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Simultaneous Raman and Rheology Measurements for Reaction and Stress Monitoring

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Abstract

Monitoring the rheology, polymerization, and stress generation of polymeric systems is essential for properly understanding encapsulation processes for weapons' components and other phase-changing systems in Sandia's mission space. Recently, a state-of-the-art diagnostic system was acquired that enables simultaneous rheological and Raman spectroscopic measurements of materials. Using this system, the evolving rheology of complex fluids can be linked to chemical or conformational changes that occur during processing such as melting, crystallization, curing, or gelation. Simultaneous measurements streamline the creation of material models that link the extent of reaction of curing polymer systems to the viscosity of the material. Uses of the technology include monitoring the crystallinity and modulus of poly(ethylene vinyl acetate) photovoltaic module encapsulants with temperature changes, curing of EPON 828 using Jeffamine for neutron generator applications, and solidification of paraffin wax which is used as a phase change material in thermal energy storage devices. Future plans for monitoring stress in polymeric systems using Raman microscopy will also be discussed, including both Raman signatures of the polymers of interest or of a tracer additive such as carbon nanotubes.

Rheo-Raman Instrumentation

A ThermoFisher Rheo-Raman device was purchased combining an iXR 150 mW 785 nm Raman spectrometer with a HAAKE MARS rheometer. The combined system is able to measure complex viscosity and shear modulus simultaneously with Raman spectroscopy (Kotula 2017). This allows the microstructural and chemical changes of the sample to be understood through the Raman signal while the consequences of these changes on the flow behavior are characterized with rheometry.

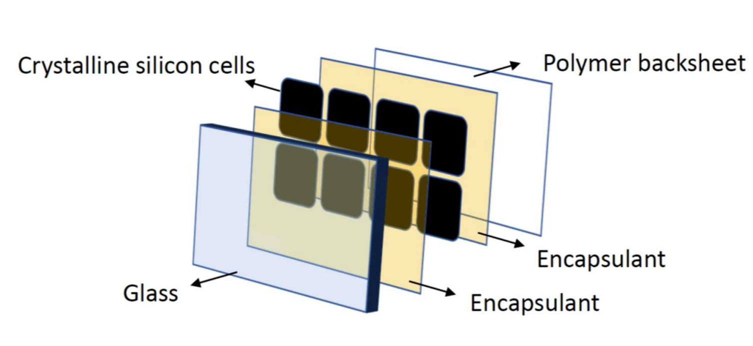
By measuring peak position and shape, Raman spectrometry is sensitive to a variety of phenomena:

Peak position	Bond chemistry
Peak shift	Temperature, stress
Peak Intensity	Concentration of bond type
Width, shoulders	Structural defects

