

Pervaporation Membranes from Natural Rubber Latex Grafted with Poly(2-hydroxyethyl methacrylate) (NR-g-PHEMA) for the Separation of Water–Acetone Mixtures

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ABSTRACT: NR-graft-PHEMA latexes were synthesized by the use of graft emulsion polymerization. By increasing the HEMA monomer concentration, we found that the grafting percentage (GP) also increased. In addition, GP increased significantly at low initiator concentrations before it leveled off at moderate concentrations, and a slight decrease was observed at high initiator concentrations. NR-g-PHEMA latexes were prepared as pervaporation membranes for the separation of water–acetone mixtures. From the equilibrium swelling, the nonideal behavior of membrane swelling in water–acetone mixtures was found such that there appeared the maximum swelling degree at a certain concentration of liquid mixtures. Moreover, the water concentration at maximum swelling shifted to high water concentration with increasing amount of graft-PHEMA. The sorption study suggested the preferential sorption of water on the membranes. Also, the sorption isotherms implied that there was a coupling

between water and acetone molecules. Pervaporation separation of water–acetone mixtures was studied with NR-g-PHEMA membranes. As the feed water concentration increased, the partial water fluxes increased in contrast to the partial fluxes of acetone. From the permeation ratio, θ_w , the strong coupling of acetone on the water transport was observed, particularly for the membrane with high graft-PHEMA under acetone-rich conditions. As the feed temperature increased, the total permeation across the membranes was enhanced. The partial fluxes of water and acetone as a function of temperature followed the Arrhenius relationship by which the activation energies for permeation were estimated as 3.53 kJ/mol for water and 21.95 kJ/mol for acetone. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3313–3321, 2009

Key words: pervaporation; natural rubber; poly(2-hydroxyethyl methacrylate); graft copolymers

INTRODUCTION

Pervaporation (PV) is an attractive membrane separation process for azeotropic mixtures and close-boiling point components because its separation efficiency does not depend upon the vapor–liquid thermodynamic equilibrium but rather relies on the capability of a membrane to specifically absorb (solubility) the separated-specie and the ability of the specie to transport through the membrane layer (diffusivity). In accord with these reasons, hydrophilic polymers such as poly(vinyl alcohol)^{1–3} or chitosan^{4–6} are used as PV membranes for the dehydration of organic–water mixtures, whereas membranes prepared from hydrophobic polymers are suitable for a separation of organic mixtures^{7,8} or an enrichment of organic from its aqueous mixtures.^{9–12}

Because of the specific interactions between a constituent of liquid mixtures and polymer molecules, polymeric membranes could experience excessive swelling, resulting in the expansion of membrane free volume and the enhancement of polymer chain mobility. As a consequence, flux across the membrane would increase at the expense of membrane selectivity. Because of these reasons, it is applicable to use hydrophobic membranes for the separation of lean organic mixtures and hydrophilic membranes for organic-rich mixtures. Nonetheless, when hydrophobic membranes are used to remove a trace organic from its aqueous mixtures, the membranes often show low organic selectivity,^{9–11} regardless of the membrane swelling effect in aqueous medium, because a water molecule diffuses through the membrane faster than does the organic molecule as the result of the large molecular size of most organics compared with the size of water molecule.¹³

To limit the swelling in aqueous media and hence improve water selectivity, membranes that consist of both hydrophilic polymers and hydrophobic elastomers could be used in the separation of organic–water mixtures. Generally, hydrophilic polymers

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provide the active interactions with water molecules whereas elastomeric polymers restrain membrane swelling as well as improve the integrity of the membrane.^{14,15} Because phase separate is inevitable for blends of hydrophilic and hydrophobic polymers, the copolymerization, e.g., graft copolymerization, could be used to improve polymer miscibility. Moreover, the grafting assures the stability of a membrane while performing a pervaporation because two polymers are bond by chemical linkages. The graft copolymerization is readily established for the emulsion system,^{16–18} where monomer can be grafted onto polymer latex particles. The amount of grafted-polymer is controlled to some extent by the monomer and initiator concentrations.

In the present study, the copolymerization of natural rubber (NR) with hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) was performed in NR latex via the graft-emulsion polymerization.¹⁷ By the use of graft-copolymer latex, PV membranes for the separation of water–acetone mixtures were readily prepared by simply casting latex films with no requiring of polymer dissolution and polymer cross-linking. Because of the presence of hydroxyl groups on the PHEMA chains, the membrane hydrophilicity is promoted.^{19,20} NR, on the other hand, is hydrophobic when grafted with PHEMA and therefore maintains water swelling in membranes. Furthermore, the elastomeric nature of NR at room temperature facilitates the formation of dense latex film. Most importantly, the performance of pervaporation separation could be expected to improve and be manageable for different water–acetone feed compositions by balancing the amount of hydrophilic PHEMA and hydrophobic NR.

