

Permeability Studies on Heterogeneous Polymer Films

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Synopsis

Oxygen permeability data on heterogeneous films prepared from mixtures of different polymer lattices were compared with predictions of a permeability theory of Higuchi based on an idealized barrier model. The theory attempts to evaluate the effect of perturbations of the diffusion process associated with the presence of a discontinuous internal-phase component. An approximate form of the theoretical permeability expression was found to render reliable predictions of the effective permeability of heterogeneous barrier systems. When the partition of the permeant between different phases of the barrier is sufficiently rapid, the theory becomes applicable to the early, nonsteady-state, stage of permeation. Implications of the general applicability of the Higuchi theory to heterogeneous systems are discussed with respect to the interaction between the constituents and the associated departures from the ideal behavior assumed for the model.

INTRODUCTION

Current scientific interest in the behavior of heterogeneous polymer materials is evidenced by the number of recent publications¹⁻⁴ which deal with studies of their properties.

In the present investigation a study has been made of gas permeability properties imparted by particles of various "hard" polymers dispersed in a matrix of soft (free-filming) polymer. The resulting filled barrier systems lend themselves advantageously to theoretical treatment, since permeability properties of their isolated polymer components can be calculated according to standard laws of diffusion from data on homogeneous films. Mixed polymer films were prepared by a procedure in which a proportion of hard polymer latex is mixed into a large proportion of latex of a softer fusible polymer. Multiphase polymer films of various composition cast from such latex mixtures are easily reproduced, and it is also possible thereby to match pairs of polymers for which there is no practical common solvent.

Although many investigations of heterogeneous systems in the literature center around analysis of mechanical behavior,^{5,6} several recent theoretical

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treatments⁷⁻⁹ have dealt with the prediction of permeability in terms relatable to Fick's laws of diffusion. The conclusions of Higuchi et al.,⁷ drawn from considerations of an idealized barrier model (depicted as a random suspension of uniformly sized spherical particles with one permeability surrounded by a continuous external phase with a different permeability), have proved to be especially relevant to the interpretation of data in the present investigation. In the analysis of their proposed model, Higuchi et al. assume that the particles of the internal phase are small compared to the thickness of the barrier, but large enough to be considered phases. In the attempt to take into account perturbations of the diffusion process in each phase introduced by the discontinuous nature of the disperse phase, Higuchi et al. draw from earlier considerations of related steady-state phenomena associated with multiphase systems. In a previous analysis of the effective dielectric properties of powders and suspensions,¹⁰ a discussion of the application of Laplace's equation to that problem led to a practical modification of Rayleigh's equation¹¹ in the attempt to allow for particle-particle interactions. This approach was shown by them to be useful in predicting effective dielectric constants of random two-phase mixtures over a broad range of internal phase volume fraction in many different systems. In a similar analysis of the permeability problem, Higuchi et al. consider the activity gradient which drives the gas, or any other solute, through the film. They point out that a solute will diffuse from a region of low concentration to a region of high concentration if the activity of the solute is less in the high concentration region. At the steady-state stage of permeation (when the concentration of the permeant in the film is no longer changing) the average activity gradient of permeant in the external phase of the barrier is visualized as a parallel and uniform field of gradient of chemical potential within which the internal phase spheres are distributed. Accordingly it is proposed that the activity gradient of permeant within individual spherical particles is determined independently as a function of both the position of the particle in the external phase gradient and its interaction with gradients in neighboring particles. The different average values of the activity gradient at the steady-state stage of permeation (F_i in the internal phase and F_e in the external phase) in the heterogeneous barrier are estimated by applying a solution of Laplace's equation. An approximate solution for this problem is given as

$$F_i = [3P_e/(2P_e + P_i)]F_e \quad (1)$$

which is tested in the present investigation. More complicated versions of eq. (1) are offered by Higuchi et al. in the extension of their analysis to include the modification of F_e induced by the response of nearby internal phase particles to the "initial" F_i field or gradient generated within the particle in question as its response to the original F_e field. In eq. (1) it is assumed that the activity gradient F_i is induced in the internal phase particle solely as a perturbation in the field F_e and is a consequence of the

presence of the individual particle in the field. In theory, eq. (1) would be expected to be decreasingly appropriate at high volume fractions of internal phase. In practice such judgments may be partially modified by effects of degree of dispersion and average particle size on the effective particle-particle separation distance at a given volume fraction. Higuchi et al. conclude their theoretical analysis of the steady-state problem by using forms of eq. (1) together with considerations of their proposed model in order to arrive at a relationship which expresses the effective permeability constant P_m , as a function of the volume fraction and the steady-state permeability of each of the component phases.

Under certain conditions (for which the theory provides a test) it becomes possible to combine the predicted effective permeability of the composite system with a form of Fick's second law of diffusion to obtain reasonably reliable estimates of the expected time lag of permeation.

The work conducted under the present investigation provides an experimental test of the validity of some of the foregoing conclusions. Oxygen permeability studies at two different temperatures have been completed on three heterogeneous polymer systems prepared from mixed latices. All three of these systems exhibit a measurable change in permeability from that of the original (bulk-phase) polymer. Comparisons between each system are facilitated by use of the same polymer as the external phase in each case.

EXPERIMENTAL

Materials

Gelva Emulsion TS-30, a low molecular weight grade of poly(vinyl acetate) latex was used as obtained from Shawinigan Resins Corporation.

Dow 586, a polystyrene latex with a molecular weight reported as 4×10^6 and an average particle diameter of 2.2×10^{-5} cm, was obtained from the Dow Chemical Company.

Daran 210, a poly(vinylidene chloride) latex, was obtained from Dewey and Almy Chemical Division of W. R. Grace and Company.

Poly(methyl methacrylate) latex used was prepared at these laboratories.

Commercial Saran Wrap and pigmented Saran (2.9% titanium dioxide by weight) were obtained from the Dow Chemical Company.