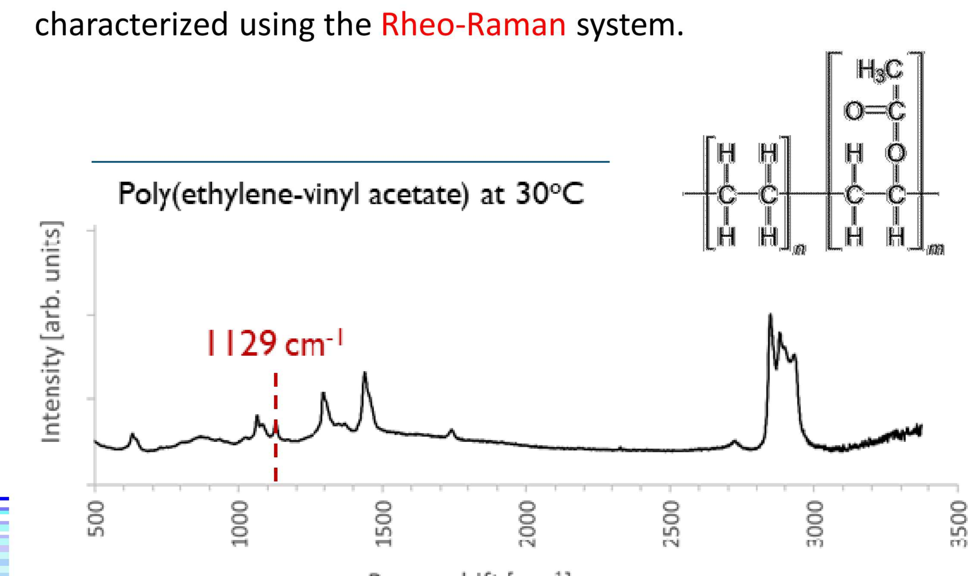
Photovoltaic Encapsulants

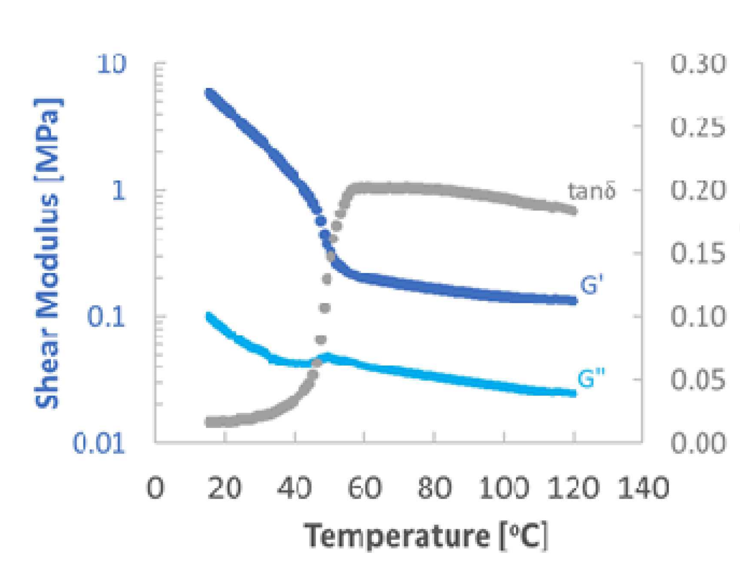
Stresses in viscoelastic encapsulants used to protect photovoltaic modules can arise due to thermal cycling and aging. A material model is being developed for poly(ethylene vinyl acetate) (EVA). This material model will then be used to populate a multi-scale finite element model for predicting module behavior (see figure on right).

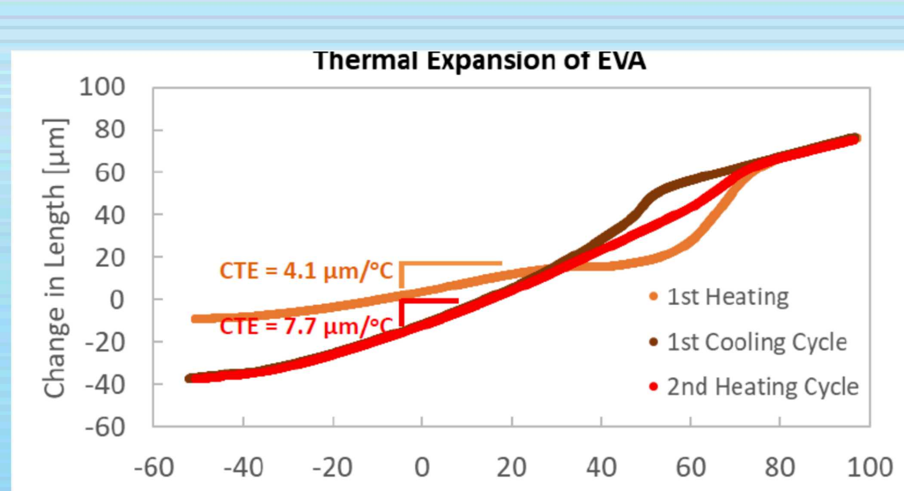
EVA copolymer is crosslinked during module fabrication. Once the module is constructed, the polymer still contains many crystalline domains that are detectable through Raman spectroscopy. The crystals melt near 40°C, which is within the operating temperature of many modules. These crystalline regions affect both the polymer modulus and the thermal expansion of the EVA copolymer. The effects of processing conditions on the crystallinity of the material are being characterized using the Rheo-Raman system.

