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Yunil Hwang^a; Janos Szamosi^a; Singa D. Tobing^b

^a Department of Chemistry, Western Illinois University, Macomb, Illinois ^b Chemical Engineering Department, Lehigh University, Bethlehem, Pennsylvania

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Enhanced Permeation Resistance in NBR/BIIR Composite Membranes¹

YUNIL HWANG and JANOS SZAMOSI†

Department of Chemistry, Western Illinois University, Macomb, Illinois 61455

SINGA D. TOBING

Chemical Engineering Department, Lehigh University, Bethlehem, Pennsylvania 18015

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Permeation-resistance and mechanical-property measurements were carried out on NBR/BIIR membranes. It was found that, in addition to good tensile strength and ultimate elongation, the composites exhibited better permeation resistance against benzene and methylethyl ketone than the pure elastomers. An explanation based on synergetics is offered, namely the observed improvement may be due to interaction effects.

KEY WORDS Membrane, permeation, breakthrough time, synergetics.

In recent years, there have been several studies on the chemical, mechanical, rheological and surface properties of polyacrylonitrile-butadiene (nitrile butadiene rubber; NBR) and brominated polybutylene-butadiene (bromobutyl rubber; BIIR), in order to determine their applicability for flexible protective coatings.^{2–8} We have focused our efforts on the identification of fundamental structure-property relationships: NBR is a polar elastomer; its polarity, as well as its resistance to hydrocarbons, increases with nitrile content. BIIR being apolar is resistant to polar solvents. Even though the latter contains only a small amount of bromine, it is also highly resistant to sunlight, aging and the passage of most gases, unlike butyl rubber (IIR).

Since a single elastomer cannot provide protection against different kinds of permeants, we decided to evaluate composite membranes made of covulcanized layers of NBR and BIIR.

EXPERIMENTAL

The base polymer, 100 parts NBR (BF Goodrich) or BIIR (Polysar), and 50 phr hydrated silica were blended with ZnO, stearic acid, antioxidant, plasticizer,

† To whom to address correspondence: Union Camp R&D, Box 3301, Princeton, NJ 08543.

accelerator and vulcanizing agent (exact composition and brand names are confidential), using a Farrell 6"-13" two-roll mill. A Lighthin air-driven mixer (Series 30) was employed for the preparation of 20 wt% solutions using a solvent blend containing toluene and MEK 4:1. Bentonite (1%) was added to the solution to increase viscosity. A silicon/silica-based defoamer was introduced to reduce foaming. After two hours vigorous stirring, the solutions were allowed to stand at room temperature in order to attain equilibrium. Uniform and composite films were made by dipping glass plates into the solutions four times; we made membranes with four layers of NBR (NNNN), four layers of BIIR (BBBB), two layers of each (NNBB), and alternating layers (NBNB). As a control, a 50:50 blend membrane was also prepared by dipping the glass plate in an equal-volume mixture of the two solutions.

Permeation resistance of the membranes against benzene and MEK was measured using ASTM F739-85, in a closed circulating system (Figure 1). The specimen with a diameter of exposed areas of 7.5 cm was placed between two chambers of the permeation cell; the stationary cell was filled with the challenge chemical, the other chamber was directly connected to the system. The collecting medium, 10% ethanol, was circulated at an approximate flow rate of 400 mL/min. A Perkin-Elmer 552 UV/vis spectrophotometer was employed for measuring the breakthrough time, i.e. elapsed time for the permeant to enter the collecting medium.

The mechanical properties (ASTM D412-86) of vulcanized films were measured with a Monsanto Tensometer 10 (capacity: 10 kN). Table I shows tensile strength and elongation at break for pure and composite membranes prepared under different vulcanization conditions. NBR had the highest tensile strength, and BIIR showed the greatest ultimate elongation at break. As for significance in differences, the result of SAS ANOVA DUNCAN analysis for tensile strength is

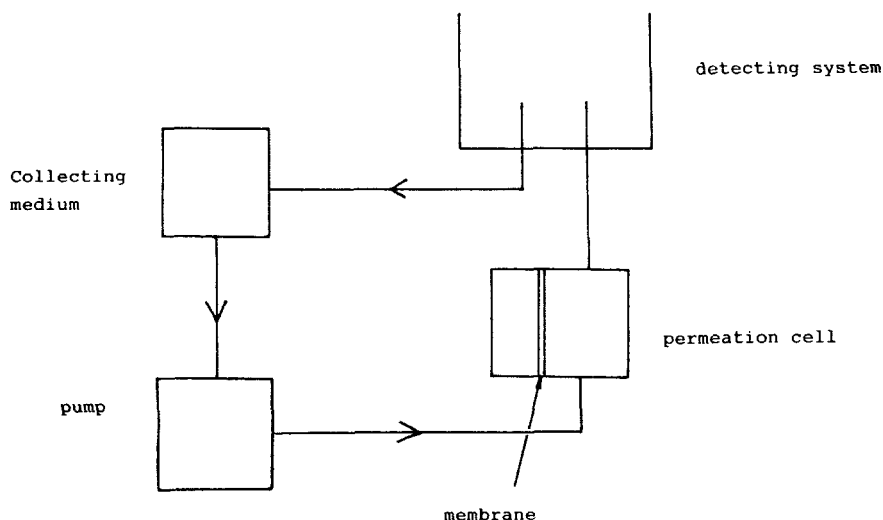


FIGURE 1

TABLE I

Tensile strength and ultimate elongation of pure and composite membranes, vulcanized at different temperatures and times

C/min	Tensile strength (MPa)			Ultimate elongation (%)		
	138/70	140/60	142/50	138/70	140/60	142/50
NNNN	26.4	24.1	25.0	459	458	447
BBBB	22.3	21.9	20.5	518	525	485
NNBB	17.5	18.0	17.8	394	406	403
NBNB	20.9	20.1	21.6	418	423	420

NBR \gg BIIR, NBNB $>$ NNBB, and for ultimate elongation BIIR \gg NBR $>$ NBNB, NNBB. In summary, the composites, especially the two-layered, are somewhat weaker mechanically than the pure elastomers, without showing any sign of grave deterioration. As far as vulcanization conditions, no significant differences can be detected: 140 C/60 min was chosen for the rest of the experiments.

RESULTS

Permeation measurements on pure, composite and blend membranes (Table II) showed that NBR provides greater resistance against benzene, and BIIR against MEK, which were expected on polarity grounds. The composites, on the other hand, produced longer breakthrough times than the pure elastomers, which was especially pronounced with the alternating layers. (Swelling tests in both benzene and MEK also showed NBNB picking up the least mass.)

Considering that permeation involves three processes, sorption, diffusion and desorption,⁹ the outcome, which was observed repeatedly, can be explained using the arguments of synergetics.¹⁰ In case of MEK, NBR resists sorption while BIIR imparts low diffusivity. Probably the opposite happens with benzene. It is also possible that at the NBR/BIIR interfaces the crosslink density is somewhat higher than in either layer.

TABLE II

Breakthrough times of pure, composite and 50:50 blend membranes, with benzene and methylethyl ketone permeants.

	Breakthrough time (min/mm ²)	
	Benzene	MEK
NNNN	78	49
BBBB	71	61
NNBB	96	74
NBNB	112	79
Blend	89	76

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