Diffusion and Permeation of Gases in Glass Ribbon-Reinforced Plastics

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PLEASE SCROLL DOWN FOR ARTICLE

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The permeation and diffusion processes in continuously reinforced polymers were investigated from both theoretical and experimental viewpoints. Composite sheets were made by reinforcing cellulose acetate with glass ribbons. These sheets exhibited good adhesion between the filler and the continuous polymer phase. The permeability in the composite films was less than in the unfilled cellulose acetate due to increased tortuosity and increased polymer phase resistance to diffusion. To explain the experimental data, a mathematical model was developed using a modified equation originally formulated by Nielsen for composite permeability. Good agreement between the model predictions and the experimental data was achieved.

INTRODUCTION

While there has been considerable research done on mechanical property characterization and prediction for reinforced polymers, physical processes such as heat conduction and diffusion have received relatively little attention. In this study the diffusion of simple gases in glass ribbon reinforced cellulose acetate films is characterized and compared to the diffusion behavior of unfilled cellulose acetate films. In particular the ribbon thickness and packing geometry were varied to vary the volume fraction of resin and the diffusion path of gas molecules. Because of the impermeable glass ribbon the gas molecules diffusing through the composite sheet have to travel a tortuous path and one might expect reduced permeability values for the filled material relative to the unfilled polymers. However it is important to know the

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magnitude of this reduction and to what degree it can be predicted for a given system.

THEORY

The diffusivity of a gas or vapor in pure polymers has been the subject of several theoretical models and both permeability and sorption methods have been used to measure diffusivities.[1,2] In composite sheets the presence of filler complicates the diffusion process and analysis of the experimental data becomes rather involved. Diffusion of a gas or vapor in composites can take place by one or more of the following modes: (a) diffusion through only the continuous matrix phase, (b) diffusion through the dispersed as well as the continuous phase, (c) diffusion through the interfacial region with properties different from the matrix phase, and (d) diffusion through cracks, pores, or small channels present in the composite due to imperfect adhesion or other structural defects. The presence of an impermeable filler in a continuous matrix can result in decreased diffusivity for two reasons. First, the activation energy can increase because the polymer chains are more restricted in their movement. Second, the effective path length of the diffusing molecules increases and the effective cross-sectional area for diffusion decreases.

For composites having impermeable fillers such as glass ribbons, the diffusivities become structure sensitive and the fluxes may no longer be inversely proportional to the thickness of the composite sheet. The diffusant molecules must travel a tortuous path by going around the ribbon in order to pass through the thickness of the film. For mathematical formulation the overall permeability of the composite is represented by permeation through a unit cell of the film as shown in cross section in Figure 1. The unit cell consists
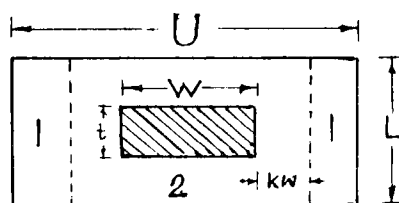

FIGURE 1   Unit cell.

of two phases. Phase one consists of only pure matrix material and permeation through this part takes place exactly as in a pure material and is thus not affected by the presence of filler. The diffusing molecules travel a straight line path perpendicular to the cross-sectional area of the film. This phase is termed

"uninfluenced". Phase two consists of both matrix material and the glass ribbon. The diffusive flow lines in this region are affected by the presence of the ribbon and undergo tortuous paths. This phase is therefore termed "influenced". The size of the influenced phase depends upon the geometry and orientation of the glass ribbons in the composite. It can be characterized by a constant K such that the diffusive flow lines are affected by the presence of the ribbon as far as a distance equal to KW from the ribbon, where W is the width of the glass ribbon.

The overall permeability of the composite P_c can now be expressed for the two phases in parallel as

$$P_c = \phi_1 P_1 + \phi_2 P_2 \tag{1}$$

where P_1 = permeability of phase 1

P_2 = permeability of phase 2

ϕ_1 = volume fraction of phase 1

ϕ_2 = volume fraction of phase 2.

Since phase 1 is uninfluenced $P_1 = P_m$ where P_m is the permeability of the unfilled matrix. The permeability P_2 for phase 2 can be expressed by Nielsen's equation[3] for composite permeability as follows:

$$P_2 = \frac{P_m \phi_{m2}}{\tau} \tag{2}$$

where ϕ_{m2} = the volume fraction of the matrix material in phase 2

τ = tortuosity factor

$= 1 + (W/2t)\, \phi_{f2}$

where ϕ_{f2} is the volume fraction of the filler in phase 2 and t is the thickness of the glass ribbon.

Substitution of Eq. (2) into Eq. (1) and a knowledge of the dimensions of the unit cell and glass ribbon results in the following expression for composite permeability,

$$\frac{P_c}{P_m} = 1 - \phi_f \left(\frac{1}{\tau} + \frac{L}{t} \right) + \frac{W(1 + 2K) - 2WK\tau}{U \cdot \tau} \tag{3}$$

where U is the width and L the thickness of the unit cell as shown in Figure 1. ϕ_f in Eq. (3) is the overall filler volume fraction of the unit cell, which is also the filler volume fraction of the composite film. Thus Eq. (3) expresses the overall permeability of the composite in terms of the permeability of unfilled matrix material, filler volume fraction, the geometry of the glass ribbon and a constant K which is characteristic of the geometry and orientation of the glass ribbon in the composite film.

