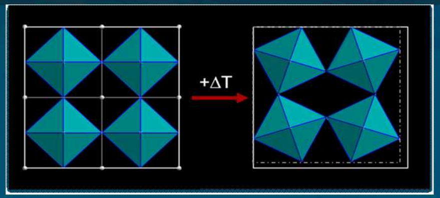
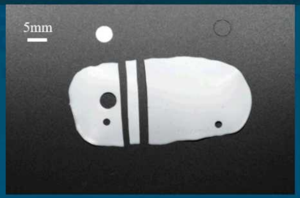
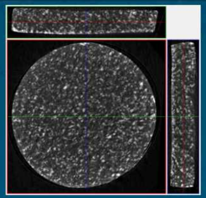
SAND2020-0006C

New Tunable Negative Thermal Expansion Ceramics in Polymer Composites





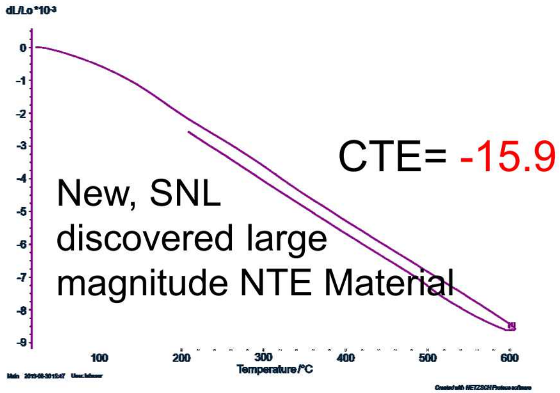


PRESENTED BY

PI: Margaret E. Gordon (SNL), Ashley Maes (SNL)

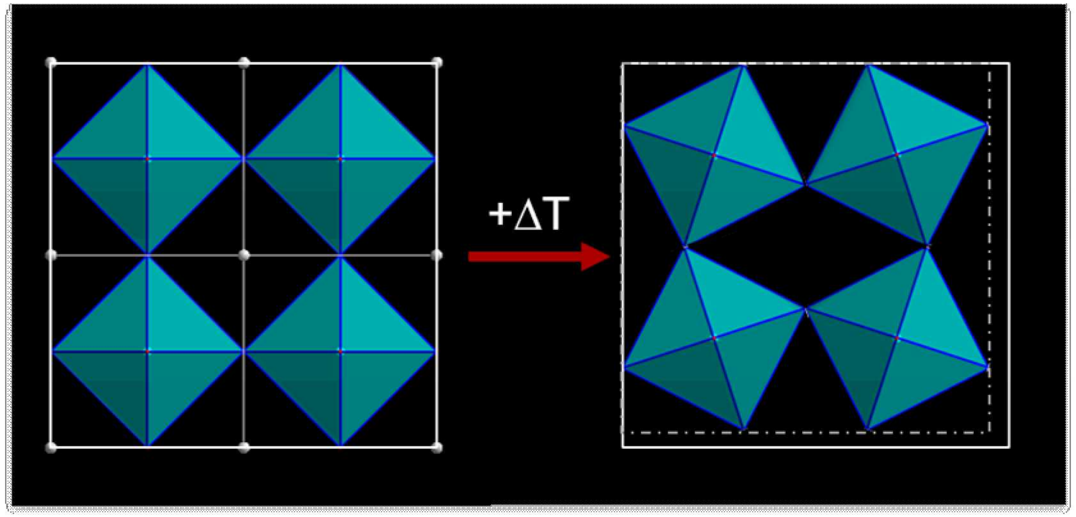
Objective

- Using newly discovered large magnitude negative thermal expansion ceramics, make a polymer ceramic composite with a tunable Coefficient of Thermal Expansion (CTE), and maintains good mechanical properties (elastic modulus).

