

Gas Permeation of Polymer Blends. IV. Poly(vinyl Chloride) (PVC)/Acrylonitrile-Butadiene-Styrene (ABS) Terpolymer

YOUNG J. SHUR and BENGT RÅNBY, *Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden*

Synopsis

The transport behavior of He, O₂, N₂, and CO₂ in membranes of poly(vinyl chloride) (PVC)/acrylonitrile-butadiene-styrene (ABS) blends has been studied at 25°C. The blends were further characterized by dynamic mechanical measurements, differential thermal analysis (DTA), density measurements, and x-ray diffraction. The equilibrium sorption of CO₂ and N₂ was measured directly at atmospheric pressure using an electromicrobalance and compared with sorption values obtained as P/D ratios from permeation measurements. The rates of permeation (P) and diffusion (D) increase with increasing ABS content in the blends. The P and D values are not additive, and only slight indications of phase inversion in the blends are observed at 5-10 wt-% ABS in the blends. Experimental densities of the blends are higher than calculated densities assuming volume additivity. The data are interpreted to mean that the PVC/ABS blends form a two-phase system composed of a soft polybutadiene (rubber) phase and a rigid PVC/styrene-acrylonitrile copolymer (SAN) phase of mutually compatible components. DTA and dynamic mechanical measurements also show a two-phase system. Sorption values of CO₂ and N₂ by equilibrium sorption measurements increase with increasing ABS content in the blends without the large fluctuations which have been observed for the sorption values obtained from the time lag method. Comparison of the two types of sorption values (from direct measurements and from P/D ratios) show larger deviations for CO₂ than for N₂. This suggests that the time lag method is not valid for permeants with polar character in heterogeneous two-phase systems where chemical immobilizing effect on the permeant molecules occurs.

INTRODUCTION

The transport of permeant molecules into and through polymer membranes depends intimately on the diffusion and sorption properties involved. These properties are sensitive to changes in membrane structure such as crystallinity, crosslinking, additives, pores, phase morphology, phase interaction, etc. For this reason, permeability measurements are a useful method to study polymer properties.

In earlier work on polymer blends,¹⁻³ we have shown how the gas transport parameters permeability (P), diffusivity (D), and activation energy of diffusion (E_D) depend on the compatibility of the two components. Changes in diffusion rate were mainly discussed as due to variations in chain segmental

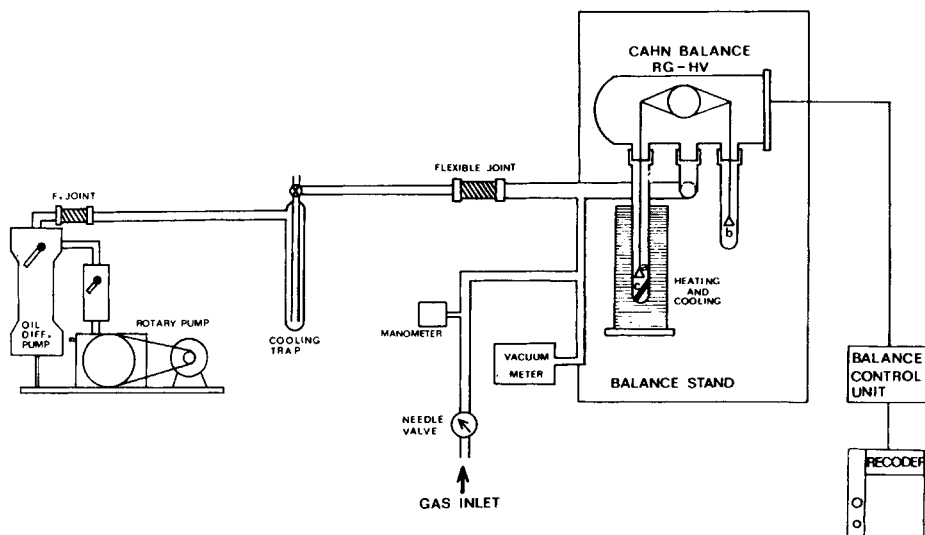


Fig. 1. Schematic diagram of a Cahn electromicrobalance for sorption measurements at equilibrium: a, sample; b, tare weight; c, ionizing unit.

mobility related to segment-segment interactions in the blends. However, the sorption characteristics were difficult to interpret as based on a single factor.

