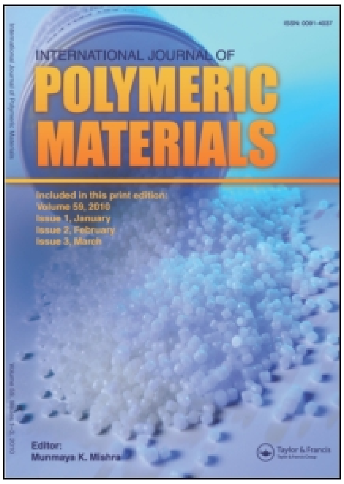

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Diffusion and Permeation of Gases in Fiber-Reinforced Composites

B. S. Mehta[a]; A. T. Dibenedetto[a]; J. L. Kardos[a]
[a] Materials Research Laboratory, and Department of Chemical Engineering Washington University, St. Louis, Missouri

To cite this Article Mehta, B. S. , Dibenedetto, A. T. and Kardos, J. L.(1976) 'Diffusion and Permeation of Gases in Fiber-Reinforced Composites', International Journal of Polymeric Materials, 5: 1, 147 — 161

To link to this Article: DOI: 10.1080/00914037608072395

URL: http://dx.doi.org/10.1080/00914037608072395

Intern. J. Polymeric Mater., 1976, Vol. 5, pp. 147–161

Printed in Reading, England

Diffusion and Permeation of Gases in Fiber-Reinforced Composites

B. S. MEHTA,† A. T. DiBENEDETTO‡ and J. L. KARDOS

Materials Research Laboratory and Department of Chemical Engineering
Washington University, St. Louis, Missouri 63130

(*Received April 14, 1975; in final form June 18, 1975*)

The presence of filler in a matrix phase greatly alters and also complicates the diffusion process, making experimental data very difficult to handle analytically. In this study both diffusion and permeability data were obtained in unfilled cellulose acetate films and cellulose acetate films filled with cheese cloth. Cheese cloth being highly permeable, the permeabilities and diffusivities of gases in the filled films are greater than in unfilled films due to reduced effective film thickness for molecular diffusion. A mathematical model has been developed which considers molecular diffusion to occur in that part of the film having no filler, while diffusion through the low-resistance cheese cloth is approximated by convective flow controlled only by the pressure gradient across the thickness of the cheese cloth yarn. The mathematical model predicts permeability values somewhat lower than experiment at low flow rates, but agrees well with experimental permeabilities at higher rates. The poor agreement between theoretical and experimental diffusivities is attributed mainly to errors involving the measurement of time lags. Morphological studies of the composite surfaces and cheese cloth filaments show that the cellulose acetate did not penetrate into the cheese cloth yarn which essentially retains its porous structure in the composite.

INTRODUCTION

While extensive experimental as well as theoretical studies[1,2] have been carried out on permeation of gases and vapors through various materials, these studies have been primarily restricted to unfilled plastic films. Diffusion and permeation in filled plastics have received relatively little attention. In a previous paper[3] we discussed the diffusion of simple gases in glass ribbon

---

†Mobil Chemical Company, Foam Products Department, Canandaigua, New York 14424.

‡Dept. of Chemical Engineering, University of Connecticut, Storrs, Conn. 06268.

reinforced cellulose acetate films. Because of impermeable glass ribbon the gas molecules diffusing through the composite film travel a tortuous path resulting in reduced permeability values for the filled system relative to the unfilled film. In this study we are concerned with determining the effect on the matrix permeability of highly permeable filler of known geometry. Cheese cloth made of porous yarn was used as the filler phase in a continuous cellulose acetate matrix phase. Because of the porous structure of the cheese cloth yarn, the gas molecules encounter very little resistance to diffusion. The overall effect of this rapid diffusion through the cheese cloth yarn is a reduction in the effective thickness of the composite film for molecular diffusion and hence an increase in the overall permeability of the film.

THEORY

The entire cross section of the composite film can be divided into the following three parallel, volume filling unit cells as shown schematically in Figure 1:

a) a portion containing no cheese cloth;

b) a portion containing only single filaments;

c) a portion containing two filaments crossecting.

Gas molecules diffusing through part (1) of the film meet the unfilled matrix phase throughout the entire thickness of the film whereas gas molecules diffusing through parts (2) and (3) have only a part of the film thickness taken up by matrix material.

