

Separation of *n*-Hexane/Acetone Mixtures by Pervaporation Using Natural Rubber Membranes

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ABSTRACT: Natural rubber (NR) membranes crosslinked by four different systems viz., conventional (CV), efficient (EV), dicumyl peroxide (DCP), and a mixture consisting of sulfur and peroxide (mixed), were employed for the separation of *n*-hexane/acetone mixtures of different compositions. The membranes exhibited preferential permeation toward *n*-hexane because of the closer solubility parameter values. The selectivity of the membranes depended on the nature and distribution of crosslinks between the macromolecular chains of the membrane but was independent on the thickness of the membrane. The effects of feed composition, cure time of the membranes, and the molecular size of the permeate on the permeation flux and selectivity were investigated.

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INTRODUCTION

Pervaporation is a fractionation process which uses a dense polymeric membrane as a separation barrier between the liquid feed and permeant vapor. It has been the object of numerous experimental and theoretical investigations over the past several years.^{1–5} The method is usually employed for the separation of azeotropes⁶ and isomers⁷ and for the removal or recovery of trace substances.⁸ Recently, interest has arisen on the application of the pervaporation process for the separation of organic mixtures in industrial processes.^{9,10}

Many interesting studies have been reported on the use of elastomeric membranes for pervaporation processes. For example, Lamer et al.¹¹ used a silicon membrane to extract aroma compounds from dilute aqueous solutions. A resistance-in-series model was used by them to describe the flux of organic compounds through the membrane. Duval et al.¹² investigated the separation properties of dense polymeric membranes to-

ward a mixture of toluene and acetone. They found that the separation properties of the membranes were improved by introducing various active carbons and zeolites into a thin polymeric film to form a heterogeneous membrane. Nijhuis et al.¹³ used a wide range of homogeneous elastomeric membranes for the removal of volatile organics from water. They related permeation and sorption data obtained for the elastomers to the chemical and physical nature of the elastomers through the solubility parameter and the glass transition temperature, respectively. They attributed the differences in the permeability of the organic component through the membrane to structural parameters in the membrane material such as the degree of unsaturation and the presence of steric side groups. Dinh et al.¹⁴ studied the transport of an ethanol/water mixture through ethylene–vinyl acetate (EVA) membranes. They observed that for a membrane with 37% vinyl acetate content ethanol permeability increased with ethanol activity in the membrane while the water permeability decreased with water activity. Lee et al.¹⁵ examined the permeation of steroids through poly(ether urethane) and EVA.

Natural rubber (NR) is one of the important

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Table I Formulation of the Mixes (phr)

Ingredients	Mixes			
	CV	EV	DCP	Mixed
Natural rubber	100	100	100	100
Stearic acid	1.5	1.5	—	1.5
Zinc oxide	5	5	—	5
MOR	0.6	—	—	0.6
TMTD	—	1	—	—
CBS	—	1.5	—	—
Dicumyl peroxide	—	—	4	1.5
Sulfur	2	0.6	—	1.5

phr, parts per hundred rubber; MOR, morpholine benzothiazyl sulfenamide; TMTD, tetramethyl thiuram disulfide; CBS, *N*-cyclohexyl-2-benzothiazyl sulfenamide.

elastomers widely used in several industrial and engineering applications. To the best of our knowledge, no systematic study has yet been carried out to explore the possibility of utilizing NR for the separation of organic liquid mixtures. The present work dealt with the pervaporation separation of mixtures of *n*-hexane and acetone of different compositions using NR membranes. The effects of feed composition, vulcanizing agents, and cure time of the membranes and the molecular size of the permeate on the separation process were examined.

EXPERIMENTAL

The NR used was of ISNR-5 grade supplied by the Rubber Research Institute of India, Kottayam, India. The solvents used were of 99.5% purity. They were double-distilled before use. The rubber ingredients used were of laboratory reagent grade.

