Preparation and Characterization of Hydrophilic Pervaporation Membranes from Natural Rubber Latex Based Polymer

Songsak Klamklang, Khantong Soontarapa* and Somsak Damronglerd

Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Phayathai Rd., Phathumwan, Bangkok 10330, Thailand.

* Corresponding author, E-mail: khantong@mail.sc.chula.ac.th

ABSTRACT To improve the hydrophilic property of natural rubber latex (NR), various methods for combining hydrophilic polymers; ie, mechanical blending (MB), semi-latex interpenetrating polymer network (semi-LIPN), and latex interpenetrating polymer network (LIPN), were studied. Polyacrylamide (PAM) and phthalated chitosan (PhChi) were chosen as hydrophilic polymers for this study. The desired membranes must possess sufficient tensile strength and high water sorption selectivity. The potential membrane usable for pervaporation dehydration of aqueous azeotrope ethanol was the LIPN type prepared from prevulcanized latex and PAM with 60/40 ratio and with 1% EGDM.

KEYWORDS: hydrophilic membrane, natural rubber latex, polyacrylamide, phthalated chitosan.

INTRODUCTION

Pervaporation separation technique is a fractionation process that uses dense or composite membranes as the separation barrier between the feed liquid and permeated vapor. Pervaporation is attractive when it is difficult to apply distillation such as in fractionation of azeotropic mixtures, close boiling point components and isomeric mixtures.[1] Transport through a pervaporation membrane takes place by a solution-diffusion mechanism; ie, the permeation rate is a function of solubility and diffusivity of the components to be separated. Total selectivity is the product of sorption selectivity and diffusion selectivity. The component that is sorbed preferentially permeates preferentially too.[2]

Thailand is the biggest world producer and exporter of natural rubber.[3] It is a challenge to develop natural rubber latex as the pervaporation membrane to be used for dehydrating azeotropic ethanol, turning it into gasohol fuel. Pervaporation dehydration needs hydrophilic membranes with proper hydrophilic-hydrophobic balance to improve the performance.

One approach includes the blending of other hydrophilic polymers into the natural rubber latex. Here, the blending of polyacrylamide and phthalated chitosan were studied. Polyacrylamide possesses highly hydrophilic character, which is greater than that of most other non-ionic water-soluble polymers.[4] Chitosan, derived from shrimp shells, is also an attractive material for hydrophilic membranes.[5] To improve the solubility of chitosan in the natural rubber latex at neutral pH or higher, it must be modified to phthalated chitosan by ring-opening reaction with some cyclic acid such as an anhydride.[6]

An interpenetrating polymer network (IPN) is an intimate combination of two polymers, at least one of which is synthesized or crosslinked in the presence of the other. There is no crosslinking between the two different polymers. When both polymers crosslink, the product is called a full IPN. If one is crosslinked and the other polymer is linear, the product is called semi-IPN. Unlike chemical blending, there is no covalent bond between the polymers.[7] Mechanical blending is the traditional way of physically combining two or more polymers by mixing, in which there is no covalent bond between the polymers.

There are a number of synthetic methods for producing IPNs, including sequential, simultaneous, latex, gradient, and thermoplastic IPN methods.[7] Each method involves controlling conditions such as the order of synthesis, the crosslink types and density, the grafting between the networks, and the relationship between gelation conditions and phase separation. In addition, the specific polymers employed, whether they are glassy, rubbery, or semi-crystalline, can be varied. Hydrophilic-hydrophobic IPN and semi-IPN as well as latex IPN (LIPN) and semi-latex IPN (semi-LIPN) are examples described in the literature.[7]

This study aims at investigating the preparation of potentially dense hydrophilic membranes from natural rubber latex for anhydrous ethanol production by pervaporation process. Only sorption characteristics are used here as the preliminary membrane selection because it is quicker and easier than a full pervaporation experiment. The suitable membrane with desired sorption characteristics and mechanical strength would be identified for further tests if the preliminary study is successful.

MATERIALS AND METHODS

Materials

Concentrated natural rubber (NR) latex and prevulcanized latex were kindly supplied by Revertex (Thailand) Co Ltd. Shrimp shell for synthesis of chitosan was supplied by Surapol Nishire Foods Co Ltd, Thailand. Other chemicals used are reagent grade.

Chitosan, a natural biopolymer, was prepared following the steps previously reported.[8] This was performed through the deproteinization of ground shrimp shells with 4% w/w NaOH at 80 °C under nitrogen atmosphere for 3 hours. Demineralization was executed overnight with 4% v/v of HCl at room temperature, drying at 60 °C. Deacetylation was performed twice with 40% w/w NaOH at 120 °C for 1 hour. The obtained chitosan was finally washed with water to neutralize, and dried at 60 °C. This transformed the chitosan into phthalated chitosan (following Sashiwa et al)[6] for enhanced solubility in latex at high pH. The procedure was conducted by dissolving 10 g of chitosan in 210 ml of 4.8% v/v lactic acid, then diluting with 800 ml of methanol, and adding phthalic anhydride amounting to 6-mole equivalent (to $-NH_2$ group in chitosan). The contents were then stirred for 24 hours at room temperature, and the pH was adjusted to 5 with 5% w/w NaOH. After filtering to collect the precipitates, the sample was dispersed in 500 ml of water. Again the pH was adjusted (this time to 12) with 5% w/w NaOH, dialyzed with dialysis membrane (MWCO = 20,000), dried in an oven at 60 °C for 2 days, and finally ground to 60 mesh.

