Flexible Food Packaging for the 21st Century and Beyond

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A Little Quote

"Knowledge and Timbers shouldn't be much used 'till they are seasoned."

Oliver Wendell Holmes, 1858

Outline

- Review of classical multi-layer film structure
- Understanding the Physics of Mass Transport
- Practical Knowledge of Barrier
- Barrier Technologies

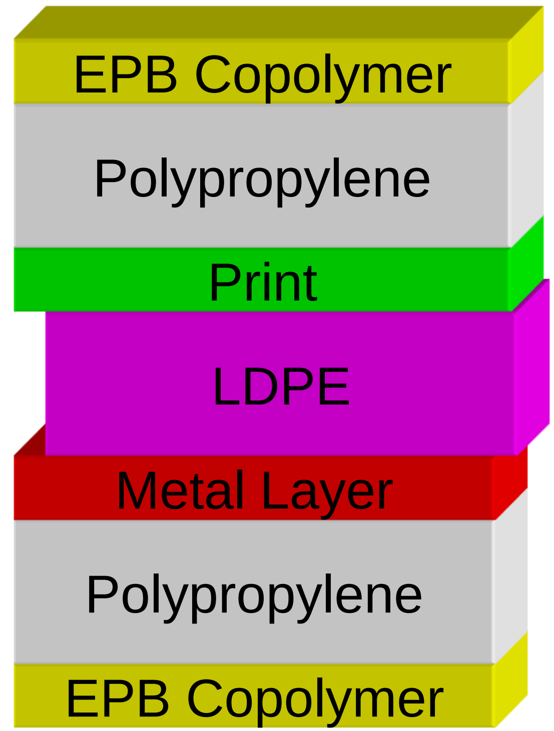
FILM STRUCTURES

Typical Opaque Laminated Film

Film Gauge: 0.0025”

- Print Film
- Lamination Layer
- Barrier Film

Cross-Section

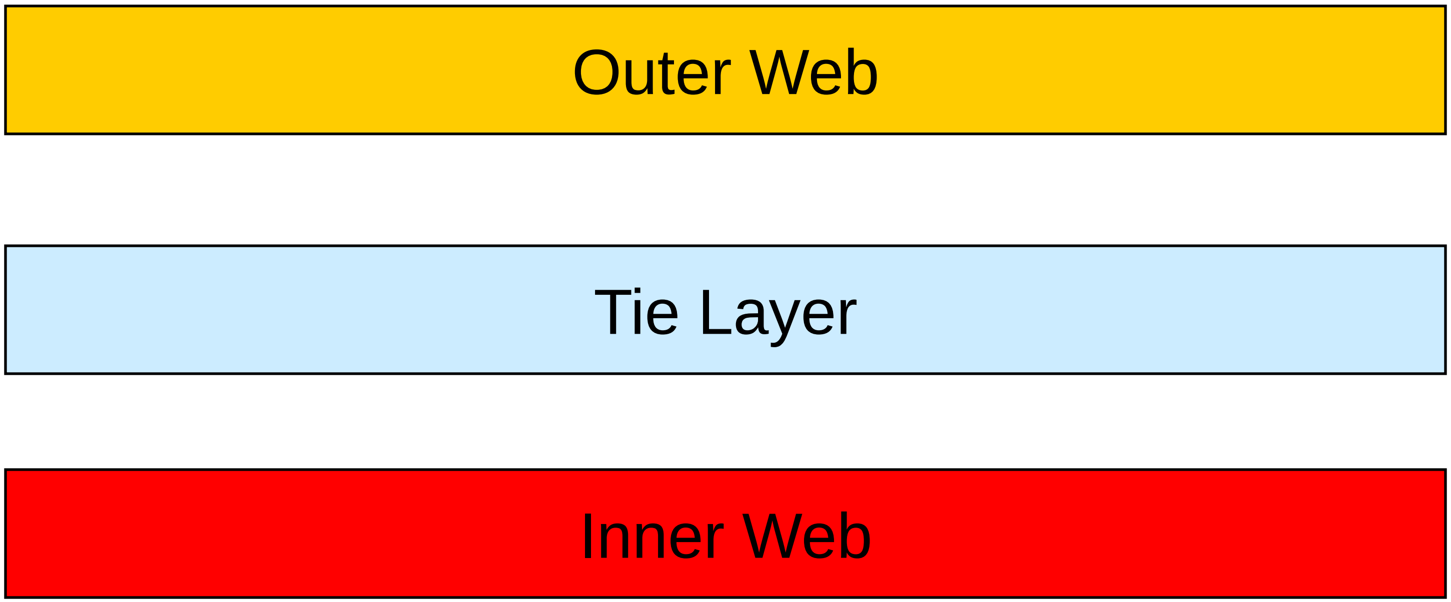


inside

Function

- Sealing
- Clarity
- Graphics
- Inter-layer Adhesion
- Barrier
- Stiffness
- Sealing

Typical Packaging Film Structure



Typical Layer Materials

Oriented Polypropylene

Polyethylene

Metalized Oriented Polypropylene

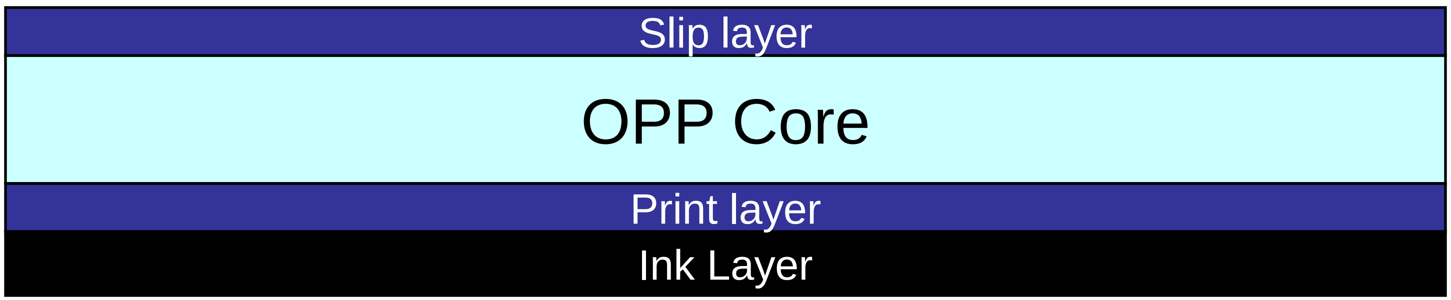
Flex. Pkg.- Materials Key Attributes

Print web: gloss (or matte), stiffness, machine-ability

Tie layer: stiffness, barrier

Barrier web: sealant, stiffness

Outer Web



The Outer web is typically a three layer structure,
Featuring a core, a slip layer, and a print surface.
Graphics are reverse printed by the converter.

