

Separation of Alkane–Acetone Mixtures Using Styrene–Butadiene Rubber/Natural Rubber Blend Membranes

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ABSTRACT: Conventionally vulcanized styrene–butadiene rubber/natural rubber blend membranes were prepared for the pervaporation separation of alkane–acetone mixtures. Swelling measurements were carried out in both acetone and *n*-alkanes to investigate the swelling behavior of the membranes. The swelling behavior was found to depend on the composition of the blend. The effects of blend ratio, feed composition, and penetrant size on the pervaporation process were analyzed. The permeation properties have been explained on the basis of interaction between the membrane and solvents and blend morphology. The SBR/NR 70/30 blend membrane showed higher selectivity among all the membranes used. Flux increases with increasing alkane content in the feed composition. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3059–3068, 1999

Key words: pervaporation; separation; polymer blend; membrane; SBR; NR;

INTRODUCTION

Membrane-based separation technology is currently regarded as a new frontier of chemical engineering. It has been widely used for the purification, concentration, and fractionation of fluid mixtures. Pervaporation is one of the most popular areas of membrane research, and the pervaporation process has been shown to be an indispensable component for chemical separations. This technique attracted the attention of specialists in the chemical, biochemical, and petrochemical industries as an energy-saving and environment-friendly technology. The pervaporation process is gaining importance because of its compactness, flexibility, simplicity, and versatility.

Pervaporation is defined as the selective evaporation of a component from liquid mixtures. The chemical potential or the temperature gradient across the membranes serves as the driving force for the process. According to the solution diffusion model,¹ pervaporation transport is described as a three step process: (1) sorption of permeant from the feed liquid to the membrane; (2) diffusion of the permeant in the membrane; and (3) desorption of the permeant to the vapor phase on the downstream side of the membrane.

The separation is based on the selective solution and diffusion, i.e., the physico-chemical interaction between the membrane and the permeating molecules. Pervaporation is a profitable complement to distillation that is an energy-intensive process. Thus, unlike other membrane separation processes, pervaporation involves a phase change of permeating species from the liquid to the vapor state.

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The application of pervaporation can be classified into three major categories: (1) removal of water from organic solvents and their mixtures;^{2,3} (2) separation of organic components from aqueous media,^{4,5} and (3) separation of liquid organic mixtures.^{6,7}

Chen and Martin⁸ investigated the separation of methanol/methyl *tert*-butyl ether/C₄'s azeotropes by pervaporation technique due to the commercial interest of producing octane enhancers for gasolines. Bagnell et al.⁹ reported that the pervaporation process can be used in reversible reaction to remove one or more product species selectively to shift the equilibrium towards the product side. Papaefstathiou and de Castro¹⁰ found that membrane pervaporation can be used as a chemical sensor in instrumental analysis. Even though numerous investigations have been carried out on the separation of organic liquid mixtures by different polymer membranes, it is the least developed applications of pervaporation because of the problems associated with membrane stability under harsh conditions. Recently in our laboratory, a series of separation studies have been conducted based on poly(ethylene-co-vinyl acetate)¹¹ and natural rubber¹² membranes. Polymer blend membranes are promising materials that can overcome the major difficulties associated with homopolymer system in the pervaporation process. Polymer blends are considered as physical mixtures of two or more polymers. In polymer blends the properties are controlled by the microstructure of the blends. There are large numbers of polymer membranes used for the pervaporation separation process. But the use of natural rubber-based blend membranes for the pervaporation process has not yet been fully tapped. Natural rubber/styrene-butadiene rubber blend membranes possess good mechanical properties. To the best of our knowledge, the use of SBR/NR blend membranes for the pervaporation process has not yet been examined.

The main objective of this work is to develop a new polymer membrane based on the SBR/NR blend for the selective separation of aliphatic hydrocarbons from alkane-acetone mixtures by pervaporation. (The alkane/acetone mixtures have been chosen to perform a basic study on the pervaporation process using the membrane). The separation efficiency has been evaluated as a function of blend ratio and feed composition.

Table I Compounding Recipe (in phr)

Ingredients	NR	SBR
Rubber	100	100
Zinc oxide	5	5
Stearic acid	1.5	2
MOR	0.6	—
CBS	—	1
TDQ	1	1
Sulfur	2.5	2.2

phr, parts per hundred rubber; MOR, morpholine benzothiazyl sulphenamide; CBS, *N*-cyclohexyl-2-benzothiazyl sulfenamide; TDQ, trimethyl dihydro quinoline.

EXPERIMENTAL

Materials

Styrene-butadiene rubber (SBR) used was styrene (1502) with 25% styrene content supplied by synthetic and chemicals Ltd. Bareilly, U. P., India. Natural rubber (NR) used in this study was of ISNR-5 grade, supplied by Rubber Research Institute of India. The solvents *n*-pentane, *n*-hexane, *n*-heptane, and acetone (Merck India Ltd., Mumbai, India) were distilled twice before use. All other rubber ingredients were of laboratory reagent grade, supplied by Bayer India, Ltd., Mumbai, India.

