Permeation of flavors and aromas through glassy polymers

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ABSTRACT: The barrier properties of polymers are often important to packaging. These polymer properties for small molecules such as oxygen, water, and carbon dioxide are well known. However, the polymer barrier properties for flavor, aroma, and solvent molecules represent relatively new territory. This paper will discuss the permeation through polymers and the sorption by polymers (scalping). The paper will also show that the diffusion of organic vapors cannot be predicted simply from the oxygen diffusion. Furthermore, glassy polymers, in general, will be shown to make good barriers to organic vapors at low activities.

KEYWORDS: Barrier properties, diffusion constant, equations, flavor, glass, odors, oxygen, penetration, polymers, solvents.

Two opinions are frequently held by many packaging professionals concerning the permeation of flavor, aroma, and solvent (F/A/S) molecules in polymers. First, many believe that the common nylons and polyethylene terephthalate (PET) have low permeabilities to F/A/S molecules. For the most part, this is true. Second, many think that the F/A/S permeabilities of polymers can be ranked according to their oxygen permeabilities. For the most part, however, this is unreliable. This paper will review published permeability data and use the simple mathematical expressions for mass transport to develop these concepts more fully.

Permeation of F/A/S molecules in glassy polymers at low concentrations will be evaluated. Low concentrations of F/A/S molecules are expected in many packaging applications, since the relative activities (partial pressure divided by the saturation vapor pressure) are often less than 20%. This treatment avoids the complications of plasticization and swelling in the polymer. To narrow the discussion, F/A/S molecules will be limited to those interesting compounds with formula weights in the range of about 75–150 daltons. Molecules with formula weights less than 50 daltons are considered to be small.

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Background and mathematical expressions

The permeability coefficient, or simply the permeability P, is useful in describing the rate of mass transport through a polymer at steady state. Equation 1 is a restatement of Fick's First Law in terms familiar to packaging individuals.

$$\Delta M_x/\Delta t = (P\ A\ \Delta p_x)/L \qquad (1)$$

where $\Delta M_x/\Delta t$ is the rate that material x permeates a polymer film with a cross-sectional area A and thickness L when a difference in partial pressure of the permeant, Δp_x, exists across the film. This equation works equally well for describing transport from the environment into the contents of a package or vice versa. It is applicable for small molecules, such as oxygen or water, and for larger F/A/S molecules.

When mass transport of one or more species through a package is an important design parameter, the permeability is the biggest variable. The permeability of a species can cover several orders of magnitude, while A is limited by the size of the contents, L is limited by the required strength and rigidity of the package, and Δp_x is defined entirely by the composition of the contents and the environment.

Since P can be very important, a closer look at its components is valuable. Equation 2 shows how P is related to two more basic properties.

$$P = D\ S \qquad (2)$$

where D is the diffusion coefficient and S is the solubility coefficient. This

describes simple solution–diffusion permeation, wherein a permeant dissolves into a polymer on the high-pressure side, diffuses through the polymer by random hops, and desorbs from the polymer on the low-pressure side. The diffusion coefficient is a kinetic term that describes how fast molecules move in a polymer host. The solubility coefficient is a thermodynamic term that describes how many molecules dissolve in a polymer host. The solubility coefficient is the reciprocal of the Henry's Law Constant.

The diffusion coefficient may be used to estimate the time interval from initial contact when a film and an environment meet until steady state is achieved. Equation 3 expresses this relationship.

$$t_{ss} = L^2/4D \qquad (3)$$

where t_{ss} is the approximate time needed to reach steady state for a film of thickness L with a diffusion coefficient D. Whenever t_{ss} is less than the time of contact between film and environment, steady-state conditions exist and Eq. 1 is applicable. For small permeant molecules in a thin, nonbarrier film, t_{ss} can be as small as a few minutes. For large F/A/S molecules in thick barrier films, t_{ss} can be much greater than any reasonable contact time. For contact times less than t_{ss}, the effective penetration depth of the permeant front, L^*, can be estimated with Eq. 4.

$$L^* = 2(Dt)^{1/2} \qquad (4)$$

In some cases, when D is very small, only a thin skin on the surface of the film will be penetrated.