Preparation of NR Membranes

Membranes out of NR were fabricated by using four vulcanizing systems, viz., conventional (CV), efficient (EV), peroxide (DCP), and a mixture consisting of sulfur and peroxide (mixed). The basic formulation of the mixes is given in Table I. The different ingredients were incorporated into the rubber using a two-roll mixing mill (friction ratio 1 : 1.4). The vulcanization behavior of the rubber specimen was studied by a Monsanto Rheometer-R100 at a rotational frequency of 100 cycles/min. The curing of rubber samples was done in such a way that all of them develop the same rheometric torque of 33.8 dNm as shown in Figure

1. This was done to minimize the differences in the magnitude and distribution of crosslinks in the membranes. The curing was done on a hydraulic press at 160°C and under a pressure of 30 tonnes. The average thickness of the membranes was 100 μm .

Swelling Characteristics

The swelling behavior of the membranes was assessed by immersing them separately in mixtures of *n*-hexane and acetone of different compositions at 28°C for 72 h. After reaching equilibrium, the membranes were taken out from the mixtures, their surfaces wiped with a filter paper, and then they were weighed immediately in an elec-

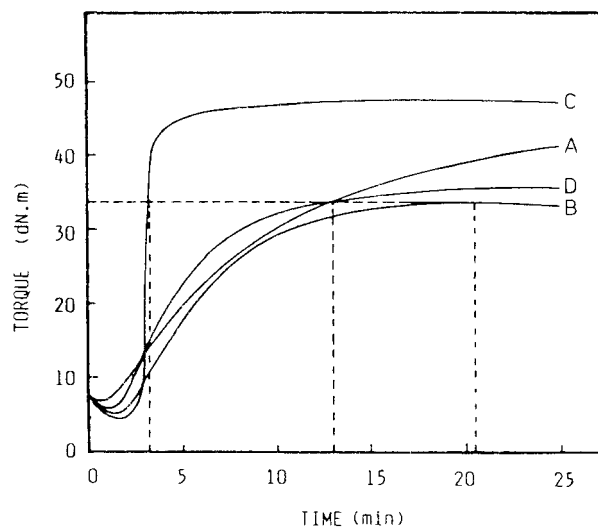


Figure 1 Rheographs indicating the curing of NR samples to a common torque of 33.8 dN m: (A) DCP; (B) CV; (C) EV; (D) mixed.

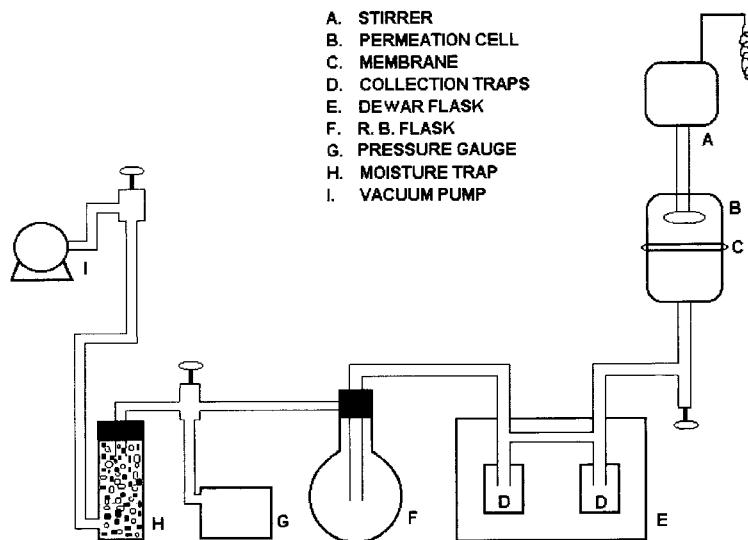


Figure 2 Pervaporation apparatus.

tronic balance that measured reproducibly within ± 0.0001 g. The swelling ratio (S) was determined as

$$S = \frac{W_s - W_d}{W_d} \quad (1)$$

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

Pervaporation Experiments

A schematic representation of the pervaporation apparatus is given in Figure 2. The membrane was placed in between the two compartments of the permeation cell. The effective surface area of the membrane was 19.4 cm^2 . The capacity of the upper compartment of the permeation cell was 150 mL. A constant downstream pressure of 3.5–4 Torr was applied throughout the process. The permeated vapors were condensed in traps dipped in dry ice–acetone mixture. The experiments were conducted at ambient temperature. The feed and permeate compositions were analyzed by gas liquid chromatography.

