Taking Plastics Packaging to the Future Through Improving Barrier Properties

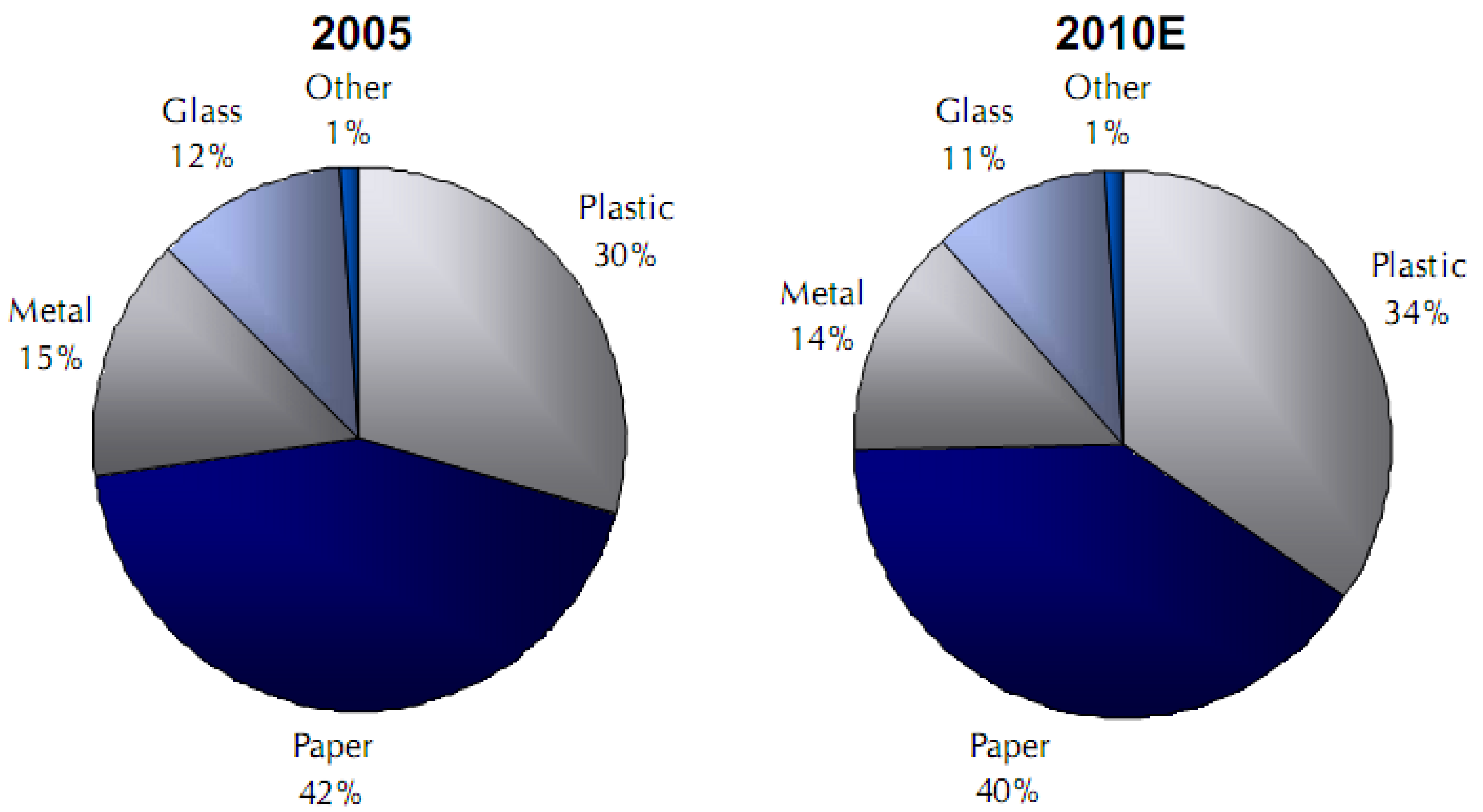
P.W Labuschagne, F.S. Moolman,

Plastic Packaging South Africa 2011

15 – 17 November 2011

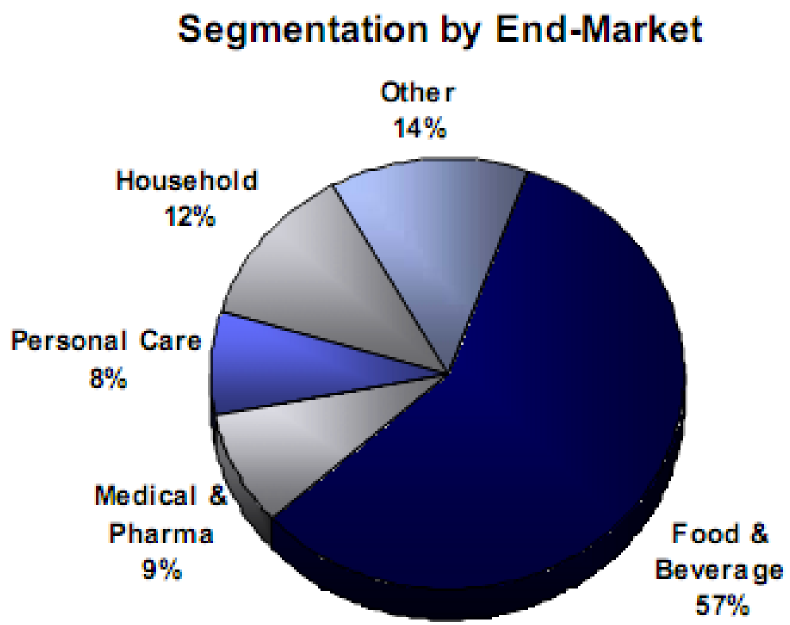
- Introduction & examining the basic principles of plastics permeability
- Increasing barrier properties with interpolymer complexes
- Increasing barrier properties with nanotechnology
- Highlighting key alternative barrier technologies

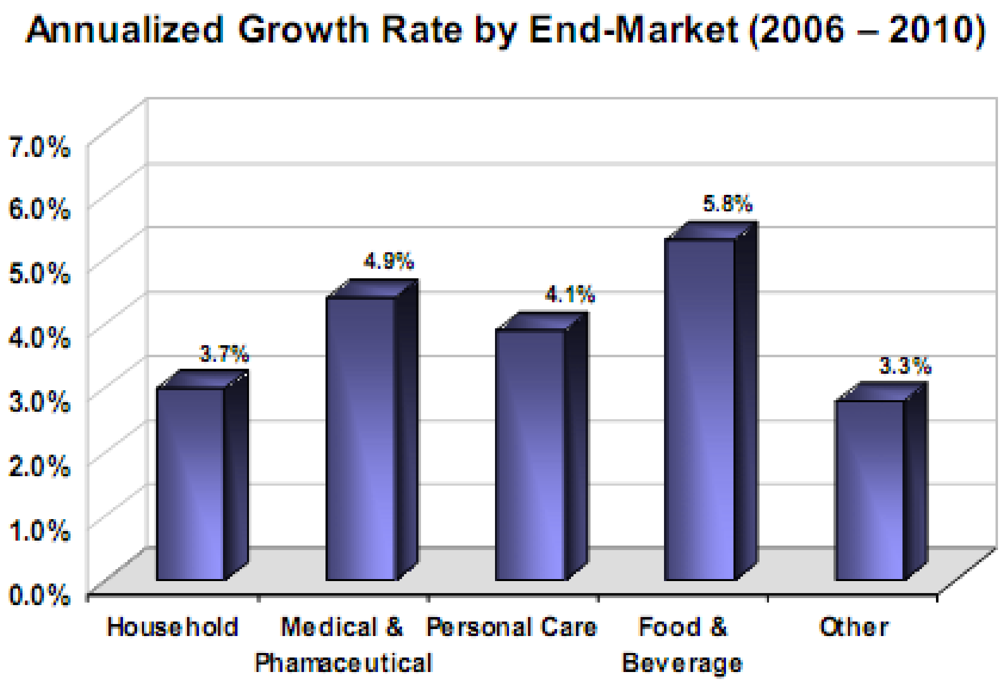
Market info



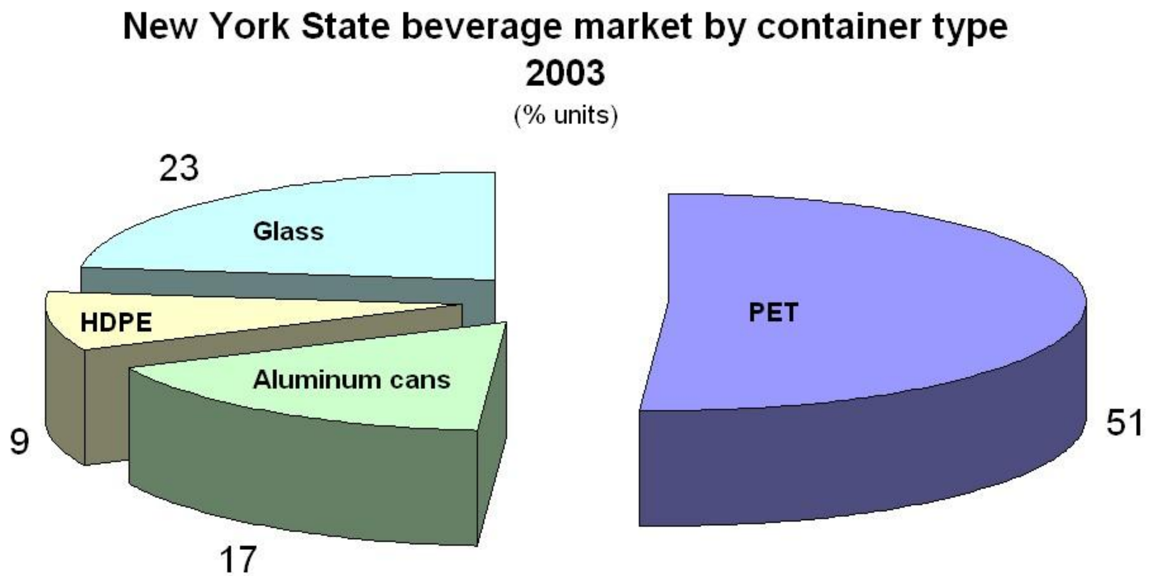
Source: PMCF Estimates and Company Data

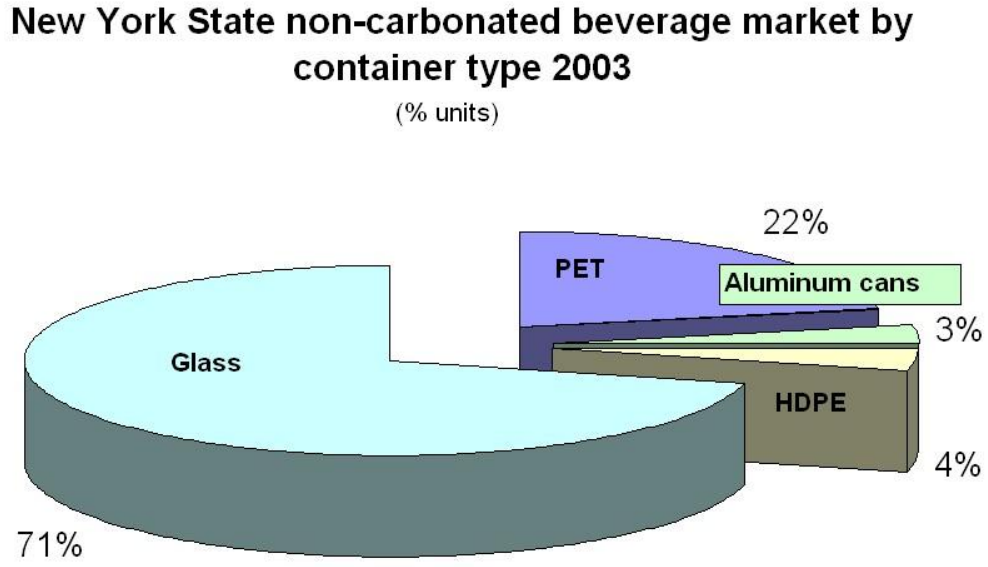
Market info





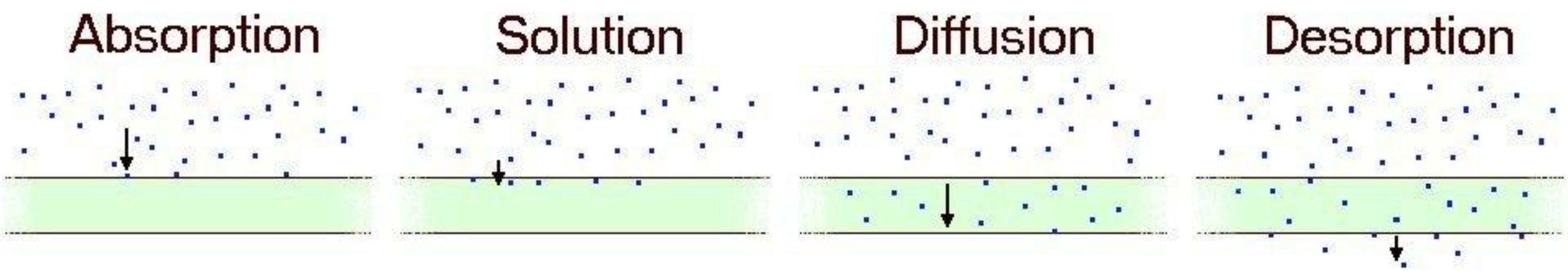
Source: PMCF Estimates and Company Data


New York State beverage market by container type
2003
(% units)
23
Glass
HDPE
Aluminum cans
9
17
PET
51


