IMPORTANT FACTORS FOR SELECTING FOOD PACKAGING MATERIALS BASED ON PERMEABILITY

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Abstract

One of the critical factors in selection of food packaging materials is permeability and/or transmission rate to help maintain food quality. Conditions of product/material use such as temperature and relative humidity are critical for determining optimal testing conditions to determine permeability rate. Basics of permeability, interpretation of data and relationship to selection of materials for specific applications will be discussed. In addition, the relationship of permeability to aroma and flavor retention will also be covered.

Introduction

The type of food, chemical composition, size, storage conditions, expected shelf life, moisture content, aroma/flavor and appearance are just a few of the characteristics that must be taken into consideration when selecting the right material for a food product. A continuing trend in food packaging is the design of packages to extend the shelf life of foods while maintaining fresh-like quality. This places a high demand on selecting materials that not only provide the needed properties to maintain the quality of the food but it must be done at a cost effective price. The permeability of the packaging material is one of the most critical features of the package for affecting the quality of the food product. Materials can be selected to provide a very long shelf life, but one must ask whether there is a need for the best barrier. Furthermore, does the extension of the shelf life justify the cost of the material and the quality of the food? Therefore, knowing the important factors for material selection based on permeability is an essential part of the package design process.

Discussion

Terminology

A discussion of permeability involves many terms that are commonly misunderstood or confused. Therefore, a definition of terms is necessary to better understand the factors that affect permeability (Robertson, 1993).

- Permeability is defined as transfer of molecules from the product to the external environment, through package or from the external environment through the package, to the product. See figure 1.
- Sorption – movement of molecules contained by the product into but not through the package. See figure 2.
- Migration – movement of molecules originally contained by the package, into the product. See figure 3.

These three components make up the majority of interactions that take place. Although permeability doesn't directly measure each of these interactions, it does have an influence on each. For example, a material such as low density polyethylene is a good water barrier but will scalp certain flavor and aroma compounds from foods. Plasticizers may be added to polymers such as polyvinyl chloride to affect their flexibility and permeability but migration of the additives is also affected.

The equation used to express permeability is expressed as follows:
P = (D)(S)
P = Permeability coefficient
D = Diffusion coefficient which is a measure of how rapidly penetrant molecules are moving through the barrier, in the direction of lower concentration or partial pressure. D is a kinetic term that describes how fast molecules move in a polymer matrix.
S = Solubility coefficient which is the amount of transferring molecules retained or dissolved in the film at equilibrium conditions. S is a thermodynamic term that relates to how many molecules dissolve in a polymer matrix.

When an equal concentration of molecules are moving through a polymer at a constant rate, a steady state is reached and is also called Fickian Behavior. When measuring water and oxygen permeability, this is common behavior for most packaging polymers such as low density polyethylene and polyester. However, some do not have steady state behavior. Polymers such as nylon and ethyl vinyl alcohol diffuse at different rates depending upon penetrant concentration and time. Polymers with this behavior are referred to as non-steady state or non-Fickian polymers. The chemical nature of the polymers and the chemical nature of the permeants are what determines whether the polymer will behave in a Fickian or non-Fickian manner.

It is also important to understand the difference between the terms permeability rate and transmission rate. According to ASTM, (1994) transmission rate (TR) is defined as the movement of a permeant in unit time through a unit area under specified conditions of temperature and relative humidity (Table 1). The thickness of the material is not incorporated into the definition but is implied to be the thickness of the test film sample. Permeability (P) is defined as the movement of a permeant through a unit area of unit thickness induced by a unit vapor pressure difference between two specific surfaces under specific conditions of temperature and humidity at each surface (Table 1). In other words, permeability is the arithmetic product of permeance and thickness.

The confusion of the proper or improper use of these terms was the topic of a paper which compared a variety of equations for predicting permeability in multilayer films cited in different packaging textbooks (Cooksey et al., 1999). In general, it was found that most of the equations were the same basic equation but stated in slightly different ways. Other equations either accurately or inaccurately dealt with permeability (P) and transmission rates (TR) to achieve the final answer. The confusion over P and TR is not new. In fact the confusion is so serious that there have been law suits that essentially center on this basic issue. The key fact to keep in mind is that permeability data accounts for thickness of the material and transmission rate assumes the thickness of the test sample. Both are useful depending on how you use the data.

