Gas Permeation of Polymer Blends. II. Poly(vinyl Chloride)/Acrylonitrile–Butadiene Copolymer (NBR) Blends

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Synopsis

The transport behavior of He, O_2, N_2, and CO_2 in a series of PVC/NBR polymer blends with varying acrylonitrile (AN) content in the NBR component has been studied at 25° and 50°C. In addition, measurements of density, crystallinity, and thermal expansion coefficients were carried out. The transport behavior of these blends is similiar to previous result for PVC/EVA.[1] With increasing AN content in NBR, the permeability (P) and diffusivity (D) of the permeants decreased while the activation energy for diffusion (E_D) increased. For the polymer blends, better additivity of permeability and diffusivity was observed with increasing AN content in the NBR component. The polymer blends also showed increasing volume contraction with increasing AN content in the NBR component. These effects have been discussed as due mainly to increased polymer–polymer interaction causing reduced segmental mobility and increased compatibility of the two polymers. The sorption values calculated from P/D ratios were largely irregular and fluctuated with the blend composition. They were less reproducible than other transport parameters, i.e., P and D measured separately. Several reasons for the irregular sorption behavior were proposed.

INTRODUCTION

The transport properties of oxygen and nitrogen through a series of poly(vinyl chloride) (PVC)/ethylene–vinylacetate copolymer (EVA) blends have been measured in a previous study[1] and related to the compatibility of the two polymers in the blends. Decrease in rate and improved additivity of permeability and diffusivity of the blends with increasing compatibility were discussed mainly as related to cooperative effects between the two types of polymer molecules in the blends, giving reduced segmental mobility of the polymer chains.

In an ideal incompatible polymer blend, as described by Higuchi's model,[2] containing a finely dispersed phase in a continuous phase, perturbations of the diffusion process will occur. However, in an ideal compatible blend, which may not exist in reality, it is expected that the diffusion process is influenced by cooperative segmental movements of the two different polymer molecules in the blend due to interaction. Such phenomena are further explored in mechanical relaxation studies of polymer blends.

The gas transport process through a polymer film cannot be interpreted as based only on segmental mobility. This process is related to a thermodynamic factor (sorption or solubility) as well as a kinetic factor (rate of diffusion). It is expected that also the sorption process is affected by changes in compatibility of the blend components. The blending of two chemically dif-

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ferent polymers is expected to cause changes in the tendency of a permeant to form a condensed phase with the polymer molecules, as proposed by Kwei et al.[3,4] Furthermore, the blending may alter the hole statistics in the blend as suggested by Stallings et al.,[5] i.e., the size and the number of holes, by which the adsorption process is changed.

The present work gives further background to our previous discussion[1] by extending it to the sorption and diffusion behavior of gases in PVC/NBR blends.

EXPERIMENTAL

Materials

The PVC used was of a suspension grade (Pevikon from KemaNord AB, Sweden) with density $d = 1.39$ g/ml at 25°C. The NBR rubbers were of three grades (supplied from B. F. Goodrich Company, U.S.A.): NBR-1 (Hycar 1024) containing 21.7% acrylonitrile (AN) with $d = 0.95$; NBR-2 (Hycar 1043) containing 29.6% AN with $d = 0.97$; and NBR-3 (Hycar 1041) with 41.6% AN and $d = 1.00$. The content of AN in the NBR samples are
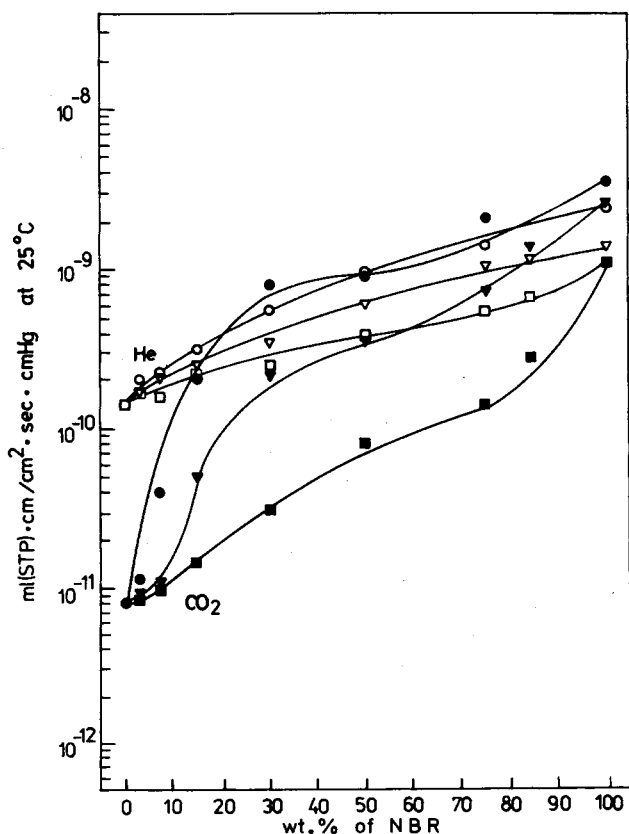

