

# Nonequilibrium Nanoblend Membranes for the Pervaporation of Benzene/Cyclohexane Mixtures

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**ABSTRACT:** Immiscible blends of polymers were cast from solution, and the rate of evaporation was controlled relative to the rate of phase separation to produce different morphologies; upon crosslinking, stable nonequilibrium nanoblends were realized. This process of forced assembly produced useful membrane materials that could be designed for solubility selectivity with the group contribution methodology. Crosslinked ternary blends of nitrile butadiene rubber (NBR), poly(methyl methacrylate) (PMMA), and a tercopolymer of ethylene oxide/epichlorohydrin/allyl glycidyl ether (Hydrin) were examined for use in the separation of benzene from cyclohexane by pervaporation. For a 50 : 50 wt % benzene/cyclohexane feed, blend 811 (containing 80 wt % NBR, 10 wt % Hydrin, and

10 wt % PMMA) gave a separation factor of 7.3 and a normalized flux of 28 kg  $\mu\text{m}^2$  h; such a performance is unmatched in the literature, with the flux being very high for the reported separation factor. Among the samples tested, the flux of the membrane increased as the amount of NBR in the ternary blend decreased; however, the separation factor was not largely affected. Blended samples showed no sign of deformation after 48 h at the operating temperature as compared to pure NBR, which did show evidence of creep. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2917–2922, 2008

**Key words:** blends; crosslinking; elastomers; membranes; separation techniques

## INTRODUCTION

The separation of aromatic–aliphatic mixtures is considered to be of significant importance in the chemical and petrochemical industries. Within the aromatic–aliphatic class of separations, the benzene–cyclohexane system poses a major problem for separation with conventional distillation.<sup>1</sup> The separation of azeotropic and close-boiling-point mixtures is a major issue when distillation is used because it depends on the relative volatility of the components. The benzene–cyclohexane mixture is a classical example of such a mixture, with a pure component boiling point difference of 0.6°C and the formation of an azeotrope. The use of a third component to split the azeotropes creates unwanted complexity and cost; the added component must be removed, and additional energy is required. These identified problems can be eliminated with pervaporation. In pervaporation, separation is dependent on the preferential permeation of the mixture components through a membrane rather than the relative volatilities. Membrane-based pervaporation is an attractive alternative for benzene–cyclohexane separations

because of its relatively low energy consumption and its capacity to break the azeotrope.

Various polymeric materials have been investigated as potential membrane candidates for the development of pervaporation for organic–organic separations.<sup>2–18</sup> Although some progress has been made, efforts are still being directed toward the development of robust materials (exhibiting chemical, thermal, and mechanical stability) with optimum performance in terms of separation factor and flux. Kusumocahyo et al.<sup>4</sup> conducted studies on the separation of benzene/cyclohexane mixtures, using a dinitrophenyl group containing a cellulose acetate (CA) membrane. A high separation factor ( $\alpha$ ) of 103 was reported for a 50 : 50 wt % mixture with the modified CA compared to a separation factor of 65 reported for the unmodified CA. However, both the modified and unmodified CA membranes exhibited extremely low permeations of 0.01 kg  $\mu\text{m}^2$  h<sup>-1</sup>. Pandey et al.<sup>19</sup> investigated the pervaporation performance of chemically modified poly(vinyl alcohol) and morphologically modified poly(vinyl alcohol) membranes. The modified membrane exhibited a higher benzene flux than the unmodified membrane. Studies have been conducted on the applications of acrylate-based polymers,<sup>6</sup> the methacrylate family of polymers,<sup>11</sup> polyimides,<sup>16,17,20</sup> poly(vinylidene fluoride),<sup>21</sup> and nylon 6,<sup>22,23</sup> just to name a few, for

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organic mixture separation. A comprehensive review of the current state of the art and the current trends for industrial pervaporation was done by Smitha et al.<sup>3</sup>