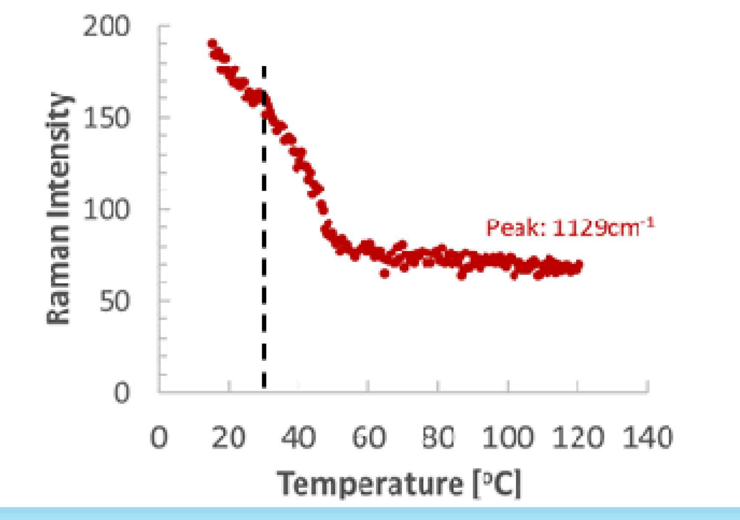


Layers in silicon PV modules



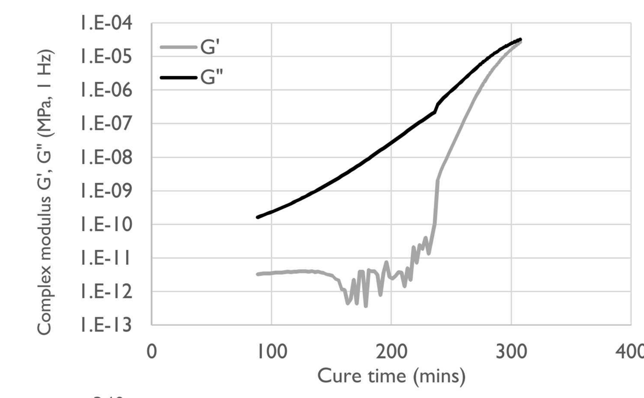






Epoxy Curing (EPON 828 Jeffamine)

Epoxies are used to encapsulate fragile electronic components. Material models describing the viscosity evolution with polymer cure aid in understanding and troubleshooting encapsulant flow during manufacturing processes. Simultaneous rheology and Raman spectroscopy supports model creation, since the extent of the curing reaction can be tracked during viscosity measurements. Here, the reaction of EPON 828 cured with Jeffamine is tracked using the epoxide ring Raman signature.



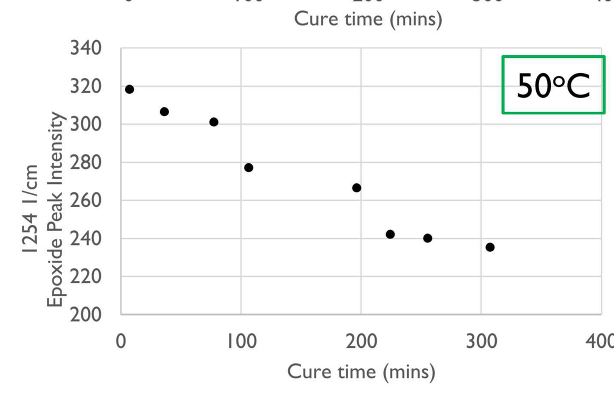
Mondy-Adolf Filled-Epoxy Model

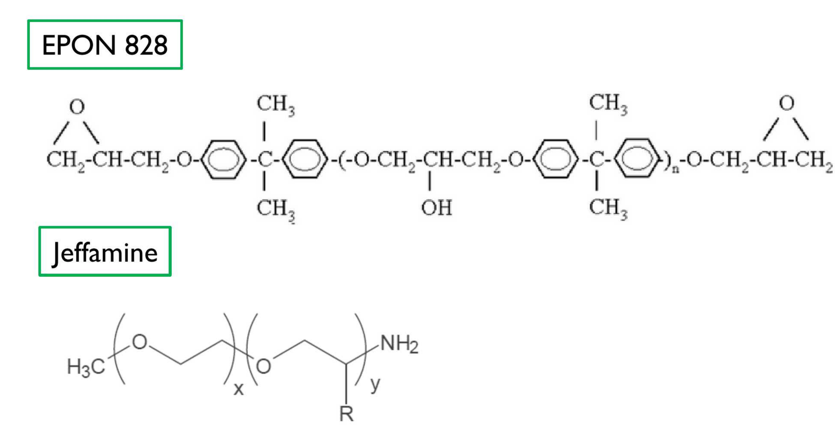
$$\frac{d\xi}{dt} = 3.3x10^6 \frac{1}{min}\left(e^{-\frac{12.5kcal/mol}{RT}}\right)(0.3+\xi)(1-\xi)^{1.5}$$

