Parametric Study of Materials for use in HEP Experiments

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Advanced Materials LDRD

- Lab Directed Research and Development
- Leverages Engineering Division resources in support of NSD, Physics, AFRD, MSD
- Generally three prongs to the effort
  - Methods to increase toughness/thermal conductivity of resins understand process variables/capabilities
  - Study of conductive foam as a heat exchange media
  - Non-destructive evaluation of assemblies (next talk)
- All goals require combined efforts from Divisions within General Science and Molecular Foundry

Areas of research

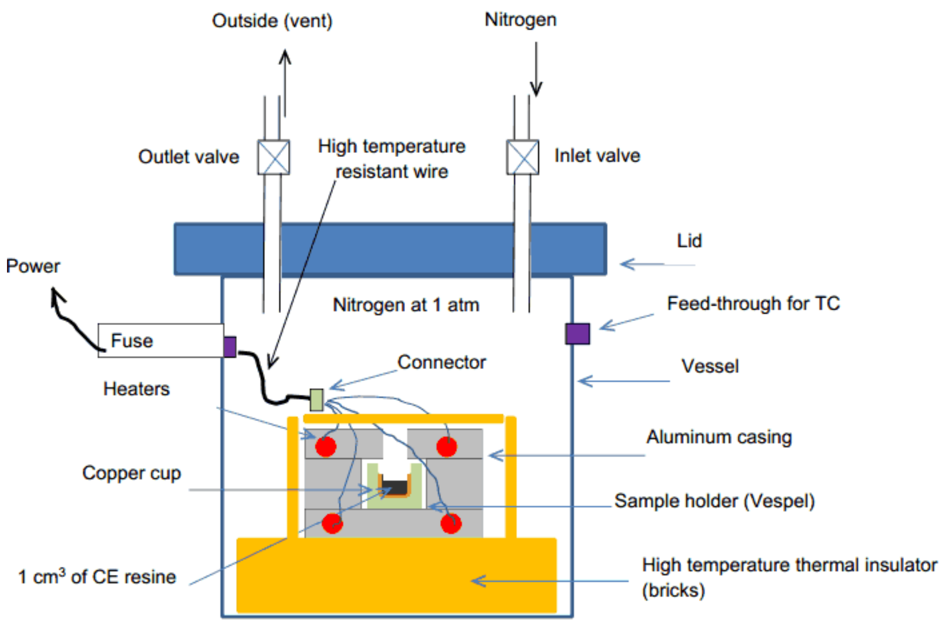
- UHV Compatible, Hi-Tg/toughness resins and laminates—compatible with RTM/potting process
- Loaded Resins/Adhesives including nano-particulates, ceramic powders and new prepregs
- Low Density, thermally conductive (carbon) foam

All material presented here is preliminary—should not be used for design

Interest in Cyanate Esters

- CE resins clearly useful for HEP detectors due to toughness and stability
- Radiation tolerance and low off-gas/adsorption also interesting
- Questions we asked:
  - Who else might be interested in similar properties
  - Are there modifications required to increase utility
  - Are there new resin systems we need to process
- Interesting applications:
  - Pot SC Magnet coils—CE may reduce training cycles
  - CE resins we already process may be UHV compatible
  - Everyone wants higher thru thickness conductivity
  - RTM Capability for SC Magnet and larger structures