EXPERIMENTAL METHOD AND MATERIALS

Apparatus

Both steady state diffusion and the time lag techniques for measuring permeability and diffusivity, respectively, require the measurement of the permeation rate of a diffusant through a membrane under well-defined conditions of surface concentrations. A constant pressure cell similar in principle to that of Geiszler, DiBenedetto and Koutsky[4] was designed for this study and is shown
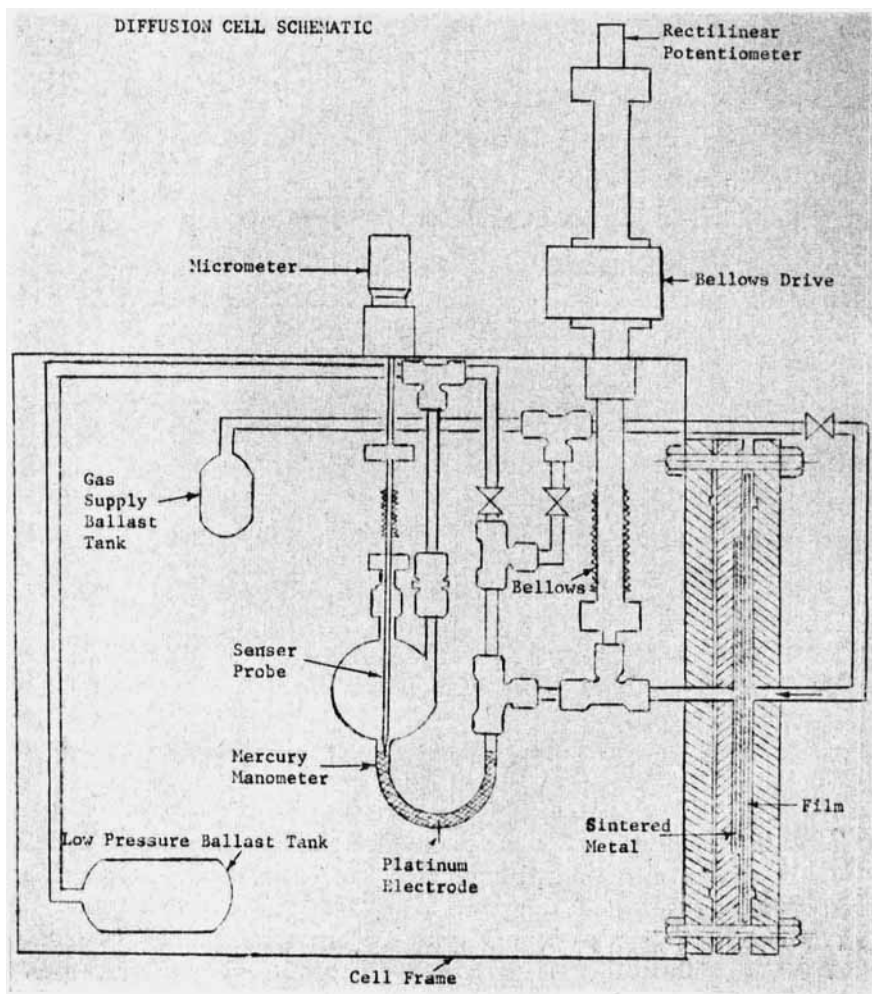

FIGURE 2   Diffusion cell schematic.

schematically in Figure 2. Two 10-inch diameter stainless steel plates serve to hold the film. With prolonged experiments, or when soft membranes are used, the high pressure in the upstream side of the film may cause the film to tear or develop cracks. To protect against any possible damage to the film, a six-inch diameter, $\frac{1}{16}$-inch thick sintered 304 stainless steel plate is mounted in the lower stainless steel plate. O-rings are provided on both sides of the film to prevent leaks from the sides. The upstream stainless steel plate is provided with a $\frac{1}{4}$-inch inlet connection in the center to admit the permeant gas to the cell. The downstream stainless steel plate is connected to the sensing and detection section.

A three-legged pyrex glass assembly, also shown in Figure 2, forms the sensing section of the cell. The U-tube portion is filled with mercury and acts as a simple pressure differential manometer. The three vertical legs of the glass assembly are connected to the mercury sensor, the low pressure ballast tank, and the downstream side of the film respectively. The two vertical legs going to the mercury sensor and the low pressure ballast tank are connected to the U-tube manometric portion through a $2\frac{1}{2}$-inch diameter bulb. A $\frac{1}{16}$-inch stainless steel rod pointed at its lower end acts as the capacitance probe of the mercury sensor and is introduced through the bulb so that its lower pointed end is above the center of the mercury surface in the U-tube below the bulb. A platinum electrode is provided in the center of the U-tube portion. The platinum electrode and the mercury sensor are connected to a relay. During the diffusion experiment a slight increase in pressure due to the permeant coming out on the downstream side of the film causes contact between the mercury surface and the sensor probe and a relay is actuated. This triggers an automatic adjustment of the volume on the downstream side, thereby bringing the pressure back to its original set value and causing the contact to break again. The constant pressure adjustment is accomplished by a bellows arrangement which is connected to a rectilinear potentiometer through two limit microswitches. The potentiometer converts the linear movement of the bellows for volume adjustment to an electrical signal for automatic readout. The relay activated by the contact between the sensor probe and mercury serves as the on-off power supply for the motor driving the bellows.

For accurate determination of permeation and diffusion constants from transient and steady state data, it is important that pressure on the two sides of the film and in the U-tube manometric portion of the sensing section are kept constant with a minimum of fluctuation. This is accomplished by using two ballast tanks shown in the schematic diagram. The entire diffusion cell is immersed in a constant temperature oil bath.