The following equations were recommended for the applications described (Cooksey et al, 1999).

- Calculating transmission rate for a multilayer laminate (TR_T) from transmission rate data is useful if you're using data instrumentally measured or comparing actual films for performance.

$$TR_T = \frac{1}{\left(\frac{1}{TR_A}\right) + \left(\frac{1}{TR_B}\right) + \ldots \left(\frac{1}{TR_N}\right)}$$

TR_{A-N} = Transmission Rate of individual layers (A, B…N (infinite number))

- Calculating transmission rate for a multilayer laminate (TR_T) permeability data would be useful if you're using published data and trying to compare to instrumentally measured data or applying published data to design a laminate for a packaging application.

$$TR_T = \frac{1}{\left(\frac{L_A}{P_A}\right) + \left(\frac{L_B}{P_B}\right) + \ldots \left(\frac{L_N}{P_N}\right)}$$

L = Thickness of individual layers (A, B…N (infinite number))
P_{A-N} = Permeability of individual layers (A, B…N (infinite number))

- Calculating permeability for a multilayer laminate (P_T) from permeability data would be useful if you're using published data and trying to estimate for theoretical laminate materials.

$$P_T = \frac{L_T}{\left(\frac{L_A}{P_A}\right) + \left(\frac{L_B}{P_B}\right) + \ldots \left(\frac{L_N}{P_N}\right)}$$

L = Thickness of individual layers (A, B…N (infinite number))
P_{A-N} = Permeability of individual layers (A, B…N (infinite number))

- Calculating permeability for a multilayer laminate (P_T) from transmission rate data would be useful if you're using instrumentally measured data from a lab and trying to convert it to data that fit the standard for published data more easily or using if for comparison with other calculated laminates.

$$P_T = \frac{L_T}{\frac{1}{(TR_A)} + \frac{1}{(TR_B)} + \ldots \frac{1}{(TR_n)}}$$

L_T = Total thickness
TR_{A-N} = Transmission Rate of individual layers (A, B…N (infinite number))

In addition to the different types of equations used to calculate permeability or transmission rates. Different units are also used to express permeability. This adds to the confusion and makes comparison of data very difficult. However, a conversion table can be helpful. See tables 2 and 3.

Variables Affecting Permeation and Diffusion

There are several variables that affect the permeation and diffusion of molecules through polymers. These include composition of the polymer and permeant, chemical composition of the material, temperature, relative humidity, crystallinity, chain packing, crosslinking, additives and orientation. Table 4 shows permeability rates for a variety of polymers in order of lowest to highest permeability for oxygen, nitrogen and carbon dioxide. According to Delassus (1997), in general, permeability ratios for nitrogen, oxygen and carbon dioxide are 1:4:14. A comparison of Table 4 to Table 5 will also show that materials that are good gas barriers are not necessarily good water barriers.

The glass transition temperature of the film is also important. For example, crystalline (glassy) films such as polystyrene have lower permeability rates than films that are semi-crystalline such as polyethylene. Crystalline polymers such as polyester are generally considered to be better barriers than semi-crytalline and glassy (amorphous) polymers. However, crystallinity can vary even for a particular polymer such as polyester, depending upon processing conditions. For example, PET film oriented at 90^oC has 22% crystallinity compared to PET film oriented at 115^oC which as 31% crystallinity. Permeation of ethyl actate was decreased by a factor of 4x in PET film with 31% crystallinity.

The length or size of the molecules involved have a strong influence on permeation of flavor and aroma compounds. Compounds of eight or more carbons are sorbed more easily than shorter chain molecules. More highly branched molecules are sorbed more than linear molecules and larger molecules are more likely to condense on the surface of a film than smaller molecules.

The presence of a functional group and polarity of a permeant can affect sorption. For example, carvone ($C_{10}H_{14}O$) and limonene ($C_{10}H_{16}$) both have 10 carbons in their chain but limonene is less polar than carvone. Limonene permeates faster through nonpolar polymers than carvone.

