FluoroConsultants Group, LLC

FAILURE ANALYSIS OF FLUOROPOLYMER PARTS – *science not art*

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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 fro data
- Example of failure
  - Application of methodology
  - Data interpretation
  - Failure scenario

INTRODUCTION

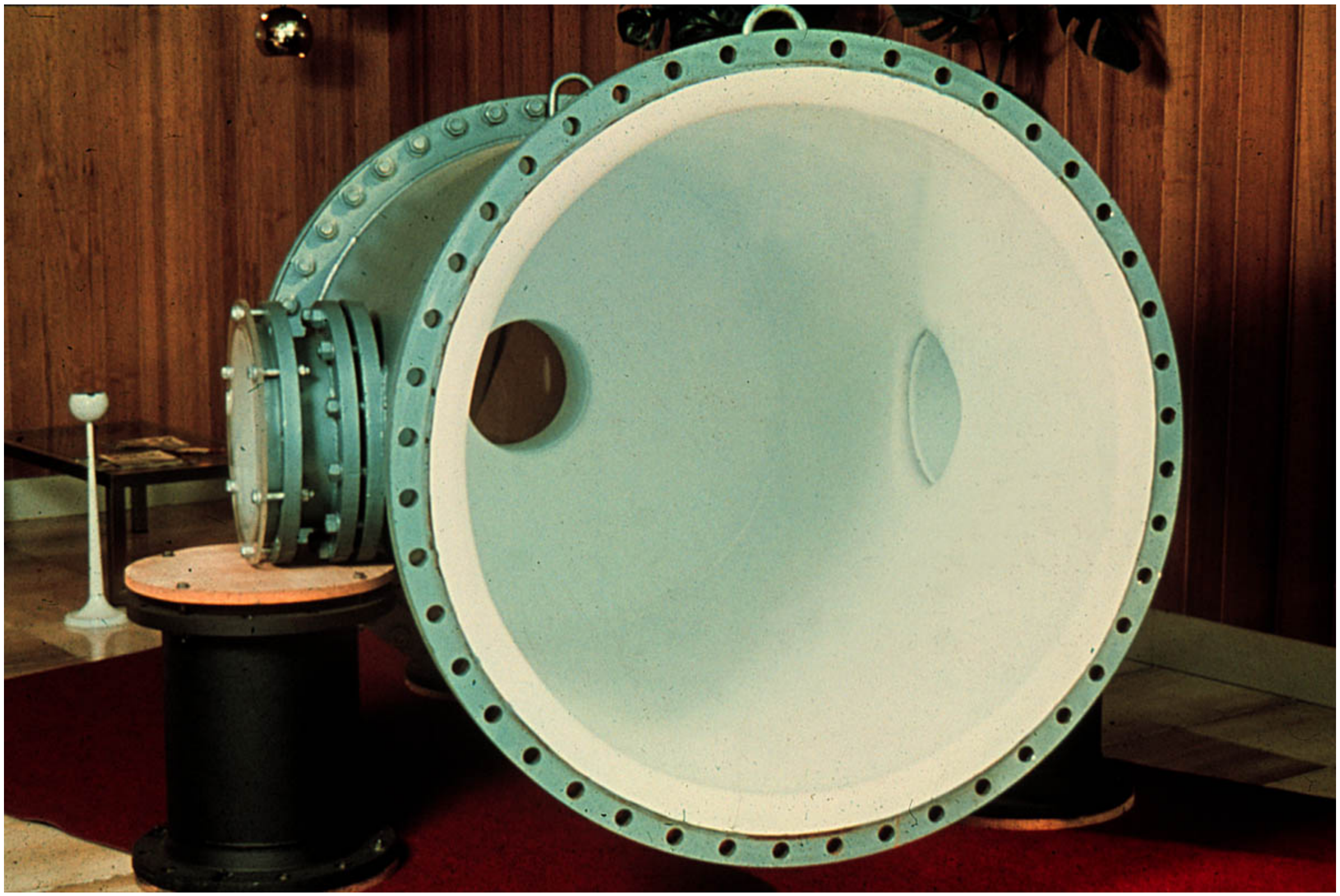
- Parts fail from time to time in chemical processing and other plants – *fact of life*
- Fluoropolymer parts last longer than most other materials
- Important to determine cause of failure because of:
  - Process hazards
  - Process up-time
  - Future improvement

EXAMPLES OF PARTS

Fluoropolymer Lined Pipe

Courtesy Crane Resistoflex Corp.