Tie Layer

Polyethylene

Polypropylene (Or EVOH)

Polyethylene

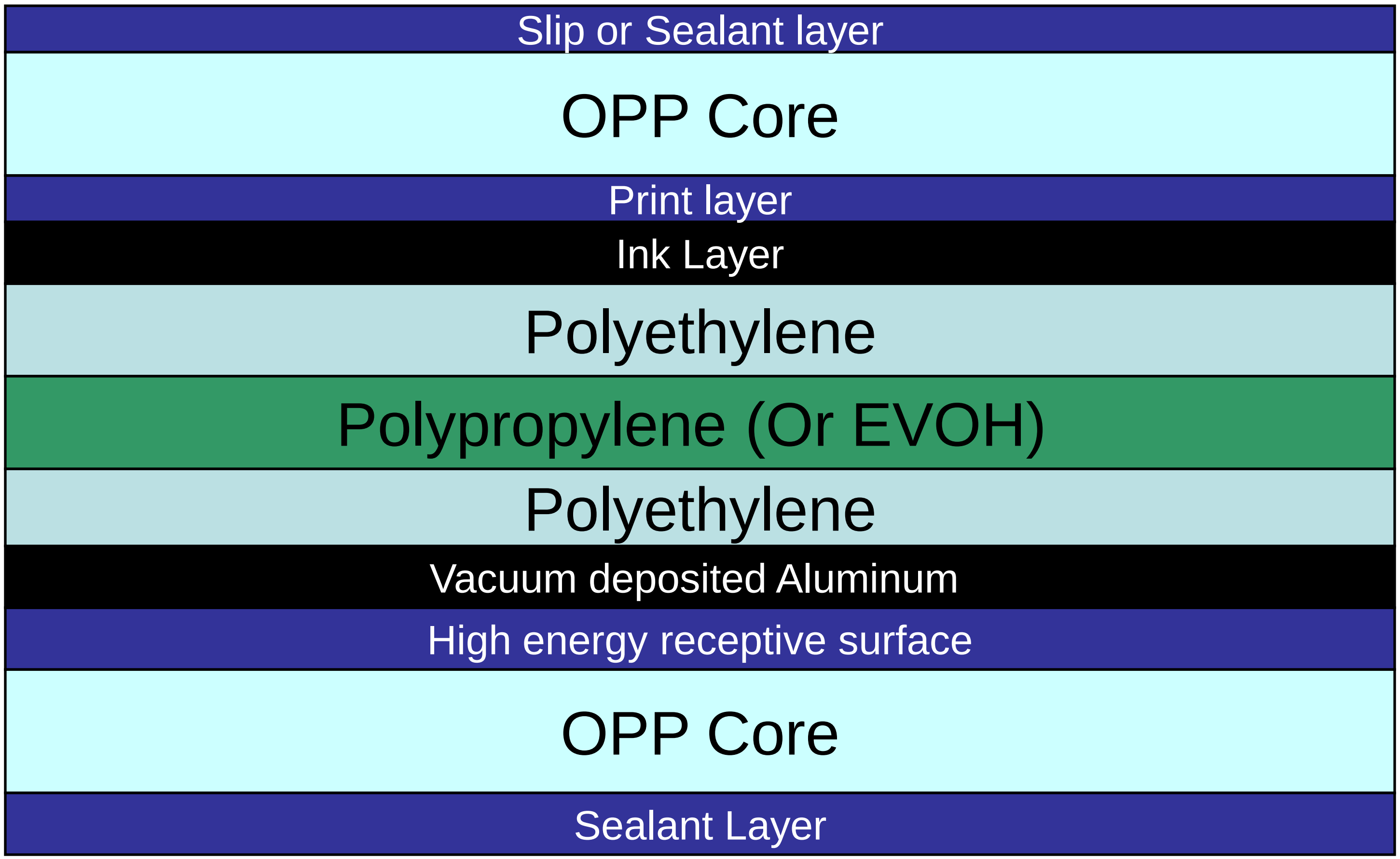
The tie layer bonds inner/outer webs together, provides stiffness, package opening for the consumer, and occasionally O_2 barrier

Inner Web

Vacuum deposited Aluminum
High energy receptive surface
OPP Core
Sealant Layer

The inner web is typically a three to four layer film, which provides heat seal, stiffness, and barrier against oxygen, moisture, and light.

Typical Packaging Film Structure



MASS TRANSPORT: THE MATHEMATICS

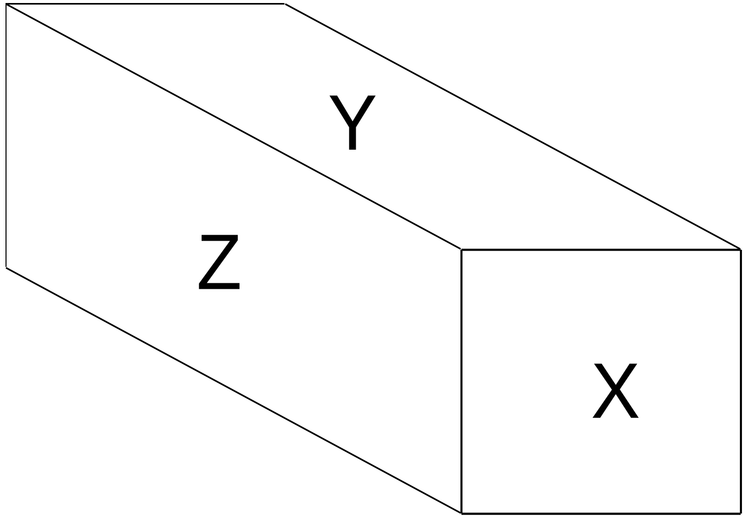
"Do not worry about your difficulties in Mathematics. I can assure you mine are still greater."