Experimental procedure

In a typical diffusion experiment the diffusion cell is immersed in the oil bath and the whole system is brought to a desired temperature. The cell is evacuated for several hours at constant temperature to remove all moisture from the film. During evacuation all valves in the system are open except for the valve at the outlet of the gas supply ballast tank. The system is evacuated to about 100 microns Hg. By momentarily opening the valve at the outlet of the gas supply ballast tank, the whole system is then filled with the diffusant gas at a pressure equal to the pressure desired on the downstream side of the film. The entire system is kept at this low pressure for a duration equal to 6–8 time lags during which both sides of the film attain equilibrium. The upstream side of the film is then isolated from the rest of the system and the upstream pressure of the gas is raised to a desired value by again opening the valve at the outlet of the gas supply tank. This outlet valve remains open throughout the experiment so that the upstream pressure of the film is essentially the pressure of the ballast tank. The automatic recorder is turned on and the downstream side is isolated from the low pressure ballast tank. During the run, the permeation process is followed automatically by the recorder. A typical permeability data curve is shown in Figure 3.

Film preparation

The reliability of diffusion data depends to a great extent on the ability to prepare films of precise physical characteristics. Unfilled cellulose acetate films as well as glass ribbon reinforced cellulose acetate films were prepared. Cellulose acetate was selected as the matrix polymer because it is relatively permeable to gases and is also relatively easy to compression mold.

Making glass ribbon-cellulose acetate composite films can be difficult and deserves detailed description.[5] First, a sheet of ribbons is formed by cutting prescribed lengths from a tape and placing them in a frame having slots and spaces to align the ribbons so that they are oriented exactly parallel and have a predetermined inter-ribbon spacing. The ribbons are held permanently in the shape of sheets with Scotch tape. The next step involves forming a laminate by laying up alternate sheets of cellulose acetate and ribbons. In the case of composites containing multilayers of glass ribbons, the successive glass layers are arranged so that ribbons in any two consecutive layers are staggered such that the spaces between the ribbons are always above and below the ribbons in adjacent layers (see Figure 4). The last step consists of compression molding at a temperature of 350°F which is high enough to ensure complete matrix melting, and 50–100 psi pressure for 15 minutes. After pressurizing at room temperature, the temperature was increased gradually with intermittent release of pressure and repressurizing until the desired temperature was reached. The
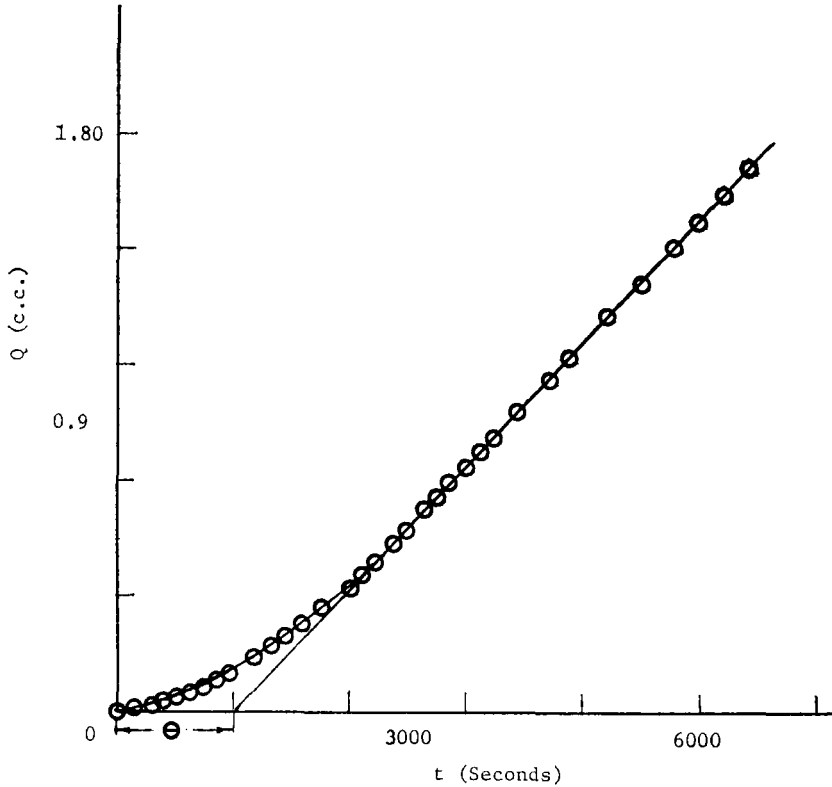
FIGURE 3   Permeation curve.

purpose of the intermittent release and increase of pressure was to ensure a more uniform infiltration of the polymer between the ribbons. After the sample had been heated at constant temperature and pressure for about 15 minutes, heating was stopped and the sample was air cooled under pressure to room temperature. The composite films were cut to the desired geometry with a diamond saw and placed in a dessicator for several days to dry completely.

Three different sizes of glass ribbons were used to make composites of various filler volume fractions, ribbon packings, and ribbon aspect ratios (Figure 4). The ribbon thickness was limited to less than or equal to 6 mils, since the thicker ribbons did not have sufficient uniformity in thickness to produce a satisfactory model system. The details of the glass ribbon-cellulose acetate films are shown in Table I. All the unit cells (shown in Figure 4) are symmetrical with the exception of film H.

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Film D	U = 167 mil
Film E	U = 334 mil
Film F	U = 644 mil
Film G	U = 334 mil
Film H	U = 167 mil
Film I	U = 167 mil
Film J	U = 167 mil
Film K	U = 100 mil

FIGURE 4   Unit cells of GRCA composite.