Preparation of Films

Heterogeneous polymer films were prepared by mixing amounts of two different latices together and casting a liquid film of the uniform mixture on a tinfoil surface with a Gardner Ultra Applicator. Films were baked until dry at 60°C.

In most instances it was necessary to take the precaution of diluting the latex which was intended to be the minor component (internal phase) of the mixture before mixing. If this is not done, the minor component latex

TABLE I

Latex	Concentration, g polymer/100 ml latex		Amount of latex mixed, g	Concentration of polymer in dried film, wt-%
	Initial	Before mixing		
Shawinigan TS-30	56.0	56.0	68.2	81.5
Dow 586	58.3	23.0	37.7	18.5

tends to agglomerate as it is added to the major component latex. An example of this preventive technique is illustrated in Table I.

Permeability Apparatus

An improved permeability apparatus was developed for use in the present study and is described elsewhere.¹²

Determination of Permeability Coefficients

The procedure followed in calculating permeability coefficients from the time rate of increase of pressure in the low pressure end of the diffusion chamber at the steady-state stage of film permeation has been outlined previously.¹³

RESULTS AND DISCUSSION

Preliminary Studies and Application of the Theory to the Steady-State Diffusion Process

Heterogeneous polymer films used in this investigation all contained poly(vinyl acetate) as the external phase. Three of these systems were studied. One system contained latex particles of polystyrene as the internal (disperse) phase. A second contained poly(vinylidene chloride) latex particles as the internal phase. The third system contained poly(methyl methacrylate) latex particles as the internal phase. Different proportions of polymer components and different systems were distinguished by various degrees of turbidity ranging to milky white. The degree of turbidity was found to be a genuinely permanent feature as evidenced by its pronounced stability even when the sample was exposed to harsh heat treatments such as melting in the flame of a Bunsen burner. In every case, sample turbidity was greater with each increase in film thickness until at about 1 cm thickness, bulk slabs prepared would transmit almost no light at all. At reduced film thicknesses used in gas permeability experiments it was noted, however, that printed patterns brought very near the reverse side of films were discerned in detail through even the most turbid-appearing samples. The uniform external appearance of individual film specimens at all thicknesses indicated that the two polymer components were reasonably well mixed, with intact particles of the internally distributed hard

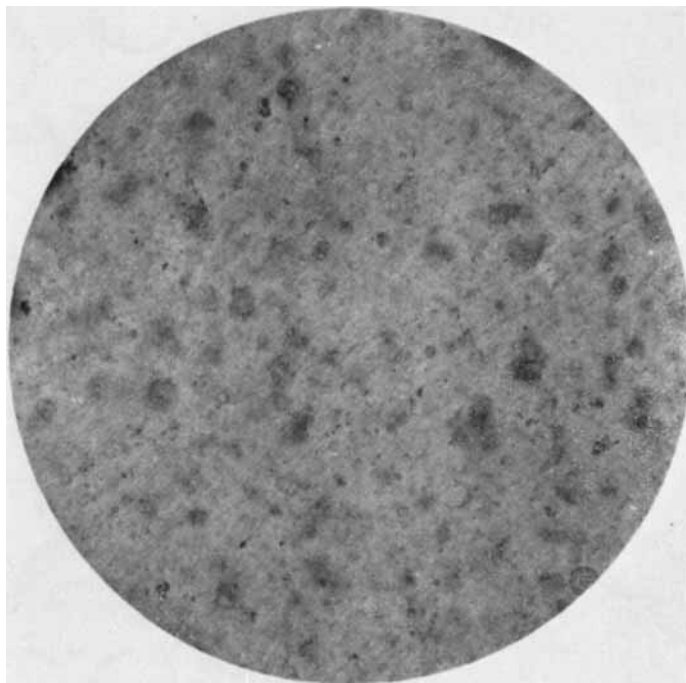


Fig. 1. Photomicrograph of a heterogeneous film prepared from mixed latices of poly-(vinyl acetate) and polystyrene. 140 \times .

polymer presumably contributing to the observed optical peculiarities of the composite.

Preliminary characterization of heterogeneous polymer films to be used in permeability studies included an assessment of gross aspects of their microstructure by light microscopy followed by a more detailed scrutiny of individual regions by means of electron micrographs.

The characteristic appearance of these films under low magnification is illustrated by a typical view using transmitted light in the micrograph in Figure 1. Most of the disperse-phase polystyrene particles in the film shown have diameters smaller than the 0.5 μ limit of resolution of the microscope. The greater part of gray blotches seen in the field reflect the positions of small clusters of particles. Some additional contribution to the mottled appearance probably comes from superimposed images of particles occupying coincident positions in the film along the path of the transmitted light. Blotches, and presumably additional unresolvable single particles of the disperse-phase resin, appear to be reasonably well distributed throughout the visible field. An electron micrograph of the surface of the same film is shown in Figure 2. At this much greater magnification, the polystyrene latex particles are seen as discrete spheres suspended in the surrounding medium of fused poly(vinyl acetate) latex. Residual pieces of polymer which could not be dissolved away from the replica cause the