Membrane Types

Concentrated natural rubber latex or prevulcanized latex was used as base polymer. To avoid the effects of non-rubber components on the properties of membrane, all membranes wer e prepared from the same lot of latex and kept at 4 °C in a refrigerator. Phthalated chitosan (PhChi) or poly-acrylamide (PAM) were used as secondary polymers. PhChi was already in polymer form. Acrylamide was polymerized to become polyacrylamide in the base polymer. Four types of membranes were prepared; ie, blending (MB), semi-latex interpenetrating polymer network (semi-LIPN) with NR network, semi-LIPN with secondary polymer network, and latex interpenetrating polymer network (LIPN). EGDM and H_2SO_4 in methanol were used as the crosslinking agents for PAM and ChPhi, respectively. Creating network of either base polymer or secondary polymer in semi-LIPN or LIPN membrane would be by using cross-linking agents.

NR-PAM Membrane Preparation

The dope solutions were prepared by dissolving acrylamide in water and mixing with NR or prevulcanized latex. Potassium persulphate and sodium lauryl sulphate were added as an initiator and surfactant in the amount of 1 and 0.1% w/w, respectively. The ratios of dry rubber content and acrylamide were varied to be 80/20, 60/40, and 40/60. To obtain polyacrylamide network, ethylene glycol dimethacrylate (EGDM) contents were varied to be 0, 1, 4, and 7% w/w acrylamide. The solutions were stirred under a nitrogen atmosphere at 70 °C for 2 hours, then left at room temperature (to remove bubbles), cast on a glass plate lined with PVC film, and finally dried in an oven.

NR-PhChi Membrane Preparation

The dope solution was prepared by first dissolving phthalated chitosan in water. The pH was adjusted to 12, and the solution was stirred for 6 hours at room temperature. NR or prevulcanized latex was added, as well as sodium lauryl sulphate 0.1% w/w as surfactant and the solution was stirred for 1 hour, and left to stand at room temperature (to get rid of bubbles). The ratios of dry rubber content and PhChi were varied to be 80/20, 60/40, and 40/60. The dope solutions were cast on a glass plate lined with PVC film, dried in an oven, crosslinked by immersing in sulfuric acid in methanol solution for different periods of time (0, 8, 16 and 24 hours), and once more, dried in an oven.

Tensile Strength Measurement

The prepared membranes were cut into dumbbell shapes and their tensile strength was measured using a universal tester. (LLOYD, LR 5K)

Sorption Experiment

For sorption experiment, the membranes were immersed in the azeotrope ethanol solution of 95% v/v at room temperature until constant weight is obtained. The sorbed compositions in membranes were desorbed under vacuum and collected in cold trap for analysis with gas chromatograph. The total sorption by the membrane and the water sorption selectivity were calculated as follows:[9]

$$S\left(\frac{g}{g\ dried\ polymer}\right) = \frac{W_s - W_d}{W_d} \qquad (1)$$

$$\alpha^s_{w/a} = \frac{M_w/M_a}{X_w/X_a} \qquad (2)$$

W_s and W_d were the weights of swollen and dried membranes. M and X were the volume fractions of components in the membrane and bulk aqueous solution, respectively. The subscripts "w" and "a" denoted water and alcohol in the alcohol-water mixture.

RESULTS AND DISCUSSION

Membrane Thickness

Several thickness levels based on dope solution were unavoidable. The dope solution should be prepared to have proper concentration for making film. This was done by trial and error. Highly viscous PAM dope solution could provide very thin membranes 57 ± 4 μm. The NR and prevulcanized latex membranes were much thicker in the range of 126 ± 6 and 171 ± 8 μm, respectively. The combination of PAM or PhChi into NR or prevulcanized latex provided membranes with thickness 111 ± 12 μm.

