

## PACKAGING PRODUCTIVITY ENHANCEMENT: SEAL, BARRIER AND ACTIVITY

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# Context...Trends

3S *pack*

In food Industry, a flexible package should contain and protect the product in the most efficient, cost effective way and be *safe*.

Flexible Packaging market value: World: 75 B\$, N.A.: 25 B\$, Canada: 2.5 B\$, 4-6% annual growth.

Consumers push: Requirements for high performance (high quality products, freshness, longer shelf life...).  
Recent contamination of food: health concerns.  
Environmental concerns.

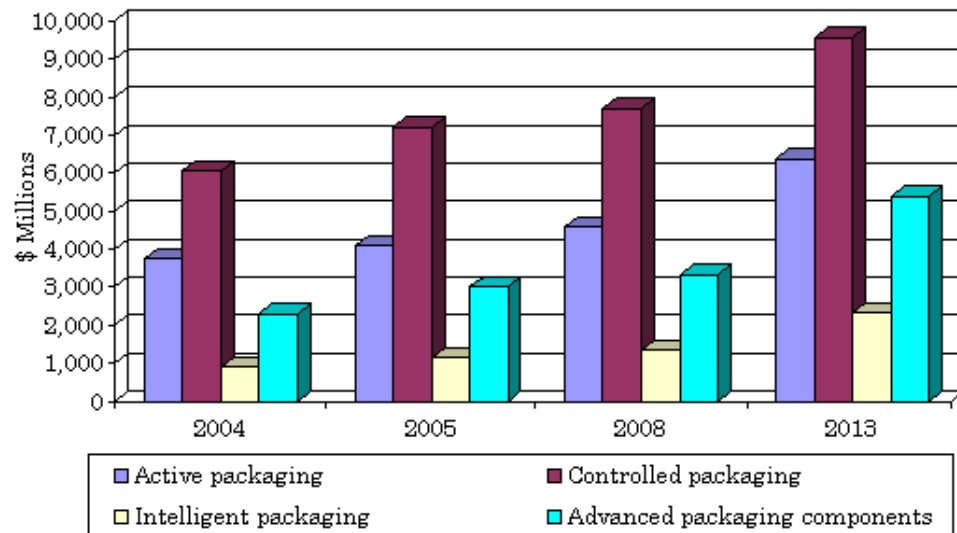
Trends: *Safety*, *Sustainability* and *Smart*.



# Functional Packaging: Food



- The current trends in packaging technology: development of functional materials that interact with the environment and with the food, and detection: growth of 10-15% per annum in US.
- Active packaging technologies: response to the market needs for minimally treated foodstuffs, preserve freshness and flavours, regulate the gas composition of the packaging headspace.  
Intelligent Packaging: detection of pathogen, history,...

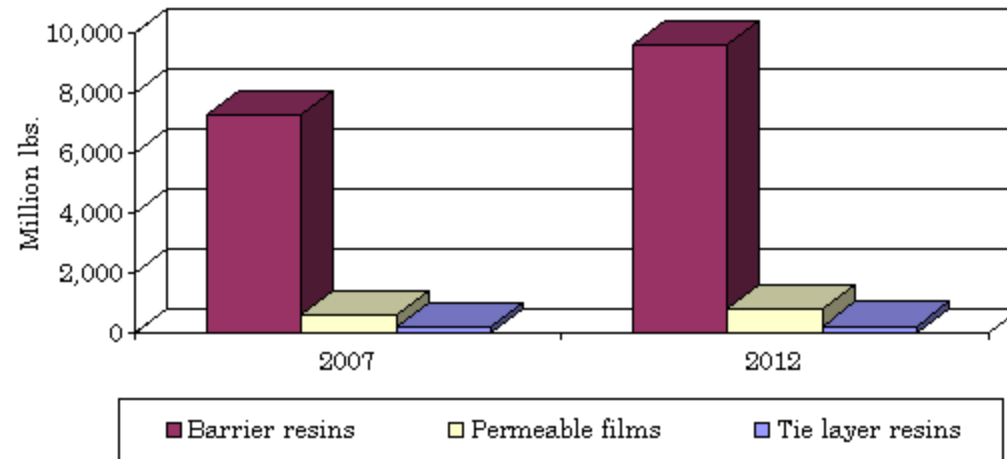


# Barrier Packaging



- The U.S. packaging barrier resin market reached 8 billion pounds in 2007. It is expected to grow by 5.8% through 2012.
- The largest market for barrier packaging is food and beverage packaging, which accounts for more than 95% of applications in the U.S.

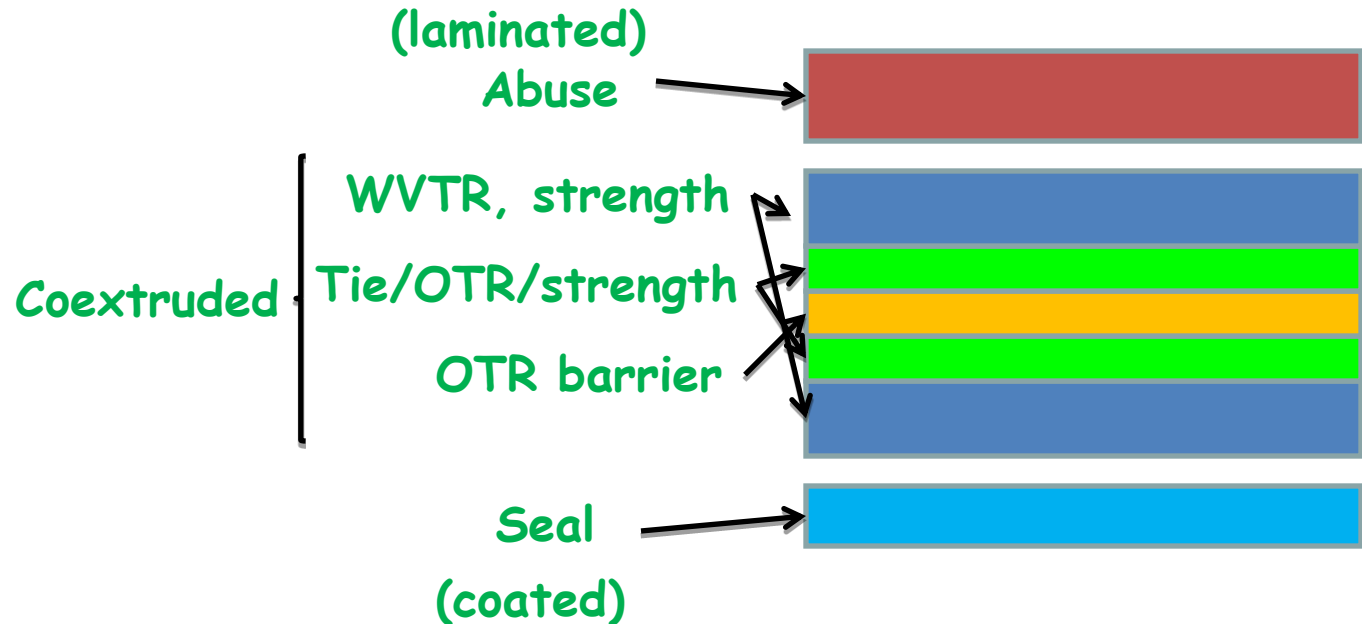
Developments in more sophisticated multilayer barrier packaging structures with nanocomposites