Due to the yarn's cylindrical shape and assuming there is no resistance to diffusion through the yarn, the effective reduction in the path of the diffusing molecules will depend upon the point on the yarn periphery intersected by the path. Thus the reduction is maximum (equal to the diameter of the filament) when the molecules meet the yarn at the top center and minimum (zero) when the molecules meet the yarn at the side as shown in Figure 1. The average reduction in the length of effective path of diffusion due to the presence of one yarn, as in (2), is

$$\frac{\int_0^{\pi/2} d\cdot\cos\theta\cdot d\theta}{\int_0^{\pi/2} \theta\cdot d\theta} = \frac{8d}{\pi^2}$$

where d is the diameter of the yarn. In (3), where the crossecting filaments are perpendicular to each other, the diffusing molecules would take an average path as in (2) through both yarns. The average reduction in the length of the effective diffusion path due to the presence of crossecting filaments in part (3) is, therefore, ($16\,d/\pi^2$). The effective lengths for diffusion in the three parts can now be written as

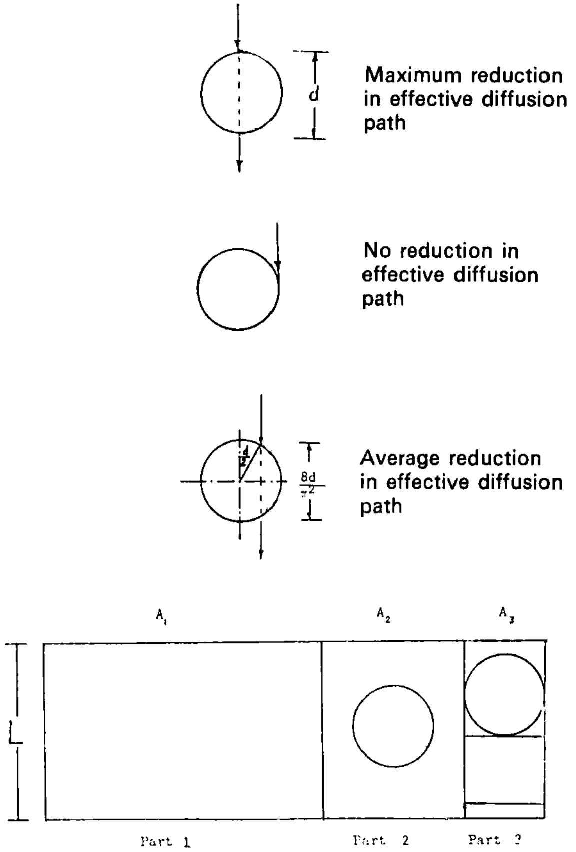

FIGURE 1 Cheese cloth-cellulose acetate composite film.

$$L_1 = L$$
$$L_2 = L - 8d/\pi^2 = L - L'_2$$
$$L_3 = L - 16d/\pi^2 = L - L'_3$$

An alternate way of viewing the film cross section is shown in Figure 2. Diffusion through part (1) takes place by molecular diffusion throughout the entire thickness L of the film. Diffusion in part (2) takes place by a molecular process through a thickness of the film equal to L_2 and by a very low resistance process through the thickness L'_2. The latter process can be approximated by convective flow which is controlled only by the pressure gradient across the channel. Similarly molecular diffusion is the rate-controlling process through that thickness of the film equal to L_3 and by convective flow through the thickness L'_3.

L

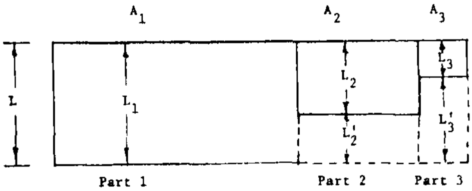

FIGURE 2 An alternate way of viewing the film cross-section shown in Figure 1.

If we neglect the flow due to convection and assume that there is no interaction between the three phases, then the steady-state molecular diffusion fluxes through the three cross-section areas of parts (1), (2) and (3) as shown in Figure 2 can be written as (1)

$$Q_1 = A_1 \frac{\bar{P}_1 \Delta_p}{L_1} (t-\theta_1) \tag{1}$$

$$Q_2 = A_2 \frac{\bar{P}_2 \Delta_p}{L_2} (t-\theta_2) \tag{2}$$

$$Q_3 = A_2 \frac{\bar{P}_3 \Delta_p}{L_3} (t-\theta_3) \tag{3}$$

where Q_1, Q_2, Q_3 are steady-state flow rates, L_1, L_2, L_3 effective diffusion path lengths, $\bar{P}_1$, $\bar{P}_2$, $\bar{P}_3$ the permeation coefficients, A_1, A_2, A_3 the cross-section areas and θ_1, θ_2, and θ_3 the time lags for the three parts (1), (2) and (3) of the film, respectively. Δ_p is the pressure difference across the thickness of the composite film. Since molecular diffusion is the rate controlling process for composite permeation (no resistance to convective flow), the pressure difference across the effective thicknesses for molecular diffusion in the three phases is also Δ_p. Since the effective diffusion process in all three processes is through matrix material only,

$$\bar{P}_1 = \bar{P}_2 = \bar{P}_3 = P_m \tag{4}$$

where P_m is the permeability coefficient for pure matrix material.