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

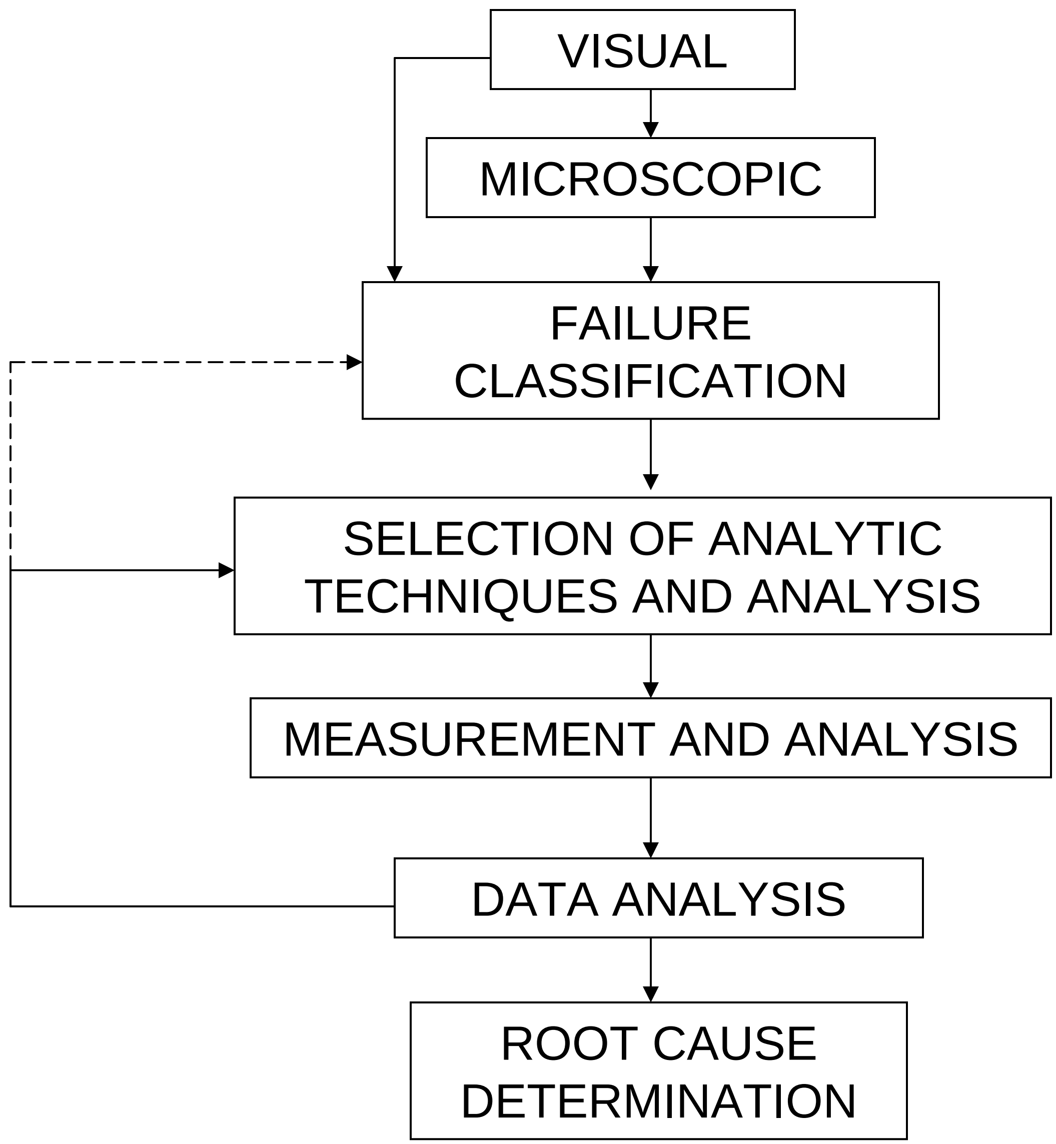
- Consequences of Routine Part Failure*
  - Emission
  - Corrosion

***Catastrophic failure is outside the scope of this presentation**

VISUAL EVIDENCE OF FAILURE

DEFECT	**POSSIBLE CAUSES**
SWELLING	SORPTION, PERMEATION
BLISTERING	PERMEATION, LOCALIZED POLYMERIZATION
DISCOLORATION	DEGRADATION, LOCALIZED POLYMERIZATION
CRACKING	STRESS, ENVIRONMENTAL STRESS CRACKING
DEFORMATION	CREEP (COLD FLOW)
GENERAL DEGRADATION	OXIDATION, CHEMICAL ATTACK

A Methodology for Failure Analysis



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)**

A Comparison of Average Sample Depth for Various Surface Analysis Techniques[18]

Analysis Method	Sampling Depth
Infrared Spectroscopy (IR)	<2 μm
Energy Dispersive X-ray (EDX)	<5,000 Å
Rutherford Back Scattering (RBS)	<400 Å
Electron Spectroscopy for Chemical Analysis (ESCA) and Auger	<40 Å
Second Ion Mass Spectroscopy (SIMS)	<4 Å
Ion Scattering Spectroscopy (ISS)	<2 Å

Ref Chapter 10, *Failure Analysis* in Fluoropolymers Applications in Chemical Processing Industries, by Ebnesajjad and Khaladkar, William Andrew Pub, Norwich, NY, 2005