New York State non-carbonated beverage market by container type 2003
(% units)
22%
PET
Aluminum cans
3%
Glass
HDPE
4%
71%

Selected Oxygen Tolerances

Food/beverage	Tolerance (ppm)	Shelf-life – PET (months)
Beer	1 - 2	0.3 – 0.7
Canned vegetables/soup	1 - 3	0.3 – 1.0
Baby Foods	1 - 3	0.3 – 1.0
Wine	2 - 5	0.7 – 1.7
Tomato-based products	3 - 8	1.0 – 2.8
High acid fruit juices	8 - 20	2.8 – 7
Oils & shortenings	20 - 50	7+
Peanut butter	30 - 100	10+
Salad dressings	30 - 100	10+



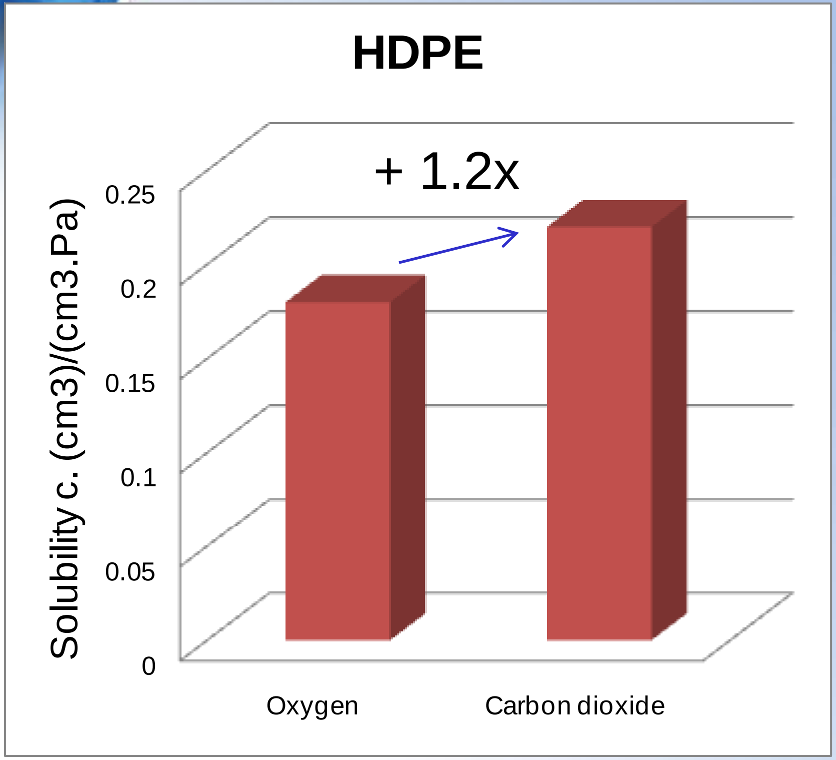
Thermodynamic component of gas transport = solubility coefficient, *S* (in mol m^{-3} Pa^{-1})

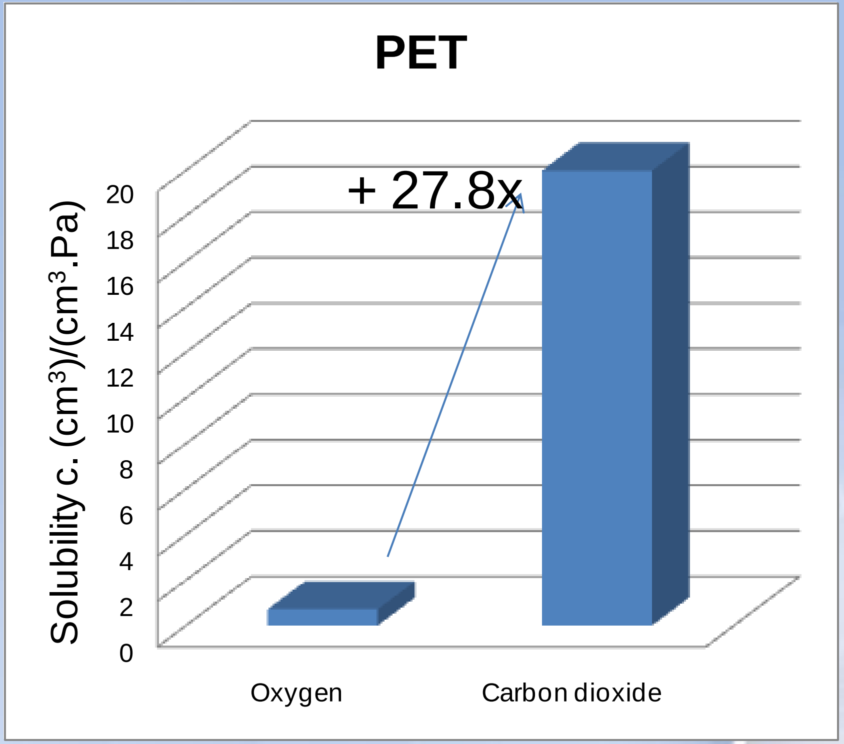
Kinetic component of gas transport = diffusion coefficient, *D* (in m^2 s^{-1})

