Pervaporation of Acetone-Chlorinated Hydrocarbon Mixtures through Polymer Blend Membranes of Natural Rubber and Epoxidized Natural Rubber

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ABSTRACT: Transparent nonporous membranes were prepared by blending natural rubber (NR) with epoxidized NR (ENR). These blend membranes were evaluated for the selective separation of chlorinated hydrocarbons from acetone. The flux and selectivity of the membranes were determined both as a function of the blend composition and feed mixture composition. Results showed that polymer blending method could be very useful to develop new membranes with improved permselectivity. Pervaporation properties could be optimized by adjusting the blend composition. NR/ENR 70/30 and NR/ENR 30/70 composition showed a decrease in flux and selectivity, whereas the 50/50 composition showed increased flux and increased selectivity. Chlorinated hydrocarbons permeated preferentially through all the tested membranes. The feed mixture composition also strongly influenced the pervaporation characteristics of the blend membranes. Permselectivity was found to depend on the molecular size of the penetrants. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2365–2379, 1999

Key words: pervaporation; polymer blend membrane; natural rubber; epoxidized natural rubber; chlorinated hydrocarbon.

INTRODUCTION

The pervaporation process is an emerging membrane separation process, where the feed mixture directly contacts one side of a dense membrane under atmospheric pressure, whereas a low partial pressure of the permeate species is maintained on the other side of the membrane by a vacuum. Important advantages (such as simplicity, low costs, acceptable flux, and high selectivity) have shown the pervaporation process to be a promising separation process.^{1–8}

In recent years, there has been increased interest in the use of the pervaporation membrane separation process for separation of organic liquid

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mixtures. The technique can be used to separate any liquid mixture in all concentration ranges. However, in practice, it is used for the separation of azeotropic mixtures, close-boiling point mixtures, or isomers, and for the removal or recovery of trace substances.⁹⁻¹¹ Many researchers reported on the separation of binary liquid mixtures by this technique. Huang and Lin¹² studied the separation of binary liquid mixtures of aqueous alcohol solution. They further established some of the characteristics of permeation. Carter and Swamy¹³ reported the separation of benzene-alcohol, ethyl acetate-carbon tetrachloride by polyethylene, and found that selectivity is related to swelling. Sweeny and Rose¹⁴ followed the influence of size and chemical nature of permeating species on pervaporation. They established the relation of selective permeation to the polarities of the liquid and the polymer.

Characteristics	NR	ENR-25
Epoxidation level (%)	_	25 ± 2
Glass transition temperature (°C)	-72	-47
Density (kg m^{-3})	0.92	0.97
Solubility parameter $(J m^{-3})^{1/2}$	16.2	17.4
Number average mol. wt. (\bar{M}_n)	$1 imes 10^{6}$	$(1–9.9) imes10^5$
Gel content (%)	_	47 ± 3

Table I Material Characteristics

Despite these studies, no large-scale application for the organic-organic mixture separation in the chemical industry can be found so far. This is due to the lack of good membranes for specific applications. Three approaches are often followed to develop pervaporation membranes: (1) synthesis of new polymers, (2) modification of existing polymers, and (3) polymer blending. Many new polymers and copolymers were synthesized and tested.^{15–17} These polymers generally showed an improved permselectivity when they contained specific groups that could preferentially interact with one component of a liquid mixture. The modification of polymers can be done through a chemical reaction, radiation or plasma treatment, or a combination of these methods. In this way, specific groups are introduced to the polymer bulk or only to the surface of polymer membranes. A third method is the blending of existing polymers to produce materials for the pervaporation of liquid mixtures, tained.^{18–21} and promising results were ob-

The objective of such material studies is to develop membranes with both a high flux and a high selectivity. However, in most cases, it is found that, as flux increases, selectivity decreases. Therefore, the performance of membranes has to be adjusted for a given separation problem to achieve optimum performance. For this purpose, a polymer blend can offer a convenient tool. The aim of polymer blending normally is to create a new polymeric material that combines the properties of two homopolymers. The physical and mechanical properties, as well as the permeation properties of the blend, can be influenced by changing the blend composition.

The main objective of this study is to develop new polymer membranes for the selective separation of organic mixtures by pervaporation. A polymer blend concept was applied for this purpose. In this study, a blend of natural rubber (NR) and epoxidized NR (ENR) was prepared. The pervaporation property of this blend was evaluated for acetone-chlorinated hydrocarbon liquid mixtures.

