

Gas Permeation Studies of Natural Rubber and Carboxylated Styrene–Butadiene Rubber Latex Membranes

Ranimol Stephen,¹ Sabu Thomas,¹ Kuruvilla Joseph²

¹School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam 686 560, Kerala, India

²Department of Chemistry, St. Berchmans College, Kottayam, Kerala, India

Received 27 July 2004; accepted 30 January 2005

DOI 10.1002/app.22075

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Predicting the permeability of natural rubber (NR), carboxylated styrene–butadiene rubber (XSBR), and NR/XSBR latex membranes has been investigated with special reference to the effects of the blend ratio, the pressure, and the nature of the permeants with oxygen and nitrogen gases. These blend membranes are a new class of materials that combine the excellent mechanical properties of NR and the weather and solvent resistance of XSBR. NR shows higher permeability than XSBR latex films. This is associated with the high extent of the flexibility of the NR network due

to its very low cohesive forces of interactions. The experimentally determined permeability values have been theoretically correlated with the Maxwell, Bruggeman, and Botcher models. The oxygen-to-nitrogen selectivity decreases with an increase in the XSBR content in the blend. Attempts have been made to correlate the transport characteristics with the morphology of the blend. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1125–1134, 2005

Key words: blends; gas permeation; latices

INTRODUCTION

The gas permeability of polymers is an important factor for various applications, including barrier materials and membranes for gas separation. The relevance of permeation studies is widely spread in the industrial zones of food packaging, encapsulation of electronic circuits, protective coatings such as paints and varnishes, biomedical devices, and so forth.^{1,2} An overview of the studies shows that this is one of the fastest growing fields of polymeric materials in the field of membranes for gas separation and liquid separation. The gas separation of polymer membranes has been studied for many years, and it depends on the selectivity of a particular gas by the membrane over other gases.^{3,4} The transport of gases through a membrane depends on various factors such as the permeant size and shape, permeant phase, polymer molecular weight, functional groups, density and polymer structure, crosslinking, crystallinity, and orientation.⁵ A better understanding of the relationship between the transport properties and chemical structure, including the effects of chain packing and flexibility, is essential for the design of new materials to meet increased performance requirements for gas-separation membranes.⁶ The wide application of membranes for gas separation has attracted many polymer

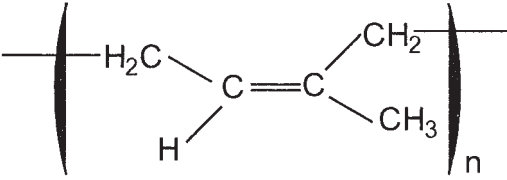
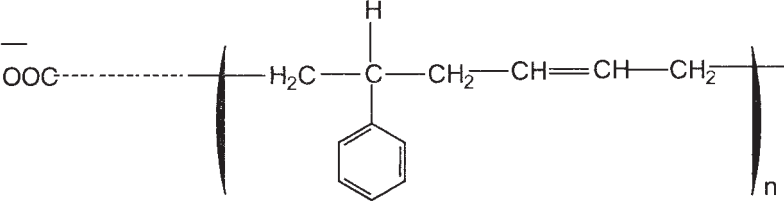
technologists to synthesize new polymeric membranes with good permeability and selectivity.^{7–9} Paul and coworkers^{10–14} investigated the relationship between gas transport and polymer structure. The introduction of functional groups into the polymer chain can alter the permeability and selectivity because of the variation in the existing free volume within the polymer.^{15,16} The selective transport of gases through polymeric membranes was reviewed by Aminabhavi et al.¹⁷

Gas-transport properties are sensitive to changes in the membrane structure, such as the crystallinity, crosslinking, additives, pores, phase morphology, and phase interaction. Thus, it is possible to get a complete picture of the system properties by permeability measurements.¹⁸ Polymer permeability properties are very sensitive to molecular packing in the amorphous state. The movement of gas molecules is dependent on the available free volume in the polymer matrix and the kinetic energy of the gas molecules for overcoming the attractive forces between polymer chains.¹⁹

The blending of polymers can result in properties that are not found in a single polymer system. This has attracted considerable attention and is widely used for various engineering applications. Blends of polymers have played an important role in many transport applications such as gas and liquid separations and barriers for packing.^{20–23} Gas transport through polymer blends has been the subject of numerous studies.^{24–27} The mechanisms of permeant diffusion in polymer blends are more complex and more difficult to interpret than those for homogeneous or idealized systems.

Correspondence to: S. Thomas (sabut@sancharnet.in).

TABLE I
Characteristics of the Polymers

NR Latex	
Supplier	Gaico Rubbers, Ltd., Kuravilangadu, Kottayam
DRC (%)	60
Total solid content (%)	61.25
XSBR Latex (PLX-802)	
Supplier	Apar Industries, Ltd., Bombay, India
DRC (%)	47
Total solid content (%)	50.66
Styrene content (%)	52

This is mainly due to (1) the perturbation of the diffusion process due to the dispersed phase, (2) the changes in the number and size distribution of the holes due to interactions of the phases, and (3) the complex transport mechanism.²⁸ The interaction of the two systems can be obtained from the permeability measurements. Recently, from this laboratory, Johnson and Thomas reported on the gas-transport properties of natural rubber (NR)/epoxidized rubber blends²⁹ and styrene-butadiene rubber/NR blends³⁰ with nitrogen and oxygen. Membrane technology can be used to separate the oxygen and nitrogen gases from air for industrial applications.³⁰ Heterogeneous polymer blends consisting of highly permeable rubbery polymers and highly selective glassy polymers have been found highly applicable for the separation of gases. The basic requirement for an ideal membrane is high permeability together with high permselectivity.