EXPERIMENTAL

Materials

Concentrated NR latex with ~ 60% w/w dry rubber content (%DRC) was purchased from Thai Hua Rubber (Udonthani, Thailand). NR latex was cleaned twice by the centrifugation–redispersion method. Cleaned NR latex was dispersed in 7% w/w ammonium hydroxide solution to prevent premature aggregation. 2-Hydroxyethyl methacrylate (HEMA) monomer supplied from Fluka/Sigma-Aldrich (St. Louis, MO) was purified by slowly passing it through a basic alumina column and was kept at 4°C for further polymerization. Initiator, potassium persulfate (KPS) was obtained from Sigma-Aldrich and used as received. The stabilizer for NR latex, sodium lauryl sulfate, was supplied from Ajax Chemicals (Auburn, NSW, Australia). Sodium bicarbonate used as a buffer was obtained from Aldrich. Water used in the experiments was distilled and deionized

(DI). Pure acetone (99.8%) was obtained from Carlo Erba Reagenti (Milan, Italy).

Grafting of PHEMA on NR latex

The graft copolymerizations were conducted batchwise in a 100-mL two-necked round-bottom flask. A total of 10 g of NR latex (60% DRC) was charged into the glass reactor with 0.5 g of buffer, 0.05 g of sodium lauryl sulfate, and 20 g of DI water. The mixture was heated to 60°C under nitrogen atmosphere and maintained at this condition for 30 min. The initiator KPS was dissolved in 20 mL of DI water before gradually being added into the reactor. The desired amount of HEMA monomer was diluted in 20 mL of DI water before being added dropwise in the reactor with the rate of one drop per second. The reaction was allowed to proceed for 24 h at 60°C with continuous stirring under nitrogen atmosphere.

After the reaction was complete, the obtained latex was coagulated, and the coagulum was washed with DI water several times before dried at 60°C for 48 h. The Soxhlet extraction was used to remove the free-PHEMA ($W_{f\text{-PHEMA}}$), using ethanol as solvent and accordingly, the weight of graft-PHEMA ($W_{g\text{-PHEMA}}$) on NR latex was calculated from the weight balance. The conversion (%) of HEMA monomer and grafting percentage (GP) of PHEMA on NR were calculated by the following equations:

$$\text{Conversion (\%)} = \frac{W_{g\text{-PHEMA}} + W_{f\text{-PHEMA}}}{W_{\text{monomer}}} \times 100 \quad (1)$$

$$\text{GP (\%)} = \frac{W_{g\text{-PHEMA}}}{W_{\text{NR}}} \times 100 \quad (2)$$

where W_{NR} is the weight of dry NR which was determined from %DRC of NR latex.

Membrane preparation

The NR-g-PHEMA latex was cast on a nylon membrane with a pore size of 0.45 μm (Osmonics Magna; Krackeler Scientific, Albany, NY). After that, it was dried at 60°C for 12 h. To remove the free-PHEMA, the membrane was placed in a flask filled with ethanol, and then the flask was subjected to a continuous shaking at 40°C for 48 h in a water bath shaker. After that, the membrane was washed with DI water to remove ethanol residue and dried at 60°C for 12 h. The membrane thicknesses were in the range of $200 \pm 10 \mu\text{m}$ measured by micrometer (Mitutoyo).

Characterizations

Fourier transform infrared spectroscopy

The grafting of PHEMA on NR was confirmed by infrared spectroscopy using PerkinElmer Fourier

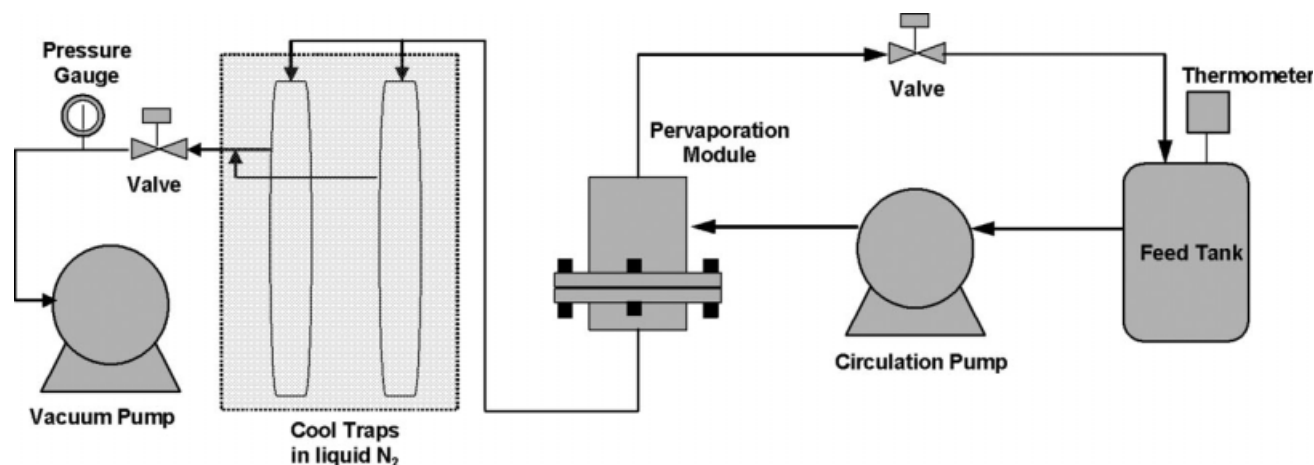


Figure 1 Schematic diagram of a pervaporation system.

transform infrared (FTIR) spectrophotometer (Spectrum One) measuring in the range of 4000–500 cm^{-1} .