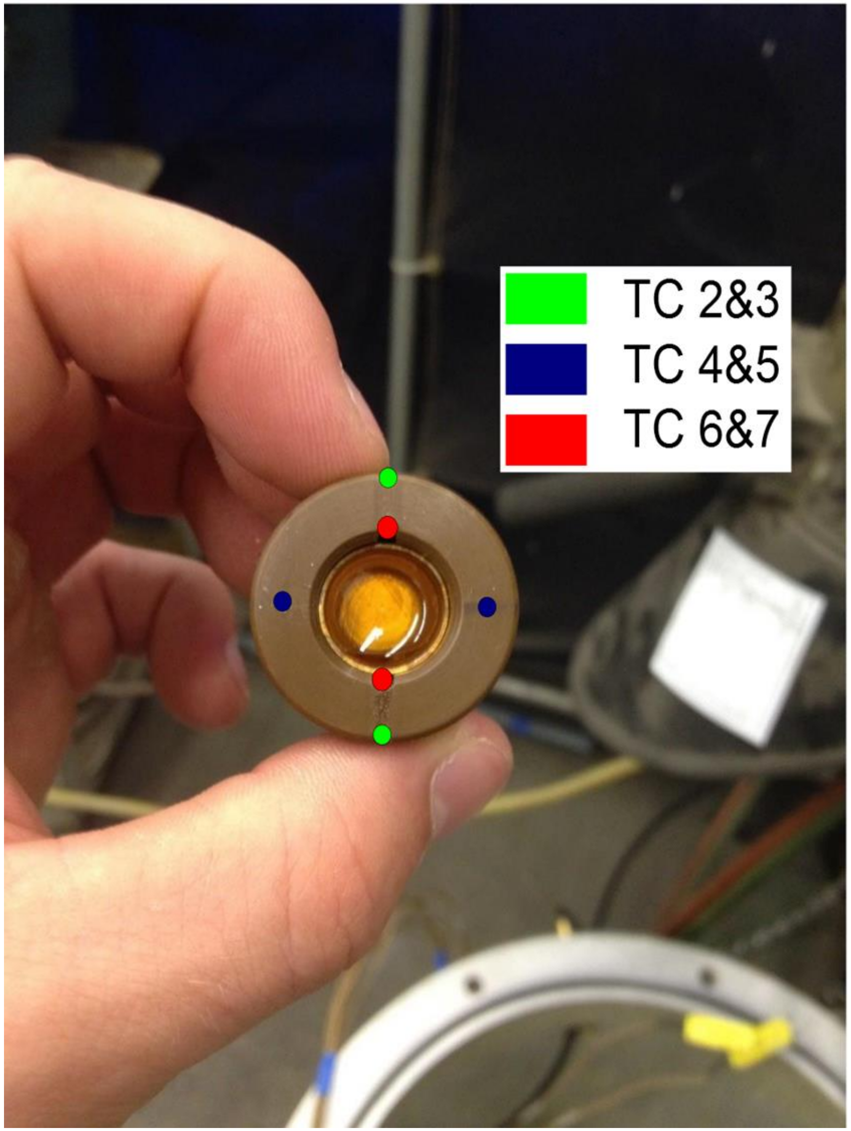
CE Resin Calorimetry



- Heat (energy) of reaction 300-700 J/g for CE
- Depending on speed of reaction, perhaps enough to vaporize…
- This is a bomb-calorimeter…
  - Without the ignition source
- This excited the safety folk
- Documentation ensued
- Want to understand process variable effect on energy release
- Want to see 'Exotherm'

