. Therefore, the presence of PS phase and crosslinker level is capable to increase the crosslink density and improve the tear strength of membranes.

Fig. 5 indicates the effect of blend ratio and crosslinker level on crosslink density. The values of  $\nu$  for both samples are in the range of 218 to 289 gmol/cm<sup>3</sup>. The figure illustrates the crosslink density increased as the content of PS increased in both cases. As PS content increases the number of crosslinks formed in unit area increase and thereby the values of  $\nu$  increase. In addition, values of  $\nu$  of 4% DVB are higher than 2% DVB. The values of  $\nu$  increase with the crosslinker level because the PS network density increases with the increment of crosslinking level. This will further improve the total crosslink density of the system. In addition, high crosslink density causes the separation factor to maximize and have good flux. It is noted that sample D<sub>4</sub>N<sub>30</sub> has the highest crosslink density value as it contains the highest PS content (70%) as well as crosslinker level (4%). On the other hand, sample D<sub>2</sub>N<sub>70</sub> has the lowest value of crosslink density due to the lowest content of PS and crosslinker level. Therefore, it is proven that the crosslink density increases as the crosslinker level increases in full-IPN system.

Figs. 6 show the effect of crosslinker level on swelling ratio of samples N<sub>30</sub>, N<sub>50</sub> and N<sub>70</sub> series respectively. It was observed that all figures showed similar trend. The swelling ratio increased as the weight percent of the MTBE increased in the mixtures. The swelling ratio shows significant increment when MTBE content is above 70 wt%. The results indicated the better similarity of membranes toward MTBE content compared to methanol. A polymer with high affinity for one feed component gives greater selectivity. However, if the affinity is too high, the membrane is excessively swollen by the component, loses its integrity and therefore selectivity loss (Villaluenga and Tabemohammadi, 2000). Consequently, it is important to suppress or control the degree of swelling by crosslinking or other method. Since the membrane affinity was towards MTBE, the molecules were allowed to diffuse in the membrane. High diffusivity leads to increase the permeability and thereby, increased the swelling ratio.

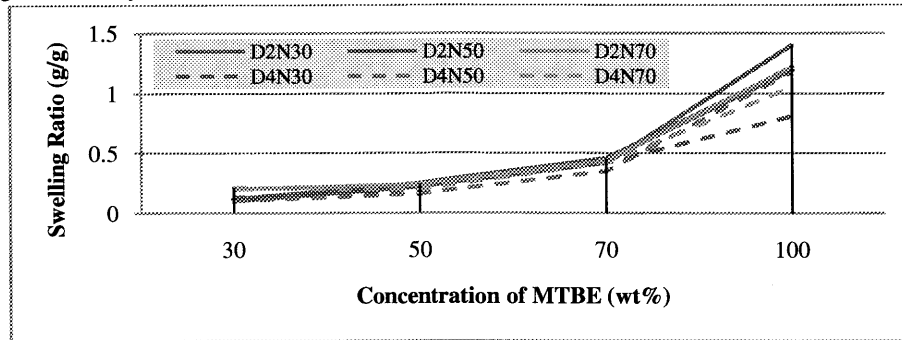


Fig. 6 : Effect crosslinker level to swelling ratio for N<sub>30</sub>, N<sub>50</sub> & N<sub>70</sub> series

Meanwhile, the swelling ratio below 70 wt% of MTBE showed no significant changes for samples N<sub>30</sub> and N<sub>50</sub> series. This is caused by the high concentration of methanol in the mixture solution. At low concentration of MTBE, methanol which is present at the high concentration is not absorbed to an appreciable extent due to presence of styrene moiety in the membrane and this is causing loss total sorption. Furthermore, the figures above shown the effect of crosslinker level on swelling ratio of MTBE-methanol mixture in varies concentration. The figures illustrated that the swelling ratio of MTBE-methanol mixture decreased with the increased of crosslinker level for all cases. The reason is due to high degree of crosslinking when increasing the crosslinker and thereby, decreased the swelling ratio. As the number of crosslink increased, the resistance offered to transport increased correspondingly. Therefore, the diffusivity of MTBE molecules towards the membranes decreased with the increasing of the number of crosslink in the samples. Degree of swelling of IPN varied with degree of crosslinking (Qi et. al, 2006).

