



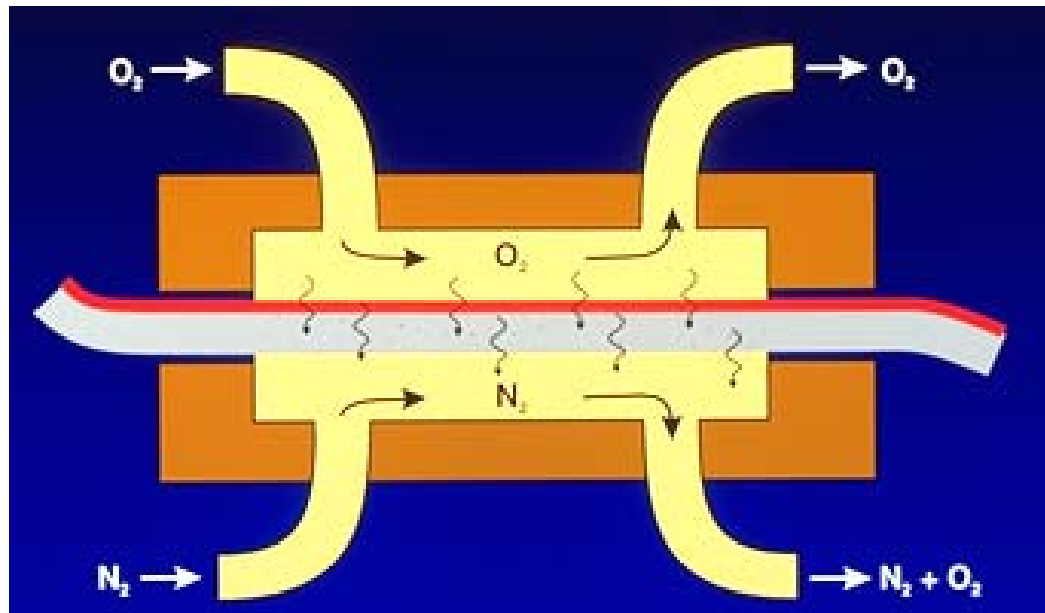
Permeation Basics II

MOCON Web Seminar Series

Presenter: Michelle Stevens

[Permeation]

The movement of gases or vapors across a packaging material



Solution-diffusion mechanism (Graham's *colloidal diffusion*)

- The gas is sorbed at the entering face and dissolved
- The dissolved penetrant molecules then diffuse through the membrane and
- Desorb at the exit face.

[Permeation]

$$J = \frac{Q}{AT}$$

Where J is the diffusive flux, Q is the total amount of permeant that has passed through area A during time t

Permeation

Fick's 1st Law:

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

Where J is the flux per unit area of permeant through the polymer, D is the diffusion coefficient, and $\delta c/\delta x$ is the concentration gradient of the permeant across a thickness δx

Permeation

Fick's second law:

$$\frac{\delta C}{\delta t} = D \frac{\partial^2 C}{\partial x^2}$$

Applies under circumstances where diffusion is limited to the x-direction and D is independent of concentration

Steady state permeation

$$J = D \frac{\partial C}{\partial x} = D \frac{(c_1 - c_2)}{X}$$

When the steady state of diffusion has been reached, $J = \text{constant}$. After integration across polymer thickness, X , and 2 concentrations:

Steady state permeation

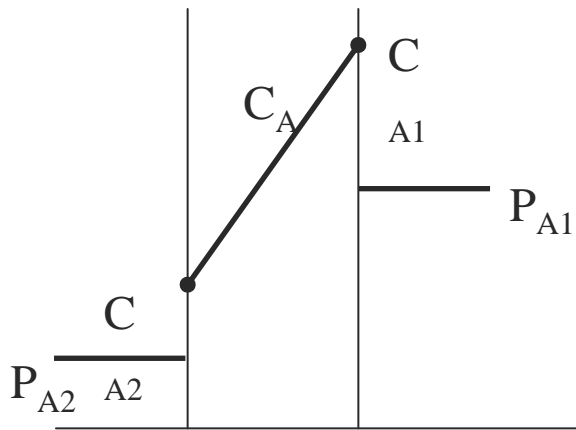
Substitution for J yields:

$$J = \frac{Q}{AT} \quad J = D \frac{(c_1 - c_2)}{X}$$

$$Q = D \frac{(c_1 - c_2)At}{X}$$

When the permeant is a gas, it is more convenient to measure the vapor pressure p which is at equilibrium with the polymer rather than the actual concentration