# Development of *Safe* Packages

3S *pack*  
■ ■ ■

Strength, Barrier, Seal, Antibacterial



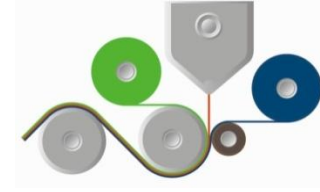
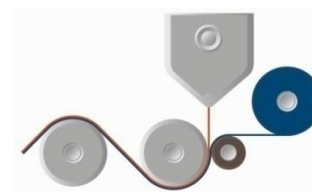
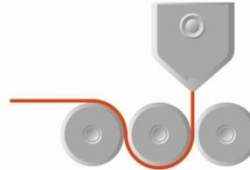
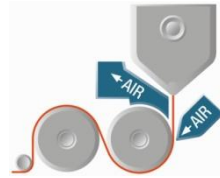
Development at laboratory scale. Pilot production for field trials.

# PILOT MULTILAYER CO-EXTRUSION LINE - POLYNOV

3S *pack*  


For Films  
production:

- Mono or multilayer  
cast film Process



- Mono or multilayer  
Bown film process

Casting, Calendering, Coating and Laminating.



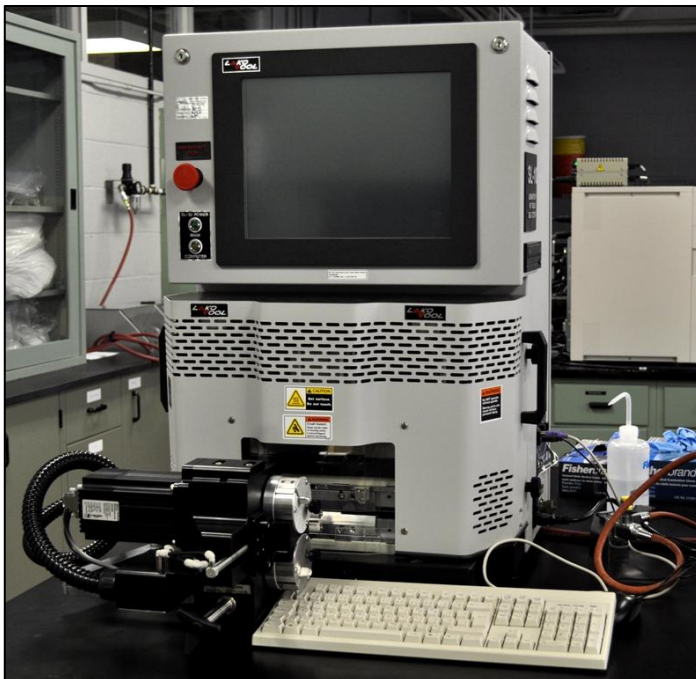
MDO



## FTIR Micro-ATR

Perkin Elmer

*Chemical bonds detection  
Identification layer by layer for multilayer films*



