Permeation Basics

Introduction

The ultimate goal of packaging is to provide a consistent barrier between a product and the surrounding environment in order to achieve the desired shelf life.

Other purposes could be to keep active ingredients inside to maintain product specifications, to keep exterior volatiles out (such as bottled soap next to water), or to encourage the exchange of oxygen and water vapor at a constant level to ensure equilibrated reaction rates for a particular product.

Permeation is defined as the movement of molecules from one side of a barrier to the other. The movement of molecules of permeant is controlled by the driving force of the test, which is the difference in concentration of molecules between the two sides of the test barrier.

The process of permeation follows a solution-diffusion mechanism where gas absorbs at the package wall (polymer), dissolves into the polymer, diffuses through the polymer due to driving force, and then desorbs/outgases on the other side (Figure 1).

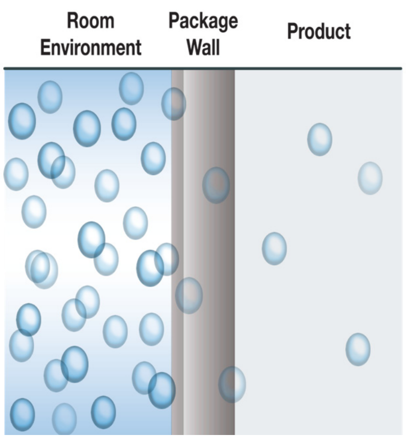

Figure 1. Permeation through a test barrier.

There is no universal time to reach equilibrium. It will be different depending on the test barrier and the test conditions. In general, the higher the barrier, the longer it will take to reach equilibrium. The permeability of a barrier material is dependent on both its solubility and diffusion.

Solubility

Solubility (S) represents the dissolution of a permeant into a polymer. It can be thought of like a sponge, where molecules move from outside the sponge (from an area of high concentration) into it (an area of low concentration). Knowing that polymers "hold" gases is important for companies because permeants such as oxygen that are within the polymer could reduce a product's shelf life. Solubility is tied to temperature; as the temperature increases, solubility decreases.

Diffusion

Diffusion (D) is the process of molecules moving from an area of higher concentration into one of lower concentration as a result of random molecular motion. Whereas solubility quantifies how many molecules are moving into a polymer, diffusion measures how quickly they are moving through the polymer (Figure 2). Diffusion is also tied to temperature; as the temperature rises, diffusion increases.

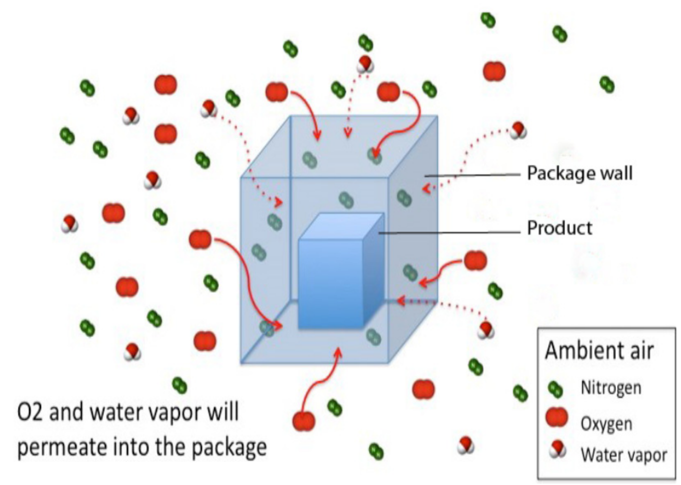

Figure 2. Diffusion into and out of a package.

Permeability

Permeability (P) is an indicator of a barrier's effectiveness. A low P value indicates a good barrier, while a high P value indicates a poorer barrier.

Permeability is defined as the product of P and S. It can also be defined as $P=(q\ell)/(At\Delta p)$, where q=the quantity of permeant transferred by a unit of area (A), t=time, ℓ=the material thickness, and Δp=the partial pressure difference. The units for OTR are given in (cc • mm)/(m^2 • day • atm), and the units for WVTR are given in (g • mm)/(m^2 • day • atm), where one atm is equal to the pressure exerted by a column of mercury 760mm high at a temperature of 0C.