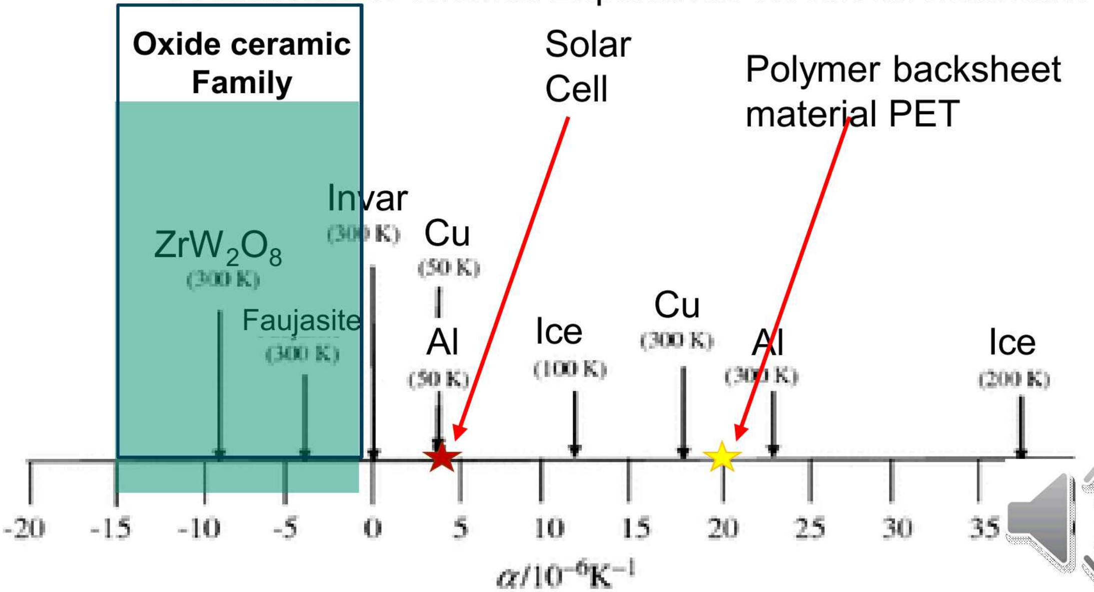


CTE= -15.9 x10^{-6} K^{-1}

NTE materials:
Thermal energy causes transverse vibrations in corner sharing polyhedra heat = shrinking!



Coefficients of Thermal Expansions for known materials.

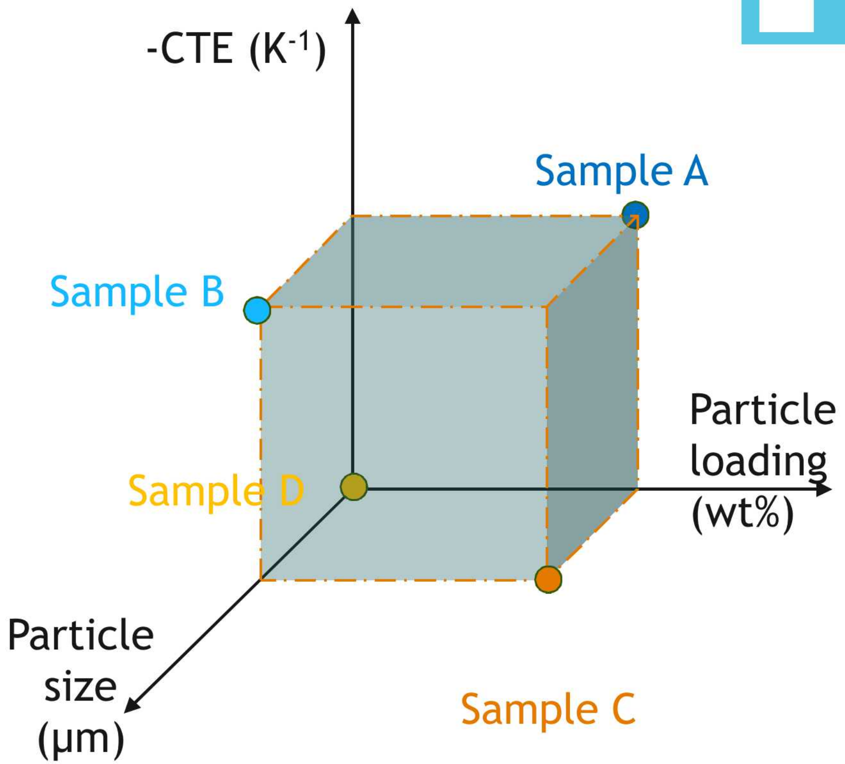


Composite sample matrix

Define a parameter space in which characteristics (mechanical, thermal) of composite are likely to be linear and will give key information on composite performance.