Swelling of the membrane

A dry membrane was cut into a square shape approximately 2 cm \times 2 cm, and then the membrane thickness was measured by the use of micrometer. Next, the dry membrane was weighed, W_d , before being immersed in liquids; that is, DI water, acetone, or water–acetone mixtures. The membrane was left in the liquid for a designated period of time. After that, the swollen membrane was taken out and blotted with filter paper to remove excess liquid on the membrane surface and then weighed, W_t . The weighing of the swollen membrane continued for allocated immersion-time periods until there was no weight change, after which the equilibrium weight, W_{eq} , was recorded. The swelling degree and the relative liquid uptake of the membrane were calculated from eqs. (3) and (4), respectively.

$$\text{Swelling degree (SD)} = \frac{W_t - W_d}{W_d} \quad (3)$$

$$\text{Relative liquid uptake (Q)} = \frac{W_t - W_d}{W_{eq} - W_d} \quad (4)$$

From the results of liquid uptake, the diffusion coefficients of water and acetone in the membranes can be estimated from a least-square fitting of the experimental Q with the solution of Fick's second law for thin-film geometry as expressed in the following equation.²¹

$$Q = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{D(2n+1)^2\pi^2 t}{l^2}\right) \quad (5)$$

where D is the diffusion coefficient (cm^2/s) of pure component in a membrane, t is liquid-membrane contacting time, and l is dry membrane thickness.

Membrane sorption selectivity

The dry membrane was immersed in water–acetone solutions for 48 h. Afterward, the swollen membrane was removed from the solution and quickly wiped out with filter paper to remove the liquid on the membrane surface. Next, the membrane was quickly placed in a dry flask that connected to a cold trap and a vacuum pump. The flask was heated to a temperature of 100°C to evaporate the liquid retained inside the membrane. The vapor was condensed in the cold trap with the use of liquid nitrogen. The condensed liquid was then analyzed with the refractive index detector (Waters RI 2414), and the acetone concentration was evaluated with the calibration curve constructed from the plot between compositions of water–acetone mixtures (%v/v) and their refractive indices. The water sorption selectivity of the membrane (α_s) was calculated from

$$\alpha_s = \frac{C_W/C_A}{X_W/X_A} \quad (6)$$

where C and X are the volume fractions either of water (W) or acetone (A) in the membrane and liquid solution, respectively.

Pervaporation

A standard pervaporation process²² was used, as schematically illustrated in Figure 1. The pervaporation module houses a membrane that sits on a ceramic porous support. The effective membrane area was 17.34 cm^2 . Vacuum was applied to the permeate side where the pressure was maintained at 1 kPa using a vacuum pump. Feed temperature was controlled by an oil-bath heater. Permeate vapor was condensed in a cold trap cooling with liquid

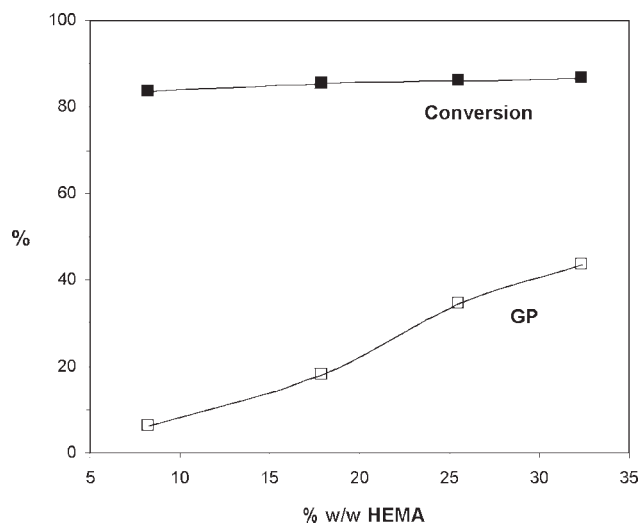


Figure 2 Effect of HEMA concentration on conversion and GP of NR-g-PHEMA latexes; initiator concentration = 0.1% w/w.

nitrogen. Before the vacuum was applied, feed solution was circulated to the feed compartment of the module for 2 h to allow the solution to swell the membrane. The pervaporation process was performed for 3 h; afterward, the vacuum was terminated and the condensed permeate was removed from the cold trap and weighed. The amount of permeate collected during the pervaporation was small compared with the amount of liquid mixtures in the feed reservoir (250 mL); hence, the composition of the feed can be assumed to be constant throughout the experiment. The composition of the permeate was determined by the use of the calibration curve of the solution compositions versus their refractive indices. The total permeate flux (J) and the water separation factor (α_p) were calculated by the following equations:

$$J = \frac{W}{A \cdot t} \quad (7)$$

$$\alpha_p = \frac{Y_W/Y_A}{X_W/X_A} \quad (8)$$

where W , A , and t represent the weight of permeate (g), the effective membrane area (m^2), and the operating time (h), respectively. Y and X are the volume fractions of water or acetone in the permeate and feed, respectively. A partial flux of each constituent in the permeate was calculated from the equation:

$$J_i = m_i \times J \quad (9)$$

where m is the weight fraction and index i denotes water or acetone.