TABLE I

Description of films

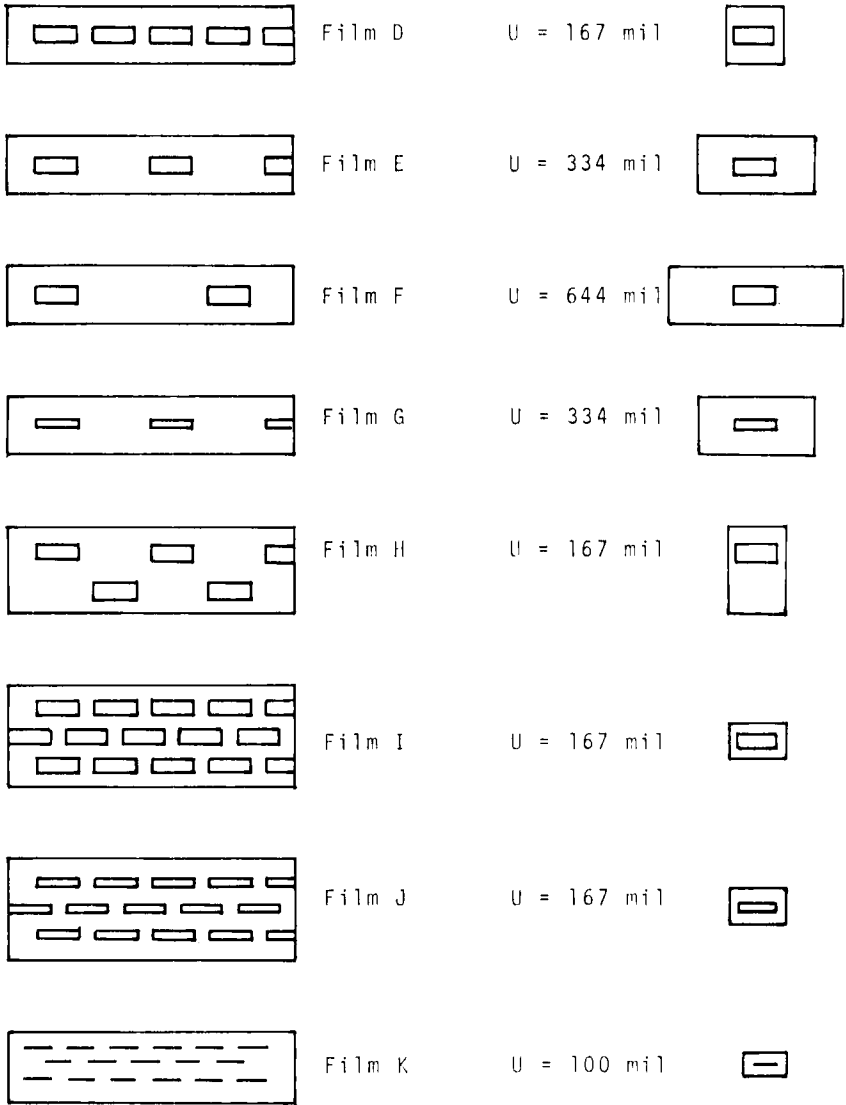| Film	Description	$<l>$ (mil)	Φ_f %	Type of filler	Width of filler (mil)	Thickness of filler (mil)	No. of filler layers in film
A	Press molded cellulose acetate	27.0	0	—	—	—	—
D	GRCA	18.5	21.0	Glass ribbon	125	5.2	1
E	GRCA	18.5	10.5	,,	125	5.2	1
F	GRCA	18.0	5.5	,,	125	5.2	1
G	GRCA	15.15	5.15	,,	125	2.4	1
H	GRCA	29.2	13.4	,,	125	5.2	2
I	GRCA	34.3	32.9	,,	125	5.2	3
J	GRCA	34.2	15.2	,,	125	2.4	3
K	GRCA	23.5	12.45	,,	60	1.5	3
L	Biaxially oriented cast cellulose acetate	20	0	—	—	—	—
M	Press molded	45.4	0	—	—	—	—
N	GRCA	45.4	34.6	GR	125	5.2	4
O	GRCA	21.2	21	,,	125	5.2	1
P	GRCA	18.0	9.15	,,	125	5.2	1
Q	GRCA	18.25	4.70	,,	125	5.2	1

GRCA = Glass ribbon/cellulose acetate.

RESULTS AND DISCUSSION

The results of the permeability experiments are summarized in Tables 2 and 3. The permeabilities were calculated by curve fitting the steady state permeation data using a least square technique and then obtaining the slope of the curve (see Figure 3). The permeability coefficients are reported in units of c.c. of gas, measured at standard temperature and pressure, passing through an area of 1 cm² of a film 1 cm thick in one second under a pressure difference of one atmosphere across the film. The diffusivities were calculated from time lag values as $D = L^2/6\theta$ where θ is the time lag on the time axis (see Figure 3) and L is the thickness of the film. The units of diffusivity are cm²/sec. The permeability coefficients and diffusion coefficients shown in Table 2, were obtained for different films and different temperatures and pressure gradients across the thickness of the film. Nitrogen and oxygen gas were used as diffusants. For unfilled, cellulose acetate (film A) the diffusion and permeation data were

