November 2, 2010

Update on:

Improved Properties of Nanocomposites for Flywheel Applications

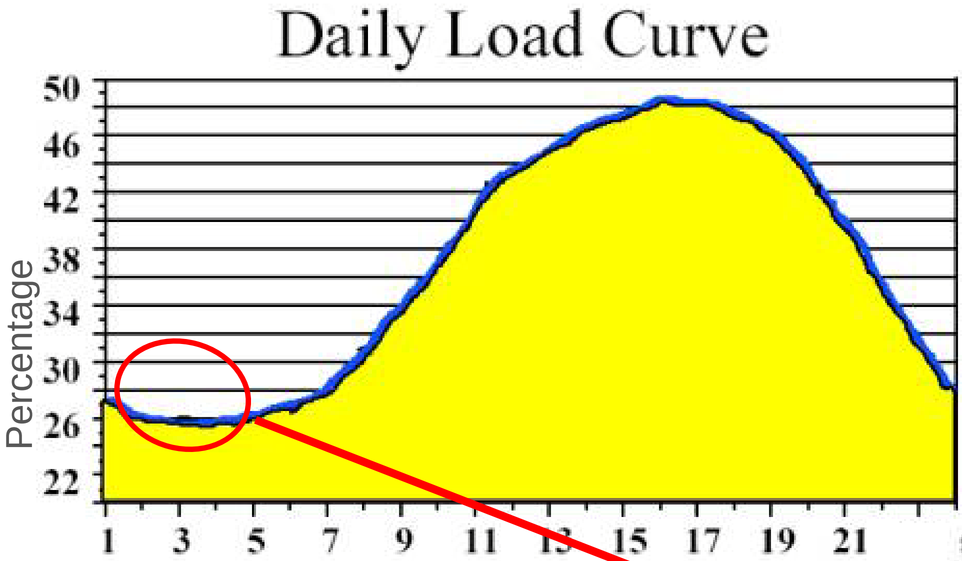
Timothy J. Boyle (1815), Mathias C. Celina (1821),
Nelson S. Bell (1816), Benjamin J. Anderson (1833)

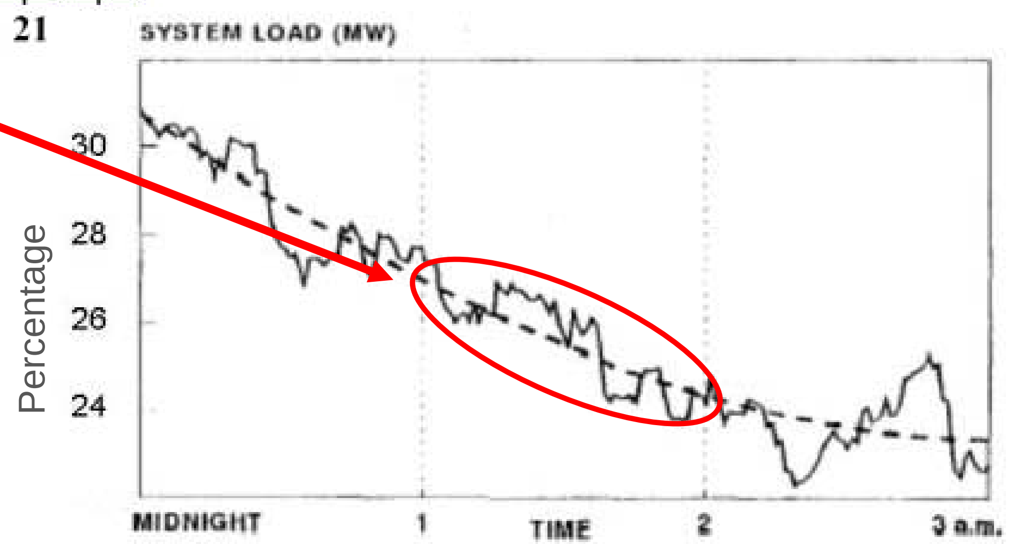
Sandia National Laboratories
Advanced Materials Laboratory
1001 University Boulevard SE
Albuquerque, New Mexico 87106
(505)272-7625
(505)272-7336
tjboyle@Sandia.gov

Funded by the Energy Storage Systems Program of the U.S. Department Of Energy through Sandia National Laboratories

This work was supported by the Office of Electricity of the Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

Optimal AC grid usage requires accurate, rapid, and continuous adjustments (frequency regulation) of power pulses.

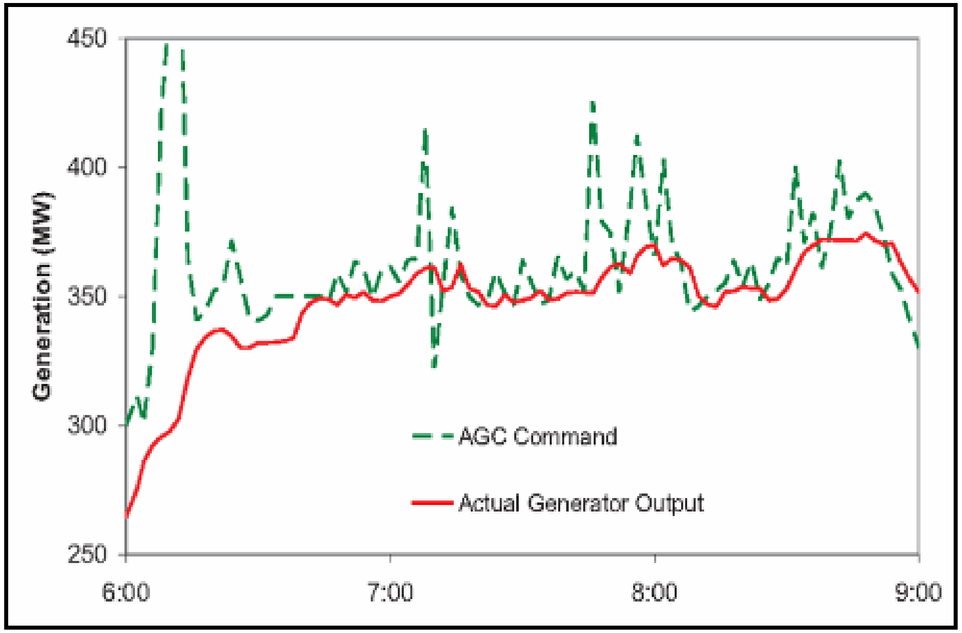




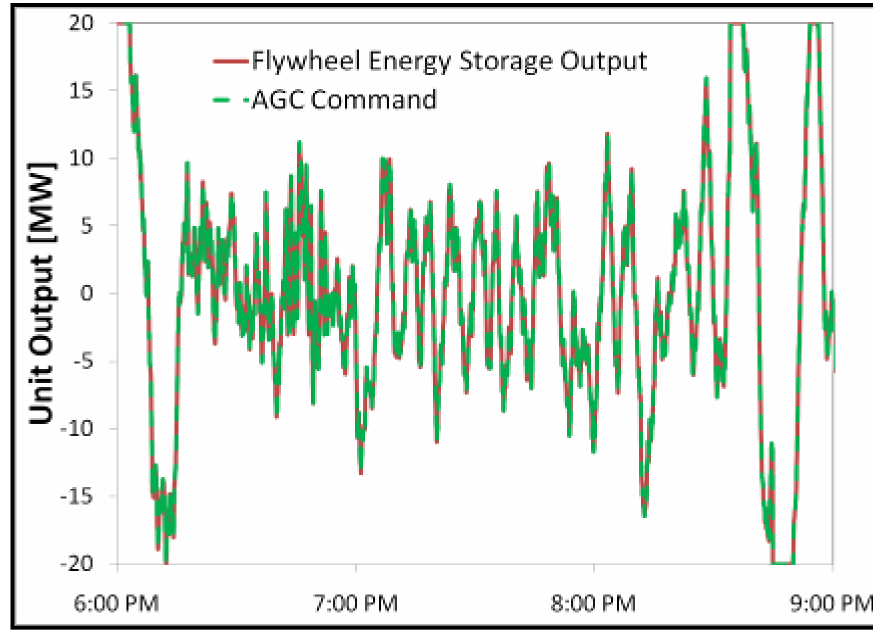
The current energy "regulation profile" is complex with demanding, small, time energy perturbations, which will be magnified upon introduction of alternative energies.

