Predicting Bond Performance of Aerospace Materials Through Non-Destructive Testing

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Agenda

• What is a surface?
• Measuring Surface Energy – why does this matter?
• Contact Angles as a convenient way to evaluate Surface Energy
• Controlling your Surface – Contamination
• The Surface Analyst™
• Applications in Aerospace
• Correlating surface energy to system performance
What is a Surface & How Does it Decay?

Surfaces tend towards a lower energy state

- Newly created surfaces are very reactive
- This reactivity is what we call surface energy
- These layers are influenced by contaminants
  - Oxygen, water vapor, oil vapor from machinery, contact contaminants, mold release

Quality of bonding is dependent upon the top few molecular layers of the surface
Contact Angles and Surface Energy

- An isolated liquid drop in the absence of external forces assumes a spherical shape.
- Upon contact with a surface, drop shape is determined by the balance of liquid-liquid vs liquid-solid forces.
- Contact angle cosine is directly proportional to surface energy of solid.
- **Surface energy is strongly affected by presence of contamination.**

Young equation:

\[ \gamma_s = \gamma_{sl} + \gamma_1 \cos \theta \]
Contact Angle of Water is Proportional to Surface Energy

• Rate of surface energy decay depends on initial surface, surface energy and environment
Adhesives are competing with contaminants and soils for active surface sites.

- **Oxide Layer**
- **Hydroxide Layer**
- **Adsorbed water**
- **Adsorbed contaminants**
- **Loosely bound Soils**
- **Oxide Layer**
- **Hydroxide Layer**
Contact Angle Behavior

Polydimethylsiloxane

Areal Density (µg/cm^2)

Contact Angle (degrees)
Contact Angle for Evaluation of Cleaning Processes**
The Surface Analyst™

- Takes sensitive surface chemistry measurements out of the laboratory and puts them in the hands of manufacturing and quality personnel
- **Fast** - <2 second inspection
- **Easy** - anyone can use it
- **Accurate** – clean to a number
- **Non-destructive** – will not harm part being inspected
- **Flexible** – multi-directional inspections, can be used in many industries and applications
- **Repeatable** – passes Gage R&R
What does the Surface Analyst™ do?

- Small droplet (<2 μl) of probe fluid is created on the surface from a pulsed stream of micro drops
- Contact angle is calculated from drop diameter
- <2 sec measurement cycle
  - Single button operation
  - No operator input
- Immediate, easy-to-understand feedback about cleanliness and reactivity of the surface: is it ready for bonding, painting, coating, sealing?
- Useful in all manufacturing industries
Characterizing Out Time of a Peeled Laminate Surface

Water contact angle

Elapsed time since peel ply removal (hours)

\[ y = 1.17 \ln(x) + 26.086 \]

\[ R^2 = 0.9683 \]
θ_{H2O} as Quantitative Prediction of Adhesion – Aluminum
$\theta_{\text{H}_2\text{O}}$ as Quantitative Prediction of Adhesion - Polypropylene

Water Contact Angle vs. ASTM Classification

Contact Angle (degrees) vs. ASTM Classification (0B-5B)
Contact Angle for Predicting Bond Performance

Single Lap Shear vs Contact Angle

Load at failure (lbs) vs Water Contact Angle (degrees)

- Aggressive, heavy sand
- Moderate sand
- Light sand
- Solvent wipe only (no sand)
Utilizing Water Contact Angle to Predict Bond Strength

Composite with PDMS (Frekote 44)

%Interfacial Failure, WCA (degrees)

GIP Panel Average

Amount PDMS Applied (ug/cm²)

%Interfacial

WCA

GIP

0 10 20 30 40 50 60

0.0 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00
• Detection of plasma treatment on wiring inside aircraft
• Predicting penetrate wettability for landing gear
• Bonding interior paneling
Plasma Treatment Effect on Surface Chemistry

- Carboxyl group incorporation plateaus after ~1 second
- Hydroxyl group concentration continues to increase
Plasma Treatment Effect on Surface Chemistry

- Control and 1s exposure time (100 watts)
- Increasing –OH; creating O-C=O (carboxylic acid)
• Passes Gage R&R
• Quantitative and objective measurement

Operator to operator correlation on prepared and unprepared:

**Aluminum**

**Isoplot**

Surface Analyst Gage – Aluminum A1007

Delta P = 115
Delta M = 16
Discrimination Ratio = 7.4

**Carbon Fiber Composite**

**Isoplot**

Surface Analyst Gage – Composite A1007

Delta P = 44
Delta M = 8
Discrimination Ratio = 5.7
Ballistic Deposition Video
σ is determined by consistency of contaminant:
Uniform surfaces have σ=1-3°
What Matters When Measuring Surface Energy?

\[ \cos \theta = \frac{(\gamma_{sl} - \gamma_{s})}{\gamma_{l}} \]

Surfaces that are prepared for adhesive bonding have high surface energy: they are chemically active and unstable.

- Decay of these surfaces is rapid.
- Rate of decay depends in the environment.

Strategies:
1. Control environment to protect surface from contamination.
2. Apply adhesive before contamination occurs.
3. Use an adhesive system engineered to displace or absorb contaminants.
XPS Analysis Techniques

1. Survey Spectral Analysis
   - Scans a broad range of binding energies
   - Quantify elements present on surface

1. Depth Profiling (2 methods)
   - Angle Resolved X-Ray Photoelectron Spectroscopy (ARXPS)
   - Ion Beam Etching

2. High Resolution Spectral Analysis
   - High res scan of small energy range
   - Identify the small shifts in binding energies that accompany formation of chemical bonds.
• Polymers have non-reactive, low energy surfaces
• Treatment frequently involves oxidation (corona, flame, plasma) to increase polarity and reactivity
• These reactive groups provide attachment sites for adhesives, inks, coatings
• Surface energy is a measure of how reactive the surface is (type and density of polar and reactive groups)
• Contact angle continues to decrease with treatment time up to ~12s
• Treatment creates low molecular weight material that is soluble in ethanol
  • Equilibrium levels of bound, oxidized material that can enhance adhesion reaches a maximum after ~0.5-1 second exposure
• Depending on adhesive,
Oxygen incorporation is approximately linear with log time

-Diminishing returns for exposures > 2s

How long will it take to achieve optimum surface chemistry?
Special form of photoemission:
Ejection of a core-level electron by an X-ray photon

\[ E_K = \text{electron kinetic energy} \]
\[ \hbar \nu = \text{photon energy} \]
\[ \Phi = \text{spectrometer work function} \]

\[ E_B = \hbar \nu - E_K - \Phi \]

**\( E_B \):**
1. Identify elements
2. Quantify elements
3. Chemical state

All within 5-10 nM of surface
Detection of Siloxane on Bond Surface via Surface Analyst™

WCA and XPS
Siloxane Contaminated Peel Ply Surfaces

Water Contact Angle, degrees

Contaminant Amount Applied, µg/cm²

17% Interfacial Failure, unacceptable amount