This article examines the transport of gases such as nitrogen and oxygen through NR/carboxylated styrene-butadiene rubber (XSBR) latex blend films. NR latex possesses a high wet gel strength, is low-cost, and has excellent physical properties. XSBR latex has better weather resistance and adhesion properties and is less permeable to gases and solvent molecules. Blending these two polymers results in new systems with better physical properties. NR is nonpolar, and XSBR is polar in nature; hence, the system is incompatible. The goals of this work are to understand the transport mechanism in these nonpolar/polar materials, to determine the potential of these materials for gas-separation applications, and to understand the structure-property relationship of these blends.

EXPERIMENTAL

Materials

The NR latex was centrifuged latex with a 60% dry rubber content (DRC). It was supplied by Gaico Rubbers, Ltd. (Kuravilangadu, India).

XSBR latex was obtained from Apar Industries, Ltd. (Bombay, India). Oxygen and nitrogen gases were supplied by Southern Gas Agencies (Coimbatore, India). The basic characteristics of the polymers are given in Table I.

Preparation of the latex films

The blending of NR and XSBR latices was done at the ambient temperature with a mechanical stirrer. The blend was then kept for 1 h to ensure homogenization and also for the sedimentation of impurities. Films with a uniform thickness were obtained via casting onto a glass plate and were allowed to dry at room temperature. NR and XSBR latices were blended in various compositions according to their DRC. The blends are designated N₇₀, N₅₀, and N₃₀, where N denotes NR and the subscripts indicate the weight percentage of NR.

Gas permeability measurements

The measurements were done with an ATS FAAR gas permeability tester (ATS FAAR, Milan, Italy) with the manometric method in accordance with ASTM Standard D 1434. A schematic representation of the experimental setup is shown in Figures 1 and 2.

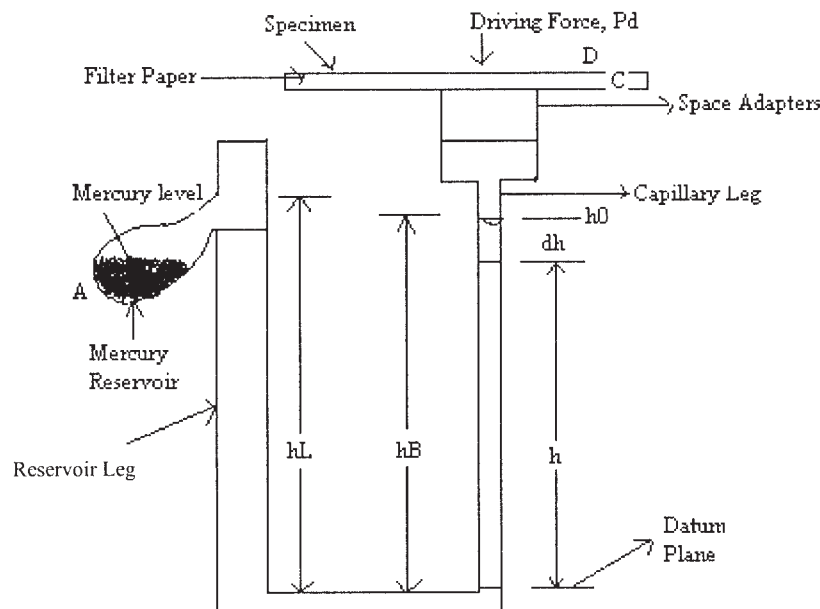


Figure 1 Experimental setup of the gas permeability tester.

The films were cut into circular pieces of the size of the test cell. Each was then fit into the test cell. The thickness of the sample over the test area was measured before the experiment. After the system was evacuated, the test gas at a constant pressure was applied. Then, the mercury was filled in the capillary after the steady-state condition was attained. The change in the mercury height in the capillary was measured with time. The experiment was carried out at various pressures.

The permeability (P) is the product of the permeance (p) and thickness (d) of a sample:

$$P = pd \quad (1)$$

p is obtained from the following relation:

$$p = g(h)/(t - t_0) \quad (2)$$

where t is the time, t_0 is the time at the start of the actual transmission run after steady-state conditions have been attained, and $g(h)$ is the gas-transmission rate.

p is defined as the ratio of $g(h)$ to the difference in the partial pressure of the gas on the two sides of the film.

$g(h)$ is defined as the quantity of a given gas passing through a unit of area of the parallel surfaces of the film in a unit of time under the test conditions:

$$g(h) = -1/ART([V_f + a_c(2P_u + h_B - h_i)] \ln [1 - (h_0 - h)/P_u - (h_L - h_0)] + 2a_c(h_0 - h)) \quad (3)$$

Most of the terms in eq. (3) are constant for this particular equipment. a_c is the area of the capillary, A is the area of the transmission, h_0 is the height of mercury in the capillary leg at the start of the transmission run after steady-state conditions have been attained, h is the height of mercury in the cell capillary leg at any given time, h_B is the maximum height of mercury in the cell manometer leg from the datum plane to the upper calibration line B (Fig. 1), h_L is the height of mercury in the cell reservoir leg from the datum plane to the top of the mercury meniscus (Fig. 1), P_u is the upstream pressure of gas to be transmitted, R is the universal gas constant, and T is the absolute temperature:

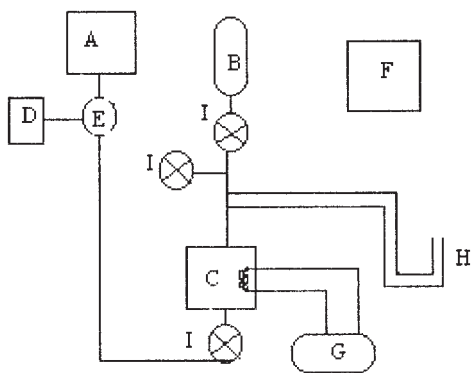


Figure 2 Experimental setup of the gas permeability tester (A = vacuum pump; B = test gas cylinder; C = gas-transmission cell; D = vacuum gauge; E = trap; F = barometer; G = automatic recorder; H = mercury manometer; I = needle valve).