For simple cases, Henry's dissolution law is valid. There are, however, complex systems which deviate from Henry's law, e.g., glassy polymers,⁴⁻⁸ heterogeneous membranes containing absorptive fillers,⁹⁻¹¹ and polymer blends.^{2,3} For some of the polymer blends studied in our earlier work,^{2,3} it seems probable that the sorption characteristic in a broad sense is fairly well interpreted with the dual sorption mechanism. The two components in the blend have different sorption properties which affect the partition rate of the given permeant molecules. Furthermore, we have observed that the sorption values of a permeant, derived from permeation and diffusion rates in the polymer blends, are rather irregular and fluctuate with the blend composition. Interpretation has been proposed for this behavior,³ e.g., the time lag method to evaluate diffusion rate and hence also sorption values is not valid, and/or the hole sorption mode of the blend varies with blend composition.

The present work gives further background to a discussion of the diffusion characteristics of polymer blends related to phase interaction in the blends. In addition, sorption values obtained from sorption equilibrium measurements are presented and the proposed factors influencing the sorption process are discussed. The present work gives the diffusion and sorption behavior of gases in PVC/ABS blends.

EXPERIMENTAL

Materials

The PVC sample was suspension grade (Pevikon, from KemaNord AB,

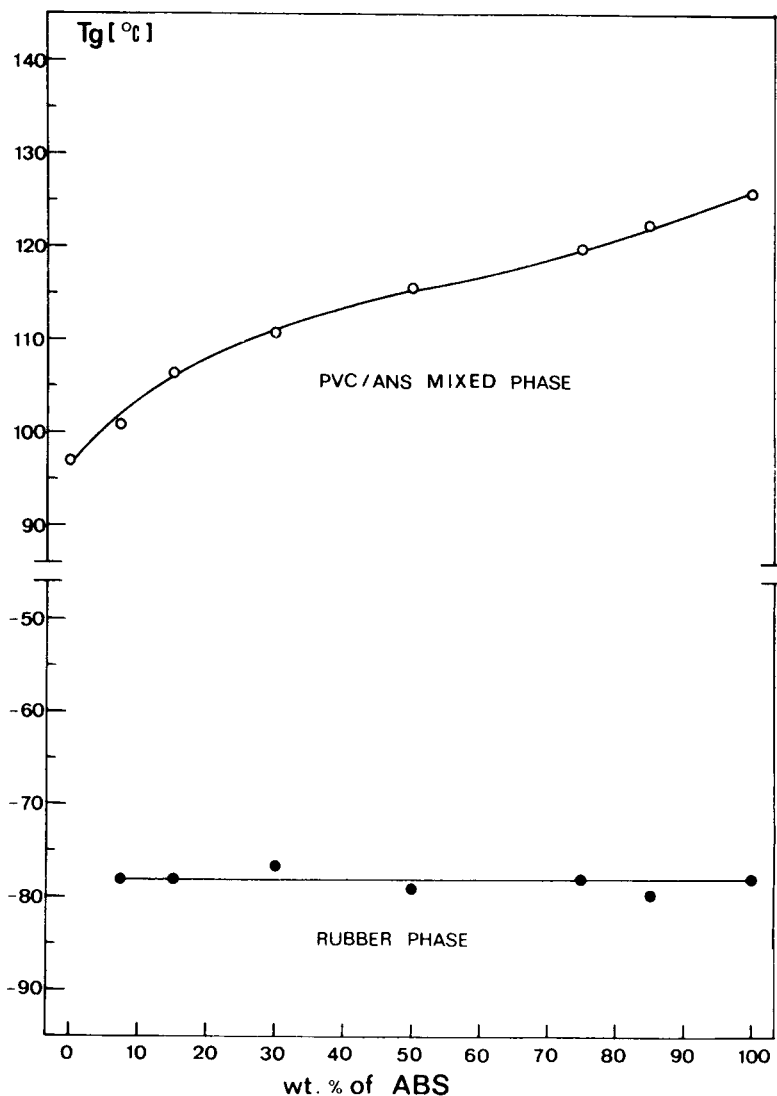


Fig. 2. Glass transition temperatures of PVC/ABS blends as a function of blend composition, measured by Rheovibron at 110 Hz.