RESULTS AND DISCUSSION

Grafting of PHEMA on NR latex

Effect of monomer (HEMA) amount

The effect of increasing monomer concentration on conversion and GP of NR-g-PHEMA latex is revealed in Figure 2. The polymerization of HEMA was almost complete for all weight percentage of HEMA, as indicated by the high conversion ($\sim 85\%$), because persulfate radicals, generated thermally, reside mostly in aqueous phase, where they can polymerize readily with water-soluble HEMA.¹⁷ Although HEMA can be polymerized considerably well, the amount of graft-PHEMA was approximately as half as its polymerized monomer for the greatest HEMA concentration. Upon reducing HEMA concentration, the grafting amount of PHEMA on NR decreased extensively. In NR latex grafting with KPS used as an initiator, persulfate radicals, once reaching the NR particle surface, attack the double bonds of isoprene units, creating the active graft-sites on NR particles. Because the polymerization of HEMA prevails in aqueous phase as the free PHEMA,²³ graft-PHEMA can be formed only when HEMA monomers reach the graft-sites and propagate via the free-radical polymerization. By increasing HEMA concentration, the probability of monomer to react with the active sites on NR particles will be increased.¹⁸

Effect of initiator concentration

Figure 3 shows the effect of initiator concentration on conversion and GP. Obviously, increasing the

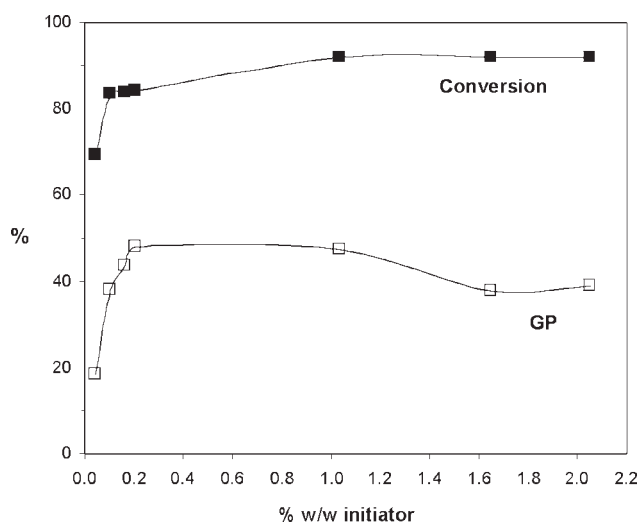


Figure 3 Effect of KPS concentration on conversion and GP of NR-g-PHEMA latexes; monomer concentration = 8.3% w/w.

initiator amount promoted the conversion of HEMA, which is caused by increasing numbers of the persulfate free-radicals. The amount of PHEMA grafting on NR increased substantially at low initiator concentration before reached the plateau at moderate concentration and finally, the grafting PHEMA slightly declined at high concentrations of initiator. Because of high water-solubility of the initiator, the radicals will partition in water phase as well as at the interfacial area between aqueous phase and NR particle surfaces. The radicals at the interface created the number of grafting sites for HEMA therefore the grafting percentage on NR enhanced with the initiator concentration. Despite the grafting enhancement with the initiator concentration, the abundance of radicals would result in a high probability of the active graft-chains to be terminated upon approaching of other radicals resulting in the decreasing of grafted-chains.²⁴

FTIR

The FTIR spectra of NR, PHEMA, and NR-g-PHEMA are shown in Figure 4. The characteristic peaks of NR can be found at 836 and 1663 cm^{-1} attributing to C=C bending and C=C stretching of the isoprene unit. PHEMA spectrum showed the characteristic absorption bands at 1730 and 1160 cm^{-1} corresponding to the carbonyl group of ester (C=O) and C—O—C stretching, respectively, whereas the hydroxyl group (—OH) of HEMA appeared as broad absorption band around 3400 cm^{-1} . Both characteristic peaks of NR and PHEMA were observed on NR-g-PHEMA spectra, indicating successful graft copolymerization of PHEMA on NR. Notably, the relative IR absorbance between characteristic NR peaks and PHEMA peaks on NR-g-

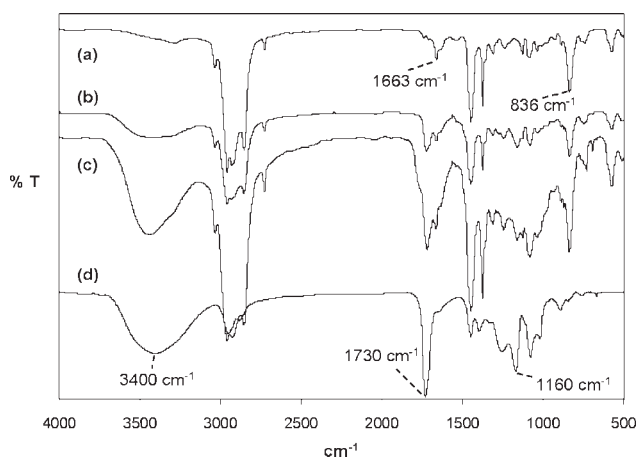


Figure 4 FTIR spectra of NR (a), 8.5%GP NR-g-PHEMA (b), 28.8%GP NR-g-PHEMA (c), and PHEMA (d).

