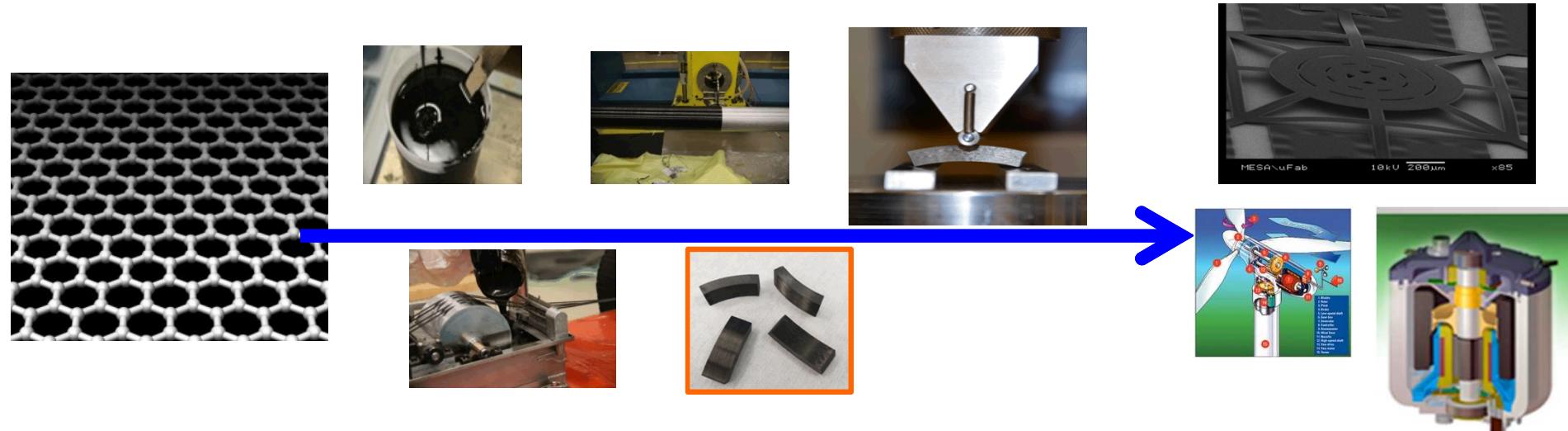


Exceptional service in the national interest

Graphene Nanocomposites



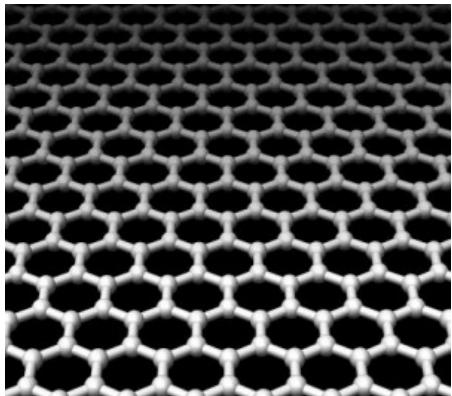
MRS, December 5th, 2014, Boston, MA

Symposium K. Graphene and Graphene Nanocomposites

Timothy N. Lambert,¹ David A. Miller,² Cody M. Washburn,¹ Nelson S. Bell,¹ Timothy J. Boyle,¹ Bernadette Hernandez-Sanchez¹

¹*Sandia National Laboratories and ²Montana State University*

Graphene – Properties and Applications

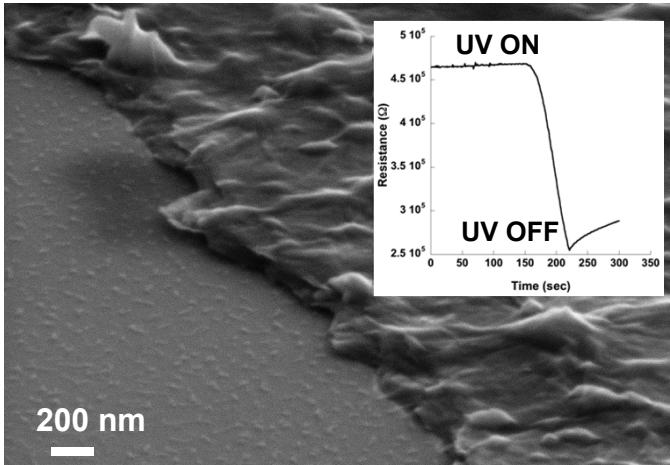


Young's modulus
Fracture Strength
Elastic Modulus
Thermal Conductivity
Mobility of Carriers
Specific Surface Area
Cost

~ 1000 GPa
~ 125 GPa
~ 0.25 TPa
~ $5000 \text{ W m}^{-1} \text{ K}^{-1}$
~ $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
= $2360 \text{ m}^2 \text{ g}^{-1}$ (calculated)
= ??????

Huge potential for applications in energy storage and reinforcing composites

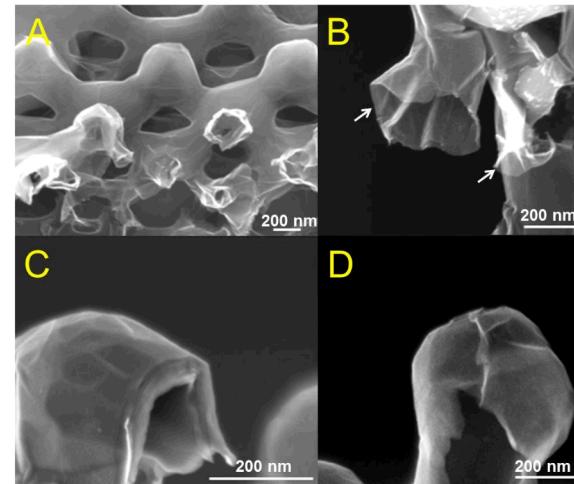
Self-Assembled TiO₂/RGO



T. N. Lambert et al. *J. Phys. Chem. C*. 2009 113 (46), 19812-19823.

T. N. Lambert et al. *Nanoscale* 2011 3(1), 188-191.

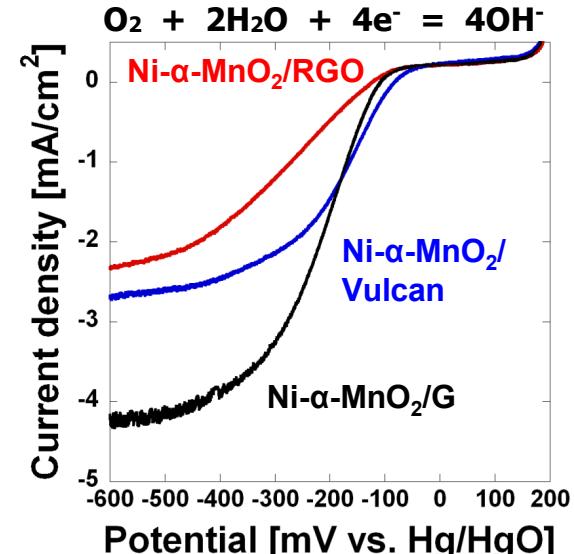
3D Graphene Electrodes



X. Xiao et al. *J. Mater. Chem.* 2012 22, 23749-23754.

X. Xiao et al. *ACS Nano* 2012 6(4), 3573-3579.

Electrocatalysts



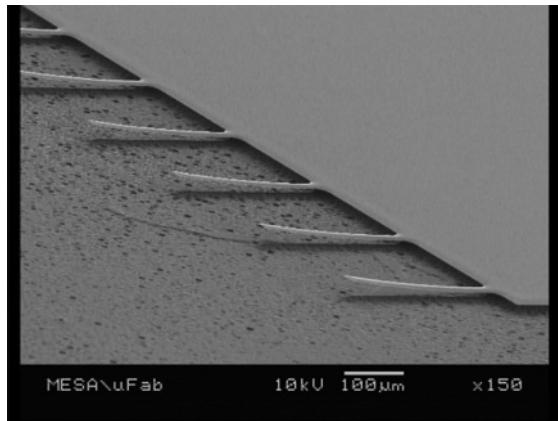
T. N. Lambert et al. *Chem. Commun.* 2012 48, 7931-7933

D. J. Davis et al. *Electroanal.* 2013, 1, 164-170.

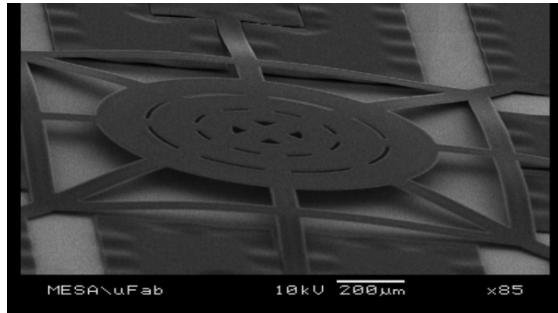
Graphene – Properties and Applications



Carbon-based MEMS Devices



C. Washburn *et al.* *J. Electrochem. Soc. Trans.* 2012, 50(12), 423-434.



Improved Composite Materials



**Building and
Testing
Prototype
Flywheels with
US Company**

T.N. Lambert *et al.*
Unpublished work



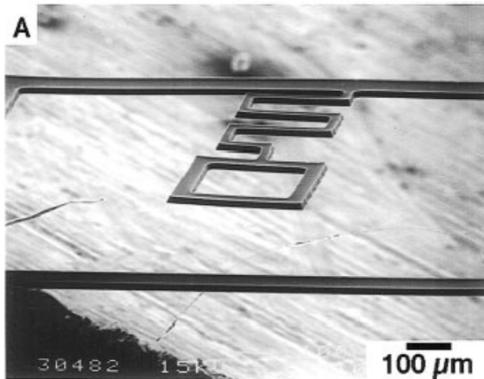
**Mechanical
Strength and
Water Uptake**

Tunable Young's Modulus in Carbon MEMS using Graphene-based Stiffeners

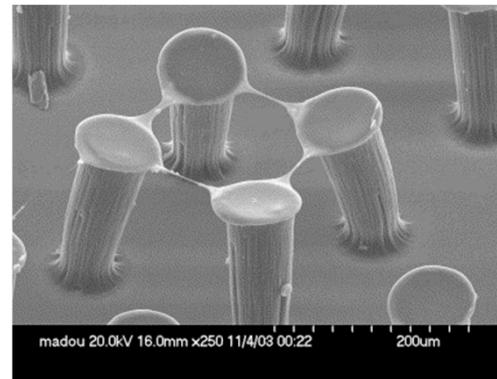
Motivation: Develop tunable carbon composite actuators and sensors.