Sweden) with density 1.39 g/ml at 25°C. The ABS used was an impact modifier for PVC (Blendex 401, Marbon Chemical Co., Netherland) with a composition ratio of acrylonitrile/styrene/butadiene 15/40/45 by weight and density 0.99 g/ml at 25°C. The ABS was prepared by emulsion polymerization and was of a slightly grafted type: polybutadiene grafted with a styrene-acrylonitrile monomer mixture (giving SAN copolymer). The methods for the preparation of membrane samples of the polymer blends used in this work are the same as those described in our previous paper.¹

Measurements

The permeation rates of gases (He, O₂, N₂, and CO₂) through thin mem-

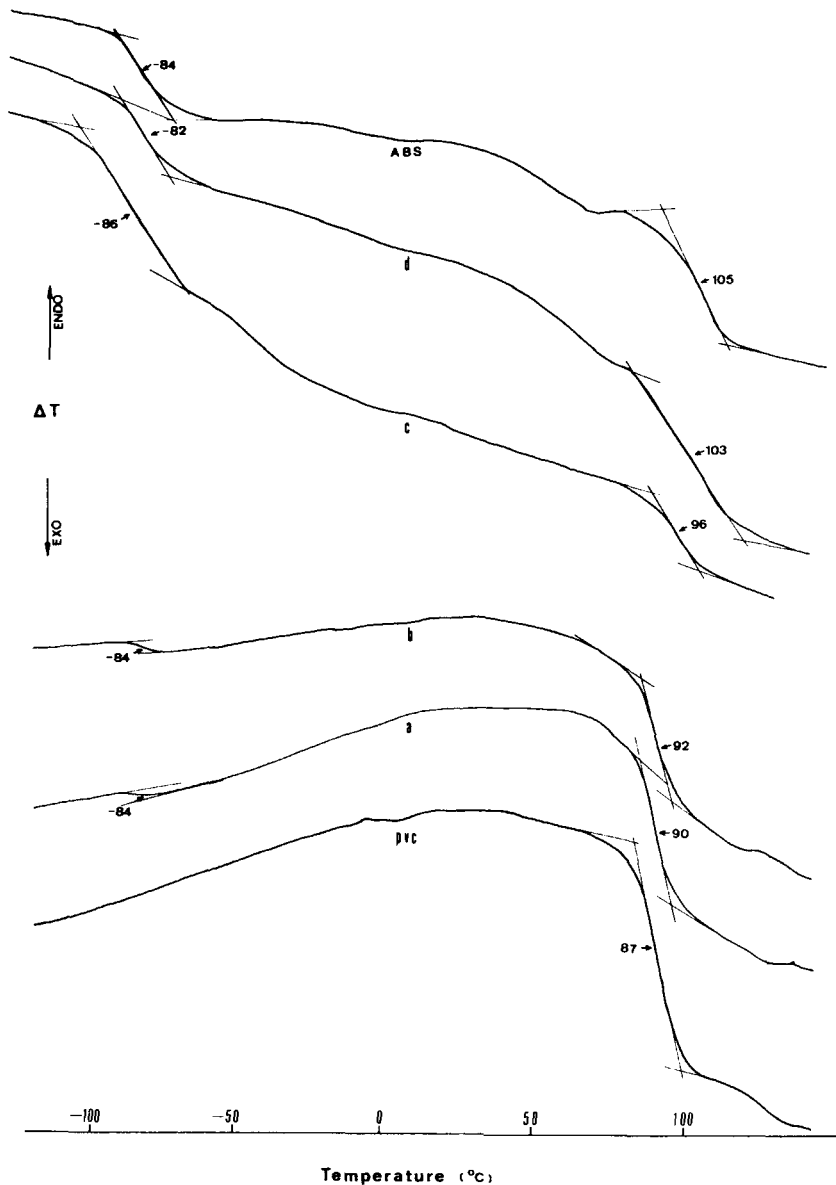


Fig. 3. DTA thermograms for PVC, ABS, and PVC/ABS blends of different blend compositions: a, 92.5/7.5; b, 85/15; c, 50/50; d, 15/85.

branes (thickness 0.04 mm) at 25°C were measured using an isostatic gas permeability meter (GPM-200, Incentive AB, Sweden) with H₂ as reference gas.

The solubility coefficients of N₂ and CO₂ for the blends were obtained by sorption equilibrium measurements and were compared with the values obtained from the *P/D* ratio. The sorption values at equilibrium were obtained by monitoring gravimetrically the weight increase with time of a membrane sample exposed to permeant gas using a Cahn electromicrobalance (Model RG). A schematic picture of this instrument is shown in Figure 1. It con-