Parameters:

1. Particle loading
   1. Literature reports composite loading 1 - 40wt%,
   2. We focused on 5% to 25% to reduce the likelihood of mechanical failure at high loadings
2. CTE value
   1. The NTE ceramics can be synthesized with CTEs that range from -5 to -15 $x10^{-6}$ K^{-1}
3. Particle size
   1. The ceramic particle sizes range from <20 to 200 micron agglomerates
   2. We chose <35 microns and 45-70 microns. Larger agglomerates are likely to split apart, smaller particles are hard to separate by sieving.

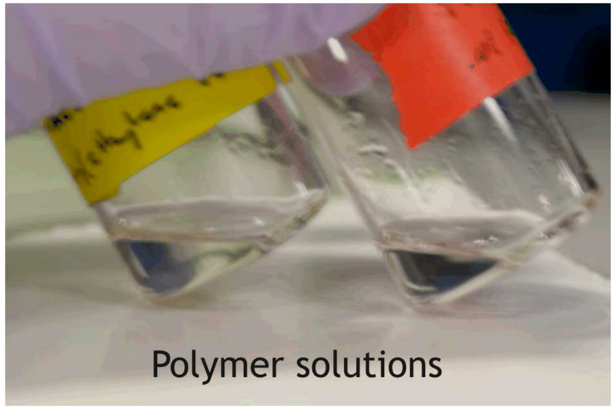


The four points depicted above were chosen.

Sample A:	25%	-15 $x10^{-6}$ K^{-1}	<35 µm
Sample B:	5%	-15 $x10^{-6}$ K^{-1}	45-70 µm
Sample C:	25%	-5 $x10^{-6}$ K^{-1}	45-70 µm
Sample D:	5%	-5 $x10^{-6}$ K^{-1}	<35 µm

Composite Processing

- Dry PET pellets dissolved in a mixture of Dichloromethane (DCM) and trifluoroacetic acid (TFA) aiming for 18 wt% PET solutions
- Sieved NTE particles added and stirred
- Solution spread on glass w/ pipette, drawn to uniform starting thickness 80 μm using a doctor blade
- Solvent allowed to evaporate slowly, final removal under vacuum and 30°C
- Cast samples were easy to handle; solvent solution was likewise easy to control and spread.