Pyrolytic Carbon is soft (15-40GPa) = needs reinforcement.

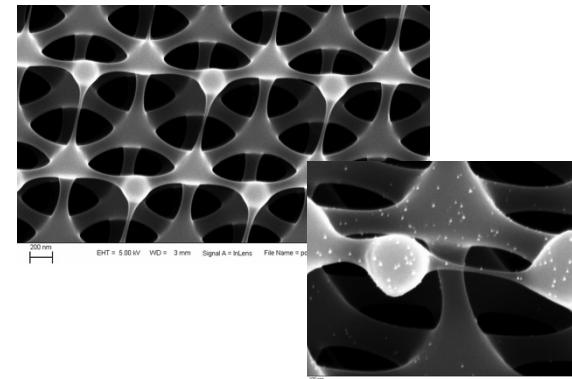
Approach: Use Photosensitive pyrolyzed carbon/graphene nanofiller



Whitesides *et al. Chem. Mat.* **1997**, 9, 1399-1406



Madou *et al. Carbon* **2006** 13, 2602-2607.

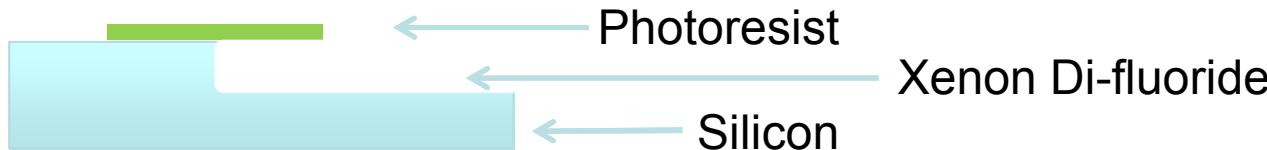


Burckel *et al. Small* **2009**, 5, 2792-2769

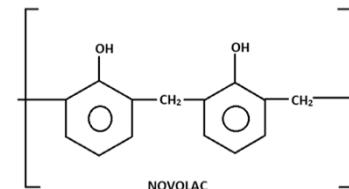
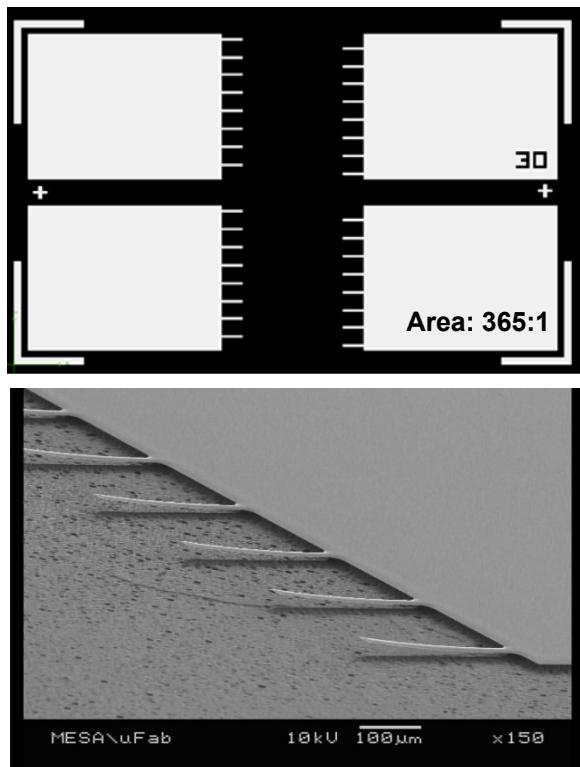
Advantages: Rapid Prototyping, Large dynamic range – tunable versus silicon?
High Fracture Toughness under loading with less abrupt failure mode than Si
(crystal fractures), Electrochemical sensitivity, Surface Chemistry

Cantilever test platform

Flexible Fabrication Approach

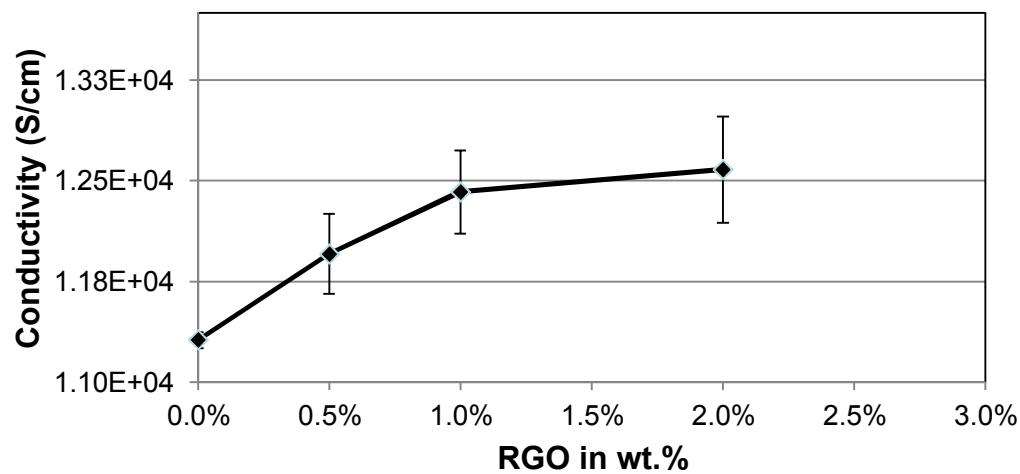


E.g. 30 μm wide X 300 μm long beams



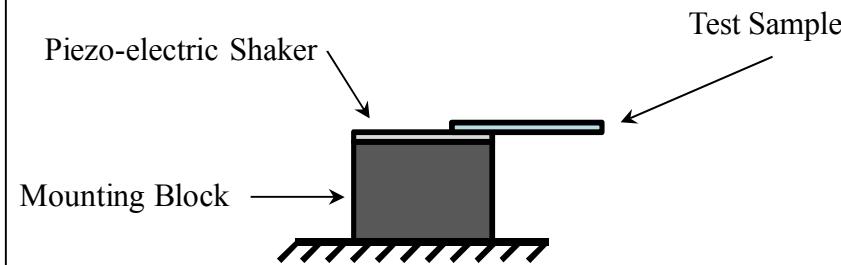
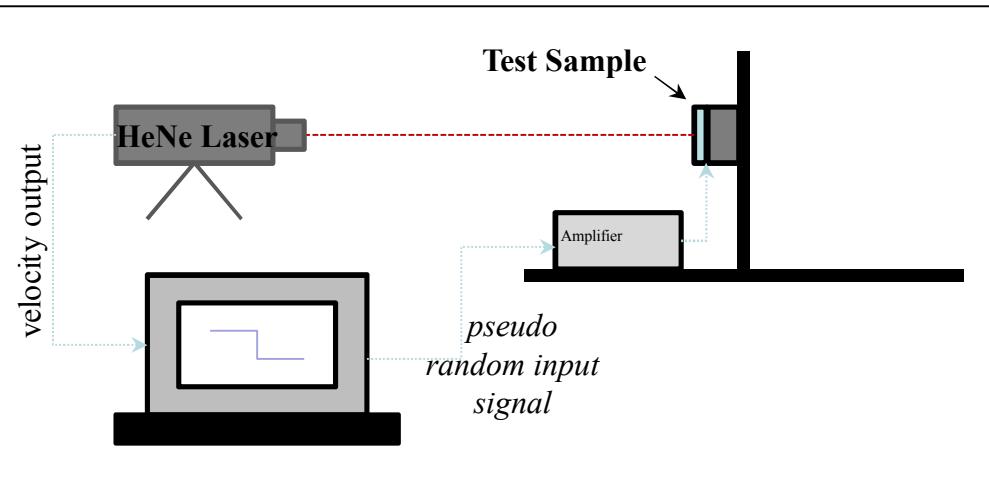
Reduced Graphene Oxide (RGO)

11% Increase with 2.5% loading
Conductivity of Pyrolytic Carbon vs. iRGO in wt.%



Laser Doppler Vibrometry (LDV)

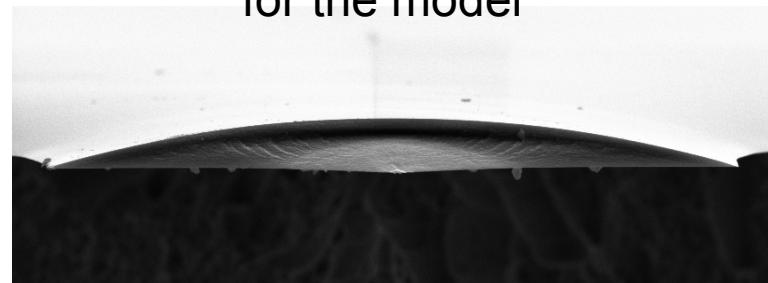
Experimental Schematic of LDV (Jill Blecke – SNL)



$$E = \frac{m}{I} \left(\frac{2\pi f_i L^2}{\lambda_i^2} \right)^2$$

Blevin's Equation
For Modulus of Elasticity
 L , beam length; M , mass/length of beam; I , moment of inertia; λ , boundary coefficient; f , frequency

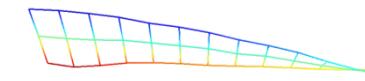
A semi-elliptical cross-section was assumed for the model



