Effect of Graphene Addition on Shape Memory Behavior of Epoxy Resins

Tiffany Williams[1], Michael Meador[1], Sandi Miller[1], Daniel Scheiman[2]

[1]NASA Glenn Research Center
Structures and Materials Division-Polymers Branch
Cleveland, OH

[2]ASRC Aerospace
Cleveland, OH

Motivation and objective

- **Motivation and objectives:**
  - Determine feasibility of using polymer matrix composites for morphing aircraft structures
  - Evaluate the use of high T_g epoxies and determine the effects of graphene nanofiller on shape memory behavior

- **Why polymer nanocomposites?**
  - Lower shape recovery with some reinforcement
  - Possibility of debonding during repetitious cycling in fiber reinforced composites

Adaptive polymers for morphing aircraft structures

- **Structures of interest**
  - Wings
  - Aircraft engine fan blades
  - Shrouded (ducted) fan blades (VTOLs)
  - Rotor blades
  - Aircraft skins
  - Chevrons
- **Benefits**
  - Reduced drag
  - Noise reduction
  - Reduced fuel consumption
  - Better engine efficiency
  - Increased aerodynamic efficiency

- **Morphing Type**
  - -Twisting
  - -Camber change
  - -Change in length
  - -Bending

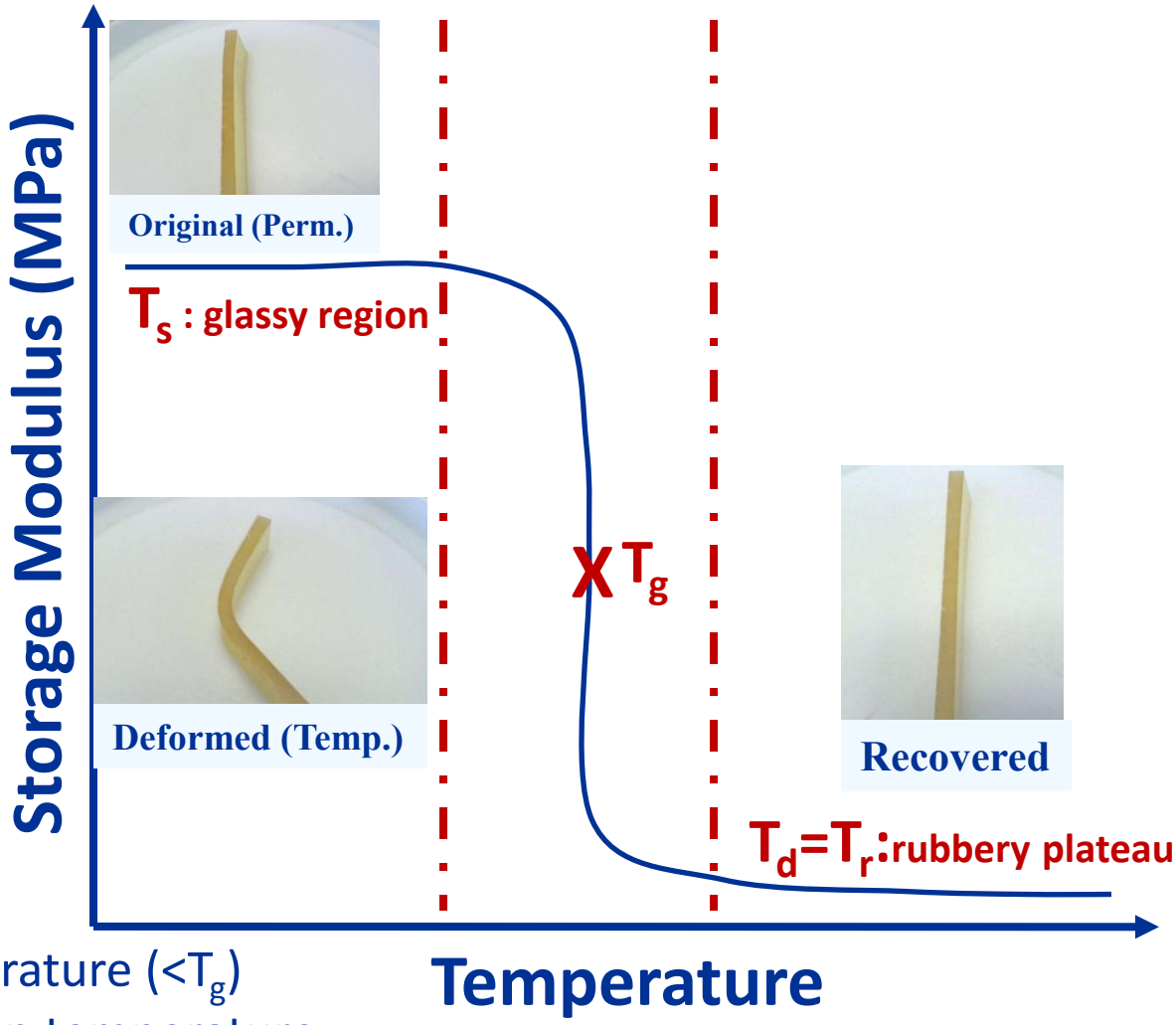
Shape memory materials

- **Shape memory alloys (SMAs)**
  - Gold-cadmium alloy (1938)
  - Nickel-titanium alloy (1963)
    - **Ni**ckel **Ti**tanium **N**aval **O**rdinance **L**ab
  - Shape change driven through temperature-dependent phase transformations

- **Shape memory polymers (SMPs) (1980's)**
  - Epoxy
  - Polyurethane
  - Polylactic acid (PLA)
  - Poly(ε-caprolactone)

- **Shape change by exceeding T_{sw} in polymer**
  - Polymer blends
  - Copolymers (block, graft, random, etc)
  - Covalent networks (crosslinking, IPNs)
- **Actuation**
  - pH
  - Temperature
  - External fields
    - Light
    - Magnetic
    - Electrical

T_s, T_d, and T_g determination for shape memory cycling

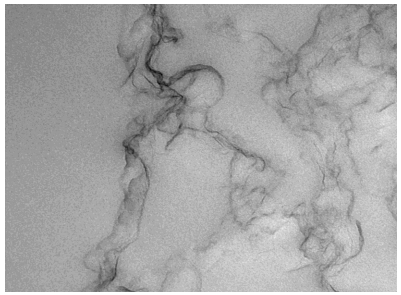


T_s: Setting temperature ($<T_g$)
T_g: Glass transition temperature
T_d: Deformation temperature ($>T_g$)
T_r : Recovery temperature ($>T_g$)

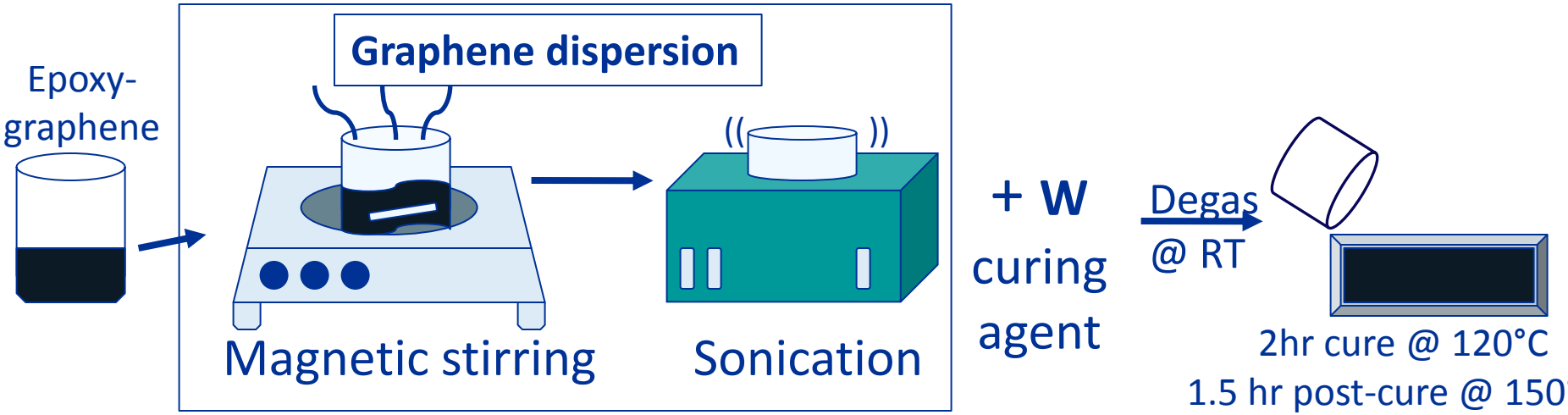
Feldkamp, D., Rousseau, I., *Macomol. Mater. Eng*. **2010**, *295*, 726-734