In order to maintain efficiencies, speed is necessary.

A coal-fired power plant poorly following a regulation command signal



A 20 MW flywheel energy storage resource accurately following a signal

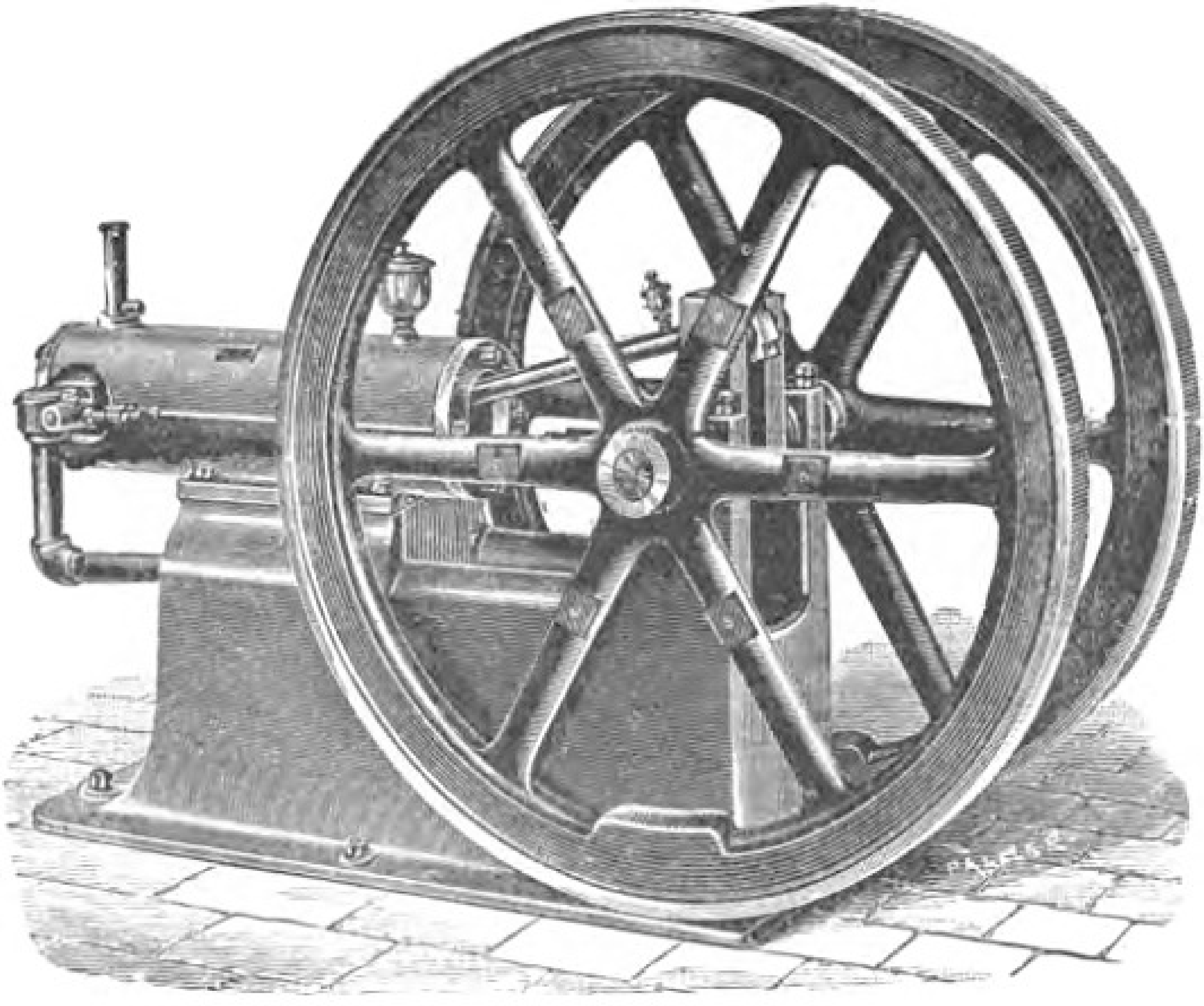


Flywheels provide "near instantaneous" response

- Zero direct carbon emissions
- 85% system efficiency at transformer
- Zero storage degradation
- 20-year design life > 150,000 100% DoD charge / discharge cycles

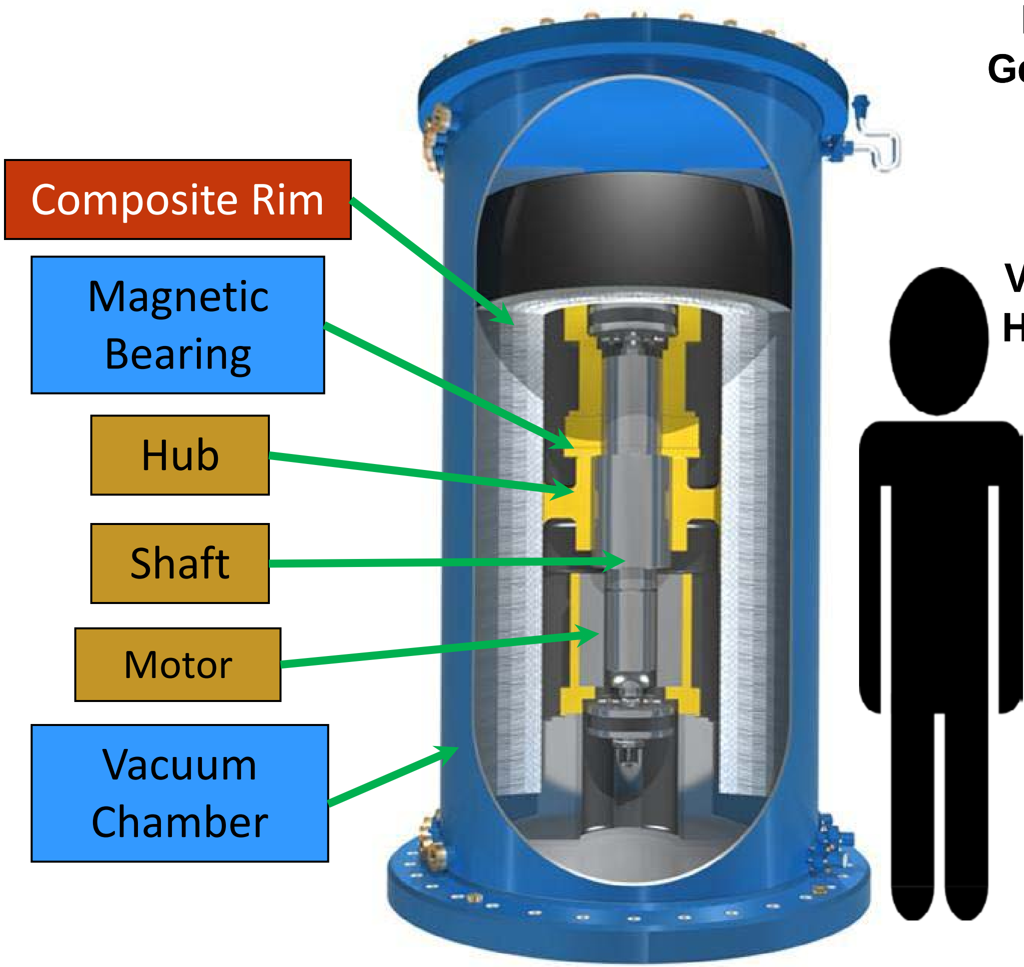
- Faster, more effective than conventional generation
  - Up to 100x faster than a traditional generator
- Available separately – without generation
- Low operating cost (no fuel)
  - Displaces higher cost deployments of traditional generators
  - Could reduce CO_2 emissions by 80 % (KEMA study)