Fickian vs. non-Fickian materials

Fick's First law states that the flux, or the flow of gas through a barrier, is dependent on the diffusion coefficient, the concentration of permeant, and the material thickness (Figure 3). With a higher concentration, the flow of gas will be higher. Greater material thickness will decrease the flow of gas.

$$F = -D\frac{\partial C}{\partial x}$$

Figure 3. Fick's First Law.

F is defined as the flow of gas, D is the diffusion coefficient, C is the permeant concentration, and x is the material thickness.

Fickian materials behave in a linear manner, while non-Fickian materials are affected by the test gas and do not behave in a linear manner after a certain point (Figure 4). For example, paper can be resilient with moderate humidity exposure, but it breaks down when exposed to high humidity. Therefore, paper is non-Fickian with respect to humidity exposure.

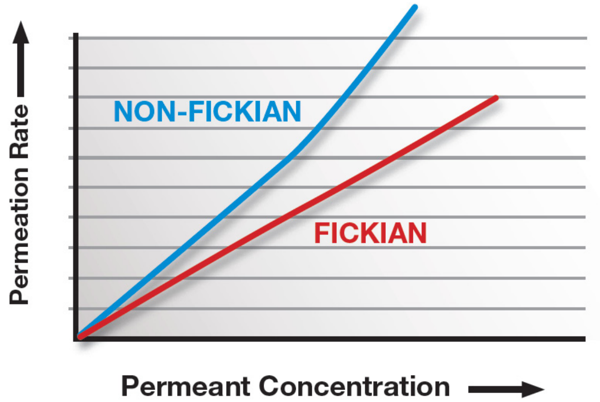

Figure 4. Fickian vs. non-Fickian behavior.

Temperature and relative humidity

Temperature has a significant effect on permeation rates. A general rule is that for every 10C increase in temperature, permeability doubles.

It is possible to decrease the time a test will take to reach equilibrium by increasing the temperature, but a factor to be aware of is that some materials have transition points where the permeation rate changes after a certain temperature. This is commonly referred to as a "glass transition point," and it must be taken into account when using higher temperatures to obtain faster results and extrapolating these results to lower temperatures.

Relative humidity (RH) also has an impact on the permeation rate of some materials, as shown below in Figure 5. Increased RH causes some materials to be less effective barriers, while others become more effective.

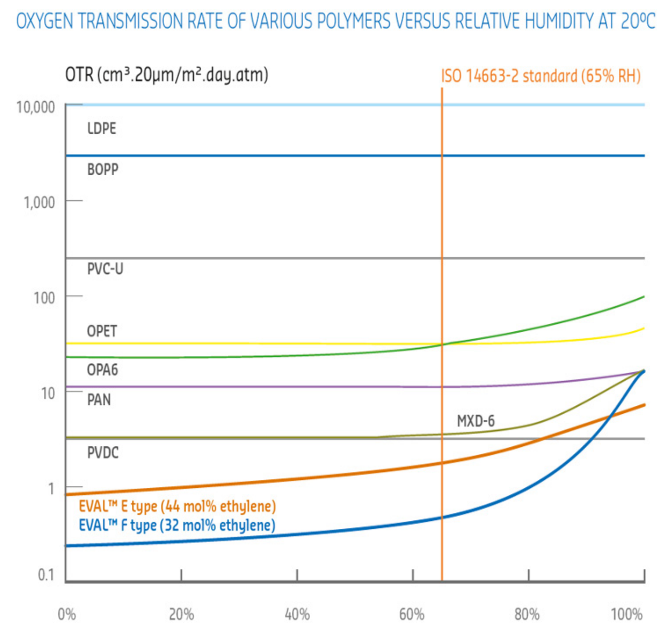

Figure 5. The effects of RH on various polymers.[1]

Because of the effects that both temperature and RH can have on permeation rates, it is necessary to take into account the conditions a product will be exposed to when conducting permeation testing. The ability to closely control test parameters such as temperature, RH, and test gas concentration is key to achieving accurate and repeatable results that can be used to ensure the desired shelf life for the product.

A common misconception is that increasing the concentration of the test gas, such as using 100% O_2 instead of 21% O_2 (room air), will decrease the testing time. In fact, while an increased concentration will indeed result in more molecules of the test gas permeating through the test barrier, it will take the same amount of time to reach equilibrium as a test that is run with a lower concentration. The only way to speed up the time to reach equilibrium is to increase the temperature at which the test is conducted.

