The Scanning Kelvin Probe Technique for Assessing Coating Degradation

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Current polyurethane (PU) based coatings experience wrinkling, cracking, and/or separation of the coating from aircraft after years of service in hot, humid climates.

Previous studies have shown that the coating system is susceptible to reversion of the polymer coating via hydrolysis.

A protocol for exposing free films of the resins to steam aging in an autoclave has been identified and has shown to be capable of replicating wrinkling as seen in the field.

Thermal Mechanical Analysis (TMA) has shown the most promise for correlating acetone extraction data with a measurable property (softening point).

Data suggest that the softening point decreases with increasing steam autoclave exposure time and increasing acetone extract value.

However, this analytical method is destructive and determines reversion has occurred after the fact.
• Problem
  – Standard lifetime predictions fail to estimate the functional lifetime of urethane coatings

• Goals
  – Develop a non-destructive evaluation technique
  – Use the scanning Kelvin probe technique to differentiate between degraded and non-degraded polyurethane coating, primer and polyurethane/primer coating system on an aluminum alloy substrate
  – Verify these results with Raman IR Spectroscopy and Thermal Mechanical Analysis
What is work function?

- **Work function** \((wf)\) is defined as:
  - Minimum amount of energy (work, measured in electron volts) required to move an electron away from the surface of a semi-conductive or conductive material (e.g. metal) to a point of zero kinetic energy.
  - The movement and “residence” of the electron at some point away from the surface of the material results in the material having an *electrical potential*.

- **Any property** of the material that will impede or enhance the electron’s ability to move away from the surface affects the amount of energy (work) required;
- Thus, different materials can have different *work functions*;
- The work function of a material is extremely sensitive to changes in the physical and chemical properties of the material;
- This measurement is made in a non-destructive manner.
SKP Operating Principle

- A) Two materials with different work functions
- B) When in electrical contact potential will be balanced by movement of electrons
- C) A PID controller nulls the current
- The probe is vibrated at 30Hz and distance \( D \)

- The capacitance, \( C \), is dependent on distance
  - \[ C = \varepsilon \varepsilon_0 \frac{A}{d + \Delta d \sin(\omega t)} \]
  - \[ i = V_{cpd} \frac{dc}{dt} \]
- PID controller balances the current generated with a bias voltage \( U \)
CAAPCOAT B-274 BLACK POLYURETHANE RAIN EROSION COATING
(PER 8010-00-459-1756)

- A) Xylene (CAS 1330-20-7)
  • 39.6%

- B) Methyl isobutyl ketone
  • 13.8%

- C) Methylenebis(4-cyclohexyl isocyanate)
  • 0.5%

- D) CARBON BLACK
  • 0.2%

- E) Isocyanate terminated polyester prepolymer
  • 46.4%
Polyurethane Decomposition

- Hydrolysis occurs on the carbonyl carbon of ester bonds

\[ \text{R} \text{O} \bigg\langle \text{H} \text{O} \bigg\rangle \text{H}_2\text{O} \xrightarrow{\Delta} \text{R} \text{OH} + \text{HO} \text{O} \text{O} \text{C} \text{H}_3 \]

- Reversion affects the urethane bond

\[ \text{NH} \bigg\langle \text{N} \bigg\rangle \text{H} \text{O} \bigg\langle \text{O} \bigg\rangle \text{O} \xrightarrow{\text{or}} \text{OH} \text{N} \text{C} \text{C} \text{H}_2 + \text{C} \text{O} \text{O} \text{O} \text{O} \text{C} \text{H}_3 \]

\[ \text{NH}_2 \bigg\langle \text{N} \bigg\rangle \text{H} \text{O} \bigg\langle \text{O} \bigg\rangle \text{O} \xrightarrow{\text{or}} \text{NH}_2 \text{C} + \text{O} \text{C} \text{O} + \text{H}_2\text{C} \text{O} \text{O} \text{C} \text{H}_3 \]
Objectives

• Simulate the conditions that lead to PU coating degradation on a 2024-T3 aluminum panel, coated with Caapcoat B-470, using elevated temperature and humidity (121 C and 100% RH).

• Characterize exposed panels with a BioLogic M470 SKP and compare them to non-exposed (pristine) samples in order to determine change in work function. Localized changes will also be identified.

• Verify chemical changes in coating structure using Raman spectroscopy

• Thermomechanical ($T_g$) properties of the reverted coatings will be measured using TMA.
Methods: Sample Preparation

1) Coat 3x6 inch 2024-T3 aluminum panel
   i. 1 mil Deft 02Y40 primer (MIL-PRF-23377)
   ii. 13 mil Caapcoat B-274 rain erosion coat (MIL-PRF-85285)
Methods: Degradation Process

1) Cut sample to make two 3”x 3” sections
2) Tape edges of one half to prevent delamination during exposure
3) Expose taped half in an autoclave at 121°C and 100% RH
4) Reconnect with conductive tape (on bare metal back)
Methods: Data Collection

1) Scan with Kelvin probe
   i. Optical surface profile (OSP) for height tracking
   ii. Kelvin scan (constant probe height)
   iii. 3 scans performed on each sample and averaged together

2) Raman Spectroscopy (Renishaw iR)
   i. 780nm (0.1mW), 10 second exposure
   ii. Interrogate 5-10 different locations on each sample
Image Analysis - ImageJ

- Highlights pixels of a certain color
- Can analyze particle grouping as well as percent surface covered