Materials & Methods

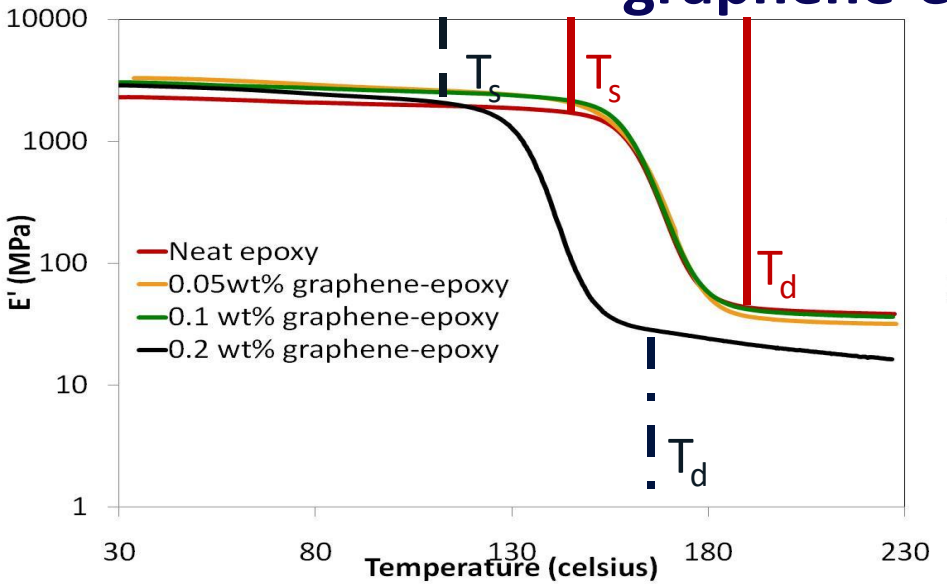
- **T_g target: >145°C**
- **SMP Epoxy:**
  - Epon 862 and Epon 828 mixture with Epikure W curing agent
- **Nanofiller**:
  - Graphene
    - 0.05 wt%
    - 0.1 wt%
    - 0.2 wt%

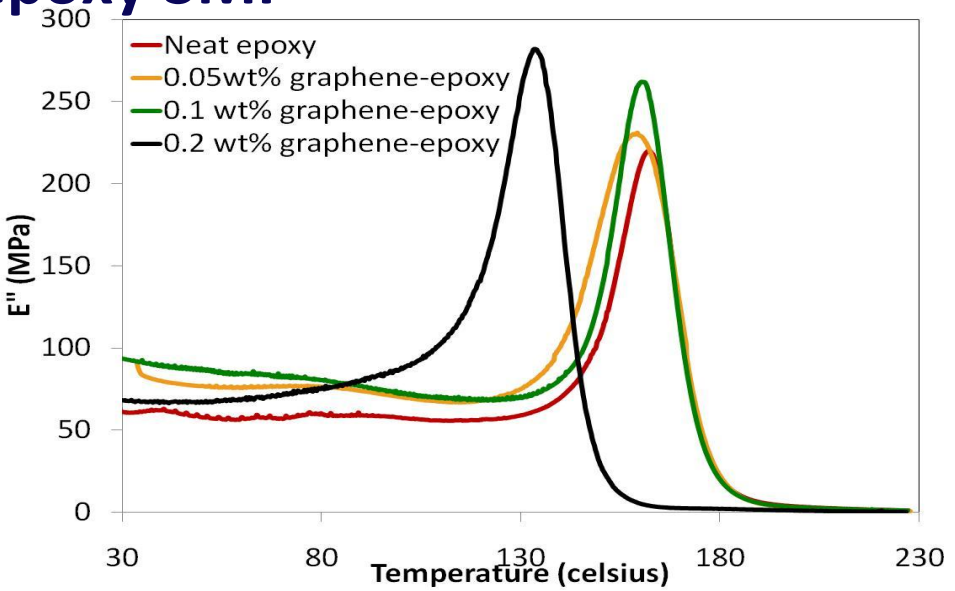


Vor-X: Surface-modified exfoliated graphene



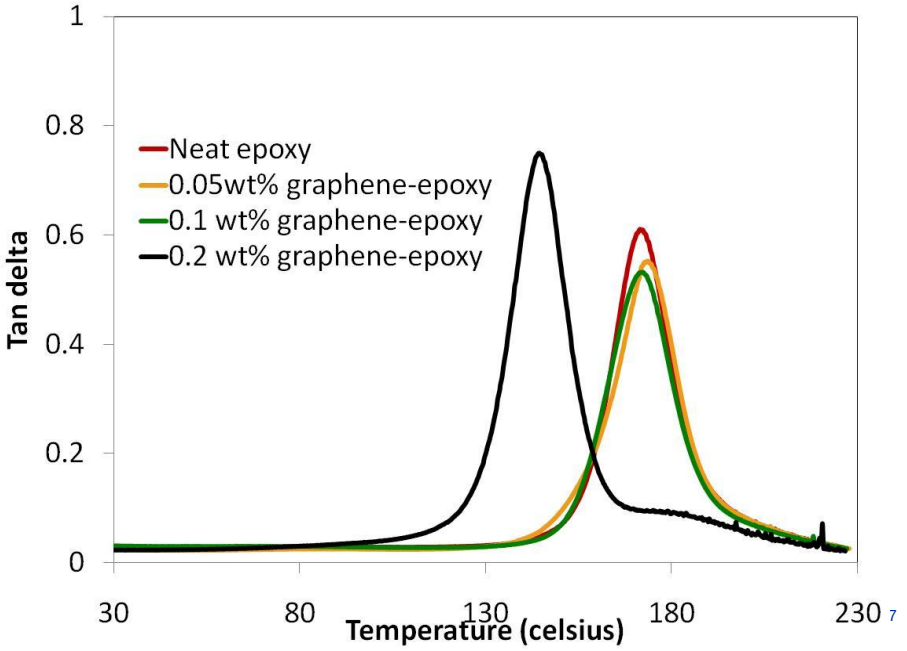
Thermo-mechanical properties of neat epoxy and graphene-epoxy SMP





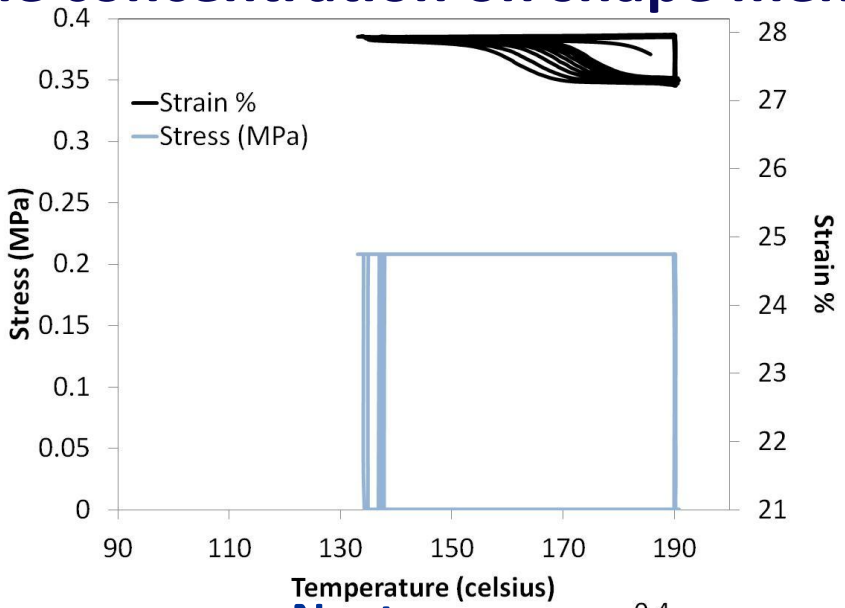
Temperature limits for shape memory cycling

	T_s (°C)	T_d (°C)	T_g (°C)
Neat epoxy	135	190	160
0.05 wt%	135	190	156
0.1 wt%	135	190	158
0.2 wt%	~100	175	132

