

Gas Permeability Studies on Poly(Vinyl Chloride) Based Polymer Blends Intended for Medical Applications

S. N. PAL,^{1,*} A. V. RAMANI,² and N. SUBRAMANIAN³

¹Division of Polymer Technology, Sree Chitra Tirunal Institute for Medical Sciences and Technology, R & D Wing, Poojapura Trivandrum, 695 012, India, ²London Rubber Co. (India) Ltd., 35 Old Trunk Road, Pallavaram Madras, 600 043, India, and ³Department of Chemical Engineering, Indian Institute of Technology, Madras, 600 036, India

SYNOPSIS

Plasticized PVC finds applications in a wide range of medical products. However, plasticizer leaching, known to take place from these conventional materials, is not desirable. A number of approaches to overcome this problem are mentioned in the literature. We suggest pursuing the polyblend approach. Plasticized PVC containing different amounts of plasticizer, binary polyblends of plasticized PVC (PPVC) with acrylonitrile-butadiene rubber (NBR1), and compounded graft polymer of vinyl chloride and ethylene-vinyl acetate copolymer (EVAPVC), and ternary blends of PPVC, NBR1, and EVAPVC, were formulated. In this article, we report our results of studies on water vapor, O₂, CO₂, and N₂ permeabilities. Increased plasticization for PVC was found to increase permeability for water vapor, O₂, CO₂, and N₂. Rise in temperature increased the permeability for water vapor and the change became faster as the materials crossed the region of T_g . A simple model suggested for permeability worked satisfactorily. The binary and ternary blends, based on PPVC, had lower O₂, CO₂, and N₂ permeability. This improvement in property is of great practical significance and interest and the results indicate that PVC-based polyblends can be investigated further for potential applications in medicine.

INTRODUCTION

A wide range of medical products are made from plasticized PVC.¹ The selection of PVC in preference to other materials is because of the wide range of properties that can be imparted to it, depending on the nature and the amount of additive.² Studies have shown that low molecular constituents of compounded PVC leach out during use and the amount of leaching depends on the chemical nature of the ingredients used in compounded PVC, the nature of the media in contact, and storage conditions.³⁻¹⁰ In case of medical applications, oily substances, such as the contents of the digestive system and blood, are capable of extracting monomeric plasticizers from PVC.^{11,12} The consequences of this are changes in properties (nonpermanence) and possible toxic

and biological effects arising from the transfer of plasticizer to a patient.

For medical devices with very short contact time, none of above effects may cause visible or apparent problems. However, the hazard to which a patient is exposed for the use of flexible PVC devices has generated lot of interest and a large number of publications have appeared regarding this.^{4,11-21} Though opinion is divided over the effect on humans, it is not desirable that patients with less than perfect health conditions should receive doses of plasticizers with the risk of possible long term effects, however minimal the possibility may be. The approaches to overcome and minimize these problems generally have been through one of the following routes:

1. Replacement of PVC.²
2. Copolymerization of vinyl chloride.²²⁻²⁴
3. Use of alternative additives.^{11,12,25}
4. Surface modification of PVC.²⁶⁻²⁹
5. Blending PVC with other polymer(s).

* To whom correspondence should be addressed.

Of all the approaches that have been adopted to overcome the shortcomings of PVC, the polymer blend approach is advantageous for a number of reasons. The important advantages are (i) changes in existing process technology are not required and (ii) the possibility of very high product cost by other approaches is avoided.

The problem of loss of plasticizer from flexible PVC can be solved in principle by blending a soft, high molecular weight polymer that is molecularly compatible with the rigid PVC.³⁰ Polyblends of rigid plastics with elastomer(s) can derive the strength and chemical resistance of plastic and the flexibility and low temperature toughness of rubber. This principle has been applied for the development of a number of commercially available poly-blend systems.³¹ Several polyblend systems, based on PVC, have also been reported in the literature.³²⁻⁴¹ Impact modification and ease of processing have been considerations for the development of such blend systems. However, there is hardly any literature that is available regarding use of PVC-based polymer blends for medical applications. It is, therefore, worthwhile to investigate the polymer blends approach and to examine whether flexibility can be achieved without making unacceptable compromise on some of the other desirable properties of PVC. There are also no reports of studies on blends of plasticized PVC with graft polymer of vinyl chloride and ethylene-vinyl acetate and ternary blends of these two polymers with acrylonitrile butadiene rubber (NBR).

In many of the medical applications, PVC-based devices are used to store substances (e.g., blood and blood products, drugs, and injectables) that require maintenance of constant microclimatic conditions without which deterioration of the contents takes place. The temperature of storage for such devices could also vary from sub-zero to about 45°C.

Knowledge regarding the permeability of gases, present in the atmosphere, through such materials is, therefore, of great interest. In this article, we present the results of permeability studies for water vapor, oxygen, carbon dioxide, and nitrogen. We have also attempted to use a simple, empirical equation to predict the permeability of polymer blends.