The use of polymer blends in the development of membranes for pervaporation applications has been studied by various researchers.<sup>7-9,24</sup> Blends are attractive as a means of tailoring material properties because they offer a wide range of functionality that allows material designs for specific applications.<sup>25</sup> Synthesizing new polymers requires extra time and is more expensive than blending commercially available polymers. Polymer blends can be easily fabricated, and homopolymers and copolymers with one or more desired properties are readily available. Synergistic effects on the combined properties of individual polymers are obtained in blends, and composition can be tailored or tuned for specific applications. The use of binary blends has received significantly more attention than ternary blends for membrane applications; this fact can be attributed to the difficulty involved in the production of miscible ternary blends. Although the ternary blends are more complex, the potential for discovering useful products is enhanced by the extra compositional degree of freedom relative to binary materials.<sup>26</sup> For example, Dorgan and Nam<sup>7</sup> investigated a ternary blend of a nitrile butadiene rubber (NBR) copolymer with 18% acrylonitrile (AN), styrene-butadiene rubber copolymer, and poly(vinyl chloride).

Elastomers are a group of polymers that offer a wide range of solubility and functionality for membrane-based separations.<sup>3</sup> Noticeable among this group of polymers are NBR, styrene-butadiene rubber copolymer, and poly(epichlorohydrin). The major limitations to the wide applications of elastomers are their thermal stability and mechanical strength when they are exposed to harsh conditions. Blending has been explored as a means of improving the properties of elastomers.<sup>7,27-34</sup>

In this study, a new membrane material comprised of ternary blends of NBR, Hydrin T3106 (a terpolymer of ethylene oxide/epichlorohydrin/allyl glycidyl ether, hereafter referred to as Hydrin), and poly(methyl methacrylate) (PMMA) was investigated for use in the separation of benzene-cyclohexane mixtures by pervaporation. Experiments were conducted over a range of benzene concentrations of 0-100 wt % at 60°C. The permeation properties, the mechanical strength and chemical resilience were enhanced through crosslinking. This study illustrated that through the proper choice of elastomers reinforced with a high glass-transition temperature ( $T_g$ ) polymer (with good mechanical integrity and an affinity for aromatics), excellent performance with respect to robustness, separation factor, and flux can be obtained.

## EXPERIMENTAL

Conceptually, many choices are available for rubbery blends. In this study, the membrane system chosen consisted of ternary blends of AN butadiene rubber copolymer (NBR), Hydrin, and PMMA. The NBR used had an AN content of 50 wt %. NBR and Hydrin were provided by Nippon Zeon Chemicals (Tokyo, Japan), and PMMA homopolymer was purchased from Aldrich Chemical Co. (St. Louis, MO). Benzene and cyclohexane (both spectroscopy grade), which were used for the feed mixtures, were also purchased from Aldrich and were used as received.

NBR (50% AN), Hydrin, and PMMA were used for the ternary blends of this study. NBR and Hydrin are known to be excellent organic solvents and possess good heat resilience; they were used here to control the permeant solubility and, thus, prevent excessive swelling of the membrane to preserve selectivity. PMMA is a highly polar, rigid and hard material and also has good heat resistance. The rigidity and hardness of PMMA helped to improve the mechanical properties of the blend. PMMA has a solubility parameter that is closer to that of benzene than cyclohexane; benzene has greater solubility in PMMA than cyclohexane, and therefore, its addition to the blend was expected to further increase the selectivity.<sup>24</sup> The chemical structures of these polymers are shown in Table I.

Membranes were prepared by solution casting from cyclohexanone solutions containing a total of 10 wt % of a blend of known composition. Blend samples are designated numerically as parts NBR, Hydrin, and PMMA. For example, 721 represents the blend containing 70 wt % NBR, 20 wt % Hydrin,

