Models for the Permeability of Filled Polymer Systems

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PLEASE SCROLL DOWN FOR ARTICLE

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Summary

A theory has been developed which predicts the minimum permeability that can be expected for a polymer filled with platelike particles. Models are also developed for the permeability of liquids through filled polymers when the liquid adsorbs or collects at the filler-polymer interface. Some of the cases discussed include different types of dispersions, orientation of filler particles, and the effects of filler aggregation. Permeability, especially of liquids, is extremely complex, and many different types of behavior can be expected.

INTRODUCTION

The permeability of gases and liquids through polymers filled with inorganic powders is an extremely complex phenomenon for which no theory exists. The possibility of developing a quantitative theory for the permeability of such systems seems very remote; there are too many factors that have to be considered. However, some simple models have been developed which show the trends and the limits to be expected for some of the effects and at the same time are a great help in interpreting the observed experimental data.

One model has been worked out that defines the maximum decrease in permeability that can be expected for the addition of a filler to a polymer. A second type of model indicates the type of changes in liquid permeability that can be expected when the liquid is partially soluble in the polymer and when the concentration of liquid at the filler-polymer interface is different from the concentration in the polymer.

MINIMUM PERMEABILITY OF FILLED POLYMERS

If the filler particles are impenetrable to a diffusing gas or liquid molecule, then the diffusing molecules must go around the filler particles. This leads to a very tortuous path for molecules traveling through a filled polymer. In addition to the tortuosity factor, permeability is cut down because not all of a given cross section of material is pure polymer. Thus, as a first approximation, an equation of the following form is often used (*1–5*):

$$P_F/P_u \doteq \phi_P/\tau \tag{1}$$

where P_F and P_u are the permeabilities of the filled and unfilled polymer, ϕ_P is the volume fraction of the polymer, and τ is the tortuosity factor. The tortuosity factor is defined by

$$\tau = \frac{\text{distance a molecule must travel to get through film}}{\text{thickness of film}}$$

In this equation it is assumed that the fractional area occupied by polymer in any cross section is equal to the volume fraction of the polymer. Although Eq. (1) has been used in the past (*1–5*), it cannot be exact, since it does not take into account such factors as horizontal variations in concentration of the permeating material as it goes around filler particles, as illustrated in Fig. 1. Because such factors are neglected, the actual permeability through filled systems is expected to be less than that predicted by Eq. (1).

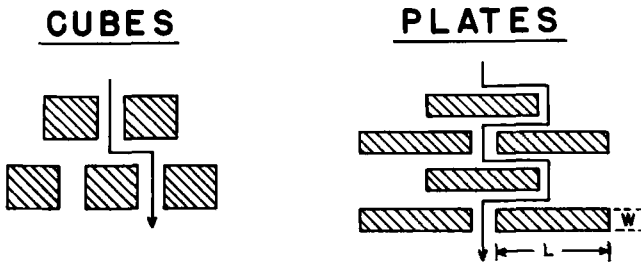If it is assumed that the filler particles are circular or rectangular

FIG. 1. Model for the path of a diffusing molecule through a polymer filled with circular or square plates.

plates and that they are uniformly and completely dispersed in the polymer and that the plates are oriented parallel to the polymer film surface, then Fig. 1 illustrates the general type of path that molecules must take to get through the polymer. These assumptions are the ones that maximize the distance a diffusing molecule must travel; that is, these assumptions give the maximum possible tortuosity factor. It can be shown by a simple averaging process with the help of Fig. 1 that, in general,

$$\tau \doteq 1 + (L/2W)\phi_F \qquad (2)$$

where L is the length of a face of a filler particle, W the thickness of the filler plates, and ϕ_F the volume fraction of filler. For the case of cubical filler particles, Eq. (2) gives exactly the same tortuosity factor that has been derived in the literature for spherical particles (5,6). This is about what one would expect. Combining Eqs. (1) and (2), the permeability equation becomes

$$\frac{P_F}{P_u} \doteq \frac{\phi_P}{1 + (L/2W)\phi_F} \qquad (3)$$

Some typical values calculated from this equation are given in Fig. 2. These curves predict that particles which are approximately cubical in shape are quite inefficient in decreasing permeability. However, thin plates with a large L/W ratio can very dramatically decrease permeability if the particles can be oriented so that their flat surfaces are parallel to the surfaces of the film. In practical cases where films are formed by melt extrusion and sometimes later given a biaxial stretching, the filler particles should be more or less oriented in this most desirable way. In general, however, incomplete filler dispersion, voids, and only partial orientation of the particles should result in higher permeabilities than this simple theory predicts.