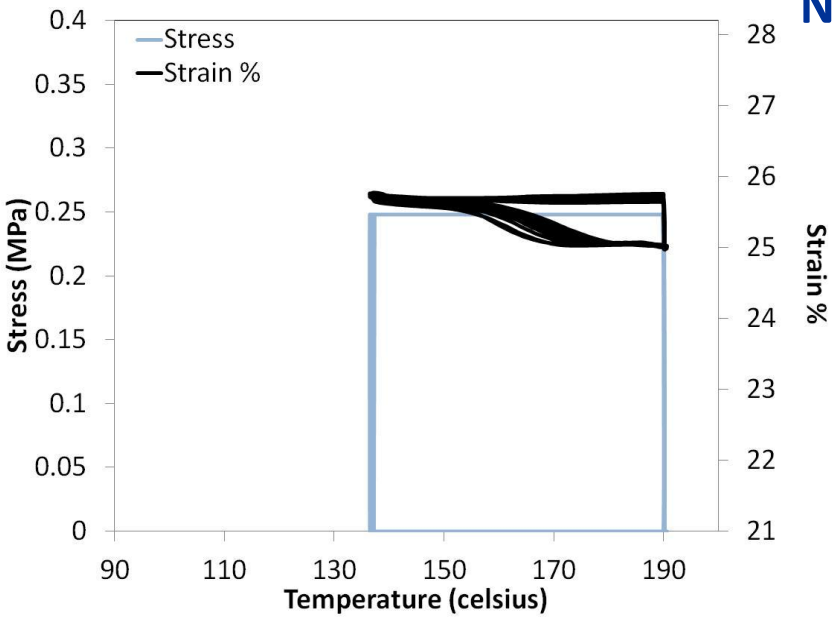


Effect of graphene concentration on shape memory behavior

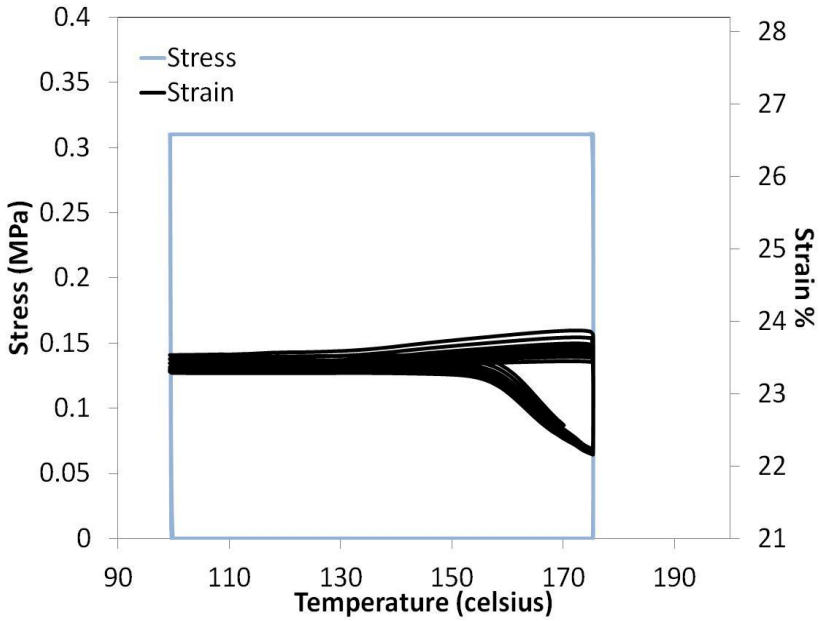
Method: DMA
 # cycles: 10



Neat epoxy

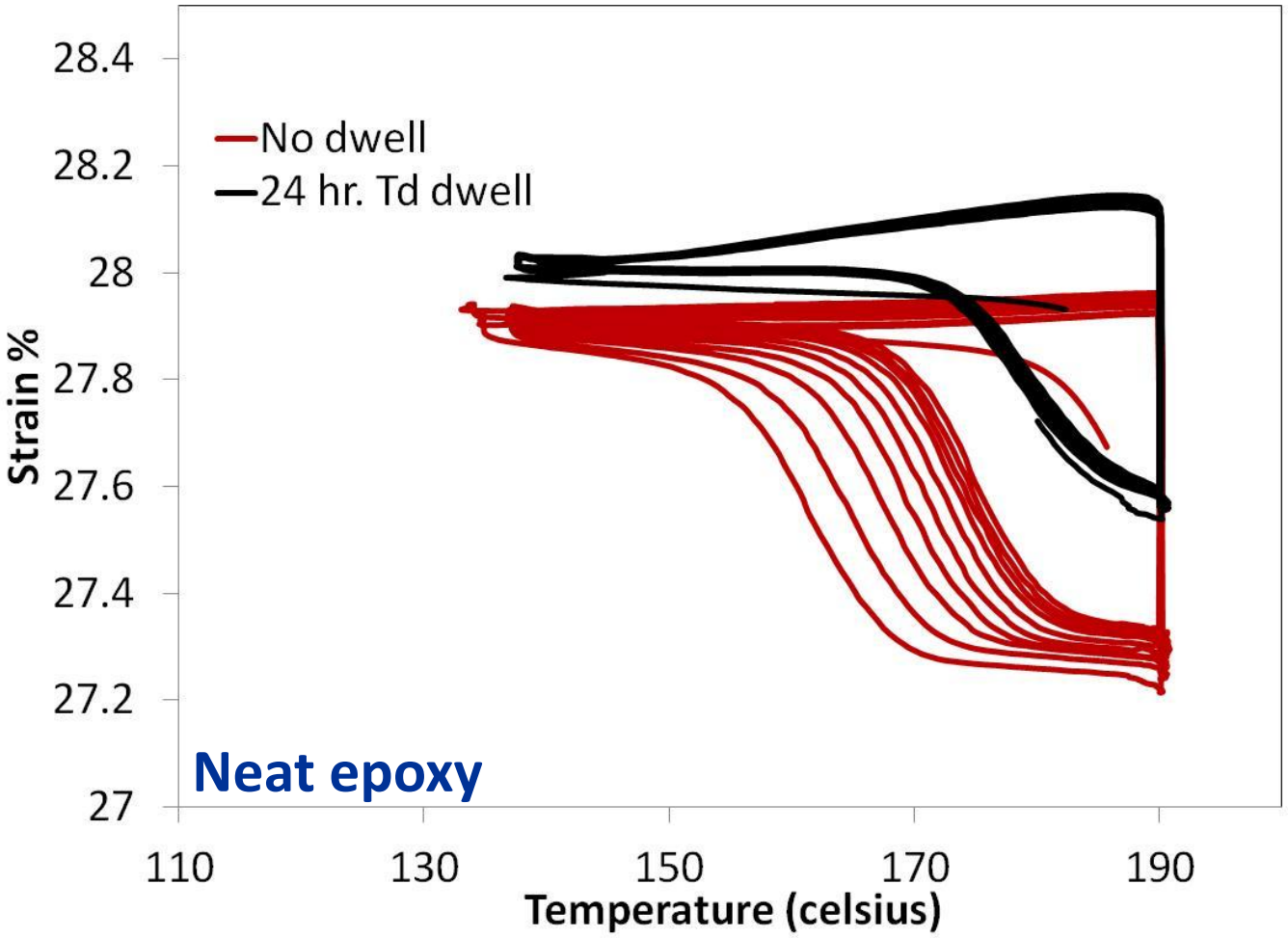


0.1 wt% graphene-epoxy



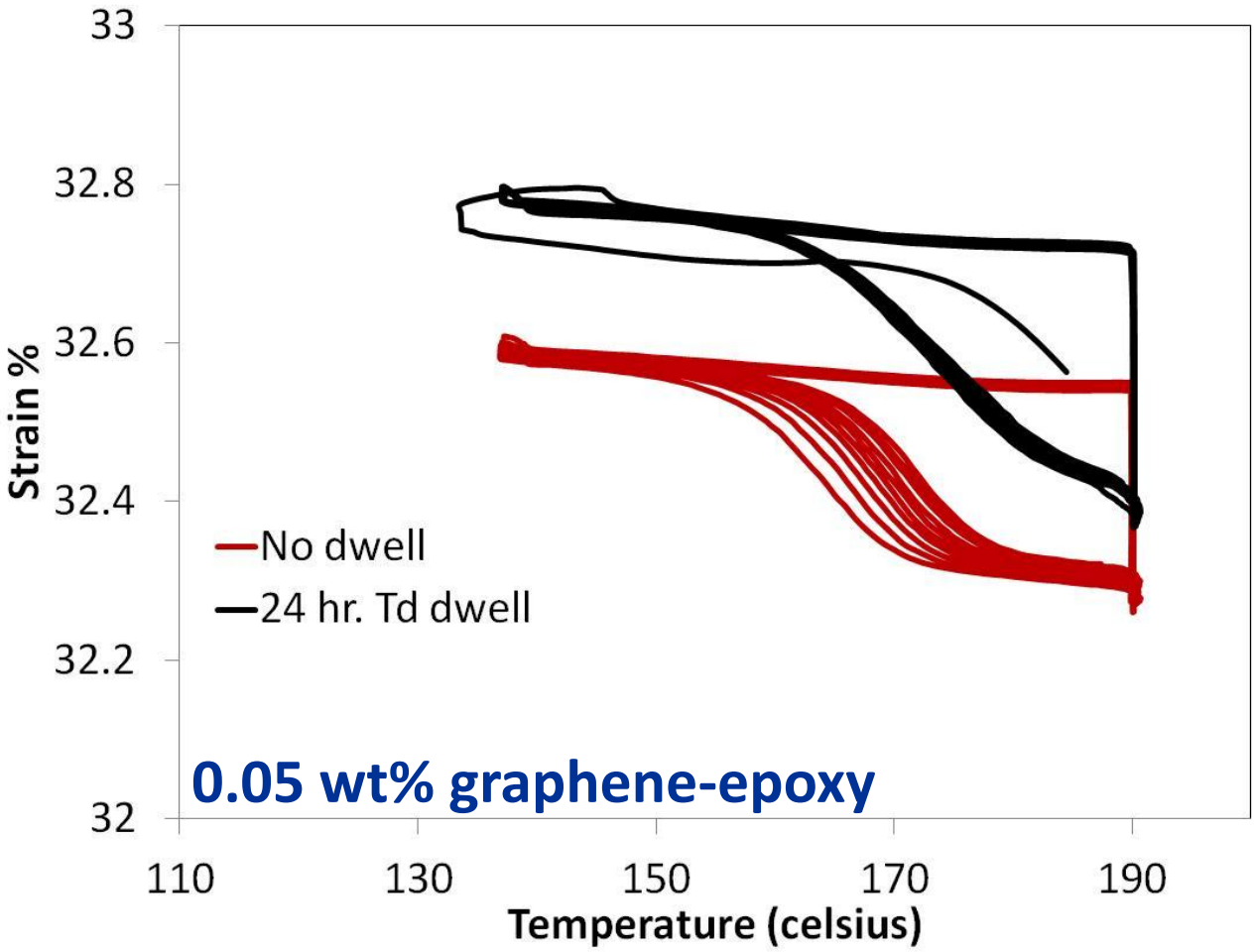
0.2 wt% graphene-epoxy

Thermal effects on shape memory behavior—24 hr. dwell at T_d