TABLE II

Experimental diffusion and permeation coefficients

Gas	Film	Temp. °C	Run	p_1 (mm Hg)	Δ_p (mm Hg)	$D \times 10^6$ cm²/sec	$P \times 10^9$ cc(STP) cm cm²-sec-atm
N_2	A	54.8	160	1015	870	2.42	9.4
		54.8	161	515	370	2.68	9.4
		64.8	162	780	635	4.08	13.5
		64.8	164	1017	872	3.86	13.7
		49.8	166	752	607	2.07	7.0
		39.8	167	767	622	1.06	4.4
O_2	A	39.8	168	750	605	2.32	13.8
		44.8	169	764	619	3.43	21.3
		54.8	171	755	610	4.41	25.3
		64.8	172	751	606	5.97	38.9
N_2	D	64.8	111	1455	1310	3.11	2.6
			112	1117	972	2.58	2.6
			113	465	320	—	3.0
			114	630	485	7.32	2.83
		49.8	115	795	650	—	3.0
			116	480	335	—	1.30
			117	1500	1355	1.85	1.20
			118	1130	985	—	1.20
		54.8	119	807	662	2.22	1.7
			120	1515	1370	1.98	1.5
			121	1170	1025	1.22	1.6
			122	530	385	—	1.7
N_2	E	54.8	123	792	647	1.670	5.7
			125	1015	870	1.920	5.0
			126	500	355	3.050	5.5
		64.8	127	1010	865	3.76	7.5
			128	755	610	2.82	8.0
			129	540	395	5.24	7.7
			130	1280	1135	2.65	7.6
N_2	E	49.8	131	565	420	2.19	4.3
			132	1025	880	1.57	4.0
			133	1255	1110	1.53	3.9
			134	760	615	1.26	4.2
	F	64.8	135	767	622	4.34	10.9
			137	570	425	4.62	10.8
			138	890	745	2.81	11.0
		54.8	139	762	617	2.65	6.6
			140	892	747	1.79	7.0
			141	575	430	2.97	6.9
			142	1070	925	1.95	6.7
		49.8	143	757	612	2.04	5.3
			145	597	452	1.80	5.6
		39.8	154	760	615	1.01	3.6
		44.8	155	770	625	1.31	4.4

TABLE II—*continued*

Gas	Film	Temp. C	Run	p_1 (mm Hg)	Δ_p (mm Hg)	$D \times 10^6$ cm²/sec	$P \times 10^9$ cc(STP) cm cm²-sec-atm
O₂	F	49.8	148	766	621	3.26	15.7
		54.8	149	790	645	3.94	19.9
			150	530	385	4.38	20.9
			151	1040	895	4.53	19.3
		34.8	152	778	633	1.96	10.2
		44.8	156	742	597	2.45	15.2
			157	1035	890	2.46	14.9
			158	545	400	2.69	15.0
N₂	G	54.8	179	1033	888	1.57	5.4
			183	757	612	1.76	5.1
			185	7111	966	1.83	5.0
			186	506	361	2.49	5.4
		49.8	180	758	613	1.93	4.3
			181	517	382	3.73	4.2
			182	1072	927	1.44	4.1
		64.8	187	744	599	3.11	7.7
			188	1137	992	3.20	7.2
			189	511	366	3.24	8.1
O₂	G	64.8	190	768	623	5.17	22.3
N₂	H	64.8	194	1135	990	5.27	4.9
			195	768	623	8.31	5.3
		54.8	197	775	630	5.27	3.1
		49.8	198	772	627	2.41	2.5
O₂	I	64.8	203	748	603	12.29	4.8
		54.8	204	763	618	3.36	3.2
		49.8	205	773	628	2.89	2.5
		64.8	206	783	638	4.55	4.7
		54.8	207	767	622	2.47	3.1
		49.8	213	794	649	5.60	2.4
	K	64.8	213	794	649	5.60	12.6

obtained for both nitrogen and oxygen. Since the steady state rate of permeation of oxygen in unfilled cellulose acetate is almost three times that of nitrogen, diffusion data for composite sheets with relatively low filler volume fraction were obtained with both nitrogen and oxygen, whereas composite sheets with relatively high filler volume fractions or having multilayers of glass ribbons, were characterized with oxygen only because of the very long times needed for nitrogen diffusion. Table III reports the relative permeabilities P_c/P_m for various composite films.

The permeability data were analysed according to Eq. (3). The diffusive flow in the unit cell can be compared with the well known pattern of fluid flow past a plate placed in a uniform laminar flow. The flow lines are disturbed by the

TABLE III
Relative permeabilities for GRCA films

Film	Gas	p_1 (mm Hg)	49.8°C $P_c \times 10^9$	49.8°C P_c/P_m	54.8°C p_1	54.8°C $P_c \times 10^9$	54.8°C P_c/P_m	64.8°C p_1	64.8°C $P_c \times 10^9$	64.8°C P_c/P_m
D	N_2	480	1.3	0.183	530	1.7	0.183	465	3.0	0.214
		795	1.4	0.197	807	1.7	0.183	630	2.83	0.203
		1130	1.2	0.169	1170	1.6	0.172	780	3.01	0.215
		1500	1.2	0.169				1117	2.60	0.186
								1455	2.60	0.186
E	N_2	565	4.3	0.606	500	5.5	0.591	540	7.7	0.550
		760	4.2	0.591	792	5.7	0.613	755	8.0	0.571
		1025	4.0	0.563	1015	5.0	0.538	1010	7.5	0.536
		1255	3.9	0.549				1280	7.6	0.543
F	N_2	597	5.6	0.789	575	6.9	0.742	570	10.8	0.771
		757	5.3	0.746	892	7.0	0.753	767	10.9	0.779
								890	11.0	0.789
	O_2	766	15.7	0.737	530	20.9	0.826			
					790	19.9	0.787			
					1040	19.3	0.763			
G	N_2	517	4.2	0.591	506	5.4	0.581	511	8.1	0.579
		758	4.3	0.606		5.2	0.559	744	7.7	0.550
		1072	4.1	0.577		5.0	0.538			
H	N_2	772	2.5	0.352	775	3.1	0.333	768	5.3	0.379
								1135	4.9	0.350
	O_2	752	7.2	0.336	768	8.6	0.340	765	12.4	0.359
		752	7.6	0.355						
I	O_2	773	2.5	0.116	763	3.2	0.126	748	4.8	0.123
J	O_2	762	2.4	0.113	767	3.1	0.123	783	4.7	0.121
K	O_2							794	12.6	0.324