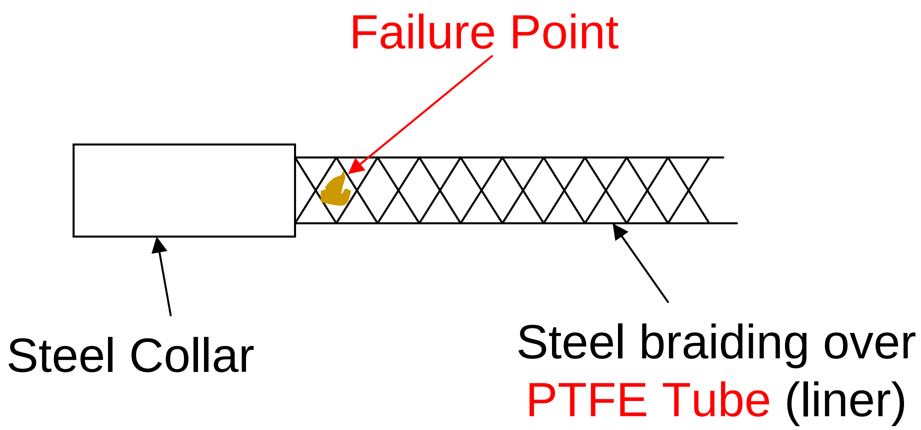
Test - Data Relationship

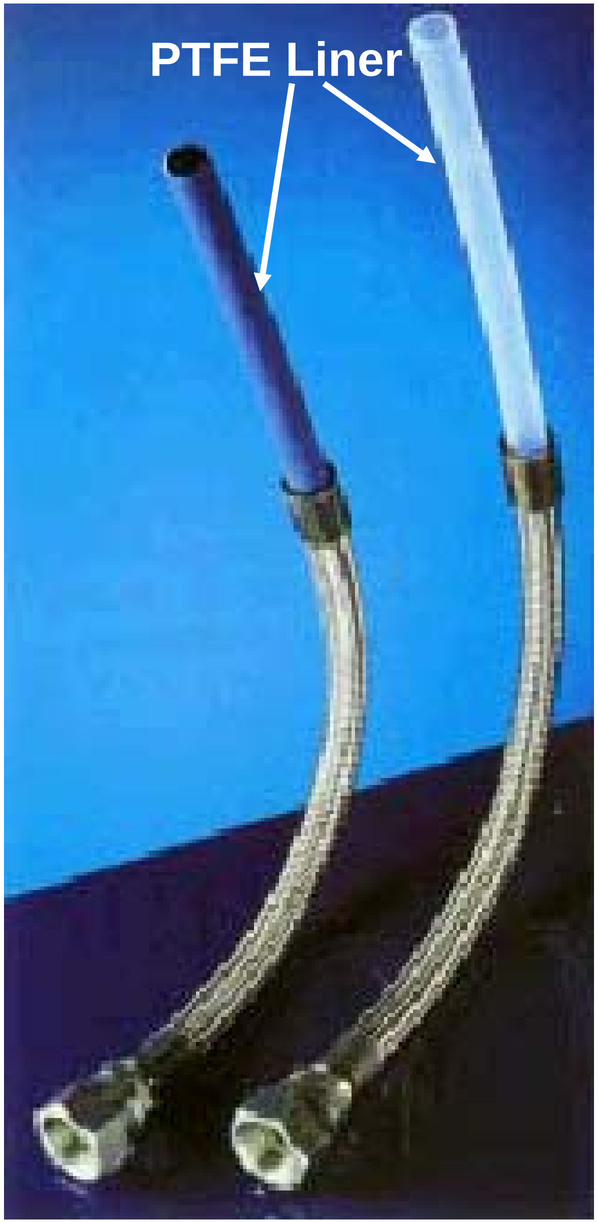
Test Method	Information Obtained from Data
OM	Appearance
SEM/TEM	Sub-microscopic Structure/Topography
EDX	Qualitative Elemental Analysis
Physical Properties	Material Degradation
Thermal Analysis	Properties, Processing, Degradation
FTIR	Material Identification
AAS	Metal Analysis
ESCA	Surface Chemical Composition (except for hydrogen)
TOF-SIMS	Composition vs Depth
AFM	Surface Roughness

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





Visual Observations

- Braid at the failure point was extremely <u>discolored</u>

- A small spot on PTFE liner was observed after removal of braid

Braid Microscopy (OM, SEM, EDX)

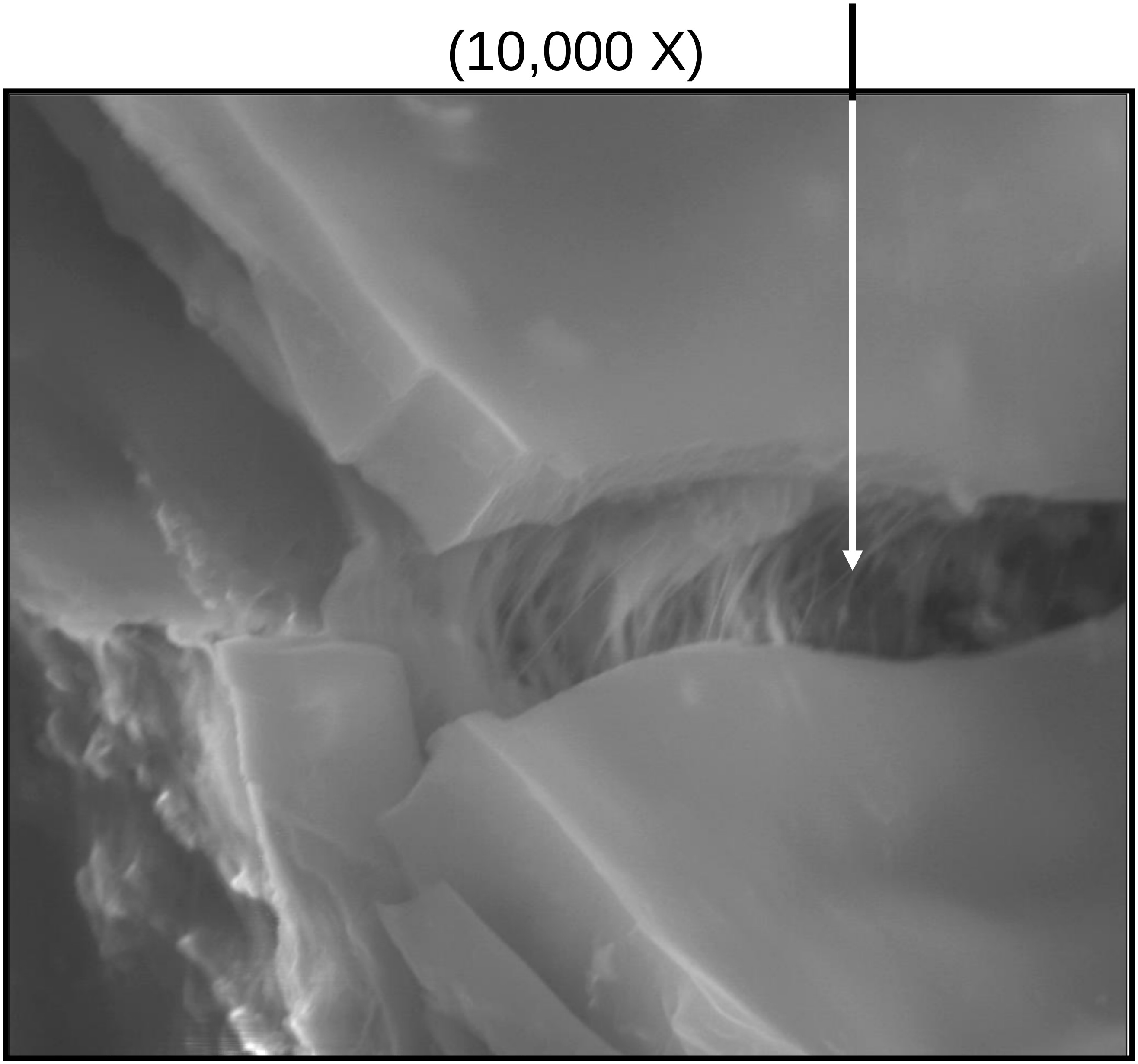
- Internal and external braid surfaces discolored → *abnormal*
  - *evidence of intense heat exposure*
- Normal weave pattern in the braid
- No “stray” wire that may have punctured tube
- Stainless Steel braid composition: Fe, Ni, Cr and Mo → *normal*