Preparation of SBR/NR Blend Membranes

The blend membranes are denoted by N₀, N₃₀, N₅₀, N₇₀, and N₁₀₀, where the subscripts denote the weight percent of natural rubber in them. The membranes were prepared by blending the respective masterbatches on a two-roll mixing mill, having a friction ratio of 1 : 1.4. The compounding recipe is shown in Table I. The cure characteristics of the membranes were studied from the elastographs shown in Figure 1. The processing characteristics are given in Table II. The sheeted out stock (about 3 g) was placed between two thin aluminum sheets and pressed for their optimum cure time on a hydraulic press at 150°C under a pressure of 25 tons. The thin membranes thus obtained were used for pervaporation experiments. Thickness of the membranes was approximately 0.3 mm.

Mechanical Properties

Tensile testing of the dumbbell-shaped membranes were performed at 25 ± 2°C according to

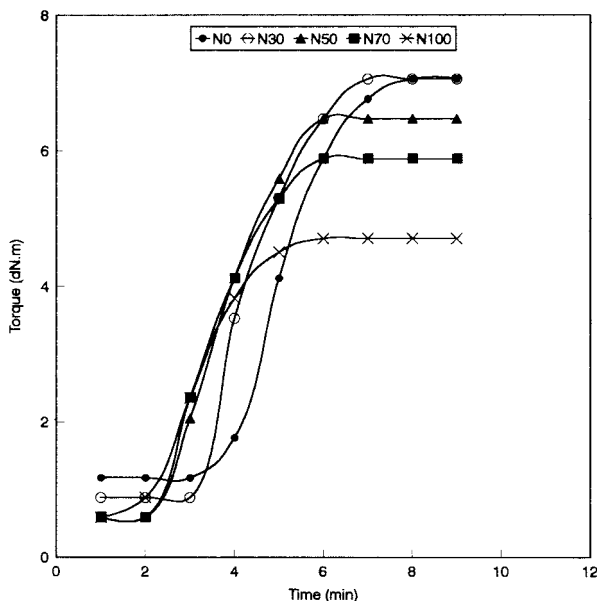


Figure 1 Elastographs of the mixes.

the ASTM 0412-80 test method, at a crosshead speed of 50 mm/min, using a Universal testing machine.

Morphology Studies

Samples for SEM studies were cryogenically fractured under liquid nitrogen. The NR phase was preferentially extracted from the cryogenically fractured samples by keeping the broken edge in petroleum ether for 72 h at room temperature. The NR-extracted samples were dried in an air oven. The dried samples were sputter coated with gold prior to SEM examination. A Phillips model scanning electron microscope operating at 10 KV was used to view the specimens.

Swelling Studies

The dried membrane was immersed in an alkane/acetone mixture. After the membrane attains an

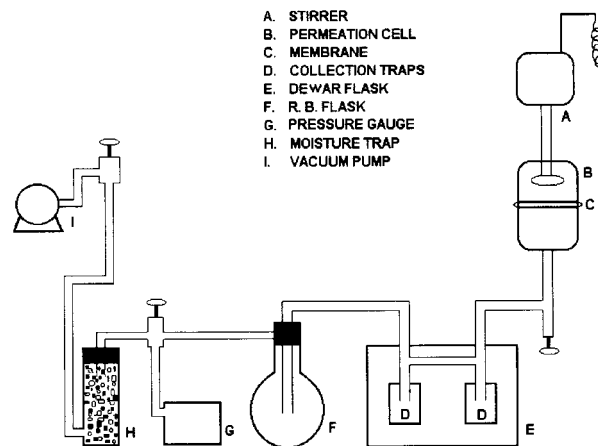


Figure 2 Schematic sketch showing the pervaporation apparatus.

equilibrium, the swelling ratio (S_R) of the membrane was calculated from the equation

$$S_R = W_s - W_d/W_d \quad (1)$$

where W_d is the weight of dry membrane, W_s is the weight of the solvent-swollen membrane.

Pervaporation Experiments

The pervaporation experiments were performed using the apparatus shown in Figure 2. The principle involved is illustrated in Figure 3. The permeation cell was assembled from two half-cells of column couplers made of glass. The capacity of each half-cell was about 100 mL, and the effective surface area of the membrane was 19.4 cm². Membranes were first immersed and swollen in the respective feed mixtures at room temperature. They were further installed in the permeation cell. The feed was circulated through the pervaporation cells from a feed reservoir kept at room temperature. The pressure at the (3.5 to 4 mm) downstream side was kept constant by a

Table II Processing Characteristics

Blend Ratio	M_L (dN · m)	M_H (dN · m)	ts_1 (m : s)	ts_2 (m : s)	t_{90} (m : s)	CRI
N ₀	1.13	7.13	7.48	8.48	17.02	11.71
N ₃₀	0.79	7.23	5.59	6.53	13.09	15.24
N ₅₀	0.65	6.72	4.59	5.54	11.40	17.06
N ₇₀	0.53	6.09	4.06	5.05	10.23	19.30
N ₁₀₀	0.61	4.85	3.12	4.46	10.05	17.89

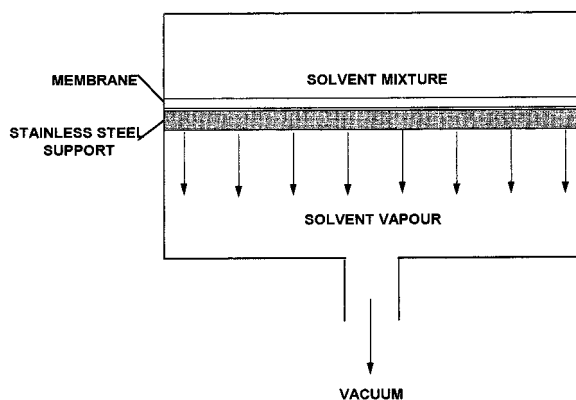


Figure 3 Schematic sketch illustrating the principle involved in the pervaporation process.

vacuum pump. The permeate was collected in cold traps cooled by liquid nitrogen. The permeate and feed compositions were analyzed by a refractometer.