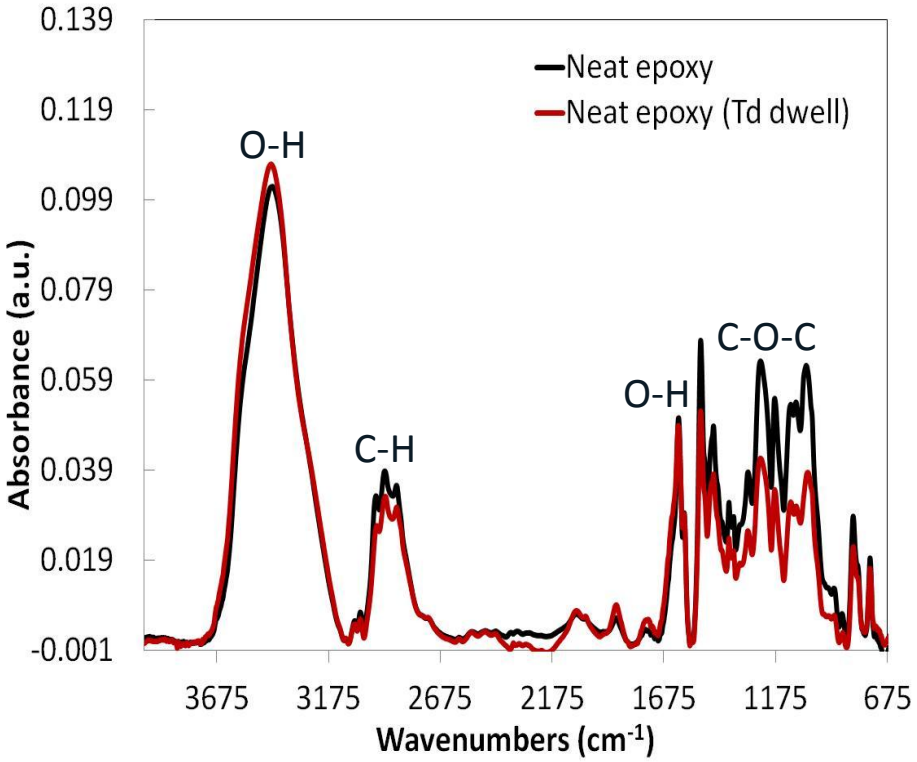
Samples heated to T_d prior to cycling showed more consistent strain response

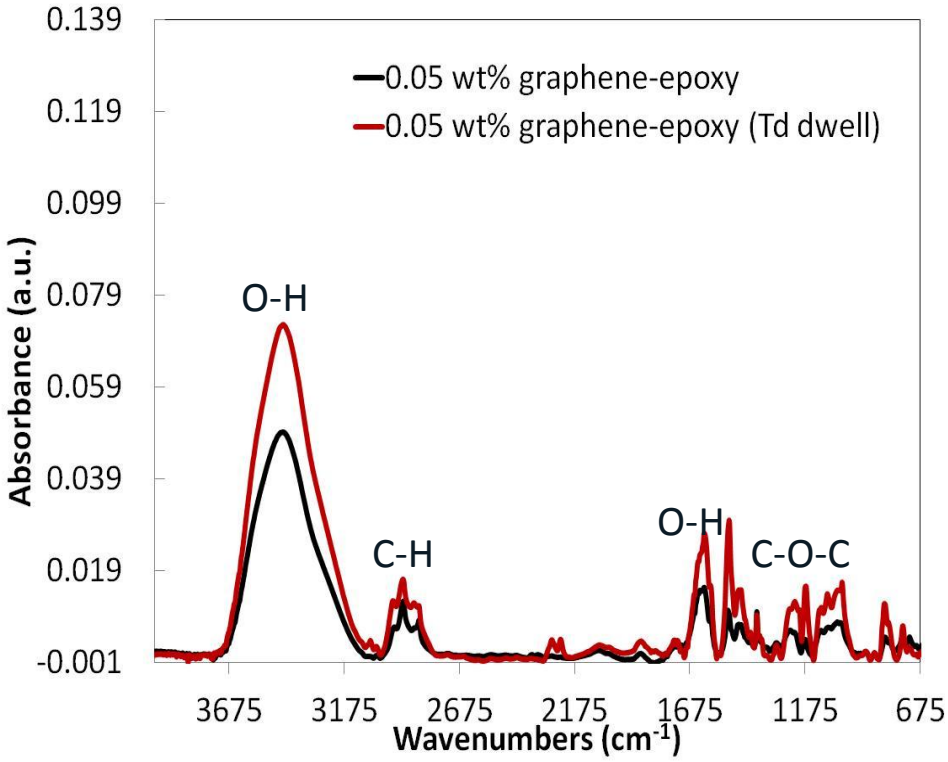
Thermal effects on shape memory behavior—24 hr. dwell at T_d



Samples heated to T_d prior to cycling showed more consistent strain response

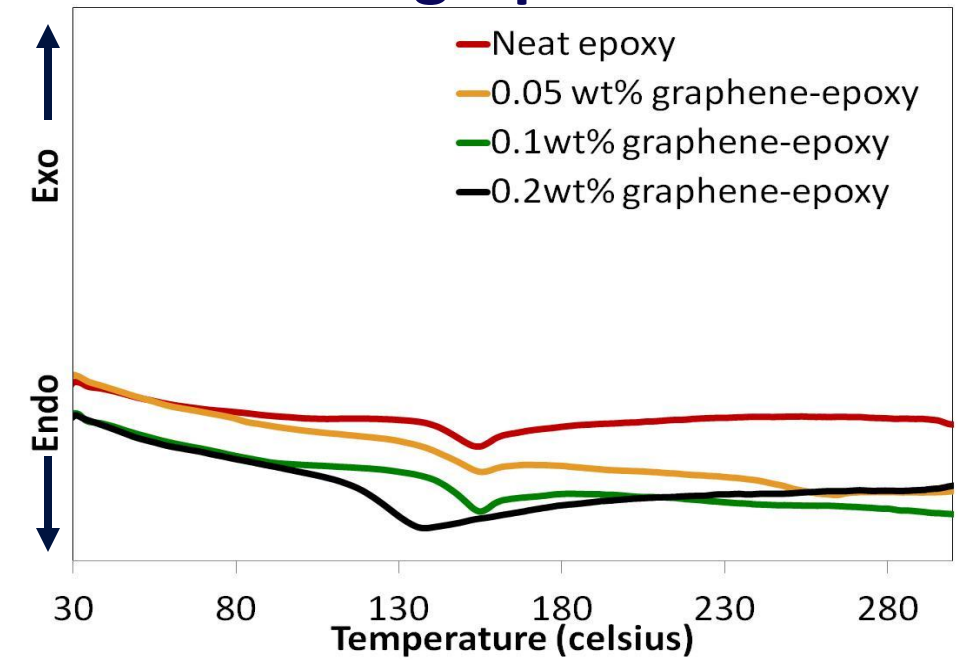
Effect of heat on chemical functionality—FTIR spectroscopy