Tensile strength

The tensile strength of NR membrane was 3.3 ± 0.5 and was increased to 16.5 ± 0.5 N/mm² for prevulcanized latex membrane. This is due to the effect of crosslinking forces between rubber chains. The effects of secondary polymer either PAM or PhChi and crosslinking agent contents on tensile strength of the prepared membranes were shown in Fig 1 and 2, respectively. In the case of MB for NR-PAM membranes in Fig 1(A), the tensile strength was improved over that of NR membrane from 4.5 ± 0.4 to 31.2 ± 1.7 N/mm² with increased PAM content due to straight long polymer chains of PAM
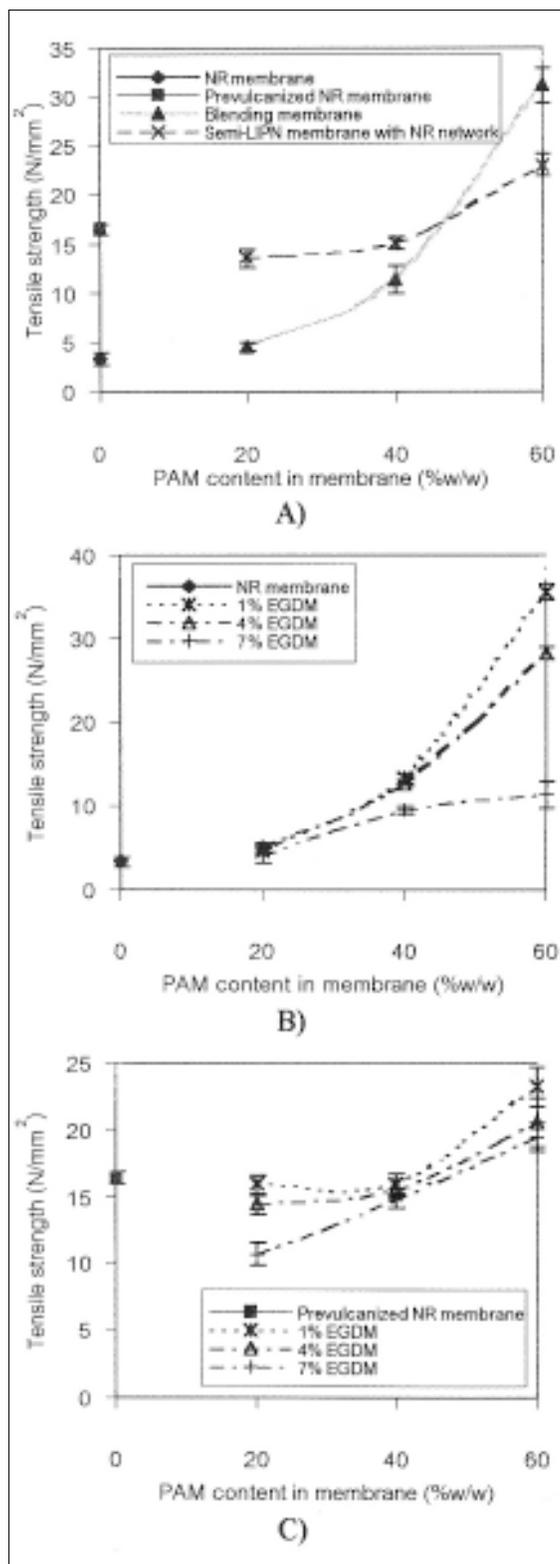
Fig 1. Effect of PAM content in membrane and EGDM content in PAM network on tensile strength of NR-PAM membrane A) Blending membrane and Semi-LIPN membrane with NR network, B) Semi-LIPN membrane with PAM network and C) LIPN membrane.
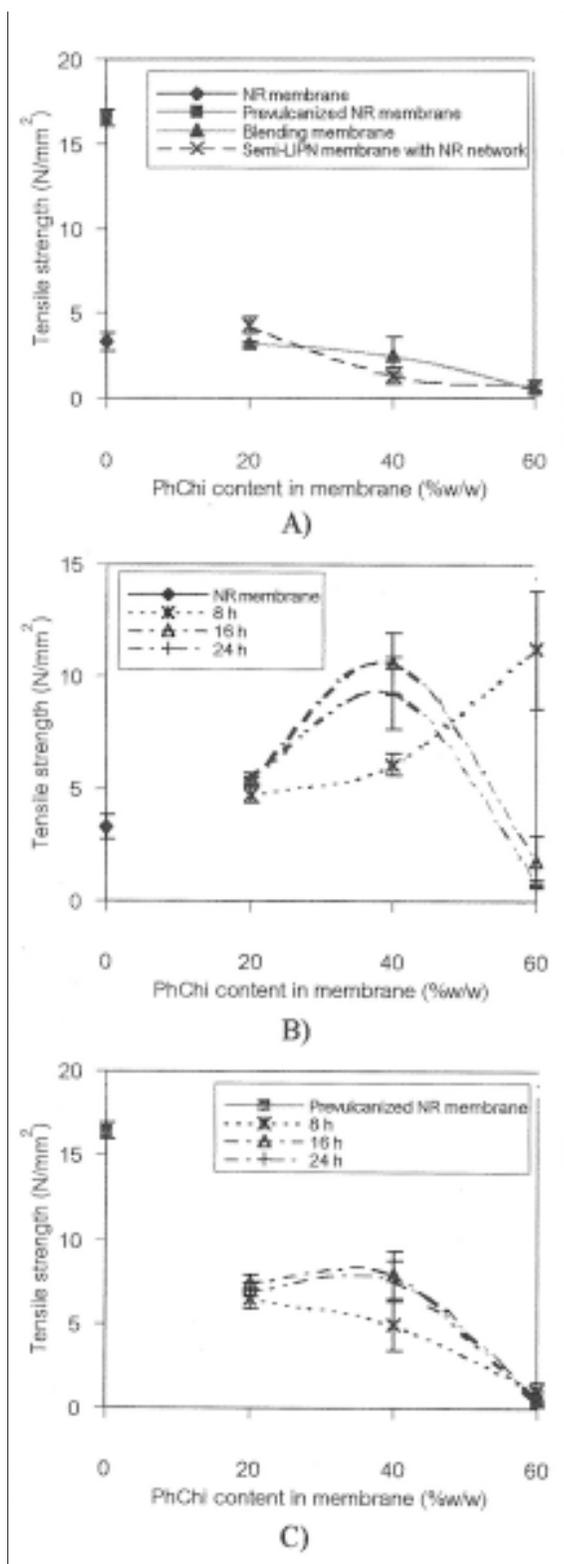
Fig 2. Effect of PhChi content in membrane and immersing time on tensile strength of NR-PhChi membrane A) Blending membrane and Semi-LIPN membrane with NR network, B) Semi-LIPN membrane with PhChi network and C) LIPN membrane.

in base polymer. However, those of NR-PhChi membranes in Fig 2(A) decreased from 3.2±0.1 to 0.6±0.2 N/mm² with PhChi content because of damaged short polymer chains[6] on ring opening reaction.

In the case of semi-LIPN with NR network for NR-PAM [as shown on the other line of Fig 1(A)], although the tensile strength increased with PAM content from 13.6±0.9 to 23.1±1.2 N/mm², the strength of prevulcanized latex membrane was worse and could only be compensated with high PAM content. For semi-LIPN with NR network of NR-PhChi membranes in Fig 2(A), the strength decreased from 4.3±0.5 to 0.8±0.3 N/mm² with PhChi content. Judging from the worsened tensile strength of NR-PhChi membranes, PhChi was not a suitable polymer. However, it was still examined for comparison with NR-PAM membranes throughout this study.

For semi-LIPN with PAM network in Fig 1(B), the tensile strengths were improved over that of NR membrane and ranged from 4.8±0.4 to 35.6±0.9, 5.2±0.4 to 28.3±0.8 and 4.2±0 to 11.4±1.9 N/mm² with increased EGDM contents from 1 to 7%, respectively. It was shown that the higher the EGDM content, the greater the deterioration of the tensile strength. This may be due to the stress occurring in over-crosslinked membranes.