EXPERIMENTAL

Materials

Suspension grade PVC, with *K* value of 66-69 (S67-311), suspension polymerized graft polymer of 50 parts vinyl chloride and 50 parts ethylene-vinyl acetate copolymer (Vinnol K 550), and acrylonitrile-butadiene rubber (Chemigum P83, coded in this article as NBR1) were procured from NOCIL, India; Wacker-Chemie GmbH, FRG, and Compagnie Française Goodyear, respectively. Other ingredients used for compounding were Di(2-ethyl hexyl) phthalate (Indo-Nippon, India), epoxidized oil (Indofil Chemicals, India), Ca-Zn stabilizer (ALA Chemicals, India), phosphite chelator (ALA Chemicals, India), and calcium stearate (New Mod. Chem. Corp., India).

Compositions

The blend compositions are given in Tables I and II. The formulations for plasticized PVC samples (Table I) were designed such that only plasticizer content varied and amount of all other ingredients remained constant. EVAPVC had a minimum amount of additive to make it easily processible without decomposition. The binary and ternary blend formulations, shown in Table II, were chosen such that the characteristics of the entire range could

Table I Formulations for Samples of Plasticized PVC and EVAPVC

Ingredients	Formulations, Parts by wt.			
	Sample Code PPVC	Sample Code PPVC2	Sample Code PPVC3	Sample Code EVAPVC
PVC Resin	100	100	100	—
Vinnol K-550	—	—	—	100
DEHP	55	30	20	5
Epoxidised Oil	10	10	10	10
Ca-Zn stabilizer	2.5	2.5	2.5	2.5
Phosphite Chelator	0.5	0.5	0.5	0.5
Ca-Stearate	0.2	0.2	0.2	0.2

be studied. Since the objective of the work is to reduce the quantity of plasticized PVC by replacing it with another polymer(s) and not to substitute it, binary blends of NBR1 and EVAPVC were not formulated.

Compounding

Master batches of dry blends of plasticized PVC and EVAPVC were made in a high speed mixer (Papenmeyer TGEHK-20), with a batch size of about 6.5 Kg. The detailed procedure has been described elsewhere.⁴² Melt blending was done in an oil-heated, laboratory-sized (6 × 13 inch), two-roll mill, having a friction ratio of 1 : 1.2 (Bonanzo Enterprise, India). When the surface temperature of the rolls reached 160°C, the gap between the rolls was adjusted to the minimum and the PPVC compound was added. After masticating for about 4–5 min, when a band formed in the front roll, the gap between the rolls was increased. For binary/ternary blends, addition of other component(s) (EVAPVC, NBR1) to PPVC was made at that stage. The band formed on the front roll was cut and put back on the nip to achieve better and quicker mixing. After mixing for 8–10 min, when the melting and mixing were complete, the band was cut and removed from the roll.

Permeability Measurements

Water Vapor

Small collapsible bags with only one 3 mm ID inlet/outlet tube were fabricated by high frequency welding (REC, Monga Electronics) technique from 0.25 mm thick films made by the two-roll mill. Two welding dies were required for the fabrication. Welding of the top side was done first, after placing the tube with a mandrel between the two sheets. After removing the mandrel, welding of the bottom side, having the 'U' shape, was done. Aluminium welding dies were used. The shape of the collapsible bags was rectangular with the dimensions 5.9 × 5.1 cm.

After filling the bags with distilled water, the inlet/outlet tube was sealed by high frequency welding and the initial weights were taken. The water-filled bags were stored in desiccators containing silica gel desiccant. The desiccators were kept at appropriate temperatures in a cold room or incubator. At desired intervals, the weights of the bags were noted. Permeability was calculated from the knowledge of water loss, its volume at the temperature of interest,

Table II Formulations for Binary and Ternary Blends

Sample Codes	Formulations, Parts by wt.		
	Ingredient PPVC	Ingredient EVAPVC	Ingredient NBR1
BB1 91	90	10	—
BB1 55	50	50	—
BB1 37	30	70	—
BB2 91	90	—	10
BB2 55	50	—	50
BB2 37	30	—	70
TB111	33.33	33.33	33.33
TB311	60	20	20
TB811	80	10	10
TB131	20	60	20
TB181	10	80	10
TB113	20	20	60
TB118	10	10	80

and other physical parameters of the barrier film. Equation (1) was used to calculate permeability constant.