RESULTS AND DISCUSSION

The plots of swelling ratio vs. feed composition for the membranes vulcanized by the four systems, viz., CV, EV, DCP, and mixed, are given in Figure

3. It is seen that the swelling ratio increases with increase in the concentration of *n*-hexane in the feed. This clearly indicates the preferential affinity of the membranes toward *n*-hexane than toward acetone. Of the four systems, the swelling ratio increases in the order $\text{DCP} < \text{EV} < \text{mixed} < \text{CV}$. To obtain additional information, the molecular mass between crosslinks (M_c) of the membranes was determined by the Flory–Rehner equation¹⁶:

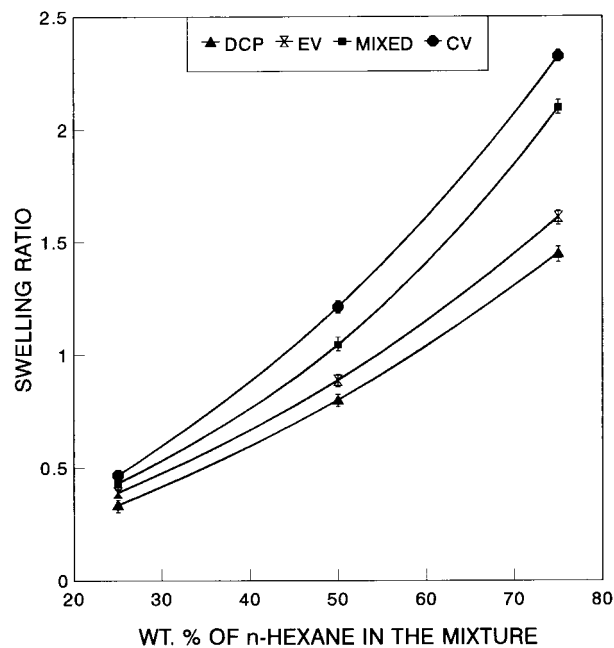


Figure 3 Variation of swelling ratio with the wt % of *n*-hexane in the feed.

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

where ρ_p is the density of rubber; V , the molar volume of the solvent mixture; ϕ , the volume fraction of rubber in the swollen membrane; and χ , the rubber-solvent interaction parameter determined by a method suggested by Aithal et al.¹⁷ The M_c values were used to compute the degree of crosslinking (ν) as $1/2M_c$. The ν values for DCP, EV, mixed, and CV membranes, in a 50/50 mixture of *n*-hexane and acetone, are 8.31×10^{-5} , 7.48×10^{-5} , 5.18×10^{-5} , and 3.61×10^{-5} g mol/cc, respectively. This clearly indicates that the membrane vulcanized by DCP has the highest degree of crosslinking, and that by the CV technique, the lowest. Since the degree of crosslinking and swelling ratio are inversely related, the differences in the swelling behavior of the four types of membranes can be attributed to the different degrees of crosslinking in them. However, Morrison and Porter¹⁸ showed that the crosslink density accounts for only a part of the swelling nature of macromolecular networks. Another major factor controlling the swelling behavior is the nature of crosslinks between the rubber chains of the membranes. This will be discussed later in this article.

