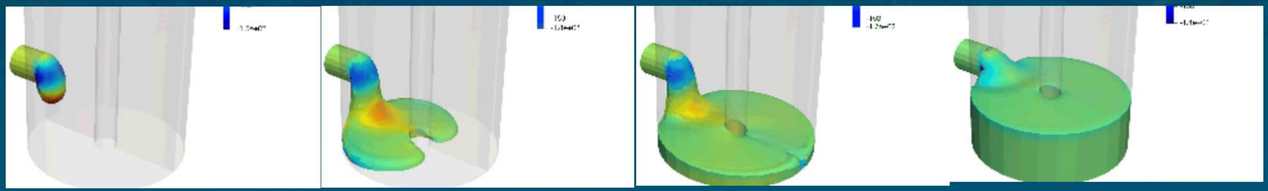
SAND2019-12736C

SIMULTANEOUS RAMAN AND RHEOLOGY MEASUREMENTS FOR REACTION AND STRESS MONITORING



PRESENTED BY

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Society of Rheology Annual Meeting, October 2019
Raleigh, North Carolina

POLYMER ENCAPSULANTS HARDEN FRAGILE COMPONENTS FROM CRADLE TO GRAVE





Encapsulation

Viscosity increase
Bubbles, voids

Cure

Cure + thermal shrinkage

Storage/Aging

Embrittlement
Incompatibilities

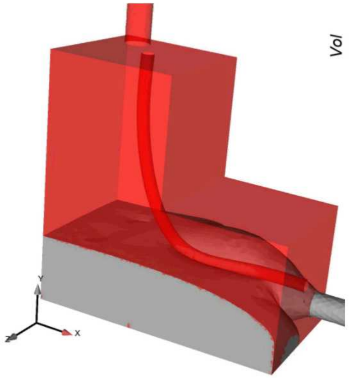
Transportation

Mechanical insult

Environments

Swelling, decomposition, thermal expansion

Design of the component is finished after the first stages



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Rheometer, FEM models

DMA,Instron, computational models

Computational models, Dynamic testing
Fiber Bragg Gratings, Crack Imaging

**Currently, models of component performance in environments do not take into account manufacturing stresses*

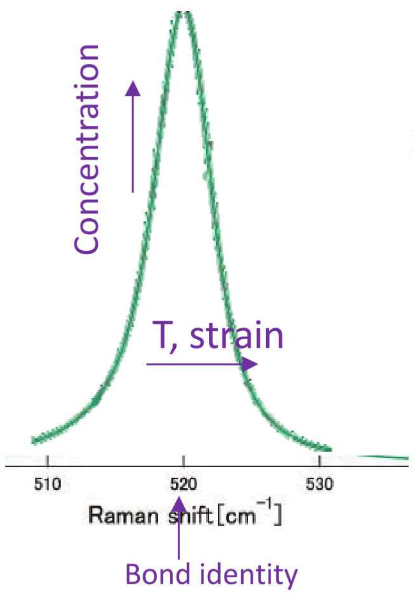
RAMAN SPECTROSCOPY

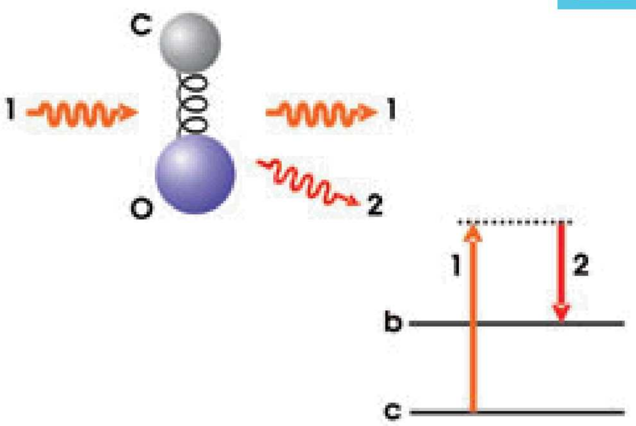
Explore Raman spectroscopy as a cradle-to-grave diagnostic

Inelastic scattering of light from molecular bonds

$$\upsilon = A\,(T_{\omega} - T_{o})^{2} + S_{\sigma}\,\sigma + \upsilon_{o}$$

Wavenumber shifts due to strain and temperature are additive

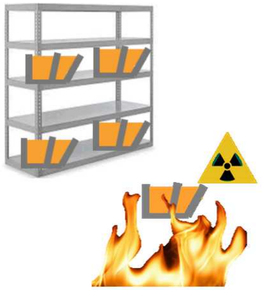




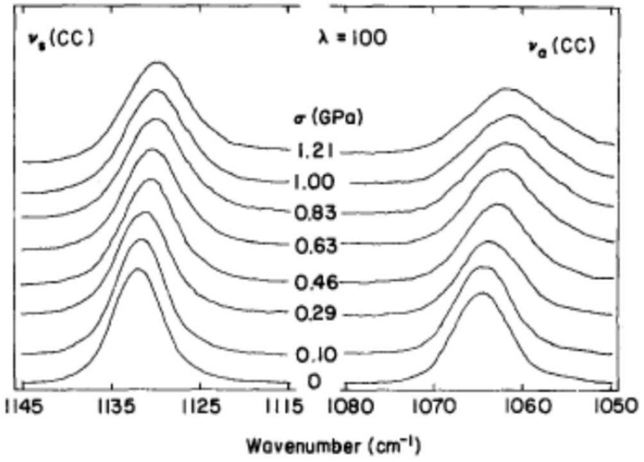
Inelastic scattering from a molecular bond (photonics.com)

Rheo-Raman tools can quantitatively monitor curing reactions simultaneously with rheology

Detect manufacturing stresses using rheo-Raman device. Calibrate strain/Raman relationships

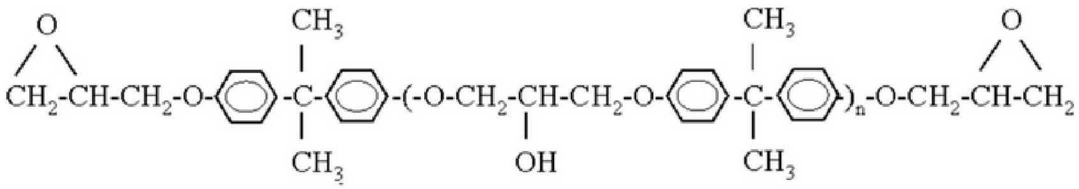


Raman detects chemical changes during aging or environmental exposure
Calibrated strain/Raman relationships quantify stresses in fielded components

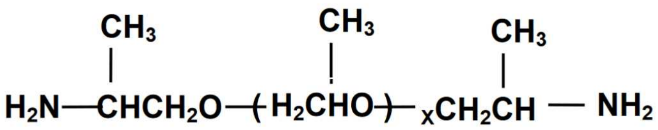


Raman spectra measured under tensile stress for polyethylene (Tashiro et al. 1988)