SEM cross section: wingshaped

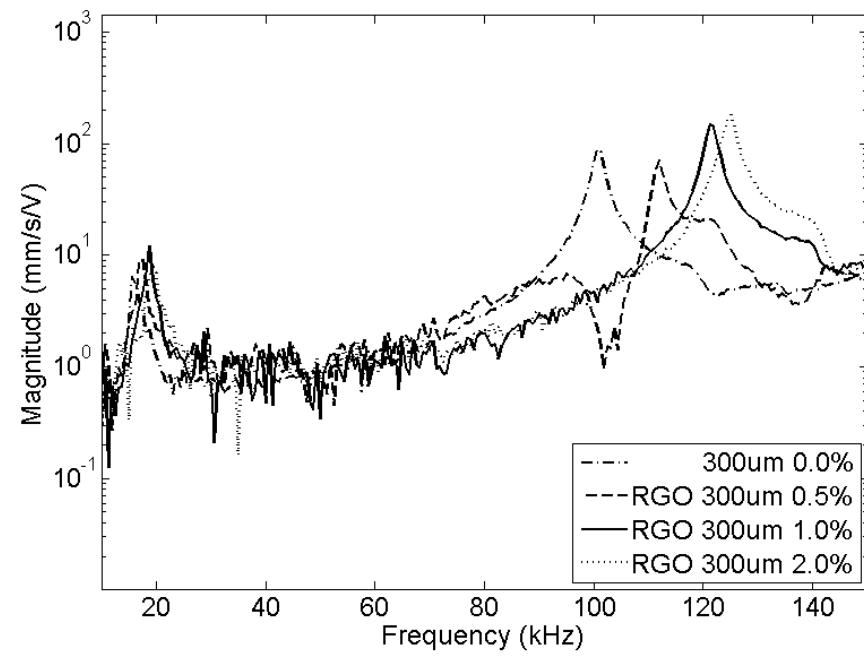
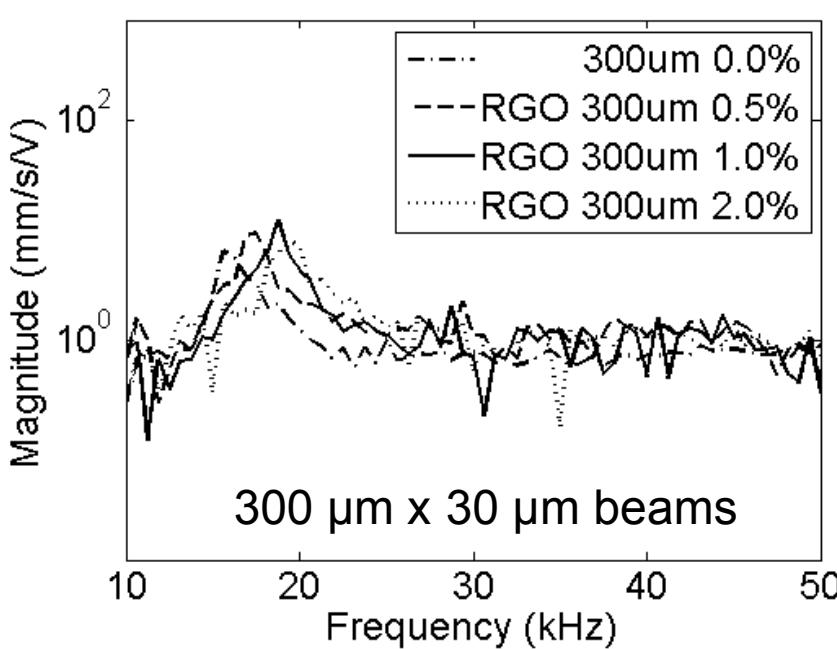
Laser Doppler Vibrometry (LDV)

Mode Shape illustrations:



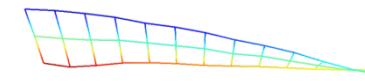
(a) first bending mode, (b) second bending mode and (c) first torsional mode

Resonant frequency response of 1st and 2nd bending modes



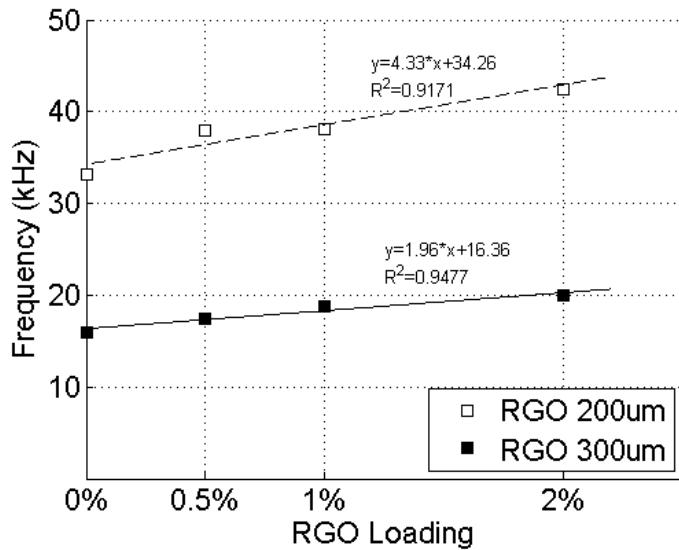
Laser Doppler Vibrometry (LDV)

Mode Shape illustrations:

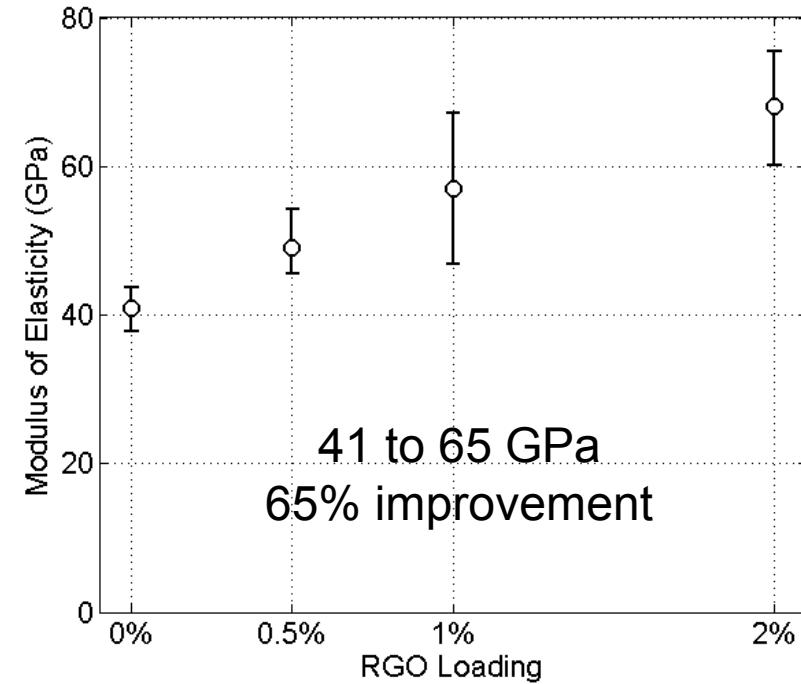


(a) first bending mode, (b) second bending mode and (c) first torsional mode

Change on 1st resonant frequency modes w/ RGO



Change in Modulus of Elasticity



OE funded Project: Improved Flywheel Materials



Problem: Flywheels used to level the AC grid need to spin faster, which requires stronger rims. Focused on the material (C-fiber, glass fiber, resin) properties of composite flywheels. *No major changes to basic design, processing parameters, and/or cost can be incurred.*



Goal: improve the overall strength of composite flywheel materials, so they can spin faster.

Approach: explore utility of nanomaterials in strengthening composite flywheel rims to improve performance. Low load levels ($\leq 5\%$) of nanoparticle fillers have led to dramatic property changes.

Energy Storage Impact: The economics of flywheel-based energy storage could potentially be improved by a factor of 3 or more. The increased storage/supply will be necessary to meet expected future complications expected as alternative energies (i.e., solar, wind, etc.) are introduced.

Energy is stored in the rotor as kinetic energy, or more specifically, rotational energy:

$$E_k = \frac{1}{2} \cdot I \cdot \omega^2$$

ω = angular velocity, I = moment of inertia of the mass about the center of rotation

The amount of energy that can be stored is dependent on:

$$S_t = \rho \cdot r^2 \cdot \omega^2$$

S_t = tensile stress on the rim, ρ = density, r is the radius, ω is the angular velocity of the cylinder.

Small % changes in the flywheel spin speed leads to magnified energy storage

16,000 rpm \rightarrow 20,000 rpm (25%)
25 kWh \rightarrow 39 kWh (56%)
of extractable energy

Flywheels

A **flywheel** is a rotating mechanical device that is used to store rotational energy.

Analogy: Electrical Motor / Generator

Benefits:

- Fast Discharge / Recharge times
- Environmentally Clean
- No Hazardous Materials
- Long Life Expectancy (e.g. 175,000 full charge/discharge)
- Potential for High Power Density (W/kg) and high energy density (W hr/kg)



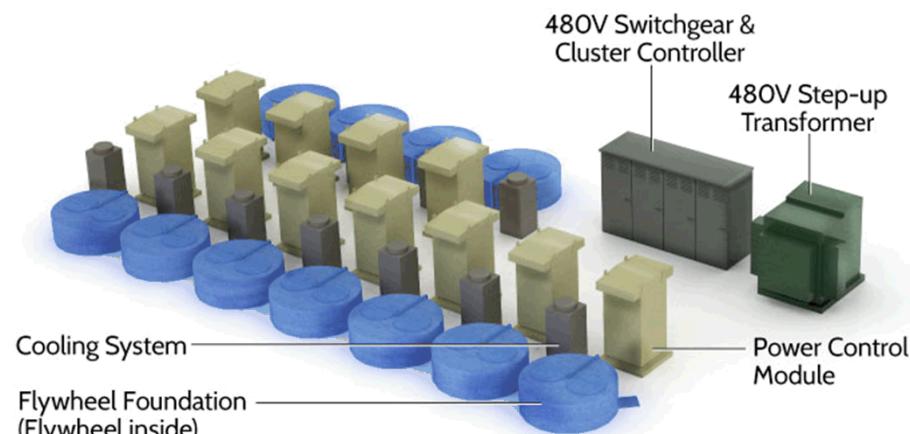
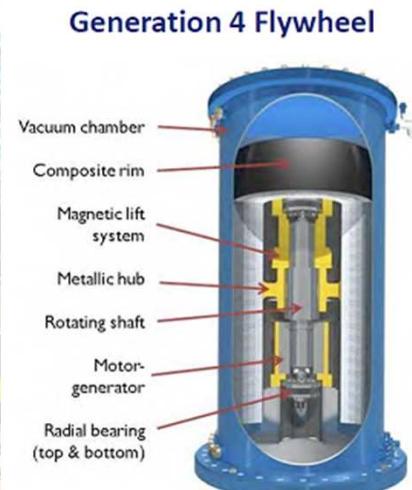
Carbon fiber materials / magnetic bearings
(spin up to 60,000 rpm!)