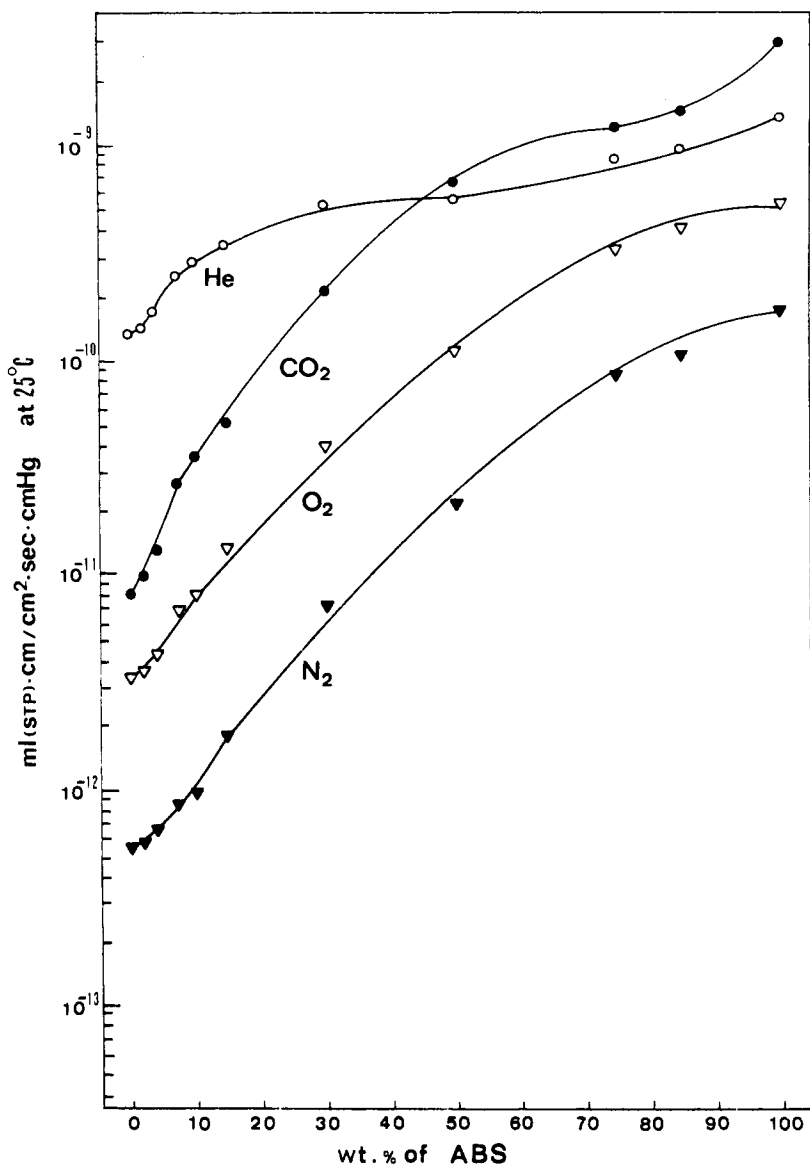


Fig. 4. Permeability coefficients at 25°C of PVC/ABS blends as a function of blend composition for He, O₂, N₂, and CO₂.

sists of three main parts: vacuum unit, balance with recording unit, and gas supply unit. For measurement, a membrane strip with dimensions $5.0 \times 1.5 \times 0.04$ cm was placed on the pan (a in Fig. 1) and evacuated under 4×10^{-7} torr at 25°C for two days. The permeant gas was thereafter introduced into the balance and the gas pressure kept constant at 760 mm Hg during the measurement. The weight increase of the membrane versus time was recorded until equilibrium, and the solubility of the gas was calculated from the weight increase at equilibrium state. The static electricity arising in the balance was eliminated by inserting an ionizing unit of ²¹⁰Po (c in Fig. 1) near