## Hottack/Seal Tester

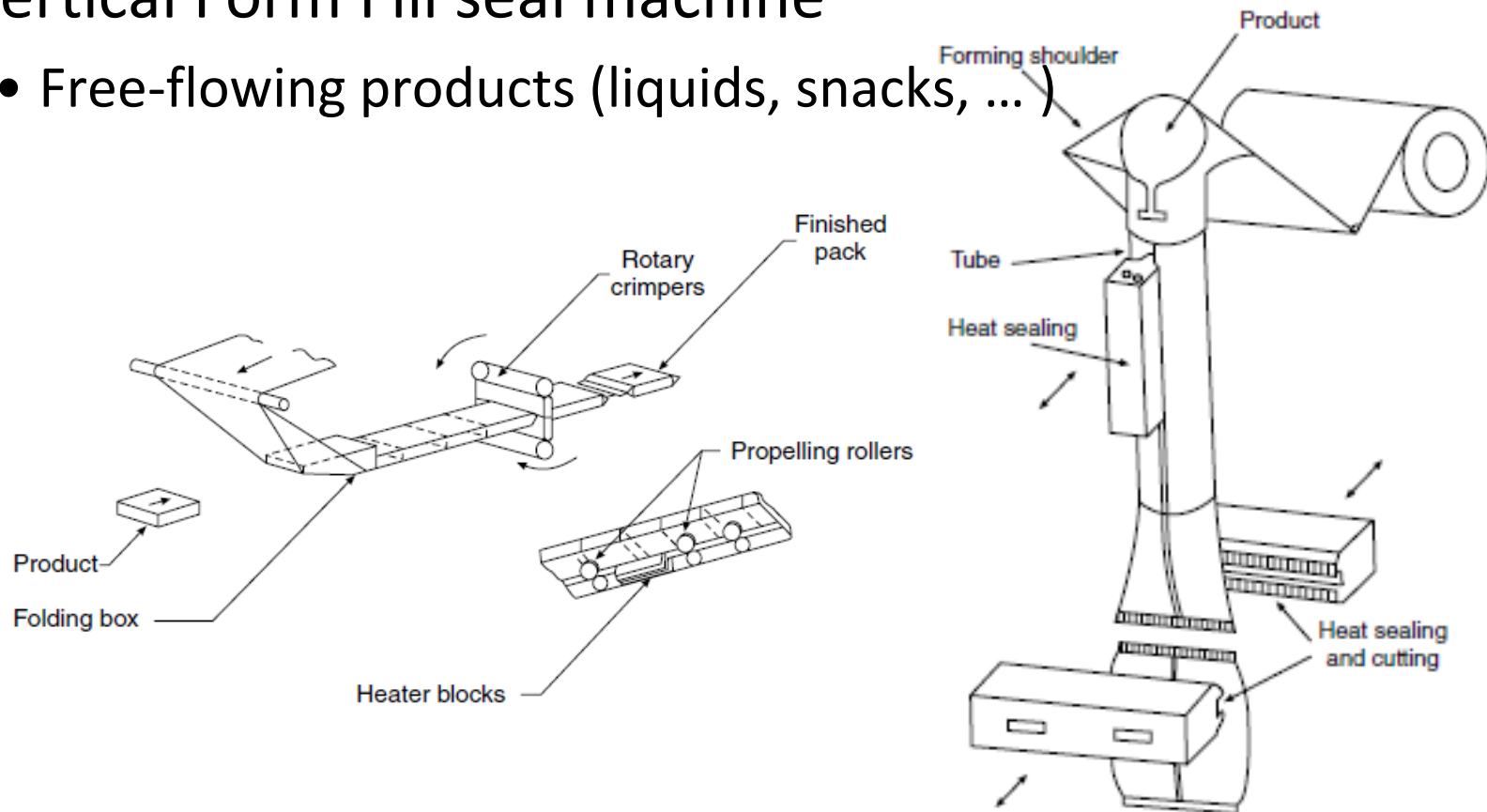
LakoTool-TMI

*Resistance of material sealing*

# Seal Layer optimisation

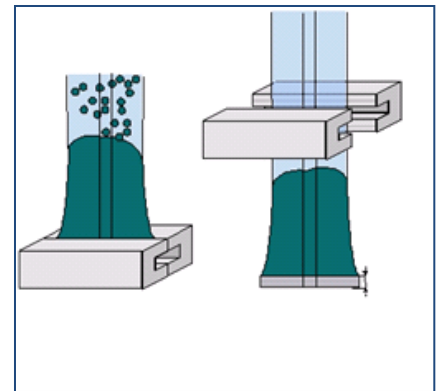
# Heat sealing process

- Fill seal machines
  - Horizontal Form Fill seal machine
    - Chocolate bars, biscuits, ...
  - Vertical Form Fill seal machine
    - Free-flowing products (liquids, snacks, ...)



# Heat sealing process variables

- Seal bar temperature
  - The temperature of heated bars
- Dwell time
  - The duration of time that the film is brought into contact by the heated bars.
- Pressure
  - The pressure is applied to the seal area



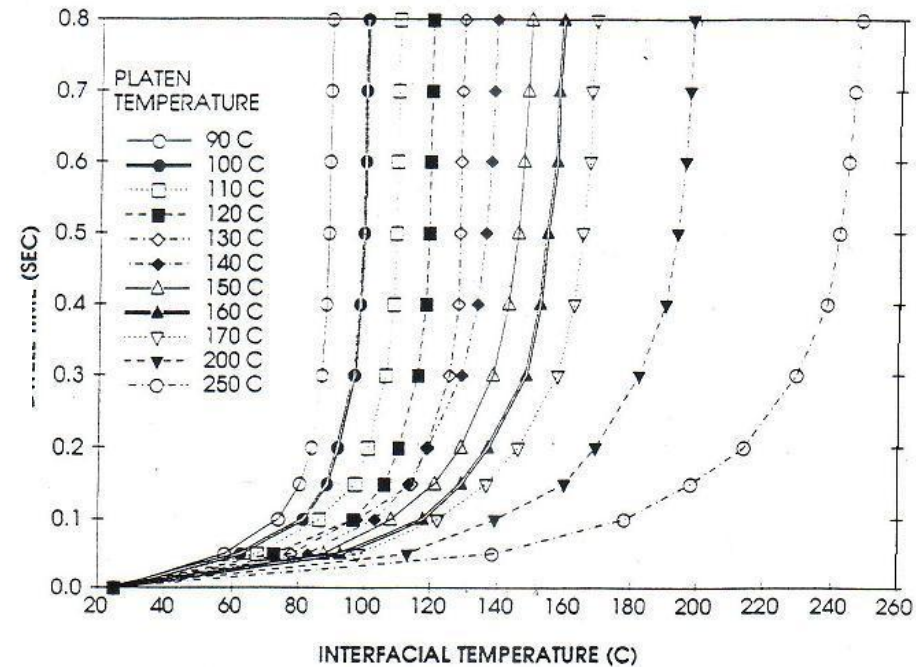
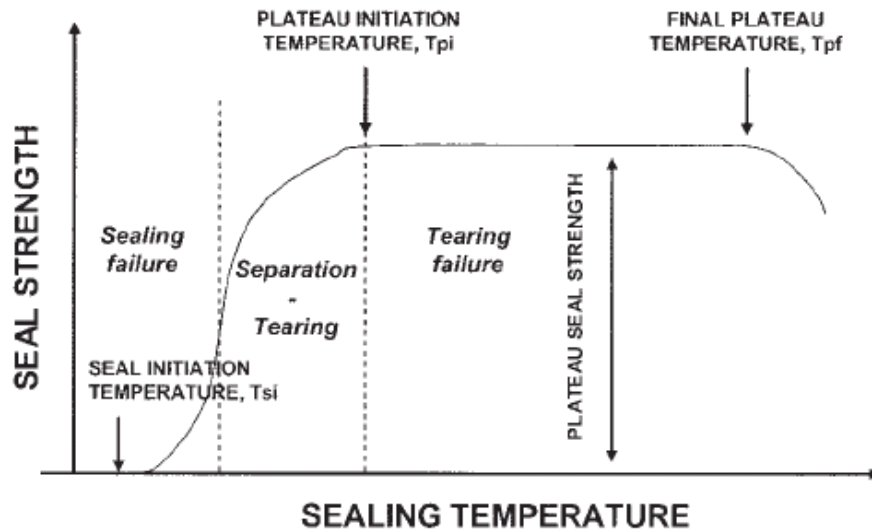
# Seal in a Structure