4 hr Exposure
4 hour Exposure

- Average work function
  - Unexposed: -0.849 V
  - Exposed: -0.671 V
  - \( \Delta \text{wf} = 0.178 \) V

- Probe height: 75\( \mu \)m

- Area
  - 35x30mm
Non-exposed surface

4 hr Exposure (representative surface)
Surface Features
6 Hr Exposure
Surface Features
6 Hr Exposure
6hr line scan

[Diagram of SKP Probe with X and Y positions and a 6hr line scan graph showing volts ranging from -1.16 to 0.067 V.]
6 hr line scan with high WF area

0.132 V
8 Hour Exposure

- Average work function
  - Unexposed -0.911 V
  - Exposed -0.837 V
  - Δwf = 0.074 V
- Probe height 100µm
- Area
  - 57x40mm
12 Hour Exposure
OSP

- 5 major craters have a depth of 300-350µm
12 Hr ImageJ Analysis

- Highlighting areas of possible reversion (black)
- Need to determine criteria
  - What quantitative change in work function values from non-exposed to exposed represents reversion
SKP (12 hr exposure)

- Average Work Function
  - a) -0.649 V
  - b) -0.406 V
  - c) -0.568 V
  - $\Delta wf = 0.081$ V
- Probe height 100µm
- Area
  - 50x26mm
12hr line scans

SKP Probe Cross-Section (H)

Potential
-0.344
-0.391
-0.438
-0.485
-0.532
-0.579
-0.626
-0.672
-0.719
-0.766
-0.813

-0.303
-0.355
-0.408
-0.46
-0.513
-0.565
-0.618
-0.67
-0.723
-0.775
-0.828

millimeters

0
5
10
15
20
25
30
35
40
45
50

0.136 V
0.088 V

Crater Area
No Crater
4, 6, 8, and 12 Hour Comparison

Work Function
Exposed and Unexposed

Change in Work Function
(Exposed-Unexposed)
Raman IR Peak Assignments

Hydrolysis of polyester polymer:

\[ R \text{CH}_2 \text{CH}_3 + H_2O \xrightarrow{\Delta} R \text{CH}_2 \text{OH} \]

- **Alcohol and Carboxylic acid O-H**
- **Ether C-O-C**
- **Ester (symmetric and asymmetric stretching) C-O-O**
- **Elastomer or Aromatic C=C**
- **CH\(_2\) bending**
- **Carbon Black**
- **Isocyanate? A little high. There is also nothing in the 500-700 cm\(^{-1}\) range**
4hr Raman (780 nm laser)

Hydrolysis of polyester polymer:

Unexposed (green)
Exposed (red)

Elastomer

C=C

Ester asymmetric stretch C=O-O

Unexposed (green)
Exposed (red)

Ester symmetric stretch C=O-O

Reversion

H₂O

Δ

Hydrolysis of polyester polymer:
8hr Raman (780 nm laser)

Hydrolysis of polyester polymer:

Unexposed (Green)
12hr Crater Bottom (Red)
12hr Crater Rim (Blue)

Reversion

Elastomer
C=C

Ester asymmetric stretch  C=O-O

Ester symmetric stretch  C=O-O
12hr Raman (780 nm laser)

Hydrolysis of polyester polymer:

\[ R\text{-}O\text{-}CH}_3 \xrightarrow{\Delta} R\text{-}OH \]

Ester asymmetric stretching C=O-O

Ester symmetric symmetric C=O-O

Unexposed (Green)
12hr Crater Bottom (Red)
12hr Crater Rim (Blue)

Reversion C=C

Raman intensity

Raman shift (cm⁻¹)
Comparison of Raman Spectra for Non-exposed, 4, 8, and 12 hr.

- There is a trend of decreasing peak intensities for ester C=O-O (1250 and 1175 cm\(^{-1}\))
  - Possible indication of hydrolysis of polyester backbone of polyurethane;
- Decreasing peak intensities for elastomeric C=C (1601 cm\(^{-1}\))
  - Indicates possible reversion of urethane bond;
- However, no observed change in urethane, ester, and carboxylic acid C=O (1733 cm\(^{-1}\)) stretching;
  - generation of CO\(_2\) due to reversion?
  - partial hydrolysis

**Figure 10:** Raman spectra comparison of unexposed (top/red), 4 hr exposed (middle/purple), 8 hr exposed (bottom dark purple), and 12 hour exposed (bottom/light green).
Conclusions

- 4, 8, and 12 hour exposures at 121 C and 100% RH resulted in degradation (hydrolysis and reversion) of polyurethane coating stack up;
  - 6 hr sample currently being analyzed by Raman spectroscopy
- SKP analysis reveals changes in work function between non-exposed and exposed coating samples for all exposure times
- Raman IR analysis shows correlation of chemical changes in polyurethane coating system with changes in work function detected by SKP
  - IR Spectroscopy shows decreasing intensities for ester and elastomer components, which make up the urethane polymer
  - Evidence of hydrolysis and reversion
- Localized areas of changes in work function correlate with changes in IR analysis
- Quantitatively shown that there is a change in work function with exposure to heat and humidity
  - Results possibly affected by other variables
  - Curing time of coating (4 hr exposure sample being repeated)
- Qualitative differences also demonstrated
- Overall, results indicate SKP is a viable non-destructive technique for early detection of hydrolysis and reversion of polyurethane coating systems.
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