Raman Spectroscopy Measurement System and Data Analysis for Characterization of Composite Overwrapped Pressure Vessels (COPVs)

Phillip A. Williams and Buzz Wincheski
Nondestructive Evaluation Sciences Branch, Research Directorate
NASA Langley Research Center
Hampton, VA 23681

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Outline

• Motivation/ COPV Stress Rupture
• Raman Spectroscopy NDE
• COPVs: Kevlar and Carbon Fiber Overwrap
• Raman Spectroscopy of Fibers
• Inspection feasibility: commercial Raman systems & 6”-diameter COPV tests
• *In situ* Raman NDE system: 40”-diameter Orbiter Kevlar COPV
• Data Analysis Techniques
• Results: - *ex situ* tests of stress-rupture-aged COPVs
  - *in situ* measurements on Orbiter COPV up to stress rupture failure
• Conclusions
Objective/Motivation

- Localized residual stress along with stress from fabrication anomalies and structural loads is an issue in a wide variety of composite structural applications, including composite overwrapped pressure vessels (COPVs).
- Evaluation of health and aging degradation in fiber composites is currently a challenge with standard NDE procedures.
  - Practical and effective NDE methods need to be developed.
  - This research upgrades and optimizes a LaRC/WSTF portable Raman spectroscopy system and utilizes other Raman spectroscopic laboratory equipment at LaRC to:
    • Accurately evaluate stress/strain related issues in fiber reinforced composites via Raman spectroscopy.
    • Evaluate *molecular* Raman-active signatures that relate to aging of fiber-matrix structure.
COPV Stress Rupture

- Pressure vessels comprised of a metal liner overwrapped with a Kevlar fiber-epoxy matrix are used for He and N gas storage on the Space Shuttle Orbiter.
- Observations of the COPV life-analysis were reviewed and raised some concerns with respect to “stress rupture” (SR) life predictions.
- SR of an Orbiter COPV on the ground or in flight would yield a catastrophic hazard
- During pressurization, volumetric changes in the COPVs induce strain-related changes in the Kevlar composite overwrap that could be a factor in predicting SR lifetime.
- Additionally, age-related degradation of COPVs could be a factor in the reliability and likelihood of failure due to SR.
- Several NDE techniques, including Raman spectroscopy, were tasked with investigation of the strain and age-related properties of the COPVs.

From R. Saulsberry, “Nondestructive Methods Supporting Shuttle and ISS Composite Overwrapped Pressure Vessel Testing”, 9th Joint FAA/DOD/NASAA Conference on Aging Aircraft, March 6-9, 2006, Atlanta, GA.
Raman Spectroscopy: Overview

- Elastic Scattering: Rayleigh scatter
- Inelastic Scattering: Raman scatter
  - Stokes shift to longer wavelengths
  - Anti-stokes shift to shorter wavelengths


\[ \nu = \frac{1}{\lambda_{\text{initial(incident)}}} - \frac{1}{\lambda_{\text{final(scattered)}}} \]

- Incident laser excitation light is focused onto the specimen.
- Stokes Raman scattered light is the light that has shifted to lower frequency than the incident beam because some of its energy has been converted to (phonon) vibrational energy.
- This shift to lower frequency due to partial conversion to vibrational energy is known as the Raman shift.
- Spectrum of scattered Raman signal is acquired for conversion and analysis of Raman shift.
Raman Spectrum

- Spectral peaks are indicative of specific vibrational modes of the molecules in specimen.
- Spectra used to determine molecular chemical structures and properties related to changes in the molecular bonds.

Typical Raman Spectrum of Kevlar

Kevlar Raman Shift Due to Strain

As previously observed in several studies, peak position of 1610 cm\(^{-1}\) in Kevlar shifts to a lower frequency with increased strain.

