FAILURE ANALYSIS OF FLUOROPOLYMER PARTS – science not art

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FluoroConsultants Group, LLC

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What you will hear in this presentation

• Brief introduction
• Examples of parts
• Part exposure and failure
• A methodology for failure analysis
• State-of-art analytic methods
  – Useful techniques
  – Expected data
  – Information obtained from data
• Example of failure
  – Application of methodology
  – Data interpretation
  – Failure scenario
INTRODUCTION

• Parts fail from time to time in chemical processing and other plants – *fact of life*

• Fluoropolymer parts last longer than most other materials

• Important to determine cause of failure because of:
  – Process hazards
  – Process up-time
  – Future improvement
EXAMPLES OF PARTS
Fluoropolymer Lined Pipe

Courtesy Crane Resistoflex Corp.

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PTFE Lined Process Vessel
PFA Parts
PTFE Lined Flexible Hose
Part Exposure and Failure

• Elements of Part Exposure
  – Mechanical
    • Stress
    • Pressure
  – Chemical
    • Organic
    • Inorganic

• Factors Intensifying Exposure
  – Temperature
  – Time

• Consequences of Routine Part Failure*
  – Emission
  – Corrosion

*Catastrophic failure is outside the scope of this presentation
## VISUAL EVIDENCE OF FAILURE

<table>
<thead>
<tr>
<th>DEFECT</th>
<th>POSSIBLE CAUSES</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWELLING</td>
<td>SORPTION, PERMEATION</td>
</tr>
<tr>
<td>BLISTERING</td>
<td>PERMEATION, LOCALIZED POLYMERIZATION</td>
</tr>
<tr>
<td>DISCOLORATION</td>
<td>DEGRADATION, LOCALIZED POLYMERIZATION</td>
</tr>
<tr>
<td>CRACKING</td>
<td>STRESS, ENVIRONMENTAL STRESS CRACKING</td>
</tr>
<tr>
<td>DEFORMATION</td>
<td>CREEP (COLD FLOW)</td>
</tr>
<tr>
<td>GENERAL DEGRADATION</td>
<td>OXIDATION, CHEMICAL ATTACK</td>
</tr>
</tbody>
</table>

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A Methodology for Failure Analysis

VISUAL

MICROSCOPIC

FAILURE CLASSIFICATION

SELECTION OF ANALYTIC TECHNIQUES AND ANALYSIS

MEASUREMENT AND ANALYSIS

DATA ANALYSIS

ROOT CAUSE DETERMINATION

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INFORMATION LIST*

• Service fluids and chemistry (design and excursions)
• Temperature, pressure and flow rate
• Material of construction
• Design details, welds etc.
• Circumstances and nature of failure: leaks, rupture
• Manufacturer of parts
• Existing industry, MIL or company standards
• Problem history, if a repeat

* Required prior to analysis
IMPORTANT ANALYTIC METHODS

- Optical Microscopy (OM)
- Physical Properties
  - Specific Gravity, Elongation, Tensile Strength,…
- (Environmental) Scanning/Transmission Electron Microscopy (SEM, TEM)
  - Energy Dispersive X-ray (EDX)
- Thermal Analysis (DSC, TGA, DMA, TMA)
  - Heat of Fusion, Melting Point, Degradation Temp.,...
- Infrared Spectroscopy (FTIR, ATR)
- Atomic Absorption Spectroscopy (AAS)
- Electron Spectroscopy for Chemical Analysis (ESCA)
- Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS)
- Atomic Force Microscopy (AFM)
- Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS)
<table>
<thead>
<tr>
<th>Analysis Method</th>
<th>Sampling Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared Spectroscopy (IR)</td>
<td>&lt;2 μm</td>
</tr>
<tr>
<td>Energy Dispersive X-ray (EDX)</td>
<td>&lt;5,000 Å</td>
</tr>
<tr>
<td>Rutherford Back Scattering (RBS)</td>
<td>&lt;400 Å</td>
</tr>
<tr>
<td>Electron Spectroscopy for Chemical Analysis (ESCA) and Auger</td>
<td>&lt;40 Å</td>
</tr>
<tr>
<td>Second Ion Mass Spectroscopy (SIMS)</td>
<td>&lt;4 Å</td>
</tr>
<tr>
<td>Ion Scattering Spectroscopy (ISS)</td>
<td>&lt;2 Å</td>
</tr>
<tr>
<td>Test Method</td>
<td>Information Obtained from Data</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------------------------------------------------------------------</td>
</tr>
<tr>
<td>OM</td>
<td>Appearance</td>
</tr>
<tr>
<td>SEM/TEM</td>
<td>Sub-microscopic Structure/Topography</td>
</tr>
<tr>
<td>EDX</td>
<td>Qualitative Elemental Analysis</td>
</tr>
<tr>
<td>Physical Properties</td>
<td>Material Degradation</td>
</tr>
<tr>
<td>Thermal Analysis</td>
<td>Properties, Processing, Degradation</td>
</tr>
<tr>
<td>FTIR</td>
<td>Material Identification</td>
</tr>
<tr>
<td>AAS</td>
<td>Metal Analysis</td>
</tr>
<tr>
<td>ESCA</td>
<td>Surface Chemical Composition (except for hydrogen)</td>
</tr>
<tr>
<td>TOF-SIMS</td>
<td>Composition vs Depth</td>
</tr>
<tr>
<td>AFM</td>
<td>Surface Roughness</td>
</tr>
</tbody>
</table>
EXAMPLE OF FAILURE ANALYSIS
Leaky Fluorine Gas Hose