Albert Einstein

Continuity Equation and Mass Transport

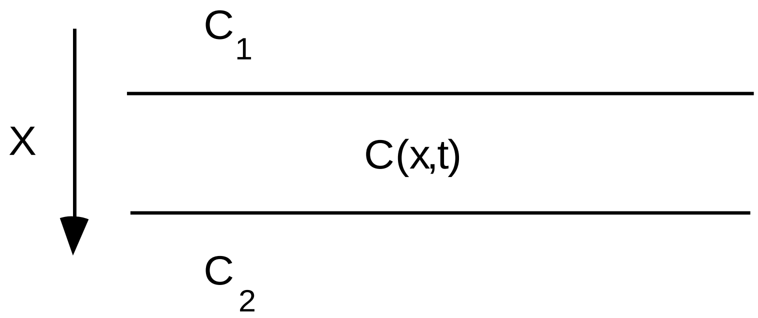
- General case of diffusion

$$\frac{\partial c}{\partial t} + \frac{\partial j_x}{\partial x} + \frac{\partial j_y}{\partial y} + \frac{\partial j_z}{\partial z} = 0$$



- One dimensional case of diffusion

$$\frac{\partial c}{\partial t} = -\frac{\partial j_x}{\partial x}$$



Fick's Laws of Diffusion

- Diffusion coefficient, D, relates concentration profiles to flux within a film (polymer).
- Fick's first law:

$$j_a = -D_{ab} \frac{\partial c_a}{\partial x}$$

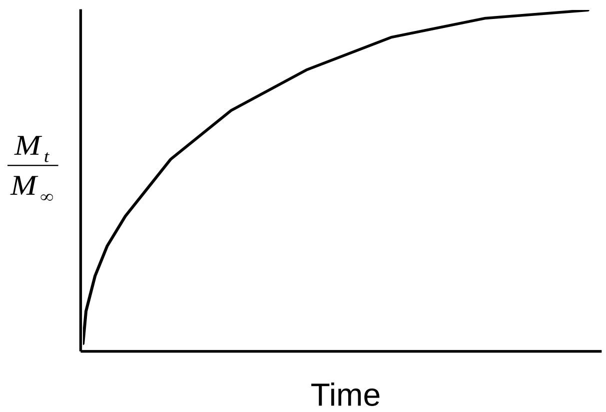
- Fick's second law:

$$\frac{\partial c_a}{\partial t} = D_{ab} \frac{\partial^2 c_a}{\partial x^2}$$

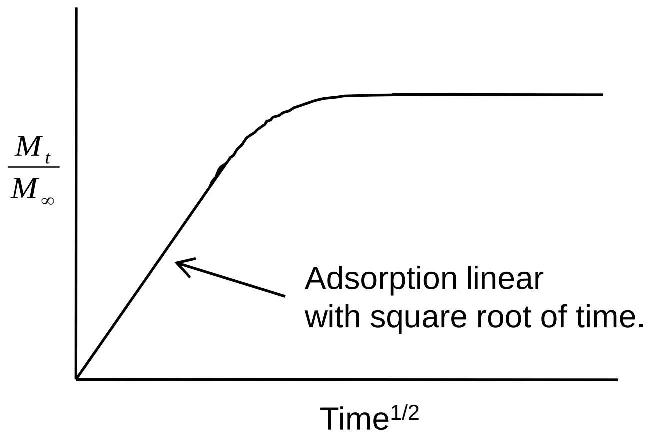
  – Case of 1-D unsteady state transport through a membrane

Different Cases of Mass Transport

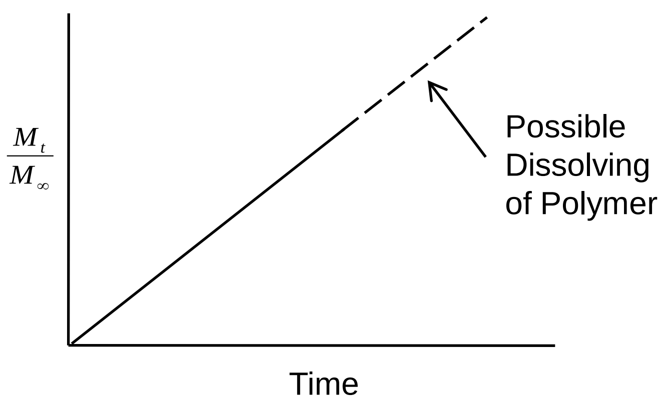
Fickian Diffusion



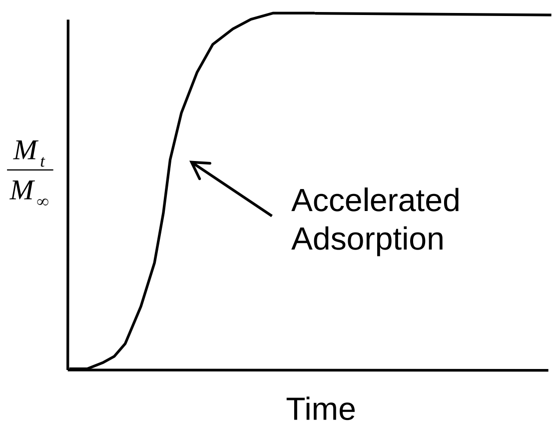
Fickian Diffusion (time$^{1/2}$)



Case II, or Solvent Front Transport



SuperCase II (Activated) Diffusion



These behaviors may be observed by measuring the weight of a film over time. A film surrounded by water vapor for example.