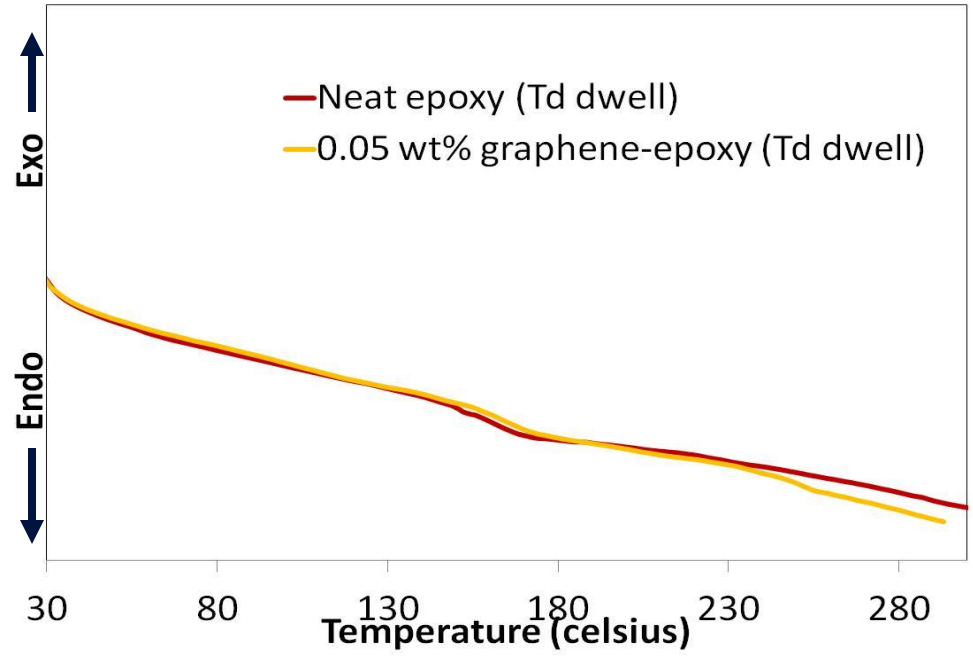


No significant chemical change when samples were heated to T_d

Effect of graphene on thermal transitions of epoxy

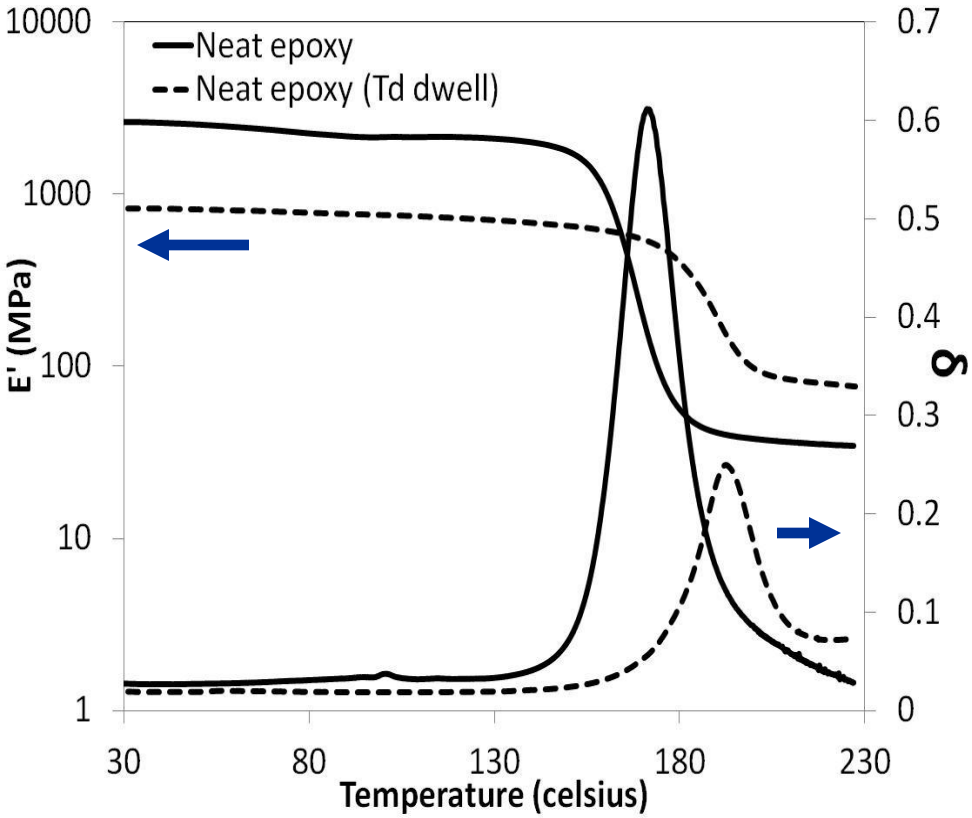


No thermal exposure	T_g (°C)
Neat Epoxy SMP	147.2 ± 1.5
0.05 wt% graphene/epoxy SMP	149.3 ± 1.4
0.10 wt% graphene/epoxy SMP	147.0 ± 6.3
0.20 wt% graphene/epoxy SMP	123.4 ± 4.1

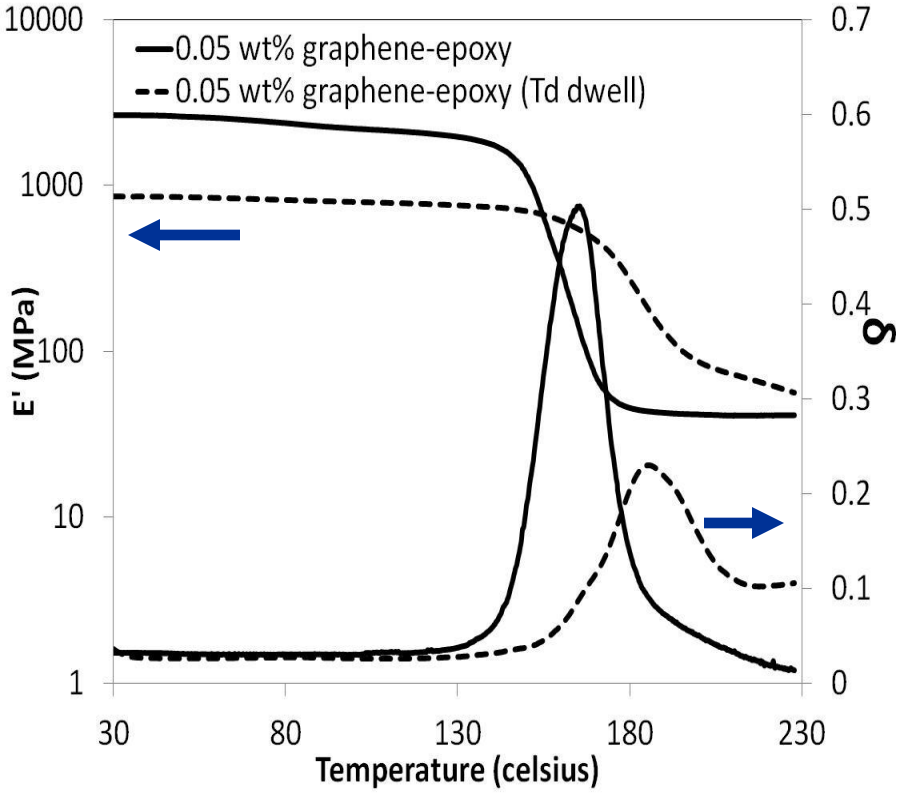


Thermal exposure	Avg. T_g (°C)
Neat Epoxy SMP	164.4
0.05 wt% graphene/epoxy SMP	163.9

Thermo-mechanical properties of epoxy nanocomposites (before and after T_d dwell)