- Seal layer
  - Internal layer of package



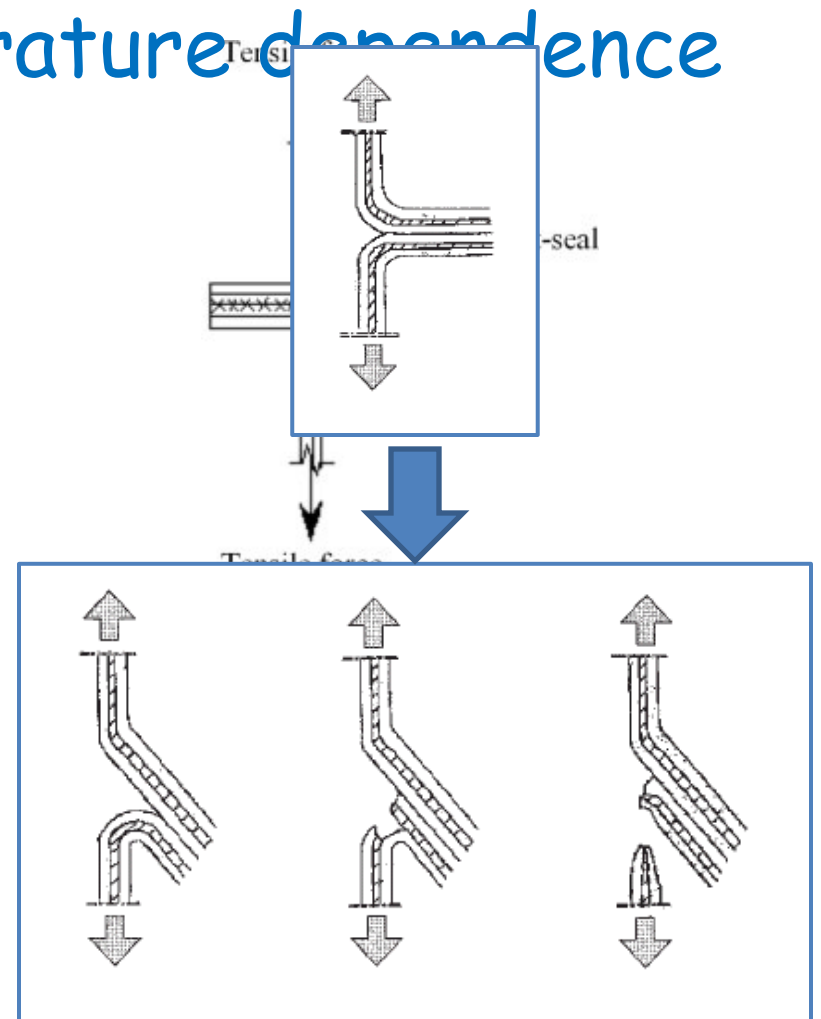
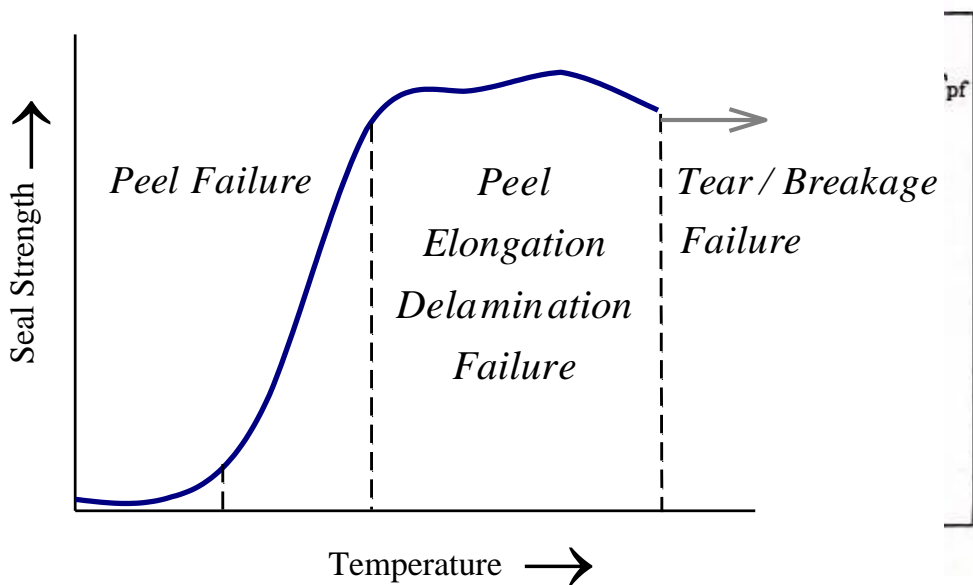
- Heat seal
  - Bonding together two polymer surfaces in the way that the surfaces are forced into intimate contact while they are in at least a partially molten state.
- Heat seal quality depends on
  - Film factors (Material, Film structure)
  - Machine factors

# Process variables and Seal properties



# Seal strength curve

- Seal Strength temperature dependence
- Failure mode analysis



# Barrier Layer optimisation

# O<sub>2</sub> and H<sub>2</sub>O Tolerances of some Food

3S *pack*  


Table I. Permeation Targets for Selected Foods

Food or Beverage	Maximum Oxygen Ingress permissible ppm (mass basis)	Maximum Water Gain or Loss % (mass basis)
Canned milk, meats, fish and poultry	1 – 5	3% loss
Beer, ale, wine	1 – 5	3% loss 20% CO <sub>2</sub> or SO <sub>2</sub> loss
Canned vegetables, soups, spaghetti, catsup, sauces	1 – 5	3% loss
Canned fruit	5 – 15	3% loss
Dried foods	5 – 15	1 % gain
Carbonated soft drinks	10 – 40	3% loss
Fruit juices, drinks	10 – 40	3% loss
Oils, shortening	50 – 200	10% gain
Salad dressings	50 – 200	10% gain
Peanut butter	50 – 200	10% gain
Jams, jellies, syrups, pickles, olives vinegar	50 – 200	3% loss

# Barrier Packaging



- Barrier properties of typical resins used in flexible packaging:

Table I. Permeability of polymers commonly used in packaging<sup>1</sup>

Polymer	Oxygen permeability at 23°C 50% or 0% RH [cm <sup>3</sup> mm/(m <sup>2</sup> dayatm)]	Water vapour permeability at 23°C 85% RH [gmm/(m <sup>2</sup> day)]
Poly(ethylene terephthalate) (PET)	1–5	0.5–2
Polypropylene (PP)	50–100	0.2–0.4
Polyethylene (PE)	50–200	0.5–2
Polystyrene (PS)	100–150	1–4
Poly(vinyl chloride) (PVC)	2–8	1–2
Poly(ethylene naphthalate) (PEN)	0.5	0.7
Polyamide (PA)	0.1–1 (dry)	0.5–10
Poly(vinyl alcohol) (PVAL)	0.02 (dry)	30
Ethylene vinyl alcohol (EVOH)	0.001–0.01 (dry)	1–3
Poly(vinylidene chloride) (PVDC)	0.01–0.3	0.1

Seal layers: modified polyolefins (plastomers)

Abuse layers: PET, PA,

Adhesives

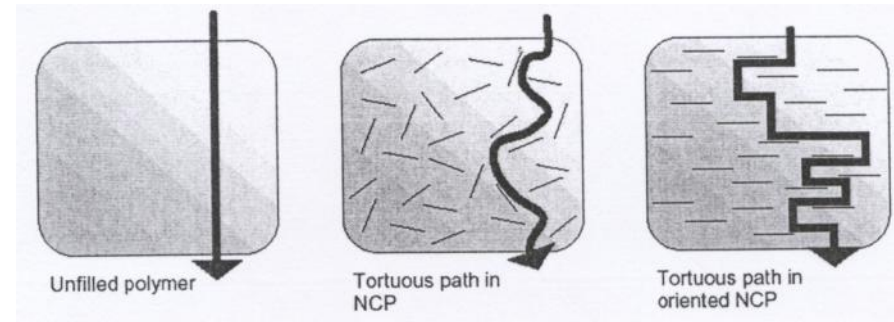
Table IV. Oxygen Permeation of EVOH - 20°C / 65% RH