Oxygen, Nitrogen, and Carbon Dioxide

Gas permeability was measured at $27 \pm 2^\circ\text{C}$ and $65 \pm 2\%$ relative humidity by using a permeability cell having 50 sq. cm as the sample (film) area. Films were made by the two-roll mill. Thickness was measured with a gauge and an average of ten readings was taken as the thickness for calculations. Helium was used as carrier gas. The amount of gas permeated was analyzed using a Gas Chromatograph after every 5 or 10 min. The apparatus used for gas permeability studies was a "Lyssy Analytical Gas Permeability Fractometer, model GPM-200." The steady difference between successive readings was taken as the amount of gas permeated within the interval. An average of 3–4 readings was used in all calculations. The details of the procedure have been described by Naik et al.⁴³ Permeability was calculated from eq. (1).

$$P = \frac{Qd}{pAt} \quad (1)$$

where,

$$P = \text{Permeability, } \frac{\text{cm}^3/\text{sec}}{\text{cm}^2(\text{cm Hg/cm of film})},$$

$$Q = \text{Volume, cm}^3 \text{ of gas at S.T.P.,}$$

A = Area, cm^2 ,
 t = Time, sec,
 p = Driving force for permeating gas, cm Hg,
 and
 d = Thickness of film, cm.

RESULTS AND DISCUSSION

Water Vapor

Plasticized PVC

Results of water vapor permeability for plasticized PVC at 37°C and 60°C are shown in Table IIIa. Increases in temperature and plasticizer content increase the permeability. Water vapor permeability increases by more than three times when the temperature is raised from 37°C to 60°C. A rise in permeability by approximately three times is also noted for the rise in plasticizer level from 25% to 40%. An increase in permeability with temperature is expected because of the increased rate of diffusion of permeate. This is due to the increased mobility of both the permeate and the local chain segment of barrier polymer. Plasticization also increases the molecular mobility of polymer chains.³⁰ Water vapor can permeate more easily through polymers having increased chain mobility. Additionally, plasticization increases the water absorption.⁴⁴ The permeability constant is dependent on diffusivity and solubility of the permeate. The differences in diffusivity in the two plasticized PVC may not significantly affect the permeability. Increased water absorption means increased solubility and, therefore, permeability goes up with an increase in the level of plasticizer.

'Pure' Components

The results of water vapor permeability for the 'pure' components are given in Table IIIa. At all the tem-

Table IIIa Water Vapor Permeability for Plasticized PVC, EVAPVC, and NBR1 at Different Temperatures

Sample Codes	Water Vapor Permeability Constants (cm^3) (cm) (cm^2) (sec) (cm.Hg), 10^{-9}		
	4°C	37°C	60°C
PPVC	0.606	16.277	50.900
PPVC3	—	5.293	20.500
EVAPVC	1.380	20.737	66.100
NBR1	4.450	34.172	102.000

Table IIIb Water Vapor Permeability Ratio for "Pure" Components at Different Temperatures

Sample Codes	Ratio of Permeability Constants		
	4°C	37°C	60°C
EVAPVC : PPVC	2.28	1.27	1.30
NBR1 : PPVC	7.34	2.10	2.00

peratures studied, water vapor permeability was in the order PPVC < EVAPVC < NBR1. This order is same as noted for water absorption.⁴⁴ The order of permeability for the 'pure' components can therefore be explained by considering solubility of water in the barrier films. Kojima et al.⁴⁵ also observed that in atactic poly(vinyl alcohol) films, the permeability of water vapor is dependent on the degree of swelling of the film.

It is interesting to note that a rise in temperature from 4° to 37° and 60°C results in increased permeability by 26 and 84 times for PPVC, 15, and 48 times for EVAPVC, and 13 and 23 times for NBR1. The difference in permeability between the three 'pure' components at 4°C is reduced as temperature is increased. This is also reflected in the permeability ratios shown in Table IIIb. This behavior can be explained by considering the T_g of the 'pure' components. The T_g values of the 'pure' components are around 17°, -1°, and -9°C for PPVC, EVAPVC, and NBR1, respectively.⁴⁶ 4°C is above the T_g of both EVAPVC and NBR1 and below the T_g of PPVC. And, therefore, PPVC has restricted chain mobility and this results in low permeability. However, 37° and 60°C are above the T_g for PPVC and the permeabilities are much higher at these temperatures. For EVAPVC and NBR1, the changes in permeabilities at these three temperatures are not as high as for PPVC because all the three temperatures are above T_g for both these materials.

Binary and Ternary Blends

Figures 1 and 2 show the results of water vapor permeabilities at 4°C, 37°C, and 60°C for binary and ternary blends. As expected, the effect of temperature on the permeability constants for all the blends are similar to the 'pure' components. Blends generally have intermediate permeabilities (of the 'pure' components) at all temperatures. The minor deviation from the intermediate behavior is too small to be considered significant.

