Condition Assessment of Kevlar Composite Materials Using Raman Spectroscopy

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Overview

• Goals & Objectives
• Hypothesis
• Kevlar Composite Material
• Raman Spectroscopy
• Review of Literature
• Experimental
• Results & Discussion
• Conclusions
Goals and Objectives

Goal: To evaluate Raman spectroscopy as a potential NDE tool for the detection of stress rupture in Kevlar.

Objective: Test a series of strand samples that have been aged under various conditions and evaluate differences and trends in the Raman response.
Hypothesis

- Reduction in strength associated with stress rupture may manifest from changes in the polymer at a molecular level. If so, than these changes may effect the vibrational characteristics of the material, and consequently the Raman spectra produced from the material.
Problem Statement

- Kevlar composite over-wrapped pressure vessels (COPVs) on the space shuttles are greater than 25 years old.
- Stress rupture phenomena is not well understood for COPVs.
- Other COPVs are planned for hydrogen-fueled vehicles using Carbon composite material.
COPVs on Shuttle Orbiter

Kevlar yarn

Kevlar/epoxy composite strand
COPVs on Shuttle Orbiter

- Composites used primarily for the high strength-to-weight ratio
Stress Rupture Phenomena

- Material under constant load over long periods of time fails without an increase in the load
- Fibers are strained at a molecular level until rupture with associated creep (exact mechanism of material weakening is not known)
- Currently there is no known method to detect stress rupture by nondestructive means
- Raman spectroscopy may be a solution to this problem
Fiber Failure

• In fiber composite material, once a fiber fails the stress is transferred to the adjacent fibers
  – This can start a chain reaction that ends in a catastrophic failure of the entire composite
    • Local variations in the state of stress/strain
• Strain associated with creep may modify the Raman spectra of a fiber
Fiber Failure

• Fibers may also degrade by chain scission
  – Breaking of interatomic bonds
  – Resulting in changes in vibrational characteristics

• General loss of order in the Kevlar polymer
  – chain cross-linking
  – Resulting in changes in vibrational characteristics
Raman Spectroscopy

- Laser technique that is sensitive to molecular interactions in materials such as Kevlar, graphite and carbon
- Measures changes in frequency (wavelength) resulting from inelastic scattering processes
Scattered Light

- Rayleigh scattered light (elastic)
- Raman scattered light (inelastic)

Raman Molecular Interaction
RAYLEIGH
\( \tilde{\nu}_o \)

STOKES RAMAN
\( \tilde{\nu}_r = \tilde{\nu}_o - \tilde{\nu}_1 \)

RELATIVE INTENSITY (counts/sec)

WAVENUMBER (ABSOLUTE)

WAVENUMBER (\text{cm}^{-1})

WAVELENGTH

\text{RAMAN SHIFTS}

647.1 nm

720.0 nm

15500 13900

1610
Raman Spectroscopy

• The shifts in frequency of the incident light relates to the vibrational properties of the molecule
  – Vibrational modes of a molecule can be modeled and Raman scattering predicted
    • Polarizability of the molecule
    • Interatomic forces between atoms
  – Peak shifts depend on
    • Strain
    • Crystallinity
    • Molecular structure
    • Temperature
Vibrational modes associated with peaks found in the Raman spectra

<table>
<thead>
<tr>
<th>Frequency / cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>630, 732, 786</td>
<td>ring vibrations</td>
</tr>
<tr>
<td>845</td>
<td>C-H out-of-plane bending</td>
</tr>
<tr>
<td>863</td>
<td>ring vibrations</td>
</tr>
<tr>
<td>1103</td>
<td>C-H in-plane bending</td>
</tr>
<tr>
<td>1181, 1277, 1327, 1514</td>
<td>C-C ring stretching</td>
</tr>
<tr>
<td>1318</td>
<td>C-H in-plane bending</td>
</tr>
<tr>
<td>1569</td>
<td>amide II (60% N-H bending; 40% C-N stretching)</td>
</tr>
<tr>
<td>1610</td>
<td>C-C ring stretching</td>
</tr>
<tr>
<td>1648</td>
<td>amide I (80% C=O stretching; 10% C-N stretching 10% N-H bending)</td>
</tr>
</tbody>
</table>

1613 cm$^{-1}$

1649 cm$^{-1}$
Kevlar Aramid Fiber

Chemical Structure of Kevlar
Review of Literature

Peak shift (~1613 cm\(^{-1}\)) With Stress

Figure 2. Raman spectra for a free-standing single fibre of Kevlar 49 subjected to tensile stress of (a) 1.76 GPa and (b) no stress.

