

Influence of Solid Loading/Dispersion on the Material Properties of Alumina and Tungsten Oxide Filled Nanocomposites

2nd Nano Today Conference 2011

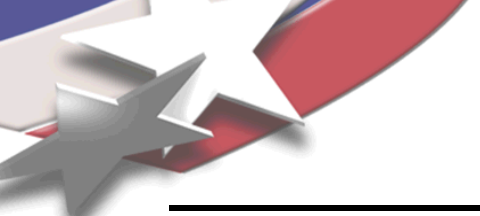
**(Tailoring of Polymeric Nanoparticles, Organic-Inorganic
Nanocomposites and Biohybrids)**

Wednesday, December 14, 2011 12:00 PM

**Roger D. Rasberry, Pin Yang, Tom Chavez, Scott
W. Spangler, Loren I. Espada, and Shawn M. Dirk**

**Sandia National Laboratories
Albuquerque, New Mexico 87185**

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



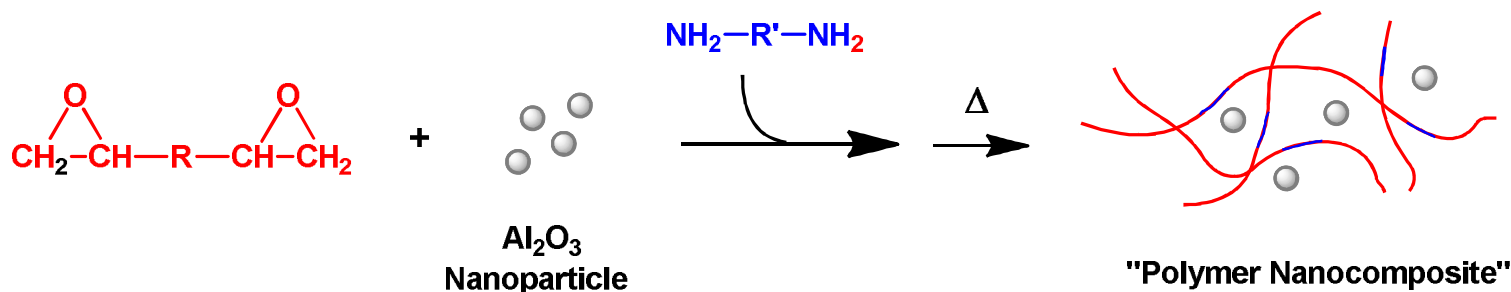
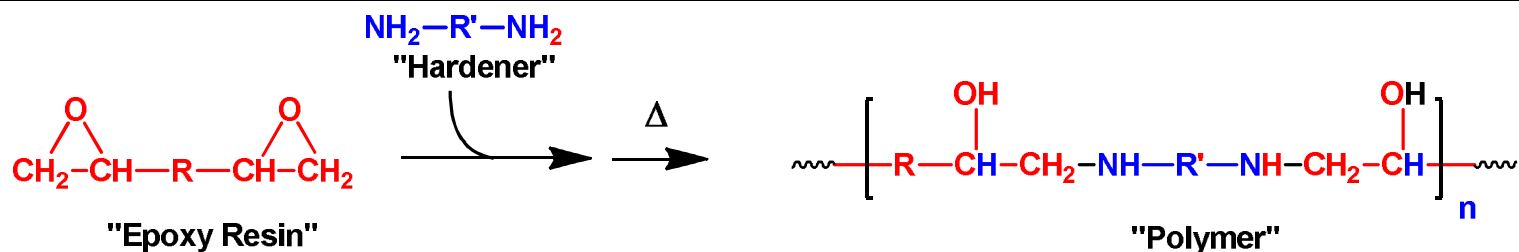
Motivation

Sandia is carrying out research on encapsulants for the prevention of high voltage breakdown

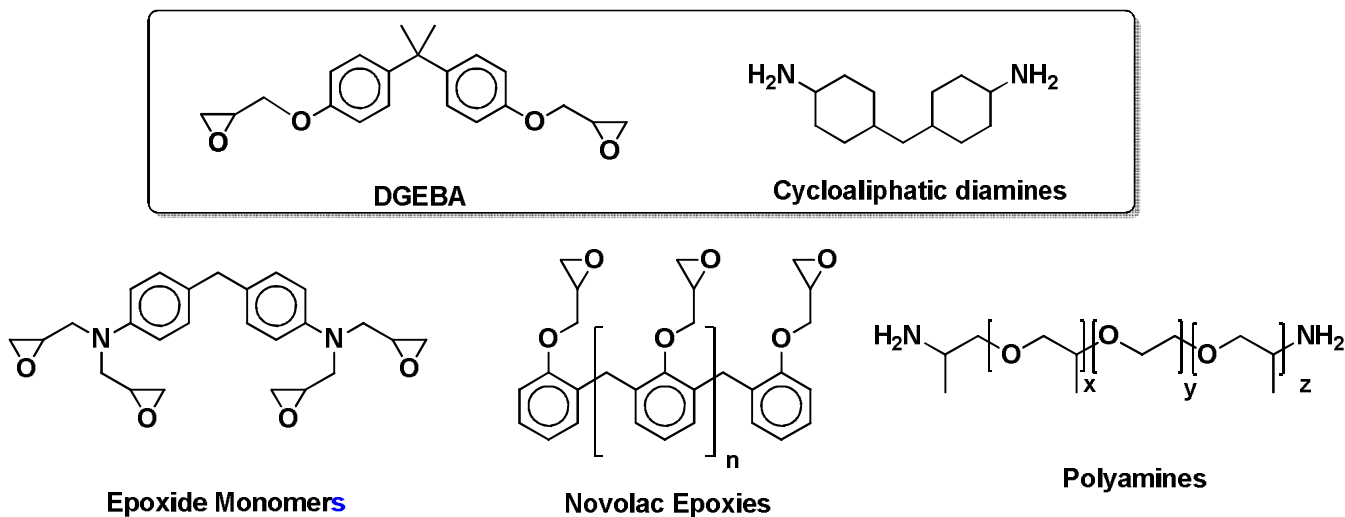
The ideal material would...

- 1) remain pourable during encapsulation**
- 2) survive thermal cycling**
- 3) operate over a wide temperature range**
- 4) sustain shock loading conditions**
- 5) withhold high voltage**