In applications such as injectable crystalloids,

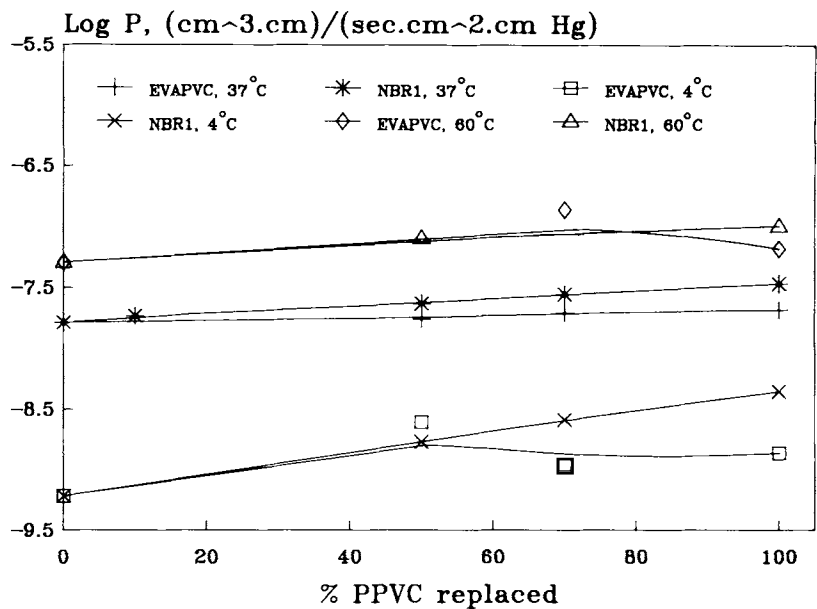


Figure 1 Water vapor permeability constants for binary blends of PPVC with EVAPVC, and NBR1 at 4°C, 37°C, and 60°C, as a function of % PPVC replaced.

blood bags containing anticoagulant solution, and CAPD bags containing dialysis fluids, a loss of too much water during storage may change the concentration of the salt solution to an unacceptable level. While recommending the blends for such applications, the difference in water vapor permeability with conventional materials, such as PPVC, should be an important consideration.

Oxygen, Nitrogen, and Carbon Dioxide

The results of oxygen, nitrogen, and carbon dioxide permeability studies are shown in Figure 3 and Table IV. All the samples studied have carbon dioxide permeability that is a little higher than those of oxygen and nitrogen. The nitrogen permeability is the lowest. Both the trend and the permeability values for

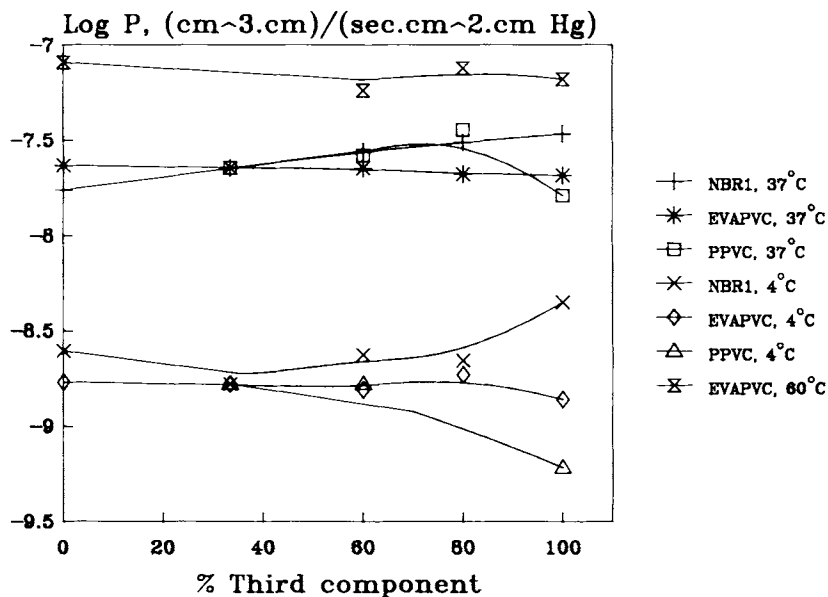


Figure 2 Water vapor permeability constants for ternary blends of PPVC, EVAPVC, and NBR1 at 4°C, 37°C, and 60°C, as a function of % third component; third component added to equal fractions of the other two components.