The solubility coefficient may be used to estimate the amount of permeant that will reside in the film. This can be important when the amount of a critical ingredient inside a package can be scalped by the package wall, leaving an unacceptable result. The equilibrium concentration, C_{eq}, of a permeant in a polymer is described by Eq. 5, where S is the solubility coefficient and p_x is the partial pressure of permeant x contacting the polymer.

$$C_{eq} = S\,p_x \qquad (5)$$

Usually, the partial pressure of the permeant is zero on one side of the film; this makes C_{eq} on that side equal to zero. Furthermore, for simple cases, the concentration gradient from the high-activity side to the low-activity side is a straight line. Hence, the average concentration, C_{avg}, is only half of C_{eq}.

$$C_{avg} = 0.5\,(S\,p_x) \qquad (6)$$

The quantity of permeant absorbed, M_{sorb}, by the package is equal to the volume of absorbing polymer times the average concentration. If steady state has been achieved, the volume of polymer is the wall thickness, L, times the area, A.

$$M_{sorb} = 0.5\,(S\,p_x\,A\,L) \qquad (7)$$

When steady state has not been achieved, the effective volume of polymer is the effective penetration depth, L^*, times the area.

$$M_{sorb} = 0.5\,(S\,p_x\,A\,L^*) \qquad (8)$$

If steady state is not achieved, substituting Eq. 4 into Eq. 8 yields Eq. 9.

$$M_{sorb} = S\,p_x\,A\,(Dt)^{1/2} \qquad (9)$$

The diffusion coefficient plays two important roles in analyzing a permeation event. First, the diffusion coefficient can be used to decide if steady state has been achieved. Second, if steady state has not been achieved, this coefficient can help estimate the sorptive loss to the package wall.

Literature review

Many references describe the diffusion of small molecules in glassy polymers. Experiments with oxygen, nitrogen, carbon dioxide, water, and other small molecules have been reported for commercial and experimental polymers. The diffusion coefficients and permeability coefficients are large enough that transmission can be detected through films after reasonable times. The polymers span the range from medium to poor oxygen barriers.

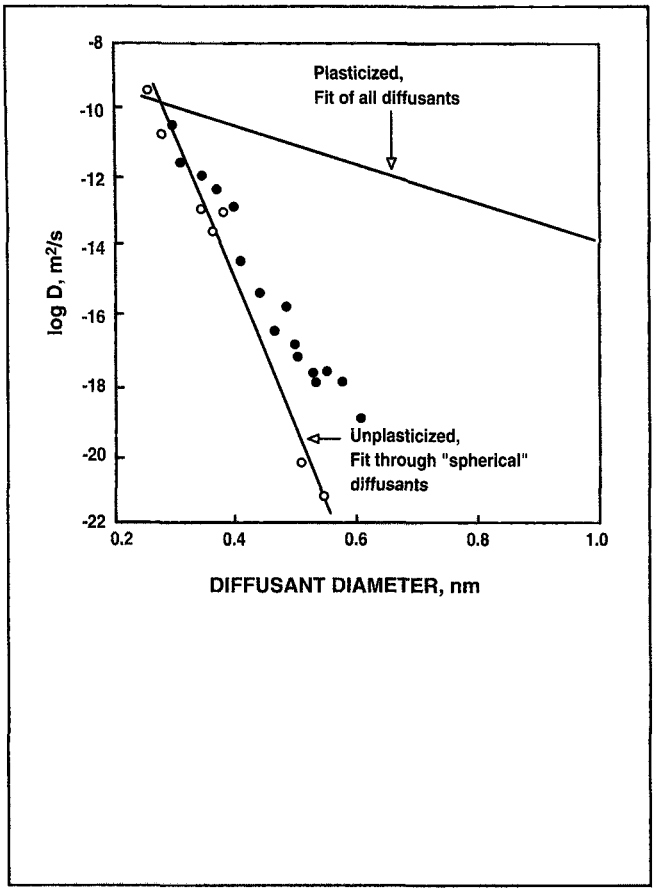
Few references describe the diffusion of F/A/S molecules in glassy polymers. The following paragraphs will show that the principal reason for this lack of information is the low diffusion coefficients. The time required for experiments is very long (see Eq. 3). Furthermore, given a low diffusion coefficient, the permeability coefficient is also likely to be small (see Eq. 2). This then might lead to flux rates that are difficult to detect and quantify, as shown in Eq. 1.