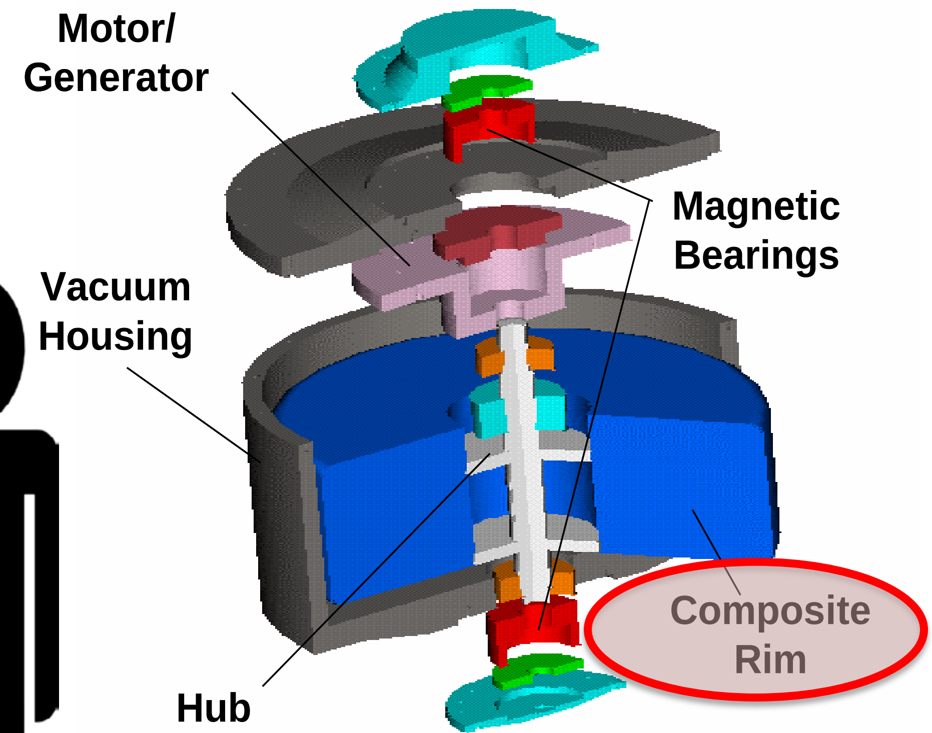
What is a flywheel?



1898 illustration of a White and Middleton stationary engine; note the large twin flywheels.

Flywheels have become much more advanced, requiring complex composite rim materials to maximize efficiency

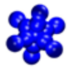




kWh/$

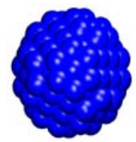
All flywheels have similar issues – the 'need for speed' - kills!

The main focus of this project is optimization the rim materials to allow for increased flywheel performance

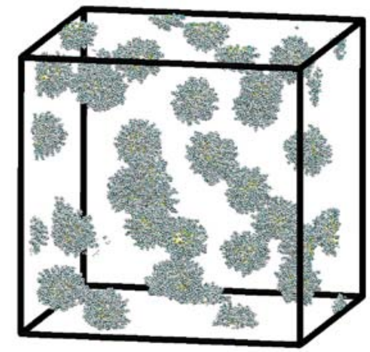


Approach: incorporation of nanomaterials into rim composite to improve flywheel performance.

Improve conductivity
Impact strength
Storage modulus,



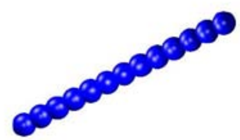
Wear resistance
Optical properties
Fracture toughness

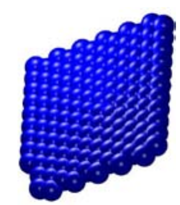


32 coated nano particles in decane (not shown)

Modification of matrices' physical properties by nanofillers is controlled by 4 phenomena:

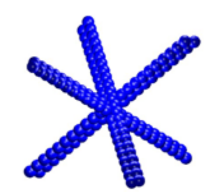
(I) Hydrodynamic effects,
(II) Occluded polymer effects,
(III) Bound polymer effects,
(IV) Interaggregate attraction.





The filler properties can be manipulated by 3 primary components of the nanoparticle which relate to its performance in a matrix:

(I) Surface area (related to size and aggregation),
(II) Filler surface energy,
(III) Filler structure in the matrix.

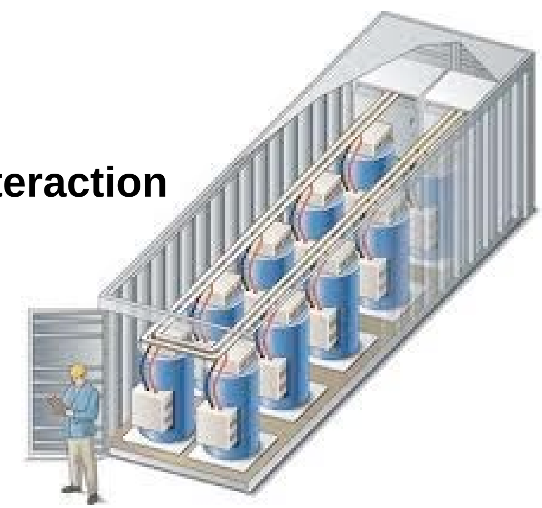


Approach based on defining 'state-of-the-art' system and elucidating nanoparticle fillers effects

- Characterize/evaluate existing high quality flywheel materials
  - (a) Existing operating material to establish baseline
  - (b) Evaluate different resins
  - (c) Evaluate nanoparticle effects on resins
  - (d) Evaluate nanoparticle effects on fibers

- Measure and optimize resin processes
  - (a) Cure kinetics determination
  - (b) Monitoring of cure chemistry

- Nanoparticle syntheses/selection
  - (a) Size
  - (b) Shape
  - (c) Phase
  - (d) Functionalization



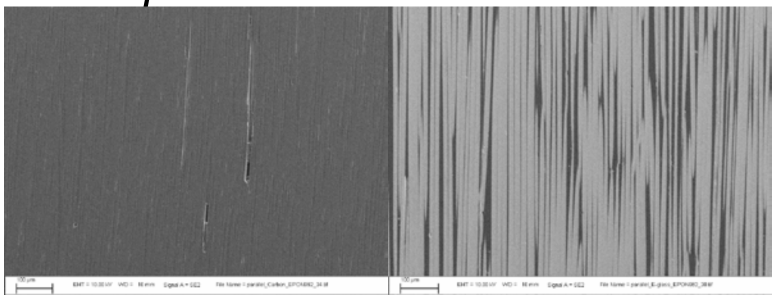
- Characterize/optimize nanoparticles/matrix interaction
  - (a) Surface charge
  - (b) Rheology
  - (c) Viscosity

- Feedback loop

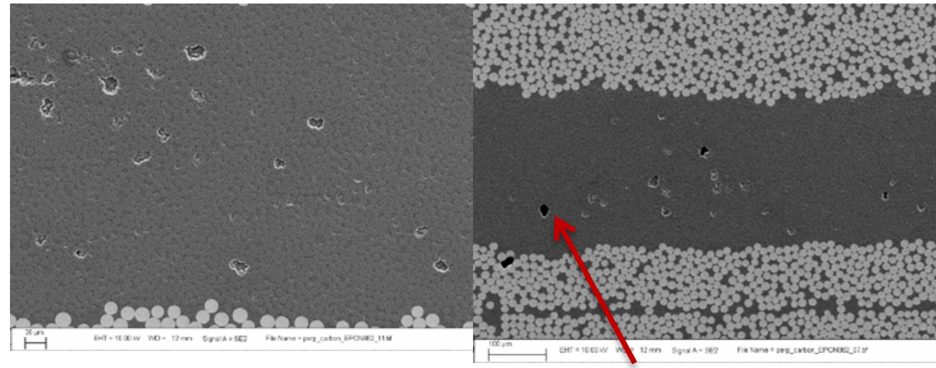
Transverse failures are observed at higher spin speeds in current flywheel materials