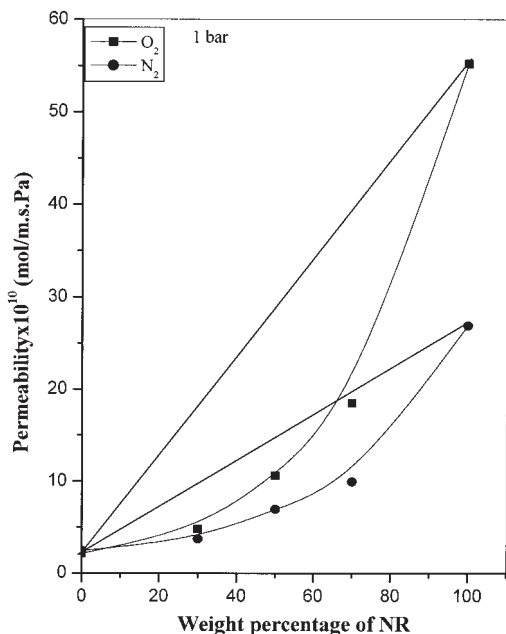


Figure 3 Effect of the blend ratio on the permeability of N₂ and O₂ gases.

$$V_f = V_{BC} + V_{CD} \quad (4)$$

where V_{BC} is the volume from B to C (Fig. 1) and V_{CD} is the volume of the depression (Fig. 1). The SI units of $g(h)$, p , and P are mol/(m² S), mol/(m² S Pa), and mol/(m S Pa), respectively.

The permeability of O₂ and N₂ gas through the NR/XSBR latex blends was tested at various pressures at the ambient temperature.

Morphology studies

The samples were cryogenically fractured and analyzed for the morphology of the blend system with a JEOL JSM-840A scanning electron microscope (JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

The immiscibility of the two systems can be obtained from dynamic mechanical analysis; the blends show two glass-transition temperatures (T_g 's) corresponding to the virgin polymers. We have already investigated the morphology and miscibility of the same system.³¹

Effect of the blend composition

The oxygen and nitrogen gas permeabilities of the NR/XSBR membranes with various weight percentages of NR are shown in Figure 3. For both O₂ and N₂ gases, the permeability of the blend systems exhibits a negative deviation from the additivity line. With an increase in the percentage of NR in the blend systems,

the permeability of the membranes increases. This behavior can be explained by the blend morphology. Immiscible polymer blends exhibit two phases, a continuous phase and a dispersed phase or a cocontinuous morphology, depending on the compositions. Scanning electron micrographs of the blend systems are given in Figure 4. In N₃₀, less permeable XSBR is the continuous phase, and NR is the dispersed phase. This inhomogeneous morphology offers a tortuous path for the permeant molecule. The N₅₀ system exhibits cocontinuous morphology, so there is a relative increase in the permeability. Because of the chain flexibility of NR, the permeant molecules have a less hindered path for penetration through the membrane in the N₇₀ blend system, for which NR is the continuous phase. As soon as phase inversion takes place, that is, when NR becomes the continuous phase and XSBR becomes the dispersed phase, the permeability is enhanced. The negative deviation of the permeability coefficients with the blend ratio can be explained in terms of the reduced permeability of one of the phases, XSBR. Because the polymer blend exhibits heterophase morphology, the permeant gas molecule may not find a continuous path for penetrating from the top to the bottom of the membrane. NR and XSBR are physically compatible but thermodynamically immiscible because of the large difference in their polarity value. The improved compatibility of NR with XSBR may be due to the increased physical interaction of the two polymers because of the molecular-level mixing during latex blending. If the two systems were highly incompatible, the permeability of the blends would be less than that of their individual components. However, in this case, the values are intermediate between the virgin polymers, and this indicates the physical compatibility between the two phases. A schematic representation of the permeation of gas molecules through latex blends is shown in Figure 5(a–e). Figure 5(a) is a schematic representation of gas transport through NR. Because of the presence of flexible chains of NR, gases can easily pass through the membrane. The permeation of gas molecules through a 70/30 NR/XSBR blend is shown in Figure 5(b). The heterogeneous phase morphology offers a more tortuous path for the permeant molecule. Figure 5(c) represents the transport of gas molecules through a cocontinuous 50/50 NR/XSBR blend system. The permeation of gas molecules through this system is very difficult because of the cocontinuous structure of XSBR, which interpenetrates with the NR phase. The movement of gas molecules in a 30/70 NR/XSBR blend system is illustrated in Figure 5(d). Because of the low permeability of the continuous XSBR phase, the path of gas molecules becomes more tortuous and extremely difficult. As explained earlier, the permeability of the XSBR latex membrane is very low, and it is shown in Figure 5(e).

