Surface and Interface Characterization of Polymer Films

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Outline

• Introduction to surface chemical techniques
  – X-ray photoelectron spectroscopy (XPS/ESCA)
  – Time-of-flight secondary ion mass spectrometry (TOF-SIMS)
• Selected examples from polymer surfaces
  – Identification of Defects on Metallized Polymer-PSA Laminate
  – Failed Heat Seal from medical packaging
• Examining the sub-surface
  – New technology available
Surface chemistry related phenomena

- Wetting (hydrophobic vs. hydrophillic)
- Corrosion/oxidation
- Coatings
- Appearance (stains, hazes, residues, etc.)
- Adhesion
- Blooming, additive migration
What tools are available to probe the surface?

1. **Microscopy** – SEM, AFM, TEM, optical microscopy
What tools are available to probe the surface?

2. **Physical properties** - hardness, wear resistance, scratch resistance, contact angle, etc

Images courtesy of www.ebatco.com
What tools are available to probe the surface?

3. **Surface chemistry** – XPS, Auger, TOF-SIMS

![Graphs and images related to surface chemistry and analysis techniques.](image_url)
Other techniques...

• Indirect “surface” techniques
  – Extraction approaches followed by GC/MS, ICP, ICP-MS, etc.

• “Bulk” techniques
  – XRF, SEM-EDS, XRD, ICP-MS, FTIR, Raman....
Comparing Analytical Techniques

Depth of Analysis

Physical Monolayer

- Sampling Volume (typical data point)
- SIMS Depth Profile
- Typical Profile Depth

Top Surface
Near Surface
Thin Film
Coating
Bulk Substrate
XPS can detect and quantify all elements except for H and He, and provide chemical state information; making it a powerful survey analysis technique.
XPS Process (Photoelectric Effect)

X-ray

X-ray penetration depth (several microns)

Sample

Photoelectrons characteristic of sample surface

Photoelectron escape depth (~100Å or less)
Typical Data - Plasma treated polystyrene

Untreated polystyrene

Treated polystyrene

Intensity (a.u.)

Binding Energy (eV)

Oxygen

Carbon

Oxygen

Nitrogen

Carbon
### Typical Data - Plasma treated polystyrene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon</th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated polystyrene</td>
<td>79.0</td>
<td>3.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Untreated polystyrene</td>
<td>99.0</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

![Graph showing binding energy distribution for treated and untreated polystyrene](image)

- **Aromatic**
- **C-O**, **C-N**
- **C-C**
- **O-C=O**, **C=O**

**Intensity (a.u.)**

**Binding Energy (eV)**

294 292 290 288 286 284 282
XPS Summary

• Strengths
  – Elemental identification of all elements except H and He
  – Chemical state identification (oxidation state)
  – Quantitative analysis
  – Can analyze insulating samples

• Limitations
  – Detection limits typically ~500 ppm
  – Smallest analytical area ~10 µm
  – Limited organic information
  – UHV technique
TOF-SIMS is a very surface sensitive technique providing full elemental and molecular analysis with excellent detection limits.
Ejected Species: Atoms, Molecules, Clusters, Ions/Neutrals (+/-)

Source for this image?

Incident Particle
Typical Data

Negative Spectrum of PET
TOF-SIMS Imaging of Alumina-Zirconia-Silica Materials

Region 1 Spectrum

Region 2 Spectrum

Primary Ion Beam

Total Ion Image

Total Area Spectrum

Chemical Map 1

Chemical Map 2
TOF-SIMS Summary

• Strengths
  – elemental and molecular information on thin (submonolayer) organic films/contaminants
  – survey analysis
  – ppm detection limits
  – small spot size (0.2 µm) and mapping
  – analyzes insulators and conductors

• Limitations
  – organic information can be limited
  – vacuum compatibility required
  – at times, too surface sensitive
Selected examples from polymer surfaces

Identification of Defects on Metallized Polymer-PSA Laminate

A laminate consisting of an acrylic-based pressure sensitive adhesive (PSA) on a polyester film bonded to a metallized PET with a silicone release layer experienced isolated defects that were 50-200 µm in size.
Was there something on the surface of the PET prior to metallization that hindered adhesion?

![Graph showing binding energies for different elements and a peak labeled "Silicone"]

![Graph showing binding energy distribution with peaks at 110-108, 106, 104, 102, 100, and 98 eV, and elements C, O, and Si marked on the graph]
Finding of silicone on PET surface under metallization seems suspicious. However, silicone release layer surrounded defect and silicones are notoriously mobile.

Underside of PSA failure confirms locus of failure is at Al-PET interface.

<table>
<thead>
<tr>
<th>Area</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal side of defect</td>
<td>67.3</td>
<td>27.9</td>
<td>0.0</td>
<td>4.7</td>
</tr>
<tr>
<td>PSA side of defect</td>
<td>43.2</td>
<td>35.4</td>
<td>17.0</td>
<td>4.5</td>
</tr>
<tr>
<td>Release layer</td>
<td>44.1</td>
<td>30.6</td>
<td>0.0</td>
<td>25.3</td>
</tr>
</tbody>
</table>

What is this carbon due to?
High resolution C 1s spectrum from underside of defect

- equal intensity C-O and O-C=O indicative of ester functional groups
- Could this be transfer of PET?
Identification of Defects on Metallized Polymer-PSA Laminate

P E T r e f e r e n c e

U n d e r s i d e o f A l d e f e c t

Binding Energy (eV)

1.54 eV

3.98 eV

1.79 eV

4.27 eV
• C 1s peak positions are consistent with aliphatic ester, not PET
  – PET surface was contaminated with some aliphatic ester prior to metallization
  – Silicones contaminated the PET after the adhesion failure
Failed Heat Seal from medical packaging

Background: A medical device sterile package experienced adhesion failure at a polyethylene-ethylene acrylic acid (co-polymer) heat seal to polyethylene interface. EAA was added at 3% to improve adhesion and lower % of crystallinity. Adhesion problems can lead to loss of sterility.