The effect of EGDM content on tensile strength of pure PAM membrane was shown in Fig 3(A). The optimum condition was at EGDM content of 1% w/w with the maximum at 73.5±15.4 N/mm². The stress induced by over crosslinking could be seen more clearly in Fig 1(C). The tensile strength was worse than that of prevulcanized latex membrane at certain ratios.

It could be stated that semi-LIPN with PAM network or LIPN membranes with 1% EGDM were promising membranes. The emphasis was to have no less than 20% and no more than 50% PAM content to obtain sufficient strength and to utilize more latex.

The tensile strength for semi-LIPN with PhChi network in Fig 2(B) showed variations, increasing with PhChi content from 4.8±0.3 to 11.2±2.6 N/mm² at 8 hour-crosslinking time. On the other hand, the strength increased to the maximum value at 40% PhChi with both 16 and 24 hour-crosslinking time. In the 16 hours case, tensile strength increased from 5.5±0.3 to 10.6±1.4 and dropped to 1.8±1.1 N/mm² with increasing PhChi content, while in the 24 hours case, it was 5.4±0.1, 9.3±1.6 and 0.8±0.1 N/mm², respectively. The presence of crosslinked PhChi in prevulcanized latex decreased the strength of the
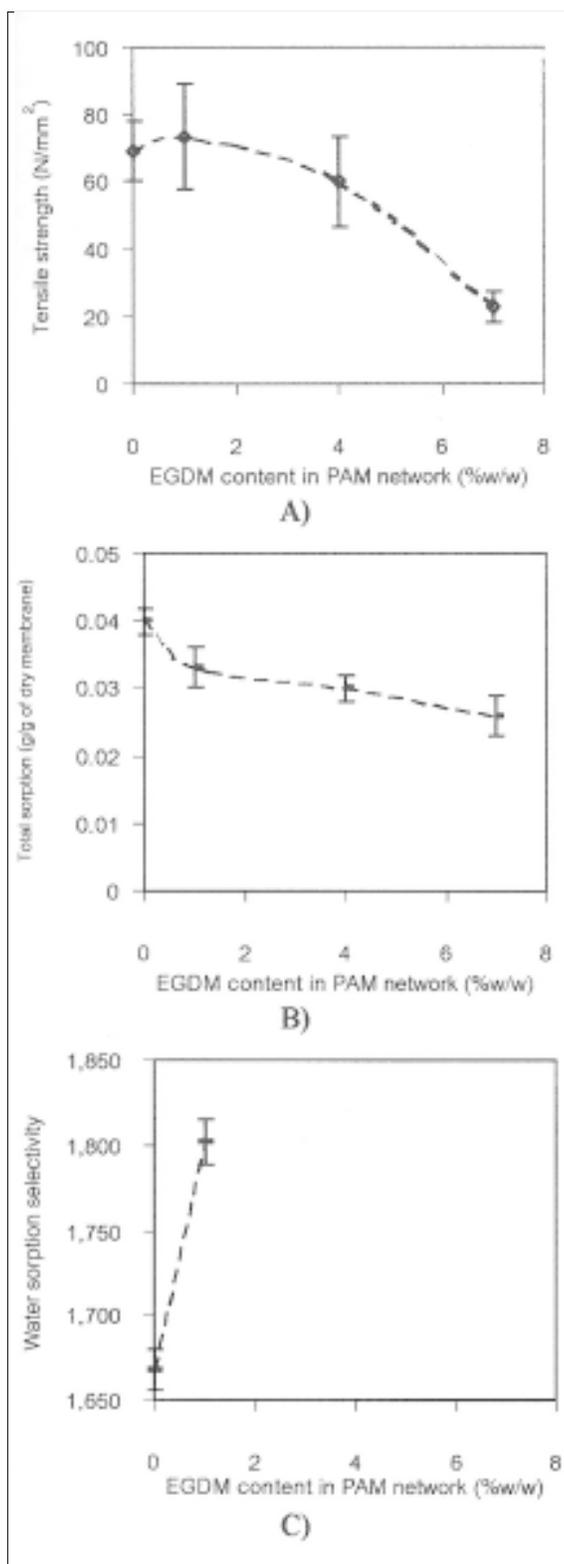
Fig 3. Effect of EGDM content in PAM network on the properties of PAM membrane A) Tensile strength, B) Total sorption and C) Water sorption selectivity.

membranes [as shown in Fig 2(C)] more than that in LIPN NR-PAM membranes because of the smaller molecular size of PhChi.

Total sorption

The total sorption of NR and prevulcanized latex were 0.159±0.016 and 0.074±0.003 g/g of dry membrane. The effects of secondary polymer content either PAM or PhChi and crosslinking on total sorption of the membranes were shown in Fig 4 and 5, respectively. In the case of MB NR-PAM membrane in Fig 4(A), the total sorption in azeotrope ethanol solution decreased with higher PAM content from 0.052±0.002 to 0.043±0.002 g/g of dry membrane. This was because of the compact structure of NR-PAM membranes due to the in-situ polymerization of acrylamide in latex and hydrophilicity effect. The sorption of components into semi-LIPN with NR network membranes was more difficult than MB membranes due to the crosslinking effect of prevulcanized latex. This resulted in lower values at all ratios ranging from 0.041±0.002 to 0.031±0.004 g/g of dry membrane [as shown in Fig 4(A)]. However, the loose blending structure between NR or prevulcanized latex and PhChi, in MB or semi-LIPN with NR network, respectively, caused both ethanol and water components to be sorbed into the membranes easier. Accordingly, the total sorption shown in Fig 5(A) increased with PhChi content in the range of 0.062±0.001 to 0.084±0 and 0.032±0.001 to 0.053±0.003 g/g of dry membrane, respectively. The solubility of both components in NR-PhChi membranes would deteriorate the selectivity property of the membrane as shown later.