PTFE Liner Microscopy (OM, SEM)

- Light impression of braiding in the tube exterior → *normal*
- A relatively large <u>void/crack</u> 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* → *normal*
- *PPVE* comonomer was also detected → *normal*

EDX

- Only F and C found in failure area → *normal*

SURFACE CHEMISTRY (ESCA)

Polytetrafluoroethylene $-CF_2-CF_2-$

- 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^{o}C (normally 327^{o}C)
  - first heat = 22.6 J/g (normally <30 J/g)
- Defect area
  - double peak at 309^{o}C and 318^{o}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

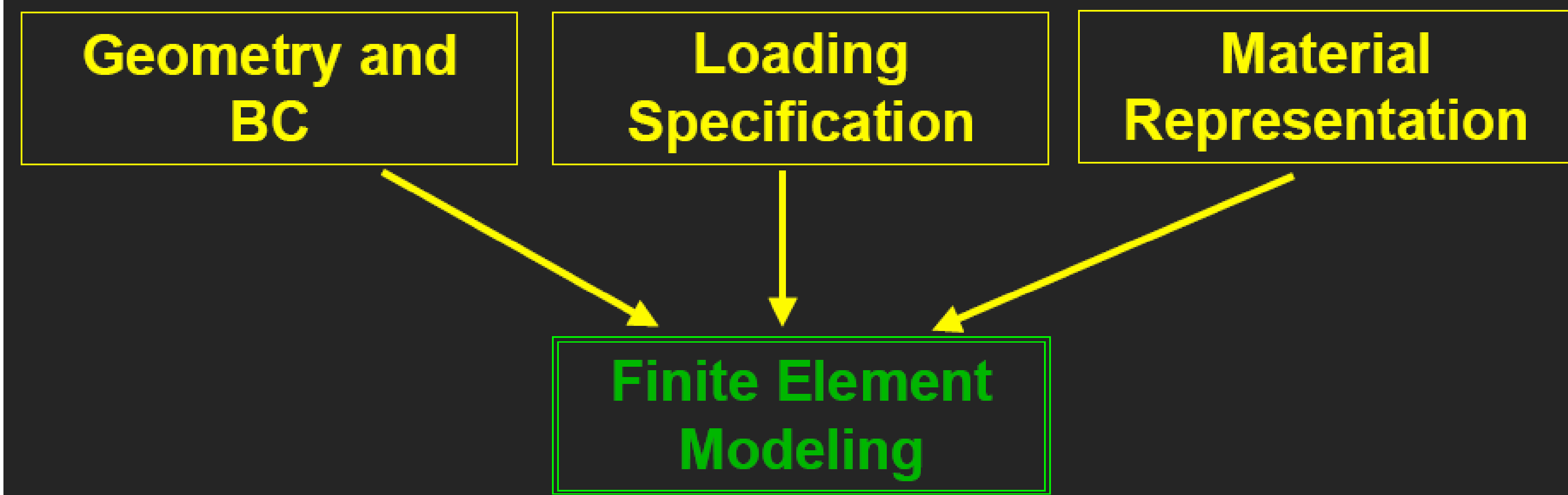
Modeling Fluoropolymer Parts

Ref Chapter 11, *Modeling and Mechanical Analysis of Fluoropolymer Components J. S. Bergström and S. Brown* in Fluoropolymers Applications in Chemical Processing Industries, by Ebnesajjad and Khaladkar, William Andrew Pub, Norwich, NY, 2005

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



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

Ref Jorgen Bergstrom, Ph.D., *Veryst Engineering, LLC*, Needham, MA
Brun Hilbert, Ph.D., P.E., *Exponent Inc*., Natick, MA

Table 11.1. Summary of Available Modeling Approaches

Technique	Advantages	Disadvantages
Linear elastic solutions from stress analysis handbooks	Relatively quick with validated results.	Does not account for polymer nonlinearity. May underestimate strains and stresses and under-estimate deformations. Standard geometries only.
Linear viscoelastic solutions from stress analysis handbooks	Relatively quick.	Small strain effects only. Simple, accepted material laws. Standard geometries only. Some material testing may be required.
Analytical viscoplastic solutions	More accurate than elastic or viscoelastic for simple geometries.	No standard solutions available. Requires some numerical analysis given complexity of material model. Some material testing may be required.
Linear elastic finite element analysis	Accommodates complex geometries. Rapid analysis possible.	Does not account for FP nonlinearity. May underestimate strains and stresses and underestimate deformations. Good only for small strains.
Hyperelastic finite element analysis	Accommodates complex geometries. Can handle nonlinearity in material behavior and large strains. Rapid analysis possible. Standard material models available.	Does not include rate-dependent behavior. Cannot predict permanent deformation. Does not handle hysteresis. Some material testing may be required. Can produce errors in multiaxial stress states.
Standard plasticity finite element analysis	Provides nonlinear behavior with large strains and permanent deformations. Standard material model.	Does not include rate-dependent behavior. Does not handle hysteresis. Not accurate for polymers.
Finite element analysis with polymer-specific material or constitutive laws	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.	Requires the most computing power. Requires the most material testing.