- Raman measurements of fibers show consistent correlation to strain in controlled tests.
- Raman shift in Kevlar has a linear correlation with strain and can be empirically calibrated to measure strain:
  - 0.26 % strain per 1.0 cm\(^{-1}\) Raman shift
  - 4.4 cm\(^{-1}\) Raman shift per 1.0% strain
Typical Raman Spectrum of Carbon Fibers


Fig. 2. Raman frequency shift of the $E_{2g}$ band as a function of tensile applied strain for four M40B carbon fibres.
Raman Spectrum of T1000 COPV Tank

$I_D/I_G$ has been reported in literature to correlate with graphene crystallite size as well as defect limited phonon mean free path. As such, the ratio is anticipated to increase with aging of carbon fibers.
Raman Spectroscopy: Instrumentation

Sample

- Excitation laser wavelengths: 532, 633, and 785 nm
- 180° light collection
- Probe contains light focusing and collection optics.
- Notch filter in spectrograph to filter Rayleigh scattered light.
- Gratings spread wavelengths of collected, scattered Raman light across camera of detector.

**Schematic of Raman spectroscopy system**

Probe head can be used in two configurations:
- microscope for small samples, e.g. tows of fibers
- remote (hand-held or mounted) for large samples & scanning, e.g. COPVs
Kevlar COPV Set-up

- Translation stages for Raman probe
- Fixture for holding COPV
- 532 nm Raman probe head

COPV
Carbon COPV Set-up

532 nm remote probe head

10x objective

Video Microscope

COPV

~ 1 mm
In situ Raman NDE Support of SR Aging Tests on 40” Orbiter Kevlar COPV

• Stress rupture tests on Orbiter 40”-diameter Kevlar COPV at NASA WSTF
• Collaboration with WSTF and GRC

From R. Saulsberry, “Nondestructive Methods Supporting Shuttle and ISS Composite Overwrapped Pressure Vessel Testing”, 9th Joint FAA/DOD/NASAA Conference on Aging Aircraft, March 6-9, 2006, Atlanta, GA.

• Portable, remote Raman system set-up at WSTF with 532-nm excitation laser and long-WD optics for in situ analysis
Experimental set-up for 40” Kevlar COPV Raman NDE

Salient features:
• MR probe head contains optics for incident, excitation laser and collection of Raman signal
• Lens is 17” working distance non-contact optic
• Shroud & cone protect against ambient, external light
• Boroscope enables viewing of region of interest on tank surface
• Mercury lamp serves as spectrometer wavelength (e.g. Raman shift) calibration reference

Raman spectra acquired on zero shear (unstressed) Kevlar tow enables reference for comparison of temperature and pressure-induced changes in the kevlar fibers on COPV surface
• Linear background removal for 1275 and 1325 cm\(^{-1}\) peaks.
• Quadratic background removal for 1610 cm\(^{-1}\) peaks.
• All curve fits calculated with MATLAB “fit” routine using “nonlinear least squares” method.

Raman spectrum acquired on 40” Kevlar COPV:
532.002 nm @ 0.2 W
15 accumulations of 1.0 s exposure
Data sectioned into regions for analysis of Kevlar peaks and Hg reference lines

- Lower (Higher) portion of background subtracted spectrum fit to 5 (4) Gaussian peaks with start points of 1327, 1275, 1180, 1250, and 1350 (1610, 1647, 1567, and 1658) cm\(^{-1}\)

- Mercury peaks searched at 1465, 1525, and 1528 cm\(^{-1}\), as calculated based upon Hg emission lines at 5769.90, 5789.66, 5790.66 angstroms

- For each peak, MATLAB routine outputs the position, amplitude (intensity), full width at half maximum amplitude (FWHM), and a goodness-of-fit-factor.
- Routine does batch processing of large sets of acquired Raman spectra files.
Ex situ Raman Measurements on 6.3” Carbon COPVs

532 nm polarized Raman data: polarization angle || to fiber direction, 50X optics, 10 accumulations @ 5.0 second exposure, 21 mW power at sample

- At 21 mW power (above), no clear trends observed in COPV due to low signal-to-noise ratio
- At 37 mW power (left), thermal damage is observed from increased laser power.
**Ex situ Raman Measurements on 6.3”Carbon COPVs**

- At lower, 6.25 mW power and much longer acquisitions (50 accumulations @ 10.0 s exposures), D and G peaks observed on COPVs.
- D to G Band intensity ratio $I_{1325}/I_{1610}$ varied widely between 6.19 and 14.6.
- Small shifts in peak position of 1610 cm$^{-1}$ band may not be out of standard deviation of measurements.