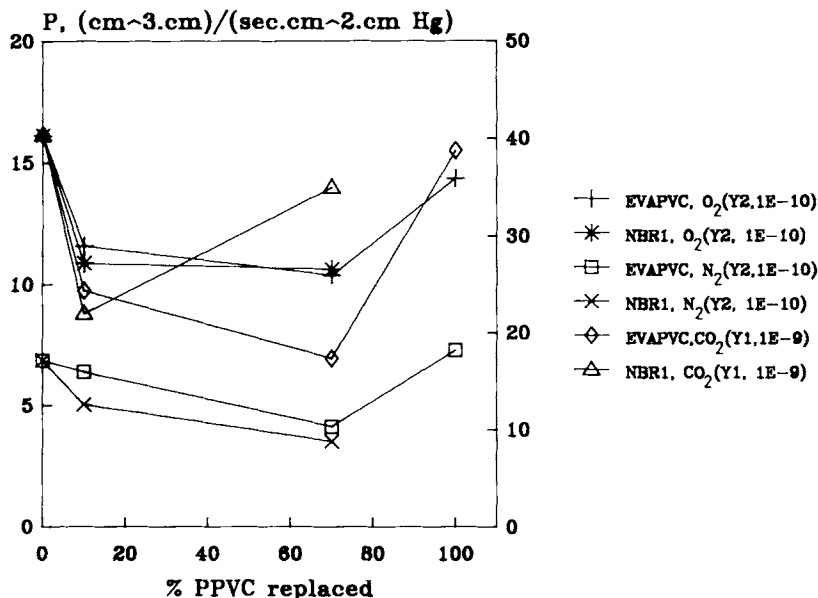


Figure 3 O_2 , N_2 , and CO_2 permeability constants for binary blends of PPVC, with EVAPVC and NBR1 as a function of % PPVC replaced.

the 'pure' components agree well with data reported in the literature.⁴⁷ Permeability values also compare well with the films used for blood bags (Table IV). The large difference in the P values of gases can have practical significance for multistage concentration and separation of gases. Tejar and Miller⁴⁸ reported such possibilities.

Comparison of P values for PPVC and PPVC2 indicates that plasticization increases permeability

for all the three gases studied, the same as observed for water vapor permeability. The reasons for this behavior are the same as for water vapor and the trend is also in agreement with other studies.⁴⁷

Blending of PPVC with a second polymer reduces the P values (Fig. 3) for all the three gases. Marked improvements in permeability characteristics in the cases of O_2 and CO_2 are noted when only 10% PPVC is replaced with EVAPVC or NBR1. However, fur-

Table IV O_2 , N_2 , and CO_2 Permeability Constants of Films

Sample Codes	Permeability Constants for Gases $\frac{(\text{cm}^3)(\text{cm})}{(\text{cm}^2)(\text{sec})(\text{cm.Hg})}, 10^{-10}$			
	Experimental O_2	Calculated O_2	Experimental N_2	Experimental CO_2
PPVC	40.3	—	17.1	161.0
PPVC2	27.1	—	8.1	84.3
BB1 91	29.0	39.8	16.0	97.5
BB1 37	25.9	37.1	10.3	69.4
BB2 91	27.2	34.9	12.6	88.0
BB2 37	26.5	19.4	8.8	140.0
TB111	24.6	26.2	10.4	80.1
TB311	31.0	30.3	10.8	99.7
TB131	25.1	29.2	9.8	86.4
TB113	31.6	20.7	11.4	81.4
TJ ^a	31.5	—	6.5	219.0
PPL ^a	25.0	—	7.4	164.0
PT ^a	26.0	—	9.5	143.0

^a Blood bag films: (TJ) Terumo, Japan, (PPL) Peninsula Polymers, India, and (PT) SCTIMST, India.

ther studies with more blend formulations would be necessary to draw conclusions regarding the binary blend compositions that give minimum permeability. The observation for ternary blends is similar to binary systems (Table IV). Paul and Barlow⁴⁹ and Masi et al.⁵⁰ also made similar observations for other systems and they observed that gas permeation rates through two miscible polymer blends were well below any additive predictions. These observations are of great practical significance and interest since reduced permeabilities of gases are expected to maintain the contents of a medical device, made from such blends, better. Reduced oxygen permeability is likely to reduce deterioration due to oxidation and reduced carbon dioxide permeability is expected to result in better maintenance of pH of the contents.

Permeability depends on the chemical structure, morphology, and polarity of the polymer, nature of the permeate, temperature, and thickness of barrier film.^{51,52} For a coherent polymer film, the permeability is the result of two distinct processes: solubility of the permeate in the polymer and diffusion. In case of noninteracting gas molecules, diffusion is the predominant factor. The rate of diffusion through a polymer film is governed by the number and size distribution of pre-existing 'holes' and the ease of 'hole' formation.⁴⁷ The first factor is dependent on chain packing and is related to the free volume and density. The ease of 'hole' formation depends on the thermal motions of the polymer chain segments as related to chain stiffness and cohesive energy forces of the polymer. The local segmental mobility, or chain stiffness, in compatible polyblends gets affected by chain interactions arising from hydrogen bonding, polar group interactions, etc. The presence of such interactions in the blends studied have been established by FTIR studies.⁴⁶ The experimental density values of binary and ternary blends are marginally lower than the values calculated by the additivity principle from the density values of 'pure' components.⁴⁴ This experimental evidence also suggests the presence of chain interactions.

From the above discussions and the experimental results, it becomes apparent that, in case of O₂, CO₂, and N₂ permeabilities for binary and ternary blends, the chain interactions between the polymers make 'ease of hole formation' difficult and, therefore, permeabilities of the blends are lower than both the 'pure' components. The predominant factor here is the 'ease of hole formation.' On the other hand, for water vapor permeability, the concentration of water in the blends and larger free volume are the predominant factors that govern the permeability.

