Flexible Barrier Materials

Charles A. Bishop
C.A.Bishop Consulting Ltd
www.cabuk1.co.uk
Barrier materials

Clay

Glass

Tin Can
Range of barrier performance

- Oxygen permeation rate (cc/m²/day)
- Water vapour permeation rate (g/m²/day)

Uncoated Polymer films
Food packaging
Medical packaging
Thermal insulation
Thin film batteries
Solar cells & OLEDs
Properties

Light barrier
Moisture barrier
Gas (Oxygen) barrier
Odour / taint barrier
Modified Atmosphere Packaging - CO₂ - ethylene – etc
Chemical / biological / anti-bacterial / anti-microbial / antiseptic
EMI/RFI screening, Anti-static
Decorative / aesthetics / convenience
Mechanical – containment – heat seal – puncture resistance

Food Degradation

Rancid – fats affected by light & oxygen
Soggy – moisture absorption
Taint - loss of flavour or alteration of aroma
Loss of colour
Loss of texture – bloom on surfaces
Degradation – mould growth, chemical interaction, etc
Total packaging performance

- Protect contents from physical damage
- Flavour loss out
- Taint in
- Brand image, Aesthetics, Product information, Contents, health, disposal, etc
- Physical properties to form package – e.g. heat seal
- Light, UV degradation i.e. rancidity
- Moisture in
- Modified gas atmosphere out
- Oxygen in
General Atomics OLED demonstration devices

Amorphous Si from Flexcell

Flexible CIGS from Daystar
Permeation

Henry’s law

desorption

absorption (sorption)

Henry’s law

Fick’s Law

diffusion
# Diffusion Coefficients

<table>
<thead>
<tr>
<th>Material</th>
<th>$D_{O_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen in air</td>
<td>$0.15 \text{ cm}^2/\text{s}$</td>
</tr>
<tr>
<td>Oxygen in Water</td>
<td>$2 \times 10^{-5} \text{ cm}^2/\text{s}$ at $20^\circ\text{C}$</td>
</tr>
<tr>
<td>Oxygen in Quartz</td>
<td>$10^{-25} \text{ cm}^2/\text{s}$</td>
</tr>
<tr>
<td>Oxygen in Silica</td>
<td>$10^{-13} \text{ cm}^2/\text{s}$</td>
</tr>
<tr>
<td>Oxygen in Silica Gel</td>
<td>$10^{-3} \text{ cm}^2/\text{s}$</td>
</tr>
<tr>
<td>Oxygen in Polypropylene</td>
<td>$10^{-7} \text{ cm}^2/\text{s}$</td>
</tr>
<tr>
<td>Oxygen in Polyester</td>
<td>$10^{-9} \text{ cm}^2/\text{s}$</td>
</tr>
<tr>
<td>Water vapour in air</td>
<td>$0.26 \text{ cm}^2/\text{s}$</td>
</tr>
</tbody>
</table>
Biaxial substrates

Diffusion path

tension
Polymers or coatings can be with or without fillers.
Barrier performance

• Performance of multi-layers dependent upon:-

• Adhesion
  • Dependent upon surface roughness, quality & cleanliness
  • Dependent upon surface energy & wetting (wetting ≠ adhesion)
  • Dependent upon amount & type of surface treatment
  • Dependent upon chemical bonding

• Quality of materials, coating technique & handling
  • Including filtration of coatings
  • Density of coatings
    – Dependent upon deposition process

• Minimise handling – protect fragile coatings
Nucleation & Film Growth

Gold nucleating onto glass

Transmission Electron Micrographs (TEM)
75,000x Magnification

The thickness indicated is for a film of equivalent mass that is continuous & parallel

R.M.Hill
Contemp Phys. 1969  Vol 10 No 9 pp 221-240
Nucleation & Film Growth

In reality the coatings can be quite thick but still contain defects or holes that reach the substrate. High surface energy & good wetting help minimise this
Microstructure modification

Slow growing crystals are shadowed & starved of material & thus stop growing, leaving the fast growing crystals to dominate.

Thicker films show more surface texture, they can even be faceted.

Following bombardment the columnar structure disappears & a denser equiaxed crystal structure is formed.

The impacting ions can displace atoms causing point defects.

Atoms can be displaced & deposit into shadowed areas.