The effect of feed composition on the pervaporation performance for the DCP membrane is given in Figure 4. It is seen that the permeation rate

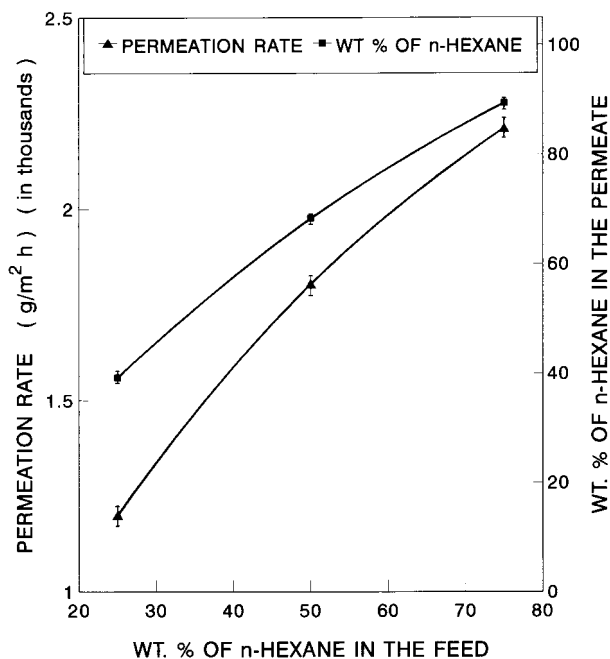


Figure 4 Pervaporation performance of DCP membrane.

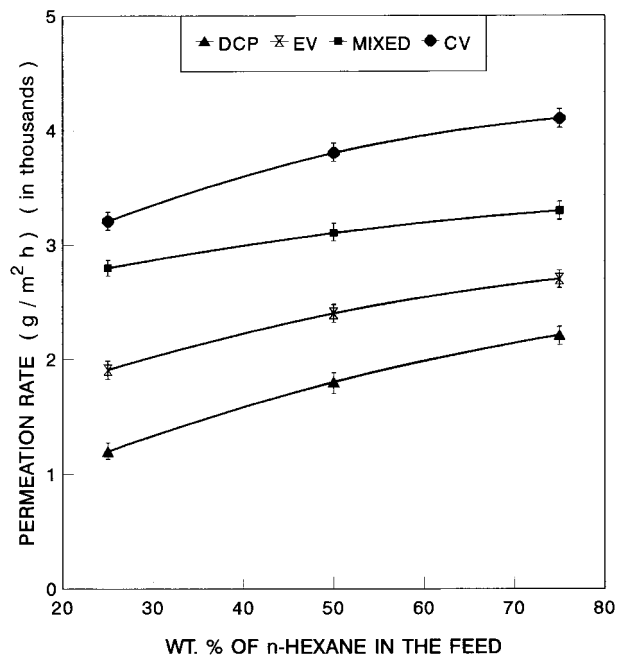


Figure 5 Effect of vulcanizing systems on the permeation rate of *n*-hexane/acetone mixture of different compositions.

through the membrane increases with increase in the concentration of *n*-hexane in the feed. This is due to the strong interaction between NR and *n*-hexane owing to the closer solubility parameter values. [The solubility parameter values of NR, *n*-hexane, and acetone are 16.2, 14.9 and 20.3 (J/m³)^{1/2}, respectively.] This interaction effectively increases the frequency and amplitude of rubber chain motions, thereby allowing the permeate molecules to pass through the membrane easily. It is also shown in Figure 4 that the wt % of *n*-hexane in the permeate increases as its concentration in the feed increases.

Figure 5 shows the variation of permeation rate as a function of wt % of *n*-hexane in the feed for the four types of membranes. It is seen that the membrane vulcanized by DCP, with the highest degree of crosslinking, exhibits the lowest flux, while that cured by CV shows the highest. These observations parallel the decrease in the values of swelling ratio which increase in the order DCP < EV < mixed < CV. However, as pointed out earlier, in addition to the degree of crosslinking, the nature of crosslinks also contribute to the permeation flux and selectivity of the membranes. The structure of the networks formed by the different vulcanization techniques¹⁹ is shown in Figure 6. The membrane vulcanized by the CV technique has predominantly polysulfidic linkages,