Mol% Ethylene	27	32	35	44	48
Oxygen Permeation (cc.mil/100 in <sup>2</sup> .day.atm)	0.010	0.020	0.028	0.076	0.163
Oxygen Permeation (cc.20 um/sq. m.day.atm)	0.2	0.4	0.6	1.5	3.2

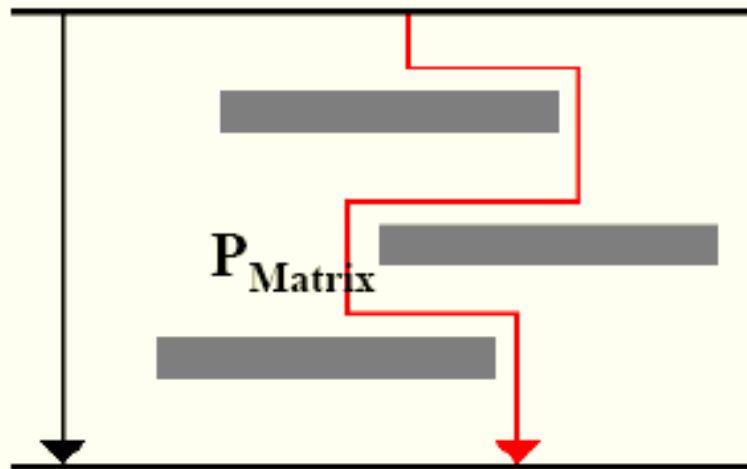
# Nanocomposites

PNC based on layered silicates have received very much attention because of their potential to improve:

- Stiffness, strength and impact resistance
- Barrier properties
- Dimensional and thermal stability



## Barrier Enhancement: Tortuous Path



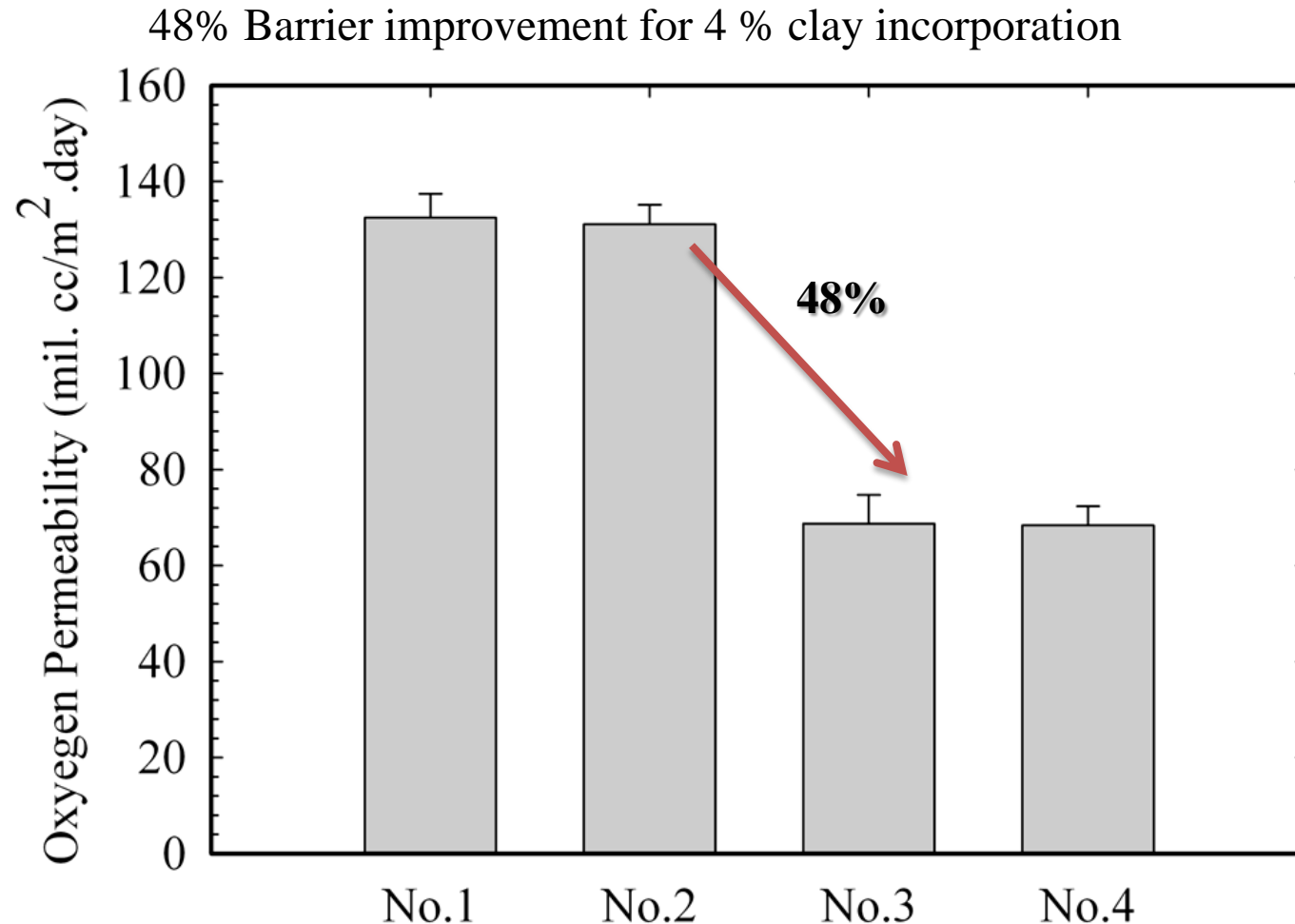
What does it take to reduce  
50% permeability?