Steel / Conventional Ball Bearings
(spin @ ~ 1,000 rpm)

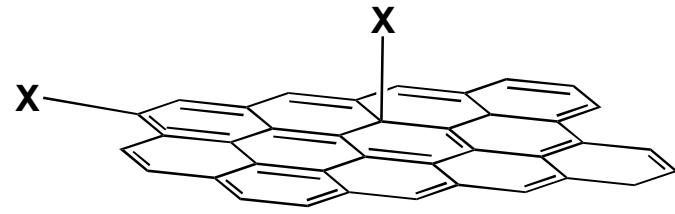
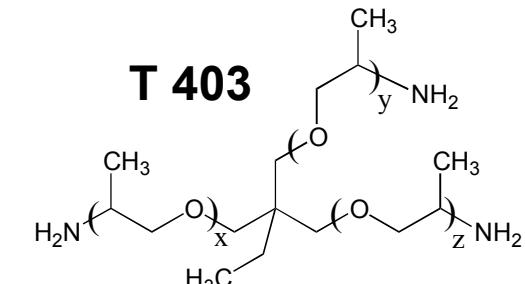
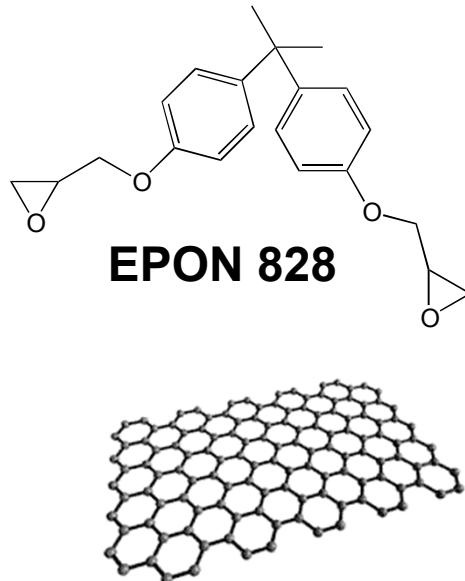
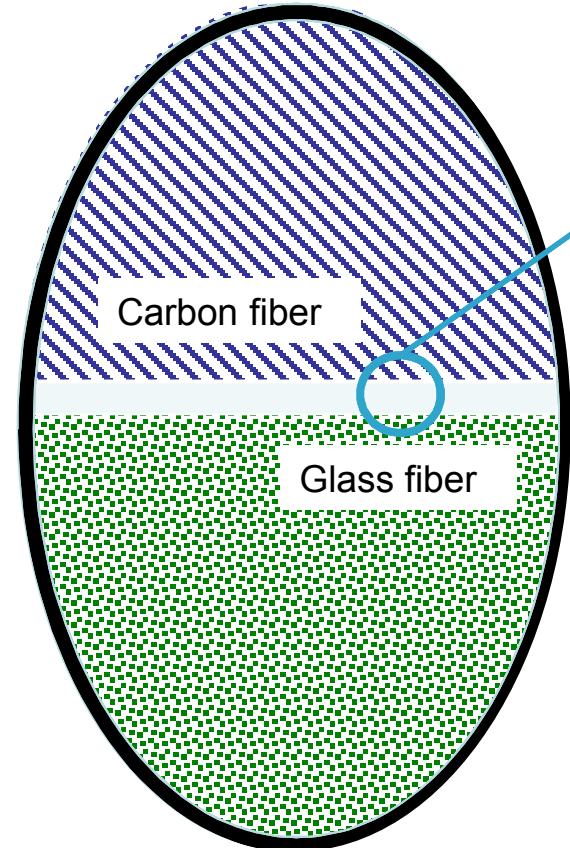
Beacon Flywheel Example

- Commercial Operation since 2008
- 400 Flywheels in use
- > 700,000 hours (16,000 rpm)
- Stephentown NY, 10% Capacity but 30% Area Control Error Correction
- Modular – 100 kW to multi MW
- 20 MW per Acre

Representative Flywheel Energy Storage Module



Approach to improving composites



Weak links are the resin and resin/CF interface.
Examine methods to:

- 1.) Increase resin strength
- 2.) Decrease water uptake in resin
- 3.) Increase interfacial resin-carbon fiber strength

Need to be mindful of amount material needed:

EPON Dogbones → gram scale

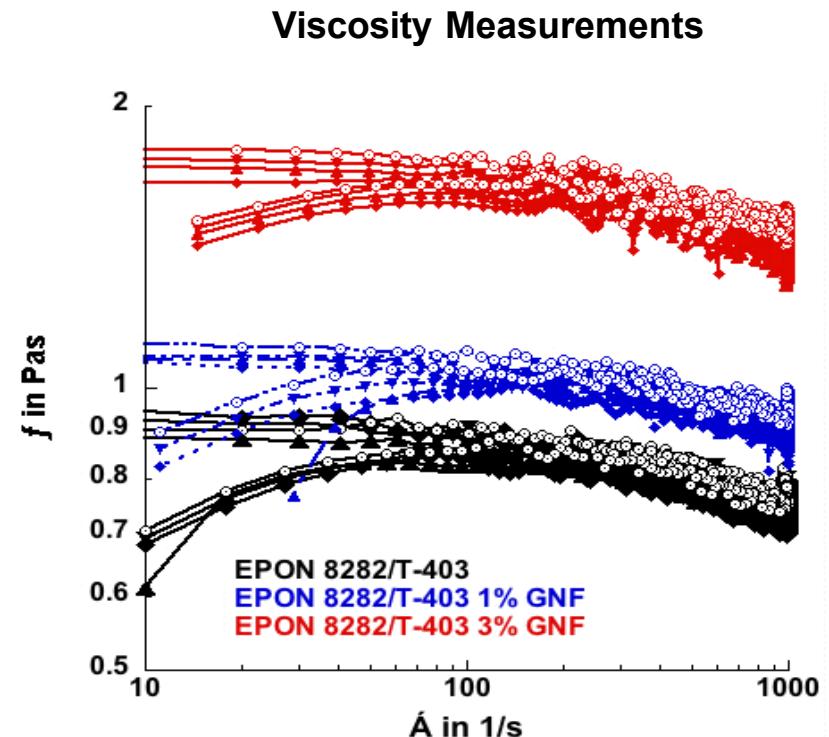
EPON/CF Arc samples → 100-200 gram scale

EPON/CF FLYWHEEL Prototype → 5 kg per wheel

Graphene/EPON828/T-403

Initial Approach:

- Mix Graphene with T-403 via sonication
- Mix with EPON 828 with hand mixing
- De-gas under vacuum (~ 30 min to 2 h)
- Pour into mold (coupons) or resin bath (test parts)



- Minimal increase in viscosity with addition of GNF
- Decrease with higher shear rate suggests plate alignment

Coupons Testing w/ LDV – Graphene/EPON828/T-403

Laser Doppler Vibrometry:

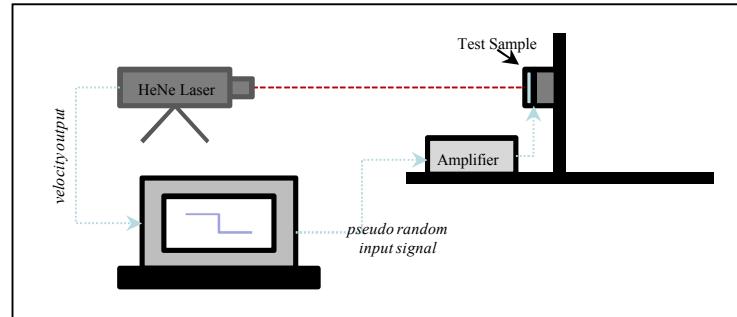
- Method for mechanical testing
- Mold-cast EPON/GNF coupons
- Sputtered Au/Pd on surface to establish reflectivity of sample
- Parts mounted on piezoelectric shaker and HeNe Laser used to measure dynamic response of the “part” Modulus of Elasticity computed w/ Blevin’s closed-form approximation from 1st bending mode frequency.
- Consistent mounting of parts is required to achieve low standard deviation (new holder solves this issue)
- Useful for studying smaller coupons (i.e., less material)

Increase in modulus w/ GNF

Sample	Modulus (GPa)	% Increase
EPON	2.09	NA
8-G (1%)	2.38	14%
RGO (1%)	2.83	35%

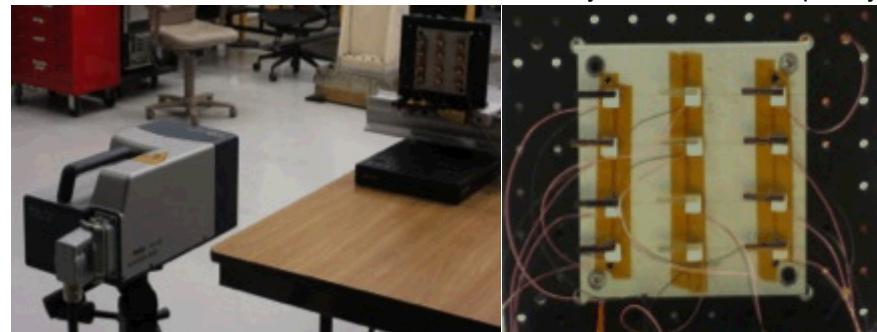
Blevins, Robert D. 1979 *Formulas for natural frequency and mode shape*.
Van Nostrand Reinhold Co., New York, NY.

Experimental Schematic of LDV (Jill Blecke – SNL)

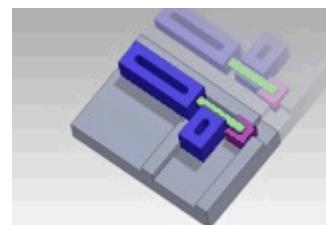


$$E = \frac{m}{I} \left(\frac{2\pi f_i L^2}{\lambda_i^2} \right)^2$$

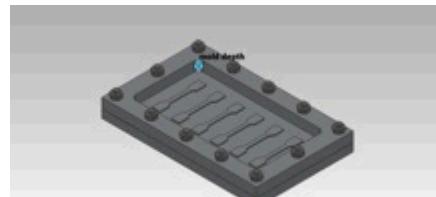
Blevin's Equation For Modulus of Elasticity
 L , beam length; M , mass/length of beam; I , moment of inertia; λ , boundary coefficient; f , frequency



LDV test is sensitive to mounting of sample: new “jig”



New mold to prepare “dogbones” –pull test vs LDV



Building of Parts – Graphene/EPON828/T-403



CF/Resin(GNF) Part Manufacture:

- Parts were fabricated in the Mechanical Fabrication and Support Area in the National Secure Manufacturing Center at the Kansas City Plant.
- Filament winding took place on a 6-Axis McClean-Anderson winder.
- Parts were oven cured on a rotating cart for 24 hours at 158 ° F.
- Mandrel designed/fabricated to spec
- Mandrel was cryogenically shrunk after being removed from oven, allowing part to easily slide off.