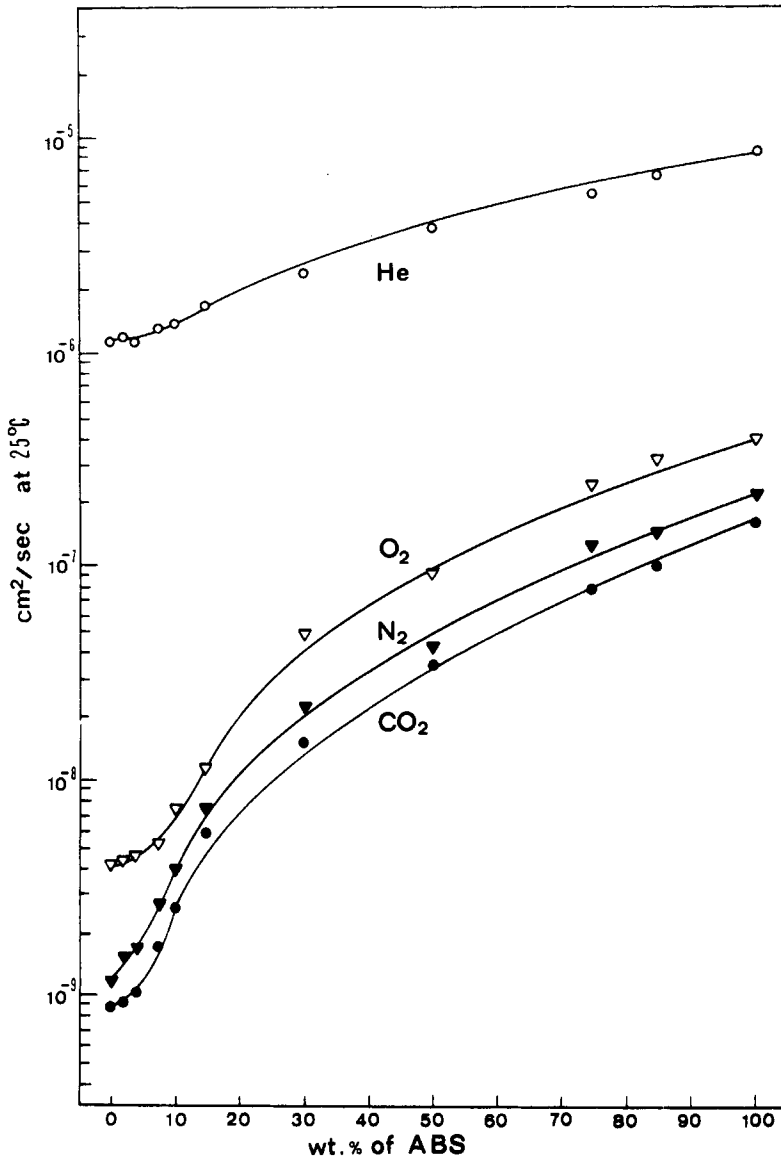


Fig. 5. Diffusion coefficients at 25°C of PVC/ABS blends as a function of blend composition for He, O₂, N₂, and CO₂.

the sample strip. In addition, the outside of the glass vessels and tubes of the balance were washed with an antistatic electricity solution.

Measurements of density and crystallinity of the blends were carried out like in previous work.¹ The compatibility of the blends was studied by determination of their glass transition temperatures using a direct-reading Rheovibron (Type DDV-II, Toyo Measuring Instrument Co., Japan) operating at 110 Hz and temperatures from -100° to +130°C and a differential thermal

analysis instrument (DTA, Type TA-2000, Mettler, Switzerland) in the temperature range from -120° to $+130^{\circ}\text{C}$. The scan speed was $20^{\circ}\text{C}/\text{min}$, and the range, $100\ \mu\text{V}$. Al_2O_3 was used as reference.

RESULTS AND DISCUSSION

Before discussing the results of the gas transport measurements, the morphology of ABS and PVC/ABS blends will be reviewed. The ABS studied consists of two incompatible phases, polybutadiene rubber phase and styrene-acrylonitrile copolymer (SAN) rigid phase. The rubber phase is finely dispersed and embedded in the rigid SAN phase as matrix. When PVC and ABS are mixed, it is probable that the PVC interacts easier with the SAN phase than with the rubber phase considering the polarity of the phases. Buchdal et al.^{12,13} have reported that PVC/polybutadiene forms an incompatible system, while Deanin et al.¹⁴ have reported that PVC and SAN of ABS are fairly compatible, providing a single continuous rigid matrix in the blend. Whether PVC and SAN are compatible in a blend or not depends, among other factors, on the level of acrylonitrile (AN) content in the SAN. For PVC/NBR blends, it is known that the minimum level of AN content giving compatibility of the blends is about 20 wt-%.² Recently, Stein et al.¹⁵ have observed that poly(methyl methacrylate)/SAN blends form a compatible system when AN content in the SAN is from 9 to 25 wt-%. Dynamic mechanical measurements and differential thermal analysis of the PVC/ABS blends show that there are only two glass transition temperatures in the whole composition range studied (Figs. 2 and 3). The T_g at high temperatures (the mixed PVC/SAN phase) is shifting toward higher temperature with increasing ABS content in the blends. The T_g at low temperature (the rubber phase), however, remains unchanged with blend composition. Hence, the PVC/ABS blends can be considered to be an incompatible system, where the rubber phase is dispersed in the mixed phase of the compatible PVC and SAN components.