EXPERIMENTAL

Materials

Indian standard NR (ISNR-5) was supplied by RRII (Kottayam, India). ENR-epoxyprene with 25 mol% epoxidation (ENR-25) was supplied by Rubber Research Institute (Malaysia). The basic characteristics of ISNR-5 and ENR-25 are given in Table I.

Membrane Preparation

The basic formulation used is given in Table II. Compounding was done on a two-roll mixing mill (friction ratio, 1 : 1.4) according to ASTM D15-627. The blends were prepared by the master-batch technique. The blend compositions are NR/ENR 70/30, NR/ENR 50/50, and NR/ENR 30/70. The compounded stock (~ 3 g) was placed between two thin aluminium sheets and pressed on a hydraulic press at 150°C and under a pressure of 25 tons to obtain membranes of ~ 0.2 mm thickness.

Table II	Compounding Recipe (Parts Per
Hundred	Parts of Rubber by Weight)

Ingredients	NR	ENR-25	
ZnO	5	5	
Stearic acid	2	2	
Calcium stearate	0	3	
CBS	1.5	1.5	
Sulfur	2.5	1.5	
TDQ	1	1	

CBS, N-cyclohexyl-2-benzothiazyl sulfenamide; TDQ, trimethyl dihydroquinoline.



(A) stirrer (B) permeation cell (C) membrane (D) collection traps (E) Dewar flask(F) R B flask (G) pressure gauge (H) moisture trap (I) vacuum pump.





Figure 2 Rheographs of the blend composition.

Sample	M_L (dN-m)	M_H (dN-m)	t_2 (min)	t_1 (min)	t ₉₀ (min)	CRI (min ⁻¹)
NR	7.5	50	6	5.5	8.25	44.44
70/30	3.5	53.5	3.5	3.25	5	66.66
50/50	1.5	50	2.5	2.25	4	66.66
30/70	2.75	47	2.75	2.5	4	80
ENR-25	3.5	45.5	3.5	3.25	4.5	100

Table III Cure Characteristics

Morphology

Morphology of the blends were studied by the ebonite method, in which the preferential reaction of one of the rubber phases with sulfur and zinc stearate effects a large increase in its electron density. The reaction medium for the ebonite treatment consists of molten sulfur/accelerator/ zinc stearate in the weight ratio 90/5/5. Small pieces of the samples are cut and are immersed in molten sulfur mixture for 8 h at 120°C. The excess sulfur was carefully scraped off from the outer surface before thin section were cut for scanning electron microscopic observations using a scanning electron microscope (SEM; Philips-Holland).



Figure 3 Swelling behavior of different blend composition with feed concentration of CH_2Cl_2 .



Figure 4 Effect of penetrant size on swelling degree.

Permeability Measurements

The permeabilities of the different solvents were determined by measuring the weight loss of small vials filled with the respective solvents and tightly closed by a membrane 1 mm thick of the individual polymers. The sorption coefficient has been determined by the gravimetric method. Diffusion coefficients (D) have been obtained from permeation (P) and sorption (S) constants by the equation:

$$P = DS \tag{1}$$

Pervaporation

A schematic representation of the pervaporation apparatus is given in Figure 1. The permeation cell consists of two half cells of column couplers made of glass, fastened together by bolted clamps. The half cells were of ~ 100 -mL capacity, and effective surface area of the membrane is 19.4 cm². Vacuum at the downstream side was main-

Solvent	NR	NR/ENR 70/30	NR/ENR 50/50	NR/ENR 30/70	ENR
Dichloromethane	3.60	3.24	3.00	2.76	2.40
Chloroform Carbon tetrachloride	$\begin{array}{c} 2.80\\ 1.40\end{array}$	$\begin{array}{c} 2.44 \\ 1.04 \end{array}$	$\begin{array}{c} 2.20\\ 0.80\end{array}$	$\begin{array}{c} 1.96 \\ 0.56 \end{array}$	$1.60 \\ 0.20$

Table IV Solubility Parameter Difference between Solvent and Polymer (kJ mol⁻¹)



Figure 5 Variation of swelling degree with solubility parameter difference between solvent and polymer.

tained using a Hondhivac (Ed-6) vacuum pump. A pressure of 6–7.5 mm was applied. Downstream pressure was measured with a vacuum gauge. Membranes were soaked in the mixture for 24 h and then kept in the pervaporation cell for ~ 2 h in each run to reach equilibrium before collecting the permeate. The permeate vapors were completely condensed in a trap placed in a Dewar flask cooled using liquid nitrogen. Complete condensation was effected by placing two traps in series. Experiments were conducted at room temperature.