Approach: Alumina Filled Polymer Composites

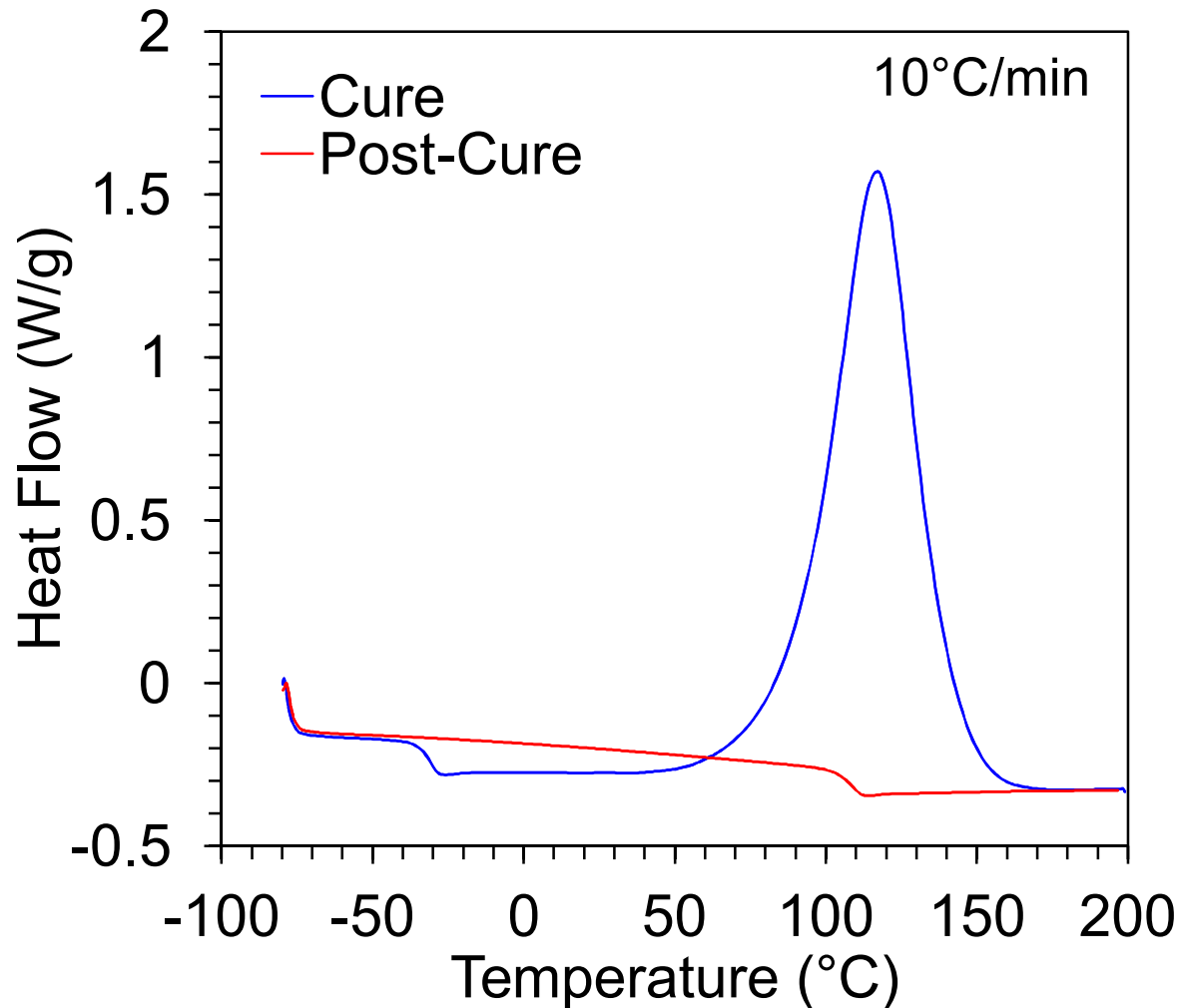


Pool of Epoxies and Hardeners



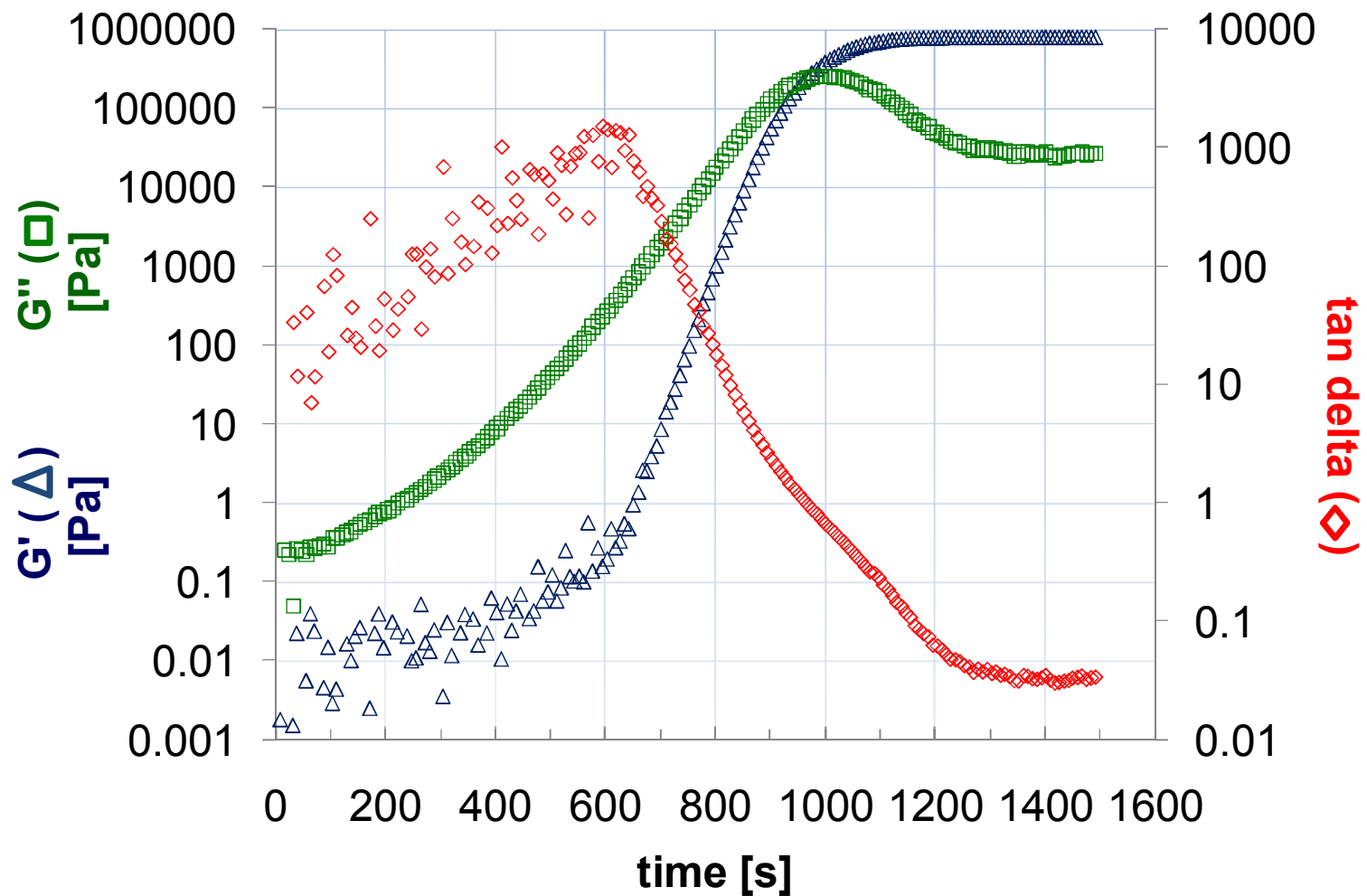
Curing Temperature

DSC Curve for Neat Polymer (1:1 Epoxy/Hardener)



Rheology Measurement

Rheology vs time for the control sample ($t = 80^\circ\text{C}$)

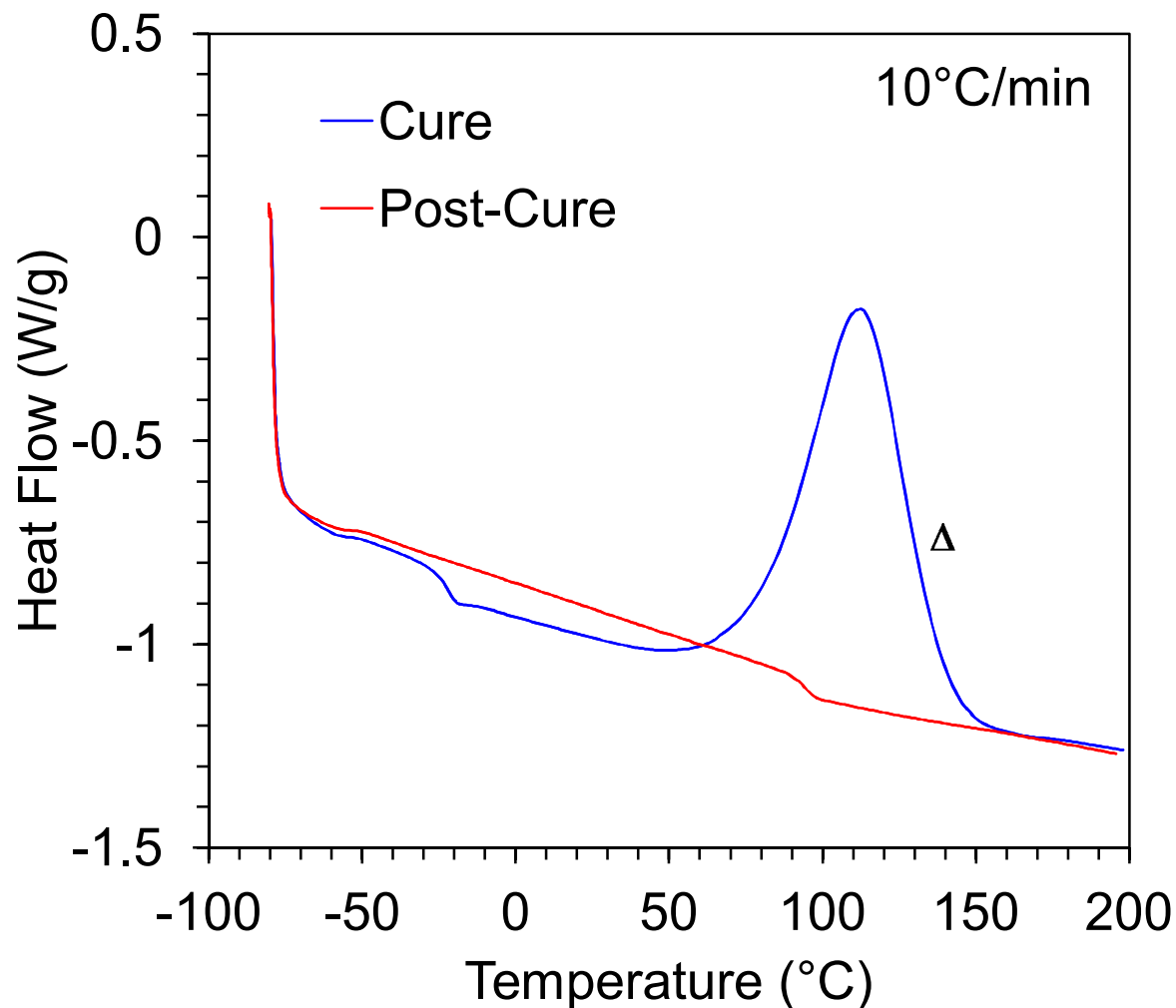
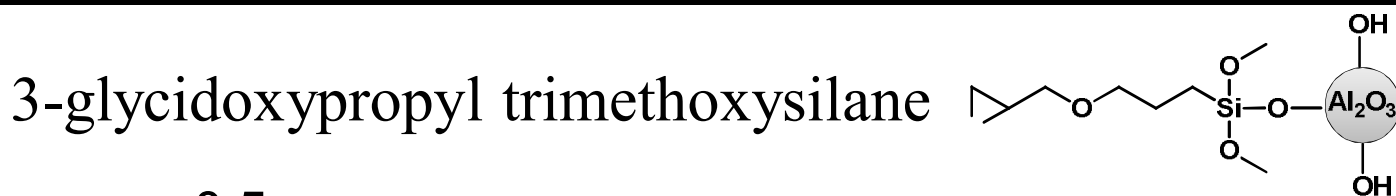


(Measured at a frequency of 1 Hz)

"Silane Coupling Agent"



DSC (10% Vol.% Functionalized Alumina)

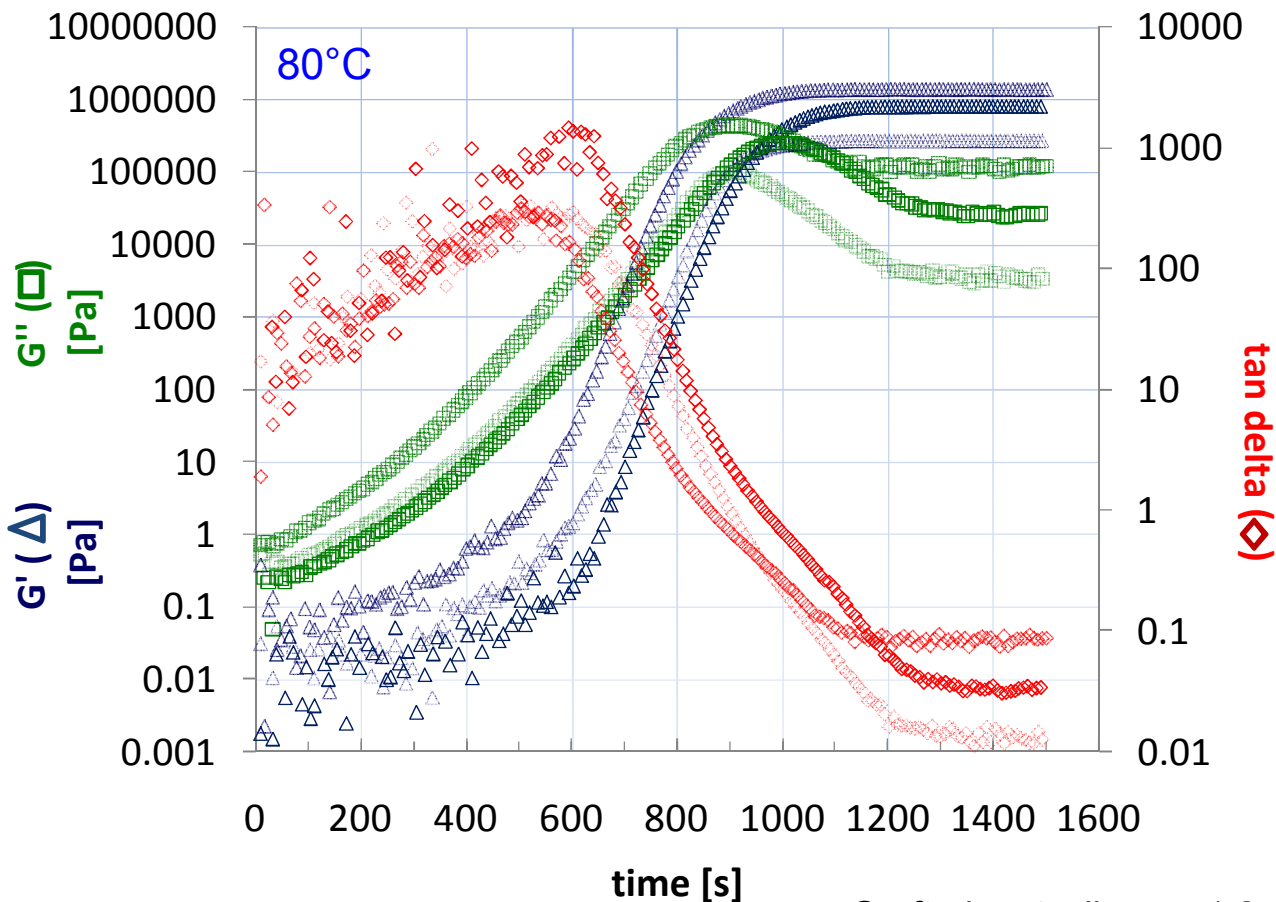
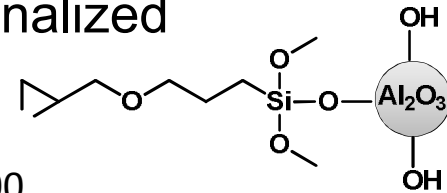