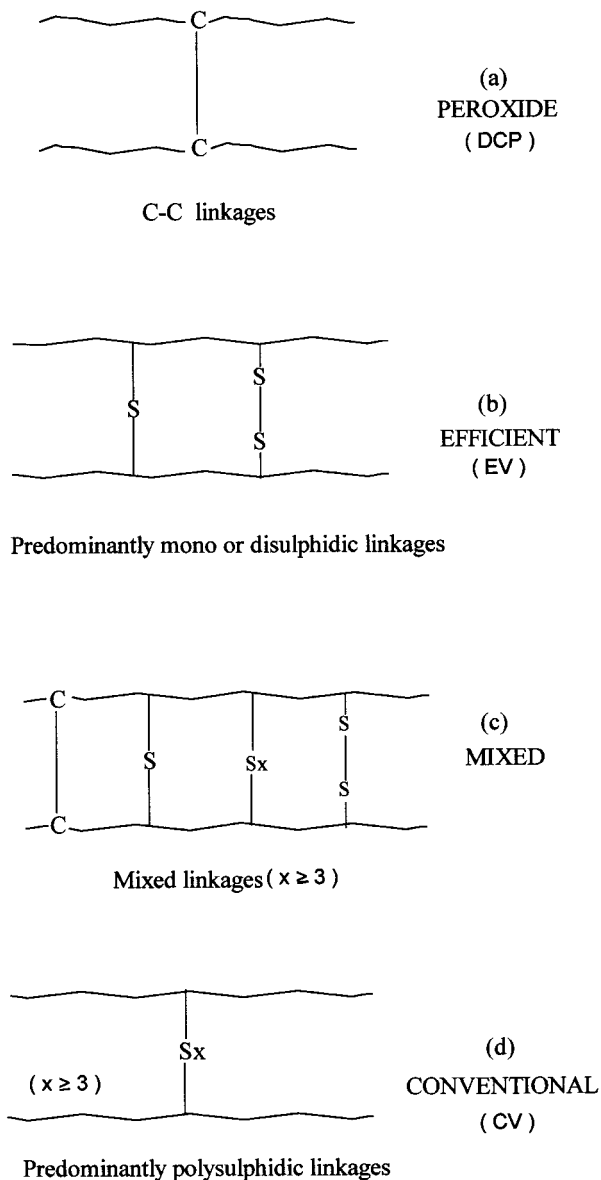


Figure 6 Structure of the networks formed by different vulcanization techniques.

with at least three sulfur atoms, between adjacent rubber chains. The presence of C—S (1.81 Å) and many S—S (1.88 Å) bonds between the macromolecular structure makes the rubber network relatively flexible. In other words, the rigidity of the three-dimensional rubber structure is decreased due to the presence of polysulfidic linkages. The flexible network of the CV membrane allows the passage of permeate molecules to be relatively easy. The membrane vulcanized by the mixed formulation also has polysulfidic linkages. The EV membrane has only mono- or disulfidic linkages between the rubber chains. The shorter crosslinks formed here bring the rubber chains

closer and thereby reduce the free volume. The DCP membrane has stable C—C (1.54 Å) linkages between the rubber chains which effectively reduces the flexibility of the network.

To determine the influence of the molecular weight of the predominantly permeating species on the separation process, mixtures of *n*-heptane/acetone and *n*-octane/acetone were also used as feed in the permeation cell. Figure 7 shows the pervaporation of 50/50 mixtures of *n*-hexane, *n*-heptane, and *n*-octane, all belonging to the same homologous series, with acetone through the four types of membranes. It is seen that the flux decreases as the molecular weight of the preferentially permeating species increases. This is in quantitative agreement with our expectation that the low molecular weight species diffuse more easily through a compatible medium. Figure 8 represents the decrease in the wt % of the three aliphatic hydrocarbons in the permeate with increase in their molecular weight.

Another significant parameter controlling the separation process was found to be the cure time of the membranes. The increase in vulcanization time increases the number of crosslinks between rubber chains, thereby enhancing the rigidity of the macromolecular network. This, in turn, reduces the flux through the membrane but enhances the separation efficiency as shown in Figures 9 and 10.