Also

$$A_1 + A_2 + A_3 = A \tag{5}$$

where A is the total cross-section area of the film.

Since the three phases are in parallel the steady-state diffusion Eqs. (1–3) for the three parts can be added to yield the overall rate of steady-state diffusion through the composite film as

$$Q = Q_1 + Q_2 + Q_3 = P_m \Delta_p \left(\frac{A_1}{L_1} + \frac{A_2}{L_2} + \frac{A_3}{L_3}\right) \left[t - \frac{\frac{A_1}{L_1}\theta_1 + \frac{A_2}{L_2}\theta_2 + \frac{A_3}{L_3}\theta_3}{\frac{A_1}{L_1} + \frac{A_2}{L_2} + \frac{A_3}{L_3}} \right] \tag{6}$$

The overall steady state flow, Q, through the composite film can also be written as

$$Q = \frac{P_c \Delta_p}{L} \cdot A \cdot (t - \theta_c) \tag{7}$$

where P_c and θ_c are the overall permeability and time lag values for the composite.

From Eqs. (6) and (7)

$$\frac{P_c}{P_m} = \frac{L}{A}\left(\frac{A_1}{L_1} + \frac{A_2}{L_2} + \frac{A_3}{L_3}\right) \tag{8}$$

and

$$\theta_c = \frac{\frac{A_1}{L_1}\theta_1 + \frac{A_2}{L_2}\theta_2 + \frac{A_3}{L_3}\theta_3}{\frac{A_1}{L_1} + \frac{A_2}{L_2} + \frac{A_3}{L_3}} \tag{9}$$

The various time lags in Eq. (9) can also be written as

$$\theta_c = L^2/6D_c \tag{10}$$

$$\theta_1 = L_1^2/6D_1 \tag{11}$$

$$\theta_2 = L_2^2/6D_2 \tag{12}$$

$$\theta_3 = L_3^3/6D_3 \tag{13}$$

where D_c is the overall diffusion coefficient for the composite and D_1, D_2, D_3 are the values of diffusion coefficients for parts 1, 2 and 3 respectively of Figure 2. Since in all three parts the effective diffusion is through the matrix phase only

$$D_1 = D_2 = D_3 = D_m \tag{14}$$

From Eqs. (9) and (10–14)

$$\frac{D_c}{D_m} = \frac{A_1(L/L_1) + A_2(L/L_2) + A_3(L/L_3)}{A_1(L_1/L) + A_2(L_2/L) + A_3(L_3/L)} \tag{15}$$

or

$$\frac{D_c}{D_m} = \frac{L}{A\phi_m}\left(\frac{A_1}{L_1} + \frac{A_2}{L_2} + \frac{A_3}{L_3}\right) = \frac{1}{\phi_m}\left(\frac{P_c}{P_m}\right) \tag{16}$$

Using Eqs. (8) and (16) the permeability and diffusivity of composites can be predicted from a knowledge of the permeability and diffusivity of the unfilled matrix phase, the volume fraction of matrix phase, ϕ_m, the cross-section areas, and the effective thicknesses for molecular diffusion of the three parts shown in Figure 2. The cross-section areas and the effective lengths of the different parts are dictated by the mesh size of the cheese cloth and diameter of the yarns.

MATERIALS AND METHODS

For permeability experiments both unfilled and filled films were prepared by compression molding between two smooth, flat plates. The unfilled cellulose acetate films were prepared by laminating several unfilled, biaxially oriented cellulose acetate sheets (obtained from Cope Plastics) and then compression molding the laminate. Bleached cheese cloth (20 × 12 mesh) made of 100% cotton, 8 mils in diameter was used as filler for the composite films. The scanning electron micrograph in Figure 3 clearly shows that each yarn strand is composed of many loosely spun cotton fibers. Cheese cloth-cellulose acetate (CC-CA) composite films were prepared by compression molding a laminate consisting of two layers of cheese cloth on one side followed by four unfilled cellulose acetate sheets. Such a composite is designated as 1,2 CCCA with cheese cloth being phase 1 and cellulose acetate phase 2. A composite film having two layers of cheese cloth on both top and bottom with six layers of cellulose acetate sandwiched in between is designated as 1,2,1 CCCA.

