Some considerations on adhesion or lack of adhesion

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Why do we need good adhesion?

Because we want to bend and stretch products

either during manufacture
  cf. high speed packaging lines

or in final use
  e.g. flexible or curved displays
       smart textiles
       barrier packaging
Flexible display

Clothing literally sparkles when made out of a light-emitting fabric. Not only for fashion, the cloth also has potential use for safety apparel.
**Twist Test – ‘gelbo’ Test**

- Coating
- Twisted material
- Polymer substrate

**Bending Test**

- Coating
- Polymer substrate
- Mandrel - reducing diameter increases severity

**Dead Fold Test - Cracks**

- Coating
- Polymer substrate
- Cracks appear at high stress point
Coated substrate changes dimension under tensile loading.

Coated substrate before any tension is applied:
- Coated substrate elongates in the direction of tension but contracts in the transverse direction.

Coated substrate once tension is applied:
- Continued elongation, stretch or tensile test – cracks widen & new cracks appear.
- Buckles appear.

Cracks:
- First crack
- More cracks

Compressed:
- Coated substrate modifies its dimension.
Elongation or % Strain

No. of cracks or Permeation or increasing electrical resistivity

Tensile test

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improved coating adhesion

reduced coating thickness

onset of cracking

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Elongation or % Strain

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No. of cracks or Permeation or increasing electrical resistivity
Oligomer

Or

Low Molecular Weight Additives
Surface energy

Time

- Fresh clean film
- Corona treatment of front surface
- In-vacuum plasma treatment
- Coated surface
- Back surface of film
‘cyclic trimer’

Cyclic tri(ethylene terephthalate)

On the surface of PET webs can be found low molecular weight oligomer that exudes to the surface with time &/or heat. These lead to reduced adhesion, pinholes & coating pick-off.
Oligomer growth

PET (442) after prolonged heating @ 140 Deg C          SEM at 2000x magnification
Showing growth of ‘mer’ units into dimers, trimers, etc.
### PET – Cyclic oligomer

<table>
<thead>
<tr>
<th>Cyclic dimer</th>
<th>175 - 224 - 229</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclic trimer (B type crystal)</td>
<td>319</td>
</tr>
<tr>
<td></td>
<td>317 – 320</td>
</tr>
<tr>
<td></td>
<td>321</td>
</tr>
<tr>
<td>Crystalline transition temperature</td>
<td>199</td>
</tr>
<tr>
<td>(A type - B type)</td>
<td>195</td>
</tr>
<tr>
<td>Cyclic tetramer</td>
<td>326</td>
</tr>
<tr>
<td>Cyclic pentamer</td>
<td>256</td>
</tr>
</tbody>
</table>

### PET – Oligomers - acyclic

<table>
<thead>
<tr>
<th>Structure</th>
<th>Molecular Weight</th>
<th>Melting Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H[AB]₁OH</td>
<td>210.2</td>
<td>178</td>
</tr>
<tr>
<td>H[AB]₂OH</td>
<td>402.4</td>
<td>200 - 205</td>
</tr>
<tr>
<td>H[AB]₃OH</td>
<td>594.6</td>
<td>219 - 223</td>
</tr>
<tr>
<td>H[AB]₁-B-H</td>
<td>254.2</td>
<td>109 - 110</td>
</tr>
<tr>
<td>H[AB]₂-B-H</td>
<td>446.4</td>
<td>173 - 174</td>
</tr>
<tr>
<td>H[AB]₃-B-H</td>
<td>638.6</td>
<td>200 - 205</td>
</tr>
<tr>
<td>H[AB]₄-B-H</td>
<td>830.8</td>
<td>213 - 216</td>
</tr>
<tr>
<td>H[AB]₅-B-H</td>
<td>1023.0</td>
<td>218 - 220</td>
</tr>
<tr>
<td>HO-A-[AB]₁OH</td>
<td>358.3</td>
<td>&gt;360</td>
</tr>
<tr>
<td>HO-A-[AB]₂OH</td>
<td>550.5</td>
<td>280 - 281</td>
</tr>
<tr>
<td>HO-A-[AB]₃OH</td>
<td>742.7</td>
<td>268 - 270</td>
</tr>
<tr>
<td>HO-A-[AB]₄OH</td>
<td>934.9</td>
<td>252 - 255</td>
</tr>
<tr>
<td>HO-A-[AB]₅OH</td>
<td>1127.1</td>
<td>233 - 236</td>
</tr>
</tbody>
</table>

O = O
C = C
A = \[
\begin{array}{c}
O \\
\hline
C \\
\hline
C \\
\end{array}
\]