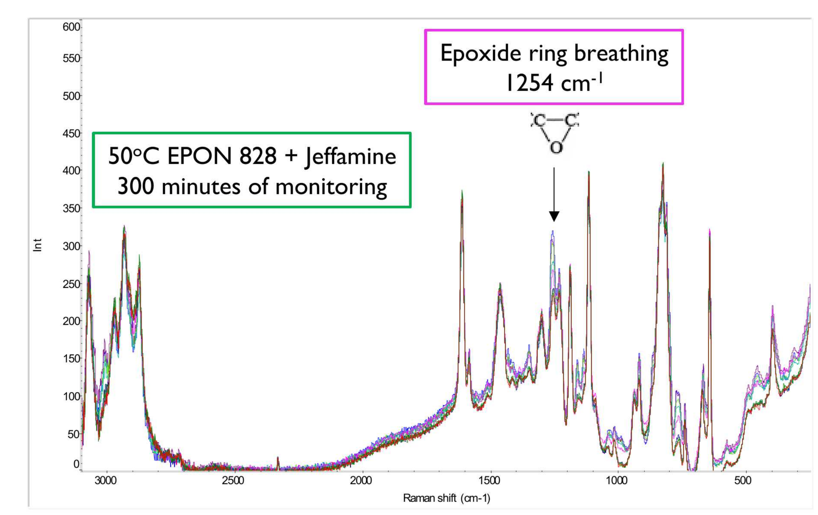
$$\mu = \mu_0(T_g)\left(1-\frac{\varphi}{\varphi_{max}}\right)^n 10^{\frac{-C_1(T-T_g)}{C_2+T-T_g}}\left(1-\left(\frac{\xi}{\xi_c}\right)^2\right)^{-1.33} \quad T_g = \frac{T_g^0}{1-A\xi^n}$$