Fig 3(B) showed the effect of crosslinking on pure PAM membrane that decreased the total sorption from 0.040±0.002 to 0.026±0.003 g/g of dry membrane with increased EGDM content. Crosslinking of secondary polymer prominently lowered the mobility of polymer chain. As a result, the total sorption of both semi-LIPN with PAM network and LIPN of NR-PAM membranes, which ranged from 0.044±0.002 to 0.028±0 and 0.041±0.002 to 0.025±0.002 g/g of dry membrane in Fig 4(B) and (C) respectively, decreased with increased PAM content and EGDM content.

Similarly, the total sorption of both semi-LIPN with PhChi network and LIPN of NR-PhChi membranes decreased with increased immersing time in crosslinking solution, ranging from 0.072±0.004 to 0.032±0.002 and 0.047±0.004 to 0.021±0.001 g/g of dry membrane as shown in Fig 5(B) and (C) respectively.
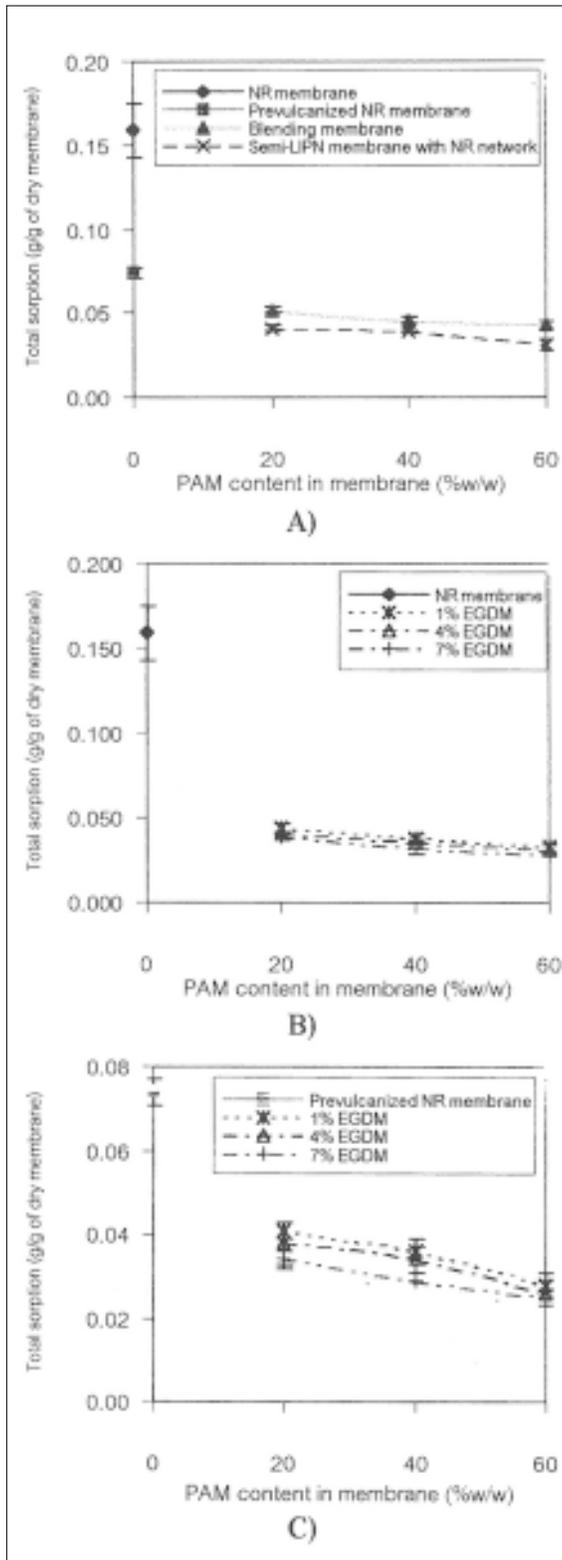
Fig 4. Effect of PAM content in membrane and EGDM content in PAM network on total sorption of NR-PAM membrane A) Blending membrane and Semi-LIPN membrane with NR network, B) Semi-LIPN membrane with PAM network and C) LIPN membrane.
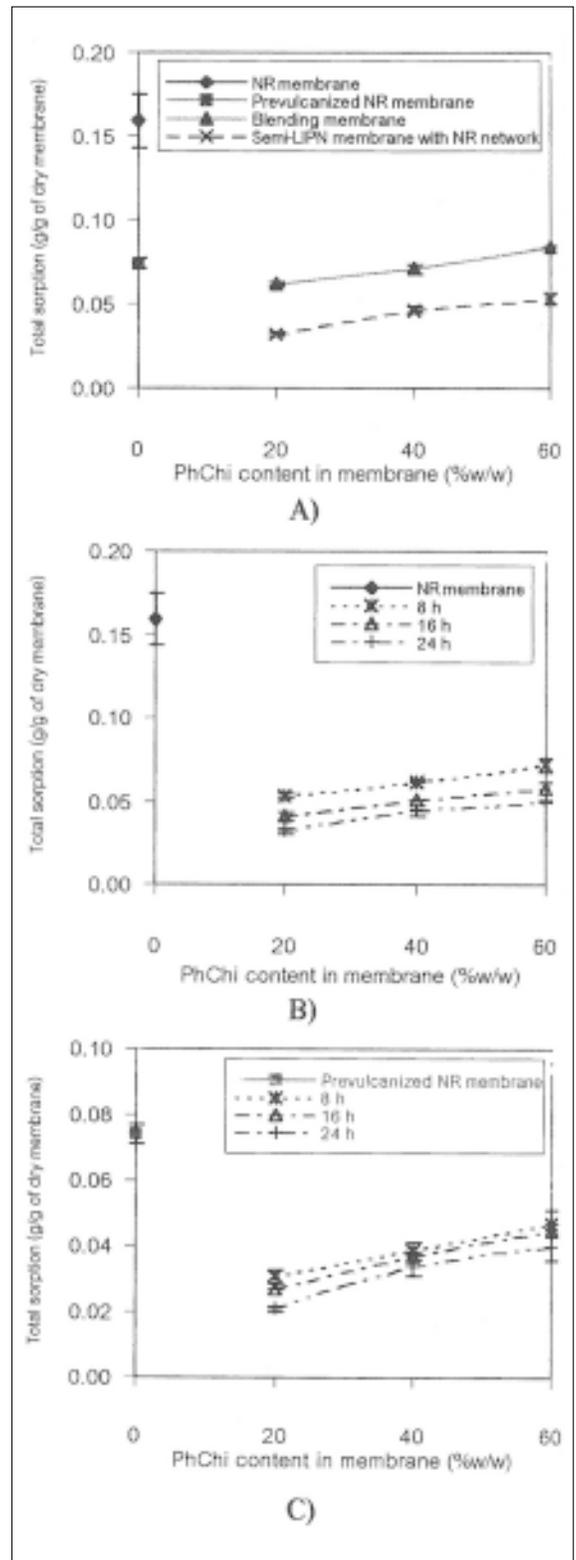
Fig 5. Effect of PhChi content in membrane and immersing time on total sorption of NR-PhChi membrane for A) Blending membrane and Semi-LIPN membrane with NR network, B) Semi-LIPN membrane with PhChi network and C) LIPN membrane.

