CHEMICAL ANALYSIS OF THE POLYESTER/METAL SURFACE OF A DELAMINATION FAILURE

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Eldridge M. Mount III
EMMOUNT Technologies
Fairport, NY
Introduction

• Problem Statement
• Approach to problem definition
• Problem analysis
  – Review manufacturing history
  – Review of components
  – Analyze the failed components
• Source of failure
Laminated structure

<table>
<thead>
<tr>
<th>Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>92 gauge PET base film</td>
</tr>
<tr>
<td>Aluminum vacuum metallized layer</td>
</tr>
<tr>
<td>Polyurethane adhesive</td>
</tr>
<tr>
<td>2.5 mil LLDPE sealant film</td>
</tr>
<tr>
<td>6 color print layer</td>
</tr>
</tbody>
</table>

Schematic diagram of the sealable printed, metallized adhesive lamination showing the delamination at the PET/Aluminum interface
The Problem

• The lamination is produced by adhesive laminating a previously printed, metallized 92 gauge polyester film to a 2.5 mil LLDPE sealant.

• The lamination shows an unexpected delamination failure.

• The lamination is found to fail by delamination between the polyester film and the metal layer with ~100% metal transfer to the sealant.
What is happening?

Adhesive/Cohesive failure

- Generally caused by **Weak Boundary** at failure surface
- Weak Boundary exists between Aluminum and PET surface or within PET surface
- No adhesion developed between Aluminum and PET interface

Formation Of Weak Boundary

- Surface Contamination before metallization
  - Low molecular weight contamine
- Poisoning of AL/PET interface after metallization
  - Ink contamination/catalyst
  - LLDPE sealant contamination
- Polymer chain scission
- Poor aluminum deposition
The approach taken is to:

1. Review manufacturing History of the process and problem onset
2. Obtain samples of good and bad material
3. Send samples to outside lab for chemical analysis of the failure surface
4. Propose a cause of the failure if possible from the analytical results
5. Review intermediate suppliers materials for source of failure based on the mechanism proposed from 3
   - a. Metallized film supplier
   - b. PET Film supplier
   - c. Component supplier ink/adhesive
   - d. LLDPE supplier
   - e. Lamination process
Failure Diagnosis

• Examine
  – Process
  – Production history
  – Inks
  – Adhesives
  – LLDPE Sealant
  – Metallized films

• Found
  – No change in process speed or conditions
  – Good with Green & Red inks
  – Adhesive consistent between Good & Bad laminations
  – Good & Bad with two lots of LLDPE sealant
  – Good with one lot of MET PET
  – Bad with one lot of MET PET
## Product Manufacturing History

<table>
<thead>
<tr>
<th>Job Number</th>
<th>Date Print (Met PET order#)</th>
<th>Date Laminated (LLDPE order)</th>
<th>Result Seen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Job 3803</td>
<td>6/25/03 (18237)</td>
<td>6/26/03</td>
<td>No Failure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>All (4/27/03)</td>
<td></td>
</tr>
<tr>
<td>Job 3801</td>
<td>7/3/03 (18237)</td>
<td>7/7/03</td>
<td>No Failure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 roll 4/27/03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 rolls 11/06/02</td>
<td></td>
</tr>
<tr>
<td>Job 3801</td>
<td>7/7/03 (19256)</td>
<td>7/8/03</td>
<td>Bond Failure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9 roll 4/27/03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 rolls 11/06/02</td>
<td></td>
</tr>
<tr>
<td>Job 3801</td>
<td>7/8/03 (19256)</td>
<td>7/9/03</td>
<td>Bond Failure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 roll 4/27/03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 rolls 11/06/02</td>
<td></td>
</tr>
<tr>
<td>Job 3801</td>
<td>7/9/03 (19256)</td>
<td>7/10/03</td>
<td>Bond Failure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 roll 4/27/03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 rolls 11/06/02</td>
<td></td>
</tr>
</tbody>
</table>
Observations of Failure

• Laminate performance failure occurs after the change in MET PET film order #
  – Metal adhesion failure in the laminations appears after change in MET PET film order #
  – Ink flaking also appears after change in MET PET film order #

• Other concurrent changes observed had no apparent impact
  – change in ink color from green to red
  – use of two lots of LLDPE film
  – Production on several days
Potential Sources of Metal Adhesive Failure

- Metallization Process
  - Poor vacuum level
  - Overheating film
  - Over treatment of film surface

- Bond poisoning
  - No evidence based on failure onset with PET lot change

- Film manufacturing process
  - Over treatment of PET film
  - Under treatment of film
  - Degraded PET added during Film making
    - Poor reclaim quality
  - Poor PET drying
Failure Surface Testing

• Chemical surface analysis of the failure surfaces
  – by X-ray photon spectroscopy (XPS)
  – IR surface analysis