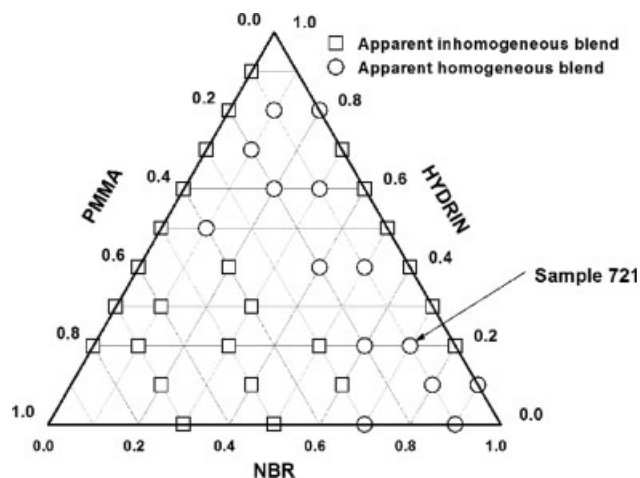
TABLE I  
Chemical Structures of NBR, Hydrin, and PMMA

Name	Chemical structure
NBR	$\left[ \text{---} \underset{\text{H}_2}{\text{C}} \text{---} \underset{\text{H}}{\text{C}} = \text{CH} \text{---} \underset{\text{H}_2}{\text{C}} \text{---} \right]_x \left[ \text{---} \underset{\text{H}_2}{\text{C}} \text{---} \underset{\text{H}}{\text{C}} \text{---} \right]_y$ $\text{C} \equiv \text{N}$
Hydrin	$\left[ \text{---} \underset{\text{H}_2}{\text{C}} \text{---} \underset{\text{CH}_2}{\text{CH}} \text{---} \text{O} \text{---} \underset{\text{H}_2}{\text{C}} \text{---} \underset{\text{H}_2}{\text{C}} \text{---} \text{O} \text{---} \right]_x \left[ \text{---} \underset{\text{H}_2}{\text{C}} \text{---} \underset{\text{H}}{\text{C}} \text{---} \text{O} \text{---} \right]_y$ $\text{Cl}$ $\text{CH}_2$ $\text{O}$ $\text{CH}_2$ $\text{HC} = \text{CH}_2$
PMMA	$\left[ \text{---} \underset{\text{H}_2}{\text{C}} \text{---} \underset{\text{CH}_3}{\text{C}} \text{---} \right]_x$ $\text{C} = \text{O}$ $\text{H}_3\text{CO}$

and 10 wt % PMMA. For blends that were cross-linked with sulfur as a crosslinking agent, activator (zinc oxide) and accelerator (dibenzothiazyl disulfide) were added to the solution. Sulfur-crosslinked blends contained 2.5 wt % sulfur and 1 wt % of each of zinc oxide and dibenzothiazyl disulfide. Blends crosslinked with peroxide contained 3 wt % dicumyl peroxide. The percentage used for the crosslinking agent concentrations was based on the total rubber content in the blend. The resulting solution was cast onto a clean  $7 \times 7$  in.<sup>2</sup> float glass plate that had been carefully shimmed to be as level as possible and subsequently dried in a fume hood for approximately 1 day (16–24 h). Before the solution was cast, masking tape was applied to the edges of the glass plate, which created a border around the perimeter of the plate. The number of layers of masking tape applied to the edges was varied to obtain the desired film thickness; for all of the membranes reported in this article, eight layers of masking tape were applied to the glass plate edges. We controlled the solvent evaporation to obtain an evenly distributed film thickness by covering the glass plate with an aluminum pan, perforated at the sides. In the case of sulfur crosslinking, cast membrane films were cross-linked in a forced conventional oven at 130°C for 24 h. Peroxide crosslinking was conducted in a vacuum oven at 130°C for 3 h. The membrane thickness was maintained in the range 150–200  $\mu\text{m}$  as determined by measurements with calipers.