The performance of a membrane in pervaporation is characterized by permeation rate or flux J ($\text{kg}/\text{m}^2\text{h}$) and selectivity α_{AB} .

The selectivity is defined by

$$\alpha_{AB} = \frac{Y_A/Y_B}{X_A/X_B} \quad (2)$$

where Y_A and Y_B represent the weight fractions of alkane and acetone in the permeate; and X_A and X_B represent those of alkane and acetone in the feed respectively.

The pervaporation separation index (PSI)¹³ has been used to evaluate the overall performance of the membranes, which can be determined from the following relation

$$\text{PSI} = J(\alpha_{AB} - 1) \quad (3)$$

RESULTS AND DISCUSSION

Processing Characteristics and Mechanical Properties of SBR/NR Blend Membranes

We have studied the processing characteristics from the elastographs (Fig. 1), and these are given in Table II. It is clear from Table II that a pure SBR membrane shows maximum optimum cure time (t_{90}) compared to all the other membranes. This was decreased with an increase of the NR content in the blend. Scorch is defined as the premature vulcanization of the rubber com-

pound. Scorch time is the time required for the torque value to increase by two units above the minimum torque. This is an indication of scorch safety. The scorch time (ts_2) decreases with an increase of NR content in the blend. Table II, where the scorch characteristics of the membranes are depicted, shows that pure SBR and the SBR/NR blend with a high SBR content exhibit better scorch safety. With increasing the NR content in the blend, the scorch safety decreases. The rheometric induction time values (ts_1) also decrease with increase in the NR content in the SBR/NR blend. N_{100} and N_{70} take minimum time to initiate vulcanization among all the blend compositions. Minimum torque values (M_L) indicate that low viscosity is expected for blend with high NR content. The slight change in M_L value in N_{100} might be due to the change in mixing time. Cure rate index (CRI), which is a direct measure of the fast curing nature of rubber compounds, is also given in Table II. Cure rate index values have been found to increase with increase of NR content in the blend. Maximum rheometric torque (M_H) is an index of crosslinking density, and these values indicate that the maximum crosslink density is possessed by N_0 and the minimum by N_{100} . The blend compositions possess intermediate values.

The mechanical properties of the blends are given in Table III. As expected, tensile strength, elongation at break E_B (%), and Young's modulus increased from N_0 to N_{100} . The mechanical strength of SBR increases upon blending it with NR. This is definitely associated with the strain-induced crystallization behavior of NR. Usually the tensile strength values of the blend composition come in between those of the homopolymers. But it was interesting to note that N_{30} , N_{50} , and N_{70} exhibit synergism in their mechanical properties. The modulus at different elongations is also given in Table III.

Pervaporation Characteristics of the SBR/NR Blend Membranes

The separation of alkane-acetone mixtures through SBR/NR blend membranes was evaluated to investigate the polymer blend concept in developing membrane materials. Effects of blend composition on flux and selectivity are presented in Figures 4 and 5, respectively. It can be observed that the transport properties of the SBR/NR blends depend strongly on the SBR/NR ratio in the blend. Pervaporation flux is greatest

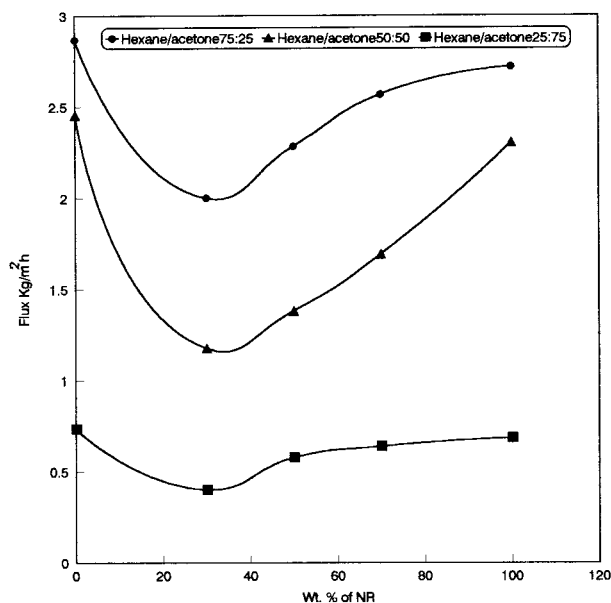
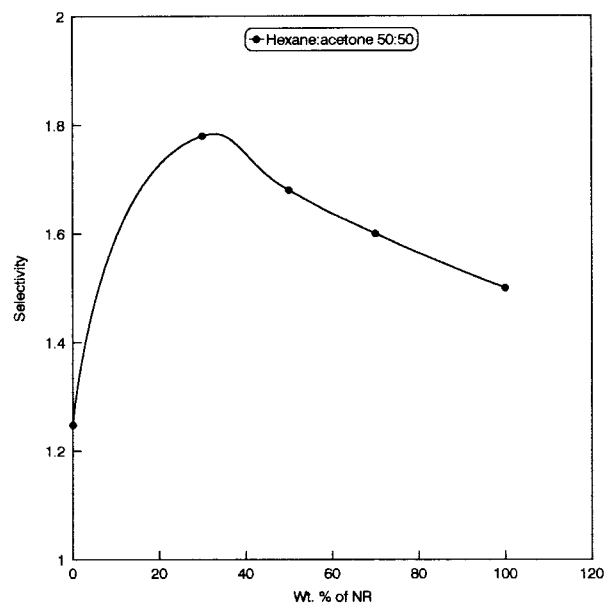
Table III Mechanical Properties

