From Dental Composites to Degraded MLI:

Selected short stories from the world of a Materials Engineer

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Chemical structure of tooth components

- **Enamel:** hard outer coating
  - 96 wt% hydroxyapatite
    - tetracalcium phosphate $\text{Ca}_4\text{O}($PO$_4$)$_2$
    - dicalcium phosphate $\text{Ca}_2\text{P}_2\text{O}_7$
  - 2 wt% proteins
  - 2 wt% H$_2$O

- **Dentin:** softer inner material
  - 70 wt% hydroxyapatite
  - 20 wt% collagen
  - 10 wt% H$_2$O
Mechanism of Dental Caries

1. Plaque bacteria ingest sugar (starch) that passes through the mouth.
2. The waste byproduct of the plaque is acidic (low pH).
3. The reduced pH increases the solubility of the hydroxyapatite causing loss of material.
4. Once the enamel has been removed the softer dentin gets attacked exposing the openings of dentin tubules.
5. Fluid then moves back and forth in the tubules due to rapid temperature changes or air passing over.
6. The moving fluid stimulates the nerves in the pulp and is registered as pain.
Carious Lesion

Cavity Prep
# Filling Materials

**Currently used (years in use)**

- Au foil (2000)
- Silver amalgam (160)
  - Ag & Sn powder
  - liquid Hg
- Composite (45)
  - organic matrix
  - inorganic filler

**Previously used**

- Bone
- Ivory
- Sea Shell
- Ceramic
- Stone
- Pb
## Advantages/Disadvantages of Composite Fillings with Adhesive Bonding

<table>
<thead>
<tr>
<th>Pro</th>
<th>Con</th>
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<tbody>
<tr>
<td>• Natural tooth color</td>
<td>• Lower service life</td>
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<tr>
<td>• Semi translucent</td>
<td>• secondary caries caused by polymerization shrinkage</td>
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<tr>
<td>• Better distribution of functional forces</td>
<td>• Lower mechanical properties</td>
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<tr>
<td>• Reinforce weakened teeth</td>
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</table>
Curing of a dental composite

cavity prep stuffed with unpolymerized composite

cured (polymerized) filling

small gap for food & plaque infiltration
Steps to Improve Bond Strength

- Surface Prep
- Like bonds to like
  - when this is impractical, use primer

- Oral environment challenges
  - patient is alive
  - hot/cold beverages
  - food/pharmaceutical staining
  - mastication - three body wear
  - aqueous/saliva
Theories of Adhesion

1. Mechanical
   - micromechanical interlocking

2. Adsorption - chemical bonds
   - Primary - ionic and covalent
   - Secondary - hydrogen, van der Waals
Acid Etching

**Enamel**
- Selective Demineralization
- Increases surface area
- Increases life of composite
- Decreases marginal staining
- Decreases secondary caries
- Decreases post-operative sensitivity
- Bond strengths » 22 - 30 MPa
- Creates high surface-energy
  - Permits efficient wetting by hydrophobic resin
  - Tag formation in microporosities

**Dentin**
- Demineralizes dentin surface
- Opens dentinal tubules
- Exposes collagen
- Conditions dentin for better wetting of the primer

Depth of demineralization depends on:
- Kind of acid
- Application time
- Acid concentration and pH
- Other components
- Moisture prevents the collapse of collagen.
Etched Enamel
Dentin Tubule Volume

Most dense tubules

Outer third

Least dense tubules

Inner third
Demineralized Dentin
Primers

- **Function:**
  - As *surface-active* compounds which may promote adhesion through functional groups
  - Provide hydrophilic monomers
  - Initiator for monomeric polymerization
    - Promote interfacial polymerization
  - Permit improved wetting for hydrophobic resin
Primer Composition

Bifunctional monomers

- Hydrophilic -COOH groups have an affinity for exposed collagen fibrils
- hydrophobic groups capable of bonding to methacrylate groups of the adhesive resin

Photoinitiators

- Camphorquinone, phosphineoxides, tertiary amine

Solvents

- Acetone, ethanol or H₂O
Adhesive Agents

4-MET

PMDM

Carboxylic acid group

Methacrylate group
What is Hybridization?