Rheology Measurements

Dark Shaded line: Control (no alumina)

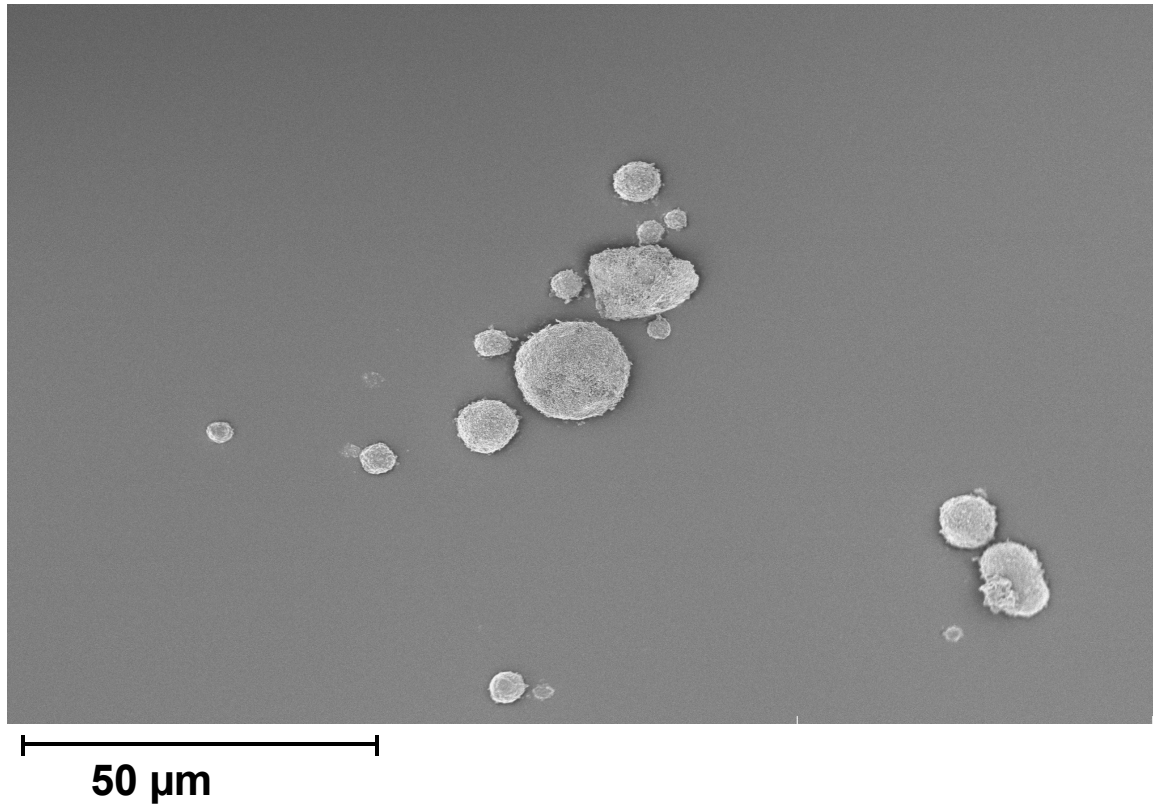
Medium Shade: 10 Vol.% alumina loading non-functionalized

Light Shade: 10 Vol.% alumina loading functionalized



Grafted amt. silane = 1.2 $\mu\text{mol/g}$

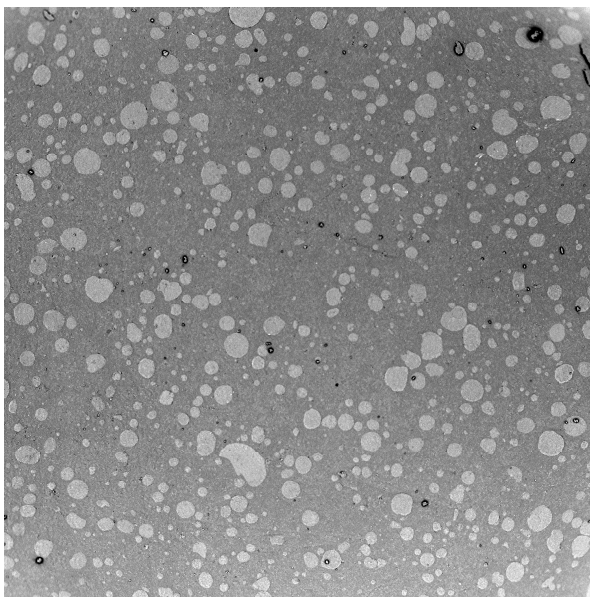
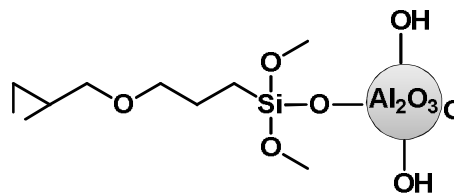
SEM Image of the As-Received Powder



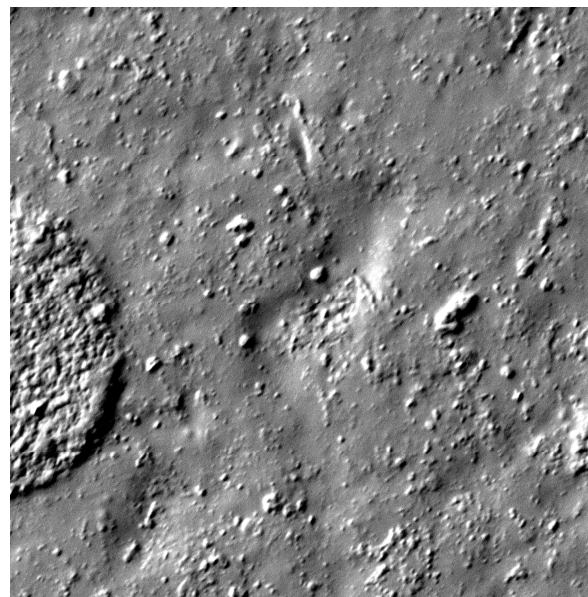
27-43 nm alumina powder

SEM Images of Functionalized Composites

10% (v/v) Nanocomposite made with alumina capped with 3-glycidoxypropyl trimethoxysilane



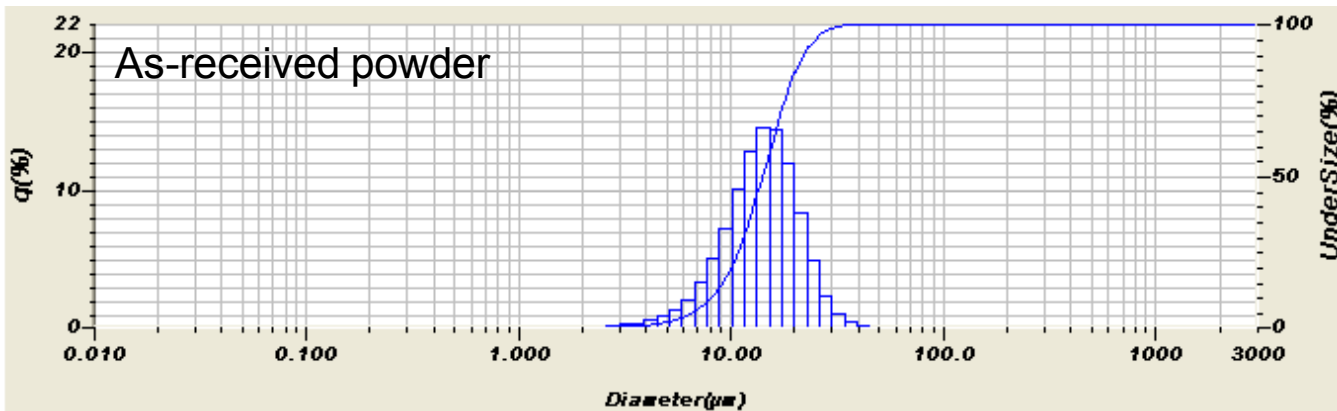
260 μm



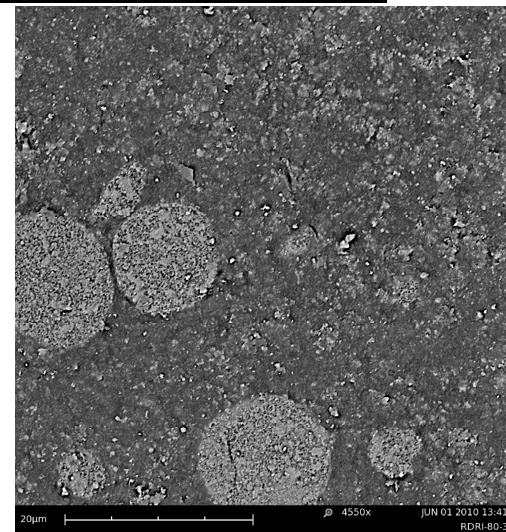
10 μm

Breaking Alumina Agglomerates

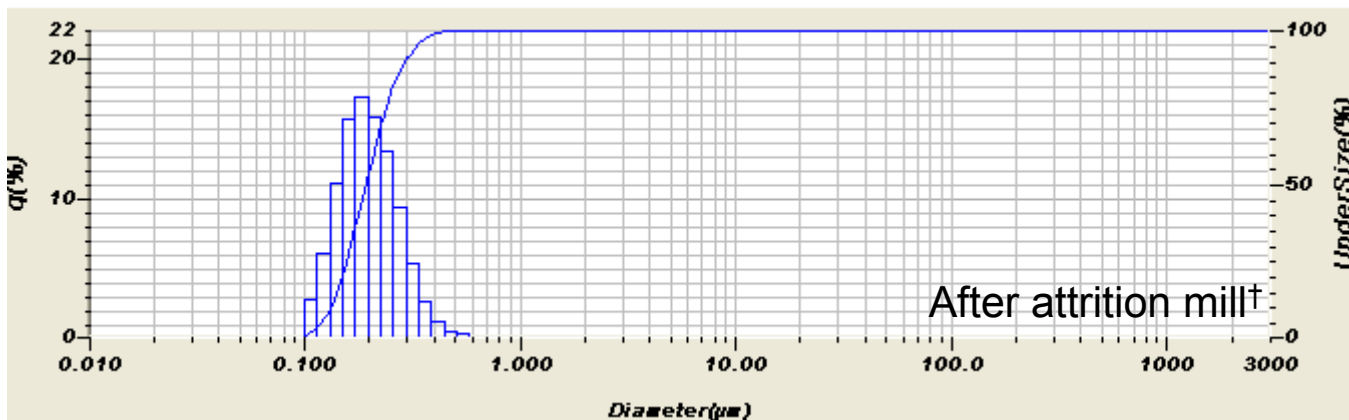
HORIBA Laser Scattering Particle Size Distribution Analyzer



