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Nitrogen/oxygen permeability of natural rubber, epoxidised natural rubber and natural rubber/epoxidised natural rubber blends

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Abstract

Pure gas transport properties of natural rubber (NR), epoxidised natural rubber (ENR) and their blends have been determined. The permeabilities of the pure polymers and blends were determined with nitrogen and oxygen. The relation between oxygen-to-nitrogen selectivity and the glass transition temperature has been studied. NR is more permeable to nitrogen and oxygen but ENR-50 shows maximum oxygen-to-nitrogen selectivity. In NR/ENR blends, permeability of the penetrant decreases with volume fraction of ENR, whereas selectivity increases with volume fraction of ENR. Pure gas permeabilities of NR/ENR blends were compared with models for permeation in heterogeneous media. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber; Epoxidised natural rubber; Permeability

1. Introduction

The permeation characteristics of a membrane material are the most important factors in deciding the economic viability of a membrane gas-separation process. Polymers for gas separation processes need to meet several criteria, such as high permeability to the desired gas, high selectivity, the ability to be formed into useful membrane configurations and resistance to processing conditions. High permeability (P) together with high permselectivity (α) is the requirement for an ideal membrane. A study of the polymer–structure permeability relationship is required for synthesising polymers with the desired permeation characteristics.

Several methods can be used for developing new materials for commercial applications; among these are the synthesis of new polymers, copolymerisation and blending of miscible polymers [1]. In principle, the most economical method is the blending of miscible materials, resulting in a product with properties that lie between those of the pure components. However, it is difficult to find polymers that are miscible, due to thermodynamic constraints arising primarily from the low combinatorial entropy of mixing of polymers [1–4].

Recent work within families of polymers has shown that structural variations leading to systematic changes in chain mobility and packing can be used to achieve increases in permeability and permselectivity [5,6]. The most detailed analysis of permeation data appears to be that of Robeson et al. [7] The gas transmission behaviour of natural rubber, blended with a variety of synthetic elastomers, has been reported by Barbier [8]. Pieski [9] has reported the effect of blending high-density (HDPE) and low-density polyethylene (LDPE) on the permeability to water vapour.

Ito [10] has determined the permeability and solubility coefficients for blends of polyethylene/polypropylene, polyethylene/polyisobutylene and blends of HDPE and LDPE. Ito reports that whereas the permeability coefficient for water, CO_2 and nitrogen all decrease monotonically as the HDPE content increased in the HDPE/LDPE blend, a distinct maximum is observed in a plot of the permeability coefficient for both CO_2 and nitrogen as a function of polypropylene content in the polyethylene/polypropylene blends.

Heterogeneous polymer blends composed of highly permeable rubbery polymers and highly selective glassy polymers have been studied with respect to their preparation and performance for the oxygen and nitrogen separation. But the permeation and diffusion mechanism of such polymeric systems is hard to analyse due to the inherently complex compatibility, intermolecular interaction and

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polarity between the component polymers. The permeation characteristics of the heterogeneous polymer membranes have been modelled with respect to the phase morphology, shape, size, etc. [11–14].

Lee and co-workers [15,16] investigated the effect of the synthesis temperature of polyurethane–polystyrene interpenetrating polymer network (IPN) membranes. The synthesis temperature included a change in the miscibility of the component polymers and the free volume of the membranes. They varied the annealing temperature to change the miscibility and the free volume of the membranes. The membranes annealed at high temperature showed an increased permeability coefficient and a decreased selectivity due to the increased free volume by the phase separation of the component polymers.

In this contribution, the permeation characteristics of natural rubber (NR), epoxidised natural rubber (ENR) and their blends are presented. The gas permeability coefficients and separation factors are measured. The present results may contribute to the investigation of a possible use of NR/ENR blends as a new membrane system for the oxygen and nitrogen separations.