Figures 4 and 5 show the permeability and diffusivity of He, O_2 , N_2 , and CO_2 for PVC/ABS blends as a function of blend composition. The P and D values gradually increase with increasing ABS content in the blends. This is interpreted as due to the presence of a highly permeable, incompatible rubber phase in the ABS matrix of the blends.

In Table I, the gas transport parameters (P , D , and S) for polybutadiene

TABLE I
Gas Transport Parameters of Polybutadiene and ABS, Measured at 25°C^a

Gas	Polybutadiene			ABS		
	P	D	S	P	D	S
O_2	23.42×10^{-10}	1.62×10^{-6}	14.44×10^{-4}	5.32×10^{-10}	0.42×10^{-6}	12.61×10^{-4}
N_2	14.70	1.32	10.11	1.78	2.24	7.95
CO_2	117.53	0.92	127.75	29.75	0.17	175.02

^a P , in $\text{cc}(\text{S.T.P.})/\text{cm}^2\text{-sec}\cdot\text{cm Hg}$; D , in cm^2/sec ; and S , in $\text{cc}(\text{S.T.P.})/\text{gas}/\text{cc}(\text{polymer})\cdot\text{cm Hg}$ and obtained from P/D ratio.

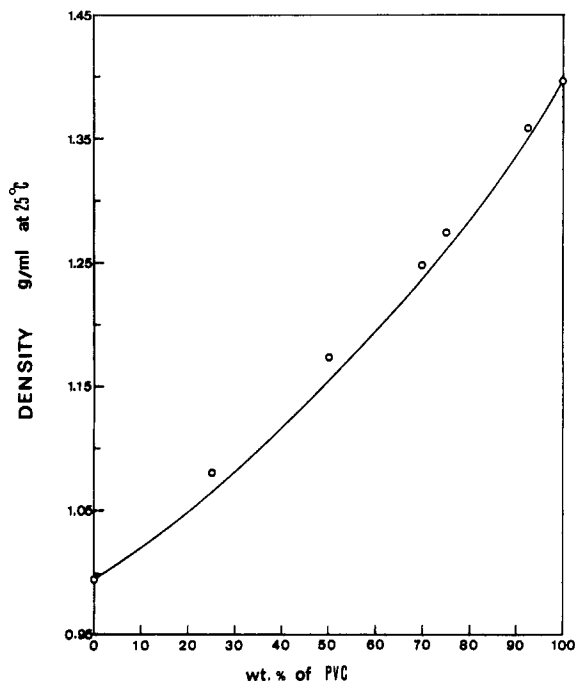


Fig. 6. Experimental and calculated densities of PVC/ABS blends vs. blend composition in wt-%: (O) experimental; (—) calculated.

and ABS are compared. Polybutadiene shows much higher P and D values than ABS. However, the sorption values of O_2 and N_2 in ABS are lower than in polybutadiene. The reverse is true for CO_2 . These data suggest that the rigid SAN phase behaves like a diffusion barrier for the inert gases (O_2 and N_2), but enhances the solubility and thus the permeation rate of a polar permeant like CO_2 due to the polar character of the SAN component.

No effect of additivity of permeability or diffusivity for the blends is observed (see Figs. 4 and 5). This could be due to the incompatibility of the rubber and PVC/SAN phases. There is slight indication of phase inversion at 5–10% ABS in the blends.

The measured densities for the PVC/ABS blends are higher than the calculated densities assuming volume additivity of the components (Fig. 6). The excess density for the 50/50 blend is 0.017 g/ml at 25°C. This is attributed to better chain packing in the blend, which probably is an effect of specific interaction between PVC and SAN. The blends are substantially amorphous with crystallinities less than 10%, suggesting that the density differences are not due to changes in crystallinity of the blends.

The sorption values of CO_2 and N_2 obtained from gravimetric measurements at equilibrium are given in Figure 7 and compared with data obtained from P/D ratios where P is measured at steady state and D from time lag. The solubility coefficients from gravimetric measurements for the blends studied increase with increasing ABS content. The deviations between the two sorption values are larger for CO_2 than for N_2 . There are large fluctuations in the sorption values from P/D ratios. In our previous work,³ abnormal sorption behavior was observed for CO_2 , but not for O_2 , N_2 , and He, i.e., a