Property	Blend Ratio				
	N ₀	N ₃₀	N ₅₀	N ₇₀	N ₁₀₀
Tensile strength (MPa)	1.82	4.59	5.24	6.09	6.63
Elongation at break ($E_B\%$)	391	862	869	1007	1069
Young's modulus (MPa)	1.36	1.22	0.80	0.62	0.35
Secant modulus					
M ₁₀₀	0.43	0.62	0.66	0.64	0.37
M ₂₀₀	1.05	1.01	0.98	0.96	0.58
M ₃₀₀	1.24	1.35	1.34	1.27	0.79

for N₀ membranes, and it decreases with the increase of NR content up to 30 wt %. Pervaporation flux again increases for all feed compositions as the NR content in the blends increases from 30 to 100 wt %. These figures show that by controlling the NR content in the blend a great variety of fluxes can be obtained for any feed composition. In the case of a feed mixtures of hexane-acetone (50/50), for example, flux increases from 1.178 to 1.69 kg/m²h as the NR content increases from 30 to 70 wt %.

The increasing NR content in the membrane has a retarding effect on the selectivity. All membranes are selective to alkane, and the selectivity increases with an increasing NR content in the blend up to 30 wt %. Then the alkane selectivity

gradually decreases from N₃₀ to N₁₀₀. Upon increasing the concentration of NR from 30 to 50 wt % there is a sudden change in the values of flux and selectivity. Pervaporation behavior could be explained based on the extent of interaction between the membrane and the solvents and the blend morphology. The solubility parameter values of NR, SBR, *n*-hexane, and acetone are 16.2, 17.2, 14.9, and 20.3 (J/m³)^{1/2} respectively. There is strong interaction between NR and *n*-hexane, owing to the closer solubility parameter values. Therefore, with increasing NR content in the blend, the interaction between the blend and *n*-hexane increases. Interaction effectively increases the frequency and amplitude of rubber chain motions, thereby allowing the permeate

**Figure 4** Effect of the blend ratio on the pervaporation flux at different hexane-acetone compositions.**Figure 5** Effect of the blend ratio on the pervaporation selectivity at 50/50 hexane-acetone compositions.

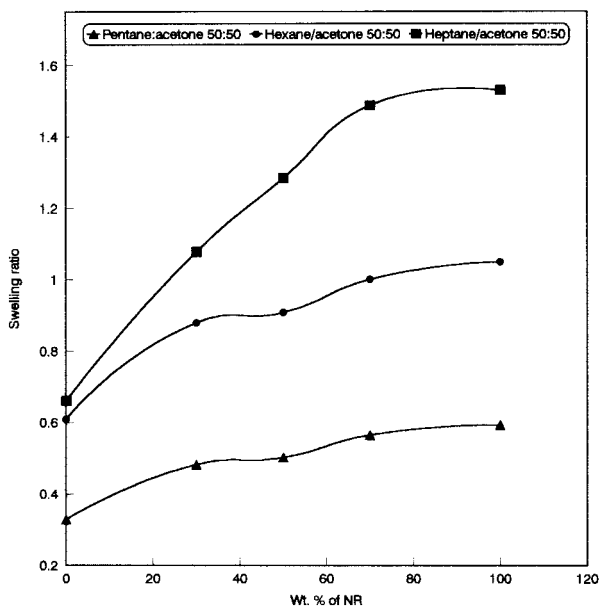
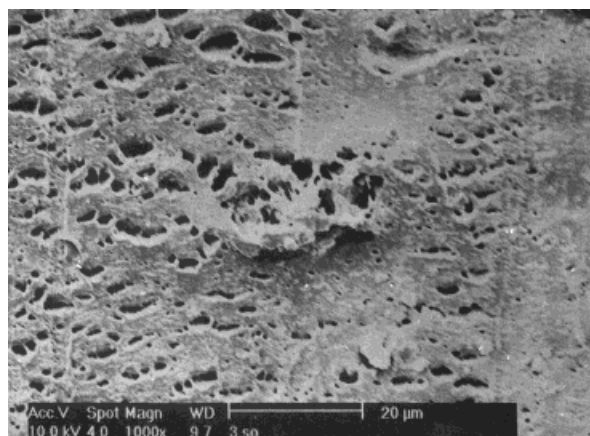


Figure 6 Effect of the blend ratio on the swelling ratio of the blend membranes.