Sample Holder

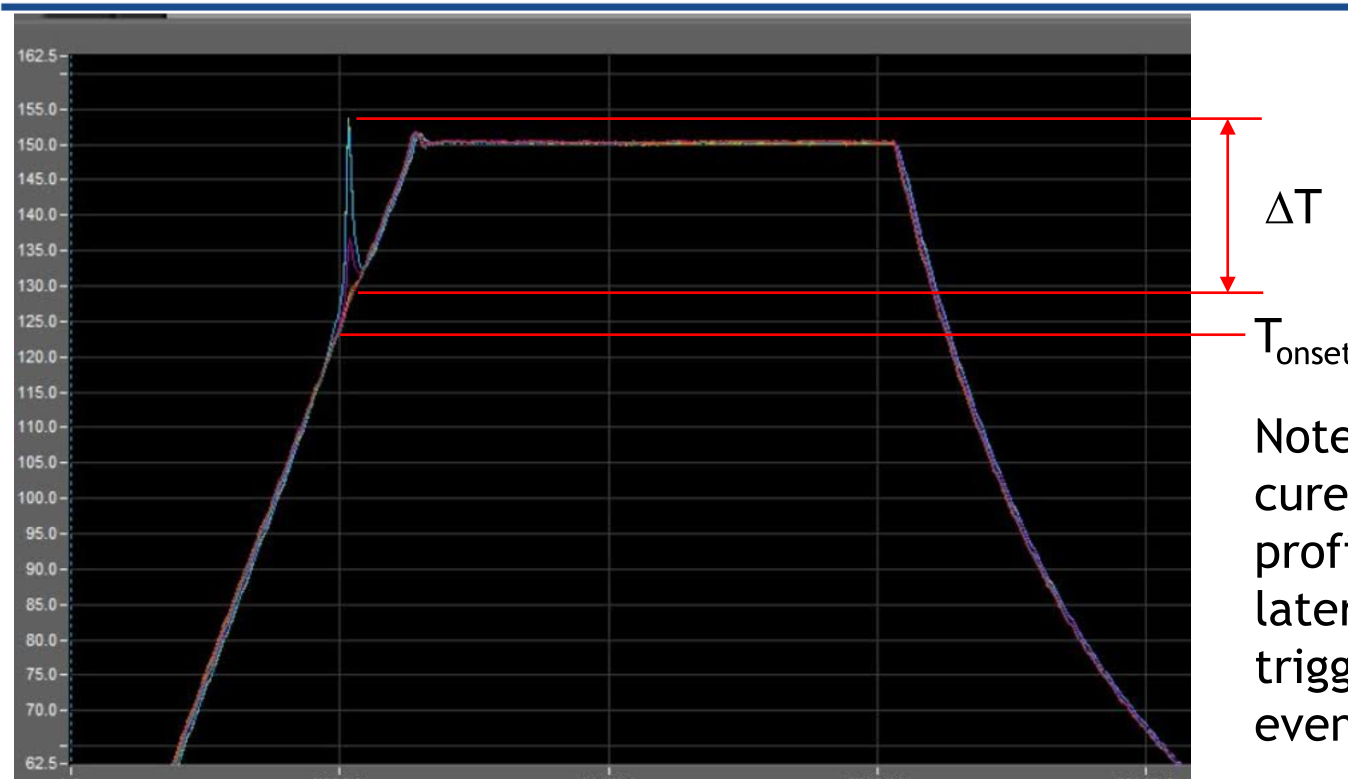
- ~1cc mixed CE resin in Cu Cup
- Tight fit in Vespel insulator
- Vespel slip fit into Al Heater blocks—TC locations indicated
- If TC 6/7 > 2/3 Heat is being generated by resin sample
- m*Cp*ΔT with appropriate inputs yields Heat of reaction
- TC 4/5 used for average T of vespel insulator for H calc
- Cured sample shown



Different Form of CE

- Composite shop uses CE regularly in prepreg
  - CE in prepreg is 'B-Staged'—partially polymerized robbing it of some heat of reaction
- Looking to use RTM CE system for SuperCon
- RTM also useful for larger Carbon Fiber parts
- RTM CE has a risk: Exo-therm (thermal run-away)
  - RTM resins have low Mol Weight—for low viscosity, require more reaction (trimerization) to fully cure
  - It *might* catch fire without proper precaution
- History of some magnet vendor(s?) finding this unsafe—mostly smoke, no fire
  - Goal is to find fully safe operating process for resins
- Small problem—Cu is the catalyst for CE resins..