Aspect ratio	Volume %
20	9%
200	1%
400	0.5%

$$P_{\text{nanocomposite}} = \frac{(\text{Matrix Volume Fraction}) * (P_{\text{matrix}})}{1 + (\text{Clay Volume Fraction}) * (\text{Clay Aspect Ratio}) / 2}$$

# PA-6 Nanocomposites: OTR

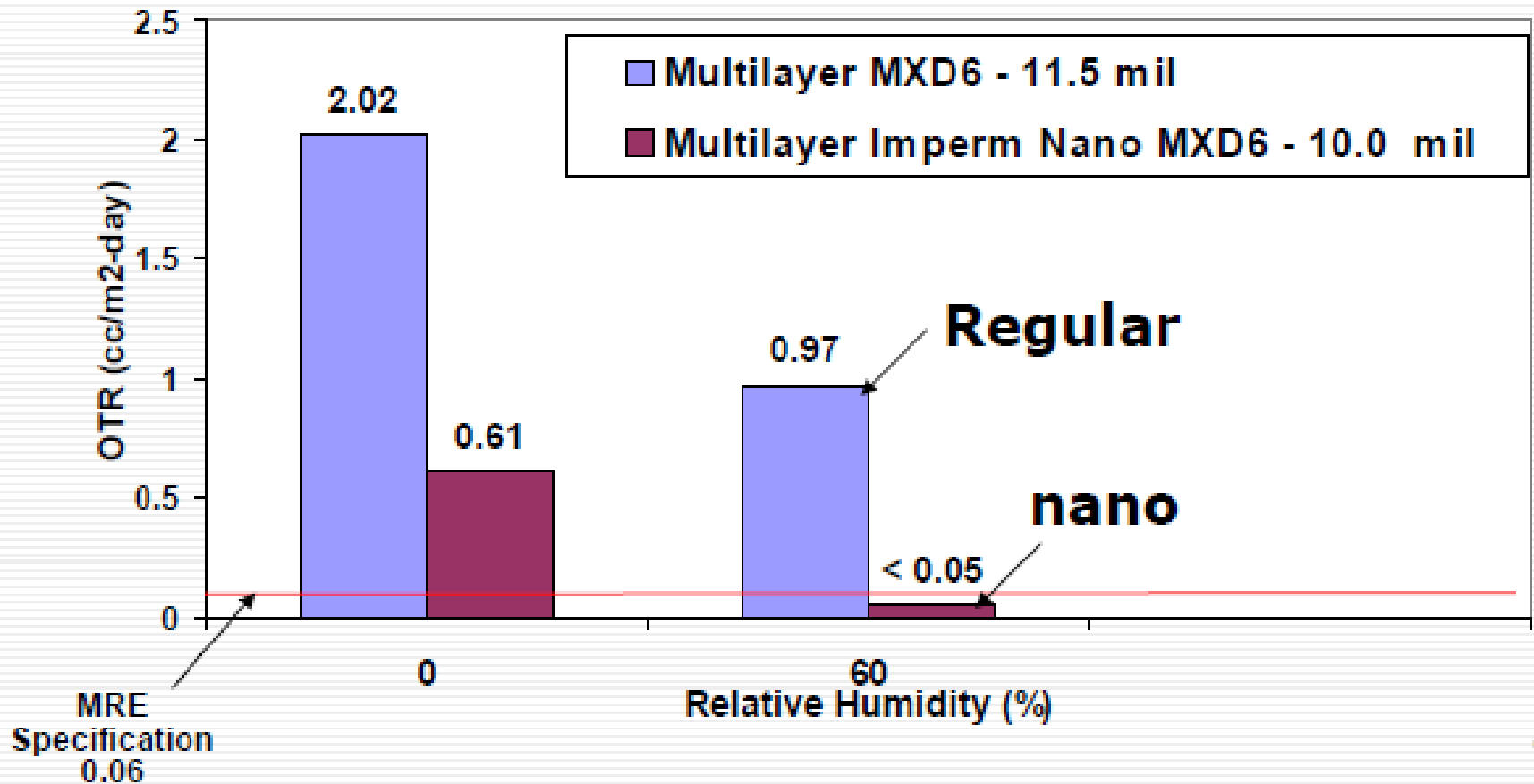
The values have been normalized



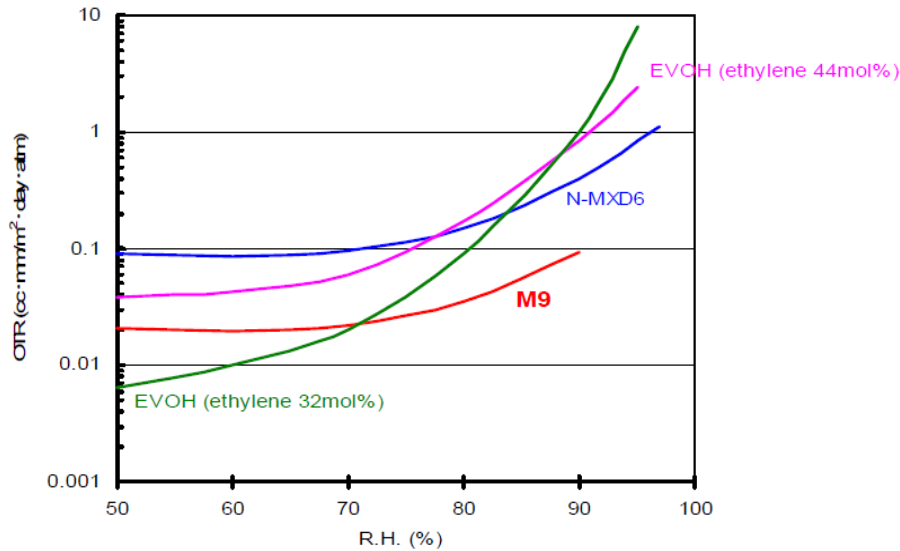
Total thickness: 50  $\mu$ m, sample 1: PA 6  $\mu$ m, 2: PA 12  $\mu$ m

# MXD-6 Nanocomposites: OTR

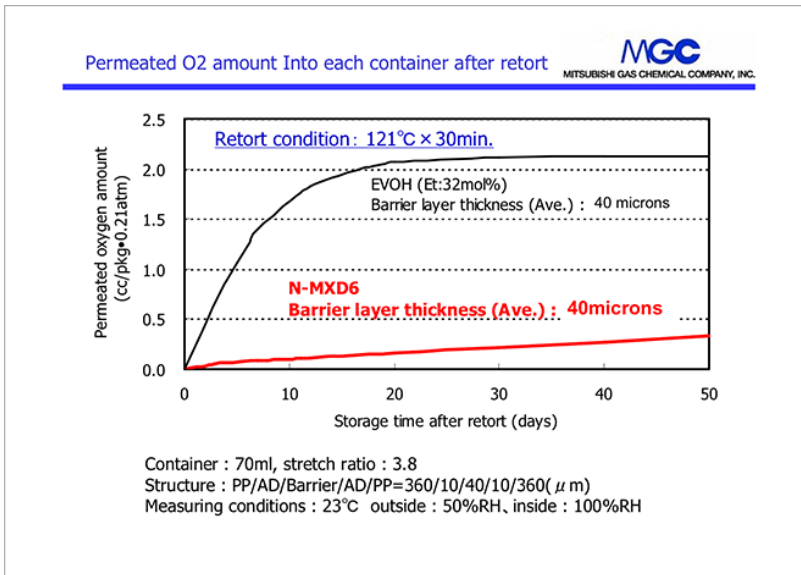
## Oxygen Transmission of Multilayer MXD6 and Imperm Films