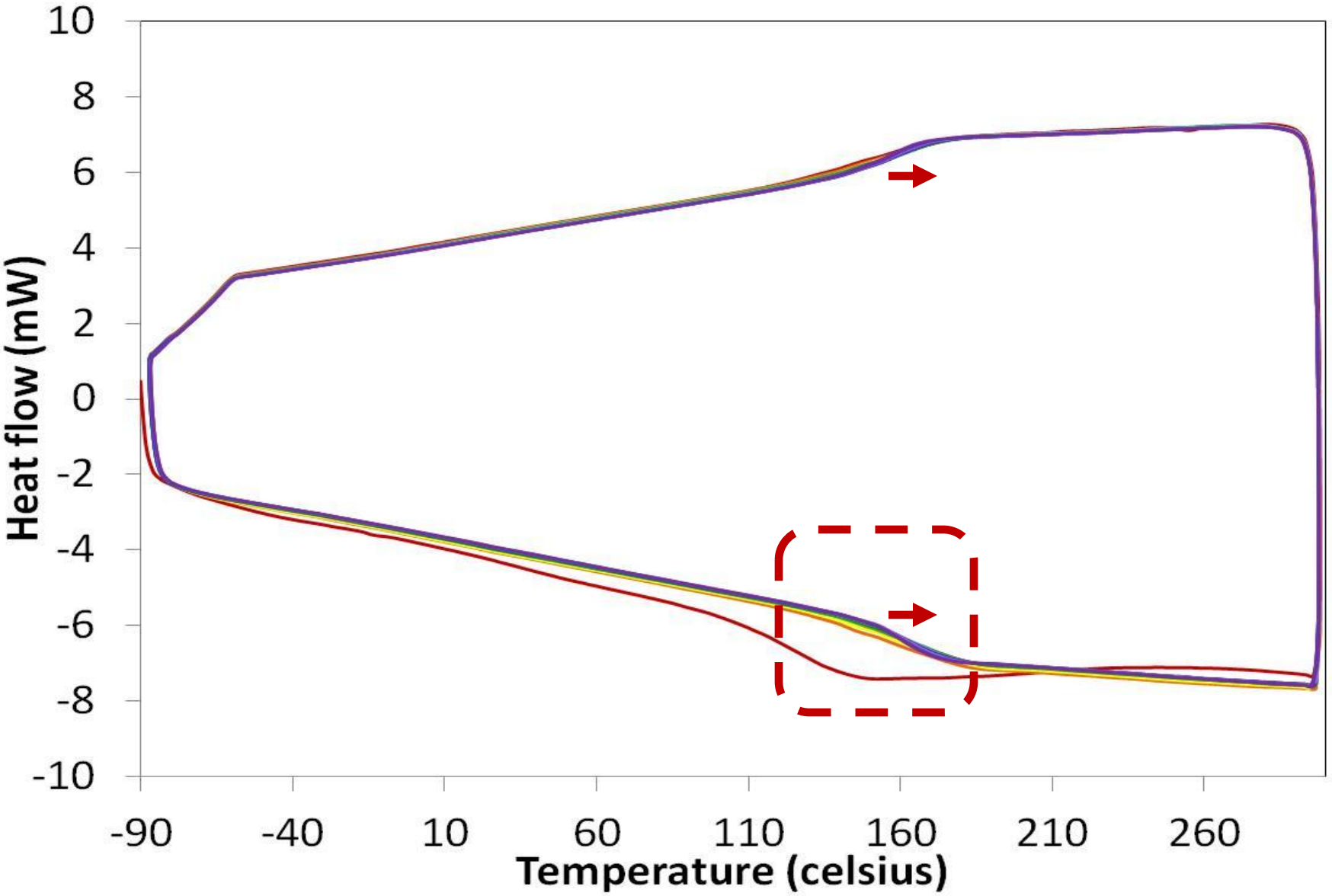


Neat epoxy

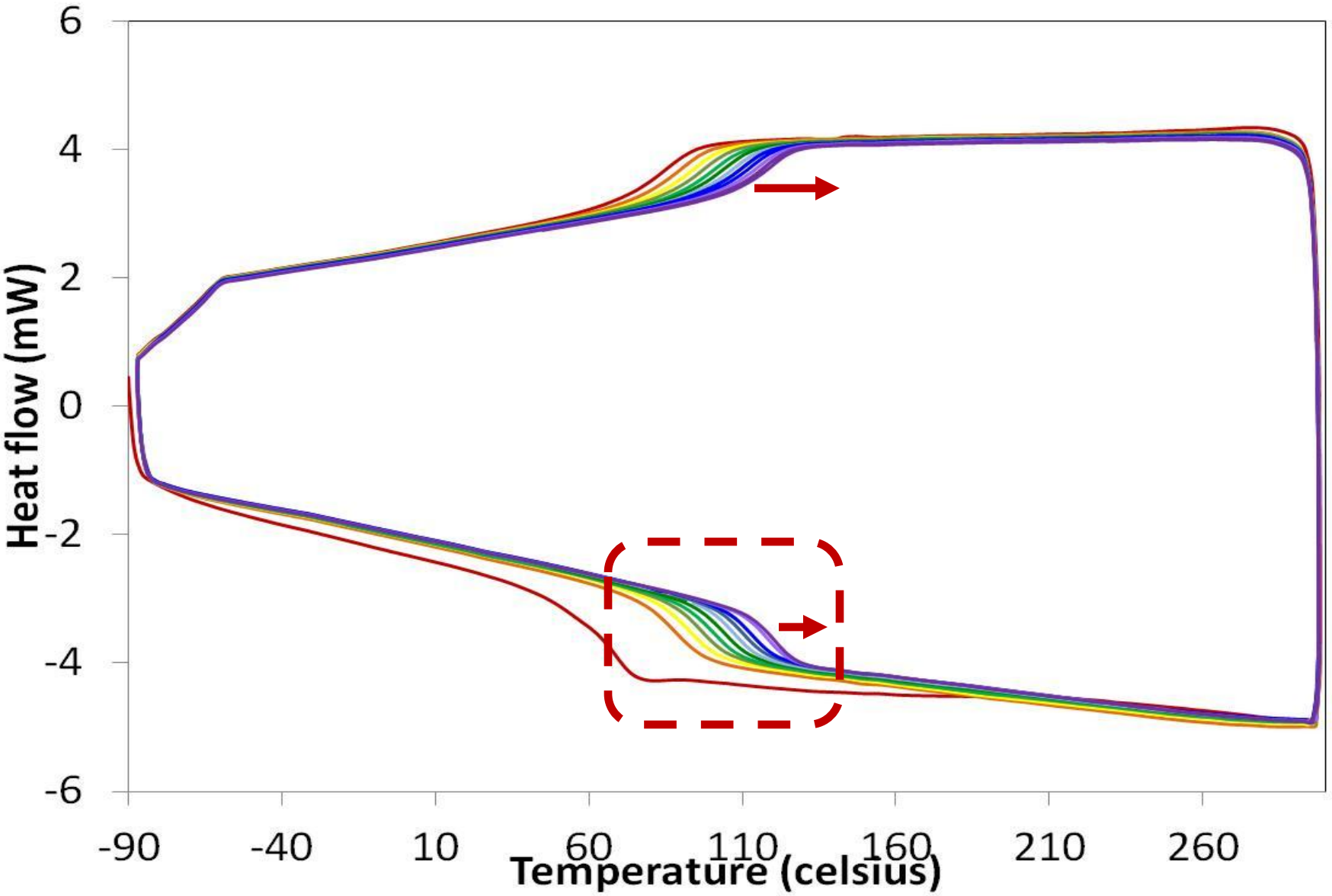


0.05 wt% graphene-epoxy

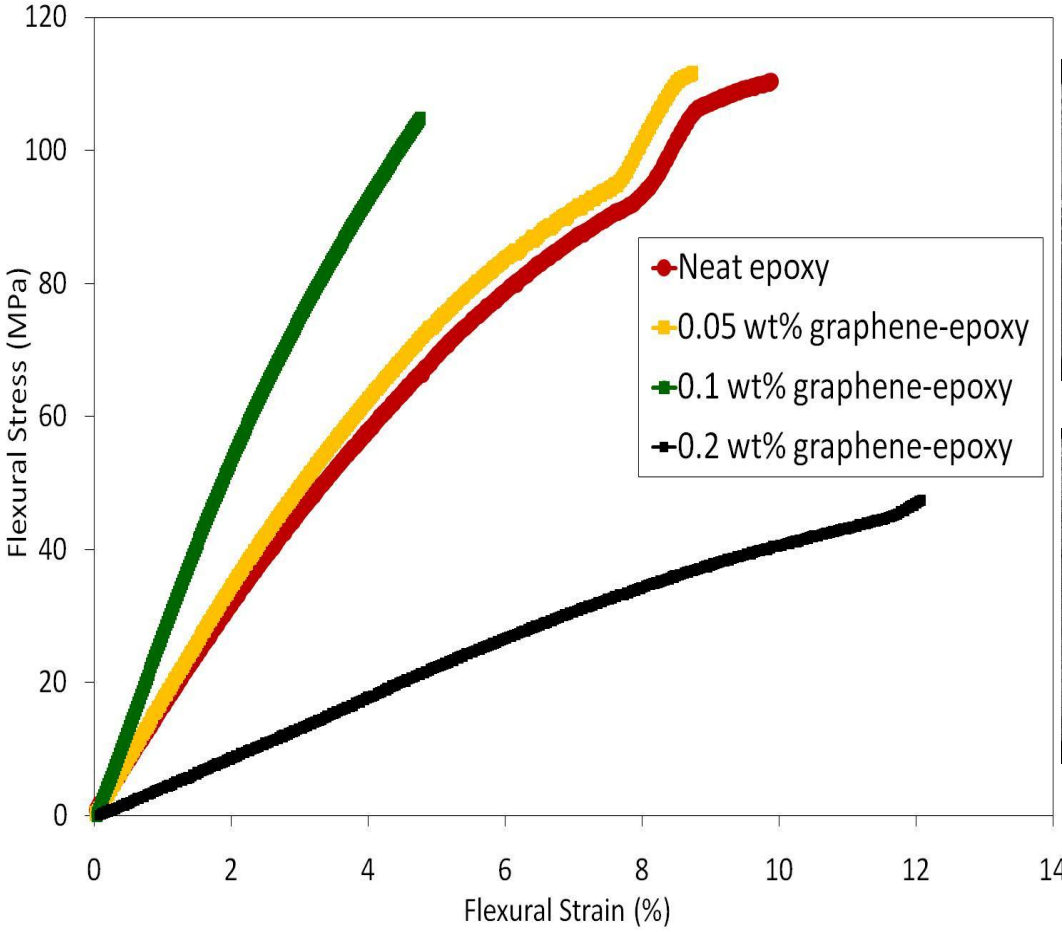
DSC temperature cycles- Neat Epon 828-W curing agent

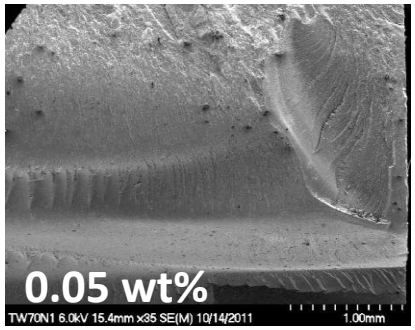


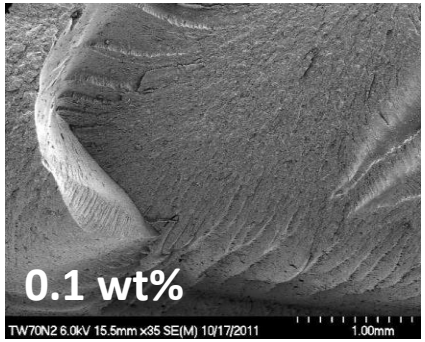
DSC temperature cycles- Neat Epon 862-W curing agent

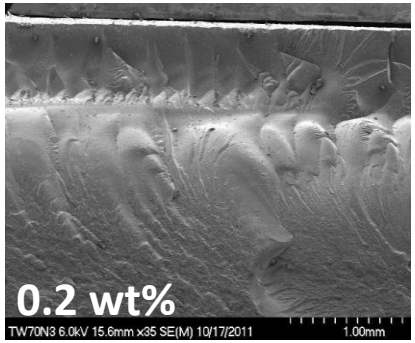


Effect of graphene on flexure properties



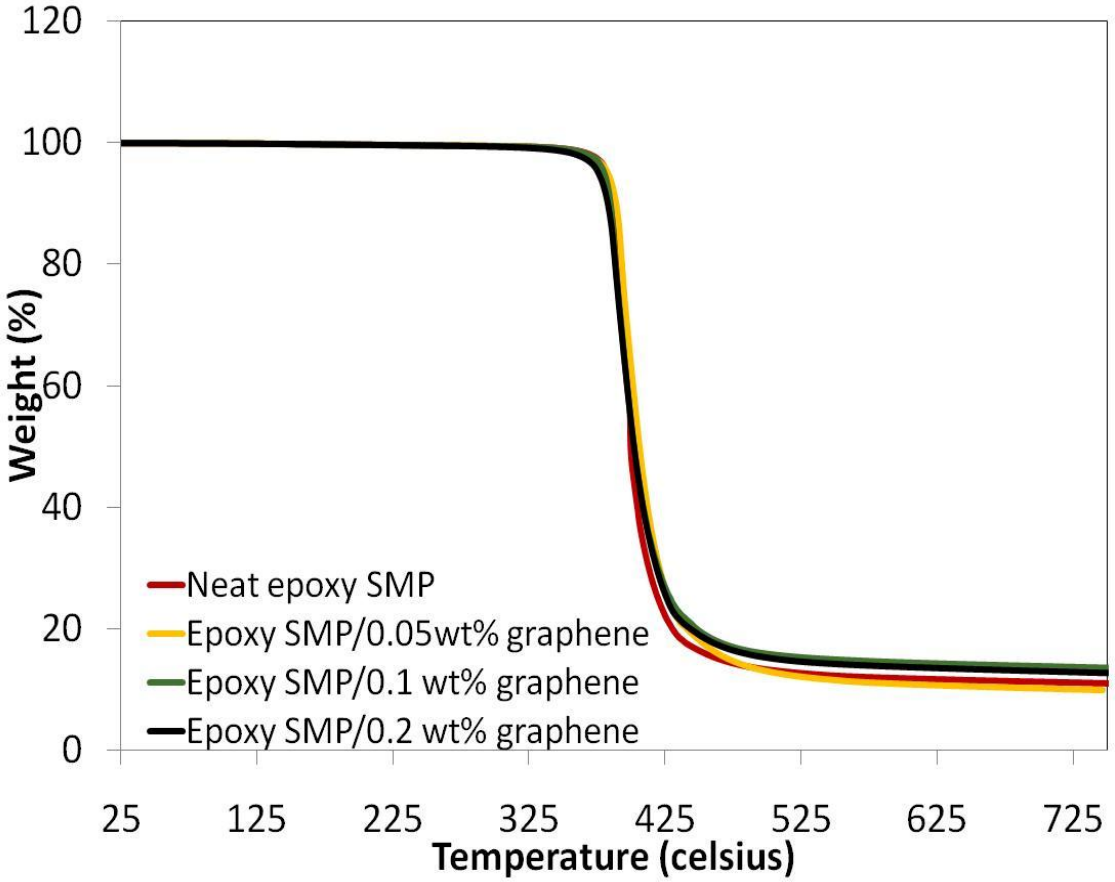






	Flexure modulus (GPa)	Flexure stress (MPa)	Flexure strain (%)
Neat epoxy	1.6 ± 0.3	108.0 ± 16.5	9.6 ± 1.6
0.05 wt% graphene-epoxy	2.4 ± 0.5	110.8 ± 15.6	7.0 ± 1.6
0.1 wt% graphene-epoxy	3.1 ± 1.0	96.2 ± 12.9	4.0 ± 0.8
0.2 wt% graphene-epoxy	0.4 ± 0.09	58.2 ± 11.8	14.1 ± 3.7

Thermal stability of epoxy nanocomposites—TGA



	T_{onset} (°C)	Char Yield % @ 600°C
Neat Epoxy SMP	385.9 ± 1.3	12.3 ± 0.8
0.05 wt% graphene/epoxy SMP	385.1 ± 1.6	11.6 ± 2.7
0.10 wt% graphene/epoxy SMP	382.4 ± 0.5	14.6 ± 0.3
0.20 wt% graphene/epoxy SMP	379.3 ± 1.2	13.0 ± 2.4

Summary

- Adding graphene improved consistency between cycles, but reduced the strain recovery range
- Samples cycled following 24 hour T_d exposure showed better shape memory behavior possibly due to structural relaxation changes
- Flexural modulus increased by at least 50% in graphene-epoxy nanocomposites, but decreased flexure stress→ low interfacial bonding
- T_{onset} decomposition of epoxy nanocomposites slightly decreased with increasing graphene concentrations