If the plates are oriented perpendicular to the surface rather than parallel to it, the tortuosity factor given by Eq. (2) should be replaced by

$$\tau = 1 + (W/2L)\phi_F$$

and Eq. (3) would be modified accordingly.
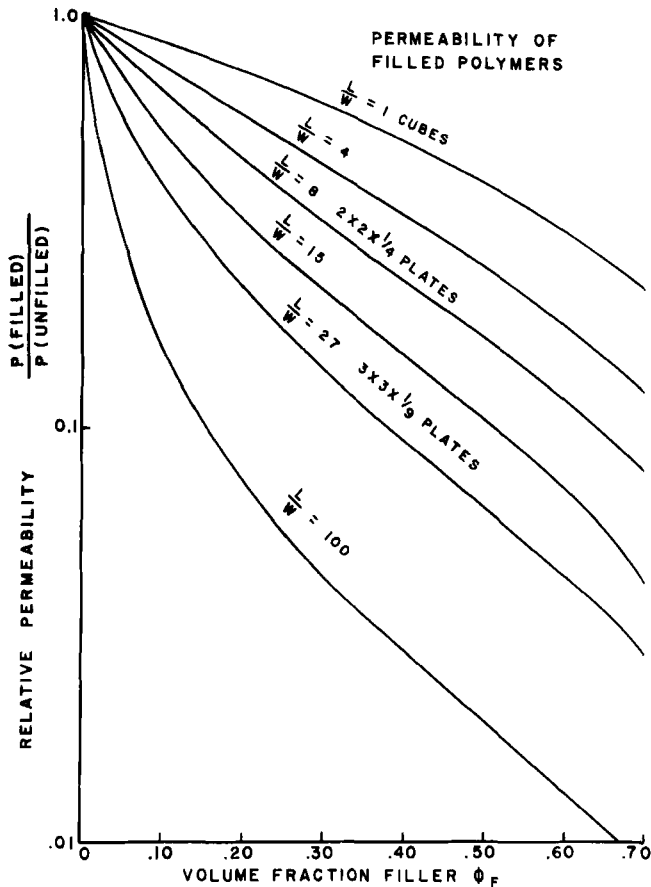
FIG. 2. Minimum permeability of gases through a polymer filled with plates of different L/W ratio oriented parallel to the surface of the film.

PERMEABILITY OF FILLED POLYMERS TO LIQUIDS

Permeability of liquids through filled polymers is much more complex than gas permeability. As is conventional in the plastics industry, liquid permeability is defined as the quantity of liquid passing through a membrane of unit area and thickness in unit time when one side of the membrane is in contact with the liquid and the other side of the membrane is swept by a flow of air or inert gas so as to keep the concentration of liquid vapor essentially at zero. Liquids often have appreciable solubility in the polymer, so that

the polymer becomes swollen. In addition, a liquid may interfere with the polymer-filler interface, and the solubility or adsorption of liquid at the interface may be different from the solubility in the bulk polymer. This may be especially true if the filler has been given some treatment where a substance (different from the polymer) has been adsorbed on the surface.

It will be assumed in the development of some simple models that around each filler particle there is an interfacial layer which has properties different from the bulk polymer saturated with liquid. There is experimental evidence that in filled systems there can be an interfacial layer with properties different from the bulk polymer (7–9). This assumption leads to a model such as is shown in Fig. 3.
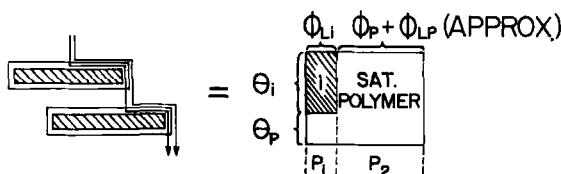

FIG. 3. Model for the permeability of a liquid through a filled polymer.