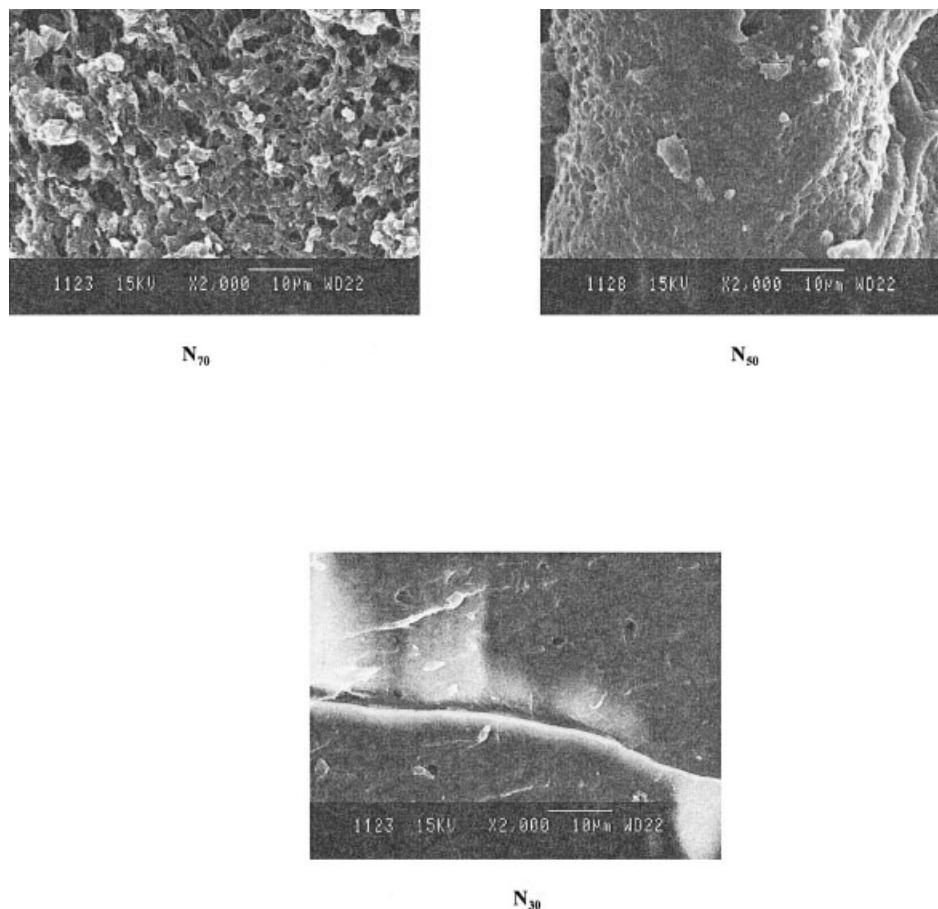


Figure 4 Scanning electron micrographs of NR/XSBR latex blends: (a) N_{70} (XSBR dispersed in NR), (b) N_{50} (cocontinuous morphology), and (c) N_{30} (NR dispersed in XSBR).

Effect of the penetrant size

The size of the permeant is one of the major factors affecting the transport of penetrants through polymeric films. In this case, oxygen shows higher permeability than nitrogen (Fig. 3). Because both oxygen and nitrogen have no interaction with these latex membranes, the higher permeability of oxygen through these polymeric membranes is due to its lower covalent radii in comparison with those of nitrogen. According to the Stoke–Einstein equation, the molecules with larger radius exert more frictional resistance during diffusion:

$$D = k_B T / f \quad (5)$$

where D is the diffusivity, k_B is the Boltzmann constant, and f is the friction factor. f is directly proportional to the radius of the diffusing molecule by the following relation:

$$f = 6\pi\mu R_0 \quad (6)$$

where R_0 is the radius of the diffusing molecule and μ is the viscosity of the solvent.

Effect of t_g

T_g of the polymers has a very marked influence on the transport properties. Because of the arresting of local motions within the system in the glassy state, the migration of diffusing gas molecules from one cavity to a neighboring cavity cannot occur.

T_g values of NR/XSBR latex blends have been obtained by the dynamic mechanical thermal analysis of those samples.³¹ The variation in the permeability of the NR/XSBR system with T_g for O_2 and N_2 gases is shown in Figure 6. Although the experiments were done above T_g , the permeability of the polymers was dependent on the flexibility of the chain segments. The T_g value obtained for NR from previous experiments is -52°C , which implies that at room temperature the networks of NR are highly flexible. However, the T_g value for XSBR is 24°C . The increased T_g value is due to the restricted mobility of the chain segments in XSBR due to the high cohesive interaction. With an increase in the XSBR phase in the blend system, T_g of the XSBR phase in the blend increases, and this indicates a decrease in the segmental mobility. The blend system becomes more rigid, and the polymer has less free volume for the penetration of the