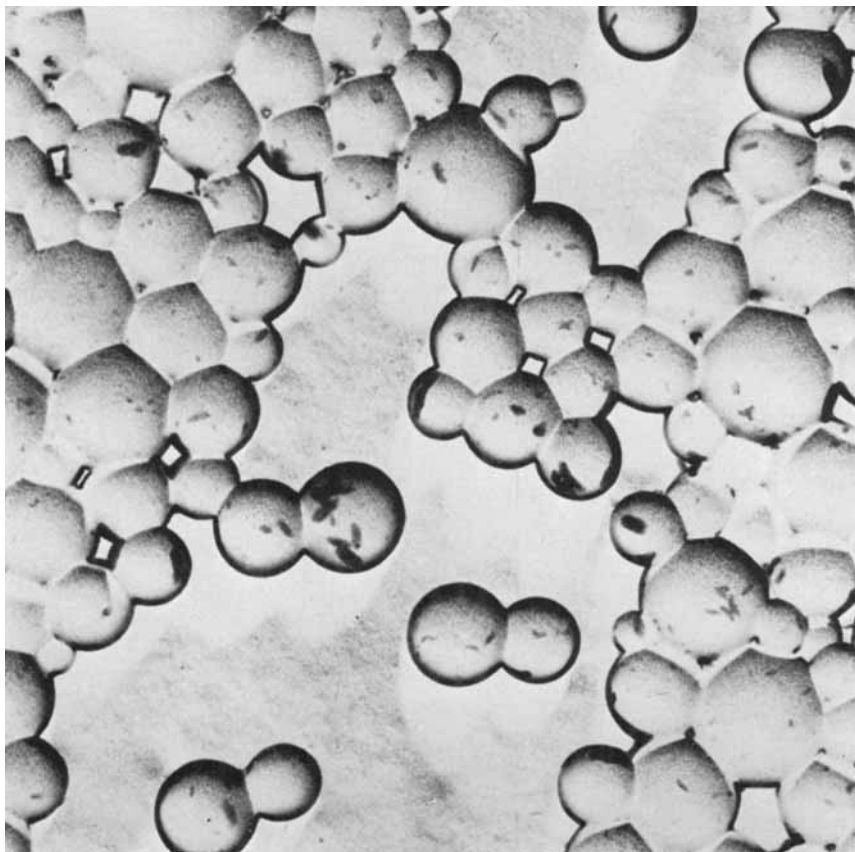


Fig. 2. Electron micrograph of the surface of the film shown in Fig. 1 from a direct (single-stage) carbon replica, preshadowed with platinum at an angle of $\tan^{-1} 1/5$. $19,200\times$.

spheres to appear flecked and portions of their outlines to be darkly accented (the latter effect in some cases leading to rough diamond-shaped enclosures). Electron micrographs were also taken of a purposely fractured surface of this film. It was hoped that close examination of such a surface would shed additional light on the arrangement of the two polymer phases in interior regions of the film. Figure 3 reveals that polystyrene latex particles in these regions remain intact although they are characteristically deformed into furrowed angular shapes. The deepest furrows in the cluster of particles shown, portions of which are darkly outlined by pieces of polymer on the replica, identify boundaries between individual particles. The deformation of these hard spheres offers impressive evidence of powerful compressive forces generated within the film by the fusion of external-phase latex particles during drying of the film after casting.

Preliminary test measurements of the rate of oxygen diffusion through homogeneous polystyrene and poly(methyl methacrylate) films prepared

from the dried latex particles dissolved in organic solvent revealed a slight increase in the permeability constant P with each increase in the applied oxygen pressure. Homogeneous poly(vinyl acetate) films cast from latex did not exhibit this behavior. Permeability data are compared in Table II. Pressure dependence of P had also been noted with samples of a commercial Saran film pigmented with titanium dioxide as well as with a commercial Saran wrapping material. The trend with the pigmented film is rather well

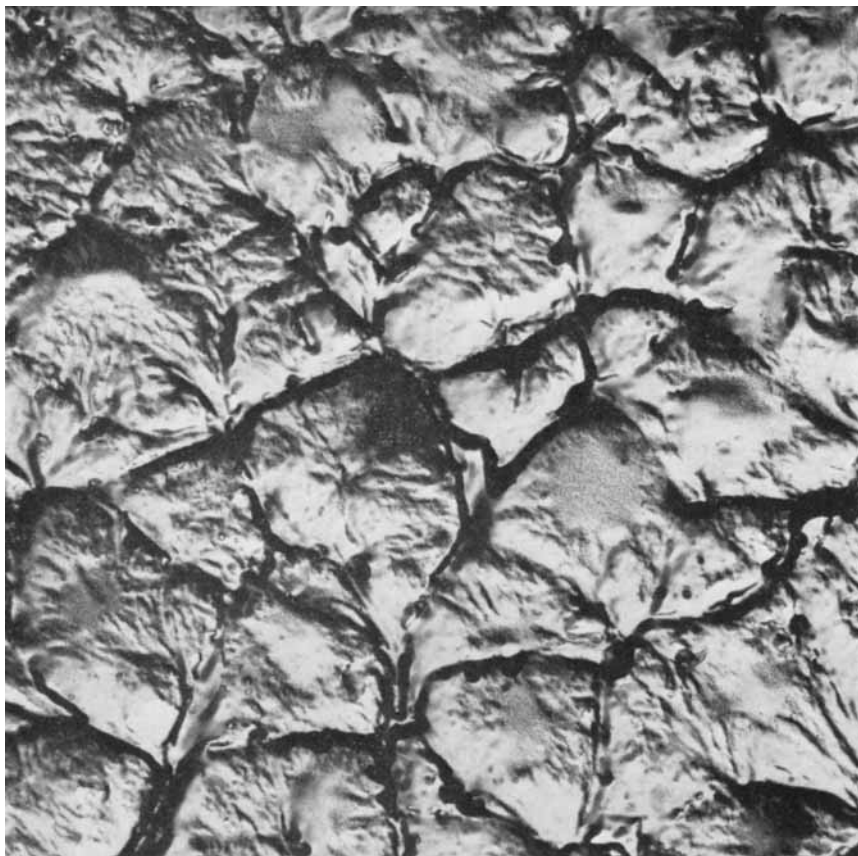


Fig. 3. Electron micrograph of fractured film surface showing the interior region of the film in Fig. 1 (for sample preparation see Fig. 2). 28,500 \times .

documented, and the data on both systems have been included in Table II for comparison. In Figure 4 the small changes in P measured with the polystyrene film are reflected solely in an inordinate steepening of the steady-state slope of the diffusion curve (increase in permeating flux) relative to the amount of increase in applied oxygen pressure. The intercept θ of the slope line with the time axis is practically identical for all three curves. The diffusion coefficient D calculated from θ did not vary significantly as shown in Table II. In light of the successive increases in the

TABLE II
Examples of Pressure-Dependent Oxygen Permeability in Various Polymer Films