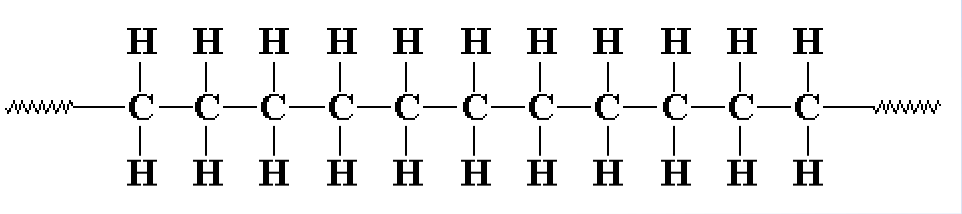
Permeability coefficient = D x S

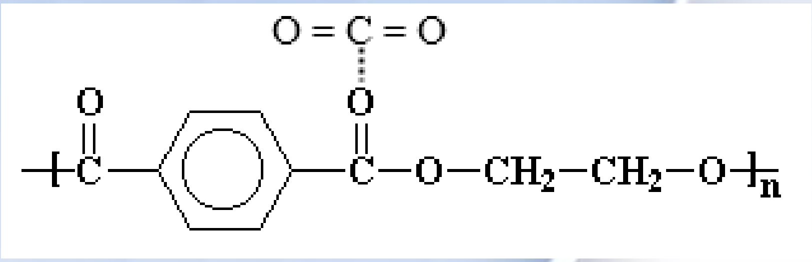
Solubility Coefficient

Permeability



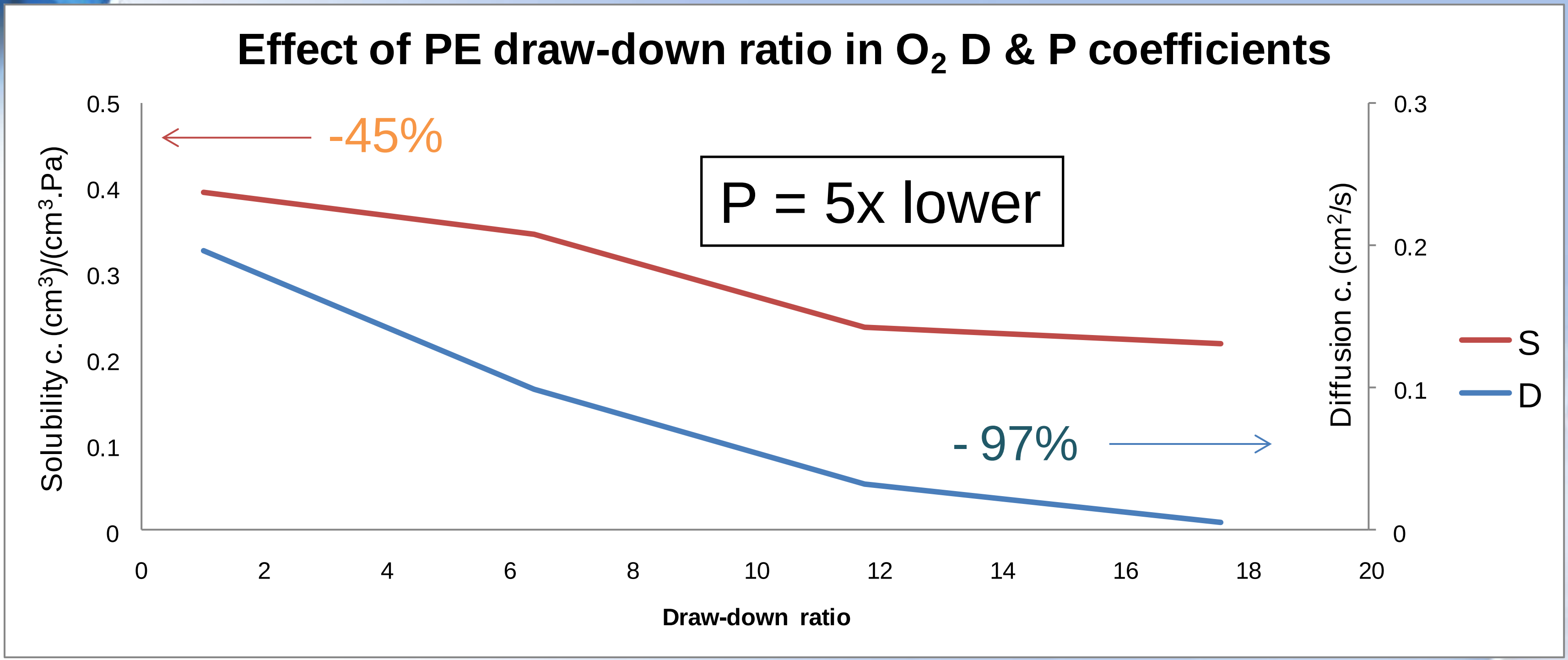


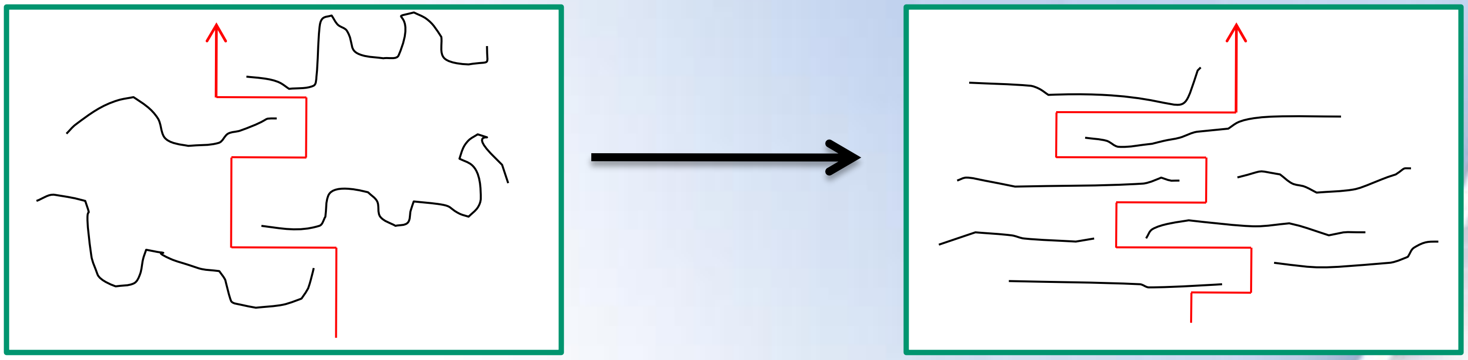




Diffusion Coefficient

Permeability





= Increased tortuous path-length

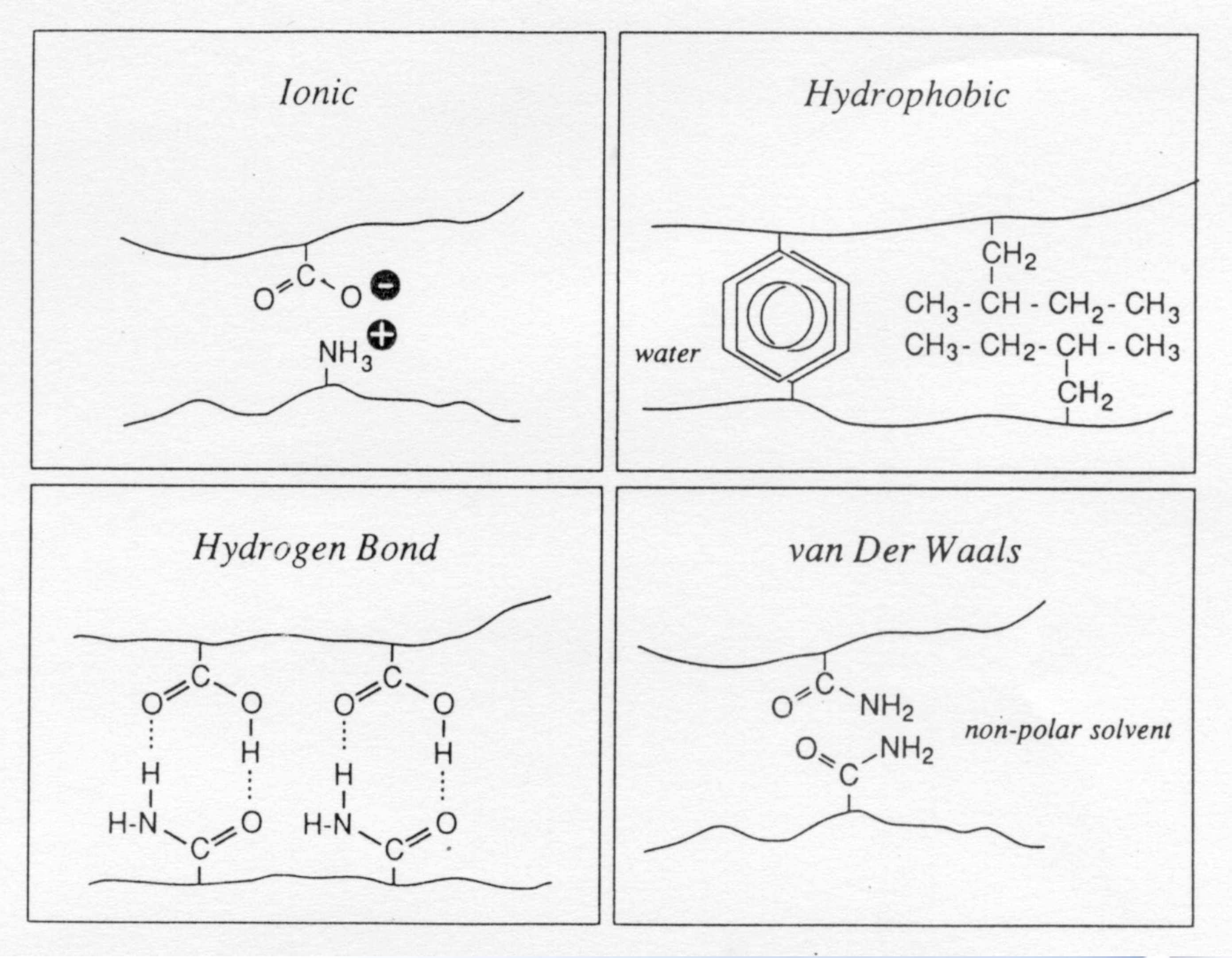
Influence of properties on polymer film permeability

Polymer	O_2 Permeability	Density (g/cm^3)	T_g (°C)	FFV	Solubility parameter
Low-density poly(ethylene)	2.2	0.92	-35	0.12	16.4
Poly(styrene)	1.9	1.04	±92	0.176	19.3
Poly(propylene)	1.7	0.903	-20	0.10	18.0
High-density poly(ethylene)	0.3	0.95	-35	0.10	18.1
Poly(ethyleneterephthalate)	0.0444	1.4	80	0.10	20.0
Nylon-6	0.0285	1.13	56	0.12	20.3
Poly(vinylidiene chloride)	0.00383	1.7	-4	n/a	21.3
Poly(acrylonitrile)	0.00015	1.17	90	0.08	27.4
Poly(vinyl alcohol)	0.00005	1.29	85	0.03	26.3

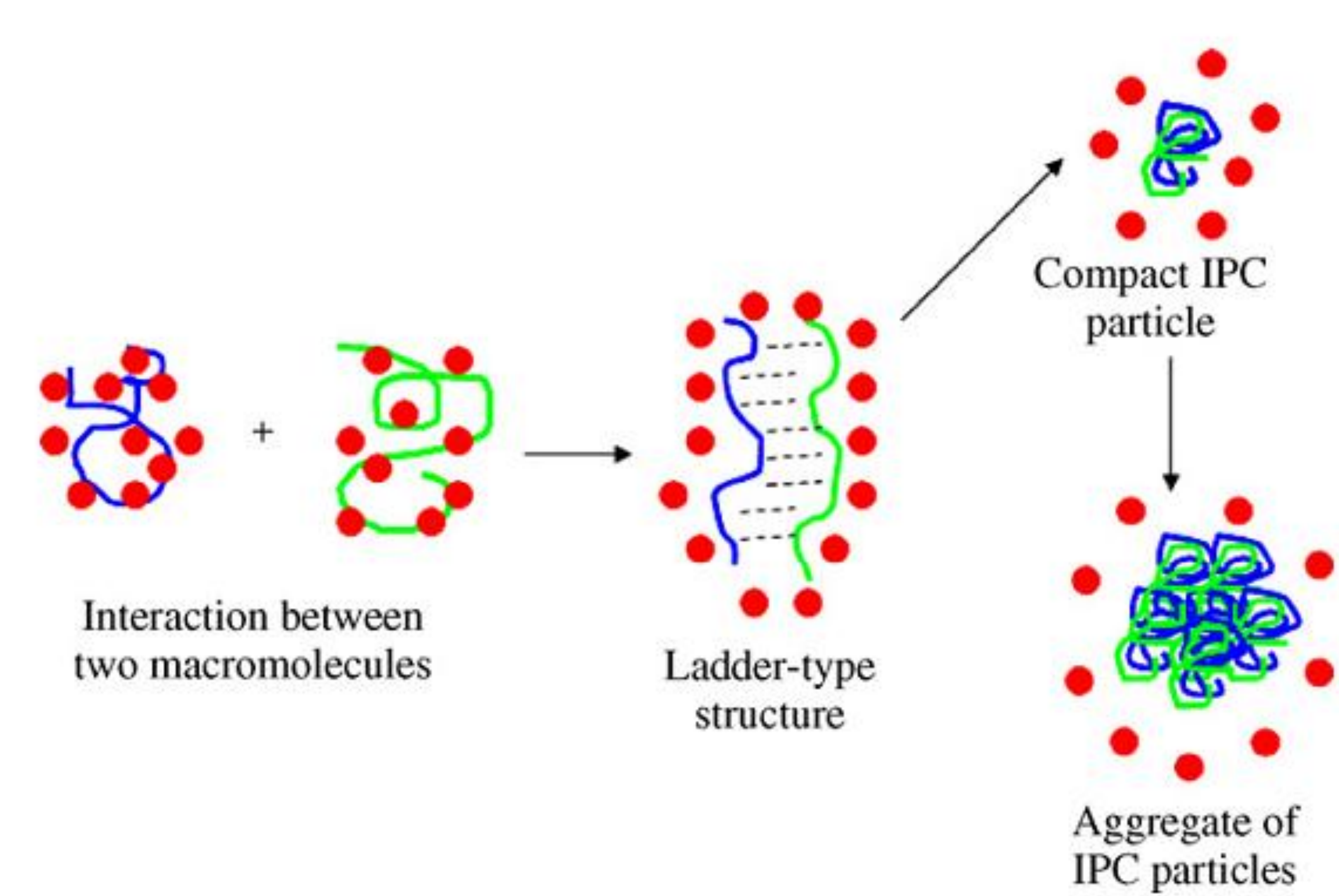
Interpolymer complexes (IPC) as oxygen barriers

- **Definition:** *Intermolecular association* of two different polymers bound together by secondary forces, resulting in *unique properties* which are essentially different from those of the initial polymers