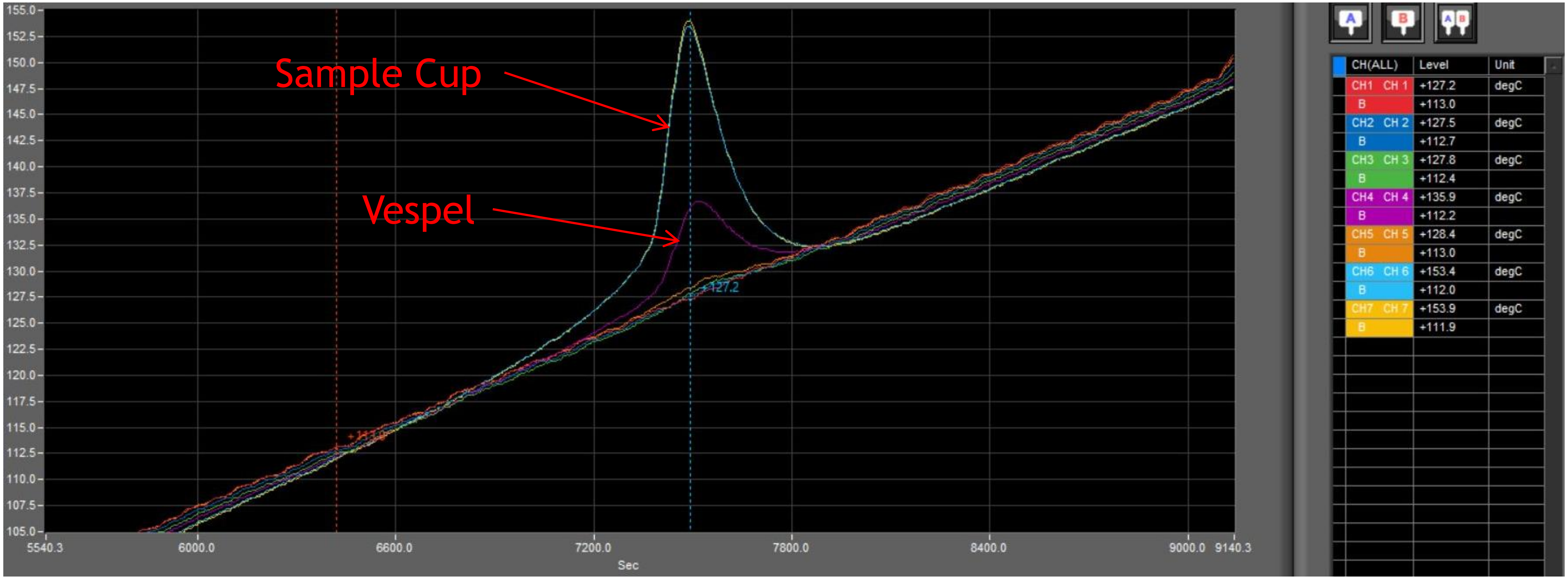
Experiment Ramp Cycle



Note: this is an aggressive cure cycle—more typical profiles will be described later. This is aimed at triggering an exothermic event.

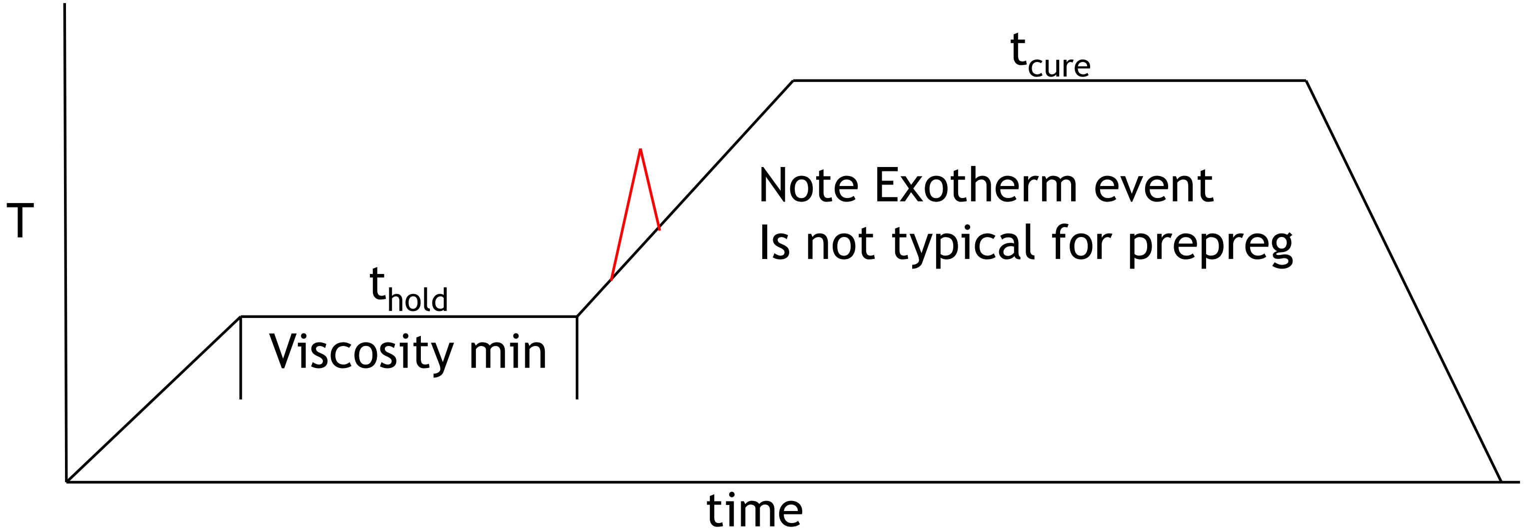
- **Ramp at Max recommended rate to cure temperature**
- **Repeat for different neat resins for baseline T_{onset}, ΔT**
- **Add materials, e.g. SC magnet wire, nano-particles, etc**
- **Increased ΔT means more heat, T_{onset} may be coupled**