Pemeance of flavor compounds can exhibit concentration dependency. For example, the permeance of such compounds through certain polymers changes with increasing or decreasing concentration. Figure 4 shows oriented polypropylene and coated oriented polypropylene. The change in permeance can be attributed to interaction between polymer and penetrant thus changing the conformation of polymer chains. The presence of a copermeant can also affect the permeance of flavor compounds. See figure 5. In this example, ethyl acetate and limonene are used with biaxially oriented polypropylene. The limonene increased permeation of ethyl acetate when limonene concentration was lower. However, limonene is more aggressive than ethyl acetate and a synergistic effect is not observed when limonene concentration is higher.

Temperature and Relative Humidity have very significant effects on the permeability of flexible films. When specifying conditions for testing it is important to consider the conditions to which the material will be exposed. In some cases, as relative humidity increases, permeability increases. See Table 6. Hygroscopic materials, nylon, polyvinyl alcohol, polyvinyl acetate and uncoated cellophane are most significantly affected by the presence of moisture. The presence of hydroxyl groups (-OH) are responsible for the phenomena observed for most of these polymers. Polyethylene (high and low density), known to be an excellent water barrier, is unaffected by humidity levels. Acrylonitrile copolymer is also unaffected by relative humidity.

A relative humidity of 50% is a common condition used for testing to simulate ambient conditions, however, the relative humidity inside most food packages can easily be 100%. Therefore, it is important to specify the % relative humidity when requesting testing of materials or when evaluating permeability data from suppliers.

An increase in temperature also causes an increase in permeability. This is not surprising since the laws of kinetics apply. As temperature increases, molecules have more energy and will move more easily through a polymer matrix. According to Delassus (1997), permeability increases proportionally to an increase in temperature, but the linear relationship between temperature and permeability rate is affected by the Tg (glass transition temperature) of the polymer. The general rule is oxygen permeability increases about 9% per ^{o}C when above Tg and about 5% per ^{o}C when below Tg. To observe the effect of temperature on flavor and aroma compounds, see Table 7. All permeants exhibit the same behavior and the transmission rate increases more significantly between 21.1 and 54.4^{o}C than between 0 and 21.1^{o}C.

Additives such as plasticizers can increase permeability rate for gas, water and flavor/aroma compounds. Small amounts (less than 1%) do not have a significant effect on permeability (Delassus, 1997) but polymers such as polyvinyl chloride (PVC) rely heavily on plasticizers for flexibility. PVC can contain as much as 50% additives (including plasticizers) to achieve the flexibility desired for most food packaging applications which can increase oxygen permeability by as much as 10 times (Delassus, 1997).

Orientation can increase the degree of "packing" which generally decreases transmission rate (Table 8). The magnitude of reduction in transmission rate differs depending on the polymer. Acrylonitrile styrene copolymer is an excellent barrier and orientation only reduces its barrier properties by 10% but polyolefins such as polypropylene and polystyrene have 45% and 29% reduction in transmission rate after orientation, respectively. The oxygen transmission rate of polyester was reduced by 50% with 500% orientation (Delassus, 1997).

Conclusions

When determining what material works best for specific food applications it is first important to understand the terminology used to describe materials. If prediction using equations is necessary, be sure the chose the equation that best fits the data provided and the information desired. Consider factors such as polymer characteristics and chemical interaction with characteristics of the permeant. Finally, determine the conditions (relative humidity and temperature) under which the material will be used. Taking all these known factors under consideration won't guarantee the best possible material for the application but will definitely provide for a more informed decision that could save time and money in the future.

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Key Words: Food packaging, permeability, material selection

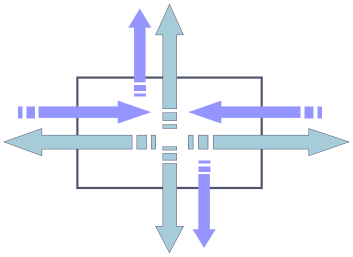

Figure 1. Permeability involves transfer of molecules into or out of the package.

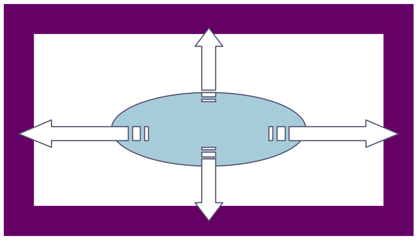

Figure 2. Sorption is the movement of molecules from the product to the package.