SYSTEM OF INTEREST



EPON 828
Diglycidyl ether bisphenol A
76 wt%



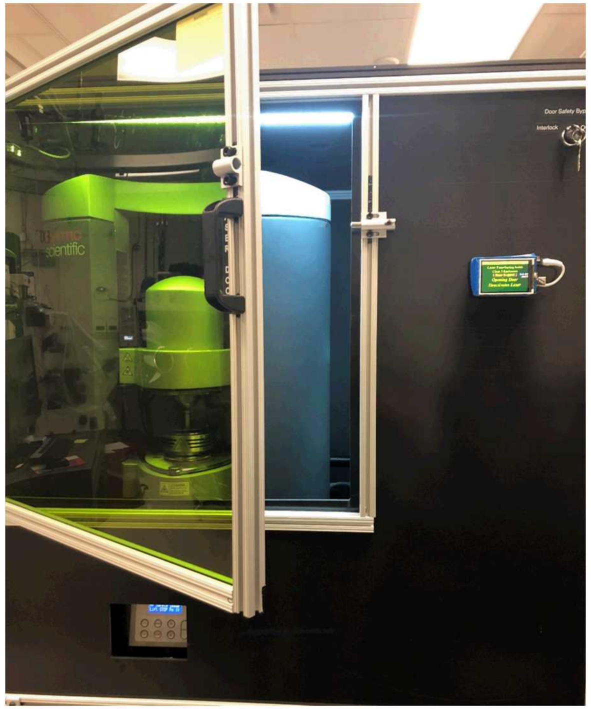
Jeffamine D-230 polyetheramine
24 wt%

Rheo-Raman systems are ideal environments for calibrating Raman shifts with strain

- Precise mechanical control up to 50 N stress (axial)
- Thermal control up to 300 ^{o}C
- Exact height measurements

Carbon nanotubes added as stress tracer materials

- 2 – 10 nm diameter, 1 – 5 micron length, 0.01 wt%

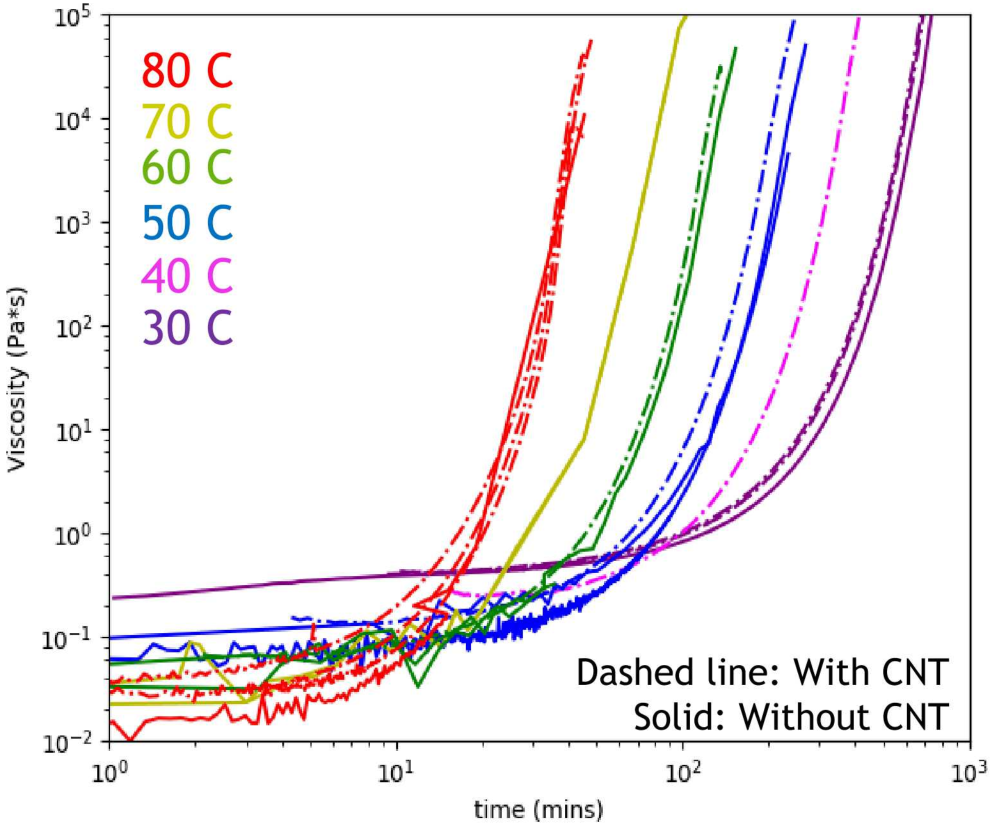


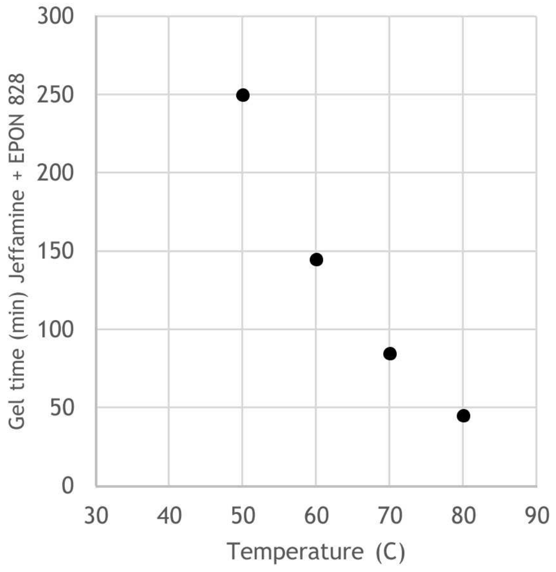
A custom interlocked box is placed around a ThermoFisher coupled Rheo-Raman system

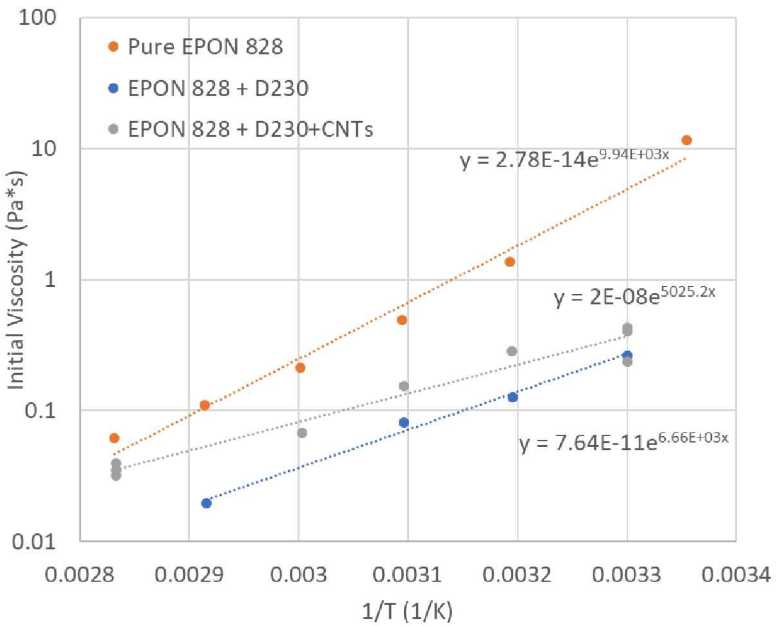
Kotula 2016, Rev. Sci. Instruments

VISCOSITY DEPENDENCE ON TEMPERATURE

Rheology measured at various temperatures:
Challenging due to fast cure times, axial stresses in rheometer



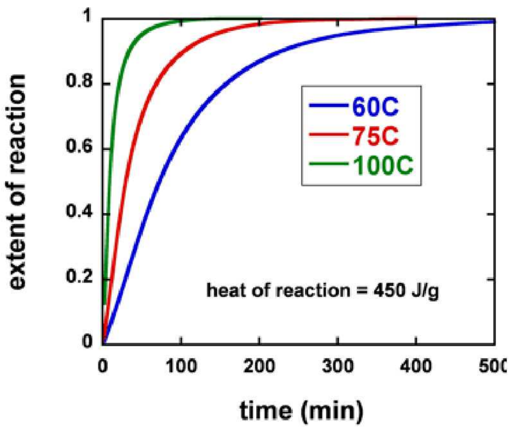




Viscosity of liquid epoxy before cure depends on temperature using an Arrhenius relationship.
Liquid viscosity is Newtonian.
Jeffamine lowers initial viscosity by almost an order of magnitude.