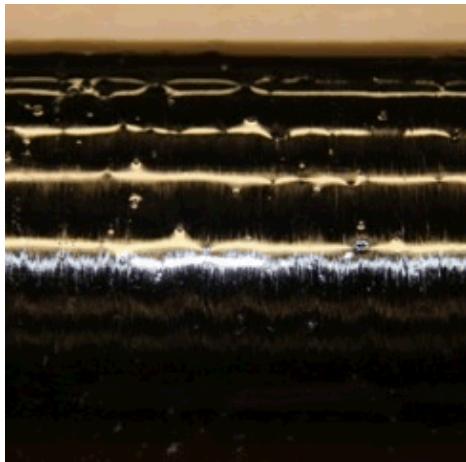
Part Manufacture:

- 4 Simultaneous Tow, no change in angle (resulting in overlap of 3 tow)
- Part Dimensions:
4' long, 4" ID, ~ $\frac{1}{4}$ " (6.35 mm),
78% Fiber Mass Fraction

Prepared 0%, 1% and 3% GNF Parts

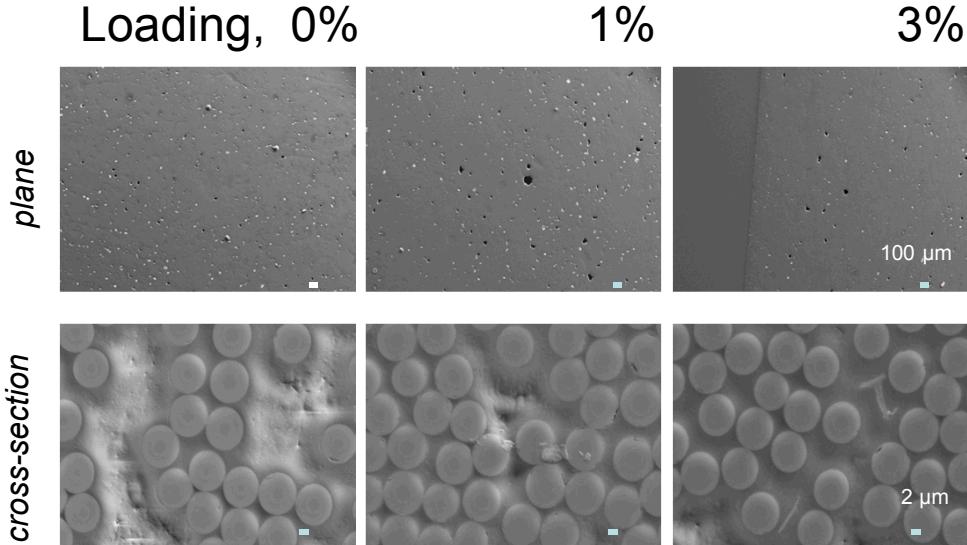
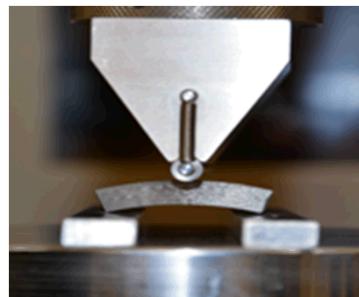
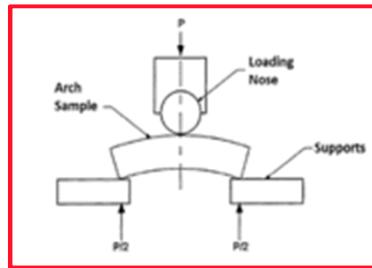
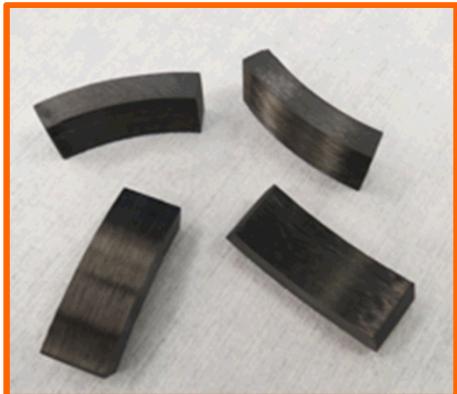
(Current parts are being manufactured with Carleton/Cobham)

Testing of Parts– Graphene/EPON828/T-403

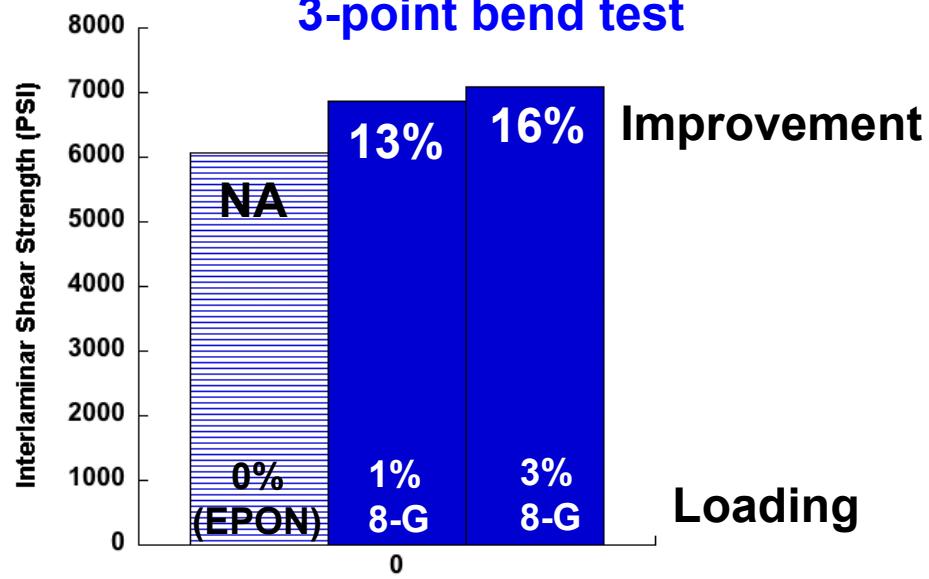


- Parts have visible bubbles on outside.
- Lathe cleaned to ensure good 3-point bend test.
- Should not effect strength just part balancing.

Test samples



3-point bend test



Summary of EPON828/T-403/CF/GNF



Sandia
National
Laboratories

- **“Large scale” samples successfully prepared, shipped, and wound**
No major changes to manufacturing process needed
- **Characterization of sample parts undertaken**
Data suggests not complete dispersion of Graphene in composite
Surface defects dependent on the filler type used – no degas used for wound part with 8-G
- **Improvement observed despite little process optimization**
Young’s Modulus for EPON828/T-403/1%G: $\geq 14\%$ (8-G) or $\geq 35\%$ (RGO)
Inter-laminar Strength \uparrow for EPON828/T-403/T700CF $\sim 15\%$ (3% 8-G)
- **Economic Cost Analysis**
Still need analysis on cost of graphene but performance based analysis indicates that the economics of flywheel-based energy storage could potentially be improved by a factor of 3 or more. (SNL, Mark Ehlen)

What about a flywheel ?



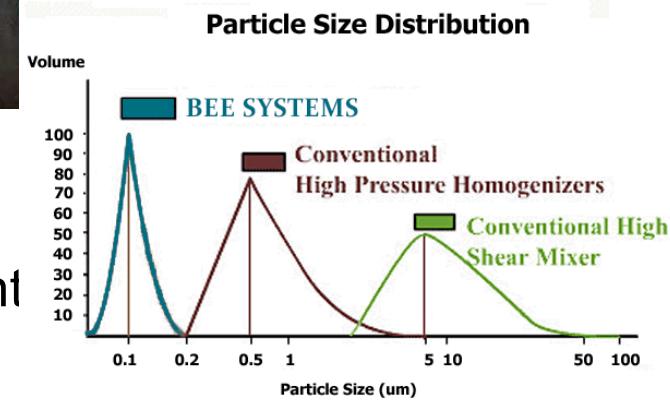
- **Need controlled, optimized blending protocol**
Bee International High Pressure Homogenizer
Initial Process parameters ✓ – needs refinement

- **Need to improve CF/resin interface**
Acoustic Emission Testing initiated

- **Need to (ideally) analyze number of filler types to used optimized material – ultimately look at surface functionalities**

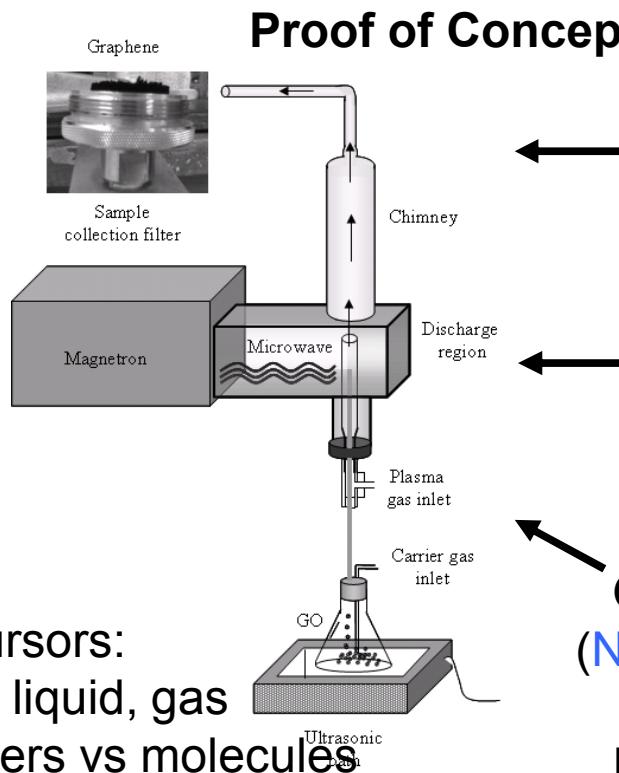
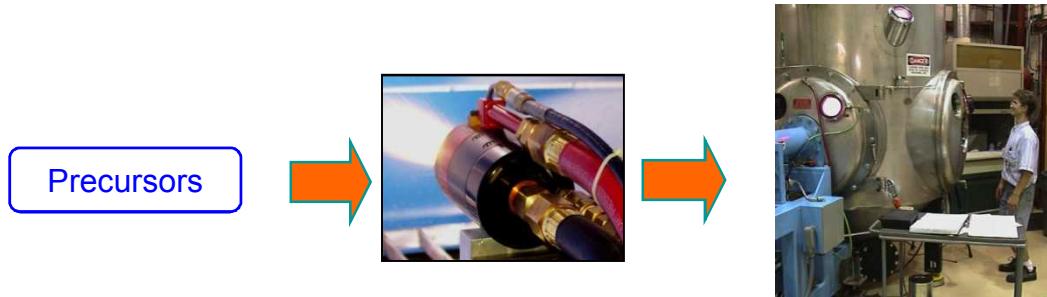
5 kg of “graphene”
95 kg of total resin