Figure 11 shows the effect of membrane thick-

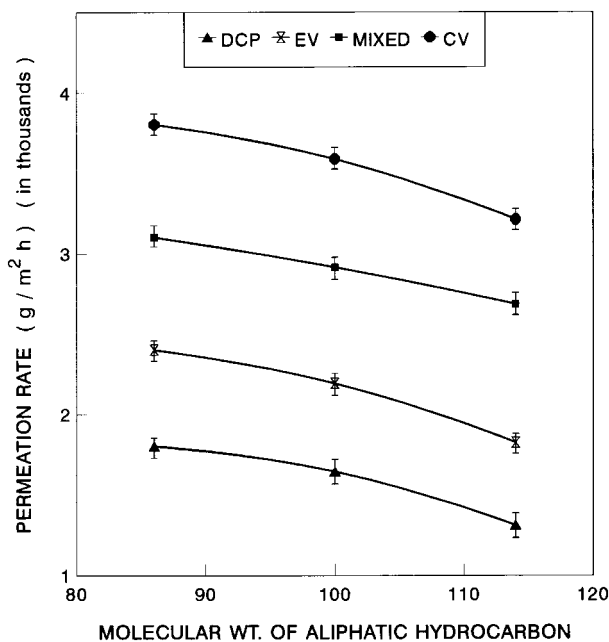


Figure 7 Effect of molecular weight of aliphatic hydrocarbons on permeation rate.

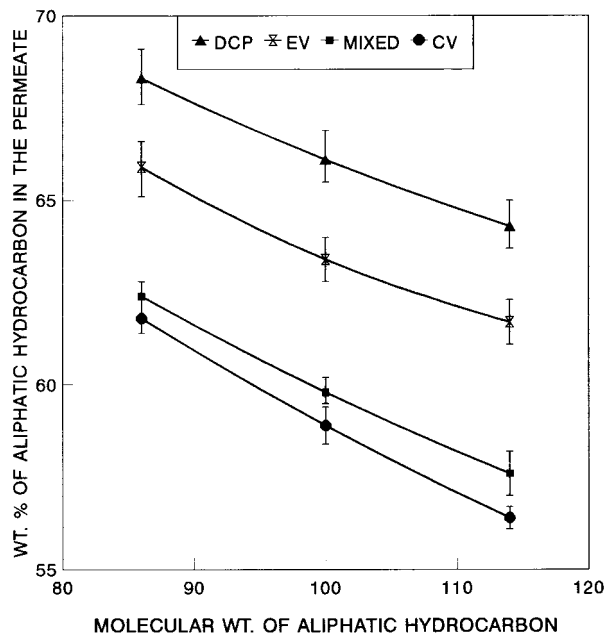


Figure 8 Variation of wt % of *n*-hexane in the permeate with molecular weight of aliphatic hydrocarbons.

ness on the permeation behavior of 50/50 *n*-hexane/acetone mixture through the DCP membrane. It is seen that the separation efficiency is independent of the thickness of the membrane but the permeation flux decreases with increase in the thickness of the membrane.

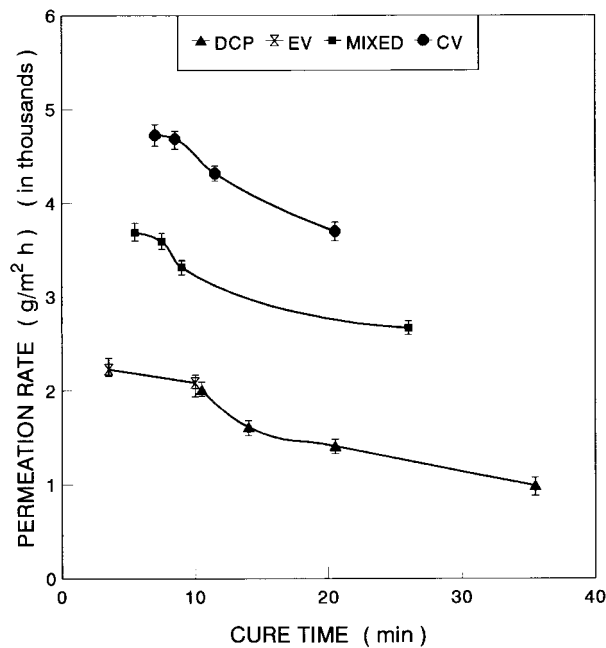


Figure 9 Effect of cure time on permeation rate through NR membranes.