Water sorption selectivity

The water sorption selectivity of NR and prevulcanized latex were 12±1 and 18±1.7, respectively. The effects of secondary polymer content on either PAM or PhChi and crosslinking on water sorption selectivity of the membranes were shown in Fig 6 and 7, respectively. The water sorption values increased with increased contents of PAM or PhChi in every type of membrane, because both PAM and PhChi show high hydrophilicity.

The mobility of polymer chains decreased with increased crosslinking agent because the polymer chains were fixed by crosslinking.[10] Consequently, the higher the crosslink density, the smaller free volume in the membrane, the higher selectivity was obtained. However, all NR-PAM membranes showed higher water sorption selectivity than those of NR-PhChi because of the more compact structure of the former as described earlier. The water sorption selectivity of pure PAM membrane was 1668±11.9 and was increased to 1802±13.1 with 1% w/w EGDM content as shown in Fig 3(C). The selectivities of the other two EGDM contents were put as infinite according to equation (2) due to the undetectable sorbed ethanol amount.

The water sorption selectivity ranges of MB, semi-LIPN with NR network, semi-LIPN with secondary polymer network and LIPN were 90±11.3 – 254±21.2, 55±11.5 – 300±13.6, 76±6.7 – 563±12.8 and 181±2.3 – 609±2.2 for NR-PAM membranes and 60±6.7 – 81±9.2, 78±6.3 – 139±8.5, 224±9.5 – 592±5.6 and 217±2.8 – 549±9.3 for NR-PhChi membranes, respectively.

Based on material balance, the candidate membrane for dehydration pervaporation of azeotropic ethanol solution to 99.5% purity should possess a water sorption selectivity property of at least 199. The water sorption selectivities of semi-LIPN with PAM network and LIPN NR-PAM membranes at 40% PAM content and using 1% EGDM were 117±8.6 and 231±8.9, respectively. It could be stated that the most suitable membrane was LIPN NR-PAM membrane with 40% PAM content and using 1% EGDM crosslinking agent.