Model

Prediction of permeabilities of gases through polymer films is difficult because a large number of variables govern the permeability. Salame⁵³ and Roberson et al.⁵⁴ have suggested empirical relationships for predicting the permeability. In a recent study, Swinyard et al.⁵⁵ employed eq. (2) to calculate the water vapor permeability of polyblends.

$$\ln P = \sum \phi_1 \cdot \ln P_1 \quad (2)$$

where

P = Permeability constant for the blend,

P_1 = Permeability constant of the component 1, and

Volume fraction of component 1 = ϕ_1

However, they reported that the calculated values differed from the experimental ones. An empirical model, consisting of terms for permeabilities and weight fractions of 'pure' components, is suggested for predicting the permeabilities of the blend systems studied for this investigation. The suggested model is given in eq. (3).

$$\frac{1}{P} = \sum \frac{x_1}{P_1} \quad (3)$$

where, x_1 = weight fraction of the component 1 in the blend.

Water Vapor

Using the model suggested [eq. (3)], the permeability constants can be calculated; from the values of permeability constants, the water loss through a film can also be predicted. The predicted and experimental loss of water at 37°C through films of representative samples of binary and ternary blends for a period of 21 days are given in Figures 4 and 5. It can be seen that the predictions are quite accurate. The deviation is maximum for TB311 (27%) and for all the other samples the deviations are well within 10%. The reason for such high deviation for TB311 can probably be attributed to experimental error for this sample. Depending on the allowable limits of water vapor permeability, this model can, therefore, be used for designing blend composition.

Oxygen, Nitrogen, and Carbon Dioxide

Due to the low strength and sticky nature of the NBR1 films, it was difficult to fix these films onto

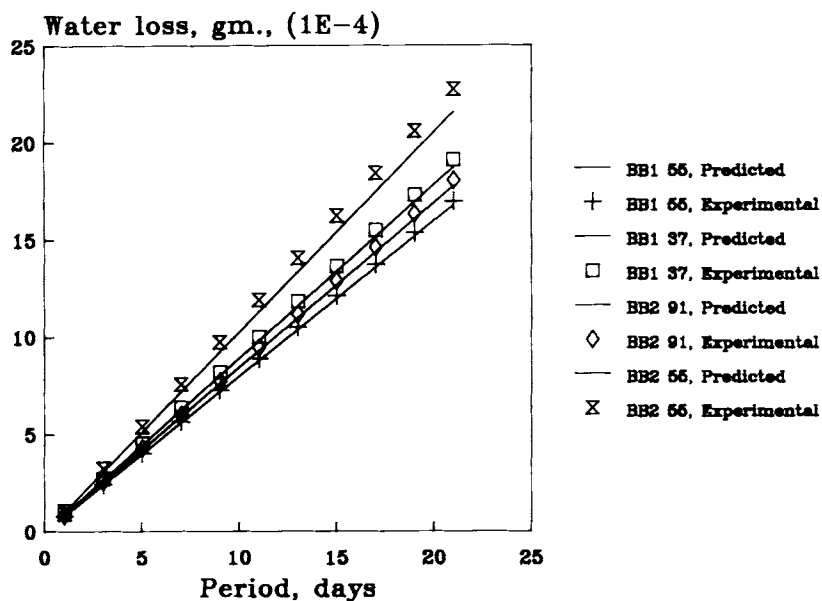


Figure 4 Experimental and predicted water loss through films of representative binary blend samples at 37°C for unit area, thickness, and pressure difference.

the permeability cell. Reproducible results for NBR1 films were difficult to obtain due to the unavoidable stretching and sticking of the film surface during fixing onto the cell. It was possible to obtain three readings, which were close only for oxygen permeability. Permeability for nitrogen and carbon dioxide could not be measured. Therefore, in the absence of data for N_2 and CO_2 , the model could be tested for

both the binary and ternary blends only in the case of oxygen. The calculated and experimental permeability constants for oxygen are presented in Table IV. Though the predictions are not as accurate as for water vapor, these are within 30% of experimental values. In an early study, Stannett and Szwarc⁵⁶ considered prediction of the P values to within a factor of 2 to be good enough. Therefore,