EXTENT OF REACTION

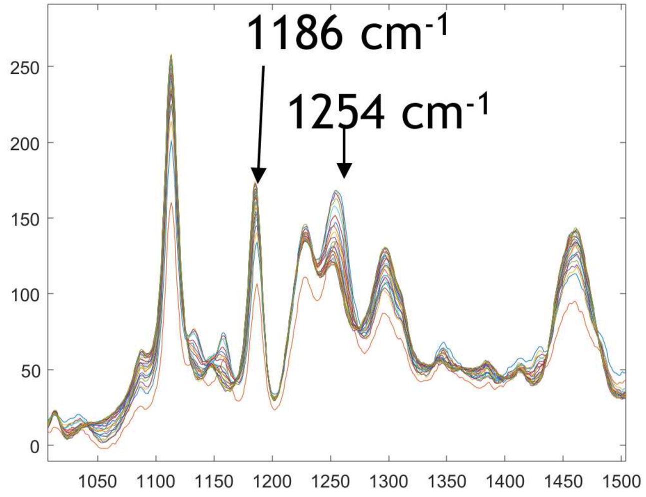
Extent of reaction was previously measured as a function of time and temperature using 3 isothermal cures by differential scanning calorimeter (Adolf).



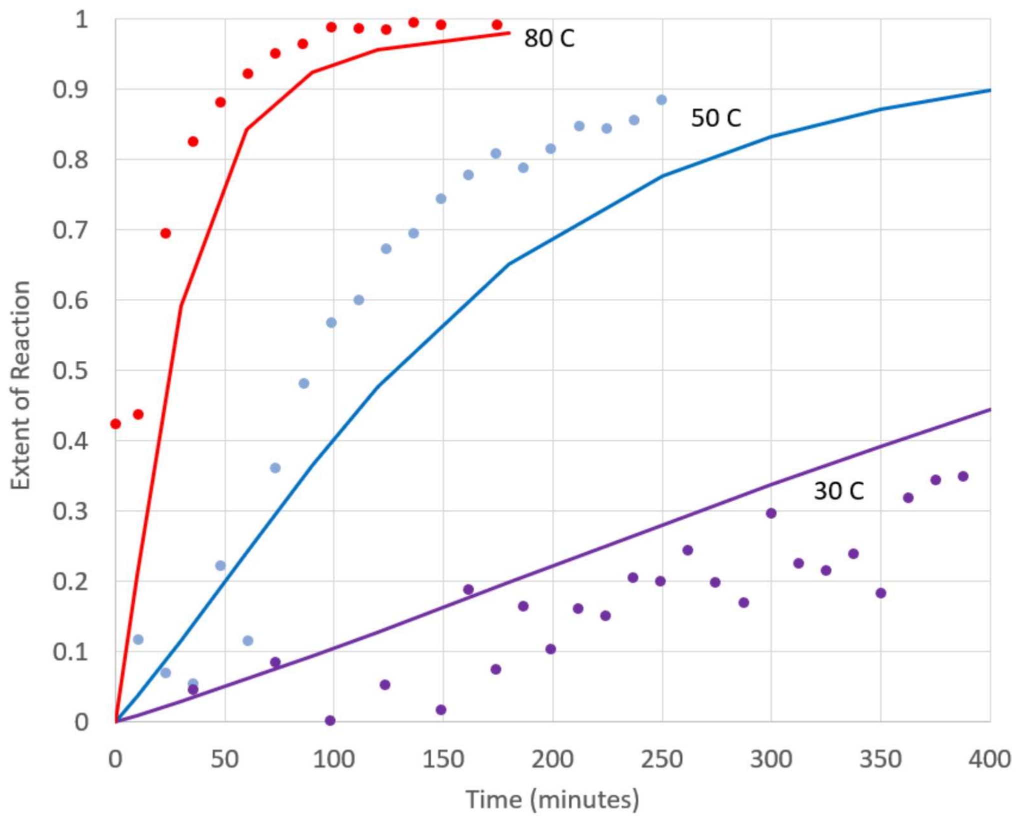
Legacy model:

$$\frac{d\xi}{dt} = 3.3x10^{6}\,\frac{1}{min}\left(e^{-\frac{12.5kcal/mol}{RT}}\right)(0.3 + \xi)(1 - \xi)^{1.5}$$

Extent of reaction defined for Raman spectra: I_{1254} / I_{1186} normalized between 0-1



Legacy model is plotted alongside Raman results. Reasonable data agreement, collected alongside rheology.



VISCOSITY MODEL

Using legacy expression for the extent of reaction, a fit is created for the viscosity as a function of time and temperature.

Mondy-Adolf Epoxy Model

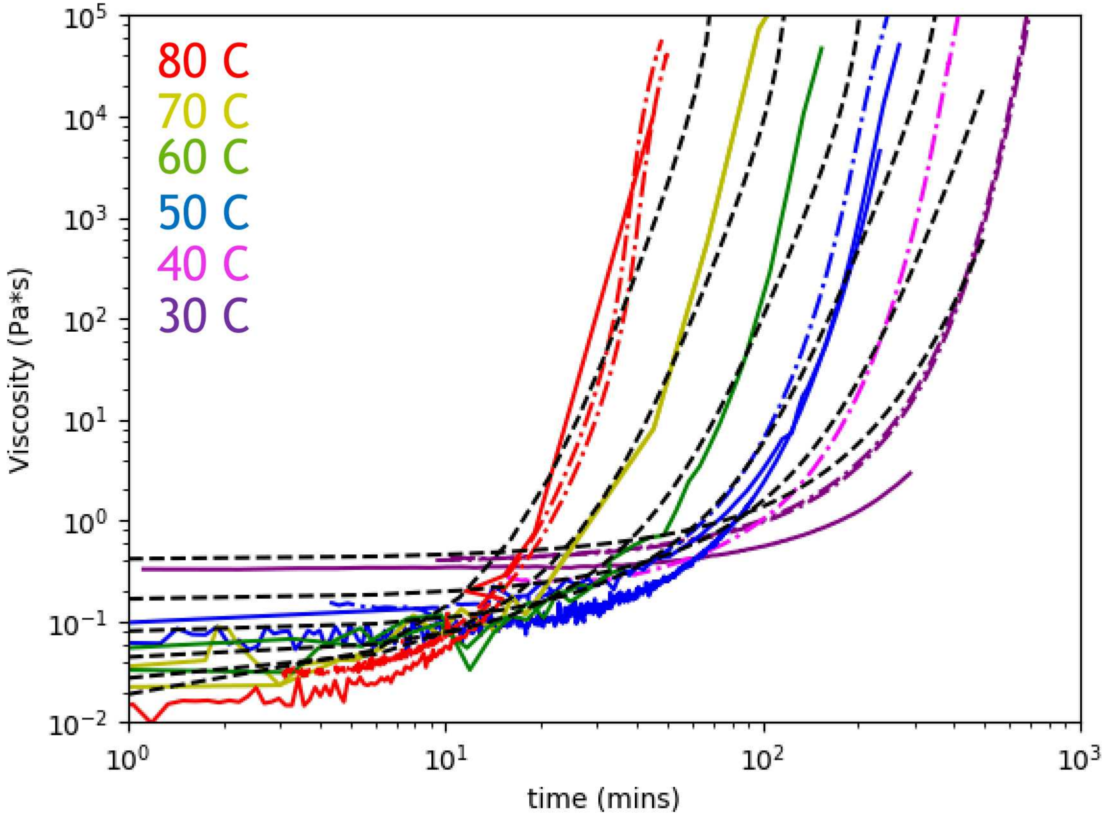
$$\frac{d\xi}{dt} = 3.3x10^{6}\,\frac{1}{min}\left(e^{-\frac{12.5kcal/mol}{RT}}\right)(0.3+\xi)(1-\xi)^{1.5}$$