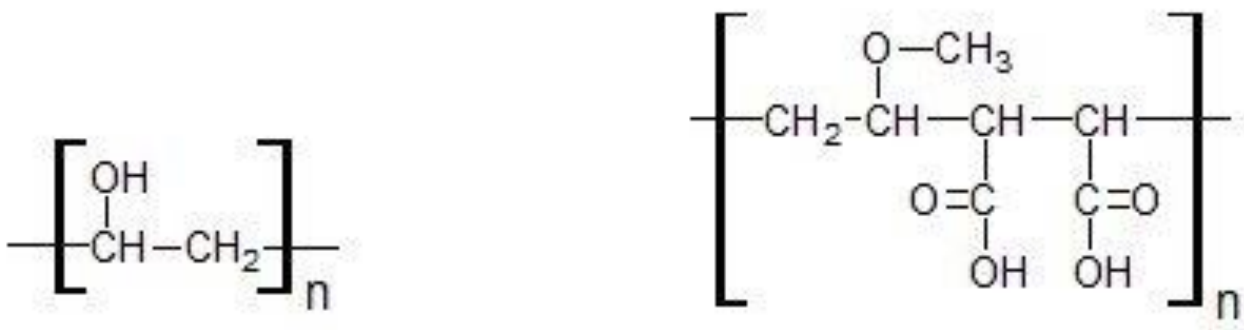
Interpolymer complexation basics



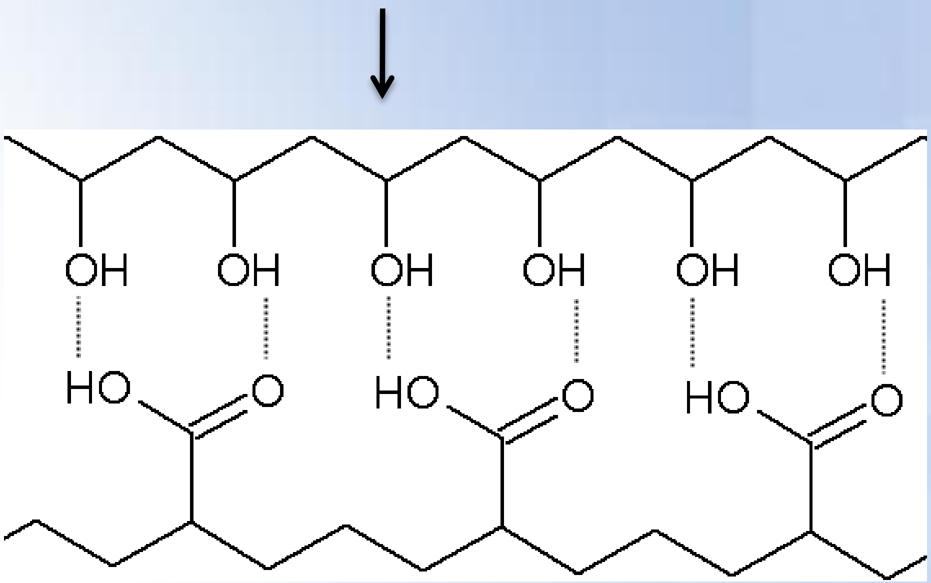
Schematic illustration of IPC



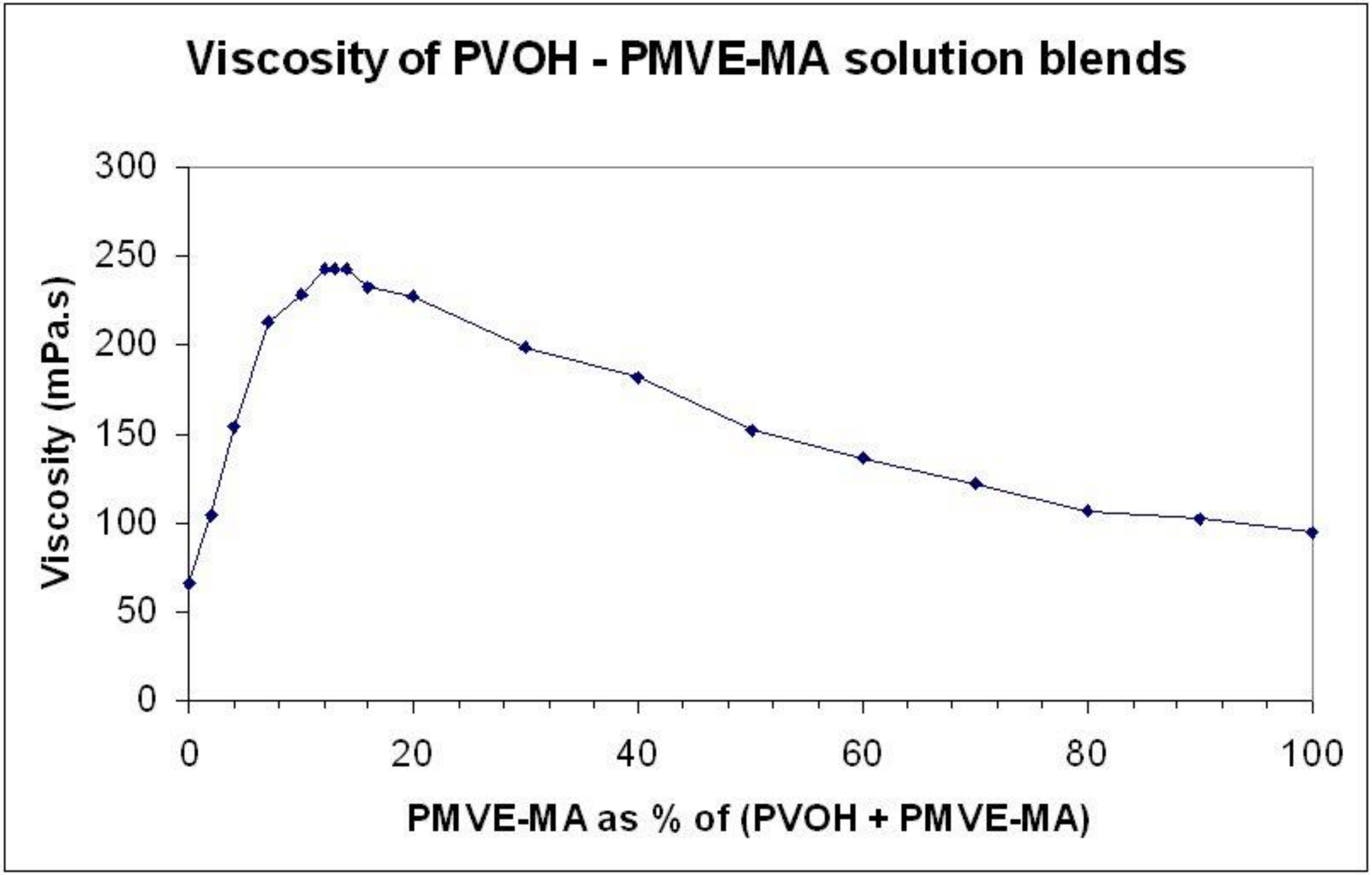
Complexation reaction



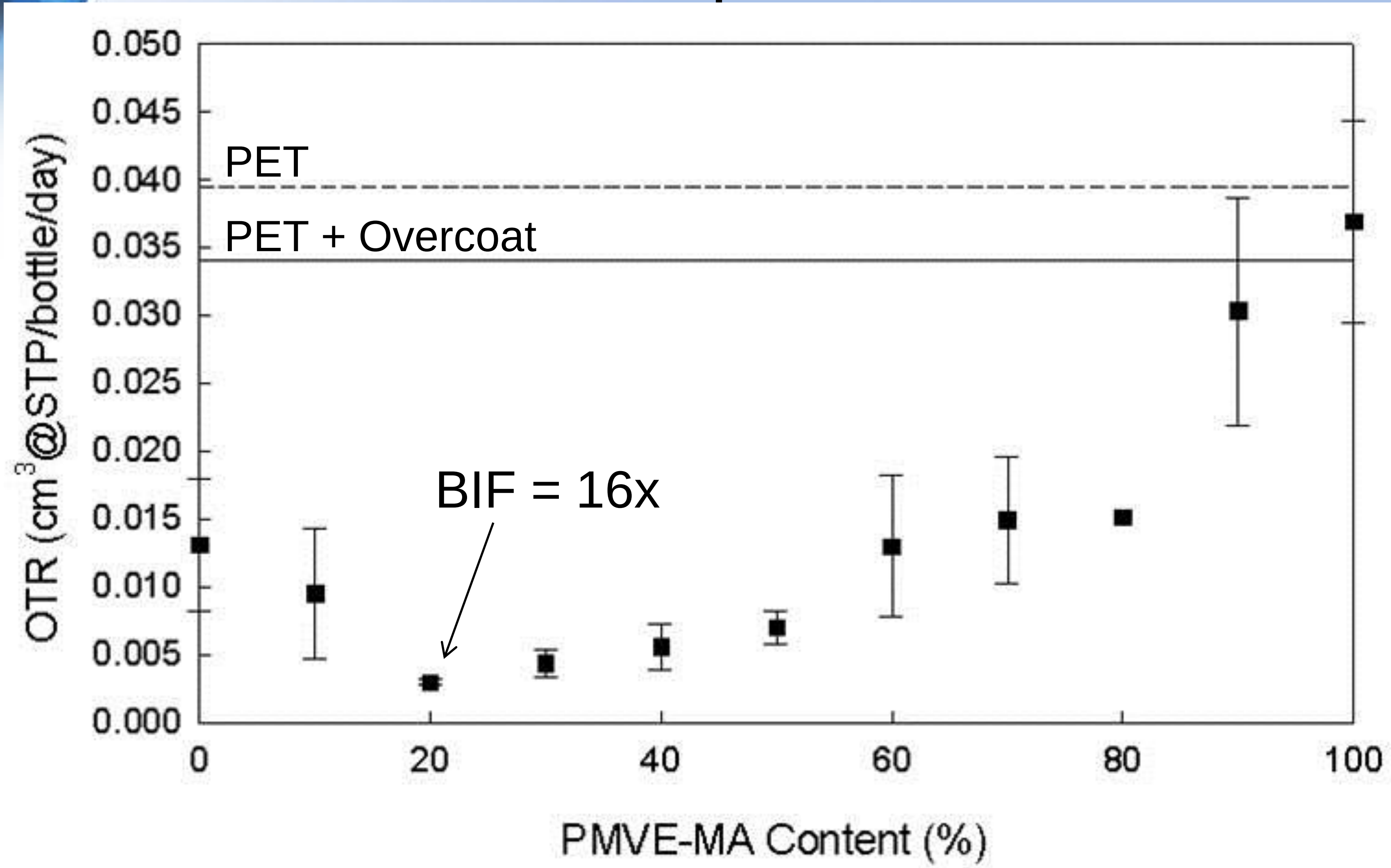
Poly(vinyl alcohol) Poly(methylvinyl ether-maleic acid)