presence of the plate and remain straight only at a great distance from it. The influenced phase of the unit cell is thus defined as consisting of disturbed diffusive flow while in the uninfluenced portion of the cell the diffusive flow lines are straight. In the development of Eq. (3), a factor K was used to characterize the extent of the influenced matrix phase. The values of relative permeabilities P_c/P_m, calculated from Eq. (3), agree within $\pm$ 10% with the experimental values when a value of $K = 0.22$ is used (Figure 5). Only film H deviates significantly from the experimental relative permeability. This is probably due to its unsymmetric unit cell as shown in Figure 4 and therefore Eq. (6) may not apply. The size of the unit cell in a composite sheet will depend upon the spacing between the adjacent glass ribbons. Furthermore, in a unit cell which has been assumed to consist of influenced phase and uninfluenced phase, the size of the influenced phase is fixed by the dimensions of the ribbon and the factor K.
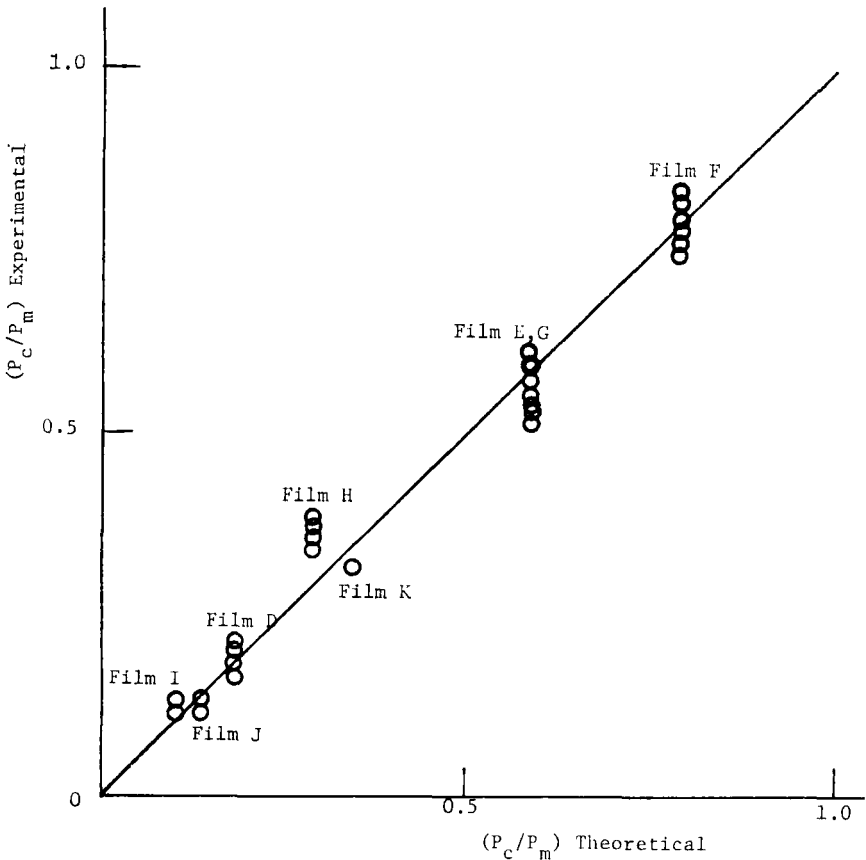

FIGURE 5   Experimental vs theoretical relative permeabilities for GRCA composites.

Therefore, as the distance between the adjacent ribbons decreases, the influenced phases around these ribbons approach each other with a simultaneous reduction in the size of the uninfluenced portions until the cells consist only of influenced matrix. Now, if two adjacent ribbons were brought even closer to each other, not only would there be no uninfluenced phase but the influenced phases of the adjacent ribbons would overlap. Thus, the actual size of the influenced phase as determined by use of the factor K would extend beyond the physical size of the unit cell and relative permeability values (P_c/P_m) should change sharply.

While the unit cells of films E, F, G, H and K have both uninfluenced and influenced phases, unit cells of films D, I and J contain only influenced material. In films D, I and J the calculated size of the unit cell is $W(1 + 2K) = 180$ mils wide, while from the geometry and the orientation of the ribbons in the films, the maximum sized unit cell can be only 167 mils wide (Figure 4); thus the theoretical unit cells must overlap as shown in Figure 6.
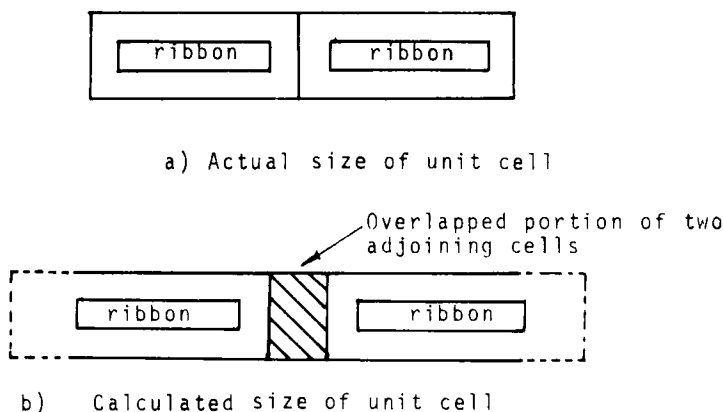

FIGURE 6   Overlapping unit cells.