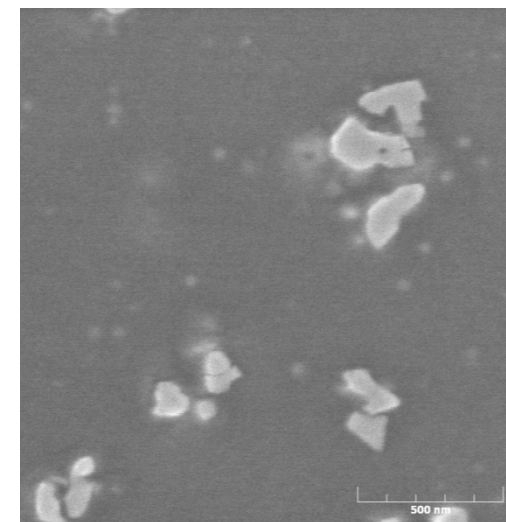
Average particle size: 14.80 μm



20 μm



Average particle size: 0.23 μm



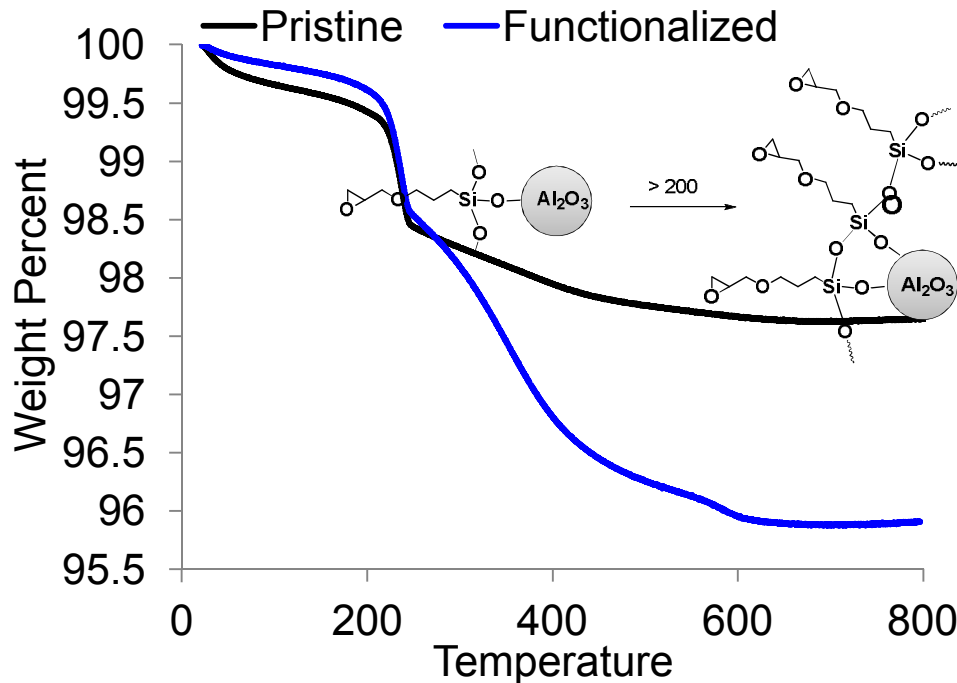
0.5 μm

†Attrition mill: 1 mm Y-ZrO₂, 150 min.



Sandia
National
Laboratories

Functionalization Characterization



α -alumina has 2.4-4.2 molecules OH/nm² for functionalization. Considering the value of 3.2 nm⁻², we achieved optimum coverage.

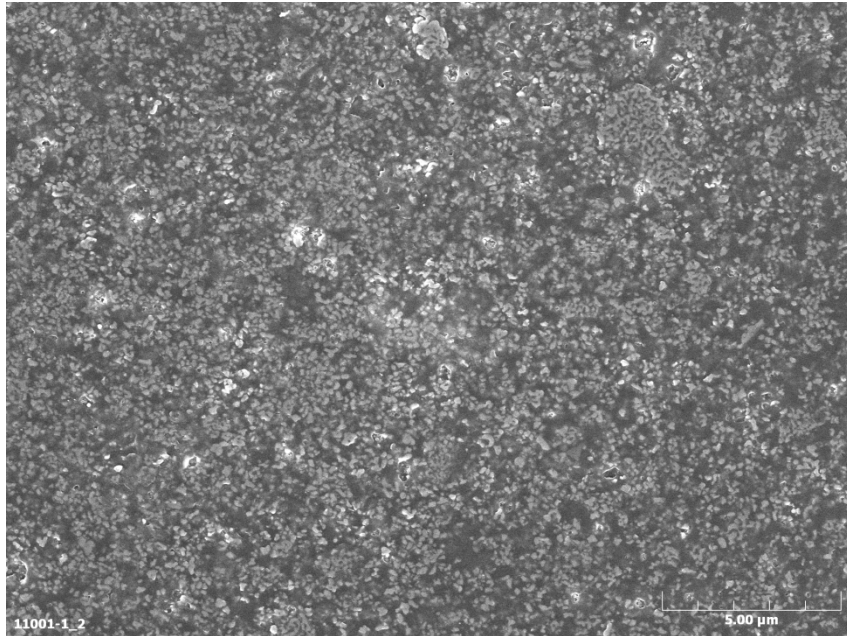
$$Q^{TGA} = \frac{\text{percent weight difference at high temp}}{\text{molecular weight organic fragment} \times \text{specific surface area } Al_2O_3}$$

$$Q^{TGA} = \frac{0.0208}{115.13 \frac{g}{mol} \times 33.9 \frac{m^2}{g} \times \frac{1 mol}{1 \times 10^6 \mu mol}} = 5.339 \frac{\mu mol}{m^2}$$

$$Q^{TGA} = 5.339 \frac{\mu mol}{m^2} \times \frac{1 m^2}{1 \times 10^{18} nm^2} \times \frac{1 mol}{1 \times 10^6 \mu mol} \times \frac{6.0223 \times 10^{23} \text{ molecules}}{1 mol} = 3.215 \text{ nm}^{-2}$$

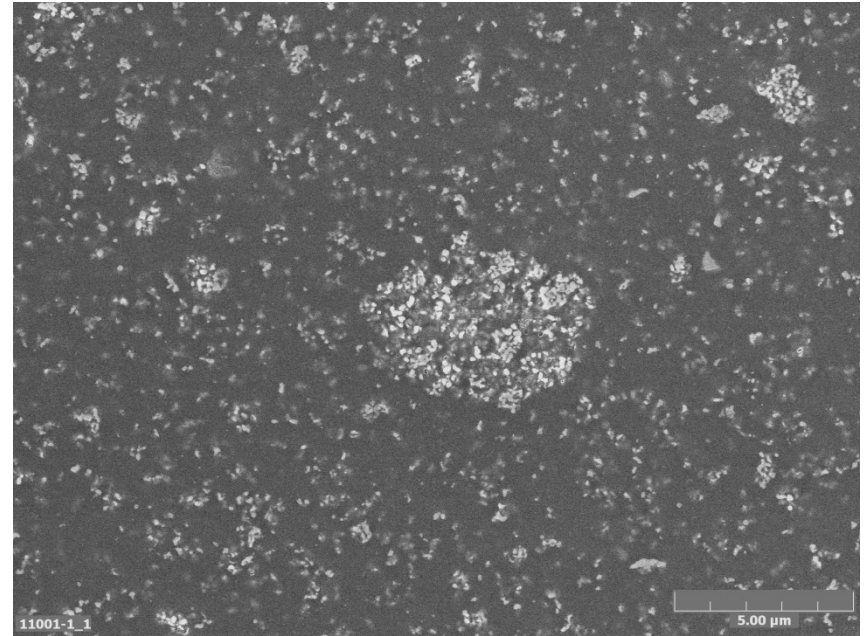
Microstructure of Nano-structured Composites (10 Vol.% alumina)