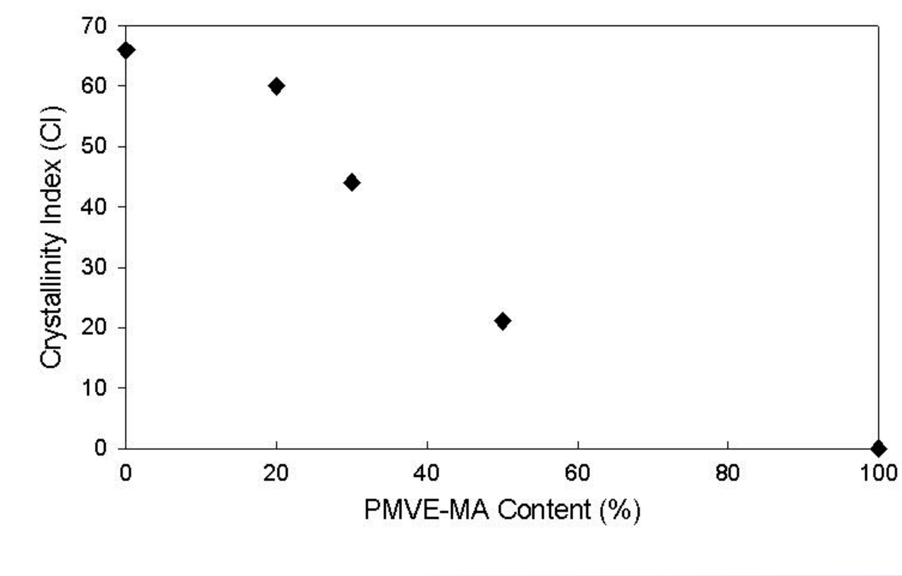
Complex formation - viscosity

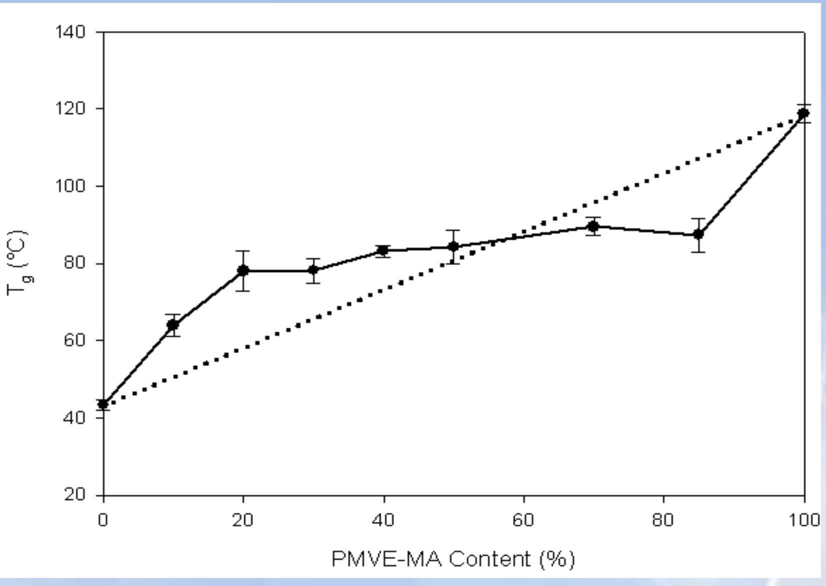


Oxygen Transmission Rate Improvement



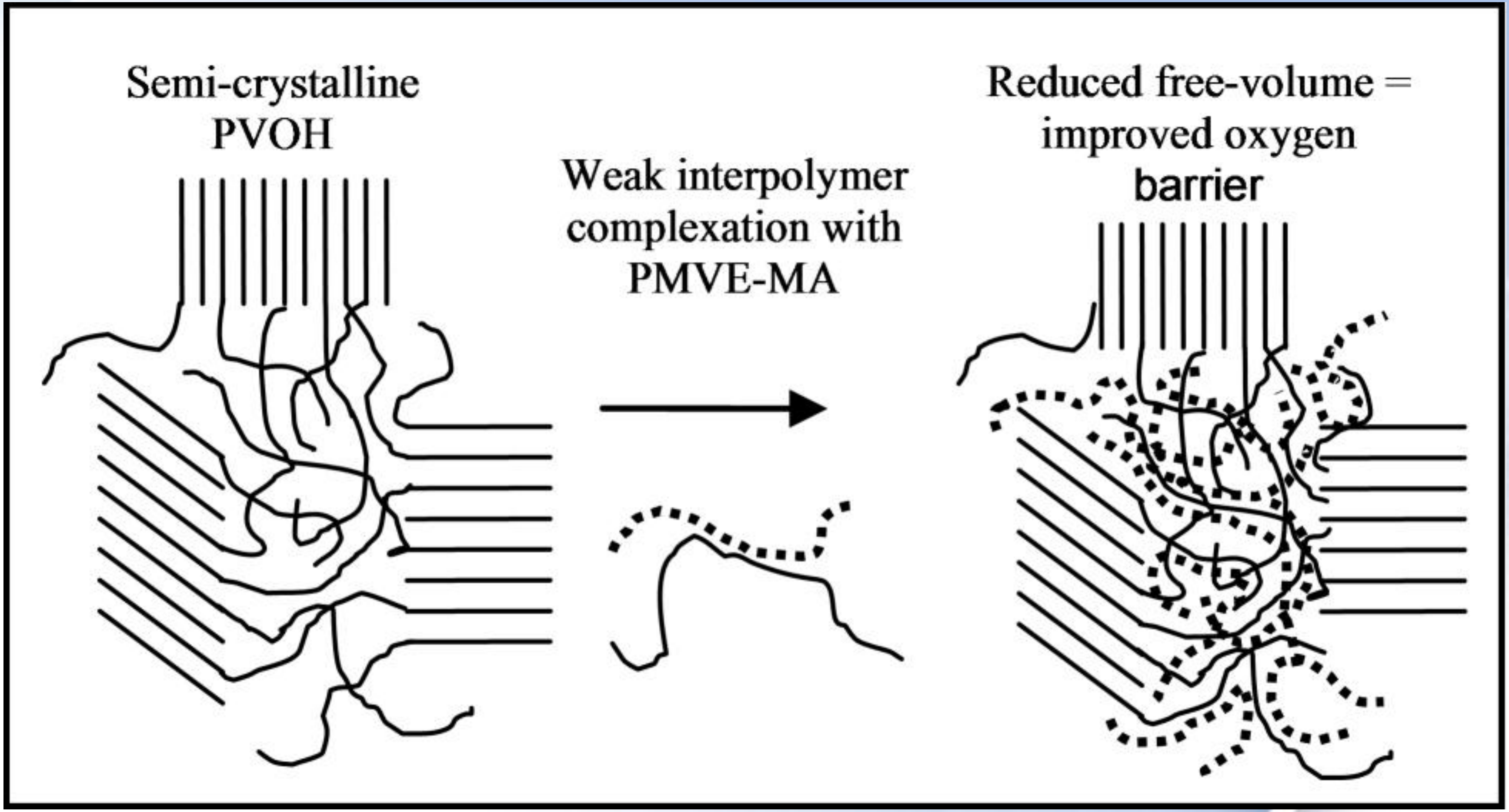
Material Properties





- PVOH crystalline fraction intact
- Positive deviation in glass transition (T_g)

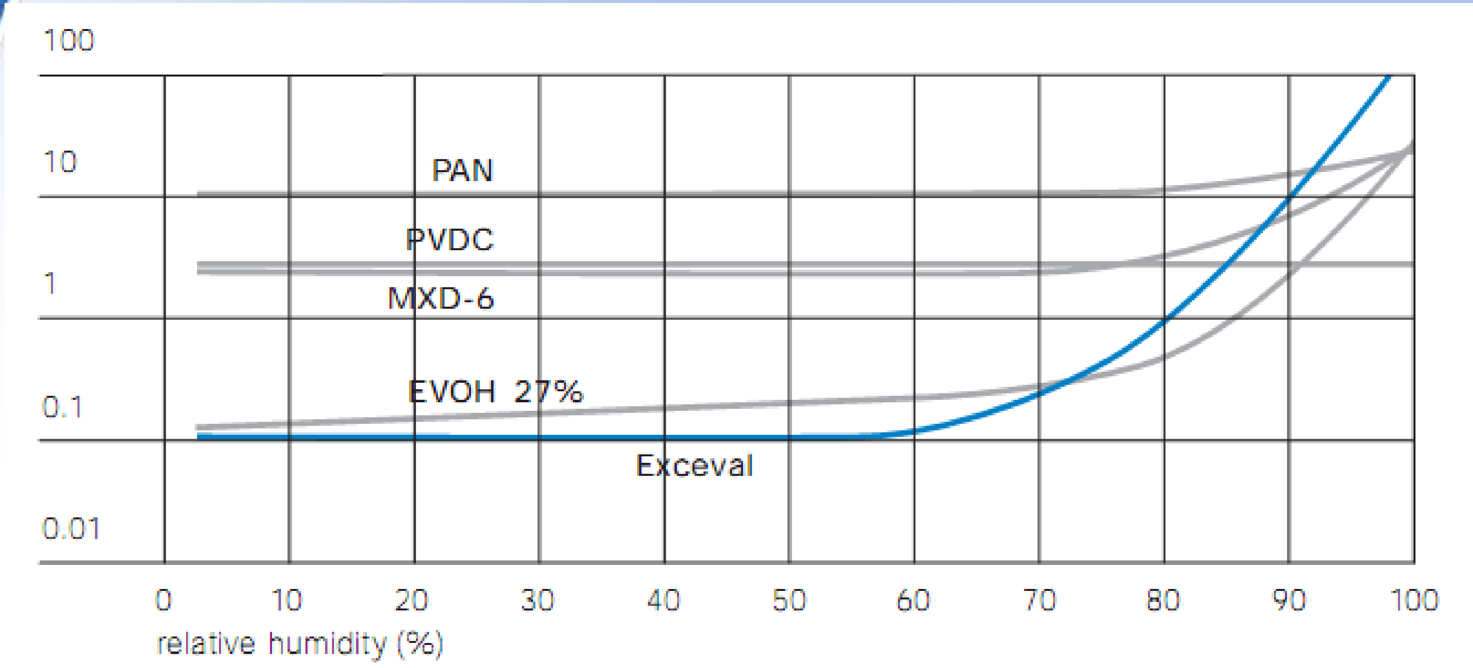
Complex Morphology



PET – uncoated & coated

PP – coated & uncoated

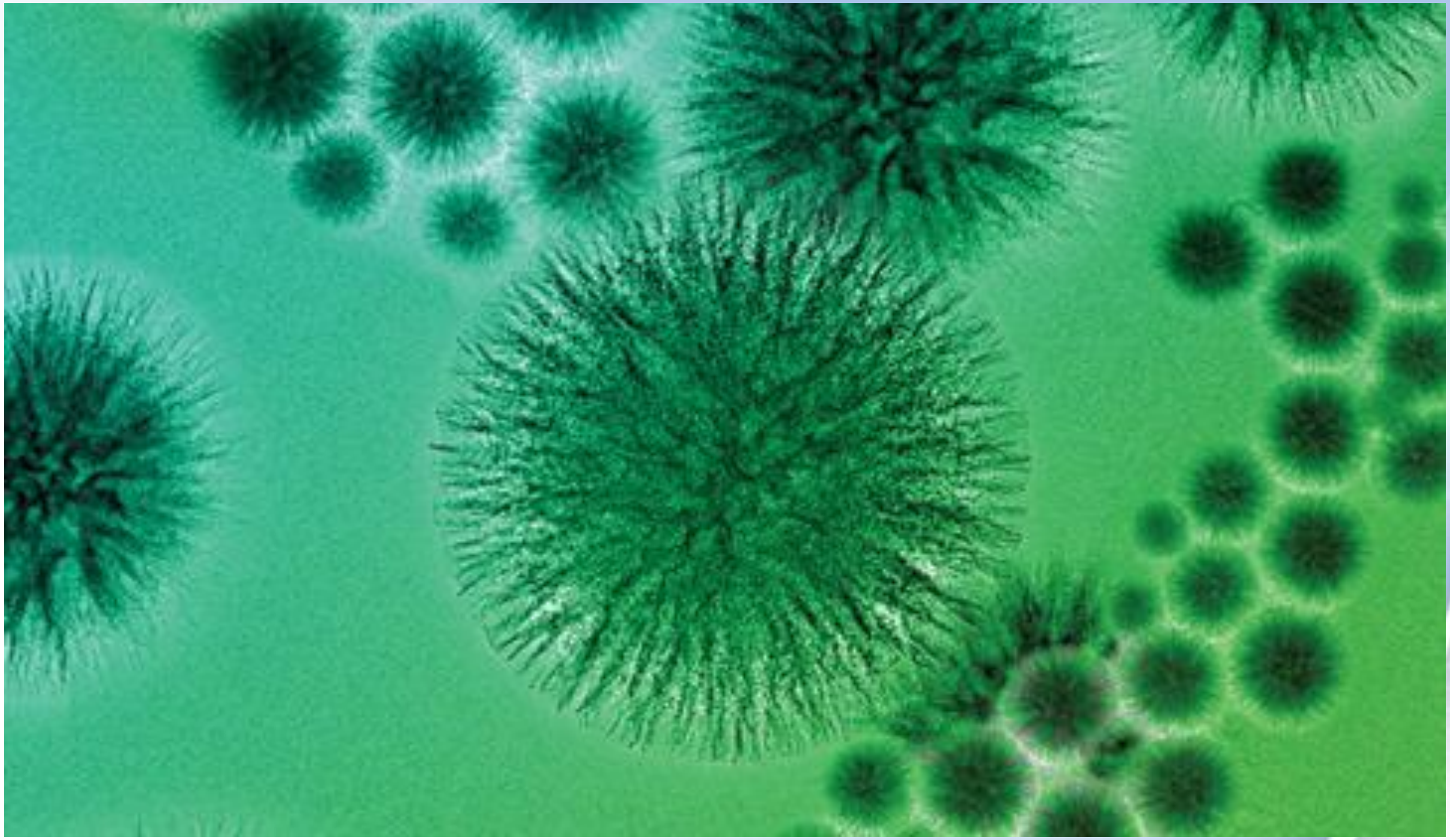
Moisture effect on O_2 barrier



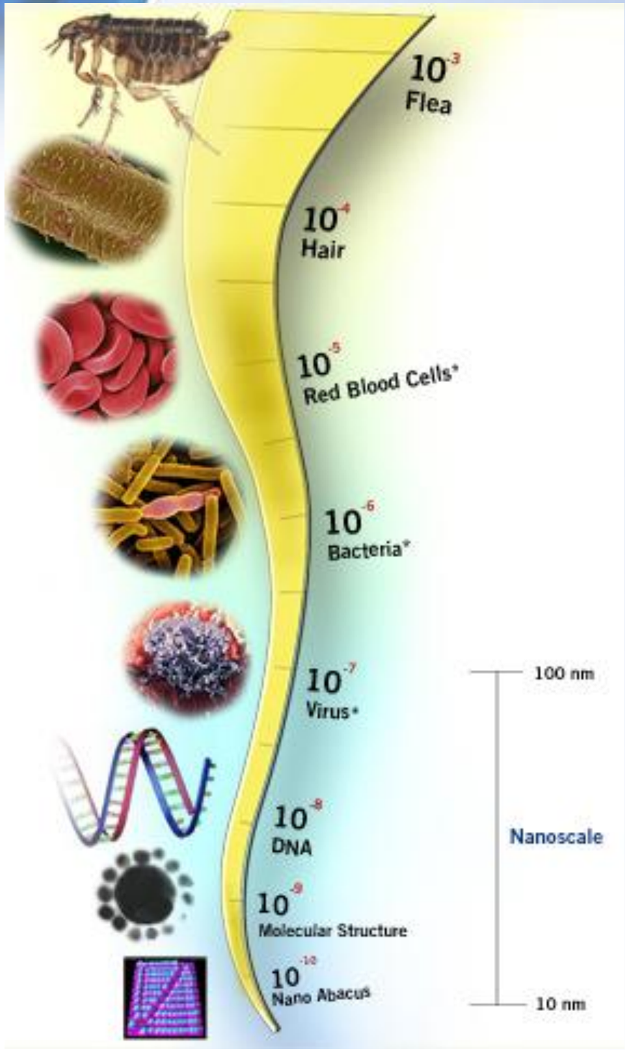
- Highly polar polymers
- H_2O binds to available functional groups – act as plasticisers
- Reduced oxygen barrier properties

- Interpolymer complexation results in closer packing (lower free-volume) and higher “rigidity”
- Increased tortuous path length for diffusing gas molecules
- Oxygen barrier properties improve: 16x for PET; 170x for PP
- However, sensitive to moisture: requires protective overcoat.