Sample or experiment	Applied gas pressure, cm Hg	Permeability P , cm ³ (STP) mm/cm ² -sec-cm Hg	Diffusion coefficient D , cm ² /sec	Solubility coefficient S_m , cm ³ (STP)/cm ³ polymer-atm
Polystyrene at 27°C				
a	5.1 ₀	16.8 ₇ × 10 ⁻¹⁰	8.35 ₈ × 10 ⁻⁸	15.3 ₄ × 10 ⁻²
b	10.1 ₇	19.3 ₆ × 10 ⁻¹⁰	8.22 ₇ × 10 ⁻⁸	17.8 ₈ × 10 ⁻²
c	14.3 ₂	21.4 ₇ × 10 ⁻¹⁰	8.29 ₂ × 10 ⁻⁸	19.6 ₈ × 10 ⁻²
Poly(methyl methacrylate) at 27°C				
	5.2 ₀	2.74 ₃ × 10 ⁻¹⁰	1.16 ₂ × 10 ⁻⁸	17.9 ₄ × 10 ⁻²
	10.1 ₃	3.25 ₄ × 10 ⁻¹⁰	1.16 ₂ × 10 ⁻⁸	21.2 ₈ × 10 ⁻²
Pigmented Saran at 25°C				
1	10.1 ₃	2.01 × 10 ⁻¹²	—	—
1	37.5 ₃	3.34 × 10 ⁻¹²	—	—
2	9.9 ₄	2.09 × 10 ⁻¹²	—	—
2	19.2 ₂	2.13 × 10 ⁻¹²	—	—
2	27.1 ₉	3.07 × 10 ⁻¹²	—	—
2	43.6 ₇	3.09 × 10 ⁻¹²	—	—
Nonpigmented Saran at 25°C				
	11.5 ₆	2.76 × 10 ⁻¹²	0.047 ₆ × 10 ⁻⁸	4.40 ₇ × 10 ⁻²
	21.6 ₅	3.21 × 10 ⁻¹²	0.047 ₆ × 10 ⁻⁸	5.12 ₅ × 10 ⁻²

value of the solubility coefficient S calculated from a, b and c diffusion data by using the relationship

$$P = DS \quad (2)$$

it appears that the anomalous permeability behavior may be attributed to a positive deviation from Henry's law such as would be manifest in a slight upward curvature of the gas sorption isotherm with pressure. Measured time lags were always constant with variation in applied oxygen pressure, and trends in solubility coefficients support the same conclusion for other systems in Table II. Possible contributions to the observed anomalous trends from voids or channels in the polymer film were also taken into consideration. The several prevalent theoretical treatments¹⁴⁻¹⁷ dealing with apparent pressure dependence in the solubility or permeability constant which stress the role of such structural defects concern either negative departures from Henry's law at high pressures or predict the simultaneous apparent dependence on pressure of both P and D . Present results do not coincide with either of these models. Although fluctuations in P with pressure observed with polystyrene and poly(methyl methacrylate) films were small and would not seriously effect the applicability of our theoretical calculations, permeability data were routinely selected from experiments conducted at as nearly the same applied pressure as feasible. Approximately 10 cm of mercury applied gas pressure was found to be a convenient

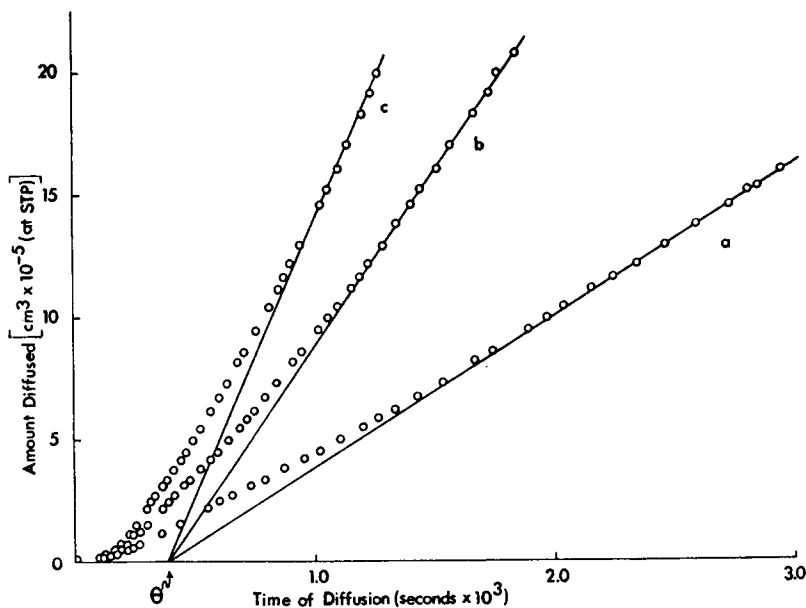


Fig. 4. Diffusion curves for oxygen permeation through polystyrene. Steady-state slopes show slightly nonlinear dependence on applied pressure gradient. Experiments shown were conducted on the same film in the sequence b to a to c (see Table II).

level at which to work in most experiments. Thus, although it was customary to measure the permeability of each film specimen at least three times at different applied pressures in order to verify the Fickian nature of the diffusion process, permeability data used in the following discussion refer to experiments which were conducted at a standard 10 cm of mercury applied oxygen pressure. Under this modest pressure gradient, distortion of the film (already minimized by firm support from a specially designed diaphragm of sintered glass) was considered negligible. Reasonably rapid rates of permeation could be obtained in this range of applied oxygen pressure using films which were between 0.5 and 5.0 mils (approximately 10^{-2} – 10^{-1} mm) thick. At the experimental temperatures (27 and 40°C) average rates of permeation corresponding to a pressure change in the low pressure side of the diffusion cell of 1.2×10^{-1} to 9.0×10^{-5} μ of mercury per second were obtained. Taking into account the small volume ($3.936_1 \times 10^{-2}$ liter) of the chamber on the low pressure side of the film, the latter figure would be equivalent to approximately 7.5×10^{-15} moles of gas passing through 1 cm^2 of film area in 1 sec. Even the lowest of these pressure changes was easily distinguished from the low measured pressure changes (less than 4×10^{-6} μ Hg/sec) associated with blank experiments in which no gas pressure was applied.