Not functionalized alumina



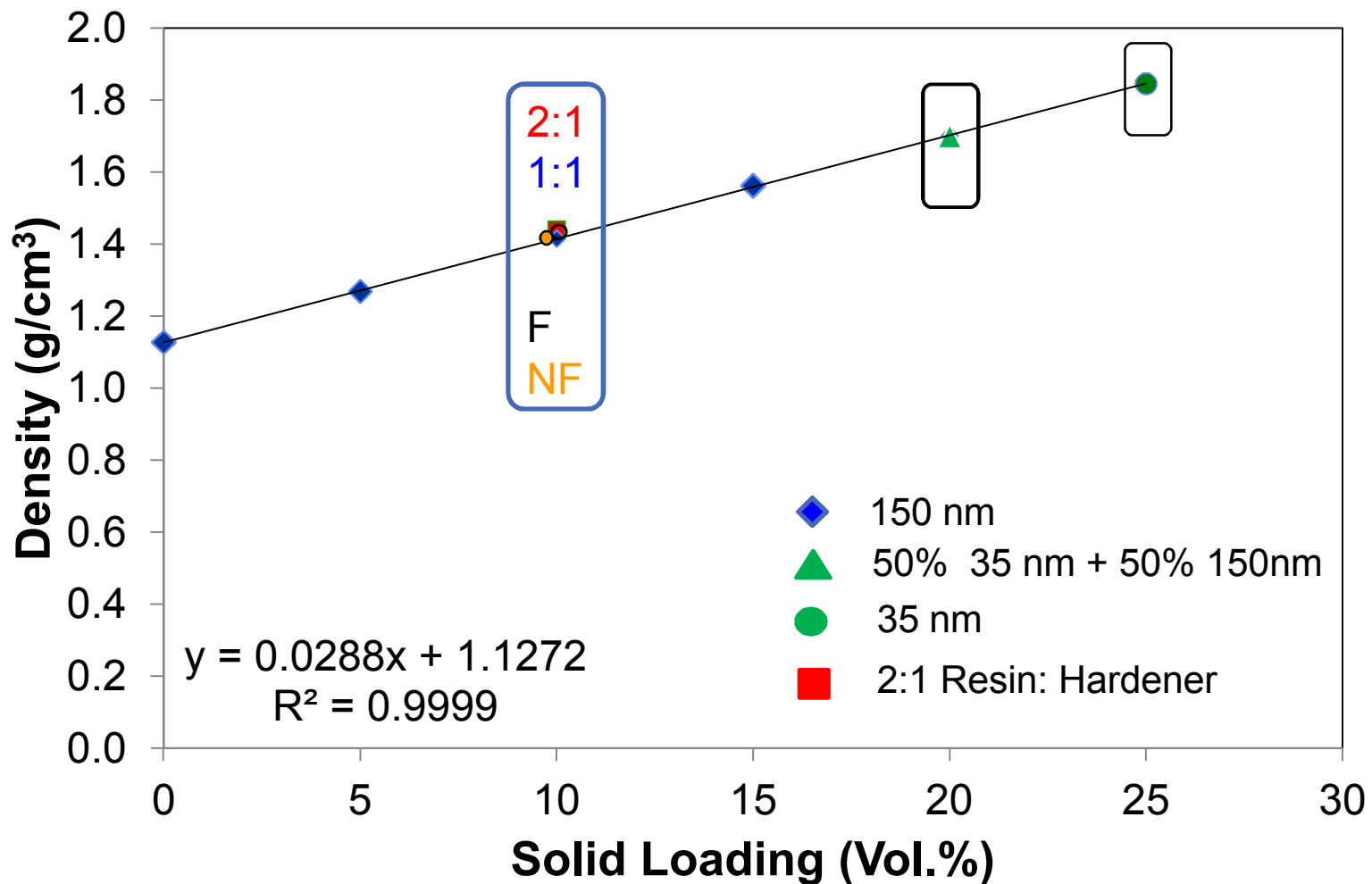
5 μm

Functionalized alumina



5 μm

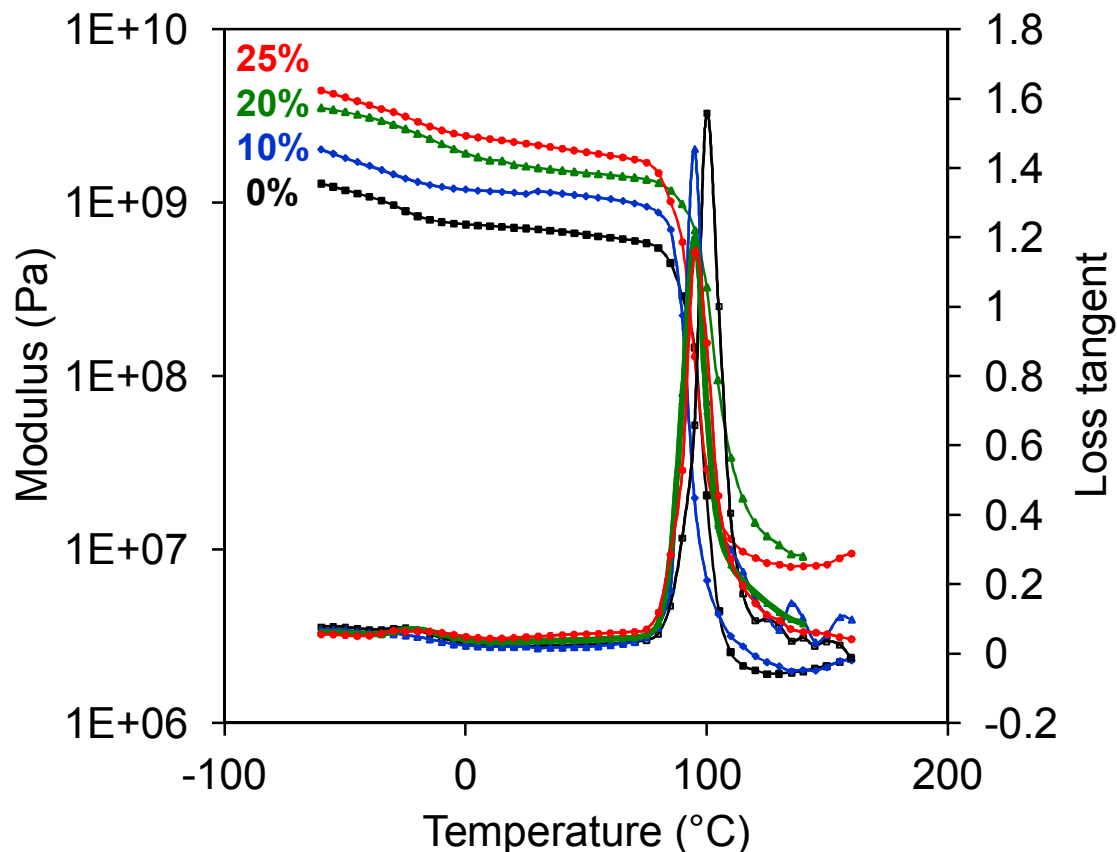
Density of the Composites



The bulk density increases linearly with the amount of solid loading.
(Determined by the Archimedes method)

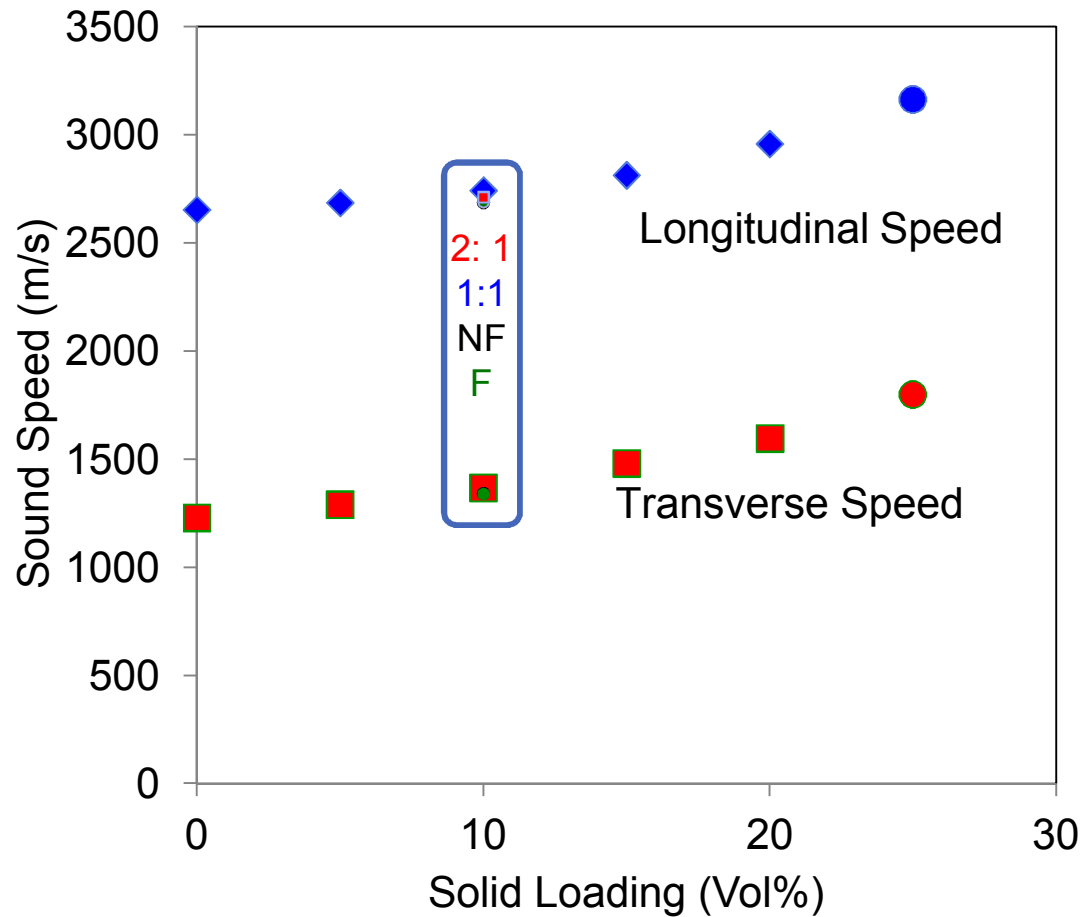
Dynamic Modulus and Tg Measurements

- The dynamic modulus of nanocomposites increases as the amount of solid loading increases.
- The glass transition temperature of our nanocomposites is between 95°C and 114°C (depending on driving frequency).



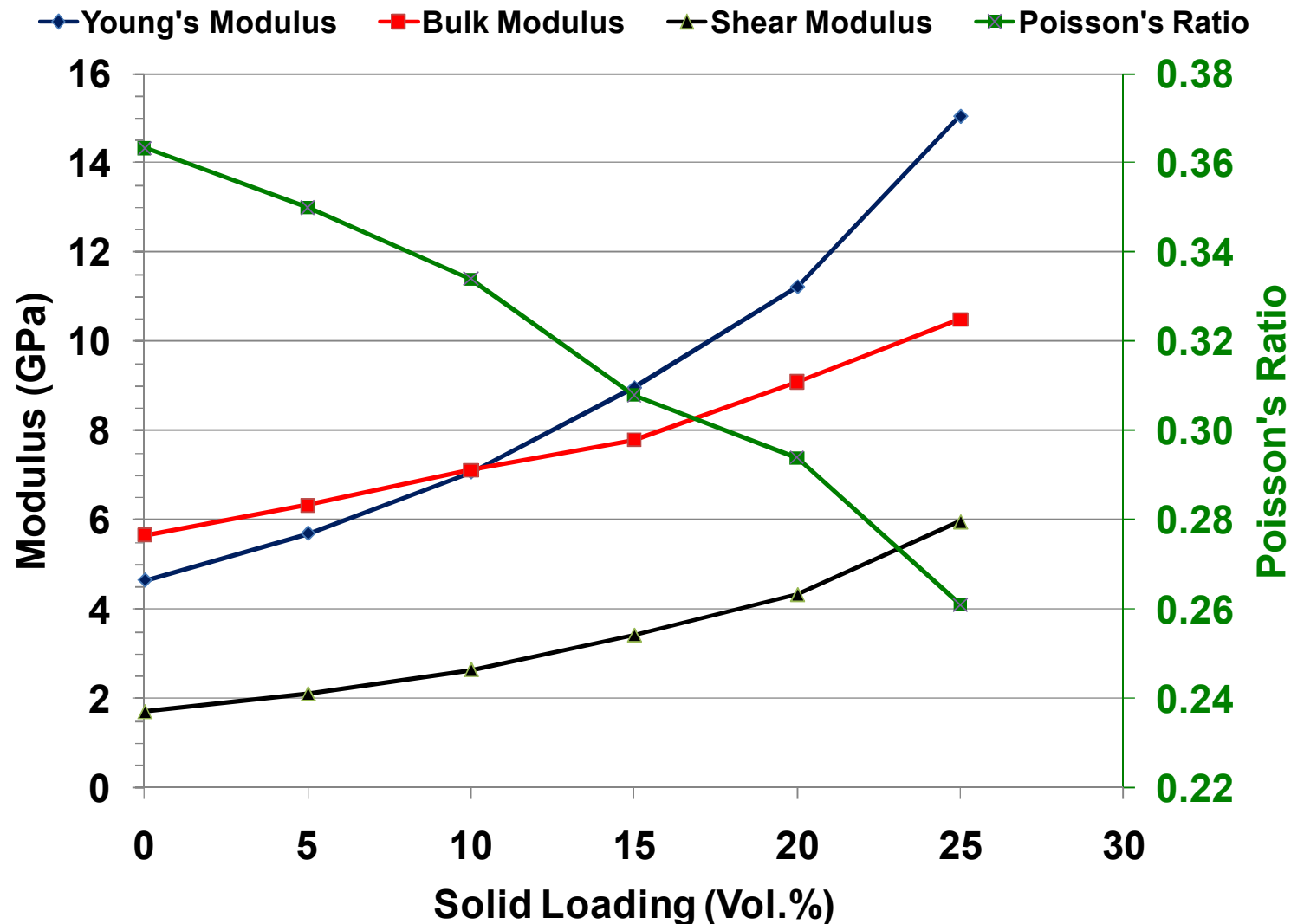


Acoustic Measurements



(Sound speed was determined pulse/echo technique at 2.25 MHz)

Elastic Modulus Measurements



(Moduli were determined by pulse/echo technique at 2.25 MHz)