Determining Transport Case

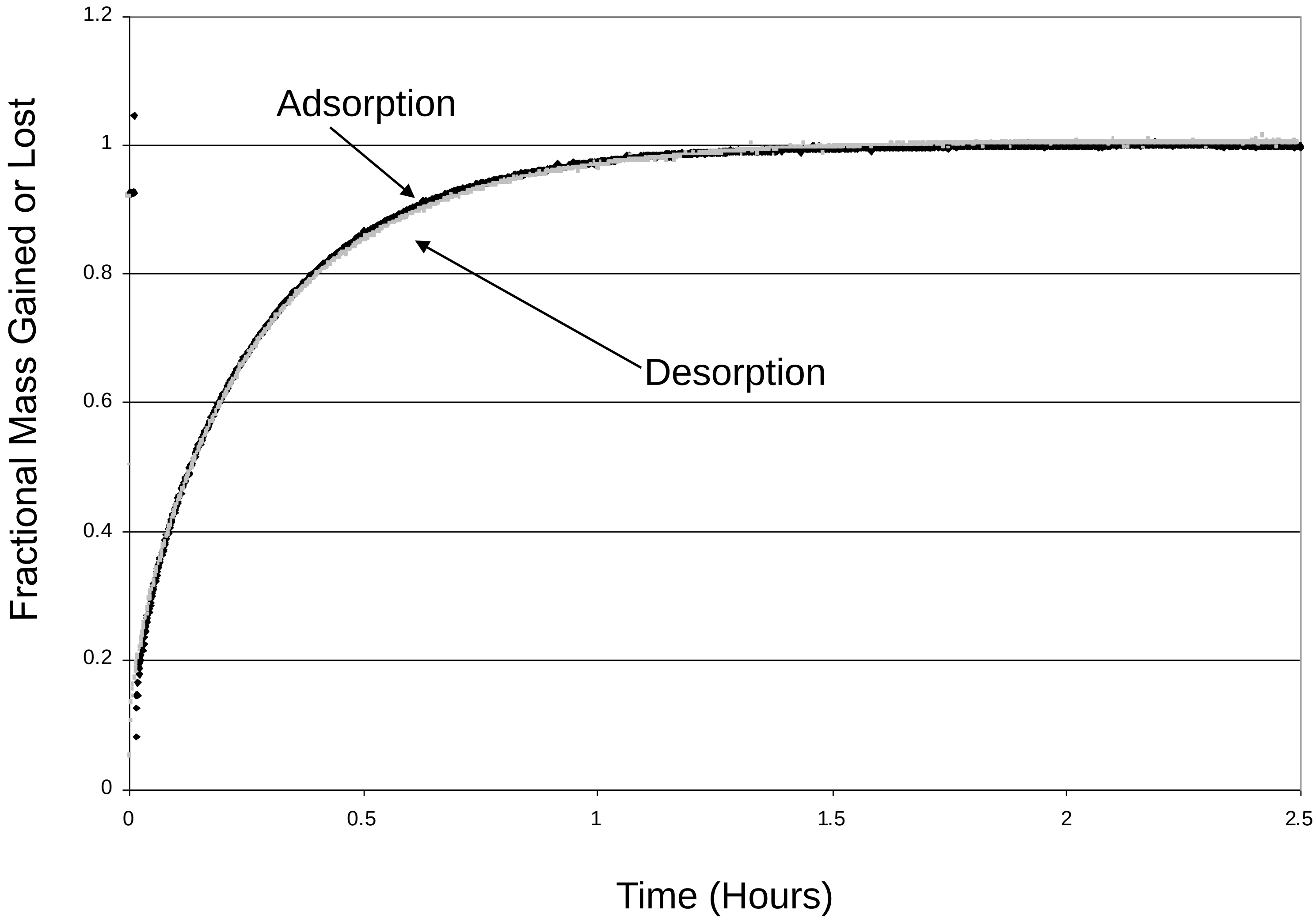
- Mass Uptake versus time:

$$\frac{M_t}{M_\infty} = kt^n$$

  - Where M_t = mass at time t
    M_∞ = mass at equilibrium
    k = proportionality constant
    n = power index
  - Power Index (n) determines Transport Case