$$\mu=\mu_0\left(T_g\right)\,\underbrace{10^{\frac{-C_1(T-T_g)}{C_2+T-T_g}}}_{\text{WLF Time/T}}\,\underbrace{\left(1-\left(\frac{\xi}{\xi_c}\right)^2\right)^{-1.33}}_{\text{Cure}}$$

$$T_g = \frac{T_g^0}{1-A\xi}$$

where A and ξ_c depend on T

μ_0	10	Pa s
c_1	6	
c_2	80	K
Tg_0	272	K
A	0.33	
ξ_{gel}	0.89	
φ_{max}	0.572	



_._._. With carbon nanotubes
_____ Without carbon nanotubes
- - - Model fit

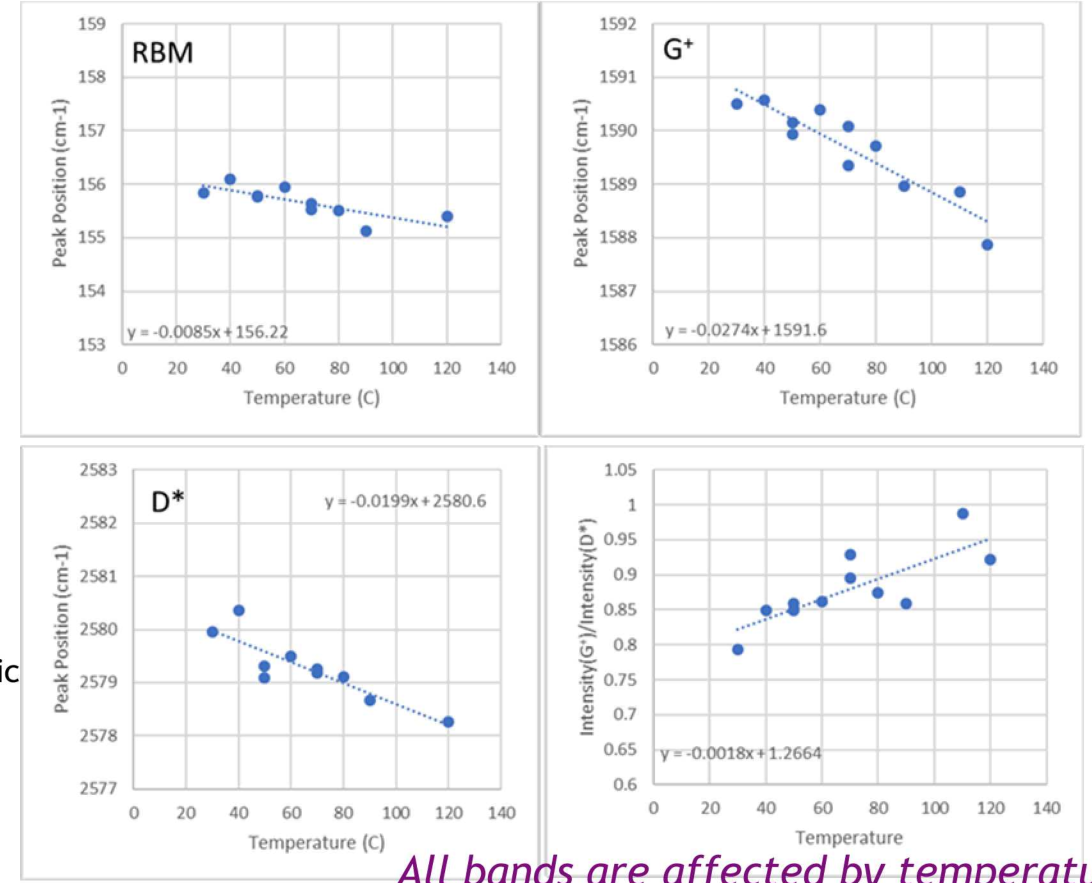
Fit to the measured viscosity is acceptable.
It is estimated that even greater success would be gained using a new extent of reaction expression.

CARBON NANOTUBES AS STRESS MARKERS

Low concentration (0.01 wt%) carbon nanotubes added to EPON 828

Several well-studied peaks are available for analysis

D* peak stands apart from EPON 828 signal



All bands are affected by temperature

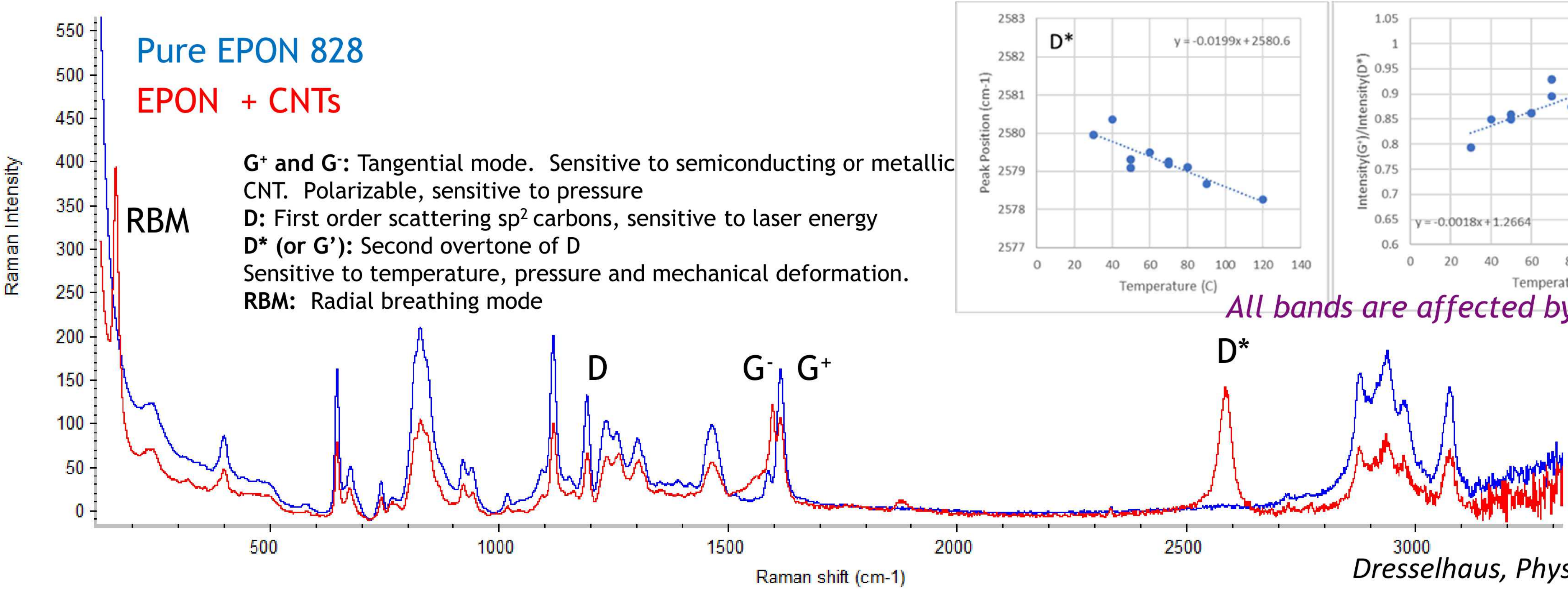
G^+ and G^-: Tangential mode. Sensitive to semiconducting or metallic CNT. Polarizable, sensitive to pressure