Analytical Approach: Examine good and bad surfaces prior to heat sealing to look for evidence of impurities with XPS and TOF-SIMS.
Failed Heat Seal from medical packaging

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good PE-EAA surface</td>
<td>98.6</td>
<td>1.4</td>
</tr>
<tr>
<td>Failed PE-EAA surface</td>
<td>97.7</td>
<td>2.3</td>
</tr>
<tr>
<td>3%EAA-PE, theory</td>
<td>98.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Sample Carbon Oxygen
Good PE-EAA surface 98.6 1.4
Failed PE-EAA surface 97.7 2.3
3%EAA-PE, theory 98.8 1.2
XPS only finds only C-C and O-C=O

• Measurable difference in amount of total O suggests either:
  – (a) difference in the amount of EAA at the surface or,
  – (b) presence of some other O-C=O containing compound on the surface of the bad heat seal

  • XPS unable to distinguish between these two scenarios
• We use the better molecular specificity inherent to TOF-SIMS to look for foreign species.
• Series of more intense peaks observed on Bad seal surface
  – Peaks are characteristic of hydroxyhydrocinnamate compounds such as Irganox® 1010 or 1076
  – 219 amu = C_{15}H_{23}O^+
  – 233 amu = C_{16}H_{25}O^+
  – 259 amu = C_{17}H_{23}O_2^+
• XPS flagged the higher O levels, but could not determine the root cause of the problem
• TOF-SIMS found clear evidence of hydroxyhydrocinnamate compounds on Bad surface
  – Low levels of hydroxyhydrocinnamate found on Good surface
Examining the sub-surface
Examining the sub-surface

What do we do when these techniques are too surface sensitive?
- buried interfaces, extraneous surface contamination, etc.

![Graph showing fraction of signal as a function of depth.](image)
Basics of sputtering process

3 kV Ar$^+$ impinging Ni\{001\}

Simulation courtesy of Barbara Garrison, PSU Chemistry
http://galilei.chem.psu.edu/organicsims/Ar3Ni.jpg

Sputtered green and red atoms

Bond breakage, atomic rearrangement in sub-surface
Typical Depth Profile: Metallized PP

![Graph showing concentration vs depth for elements C, O, and Al.](image-url)
Aluminum Spectra

Al\textsubscript{2}O\textsubscript{3}

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What about profiling organics?

PET

After ~10 nm of sputtering
What about profiling organics?

![Graph showing concentration of Carbon and Oxygen with depth](image)

- **Carbon**: Concentration at 28.4% at depth 0 nm, decreasing to negligible amounts at higher depths.
- **Oxygen**: Concentration at 2.7% at depth 0 nm, remaining constant at lower depths.

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Cluster Ion Beams

Producing higher mass projectiles to increase sputter yield and decrease damage depth

\[ \text{SF}_5^+, m = 127 \]
\[ \text{Au}_3^+, m = 591 \]
\[ \text{C}_{60}^+, m = 720 \]

Most recent creation
\[ \text{Ar}_{10,000}^+, m = 40,000! \]
Erucamide Chemical Mapping-Surface

300 µm X 300 µm field of view

C_{22}H_{44}NO^+
300 µm X 300 µm field of view

Erucamide Chemical Mapping-Sub-Surface

Mass-to-charge

$\text{C}_{22}\text{H}_{44}\text{NO}^+$
## Summary

<table>
<thead>
<tr>
<th>Surface Technique</th>
<th>XPS/ESCA</th>
<th>TOF-SIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical applications</td>
<td>Corona/plasma treatments</td>
<td>Defect analysis</td>
</tr>
<tr>
<td></td>
<td>Adhesion failures</td>
<td>Adhesion failures</td>
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<tr>
<td></td>
<td>Additive blooming studies</td>
<td>Additive blooming</td>
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<tr>
<td></td>
<td>Reverse engineering of nm coatings</td>
<td>Surface contaminants</td>
</tr>
<tr>
<td></td>
<td>Surface contaminants</td>
<td>Molecular identification on surfaces</td>
</tr>
<tr>
<td>Signal detected</td>
<td>photoelectrons</td>
<td>sputtered ions</td>
</tr>
<tr>
<td>Elements detected</td>
<td>Li-U</td>
<td>H-U (including isotopes) and molecular species</td>
</tr>
<tr>
<td>Organic info</td>
<td>Yes, nearest neighbor bonding</td>
<td>Yes, molecular info</td>
</tr>
<tr>
<td>Quantitative</td>
<td>Yes</td>
<td>Qualitative</td>
</tr>
<tr>
<td>Detection limits</td>
<td>0.01-1.0 atom%</td>
<td>ppm</td>
</tr>
<tr>
<td>Sampling depth</td>
<td>1-10nm</td>
<td>1-2 monolayers</td>
</tr>
<tr>
<td>Depth profiling</td>
<td>Yes, limited info on organics</td>
<td>Yes, for most organics</td>
</tr>
<tr>
<td>Imaging/mapping</td>
<td>Yes-limited</td>
<td>Yes, elemental and molecular imaging</td>
</tr>
<tr>
<td>Spatial resolution</td>
<td>$\geq$10,000 nm (10 $\mu$m)</td>
<td>$\geq$200 nm</td>
</tr>
</tbody>
</table>
Questions Welcome

- Materials Characterization
- Microelectronics Test and Engineering
- Environmental Fate, Chemistry and Ecotoxicology

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