Henry's Law



The concentrations are related to the partial pressures by a solubility coefficient, S (the reciprocal of Henry's Law coefficient)

$$C_A = P_A S_A$$

Substitution yields:

$$Q = DS \frac{(p_1 - p_2)At}{X}$$

Steady state permeation

The product DS is referred to as the permeability coefficient, P .

Substitution and rearrangement gives:

$$P = \frac{QX}{At(p_1 - p_2)}$$

$$\frac{cc \times mil}{m^2 \times day \times atm}$$

Pasternak's Solution of Fick's Law

$$F(x) = -D(dc/dx)$$

Assumptions:

The diffusion coefficient D is not a function of the concentration

The surface concentration is proportional to the pressure of the permeant

The swelling of the polymer is negligible.

Pasternak's Solution of Fick's Law

Boundary conditions:

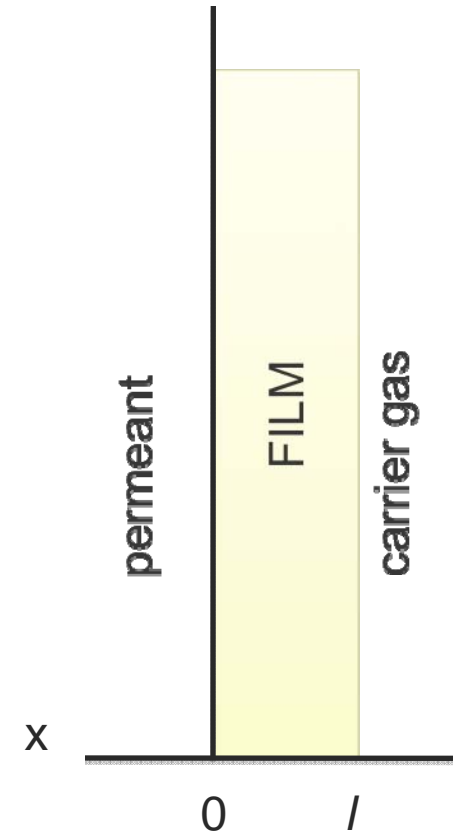
$$x = 0 \quad c = 0 \quad t = 0$$

$$0 \leq x \leq l \quad c = 0 \quad t = 0$$

$$x = 0 \quad c = c_f \quad t > 0$$

$$x = l \quad c = 0 \quad t \geq 0$$

$$0 \leq x \leq l \quad c = c_f(l-x)/l \quad t = \infty$$



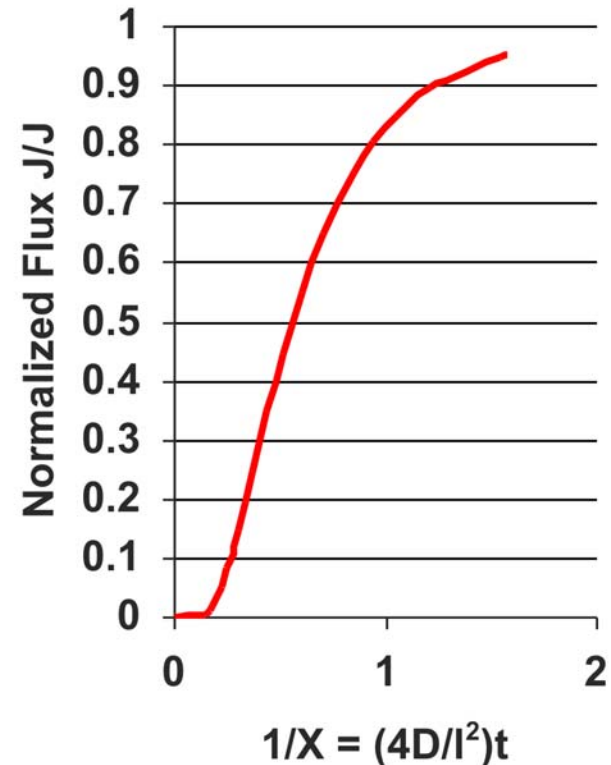
Pasternak's Solution of Fick's Law

Theoretical permeation curve for constant diffusion coefficient

$$\frac{\Delta J}{\Delta J_{\infty}} = \left(\frac{4}{\sqrt{\pi}} \right) \sqrt{X} \exp\{-X\}$$