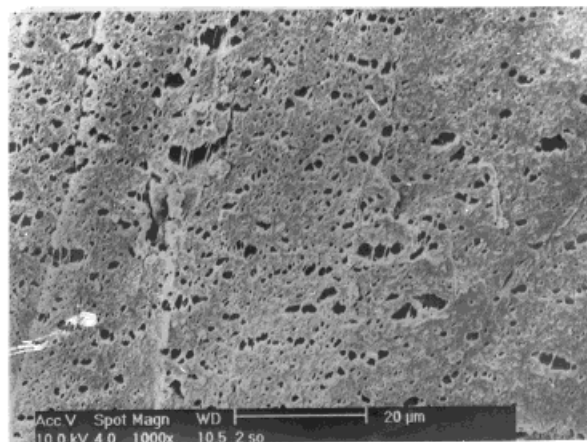
molecules to pass through the membrane easily. Thus, the permeation rate increases, and the selectivity decreases. The swelling behavior of the membranes also shown in Figure 6.

Instead of a regular increase in the flux, we observed a decrease at the N_{30} blend even though the interaction between the membrane and alkane increases with increasing NR content in the blend. This is due to the hetrophase morphology existing in the N_{30} blend. SEM photographs of the morphology of the blends are shown in Figure 7. Figure 7(a) shows the morphology of the N_{30} blend, where NR is dispersed as domains in the continuous SBR matrix. The voids are found to be the etched out NR particles. The average domain size of the dispersed particles is $3.2 \mu\text{m}$. The two phase morphology retards the passage of the solvent mixture. The dispersed NR makes a tortuous path for the penetrant. Hence, the flux is less, and selectivity is higher. But in the N_{50} blend NR becomes continuous, and the system exhibits a cocontinuous morphology, as shown in Figure 7(b). In the N_{70} [Fig. 7(c)], a cocontinuous morphology was also observed. Due to the cocontinuous morphology of N_{50} and N_{70} blends, passage of the penetrant becomes easier and, hence, flux increases and permselectivity decreases. A similar behavior has been observed in the case of heptane/acetone and pentane/acetone, as shown in Figure 8.

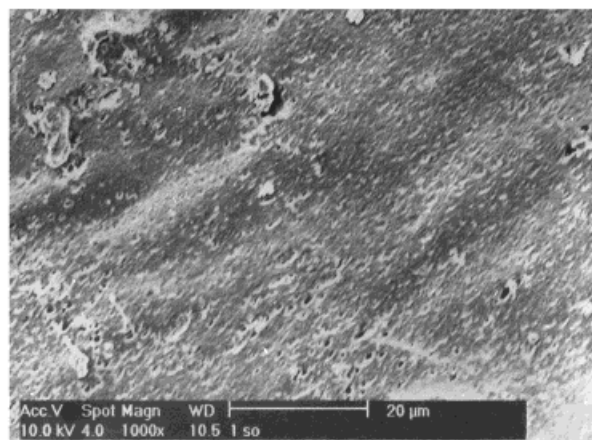
A schematic representation of pervaporation process in the SBR/NR blends is shown in Figure



(a)



(b)



(c)

Figure 7 SEM photographs of morphology of the SBR/NR blends: (a) N_{30} , (b) N_{50} , and (c) N_{70} .

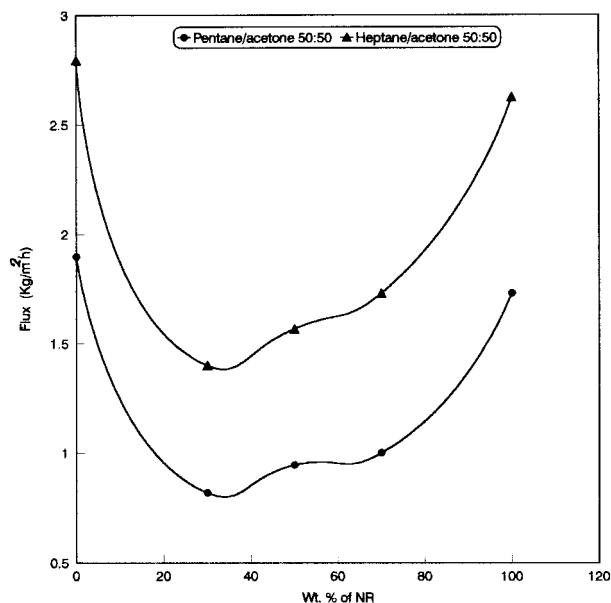


Figure 8 Effect of the blend ratio on the pervaporation flux.

9. As the model indicates, sorption of the alkane/acetone mixture at the membrane surface takes place at first, followed by diffusion in the bulk, and then permeation or evaporation from the other side of the membrane. In the N_0 membrane, sorption, diffusion, and permeation takes place quickly, as shown in Figure 9(a). In the N_{30} membrane, NR is dispersed in the continuous SBR matrix [Fig. 9(b)]. The two-phase morphology present in the system restricts the passage of the alkane/acetone mixture. Hence, the total flux is less. Due to the cocontinuous morphology of the N_{50} membranes [Fig. 9(c)], the rate of diffusion and permeation increases after the sorption process. Therefore, the total flux increases. Similarly, in the N_{70} membrane, dispersal and permeation of permeant molecules takes place quickly due to the cocontinuous morphology [Fig. 9(d)]. Just like N_0 , the sorption, diffusion, and permeation processes occur in the N_{100} membrane due to the single-phase morphology.