Stability and Structure

Table 1 lists the membranes used for testing sorption stability based on their performance. The relationship between the selective performance and number of sorption repetitions was plotted in Fig 8. It was shown that the membrane still had stable selective performance, even after 4 repetitions of sorption.
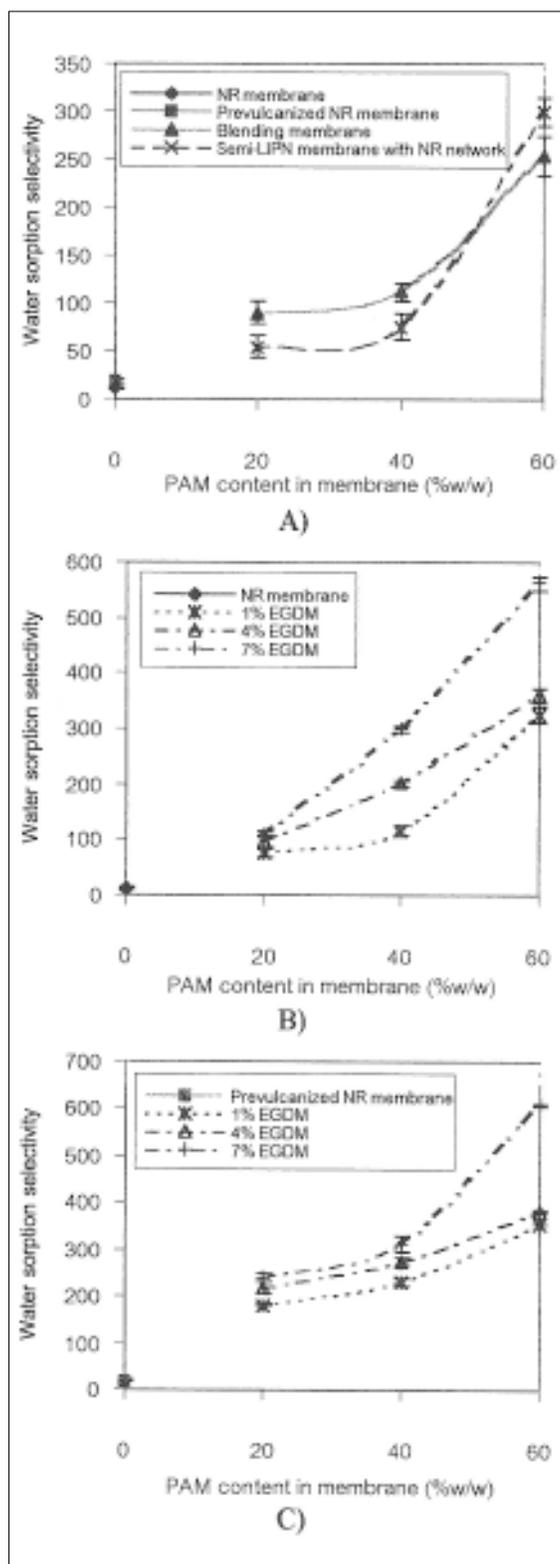
Fig 6. Effect of PAM content in membrane and EGDM content in PAM network on water sorption selectivity of NR-PAM membrane A) Blending membrane and Semi-LIPN membrane with NR network, B) Semi-LIPN membrane with PAM network and C) LIPN membrane.
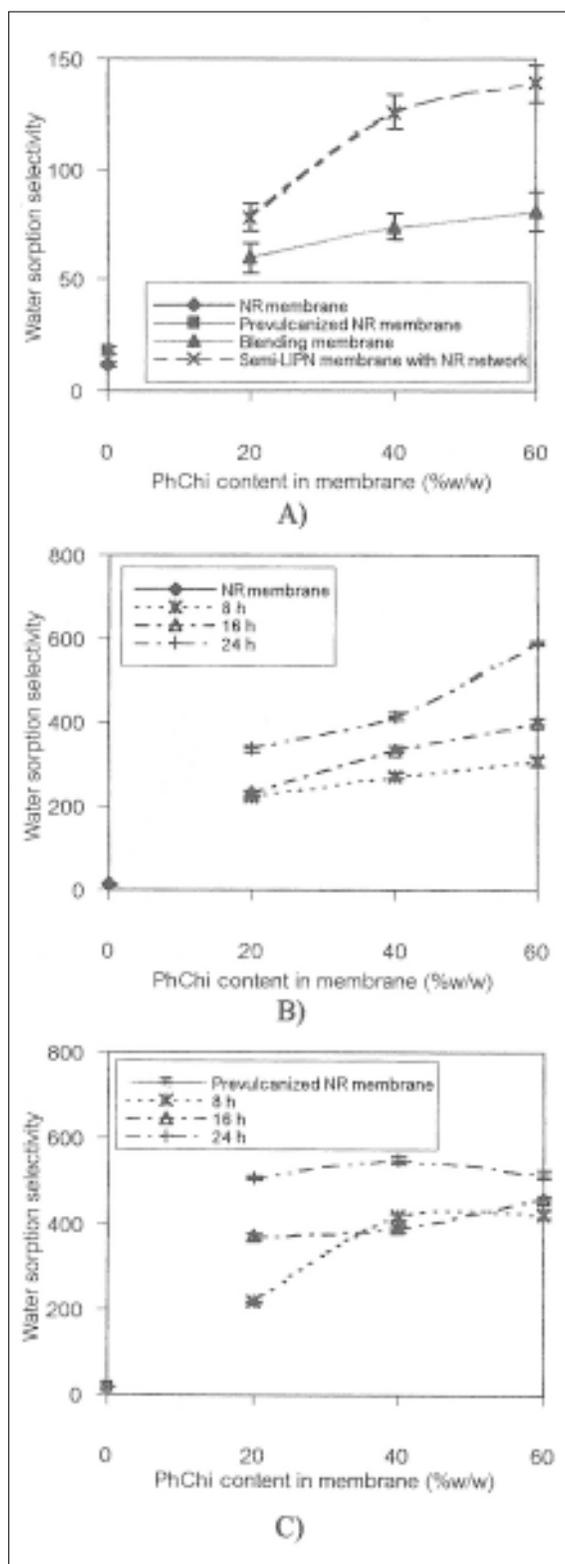
Fig 7. Effect of PhChi content in membrane and immersing time on water sorption selectivity of NR-PhChi membrane for A) Blending membrane and Semi-LIPN membrane with NR network, B) Semi-LIPN membrane with PhChi network and C) LIPN membrane.

Fig 9 represents the scanning electron micrograph of a cross section of the candidate membrane for NR-PAM or NR-PhChi usable as dehydration pervaporation membrane of azeotrope ethanol solution. Both are LIPN types with prevulcanized latex content of 60 %w/w, using EGDM content of 1% for NR-PAM membrane (CP604001) or cross-linking time of 16 hours for NR-PhChi (CC604016). They were homogeneous dense membranes as required for a pervaporation membrane.

CONCLUSIONS

1. Hydrophilic membrane from natural rubber latex could be obtained by combination with other hydrophilic polymers.
2. The preparing method for secondary polymer in the base polymer caused significant differences in sorption characteristics between NR-PAM (natural latex – polyacrylamide) and NR-PhChi (natural latex - phthalted chitosan) membranes.
3. The interpenetrating polymer network of prevulcanized latex and PAM (at ratio 60:40 and using 1% of EGDM) was the most appropriate membrane in view of strength and water sorption selectivity, as a dehydration pervaporation membrane for azeotropic ethanol solution.
4. The characteristics of the above membrane were as follows:
   - Tensile strength = 16 ± 0.81 N/mm^2
   - Total sorption = 0.036 ± 0.003 g/g of dry membrane
   - Water sorption selectivity = 231 ± 8.9

ACKNOWLEDGEMENTS

REFERENCES

1. Wei Y and Huang RYM (1993) Pervaporation with latex membranes. I Latex membrane preparation and characterization. *J Membr Sci* **82**, 27-42.
2. Mulder MHV and Smolders CA (1986) Pervaporation, solubility aspects of the solution-diffusion model. *Sep Purif Methods* **15** (1), 1-19.
3. Economical Planning Division (1998) *Cost Prediction Report of Importance Thailand's Exports (20 items)*. Institute for Thailand Development, Bangkok.
4. Molyneux P (1983) *Water-soluble synthetic polymers: properties and behavior*. CRC Press, Boca Raton.