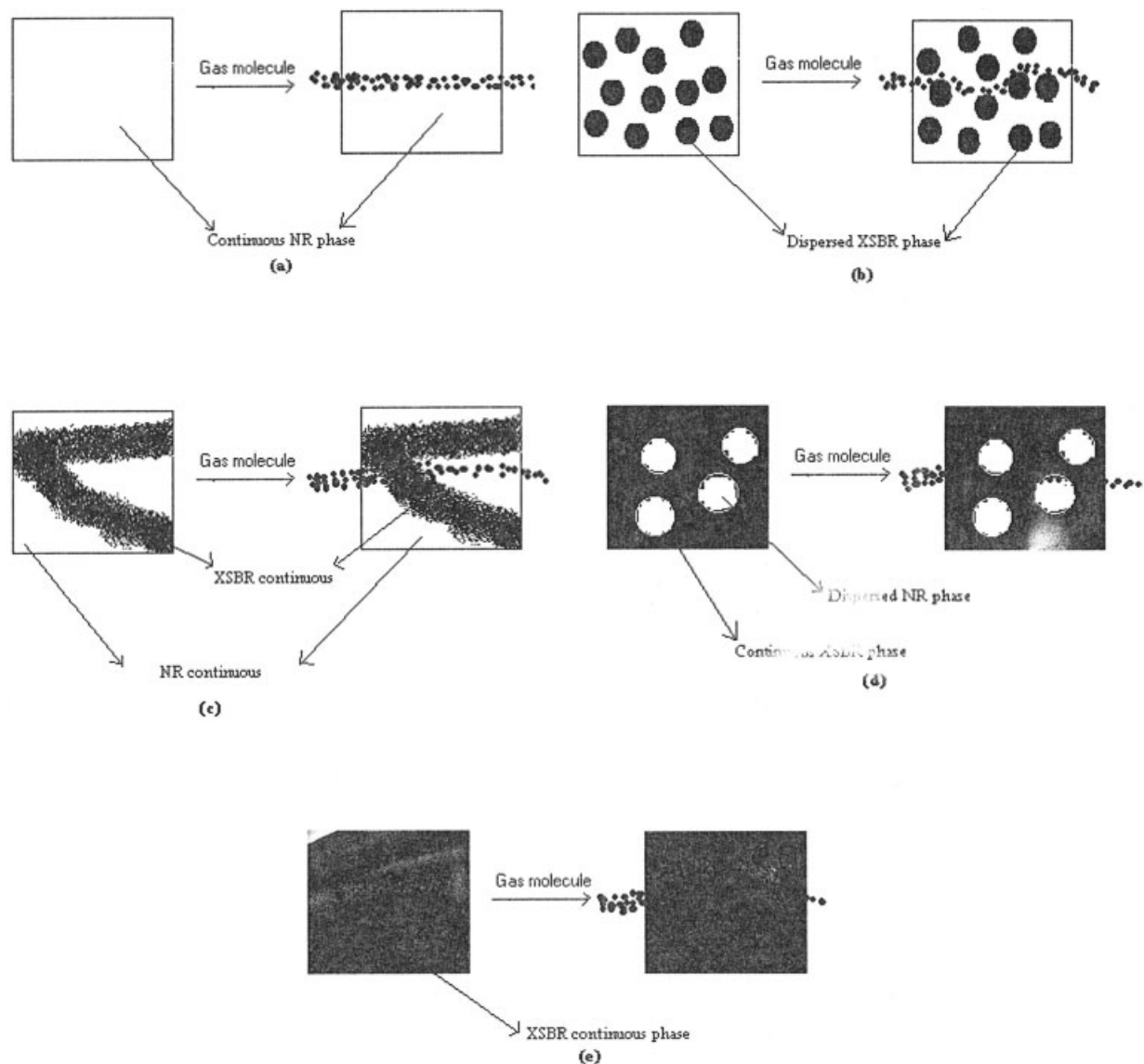


Figure 5 Schematic representation of the permeation of gas molecules through blends: (a) NR continuous phase, (b) 70/30 NR/XSBR, (c) 50/50 NR/XSBR, (d) 30/70 NR/XSBR, and (e) XSBR continuous phase.

permeant molecule. Obviously, the gas permeability coefficient of the latex membrane decreases. It is well known that the permeation depends on D and the solubility coefficient, S , where D is a kinetic parameter related to the polymer-segment mobility and S is a thermodynamic parameter that depends on the polymer-permeant interaction.⁵

Effect of the pressure

According to the literature,³² an increase in pressure will enhance the segmental mobility and will result in the occupation of gas molecules in the voids. The effect of pressure on the transport of O_2 and N_2 gases through NR/XSBR systems is shown in Figures 7 and 8. For O_2 and N_2 gases, the permeability increases with

an increase in pressure for the NR/XSBR systems. The effect is sharper in N_{100} . The application of pressure to the NR membrane enhances the segmental mobility, and the gas molecules can easily permeate it. In non-polar systems, the permeability increases continuously with pressure. NR is the continuous phase in the 70/30 NR/XSBR blend system, so it shows increased permeability with pressure.

We have observed only a marginal effect of pressure on the permeability of O_2 and N_2 gases through the 30/70 and 0/100 NR/XSBR latex membranes. The cohesive energy density is a better parameter for correlating the permeabilities of polymers with polar substituents because polar substituents affect the localized chain mobility. Therefore, the cohesive energy density is in fact an indirect measure of the chain

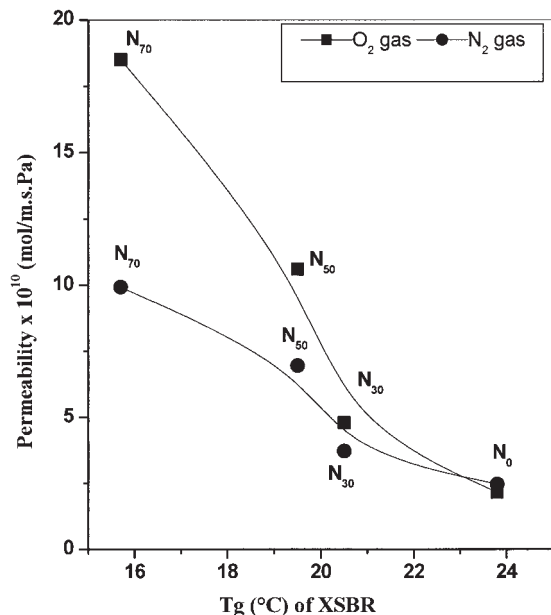


Figure 6 Variation in the permeability with T_g of the XSBR phase.

mobility. Because the cohesive energy density of XSBR is higher than that of NR, the pressure does not show much effect on the permeability of blend systems in which XSBR is the continuous phase.

Selectivity of the membranes

In membrane applications, polymers with high permeability and high selectivity are needed. Faupel et al.³³ studied the influence of the free volume on the

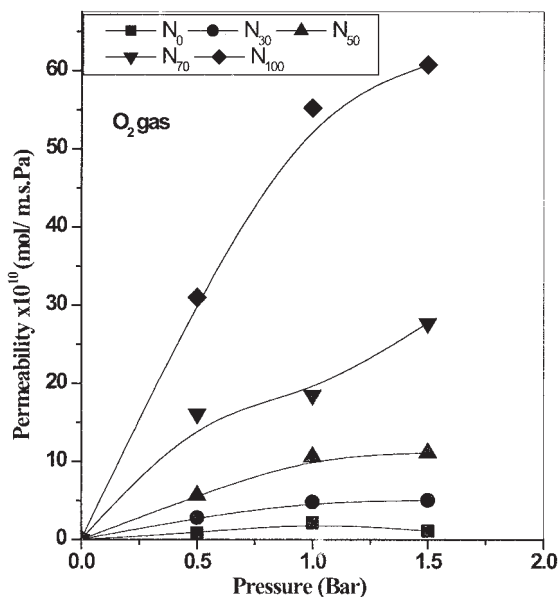


Figure 7 Effect of pressure on O_2 gas permeation through NR/XSBR latex blends.