Exotherm Peak detail



- Linear fit to heater block temp subtracted from Ts/Tv
- DT of each with m*Cp of appropriate constituents used to calculate Joules ~250J in this case
- Lower than expected, but may not have all energy release channels—OK for relative measurements…

Typical Cure cycle for CE Resins



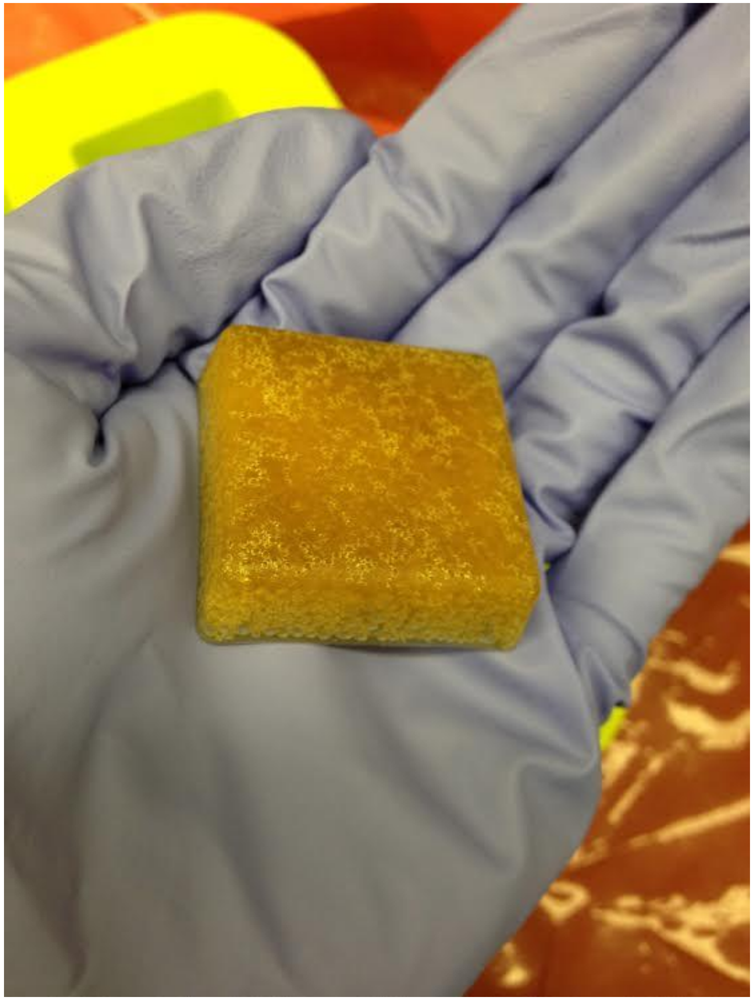
- (T, t_{hold}) aimed at max flow in RTM, max compression in prepreg for part quality (also last chance if bag leaks)
- Extending t_{hold} beyond some value increases viscosity via slow reaction—i.e. reduces energy available for exotherm
- In all cases t_{hold} should be below T_{onset} with some margin
- ΔT should decrease and T_{onset} increase with extended t_{hold}