Fig. 1. Permeability coefficients of He and CO_2 vs. polymer blend composition. P of He: (O) in PVC/NBR-1 blends; (△) in PVC/NBR-2 blends; (□) in PVC/NBR-3 blends. P of CO_2: (●) in PVC/NBR-1 blends; (▲) in PVC/NBR-2 blends; (■) in PVC/NBR-3 blends.
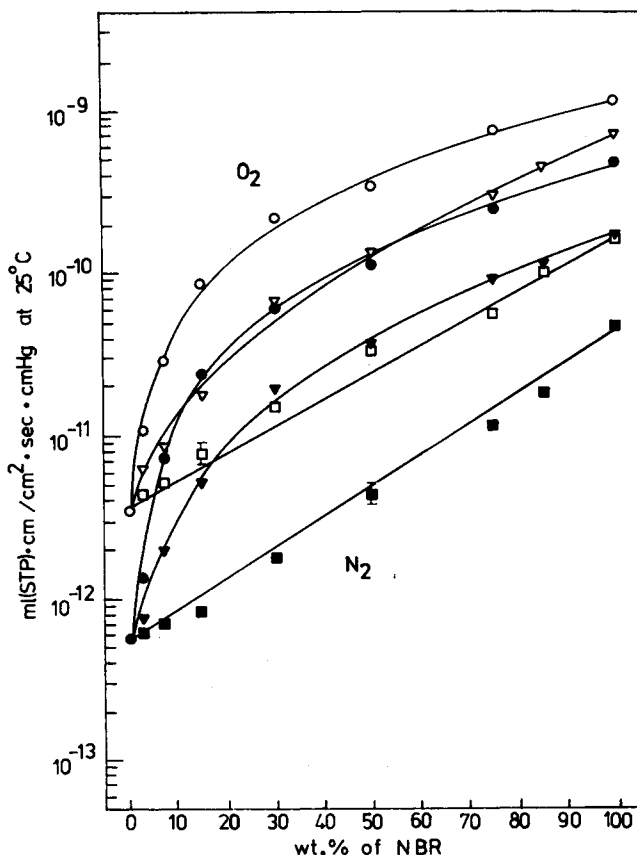
Fig. 2. Permeability coefficients of O_2 and N_2 vs. polymer blend composition. P of O_2 and P of N_2: with the same polymer blends as in Fig. 1.

taken from the data reported by Jorgensen et al.[6] The methods for preparation of the films and for measurements of permeation of gases through the polymer blends are the same as described in our previous work.

Measurements

Permeation measurements of He, O_2, N_2, and CO_2 were performed for thin membranes (thickness about 0.03 mm) at 25° and 50°C, using the isostatic gas permeability meter (GPM-200, Incentive AB, Sweden) which gives rate of permeation (P) as previously described with hydrogen as reference gas. The coefficients of diffusion (D) and solubility (S) can be obtained from the time lag of permeation and from P/D, respectively. The solubility data, however, are not reported here because of low reproducibility. This will be discussed later. No separate solubility measurements were made.

