

Sorption and Diffusion of Water in Glass Ribbon-Reinforced Composites*

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Synopsis

The processes of sorption and diffusion of water in anisotropic glass ribbon-reinforced composite films of controlled structural and physical characteristics were investigated in terms of the film properties, e.g., geometry, orientation, and volume fraction of the filler; molding characteristics of the composite film; and the adhesion between the glass ribbon and continuous cellulose acetate matrix. While the diffusion of water through unfilled cellulose acetate film was found to be a simple activated process with very little concentration dependence, the diffusion behavior of glass ribbon-reinforced cellulose acetate was found to be anomalous and concentration dependent.

INTRODUCTION

The long-range mechanical performance of glass-reinforced plastics depends on their stability in varying environmental conditions. There is a particular need for knowledge of the effect of water on these materials. Water, a universally present compound, is capable of diffusing in most materials. Glass-reinforced plastics tend to absorb moisture after extended periods of exposure to high humidity, and this moisture often degrades their mechanical and structural integrity. A knowledge of the mechanism and the rate of diffusion of water in composites thus becomes very important.

The sorption and diffusion of low molecular weight substances such as water by polymers is often sensitive to any change in segment mobility or spatial arrangement of polymer chains. In the case of composite materials, the filler phase incorporated in a matrix material plays an important role in the solution and diffusion processes. Most of the literature concerning diffusion and sorption in heterogenous media deals primarily with crosslinked and crystalline polymers where the crosslinks or crystallites act as the dispersed phase in the continuous amorphous phase. Relatively little work has been reported on diffusion in composite media made by combining two physically different materials.

Nielsen¹ studied the permeability of polymer systems filled with plate-like particles. He developed phenomenological equations to predict the maximum decrease in composite permeability that can be expected for the addition of a filler to a polymer. He extended his analysis to permeability of liquids through

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filled polymers when the liquid adsorbs or collects at the filler-polymer interface. Ruhman and Wu² have studied the effect of anisotropy on the sorption of benzene vapor in glass-epoxy composite specimens. They also studied the role of internal stresses generated as a result of the dilatation which accompanies the sorption of the organic solvent in a filled system. Very recently, Shen and Springer³ have studied the absorption and desorption in moisture in Graphite-Fiberite composites under controlled environmental conditions. They developed expressions for the moisture distribution and moisture content as a function of time of one-dimensional homogeneous and composite materials exposed either on one side or on both sides to humid air or to water.

SORPTION AND DIFFUSION IN COMPOSITES

In a composite material with two components A and B, a component A may be in direct contact with component B to produce a two-phase system. Sometimes, there may be an intervening phase between components A and B, thus making it a three-component system. The intervening phase may be deliberately added to improve adhesion, or it may be the result of a chemical reaction between A and B. In the case of poor adhesion, this phase may be air. The simplest case to consider is the case where A and B meet at an interface in the absence of a third phase. Most theoretical studies of the effect of disperse phases on the physical and mechanical properties of composite materials assume perfect adhesion at the interface for simplicity of treatment. This is only a reasonable assumption where such complicating factors as imperfect adhesion leading to the presence of cracks, pores, or small channels, or the presence of impurities at the interface can be neglected. If the composite material is considered to consist of two phases, matrix material and filler, such that these phases can be regarded independent of each other and there is no interaction between matrix and the filler, then the solubility coefficient of the penetrant in the composite system S is given by Barrer:⁴

$$S = S_m \phi_m + S_f \phi_f \quad (1)$$

where ϕ_m and ϕ_f are the volume fractions and S_m and S_f are the solubility coefficients of the matrix and the filler phase, respectively. Equation (1) is an oversimplification of the solution process because it does not account for the adsorption that occurs at the interface. In real situations, the matrix material and filler may not be independent of each other. The matrix material may wet the filler surface and so compete with the vapor for the surface.

When the filler phase is impermeable ($S_f = 0$), eq. (1) becomes

$$S = S_m \phi_m \quad (2)$$

and the solubility equation can be written as

$$C = S_m \phi_m P \quad (3)$$

where C is the concentration of water vapor in the composite and p is the equilibrium pressure. When the adhesion between the filler and the matrix material is not perfect, the existence of holes or microvoids may act as a stable phase. The solution process can in this case be considered to consist of two mechanisms,⁵⁻⁷ namely, the ordinary dissolution and the hole-filling processes, and can be described quantitatively as follows:

$$C = C_D + C_H = S_m \phi_m P + \frac{C_h' b_p}{1 + b_p} \quad (4)$$

where ordinary dissolution C_D is represented by the Henry's law term, and the sorption of penetrant into holes, C_H , is represented by the nonlinear Langmuir expression where C_h' is the hole-filling constant and b is the hole affinity constant.

While the diffusion behavior for most of the unfilled polymers can be explained by simple Fickian phenomena where diffusivity is constant and independent of solute concentration, in the case of composites the presence of filler makes the diffusion process more complicated 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: (i) diffusion through the continuous matrix phase, (ii) diffusion through the dispersed and matrix phases, (iii) diffusion through the interfacial region with properties different from the matrix phase, (iv) diffusion through cracks, pores, or small channels present in the composite due to imperfect adhesion or other structural defects.

The presence of impermeable fillers in composites increases the effective length that the diffusing molecules must travel and restricts the effective cross-sectional area for diffusion. It also can reduce the chain mobility of the polymer phase adjacent to the filler surface. For impermeable fillers such as glass ribbons, the diffusion coefficients of composites become very structure sensitive and fluxes may no longer be inversely proportional to the thickness of the composite film. Barrer et al.⁸ have shown that for diffusion through composites having impermeable fillers, a simplified equation for diffusion through the composite medium can be written as follows:

$$\frac{\partial c}{\partial t} = \phi_m K D_m \frac{\partial^2 C_m}{\partial x^2} = D_c \frac{\partial^2 c}{\partial x^2} \quad (5)$$

where D_m is the diffusivity of the matrix phase, ϕ_m is the volume fraction of the matrix material in the composite film, K is the structure factor for diffusion in the x -direction, and D_c is the diffusivity of the composite film. The structure factor K is a function which describes the reduction of the diffusion coefficient of the composite below the value D_m of the matrix material due to distortion of the path of molecular diffusion around the filler particles dispersed throughout the matrix phase. Equation (5) is applicable only if the composite film is macroscopically isotropic, or, failing that, if the diffusion occurs in only one of the principal directions of the anisotropic composite.