Future work

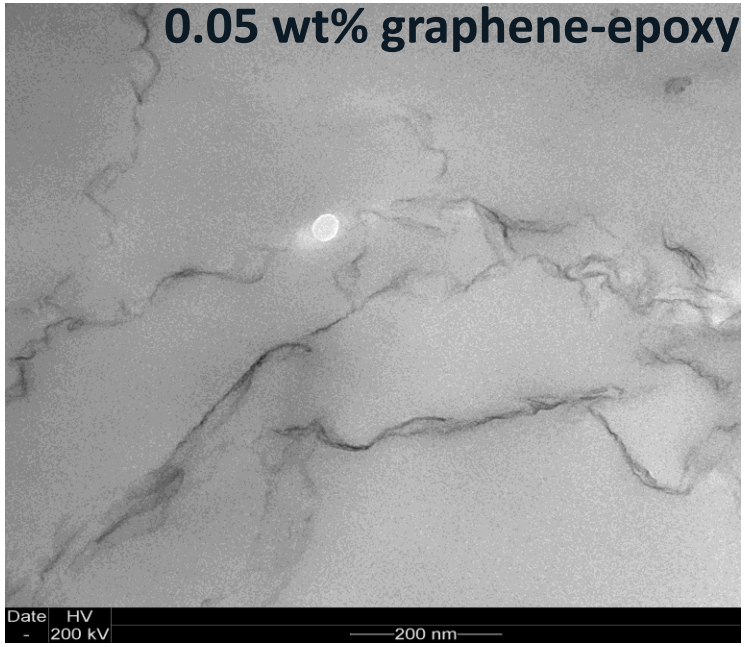
- Incorporate more compatible functionalized nanofillers to improve interfacial adhesion
- In depth analysis of relaxation behavior

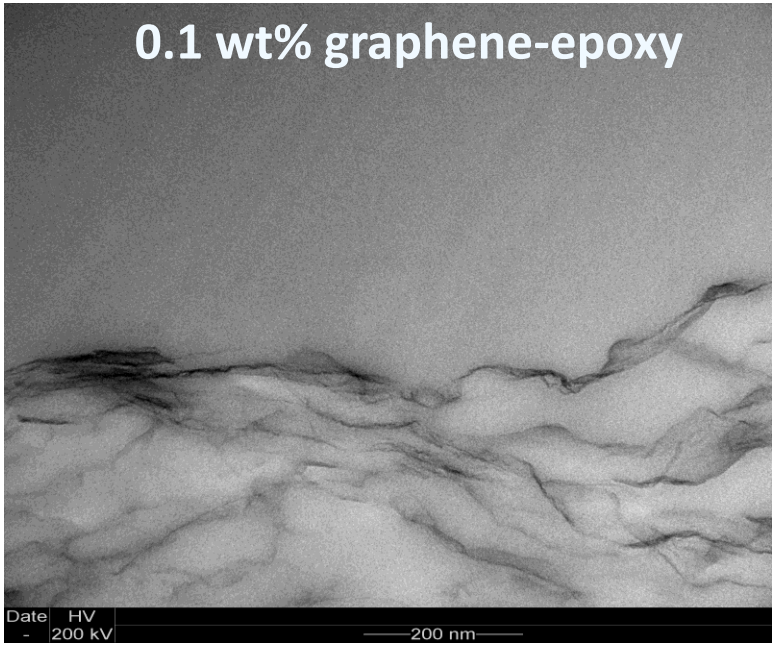
Acknowledgements

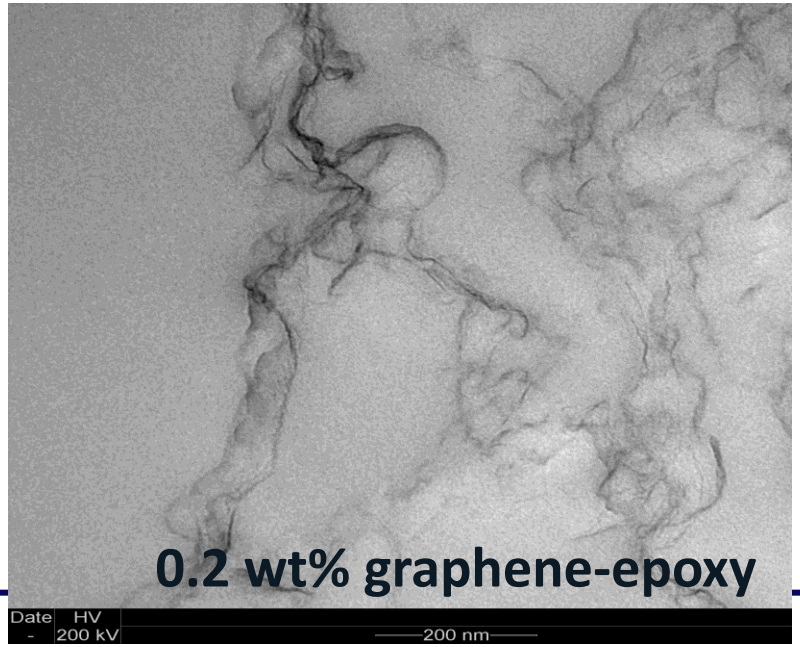
- Derek Quade: Mechanical property testing
- Linda McCorkle: SEM analysis
- David Hull: TEM analysis
- Vorbeck Materials: Supplier of exfoliated graphene sheets
- Funding Program: Subsonic Fixed Wing

Questions?

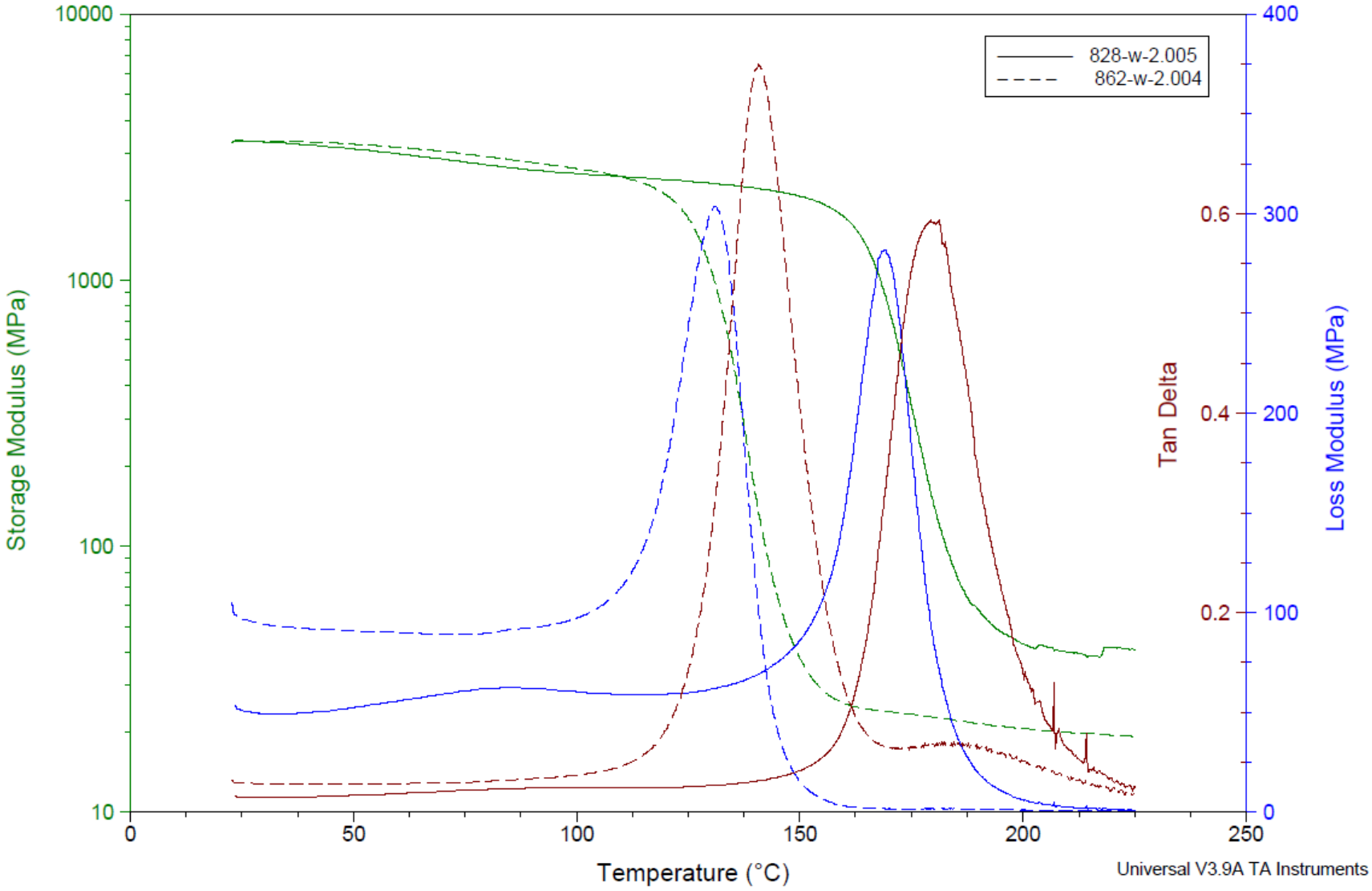
Dispersion of graphene nanofiller in epoxy







Neat Epon 862 vs. neat Epon 828 with Epikure W curing agent



Epon 828 vs. Epon 862-828 mixture