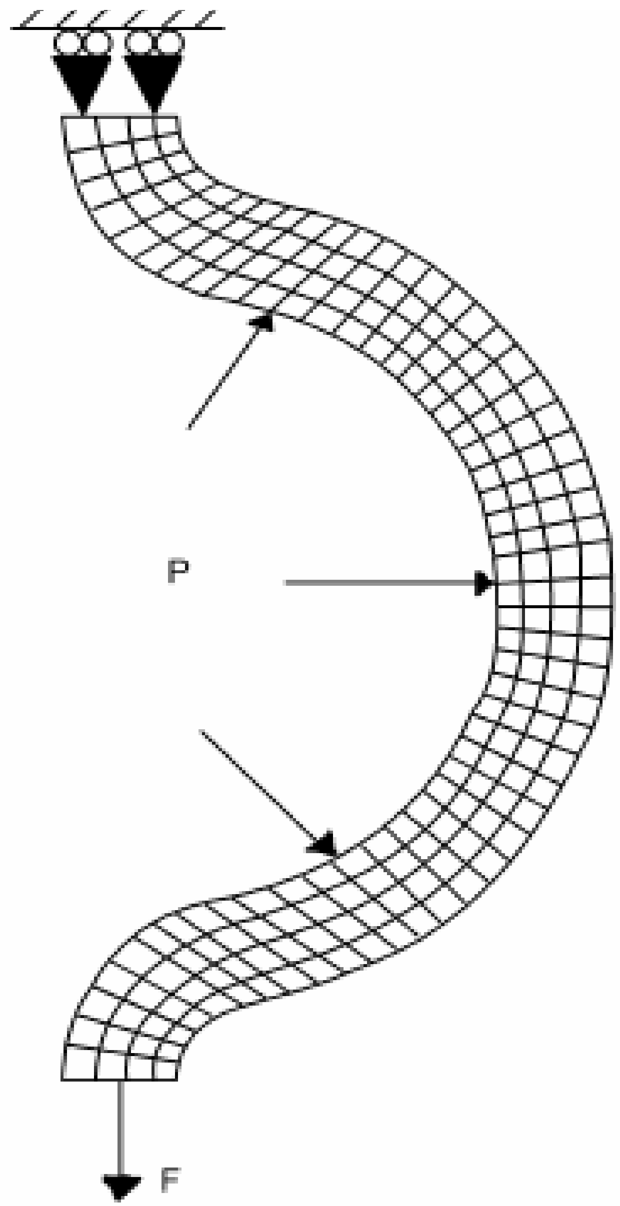


Figure 11.8 Axisymmetric representation of the hose showing the axial load (F) and the internal pressure (P).