The pervaporation properties are characterized by the flux, J, and selectivity α_{ij} . Flux was determined by measuring the weight of liquid collected in the cold traps during a certain time at steady-state condition. The pervaporation selectivity α_{ij} is defined as

$$\alpha_{ij} = (Y_i/Y_j)/(X_i/X_j) \tag{2}$$

where X and Y represent the concentration in the feed and in the permeate respectively. Indices i and j refer to the more permeable component (chlorinated hydrocarbon in this study) and the less permeable one (acetone), respectively.

RESULTS AND DISCUSSION

Cure Characteristics

The rheographs of the mixes are given in Figure 2, and cure characteristics in Table III. The minimum torque in the rheograph is presented as the minimum viscosity (M_L) value and is a measure of the extent of mastication. The low M_L value of 50/50 composition indicates its higher extent of mastication during mixing. The maximum torque in the rheograph is presented as maximum viscosity M_H . Values are higher and comparable for NR, NR/ENR 70/30, and NR/ENR 50/50.



Figure 6 Effect of blend composition on pervaporation fluxes for 50/50 composition of acetone/chlorinated hydrocarbons.

The induction time t_1 , determined from the rheograph, is the time taken to start the vulcanization process. It is clear from the data that the vulcanization of 50/50 blend starts first. This may be due to a fine dispersion of compounding ingredients in 50/50 blend. The rheometric scorch time, t_2 (premature vulcanization time) is the time taken for minimum torque value to increase by 2 units. Pure NR mix shows maximum scorch safety, whereas a 50/50 blend is scorchy. Optimum cure time (t_{90}) is the vulcanization time to get optimum physical properties and is calculated using the equation

$$t_{90} = (M_H - M_L) \times 0.9 + M_L \tag{3}$$

where t_{90} is the optimum cure torque. Optimum cure time t_{90} is the time corresponding to optimum cure torque. NR takes maximum cure time, whereas NR/ENR 50/50, ENR-25, and NR/ENR 30/70 show comparatively lower values. Cure rate index (CRI) is calculated using the equation

$$CRI = 100/t_{90} - t_2 \tag{4}$$

The higher the CRI values, the higher the vulcanization rate. From the table, it can be seen that ENR-25 has the highest cure rate, and NR the minimum. The cure-activating component is ENR; therefore, 30/70 composition has the highest cure rate among the blend compositions.

Swelling Degree

A piece of dry membrane was weighed and swollen in the acetone/chlorinated hydrocarbon mixture of known composition at room temperature. After equilibrium swelling, it was again weighed. The swelling ratio was calculated using the equation



Figure 7 Variation of permeation coefficient and sorption coefficient with volume fraction of NR.

$$S = \frac{W_s - W_d}{W_d} \tag{5}$$

where W_d denotes the weight of the dry membrane, and W_s is the weight of the solvent swollen membrane. Figure 3 shows the swelling behavior of the different blend compositions with feed concentration of dichloromethane and Figure 4 for different types of solvent mixtures. It is observed that the swelling degree increases with volume fraction of ENR and reaches the maximum for neat ENR-25. However, the swelling index decreases as the concentration of dichloromethane in the feed decreases. Figure 4 shows that the swelling degree increases as the size of the chlorinated hydrocarbon increases.

Generally, if the affinity between the permeant and the polymer membrane is strong, the solubility of the permeant is high. The solubility parameter is a convenient measure of the affinity between a polymer and penetrant. The difference in the solubility parameters between the polymer and the penetrant is often used to characterize the sorption behavior of the penetrant in the polymer membrane.²²⁻²⁵ The solubility of the penetrant generally becomes high when the difference in the solubility parameters between the polymer and penetrant is small. These values for the different polymer-penetrant systems are given in Table IV. As the volume fraction of ENR increases, these values decrease with a consequent increase in solvent sorption. Furthermore, Figure 5 shows the variation of swelling degree with solubility parameter difference between solvent and polymer. As the chlorinated hydrocarbons have preferential sorption compared with acetone, an increase in acetone concentration in the feed decreases the overall sorption. Furthermore, the solubility parameter difference values explain the swelling behavior of different chlorinated hydrocarbons.