In the case of films D, I, and J, Eq. (3) predicts that all the matrix in the unit cell is influenced. However, the permeability must be corrected for the fact that the actual unit cell is physically smaller than the cell calculated using Eq. (3). This is done by using the factor, ϵ, which is the ratio of the size of the actual unit cell to that of the theoretical unit cell ($U/w(1 + 2k)$). The permeability must be further corrected to account for the fact that the flux lines interact in the overlapped region; this is accomplished with the empirical factor λ. The permeability of the composite can now be written as:

$$P_c = P_2 \cdot \epsilon \cdot \lambda \tag{4}$$

where P_c is the permeability of the composite, P_2 the permeability of the theoretical influenced phase, the size of which is calculated by the factor k. In the case of films D, I and J, from Eqs. (3) and (4), the value for λ is found to be approximately 0.84. In Eqs. (3) and (4), Nielsen's permeability equation was used for the influenced portion of the unit cell where all the diffusive flow lines are disturbed and travel a tortuous path. In films D, I, and J where unit cells consist only of influenced flow, Nielsen's model was applied directly to calculate the relative permeabilities. The resulting values of P_c/P_m are considerably higher than experiment shows (Table IV). However if we account for

TABLE IV

Comparison of experimental permeabilities with permeabilities of composites (P_c) predicted by Nielsen's model and Eq. (3)

Film	D	I	J
Eq. (3)	0.186	0.112	0.142
Nielsen's P_c/P_m	0.226	0.134	0.170
Experimental P_c/P_m	0.214	0.123	0.121
	0.202	0.126	0.123
	0.215	0.117	0.113
	0.186		
	0.186		
	0.183		
	0.172		
	0.183		
	0.197		
	0.169		
	0.169		

the overlapping effect as in Eq. (4), Nielsen's equation can be rewritten as

$$P_c = P_N \cdot \lambda \tag{5}$$

where P_N is the permeability as calculated by Nielsen's equation in the actual unit cell. Again using Eqs. (3) and (5), an approximate value of 0.84 results for the overlapping factor λ.

   Due to material anisotropy, the process of diffusion through glass ribbon/ cellulose acetate films is direction dependent. Even when the flow is maintained in one direction only, i.e., along the thickness of the film, the diffusing molecules have to go around the impermeable glass ribbons. This causes concentration gradients to develop along the width of the ribbons and the flux in the direction of flow will gain an additional component. The classic time lag expression therefore cannot be applied to glass ribbon/cellulose acetate films due to two-dimensional flow. The time lag technique could also not be correctly applied to determine diffusion coefficients because the permeability data showed anomalous behavior in the transient state region. In some experiments, a high

initial permeation rate, which gradually decreased to the final steady state
value was observed as shown in Figure 7. These experiments gave anomalous
time lags which are effectively negative numbers (runs 113, 115, 116, 118 and
122 in Table 2). In other experiments the time lags were very small resulting in
high diffusivities. It is clear that anomalous permeation behavior makes a
quantitative determination of time lags very difficult and experimental data
cannot be reliably used to predict diffusion coefficients.

Park[6] observed similar anomalous behavior for methylene chloride diffusing
through polystyrene films. Meares[7,8] also observed similar but more complex
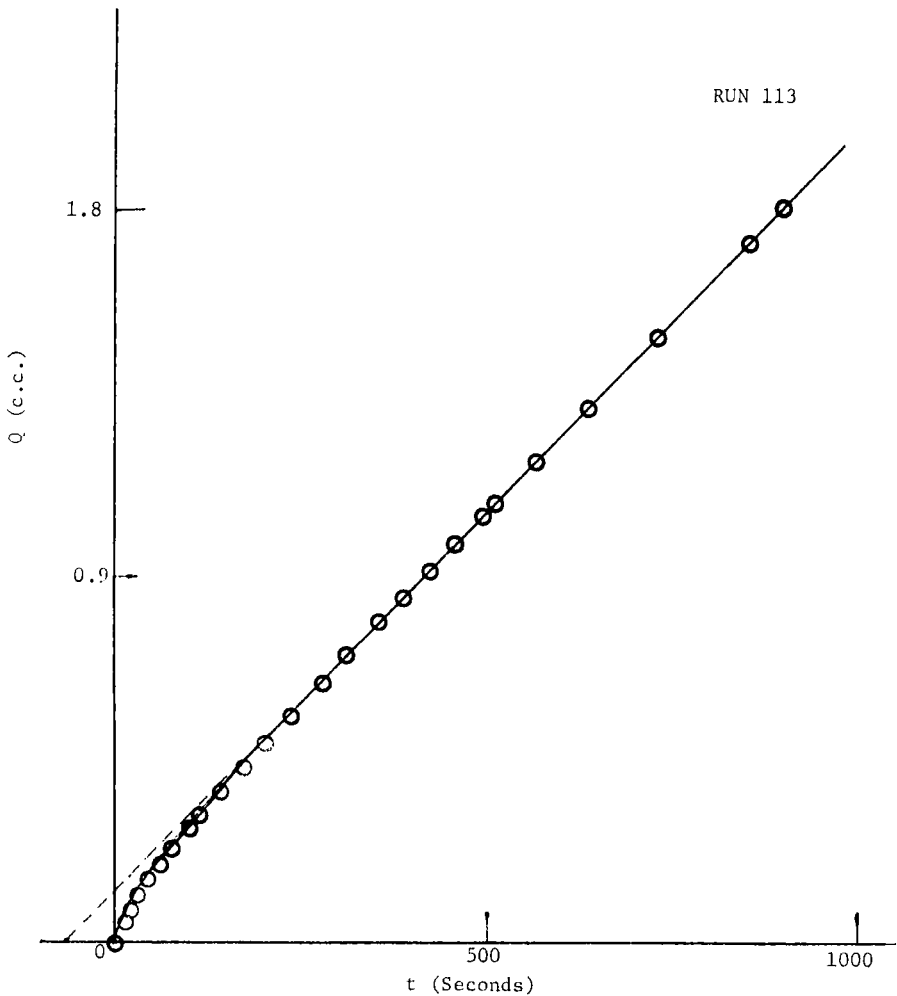