- Inner Ring

Hoop x-section



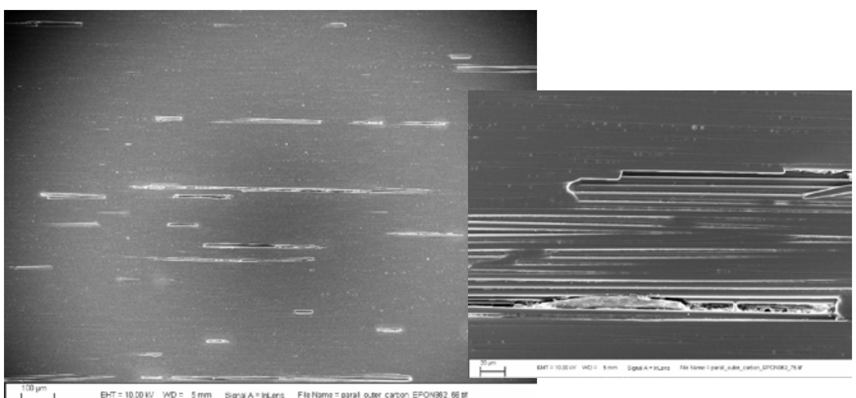
Radial x-section



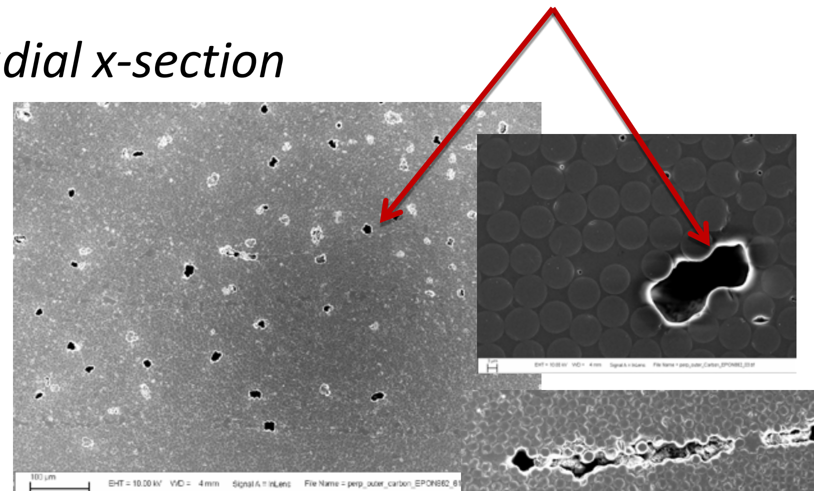
- Outer Ring

Voids

Hoop x-section

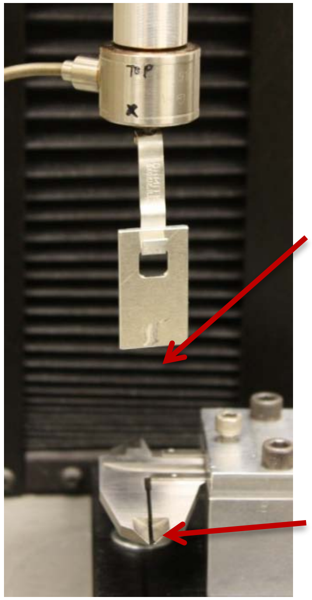


Radial x-section



SEM images reveal 'void' formation occurring in both the inner and outer rims

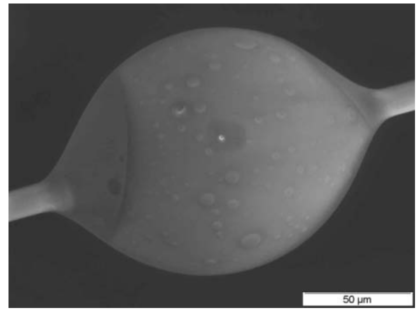
Microdroplet test of the epoxy/ E- glass fiber adhesion strength undertaken



Fiber w/ microdroplet

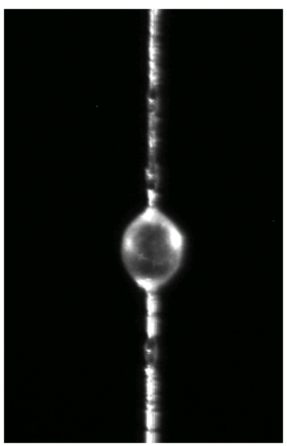
Microdroplet de-bonded by calipers

Epoxy Microdroplet



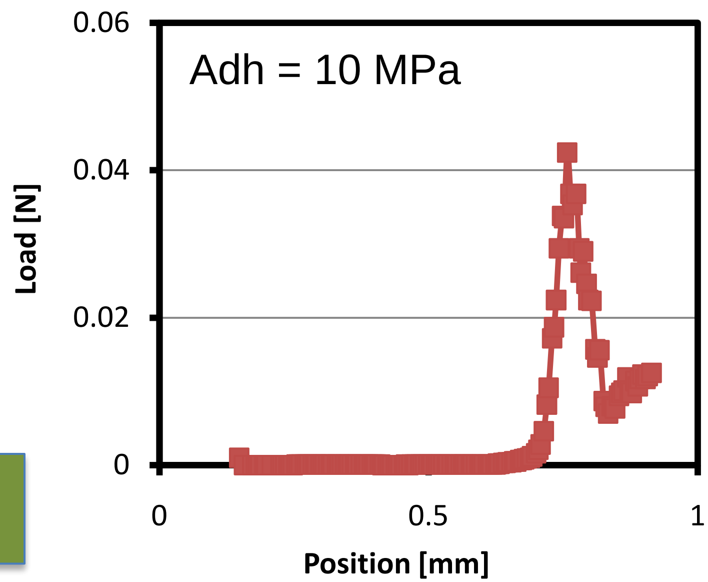
on E-glass fiber

Ultimate strength of adhesion found to depend on the cure schedule:
Droplets cured to 150 ^{o}C have 5x higher adhesion strength