Figure 8 Variation of permeation coefficient and diffusion coefficient with volume fraction of NR.

Pervaporation Analysis

Effect of Blend Composition

The separation of acetone-chlorinated hydrocarbon mixtures through NR/ENR-25 blend membranes with compositions of NR/ENR 70/30, NR/ ENR 50/50, and NR/ENR 30/70 was evaluated to investigate the polymer blend concept in developing membrane materials. The blend membranes were preswollen in the feed before pervaporation experiments. Figure 6 shows the pervaporation flux for NR/ENR-25 blend membranes for chlorinated hydrocarbon/acetone mixtures. In this figure, the flux is given as a function of the ENR concentration in the blend. The flux calculated according to eq. (2) shows an interesting trend. The flux is maximum for NR and decreases with the concentration of ENR in the blend. But, among the blend compositions, the NR/ENR 50/50 composition shows a flux maximum, and NR/ENR 70/30 composition shows a flux minimum. But,

Figure 3 shows that the swelling degree increases with an increase in ENR concentration in the blend. This should increase the flux with ENR concentration in the blend. However, the observed phenomenon can be explained by the solution-diffusion model of pervaporation. The mechanism of transport by pervaporation is described as comprising three consecutive steps: (1) sorption of components from a liquid phase at the membrane surface; (2) diffusion of the sorbed components through the polymer matrix; and (3)evaporation from the polymer into the vapor phase on the permeate side of the membrane. The efficiency of the pervaporation process is controlled mainly by the intrinsic properties of the polymers used for membrane preparation.

Figure 7 shows the variation of the permeation and sorption constants with the volume fraction of NR in the blend. The sorption constant increases with the concentration of ENR and is a maximum for ENR-25. However, the permeation



NR/ENR:30/70

Figure 9 SEM photographs of different blend membranes.

coefficient shows a different behavior. Permeability increases with the volume fraction of NR. But, the blend composition shows a different behavior. The permeability of NR/ENR 70/30 and NR/ENR 30/70 is lower, compared with NR/ENR 50/50.



Figure 11 Effect of blend composition on selectivity for the 50/50 composition of acetone/chlorinated hydrocarbons.

The observed behavior in permeability can be related to the diffusion constants of the different hydrocarbon through the membranes. Figure 8 shows the variation of the permeation and diffusion coefficients. Thus, the decrease in permeation rate can be attributed to the decreased diffusion coefficient values.

This interesting transport phenomena can be related to the unique morphology of NR/ENR-25 blends. Figure 9 shows the SEM photographs of the different blend composition, and Figure 10 shows the tentative model representing the permeation of penetrant molecules through different blend membranes. NR/ENR-25 70/30 shows a two-phase morphology in which ENR-25 is the dispersed phase. The dispersed ENR domains affects the phase continuity of NR. This leads to reduced permeability due to the more tortuous path that must be taken by penetrants. This is clear from the model given in Figure 10. But, NR/ENR-25 50/50 presents a fully cocontinuous morphology that increases the permeability. The enhanced permeability of NR/ENR 30/70, compared with ENR-25, is due to partial cocontinuity, as can be seen from the SEM photograph.

Thus, the observed flux values in NR/ENR blend membranes is the result of the unique morphology of these membranes that affects the solvent permeability through these membranes.

Figure 11 shows the effect of blend composition on the selectivity of the membranes. NR membrane shows the minimum selectivity and ENR the maximum. The increased selectivity of ENR-25 results from the decreased chain mobility of ENR-25. Another factor contributing to the increased separation efficiency is the polar nature of ENR network and the higher hydrogen bonding efficiency of acetone, compared with the chlorinated hydrocarbon. With epoxidation, the polarity increases and, consequently, extent of hydro-



Figure 12 Infrared spectrum of ENR swollen in acetone.

gen bonding with acetone and ENR-25 increases, resulting in improved separation for ENR-25. This is clear from the infrared spectrum of ENR swollen with acetone given in Figure 12. The spectrum shows a peak at 1690 cm^{-1} . The characteristic peak of -C=O stretching in acetone is expected in the range of $1730-1705 \text{ cm}^{-1}$. The shift in this peak to 1690 cm^{-1} results from the hydrogen bonding of acetone with ENR. Comparing the different blend composition, it is seen that NR/ENR 70/30 has the lowest selectivity. This is because the dispersed domains hinder permeability of the comparatively bigger chlorinated hydrocarbon molecules, resulting in reduced selectivity. The cocontinuous nature of the 50/50 composition offers a smooth passage of the penetrants and hence shows increased selectivity. The decreased selectivity of the NR/ENR 30/70 composition results from its heterogeneous nature, which again affects the permeability of the bigger chlorinated hydrocarbon molecules.