FIGURE 7   Anomalous permeation curves.

behavior in which the initial high permeation rate decayed in a relatively short time interval, gradually increased, and then eventually approached a steady state. Fujita[9] has proposed three possible mechanisms to explain such anomalous behavior: (1) the presence of a convective flow or of two or more diffusion flows having different diffusivities, (2) a time dependence on D proposed by Crank and Park,[10] and (3) stress effects on the diffusion process. Park[6] suggested that the initial high rate of permeation may be due to rapid penetration of vapor through cracks or internal pores with the subsequent decay to a steady state level arising from sealing up of such cracks by absorbed vapor. In the case of glass ribbon/cellulose acetate composites, the presence of minute cracks forming microchannels for the whole distance through the film cannot be completely ruled out. However, as the upstream pressure of the film is increased, the convective contribution to permeability due to flow through channels should increase. There was no such evidence from the experiments done at different pressures and the glass ribbon/cellulose acetate composites cannot, therefore, be assumed to have an internal capillary system to a significant extent. Meares[8] in his sorption studies observed that stress effects seem to be important for glassy polymers. The molecular layers on the surface in contact with a given vapor tend to expand and impart strain in the underlying polymer. The strain causes relaxation motions of long-chain molecules which reduces the microheterogeneity of the structure and thus make it less permeable. Further penetration of the gas molecules will have to occur through less permeable material. Ruhmann and Wu[11] have studied the effect of internal stresses on liquid diffusion in composites. In their sorption studies of benzene vapor in glass-epoxy composite specimens they observed two competing phenomena. First, an increase in the rate of sorption takes place because of channeling etc. whereas a reduction in the rate of sorption occurs due to severe restraint on the matrix swelling dilation by the filler, which results in the generation of internal stresses. All things considered, it seems that neither the dependence of diffusivity on concentration nor the time-dependent surface concentration can explain the occurrence of the anomalous behavior in cellulose acetate-glass ribbon system.

CONCLUSIONS

The presence of glass ribbon reduces the permeability of the unfilled cellulose acetate to a much greater degree than would be warranted by the filler volume fraction. The composite permeability data can be explained in terms of molecular diffusion through a unit cell. Use of Nielsen's equation for composite permeability, along with a reduced parameter K to characterize the extent of the disturbed phase, gives theoretical permeability values which

agree within $\pm 10\%$ of the experimental values. Equation (3) is a realistic model when unit cells contain both uninfluenced and influenced phases. Equation (3) is not a physically realistic model when the unit cells contain only influenced phase and the calculated influenced phases of two adjacent unit cells overlap.

However, Eq. (4) derived from a knowledge of the size of the theoretical unit cell, the actual size of unit cell and the use of a factor λ for the flux line inter-action offers reasonable agreement with experimental data. Nielsen's permeability equation which actually predicts higher permeability values for films having overlapping unit cells also shows better agreement with experimental data when the factor λ is used to account for flux line interaction (Eq. (5)). Diffusivities of glass ribbon/cellulose acetate composites cannot be calculated from time lag measurements due to two-dimensional flow and anomalous time lag behavior.

Acknowledgements

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.   L. E. Nielsen, Models for permeability of polymer systems, *J. Macromol. Sci. (Chem.)* A1(5), 929–942 (1967).
4.   W. A. Geiszler, *Diffusion and Permeation of Gases in Amorphous Polymers*, Ph.D. Thesis, University of Wisconsin, 1968.
5.   T. B. Lewis, *Ribbon Reinforcements in Composite Materials*, Reinforced Plastics/ Composites Division, The Society of the Plastics Industry, Inc., 25th Annual Technical Conference, 1970.
6.   G. S. Park, The diffusion of some halo-methanes in polystyrene, *Trans. Faraday Soc.* **46**, 684 (1950).
7.   P. Meares, Diffusion of allyl chloride in polyvinyl acetate Part I. The steady state of permeation, *J. Polymer Science* **27**, 291 (1958).
8.   P. Meares, Diffusion of allyl chloride in polyvinyl acetate Part II. The transient state of permeation, *J. Polymer Science* **27**, 405 (1958).
9.   Hiroshi Fujita, Diffusion in polymer-diluent systems, *Forthschr. Hochpolym.-Forsch.*, Bd. 3, S.1–47 (1961).
10.   J. Crank and G. S. Park, An evaluation of the diffusion coefficient and its concentration dependence from sorption experiments, *Transactions of Faraday Society* **51**, 1632 (1955).
11.   D. S. Ruhmann and E. M. Wu, The effect of stress on diffusion in composites, *Polymer Preprints*, American Chemical Society 475–480, Vol. 14, Number 1, May 1973.