Where $X = l^2/4Dt$

This first order approximation of the previous equation holds for $\Delta J / \Delta J_{\infty} < 0.95$



Permeability

- Permeability can be defined as the product of the solubility coefficient and the diffusion coefficient
- $P=S \cdot D$
- Generally, P and S can be directly measured and D can be calculated.
- However, there are indirect methods for measuring D as well.

[Diffusion]

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions.

Diffusion refers to the net transport of material within a single phase in the absence of mixing.

In Fickian systems, D is independent of concentration.

Units of D : $\frac{cm^2}{sec}$

[Solubility]

Solubility represents the dissolution of permeant into polymer and relates the concentrations within the film to the partial pressure of the permeant.

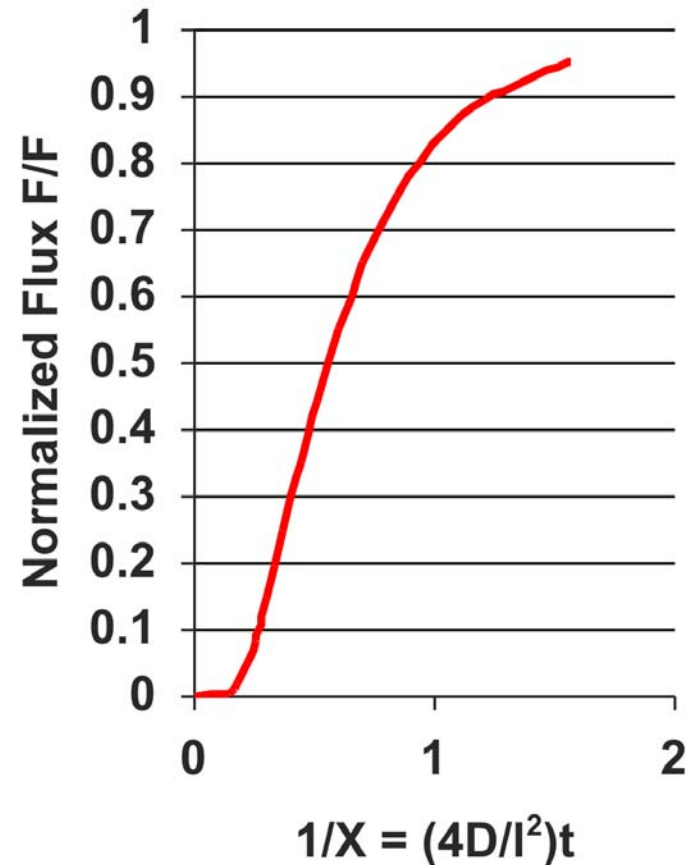
Solubility is dependent upon permeant concentration or driving force.