2. Theory

The permeability of a polymer to a pure penetrant, P, is often written as

$$P = S \times D \tag{1}$$

where S, the apparent solubility coefficient, is the ratio of the penetrant concentration in the polymer to the penetrant pressure in the contiguous gas or vapour phase [17]. D is the penetrant diffusion coefficient in the polymer [18]. The ideal selectivity for penetrant A relative to penetrant B, α_{AB}, is defined as the ratio of the permeability coefficients of the gases:

$$\alpha_{AB} \equiv \frac{P_A}{P_B} = \left[\frac{D_A}{D_B}\right] \times \left[\frac{S_A}{S_B}\right] = \left[\begin{matrix}\text{Diffusivity}\\ \text{selectivity}\end{matrix}\right] \times \left[\begin{matrix}\text{Solubility}\\ \text{selectivity}\end{matrix}\right] \tag{2}$$

Selectivity, as defined by Eq. (2), is a product of two terms. The first term is the ratio of the diffusion coefficients and is called the diffusivity or mobility selectivity. This term depends on the size of the permeants relative to the chain mobility and inter- and intramolecular chain spacing of the polymer. In the separation of organic vapours from permanent gases, the diffusion coefficient of the organic vapour is always less than that of the permanent gas; thus, the diffusivity selectivity term is less than one. The second term is the sorption or solubility selectivity and reflects the relative sorption of the two permeants. In general, the more condensable the component, the higher is its sorption in the polymer. Thus, in the separation of organic vapours from permanent gases, the sorption selectivity term will be greater than one. Whether a particular membrane material is organic vapour selective or permanent gas selective depends on the balance between these two terms. In general, gas transport through rubbery polymers is dominated by the solubility term. On the other hand, transport through conventional low free-volume glassy polymers is dominated by the diffusion term.

3. Experimental

3.1. Measurement of gas permeability

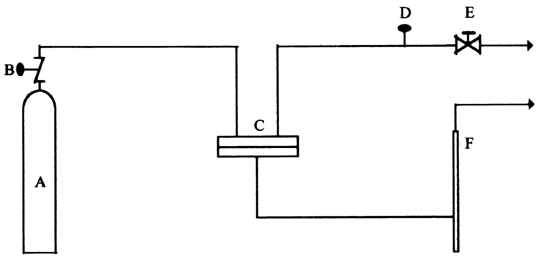
A schematic of the gas permeability measurements is given in Fig. 1.

The permeability of NR, ENR-25 and ENR-50 and their blends to pure nitrogen and oxygen were determined at 25°C using the constant pressure/variable volume method. The feed side pressure of the gases was 90 PS. The permeant side was maintained at atmospheric pressure.

The test cell was constructed of stainless steel. The effective area inside the cell was 3.14 cm^2. The gas permeated from the active membrane was passed through the supporting medium of a porous stainless steel plate. Two O-rings were used as the sealing agent.

4. Results and discussion

Oxygen and nitrogen permeabilities and oxygen-to-nitrogen selectivities with mol% epoxidation are given in Figs. 2 and 3, Fig. 2 shows that the permeability of oxygen and nitrogen decreases with mol% epoxidation. Fig. 3 shows that a membrane with high oxygen permeability exhibits low selectivity and that with high selectivity exhibits low permeability. Natural rubber, which has the highest oxygen permeability, has an oxygen-to-nitrogen selectivity of about 2.9. With epoxidation, the permeability to larger penetrants decreases more compared to smaller penetrants. Thus the ENR membranes have higher oxygen-to-nitrogen selectivity.



A - gas cylinder; B - line regulator; C - test cell;
D - pressure gauge; E - micro valve; F - mercury flow meter

Fig. 1. Schematic representation of gas permeation apparatus.

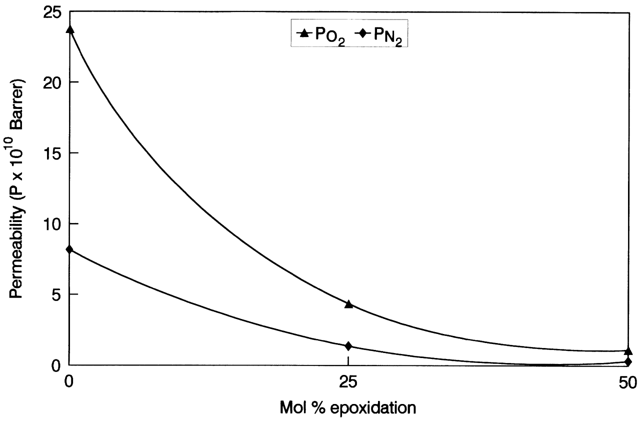


Fig. 2. Oxygen and nitrogen permeability with mol% epoxidation.