Schadler et al. (1995)

• As a material is strained, the interatomic distance changes resulting in a change in the interatomic force, and thus a change in the vibrational frequency
• The $\sim 1613$ cm$^{-1}$ peak exhibits the highest sensitivity with stress/strain

Prasad et al. (1990)

• Raman band broadening due to defects in the molecular chain
• Defects possibly from stress or harsh environmental conditions
Stuart (1995)

- Used a 1064 nm incident laser to investigate water absorption in Kevlar.
- Found a decrease in intensity for the 1613 cm\(^{-1}\) Raman band.
Experimental

- Renishaw Raman inVia spectrometer
- FT Raman system
• Typical Micro-Raman Spectrometer
Spectra from Kevlar with incident laser wavelengths of 647, 752 and 1064 nm
Spectra from Kevlar with Incident laser wavelengths of 488 nm
Fiber Alignment

90° 0°
# Comparison of Raman Peaks for Kevlar

<table>
<thead>
<tr>
<th>RAMAN PEAKS (cm⁻¹)</th>
<th>TEST TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kevlar yarn</td>
</tr>
<tr>
<td></td>
<td>(647 nm)</td>
</tr>
<tr>
<td>Penn and Milanovich Peaks</td>
<td>Kim et al. Peaks</td>
</tr>
<tr>
<td>698</td>
<td>694</td>
</tr>
<tr>
<td>734</td>
<td>725</td>
</tr>
<tr>
<td>789</td>
<td>773</td>
</tr>
<tr>
<td>-</td>
<td>853</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1104</td>
<td>1106</td>
</tr>
<tr>
<td>1187</td>
<td>1184</td>
</tr>
<tr>
<td>1192</td>
<td>1188</td>
</tr>
<tr>
<td>1279</td>
<td>1283</td>
</tr>
<tr>
<td>1331</td>
<td>1332</td>
</tr>
<tr>
<td>1409</td>
<td>1400</td>
</tr>
<tr>
<td>1518</td>
<td>1516</td>
</tr>
<tr>
<td>1570</td>
<td>1567</td>
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<tr>
<td>1615</td>
<td>1615</td>
</tr>
<tr>
<td>1649</td>
<td>1654</td>
</tr>
</tbody>
</table>


Kevlar yarn vs composite strand

[Graph showing the relative intensity (counts/sec) across different wavenumbers (cm\(^{-1}\)) for Kevlar epoxy strand and Kevlar yarn.]
# Strand Samples

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Notes</th>
<th>488 nm</th>
<th>647 nm</th>
<th>752 nm</th>
<th>1064 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRI Virgin Kevlar 49 Strands</td>
<td>original virgin strands, 1140 denier</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>TRI Virgin Kevlar 49 Yarn</td>
<td>original virgin yarn, 1420 denier</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>TRI Creep Test Samples</td>
<td>65% ult strength (65 lbs) at different times and temperatures</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Fleet Leader Tank SN007</td>
<td>S/N 007, 50% pressure ~4200 psi</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Fleet Leader Tank SN032</td>
<td>SN032, pressure 50% ~4200 psi</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>ATK Kevlar prepreg</td>
<td>4560 denier, cured and uncured</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>SIM Kevlar Strands</td>
<td>Stepped isothermal strands; 14o5, 21o5, 23d5, 23o5</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>
## Strand Specimens

### SIM Strands

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength</th>
<th>Temp (°C)</th>
<th>Time at Failure Temp (sec)</th>
<th>Total Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1405</td>
<td>65%</td>
<td>90</td>
<td>8770</td>
<td>58770</td>
</tr>
<tr>
<td>2105</td>
<td>65%</td>
<td>90</td>
<td>480</td>
<td>50480*</td>
</tr>
<tr>
<td>23d5</td>
<td>65%</td>
<td>103</td>
<td>8130</td>
<td>68130</td>
</tr>
<tr>
<td>23e5</td>
<td>65%</td>
<td>104</td>
<td>210</td>
<td>60210</td>
</tr>
</tbody>
</table>