Units of S: $\frac{cm^3 (STP)}{cm^3 - mmHg}$

Isostatic permeation measurement

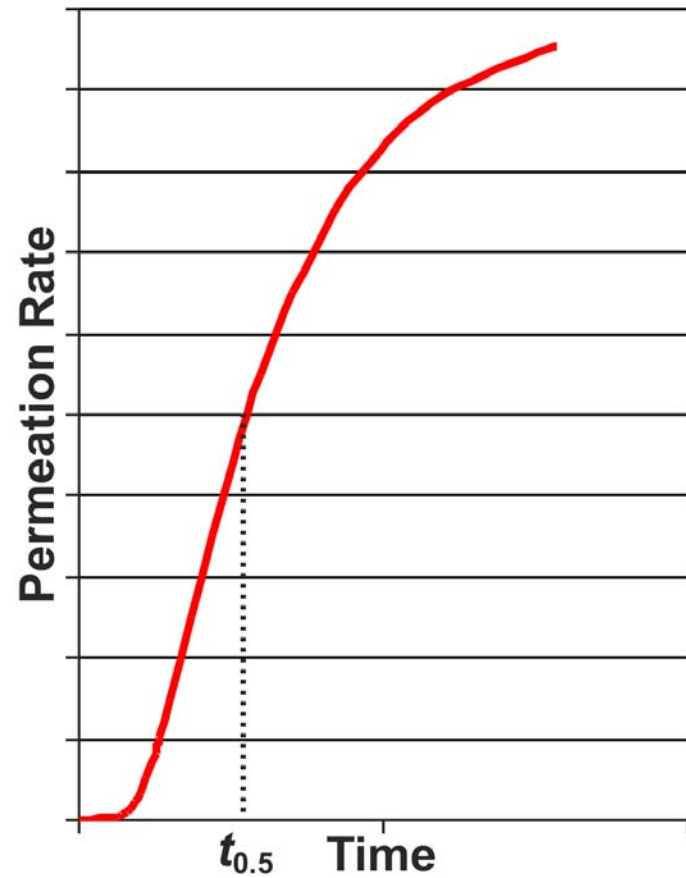
$$\frac{\Delta F}{\Delta F_{\infty}} = \left(\frac{4}{\sqrt{\pi}} \right) \sqrt{X} \exp\{-X\}$$

Theoretical permeation curve for constant diffusion coefficient

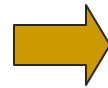
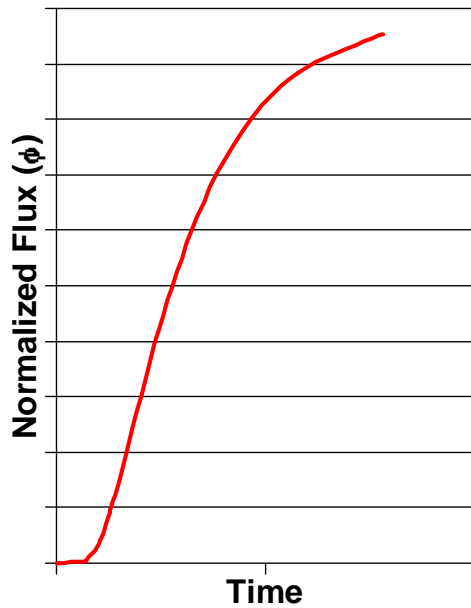


[Half-time method]

$$D = \frac{\ell^2}{7.199t_{0.5}}$$

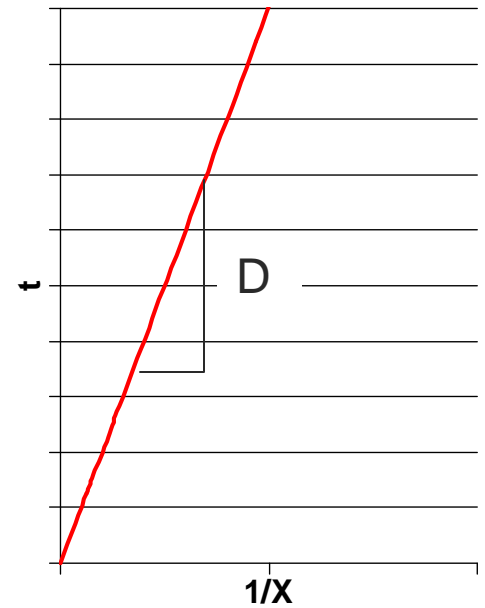
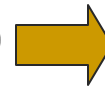