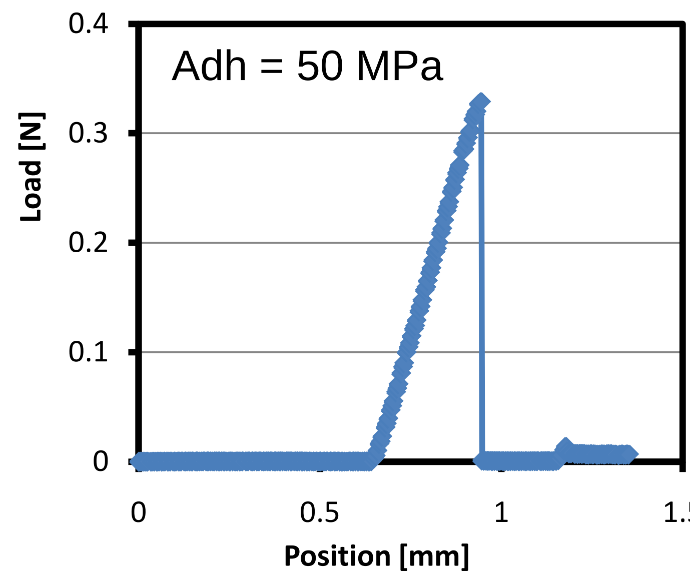


$$\text{Adh} = \frac{\text{Force}}{\text{Interfacial Area}}$$

100 ^{o}C max cure

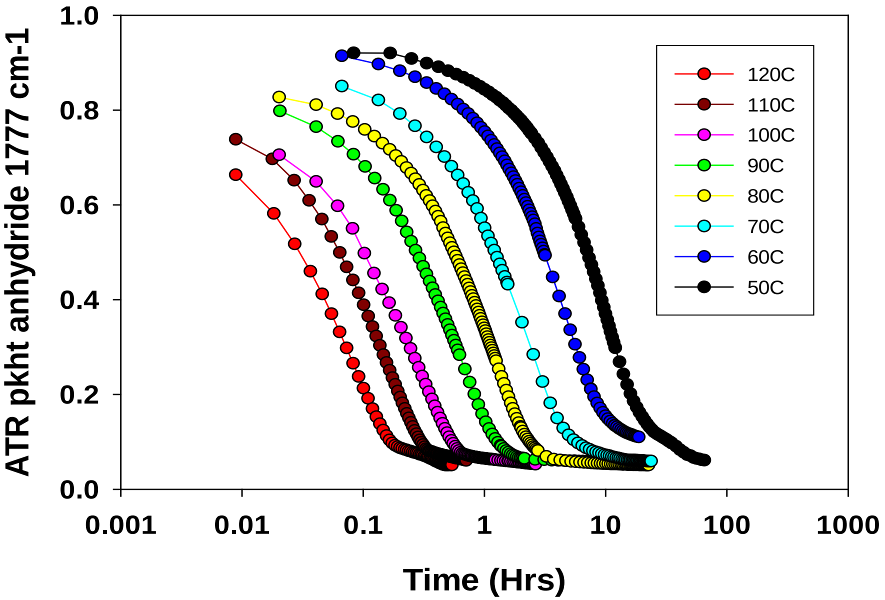


150 ^{o}C max cure

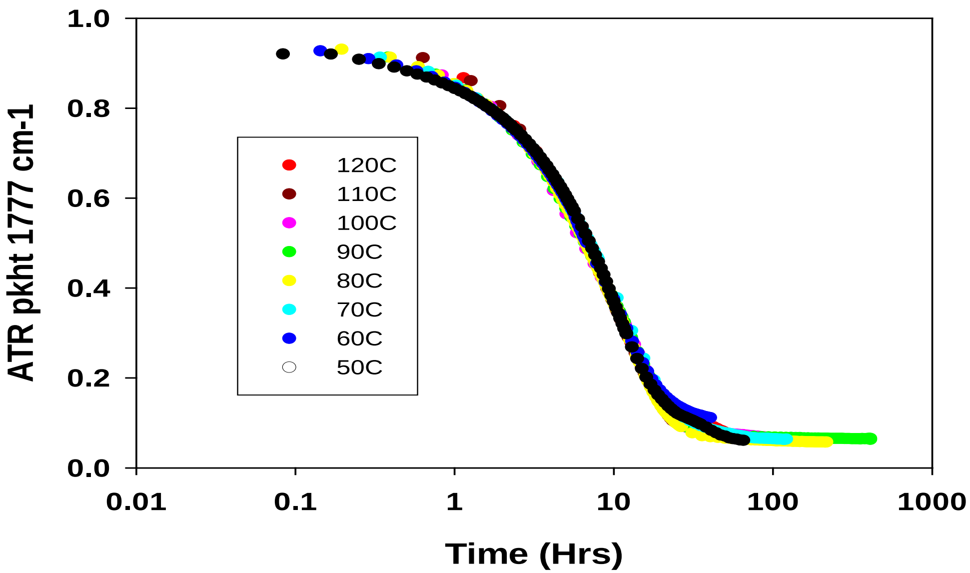


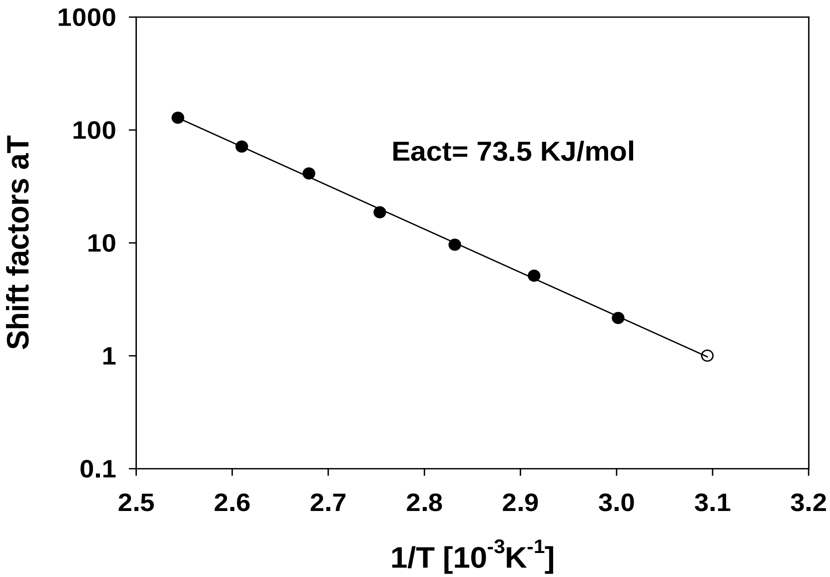
Isothermal cure kinetics of the anhydride epoxy reaction realized from IR spectroscopy measurements

- Cure chemistry as a function of time (t) and temperature (T)
- Correlation with cure viscosity
- Use data as model input for autocatalytic behavior

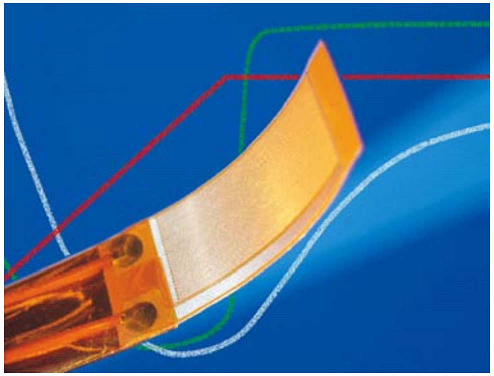


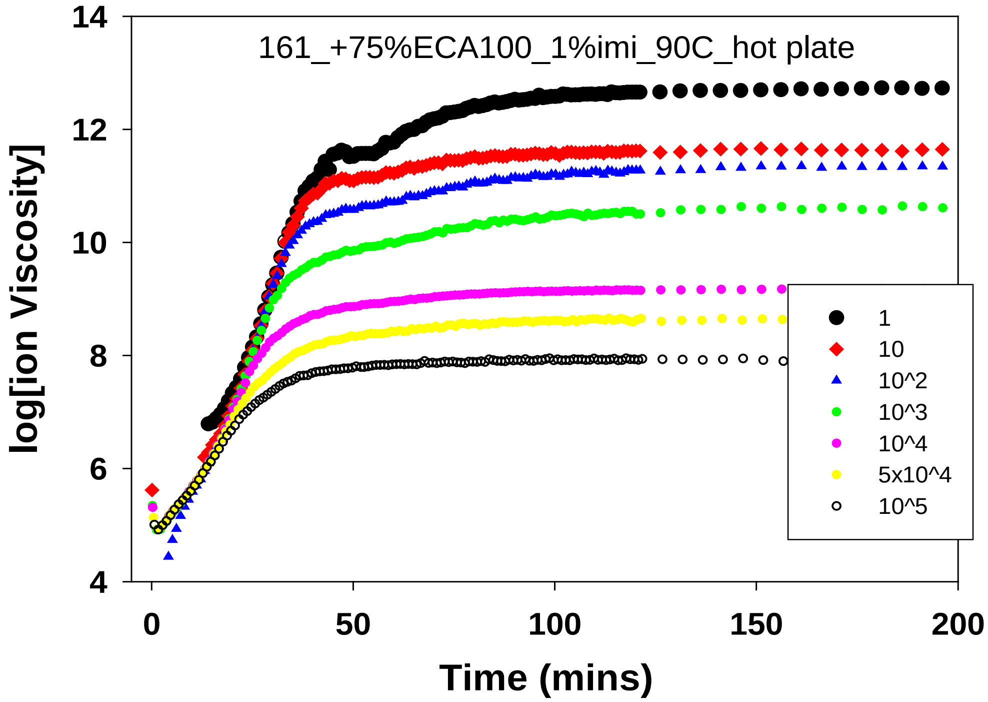
Epon862:LSK81 = 1:1 system





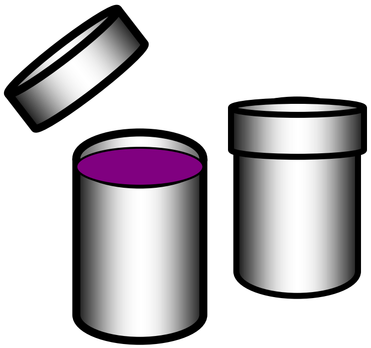
Cure viscosity monitoring using dielectric analysis and its correlation with cure chemistry