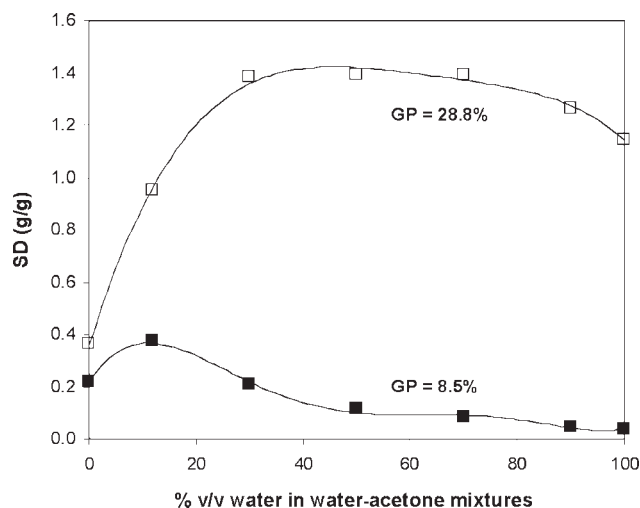


Figure 5 Equilibrium swelling of NR-g-PHEMA membranes in water-acetone liquid mixtures.

PHEMA spectra depended upon the grafting amount of PHEMA on NR.

Membrane swelling

Equilibrium swelling

Swelling behaviors of NR-g-PHEMA membranes in water-acetone mixtures are illustrated in Figure 5. Both membranes at different GP showed the non-ideal swelling pattern such that there was the composition of water-acetone mixtures where the swelling degree was greater than the corresponding swelling values in pure components. The composition at maximum swelling changed with the grafting amount of PHEMA on NR. At GP of 8.5%, the maximum was found in the acetone-rich region ($\sim 10\%v/v$ of water) whereas it shifted to the water-rich region for 28.8%GP ($\sim 40\text{--}50\%v/v$ of water). This maximum-swelling is caused by the mutual interactions between water and acetone within the membranes so called the coupling effect.^{23,24} The coupling effect induces a formation of water-acetone clusters which could expand the membrane structure in a larger extent than do the water or acetone nonassociated molecules.

Because PHEMA is the hydrophilic polymer comprising hydroxyl groups that are capable of attracting water molecules via the hydrogen bonding whereas NR is hydrophobic, with a solubility parameter ($\delta_{\text{NR}} = 17 \text{ MPa}^{1/2}$) comparable with that of acetone ($\delta_{\text{acetone}} = 20.3 \text{ MPa}^{1/2}$; $\delta_{\text{water}} = 47.9 \text{ MPa}^{1/2}$),²⁷ the ratio between PHEMA and NR affected the membrane swelling in pure components. Evidently, at low PHEMA grafting, the membrane was found to swell greater in acetone. For high graft-PHEMA, on the contrary, the water swelling

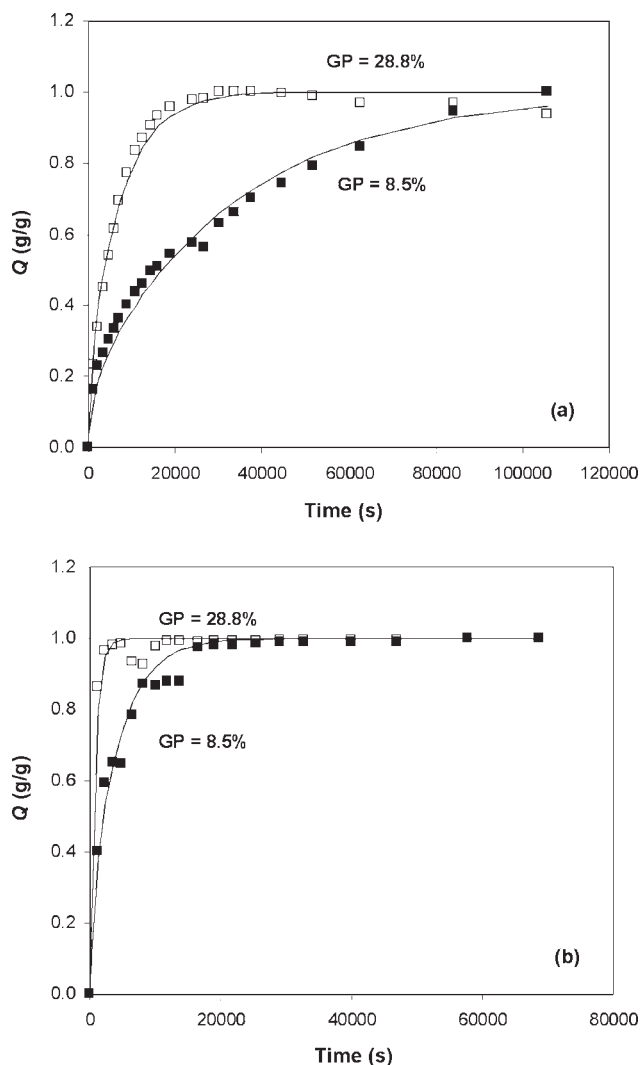


Figure 6 Relative liquid uptake (Q) of NR-g-PHEMA membranes for swelling in water (a) and acetone (b); symbols represent experimental Q and lines are calculated from eq. (5).

was greater affirming the preferential sorption of water.