A diffusing molecule can get through the filled system by going only through the polymer, or it can diffuse along a path which consists of both polymer and the interface. Thus the total permeability is divided into two parts:

$$P_{FL} \doteq P_1 \left(\frac{\phi_{Li}}{\tau^*} \right) + P_2 \left(\frac{\phi_P + \phi_{LP}}{\tau} \right) \tag{4}$$

P_{FL}, P_1, and P_2 are the permeabilities of liquid through: (1) the filled polymer, (2) the interfacial part, and (3) the saturated bulk polymer. P_2 is equal to the permeability of the liquid through the unfilled polymer P_{PL} unless the filler induces changes in the polymer. τ^* is a tortuosity factor for the interfacial part; it may or may not be the same as τ. ϕ_{Li} is the volume fraction of liquid collected in the interfacial region while ϕ_{LP} is the volume fraction of liquid dissolved in the polymer. For the whole system

$$\phi_P + \phi_F + \phi_{Li} + \phi_{LP} = 1 \tag{5}$$

These volume fractions are for the swollen system, not the original dry values. In practice ϕ_{Li} in the model may be larger than the

value of ϕ_{Li} calculated from experimental data on the excess solu-
bility of the permeating liquid in a filled system. One of the reasons
for this is that most diffusing molecules will at one time or another
enter the interfacial layer for a portion of their journey through the
film or sheet, even though for any given cross section the area of
the interface is small compared to the total area of the section. In
general, ϕ_{Li} should be directly proportional to the surface area of
the filler, which in turn for a given particle size is proportional to
the volume fraction of filler.

The permeability P_1 through the interfacial region will be calcu-
lated first. In this section the liquid must in general go through both
the interface and a polymer to get through the film. In this region
reciprocal permeabilities are additive. Therefore,

$$\frac{1}{P_1} = \frac{\theta_i}{P_i} + \frac{\theta_P}{P_{PL}} \tag{6}$$

or

$$P_1 = \frac{P_i P_{PL}}{P_{PL}\theta_i + P_i\theta_P} \tag{7}$$

where θ_i and θ_P are the fractional length of diffusion path through
the model for the interface and polymer, respectively. $\theta_i + \theta_P = 1$.
P_i is the permeability of the liquid in the interface, which generally
would be expected to be much greater than P_{PL}.

The desired equation is now obtainable from Eqs. (4) and (7):

$$P_{FL} \doteq \frac{P_i P_{PL}}{P_{PL}\theta_i + P_i\theta_P}\left(\frac{\phi_{Li}}{\tau^*}\right) + P_{PL}\left(\frac{\phi_P + \phi_{LP}}{\tau}\right) \tag{8}$$

All the quantities in Eq. (8) are obtainable experimentally except
P_i, θ_i, and τ^*. Different cases will now be considered where one or
more of these quantities can be estimated and checked experi-
mentally. In general, θ_i will be some function of the volume fraction
of filler θ_F and the tortuosity factor.

The problem now is to calculate θ_i and θ_P. Solutions shall be
given for thin plates and for cubes. To do this it will be necessary
first to calculate the thickness of polymer between filler particles.
For cubical particles the arrangement might be something like the
case shown in Fig. 4; the exact arrangement is not important to
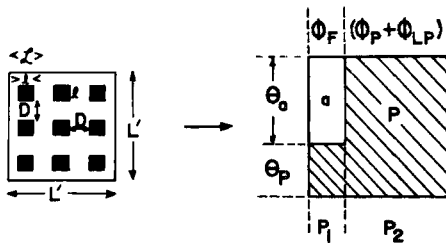a first approximation. The following notation will be useful:

FIG. 4. Model for calculating the minimum separation of particles in a filled system (left side). On the right side is the derived model for the case where the filler particles are porous aggregates.