} Per flywheel (*For now using commercial material*)



BEE International High Pressure Homogenizers
for a tight distribution of smaller particles

Plasma Processing of Graphite Oxide



secondary gas (reactive)

Time: 0.1 sec

Temp: Variable ~ 2500-15,000 °C

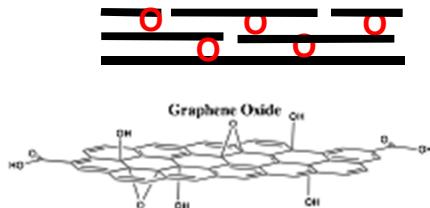
Energy: (500 W to 100 kW)

Gas: Reactive (NH_3) vs. Passive Oxidizing, Reducing (H_2)

T. N. Lambert *et al.* *Carbon* 2010 48, 4081-4089

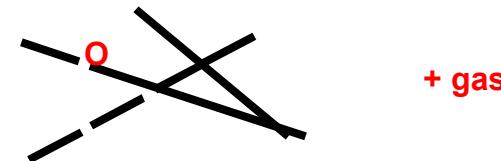
Plasma Processing of Graphite Oxide

Graphite oxide (GO)



Thermal
exfoliation and
reduction

Established
mechanism

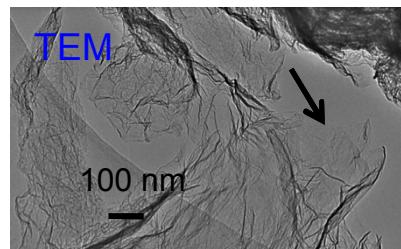


Graphene or Plasma reduced graphene oxide (PRGO)

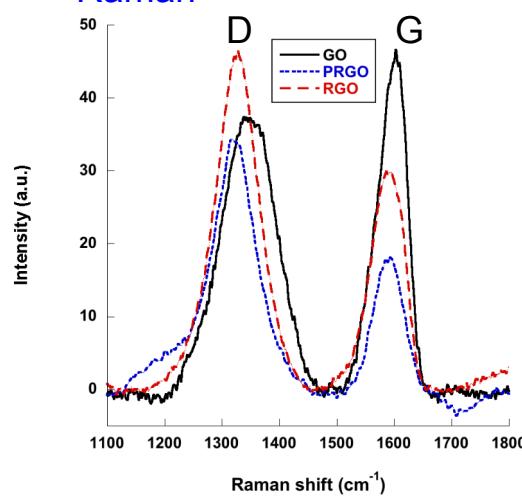
Surface Area $\sim 650 \text{ m}^2/\text{g}$

sheets $\sim 3\text{-}4$

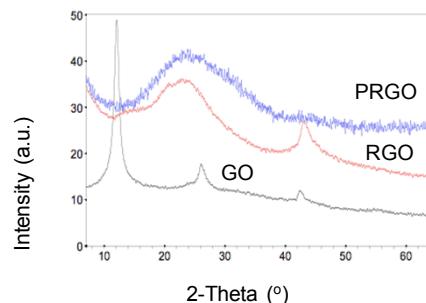
2-4% oxygen



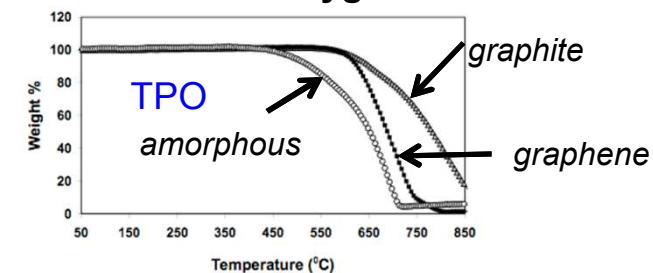
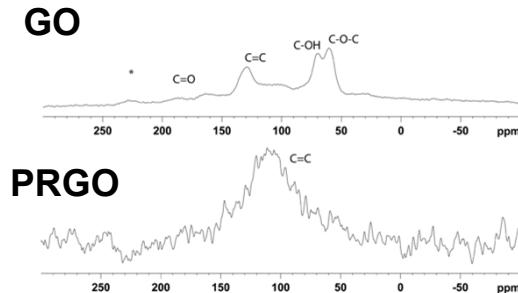
Raman $I_D/I_G = 1.8$



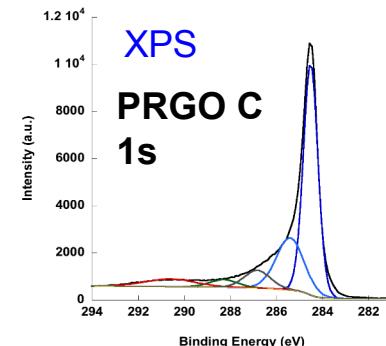
PXRD



NMR



XPS PRGO C 1s



What about a Flywheel ?

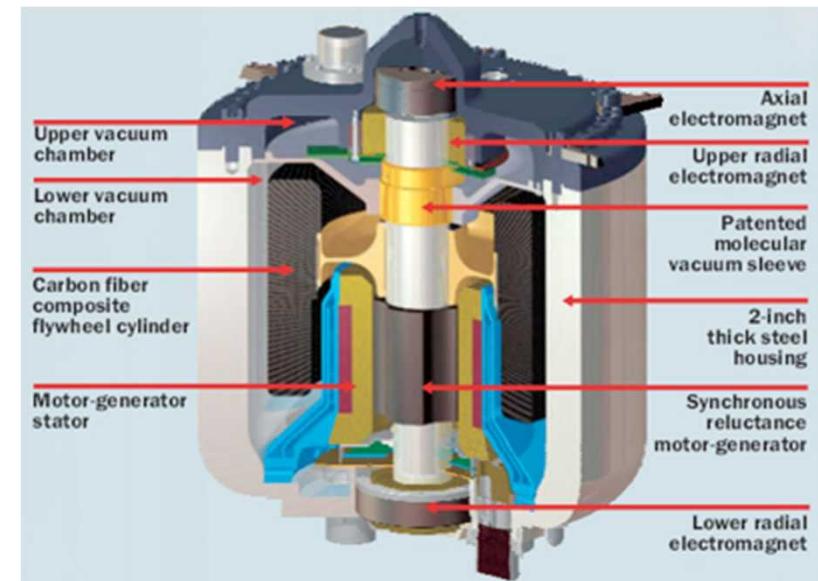
PowerThru formed in 2010 from Pentadyne
Power Corporation/ Beaver Aerospace and Defense.



POWERTHRU designs and manufactures advanced flywheel energy storage systems that provide ride-through power and voltage stabilization for power quality and power recycling applications. Designed to provide high-power output and energy storage in a compact, self-contained package.

POWERTHRU flywheel products are a long-lasting, low-maintenance, lightweight, and environmentally-sound alternative to flooded and valve regulated lead-acid (VRLA) batteries in uninterruptible power supply (UPS) systems. POWERTHRU products are developed for commercial application and not home use.

POWERTHRU shipped its first commercial production flywheel in 2004, and continues to provide award-winning flywheel products to critical applications around the world. Flywheels are built in Michigan (seismic Zone 4 rated).



3-way NDA in place. Benefits to all involved are anticipated for the Carleton/Cobham, PowerThru, Sandia, and OE Collaboration.



- Selected C/C due to experience with Beacon processes
- PowerThru selected due to smaller sized flywheels (PoC)

Carleton/Cobham

- Develops a process for winding nano-loaded flywheels

PowerThru

- Improved flywheels
- Comparative analysis of flywheel produced using a different resin system
- New Tech Develop with NW usage