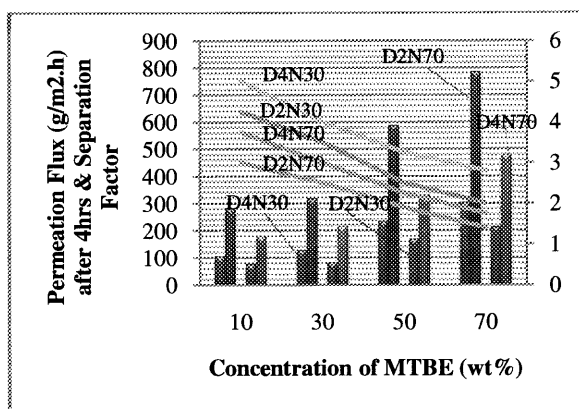


Fig. 7 : Permeation flux & separation factor of IPN natural rubber membranes at 25°C

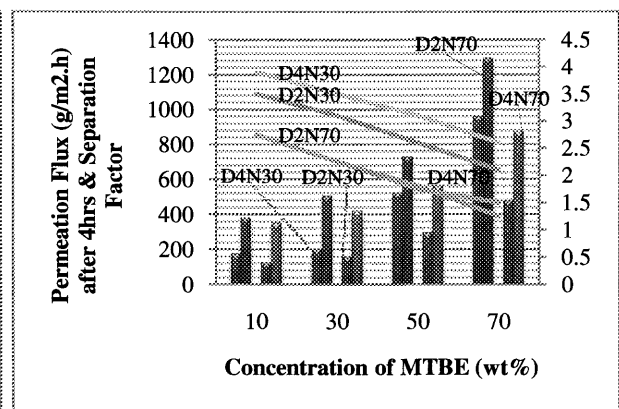


Fig. 8 : Permeation flux & separation factor of IPN natural rubber membranes at 55°C

Fig. 7 and Fig. 8 indicate permeation flux and separation factor performances of developed IPN natural rubber membranes at different temperatures. At both temperatures, D<sub>2</sub>N<sub>70</sub> shown the highest permeation flux for each

concentration of MTBE (wt%). It is seen that the permeation flux through IPN natural rubber/polystyrene membranes increased with increased in the concentration of MTBE in the feed. This is due to the strong interaction between natural rubber and MTBE. This interaction effectively increases the frequency and amplitude of rubber chain motions, thereby allowing the permeate molecules to pass through the membrane easily (Das *et al.*, 2006). At 70 wt% MTBE, the impact of temperature changed shows  $D_2N_{70}$  permeation flux increased by 64.50%. At high temperature, kinetic energy of molecules is at high level directly increase the molecules movement through membranes surface and therefore increasing the permeation flux. However for separation factor,  $D_4N_{30}$  showed high separation factor and this performances was vice versa. As the DVB level increased, separation factor of IPN natural rubber/polystyrene increased. A same performance has been reported by Hilmioglu and Tulbentci, 2004 whereby increasing the crosslinker PAA content in the membranes, solubility and fluxes decreased and selectivity increased. Higher DVB level increased the crosslinking in polystyrene phase and directly decreased the interaction of MTBE molecules to natural rubber.

## CONCLUSION

6 series of IPN NR/PS membranes were successfully developed using natural rubber. Observation from Scanning Electron Microscopy (SEM) showed that the membranes were dense and appropriated for the pervaporation process application. From the pervaporation of MTBE and methanol, IPN NR/PS membranes of series  $D_4N_{30}$  shown low permeation flux of MTBE but high separation factor while  $D_2N_{70}$  membranes was vice versa for both temperature of 25°C and 55°C.

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