# Oxygen Transmission Rate vs. Relative Humidity for Oriented Barrier Films



Between 0 and 100% RH, the oxygen permeability of nylon-6 increases by a factor of 2 the oxygen permeability of EVOH with 44 mol % ethylene increases by a factor of 40. Surprisingly, the oxygen permeability of **MXD6** decreases by a factor of 2 between 0 and 70% RH but increases at higher RH values



Active Packaging:  
Antibacterial and Oxygen  
Scavenging Films

# Development of Antibacterial films

## Antibacterial efficiency

Minimum inhibitory concentration for various essential oil compounds on *Staphylococcus aureus* :

Carvacrol	- 0.45	mg/mL
Eugenol	- 0.9	mg/mL
Thymol	- 0.0125	mg/mL
Mint	- > 0.8	mg/mL
Oregano	- [0.4, 0.8]	mg/mL

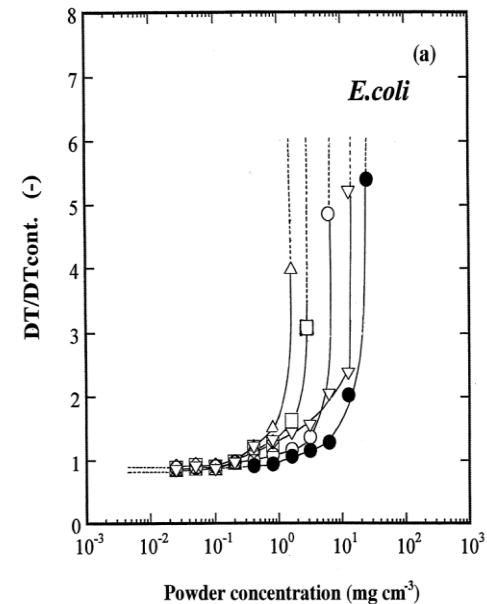


Fig. 3. Comparison of the antibacterial activity of the powder samples with respect to (a) *E. coli* and (b) *S. aureus*: ( $\Delta$ ) ZO-1, ( $\square$ ) ZO-2, ( $\circ$ ) ZO-3, ( $\nabla$ ) ZO-4, ( $\bullet$ ) ZO-5.

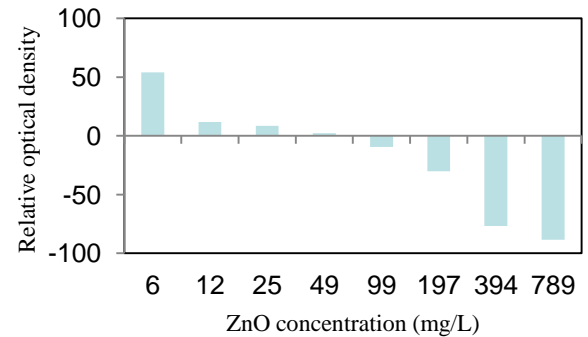
Table 1

Antibacterial parameters of ZnO, CaO and MgO powders against *S. aureus* and *E. coli*

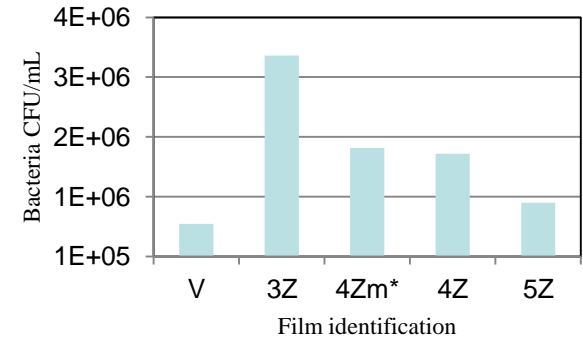
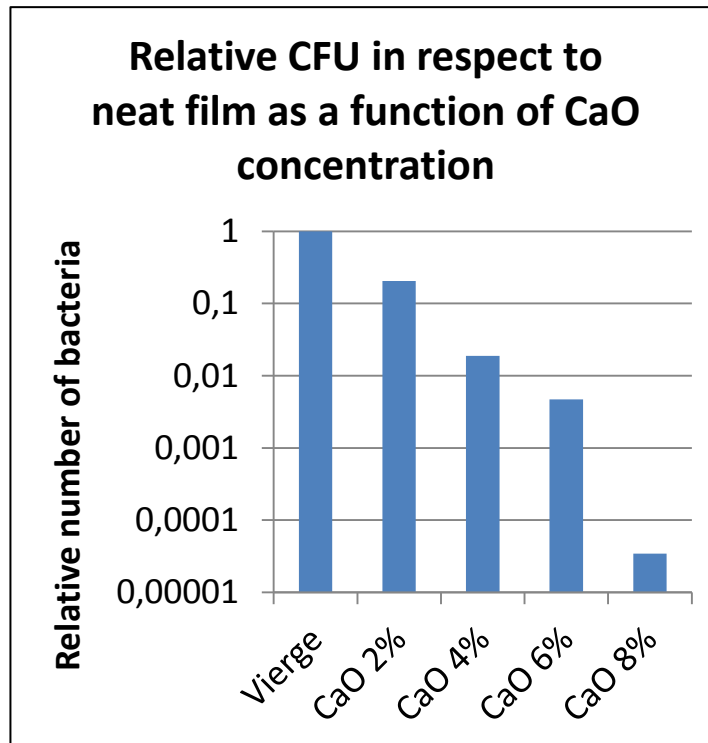
Microorganisms	Substance	$m$	$K_d$	$[I]_{50}$ (mg/ml)	$a$	$b$	$[I]_{100}$ (mg/ml)
<i>S. aureus</i>	ZnO	2.60	0.35	0.67	1.01	1.90	0.99
	CaO	1.53	9.37	4.30	0.07	1.61	5.08
	MgO	3.78	141	3.71	0.01	2.82	5.00
<i>E. coli</i>	ZnO	1.49	30.2	9.85	0.07	0.75	32.4
	CaO	3.49	18.3	2.30	0.06	2.56	3.06
	MgO	3.78	167	3.87	0.01	2.62	5.58

# Development of Antibacterial films

- Prepare LDPE film with a range of antibacterial filler concentration.
- Addition of a range of slip and anti-block additives.
- Perform antibacterial, Mechanical and COF tests for the combined systems.