Berens and Hopfenberg have studied the diffusion of gases and organic vapors at low concentrations in glassy polyvinyl chloride (PVC), polystyrene (PS), and polymethyl methacrylate (PMMA) *(1)*. They worked with fine powders of these polymers. While the PS and PMMA powders were a few micrometers in diameter, the PVC powders were somewhat larger. The small diameters were necessary to complete the experiments and will be discussed later. Helium was the smallest molecule for the study, and alkanes with as many as six carbon atoms were the largest molecules. The diffusion coefficients decreased by 10 or more orders of magnitude as larger diffusing molecules were tested.

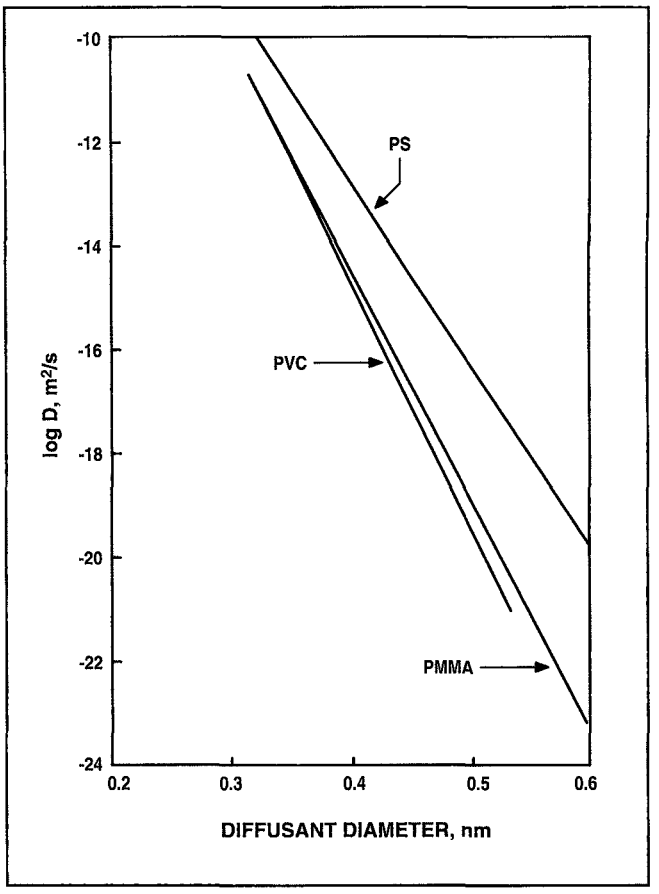
The lower line in **Fig. 1** is a fit of the diffusion coefficient at 30°C as a function of diffusant size through glassy PVC for "spherical" molecules. Diffusion coefficients for other molecules that were not spherical, but rather somewhat elongated, lie above the line. Elongated molecules can have diffusion coefficients several orders of magnitude larger than spherical molecules with the same mean diameter. For example, the diffusion coefficient of normal pentane in PMMA is nearly 1000 times greater than that of neopentane in PMMA. **Figure 2** shows the best fits of the diffusion coefficients of spherical molecules in PVC, PS, and PMMA.

The slopes of the three lines are nearly equal. Equation 10 defines the slope, where log is the base-10 logarithm, D is the diffusion coefficient, and d_{mean} is the mean diameter.