- **Service**: Fluorine gas
- **Hose Assembly**: nipple, collar, hose and steel braid
- **Nature of Failure**: leak
- **Location of Failure**: in PTFE tube near the collar

![Image of hose assembly showing failure point and components](image-url)
Visual Observations

• Braid at the failure point was extremely discolored

• A small spot on PTFE liner was observed after removal of braid
Braid Microscopy (OM, SEM, EDX)

- Internal and external braid surfaces discolored \(\rightarrow\) *abnormal*  
  - evidence of intense heat exposure
- Normal weave pattern in the braid
- No “stray” wire that may have punctured tube
- Stainless Steel braid composition: Fe, Ni, Cr and Mo \(\rightarrow\) *normal*
PTFE Liner Microscopy (OM, SEM)

- Light impression of braiding in the tube exterior → normal
- A relatively large void/crack found in the failure area → abnormal
- SEM showed presence of voids and primary PTFE particles and fibrils → abnormal
  - Suggesting processing problem of PTFE liner (Incomplete Sintering)
PTFE Liner Crack
(10,000 X)
Tube Composition

FTIR

• Determined tubing was PTFE $\rightarrow$ normal
• PPVE comonomer was also detected $\rightarrow$ normal

EDX

• Only F and C found in failure area $\rightarrow$ normal
SURFACE CHEMISTRY (ESCA)

Polytetrafluoroethylene -CF₂-CF₂-

- Ideal $F:C$ Ratio = 2 (actual 1.8-1.9) and $O:C$ Ratio = 0
- Defect area $F:C$ Ratio = 0.9 and $O:C$ Ratio = 0.09
- Adjacent Area $F:C$ Ratio = 1.3 and $O:C$ Ratio = 0.05
- Conclusion: loss of F due to oxidation at failure point
Differential Scanning Calorimetry (DSC)

• **Adjacent area**
  – single peak, melting point = 321°C (normally 327°C)
  – first heat = 22.6 J/g (normally <30 J/g)

• **Defect area**
  – double peak at 309°C and 318°C
  – first heat 30.9 J/g + 12.5 J/g = 43.4 J/g

• **Conclusion**: severe degradation at failure point
A likely scenario for the failure

- A contaminant was probably trapped inside tube wall where the void has been formed.
- Fluorine diffuses over time and reaches the contaminant.
- Exothermic reaction of fluorine with contaminant takes place (most materials react with fluorine) – *it disappears*.
- A hot spot develops at leak area.
- Intense heat melts the PTFE and creates a leakage point.
- PTFE is severely degraded at failure point, thus has lower molecular weight → depressed melting point.
- PTFE loses fluorine because of intense heat exposure.
- $O_2$ replaces some of $F_2$ lost from PTFE.
Modeling Fluoropolymer Parts

Modeling Fluoropolymer Parts

• Advanced finite element techniques are available for modeling fluoropolymer
  – dramatic improvements made in modeling accuracies

• Models allow designers and engineers to advance sophistication of component designs
  – understand where problems may develop
Finite Element Modeling

- Geometry and BC
- Loading Specification
- Material Representation

Finite Element Modeling

- The results from FEA are only as accurate as the input values

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Brun Hilbert, Ph.D., P.E., Exponent Inc., Natick, MA

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<table>
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<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tr>
<td>Linear elastic solutions from stress analysis handbooks</td>
<td>Relatively quick with validated results.</td>
<td>Does not account for polymer nonlinearity. May underestimate strains and stresses and under-estimate deformations. Standard geometries only.</td>
</tr>
<tr>
<td>Linear viscoelastic solutions from stress analysis handbooks</td>
<td>Relatively quick.</td>
<td>Small strain effects only. Simple, accepted material laws. Standard geometries only. Some material testing may be required.</td>
</tr>
<tr>
<td>Analytical viscoplastic solutions</td>
<td>More accurate than elastic or viscoelastic for simple geometries.</td>
<td>No standard solutions available. Requires some numerical analysis given complexity of material model. Some material testing may be required.</td>
</tr>
<tr>
<td>Linear elastic finite element analysis</td>
<td>Accommodates complex geometries. Rapid analysis possible.</td>
<td>Does not account for FP nonlinearity. May underestimate strains and stresses and under-estimate deformations. Good only for small strains.</td>
</tr>
<tr>
<td>Finite element analysis with polymer-specific material or constitutive laws</td>
<td>Accommodates complex geometries. Can handle nonlinearity in material behavior and large strains. Rapid analysis possible. Can predict very complicated polymer behavior, including filled polymers and complex temperature-loading histories.</td>
<td>Requires the most computing power. Requires the most material testing.</td>
</tr>
</tbody>
</table>
Figure 11.8 Axisymmetric representation of the hose showing the axial load (F) and the internal pressure (P).
Figure 11.10 Contours of maximum principal stress in the hose at 20°C, $P = 0.6$ MPa, $F = 280$ N, after a loading time of 1 min.
Threaded Connection Simulation

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Threaded Connection Simulation

What is the pressure between the Teflon seal and the steel pipes at different temperature and times?

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Threaded Connection Simulation

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Conclusions

• Methodology and advanced techniques are available for failure analysis of fluoropolymer parts using engineering/scientific principles.

• Stress development in fluoropolymer parts can be studied by modeling to understand where problems may arise and enhance component design.