- Formation of a hybrid layer following demineralization with an acidic conditioner.

What is the Hybrid Layer?

- A zone
- Resin micromechanical interlocking with dentinal collagen
Resin composite

Hybrid Layer

Dentin (mineral and collagen)
Hybrid Layer

Hybrid layer

Bonding agent

Dentin

1000X 15 kV

10µ
Good seal  
Well-hybridized resin tag  

Poorly hybridized resin tag  
Nanoleakage  
Internal gap  
No tag  
Dentin sensitivity  
External gap  
Bacteria invasion  
Pulpal irritation

Modified from Hybridization of Dental Hard Tissues (1998), Nakabayashi & Pashley, Quintessence Publishing Co., Ltd., Pulp
What bond strength is required?

• Adequate bond strength is required to overcome the stresses associated with polymerization shrinkage of the resin composite restorative material.

• 20 MPa*

Types of Tests

• Adhesion or Bond Strength
  • Tensile, Microtensile
  • Shear, Microshear

• Thermal cycling

• Microleakage

• Bond Observations
  • SEM
  • TEM
  • Mode of Failure
1. Cut the tooth/composite assembly into a cube-shaped block.
2. Cut two grooves on the long sides of the cube parallel to and centered on the resin-dentin interface, and machine the resin-dentin block into an hour-glass shape.
3. Cut the resin-dentin block into several slices and measure bond interface areas.
4. Fix the specimen to a specially designed holder with Loctite®.
5. Mount in a universal testing machine and stress at a crosshead speed of 1 mm/min.
**Shear Bond Tests**

- Metal Iris
- Single plane lap shear (SPLS)

Milos and Dickens, IADR 1997
Polymerization Shrinkage

Van der Waal’s distance apart

pre-cured monomer

covalent bond distance apart

polymer
Free Radical Ring Opening Polymerization to Minimize Polymerization Shrinkage

Based in ring size, number of rings, degree of conversion, etc., reduced shrinkage and even net volume increase possible.

Mechanical properties tend to suffer
- compressive modulus
- wear resistance
Acknowledgements

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COS Interpoint DC-DC Power Converter Failure in Vacuum

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March 4, 2008
Cosmic Origins Spectrograph (COS)

- HST axial scientific instrument the size and shape of a phone booth.
- Designed to study the large-scale structure of the universe and how galaxies, stars and planets formed and evolved.
- Will replace COSTAR which is no longer needed.
- The prime contractor for the design and assembly is Ball Aerospace and Technologies Corp., Boulder, CO.
Background

• COS successfully completed instrument level ambient functional testing in 2003.
• Subsequently, moved into a thermal vac chamber at Ball where during the initial instrument checkout an anomaly was noted.
• The Calibration Lamp Converter 30V output was reading only 14V.
• The low voltage power supply board #2 was removed from the instrument.
• Following trouble shooting at Ball the Interpoint dual power converter, MFL2815D, was removed and shipped to GSFC.
COS LVPS2
photo dated 2001

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.
Materials Branch Investigation

- A halo was observed around the ‘foot’ of the L5A inductor lead.
- The converter was then installed in a vacuum bell jar, mounted to the real time radiography manipulation stage, and configured with continuous impedance monitoring of the -15V output.
- This allowed realtime telemetry of the circuit resistance while observing any internal movement as a function of external pressure.
- BTW, Interpoint power converters are hermetically sealed with ambient pressure inside.
MFL2815D with Lid Removed
Internals of Interpoint 2815D, LDC 9846
Root Cause

- Detrimental combination of:
  - L5 inductor bonded to lid
  - lid bowing outward upon vacuum acquisition
  - lack of adequate strain relief of L5 leads