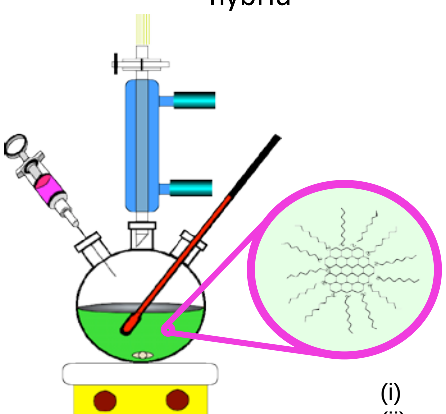
- Interdigitated electrodes detect cure state via dielectric loss spectroscopy
- Remote sensing of cure conversion as a function of time (t) and temperature (T)
- Correlation with cure chemistry and rheology
- Input for 3D models linking evolution of chemistry and physical properties

Ceramic nanoparticles selected as filler based on multiple intrinsic characteristics/properties

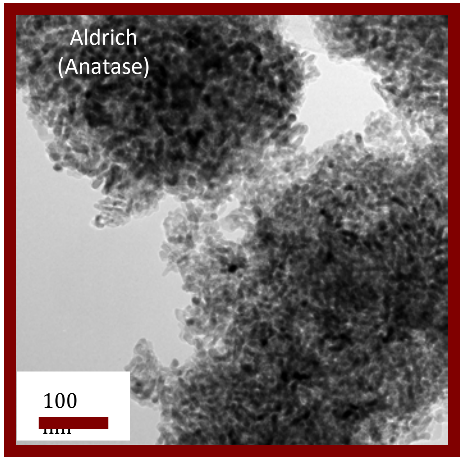


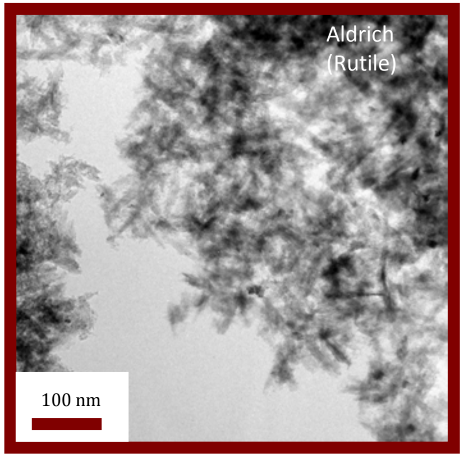
solvothermal

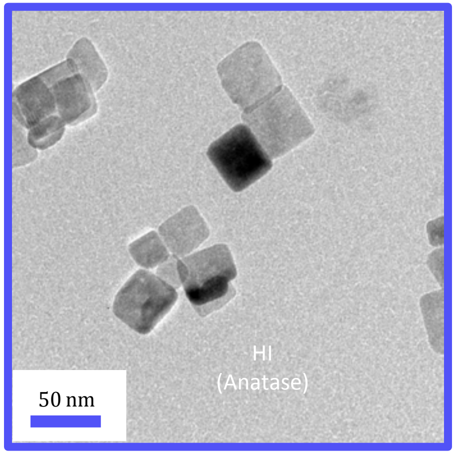
hybrid

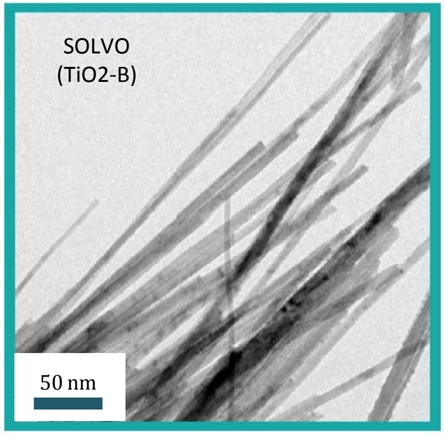


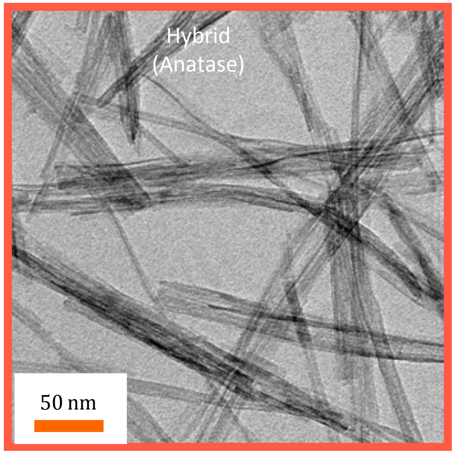
Solution precipitation











(i) Sarwar et al. *J. Sol-Gel Sci Tech*. (**2007**) 44, 4.
(ii) Adler-Abramovich et al. Angewandte Chemie (**2010**) 49, 1-5.
(iii) Kane et al. J Appl. Cryst. (**2009**) 42, 925.
(iv) Sumfleth et al *Polymer* (**2008**) 49, 5105.
(v) Sangermano et al. Macromol. Mater. Eng. (**2006**) 291 517.

Controlling the dispersion of the nanoparticles requires tailored surface chemistry

Surface Modification in volatile solvent (acetone)

↓

Dispersion of Solids in chosen phase (resin, hardener)

↓

Hi Shear Mixing with second phase

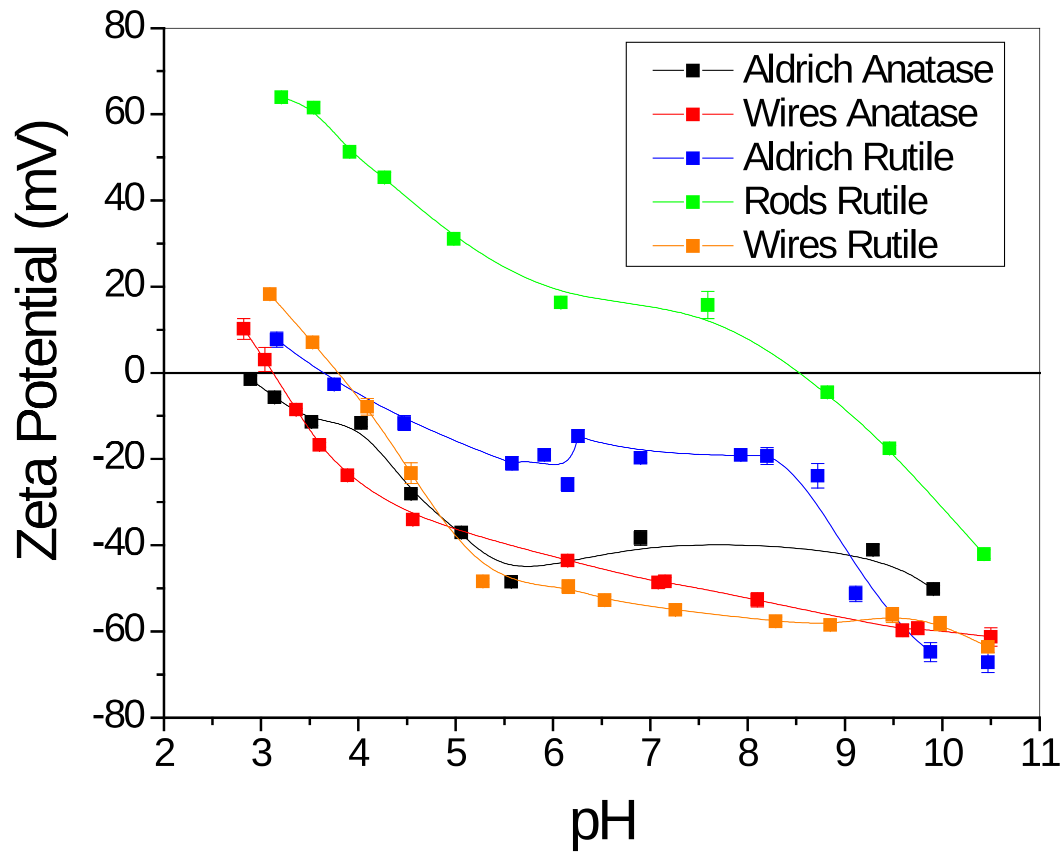
↓

Degassing

↓

Casting or Processing

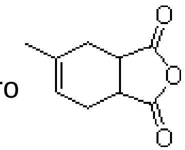
The surface chemistry of the TiO_2 nanoceramics were studied by comparing ζ-potential measurements.