Dynamic swelling

Figure 6 compares Q of water and acetone in the NR-g-PHEMA membranes obtained from the dynamic swelling and calculated by eq. (5). The correlation coefficients (r^2) of the least square fitting were more than 0.975 for all swellings, indicating that the transport process of water and acetone through these membranes is governed mainly by Fickian diffusion. Table I shows the water and acetone diffusion coefficients through NR-g-PHEMA membranes obtained from curve-fitting. Accordingly, the diffusion coefficients indicate that acetone can diffuse through NR-g-PHEMA faster than water molecules. When the amount of graft-PHEMA increased, the increasing of membrane hydrophilic-

TABLE I
Diffusion Coefficients of Water and Acetone Estimated from Dynamic Swelling of NR-g-PHEMA Membranes

GP (%)	Diffusion coefficients (cm^2/s)	
	Water	Acetone
8.5	7.42×10^{-8}	5.72×10^{-6}
28.8	1.63×10^{-6}	4.55×10^{-6}

ity limited the transport of acetone molecules but provided larger pathways for water molecules to diffuse through the membrane. As a result, the diffusion coefficient of acetone decreased with the increase of water diffusion coefficient.

Membrane sorption

Figure 7 shows the water sorption isotherms of NR-g-PHEMA membranes for sorption in water–acetone mixtures. The isotherms revealed preferential sorption of water for all water–acetone compositions. The water preference of the membrane was more pronounced with increasing of graft-PHEMA as indicated by higher concentration of water for the membrane with 28.8%GP than those for 8.5%GP membrane. The upturn of water sorption isotherms suggests that the mutual interaction of water and acetone molecules in the membranes is stronger than their interactions with the copolymer membranes which leads to the formation of water–acetone clusters inside the membrane matrix.^{13,28}

Pervaporation

Effect of feed concentration

The influence of water–acetone compositions on the permeation fluxes through the NR-g-PHEMA

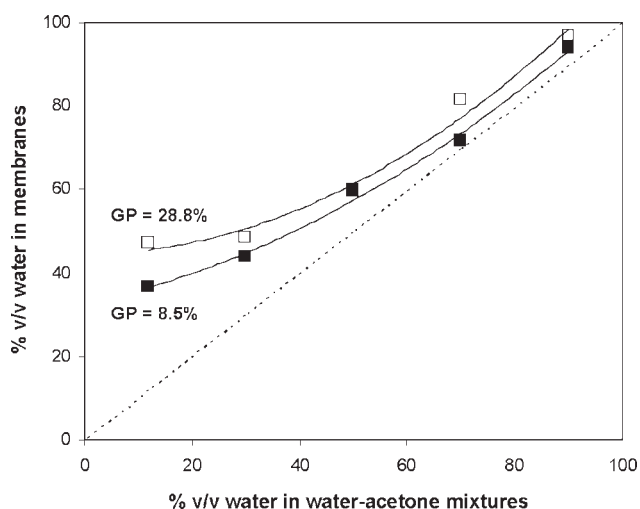


Figure 7 Water sorption isotherms of NR-g-PHEMA membranes.

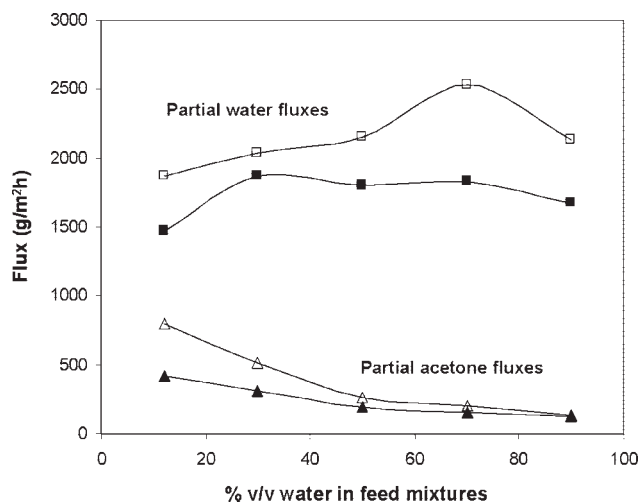


Figure 8 Partial fluxes of water and acetone through NR-g-PHEMA membranes as a function of feed-water concentration, feed temperature is 30°C; closed symbols are for GP = 8.5% and opened symbols are for GP = 28.8%.

membranes is revealed in Figure 8. The partial water fluxes were significantly greater than those of acetone, suggesting a feasibility of the membranes for the dehydration of water–acetone mixtures. When increasing the feed–water concentration, the partial water fluxes increased, which was in opposition to the partial fluxes of acetone. An enhancement of the water flux is attributable to interactions between the functional groups of PHEMA and water molecules, that is, such interactions induce the water molecule to be able to attract other water molecules with resulting in the formation of water clusters. Consequently, these water clusters might deter the penetration of acetone molecules through membranes, thus suppressing the acetone flux.²⁹ In addition, both partial fluxes of water and acetone were augmented with the amount of graft-PHEMA which was expected because more functional groups of PHEMA were available to interact with the water molecules.