D = minimum distance between the cube faces, i.e., thickness of polymer layer separating particles

l = length of cube faces of filler

$\mathscr{L}$ = length of "unit cell"

L' = size of specimen; let $L' = 1$ for convenience

m = number of filler particles; if $L' = 1$, then m is the number number of filler particles per cubic centimeter

From the illustration, the total volume allocated to each filler particle is

$$\mathscr{L}^3 = V/m \qquad \text{and} \qquad \phi_F = ml^3/L'^3$$

where V is the total volume, that is, L'^3. Since

$$D = \mathscr{L} - l$$

$$D = \left(\frac{V}{m}\right)^{1/3} - l \; = \frac{L'}{m^{1/3}} - L' \left(\frac{\phi_F}{m}\right)^{1/3} = \frac{L'}{m^{1/3}} (1 - \phi_F^{1/3}) = \frac{1 - \phi_F^{1/3}}{m^{1/3}}$$

the total fraction of the thickness that is represented by polymer between particles is $m^{1/3}D$. Therefore,

$$m^{1/3}D = (1 - \phi_F^{1/3}) = \theta_P \tag{9}$$

If one carries out a similar analysis for thin plates ($L/W \to \infty$) that are oriented parallel to the film surface, the fractional length of the thickness occupied by polymer is ϕ_P or $(1 - \phi_F)$.

In general $\theta_i = \phi_F^n$ and $\theta_P = 1 - \phi_F^n$, where n is a constant between zero and one which denotes the fractional length of the average diffusion path that is through polymer. The constant n will depend upon particle shape and orientation as well as upon such factors

as aggregation of filler particles. For cubical or spherical particles n should be roughly $\frac{1}{3}$, while for thin plates with $L/W \to \infty$, n would approach 1.0 if the plates are oriented parallel to the plane of the sheet. For plates with $L/W \to \infty$ oriented perpendicular to the plane of the sheet, n should approach zero, and something approaching channels through the sheet could result.

Thus Eq. (8) for the diffusion of a liquid through a filled sheet or film becomes

$$\frac{P_{FL}}{P_{PL}} \doteq \frac{P_i}{P_{PL}\phi_F^n + P_i(1 - \phi_F^n)} \left(\frac{\phi_{Li}}{\tau^*}\right) + \left(\frac{\phi_P + \phi_{LP}}{\tau}\right) \tag{10}$$

This equation will now be used to illustrate some of the various types of behavior that can be expected.

Case 1: Channels

One case is where the interface forms channels all the way through the film so that $n = 0$. For channels, Eq. (10) becomes
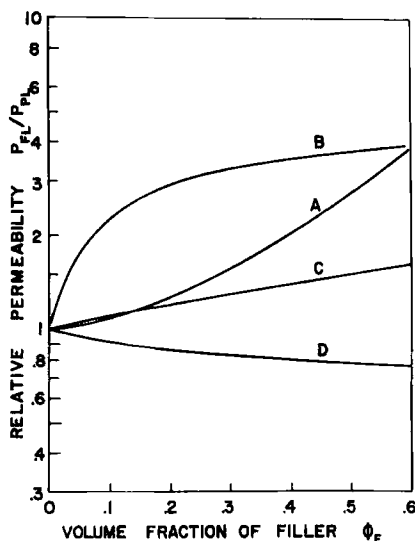

FIG. 5. Various types of relative permeability curves that can be expected when there are channels through the polymer film. A, A comparative curve for porous aggregates rather than channels. $P_i/P_{PL} = 50$, $\phi_{LP} \doteq 0$. B, Channels with $P_i/P_{PL} = 50$, $\phi_{Li} = 0.5\phi_F$, $\tau^* = \tau = 1 + 5\phi_F$, $L/W = 10$. C, $P_i/P_{PL} = 20$, $\phi_{Li} = 0.2\phi_F$, $\tau^* = 2$, $\tau = 1$. D, $P_i/P_{PL} = 10$, $\phi_{Li} = 0.15\phi_F$, $\tau^* = 2$, $\tau = 1 + 0.5\phi_F$ (cubes).