By definition, the concentration of a gas in a composite film is given by

$$C = C_m \phi_m + C_f \phi_f \quad (6)$$

assuming that there are no cracks or microvoids in the composite. When the filler is impermeable, $C_f = 0$, and eq. (6) is reduced to

$$C = C_m \phi_m \quad (7)$$

Substituting eq. (7) in eq. (5) yields

$$D_c = K D_m \quad (8)$$

Nielsen,¹ in his models for the permeability of filled polymer systems, defined

the reduction in molecular diffusion path caused by the structure factor K to be inversely proportional to the tortuosity ζ such that $K = 1/\zeta$. The tortuosity ζ is a function of the filler volume fraction, the geometry of the filler particles, and their orientation in the composite. For plate-like particles, e.g., glass ribbons, Nielsen developed the following equation for tortuosity ζ :

$$\zeta = 1 + (W/2t) \phi_f \quad (9)$$

where W is the width of the glass ribbon, t is the thickness of the ribbon, and ϕ_f is the filler volume fraction. However, Nielsen pointed out that the actual value of the structure factor would be less than that predicted by eq. (9) because of the variation of concentration of the diffusant perpendicular to the major flux direction (x) as it goes around the filler. Klute⁹ and Bixler et al.¹⁰ have proposed that the structure factor actually consists of two impedance factors and can be expressed as

$$K = 1/\zeta\beta \quad (10)$$

where ζ is the tortuosity factor accounting for the increase in diffusion path length caused by the presence of the filler particles and β is a chain immobilization factor which takes into account the reduction in matrix chain segment mobility due to proximity of the filler particles. The chain immobilization factor is greater than 1.0 if there is some interaction between filler and matrix material. If there is no immobilization effect, $\beta = 1$. Mehta et al.¹¹ applied Nielsen's model for composite permeability to interpret the permeability of nitrogen and oxygen gases in anisotropic composite films made by reinforcing cellulose acetate with glass ribbons. They also found that reduction in composite permeability was more than warranted by tortuosity alone. They explained this further reduction in terms of the size of the influenced matrix phase portion of the unit cell of the composite film.

In this paper, we discuss the application of the above models, eqs. (1)–(10), to explain the diffusion and sorption of water in reinforced anisotropic composites.

EXPERIMENTAL

Materials

For sorption experiments, both unfilled and filled films were prepared by compression molding between two smooth, flat plates. Cast cellulose acetate sheets used for the matrix phase of the composite films were made by XCEL Corporation. The cellulose acetate had 2.5 degrees of substitution and contained about 20%–30% diethyl phthalate plasticizer. The unfilled cellulose acetate films were prepared by laminating several unfilled, cast cellulose acetate sheets and then compression molding the laminate. Making glass ribbon–cellulose acetate composite film is more involved and has been discussed in detail elsewhere.^{12,13} 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

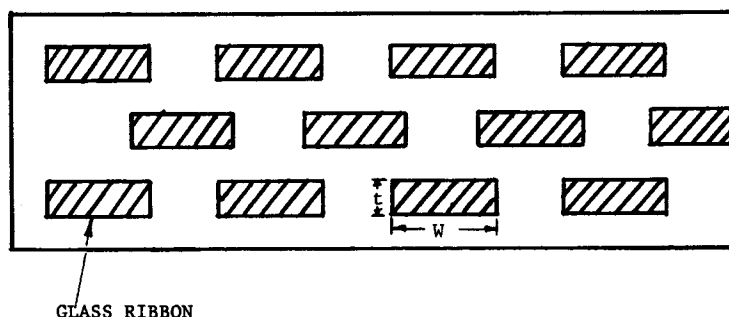


Fig. 1. Distribution of filler in glass ribbon-reinforced cellulose acetate film.

of glass ribbons, the successive glass layers are arranged so that ribbons in any two consecutive layers are staggered causing the spaces between the ribbons to be always above and below the ribbons in adjacent layers (see Fig. 1). The last step consists of compression molding.

Both unfilled and filled films were made by compression molding for about 15 min 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 min, 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 glass ribbons are totally embedded, while it at the same time prevents excess flashing and the development of high molded-in stresses. The films were then placed in a desiccator for several days to keep them dry. The details of the films used for sorption experiment are listed in Table I.

Apparatus and Procedure

The experimental setup used for sorption for this investigation is similar in principle to that used by Prager and Long.¹⁴ The apparatus is schematically

TABLE I
Description of Films^a

Film description		$\langle l \rangle$, mil	ϕ_f , %	No. of filler layers in film
I.D.	Type			
L	Biaxially oriented cast cellulose acetate	20	0	—
M	press molded	43	0	—
N	GRCA	45.4	34.6	4
O	GRCA	21.2	21	1
P	GRCA	18.0	9.15	1
Q	GRCA	18.25	4.70	1

^a All composite films were made by using glass ribbon 125 mil in width and 5.2 mil thick. GRCA = Glass ribbon/cellulose acetate.

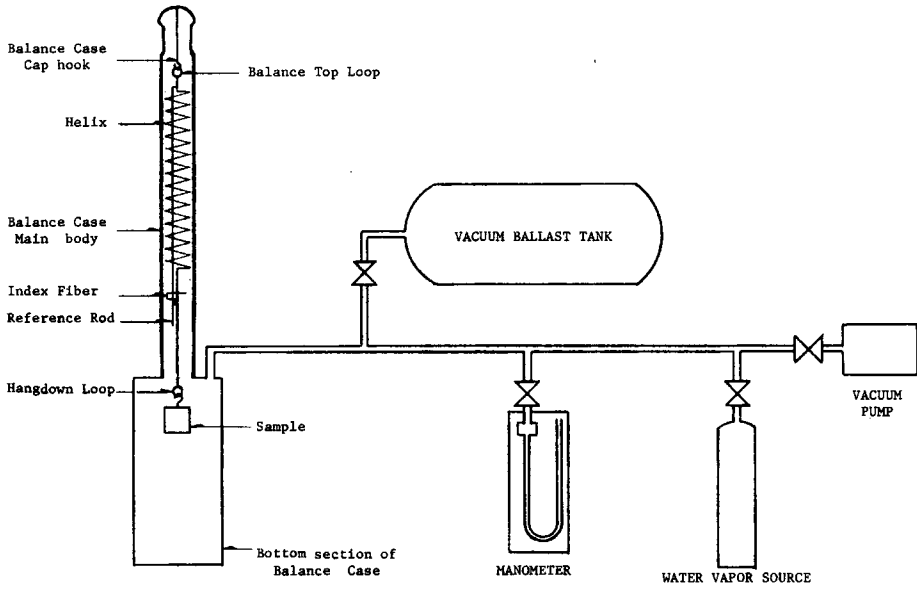


Fig. 2. Sorption cell schematic.