The concentration of permeants as increasing of feed–water concentration was plotted in Figure 9. It is evident that the NR-g-PHEMA membranes were capable of separating water from water–acetone mixtures. However, when considering the water separation factor (α_p), as also shown in Figure 9, it was seen that α_p declined with more water content in the feed. This is because the membrane, especially at 28.8%GP, was in the state of excessive swelling due to the interactions of water molecules with PHEMA. Such condition accommodates the transport of acetone molecules through the membrane since the swollen membrane matrix was expanded. Despite the decreasing trends of acetone concentration in the permeate with the feed water content, the ability of

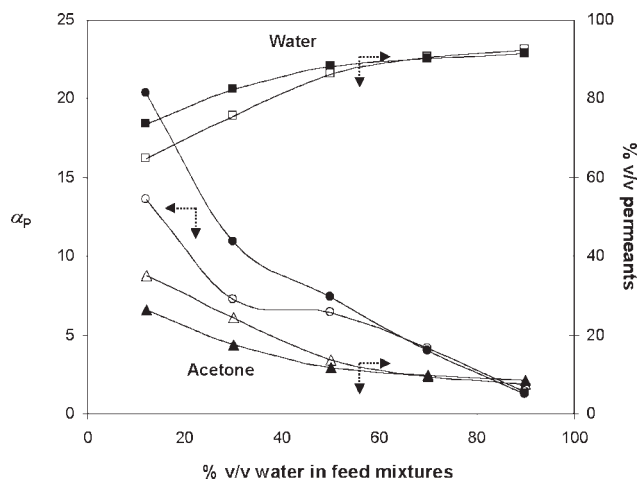


Figure 9 Concentration of permeants (% v/v) and water separation factor (α_p) as a function of feed–water concentration, feed temperature is 30°C; closed symbols are for GP = 8.5% and opened symbols are for GP = 28.8%.

acetone penetration was enhanced with the aid of water molecules so called the plasticization effect.

The permeation of water through NR-g-PHEMA membranes was affected not only by the swelling, which leads to the plasticization effect but also the coupling of water and acetone molecules. To disclose the coupling effect of acetone on water, the water permeation ratio (θ_w)³⁰ was plotted against feed water concentration as displayed in Figure 10. The θ_w is a ratio of an actual partial water flux (J_w) to an ideal water flux (J_w^o) by which J_w^o is calculated from a product of the weight fraction of water in feed with the permeation flux obtained when the

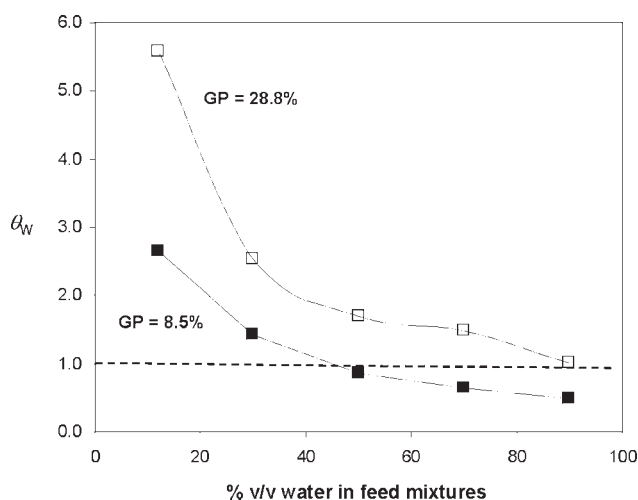


Figure 10 Water permeation ratio (θ_w) of NR-g-PHEMA membranes as a function of feed–water concentration; feed temperature is 30°C.

pervaporation operates with pure water.³¹ θ_w more than unity suggests, at least qualitatively, the occurrence of water–acetone coupling as causing from the greater water–acetone interactions than the interactions of water with a membrane.¹³ As observed in Figure 10, the coupling occurred in the membranes more extensively for high graft-PHEMA. However, the degree of coupling for both membranes declined as the feed water concentration increased. Under the strong coupling effect, large clusters could be formed that may inhibit the transport of water molecules through membrane and as a consequence, the water flux across the membrane would reduce with increase of the acetone flux.

Effect of feed temperature

Effect of feed temperature on the permeation fluxes was revealed in Figure 11 for the NR-g-PHEMA membrane with 28.8%GP and the feed water concentration of 12% v/v. The total permeate flux was found to increase with the feed temperature such that the increasing of flux mainly arose from the enhancement of acetone permeation. As increasing temperature, polymer chains will be more agitated which promotes the diffusion of penetrating molecules.³² Additionally, because of high thermal energy, the free volume of polymeric membrane will be expanded giving a loose structure of polymer networks and thus both water and acetone molecules transport through the membranes more conveniently.³³