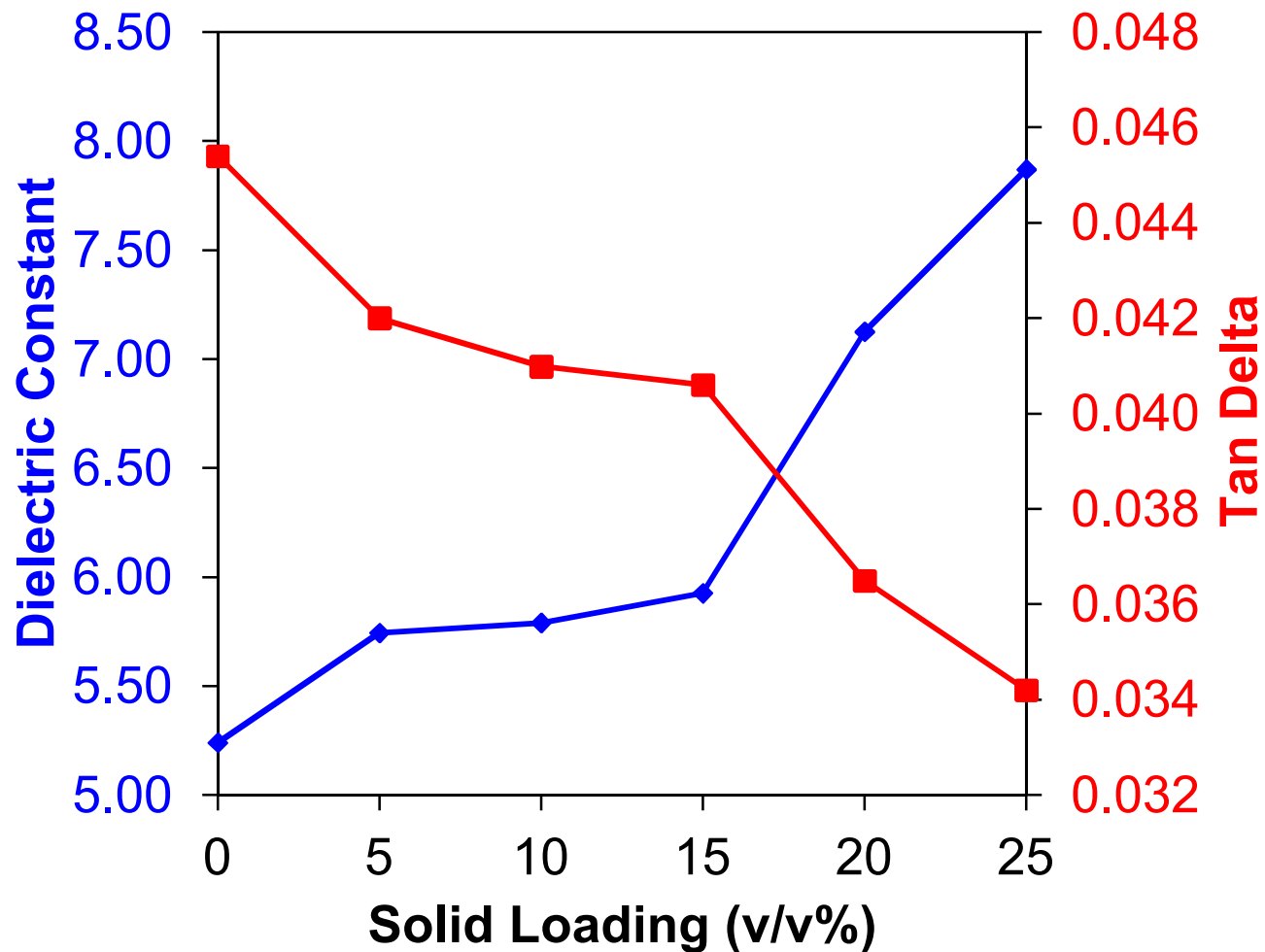
Summary – Density, Elastic, and Acoustic Measurements

Solid loading (vol.%)	Density (g/cc)	Speed (m/sec) Longit.	Speed (m/sec) Shear	Youngs Modulus (GPa)	Shear Modulus (GPa)	Bulk Modulus (GPa)	Poisson's Ratio
10	1.416	2742.44	1368.04	7.07	2.65	7.12	0.334
20	1.702	2957.07	1596.39	11.23	4.34	9.10	0.294
20	1.700	3007.61	1641.60	11.80	4.58	9.27	0.288
10°	1.440	2711.70	1358.65	7.08	2.66	7.04	0.332
10 [#]	1.410	2686.56	1342.39	6.78	2.54	6.79	0.334
10 [†]	1.404	2688.84	1339.60	6.73	2.52	6.79	0.335

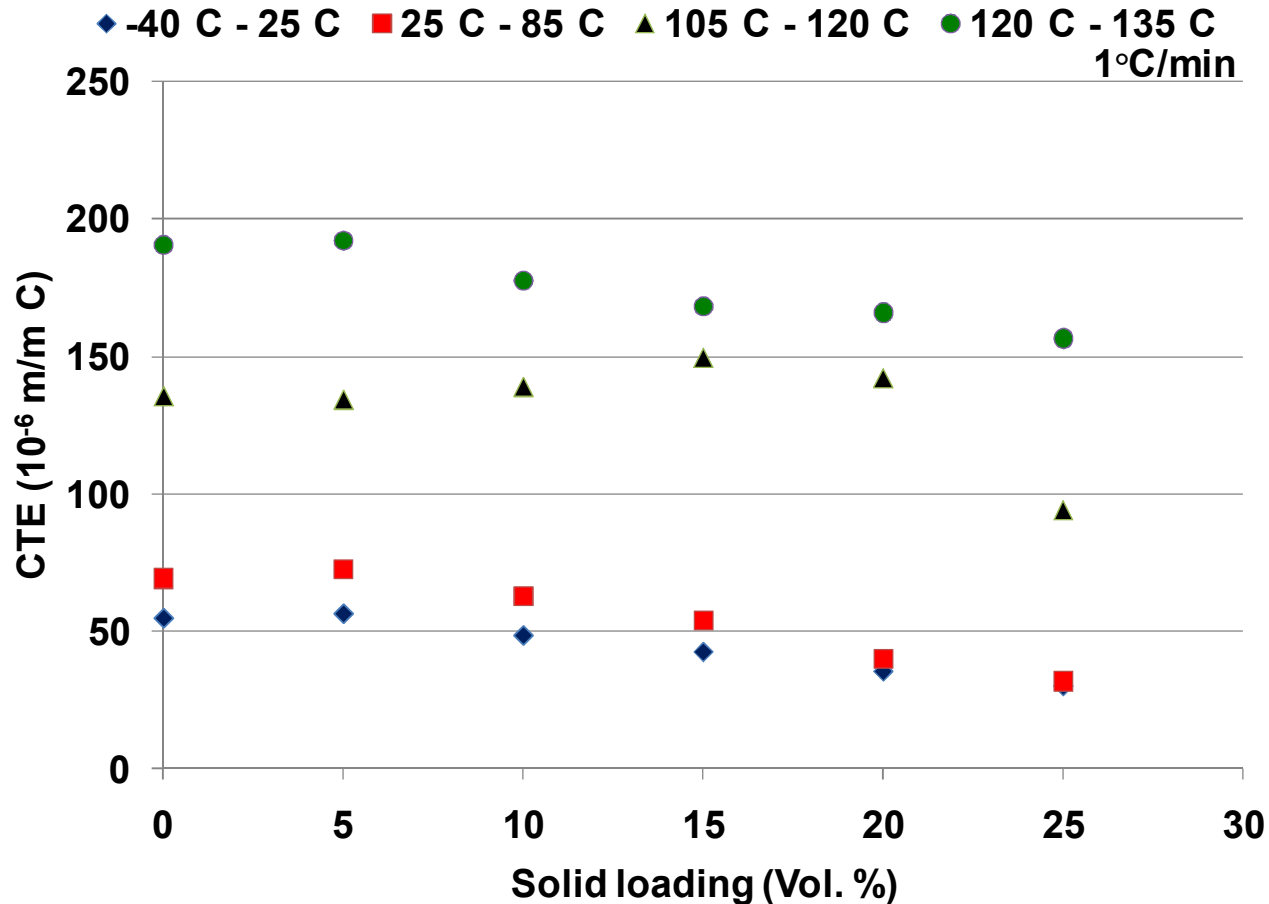
* 150 nm alumina, 20 nm + 150 nm alumina, °2:1 cross-linked, # Attrition milled, but not functionalized alumina, † attrition milled, functionalized

- The amount of solid loading appears to have the most impacts on the elastic properties of these nanocomposites, despite of
 - The size of the alumina filler (150 nm and/or 35 nm)
 - The amount of cross-linking (1:1 or 2:1)
 - Surface modification by silane coupling agent (functionalized and not-functionalized)

Dielectric Constant Measurements



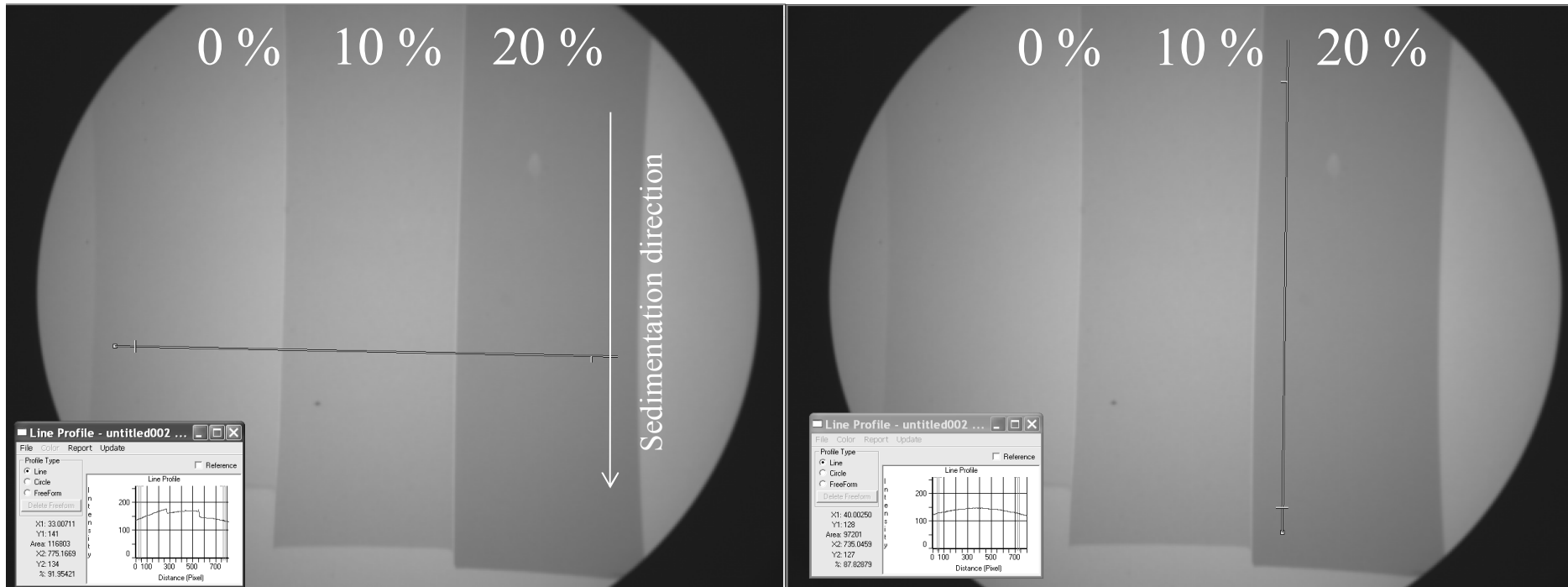
Coefficient of Thermal Expansion Measurements



- In general, the CTE value decreases as the amount of filler increases.
- The difference in CTE values between two sections below the glass transition ($T_g \sim 80\text{-}90^\circ\text{C}$) temperature decreases as the amount of solid increases.