As an added precaution, steps were taken to avoid any ordered sequence of experimental conditions used in the measurements such as might conceivably engender unsuspected irreversible alterations of film barrier proper-

TABLE III
Reproducibility of Permeability Data at a Constant Applied Gas Pressure^a

Applied gas pressure, cm Hg	Permeability P_m , cm ³ (STP) mm/cm ² -sec-cm Hg)	Diffusion coefficient D_m , cm ² /sec	Solubility coefficient S_m , cm ³ (STP)/cm ³ polymer-atm
10.9 ₀	$1.92_0 \times 10^{-10}$	$2.88_1 \times 10^{-8}$	$5.06_5 \times 10^{-2}$
10.0 ₃	$1.93_1 \times 10^{-10}$	$2.89_0 \times 10^{-8}$	$5.07_8 \times 10^{-2}$

^a Poly(vinyl acetate) containing polystyrene at 27°C.

ties. In each case (for example) the permeability was measured alternatively at a higher and then a lower applied oxygen pressure rather than in any sequence of constantly increasing or constantly decreasing pressure.

With reasonable care the reproducibility of permeability determinations was found to be highly satisfactory as illustrated by data from a heterogeneous film sample shown in Table III. The first and second sets of permeability data compared in the example shown were measured respectively before and after an oxygen permeability experiment was conducted on the same film at 40°C.

Experimental results from studies at two different temperatures of the steady-state oxygen permeability of the three mixed polymer films under investigation and the four homogeneous films of their component polymer phases are summarized in Tables IV and V. As shown in Table IV, the oxygen permeability of homogeneous films prepared from each of the polymer components decreased in the order: polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc), poly(vinylidene chloride) (PVCl₂). Values of P and S in the case of PVAc at 27°C compare favorably with estimates from Meares' data¹³ [$P = 3.93 \times 10^{-10}$ cm³ (STP) mm/cm²-sec-cm Hg and $S = 6.42 \times 10^{-2}$ cm³ (STP)/cm³ polymer-atm] with oxygen at the same temperature. The latter data were obtained on films of very high molecular weight PVAc which had been purified before casting on a mercury substrate. Results with films of the mixed polymer components

TABLE IV
Averaged Results from Oxygen Permeability Experiments
with Homogeneous Films of Mixed Polymer Film Components

Film	Temperature, °C	Permeability P , cm ³ (STP) mm/cm ² -sec-cm Hg	Diffusion coefficient D , cm ² /sec	Solubility coefficient S_m , cm ³ (STP)/cm ³ polymer-atm
PVAc	27	$0.96_4 \times 10^{-10}$	$2.20_5 \times 10^{-8}$	$3.32_3 \times 10^{-2}$
PS	27	$19.3_6 \times 10^{-10}$	$8.22_7 \times 10^{-8}$	$17.8_8 \times 10^{-2}$
PVCl ₂	27	$0.009_0 \times 10^{-10}$	$0.19_4 \times 10^{-8}$	$0.35_5 \times 10^{-2}$
PMMA	27	$3.25_4 \times 10^{-10}$	$1.16_2 \times 10^{-8}$	$21.2_8 \times 10^{-2}$
PVAc	40	$2.64_1 \times 10^{-10}$	$2.48_1 \times 10^{-8}$	$8.09_0 \times 10^{-2}$
PS	40	$23.3_0 \times 10^{-10}$	$13.7_0 \times 10^{-8}$	$12.9_3 \times 10^{-2}$

given in Table V were determined in each case with films which contained a volume fraction 0.28 of the added disperse-phase polymer. Mixed polymer films exhibited no measurable pressure dependence in barrier properties. Comparing permeability values, it can be seen that the addition of PS latex particles in the indicated proportion doubles the oxygen permeability of PVAc film at 27°C and almost doubles it at 40°C. In contrast, the incorporation of PVCl₂ latex particles caused a reduction in the oxygen permeability of PVAc at both temperatures to about one-half its homogeneous value. PMMA particles were found to impart an increase in oxygen permeability to PVAc at 27°C.

TABLE V
Averaged Results from Oxygen Permeability Experiments
with Mixed Polymer Films

Film	Temperature, °C	Permeability P_m , cm ³ (STP) mm/ cm ² -sec-cm Hg	Diffusion coefficient D_m , cm ² /sec	Solubility coefficient S_m , cm ³ (STP)/ cm ³ polymer-atm
PVAc + PS	27	$1.93_1 \times 10^{-10}$	$2.88_5 \times 10^{-8}$	$5.08_7 \times 10^{-2}$
PVAc + PVCl ₂	27	$0.57_1 \times 10^{-10}$	1.37×10^{-8}	3.17×10^{-2}
PVAc + PMMA	27	$1.38_0 \times 10^{-10}$	9.27×10^{-8}	1.13×10^{-2}
PVAc + PS	40	$4.60_3 \times 10^{-10}$	$3.06_1 \times 10^{-8}$	$11.4_3 \times 10^{-2}$
PVAc + PVCl ₂	40	$1.25_1 \times 10^{-10}$	$3.51_9 \times 10^{-8}$	$2.70_2 \times 10^{-2}$

The applicability of the theoretical analysis outlined by Higuchi et al. to interpretation of steady-state oxygen permeability through mixed polymer films was tested by comparing the experimentally determined effective permeability of each heterogeneous system given in Table V with the value predicted by the relationship

$$P_m = \frac{3P_e P_i V_i + 2(P_e)^2 V_e + P_i P_e V_e}{3P_e + V_e (P_i - P_e)} \quad (3)$$

Equation (3) follows from the application of eq. (1) and is derived by those authors in the course of their discussion. According to this equation, to predict the effective permeability P_m of the composite film from a knowledge of the external phase (in the present case, PVAc) permeability P_e and the permeability of the added polymer particles P_i , it is necessary only to know the volume fraction of the film occupied by each of the two components. A value of 0.72 for V_e follows from the previously mentioned constant volume fraction (V_i) of added polymer particles used. The oxygen permeabilities of polymer components used in calculations with eq. (3) are listed at the corresponding temperature in Table IV. Values of P_m predicted from these data by eq. (3) for each of the heterogeneous polymer combinations studied are listed in Table VI. The close agreement between these theoretically predicted values and the experimentally verified values of P_m given in Table V is evident.