Measurements of density and crystallinity were made like in previous work.[1] Measurements of the thermal expansion coefficients for 50/50 blends were carried out using a thermomechanical analyzer (Perkin-Elmer Model TMS-1). In order to avoid effects of mechanical stress in the samples induced during sample preparation, heat treatment of the samples at about
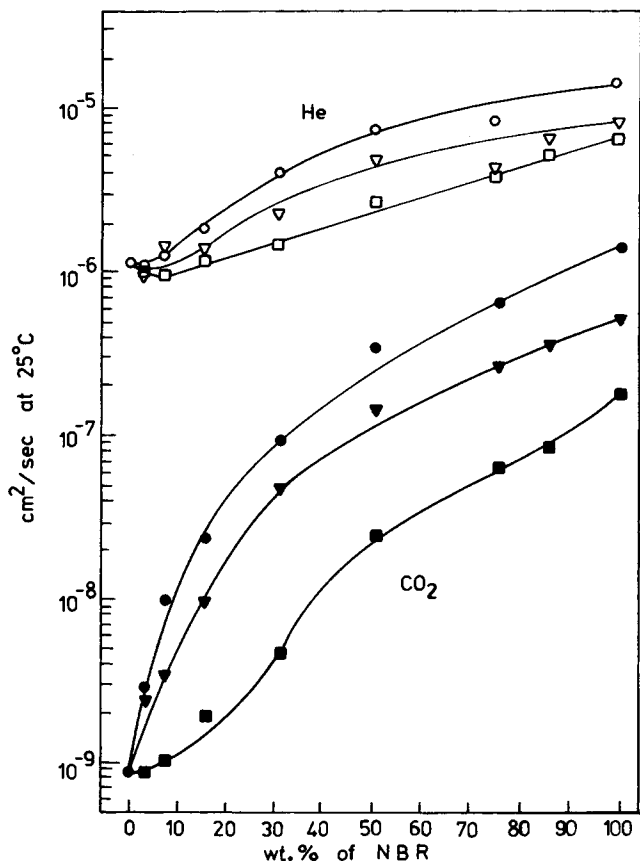
Fig. 3. Diffusion coefficients of He and CO_2 vs. polymer blend composition. D of He and D of CO_2: with the same polymer blends as in Fig. 1.

90°C was made before measurements. Sensitivity 10, heating rate 10°C/min, and loading 3 g were applied in the TMS analyzer.

RESULTS AND DISCUSSION

The diagrams in Figures 1 to 4 present analogous results to those obtained for PVC/EVA blends.[1] With increasing AN content in NBR, the P and D values of a given gas for the blends decrease and increasing additive behavior of these transport parameters are obtained, i.e., the relations P and D versus blend composition approach linearity.

There are also some indications of phase inversion (compare with ref. 1) for the PVC/NBR blends at low NBR content (~5%), e.g., from the permeability measurements with CO_2 (see Figs. 1 and 5).

Why does the change in AN content of the NBR component cause such pronounced effects? No doubt this is due to the highly polar character of the nitrile (—C≡N) groups. For a series of vulcanized NBR rubbers, van Amerongen[7] has shown that increasing AN content in the rubbers cause considerable decrease in P and D for He, O_2, N_2 and CO_2.
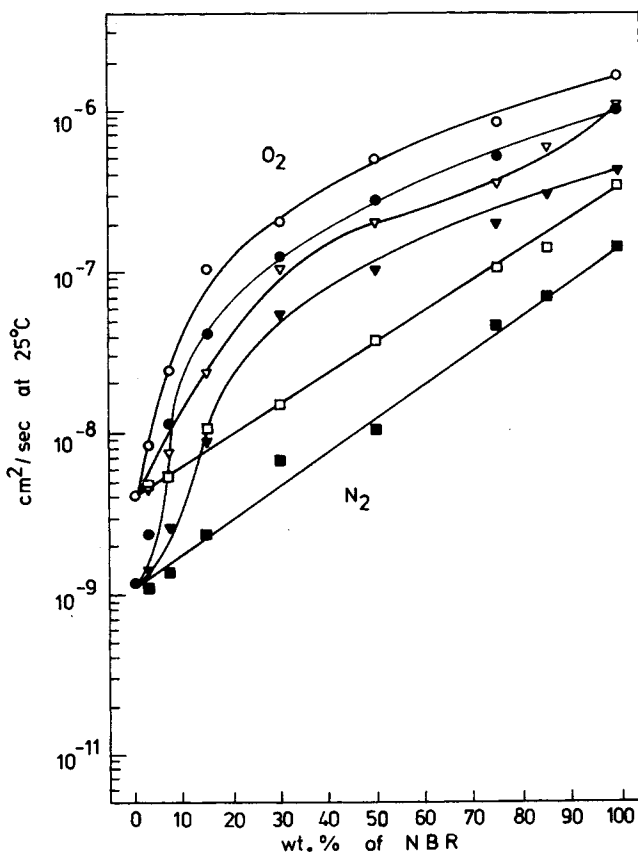
Fig. 4. Diffusion coefficients of O_2 and N_2 vs. polymer blend composition. D of O_2 and D of N_2: with the same polymer blends as in Fig. 1.