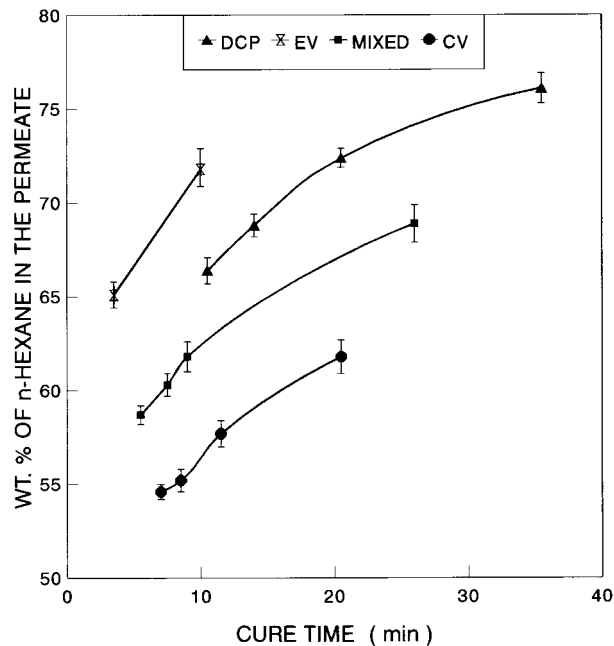


Figure 10 Effect of cure time on separation efficiency of NR membranes.

CONCLUSION

The feasibility of a pervaporation technique for the separation of mixtures of *n*-hexane and acetone using natural rubber membranes, vulcanized by four different systems, was investigated. It is ob-

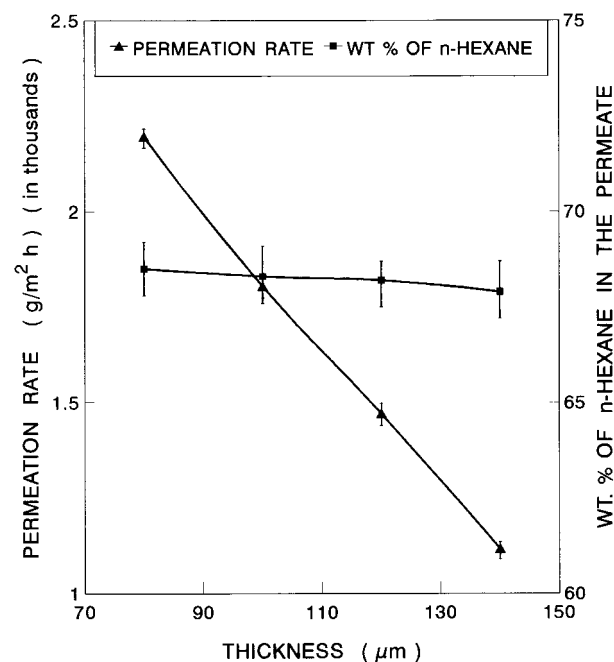


Figure 11 Effect of thickness of DCP membrane on permeation rate.

served that the membranes exhibit permselectivity toward *n*-hexane, due to the closer solubility parameter values. The pervaporation efficiency increases with increase in the concentration of *n*-hexane in the feed. Of the four vulcanizing systems, the membrane vulcanized by DCP exhibits the highest separation efficiency. The differences in the pervaporation efficiency of the membranes was explained in terms of the different degrees of crosslinking as well as the different physicochemical nature of the crosslinks in them. The flux through the membranes was found to decrease with increase in the molecular weight of the predominantly permeating species. The cure time of the membranes and the separation efficiency was found to be directly related. The selectivity of the membranes appears to be independent of their thickness while the flux decreases with increase in membrane thickness.

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