The total flux J can be divided into the component flux of alkane, J_{alkane} and that of acetone, J_{acetone} using the permeate composition data.¹⁴

$$J_{\text{alkane}} = J \times Y_{\text{alkane}} \quad (4)$$

$$J_{\text{acetone}} = J \times Y_{\text{acetone}} \quad (5)$$

where Y_{alkane} and Y_{acetone} are the concentration of alkane and acetone in the permeate, respectively.

As an example, the component fluxes of a heptane-acetone (50 : 50) mixture calculated from these equations are given in Figure 10 as a function of the blend composition. This figure clearly indicates that for this system the decrease in selectivity is attributed to a more rapid increase in the acetone component flux compared to heptane with increasing NR content. As the heptane concentration increases in the membrane, it plasticizes the membrane, and thereby the low swelling component (acetone) permeates quickly. The pervaporation separation index (PSI) was calculated using eq. (2) and is plotted as a function of the blend composition, as shown in Figure 11 for hexane/acetone 50 : 50 composition. It is very clear from the figure that the overall performance of the blend membrane increases with the increase

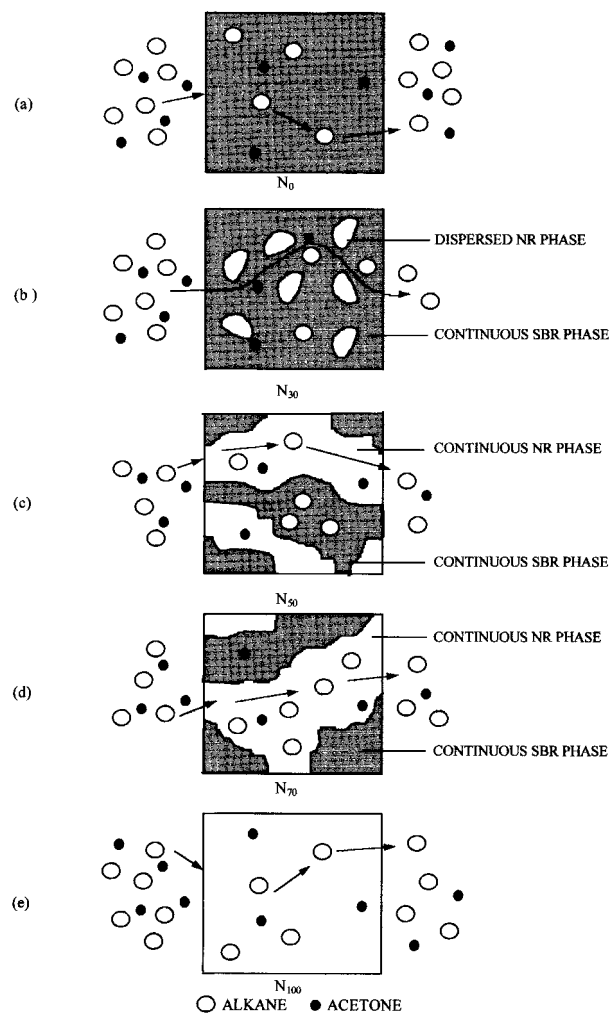


Figure 9 Schematic model illustrating the pervaporation process in the SBR/NR blends: (a) N_0 , (b) N_{30} , (c) N_{50} , (d) N_{70} , and (e) N_{100} .

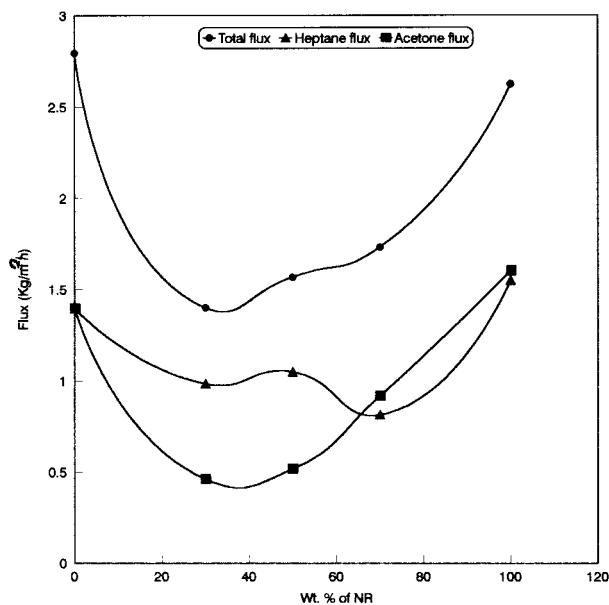


Figure 10 Effect of the blend ratio on total and component fluxes of heptane-acetone mixture.

of NR content in the blend. The positive deviation exhibited by the blend membranes suggest that they can be used as potential membranes for separating liquid mixtures.