Before choosing blend compositions for membrane preparation, we observed films of over 30 samples with different compositions using optical microscopy to determine regions of apparent blend miscibility and immiscibility. Differential scanning calorimetry (DSC) experiments were performed on the dry membrane blends, approximately 20 mg by weight, sealed in aluminum pans. A PerkinElmer (Waltham, MA) DSC 7 instrument was used in these experiments. Samples were conditioned by heating from  $-80$  to  $140^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ ; samples were then held at  $140^\circ\text{C}$  for 5 min and subsequently cooled to  $-80^\circ\text{C}$  and held at this temperature for 5 min. Thermograms were recorded on the second heating from  $-80$  to  $140^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . The  $T_g$  for each of the blends was determined with the half- $C_p$  (specific heat capacity) method for the calculation of  $T_g$ . Information obtained from microscopy and DSC was used to construct an operational ternary phase diagram, which is shown in Figure 1. This diagram does not represent the equilibrium phase diagram but rather the outcome from the controlled evaporation processing; this is the meaning of an operational phase diagram: a single phase in this case refers to material blends that upon casting and crosslinking exhibited a single  $T_g$ .

Pervaporation experiments were carried out with laboratory scale equipment consisting of a Millipore



**Figure 1** Ternary phase diagram for the blends of NBR (50% AN), Hydrin, and PMMA obtained from optical microscopy analysis.

(Billerica, MA) membrane holder (with an effective membrane area of  $13.8 \text{ cm}^2$  in contact with the feed liquid). The feed liquid was continuously circulated from and returned to a 3-L reservoir maintained at  $60^\circ\text{C}$ . The downstream pressure was maintained below 2 Torr, typically at about 1.5 Torr. After an equilibration period of at least 2 h, the permeate was collected at constant time intervals by means of freezing in the glass cold finger cooled by submersion in a liquid-nitrogen-filled Dewar. Analysis of the feed and permeate compositions was performed by gas chromatography/mass spectrometry (Agilent, Santa Clara, CA, GC-MS G2570A) and was checked by simple refractive index measurements.

Membrane performance was characterized by the separation factor ( $\alpha$ ) and permeation rate or flux. The separation factor and permeation rate are defined in the usual manner as follows:

$$\alpha = \frac{w_{P,\text{Benzene}}/w_{P,\text{cyclohexane}}}{w_{F,\text{Benzene}}/w_{F,\text{cyclohexane}}} \quad (1)$$

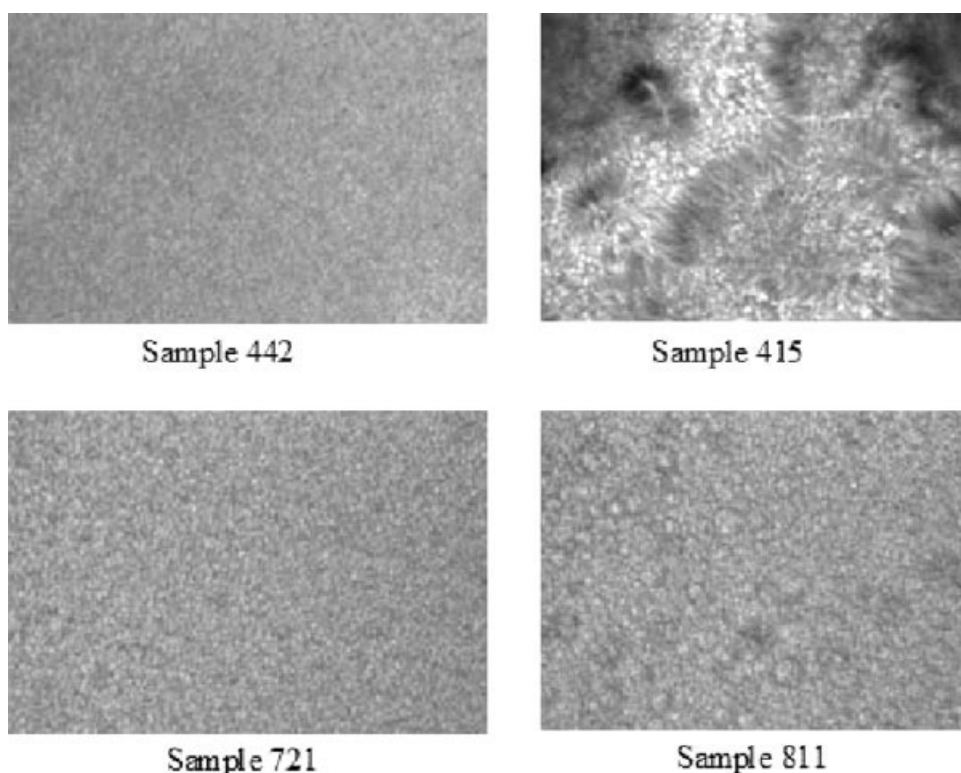
$$Q = \frac{q \times L}{A \times t} \quad (2)$$