The relation between the oxygen-to-nitrogen selectivity and oxygen permeability is given in Fig. 4. It is seen from this figure that O_2/N_2 selectivity decreases with an increase in O_2 permeability. In general, an approximately linear relation with negative slope exists between the oxygen-to-nitrogen selectivity and oxygen permeability. Also, it is said that gas permeability follows the solution diffusion mechanism. If gas permeability follows the solution diffusion mechanism, the glass transition temperature of the polymer membrane and the diffusion constant are the important factors, and an approximately linear relation exist between them. The relation between the glass transition temperature of the polymers and oxygen permeability is shown in Fig. 5.

As gas molecules pass through the molecules of the polymer, the rate is higher if the molecular structure is not rigid or the polymer has a high free volume; that is, the polymer having a lower glass transition temperature has higher gas permeabilities.

4.1. Gas permeability of NR/ENR blends

The permeability coefficients of NR/ENR-25 and NR/ENR-50 blends to O_2 and N_2 are shown in Figs. 6 and 7. In all cases gas permeability decreases with ENR concentration. Compared to oxygen, nitrogen exhibits lower permeability. With increasing ENR concentration, permeability to larger penetrants decreases than the permeability of smaller penetrants. The permeability of the polymer appears to be a very sensitive function of penetrant size. With increasing covalent radii of nitrogen, the permeability coefficient decreases.

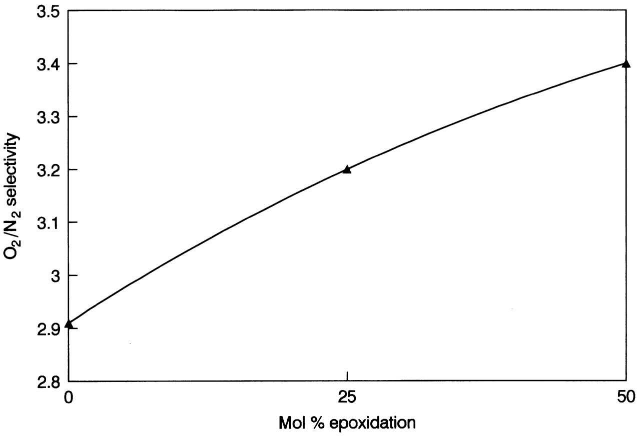


Fig. 3. Variation of oxygen-to-nitrogen selectivity with mol% epoxidation.

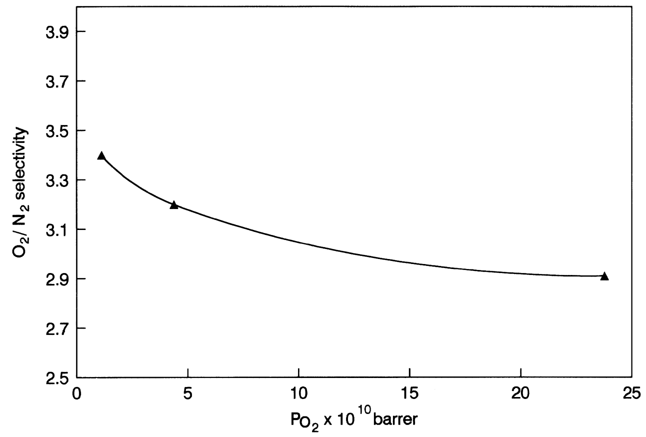


Fig. 4. Relation between oxygen-to-nitrogen selectivity and oxygen permeability.

4.2. Comparison of pure gas permeability of NR/ENR blends with models for permeation in heterogeneous media

The experimental gas permeabilities in NR/ENR blends are compared with several models of permeation in heterogeneous blends [19,20]. The following empirical model has been used to describe permeability values in both homogeneous and heterogeneous binary blends and copolymers.

$$\log P_{\text{blend}} = \phi_1 \log P_1 + \phi_2 \log P_2 \qquad (3)$$

where P_{blend} is the blend gas permeability, ϕ_1 and ϕ_2 are the volume fractions of polymers 1 or 2 in the blend, and P_1 and P_2 are the permeabilities of pure polymers 1 and 2. Fig. 8 shows the experimental and theoretical blend