Liquid CE Resins Tested

- EX 1510 (Tencate Advanced Composites)
  - RTM version of EX1515, close to what we typically process
  - TCAC also sells RS-14, has history in magnet potting
- 403 and 425 (Composites Technology Development
  - 403 is pure CE—exotherm curve shown
  - 425 is a mixture of CE and Epoxy currently used on ITER
  - 403 has extensive testing for radiation tolerance: GGy, but also resin some vendors might want to avoid…
- EX1510 showed no exotherm bump on test ramp
  - Mixed with Cu NiSn cuttings, causes an exotherm
  - Perhaps also nano particles (later slide)
- Continue testing baseline response to added materials before moving to t_{hold} studies

Filled Resin Study

- Original intent was to concentrate on CE resins, both Liquid RTM resins and EX1515 (prepreg film)
- Delayed calorimetry made it unwise to start with liquid CE—wait for more results before moving ahead (safety)
- Developed technique to mix powders into resin film—essentially like making pastry (mille fuille)
- Original attempts cured in oven, then in autoclave no bag, then autoclave with pressurized tool
  - Need pressurized tooling to remove bubbles from B-stage resin
  - Also need absence of O2 when curing CE Resins



Autoclave Cycle EX1515 nano BN

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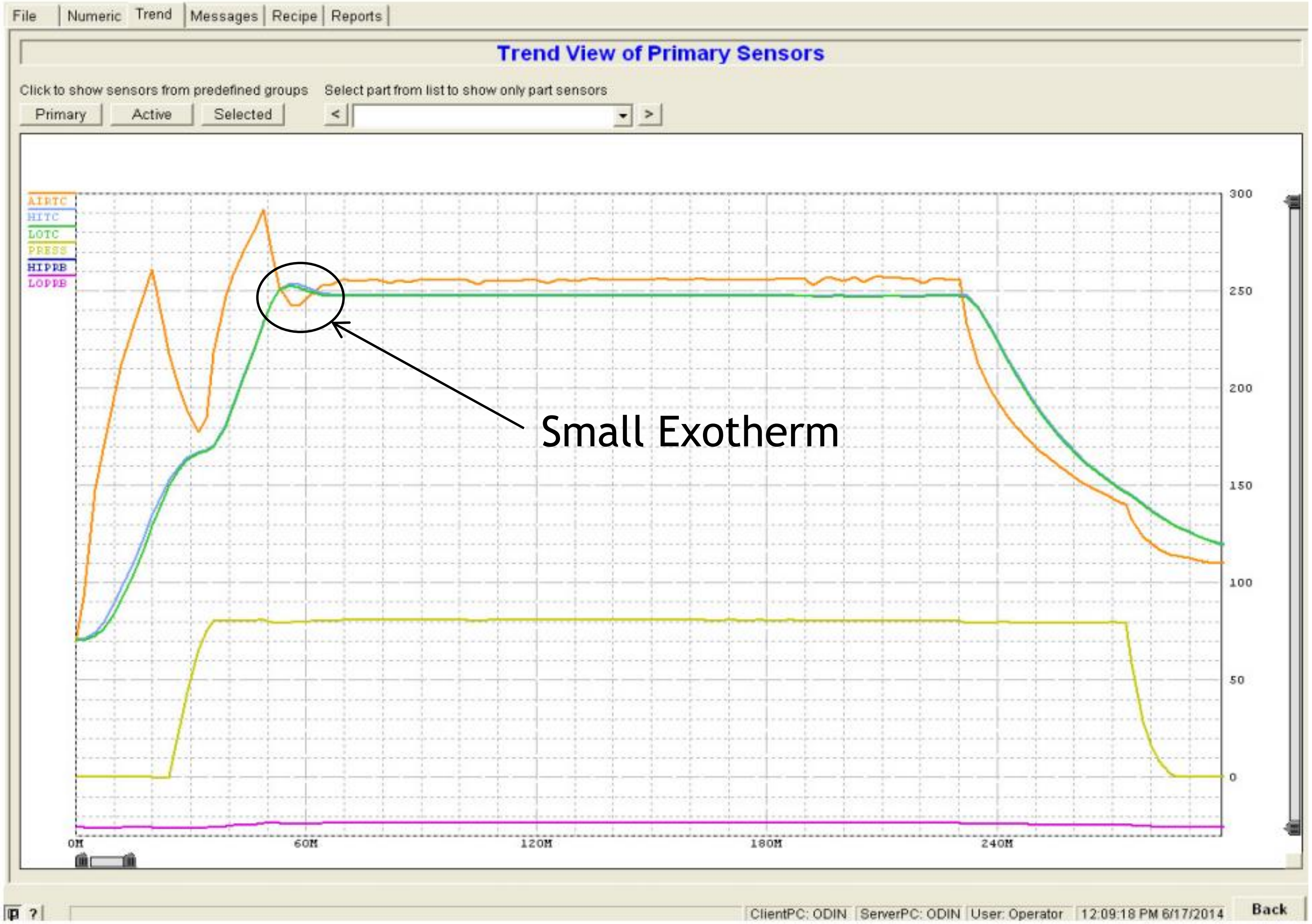
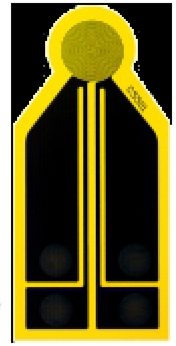