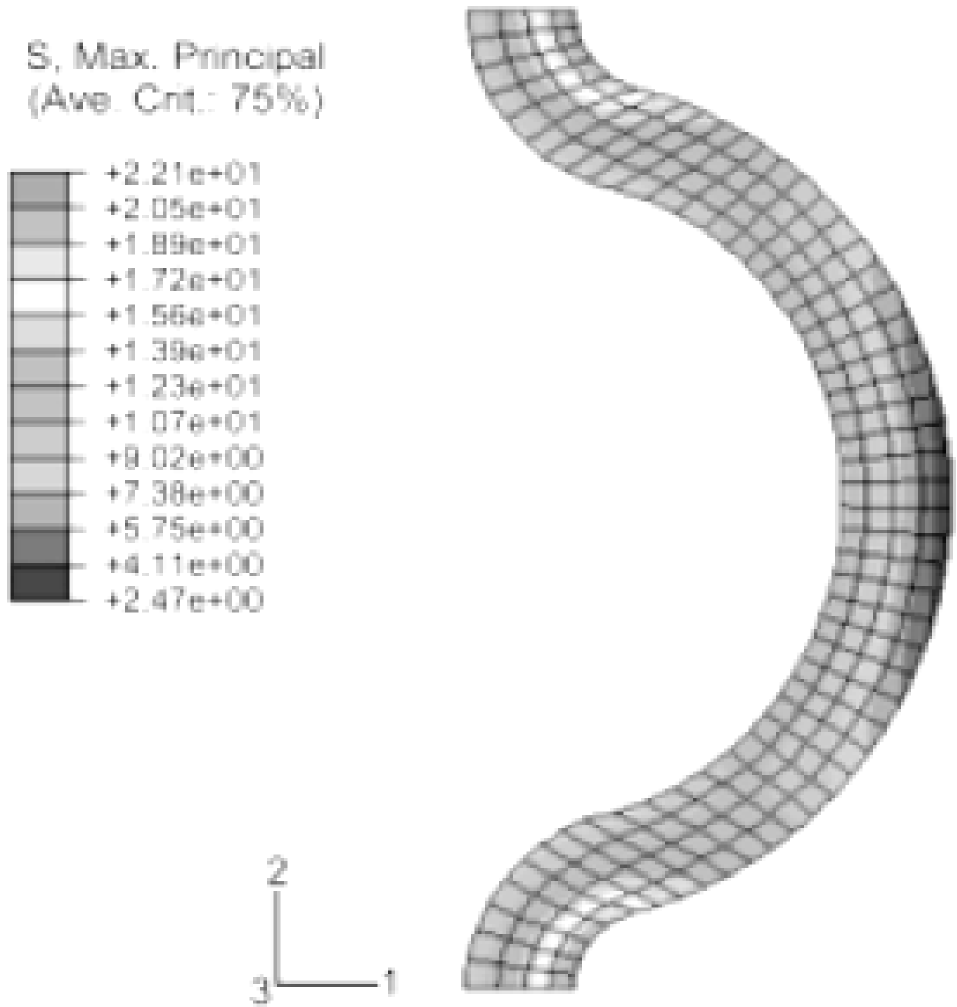
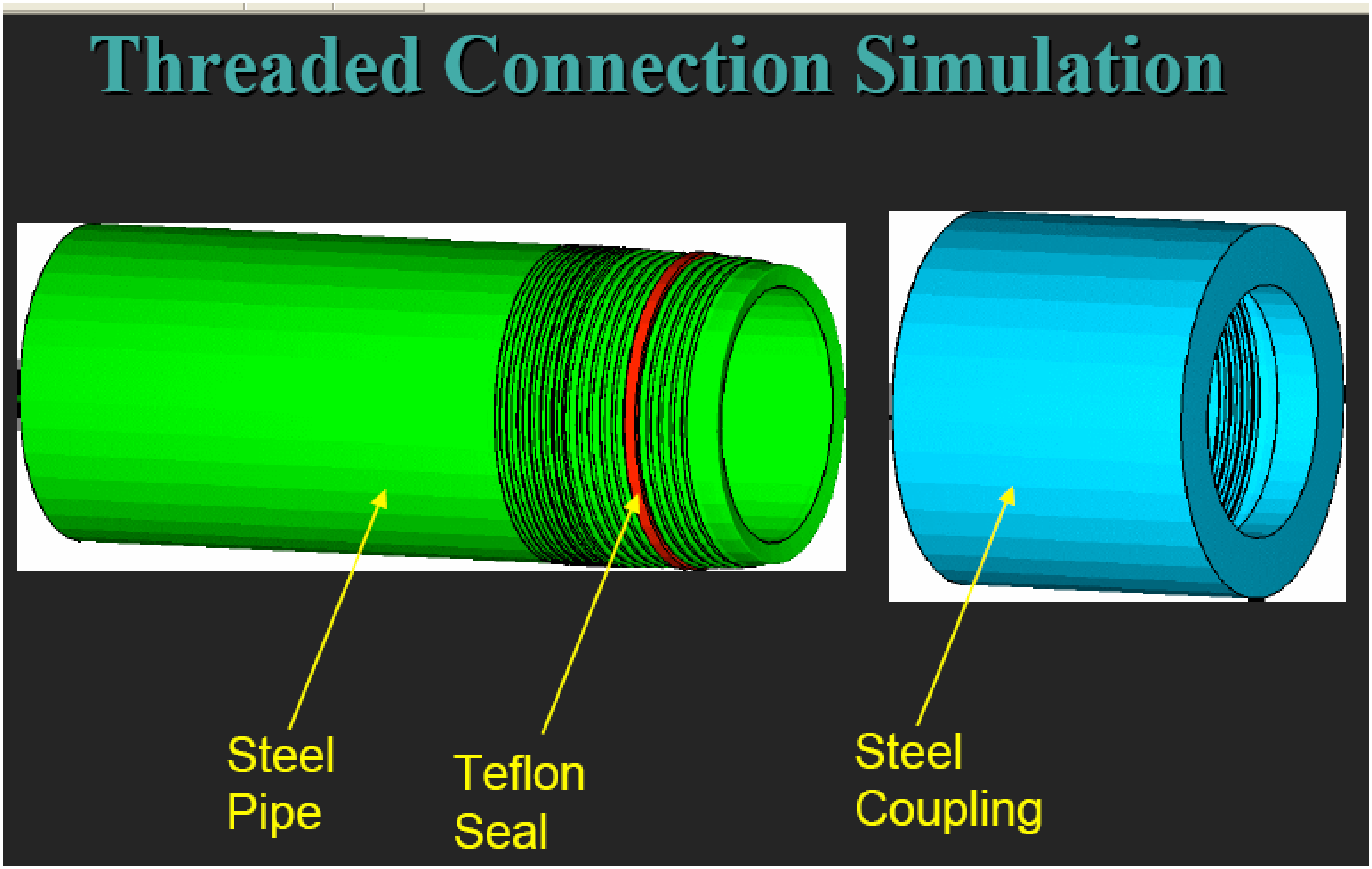


Figure 11.10 Contours of maximum principal stress in the hose at 20°C, P = 0.6 MPa, F = 280 N, after a loading time of 1 min.