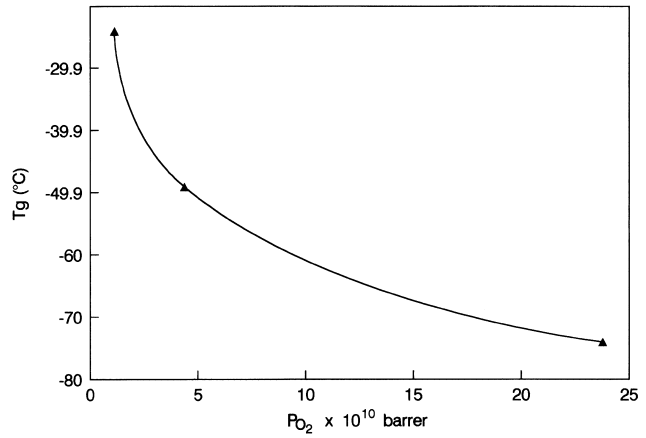


Fig. 5. Relation between glass transition temperature T_g and oxygen permeability.

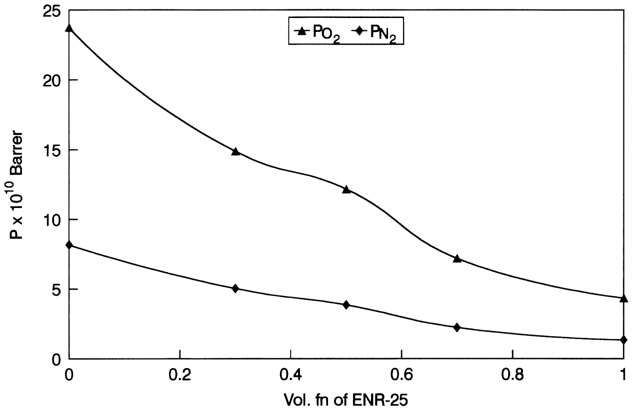


Fig. 6. Permeability coefficients of NR/ENR-25 blends to oxygen and nitrogen.

permeabilities. However, there appears to be no strong linkage between the empirical model and the morphology or spatial distribution of the blend components [21].

Two theoretically based models that were developed to describe transport properties in microparticulate dispersion of one component in a continuous matrix of a second component are also applied to fit the permeation data [20]. Our objective in considering these theoretical models is to obtain a qualitative, rather than quantitative, understanding of their ability to describe the experimental permeation properties, and to use the theoretical models to provide insights into the structure of NR/ENR blends.

The Maxwell model was originally applied to permeation in systems in which the dispersed phase consisted of a low fraction of spherical particles [22]. According to Petropolous [20], Maxwell's model is valid over the whole composition range for dispersion of isometric particles of such shape and mode of packing that the interparticle gaps are uniformly maximised. The Bruggeman model corresponds to a random packing of dispersed, isometric particles. A schematic model of the dispersed phase in the Maxwell model and the Bruggeman model is given in Fig. 9. When the low permeability component is the continuous phase, the Maxwell model gives lower estimates of permeability than the Bruggeman model. When the high permeability component is the continuous phase the Maxwell model predicts higher permeability coefficients than the Bruggeman model [19]. The permeability properties of the components comprising the dispersed and continuous phase are presumed to be the same as the pure component permeability properties. The mathematical forms of the two models are given below.

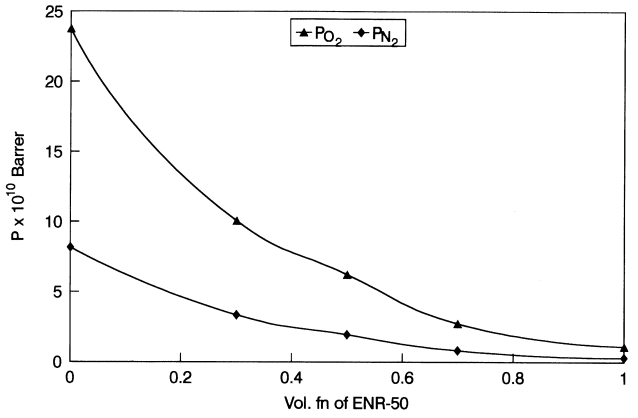


Fig. 7. Permeability coefficients of NR/ENR-50 blends to oxygen and nitrogen.