Table 1. List of membranes tested for sorption stability and membrane morphology.

Membrane	Amount of latex in dry membrane (%w/w)	Amount of PAM in dry membrane (%w/w)	Amount of PhChi in dry membrane (%w/w)	Amount of EGDM in PAM network (%w/w)	Immersing time (h)	Tensile strength (N/mm²)	Total sorption (g/g of dry membrane)	Water sorption selectivity	Remark
LP604000	60	40	-	0	-	11.4±1.4	0.046±0.002	112±9.8	MB of NR-PAM
LP604001	60	40	-	1	-	13.3±0.7	0.038±0.003	117±8.6	Semi-LIPN with PAM network
CP604000	60	40	-	0	-	15.1±0.6	0.039±0.001	76±13.0	Semi-LIPN with NR network
CP604001	60	40	-	1	-	16±0.8	0.036±0.003	231±8.9	LIPN
LC604000	60	-	40	-	0	2.5±1.1	0.071±0.003	74±5.8	MB of NR-PhChi
LC604016	60	-	40	-	16	10.6±1.4	0.051±0.000	334±7.7	Semi-LIPN with PhChi network
CC604000	60	-	40	-	0	1.3±0.5	0.047±0.002	126±7.4	Semi-LIPN with NR network

A)
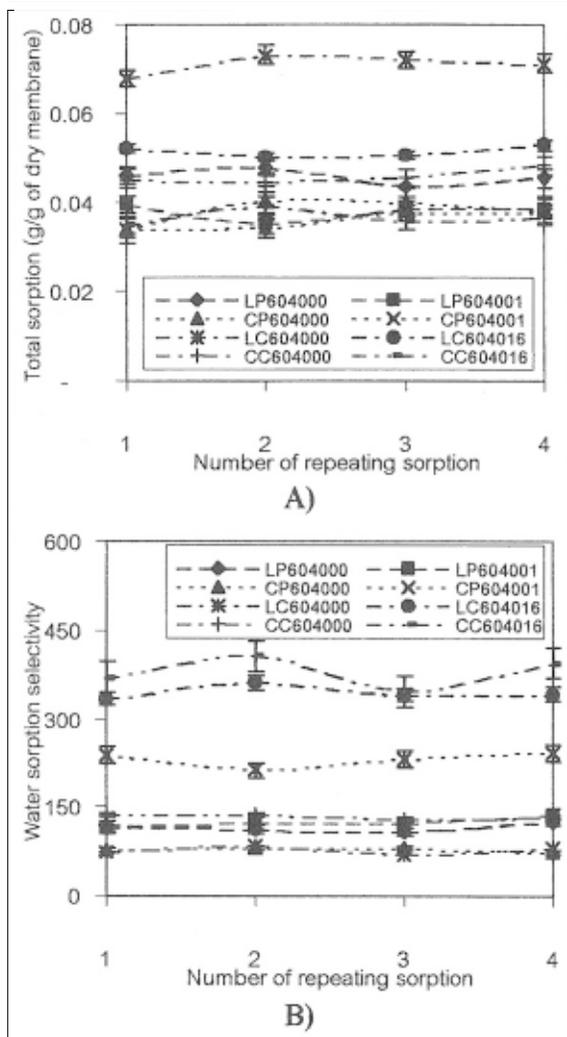
Fig 8. Effect of repeating sorption on the sorption stability of membrane A) Total sorption and B) Water sorption selectivity.
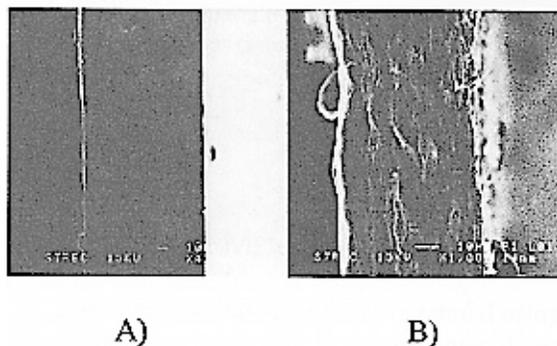
Fig 9. Scanning electron micrograph of the membrane A) LIPN of NR-PAM (CP604001) and B) LIPN of NR-PhChi (CC604016).

5. Chanachai A, Jiraratananon R, Uttapap D, Moon GY, Anderson WA and Huang RYM (2000) Pervaporation with chitosan/hydroxyethylcellulose (CS/HEC) blended membranes. *J Membr Sci* **166**, 271-80.
6. Sashiwa H and Shigesama Y (1999) Chemical modification of chitin and chitosan 2: preparation and water-soluble property of N-acrylated or N-alkylated partially deacetylated chitin. *Carbohydr Polym* **39**, 127-38.
7. Klempner D, Sperling LH and Utracki LA (1991) *Interpenetrating polymer networks*. Advances in Chemistry Series 239, American Chemical Society, New York.
8. Chitin/Chitosan Research Group (1999) Private communication. National Metal and Materials Center (MTEC), Bangkok.
9. Wei Y and Huang RYM (1994) Selective sorption of latex membranes with ethanol-water mixtures. *Sep Sci Technol* **29**, 301-14.
10. Ruckenstien E and Liang L (1996) Pervaporation of ethanol-water through polyvinyl alcohol-polyacrylamide interpenetrating polymer network membranes unsupported and supported on polyethersulfone ultrafiltration membranes: a comparison. *J Membr Sci* **110**, 99-107.