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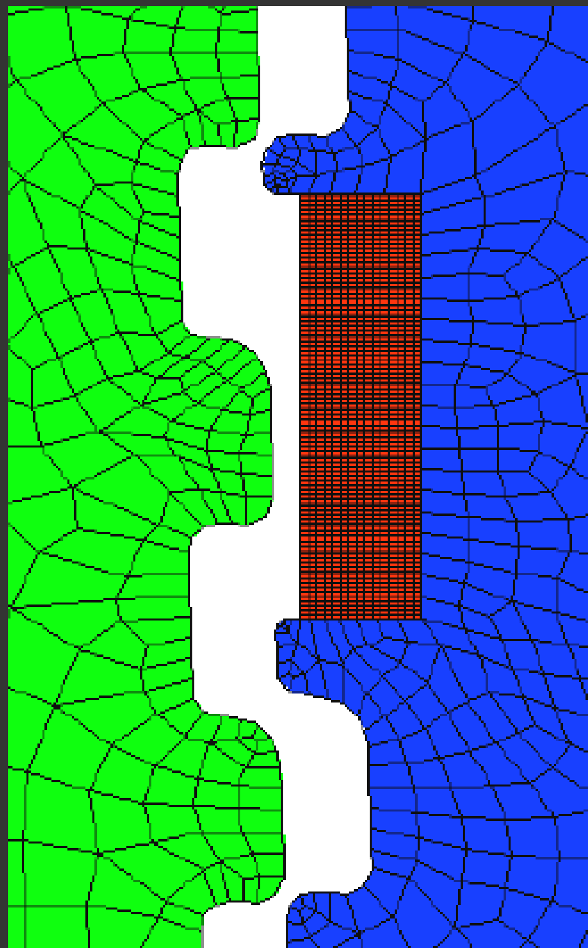
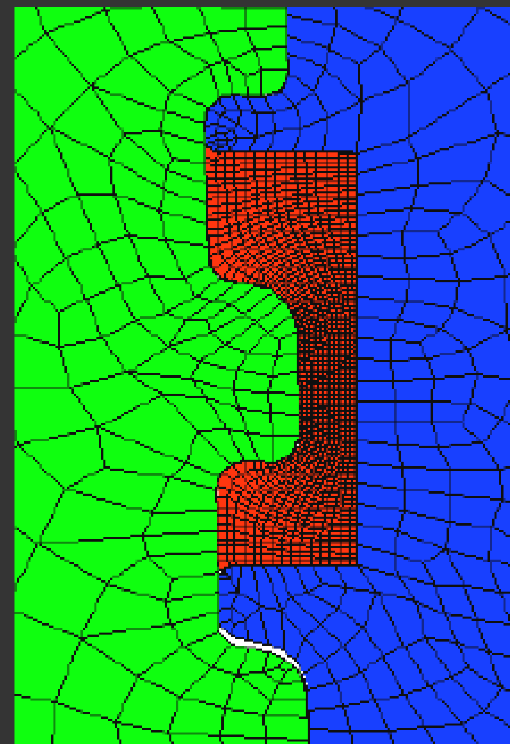
Threaded Connection Simulation





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

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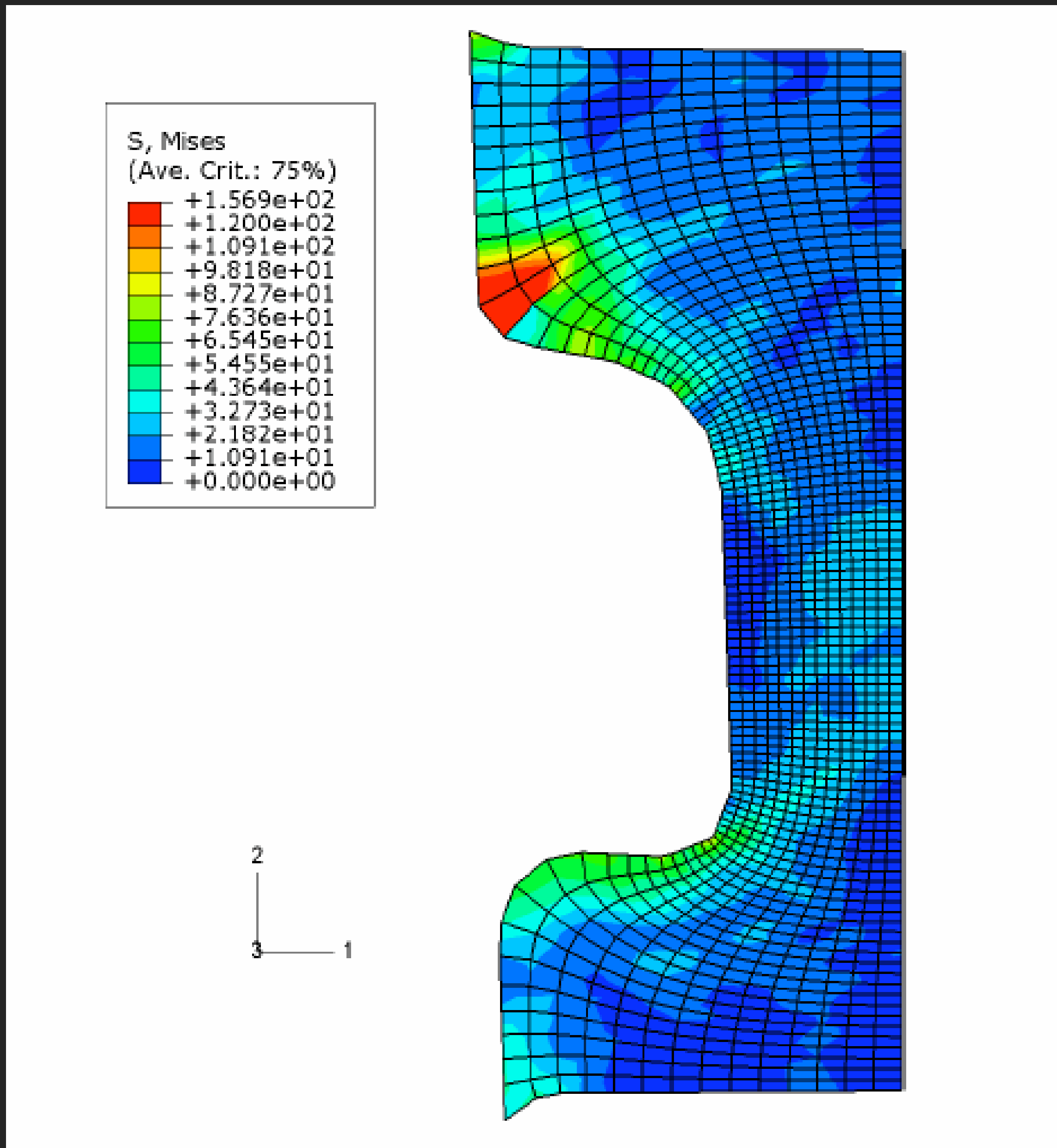