- Beam focus found to be critical, with manual adjustment of beam position on COPV and focal distance to COPV surface required to obtain usable spectra.
- At lower power, total acquisition time for each spectra was ~ 2000 seconds.
- At present, the criticality of the focus combined with the long acquisition times make Raman scanning and health monitoring of carbon COPV vessels impractical with aforementioned systems; however, recent improvements in Raman instrumentation may overcome these limitations and should be studied.
Ex situ Raman Measurements on 6.3” Kevlar COPVs

Analysis of position of 1610 cm⁻¹ peaks confirm increased strain in aged vessels (SN 28 is virgin, unaged), corroborating diameter measurements.
Raman Measurements on 6.3” Kevlar COPVs

1610/1278 Intensity Ratio

- Aged vessels exhibit a decrease in the intensity (amplitude) of 1610 cm\(^{-1}\) band normalized to that of 1278 cm\(^{-1}\) band, as compared to unaged vessel (SN28).
- No clear correlation was observed for normalization with 1325 cm\(^{-1}\) band of COPVs nor for intensity ratios of Kevlar fibers.
Raman Measurements on 6.3” Kevlar COPVs

1610/1325 FWHM ratio

• Aged vessels exhibit an increase in the FWHM (broadening) of 1610 cm\(^{-1}\) band normalized to that of 1325 cm\(^{-1}\) band, as compared to unaged vessel (SN28).
• No clear correlation was observed for normalization with 1278 cm\(^{-1}\) band of COPV nor for FWHM of Kevlar fibers.
**Ex situ** Raman Measurements After Continued Aging

- Trend shows clear increase in FWHM ratio with increased aging.
- Plotted values represent average of 27 measurements per bottle, standard deviation of each bottle approx. ±05 units.
In situ Raman Data of 40” Kevlar COPV During Stress Rupture Testing

Raman shifts correlate well with variations in pressure, i.e., lower Raman shift with higher pressure/strain.
In situ Raman Data of 40” Kevlar COPV During Stress Rupture Testing

1610 cm\(^{-1}\) Peak Position 5/4/2009 - 10/22/2009

Stable measurements of the 1610 cm\(^{-1}\) peak position were observed during the constant pressure phases of the stress rupture testing of the vessel.
In situ Raman Data of 40” Kevlar COPV During Stress Rupture Testing

During the final 10 days of testing, the normalized FWHM of the 1610 cm$^{-1}$ peak showed significant increase with a maximum value before final COPV rupture.
Conclusions/Summary

• Feasibility of the use of Raman spectroscopy an NDE tool for the evaluation of Kevlar and carbon COPVs was demonstrated.

• Stress rupture aging protocols used on the Kevlar COPVs induced an increase in both the diameter (strain) and the stress rupture age, shown via Raman analysis.

• Data suggest that measurements of the Raman shift of the 1610 cm⁻¹ band potentially can be used for accurate measurements of the fiber strain, independent of aging, while measurements of the 1610/1325 FWHM ratio and the 1610/1278 intensity ratio can quantify aging effects independent of strain.

• Future work should include:
  • Modeling of Raman phenomena and composite material interactions to aid in the inspection design and in understanding the correlation between the Raman measurements and physical behavior of the composites.
  • Study of recent improvements in Raman spectroscopy instrumentation to overcome limitations and issues encountered during these studies.

• Raman measurements, which provide information on the molecular level changes in composite fibers, could lead to a universal, nondestructive method for characterizing both strain and stress rupture age in fiber overwrapped COPVs.