- May be determined plotting by weight uptake over time

Example of Fickian Diffusion

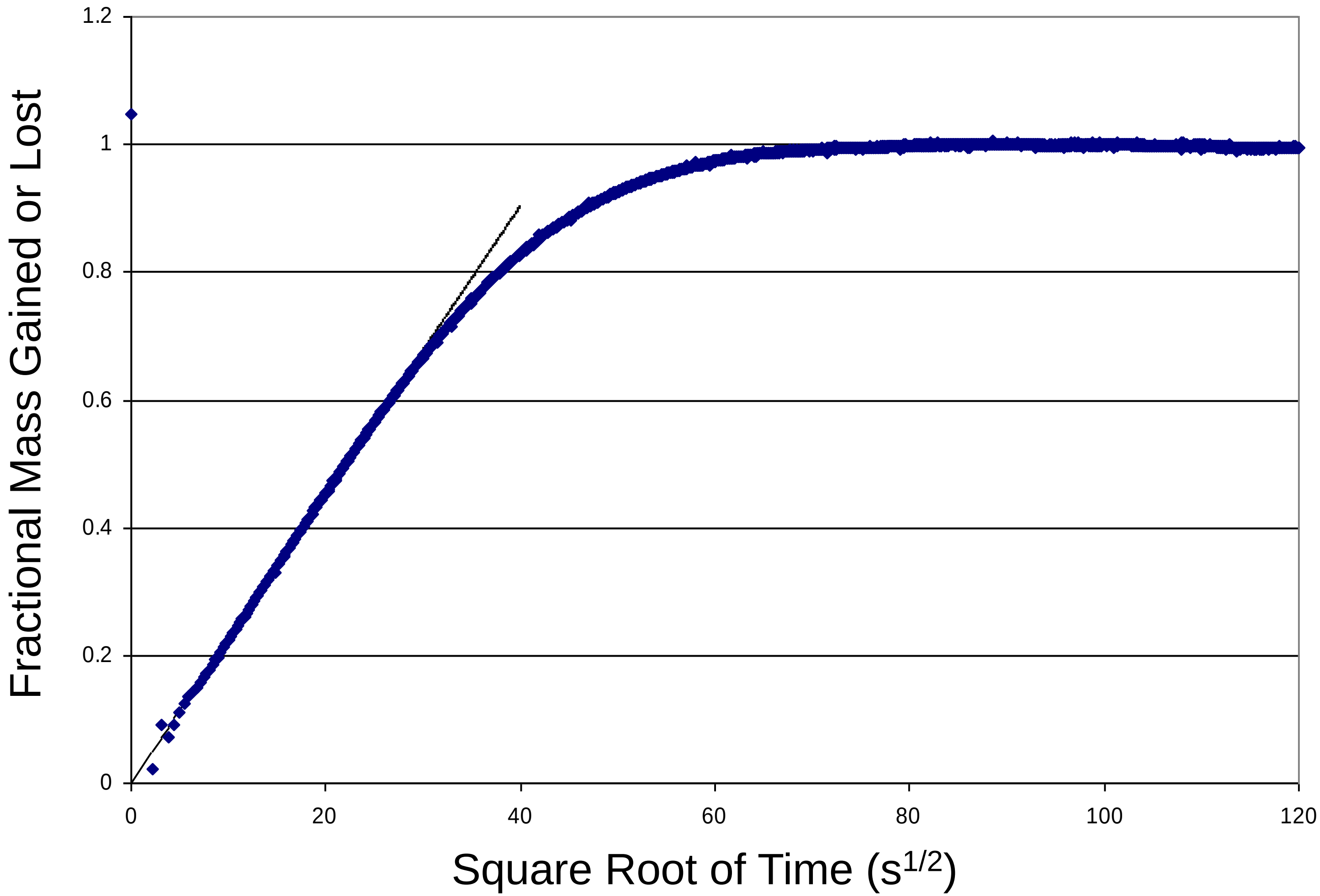


Fickian Diffusion -- Curve of CO_2 Ad/desorption within Polymer Film

Fickian Diffusion vs. Time$^{1/2}$

1 hr = 3600s;

$\sqrt{3600} = 60$



Fickian Diffusion – Demonstration of linear behavior

Diffusion Coefficient by 'Initial Slope' Method

- 'Initial Slope Method'

$$\frac{M_t}{M_\infty} = 8\left(\frac{Dt}{L^2}\right)^{1/2}\left[\pi^{-1/2} + 2\sum_{m=0}^{\infty}(-1)^m \, ierfc\,\frac{mL}{4(Dt)^{1/2}}\right]$$

Crank, "Mathematics of Diffusion", 1975.

- Fickian diffusion
  - Initial slope of mass uptake is linear with $t^{1/2}$.

- For short times and Fickian diffusion,

$$\frac{M_t}{M_\infty} = \frac{8}{L}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2}$$

Other Methods to Extract D_{eff}

- 'Half-time Method'

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left(-\frac{4D(2m+1)^2\pi^2 t}{L^2}\right)$$

Crank, "Mathematics of Diffusion", 1975.

D from half time of mass uptake: $D = \frac{L^2}{4\pi^2 t_{1/2}} Ln\frac{16}{\pi^2}$

- 'Limiting Slope Method'

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\frac{8}{\pi^2} - \left(\frac{4D\pi^2 t}{L^2}\right)$$

Berens, A. R., *Polymer* **1977**, *18,* 697.

Slope of $\ln\left(1 - \frac{M_t}{M_\infty}\right)$ versus time $\longrightarrow -\left(\frac{4D\pi^2}{L^2}\right)$

Other Methods to Extract D_{eff}

- 'Half-time Method'

Plenty of methods to compute D_{eff}, each has its own built-in assumptions and accuracies.

$$\ln\left(1-\frac{M_t}{M_\infty}\right) = \ln\frac{8}{\pi^2} - \left(\frac{4D\pi^2 t}{L^2}\right)$$

Slope of

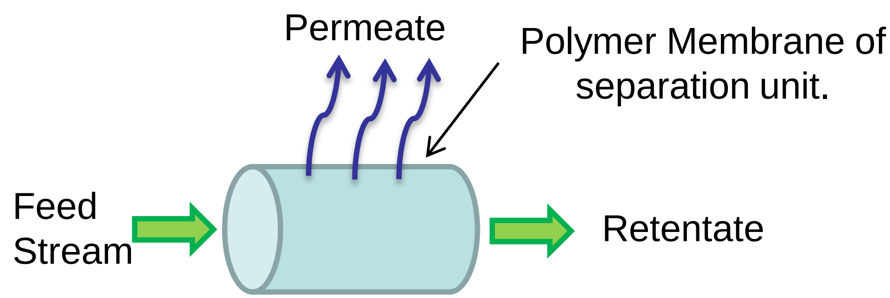
$$\ln\left(1-\frac{M_t}{M_\infty}\right) \longrightarrow -\left(\frac{4D\pi^2}{L^2}\right)$$