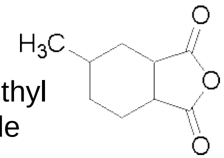
Variations noted for different TiO_2 nanomaterials, which will allow for fine tuning interaction.

The dispersion of the nanoparticles is highly dependent on the curative agent and nanoparticle

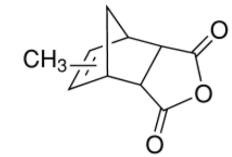
MTHPA
Methyl 1,2,3,6-tetrahydro phthalic anhydride

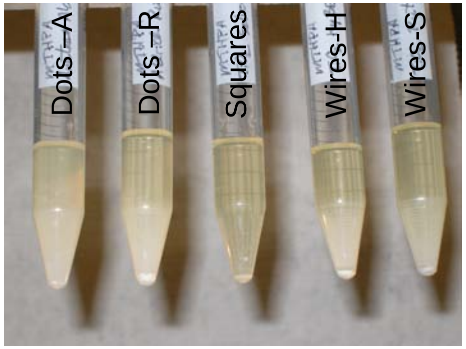


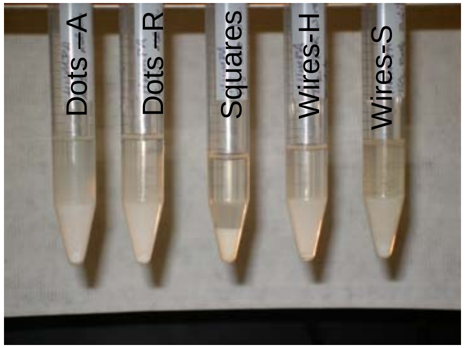
HHMPA
Hexahydro-4-methyl phthalic anhydride

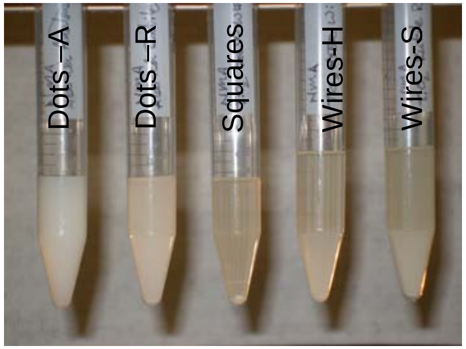


NMA
Nadic methyl anhydride

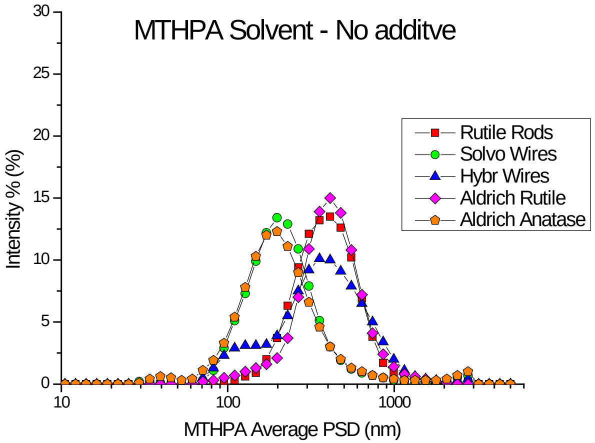


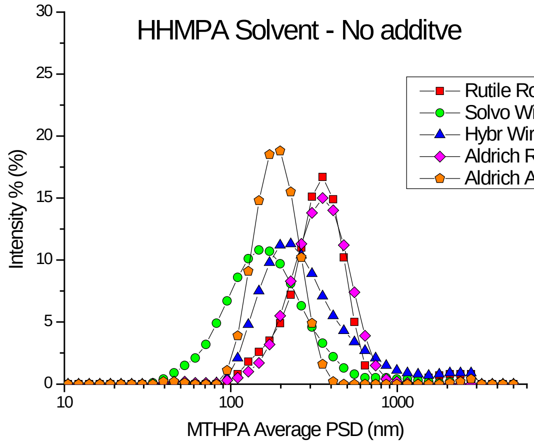


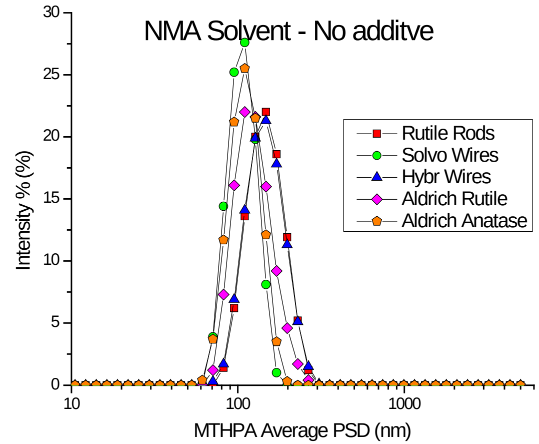




Optical Light Scattering







- NMA fluid gives smaller particle sizes and most stable dispersion.
- MTHPA and HHMPA fluids lead to particle aggregation and sedimentation; however, molecular structures are not greatly different between the three resin curatives.
- Of the resin curatives properties, NMA has highest viscosity of the three systems tested.

Dissemination of technical information as ***Papers, Patents, and Presentations*** is forthcoming

Papers:

(iii) Celina *et al*. "Cure reactions of advanced composite resins explored by high temperature micro ATR-IR"   241st ACS National Meeting, Anaheim, CA. Program Area: POLY: Division of Polymer Chemistry Symposium (POLY002) Polymers for Energy Storage and Delivery

(ii) Bell and Boyle "Nanoparticle stabilization mechanisms in epoxy curative fluids: wetting interaction and Van Oss model parameters" (*in prep* for J. Materials Chemistry)

(i) Boyle and Ottley "Structural Characterization of a Novel Family of Cesium Aryloxide" (*in prep* for Inorganic Chemistry).

Patents/Technical Advances:

None

Presentations:

(a) Saad et al. "Synthesis of Barium/Cesium Alkoxide Precursors for the Application of Nitrogen Phosphorus Detectors" Rio Grande Regional Meeting (OCT 2010 – Albuquerque).