Gavara and Hernandez



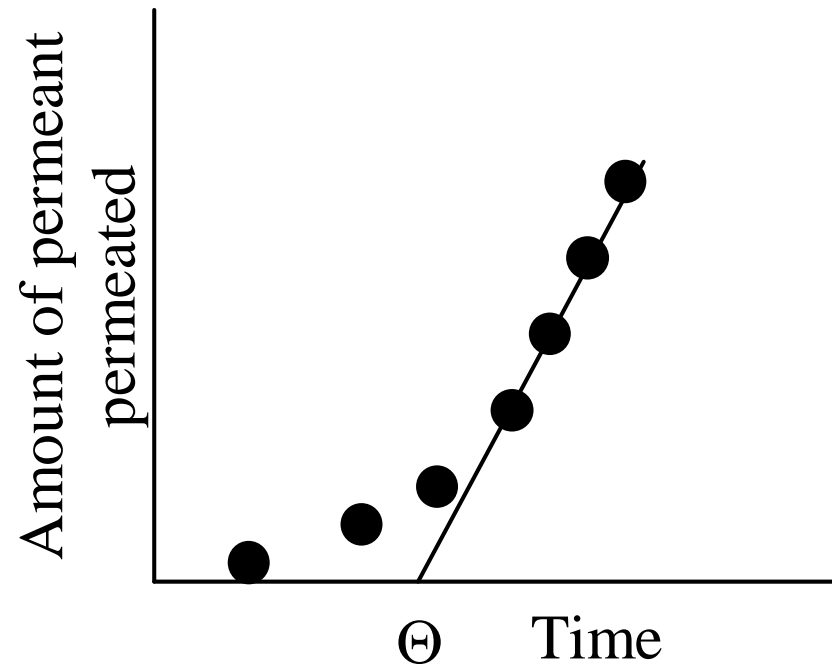
$$\phi = \left(\frac{4}{\sqrt{\pi}} \right) X^{\frac{1}{2}} \exp(-X)$$

(Newton-Raphson)



Time lag method

$$D = \frac{l^2}{6\Theta}$$



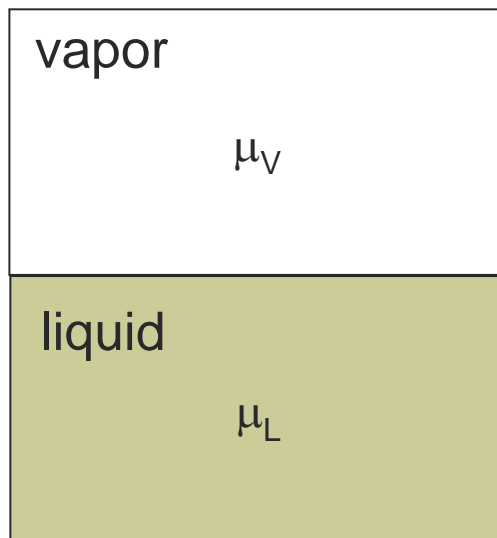
Effective diffusion coefficient

- Isostatic permeation experiment to directly measure equilibrium P
- Directly measure equilibrium S
 - Desorption
 - Gravimetric
- Calculate effective D
 - $P=(S)(D)$

Chemical Potential

Chemical potential, μ , is the actual driving force for permeation.