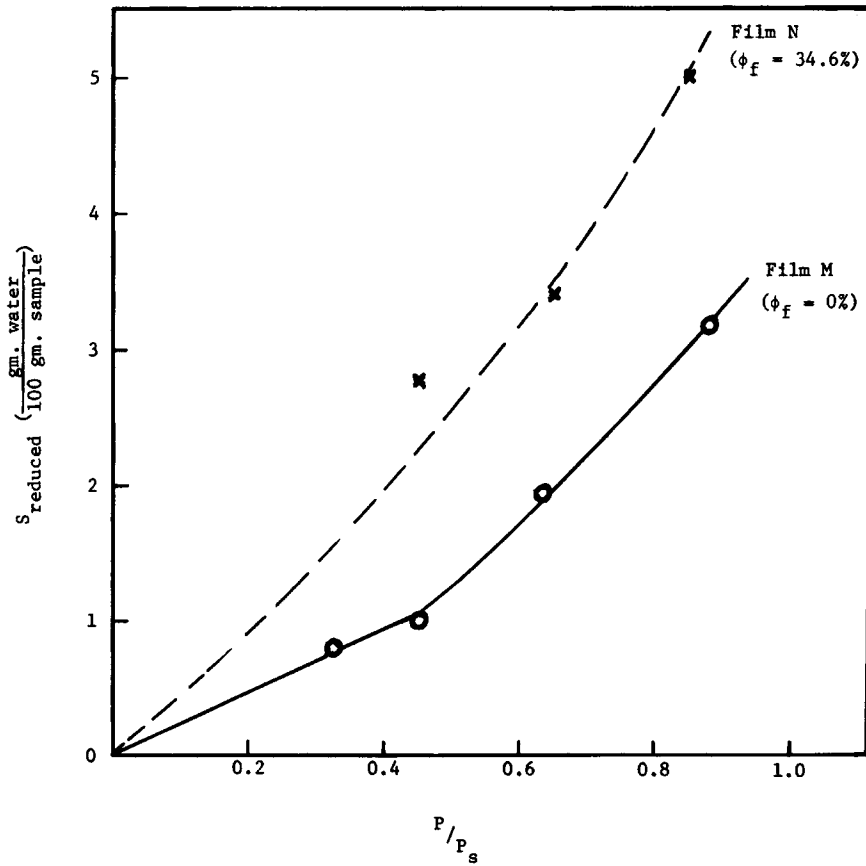


Fig. 3. Equilibrium sorption isotherms at 39.8°C.

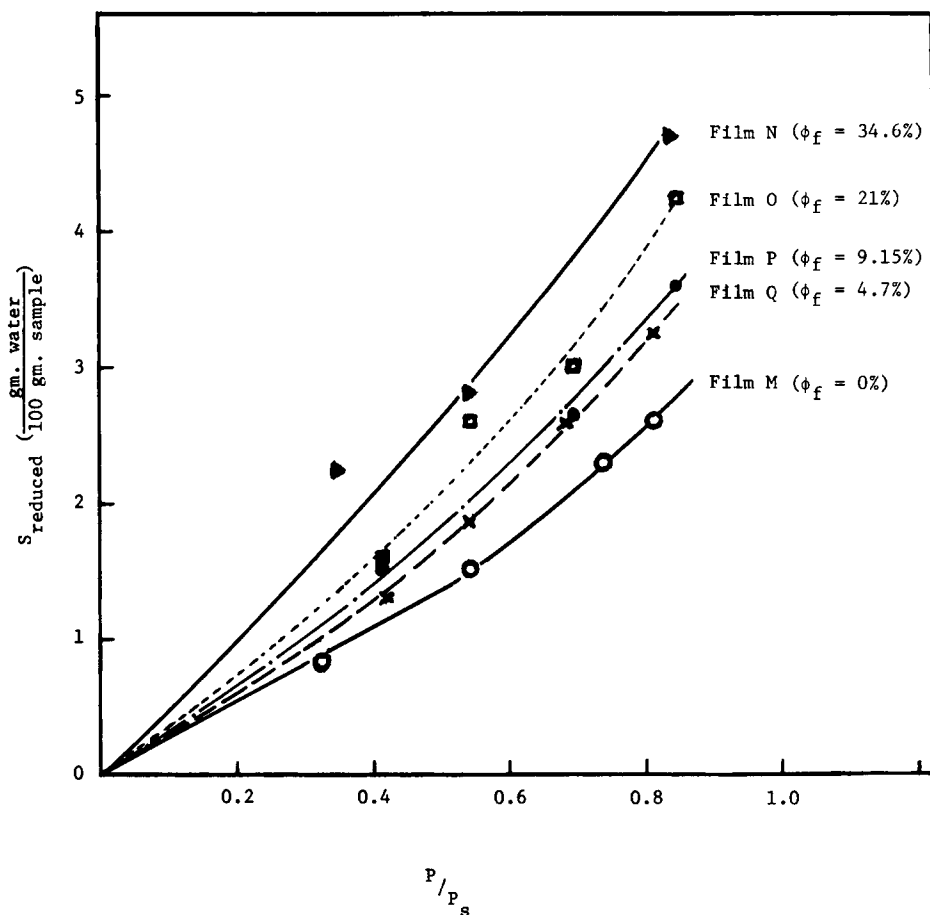


Fig. 4. Equilibrium sorption isotherms at 49.8°C.

shown in Figure 2. In this setup, a specimen of known shape and size is suspended from a sensitive quartz helix spring in an evacuated chamber to keep the specimen in an atmosphere of constant water vapor pressure. The increase in weight of the specimen due to absorption of vapor is then measured as a function of time by observing the extension of the spring using a cathetometer. The quartz spring was obtained from Misco Scientific Co., Berkeley, California. The spring has high tensile strength, negligible coefficient of expansion at all temperatures, and is noncorrosive and practically inert. The cathetometer (obtained from Gaetner Scientific Corporation, Chicago, Illinois) can measure an extension of the spring up to 10 cm and read to within 10^{-4} cm.