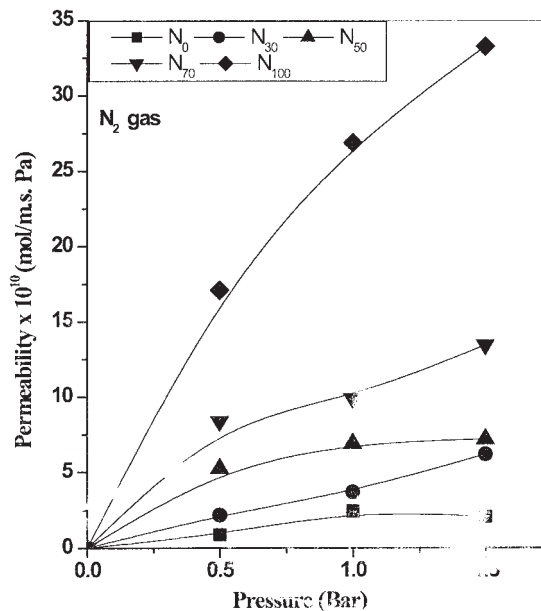


Figure 8 Effect of pressure on N_2 gas permeation through NR/XSBR latex blends.

gas-transport properties of highly selective polymer membranes. The permselectivity efficiency of a membrane to the transport of O_2 to N_2 gas [$\alpha(O_2, N_2)$] is given by

$$\alpha(O_2, N_2) = \frac{P(O_2)}{P(N_2)} \tag{7}$$

where $P(O_2)$ is the permeability of oxygen gas and $P(N_2)$ is the permeability of nitrogen gas.

The values of $\alpha(O_2, N_2)$ are plotted against the weight percentage of NR in Figure 9. The permselectivity of all those membranes is greater than 1. In general, an approximately linear relation exists between the O_2/N_2 selectivity and weight percentage of NR. It is clear from the plots that the selectivity and permeability of the blend system depends on the nature of the continuous phase.

Theoretical comparison of the permeability coefficients of the latex films

The gas permeability of the weakly interacting polymer blends have been shown to follow a logarithmic additivity rule given by³⁴

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 \tag{8}$$

where ϕ_1 and ϕ_2 are the volume fractions of the two homopolymers. Figure 10 shows the experimental and theoretical blend permeabilities. The theoretical and experimental values are different for these blends because of the heterophase nature. In fact, the experi-

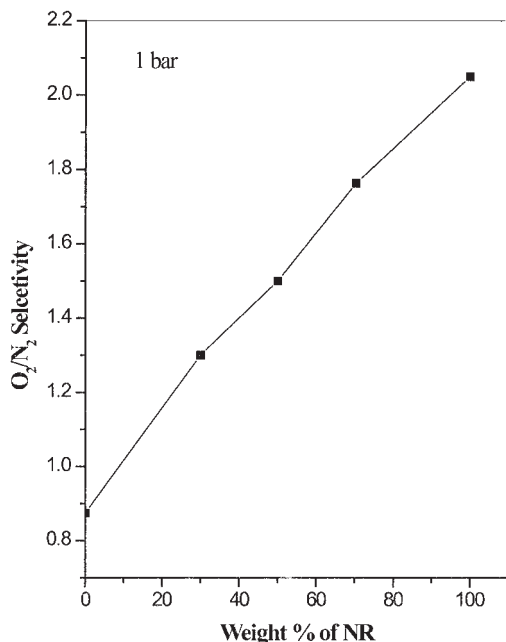


Figure 9 Variation in the oxygen-to-nitrogen selectivity with the blend composition.

mental values are slightly lower than the theoretical values. However, at a 50/50 ratio, the values are almost the same. This can be explained in terms of the cocontinuous morphology of the system at a 50/50 ratio as shown by the morphology.

Most of the theoretical predictions developed for the transport properties of heterogeneous polymeric systems are considered to consist of a microparticulate dispersion of one component in a continuous matrix of the other.³⁵ The structure of such a system can be specified in terms of the particle shape, size, orientation, and mode of packing. The Maxwell model can be applied to a system in which interparticle distances are sufficiently large to ensure that the flow line pattern around any one sphere is practically undisturbed by the presence of the others. In this case, the system is considered a dilute dispersion of spheres.³⁴ Other formulas, such as the Bruggeman, Bottcher, and Higu-chi formulas, are considered to be applicable to random dispersions of spherical particles.³⁵⁻³⁷

The transport behavior of blends can be related to the interaction between the two systems. Permeation through a biphasic, in which one phase is dispersed in the other, can be explained well by the Maxwell model:

$$P_{\text{blend}} = P_c \left[1 + \frac{3\phi_d}{\frac{P_d}{P_c} + 2} - \phi_d \frac{\frac{P_d}{P_c} - 1}{\frac{P_d}{P_c} + 1} \right] \quad (9)$$

where P_{blend} is the permeability of the blend, 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 Maxwell model may be considered to be valid over the whole composition range for a dispersion of isometric particles of such shape and mode of packing that the interparticle gaps are uniformly maximized.³⁵