Enhanced diffusion including at the interface & into the substrate surface giving interfacial mixing.
Onset of cracking

![Graph showing the onset of cracking for different SiOx thicknesses.]

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiOx thickness [nm]</th>
<th>Crack Onset Strain [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOx / PET (RDO12)</td>
<td>20</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.5</td>
</tr>
</tbody>
</table>
**Materials**

**Polymers / organic materials**

**Substrates**
- Polyester (PET, PEN)
- Polypropylene (PP, OPP, CPP)
- Polyethylene, (PE, LDPE, HDPE, Linear LDPE, ULDPE….)
- Polyamide (Nylon)
- Biopolymers
- Others
  - Cyclic Oxalic Copolymers (COCs)
  - Liquid Crystal Polymers (LCPs)
  - Polycarbonate (PC)

**Coatings**
- Ethylene vinyl alcohol (EVOH) - Polyvinyl alcohol (PVOH)
- Poly vinyl dichloride (PVdC) – *(banned in some countries)*
- Adhesives (heat seal, lamination, polyurethanes, polyethylene….)
- Acrylates (inc. in-vacuum coatings)

**Inorganic coatings**

**Compounds**
- Silica, silicates
- Alumina
- Metal oxides – ITO, SnO, ZnO, etc
- Metal nitrides
- Metal oxynitrides
- Metal carbides, oxycarbides, etc
- Graded compounds

**Metals**
- Aluminium

**Others**
- Carbon
- Melamine (1,3,5-triazine-2,4,6-triamine)
An inorganic compound is dispersed in a polymeric matrix, to create a tortuous path for gas molecules (long gas diffusion path).

Molecular movement of the polymer chain is restricted by the inorganic compound (low gas diffusion rate).

Magnification of the gas barrier layer: less than 5nm.
<table>
<thead>
<tr>
<th>Barrier Material</th>
<th>Thickness</th>
<th>Oxygen Transmission [ccm/m²/day/atm]</th>
<th>Water Vapour Transmission [g/m²/day/atm]</th>
<th>Deposition Process</th>
<th>Coating type</th>
<th>Relative cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET / Blank</td>
<td>12.00 μm</td>
<td>100</td>
<td>64.64</td>
<td></td>
<td></td>
<td>1x</td>
</tr>
<tr>
<td>PVDC</td>
<td>24.00 μm</td>
<td>8</td>
<td>0.3</td>
<td></td>
<td></td>
<td>3x</td>
</tr>
<tr>
<td>EVOH</td>
<td>24.00 μm</td>
<td>0.16 - 1.86 *</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-OPA</td>
<td>15.00 μm</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminized PET (single)</td>
<td>~ 30nm</td>
<td>0.31 - 1.55</td>
<td>0.31 - 1.55</td>
<td>Evaporation</td>
<td>Al</td>
<td>2x</td>
</tr>
<tr>
<td>Aluminized PET (double)</td>
<td>~ 30nm each</td>
<td>0.03</td>
<td>N/A</td>
<td>Evaporation</td>
<td>Al</td>
<td>~3x</td>
</tr>
<tr>
<td>Aluminium on PE</td>
<td>7μm Al</td>
<td>0.001</td>
<td>N/A</td>
<td>Laminated</td>
<td>Al</td>
<td></td>
</tr>
<tr>
<td>SiOx on PET</td>
<td>10 - 80 nm</td>
<td>0.35 - 10**</td>
<td>0.46 - 1.24</td>
<td>Evaporation</td>
<td>SiOx</td>
<td>3x</td>
</tr>
<tr>
<td>SiOx on PET or SiOx containing Carbon</td>
<td>10 - 80 nm</td>
<td>0.08 - 1.55</td>
<td>0.5 - 5.0</td>
<td>PECVD</td>
<td>SiOx or Si(C)Ox</td>
<td>3x</td>
</tr>
<tr>
<td>Al2O3 on PET</td>
<td>20 nm</td>
<td>1.5</td>
<td>5</td>
<td>Evaporation, or Reactive Evaporation</td>
<td>Al₂O₃</td>
<td>2.25x - 2.5x</td>
</tr>
<tr>
<td>Al₂O₃/SiOₓ on PET</td>
<td>50 nm</td>
<td>2.0 - 3.0</td>
<td>1</td>
<td>Evaporation</td>
<td>Al₂O₃/SiOₓ</td>
<td>2.5x - 3x</td>
</tr>
<tr>
<td>Al₂O₃ on PET</td>
<td>&lt;5 nm</td>
<td>~1.5 (improving 0.0001 claimed)</td>
<td>~5 (improving 0.0001 claimed)</td>
<td>ALD - Atomic Layer Deposition</td>
<td>Al₂O₃</td>
<td>aim to be &lt; 2x</td>
</tr>
<tr>
<td>Diamond-like Carbon on PET</td>
<td>20 nm</td>
<td>2</td>
<td>1.5</td>
<td>PECVD</td>
<td>Carbon (DLC)</td>
<td>2.5x - 3x</td>
</tr>
<tr>
<td>Melamine on PET</td>
<td>12.00 + 0.25μm</td>
<td>&lt;5</td>
<td></td>
<td>PVD</td>
<td>Triazine</td>
<td>2.5x - 3x</td>
</tr>
<tr>
<td>Melamine on OPP</td>
<td>20.00 + 0.25 μm</td>
<td>30</td>
<td></td>
<td>PVD</td>
<td>Triazine</td>
<td>2.5x - 3x</td>
</tr>
<tr>
<td>OPP / Blank</td>
<td>20.00 μm</td>
<td>1600</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- * depending on relative humidity and ethylene content
- ** depending on process
Foil may be annealed periodically.