Sandia

- Lab scale idea implemented
- Another happy customer

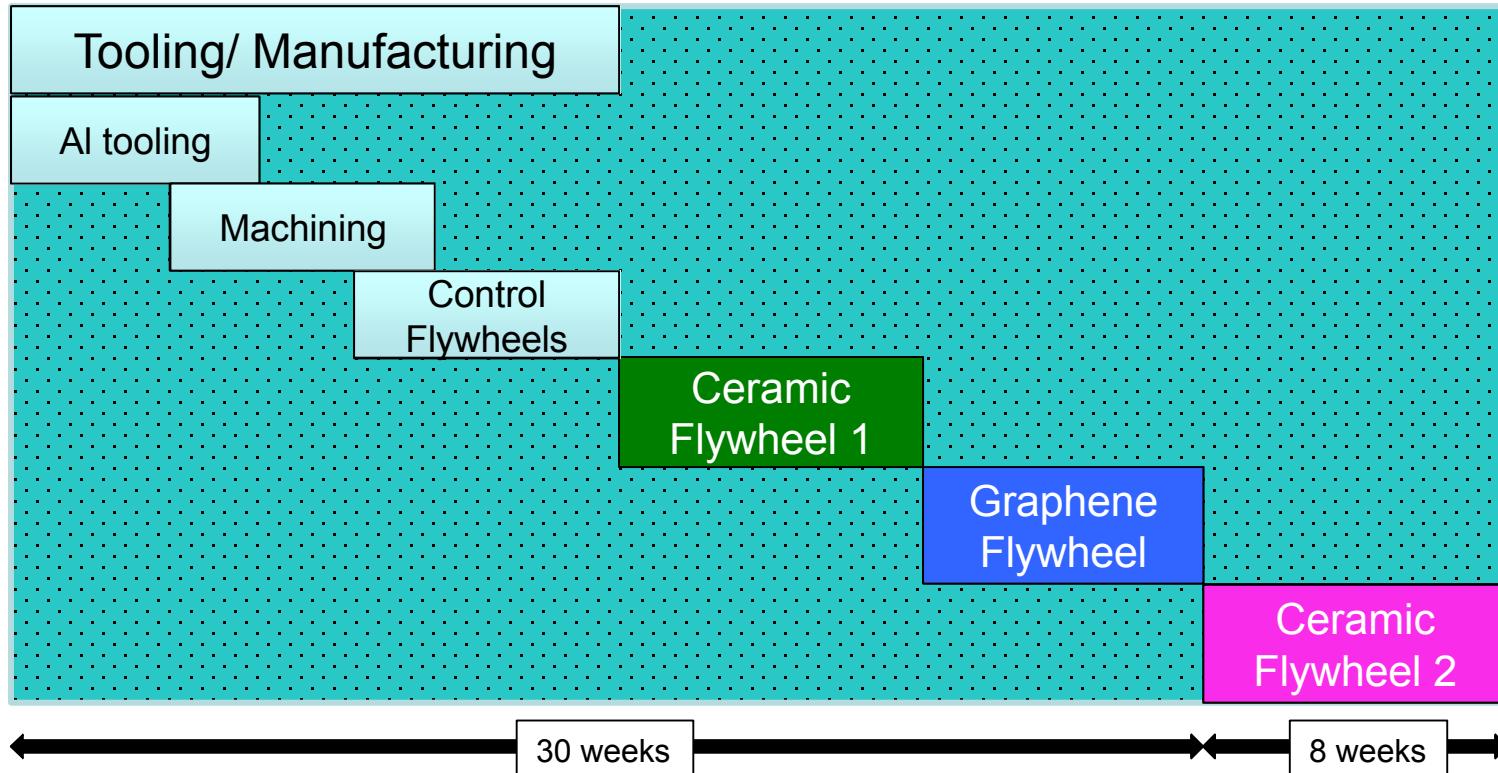
EERE/OE

- Reliable electricity for grid
- Tech Transfer: TRL 1 to ~7
- US jobs

If nano-loaded flywheels provide improved performance:

- PowerThru will have the ability to improve their commercial and defense related UPS product
- C/C will have developed a new capability outside of their current manufacturing scope
- New job potential as C/C may assume overseas manufacturing of flywheels; incorporation of nano-wires into an existing composite product can provide an overarching effect for other technologies
- Product viability provides stepping stone for incorporation into larger grid-based flywheel systems.

Timeline for flywheel production determined and initiated.



16 weeks to produce the first unfilled flywheel (includes)

- Manufacturing aluminum tooling to wind rim parts
- Time for machining filament wound rim parts
- Manufacturing time for aluminum tooling to press hub into rim

~ 8 weeks to produce each flywheel

Marine Hydrokinetic Applications

Sandia's Water Power Technologies Advanced Materials Program: SNL contact: Bernadette Hernandez-Sanchez

Applied Research program:



Industrial Guidance

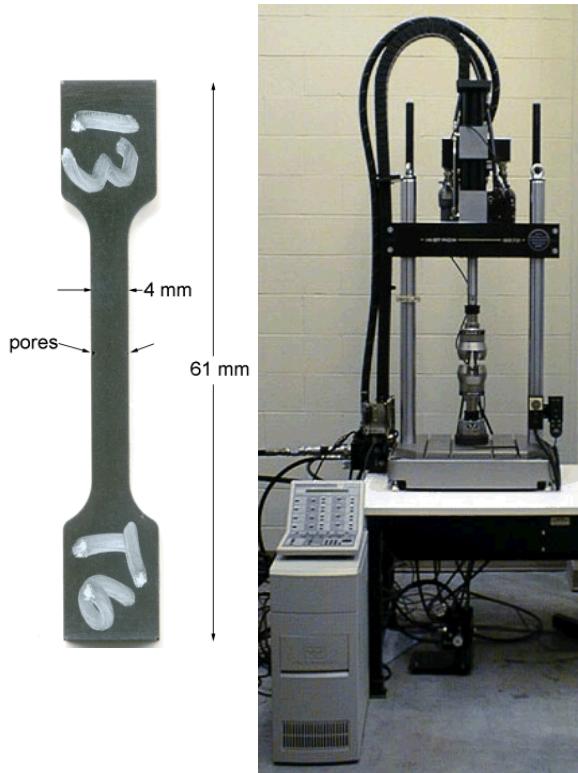
Technology Transfer

Novel Materials & Coatings

Our Small effort:

- Can incorporation of graphene reduce water uptake in composite materials ?
- Establish and obtain dogbone tensile testing – improve mechanical properties ?

Dogbone Testing at MSU



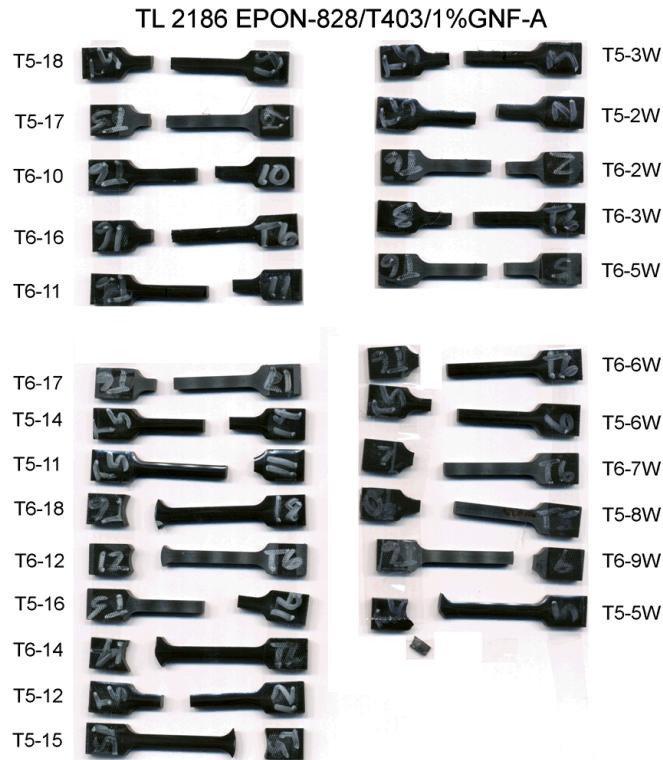
Instron 8872

*Alignment, calibration etc. followed:
ASTM standards E4, E74, E83, E251, E3039.*

Clamping pressures
< 2 MPa to reduce grip area failures

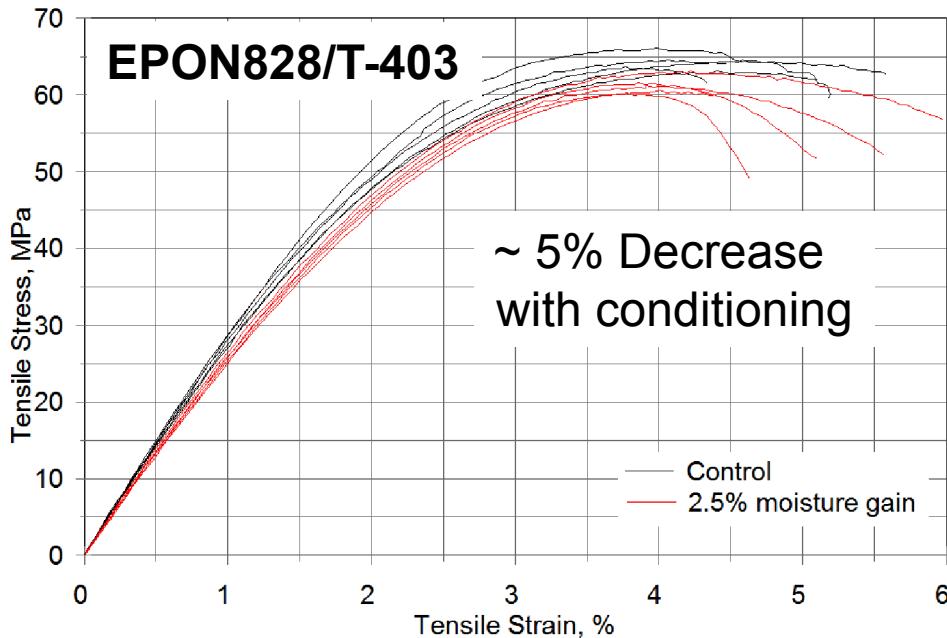
Tests:
22 to 24 °C, 23 - 50%
relative humidity,
samples air cooled

Static and Fatigue tests



Water uptake in EPON

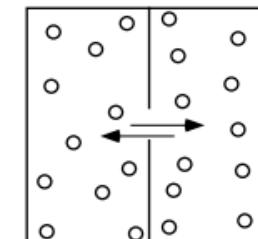
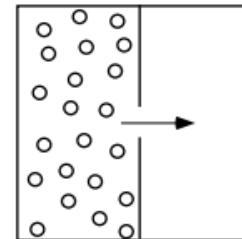
Water uptake in composites is known to be detrimental