It has also been found that the compatibility of PVC with NBR is improved with increasing AN content in the NBR component.[6,8–10] Matsuo et al.[8] have reported that PVC can form a compatible system with NBR containing about 40% of AN by weight but forms a semicompatible system when AN content is about 20%. Zakrewski[9] has also reported the formation of compatible blends of PVC with NBR within the AN range of 23–45% in NBR. Horvath et al.[10] have observed complete mixing of PVC with an NBR containing 32% AN.

The decrease in P and D with increasing AN content in the NBR component are difficult to interprete, i.e., to what extent they are due to the polar character of AN groups or to the improved compatibility of the blend components. The two factors may effect the transport process in the same direction. A better additivity of P and D may, however, mainly be attributed to increased blend compatibility. Thus, cooperative molecular phenomena of the two polymers may govern the transport process through the polymer blends. The P and D values for CO_2 at various NBR contents deviate more from additivity than those for other gases. This may be interpreted as due to irregular changes in the gas sorption process. The increased AN content may
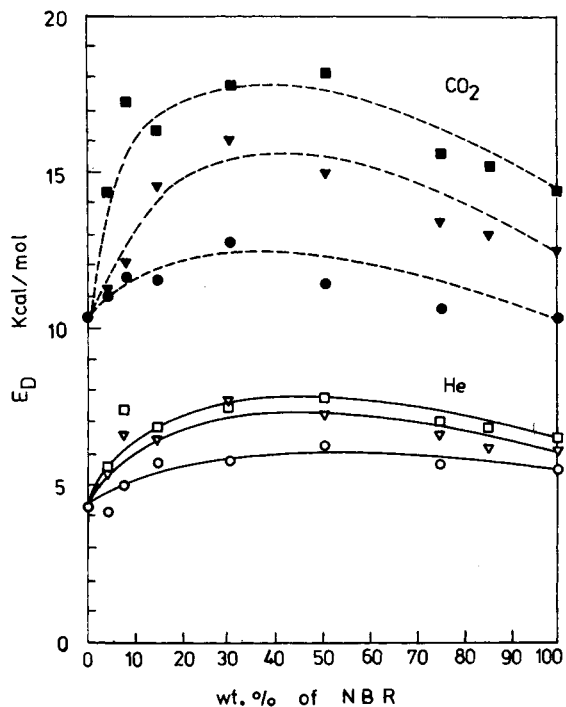
Fig. 5. Activation energy of diffusion for He and CO_2 vs. polymer blend composition.
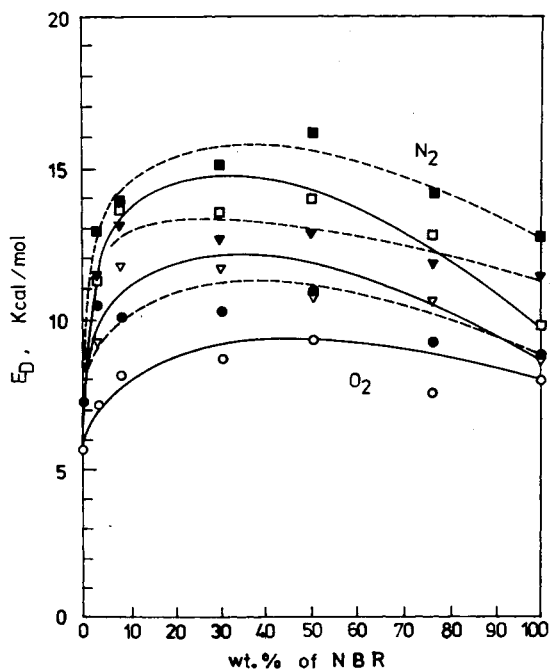