1. Diffusion coefficients in PVC at 30°C



2. Diffusion coefficients for spherical molecules in PVC, PMMA, and PS at 30°C



$$slope = -\Delta \log D / \Delta d_{mean} \qquad (10)$$

The slopes for PS, PMMA, and PVC are 38 nm^{-1}, 43 nm^{-1}, and 44 nm^{-1}, respectively.

Only the largest molecules of this study approached the arbitrary definition of an F/A/S molecule; the principal reason for this is the experimental time. Equation 11 gives the time for a sphere to reach about 95% of the equilibrium sorption, where r is the radius.

$$t_{95\%} = 0.5\ (r^2/D) \qquad (11)$$

For a sphere with a radius of 0.5 μm and a diffusion coefficient of 10^{-18} m^2/s, the experimental time would be nearly a day. For some of the experiments in this paper, the experimental times were nearly a month. Larger diffusant molecules would have had smaller diffusion coefficients, but this would have made prohibitively long experiments.

In subsequent studies, Berens evaluated the diffusion coefficients of many of the same molecules through plasticized PVC *(2)*. The best straight-line approximation for these data is given in Fig. 1. The slope, as defined by Eq. 10 for this line, is only 5.5 nm^{-1}. This is consistent with the diffusion coefficients in rubbery polymers, i.e., polymers above their glass transition temperature, T_g. For a series of linear esters, the slope was about 4.8 nm^{-1} in a vinylidene chloride copolymer at 85°C and about 4.6 nm^{-1} in low-density polyethylene at 30°C *(3)*. Since these slopes are for nearly linear molecules, the slope for spherical molecules would be a little larger, perhaps 10 nm^{-1}. For a variety of diffusant molecules, Zobel found a slope of about 8.8 nm^{-1} in polypropylene at 30°C *(4)*. The diffusant molecules for this slope were neither linear nor spherical; hence, a slightly larger slope would be expected for spherical molecules. For all polymers, the diffusion coefficient is smaller for a larger diffusant than for a smaller diffusant. However, for a polymer above T_g, the diffusion coefficient changes by a smaller amount as the size of the diffusant increases. The magnitude of the slope conveys this: compare about 40 nm^{-1} for glassy polymers to about 10 nm^{-1} for rubbery polymers.

Chen studied permeation in films of three glassy polymers *(5, 6)*. For the polycarbonate of bisphenol-A(PC), the diffusion data for spherical or nearly spherical molecules at 120°C have a slope of about 30 nm^{-1}. However, the largest diffusant molecule was neopentane. For polyethylene terephthalate (PET), the diffusion data for nonspherical diffusant molecules had a slope of about 20 nm^{-1}. The slope would be larger for spherical molecules. The largest diffusant molecule in PET was isobutane. Insufficient data are given to calculate a credible slope for

PMMA at 55°C. Diffusion coefficients for small molecules only are given.

New experimental attempts

Permeation experiments were attempted in this laboratory with thin polystyrene, PET, and nylon-6 films. The experiments used low activities of several F/A/S molecules, including d-limonene, linear and branched esters, and ketones. The very sensitive permeation instrumentation developed in this laboratory and described elsewhere was used *(7, 8)*.

No measurable permeation was observed in any case. Elevated temperatures were used, and experimental times ran to 1000 min. If the ultimate steady-state permeation rates would have been large enough to observe with the instrumentation, an upper bound for the diffusion coefficient could be calculated using Eq. 12, where $t_{0.5}$ is the time for permeation rate to reach half of the steady-state rate *(9)*.

$$D = L^2/(7.2\ t_{0.5}) \qquad (12)$$

For a thickness of 12 μm (0.5 mil) and $t_{0.5}$ greater than 120,000 s (2000 min), the diffusion coefficient is less than 1.7 x 10^{-16} m^2/s. These experiments were conducted at higher temperatures. The diffusion coefficients at lower temperatures would be smaller. For example, Berens shows that, for PS, the diffusion coefficients for the largest molecules would drop by about a factor of 100 going from 90°C to 30°C *(1)*. Hence, our experiments indicate that the diffusion coefficients for F/A/S molecules in glassy polymers at 30°C are less than 10^{-17} m^2/s, possibly orders of magnitude lower.