Both unfilled and filled films were made by compression molding for about 15 minutes at 350°F and 50–100 psi pressure. The compression was always started from room temperature and the temperature increased gradually with intermittent release of pressure and repressurizing until the desired temperature was reached. The intermittent release of pressure and repressurization helped in pushing out entrapped air bubbles. After the laminate had been heated at the final constant temperature and pressure for about 15 minutes, the heating was stopped and the film air cooled under pressure to room temperature. This molding cycle ensures complete melting of the matrix so that the cheese cloth is totally embedded, while at the same time preventing excess fleshing and the development of high molded-in stresses. The films were then placed in a dessicator for several days to keep them dry.

It was of some consequence to know to what degree the matrix wetted the

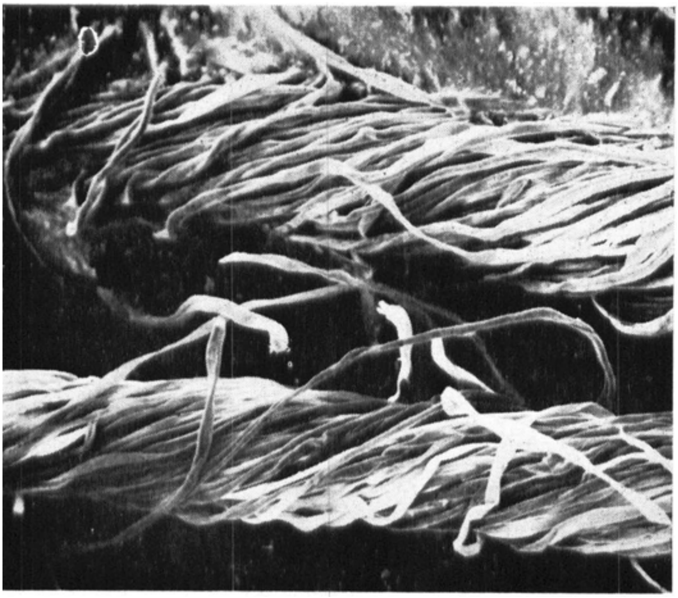

FIGURE 3 Structure of cheese cloth yarn.

fiber bundles (yarn), since our assumptions in the theoretical development called for convective or at least very-low-resistance transport through the filler phase. First, scanning microscopy showed that the cheese cloth yarns were totally embedded and not exposed on the surface. Secondly, composite films were cut with a microtome and examined under the scanning microscope. Figure 4 shows a section through the interior of a yarn whose diameter runs from the top to the bottom of the micrograph. There are large, obvious voids between individual fibers in the interior of the yarn where the matrix did not penetrate. This porous yarn interior is also visible on tensile fracture surfaces of the composites as shown in the scanning micrograph of Figure 5. An outer sheath of matrix containing fibers has peeled away leaving behind a porous core of fibers unwetted by matrix (top of micrograph). Thus, it seems clear that the cellulose acetate wets and engulfs the outermost fibers in the yarn, but a large porous core remains untouched by the resin.

A diffusion cell was designed for obtaining the permeability data and the details of the apparatus and method of obtaining experimental data have been discussed in detail elsewhere.[3,4] A constant pressure is maintained at both faces of the film during the permeation process, thereby maintaining the boundary conditions employed in the mathematical development of the time lag technique. The permeation curve can be traced automatically on a recorder chart. Experimental permeation data were obtained for nitrogen gas in both

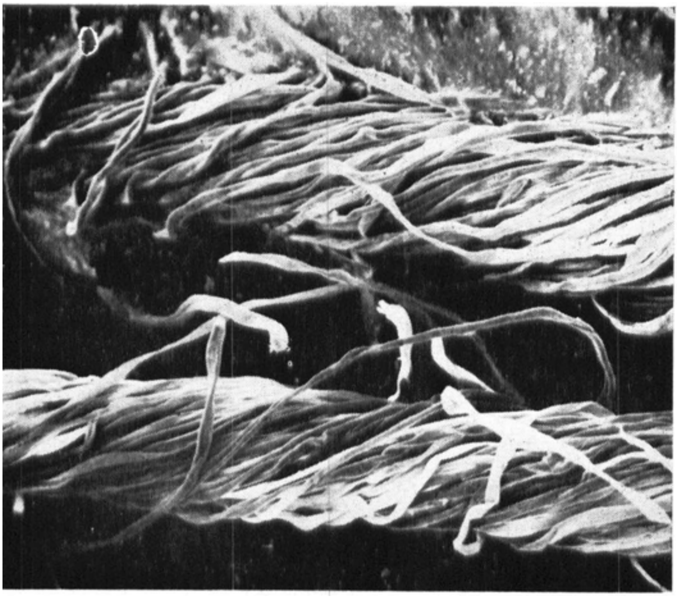

FIGURE 4 Surface of cheese cloth-cellulose acetate composite cut by microtome glass blade.