Polymer solutions

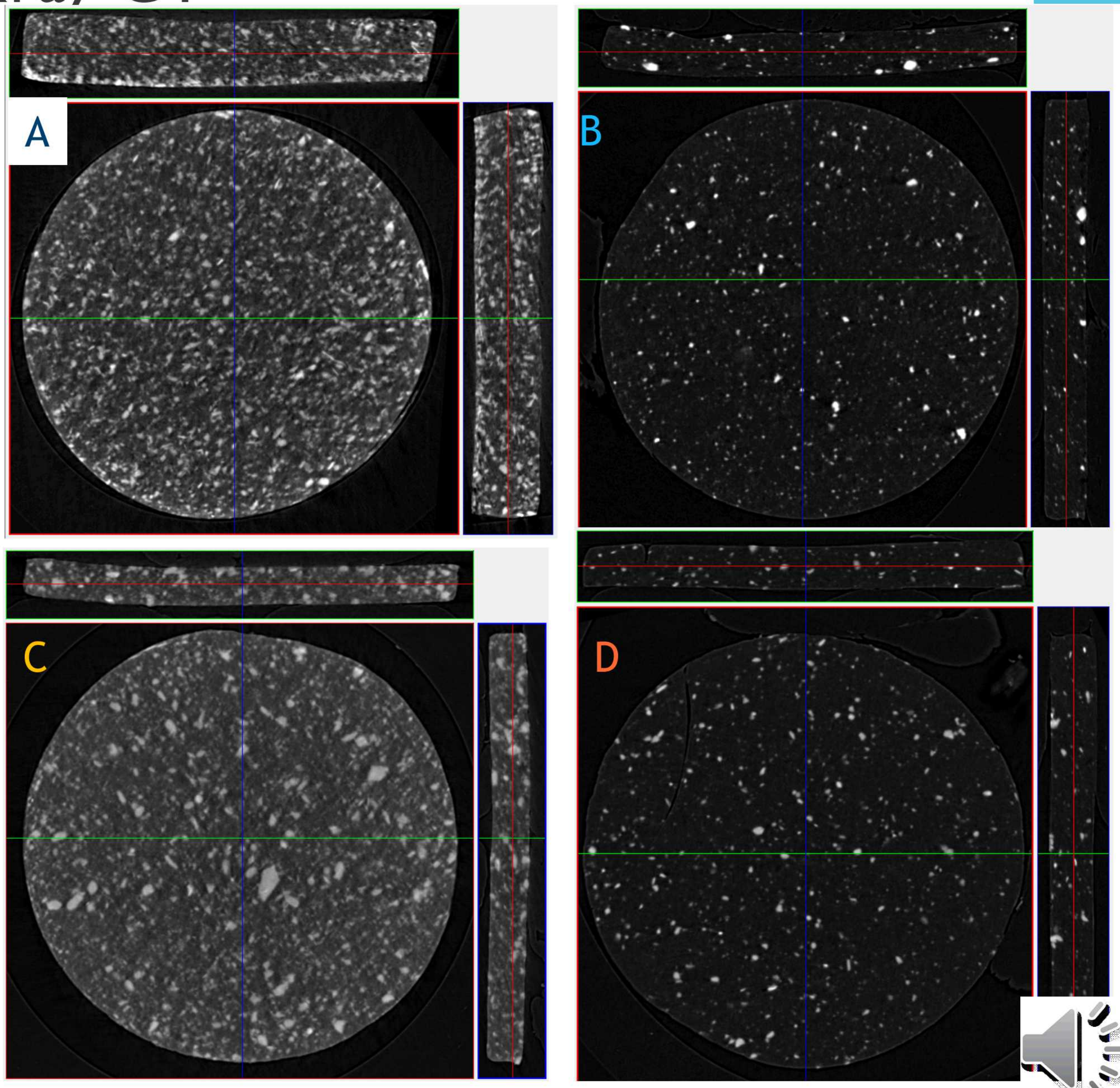

NTE particles in polymer solution


Drawn solution on glass, covered


Pure PET, Samples A, B, C, and D

Composite Characterization – Xray CT

- X-ray CT analysis shows that
  - The particles remain suspended during casting
  - Particles mix well in the polymer: there are no bubbles present around the particles and particles do not agglomerate in the composite
  - Further analysis to quantify particle distribution is underway
- Larger particles are clearly visible in sample C, but difficult to discern in sample B.
- High loading vs low loading is easily visible