where  $w_{P,i}$  is the weight fraction of component  $i$  in the permeate,  $w_{F,i}$  is the weight fraction of component  $i$  in the feed,  $Q$  is the normalized flux or permeation rate, and  $q$ ,  $L$ ,  $A$ , and  $t$  represent the mass of collected permeate (g), the membrane thickness ( $\mu\text{m}$ ), membrane area ( $\text{m}^2$ ), and operating time (h), respectively.

## RESULTS AND DISCUSSION

Optical microscopy and DSC were used to analyze the blend characteristics. The microstructure of the polymer blend was observed with optical micros-





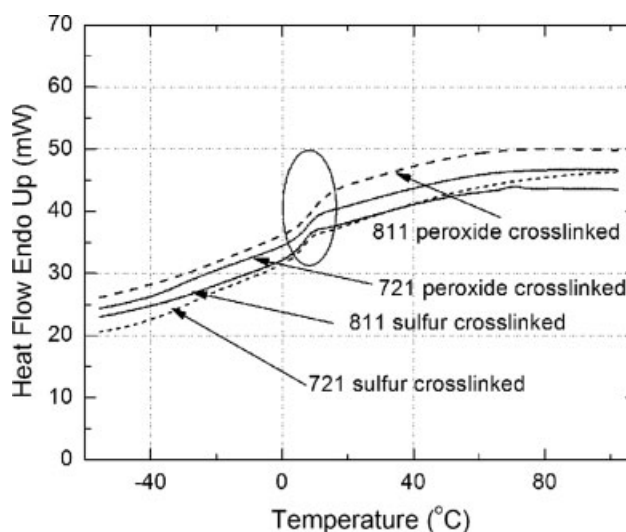
**Figure 2** Sample morphology taken with optical microscopy with a magnification of 20 $\times$ .

copy; a continuous (homogeneous) microstructure was taken to be an indication of miscibility and vice versa. The ternary diagram showing the apparent miscible and immiscible regions is shown in Figure 1. Additionally, Figure 2 shows that samples 442, 721, and 811 were apparently miscible, as evidenced by the continuous surface microstructure, in contrast to the nonhomogeneous nature of sample 415. Figure 3 shows the DSC curves for samples 721 and 811, which exhibited a single transition region. If a blend exhibited a single  $T_g$  in the DSC experiment, it was considered miscible. Because the films were cast from solution and may have been vertically trapped, the operational definition associated with the phase diagram was based on the existence of a single  $T_g$ .

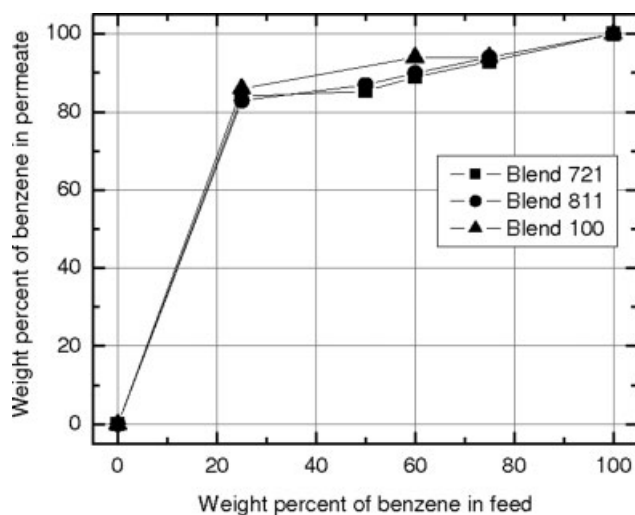
In Figure 4, the permeate concentration of the membrane samples 721, 811, and 100 (sulfur-crosslinked) is shown as a function of the benzene concentration in the feed. As expected, the benzene composition in the permeate increased with increasing benzene composition in the feed. Sample 100 (pure NBR) gave better performance with respect to separation factor (better enrichment) than the other samples. However, the extent was minor.