Fig. 6. Activation energy of diffusion for O_2 and N_2 vs. polymer blend composition.
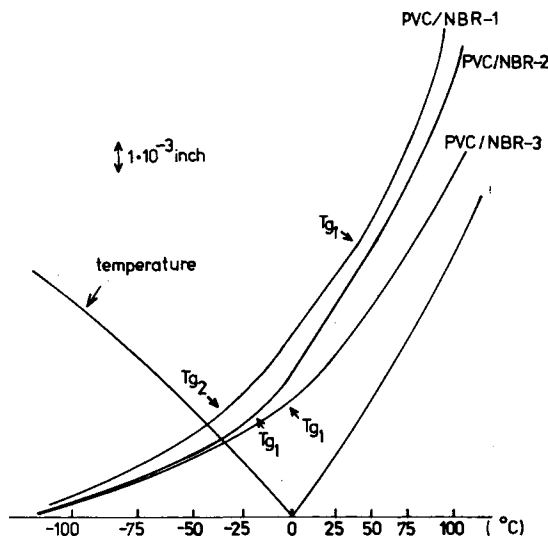
Fig. 7. Length expansion of PVC/NBR (50/50) blends vs. temperature.

alter both the segmental mobility through polymer–polymer interaction, and the gas sorption character of the blends by changing the condensed phases between the polymer and permeant molecules and by altering the hole adsorption mode. To obtain a clear picture, it is necessary to separate these two factors, i.e., the kinetic and thermodynamic factors.

Figures 5 and 6 show the increased activation energy for diffusion (E_D) through PVC/NBR blends with increasing AN content in the NBR component. This is interpreted as kinetic evidence that segmental mobility is reduced with increasing AN content due to increased polymer–polymer interaction, i.e., PVC-to-NBR.

Some other indications of polymer–polymer interaction are shown in Figure 7 which gives data for length expansion of the three 50/50 blends within a wide temperature range (−100° to +100°C). With increasing AN content in NBR, lower thermal expansion is clearly indicated and also improved compatibility as earlier reported. Jorgensen et al.[6] have observed two transitions for a PVC/NBR blends with 32% AN. We have observed only one transition for the 50/50 blends of PVC with NBR-2 (29.6% AN) and NBR-3 (41.6% AN), but two transitions for PVC/NBR-1 (21.7% AN) (see Fig. 7). The transition at high temperature for PVC/NBR blends was assigned by Matsuo et al.[8] to a mixed phase of compatible polymer components. For the PVC/NBR-1 blend, it was observed that T_{g_1} for the mixed phase is shifted to lower temperature while T_{g_2} for NBR-1 phase remained unchanged. Thus, PVC/ NBR-1 seems to form a semicompatible system as reported by Matsuo[8] like corresponding PVC/EVA-65 blends milled at 160°C.[1] The thermal expansion coefficients obtained graphically 10°C below T_{g_1} were 1.42×10^{-4}/°C
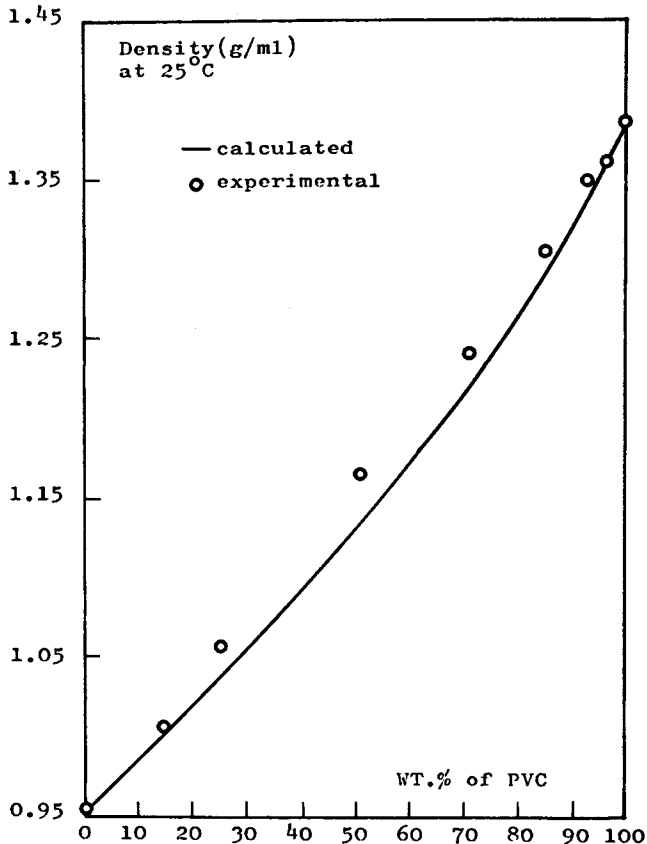
Fig. 8. Density of PVC/NBR-1 blends vs. blend composition.