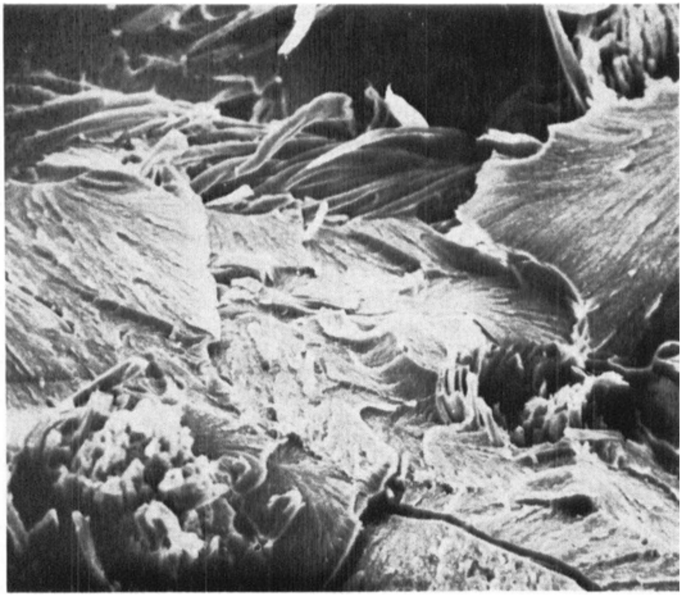

FIGURE 5 Fracture surface of cheese cloth-cellulose acetate composite pulled in tension.

unfilled cellulose acetate films and cellulose acetate films filled with cheese cloth yarn.

RESULTS AND DISCUSSION

The resulting permeability data are summarized in Tables I to IV. The permeation and diffusion coefficients were calculated by curve fitting the steady state permeation data as shown in Figure 6 which is a plot of the volume Q

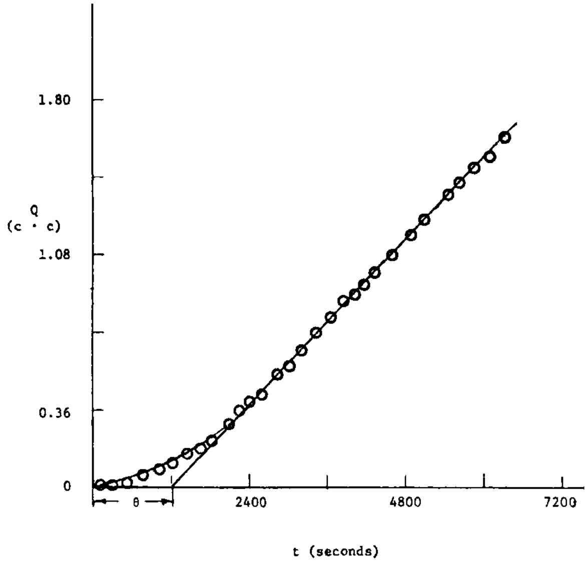

FIGURE 6 Permeation curve for 1,2 CCCA film at 54.8°C, $p1$ = 950 mm Hg and $p2$ = 145 mm Hg.

TABLE I

Experimental diffusion and permeation coefficients of unfilled cellulose acetate maxtrix

(Permeant gas: nitrogen. Film thickness = 27 mil)

Temp. °C	Upstream pressure (mm Hg)	ΔP (mm Hg)	$D_m \times 10^6$ cm^2/sec	$P_m \times 10^9$ $\frac{\text{cc(STP)cm}}{\text{cm}^2\text{/sec/atm}}$
39.8	767	622	1.06	4.4
49.8	752	607	2.07	7.0
54.8	515	370	2.68	9.4
54.8	1015	870	2.42	9.4
64.8	780	635	4.08	13.5
64.8	1017	872	3.86	13.7

TABLE II

Experimental diffusion and permeation coefficients of 1,2 CCCA composite (Permeant gas: nitrogen. Film thickness = 18.5 mil)