In Figure 2, the smaller tank contains liquid water which acts as a supply source for water vapor. The vapor pressure of water is adjusted by control of the temperature of the liquid water, and the relative humidity of the water vapor in the weighing chamber containing the quartz spring and the suspended sample is controlled by a regulating needle valve provided at the outlet of the smaller tank. The bigger tank connected to the weighing chamber acts as a ballast tank and helps keep the water vapor pressure in the chamber constant with a minimum of fluctuation. A vacuum pump is used as the vacuum source for the sys-

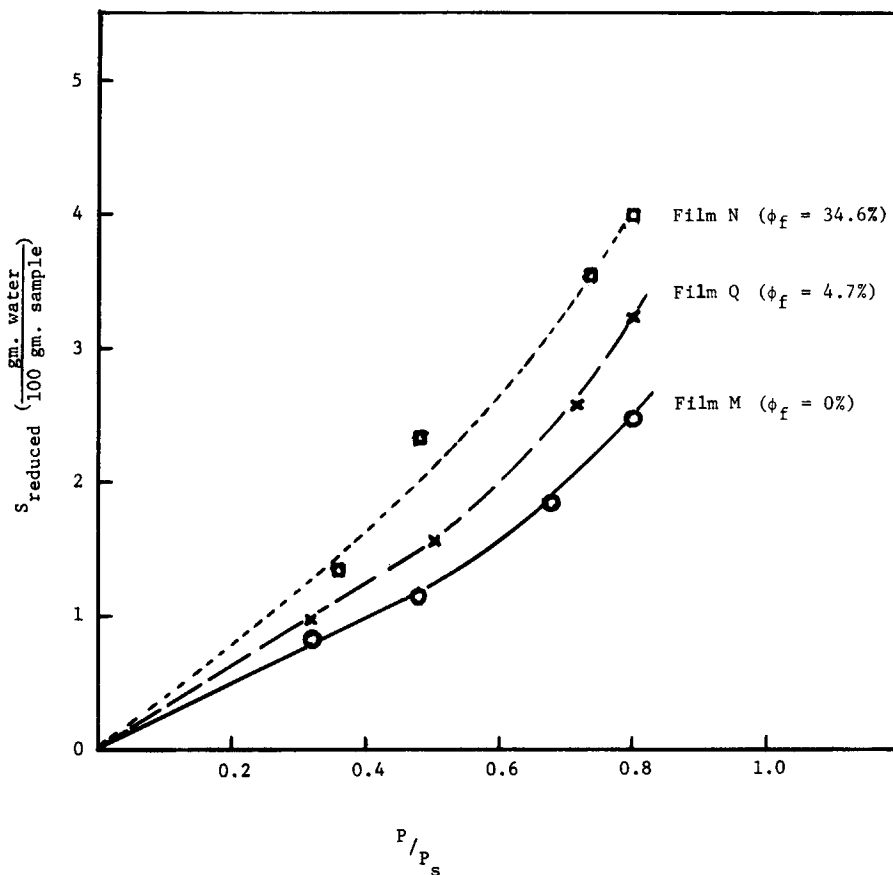


Fig. 5. Equilibrium sorption isotherms at 56.3°C.

tem, and a mercury manometer is used to measure the pressure of the system. The whole sorption system is enclosed in a constant-temperature air bath.

RESULTS AND DISCUSSION

Water sorption data for both unfilled and filled cellulose acetate films were obtained at several temperatures ranging from 39.8 to 64.8 °C and for various relative pressures. The experimental equilibrium sorption isotherms for both unfilled and filled cellulose acetate films are shown in Figures 3–6. While the water uptake by the films is fairly linear at low relative pressures, it increases sharply at high relative pressures. This behavior is very typical of sorption of water in cellulose derivatives and can be interpreted as initial sorption on specific sites followed by some kind of mixing process, e.g., clustering of water molecules in the matrix polymer, possibly in preexisting cavities,¹⁵ and in the case of glass ribbon-reinforced composite films by clustering of water on the surface of hydrophilic glass ribbons also.

The solubility data are sensitive to the mode of preparation of the film. The equilibrium sorption coefficient in the compression-molded film (unfilled) was found to be about 40% lower than the solubility coefficient for a biaxially oriented

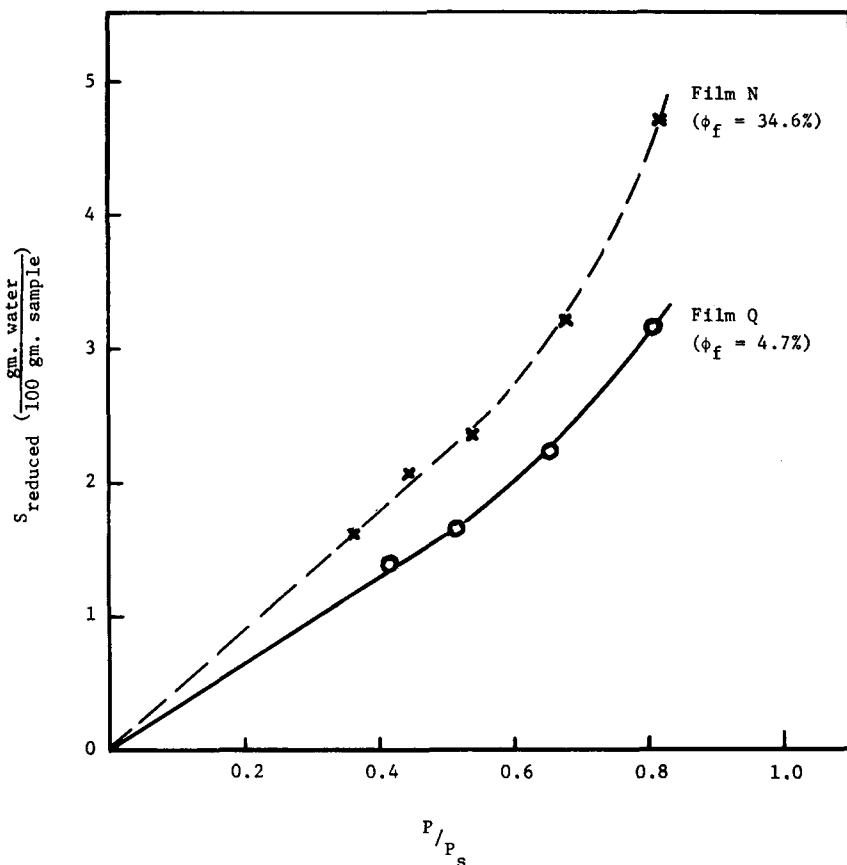


Fig. 6. Equilibrium sorption isotherms at 64.3°C.

cast film. Compression molding the cast film can result in change of its density, orientation, and molecular structure which can affect the solubility coefficient.