(PVC/NBR-1), 1.29 × 10⁻⁴/°C (PVC/NBR-2) and 1.09 × 10⁻⁴/°C (PVC/
NBR-3) for the three 50/50 blends.

Independent evidence of PVC–NBR interaction can also be derived from
density measurements (see Figs. 8–10). When interaction occurs, experimen-
tal densities for the blends are higher than those calculated assuming volume
additivity for the components. The difference between experimental and
calculated values, i.e., the volume contraction, is larger with higher AN con-
tent in the NBR component. For the 50/50 blends, the differences are 0.034
(PVC/NBR-1), 0.042 (PVC/NBR-2), and 0.048 g/ml (PVC/NBR-3). In order
to separate density changes due to possible changes of crystallinity in the
blends from density changes due to better chain packing from increased mo-
lecular interaction and compatibility, crystallinity measurements by x-ray
diffraction were carried out for each blend at room temperature. The x-ray
data showed that all blends are substantially amorphous with crystallinities
less than 10%. It is therefore reasonable to conclude that the volume con-
traction of the blends is due to increased molecular interaction of PVC with
NBR with increasing AN content in the NBR component.

The change in activation energy of diffusion (E_D in Figs. 5 and 6) is inter-
preted as mainly due to changes in segmental mobility and also related to the
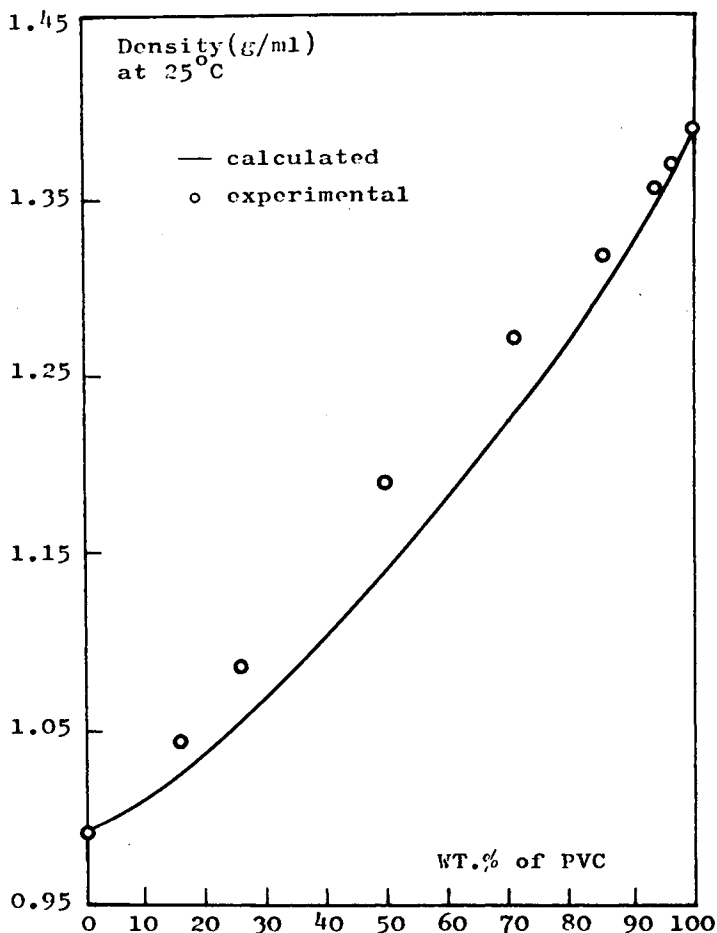
Fig. 9. Density of PVC/NBR-2 blends vs. blend composition.

molecular size of the permeant. In polymer blends, the segmental mobility is strongly affected by interaction between the two types of polymer molecules in the blends. In discussion of mechanical relaxations and bulk viscosity of a polymer and of transport processes through a polymer, it is necessary to consider the interaction of a certain chain segment with the surrounding segments rather than the motion of an individual segment. In polymer blends, this situation will become more complicated because of interaction between two different polymers. Generally speaking, we can expect that stronger interaction between segments of the two polymers in the blend will result in less segmental mobility. Hence, hindrances to the transport process (lower rate) and higher activation energy of diffusion are related to increased chain interaction. This general discussion is in good agreement with our experimental results.