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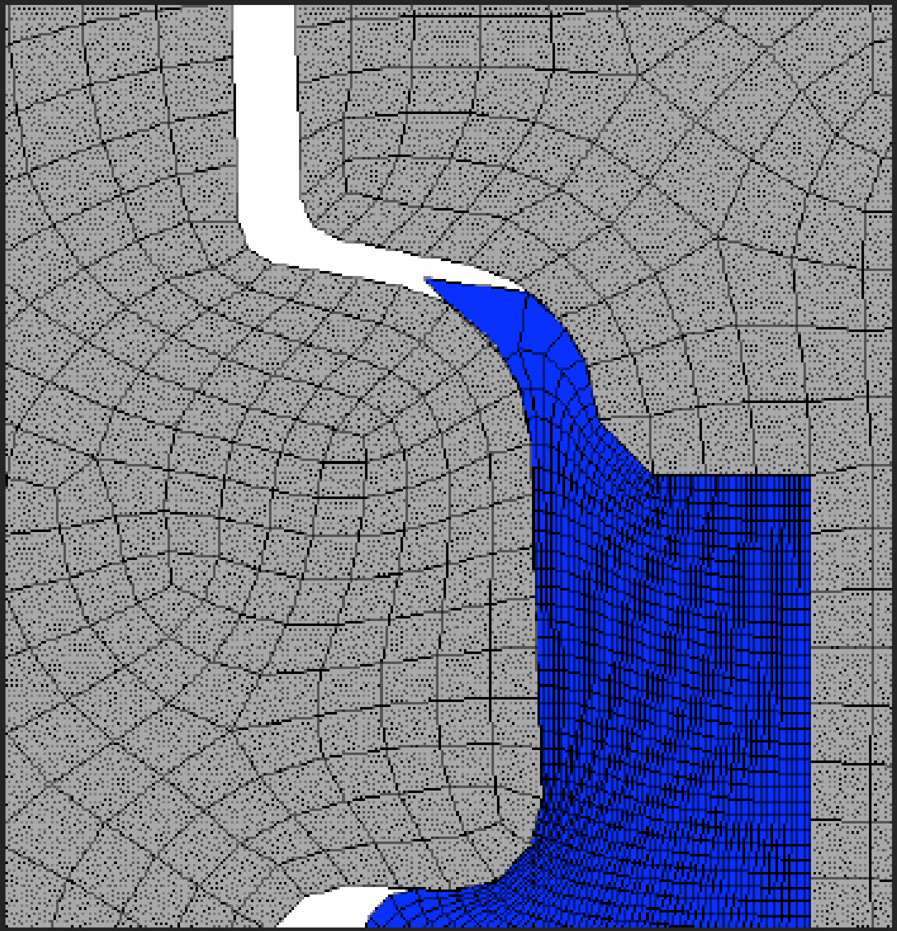

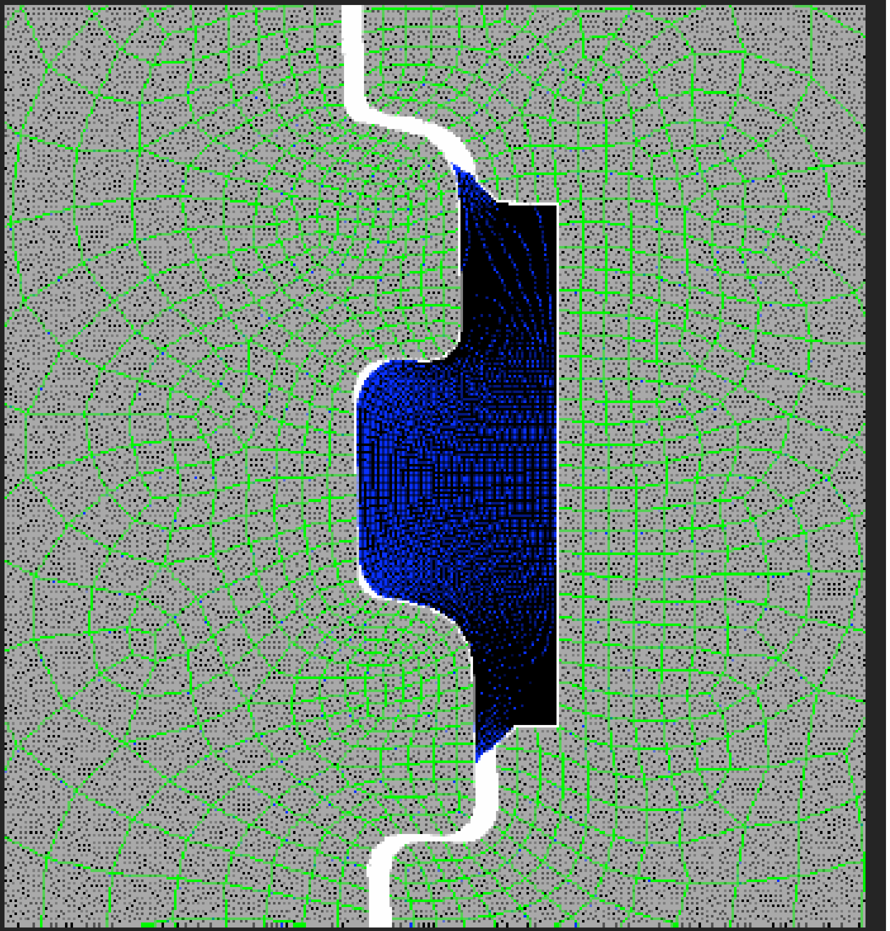

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Conclusions

- 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