To make a reasonable evaluation of the effect of the presence of glass ribbon

TABLE II
Solubility Coefficients for GRCA Films

Film	39.8°C			49.8°C			56.3°C			64.8°C		
	P/P_s	S_{exp}	S_{red}	P/P_s	S_{exp}	S_{red}	P/P_s	S_{exp}	S_{red}	P/P_s	S_{exp}	S_{red}
N	0.454	1.29	2.79	0.348	1.04	2.25	0.360	0.62	1.34	0.364	0.75	1.62
	0.654	1.57	3.40	0.543	1.29	2.79	0.480	1.08	2.34	0.446	0.96	2.08
	0.854	2.31	5.00	0.837	2.18	4.72	0.736	1.64	3.55	0.540	1.09	2.36
							0.800	1.84	3.98	0.679	1.49	3.23
O				0.413	1.00	1.59				0.818	2.18	4.72
				0.543	1.64	2.60						
				0.696	1.89	3.00						
				0.848	2.68	4.24						
P				0.413	1.24	1.55						
				0.696	2.11	2.65						
				0.848	2.87	3.60						
Q				0.424	1.17	1.30	0.32	0.88	0.985	0.417	1.26	1.40
				0.543	1.68	1.86	0.504	1.42	1.57	0.513	1.50	1.66
				0.685	2.34	2.59	0.720	2.33	2.58	0.652	2.03	2.25
				0.815	2.93	3.25	0.800	3.01	3.24	0.807	2.86	3.17

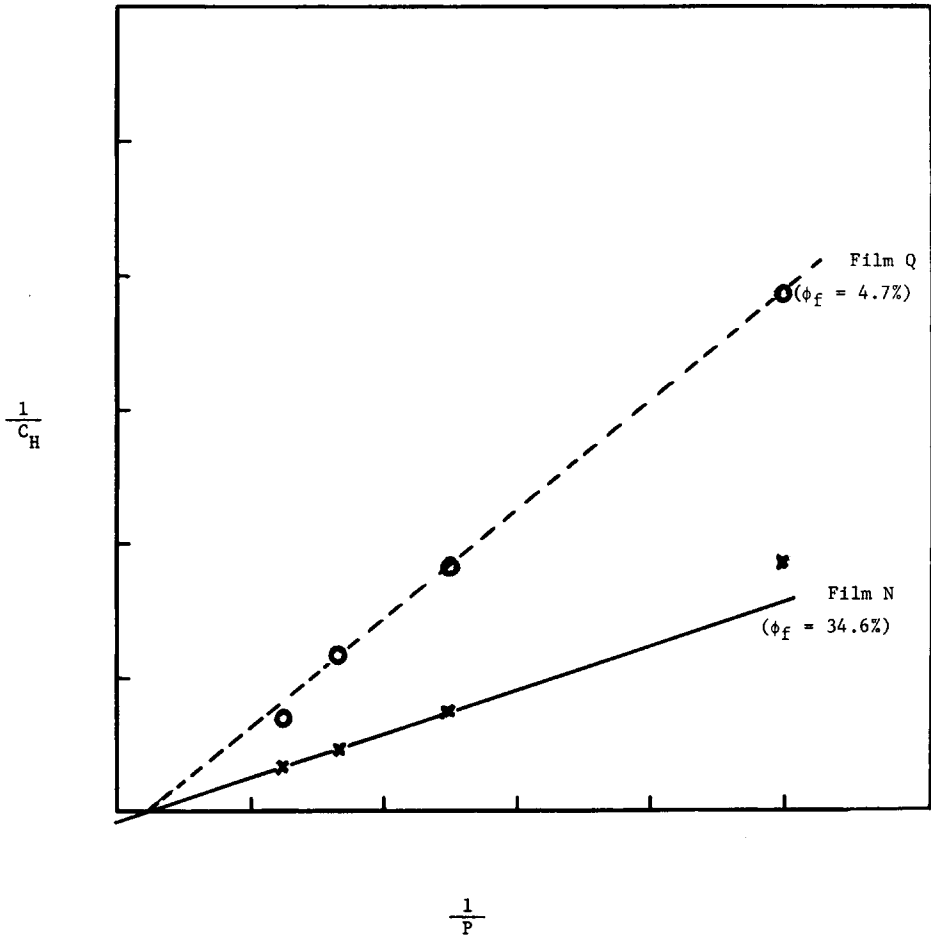


Fig. 7. Langmuir plots for water sorption by hole filling in glass ribbon-reinforced cellulose acetate films at 56.3°C.

in the matrix phase on the overall composite solubility, the experimental solubilities (S_{exp}) were reduced to equilibrium solubility coefficients (S_{red}) based on the weight of the matrix material present in the composite films such that

$$S_{\text{red}} = \frac{S_{\text{exp}} \times W_c}{W_c - W_f} \quad (11)$$

where W_c and W_f are the weights of composite film and the filler in the composite film, respectively.

The values of solubility coefficients for glass ribbon-cellulose acetate composites show a consistent increase with filler volume fraction. This could possibly happen for two reasons. First, the glass is very hydrophilic and will have a tendency to absorb water on its surface. The other reason is that during compression molding the solubility characteristics of the film change. The presence of glass ribbon can constrain the free and uniform flow of cellulose acetate in all directions during molding. This could have a twofold effect. Because of the nonuniform flow, wetting may not be complete, and voids can result along the

TABLE III
 Sorption and Diffusion Data

Film	Temp., °C	Run no.	p , mm Hg	p/p_s^a	S ,	$D_s \times 10^7$,	$D_d \times 10^7$,	$\langle D \rangle =$	
					$\frac{\text{g water vap.}}{100 \text{ g sample}}$			$\frac{2}{D_s + D_d}$	
						cm^2/sec	cm^2/sec	$\times 10^7$,	
								cm^2/sec	
L	39.8	S-1	32	0.582	2.89	1.19	1.28	1.24	
M	39.8	S-2	18	0.327	0.80	1.45	0.43	0.94	
		S-3	25	0.454	0.99	1.87	0.52	1.19	
	49.8	S-4	35	0.636	1.94	0.98	0.87	0.93	
		S-5	48.5	0.882	3.36	0.89	1.18	1.04	
		S-6	30	0.326	0.84	2.22	1.96	2.09	
		S-7	50	0.543	1.52	1.88	1.85	1.86	
		S-8	68	0.739	2.30	1.88	1.72	1.80	
		S-9	75	0.815	2.62	2.00	1.92	1.96	
		S-10	40	0.320	0.93	3.18	3.91	3.05	
	56.3	S-11	60	0.480	1.15	3.29	2.55	2.92	
		S-12	85	0.680	1.85	3.29	2.55	2.92	
		S-13	100	0.800	2.48	3.18	2.86	3.02	
N	39.8	S-19	25	0.454	1.29	0.86	1.34	1.10	
		S-20	36	0.654	1.57	1.49	2.20	1.85	
	49.8	S-21	47	0.854	2.31	1.33	1.31	1.32	
		S-22	32	0.348	1.04	0.89	2.51	1.70	
		S-23	50	0.543	1.29	2.15	1.51	1.83	
		S-24	77	0.837	2.18	2.62	2.41	2.51	
		S-25	45	0.360	0.62	3.83	2.36	3.10	
		S-26	61	0.488	1.08	3.10	4.00	3.55	
		S-27	92	0.736	1.64	3.67	5.35	4.51	
N	64.8	S-29	68	0.364	0.75	0.28	1.83	3.06	
		S-30	83.5	0.446	0.96	3.91	2.92	3.14	
		S-31	101	0.540	1.09	3.91	1.53	2.72	
		S-32	127	0.679	1.49	4.21	5.34	4.78	
		S-33	153	0.818	2.18	3.00	4.96	3.98	
O	49.8	S-34	38	0.413	1.00	2.52	1.85	2.18	
		S-35	50	0.543	1.64	1.52	1.83	1.67	
		S-36	64	0.696	1.89	2.34	1.50	1.97	
		S-37	78	0.848	2.68	1.80	3.30	2.54	
P	49.8	S-38	38	0.413	1.24	1.50	1.45	1.48	
		S-40	64	0.696	2.11	1.75	2.09	1.92	
		S-41	78	0.848	2.87	1.67	0.96	1.31	
Q	49.8	S-42	39	0.424	1.17	1.98	1.78	1.88	
		S-43	50	0.543	1.68	1.96	1.45	1.70	
		S-44	63	0.685	2.34	1.51	1.73	1.61	
		S-45	75	0.815	2.93	1.73	1.83	1.78	
		S-46	40	0.32	0.88	2.75	2.00	2.38	
	56.3	S-47	63	0.504	1.42	2.26	1.87	2.06	
		S-48	90	0.720	2.33	2.35	2.39	2.37	
		S-49	100	0.800	3.01	2.41	2.19	2.30	
		64.8	S-50	78	0.417	1.26	2.95	2.33	2.64
			S-51	96	0.513	1.50	3.45	3.20	3.33
			S-52	122	0.652	2.03	3.50	3.39	3.45
S-53	151	0.087	2.86	2.89	2.85	2.87			