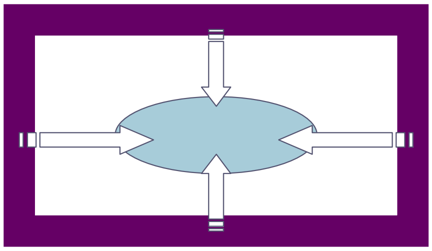

Figure 3. Migration is the movement of molecules from the package to the product.

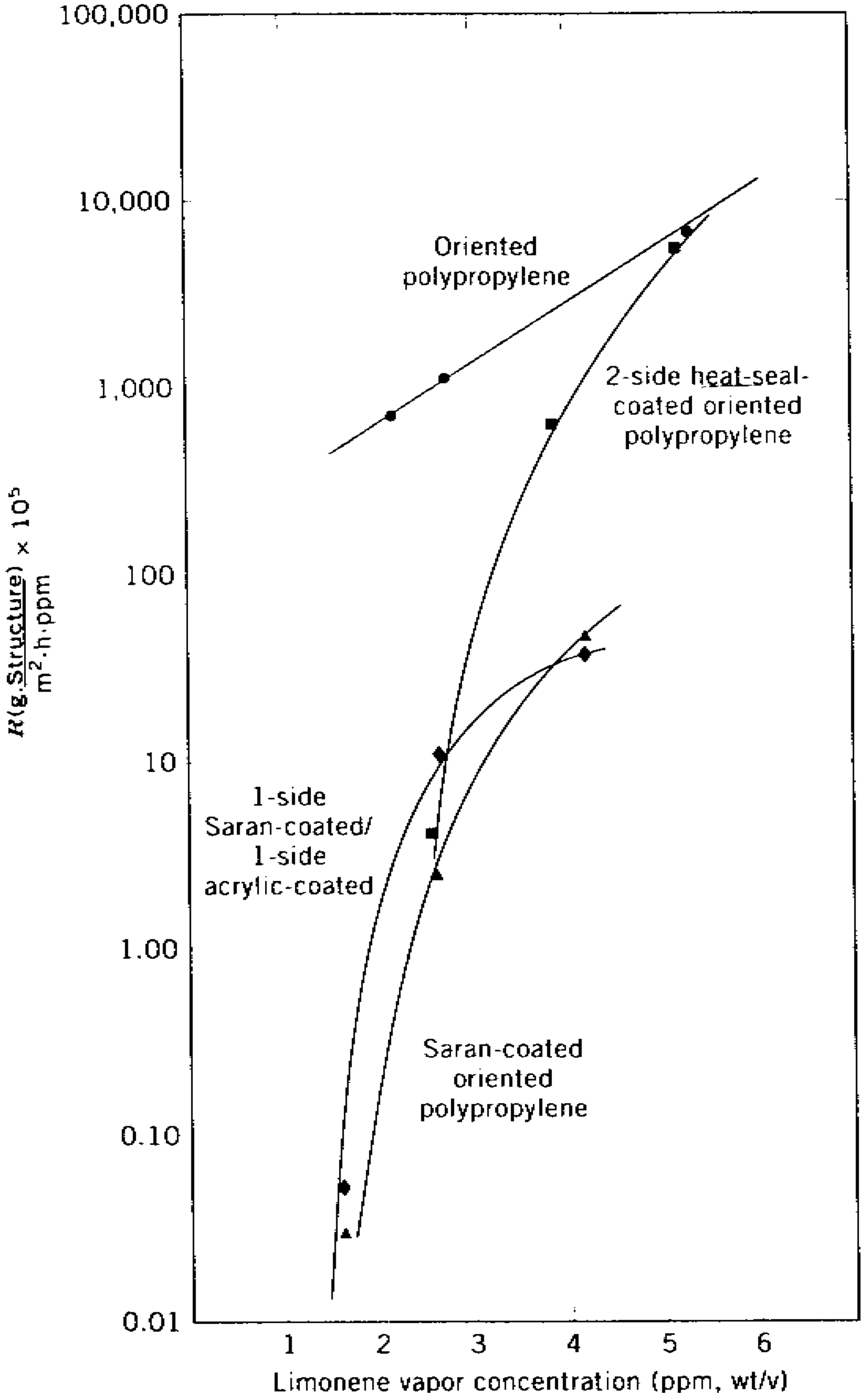

Figure 4. Concentration Dependency of Limonene in coated and uncoated oriented polypropylene (Giacin and Hernandez, 1997).