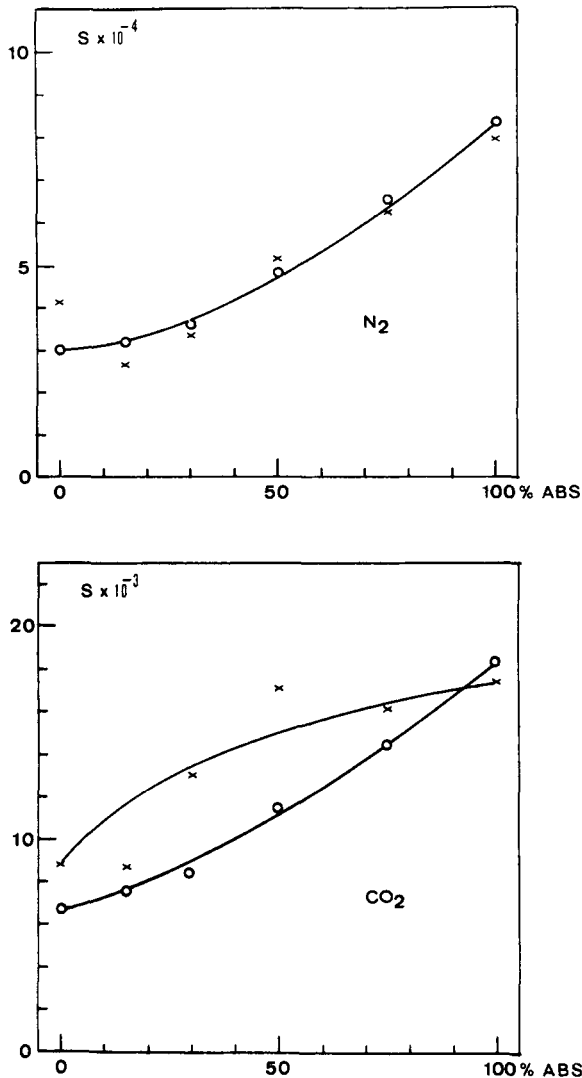


Fig. 7. Gas solubility coefficients at 25°C of PVC/ABS blends vs. blend compositions in wt-%: (x) from P/D ratios; (O) by equilibrium sorption measurements.

deviation of linearity of $\ln S$ versus ϵ/κ . Larger deviation from linearity was observed with increasing chlorine content in CPE. This suggests that increasing interaction between CO₂ and polymer molecules causes a larger deviation. These results indicate that due to interaction, the sorption process of permeants having a polar character like CO₂ is more complex than that of nonpolar ones such as O₂, N₂, and He.

The sorption of a mobile component in a solid could be both a physical and chemical process. Physical sorption occurs as the result of nonspecific forces of attraction between permeant molecules and solid phase, i.e., van der Waals forces. This sorption occurs on the surface and in voids of the solid. Chemical sorption involves some degree of specific chemical interaction between

molecules of the permeant and the solid component. It usually leads to pronounced hysteresis effects in a cyclic sorption process.

When two incompatible polymers of different chemical and physical characters are mixed, it is assumed that the effect on the sorption process is due to changes in hole statistics by blending as proposed by Stannett et al.¹⁶ The sorption of a permeant in a blend can simply be expressed as additive,^{17,18} i.e.,

$$S = S_1V_1 + S_2V_2 + S_hV_h$$

where S_1 , S_2 , and S_h are the solubilities of the permeant in pure polymers (1 and 2) and in holes, respectively; V_1 , V_2 , and V_h are the corresponding volume fractions of the two polymers and the holes in the blend.

In the extreme case, where the specific interaction of the permeant molecules with the substrate is much larger in one phase than in the other phase of the blend, an immobilizing effect on the permeant molecules will be exerted in the highly interacting phase. The result would, in effect, be a delay in the attainment of steady-state diffusion. This may, in the extreme case, cause a leveling-off in the diffusion rate through the membrane. The D values obtained from the intercept of the permeation curve (the time lag), hence, would not be the true values. Such an immobilizing effect may be analogous to that showed in the dual sorption process for a glassy polymer and a filled system. We may call our concept of immobilizing effect for a two-component system *chemical immobilization*, while that of a dual sorption system may be called *physical immobilization*. These two effects lead to critical difficulties when the classical time lag technique is applied to measure the gas transport parameters in systems where a dual sorption process is involved. This situation would be more pronounced for polar and large permeants.