D: First order scattering sp^2 carbons, sensitive to laser energy

D* (or G'): Second overtone of D

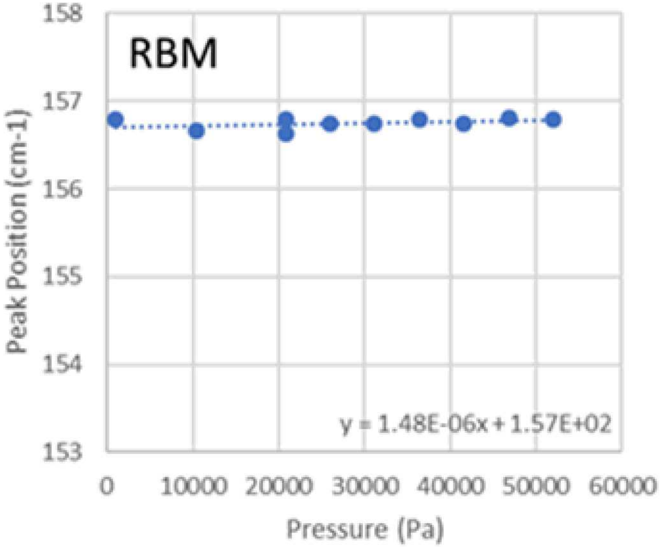
Sensitive to temperature, pressure and mechanical deformation.

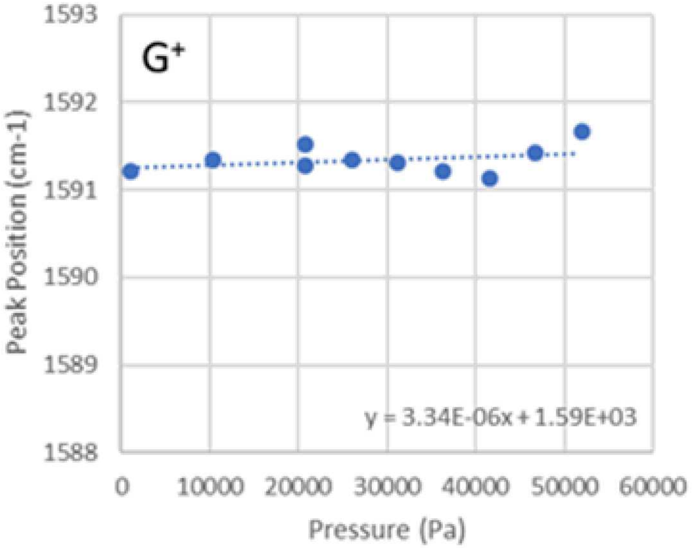
RBM: Radial breathing mode

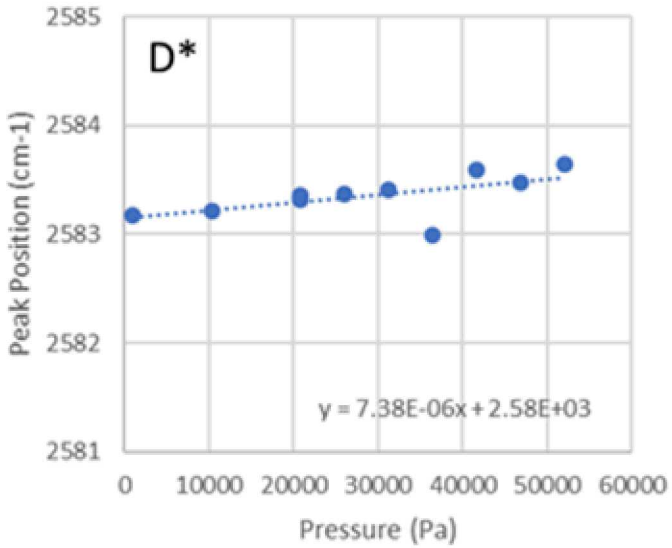


Dresselhaus, Phys Reports, 2005

CALIBRATION: RAMAN SHIFTS OF CNT'S IN CURED EPON 828

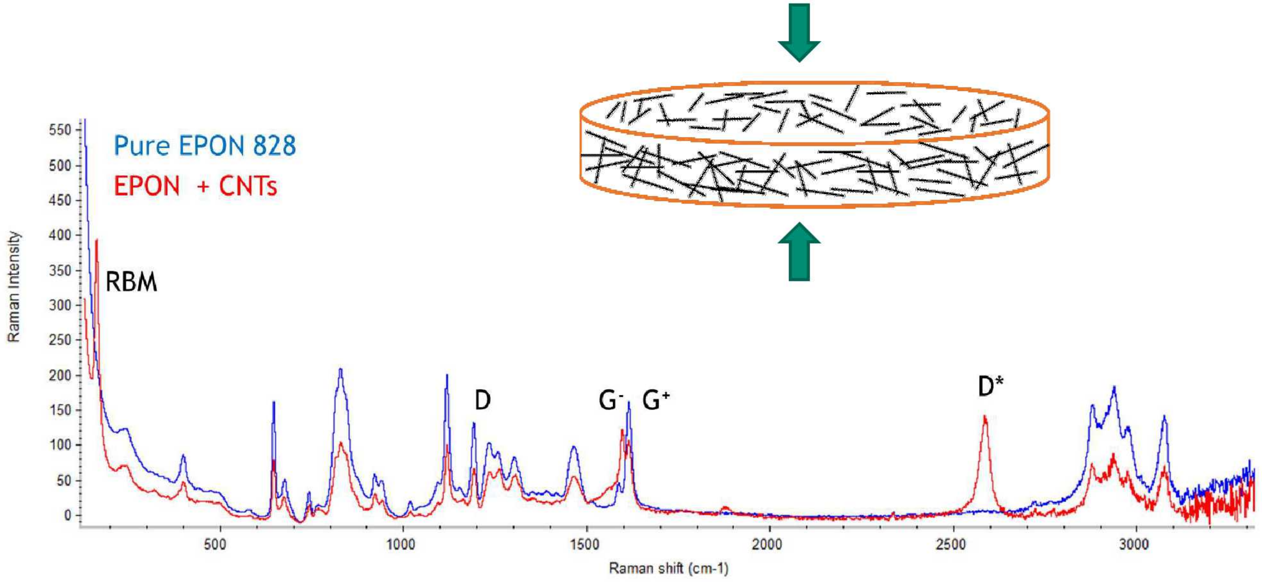






EPON 828 + 0.01% CNT is cured in a petri dish at 70 ^{o}C and then exposed to axial pressure at room temperature.