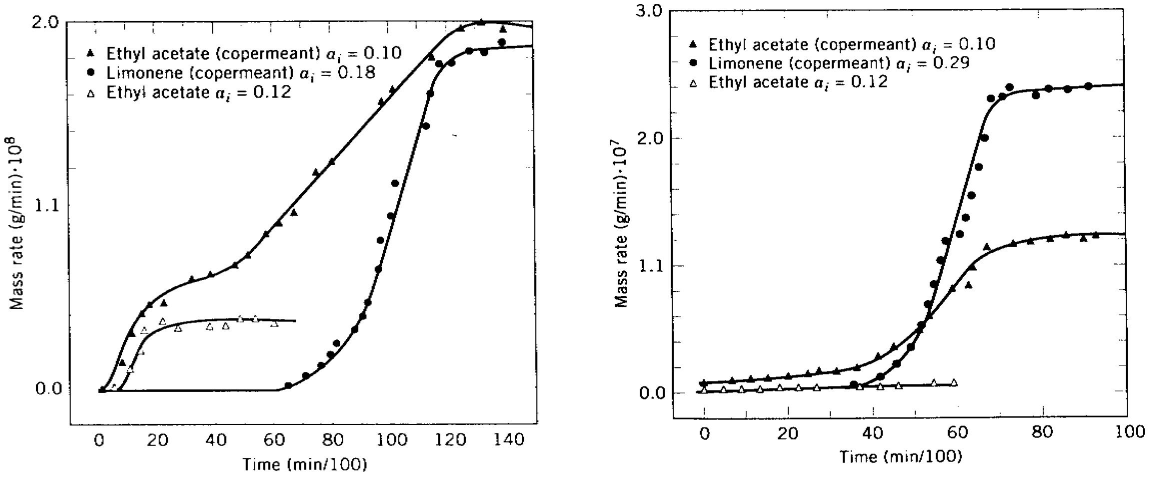

Figure 5. Effect of Copermeant on permeation

Table 1. Units used to express Permeability and Transmission Rates (Cooksey et al., 1999)

Term	Units
Permeability	cc*mil/100in^2*24h*ATM @ %RH & temp.
Transmission Rate	cc/100in^2*24h *ATM @ %RH & temp.

Table 2. Conversion units for water vapor permeability assuming standard temperature and pressure conditions. (adapted from Krochta, et al., 1994)

Units Given	Units Desired (Multiply the values represented in the units provided in the first column by the Values Listed Below				
	g*mm/ m^2*d*kPa	g *mil/ m^2*d*mmHg	g*mil/ 100^2*s*cmHg	g/m*s*Pa	cm^3*cm/ cm^2*s*cmHg
g *mm/m^2*d*kPa	1	5.25	$3.91x10^{-5}$	$1.16x10^{-11}$	$1.92x10^{-7}$
g *mil/m^2*d*mmHg	$1.90x10^{-1}$	1	$7.46x10^{-6}$	$2.20x10^{-12}$	$3.66x10^{-8}$
g*mil/100^2*s*cmHg	$2.25 \text{ x } 10^{4}$	$1.34x10^{5}$	1	$2.95x10^{-7}$	$4.90x10^{-3}$
g/m*s*Pa	$8.62x10^{10}$	$4.54x10^{11}$	$3.39x10^{6}$	1	$1.66x10^{4}$
Cm^3*cm/cm^2*s*cmHg	$5.20x10^{6}$	$2.73x10^{7}$	$2.04x10^{2}$	$6.02x10^{-5}$	1

Table 3. Conversion units for oxygen permeability assuming standard temperature and pressure conditions. (adapted from Krochta, et al., 1994)