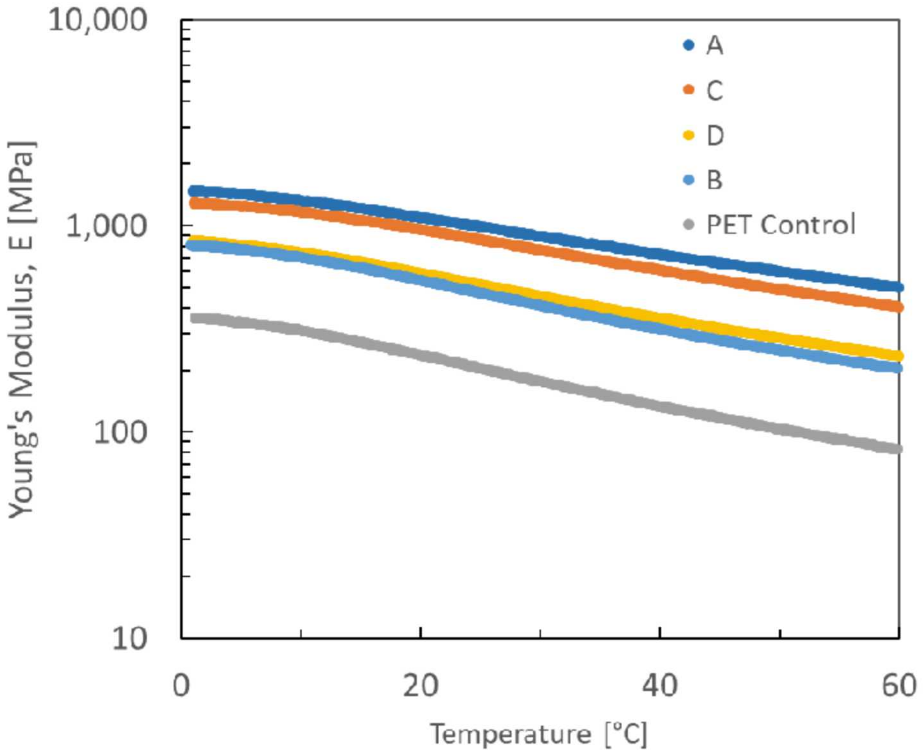


Sample A:	25%	-15×10^{-6} K^{-1}	<35 µm
Sample B:	5%	-15×10^{-6} K^{-1}	45-70 µm
Sample C:	25%	-5×10^{-6} K^{-1}	45-70 µm
Sample D:	5%	-5×10^{-6} K^{-1}	<35 µm

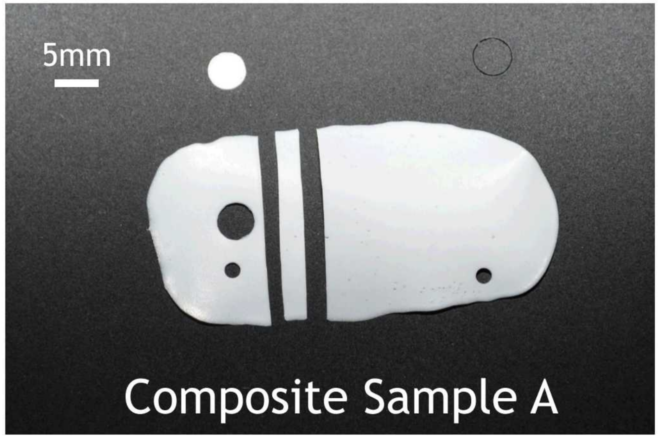
Composite Characterization

- Sample pairs A&C and B&D behaved similarly in tests to measure their elastic modulus.
    - For this characteristic, particle loading is the most influential parameter
    - Then followed by a small effect of particle size – within the loading pairings, the larger particle size samples B and C were less stiff than the smaller particles sizes.

Sample A:	25%	-15×10^{-6} K^{-1}	<35 µm
Sample B:	5%	-15×10^{-6} K^{-1}	45-70 µm
Sample C:	25%	-5×10^{-6} K^{-1}	45-70 µm
Sample D:	5%	-5×10^{-6} K^{-1}	<35 µm



- CTE's were measured using a dynamic mechanical analyzer in tension. Temperature range was set to exclude the glass transition temperature of the pure PET polymer control
- Samples A&C showed the largest difference in CTE compared to the pure PET control
    - Again, particle loading is the most influential parameter.
    - Lower loading was not compensated much by a larger CTE (consider sample B vs sample D)



Composite Sample A

Sample	Measured Linear CTE	Predicted Linear CTE
	$[10^{-6}$ m/m °C]	
A	95.0	88.1
B	111.2	115.7
C	96.9	90.6
D	114.1	116.2
Control	122.5	-

Summary

- A new polymer– ceramic (PET - ZrWPO) composite family was synthesized and characterized
- The composite CTE can be tuned depending on primarily particle loading and secondarily on particle CTE
- Elastic modulus can be tuned depending on primarily particle loading and secondarily on particle size. Elastic modulus remained in an acceptable range for photovoltaic backsheet materials
- Within this study a decrease in CTE of **27.5 x 10^{-6} K^{-1} or 22%** was achieved
- Successful completion of this proof of concept project
  - Provides data on these composites for use in future proposals.
  - Moved this idea from conception (TRL1) to a tested material prototype (TRL 3/4)
- Further optimizations are possible
  - for greater reductions to CTE
  - Use in other polymers and epoxies
  - In processing to different forms – thin films, thermoplastics, curing systems

Thank you!

Margaret Gordon, megord@sandia.gov