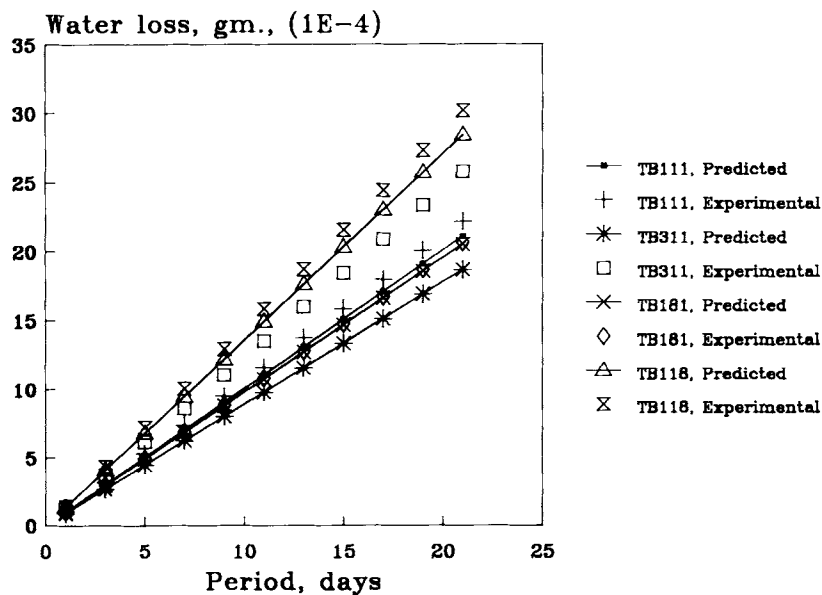


Figure 5 Experimental and predicted water loss through films of representative ternary blend samples at 37°C for unit area, thickness, and pressure difference.

these predictions could be used at least as a rough guide for considering the oxygen permeability of polyblends while designing the blend formulations. The reason that the model works better for water vapor, as compared to oxygen, is probably the different controlling factors that govern the permeability for these two gases. For reasons of simplicity, the interactions between polymers have not been considered for this model. 'Ease of hole formation' is influenced by the interactions and, hence, a more complex equation with these considerations should work better for predicting oxygen permeability.

CONCLUSIONS

Increased plasticization for PVC increases permeability for water vapor, O₂, CO₂, and N₂, due to increased chain mobility. The trend for water vapor permeability for 'pure' components is the same as observed for water absorption, suggesting that solubility of water in barrier films is the predominant factor that determines water vapor permeability in these cases. While temperature increases permeability, the change is faster as the materials cross the region of T_g . Blending PPVC with EVAPVC and/or NBR1 (binary and ternary blends) results in reduced O₂, CO₂, and N₂ permeability. This improvement in property is of great practical significance and interest, since, in medical applications, plasticized PVC is mainly used for storing substances that are affected by permeating gases. The model suggested for permeability of gases through polyblends works well for water vapor and is satisfactory for oxygen. This should help in designing the blend composition and the validity of the model could also be investigated for other polyblend systems. Results on permeability studies are very encouraging and PVC-based polyblends should be investigated further for potential medical applications.

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REFERENCES

1. V. Kalliyankrishnan, S. N. Pal, and A. V. Ramani, *Biomedical Applications of Polymers: An overview*, in Proc. of Polymers: Res. & Ind. Meet., IPCL, Baroda, January, 1987, p. 284.
2. W. W. Vincent, *Biomaterials*, **2**, 194 (1981).
3. H. Daun and S. G. Gilbert, *J. Food Sci.*, **42**, 561 (1977).
4. R. J. Jager and R. J. Rubin, *New Eng. J. Med.*, **287**, 1114 (1972).
5. J. R. Wiethy, *Environ. Health Perspect.*, **17**, 125 (1976).
6. T. R. Cromton, in *Additives Migration from Plastic into Food*, Pergamon, Great Britain, 1979.
7. P. S. Srivasthava, A. K. Saxena, and P. K. Seth, *Ind. J. Pharmaceutical Sci.*, **July-Aug.**, 156 (1985).
8. V. K. Sherwin and M. S. Jacobson, *Environ. Health Perspect.*, **45**, 57 (1982).
9. G. Wildbrett, *Environ. Health Perspect.*, **3**, 29 (1973).
10. J. L. Miripol and I. J. Stern, *Transfusion*, **17**, 71 (1977).
11. M. S. Biggs and J. Baldwin, in *Plastics in Medicine and Surgery III*, PRI, London, 1979, p. 7.1.
12. S. V. Kevy, M. S. Jacobson, and W. E. Harmon, *Trans. Amer. Soc. Artif. Int. Organs*, **XXVII**, 386 (1981).
13. E. G. Hayhurst and M. Wyman, *Am. J. Dis. Children*, **129**, 72 (1975).
14. H. K. Prins and H. M. Scheepatra, in *Plastics in Medicine and Surgery III*, PRI, London, 1979, p. 24.1.
15. P. W. Albro, J. T. Crobett, J. L. Schroeder, and S. C. Jardon, *Environ. Health Perspect.*, **45**, 19 (1982).
16. I. Tomita, Y. Nakamura, N. Aoki, and N. J. Inui, *Environ. Health Perspect.*, **45**, 19 (1982).
17. R. J. Jager and R. J. Rubin, *Science*, **170**, 460 (1970).
18. W. Geertz, K. Dyer, D. Johnson, B. Miller, B. Taylor, and W. Sharp, *Trans. Amer. Soc. Artif. Int. Organs*, **XX**, 42 (1974).
19. J. H. Turner, J. C. Petricciani, M. L. Crouch, and S. Wenger, *Transfusion*, **14**, 560 (1974).
20. R. J. Rubin and C. A. Schiffer, *Transfusion*, **16**, 330 (1976).
21. R. W. R. Baker, *Toxicology*, **9**, 319 (1978).
22. W. M. Kline and N. E. Skiest, in *Encyclopedia of PVC*, I. L. Nass, Ed., Vol. 1, Chap. 4, Marcel Dekker, New York (1976).
23. D. J. Walsh and G. L. Cheng, *Polymer*, **25**, 495 (1984).
24. D. J. Walsh and G. L. Cheng, *Polymer*, **25**, 499 (1984).
25. C. R. Blass, in *4th Intl. Conference on PVC-90*, PRI, 8/1, April 24-26, (1990).
26. V. Kalliyana Krishnan, A. Jayakrishnan, and J. D. Francis, *J. Mater. Sci.: Mater. Medicine*, **1**, 185 (1990).
27. *Inside R & D*, **14**(47), (1985).
28. R. Ludwig, *Plasma Polymerization—A new Technology for Surface Modification*, in Proc. of ANTEC 89, May 1-4, New York, 1989, p. 915.
29. *Bev-a-line*, Trade Literature of Thermoplastic Scientifics Inc.
30. C. F. Hammer, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Vol. 2, Academic, New York, 1978, p. 219.
31. *Polymer Blends and Alloys-Guidebook to Commercial Products*, Technomic, Pennsylvania, 1988.