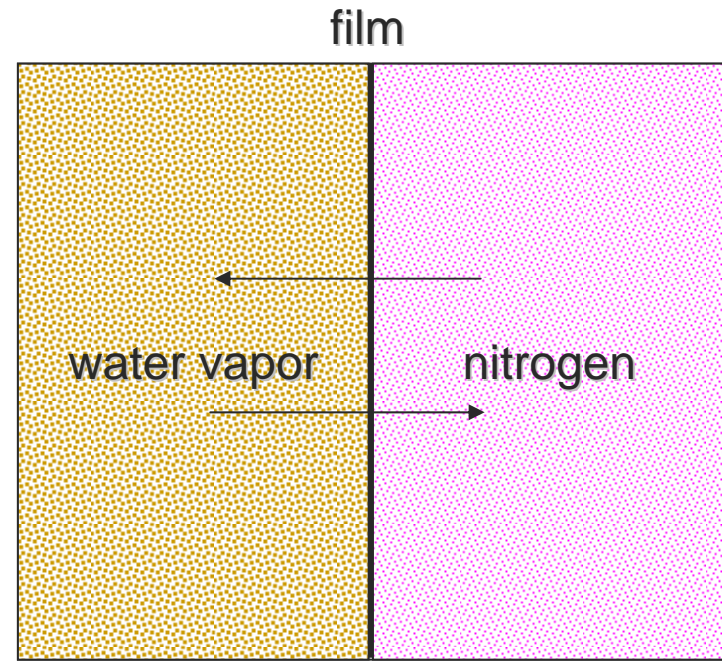
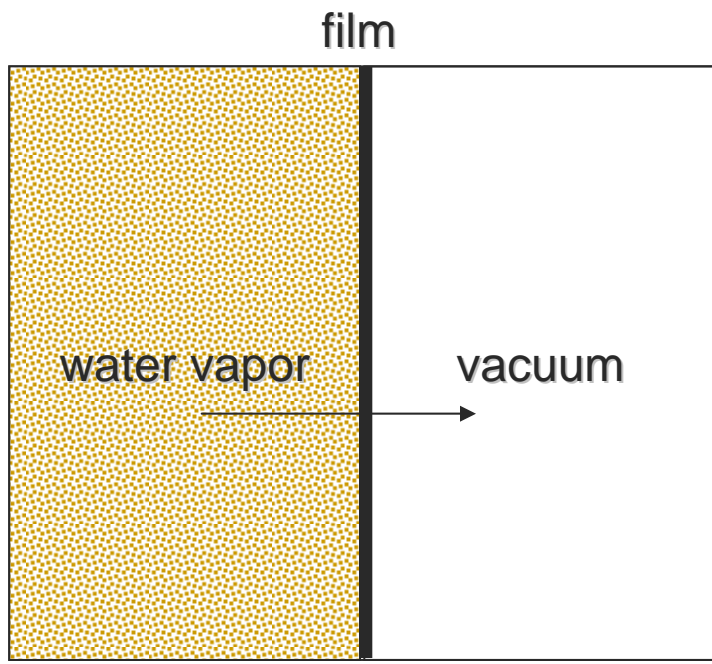
Chemical potential is a thermodynamic property related to pressure.



For *Vapor Liquid Equilibrium* (VLE),

$$\mu_L = \mu_v$$

[Permeation]



$$P_{wv} = X \quad \longleftrightarrow \quad \begin{matrix} P_{wv} = X \\ P_{nitrogen} = y \end{matrix}$$

Temperature

Arrhenius equation:

$$P = P_0 e^{\frac{-E}{RT}}$$

P = Permeation rate

P_0 = Permeability constant

E = Activation energy

R = Gas constant

T = Temperature



MATERIAL PROPERTIES

[Polymer backbone]

Polymer chains must “move aside” or “open up” to allow permeation.

The weaker the forces holding the chains together, the more rapidly the permeation will occur.

The chain-to-chain forces are determined by the chemical nature of the backbone.

Polymer backbone

POLYMER	STRUCTURE	OXYGEN PERMEATION*	COMMENTS
Polyethylene	$\text{H}_2\text{C}=\text{CH}_2$	480	Low polarity, very little cohesion between chains
Polypropylene	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{CH}_3 \end{array}$	150	Chains are a little stiffer, but very little cohesion or attraction
Poly(methyl methacrylate)	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}$	17	Chains are much stiffer due to steric hindrances; polarity results in chain-to-chain attraction superior to hydrocarbon polymers
Poly(vinyl chloride)	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{Cl} \end{array}$	8	Chain-to-chain attraction very high due to chlorine electrons; movement of chains restricted

* cc-mil/100 in²-day-atm

The degree of packing, crystallinity, and orientation of the molecular chains

Close packing and/or high crystallinity results in low free volume and better barrier.

Orientation results in better barrier by creating a more tortuous diffusion path.

POLYMER	MORPHOLOGY	O ₂ PERMEATION*	COMMENTS
PET (poly(ethylene terephthalate))	10% crystalline	10.0	
PET	50% crystalline	5.0	Higher crystallinity reduces the available sites for permeation
PET	50% crystalline and oriented	3.0	Crystallinity and orientation produces more tortuous path for permeation

The susceptibility to moisture and other possible interactants with the chains

- Some chemical species are adversely affected by moisture absorption and thus barrier is reduced.
- Water, which is highly polar, will only react this way with polar polymer groups that depend upon hydrogen bonds.
- Other polar groups, although they might absorb water, are not affected since their barrier properties do not depend upon hydrogen bonds.