Figure 5 illustrates the effect of feed composition on the permeation rate. A significant increase in permeability was observed with increasing feed composition. There was a significant difference between the

fluxes obtained for the different membrane samples compared to the slight difference observed for permeate composition. The membrane sample with 70 wt % NBR showed greater flux over samples with 80 and 100 wt % NBR. This suggests that the reduction in NBR content in the blend and the concurrent increase in Hydrin content enhanced the flux as



**Figure 3** DSC curves for samples 721 and 811 indicating homogeneous samples by the presence of a single  $T_g$ .

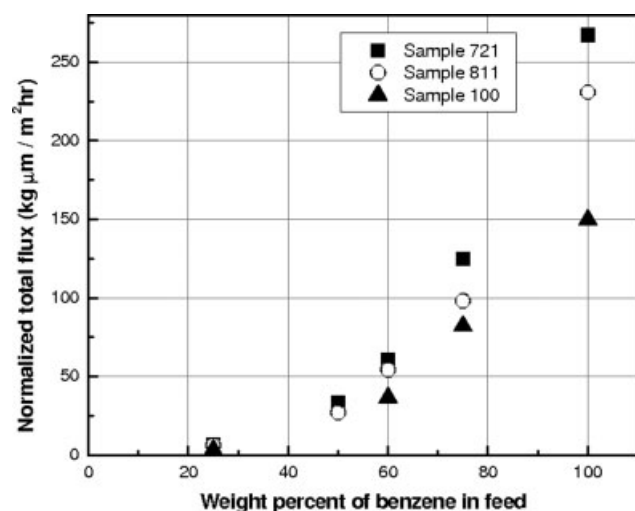


**Figure 4** Effect of the benzene composition (wt %) in the feed on the composition (wt %) of benzene in the permeate for the sulfur-crosslinked blends.

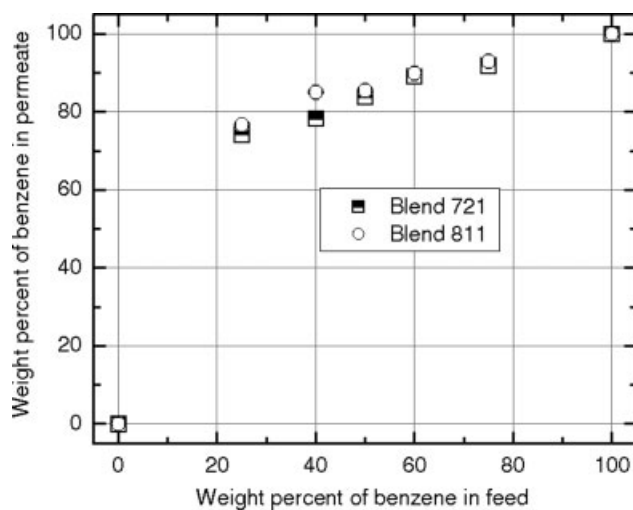
compared to NBR alone without significant decreases in separation factor.

In Figure 6, the effect of feed concentration on the permeate composition for samples crosslinked with dicumyl peroxide is illustrated. The results show similar trends to that of the sulfur-crosslinked samples but with a slight decrease in benzene composition in the permeate.