$$P_{FL} = \frac{P_i \phi_{Li}}{\tau^*} + P_{PL} \left(\frac{\phi_P + \phi_{LP}}{\tau} \right) \tag{11}$$

This type of situation would be expected to occur where thin plates are oriented perpendicular to the surface or where the particles are not completely dispersed but form certain types of aggregates. For the oriented plates and for through-going permeable aggregates, $\tau^* \doteq 1$, while for impermeable aggregates with a through-going interfacial layer, τ^* could be as large as 2.0. Since τ can be independently estimated from gas-permeability measurements, and ϕ_{LP} and ϕ_{Li} can be determined from solubility tests, the only unknowns in Eq. (11) are P_i and possibly τ^*. Figure 5 shows examples of the manner in which channels can affect liquid permeability. The permeability of the filled system can be either greater than or less than the permeability of the unfilled polymer, depending upon the relative magnitudes of the tortuosity and ease of diffusion through the channels, i.e., upon $P_i \phi_{Li}$.

Case 2: Permeability When Filler Particles Are Porous Aggregates

If the filler particles are not completely dispersed, they will form porous aggregates which contain more or less free volume, and the density of the mixture will be less than expected.

If one assumes that the filler particles shown on the left side of Fig. 4 are really highly permeable aggregates instead of individual impermeable filler particles, a model such as shown on the right side of Fig. 4 should apply. In this case $\theta_P + \theta_a = 1$, where θ_P and θ_a are the fractional lengths of the diffusion path that are in polymer and aggregates, respectively. From the analysis leading to Eq. (9), it is expected that $\theta_P = 1 - \phi_F^{1/3}$ and $\theta_a = \phi_F^{1/3}$. Also, $\tau^* \doteq \tau \doteq 1$ in many cases. Because of the void volume in the aggregates, the permeability of the liquid through them should be very high since capillary attraction and "wicking" can occur. Thus $P_a \gg P_{PL}$, where P_a is the permeability of the liquid through the aggregate. From the model shown in Fig. 4 by the methods already used, Eq. (10) can be modified to give the approximate equation:

$$\frac{P_{FL}}{P_{PL}} \doteq \frac{P_a \phi_F}{P_{PL} \phi_F^{1/3} + P_a (1 - \phi_F^{1/3})} + (\phi_P + \phi_{LP}) \tag{12}$$

The type of behavior that can be expected from systems containing
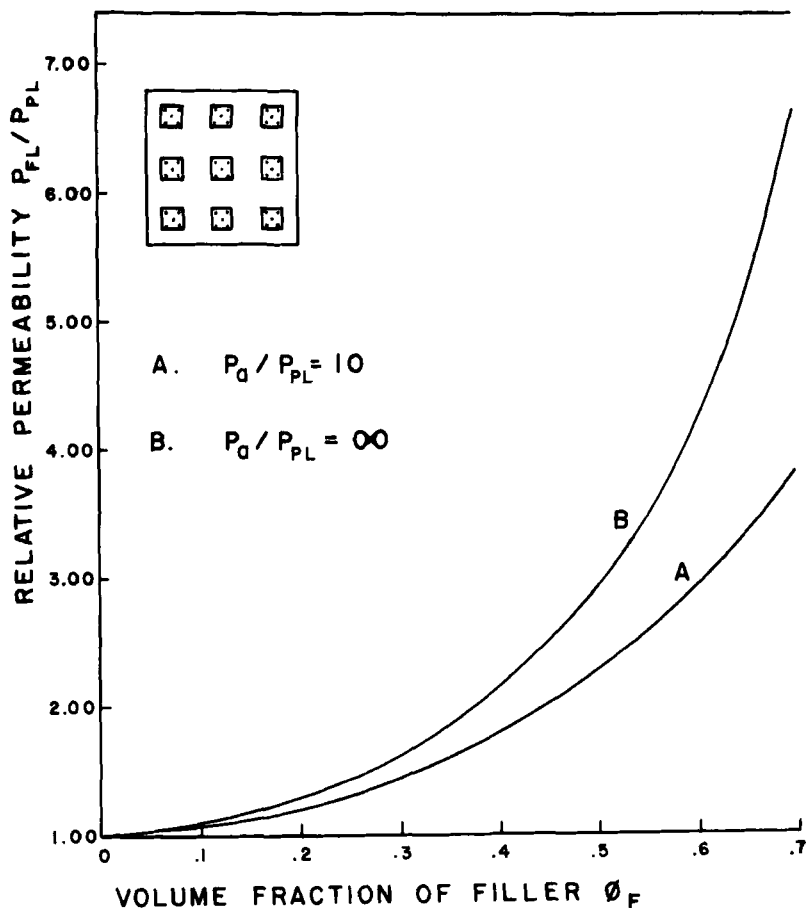
FIG. 6. Relative liquid permeability for polymers filled with porous aggregates. Curve A, $P_a/P_{PL} = 10$. Curve B, $P_a/P_{PL} = \infty$.