Influence of Feed Composition

According to the solution-diffusion model previously described, the permselective properties of pervapo-

ration membranes are determined by solubility and diffusivity of the permeating components in the membrane. Because both sorption and diffusion phenomena are dependent on the composition of the liquid mixture, permeation characteristics of membranes are usually strongly influenced by the feed composition.

The effect of the feed composition on the flux and selectivity is clear from Figures 13 and 14. The flux values decrease, whereas the selectivity increases with increase in acetone concentration in the feed. When a penetrant *i* diffuses through a membrane, the flux J_i is the product of the concentration C_i and the linear velocity ν_i of the penetrant inside the membrane. The velocity is the product of mobility B_i and driving force. In the case of pervaporation, the driving force is a gradient in the chemical potential across the membrane (i.e., $-d\mu_i/dx$). Therefore, the following relation expresses the flux in a pervaporation process.²⁶

$$J_i = \nu_i C_i = -C_i B_i \, d\mu_i / dx \tag{6}$$

According to this relation, the flux should decrease as the activity (i.e., the chemical potential



Figure 13 Effect of feed composition on pervaporation flux.

of a mixture component in the feed) decreases because the activity in the permeate side is kept constant by continuous evacuation. Thus, as the concentration of dichloromethane in the feed decreases, the flux decreases. But, the selectivity values show the reverse trend. This is because of the decreased swelling with increasing feed concentration of acetone. The decreased swelling hinders the passage of acetone molecules, thereby increasing the selectivity.

Effect of Penetrant Size

Figure 6 shows the variation of the pervaporation flux for acetone/chlorinated hydrocarbon 50/50 compositions. The figure shows that the pervaporation flux decreases with increase in penetrant size. However, Figure 4 shows that the swelling degree increases with increase in penetrant size. This should increase the flux as we move from CH_2Cl_2 to CCl_4 . But the flux values are found to decrease with increase in penetrant size. This may be again attributed to the decreased diffusivity as seen from Figure 8, with increased penetrant size. Thus, even though the sorption constant increases, the decrease in diffusivity reduces overall flux.

The variation of selectivity with penetrant size is evident from Figure 11. Usually, a decrease in flux value increases the separation factor. But, the observed decrease in selectivity may be explained by the increased sorption with increase in penetrant size. This effect plasticizes the polymer matrix, allowing the passage of comparatively smaller acetone molecules, which tends to decrease the selectivity.

CONCLUSIONS

Transparent nonporous membranes could be prepared from a blend of NR with ENR. Their per-



Figure 14 Effect of feed composition on selectivity.

vaporation properties were investigated by using chlorinated hydrocarbon/acetone mixtures. The flux and selectivity depend on blend composition. The swelling degree increases with an increase in the concentration of ENR in the blend. But, the flux values behave differently. The decreased flux for NR/ENR 70/30 and NR/ENR 30/70 compositions is the result of decreased diffusivity of the penetrant through the membranes. This decrease is attributed to the particular morphology of NR/ ENR 70/30 and NR/ENR 30/70 compositions. But the 50/50 composition shows both higher flux and higher selectivity. This results from the cocontinuous nature of the 50/50 composition, which increases the diffusivity of the penetrants through the membrane. This implies that such a polymer blend can offer a convenient way to optimize the separation characteristics of a membrane for a particular separation task. This means that the separation characteristics of a blend membrane can easily be adjusted by varying the blend composition.

It was also observed that membrane performance was strongly influenced by the feed mixture composition. The flux decreased, but selectivity increased with increasing acetone concentration in the feed. The penetrant size was also found to affect both flux and selectivity. Flux values decrease with an increase in penetrant size due to the decreased diffusivity of the penetrant as the size increases. Selectivity was also found to fall due to the increased sorptivity, with an increase in penetrant size, which plasticizes the polymer matrix and also allows for the penetration of acetone molecules.

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