According to Meares,[11] the activation energy of diffusion is taken to be the energy required to overcome segmental interaction forces to the extent that a cylindrical passageway with the volume $(\pi/4)d_G{}^2 L_D$ is formed, where L_D is the length of the passageway and d_G the collision diameter of the permeant
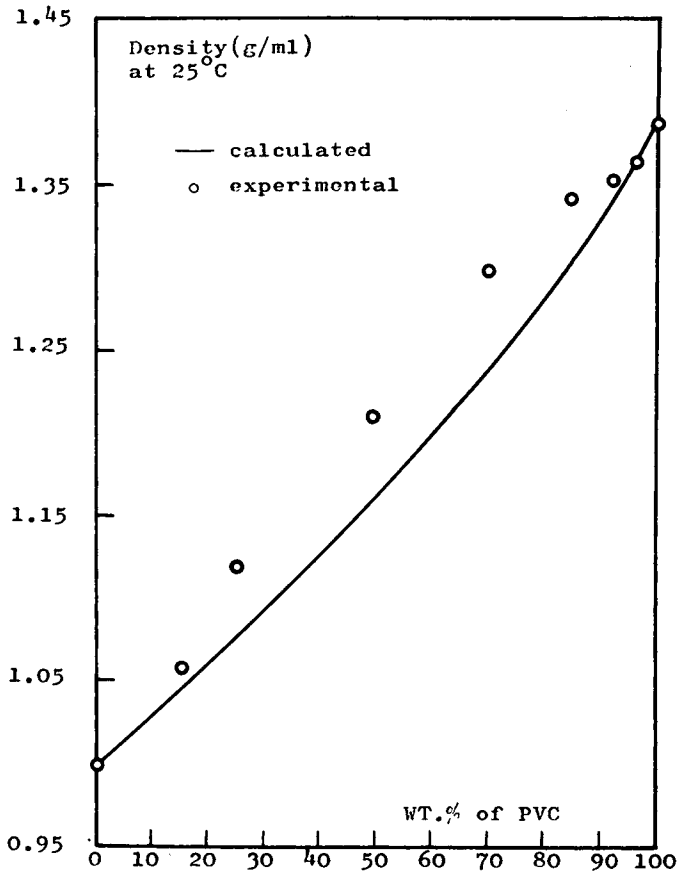
Fig. 10. Density of PVC/NBR-3 blends vs. blend composition.

molecule. The activation energy is then calculated by multiplying this volume with the cohesive energy density of the polymer. The volume of the passageway is created by the segmental motion. Small permeants such as He would require small vibrational and rotational oscillations of the polymer chain segments for diffusion through the polymer, while larger permeants such as CO_2 would require larger oscillations. Therefore, Meares[11] has concluded that the diffusion of large permeants is controlled by the motion of chain segments, while small permeants may diffuse through voids (holes). Hence, the activation energy of diffusion for small permeants would depend on the permeant size and the changes of hole statistics (in polymer blends), while for large permeants it would mainly depend on the polymer chain mobility.

The sorption values calculated by the classical relationship $S = P/D$, for the gases through the polymer blends were examined. The S values of He are small and almost the same for all blends but for other gases they were changed and showed considerable fluctuations with blend composition, especially for CO_2. Thus, the sorption values obtained from P/D ratios seem less reproducible for the large permeants than for the small one. According to the classical relationship in gas transport through polymers, the solubility of

gases obtained from P/D is deduced under the assumption that the partition of the gases through a membrane in the nonsteady state of the diffusion is uniform. However, this ideal situation is hardly probable for a heterogeneous polymer systems, e.g., semicrystalline polymers, filled polymers and polymer blends. Deviation from ideality may be chiefly due to different rate of establishment of equilibrium partition of permeant, between crystalline and amorphous phases in semicrystalline polymers and between the components and/or mixed phases (if a blend is miscible) in polymer blends. Different rates to reach equilibrium of permeant partition would then affect the time interval to steady state, i.e., the time lag in gas permeation. If it is assumed that the rates to reach equilibrium are the same between the components of the blend or between components and mixed phases, or if the partition process is sufficiently rapid so that the time lag is small compared to the time for a unit change in local concentration of the permeant, Fick's second law would be applicable in a gas transport study for polymer blends. However, that is not probable for practical cases like those we have studied. The rate to reach equilibrium would depend on the interaction between the permeant and the polymer molecules. For inert gases like He, O_2, and N_2, Fick's law may be applicable with small deviations also for polymer blend barriers, while reactive and polar permeants such as organic gases and vapors, H_2O, and NH_3 are expected to give large deviations from ideal gas transport behavior.