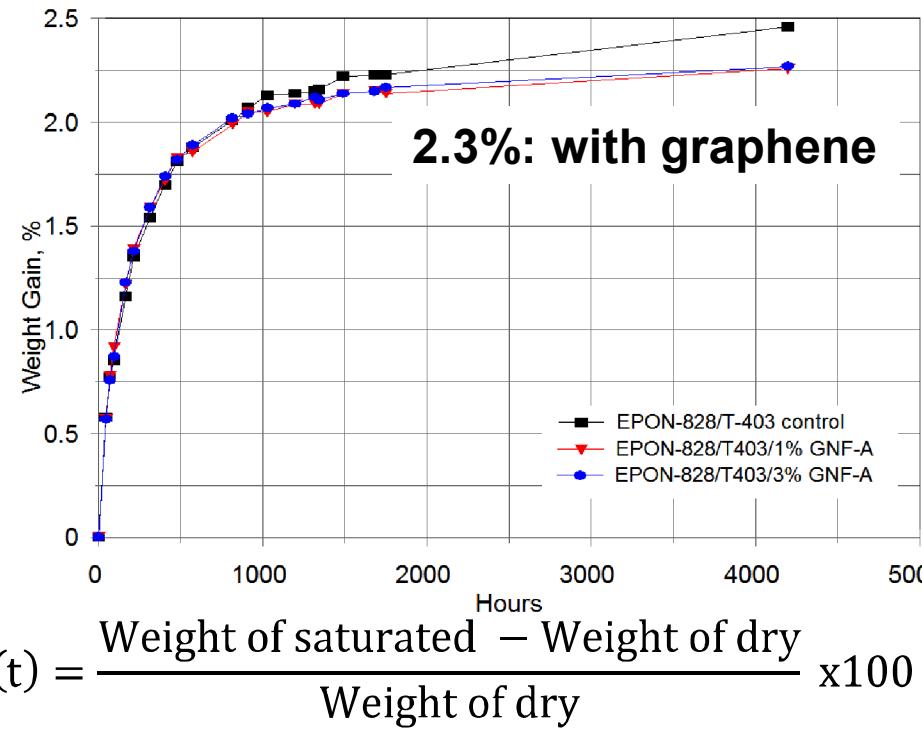
Water uptake decreases Strength

Graphene results in ~ 8% decrease in water uptake in EPON 828

Moisture saturation in 50 °C

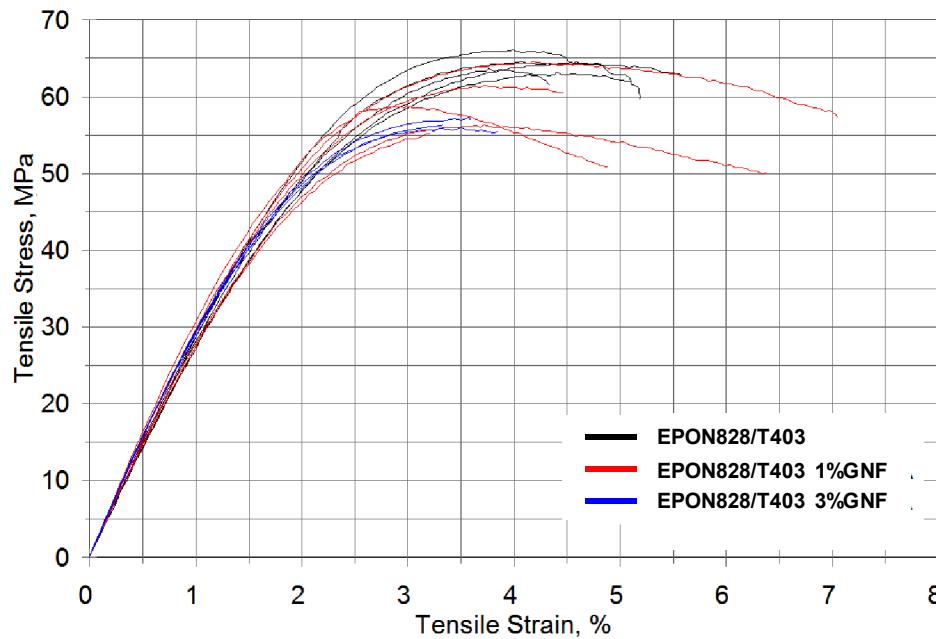


2.5%: EPON828/T-403

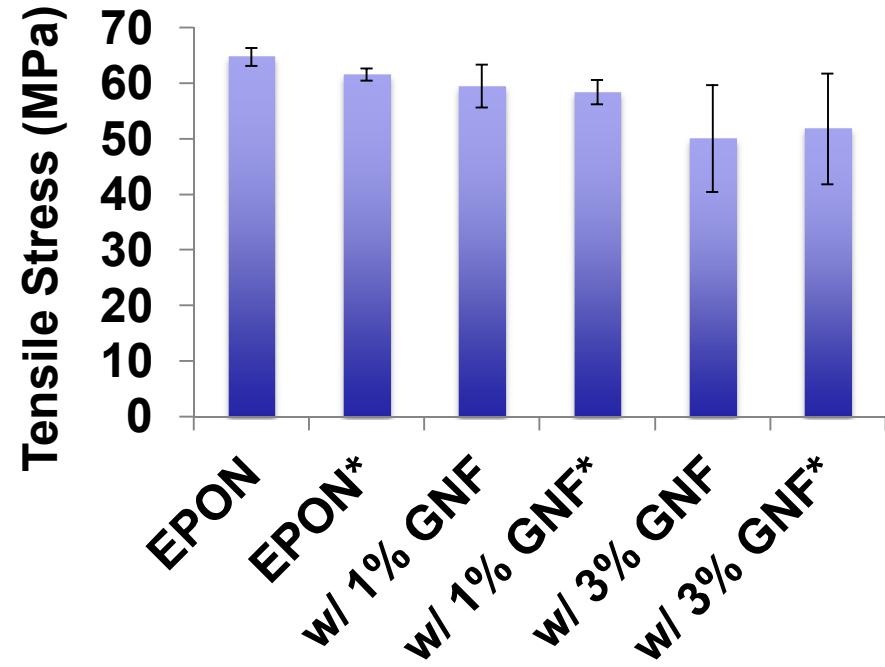


Mechanical Testing

Stress-strain curves



Ultimate Stress

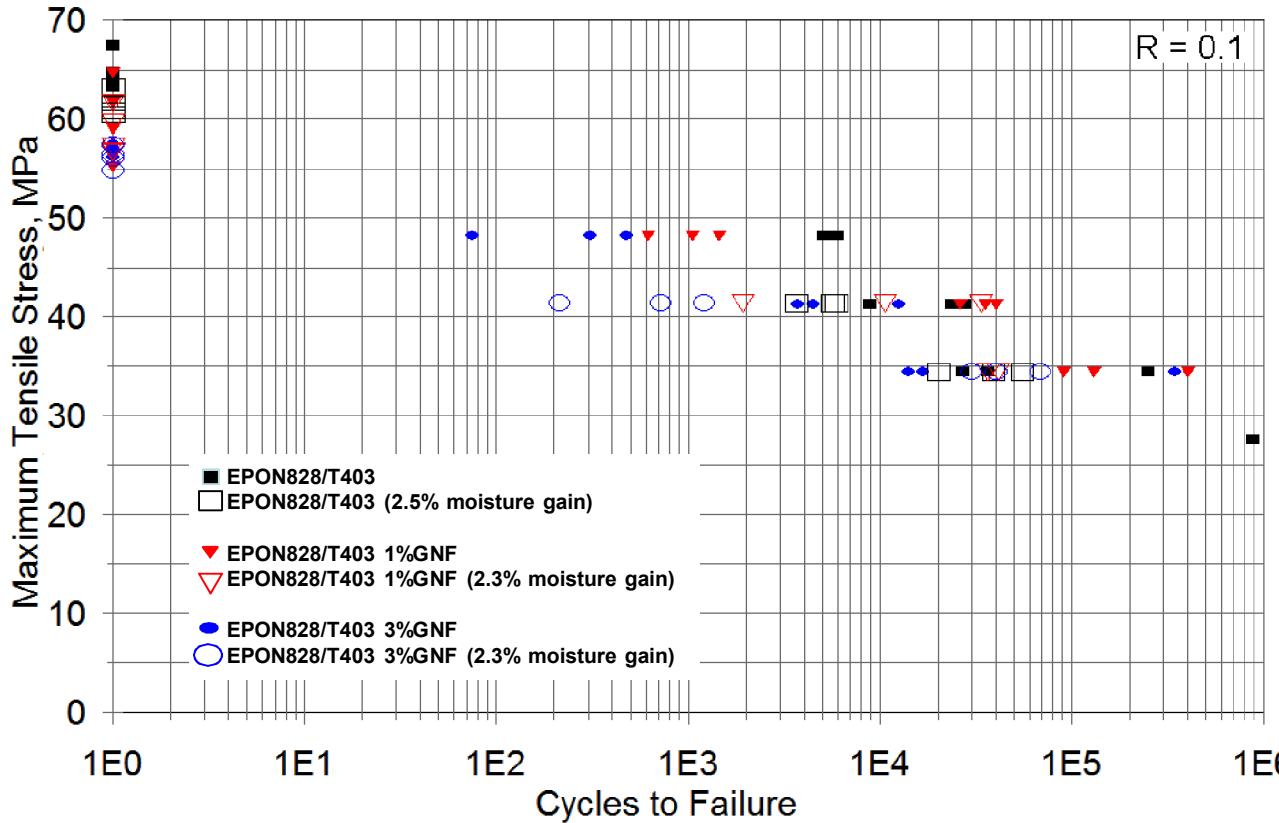


Defect driven results observed for 8-G Dogbones

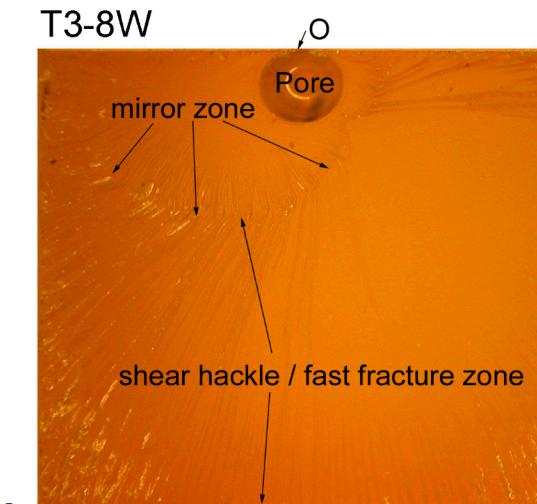
Larger Standard Deviations observed, Some visible pores, degas not complete with GNF, visible aggregation of GNF observed on surface → Need better dispersion methods or use different filler type.

Fatigue Testing

Fatigue test results for all test cases with known pore coupons removed.



Brittle transverse crack growth leads to failure



Results consistent with Ultimate Strength tests – defect driven.

Summary of MHK Test Samples



- **Inclusion of Graphene lowers water uptake**
Would expect better mechanical properties after water saturation
- **Results on dog-bones were defect driven**
Voids consistent with air bubbles in Flywheel parts
Better degas mixing required
- **Dogbones and Acoustic Testing**
Will allow for commercial and custom graphene samples to be screened

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Program Manager – Drs. Jim Alghrim and Ryan Sun Chee Fore

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END