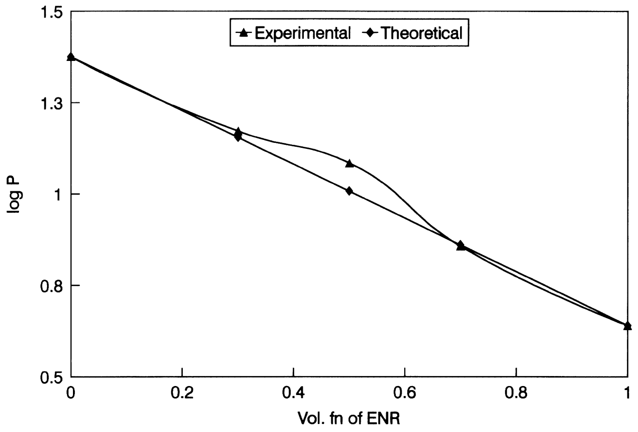


Fig. 8. Experimental and theoretical blend permeabilities of NR/ENR-25.

Maxwell

$$P_{\mathrm{blend}} = P_{\mathrm{c}} \left[1 + \frac{3\phi_{\mathrm{d}}}{\left[\dfrac{P_{\mathrm{d}}/P_{\mathrm{c}} + 2}{P_{\mathrm{d}}/P_{\mathrm{c}} - 1} \right] - \phi_{\mathrm{d}}} \right] \tag{4}$$

Bruggeman

$$P_{\mathrm{blend}} = P_{\mathrm{c}} \left[\frac{P_{\mathrm{d}}/P_{\mathrm{c}} - P_{\mathrm{blend}}/P_{\mathrm{c}}}{(1-\phi_{\mathrm{d}})(P_{\mathrm{d}}/P_{\mathrm{c}} - 1)} \right]^3 \tag{5}$$

where P_{blend} is the blend permeability, P_{c} is the permeability of the continuous phase, P_{d} is the permeability of the dispersed phase, and ϕ_{d} is the volume fraction of the dispersed phase.

The volume fraction of ENR in the blends was estimated from

$$\phi_{\mathrm{ENR}} = W_{\mathrm{ENR}} \frac{\rho_{\mathrm{blend}}}{\rho_{\mathrm{ENR}}} \tag{6}$$

where W_{ENR} and ρ_{ENR} are the weight fraction and density of ENR in the blend, respectively. The blend density, ρ_{Blend}

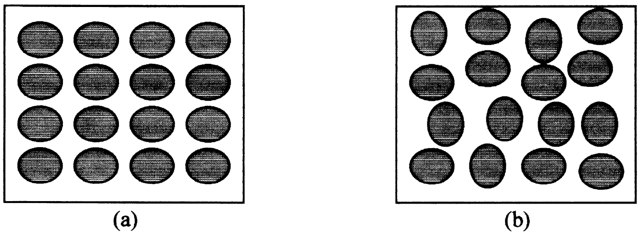


Fig. 9. Schematic model representing (a) the Maxwell model and (b) the Bruggeman model.

was calculated from

$$\rho_{\mathrm{blend}} = \frac{1}{\dfrac{W_{\mathrm{ENR}}}{\rho_{\mathrm{ENR}}} + \dfrac{W_{\mathrm{NR}}}{\rho_{\mathrm{NR}}}} \tag{7}$$

W_{NR} and ρ_{NR} are the weight fraction and density of NR in the blend respectively.

Using pure component permeability values for each penetrant in NR and ENR, the Maxwell and Bruggeman models predict the dependence of permeability on blend composition. A comparison of blend permeability values predicted by these models and the experimental data is shown in Fig. 10 for oxygen. The nitrogen result was qualitatively similar to the behaviour of oxygen. The model predictions are shown for both NR and ENR as the continuous phase. As expected, the Maxwell model predicts lower blend permeabilities than the Bruggeman model when ENR is treated as the continuous phase, and when NR is treated as the continuous phase the Maxwell model predicts higher blend permeability than the Bruggeman model.

4.3. Effect of blend composition on oxygen-to-nitrogen selectivity

Pure gas oxygen/nitrogen selectivity is given in Fig. 11. Oxygen permeability decreases as the content of ENR in the blend increases. In contrast, the O_2/N_2 selectivity is almost constant at low fractions of ENR. With increasing concentration of ENR in the blend, the O_2/N_2 selectivity increases and at high ENR concentration, the selectivity is almost constant.