such aggregates is illustrated in Fig. 6. It will be noted that such aggregates always increase the permeability rather than decrease it. They should increase gas permeability as well as liquid permeability. Figure 6 shows the limiting value of the permeability as P_a increases to infinity. For instance, the permeability when $P_a/P_{PL} = \infty$ is not much greater than when $P_a'/P_{PL} = 10$. The difference in the permeability behavior as a function of filler concentration for discrete aggregates and for channels is shown in Fig. 5.

Case 3: Discrete Particles with Uniform Dispersion

The permeability behavior of liquids through filled systems can assume a wide variety of forms as the concentration of filler increases. The main factors are the concentration dependence of the tortuosity factor, the concentration of liquid at the interface, and the rate of diffusion of the liquid through the interfacial layer. Figure 7 illustrates the effect of some of these variables and compares liquid and gas permeability on the same materials for $n = 1$. The difference between liquid and gas permeability gets greater as the concentration of filler increases and as the interfacial part of the process becomes more important.
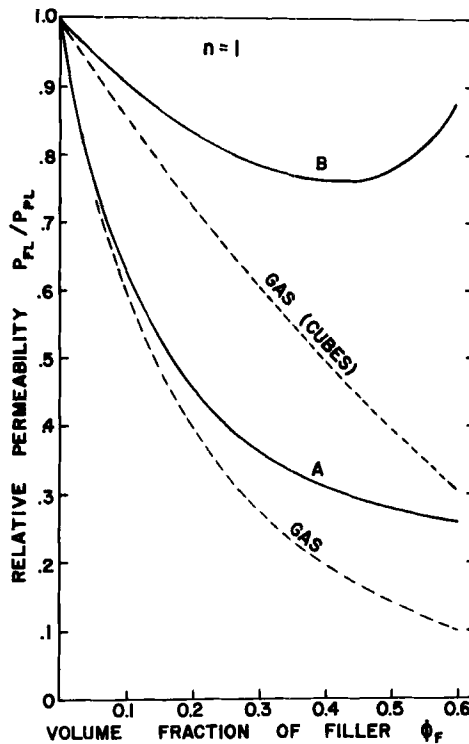