32. R. P. Petrich, *Impact Reinforcement of PVC*, Paper presented at SPE RE/TEC Meeting, Cleveland, Ohio, March 7, 1972.
33. M. Matsuo, *Japan Plast.*, **2**, 6 (1968).
34. R. G. Bauer and M. S. Guillod, in *Copolymers, Polyblends, and Composites*, N. A. Platzer, Ed., ACS 142, Washington DC, 1977, p. 231.
35. *IPI Transactions, News Abstracts*, **V** (3,4), 11 (1990).
36. H. F. Schwarz and J. W. F. Bley, in *Advances in Polymer Blends and Alloys Technology*, M. A. Kohudic, Ed., Vol. 1, chap. 10, Technomic, Pennsylvania, 1988.
37. K. T. Varughese, G. B. Nando, P. P. De, and S. K. De, *J. Mater. Sci.*, **23**, 3894 (1988).
38. K. T. Varughese, P. P. De, S. K. Sanyal, and S. K. De, *J. Appl. Polym. Sci.*, **37**, 2537 (1989).
39. G. Menzel, *Kunststoffe*, **69**, 480 (1979).
40. B. Terselius and B. Ranby, *Pure Appl. Chem.*, **53**, 421 (1981).
41. *Plast. Technol.*, **Nov.**, 34 (1989).
42. A. Saxena, V. Kalliyankrishnan, and S. N. Pal, *J. Appl. Polym. Sci.*, **34**, 1727 (1987).
43. V. G. Naik, R. Rangaprasad, and D. D. Kale, *Permeability of Gases through Polymer Packaging Films*, Packaging India, to appear.
44. S. N. Pal, A. V. Ramani, and N. Subramanian, submitted for publication.
45. Y. Kojima, K. Furuhashi, and K. Miyasaka, *J. Appl. Polym. Sci.*, **28**, 2401 (1983).
46. S. N. Pal, A. V. Ramani, and N. Subramanian, (submitted).
47. C. E. Rogers, M. Fels, and N. N. Li, in *Recent Developments in Separation Science*, N. N. Li, Ed., Vol. II, Chap. 7, CRC Press, Cleveland, Ohio, 1976.
48. J. G. Tejar and I. Miller, *Facilitated Versus Non-facilitated Permeation through Polymer Membranes*, in Proc. of 68th National A.I.Ch.E. Meeting, 1971.
49. D. R. Paul and J. W. Barlow, in *Polymer Compatibility and Incompatibility-Principles and Practices*, K. Solc, Ed., Harwood Academy, New York, 1982, p. 18.
50. P. Masi, D. R. Paul, and J. W. Barlow, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 15 (1982).
51. R. J. Ashley, in *Polymer Permeability*, J. Comyn, Ed., Elsevier, London, 1985, Chap. 7, p. 269.
52. P. M. Subramanian, *Polym. Eng. Sci.*, **25**, 483 (1985).
53. M. Salame, *A.I.Ch.E. Meeting Preprints*, Atlanta, 1970, p. 281.
54. L. M. Robeson, A. Noshey, M. Matzner, and C. N. Merriam, *Angew. Makromol. Chem.*, **29/30**, 47 (1973).
55. B. T. Swinyard, P. S. Sagoo, J. A. Barrie, and R. Ash, *J. Appl. Polym. Sci.*, **41**, 2479 (1990).
56. V. Stannett and M. Szwarc, *J. Polym. Sci.*, **16**, 89 (1955).

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