The Bruggeman and Bottcher models for the random packing of the dispersed phase are given as eqs. (10) and (11), respectively.³⁶

$$P_{\text{blend}} = P_c \left[\frac{\frac{P_d}{P_c} - \frac{P_{\text{blend}}}{P_c}}{(1 - \phi_d) \left(\frac{P_d}{P_c} - 1 \right)} \right]^3 \quad (10)$$

$$\left(1 - \frac{P_c}{P_{\text{blend}}} \right) \left(\alpha + \frac{2P_{\text{blend}}}{P_c} \right) = 3v_d(\alpha - 1) \quad (11)$$

The terms P_c , P_d , and ϕ_d in eqs. (8) and (9) represent the permeability of the continuous phase, the permeability of the dispersed phase, and the volume fraction of the dispersed phase, respectively, as those in the Maxwell model; α is the ratio of the permeability of the dispersed phase to that of the continuous phase; and v_d is the volume fraction of the dispersed phase.

A comparison of the experimental values with the theoretical predictions of the permeability of O₂ gases through latex membranes is given in Figure 11. These models predict the dependence of the permeability on

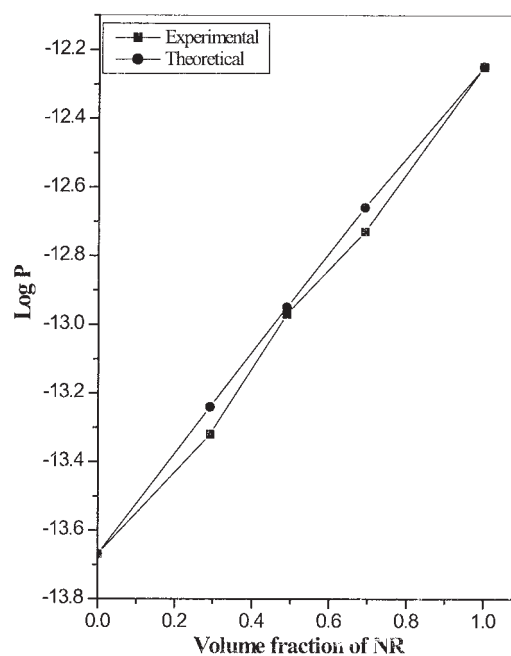


Figure 10 Experimental and theoretical permeabilities of NR/XSBR latex membranes.

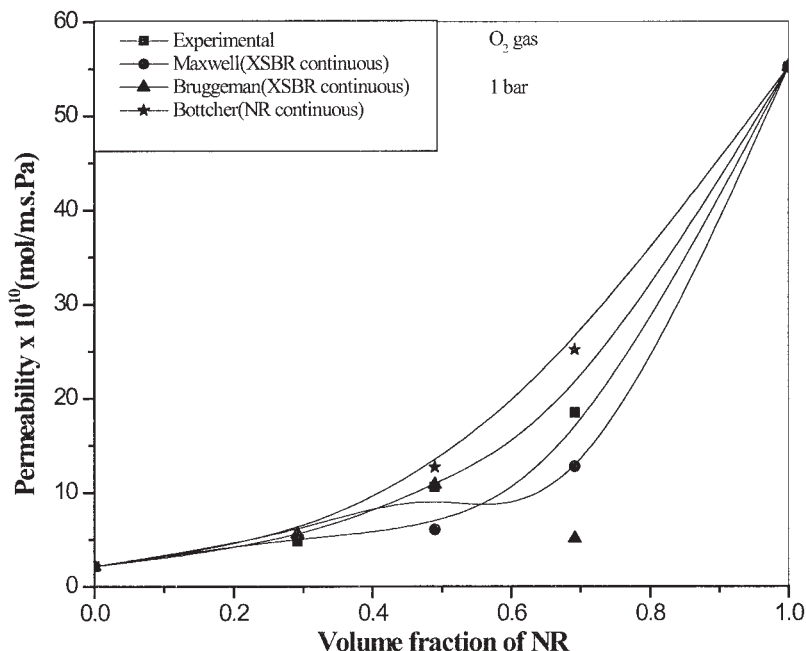


Figure 11 Theoretical modeling of the permeability values of NR/XSBR latex blends.

the blend composition and morphology. Theoretically predicted values agree well with experimental results at a lower concentration of NR, that is, the N₃₀ system. The Bottcher and Bruggemann models fit well the experimental values of the 50/50 ratio for the NR continuous phase and XSBR continuous phase, respectively. In the blend systems, the Bottcher model exhibits higher permeability when NR is considered the continuous phase. This model corresponds to the perfectly random mixing of physically equivalent components of A and B. In the case of the 70/30 NR/XSBR blend system, the theoretical values do not agree with the experimental results. This system shows two-phase morphology, that is, the XSBR phase dispersed in the NR continuous phase. All these models predict the heterophase structure of the NR/XSBR blends.

CONCLUSIONS

The gas-transport behavior of NR, XSBR, and NR/XSBR latex membranes has been studied with oxygen and nitrogen gases. The permeability coefficient with special reference to the blend ratio and pressure has been investigated. There is a drastic change in the permeability when NR becomes the continuous phase. This is due to the high extent of the flexibility of NR in comparison with that of XSBR. The variation in the permeability with the blend composition has been explained by the consideration of the blend morphology. When less permeable XSBR is the continuous phase, the gas molecules have a tortuous path for permeation. The permeability shows a sharp increase

with an increase in pressure for NR and 70/30 NR/XSBR latex blends. The 50/50, 30/70, and 0/100 NR/XSBR systems exhibit only a slight variation in permeability with pressure. Because of the difference in the covalent radii of the two gases, O₂ shows higher permeability than N₂ gas. As T_g of the blend increases, the permeability decreases because of the decrease in the chain mobility.