Foil - 2.2m wide 2,500 m/min 6 microns thick

<table>
<thead>
<tr>
<th>Foil Gauge</th>
<th>Foil Caliper, μ</th>
<th>Average</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.5</td>
<td>7</td>
<td>423</td>
<td>1584</td>
</tr>
<tr>
<td>35</td>
<td>9</td>
<td>211</td>
<td>1056</td>
</tr>
<tr>
<td>50</td>
<td>13</td>
<td>85</td>
<td>528</td>
</tr>
<tr>
<td>75</td>
<td>18</td>
<td>21</td>
<td>106</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Examples of Typical Foil Pinholes

- Pinholes from Al-Fe-Si Constituents
- Pinhole from Depression in Foil
- Pinhole from rolling Debris
- Pinhole from Aluminum Fines Damage
Pinholes

- Debris typically >0.5 microns
- Metalized layer 20 – 100nm
ALD provides conformal coating over whole surface including into root of debris contamination or defects.

Loss of coating due to shadowing by debris from coating point source

Metallization or other PVD process

Atomic Layer Deposition (ALD)
Surface defects

Incident Dark Field Optical Microscopy
Or
Differential Interference Contrast Microscopy

Area used for the analysis was 170 x 170 microns

Magnification 400x.

Average of 6 different fields of view
Comet debris slides causing pinhole and scratch.
SEM of defects – FEP IVV Freising
Resolution of eye
A working value ~50 microns (quoted range 10 – 100 microns)

Practical example
Human inspection expected to resolve 50% of 50 microns debris on a surface

Source of debris

People emit a very large number of particles
standing still humans emit 100,000 particles per minute (ppm)
standing up from a sitting position humans emit 2,500,000 ppm
(definition of a particle is debris of 0.5 microns or larger)

This comprises hair, skin and micro-salt crystals
skin in the range  0.1 – 5 microns     Hair in the range  5 – 100 microns

<table>
<thead>
<tr>
<th>Activity generating particles</th>
<th>microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pollens</td>
<td>10 - 100</td>
</tr>
<tr>
<td>Rubbing ordinary painted surface</td>
<td>90</td>
</tr>
<tr>
<td>Sliding metal surfaces (unlubricated)</td>
<td>50 to 150</td>
</tr>
<tr>
<td>Crumbling or folding paper</td>
<td>60</td>
</tr>
<tr>
<td>Rubbing epoxy painted surfaces</td>
<td>30 to 75</td>
</tr>
<tr>
<td>Seating and unseating screws</td>
<td>25 to 120</td>
</tr>
<tr>
<td>Belt drive</td>
<td>5 to 35</td>
</tr>
<tr>
<td>Writing with ballpoint pen on paper</td>
<td>15 to 30</td>
</tr>
</tbody>
</table>
Oligomer growth

PET (442) after prolonged heating 1hr @ 140 Deg C  SEM at 2000x magnification
Showing growth of ‘mer’ units into dimers, trimers, etc
The atoms nucleate on the higher surface energy part of the substrate but not on the low molecular weight contamination.