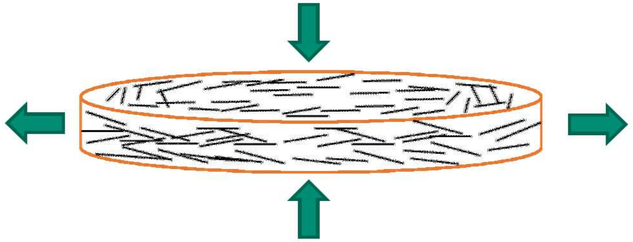
Sensitivity of Raman signal to pressure is not strong.



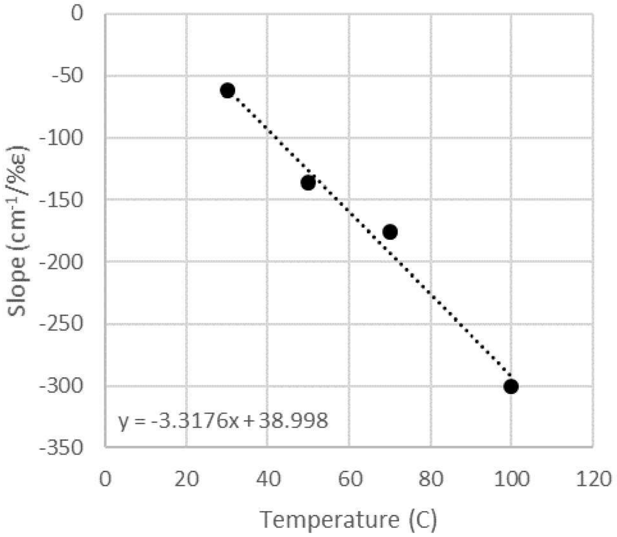
CALIBRATION: RAMAN SHIFTS OF CNT'S IN CURED EPON 828

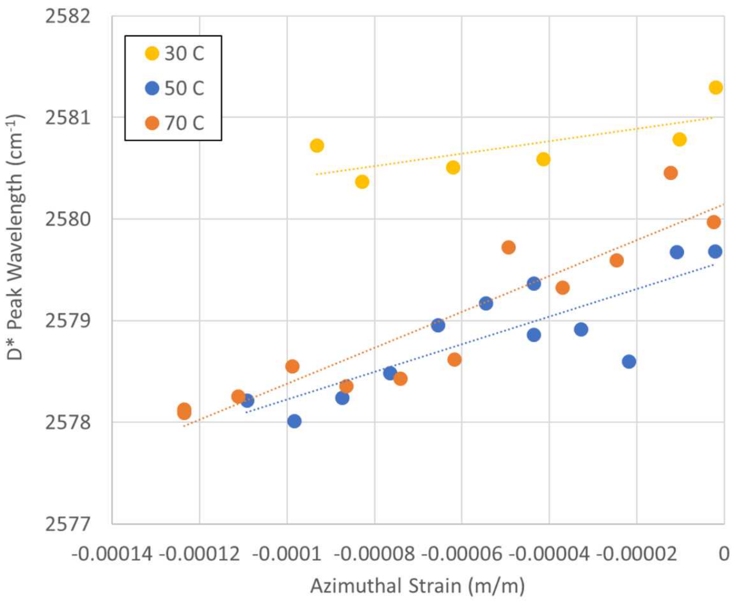
Given a preshear, alignment of the nanotubes creates a strong Raman signal.

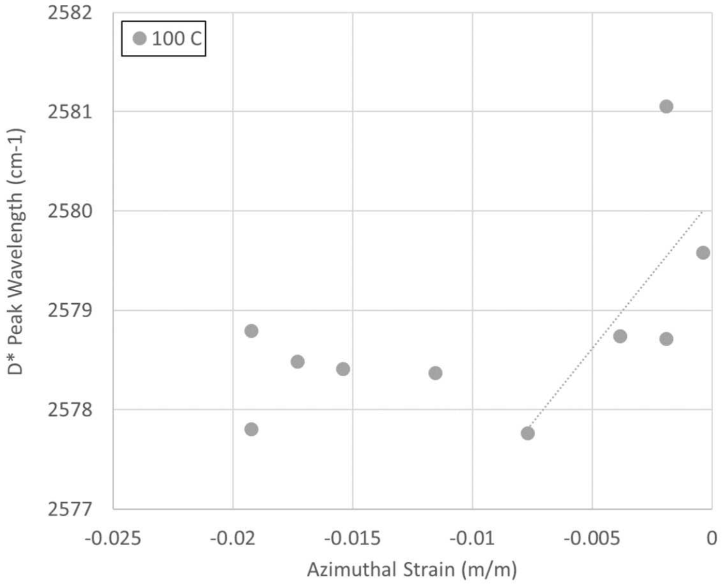
Axial pressure creates an azimuthal tension that is detectable by the Raman signal of the nanotubes.