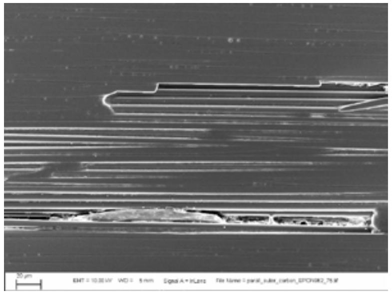
(b) Ottley et al. : "A Novel Family of Cesium Alkoxides as Novel Resin Catalysts" 241st ACS National Meeting, Anaheim, CA. Program Area: Materials Chemistry (*upcoming*)

(c) Boyle and Bell: "Novel Precursors for production of complex well-characterized nanoceramic materials" 241st ACS National Meeting, Anaheim, CA. Program Area: Materials Chemistry (*upcoming*)

(d) Celina: "Cure reactions of advanced composite resins explored by high temperature micro ATR-IR" 241st ACS National Meeting, Anaheim, CA. Program Area: POLY: Division of Polymer Chemistry Symposium (*upcoming*)

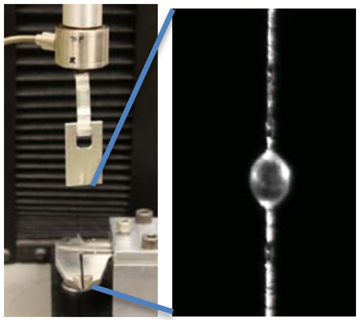
Project initiated February 2010

Summary and Conclusion

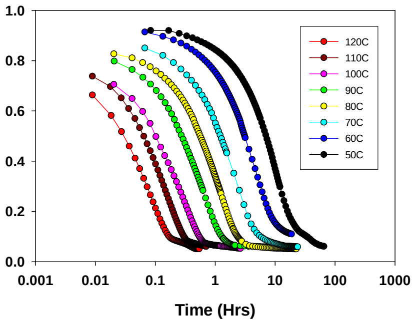


SEM image of outer ring

- Voids observed in the rim materials of flywheel
- Ultimate strength of adhesion found to depend on the cure schedule



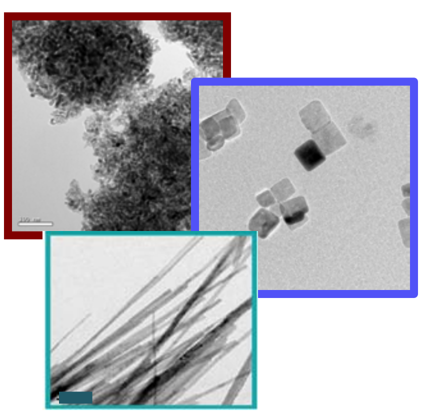
microdroplet testing of epoxy-fiber strength



isothermal cure kinetics

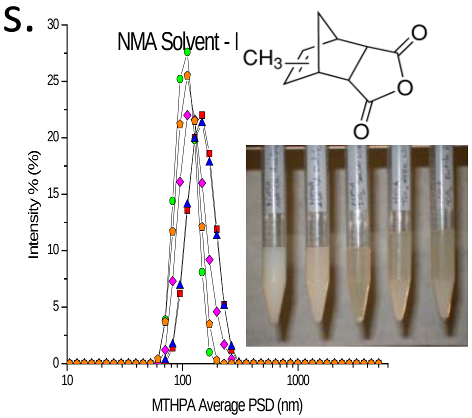
- Isothermal cure kinetics of the anhydride epoxy reaction realized from IR spectroscopy measurements

- Nanoceramic materials developed with different morphologies.



nanoceramic filler materials

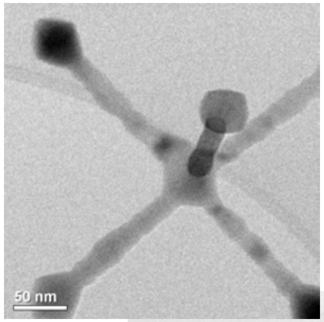
- Variations noted for different TiO_2 nanomaterials surface chemistry and behavior in resin curatives, which will allow for fine tuning interaction.

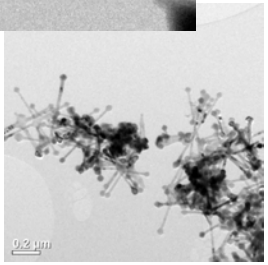


Optical scattering of NMA

Future Aims

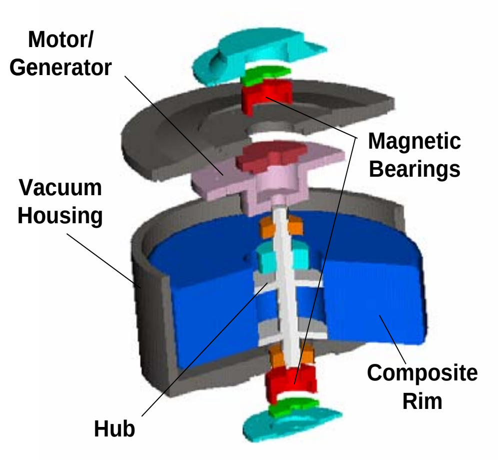
- Optimize interaction of nanoparticle and curative agent.
- **Introduction of morphologically varied NP into fully characterized system for impact determination.**
- Complete characterization of epoxy/fiber (glass and carbon) adhesion through microdroplet de-bonding measurements for different cure schedules
- Measure transverse yield stress of epoxy/fiber composites for different cure schedules
- **Investigate 3-D nanoparticles**





- Explore measuring stress strain behavior in pure resin cylindrical specimens using compression.
- Develop the 1D FE models linking resin cure with position-dependent thermal conditions.
- Develop the measurement of thermal gradients and maximum cure temperature variations in thick resin specimens as a function of cure time.
- Initiate nanoparticle on C-wire surface
- **Magnetic component for 'hubless' design study initiated**.

Increasing the strength of the rim of the flywheel is necessary to store more energy.



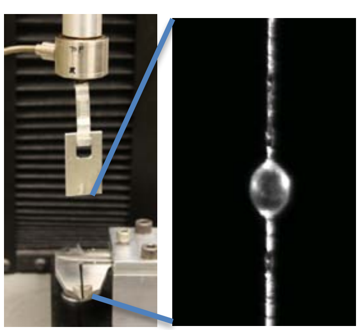
- Kinetic energy depends on speed of wheel which is limited by the tensile strength of the rim material

$$E_k = ½ \bullet I \bullet \omega^2$$

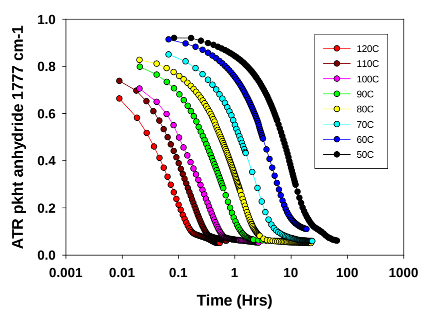
$$\sigma_t = \rho r^2 \omega^2$$

Our approach is to introduce nanoceramic fillers into the resin to increase the strength of the rim material. These nanoparticles will not significantly increase the weight of the rim but should allow for faster spin speeds and thus more stored energy

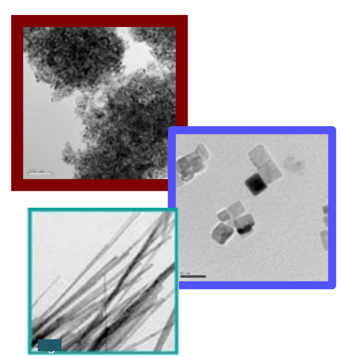
Approach is to initially determine the properties of the 'state-of-the-art' commercial system (Beacon Power) through (i) mechanical and (ii) chemical testing. With this baseline information, we can then introduce well-characterized nanoparticles - both in (iii) physical (i.e., size,shape) and (iv) chemical properties (i.e., solubility) to elucidate/optimize changes.



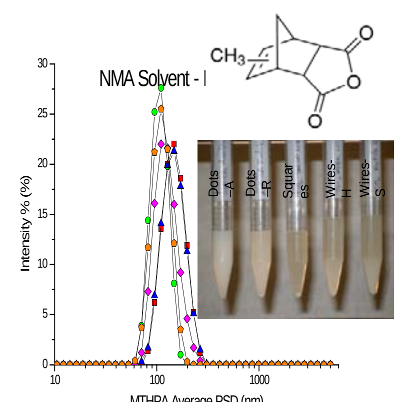
(i) Microdroplet testing of epoxy-fiber strength



(ii) Isothermal cure kinetics determined by IR spectroscopy



(iiii) nanoceramic filler materials



(iv) Optical scattering of different curative agents