In general, the sorption of a permeant in a polymer phase obeying Henry's law is a simple solution process. Recently, a dual sorption process has been proposed for glassy polymers[12–14] and filled polymers.[15] In a broad sense, it is probable that the sorption characteristics of a polymer blend can be fairly well interpreted with the dual sorption process. By blending two chemically different polymers, assuming that they form an incompatible blend, there will be two components with different sorption characteristics and having different partition rates in the blend. In this case, the composition of the two components in the blend will be the main factor in discussions of the overall sorption values. In compatible polymer blends, on the other hand, the overall sorption process will be more or less influenced by the cooperative characteristics of the two components. How much this will affect the sorption process is dependent on the level of compatibility of the blend components.

According to Kwei and Arnheim,[3] the solubility coefficients (S) of nonpolar gases in polymers, such as the inert gases studied here, can be expressed with the assumption that the dissolved gas molecules are located in the free volume of the polymer without any disruption of polymer–polymer contacts, as follows:

$$RT \ln S = -\Delta H_s + RT \ln V_{fp} - RT(T/273) - RT$$

where ΔH_s is the heat of solution and V_{fp} is the fraction of free volume in the polymer phase. The value of ΔH_s depends on the properties and the interaction of permeant and polymer molecules, i.e., the molar heat of condensation of the permeant and the internal pressure of the polymer. The molar heat of condensation is mainly determined by the polarity of the polymer and the permeant molecules, while the free volume (V_{fp}) is determined by the physi-

cal characters of the polymer chains. It is very difficult to predict which factor will dominate in the sorption process. For polar or condensable permeants in a polar polymer, the interaction between the polymer and the permeant molecules has a strong effect on the sorption process. The free volume factor will be more effective for nonpolar permeants as suggested by van Amerongen[7] and Rogers.[16] For our system, the free-volume factor may be more significant in the sorption process for He, O_2, and N_2. But for CO_2, the two factors (condensation and free volume) may influence simultaneously for the sorption process. It should also be noticed that the activation energies of the gases have a maximum at about 50/50 blend composition where the solubility values show a minimum.

There is also another problem in the sorption process for polymer blends. If blending of the two polymers brings changes in the hole (or void) statistics (size and number), it is possible that the adsorption process is altered as proposed by Stallings et al.[5] If the blending of PVC and NBR causes changes in the adsorption process due to changes in the hole statistics, noticeable changes in the transport properties will be the result. With changing composition of the blends and changing AN content in the NBR, the transport parameters (P, D, and S) for He are not significantly changed. Furthermore, the activation energy (E_D) for He also changes very little with varying AN content. This may indicate that changes of hole size and redistribution of holes by blending may be less significant for He transport. We may also assume that the holes in pure polymers and in the polymer blends are larger than the size of He molecules. In this way, the adsorption process of He may not be noticeably influenced by blending.

The preparation of the polymer blends is another factor which could affect the gas permeation. It is very difficult to avoid thermal oxidation in preparation of blends by melt blending under air atmosphere. Thermal oxidation creates polar groups on the polymer chains, e.g., —OH, —C=O, and —COOH, and may also produce crosslinks. This is true for PVC/rubber blends, where the rubber phase is more easily oxidized, if it is a diene polymer. These extraneous groups can influence the gas transport properties, especially the sorption process. The crosslinks may even exert immobilizing effects as considered in the dual sorption process, depending on the type of crosslinking and the density of the crosslinks. Then, the time-lag method may be less reliable for a quantitative analysis of the sorption and diffusion processes as pointed out by Paul et al.[14]

In conclusion, it is more difficult to interpret the sorption process than the diffusion kinetics of permeation in polymer blends. The sorption process is affected by changes in morphology, molecular coordination of the two polymers in the blends, and interaction of the permeant molecules with the polymer molecules in the pure and the mixed phases.

Further investigations on the sorption behavior and the preparation factors on the gas transport in polymer blends are required and are in progress in our laboratory.

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