Figure 7 shows how the permeation rate for peroxide-crosslinked samples changed with benzene composition in the feed. The flux again increased with increasing benzene composition in the feed. The normalized fluxes obtained over the entire composition range were lower than the ones obtained for the



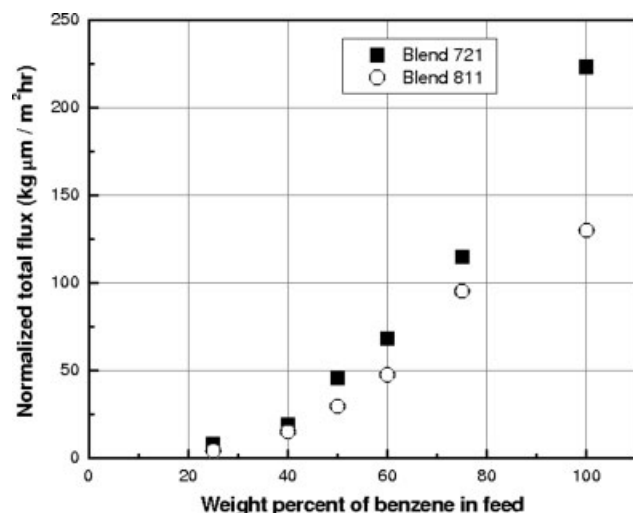
**Figure 5** Effect of the benzene composition (wt %) in the feed on the normalized total flux for the sulfur-crosslinked blends.



**Figure 6** Effect of the benzene composition (wt %) in the feed on the composition (wt %) of benzene in the permeate for the peroxide-crosslinked blends.

sulfur-crosslinked samples shown in Figure 5. The lower flux obtained for the peroxide systems could be explained by the fact that peroxide is a more effective crosslinking agent.<sup>32</sup> The reduced flux implies a greater crosslinking density.

The increase in flux obtained as a result of the change in NBR content from 80 to 70 wt % and the increase in Hydrin content in the blend could be ascribed to the preferential permeation of benzene through the ethylene oxide and ether segments present in the Hydrin terpolymer chain. Tanihara et al.<sup>10</sup> observed this type of permeation associated with the poly(ethylene oxide) segment in poly(ether imide) segmented copolymers. The ethylene oxide segment was highly hydrophilic and thus contributed to the



**Figure 7** Effect of the benzene composition (wt %) in the feed on the normalized total flux for the peroxide-crosslinked blends.

high polarity of Hydrin and thereby created more affinity for benzene than for cyclohexane. Also, the decrease in the NBR composition in the blend implies that the rigidity offered by the AN content was substituted with more flexible chains as available in Hydrin, this could have caused an increase in the permeability of the penetrants.

On the basis of the membrane performance of the NBR/Hydrin/PMMA ternary blends presented here, it is evident that such blends of elastomers reinforced with a thermoplastic could provide a great means of tailoring membrane performance for targeted applications. Elastomers offer a wide range of solubility and functionality; these characteristics can be explored for separations advantage. The ternary blend membranes reported in this article have not been applied to any other mixture apart from the benzene–cyclohexane separation discussed herein; nonetheless, they should be applicable to mixtures that can be characterized as aromatic/nonaromatic mixtures.

### CONCLUSIONS

Ternary blends of two elastomers and a thermoplastic polymer with a higher  $T_g$  were capable of giving good separation factor and fluxes at elevated temperatures for the separation of benzene/cyclohexane mixtures by pervaporation. For a 50 : 50 wt % benzene/cyclohexane feed at 60°C, blend 811, containing 80 wt % NBR, 10 wt % Hydrin, and 10 wt % PMMA, gave a separation factor of 7.3 and a normalized flux of 28 kg  $\mu\text{m}^{-2} \text{h}^{-1}$ . Permeate analyses showed that the benzene/cyclohexane azeotrope could be split to greater than 85 wt % benzene in the permeate with much improved fluxes. The permeation flux and separation factor for the NBR/Hydrin/PMMA blend showed strong dependence on the composition of benzene in the feed and also on the blend composition of the membrane. Also, benzene permeation was observed to be favored over that of cyclohexane. The permeation results show that the design of rubbery blends with controlled permeation characteristics is a promising approach to the development of materials for pervaporation applications.

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