The Effect of Feed Composition

The permeation properties of the membranes are also strongly influenced by the feed composition, because both sorption and diffusion are phenom-

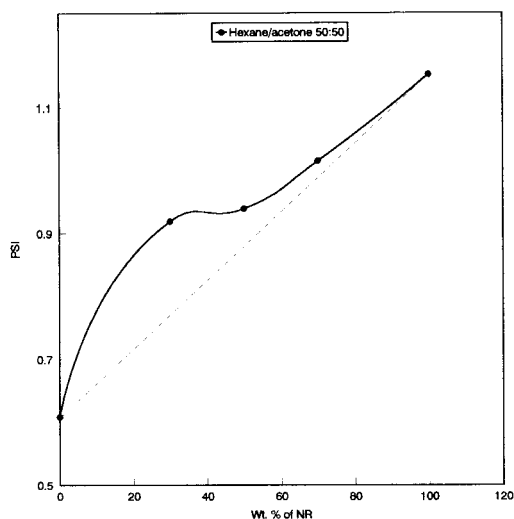


Figure 11 Effect of the blend ratio on the pervaporation performance of the membranes.

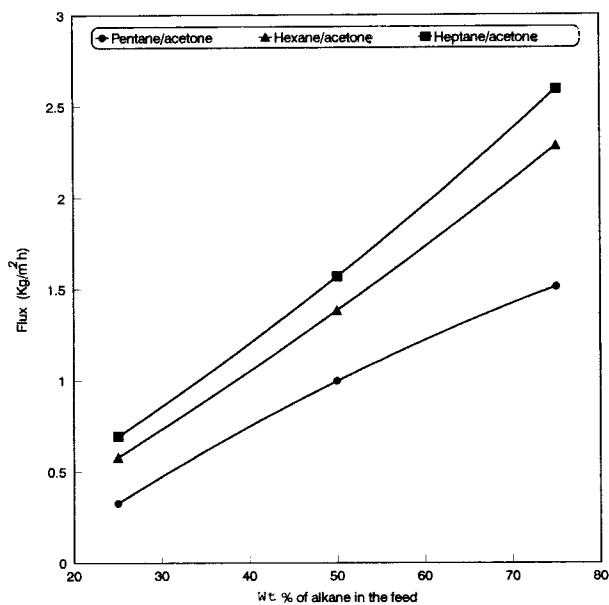


Figure 12 Effect of the feed composition on the pervaporation flux.

ena dependent on the composition of the liquid mixtures. The effect of the feed composition on the pervaporation fluxes is shown in Figure 12. Low fluxes are obtained when the alkane content in the feed composition is low. The fluxes increase strongly with an increase of the alkane concentration in the feed. This is the same behavior observed for all compositions of the three alkane/acetone mixtures. This behavior can be explained on the basis of a general pervaporation equation as well as the interaction between the membrane and penetrants.

The flux in pervaporation process can be given as¹⁵

$$J = v_i C_i = -C_i B d\mu_i/dx \quad (6)$$

where v_i and C_i are, respectively, the concentration and velocity of the penetrant inside the membrane. The velocity is the product of mobility B and the driving force. Here, the driving force is the chemical potential gradient across the membrane, i.e., $d\mu_i/dx$. According to this relation, the flux should increase as the activity, i.e., the chemical potential of a mixture component in the feed increases, because the activity in the permeate side is kept constant by continuous evacuation. Therefore, with increasing alkane concentration in the feed, the flux also increases. It is also significant to note that as the concentration in the

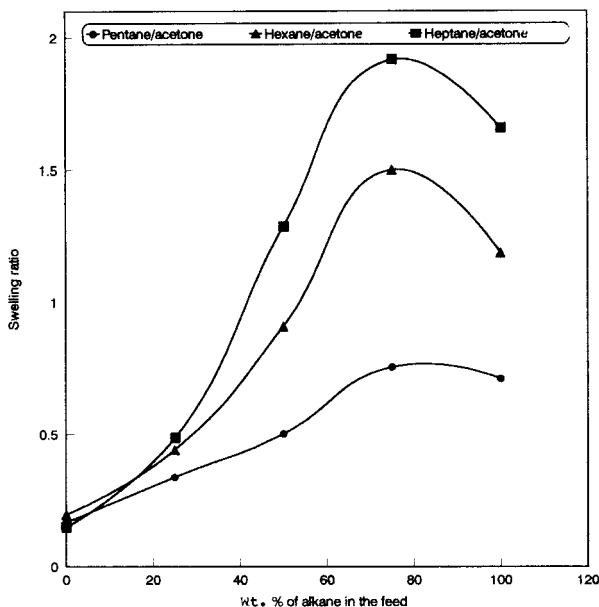


Figure 13 Effect of the feed composition on the swelling ratio of the membranes.

alkane concentration in the alkane/acetone mixture increases, the interaction between the alkane and the membrane also increases. This interaction increases the flexibility of the rubber chains, which results into an increased permeation rate. The swelling behavior of the N₅₀ membranes in different solvents given in Figure 13 is also in agreement with this observation. It is evident from the Figure 13 that swelling increases with the increase of alkane content in the feed up to 75 wt %, and then decreases. The maximum is observed at 75 wt % of alkane due to the nonsolvent effect of acetone.