Applications

These low-diffusion coefficients will lead to low sorption by the polymer in packaging applications. For a diffusion coefficient less than 10^{-17} m^2/s and a flexible package wall thickness of 25 μm (1.0 mil), Eq. 3 predicts that the time to reach the steady-state permeation rate would be greater than 180 days. For a rigid package wall thickness of 500 μm (20 mil), the time to reach steady state would be greater than 200 years!

Equation 4 predicts that, for these low diffusion coefficients, the penetration depths would be small. In a year, the effective penetration depths would be no larger than 35 μm. For larger F/A/S molecules with diffusion coefficient orders of magnitude less than the arbitrary 10^{-17} m^2/s considered thus far, the penetration depths would be much less, perhaps only a few micrometers. Even for very large solubility coefficients (e.g., 1.0 $kg/m^3 \cdot Pa$), the sorption by a package wall would be virtually nothing, perhaps a few micrograms, for these shallow penetration depths.

This judgment does not apply to polyolefin packages. The diffusion coefficients would be large, and steady-state permeation would be established quickly. The entire package thickness would participate in sorption.

Relation to oxygen diffusion

Table I shows the diffusion coefficients for oxygen in several polymers at 30°C. The vinylidene chloride copolymer has the lowest diffusion coefficient, which is consistent with its commercially important low oxygen permeability. The PS has a high diffusion coefficient, comparable to the polyolefins.

Table I also contains a qualitative comment on the diffusion coefficients for F/A/S molecules in these polymers. The polyolefins have shown high diffusion coefficients in experiments. Vinylidene chloride copolymers have very low diffusion coefficients, but they are barely measurable. This polymer still would have a valuable barrier for F/A/S applications. The glassy polymers have such low diffusion coefficients that they cannot be measured by macroscopic techniques. The diffusion data of Berens indicate that the ranking of glassy polymers for F/A/S diffusion is similar to the ranking for oxygen diffusion *(1)*. Furthermore, the ranking of rubbery polymers for F/A/S diffusion is similar to the ranking for oxygen. However, rankings between rubbery and glassy polymers cannot be compared. For example, the diffusion coefficient for oxygen in PS is 1000 times greater than that for oxygen in a vinylidene chloride copolymer, while the diffusion coefficient for F/A/S molecules in PS is lower than in a vinylidene chloride copolymer. This represents a stark reversal.

I. Diffusion of oxygen and organic vapors at low activities in polymers at 23°C

Polymer	*Oxygen diffusion, m^2/s (10)*	*F/A/S molecule diffusion*
Vinylidene chloride copolymer	1.2×10^{-14}	Low
PET	2.7×10^{-13}	Very low
PVC (rigid)	1.2×10^{-12}	Very low
Polypropylene	2.9×10^{-12}	High
PS	1.1×10^{-11}	Very low
High-density polyethylene	1.6×10^{-11}	High
Low-density polyethylene	4.5×10^{-11}	Very high

Summary

Glassy polymers have medium and high diffusion coefficients for oxygen and very low coefficients for flavor/aroma/solvent molecules at low concentrations. Typically, these are too low to measure by macroscopic means. Vinylidene chloride copolymers have low diffusion coefficients for oxygen and flavor/aroma/solvent molecules. Polyolefins have high diffusion coefficients for both oxygen and F/A/S molecules.

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CORRECTION

In the article, "Corrugated containers take on added value," which appeared in the Focus on Corrugated Containers special supplement (*Tappi J.*, 76(10):17(1993)), the F-flute height of 0.003 in. is incorrect. The correct height is 0.03 in.