TABLE VI
Predictions of Oxygen Permeability and Solubility Coefficients in Mixed Polymer
Films According to the Higuchi Permeability Theory

Film	Temperature, °C	Permeability P_m , cm ³ (STP) mm/ cm ² -sec-cm Hg	Solubility coefficient S_m , cm ³ (STP)/ cm ³ polymer-atm
PVAc + PS	27	1.89×10^{-10}	7.40×10^{-2}
PVAc + PVCl ₂	27	0.61×10^{-10}	2.49×10^{-2}
PVAc + PMMA	27	1.37×10^{-10}	8.35×10^{-2}
PVAc + PS	40	4.65×10^{-10}	9.45×10^{-2}

Although eq. (3) should tend to yield increasingly approximate predictions of P_m at high values of V_i , it may be worthwhile at this point to estimate the range of effective permeability which can be expected in heterogeneous systems. It is seen that when P_i is equal to zero (as when a pigment has been incorporated as the internal phase), P_m may be expressed as

$$P_m = P_e \{ 2 / [(3/V_e) - 1] \} \quad (4)$$

where as V_i nears a value of 0.5, P_m should approach a lower limit of $0.4P_e$. It is assumed in eq. (3) that the properties of either component phase are not altered by the presence of the other phase, and therefore no allowance is made for such complicating interactions as have been postulated for pigmented systems.^{18,19} In the case of pigmented and nonpigmented Saran found in Table II it has been shown²⁰ that an apparent deviation from eq. (4) could be reasonably explained on the basis of such an interaction. However, differences in sample history could not be ruled out with these commercial samples; and it was considered that the observed discrepancy could be as easily attributed to such causes. By dividing eq. (3) by $P_i P_e V_e$ it can also be shown that

$$P_m = \frac{P_i P_e V_e}{3P_e + V_e(P_i - P_e)} [1 + (2P_e/P_i) + (3V_i/V_e)] \quad (5)$$

If P_i is much greater than P_e , then $P_i - P_e \cong P_i$ and $P_e/P_i \cong 0$. It can then be shown that

$$P_m = [P_i P_e / (3P_e + V_e P_i)] (V_e + 3V_i) \quad (6)$$

Since P_e is relatively small with respect to P_i , we may neglect $3P_e$ as an approximation, leading to

$$P_m = P_e [1 + (3V_i/V_e)] \quad (7)$$

which indicates that as V_i nears the value of 0.5, P_m should approach the value $4P_e$.

As a test of the consistency of the model proposed by Higuchi et al. it was considered worthwhile to compare the effective oxygen solubility in mixed polymer films calculated at the steady-state stage of permeation

according to eq. (2) with the solubility expected according to the model from a knowledge of the steady-state solubility in homogeneous films of each component phase. Solubility values for components of each mixed polymer film at the temperature studied are listed in Table IV. According to the model, the overall effective solubility S_m should be expressed in terms of the solubilities (S_i, S_e) and volume fractions (V_i, V_e) associated with the internal and the external phase as

$$S_m = S_i V_i + S_e V_e \quad (8)$$

Provided that equilibrium partition of the oxygen diffusant between the two polymer phases is attained rapidly enough with respect to the time scale of the permeability experiment, the overall effective solubility ($S_m = P_m/D_m$) determined from the diffusion curve should be in good agreement with the value calculated from eq. (8). Values of S_m determined from the mixed polymer diffusion curves are given in Table V. Estimates of S_m according to eq. (8) are shown in Table VI. It can be seen that the predictions of eq. (8) and the solubility values determined from the diffusion curve and eq. (2) are in fairly reasonable agreement for all but one of the mixed polymer films studied. Ordinarily, uncertainties which may arise between the two values would be chiefly associated with slow rates of establishment of equilibrium partition of the diffusant between the internal and the external phase during the initial moments of its penetration of the film. Such an effect alters the shape of the diffusion curve in the early stage of film penetration leading to errors in extrapolation to the θ intercept. This effect does not change the permeability of the film, which is measured at the later, steady-state stage of film penetration. Only in a very extreme case would the rate of partition between phases be so slow as to continue into very late stages of the permeation process. The result would be an effective delay in the attainment of steady-state diffusion through the film so that plots of the diffusion curve would not tend to level off until very large times of diffusion. Discussion of factors which may limit the rate of the partition process and how to test for them will be postponed for further consideration under the following section.

Application of the Theory to the Nonsteady-State Stage of the Diffusion Process

Higuchi et al.⁷ also discuss the feasibility of using their permeability theory to predict the barrier behavior of a heterogeneous film in the early, nonsteady-state stage of the permeation process. Such a prediction of barrier performance for a heterogeneous film, which would encompass the early stages of penetration (from the instant that the permeant comes into contact with the film until it begins to emerge at a constant, maximum rate from the other side) while utilizing terms and values consistent with the steady-state expression given by eq. (3) could be regarded as strong sup-

port for the validity of their theoretical approach. It is reasoned that the success of such an analysis would depend critically upon the proportion of the nonsteady-state stage of permeation which would unavoidably coincide with the completion of partition of the permeant between the immiscible phases of the film. They consider the case where the partition process is sufficiently rapid that the time consumed in establishing the steady-state stage of permeation within any microscopic region of heterogeneity in the barrier is small compared to the time for a unit change in local concentration (or activity) of the diffusing permeant associated with its penetration of the region. Under this condition there would be the least variance between such transient, effective values as the diffusion coefficient might have in the early stages of the penetration of such a region and its eventual (measurable) value D_m (equal to P_m/S_m) which would prevail in the barrier once the steady-state stage of permeation became established throughout all regions of the film. Under such a circumstance the nature of the permeation process in the early stages of penetration of the heterogeneous barrier would more nearly approximate Fickian behavior in a simple homogeneous barrier. In such instances it might be reasonable to expect the behavior of the heterogeneous barrier in both the nonsteady-state and the steady-state stage of permeation to be related (in the usual sense) through Fick's second law.