Material thickness and multilayered materials

The thickness of a test barrier also impacts the time to reach equilibrium. If the thickness doubles, the transmission rate decreases by half. This means it will now take four times as long to reach equilibrium.

Multilayered materials often have longer times to equilibrium. The transmission rates (TR) of materials that obey Fick's Law can be added by means of the parallel resistance equation to determine the overall permeation rate of a multilayered material (Figure 6).

$$\frac{1}{TR_{total}} = \frac{1}{TR_A} + \frac{1}{TR_B} + \cdots$$

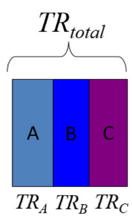

Figure 6. The parallel resistance equation.

Testing films and packages

The process of testing flat films involves mounting the film in a test plate, sweeping one side of the film with nitrogen to eliminate the test gas, and then allowing the test gas to permeate through the film until it reaches equilibrium. The test gas is swept along with the nitrogen into a sensor, where the permeation rate is measured (Figure 7).

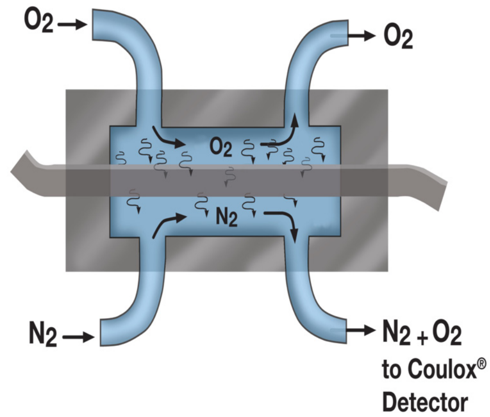

Figure 7. The setup for testing a film.

The process of testing packages is similar, except that instead of a film being placed in a test cell, the package itself is being analyzed. One side of the package (usually the interior) is swept with a carrier gas, while the other side is challenged by the test gas (Figure 8).

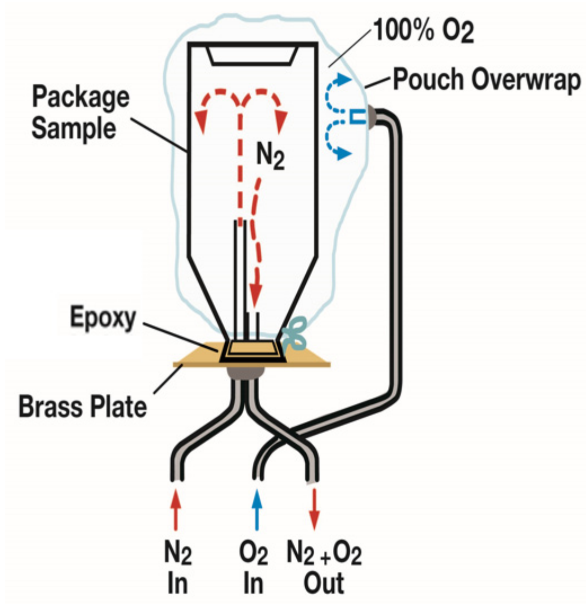

Figure 8. A setup for testing a package.

It is important to test the permeation rate of the completed package and not just films, because the process of creating the package can introduce factors such as seams, creases, and closures that may impact the permeation rate of the overall system. This is shown in Table 1 below; the OTR film testing showed results that were below the detection limit of the instrument used, but when finished packages were analyzed the OTR was significantly higher.

Sample ID	OTR - Film ($cc/m^2 \cdot day$)	OTR - Package (cc/day)
A	<0.005	0.011
B	<0.005	0.032
C	<0.005	0.040
D	<0.005	0.036
E	<0.005	0.052

Table 1. OTR test results for films and packages.

Conclusion

Permeation testing is necessary to ensure that a product's packaging will provide the desired shelf life. Understanding the factors that contribute to a material's permeation rate will lead to a greater knowledge of how to develop packaging that will provide enough protection to the product to provide the desired shelf life.

[1]Source: http://www.eval.eu/media/120492/otr_vs_rh_plastics_en.png

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