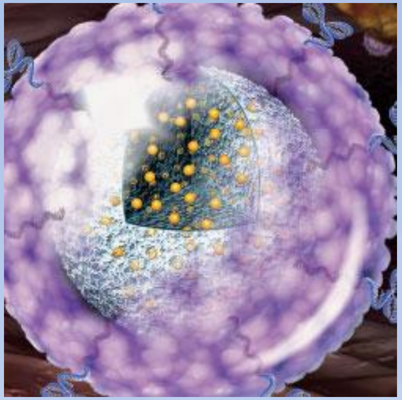
Increasing barrier properties with nanotechnology

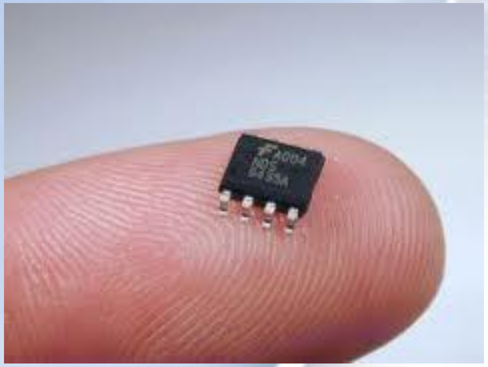


Nanotechnology defined:

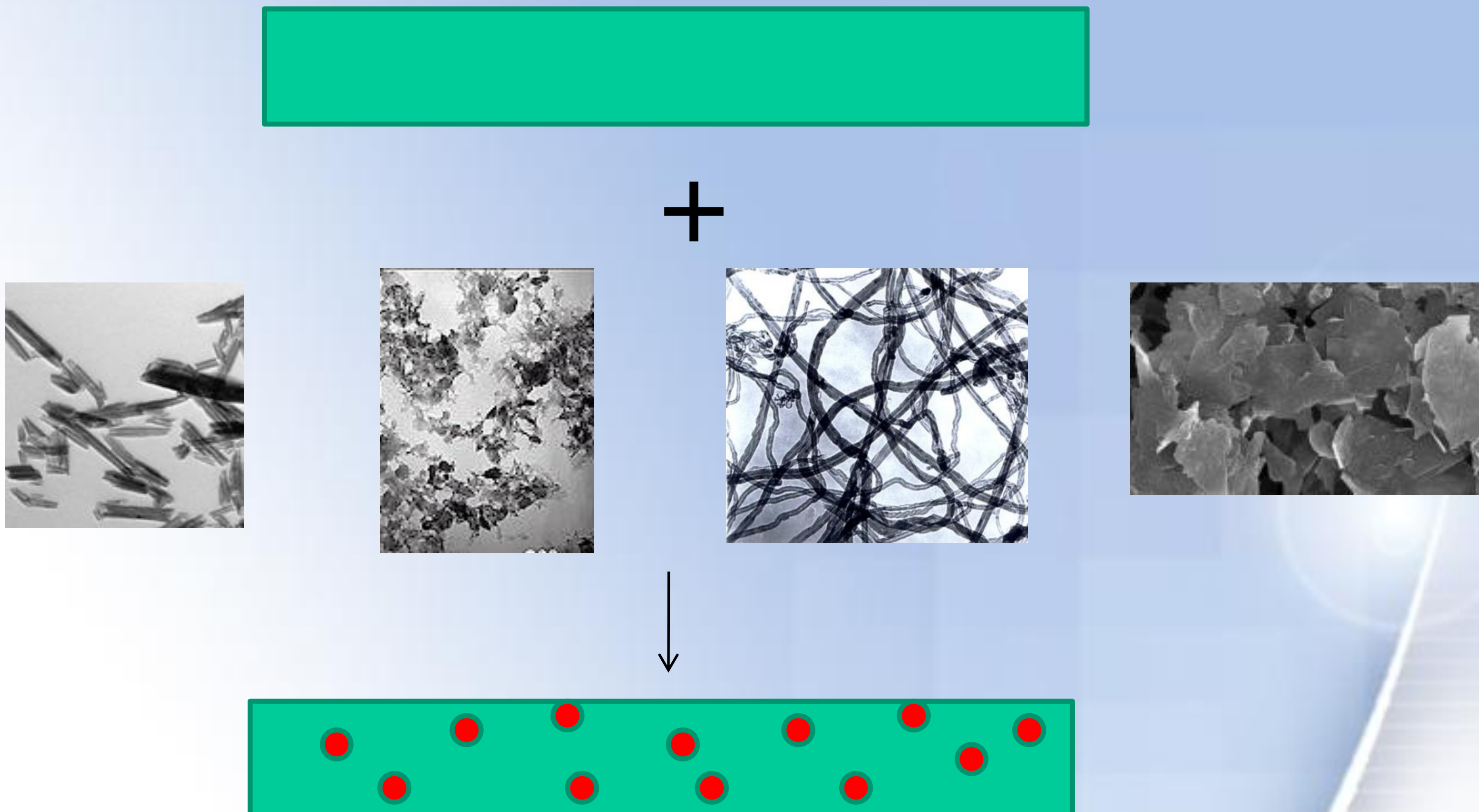


Dramatic change in bulk properties due to ingredients of nano-scale proportions:





Nanotechnology in plastics



↑ Heat resistance

↑ Stiffness

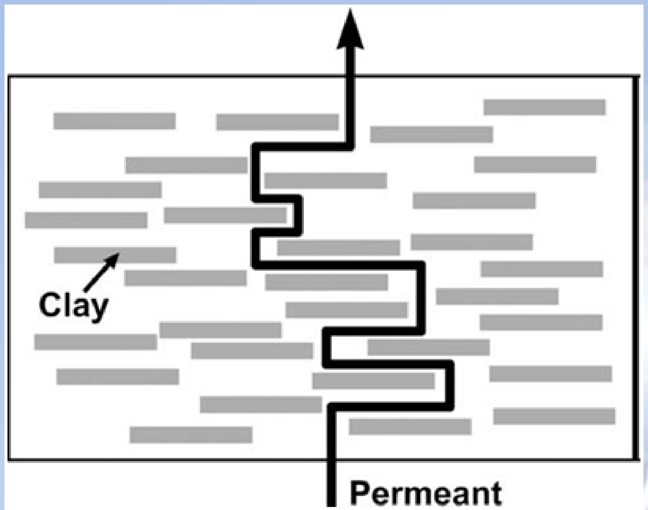
↑ Dimensional stability

↑ Flame retardancy

Polymer/layered silicate nanocomposites

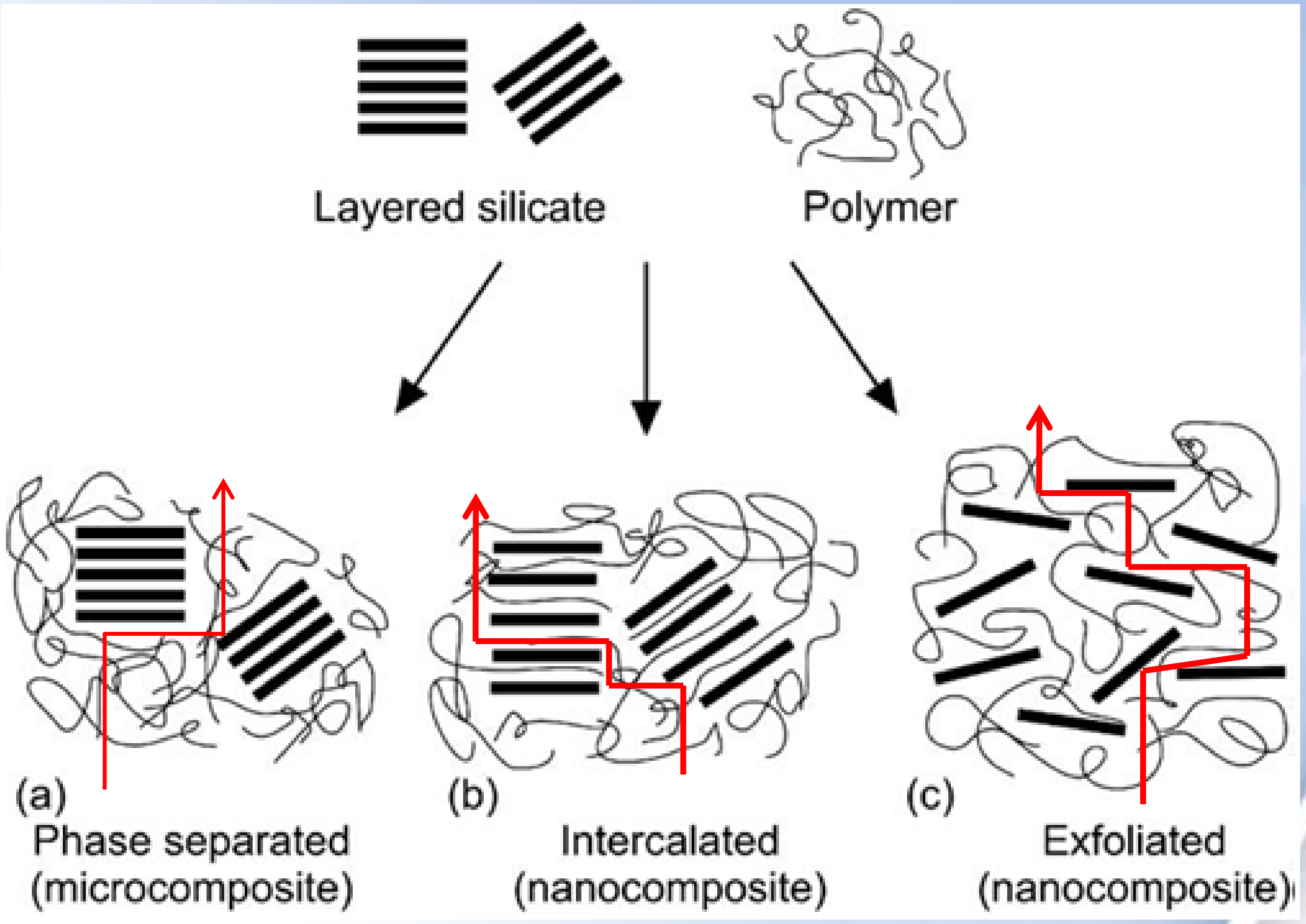
Layered silicate clay, e.g. Montmorillonite:

l = 30 – 2000nm
t = ±1 nm



$$\tau \equiv \frac{\ell'}{\ell^{o}} \longrightarrow D = D_{o}\tau$$

Factors affecting τ :



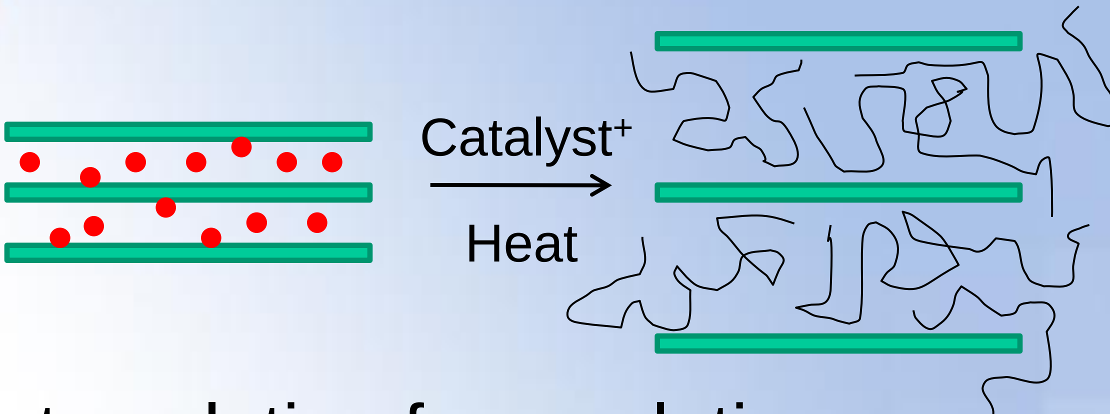
Factors affecting clay intercalation/exfoliation:

- Preparation method
- Polymer chemistry
- Clay surfactant
- Clay loading

Preparation methods

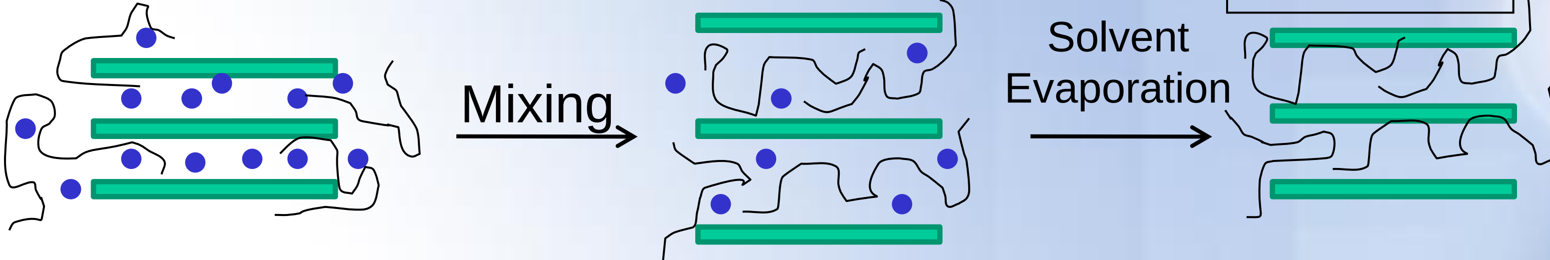
- In-situ intercalative polymerisation:

BIF: 2 - 15x



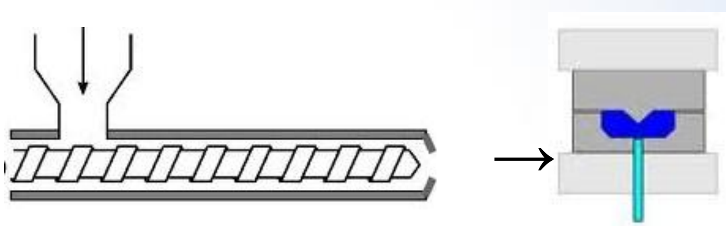
- Intercalation from solution:

BIF: 1.5 – 3x

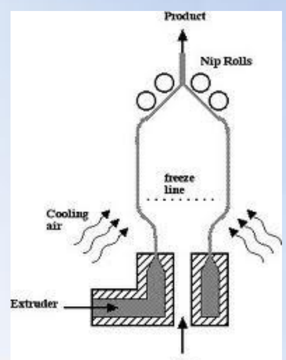


- Melt intercalation:

BIF: 1.2 - 4x

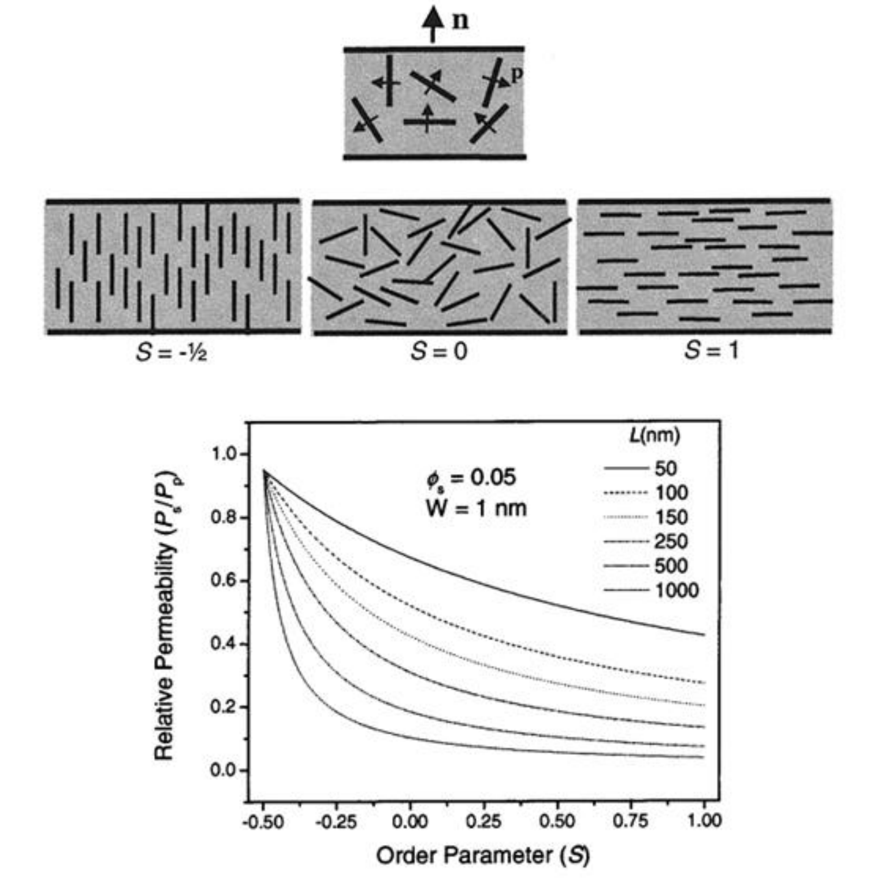


or



=

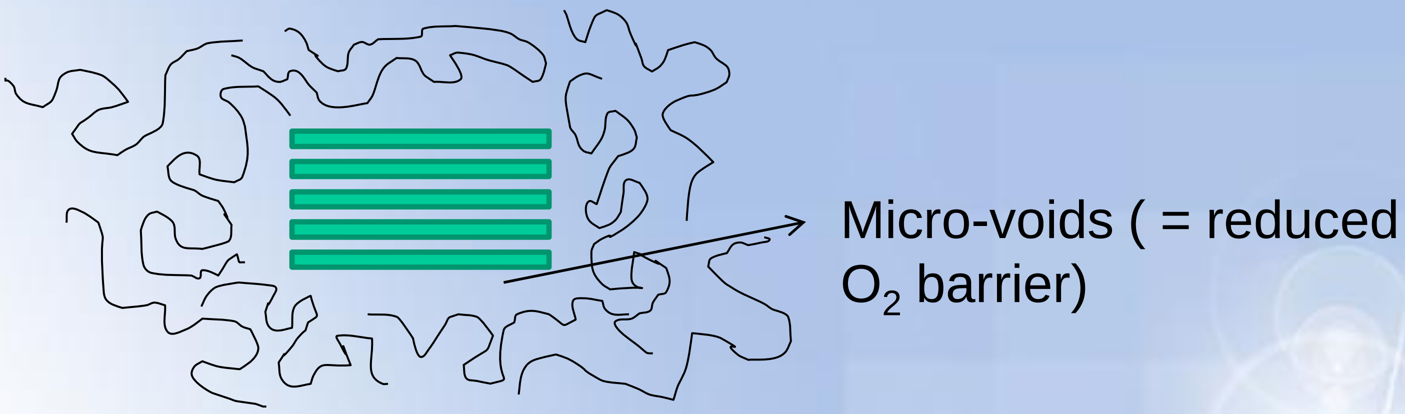
Sheet orientation



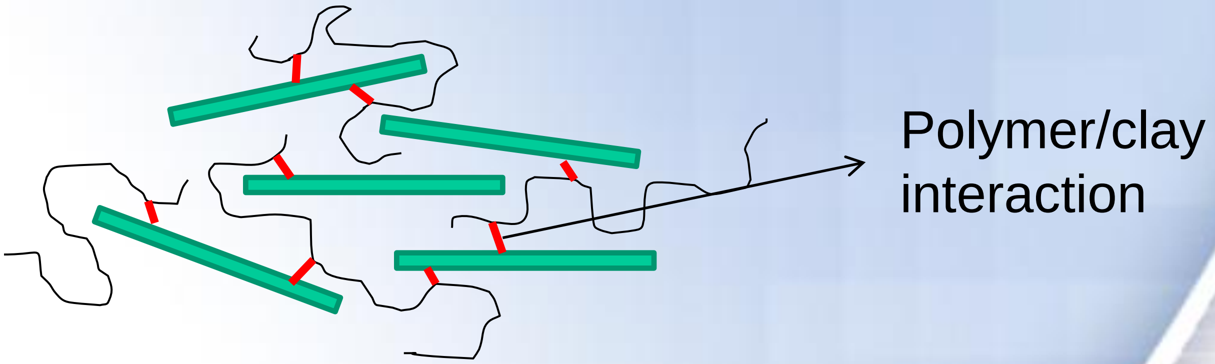
Film blowing – draw down ratio's

Polymer functionality

- Non-polar polymers (PE, PP):

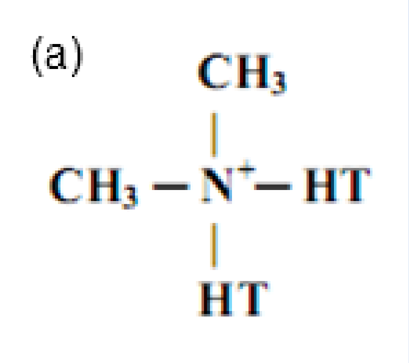


- Polar polymers (PET, PA, PP-g-MA):

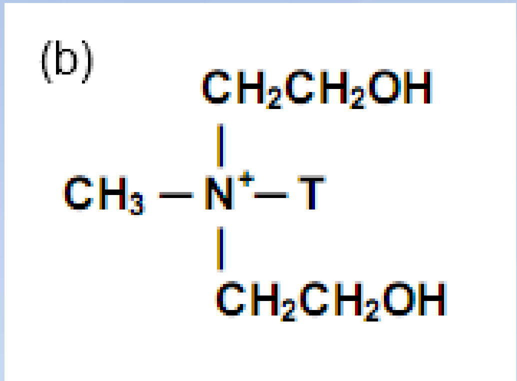


Clay surfactant

- To enhance polymer-clay interaction – clay surface organophilic
- Cationic surfactants:

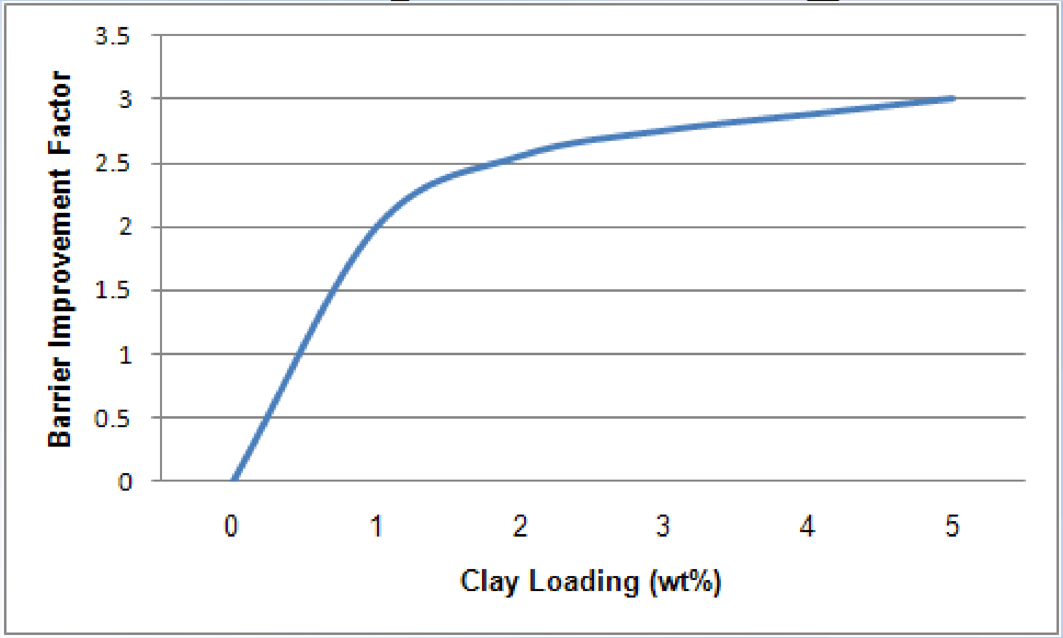


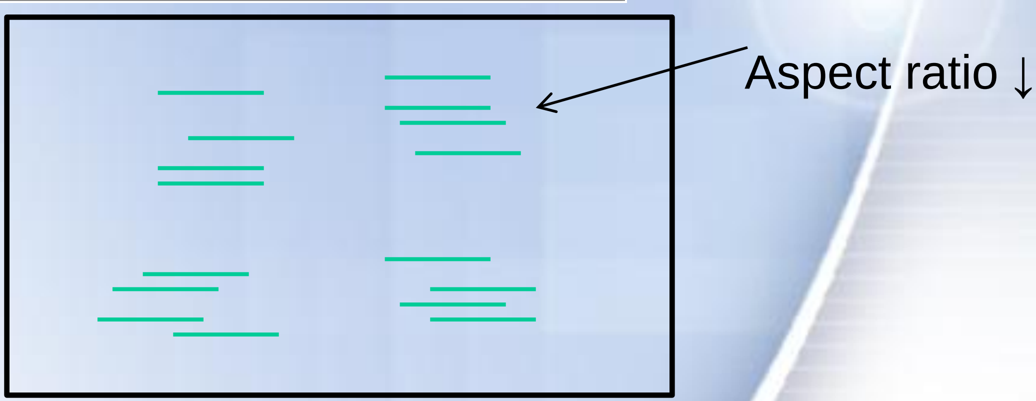
Non-polar polymers



Polar polymers

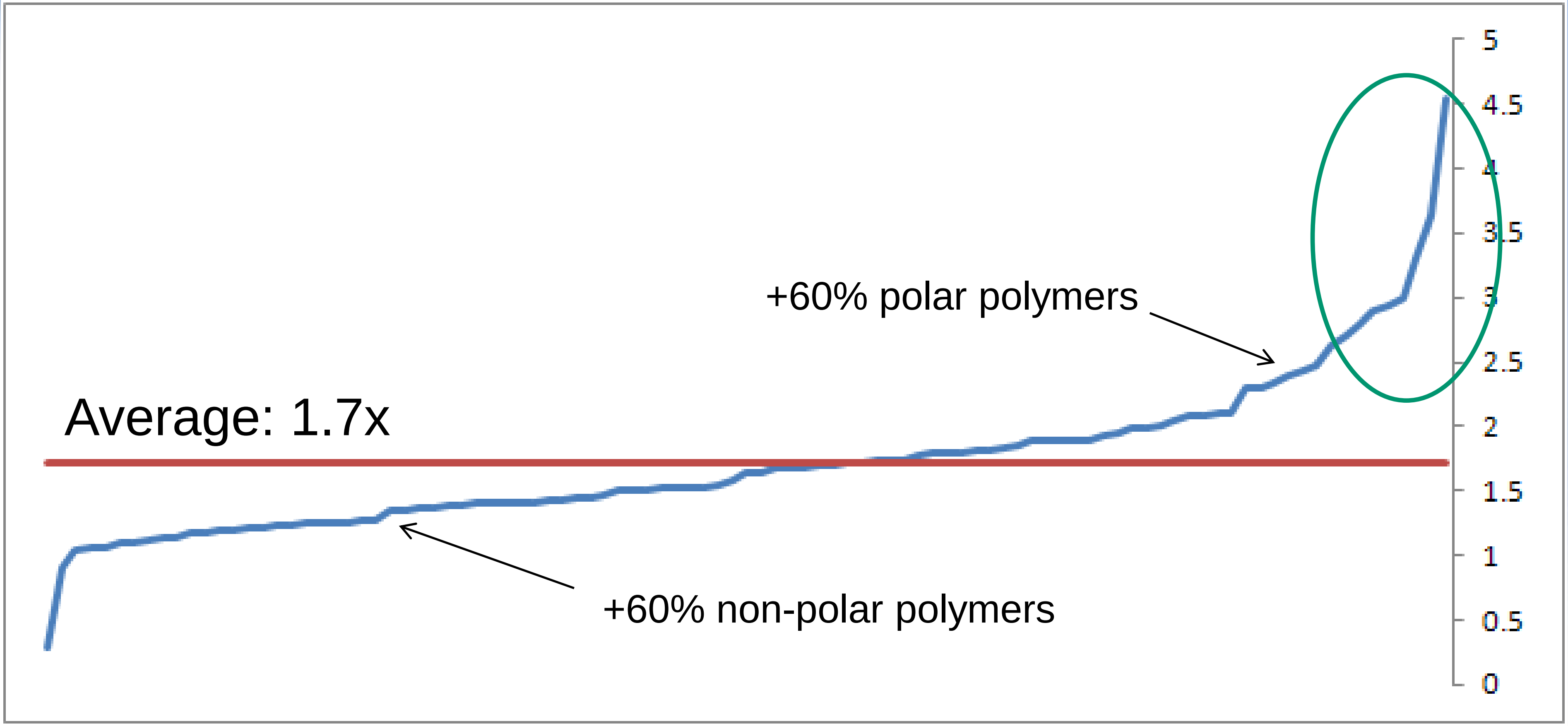
Clay loading





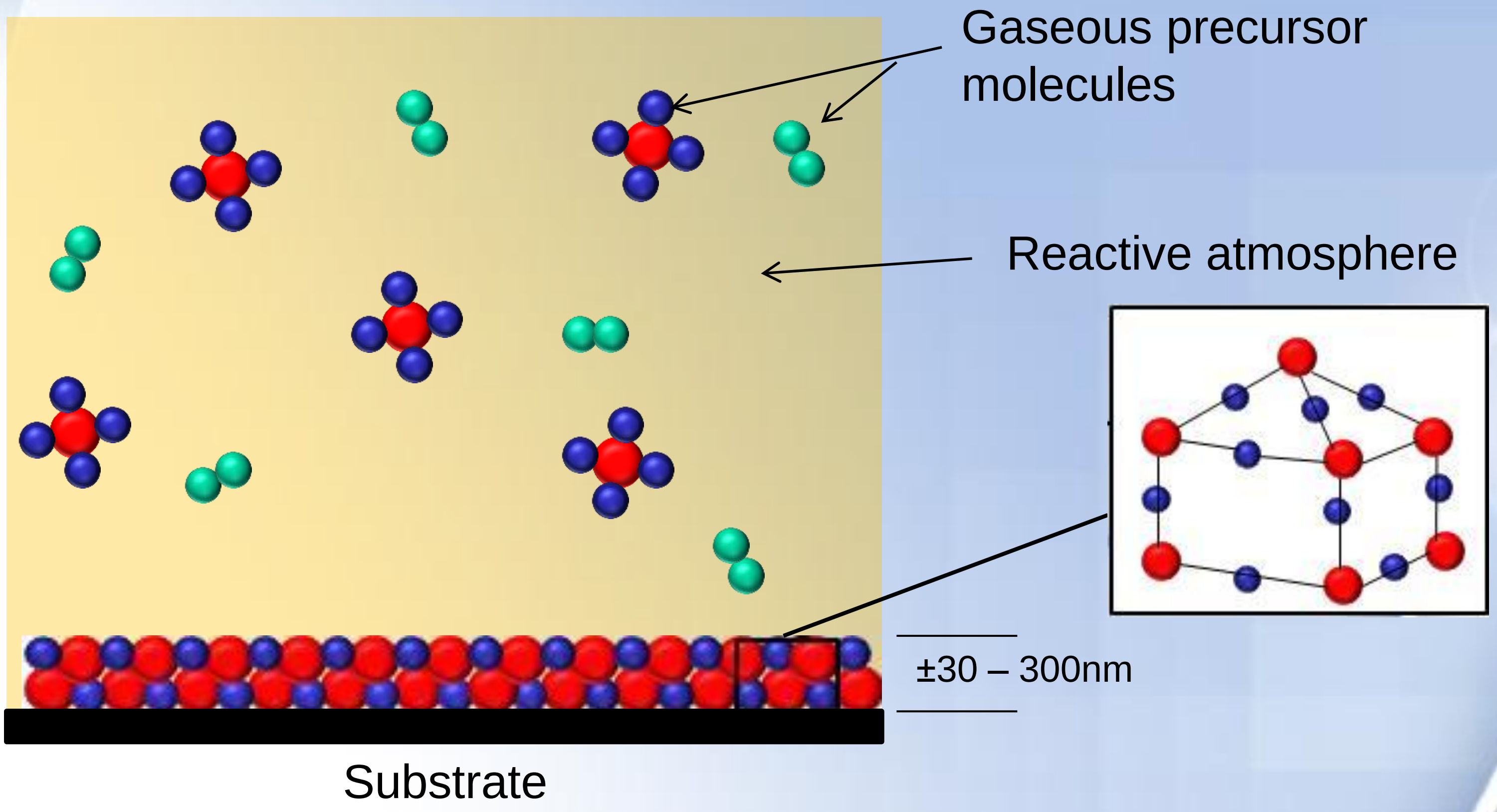
- Polymer/clay incompatibility
- Limited polymer chain mass transport between sheets

Literature summary: BIF's

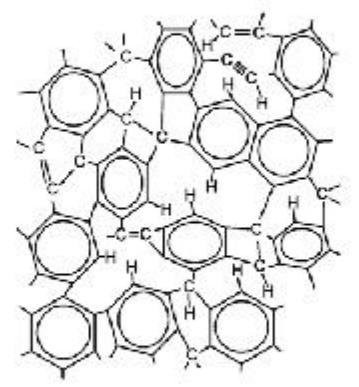


Key Alternative Barrier Technologies…

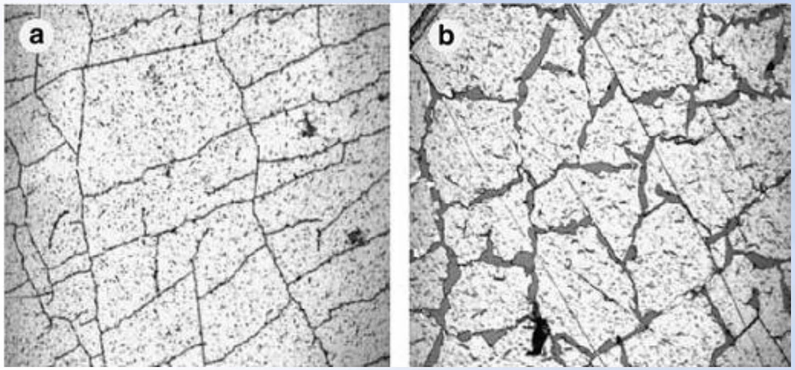
Chemical Vapour Deposition (CVD)



Diamond-like Carbon (DLC)

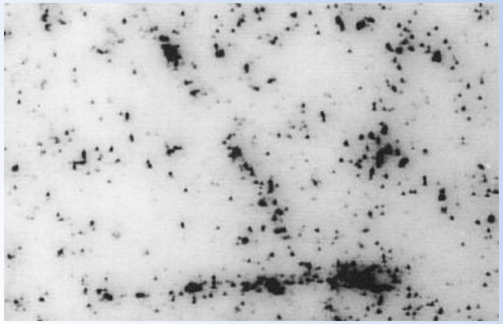


- Precursors: acetylene, methane + argon, helium, nitrogen
- Mech. properties: between graphite/diamond
- Process variables: pressure, gas, power, pulse
- BIF PET: 5 – 100x
- Increased *d* leads to increased brittleness:



Metal-oxides (SiO_x; Al_xO_y)

- Precursors: organo-(silicones/aluminiums) e.g., tetramethoxysilane, trimethylaluminium) + O_2, Ar
- Covalently bonded to substrate – adhesion ↑; brittleness ↓
- Process variables: power, pressure, O_2 %
- BIF PET: 5 – 200x; PP: 2 – 60x
- Prone to pinholes (contaminants), microcracks:



Summary

- Reducing diffusion coefficient (tortuosity) contributes most to increased O_2 barrier
- Interpolymer complex = close packing of chains: BIF PET = 16x; PP = 170x
- Nanoclays = impermeable nanoplatelets: BIF polymers →4x
- Challenges in clay dispersion/stability
- CVD coating = dense, rigid inorganic network
- BIF PET = →200x; PP = →60x
- Coating brittleness

Conclusions

- Poor barrier properties of plastics big limitation for replacing glass/metal
- All technologies have pro's & con's
- Many technical/cost/aesthetic requirements
- No "silver bullet" technology yet