Units Given	Units Desired (Multiply the values represented in the units provided in the first column by the Values Listed Below				
	g/m*s*Pa	mol/m*s*Pa	cm^3*µm/ m^2*d*kPa	cm^3*mil/ m^2*d*atm	cm^3*mil/ 100in^2*d*atm
g/m*s*Pa	1	$3.2x10^{-2}$	$6.05x10^{16}$	$2.41x10^{17}$	$1.56x10^{16}$
mol/m*s*Pa	$3.2x10^{1}$	1	$1.94x10^{18}$	$7.72x10^{18}$	$4.98x10^{17}$
Cm^3*µm/m^2*d*kPa	$1.65 \text{ x } 10^{-17}$	$5.15x10^{-19}$	1	3.99	$2.57x10^{-1}$
Cm^3*mil/m^2*d*atm	$4.14x10^{-18}$	$1.30x10^{-19}$	$2.51x10^{-1}$	1	15.5
Cm^3*mil/100in^2*d*atm	$6.42x10^{-17}$	$2.01x10^{-18}$	3.89	$6.45x10^{-2}$	1

Table 4. Gas permeability of selected polymers (cc*mil/100in^2*day*atm) (Delassus, 1997).

Polymer	Oxygen	Nitrogen	Carbon dioxide
Vinylidene chloride copolymer	0.01-0.15	0.003-0.035	0.05-0.75
Ethylvinyl alcohol, dry	0.007-0.048	----	----
Ethylvinyl alcohol, 100% RH	1.1-0.55	----	----
Nylon – MXD6	0.15	----	3-4
Acrylonitrile	0.9-1.0	----	10-12
Nylon 6	2-3	----	15-25
Polyethylene terephlate	3-4	0.7	20-50
Polyvinyl chloride	5-20	----	600-700
High density polyethylene	100-200	40-60	500-700
Polypropylene	150-250	30-50	1000-2000
Low density polyethylene	250-350	100-200	700-1500
Polystyrene	250-400	40-60	

Table 5. Water Vapor Transmission Rates for Selected Polymers (Delassus, 1997).

Polymer	WVTR (cc/100in^2*day*atm @38^{o}C, 90%RH)
Vinylidene chloride copolymer	0.003-0.25
High density polyethylene	0.48
Polypropylene	0.08
Low density polyethylene	0.175
Ethylvinyl alcohol (44% ethylene)	0.175
Polyethylene terephlate	0.225
Polyvinyl chloride	0.275
Ethylvinyl alcohol (32% ethylene)	0.475
Acrylonitrile	0.75
Polystyrene	0.9
Nylon 6	1.35
Polycarbonate	1.4
Nylon 12	7.95

Table 6. Effect of Relative Humidity on Oxygen Permeability (10^{11} mL*cm/cm^2*sec*cmHg) of Selected Films measured at 25^{o}C (adapted from Robertson, 1993)

Polymer	0%RH	100%RH
Poly(vinyl alcohol)	0.0006	1.5
Uncoated Cellophane	0.0078	12.0
Nylon 6	0.06	0.3
Poly(vinyl acetate)	3.3	9
Acrylonitrile-styrene copolymer	0.06	0.06
High density polyethylene	6.6	6.6
Low density polyethylene	28.8	28.8

Table 7. Transmission Rate (g*mm/m^2/day) of selected organic compounds through low density polyethylene. (adapted from Robertson, 1993)

Permeant	0^{o}C	21.1^{o}C	54.4^{o}C
Acetic acid	0.14	1.22	25.9
Benzaldehyde	0.15	2.67	81.0
Ethyl alcohol	0.75	6.5	149
Phenol	0.04	0.2	9.4
Propyl Alcohol	0.03	0.2	8.8
Toluene	22.7	199	2270
Xylene	14.2	101	1420

Table 8. Oxygen transmission of polymers in relationship to effect of orientation (Delassus, 1997).

Polymer	% Orientation	Oxygen transmission (cc/100in^2*day*atm)
Polypropylene	0 300	150 80
Polystyrene	0 300	420 300
Polyester	0 500	10 5
Acrylonitrile 70%/ Styrene 30% copolymer	0 300	1.0 0.9