$$\partial C/\partial t = D(\partial^2 C/\partial x^2) \quad (9)$$

The otherwise limited range of useful application of eq. (9) to the disperse type of heterogeneous barrier studied in the present investigation would be broadened in such cases to include valid application to even the early stages of film penetration. It would then be feasible to combine the value of the predicted effective permeability of the system at steady state [obtained from eq. (3)] with a form of eq. (9) in order to calculate the expected shape of the entire permeability curve starting at time zero. Barrer's²¹ solution of eq. (9) for the boundary conditions of the present permeability experiments is

$$M = \left(\frac{D_m S_m C_0 t}{h} \right) + \frac{2h S_m C_0}{\pi^2} \sum_{n=1}^{\infty} \frac{\cos n\pi}{n^2} \left(1 - \exp \left\{ \frac{-D_m n^2 \pi^2 t}{h^2} \right\} \right) \quad (10)$$

where M is the total amount of permeant penetrating the barrier in a given time t per square centimeter of film area, subsequent to its initial contact with the film.

The basis for a simple mathematical test to determine whether permeability data obtained with a given heterogeneous (mixed polymer) barrier may or may not be amenable to treatment with eq. (10) is as follows. To complete the test in the case of a particular mixed polymer system a knowledge of the permeability and solubility in the two component polymer phases, and an estimate of the film thickness and the average internal-phase particle size is required. Briefly, the test method reviews conditions which could bring about a critical delay in the establishment of equilibrium parti-

tion of the permeant between the internal and the external phase (so that completion of this process would coincide with and compete with the permeation process). Two possible situations are recognized. In the first instance, the critical delay in the completion of partition would come about as a result of the slow rate of diffusion of permeant into the interior regions of individual internal-phase particles. The average time τ_1 for this slow rate-determining step would be estimated to a rough order of magnitude as

$$\tau_1 \cong r^2/15D_i \quad (11)$$

according to Glueckauf's²² formulae for diffusion into spheres, where r is the radius of the equivalent volume sphere of the internal phase. Alternatively, the critical delay in regional relaxation could come about through the slow rate of the diffusion of permeant into each particle through the surrounding external phase. In this case the time delay considered would be the time required for diffusion through a unit volume which would just include one internal-phase particle and the small region of external phase associated with it. This volume V may be represented as²³

$$V = 4/3\pi r^3[1 + (V_e/V_i)] \quad (12)$$

If it is assumed that V is a cube with sides of dimension l , the time delay τ_2 involved in diffusion through V (the relaxation time in this volume) would be approximately equal to

$$\tau_2 = l^2/6D_m = \{4/3\pi r^3[1 + (V_e/V_i)]\}^{2/3} (1/6D_m) \quad (13)$$

If the slow step in the permeation of V is the diffusion through its external-phase component, the effective permeability of V may approach the value of P_e . For their publication Higuchi et al.⁷ use P_e/S_m as an approximation for D_m in an equation similar to eq. (13) and arrive at a final expression for τ_2 given by eq. (14).

$$\tau_2 \cong (2S_m r^2/P_e)(1/V_i)^{2/3} \quad (14)$$

The criterion for successful application of eq. (10) to the interpretation of permeability data from a given heterogeneous barrier system is that partition of the permeant concerned between the internal and the external phase in each microscopic region of the film must be completed at a far more rapid rate than the rate at which that region would be penetrated by the permeant. Thus the larger (partition, rate-determining) value of τ_1 or τ_2 delay times must be very small compared to $(\Delta t/\Delta c)_x$, the span of time within which permeation in the neighborhood of the particle would cause a unit change in local permeant concentration. From a solution given by Barrer²¹ to the one-dimensional barrier problem in diffusion through an infinitely thick barrier, Higuchi et al. select a relationship

$$\partial C/\partial t = [S_m C_0 x/2(\pi D_m)^{1/2} t^{3/2}] \exp \{(-x^2/4D_m t)\} \quad (15)$$

which they use to estimate the value of $(\Delta c/\Delta t)$ at some point x in the thickness of a heterogeneous film at a time t in the early stage of permeation as a

function of the effective diffusion coefficient and the effective solubility of the permeant in the film. The rate of partition and the maximum initial rate of change in permeant concentration in an average microscopic region at x may then be compared by evaluating the ratio R between $(\partial t/\partial C)$ [the reciprocal of eq. (15)] and the larger value of either τ_1 or τ_2 as is done eq. (16).

$$R = [2(\pi D_m)^{1/2} t^{3/2} / \tau_2 S_m C_0 x] \exp \{x^2 / 4 D_m t\} \quad (16)$$

If the value of R throughout the range of $0 < x < h$ (where h is the film thickness) is found to average much greater than unity during the early stages of film permeation, the partition of diffusant between the internal and the external phase of the heterogeneous film would be expected to take place rapidly enough at all times that it would not interfere with permeation through any region.