Effect of Relative Humidity on OTR

Polymer	0%RH	100%RH
PVOH	0.0006	1.5
Uncoated Cellophane	0.0078	12.0
Nylon 6	0.06	0.3
PVA	3.3	9.0
ABS	0.06	0.06
HDPE	6.6	6.6
LDPE	28.8	28.8

The nature of the polymer surface contacting the permeant

- The nature of the surface can determine the permeability as much as the polymer bulk.
- An example is hydrocarbon permeation through polyethylene:
 - Polyethylene polymer is very nonpolar and thus a very poor barrier to nonpolar permeants such as hydrocarbon liquids.
 - By treating the surface with fluorine gas, the fluorine adds on to the chains at or near the surface and by virtue of its bulk and polarity prevents hydrocarbon liquids from entering the polymer

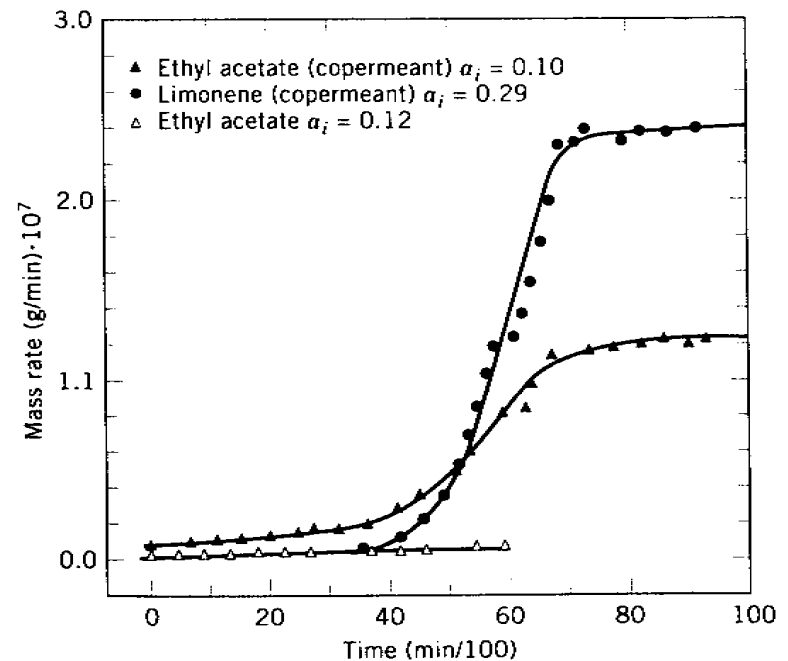
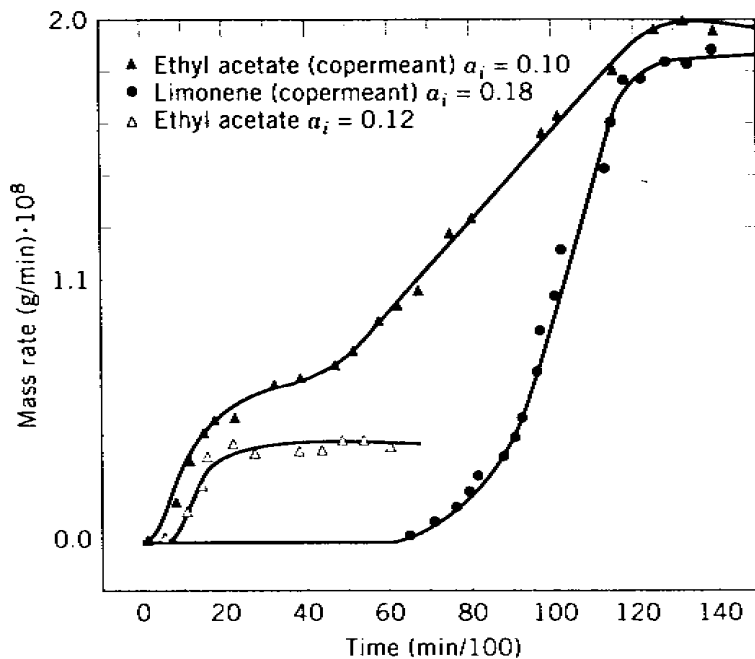
Additives used in manufacturing or modifying the polymer

- Depending upon the chemical nature, as well as the manner which the additive is blended, the barrier can be either enhanced or reduced.