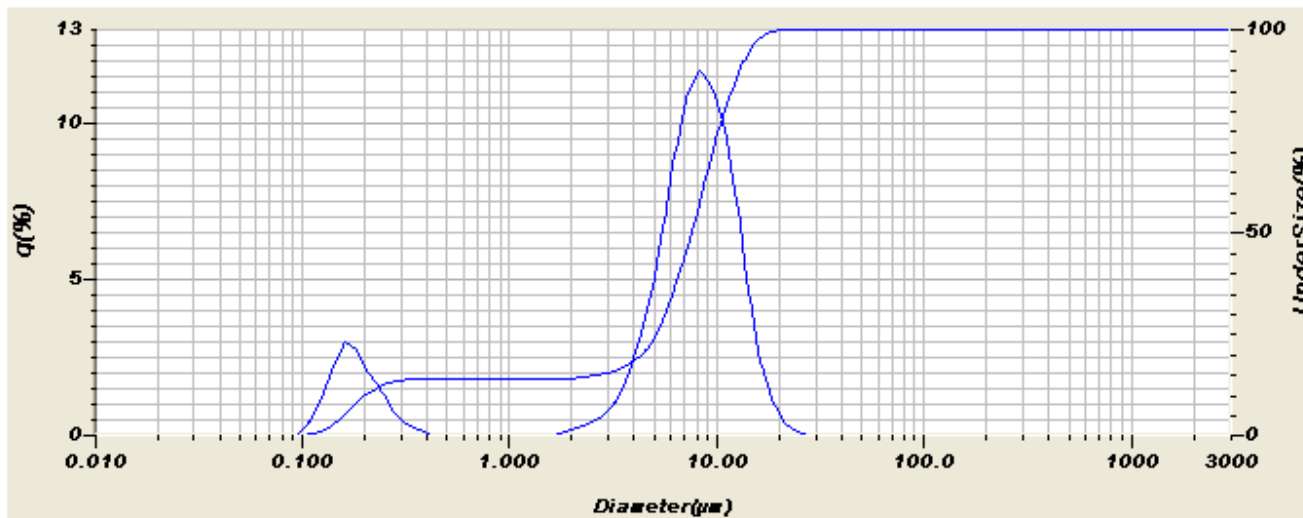
Sedimentation Measurements

X-ray Radiography Analysis

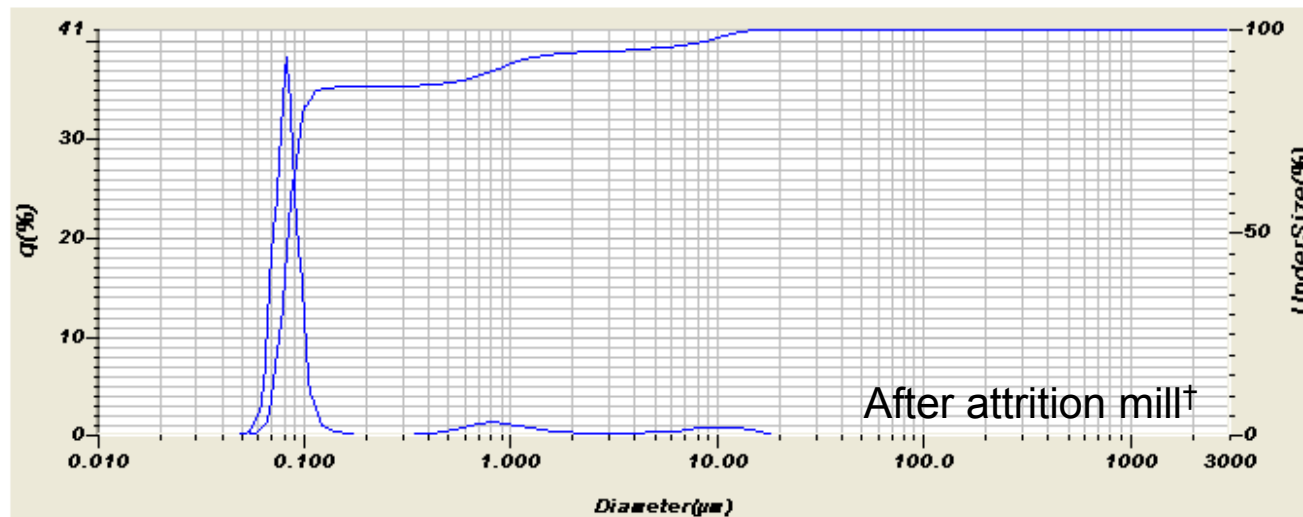
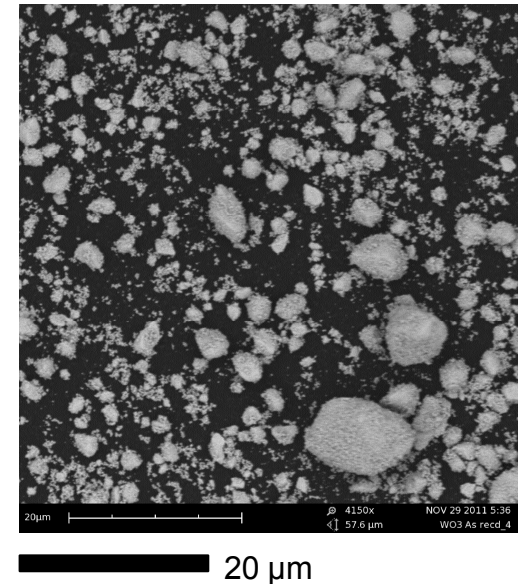


- The mixture of alumina and epoxy resin can be easily poured into a mold.
- No evidence of sedimentation was observed, i.e., alumina is homogeneously distributed in the nanocomposites.

WO₃ Powder Processing



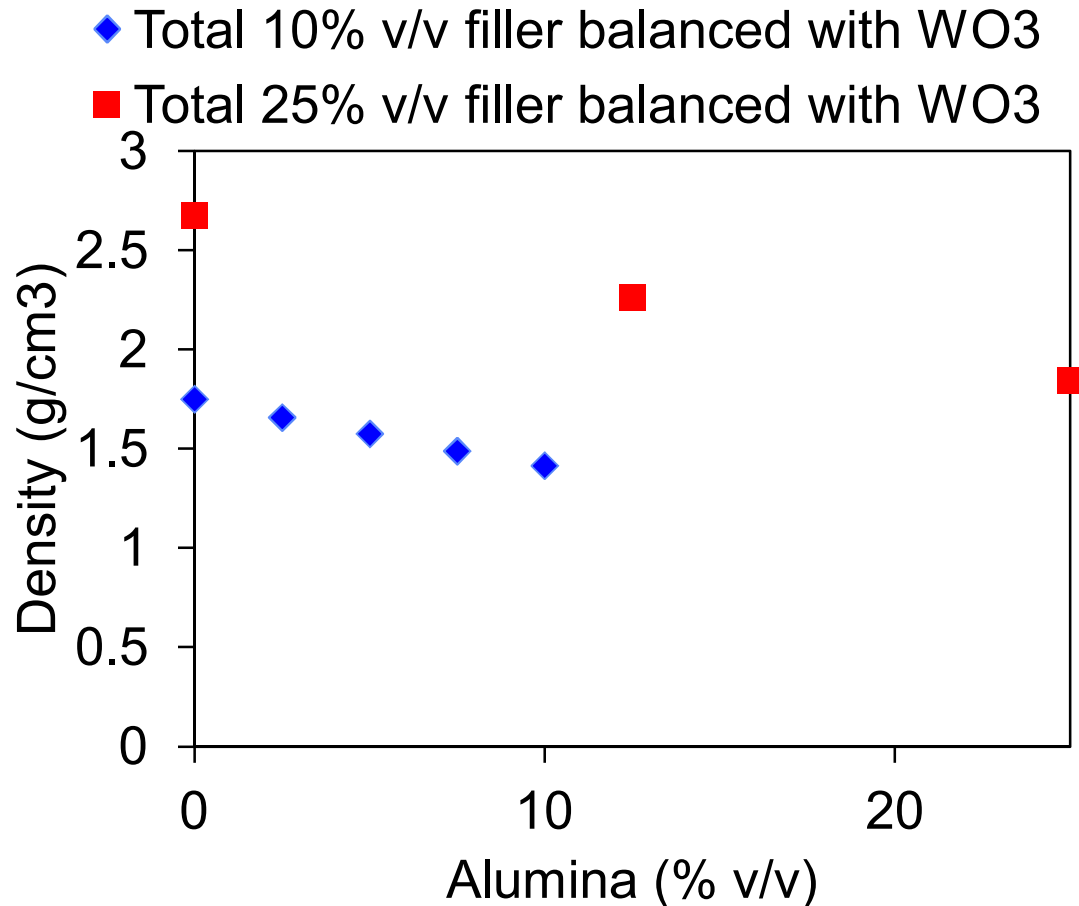
Average particle size: 8.080 μm



Average particle size: 0.083 μm

[†]Attrition mill: 1 mm Y-ZrO₂, 150 min.