The temperature dependence of permeation fluxes can be described by the Arrhenius type relationship.³²

$$J_W = J_{OW} \exp(-E_{JW}/RT) \quad (10)$$

$$J_A = J_{OA} \exp(-E_{JA}/RT) \quad (11)$$

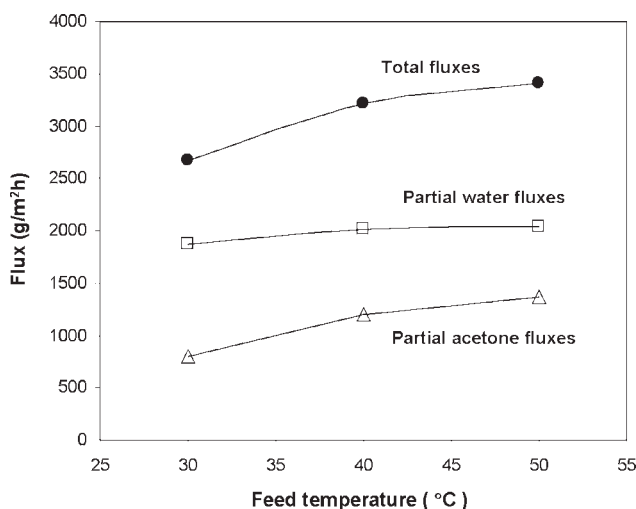


Figure 11 Effect of feed temperature on permeation flux across 28.8%GP NR-g-PHEMA membrane using 12% v/v feed water concentration.

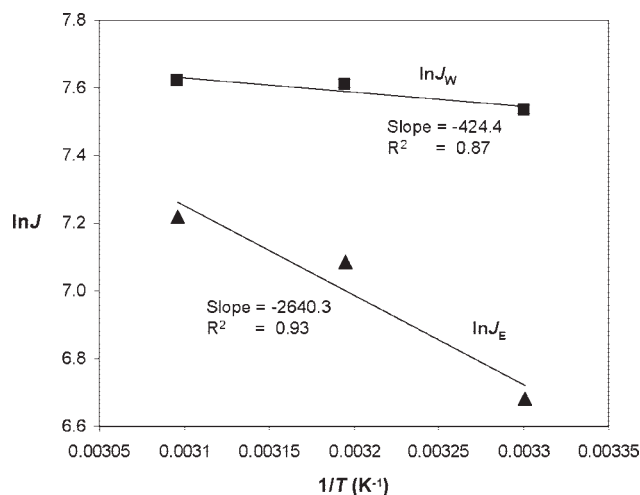


Figure 12 Arrhenius plot of $\ln J$ versus $1/T$ for partial water flux (J_W) and partial acetone flux (J_E) across 28.8%GP NR-g-PHEMA membrane with 12% v/v feed water concentration.

where E_J is the activation energy for permeation and J_o is the preexponential term. Figure 12 shows the plot between $\ln J$ and $1/T$ for the partial permeation fluxes of water and acetone reported in Figure 11. Evidently, the linear relationships were obtained suggesting the Arrhenius relationships of permeation through the membrane. The activation energies were estimated as 3.53 kJ/mol for water permeation and 21.95 kJ/mol for the permeation of acetone. The lower E_{JW} indicates that water molecules can penetrate through the membrane more easily than acetone due to its lower energy barrier.

CONCLUSIONS

The grafting of PHEMA on NR latex was performed by the use of graft-emulsion polymerization. The FTIR analysis indicated the successful grafting of PHEMA on NR. The grafting percentage (% GP) of PHEMA on NR depended on the amounts of HEMA monomer and initiator. By increasing HEMA concentration, % GP was found to increase, suggesting that the probability of HEMA to react with the active sites on NR particles was increased. On the other hand, % GP responded differently upon increased initiator concentration. The % GP increased significantly at low initiator concentrations as a result of the increased number of free radicals before it leveled off at moderate concentrations and, finally, a slight decrease was observed for high initiator concentrations caused by the greater probability of self-termination of radicals with active oligomers or graft-chains. NR-g-PHEMA latexes were prepared as pervaporation membranes for a dehydration of water–acetone mixtures. The equilibrium swelling was conducted for various concentrations of water–

acetone mixtures. The nonideal swelling behaviors of the membranes were found such that there appeared the maximum swelling degree at a certain concentration of liquid mixtures, which was dependent on the amount of graft-PHEMA. The diffusion coefficients of pure components, water and acetone, were estimated from the dynamic swelling of the membranes. The diffusion coefficients of acetone were greater than those of water. However, the diffusion coefficient of water increased with the amount of graft-PHEMA because of the increasing of membrane hydrophilicity. The sorption study suggested the preferential sorption of water on the membranes. In addition, the sorption isotherms implied the occurrence of coupling effect in which interactions between water and acetone molecules are more prominent than the water-membrane interaction. Pervaporation separation of water-acetone mixtures was investigated, considering the effects of feed water concentration and feed temperature. As the feed-water concentration increased, the partial water fluxes increased in contrast to the partial fluxes of acetone. This enhancement of water flux is mainly attributable to the interactions between functional groups of PHEMA and water molecules. To observe the coupling effect in pervaporation, the permeation ratio, θ_w , was estimated, and θ_w indicated that there was a coupling of acetone on the water transport through membrane especially for the membrane with high graft-PHEMA under acetone-rich conditions. For the effect of feed temperature, it was found that increasing the feed temperature would promote the total permeation across the membranes because of the increasing polymeric chain mobility. The partial fluxes of water and acetone as a function of temperature followed the Arrhenius relationship by which the activation energies for permeation were estimated as 3.53 kJ/mol for water and 21.95 kJ/mol for acetone.

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