The selectivity of the membranes has been determined. The results reveal that blending with NR can enhance the permeability and selectivity of XSBR membranes. The Maxwell, Bruggemann, and Bottcher models have been used to correlate the experimental values. The dependence of the blend ratio on the permeability has been predicted. From the plots, it is clear that phase inversion occurs in the system in the range of 30–70 wt % NR. The theoretical correlations suggest that the permeability of the blend membranes depends on the nature of the continuous phase. The experimentally determined permeability coefficient of the 30/70 NR/XSBR blend matches the theoretically predicted values. The theoretical predictions also confirm the two-phase morphology of the 70/30 and 30/70 NR/XSBR systems.

References

1. Chiou, J. S.; Maeda, Y.; Paul, D. R. *J Appl Polym Sci* 1987, 33, 1823.
2. George, S. C.; Thomas, S. *Prog Polym Sci* 2001, 26, 985.
3. Thorman, J. M.; Rhim, H. K.; Hwang, S. T. *Chem Eng Sci* 1975, 30, 751.
4. Lonsdale, H. K. *J Membr Sci* 1982, 10, 81.

5. Naylor, T. Handbook of Comprehensive Polymer Science, 1st ed.; Pergamon: United Kingdom, 1989; Vol. 2; p 643.
6. Singla, S.; Beckham, H. W.; Rezac, M. E. *J Membr Sci*; Elsevier: New York, 2002, 208, 257.
7. Compan, V.; Zanuy, D.; Andrio, A.; Morillo, M.; Aleman, C.; Guerra, S. M. *Macromolecules* 2002, 35, 4521.
8. Arnold, M. E.; Nagai, K.; Freeman, B. D.; Spontak, R. J.; Betts, D. E.; De Simone, J. M.; Pinnau, I. *Macromolecules* 2001, 34, 5611.
9. Barbi, V.; Funari, S. S.; Gehrke, R.; Scharnagl, N.; Stribeck, N. *Macromolecules* 2003, 36, 749.
10. Pixton, M. R.; Paul, D. R. *Macromolecules* 1995, 28, 8277.
11. (a) Vega, M. A.; Paul, D. R. *J Polym Sci Part B: Polym Phys* 1993, 31, 1599; (b) Vega, M. A.; Paul, D. R. *J Polym Sci Part B: Polym Phys* 1993, 31, 1577.
12. Aitken, C. L.; Koros, W. J.; Paul, D. R. *Macromolecules* 1992, 25, 3651.
13. Mc Hattie, J. S.; Koros, W. J.; Paul, D. R. *Polymer* 1992, 33, 1701.
14. Mc Hattie, J. S.; Koros, W. J.; Paul, D. R. *Polymer* 1991, 32, 2618.
15. Tiemblo, P.; Guzman, J.; Riande, E.; Mijangos, C.; Reinecke, H. *Macromolecules* 2002, 35, 420.
16. Neilson, P. W.; Xu, G. F. *Macromolecules* 1996, 29, 3457.
17. Aithal, U. S.; Balundgi, R. H.; Aminabhavi, T. M.; Shukla, S. S. *Polym Plast Technol Eng* 1991, 30, 299.
18. Shur, Y. J.; Ranby, B. *J Appl Polym Sci* 1976, 20, 3121.
19. Cornelius, C. J.; Marand, E. *J Membr Sci* 2002, 202, 97.
20. Hopfenberg, H. B.; Paul, D. R. In *Polymer Blends*; Paul, D. R.; Newman, S., Eds.; Academic: New York, 1978; Vol. 1, Chapter 10.
21. Subramanian, P. M.; Poltzker, I. G. In *Polymer Blends*; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 2, Chapter 30.
22. Koros, W. J.; Flemming, G. K. *J Membr Sci* 1993, 83, 1.
23. Koros, W. J.; Paul, D. R. In *Synthetic Membranes*; Chenoweth, M. B., Ed.; MMI Press Symposium Series 5; Harwood Academic: New York, 1984; p 354.
24. Muruganandan, N.; Paul, D. R. *J Membr Sci* 1987, 34, 185.
25. Chiou, J. S.; Paul, D. R. *J Appl Polym Sci* 1987, 33, 2935.
26. Kim, M. H.; Kim, J. H.; Kim, C. K.; Kang, Y. S.; Park, H. C.; Won, J. O. *J Polym Sci Part B: Polym Phys* 1999, 37, 2950.
27. Moon, E. J.; Yoo, J. E.; Choi, H. W.; Kim, C. K. *J Membr Sci* 2002, 204, 283.
28. Shur, Y. J.; Ranby, B. *J Appl Polym Sci* 1975, 19, 1337.
29. Johnson, T.; Thomas, S. *Polymer* 1999, 40, 3223.
30. George, S. C.; Ninan, K. N.; Thomas, S. *Eur Polym J* 2001, 37, 183.
31. Stephen, R.; Raju, K. V. S. N.; Nair, S. V.; Varghese, S.; Thomas, S.; Oommen, Z. *J Appl Polym Sci* 2003, 88, 2639.
32. Crank, J.; Park, G. S. *Diffusion in Polymers*; Academic: New York, 1968.
33. Nagel, C.; Gunther, K.; Fritsch, D.; Strunskus, T.; Faupel, F. *Macromolecules* 2002, 35, 2071.
34. Muruganandan, N.; Paul, D. R. *J Polym Sci Part B: Polym Phys* 1987, 25, 2315.
35. Petropoulos, J. H. *J Polym Sci Polym Phys Ed* 1985, 23, 1309.
36. Higuchi, W. I. *J Phys Chem* 1958, 62, 649.
37. Petropoulos, J. H. In *Polymeric Gas Separation Membranes*; Paul, D. R.; Yampoliskii, Y. P., Eds.; CRC: Boca Raton, FL, 1994; p 17.