B = O – CH₂ – CH₂ – O

Melting point of some oligomers much lower than polymer melting point.
Low molecular weight material will migrate to the surface

LMW material will transfer from the film back surface to freshly coated front surface when film is wound into roll
Substrate Cleaning

To get good coating adhesion needs an atomically clean surface

NOT JUST A VISIBLY CLEAN SURFACE

Low molecular weight contamination on substrate surface

Contamination leading to poor coating adhesion
Thin film coating

Substrate - unfilled coextrusion

Substrate - filled coextrusion

Thin film coating picked off

Resulting pinhole

High points on the substrate back surface produced by the inclusion of fillers press into the thin film coating & if adhesion is poor, can ‘pick off’ the coating leaving a pinhole.
Reticulation pinholes

The atoms nucleate on the higher surface energy part of the substrate but not on the low molecular weight contamination.

Low molecular weight contamination may be vapourized by depositing atoms and radiant heating thus preventing any deposition. This low molecular weight material may be oligomer.
Cleaning options

Cloth wipe
Static brush
Rotating brush
Air blower / knife
Vacuum cleaner
Combined ultrasonic air jet & vacuum
Transfer tack rolls
Planarisation and/or Overcoating
Carbon Dioxide ‘snow jet’
Washing
Wiping with Rags

- Limitation – accumulation of debris at contact point, may cause scratching

Wiping with fabric roll / belt

- Roll can be rotated to refresh contact area with clean fabric
- Roll/belt system can work well with hard surfaces such as foils or drums
Casting drum covered with PET oligomer.

Casting drum with oligomer cleaned off.

Cleaning fabric.

Image courtesy of PolymagTek.
Tack roll cleaning

High adhesive tack roll -
As layer fills with dirt it is peeled off giving fresh surface

Clean Surface presented to the incoming Material - No repeater’s

Tack roll - picks up debris

Idle Roller - provides nip

Adhesive roll

High adhesive tack roll - picks up debris from Blue tack roll – keeping blue roll clean
Tack roll cleaning

This shows an example of a wide tack roll assembly used on a production film line prior to the wind-up. The blue roll is the low tack roll that is in contact with the web. The upper white roll is the high tack collection roll.

Courtesy of Teknek
Tacky roll cleaning

Before Cleaning
Particle Count = 2828

(10 micron particles on film)
Photographed at 125X magnification

After Cleaning
Particle Count = 87

Cleaning Efficiency = 96.9%

Image courtesy of PolymagTek
Pretreatments - warning

A little treatment is good – too much may be as bad as no treatment

Surface energy ≠ adhesion
Both of these two polymer chains are entangled in the bulk polymer. If the chains are broken in the region of the arrow head and the coating bonds to the ends of the chains the bond strength will be high due to entanglement.

If the chains are broken at multiple points the fragmentation of the chains means that even if the coating bonds onto the chain ends the polymer chain fragments are not bonded into the bulk polymer and bonding will be weak.
Contamination – wet cleaning

Wash
Rinse
Air knife
Dry

Even 1 monolayer of contamination interferes with adhesion
~0.1 microgram/sq cm of organic contamination.
~equivalent to 1 drop of liquid containing < 10 ppm non-volatile organics

It is extremely difficult to obtain solvents/water with <10 ppm non-volatiles – even a rinse is likely to leave a residue
Coatings bonded to crystalline polymer has little elasticity & adhesion equates to bond strength.

Coatings bonded to amorphous polymer has some elasticity which absorbs energy & adhesion may be higher than simple bond strength.
Conductive track
Shape designed to allow distortion

The serpentine metal track can bend without overloading the adhesion allowing the substrate to be stretched more than possible with a straight conductive track.
Electronic devices with extending linking connections deposited onto rigid substrate then encapsulated with silicone or polyeurethane & transferred to fabric laminated with pliable high adhesive
Good adhesion is promoted by:

- Entanglement
- Strong atom-atom bonding at interface *(clean surfaces essential)*
- Low local stress levels
- No easy deformation or fracture modes
- No long term degradation modes

• **Surface energy** – does **NOT** equate to adhesion
  
  Proximity bond = low adhesion
  
  Double surface area *(roughness)* only doubles adhesion
  
  Step change in adhesion *(10x -100x)* needs entanglement
  
  Plasma treatment to remove low molecular weight contaminants
  Plasma treatment may give chain scission & aid bonding to bulk polymer **BUT** may also fragment the surface & weaken interface
Thank you

Any questions?