Temp. °C	Upstream pressure P_1 (mm Hg)	ΔP (mm Hg)	$P_c \times 10^9$ $\frac{\text{cc(STP)cm}}{\text{cm}^2\text{/sec/atm}}$	P_c/P_m	$D_c \times 10^6$ cm²/sec	D_c/D_m
39.8	510	365	7.2	1.63	1.55	1.46
	645	500	7.0	1.59	1.29	1.21
	770	625	6.9	1.56	1.46	1.37
	865	720	6.6	1.50	1.48	1.39
	870	725	6.9	1.56	1.58	1.48
	1030	885	6.7	1.52	1.47	1.38
	1290	1145	6.3	1.43	1.49	1.40
49.8	500	355	11.7	1.64	2.76	1.33
	755	610	11.1	1.56	2.59	1.26
	800	655	11.1	1.56	2.93	1.41
	845	700	11.5	1.62	3.08	1.49
	990	845	10.3	1.45	2.65	1.28
	1145	1000	10.3	1.45	2.41	1.17
54.8	475	330	13.6	1.46	3.57	1.48
	510	365	14.7	1.58	3.22	1.33
	580	435	13.2	1.42	2.96	1.22
	760	615	13.6	1.46	3.47	1.43
	852	707	13.9	1.49	3.08	1.27
	945	800	13.8	1.48	3.47	1.43
	950	805	12.8	1.38	3.09	1.28
	990	845	13.7	1.47	3.02	1.25
	1060	915	13.4	1.45	3.52	1.45

TABLE III

Experimental diffusion and permeation coefficients of 2,1 CCCA composite (Permeant gas: nitrogen. Film thickness = 18.5 mil)

Temp. °C	Upstream pressure P_1 (mm Hg)	ΔP (mm Hg)	$P_c \times 10^9$ $\frac{\text{cc(STP)cm}}{\text{cm}^2\text{/sec/atm}}$	P_c/P_m	$D_c \times 10^3$ cm²/sec	D_c/D_m
49.8	500	355	11.3	1.59	2.47	1.20
	755	610	10.2	1.43	2.45	1.20
	1000	855	10.4	1.46	2.07	1.00
	1520	1375	10.1	1.42	2.07	1.00
54.8	470	325	13.5	1.45	4.58	1.90
	587	442	13.5	1.45	3.02	1.25
	745	600	12.9	1.38	3.31	1.37
	940	795	12.6	1.35	2.99	1.24
	1090	945	12.1	1.30	3.15	1.30

TABLE IV

Experimental diffusion and permeation coefficients of 1,2,1 CCCA composite (Permeant gas: *nitrogen*. Film thickness = 37.25 mil)

Temp. °C	Upstream pressure P_1 (mm Hg)	ΔP (mm Hg)	$P_c \times 10^9$ $\frac{\text{cc(STP)cm}}{\text{cm}^2\text{/sec/atm}}$	P_c/P_m	$D_c \times 10^5$ cm²/sec	D_c/D_m
34.8	608	463	5.3	1.58	1.50	1.85
	695	550	5.0	1.49	2.01	2.48
	750	605	4.9	1.46	1.66	2.05
	860	715	5.0	1.49	1.58	1.95
39.8	657	512	6.9	1.57	1.47	1.38
	700	555	6.6	1.50	2.62	2.46
	750	605	6.5	1.48	2.10	1.97
	760	615	6.9	1.57	2.08	1.96
	855	710	6.5	1.48	1.96	1.84
49.8	645	500	11.4	1.61	3.79	1.83
	700	555	10.8	1.52	4.02	1.94
	750	605	10.3	1.45	3.02	1.45
	755	610	10.3	1.45	2.58	1.25
	800	655	10.0	1.41	2.62	1.26
54.8	650	505	13.9	1.49	4.70	1.94
	700	555	13.2	1.42	4.10	1.69
	750	605	12.7	1.37	3.91	1.61

of the diffusant gas measured as a function of time on the downstream side. The diffusion coefficients were obtained from the time lag values θ by using Dayne's[5] equation, $D = l^2/6\theta$, where l is the thickness of the film and D the diffusion coefficient. The diffusion coefficients are reported in units of cm²/sec while the permeation coefficients, as measured from the steady state slope of the Q vs. t plot of Figure 6, are given in units of c.c. of gas measured at standard temperature and pressure passing per second through an area of 1 cm² of a film 1 cm thick under a pressure difference of one atmosphere across the film. The experimental data for the 1,2 CCCA and 2,1 CCCA composites (Tables II and III) were obtained by using the same film except that the sides of the film exposed to the upstream and downstream pressures were reversed.

Permeability experiments were carried out at several temperatures ranging from 34.8 to 64.8°C. For both unfilled and filled films, experimental data were obtained for several upstream pressures at each temperature to determine the concentration dependence of the permeation and diffusion coefficients. The area fractions for the three different parts shown in Figure 2 and the overall filler volume fraction of the composite film were calculated from a knowledge of the mesh size, filament diameter, and the number of cheese cloth layers used in the films. The theoretical permeability ratio (composite/unfilled matrix material, P_c/P_m) were then calculated using Eq. (8) which yielded 1.37 for the

1,2-CCCA and 2,1-CCCA composites and 1.38 for the 1,2,1-CCCA composite. The corresponding theoretical ratio of the diffusion coefficients for all composites considered is 1.65.