^a p_s = Saturation vapor pressure at the temperature of the sorption-desorption experiment.

interface which will provide additional sites for absorption of water. Also due to nonuniform flow, the overall characteristics of the matrix phase may be somewhere between those of cast cellulose acetate and the unfilled compression-molded cellulose acetate, but possibly much closer to the latter. Since cast cellulose acetate has a higher solubility, it might contribute to the higher solubility of composites which were evaluated on the basis that the matrix phase behaves only like compression-molded cellulose acetate. The thickness of the water layer adsorbed on the glass surface, calculated on the assumption that adsorption on the glass surface is the only source of water uptake beside the matrix phase, was found to range from 200 to 600 Å for different composite films. A realistic value for the thickness of the water layer could be of the order of 10–20

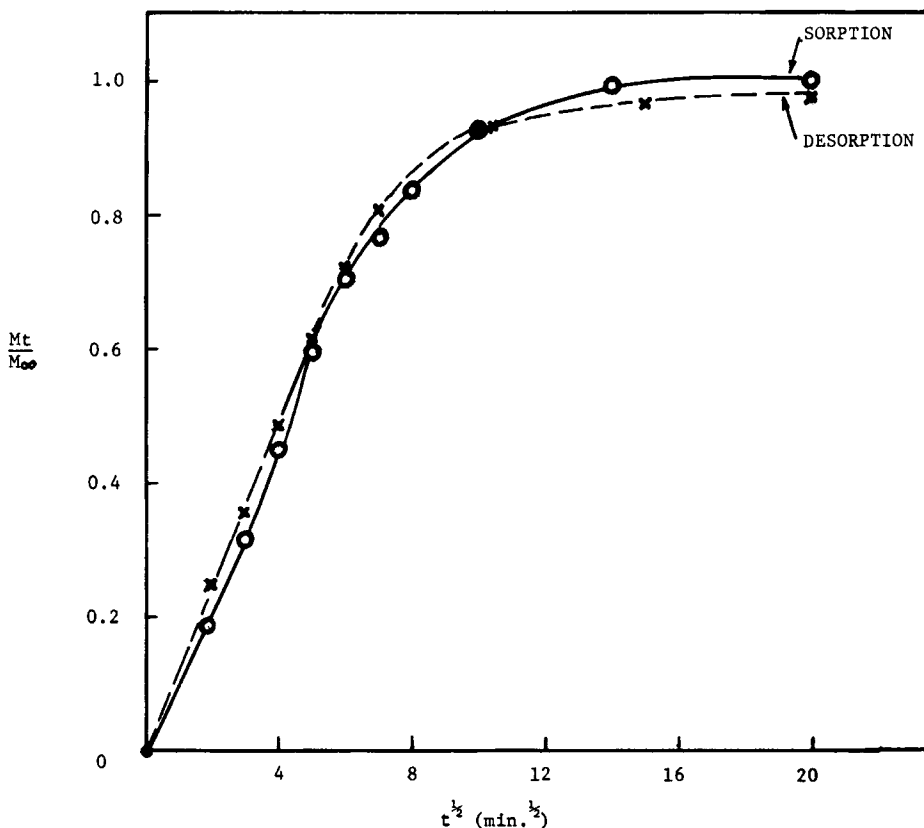


Fig. 8. Sorption-desorption curves for biaxially oriented cast film (20 mil thick; weight of sample 7.433) at 39.8°C and 32 mm Hg of water vapor pressure.

molecular layers of water, which would imply a thickness of the order of approximately 50 Å. In view of the high value of the calculated thickness of the water layer, it seems reasonable to assume that there are some water-absorbing voids present in the composite system, and clustering seems to be a real phenomenon in composite films.

The clustering of water molecules in the composite films can result if there are microcavities in the matrix phase or if imperfect adhesion between the matrix and filler phase exists along the interface between the glass ribbon and cellulose acetate. Mehta et al.⁹ used a similar composite system to measure diffusion of permeant gases and observed good adhesion between the glass ribbon and cellulose acetate. However, with water as the diffusant, the cellulose acetate matrix phase has a tendency to swell and this swelling action results in internal compression-extension stresses.¹⁶ These stresses can cause craze cracking, and water can enter these cracks from which attack then occurs on the glass ribbon bond. A quantitative analysis of the clustering can be made using eq. (4) and Figures 3-6. The amount of water present as clusters can be determined by subtracting the solubility of the unfilled matrix material (film M) from the reduced solubility of the composite film (films N, O, P and Q) at any given temperature and relative pressure (Figs. 3-6).