Particles — WLF Time/T — Cure

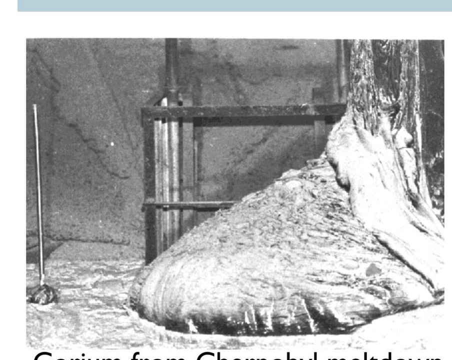
where A and ξ_c depend on T





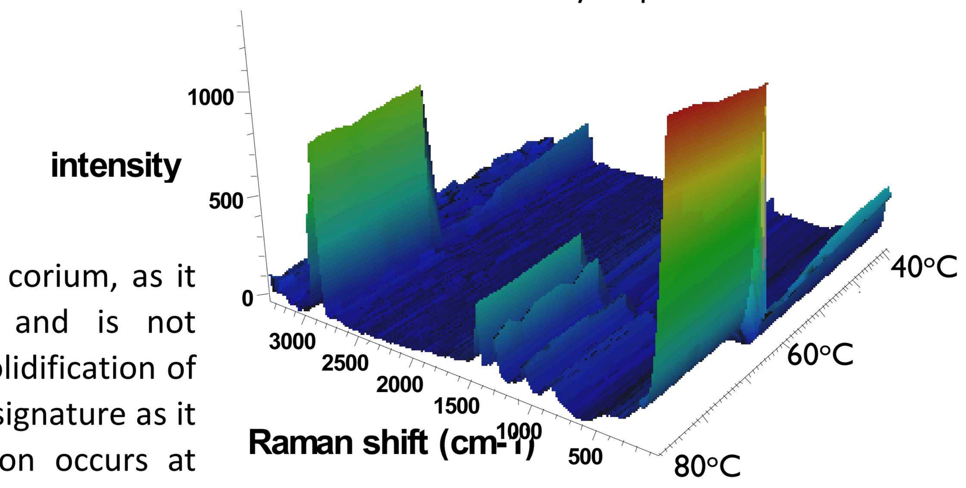


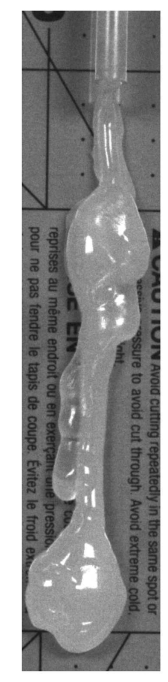
Crystallization of Paraffin Wax



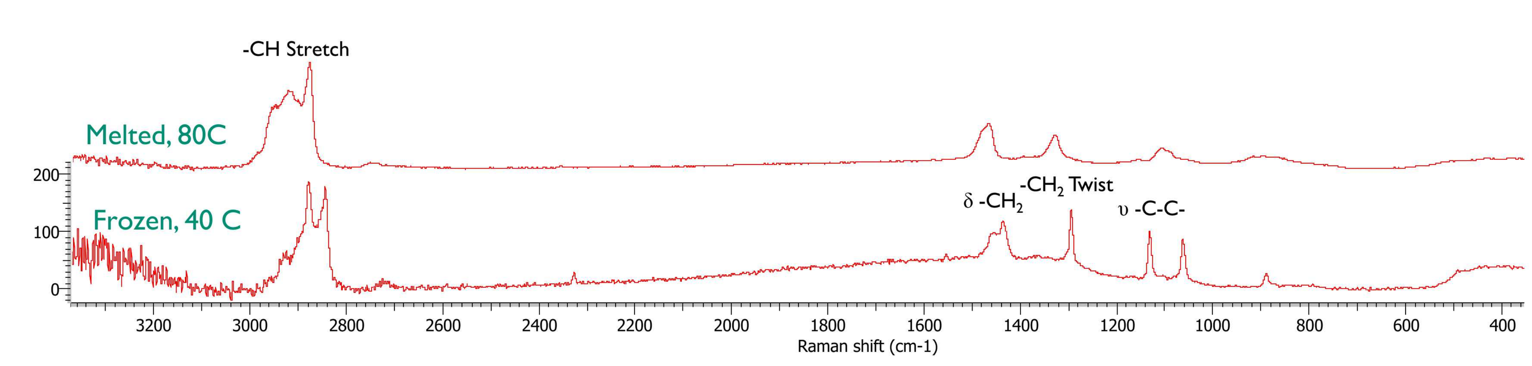
Corium from Chernobyl meltdown

Modeling solidifying systems is a challenge for numerical methods since liquids and solids coexist, interact, and transform into each other during the same simulation. Predicting the spread of corium, for example, in a nuclear reactor accident is difficult since the solid crust that forms severely impacts the flow of liquid beneath.





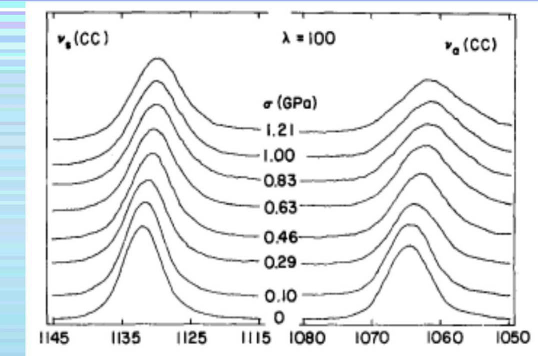
Paraffin wax is used as an analogue for corium, as it solidifies at laboratory temperatures and is not radioactive. Here (right & below), the solidification of paraffin wax is tracked using the Raman signature as it cools from 80°C to 40°C. Crystallization occurs at approximately 58°C. Models for wax viscosity versus crystallization will be implemented into Sierra Mechanics. Validation experiments include the one shown (left) of dripping wax down an incline plane.



Conclusions and Future Work

Simultaneous Raman spectroscopy and viscosity measurements streamline parameterization and increase the fidelity of material models for soft materials. Here, measurements for crystallization and curing kinetics of polymers are demonstrated.

In the future, Raman spectroscopy will be expanded to monitoring stress in materials. As polymer backbones are strained, the characteristic vibration of the bonds will shift in wavelength, giving a measure of strain. When the bulk material is unsuitable for these measurements, carbon nanotubes will be added as a tracer. These types of measurements will be useful for composites where the local stress state in a material is not always the same as the bulk.



Raman spectra measured under tensile stress for polyethylene, taken from Tashiro et al. 1988

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