A review of Table II thru IV shows that the experimental values for P_c/P_m are higher than those predicted from the model by about 15% at relatively low Δ_p and about 5% at high Δ_p. At any one temperature, the difference between the experimental permeability and that predicted by the model tends to decrease with increase in the upstream pressure. A leakage either around the O'rings used to compress the film or on the downstream side of the film could cause an increase in the experimental permeability. As Δ_p increases, the relative magnitude of this leakage, compared to the total flux, decreases. The larger flux thus is measured with better accuracy and permeabilities at high upstream pressures are relatively more accurate. They also show better agreement with the theoretical values.

The theoretical relative permeabilities, P_c/P_m, are almost the same, for all three composite films (Tables II–IV). This indicates that permeability is primarily a function of volume fraction of reinforcement (which is about 16% for all composites examined) and not strongly dependent on (a) the geometric arrangements such as number of layers of cheese cloth in the film, (b) whether the cheese cloth was placed on one or both sides of the film and, (c) for films having cheese cloth on one side only, which side of the film was exposed to the high pressure. This also corroborates the earlier observation that although cheese cloth is placed on the sides of the film before compression molding, it actually is uniformly embedded into the matrix phase and results in a macroscopically uniform composite.

The diffusion data for cheese cloth-cellulose acetate composites show considerable scatter and it is very difficult to make a reliable estimate of effective diffusion coefficients. The theoretical model (Eq. (16)) predicts that the diffusion coefficients for composites should be approximately 1.65 times the value for unfilled matrix. However, from Tables II–IV one can see that most of the experimental values of relative diffusivities, D_c/D_m, as calculated from the measured time lags range from about 1.2 to 1.6 with a number of experiments showing values as low as 1.0 and as high as 2.4. The range of variation in the experimental measurement of diffusion coefficients for this system by time lag analysis is estimated to be no better than ±15–25%, which encompasses most of the data. There are several factors which can cause this error. The diffusion coefficients depend upon the accuracy of measurements of film thickness and the intercept θ on the time axis of the permeation plot. Faster permeation rates in the case of cheese cloth-cellulose acetate films results in more data scatter in the steady state portion of the permeation plot, which leads to error in the slope and this can very significantly affect the time lag calculations.

The calculation of the diffusivity requires an accurate extrapolation of the steady state portion of the Q versus t curve back to the zero value of Q, the intercept on t-axis being time lag.[6]

From Figure 6

$$Q = (dQ/dt)\,t - b \tag{17}$$

and

$$\theta = \frac{b}{(dQ/dt)} \tag{18}$$

Differentiation of Eq. (18) gives

$$\Delta\theta = \frac{\Delta b}{(dQ/dt)} - \frac{\theta \cdot \Delta(dQ/dt)}{(dQ/dt)} \tag{19}$$

In the usual permeation experiments the rate of permeation has acquired steady state at and beyond $t = 3\theta$ and it is safe to draw a straight line through permeation data points after $t = 4\theta$ where Eq. (17) becomes

$$(Q)_{t=4\theta} = (dQ/dt) \cdot 4\theta - b \tag{20}$$

Differentiation of Eq. (20) and substitution of (18) and (19) in it gives

$$\frac{\Delta\theta}{\theta} = 3\frac{\Delta(dQ/dt)}{(dQ/dt)} \tag{21}$$

which means that relative error in θ is almost three times that in slope. Therefore for a ±5% error in slope the error in θ is ±15%. Diffusivity is measured from time lag data by the relation

$$D = l^2/6\theta \tag{22}$$

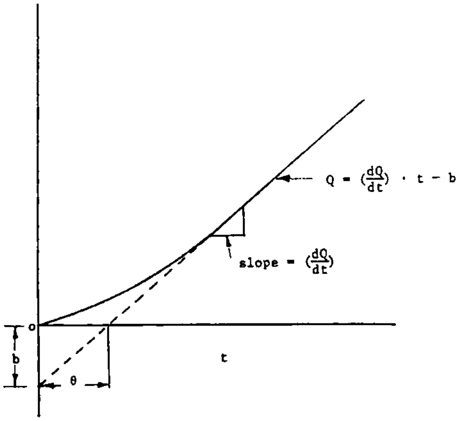

FIGURE 7 Time lag curve.