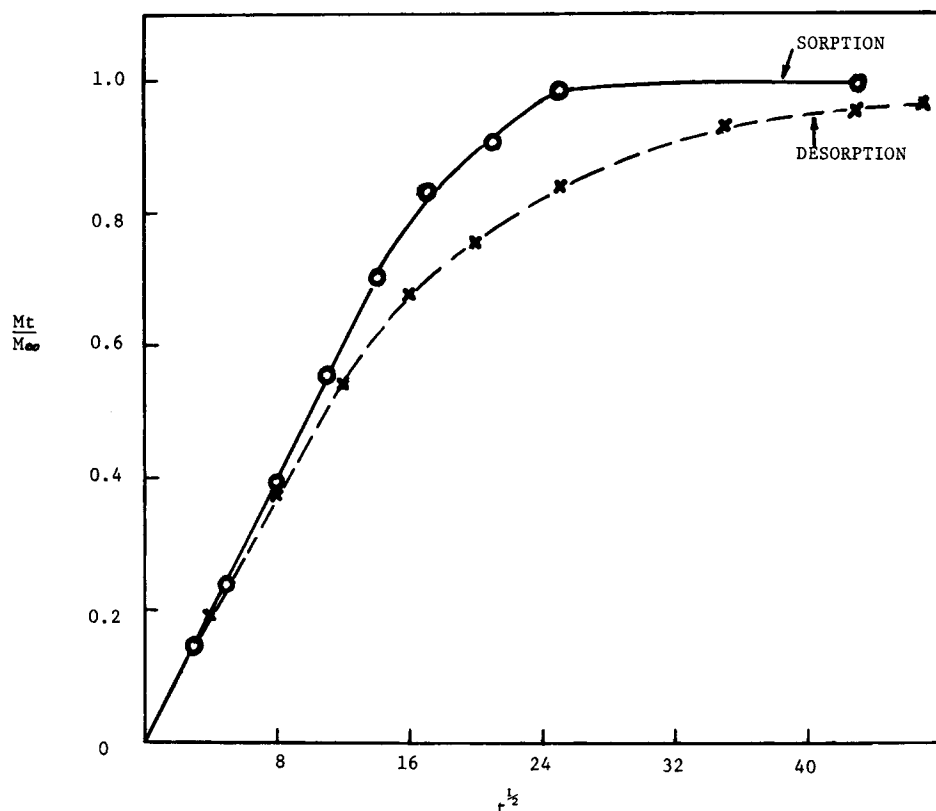


Fig. 9. Sorption-desorption curves for compression-molded film (43 mil thick, weight of sample 8.327 g) at 39.8°C and 35 mm Hg of water vapor pressure.

Such an analysis was done for films N and Q at 56.3°C (Fig. 5), and these data are plotted in Figure 7 according to eq. (4) wherein

$$C_H = \frac{C_h'bp}{1 + bp} \quad (12)$$

or

$$\frac{1}{C_H} = \frac{1}{C_h'} + \frac{1}{c_h'b} \cdot \frac{1}{P} \quad (13)$$

The plots of $1/C_H$ versus $1/P$ are straight lines, and the clustering of water in composites can be approximated by the nonlinear Langmuir expression.

The sorption data for both unfilled as well as filled films were obtained by observing the uptake M_t of the diffusant in the film in time t . The uptake data are plotted in terms of reduced uptake M_t/M_∞ versus $(t)^{1/2}$, where M_∞ is the equilibrium sorption obtained theoretically after infinite time. The value of D can be deduced from an observation of the initial gradient of the graph of M_t/M_∞ as a function of $(t/1^2)^{1/2}$. Similarly, with suitable interpretation of M_t and M_∞ , desorption data can also be used to determine the diffusion coefficient. Since both sorption and desorption data were obtained for a concentration in-

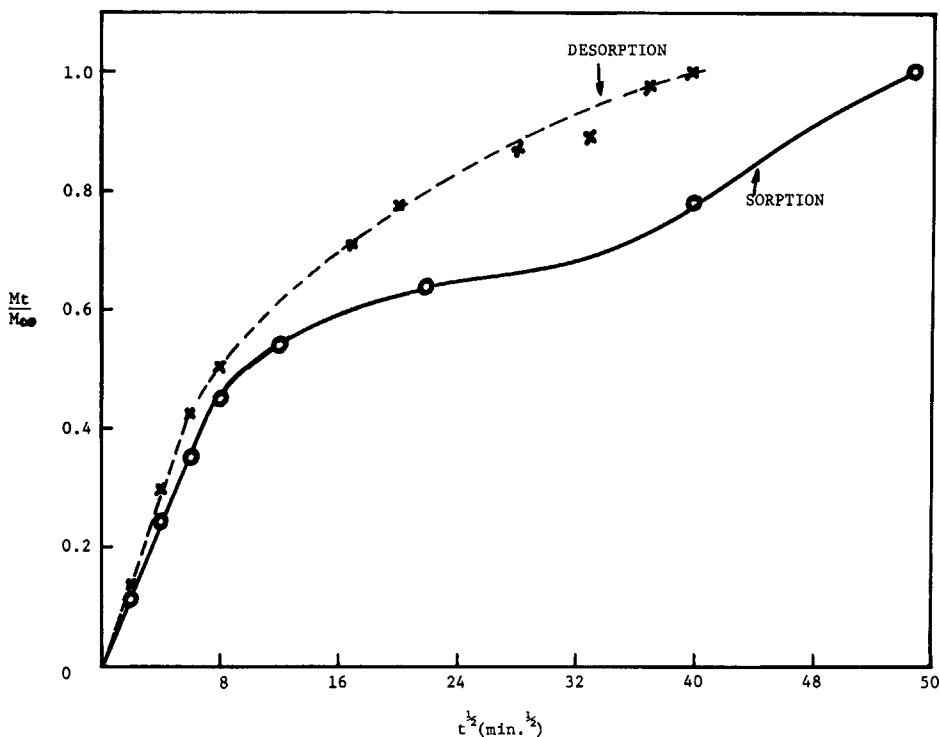


Fig. 10. Sorption-desorption curves for glass ribbon-reinforced plastic film (film N, weight of sample 5 g) at 39.8°C and 36 mm Hg of water vapor pressure.

terval of $0 \rightarrow C_{\text{final}}$, the integral diffusion coefficients at the concentration C_f were calculated as follows:

$$D = \frac{1}{C_f} \int_0^{C_f} D dc = \frac{\pi}{32} (K_s^2 + K_d^2) \quad (14)$$

where K_s and K_d are initial slopes for sorption and desorption, respectively. The diffusion coefficients thus calculated are shown in Table III. Typical sorption-desorption kinetics for the biaxially oriented cast film (film L), compression-molded film (film M), and glass ribbon-reinforced film (film N) are shown in Figures 8-10. While the sorption-desorption curves for the compression-molded film indicated Fickian behavior, the sorption-desorption curves for films L and N showed anomalous behavior. The anomalies are of two types: (a) the sorption curves assume a sigmoidal shape, and (b) desorption becomes faster than sorption. Blackladder et al.¹⁷ explained these anomalies by invoking the effect of internal stress in a film approaching equilibrium from an initially solvent-free state. Sorption of water into initially dry biaxially oriented film and glass-reinforced film will result in an attempt by the outer regions to swell. But the inner matrix phase, especially the portion which is relatively immobilized by adhesion to the glass ribbon, will tend to restrain the increase in volume. This can have a twofold effect. First, swelling of the outer regions of the specimen will cause the core to be stretched. Second, the surface concentration will not immediately reach the true equilibrium value appropriate to unconstrained polymer.