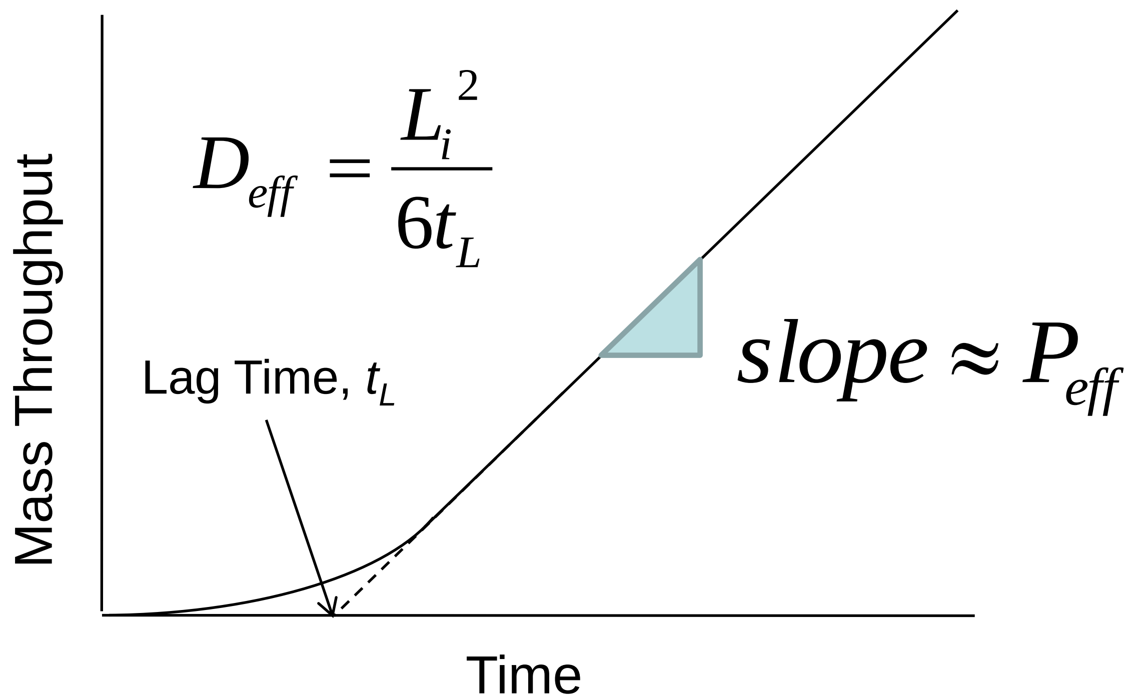
versus time

Berens, A. R., *Polymer* **1977**, *18,* 697.

Lag Time Method

Employed with Permeation Cells



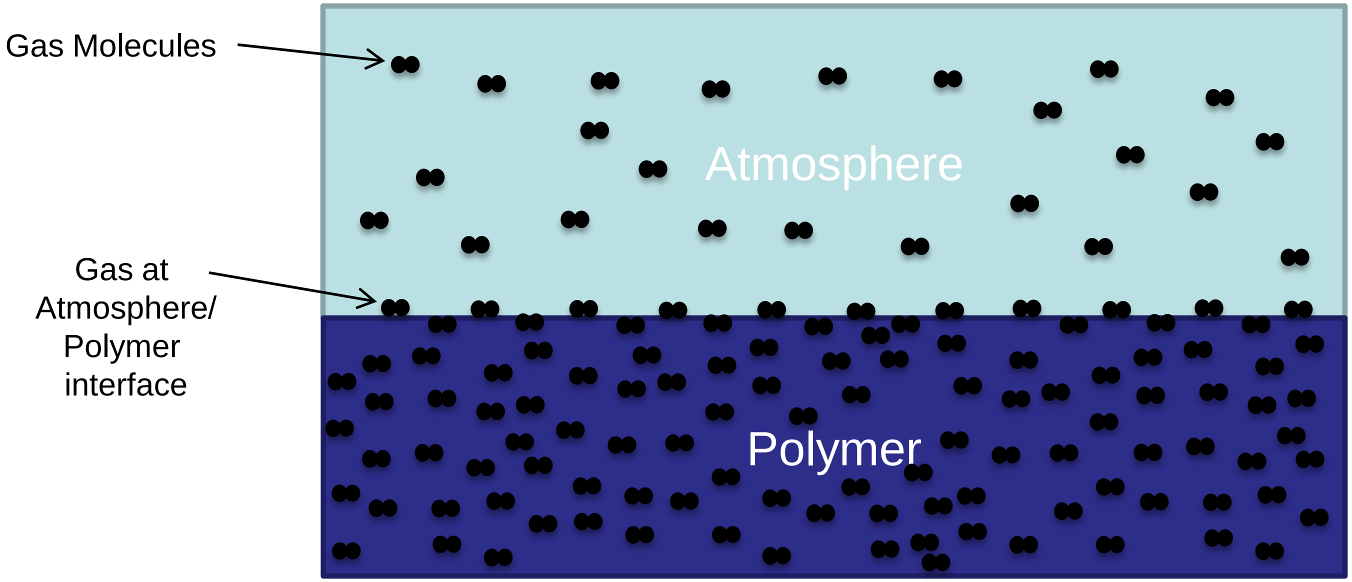


$$D_{eff} = \frac{L_i^{2}}{6t_L}$$

$$slope \approx P_{eff}$$

Solubility

- Solubility coefficient, S
  - Partitioning of a component within two different phases
- Gas solubility in a solid
  - Henry's Law: $c_i = S_i p_i$



MASS TRANSPORT:
THE APPLICATION

"Permeation by the Units"

- Permeation, Diffusion, and Solubility Coefficients:

$$P = D * S$$

Penetration distance

- D [=] $cm^2/s \equiv cm * (cm/s)$ ← Penetration Velocity

Volume of Adsorb Gas

- S [=] cc (STP) /(cm^3 {polymer} * atm)

Volume of Solid

Driving Force

- P [=] (cc (STP) * cm) / (cm^2 * s * atm) ≡ (cc(STP)/cm^2 * s) * cm* (1/atm)