The compression molded cheese cloth-cellulose acetate films exhibited a variation of ±5% in thickness, l. Thus Eq. (22) can be written to relate the actual (theoretical) diffusivities with those experimentally measured as below

$$D_{\text{theoretical}} = \frac{(1 \pm 0{\cdot}00)^2 l^2}{6(1 \pm 0{\cdot}15)\theta} = (1 \pm 0{\cdot}297)\, D_{\text{experimental}}$$

Therefore $D_{\text{theoretical}}$ can differ from $D_{\text{experimental}}$ by as much as ±30% due to experimental errors. In light of these facts the scatter in the diffusivity data is not very surprising.

The mathematical development of the model for permeation through films containing highly permeable fillers considered the steady state diffusion (Eq. 7) wherein the presence of filler was ignored except that it reduces the overall effective thickness of the film. In reality, however, during the permeation process, gas molecules can be absorbed by the cheese cloth yarns and deposited in the porous cores. Meares,[7] has suggested that these molecules are immobilized and do not participate in diffusion. The time lag expression takes into account the mobile molecules and cannot be quantitatively applied for determining diffusion coefficients when immobilization is occurring. Michaels[8] and Vieth *et al.*[9,10] expanded on Mearers' idea and concluded that two types of sorption are operative, i.e., one which is identified with a Henry's law term and the other with gas deposited in the holes. Michaels, Vieth *et al.*[9,10] have postulated that the hole-filling process obeys a Langmuir-type isotherm. Paul[11] used the dual sorption model proposed by Vieth *et al.*[9,10] and computed time lags by making necessary modification of the Fick's second law to take into account the accumulation term. His calculations show that due to immobilization, the time lag will be larger because it includes the time taken for hole filling although only the dissolved species may supply the concentration gradient for the diffusion process. Although the above theory was not used to quantitatively predict the effect of the immobilization factor on the time lags in this study, but absorption on surfaces and in voids probably causes an increase of the measured time lags and could account for the somewhat low experimental diffusivities.

CONCLUSIONS

A mathematical model for permeation of gases in a composite having a highly permeable filler has been formulated. When cheese cloth yarns which consist of spun cellulose fibers are used as filler in a cellulose acetate matrix, they retain a porous core structure in the composite even though the outer fibers of the yarn are well wetted with matrix. Because of this high porosity core, the gas molecules diffuse extremely rapidly through the yarn resulting in a decrease in the effective thickness of the composite film. The relative permeabilities found experimentally agree with values calculated from the mathematical model (Eq. (8)) within 5% at large pressure gradients and 15% at low pressure gradients. However, diffusion data for this system show considerable scatter due most likely to errors in the time lag measurements. Immobilization effects could explain why experimental diffusivities are somewhat lower than the theoretically predicted values.

Acknowledgements

This work is part of research conducted by the Monsanto/Washington University Association sponsored by the Advanced Research Projects Agency, Department of Defense and the office of Naval Research under contract No. N00014-67-C-0218.

References

1. J. Crank and G. S. Park, Eds., *Diffusion in Polymers*, Academic Press, New York (1968).
2. R. M. Barrer, *Diffusion In and Through Solids*, University Press, Cambridge (1941).
3. B. S. Mehta, A. T. DiBenedetto and J. L. Kardos, Diffusion and permeaton of gases in glass ribbon—reinforced plastics, *Inter. J. Polymeric Mater.* **3**, No. 4, 1975.
4. B. S. Mehta, *Diffusion and Permeation of Gases in Fiber-reinforced Composites, Doctoral Dissertation*, Washington University, 1972.
5. H. A. Daynes, The process of diffusion through a rubber membrane, *Proc. Royal Soc.*, **97A**, 286 (1920).
6. R. D. Siegel and R. W. Coughlin, "Errors in diffusivity as deduced from permeation experiments using the time lag technique", unpublished.
7. P. Meares, The solubilities of gases in polyvinyl acetate, *Tran. Faraday Soc.*, **54**, 40 (1958).
8. A. S. Michaels and H. J. Bixler, Solubility of gases in polyethylene, *Journal of Polymer Science*, **L**, 393–412 (1961).
9. W. R. Vieth and K. J. Sladek, A model for diffusion in glassy polymers, *J. Colloid Sciences* **20**, 1014–1033 (1965).
10. W. R. Vieth, P. M. Tam and A. S. Michaels, Dual sorption mechanisms in glassy polystyrene, *J. Colloid and Interface Science* **22**, 454–461 (1961).
11. D. R. Paul, Effect of immobilizing adsorption on the diffusion time lag, *Journal of Polymer Science*, Part A-2, Vol. 7, 1811–1818 (1969).