Corrective Actions

- All dual power converters, on all PWAs, were radiographed to assess the inductor strain relief.
- Subsequently, Kovar plates were bonded to the lids to stiffen and thereby minimize deflection.
- For unrelated reasons, all Interpoint power converters were removed and replaced.
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HST SM4
Exterior Materials
Awareness Briefing

Benjamin Reed
NASA/GSFC
March 3, 2007
HST Servicing History

total years between

- Deploy: Apr 1990
- SM1: Dec 1993 3.6 3.6
- SM2: Feb 1997 6.8 3.2
- SM3A: Dec 1999 9.7 2.9
- SM3B: Feb 2002 11.9 2.2
- SM4: Sep 2008 18.4 6.5
Overview of HST Exterior

**Equipment Bays:**
combination of MLI, FOSR, NOBL

**MLI construction:**
- space
- 5 mil Al Teflon
- 1/3 mil double Al Kapton embossed x 15 layers
- 1 mil Al Kapton
- telescope

**FOSR Tape:**
- space
- 5 mil Ag Teflon acrylic adhesive
- telescope

**Handrail & scuff plate paint:**
- space
- Silicone overcoat
- Polyurethane binder with inorganic pigment
- telescope
HST Damage Map as of Mar 2002
JSC ISAG Survey
Damage Map Summary

- SM2: 96 cracks all 5 inches or longer (light green)
- SM3A: 150 total cracks, 9 existing much longer (dark green)
- SM3B: 260 total cracks, 38 existing grew longer (violet)
  - 75% of cracks are on +V3
SM4 MLI Crack Prediction

Hundreds of new cracks; average length 20 cm; a few much larger cracks.
MLI Degradation Example
+V3 Light Shield and SM2 installed patches

SM1  SM2  SM3B

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.
Bay 8 Details

- Original 17 layer MLI on Bay door cracked but in place
- Patches installed Feb 1997 - single layer 2 mil FEP Teflon aluminized
- Electronic equipment inside at risk of exceeding upper temp limit
- Patches & MLI to be removed and replaced with a NOBL
Bay 10 Patch Prior to Installation
Bay 10 On Orbit
Prior to MLI
Removal

Bay 10 MLI in its
EVA Transport
Bag
SEM images of 5 mil Teflon
9.8 years exposure

- Cracks initiate on the space exposed, embrittled, side—propagate through the thickness, then laterally. The slow crack growth is a low stress event.
# Brief History of HST MLI

<table>
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<tr>
<th>SM1</th>
<th>Observations</th>
<th>Installed</th>
<th>Retrieved</th>
<th>Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No mention of cracks by crew; cracks visible in post-flight observations &amp; photographs</td>
<td>Magnetometer cover-R &amp; SA2</td>
<td>Magnetometer cover MLI &amp; SA1 drive arm MLI</td>
<td></td>
</tr>
<tr>
<td>SM2</td>
<td>Crew noted significant damage to MLI, ad-hoc photo survey - 95 cracks greater than 5” &amp; yellow pigment on EVA gloves</td>
<td>Patches: two 17 layer (5 mil outer layer) on LS &amp; 4 single layer (2 mil) on Bays 8 and 10. Wire/Ty-Raps</td>
<td>~12 in² 5 mil aluminized Teflon from LS &amp; FOSR tape from cryo-vent cover</td>
<td>Synergistic effect of thermal cycling, deposited e⁻ and H⁺, and solar radiation =&gt; slow crack growth</td>
</tr>
<tr>
<td>SM3A</td>
<td>150 total cracks, 9 existing much longer, yellow pigment on EVA gloves</td>
<td>Contamination covers - handrail (5), door knob (2) and handle (1); and NOBLs (3)</td>
<td>~1800 in² Bay 10 MLI (17 layers 5 mil VDA FEP top layer) &amp; 2 Bay 10 patches (2 mil single layer)</td>
<td>Synergistic effect confirmed, contribution of peak temperature established</td>
</tr>
<tr>
<td>SM3B</td>
<td>260 total cracks, 38 existing grew longer, yellow pigment on EVA gloves. Complete photo survey executed.</td>
<td>Installed NOBL on Bay 6</td>
<td>SA2 drive arm MLI &amp; bi-stem thermal shield (BSTS), diode box FOSR tape, one flake of paint</td>
<td>Synergistic effect confirmed, AO erosion of 1/3 mil VDA2 Kapton measured. Effect of temperature on embrittlement confirmed: solar facing BSTS fully embrittled, anti-solar not.</td>
</tr>
</tbody>
</table>
Outer Layer MLI
SM4 Predicted Condition