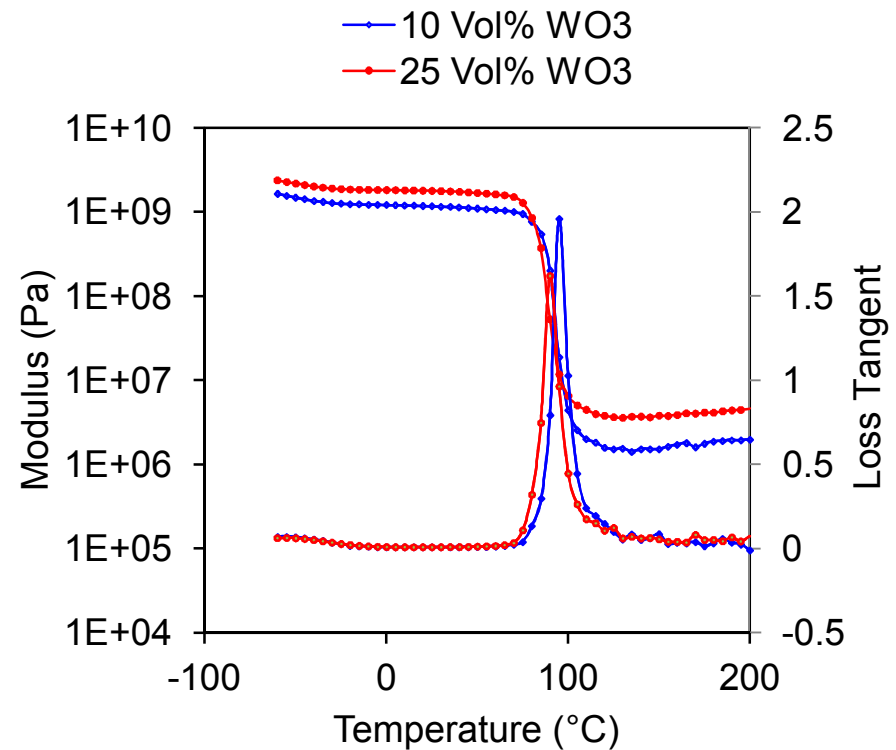
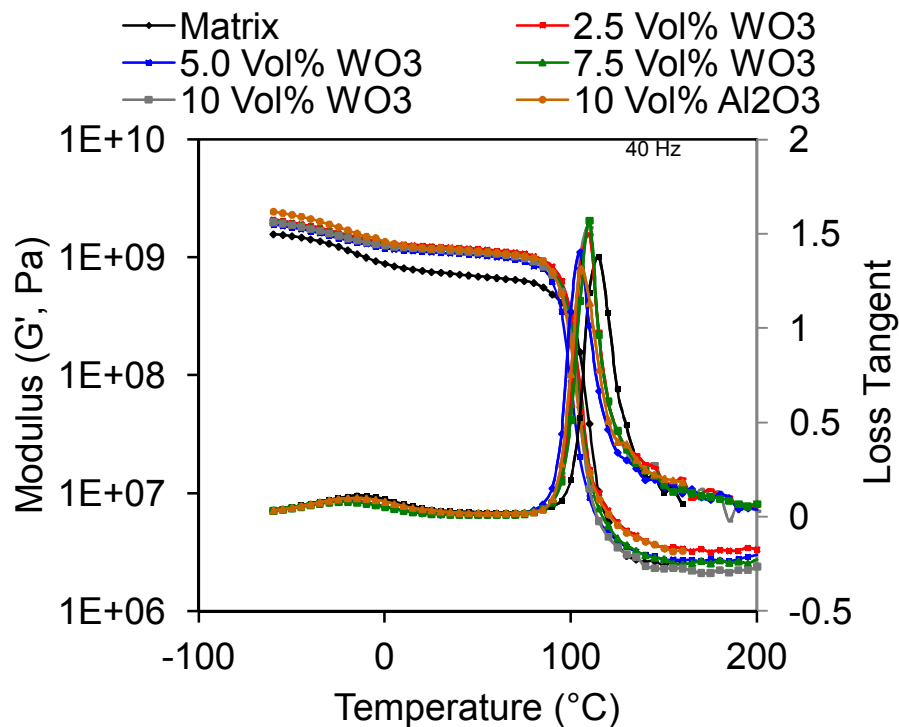
Alumina/WO₃ Composite Density



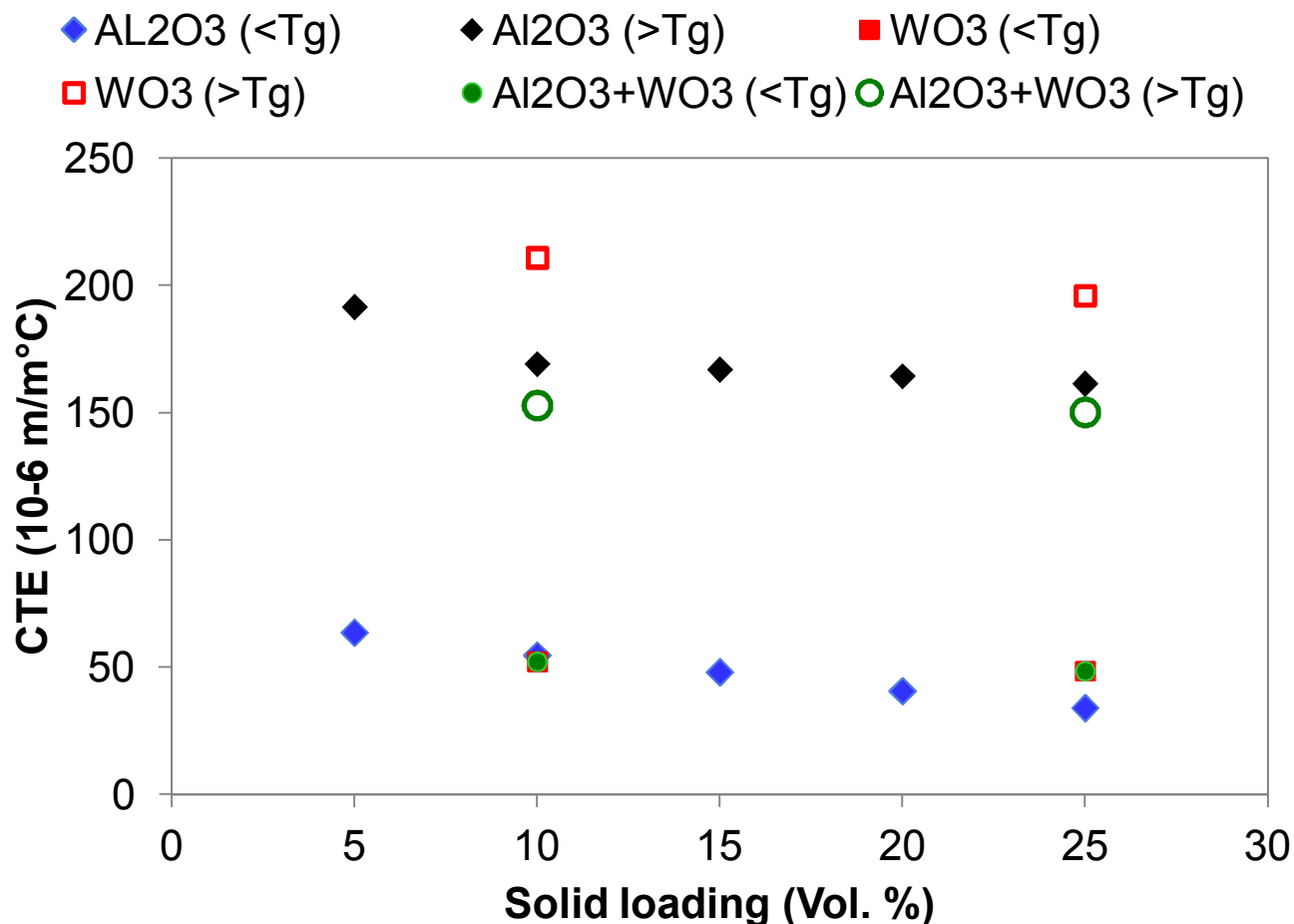
(Determined by the Archimedes method)

Alumina/WO₃ Dynamic Modulus and T_g

- The glass transition temperature of our nanocomposites is between 100°C and 120°C.
- The dynamic modulus appears to be independent of the type of filler used.

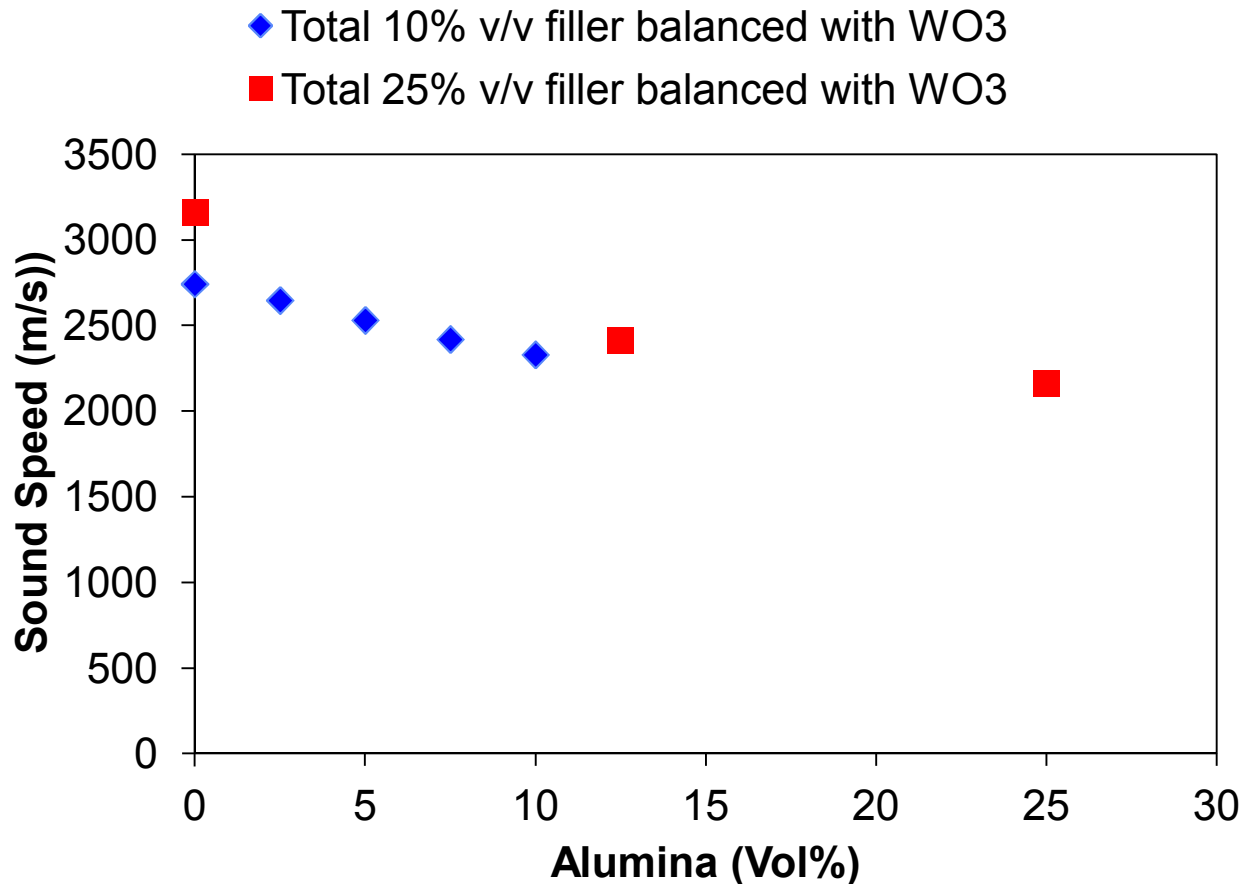


Alumina/WO₃ Coefficient of Thermal Expansion



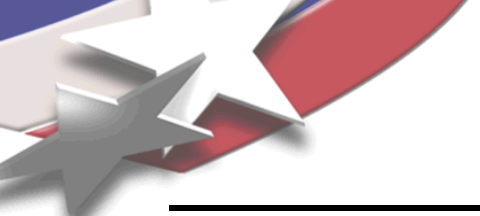
- In general, the CTE value decreases as the amount of filler increases.
- The difference in CTE values between two sections below the glass transition (T_g ~ 80-90°C) temperature decreases as the amount of solid increases.

Alumina/WO₃ Acoustic Measurements



(Sound speed was determined pulse/echo technique at 2.25 MHz)

WO₃ leads to enhanced sound speed whereas alumina lowers it.



Conclusions

- Alumina and WO_3 filler enhances the thermal, acoustic, and dielectric properties of an epoxy based polymer matrix.
- The high specific surface area of nanofiller ($>30 \text{ m}^2/\text{g}$) leads to aggregation outside of the nano-range.
- Attrition milled alumina and WO_3 powder creates more homogenous nanocomposites.
- The silane coupling agent improves the dispersion of alumina into the polymer matrix.
- Alumina increases the viscosity of the polymer matrix prior to curing but remains pourable at high loading (25%).
- The physical properties of these composites strongly depend on the solid loading.
- The elastic responses of these composites are still dominated by the compliant matrix material.