### TRI Creep Strands

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Aged (hrs)</th>
<th>Temp (°C)</th>
<th>Failed?</th>
</tr>
</thead>
<tbody>
<tr>
<td>2F1</td>
<td>9</td>
<td>92</td>
<td>yes</td>
</tr>
<tr>
<td>Virgin</td>
<td>0</td>
<td>room</td>
<td></td>
</tr>
<tr>
<td>2F9</td>
<td>1</td>
<td>90</td>
<td>yes</td>
</tr>
<tr>
<td>2F10</td>
<td>4</td>
<td>90</td>
<td>yes</td>
</tr>
<tr>
<td>2F11</td>
<td>9</td>
<td>92</td>
<td>yes</td>
</tr>
<tr>
<td>2F12</td>
<td>1</td>
<td>76</td>
<td>yes</td>
</tr>
</tbody>
</table>
Full width at half maximum (FWHM) ratio

\[ \eta_i = \frac{FWHM_i}{FWHM_{1278}} \]

Intensity ratio

\[ \chi_i = \frac{I_i}{I_{1278}} \]
Intensity Variations (relative to 1278 cm\(^{-1}\)) for Virgin Strands, 647 nm incident wavelength

Variations in the intensity of different virgin materials

st dev: 0.10
Inteensity Variations (relative to 1278 cm⁻¹) for Virgin Strands vs SIM specimens, 647 nm

st dev: 0.09
Intensity Variations (relative to 1278 cm$^{-1}$) for Virgin Strands vs SIM specimens, 647 nm

- **VIRGIN**
- $\triangle$ 14o5
- $\triangleleft$ 21o5
- $\square$ 23d5
- $\times$ 23o5
- $\bullet$ VIRGIN_high
- $\bullet$ VIRGIN_low
- $\square$ 23d5_high
- $\square$ 23d5_low
- 1613 cm$^{-1}$ band
- VIRGIN
- 23d5

Inters 647 nm
Intensity Variations (relative to 1278 cm\(^{-1}\)) for Virgin Strands vs Fleet Leader specimens, 647 nm incident wavelength

st dev: 0.08
Intensity Variations (relative to 1278 cm\(^{-1}\)) for Virgin Strands vs Fleet Leader specimens, 647 nm incident wavelength.
FWHM (relative to 1278 cm$^{-1}$) for Virgin Strands vs Fleet Leader specimens, 647 nm incident wavelength

st dev: 0.04
FWHM (relative to 1278 cm\(^{-1}\)) for Virgin Strands vs Fleet Leader specimens, 647 nm incident wavelength

- **VIRGIN**
- △ SN007a
- — SN007b
- □ SN032a
- ✶ SN032b
- ✦ VIRGIN\_high
- ✦ VIRGIN\_low
- □ SN032a\_high
- □ SN032a\_low

1613 cm\(^{-1}\) band

SN032a
FT Results – Fleet Leader

![Graph showing FT Results for Fleet Leader](image)
Peak shifts for all strand specimens
1613 cm$^{-1}$ Peak Shift with Applied Force, 647 nm

\[ y = -0.1472x + 1612.5 \]
Defects in molecular structure

-perhaps for hydrogen bonds

Chemical Structure of Kevlar

-1613 cm⁻¹
Fiber Optic Raman Systems

The laser beam is directed through a fiber optic probe which can be taken out in the field for measurements.

Renishaw

Avalon Inst.
Summary

• Raman spectroscopy is being explored as an NDE technique to predict the onset of stress rupture in Kevlar composite materials
• Test aged Kevlar strands to discover trends in the Raman response
• Strength reduction in Kevlar polymer will manifest itself on the Raman spectra
Conclusions

Raman spectroscopy has shown

- Relative changes in the intensity and FWHM of the \( \sim 1613 \) \( \text{cm}^{-1} \) peak
  - Reduction in relative intensity for creep, fleet leader, and SIM specimens compared to the virgin strands
  - Increase in FWHM has been observed for the creep and fleet leader specimens compared to the virgin strands
  - Changes in the Raman spectra may result from redistributing loads within the material due to the disruption of hydrogen bonding between crystallites or defects in the crystallites from aging the Kevlar strands
- Peak shifting has not been observed to date. Analysis is ongoing......
- Stress measurements may provide a tool in the short term
Questions?
Thank You