Sensitivity of wavelength to strain is increased at increased temperatures







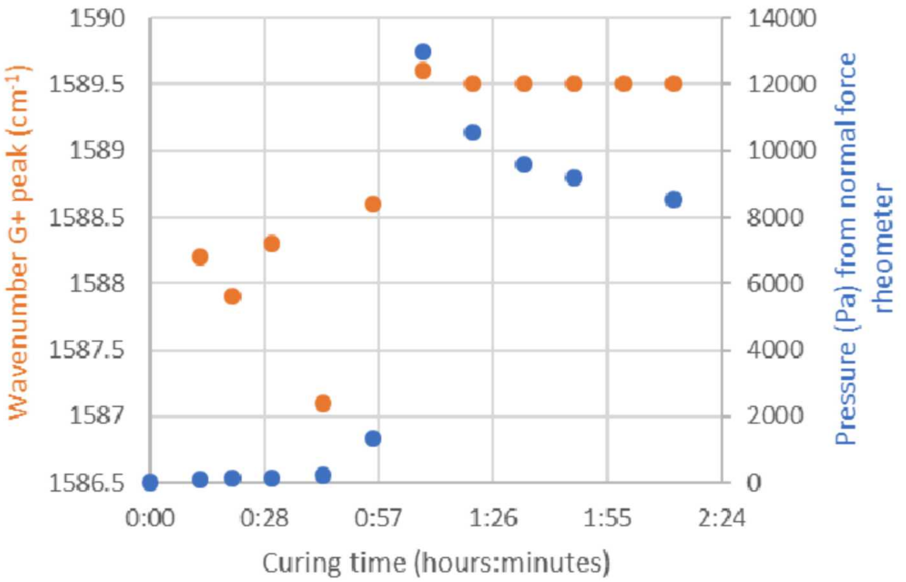
STRESSES DURING CURE

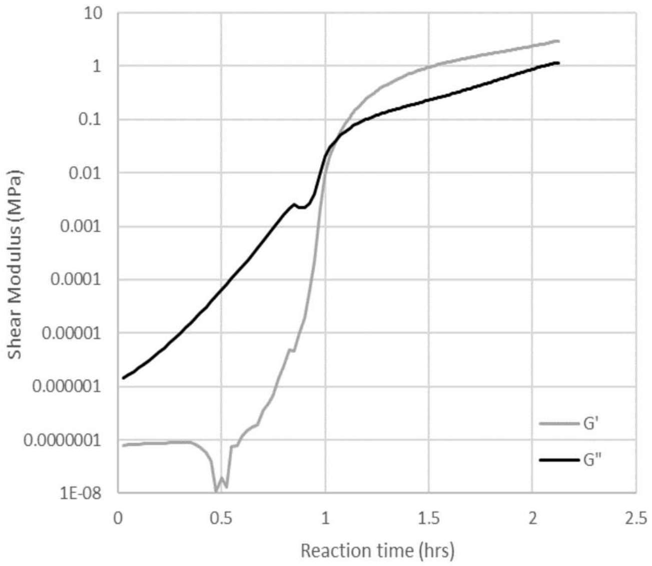
Sample is cured at 70 C on rheometer after a preshear and then exposed to 1 Hz, 1% strain oscillations

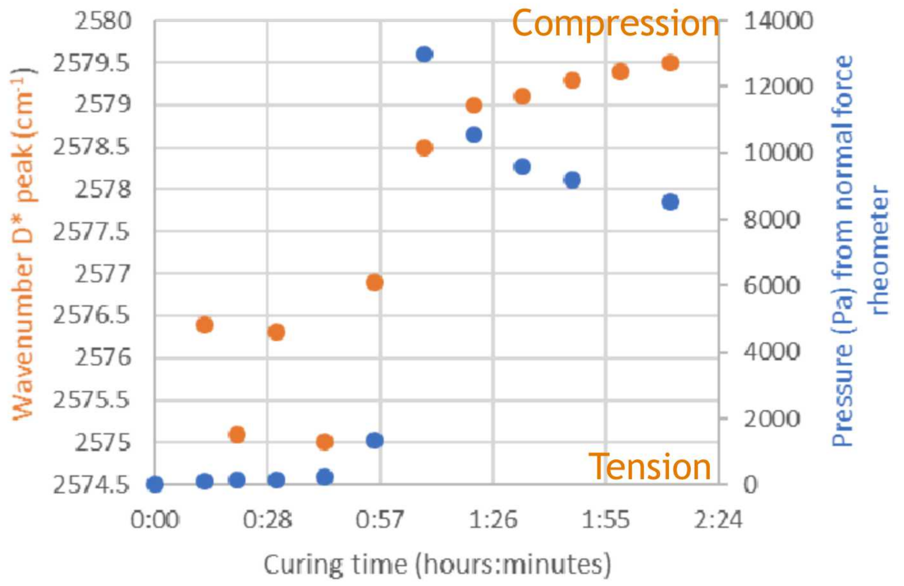
Gel point is observed after 1 hour

Raman signal detects compression in the carbon nanotubes at the gel point (cure shrinkage).

Normal force is also measured by rheometer at this time.



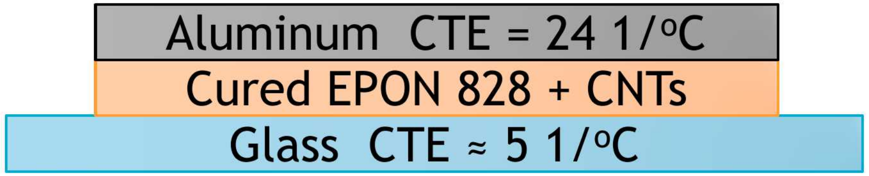


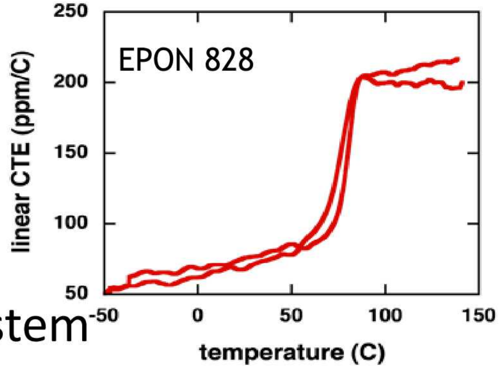


THERMAL EXPANSION OF A CONFINED SAMPLE

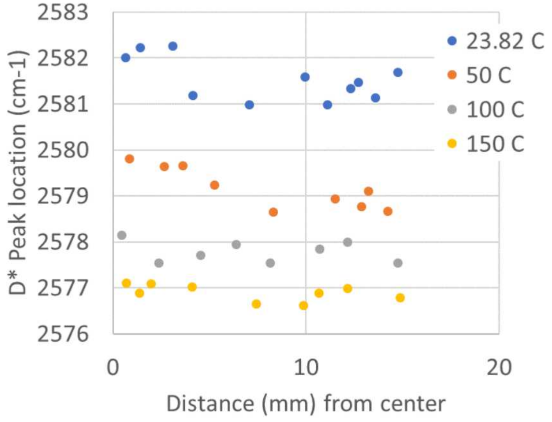
In practice, encapsulants are bonded to dissimilar materials

Temperature excursions are common

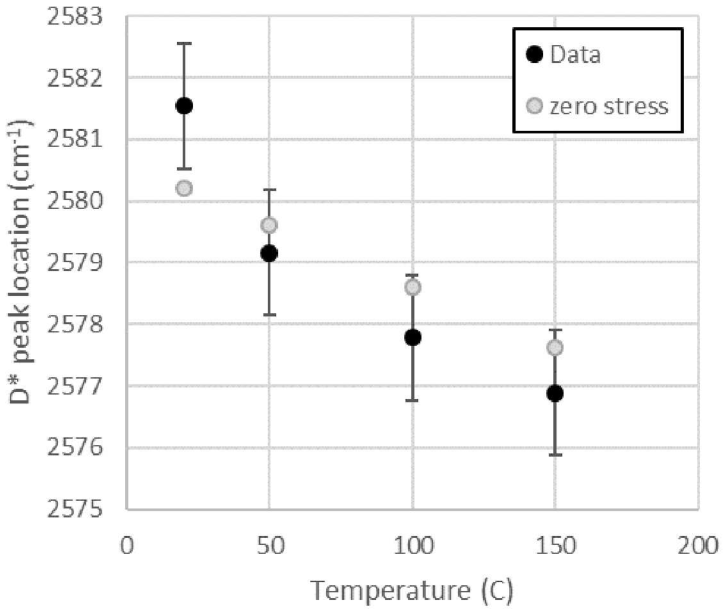


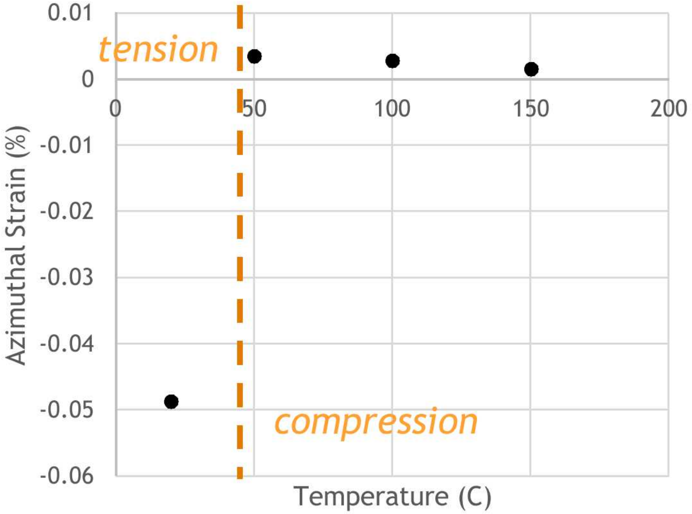


Sample is cured at 70 °C on Rheo-Raman system in a shearing flow. It is then exposed to temperatures