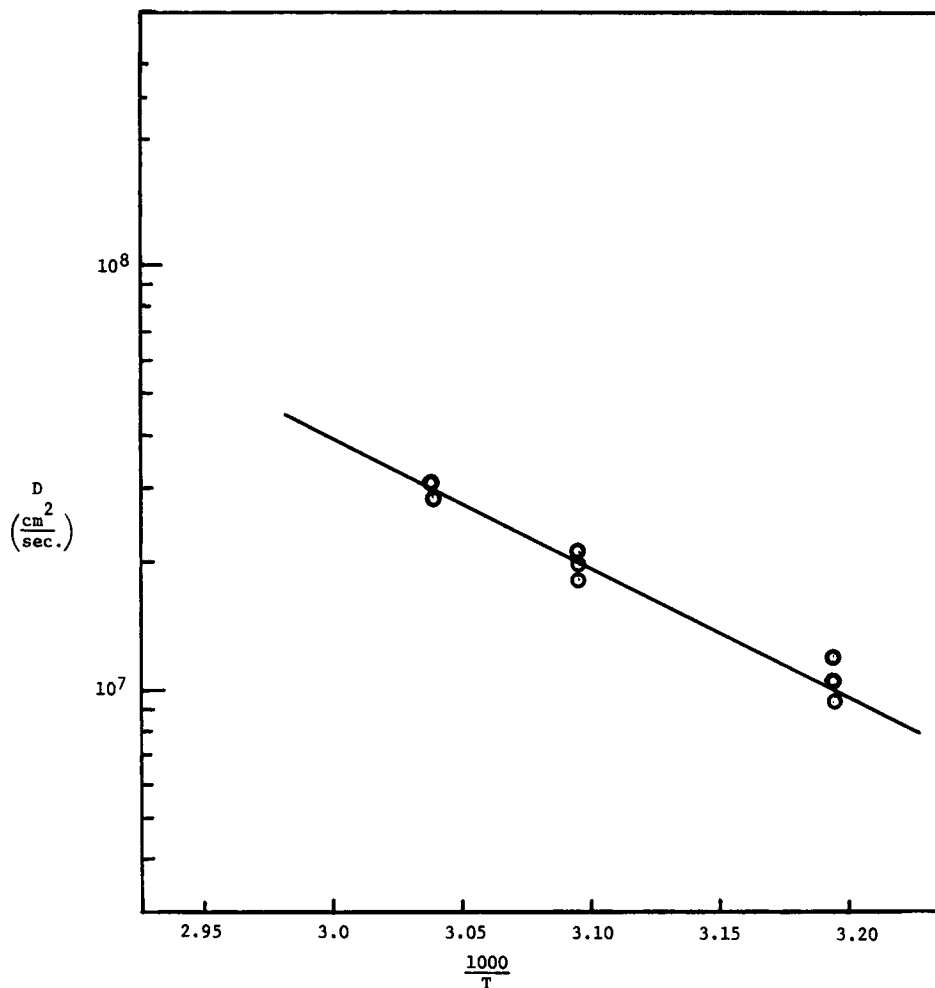


Fig. 11. Water diffusivity in unfilled cellulose acetate.

In the case of compression-molded film, most of the built-in stresses of the cast film were released during molding, and the sorption-desorption kinetics were subject to relatively less internal stress effects. Crank,¹⁴ from his studies of anomalous diffusion, concluded that compression-extension effects caused by internal stresses lead to sigmoidal curves and this effect manifests itself more in the sorption curve than the desorption curve.

The diffusion data for unfilled cellulose acetate film plotted as $\ln D$ versus $1/T$ (Fig. 11) shows a straight-line relationship which is indicative of the exponential activated process described by Fick's law of diffusion. The diffusion data for glass ribbon-reinforced films were very scattered (Table III) and presented irregular trends. Whereas, according to eqs. (8)–(10), the diffusivities for filled films should be far lower than the corresponding diffusivities for the unfilled films due to tortuosity effects and the immobilization effects, they were actually found either equal to or greater than the unfilled systems. Because of significant internal stress effects, sorption-desorption data for filled films become difficult to use for determining diffusion coefficients. However, the initial portions of

the M_t/M_∞ versus $t^{1/2}$ curves for most filled films were found to be approximately straight lines, and their slopes could be used to predict diffusion coefficients. The reason for initial straight-line behavior probably is that all composite films had cellulose acetate on both sides of the film exposed to the water vapor, and Fickian behavior is expected for unfilled material. However, as the process of sorption proceeds, the diffusant molecules meet regions close to glass ribbons where polymer segments rearrange themselves more slowly, thus making changes in the time dependence of the diffusion process. This complicates any further analysis of the data.

CONCLUSIONS

1. While the equilibrium solubility coefficients of filled systems should decrease in proportion to the glass ribbon content in view of the impermeable nature of glass ribbons, they were actually found to be higher than those of unfilled cellulose acetate, and these solubility coefficients were found to increase with increase in filler volume fraction. Three explanations are offered for this behavior: (a) The adhesion between glass ribbon and cellulose acetate matrix can fail, resulting in the adsorption of water on hydrophilic glass ribbons. (b) During compression molding of glass ribbon-cellulose acetate film, the solubility characteristics of the cellulose acetate matrix change. (c) The presence of glass ribbon can constrain the free and uniform flow of cellulose acetate in all directions during molding; this may result in incomplete wetting between the filler and matrix phase and can cause voids along the interface, which provide additional sites for absorption of water.

2. The integral diffusion coefficients were calculated from an observation of the initial gradient of the plot of reduced uptake of water by the sample, (M_t/M_∞) , as a function of $(t/l^2)^{1/2}$ both for unfilled and filled systems. Diffusion of water through unfilled cellulose acetate was found to be a simple Fickian activated process and showed very little concentration dependence. The sorption-desorption kinetics of composite films exhibited non-Fickian behavior with two distinct anomalies: (a) the sorption curves assume a sigmoidal shape, and (b) desorption becomes faster than sorption.

The anomalies are typical of internal stress phenomena which make prediction of diffusivities from sorption kinetics difficult.

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