Low molecular weight contamination can be vaporized by depositing atoms preventing any deposition. This low molecular weight material may be oligomer.
Stress raisers

Surface defects i.e. dents or bumps lead to defects in the coatings

The coating thinner over the defect (> surface area for same coating thickness) & also the edges of the defect are prone to cracking

Substrate
Cleaning options

Options for cleaning polymer film surfaces

– Cloth wipe
– Static brush
– Rotating brush
– Air blower / knife
– Vacuum cleaner
– Electrostatic neutralised ultrasonic pulsed air jet & vacuum extract
– Transfer tack rolls
– Planarization and/or Overcoating (best combined with pre-cleaning first)
– Carbon Dioxide ‘snow jet’
Polymer pre-layer

No cleaning requires thick coating

Large debris

Cleaning = fewer, smaller debris & thinner coating
General Atomics – Super sapphire

Regular sputtered Al₂O₃

Sputtered Super Sapphire
Ultrasonic atomisation of monomer feed

Heated plates flash evaporate the atomised monomer into a vapour

The vapour passes through baffles to ensure the vapour pressure is uniform at exit slit

electron gun (shown) or UV source

Cooled Deposition Drum
Pre / Post Acrylate Monomer Printing

- gravure roll
- transfer roll
- anilox roll
- doctor blade
- polymer source
- UV or EB curing
- aluminium evaporation
- polymer source
- UV or EB curing
- gravure roll
- transfer roll
- anilox roll
- doctor blade
Polymer layers

Sigma International - Benefits of polymer layers.

<table>
<thead>
<tr>
<th>Materials</th>
<th>No. pinholes/unit area</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPP + Al</td>
<td>1760</td>
</tr>
<tr>
<td>OPP + Polymer + Al</td>
<td>590</td>
</tr>
<tr>
<td>OPP + Al + Polymer</td>
<td>35</td>
</tr>
</tbody>
</table>

- Polymer acrylate hides some debris & prevents some others from being moved. If debris is moved the polymer protects the metal coating.
The polymer is drawn by capillary action into pores thus partially sealing them. Adding a nano-flake further improves the diffusion coefficient of the coatings. Ideally the flake size is small enough to fill and plug any cracks, pores or pinholes in the coating.
## Barrier performance

<table>
<thead>
<tr>
<th>Material</th>
<th>Spacing</th>
<th>Diffusion Path</th>
<th>Method</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminised PET (single)</td>
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</tr>
</tbody>
</table>

When the defect spacing is large compared to the thickness the diffusion path becomes very long as shown above.

By comparison a greater density of defects results in the diffusion distance being ~ = equal to the polymer thickness.
Polymer / oxide barriers - Barix

a) Basic 4 dyad structure

b) Barrier structure on OLED cathode

c) Barrier structure on substrate defect

d) Basic polymer planarization layer on a test grating to evaluate planarising effect
Multi-dyad barrier

Fracture cross-section SEM of generic Barix ™ film
Glass - Float line process

Fusion process

Rolls of glass down to 50 microns thick
Glass substrates

30 microns (R &D)
50 microns pilot production

The photograph from Corning shows the edges protected by Kapton tape
Conclusions

Key to good barrier:

Substrate quality
- Surface – clean, smooth, flat, minimal defects
- Bulk - thermally stable, good gauge, well wound
  zero or minimal exudate contamination

If you do not get the substrate right – do not bother coating

Deposition process
- High quality winding – tension control
- Good quality deposition system hygiene
- Dense coating – minimise defects
- Maximise adhesion
- Minimal front surface contact – protect coating
- High quality handling & storing rolls

Manage substrate surface
Conclusions

All webs are contaminated with debris (both sides)

Most webs would benefit from a physical clean such as by tack-roll (both sides)

Many would also benefit from a molecular clean to raise the surface energy to modify chemistry to improve adhesion

Alternative strategy - cover debris using polymer coating - coating may also need plasma treating

Densify coating – minimise porosity & defects
Thank you for listening

Charles A. Bishop
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