PVC		
Poly (vinyl chloride)		
Material state	Pure, rigid PVC	Plasticized, soft PVC
O ₂ Permeation rate (cc-mil/100 in ² -day-atm)	8	150

Presence of Copermeant

Example – ethyl acetate and limonene, used with BOPP



Thickness

- Typically the transmission rate is inversely proportional to the thickness of the material

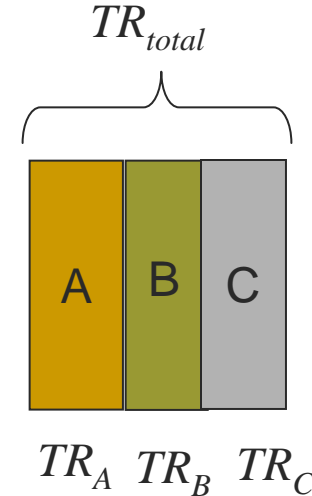
thickness ↑ transmission rate ↓

- This may not apply for very thin materials where structural changes or surface phenomena may have occurred.

Multiple layers

- Multi-layer materials obeying Fick's Law can be mathematically “added” by means of the *Parallel Resistance Equation*.

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

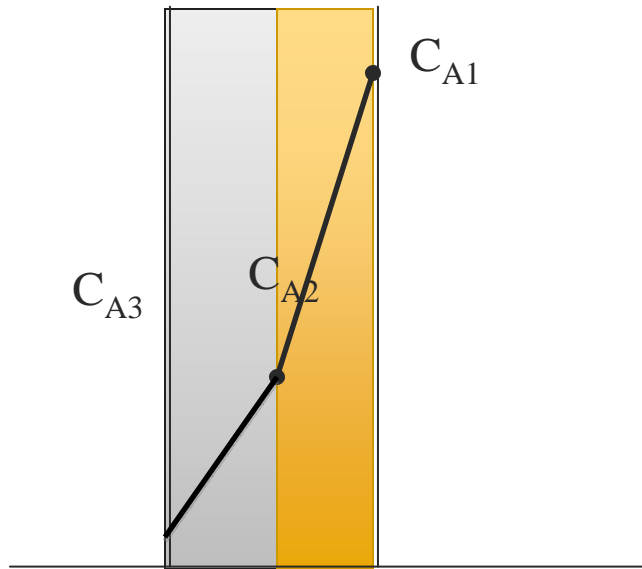




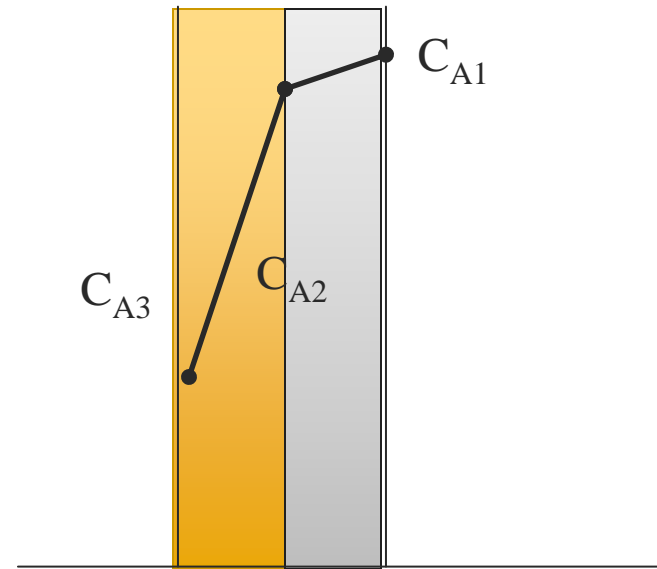
**MOISTURE INGRESS = MOISTURE EGRESS
(USUALLY!!!)**

WVTR of multi-layer material containing moisture sensitive layer

Moisture sensitive side protected



Moisture sensitive side exposed



= water vapor barrier



= water vapor sensitive

Thank You!

Questions?

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