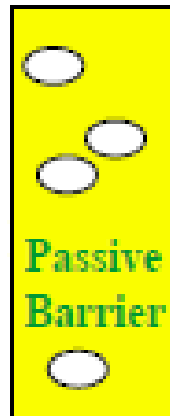
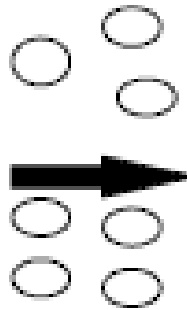
Relative Optical Density as Function of ZnO Concentration



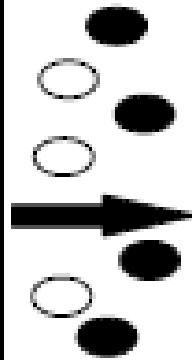
Colony forming units as function of film.  
\*m stands for thin film

# Definition of an active layer using OS

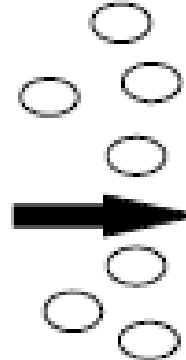
Outside  
Container



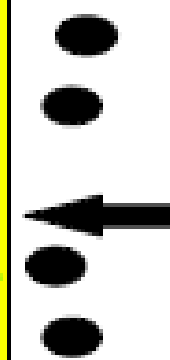
Inside  
Container



Outside  
Container



Inside  
Container



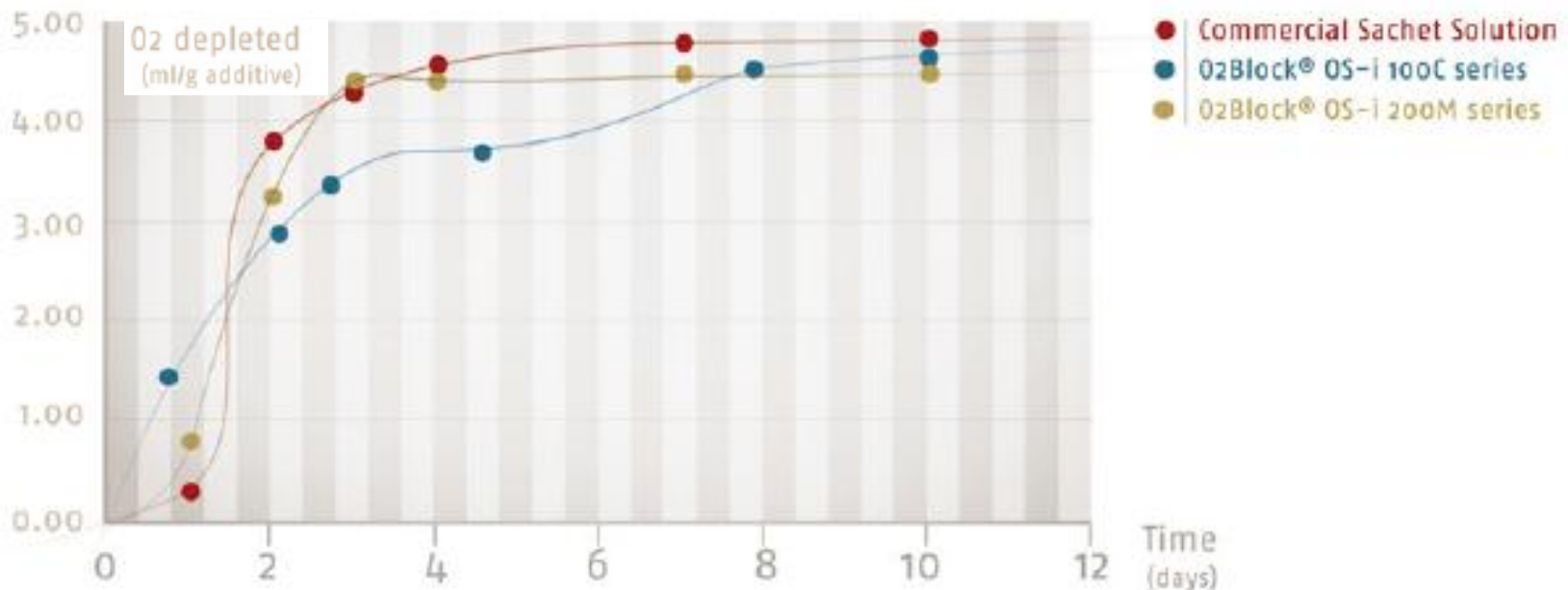
○ = Oxygen molecule initially outside container

● = Oxygen molecule initially inside container

# Fe-based OS films

More useful in applications where transparency is not an issue.

- Amosorb (Color Matrix) → PET-based OS for bottles
- Oxyguard (Tokio Seikan) → Tray, film, closure liner
- ShelfPlus (Albis Plastics, before Ciba) → masterbatch
- O2Block (Nanobiomatters) → Powder of masterbatch
  - OM-Silicate clay functionalized with Fe linked to clay surface



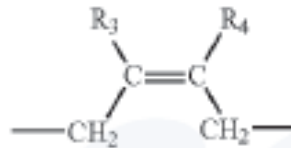
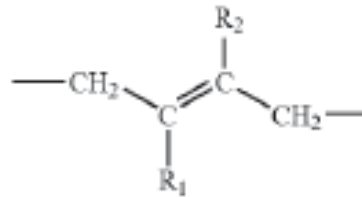
# Ascorbic Acid/derivates

- Technology developed by Toppan Printing (Japan).
- Daraform -> Plastic bottle linings (Grace Performance chemicals)
- Darex -> bottle-cap gaskets for beer bottles (Grace Performance Chemicals)
- DarEval (Grace+Kuraray) for PET beer bottles: EVOH + Asc. Acid



# Diene Polymers

- Polybutadiene, Polyisoprene, Polyoctenylene, etc + Metal Catalyst (Sealed Air Co. → Cryovac)



- **EMCM** Poly (ethylene/methyl acrylate/ cyclohexene methyl acrylate) (Chevron) + Catalyst + Photoinitiator + UV light.
- ❑ Current Cryovac OS200 film

# Oxygen Scavenger structure for study

- 5 layer film
- “Generic structure”
- Oxygen Scavenging capacity
- Oxygen Barrier
- Moisture barrier
- Transparency is not important.

thickness, $\mu\text{m}$	Layer type
20	LLDPE
8	tie
30-50	<b>Active Barrier Layer (OB+OS)</b>
8	tie
20	LLDPE

THANK YOU!