The change in selectivity with blend composition may be related to phase inversion occurring over a narrow concentration range. NR is much more permeable than ENR to N_2 and O_2. Thus, for the theoretical models, if NR is the continuous phase, then $P_d/P_c \ll 1$; if ENR is the continuous phase, then $P_d/P_c \gg 1$. In either of these limits, the Maxwell model yields the following prediction for blend selectivity.

$$\alpha_{\mathrm{A,B}} = \frac{P_{\mathrm{c,A}}}{P_{\mathrm{c,B}}} \tag{8}$$

where $\alpha_{\mathrm{A,B}}$ is the ratio of permeability of penetrants A and B in the blend. The permeabilities of the continuous phase to penetrants A and B are $P_{\mathrm{c,A}}$ and $P_{\mathrm{c,B}}$ respectively. According to the Maxwell model, the blend selectivity should be the selectivity of the continuous phase, and selectivity should be independent of blend composition as long as phase inversion does not occur. These predictions are consistent with the experimental data if phase inversion occurs below 30 wt% ENR. At blend concentrations below 30 wt% ENR, NR is the continuous phase. ENR is the continuous phase at concentrations greater than 70 wt% ENR. At concentrations between 30 and 70 wt% ENR, the data suggest a co-continuous structure, with both components being continuous. This interpretation of the NR/ENR blend results is substantiated by the earlier work of Shur and Ranby [23].

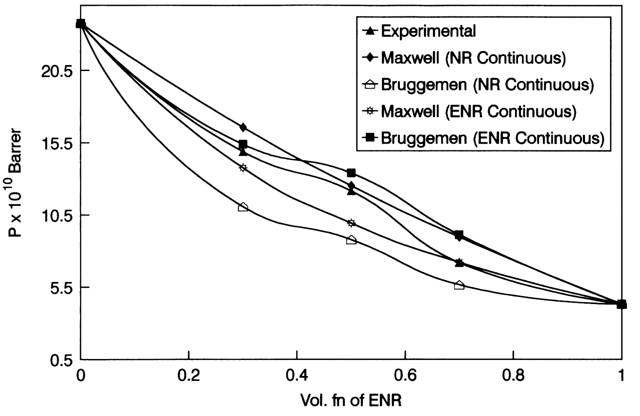


Fig. 10. Comparison of blend permeability with theoretical models.

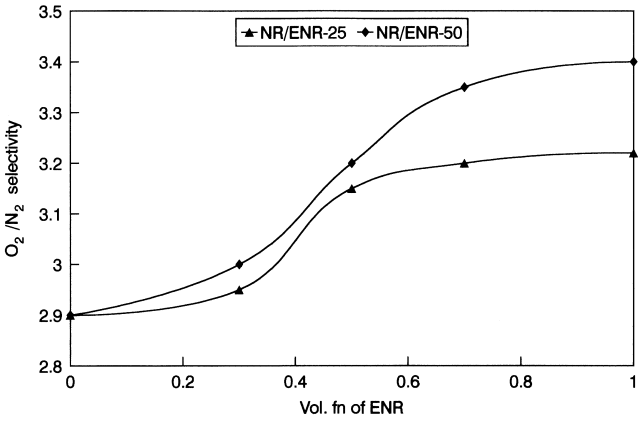


Fig. 11. Variation of oxygen-to-nitrogen selectivity with volume fraction of ENR.

5. Conclusion

The permeability and selectivity of natural rubber, epoxidised natural rubber and their blends were investigated. It was found that membranes with high oxygen permeability exhibit low selectivity. ENR-50 membrane had the highest oxygen-to-nitrogen selectivity. An almost linear relation was observed for oxygen-to-nitrogen selectivity and oxygen and nitrogen permeability with mol% epoxidation.

Permeability of the blends to oxygen and nitrogen decreases with increasing ENR content. Larger penetrant molecules exhibited a greater permeability reduction than smaller penetrants with increasing ENR content. Maxwell and Bruggeman models were used to predict the dependence of permeability on blend composition. Comparison of blend permeability values predicted by these models and the experimental data show that the Maxwell model predicts lower blend permeabilities than the Bruggeman model when ENR is treated as a continuous phase. As the ENR content in the blend increases, permeation results suggest a phase inversion in the range of 30–70 wt% ENR.

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