Flux

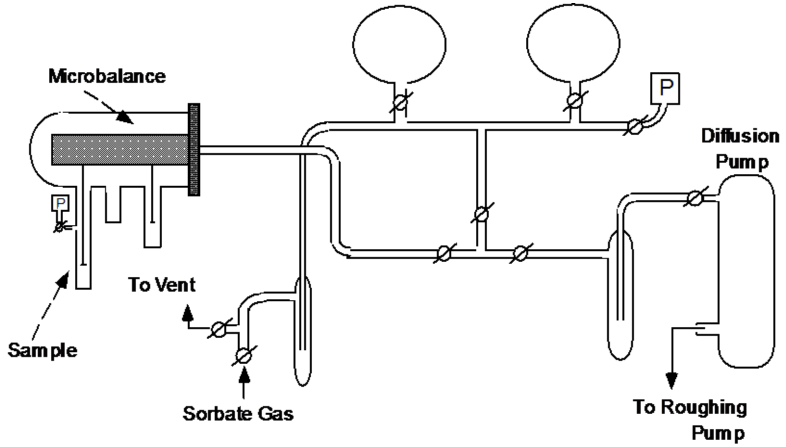
Gauge

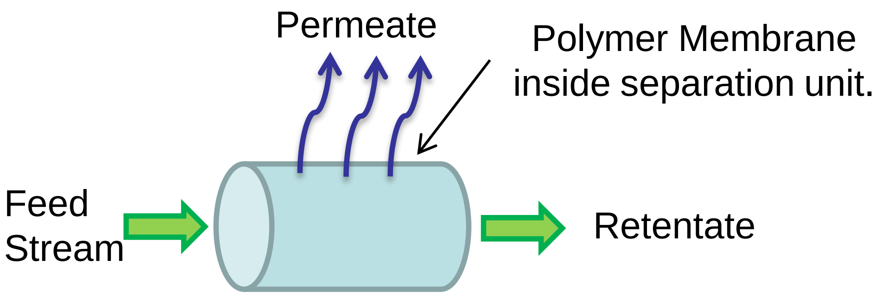
Driving Force

Permeation, Permeance, and Transmission Rate

- Permeation Coefficient
  – P [=] mass * film gauge / (area * time * (delta) pressure)
  – Mass Transport normalized to gauge and conditions
- Permeance
  – Permeance [=] mass / (area * time * (delta) pressure)
  – Mass Transport normalized to conditions for a specific film gauge
- Transmission Rate
  – TR [=] mass / (area * time) ≡ flux
  – Mass Transport at specific gauge and conditions.

Methods of Mass Transport Measurement





- Gravimetric Sorption
  - Easy to identify types of transport behavior.
  - Samples may exhibit a low mechanical integrity.
  - Fluids must have a high solubility in the polymer to observe transport.

- Permeation Cell
  - Standardized characterization technique.
  - Samples must form mechanically stable, continuous film.
  - Fluids are not required to be highly soluble in order to observe transport behavior.

Mocon Permatran (http://www.mocon.com)

Oxygen vs. Water: Differences in Barrier

Property	*Oxygen*	*Water Vapor*
Composition of Atmosphere	21%	1%
Gas	Permanent	Condensable
Polarity	Non-Polar	Polar
Diffusion	Fickean	Fickean and Type II
Solubiilty	Low for all polymers	Low for polyolefins (hydrophobic) and High for cellulose/EVOH (hydrophilic)
Permeation Control	Diffusion	Diffusion and Solubility
Barrier Effectiveness	Pin Hole Defects	Surface Area Coverage

Oxygen requires only a diffusion barrier;
Water requires both diffusion and solubility barriers.

Transmission Rates;
An example from the web.

	Low	Average	High	Units
PP, WVTR	0.122	0.311	0.702	g/100 in²/day
PP, OTR	0.00644	2.02	4.51	cc/100 in²/day
PET, WVTR	0.0316	0.265	0.386	g/100 in²/day
PET, OTR	13	28.2	58.4	cc - mil/100 in²/day/atm

Red = PP with functional barrier, PVDC or metallization
Blue = PP with no functional layers

Source: http://www.matweb.com

Transmission Rates: The Literature

Film Classification ASTM D-1600	Film Modification	Permeability, 25ºC (cc * mil)/(100 in² * day * atm) Oxygen ASTM D-1434	Permeability, 25ºC (cc * mil)/(100 in² * day * atm) Carbon Dioxide ASTM D-1434	Water Vapor Transmission Rate 38ºC, 50 to 100% RH (cc * mil)/(100 in² * day) ASTM E-96
Polyamide	None	2.6	11 ± 1.0	19 ± 3
Polyamide	Biaxially Oriented	1.3	No Data	10.5
Polyamide	PVDC Coated	0.5	1.4	0.2
Polyamide	Metallized	0.05	No Data	0.2
PET	None	4.5 ± 1.5	20 ± 5	1.2
PET	PVDC Coated	0.4	No Data	0.9
PET	Metallized	0.08	No Data	0.1
LDPE	None	500	2700	1.3
LLDPE	None	545 ± 295	2750 ± 2250	1.2
HDPE	None	185	580	0.3
PP	None	250 ± 160	925 ± 425	1.75 ± 0.25
PP	Biaxially Oriented	135 ± 25	390 ± 150	0.5 ±0.2
PP	Metallized	3	No Data	0.33 ± 0.08
PS	None	330 ± 165	1160 ± 520	8.5
PVC	None	17 ± 13	27 ± 23	3.0 ± 2.0
PVC	Plasticized	450 ± 150	4500 ± 1500	17 ± 12
PVDC	None	3.9 ± 3.0	24 ± 20	0.35 ± 0.3

R. Tock, *Advances in Polymer Technology*, Vol. 3, No. 3 (1983), pp. 223-231

Select Coefficients for Film

Polymer	Oxygen		Carbon Dioxide	
	D cm^2/s	S cc (STP)/(cc * atm)	D cm^2/s	S cc (STP)/(cc * atm)
EVOH, 42% ethylene	7.2E-10	5.9E-03		
PET	2.7E-09	6.9E-02	6.2E-10	2.0E+00
PVC	1.2E-08	3.0E-02	8.0E-09	2.4E-01
PP	2.9E-08	2.7E-01	3.2E-08	8.4E-01
HDPE	1.6E-07	1.8E-02	1.1E-07	1.1E-01
LDPE	4.5E-07	5.0E-02	3.2E-07	3.0E-01

Diffusion and Solubility Coefficient Data is difficult to obtain from literature.