Molecular Size of the Permeating Species

With the increase of the size of the alkane content in the alkane/acetone mixture, the pervaporation flux increases, as shown in Figure 14, irrespective of the blend composition used. The pervaporation of 50 wt % pentane–acetone, hexane–acetone, and heptane–acetone mixtures were followed. It was observed that as the number of carbon atoms in the aliphatic hydrocarbons increases, pervaporation flux increases. This might be due to the different degree of interaction, as earlier discussed. Heptane shows a stronger affinity for the blend than other alkanes. This is due to the fact that the difference in solubility parameter between the membrane and heptane is the lowest among the

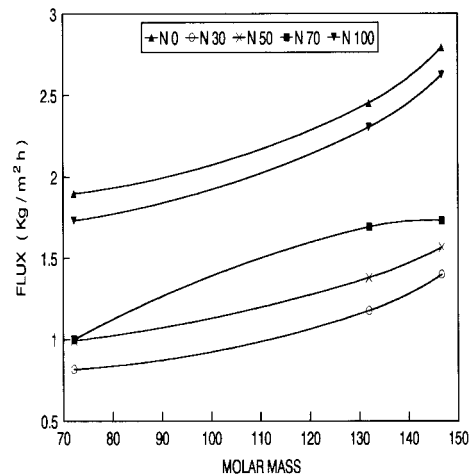


Figure 14 Effect of the molecular size of alkane in the alkane–acetone mixture on the pervaporation flux.

other two membrane–alkane systems. This is well illustrated in Figure 15. This stronger interaction results in higher sorption, and thereby a higher permeation of the heptane mixtures than the other solvents. The diffusion profile shown in Figure 16 is also in agreement with this observation.

CONCLUSION

SBR/NR blend membranes were prepared, and their pervaporation performance investigated in

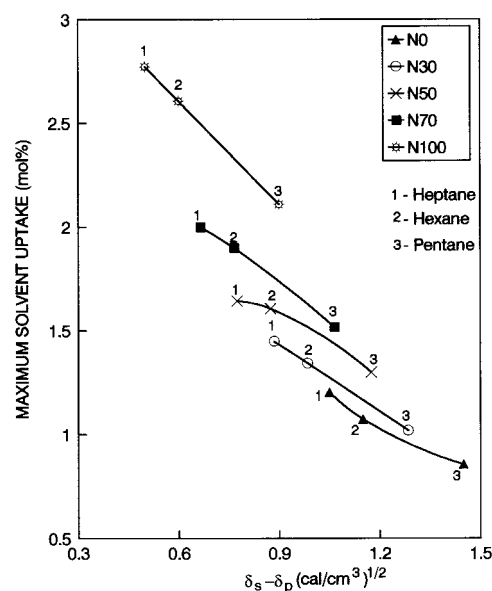


Figure 15 Variation of the maximum solvent uptake with the solubility parameter difference between the membrane and *n*-alkanes.

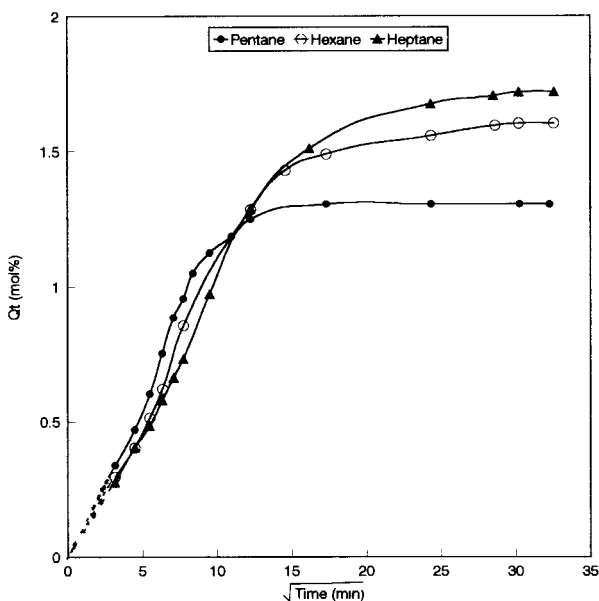


Figure 16 Diffusion profiles of the N_{50} membrane in n -alkanes.

the alkane–acetone mixtures. The flux increased as the NR content in the blend increased, whereas the selectivity decreased. This behavior is associated with the interaction between the membrane and the penetrants, besides the morphology of the blend system used. The interaction between the membrane and the solvents increasing with increasing the NR content in the blend is due to the closer solubility parameter values. In the N_{30} blend, the dispersed NR makes a tortuous path for the passage of the penetrant molecules. Hence, the two-phase morphology reduces the permeation rate and increases the selectivity. But in N_{50} and N_{70} blends, NR becomes continuous, and the resulting cocontinuous morphology increases the permeation rate and slightly reduces the selectivity. This implies that such a polymer blend can offer a convenient way to optimize the separation characteristics by varying the blend composition.

It was also observed that the membrane performance was strongly influenced by the feed mix-

ture composition. For all the alkane–acetone mixtures the flux increased with increasing alkane concentration in the feed. As the alkane concentration in the feed increases, the interaction between the membrane and penetrant increases, and thereby the flux. The overall pervaporation performance increased with increasing NR content in the blend. Work is in progress using the separation of chlorohydrocarbon/acetone mixtures using different crosslinked SBR/NR blends.

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