Some trial calculations with eqs. (11) and (14) were carried out by using data from oxygen permeability experiments with a mixed polymer film composed of poly(vinyl acetate) which contained 28 vol-% polystyrene particles. Data taken from experiments with this film and films of its separated components at 27°C (see Tables IV and V) gave τ_2 a much larger numerical value than τ_1 , as indicated in Table VII. The use of a value of S_m either calculated from the composite film diffusion curve according to eq. (2) or estimated according to the theoretical model by using eq. (8) gave only slightly different values for τ_2 , but produced no significant change in the outcome of the test comparison. The value of τ_2 shown in Table VII was calculated by using an average of S_m determined by the two

TABLE VII
Estimates of Unit Volume Relaxation Time in a Mixed Polymer Film^a

Test	Time delay, sec
τ_1	9.80×10^{-6}
τ_2	4.82×10^{-2}

^a Poly(vinyl acetate) containing polystyrene particles at 27°C.

methods. In the absence of more direct experimental data on S_m , an estimate of its value in accordance with eq. (8) could have been used. In view of the far greater value found for τ_2 compared to τ_1 , the rate-determining step in the partition of the oxygen permeant in this case would appear to be the slow rate of diffusion of oxygen to the internal-phase (polystyrene) particle compared to the rapid rate at which the particle is capable of absorbing it. The test procedure for determining the applicability of eq. (10) to this system under the experimental conditions was completed by using eq. (16) and the value of τ_2 to estimate a representative value of R in the early, presteady-state stage of film permeation. A region in the film located at x equal to 5×10^{-3} cm midway between the high and the low pressure side of the film was selected for the calculation of

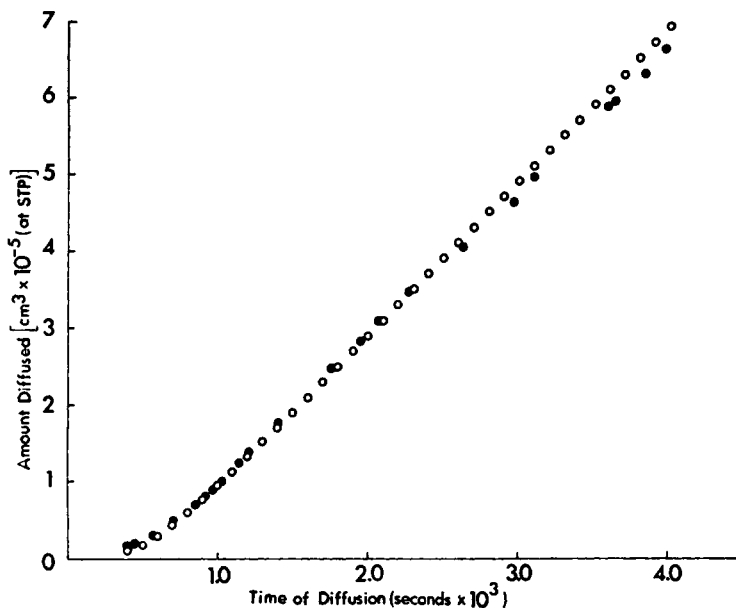


Fig. 5. Comparison of (○) theoretically predicted diffusion curve with (●) experimental results for oxygen permeation through poly(vinyl acetate) containing 0.28 volume fraction of polystyrene latex particles.

R at a time t equal to 3×10^2 sec halfway between the initial instant of contact of oxygen with the high pressure side of the film and the time θ which would have elapsed when it first begins to reappear at a constant rate at the opposite side. The effective diffusion coefficient D_m used in this calculation was estimated from the experimentally determined effective permeability and the same average value of S_m used in calculating τ_2 . The value of R under these conditions was found to be 7.13×10^7 and was therefore much greater than unity. If this value of R may be considered representative of its value throughout the film in question during the early stages of permeation, eq. (10) should be applicable to the experiment. The series in eq. (10) was summed to the fourteenth term at different values of diffusion time t . The results of the summation were applied with eq. (10) to the prediction of the experimental diffusion curve. The applicability of eq. (10) to this barrier system was demonstrated.

It is of interest to note that the use of a value for S_m which was calculated from the value of D_m obtained experimentally produced a better fit of the predicted diffusion curve with the curve for the experimental data at all stages of permeation than did a value of S_m based on eq. (8). The curve predicted from the former value of S_m is compared with the experimental curve in Figure 5. From the close fit obtained, the overall shape of the experimental curve appears to be Fickian. Therefore it would be difficult to attribute the discrepancy between predicted and observed oxygen solubility in the mixed polymer film to uncertainties connected with the rate of

attainment of equilibrium partition between the polymer phases. To the extent that oxygen solubility in the component phases may be legitimately represented in eq. (8) by the values determined separately in Table IV, an implication of these findings would be that this equation based on the additivity of solubilities from each polymer component may not be exactly obeyed. Alternatively, a possible explanation of some, though not all, discrepancies with this equation may be sought in the effect of undetected polymer voids on the time-lag estimate of solubility applied to the glassy polymer components of Table IV. According to a postulated mechanism which is accurately described elsewhere,¹⁵ voids in the glassy polymer network may act to withdraw diffusant molecules from participation in the permeation flux thereby delaying the achievement of steady-state diffusion in the barrier. Theoretically, if partition of the diffusing gas between the microscopic voids or "holes" and surrounding regions of the polymer is sufficiently rapid the resulting diffusion plots would be expected to retain the characteristic Fickian curvature and the misinterpreted significance of the measured time-lag may lead to erroneous high estimates of the solubility coefficient. Thus determined (as conceivably in the case of polystyrene in Table IV) a high value of S_i inserted in eq. (8) could contribute to slightly high estimates of S_m in Table VI.

CONCLUSIONS

Preliminary results reported in the present investigation support the applicability of eq. (3) to prediction of effective permeability coefficients in mixed polymer films. The neglect of refinements in the theoretical treatment with regard to the effect of particle-particle interaction and particle shape as mentioned by Higuchi et al. does not appear to hamper seriously the agreement between predictions and experimental findings. That eq. (1) appears to be valid for the relatively high concentrations of internal phase used in the present study may be attributable to a fairly high degree of agglomeration in the systems investigated in which small clusters of internal-phase latex particles may be separated from neighboring clusters by relatively large distances. An important consequence of the applicability of eq. (3) lies in the possibility that occasional large deviations from predicted behavior in heterogeneous systems may provide a measure of the degree of interaction between component phases and associated departures from ideality in the system.

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