FIG. 7. Various types of liquid permeability curves for $n = 1$, and the comparison of liquid permeability with idealized gas permeability. A, $P_l/P_{PL} = 50$, $\phi_{Li} = 0.5\phi_F$, $\tau^\circ = \tau = 1 + 5\phi_F$, $L/W = 10$. B, $P_l/P_{PL} = 20$, $\phi_{Li} = 0.5\phi_F$, $\tau^\circ = \tau = 1 + 0.5\phi_F$, $L/W = 1$ (cubes).
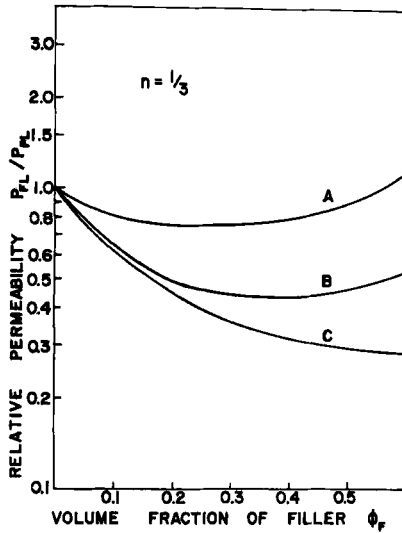
FIG. 8. Various types of liquid permeability when $n = \frac{1}{3}$. A, $P_i/P_{PL} = 10$, $\phi_{Li} = \phi_F$, $\tau^\circ = \tau = 1 + 3\phi_F$, $L/W = 6$. B, $P_i/P_{PL} = 50$, $\phi_{Li} = 0.5\phi_F$, $\tau^\circ = \tau = 1 + 5\phi_F$, $L/W = 10$. C, $P_i/P_{PL} = 10$, $\phi_{Lt} = 0.3\phi_F$, $\tau^\circ = \tau = 1 + 5\phi_F$, $L/W = 10$.
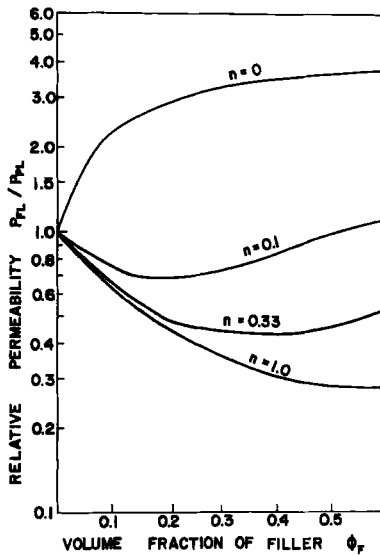

FIG. 9. Various types of liquid permeability when all variables except n are held constant. $P_i/P_{PL} = 50$, $\phi_{LP} \doteq 0$, $\phi_{Lt} = 0.5\phi_F$, $\tau^\circ = \tau = 1 + 5\phi_F$, $L/W = 10$.

Figure 8 shows some of the possible curves for the case where $n = \frac{1}{3}$. The permeability of the filled polymer can be either greater or less than that of the unfilled material, and under some conditions a definite minimum in permeability is found.

Figure 9 illustrates the types of behavior that can be found by changing only the factor n, holding all the other variables constant. To achieve the maximum reduction in permeability, n should be as large as possible. If the variation in n is due to orientation of platelike particles rather than aggregation, etc., Fig. 9 indicates that the plates should be oriented parallel to the surface rather than perpendicular to it. This is, of course, what one already suspects, but it is gratifying that a simple theoretical model can make such a prediction. Although not too much emphasis can be placed upon the quantitative aspects of these models, experiments on filled systems have been able to produce nearly all the types of curves shown in Figs. 5 to 9.

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Zusammenfassung

Eine Theorie wurde entwickelt welche es erlaubt, die minimale Permeabilität vorauszuberechnen, die für ein mit blättchenförmigen Partikeln gefülltes Polymerisat zu erwarten ist. Ebenfalls wurden Modelle für die Permeabilität von Flüssigkeiten durch gefüllte Polymere entwickelt, wobei die Flüssigkeit an der Grenzfläche Füllmaterial-Polymer adsorbiert wird oder sich ansammelt. Einige der hier besprochenen Fälle schliessen verschiedene Arten von Dispersionen, die Orientierung der Füllmaterialpartikel und die Effekte der Füllmaterialaggregation ein. Die Perme-

abilität, besonders von Flüssigkeiten, ist äusserst kompliziert und viele verschiedenartige Erscheinungsformen können erwartet werden.

Résumé

On a developpé une théorie qui prévoit la perméabilité minime qu'on peut attendre d'un polymère chargé avec des particules en plaquettes. On a aussi developpé des modèles pour la perméabilité des liquides à travers des polymères chargés lorsque le liquide s'adsorbe ou se collecte à l'interface polymère-charge. On discute dans quelques cas les maniéres variées de dispersion, l'orientation des particules chargées et l'effet de leur aggregation. La perméabilité, en particulier, celle des liquides est extrèmement complexe, et on doit s'attendre aux modes divers de comportement.