P. DeLassus, "Barrier Polymers," H. Tung, *Ed.*, Kirk-Othmer Encyclopedia of Chemical Technology – 4th Ed., Vol. 3 (1992), pp. 931-962.
(Multiple References)

Permeation Coefficients: A Comparison

Permeation Coefficients

Film Classification	*Tock 1983 (cc * mil)/(100 in² * day * atm)*		*DeLassus (Dow Chemical) (cc * mil)/(100 in² * day * atm)*		*DeLassus (D & S data) cc(STP) * mil /(100 in² * day * atm)*	
	Oxygen	*Carbon Dioxide*	*Oxygen*	*Carbon Dioxide*	*Oxygen*	*Carbon Dioxide*
PET	4.5 ± 1.5	20 ± 5	3 ± 0.5	20 ± 5	4	27
PVC	17 ± 13	27 ± 23	12.5 ± 7.5	35 ± 15	8	42
PP	250 ± 160	925 ± 425	200 ± 50	650 ± 150	173	591
HDPE	185	580	150 ± 50	650 ± 50	63	257
LDPE	500	2700	300 ± 50	1100 ± 400	489	2086

$$P = D * S$$

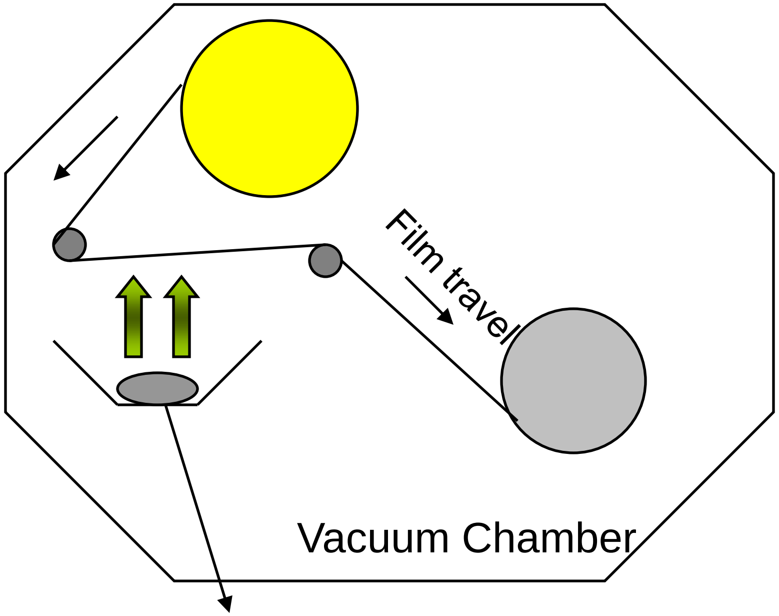
Coefficients from different sources generally agree.
Some error is present in Mass Transport measurements.

P. DeLassus (Dow Chemical Data), “Barrier Polymers,” H. Tung, *Ed.*, Kirk-Othmer Encyclopedia of Chemical Technology – 4th Ed., Vol. 3 (1992), pp. 931-962.
(Permeation data from Dow Chemical Brochure)

BARRIER TECHNOLOGY

Vacuum Metallization

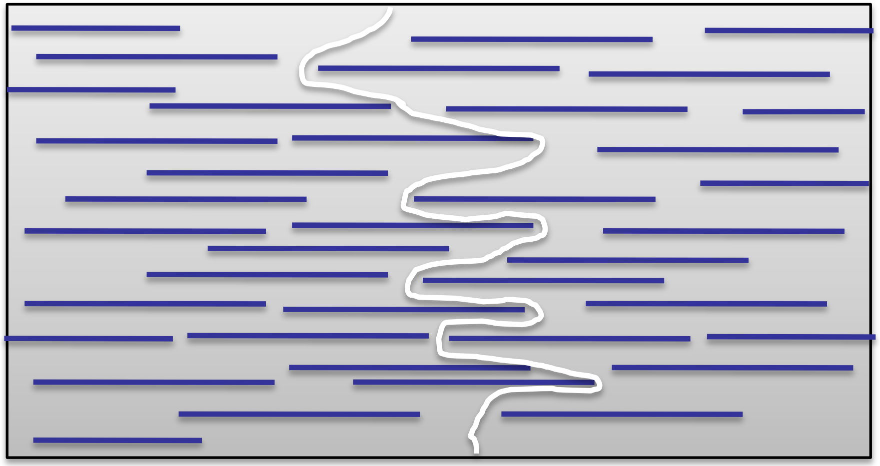
- Properly prepared roll of OPP placed inside vacuum chamber
- Vacuum drawn to < 10^{-4} mm Hg (10^{-6} atm)
- Rewound and passed over molten Al
- Al vapor deposited on surface of film



Nanotechnology Barrier

- Clay Platelet
  - Aspect Ratio 100 to 1000 for length to gauge.
  - Impenetrable to permeate gas.
- Barrier formed by tortuous path of platelet.
  - Platelet perpendicular to direction of permeation gives maximum barrier.
- Application methods
  - Aqueous solutions
  - Extrusion

Polymer film with nanoparticle platelets



- Diffusion controlled by number and orientation of platelets.
- Solubility controlled by polymer binder.

IN CONCLUSION

Summary

- Packaging film structures are complex assemblies with specialized layers for barrier.
- The type of mass transport, Fickian vs. Case II (solvent front), will determine the type of measurements and models employed.
- Permeation: P = D * S
- Consider both diffusion and solubility for barrier.
  - Oxygen requires only a diffusion barrier;
    Water requires both diffusion and solubility barriers.

A Final Word

“Knowledge is power.”

Sir Francis Bacon (1561 - 1626)

Whatever technology is employed to obtain barrier in the 21st century, knowledge of mass transport fundamentals will allow you to leverage that technology to the fullest.