• Nominal MLI Outer Layer
  • **best case**: continued linear progress in crack initiation and propagation
    • Many small cracks initiated
    • Some propagation of existing cracks
    • Partially embrittled Teflon **will not** crack upon crew contact
  • **worst case**: high dose rate and increased total dose significantly increase degradation rate
    • Many small and large cracks occur
    • Significant propagation of existing cracks
    • Numerous intersecting cracks lead to “islands” of free material
    • Fully embrittled Teflon **will** crack upon crew contact - much debris generated

• Patches
  • Best case: small cracks progress, not visible on orbit
  • Worst case: attachment failure; significant material loss

SM4 Mitigation Techniques

• Ordering of tasks
• Flight Rules
• FOD checks for all connectors
• Inspection/Cleaning of EMUs prior to donning
Outer Layer MLI Degradation Mechanism

- **Cracking Mechanism:**
  - Synergistic effects of load (stress concentrations), total dose, dose rate, temperature and film thickness
  - Load from stress concentrations inherent in manufacturing process, shrinkage, blanket build and installation, and thermal cycling
  - Dose rate is a function of solar cycle
  - The higher the upper temperature limit during thermal cycling, the more severe the degradation
  - The thinner the film for identical exposure conditions, the more degraded it will be

- **Factors by Mission**
  - Launch to SM1: high dose rate but not total dose
  - SM1 to SM2: detrimental combination of load, dose and t-cycles
  - SM2 to SM3A: lower dose rate and lower load (relieved by cracking)
  - SM3A to SM3B: moderate dose rate
  - SM3B to SM4: high dose rate and total dose and ~ 107,500 thermal cycles
Handrail, Doorknob & Handle Paint
SM4 Predicted Condition

- Free pigment on all painted surfaces
  - Handrails
  - Doorknobs
  - Door handles

Mitigation Techniques

- Flight rules
- Glove inspection prior to opening of Aft Shroud
- Contamination covers if necessary
  - Installed on SM3A
    - 5 handrail covers
    - 2 knob covers
    - 1 handle cover
Handrail Paint Degradation Mechanism

- Handrail Paint:
  - Silicone overcoat on top of polyurethane paint with inorganic pigment
- Free pigment
  - Atomic oxygen (AO) undercuts silicone, erodes binder
  - Pigment left on surface and transfers to gloves when touched
  - Occurs all around telescope
- Flaking (peeling, scaling, lifting; not discoloration)
  - UV + AO damage shrinks silicone
  - Good bond between silicone and paint;
  - Failure between paint and aluminum
  - Occurs with high solar exposure (+V3)
SM4 Task Summary

- Debris generating tasks follow debris sensitive tasks.
- Debris sensitive tasks are surrounded by FOSR (tape), not MLI.
- Handrail/handle covers may be installed as their condition dictates.

Debris generating task

Debris sensitive task

![Diagram showing task areas and markings]
SM4 Mission Summary

• MLI outer layer will look bad

• Some locations (hot spots) will be brittle, most will not

• Majority of SM4 tasks are independent of MLI, mitigation strategies are in place
Figure 6. Bottom MLI grid pattern and MMOD map.
Detail of a Through-Hole
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