No discernable effect of radial position in sample

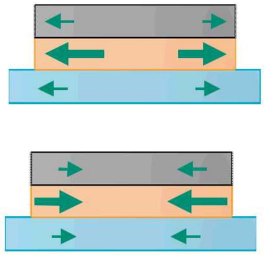




Above the cure temperature, CNTs detect compression

Below the cure temperature, CNTs detect tension

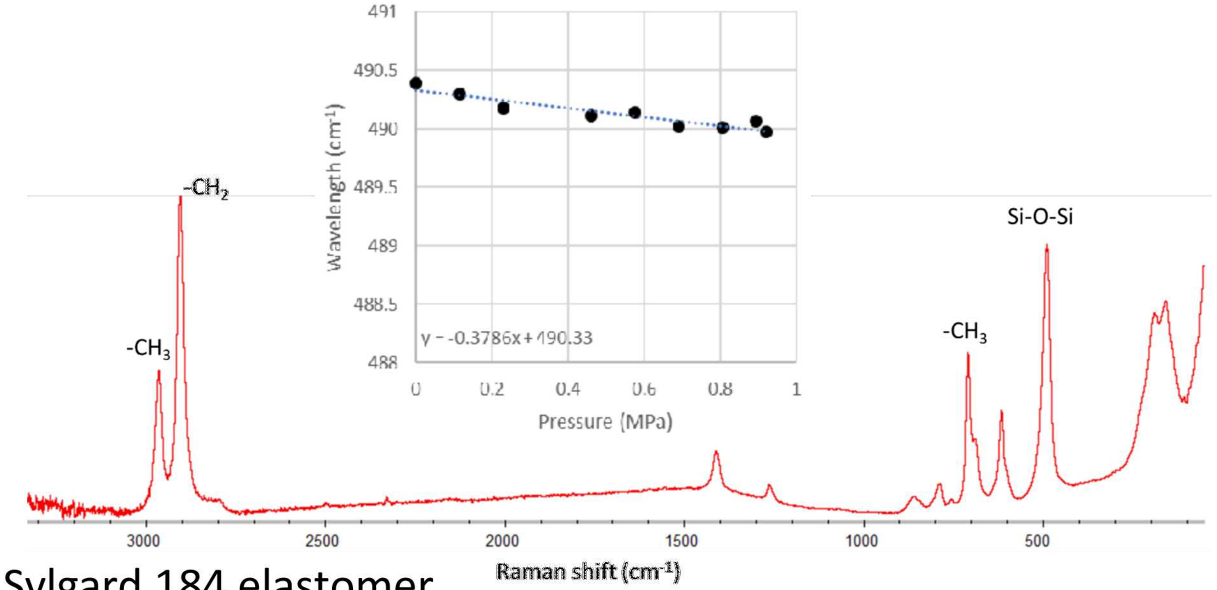
Much less strain above the T_g of the material



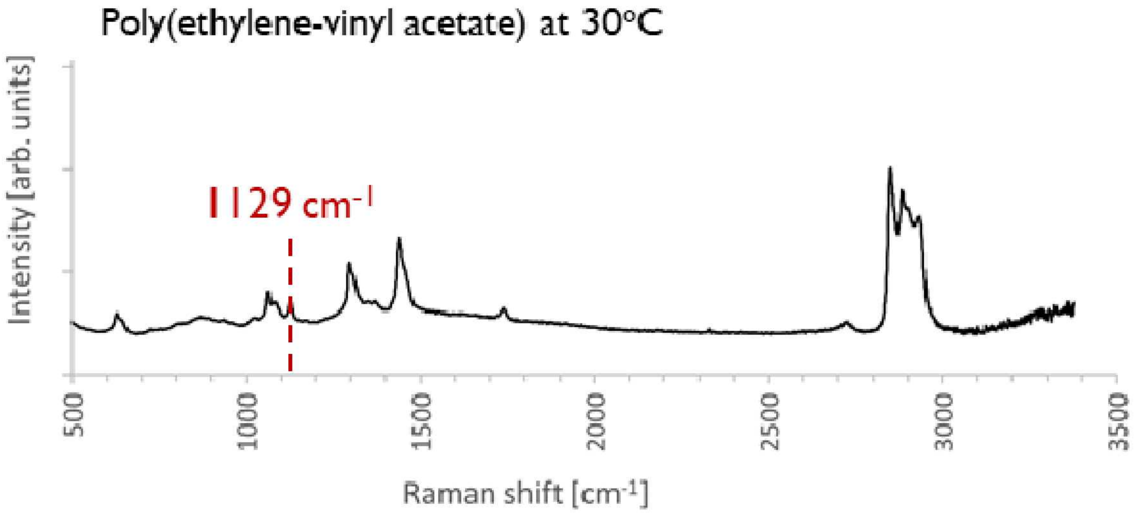
OTHER EXPLORATIONS

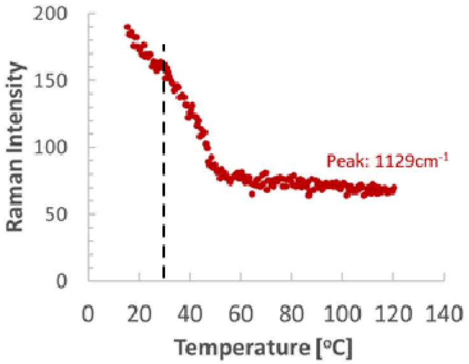
In the future, would prefer no tracer materials. Sylgard 184, for example, natively contains a peak susceptible to stress.

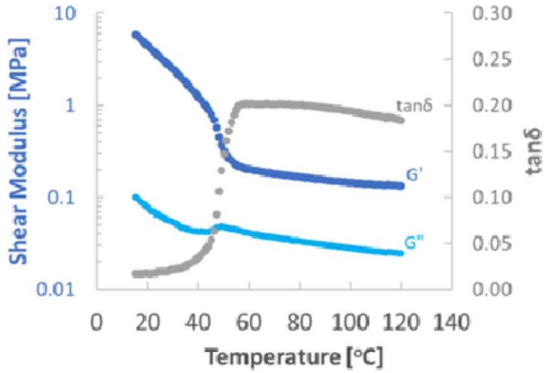
See Ashley Maes' talk (Thurs) for discussion on photovoltaic module encapsulants



Sylgard 184 elastomer







CONCLUSIONS

For an encapsulation material within Sandia's mission space:

Rheo-Raman was used to calibrate a viscosity model vs cure temperature

Effects of dwell time on polymer viscosity, flow into mold

Cure stresses can be tracked during solidification

Optimization of cure schedule to reduce manufacturing stresses

Stresses tracked during thermal excursions for a cured sample

Observations of strains due to CTE mismatches

Detection of delamination/cracks