• Test Sample

[Diagram showing a test sample with layers of PET and aluminum, with an exposed PET surface.]
Determine Failure mechanism

• Obtain XPS measurements in areas of metal failure to determine chemical composition (Carbon/Oxygen/Nitrogen) of the PET surface and transfer of PET or other materials on the surface of the removed metal layer

• Look for the presence of nitrogen in the XPS results to differentiate between surface failure of the PET and bond poisoning from catalyst diffusion to the metal interface.
**XPS: X-ray Photoelectron Spectroscopy**

- Irradiate sample with X-rays of known energy \((Hv)\)
- Electron ejected with kinetic energy \(E_k\)
- Binding energy \(E_b\) calculated and atom from which it was ejected is determined
- \(E_b = Hv - E_k\)
- \(E_b\) is characteristic of Specific atoms and “Shells” of Bohr atom model

**Diagram:**
- **Photoelectron (e^{-1}):** X-ray energy \((Hv)\) hits inner K level electron ejecting it from the atom
XPS
X-ray Photoelectron Spectroscopy

- Binding energies range from 14 to 1194 electron volts for H to Zn atoms
- Spectra can be obtained from:
  - All electrons in a single atoms
  - from multiple atoms in a single specimen
- Atoms joined by chemical bonds shift binding energies
Typical Low Resolution XPS of Laminate Test Sample

031818210.spe: Sample#1 exposed PET
03 Oct 8 Al mono 350.0 W 0.0 65.0° 187.85 eV
Sur1/Full/1

Evans East
2.6534e+005 max 4.50 min

Binding Energy (eV)

C 1s
O 1s
Al 2s
Al 2p
High Resolution XPS: PET Verses Sample 1
(Good bond performance)
Sample 1 Verses Sample 2

(Good bond performance vs. poor bond performance)
Sample 1 Verses Sample 3

(Good bond performance vs. poor bond performance)
<table>
<thead>
<tr>
<th>Sample</th>
<th>O</th>
<th>N</th>
<th>C</th>
<th>Cl</th>
<th>Si</th>
<th>Al</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample#1 aluminum surface</td>
<td>29.4</td>
<td>0.7</td>
<td>59.4</td>
<td>ni</td>
<td>3.0</td>
<td>7.6</td>
<td>nd</td>
</tr>
<tr>
<td>Sample#1 exposed PET</td>
<td>29.4</td>
<td>nd</td>
<td>69.8</td>
<td>ni</td>
<td>0.1</td>
<td>0.7</td>
<td>nd</td>
</tr>
<tr>
<td>Sample#2 aluminum surface</td>
<td>25.5</td>
<td>1.4</td>
<td>68.3</td>
<td>0.2</td>
<td>1.0</td>
<td>2.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Sample#2 exposed PET</td>
<td>29.5</td>
<td>0.4</td>
<td>68.6</td>
<td>0.1</td>
<td>0.2</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample#3 aluminum surface</td>
<td>29.8</td>
<td>1.2</td>
<td>56.5</td>
<td>0.1</td>
<td>2.2</td>
<td>9.4</td>
<td>0.8</td>
</tr>
<tr>
<td>Sample#3 exposed PET</td>
<td>26.5</td>
<td>0.9</td>
<td>69.8</td>
<td>nd</td>
<td>2.4</td>
<td>0.4</td>
<td>nd</td>
</tr>
</tbody>
</table>
Conclusions

- PET surface polymer is clearly degraded
- Bond failure at both film surfaces
  - Metal
  - Ink flaking
- Either the Metallizer or Film Manufacturer at fault
  - Treatment process
    - (Metallizer or Film supplier process audit)
  - Reclaim levels and PET Process temperatures
    - Bulk Chemical testing
    - Film IV
Acknowledgement

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EMMOUNT Technologies
Consulting and Technical Services To the Polymer Extrusion and Film Converting Industries
ph 585.223.3996
fax 585.223.3480
emmount@earthlink.net
www.emmount-technologies.com

- Polymer Processing and Troubleshooting
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- Literature Searches and Technology Reviews
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- Confidentiality
- Complete confidentiality of client information with no disclosure of confidential information
- Ethical
- All patentable concepts developed while working for client, disclosed and assigned to client,
- Efficiency
- A knack for being able to “zero-in” on the problem at hand and to systematically identify solutions,
- Team Player/Excellent Communicator
- Able to work well with line-operators, engineering staff and management to cross-communicate technical information,
- LIFETIME EXPERIENCE/ TOP-NOTCH KNOWLEDGE
- Troubleshoot or focus your R & D having the advantage of a lifetime of learning and experience,
- Continuous Improvement
- Goal is to exceed the client’s expectations and to provide information about the most recent advancements in the field,
- References
- Professional references gladly provided.