Chemical immobilization of permeant molecules would tend to increase with increasing permeant molecule-polymer interaction. Rogers has noted that the Langmuir isotherm is best fitted in chemisorption and in adsorption of large permeant molecules.¹⁹ This suggests that sorption in polymer blends having a chemical immobilizing effect may be explained by the dual sorption process. In the PVC/ABS blends, the sorption behaviors of CO_2 and N_2 in the rubber phase and the mixed PVC/SAN phase are, of course, different. The chemical immobilization effect (at least in the earlier stage of diffusion) is expected to be pronounced for CO_2 in the PVC/SAN mixed phase due to the polar character of both permeant and polymer phase. If this is true, the sorption values for PVC/ABS blends obtained from the time lag method are expected to be less reliable for CO_2 than for N_2 . This is verified by the experiments. As shown in Figure 7, the sorption values for CO_2 obtained by the two different methods show larger deviations than those for N_2 . The equilibrium sorption values for the blends are "true" values since they are not affected by time-dependent immobilizing effects.

If blending of PVC and ABS changes hole statistics, i.e., size and number of holes in the blends, the term S_hV_h in eq. (1) will be changed. This will affect the physical sorption process of the blend. The changes in hole statistics may differ in different blend compositions. It may cause the fluctuation of sorption values in the blends having different blend compositions. The ef-

fect of changes in hole statistics on the sorption process should be considered in relation to the size of permeant molecules. Thus, the size of holes created or changed owing to blending may not be so much larger or smaller than the size of the permeant molecules. The sorption values obtained from equilibrium sorption measurements showed a steady increase with increasing ABS content in the blends. This may suggest that the effect of hole statistics changes may not exist or may be less significant than the changes of other factors which influence the overall sorption process, e.g., the molar heat of condensation of permeant molecules in different blend compositions and the level of interaction between the two polymers in the blends having different blend compositions.

It is interesting to further study the sorption values of N₂ and CO₂ in pure PVC. Although PVC is a one-component system, there are large deviations between the two types of sorption values (see Fig. 7). It has been shown that PVC milled at 160°C is morphologically heterogeneous.¹ It contains two fractions, one having partly crystalline, unmelted particles and the other consisting of an amorphous fraction of melted particles. Our results could be due to the presence of unmelted PVC particles, which behave like a dispersed phase and immobilize the permeant molecules. This interpretation is tentative. More conclusive evidence is needed, e.g., from determination of sorption values for PVC prepared at different milling temperatures and from morphologic studies by electron microscopy.

The authors wish to express their gratitude to the Swedish Polymer Research Foundation and Carl Tryggers Stiftelse for financial support and to KemaNord AB for preparation of special samples and for useful information about their properties. The authors also wish to acknowledge the contribution of Hugo Tillqvist AB, Sweden, in measurements of DTA.

References

1. Y. J. Shur and B. Rånby, *J. Appl. Polym. Sci.*, **19**, 1337 (1975).
2. Y. J. Shur and B. Rånby, *J. Appl. Polym. Sci.*, **19**, 2143 (1975).
3. Y. J. Shur and B. Rånby, *J. Appl. Polym. Sci.*, **20**, 3105 (1976).
4. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 1 (1963).
5. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 13 (1963).
6. W. R. Vieth and J. A. Eilenberg, *J. Appl. Polym. Sci.*, **16**, 945 (1972).
7. W. R. Vieth, H. H. Alcalay, and A. J. Frabetti, *J. Appl. Polym. Sci.*, **8**, 2125 (1964).
8. W. R. Vieth and K. J. Sladek, *J. Colloid Sci.*, **20**, 1014 (1965).
9. D. R. Kemp and D. R. Paul, *J. Polym. Sci.*, **12**, 485 (1974).
10. D. R. Paul and D. R. Kemp, *J. Polym. Sci.*, **C-41**, 79 (1973).
11. W. I. Higuchi and T. Higuchi, *J. Amer. Pharm. Assoc. Sci.*, **49**, 598 (1960).
12. R. Buchdal and L. E. Nielsen, *J. Polym. Sci.*, **15**, 1 (1955).
13. S. Krause, *J. Macromol. Sci. Rev.*, **C7**, 251 (1972).
14. R. D. Deanin and C. Moshar, *ACS Polym. Prepr.*, **15**(1), 403 (1974).
15. Von D. J. Stein, R. H. Jung, K. H. Illers, and H. Hendus, *Angew. Makromol. Chem.*, **36**, 89 (1974).
16. R. T. Stallings, H. B. Hopfenberg, and V. Stannett, *J. Polym. Sci.*, **C-41**, 23 (1973).
17. G. J. van Amerongen, *Rubber Chem. Technol.*, **37**, 1065 (1964).
18. C. C. Monks and B. Ellis, *J. Polym. Sci.*, **11**, 2089 (1973).
19. C. E. Rogers, in *Engineering Design for Plastics*, E. Baer, Ed., Reinhold, New York, 1964, p. 609.

Received November 25, 1975