Thermal Test Instrument



- It requires two bulk samples of >5mm
- Range of T = [30K-1000K]
- K range=[0.01-500 W/mK]
- Typical Sample sizes [1-10cm^3]
- Size of the sample surface should be appreciable larger than the diameter of the Hot Disk Sensor in order to allow for a not to slow transient recording.
- Thickness of the sample should not be less than the radius of the hot disk.

- **Acquired TPS500s (http://www.thermtest.com/Products/TPS500S.aspx)**
  - **Hot Disk Transient plane source**
  - **Direct measurement of thermal conductivity and thermal diffusivity no calibration required**
- **'Smooth' surfaces, but not contact compound is required**

Sample Example Datasheet

	A	B	C	D	E	F
1		**Note: This sample is not included in the plots**				
2		Sample #2				
3		Components	Product Number	Brand	Density [g/ml]	
4		PolarTherm Boron Nitride Powder PT 140 (9-12um)	PT140	Momentive Performance Materials Inc	2.25	
5		Hysol EA 9396	9396	Henkel	1.14 (of mixture)	
6						
7			Degassed?	Curing Method	Filler Volume Fraction	Thickness [cm]
8			No	Cured in the oven at 67 C for 1hr	10%	6.5
9			Weight Hysol [g]	Weight of Filler [g]	Thermal Conductivity [W/	Thermal Diffusivity [mm^2/sec]
10			16.62	3.64	0.6086	0.4113

- Samples are Serialized, and various data is entered into a standardized spreadsheet
- It has taken 16 or so samples of varying composition to track what data needs to be recorded and to understand quality control variables for sample production

Materials tried so far

Material	Product number	Supplier
Hysol EA 9396	9396	Henkel
PolarTherm Boron Nitride Powder PT 140 (9-12um)	PT140	Momentive Performance Materials Inc
Boron Nitride Nanopowder, (BN, 99.8+%, 70-80 nm, Hexagonal)	US2019	US Research Nanomaterials Inc
Aluminum Nitride Nanopowder, (AlN, 99.5%, 65-75 nm, Hexagonal)	US2010	US Research Nanomaterials Inc
Carbon Black, acetylene, 50% compressed, 99.9+% (metal basis)	39724	Alfa Aesar
Graphite Flakes, +100mesh (>=75% min)	332461	Sigma-Aldrich
Graphite Powder, natural, high purity,-200 mesh99.9999% (metals basis	14734	Alfa Aesar

- **EX1515 samples difficult to produce quickly—decided to change to Hysol EA9396 (liquid resin)**
- **Move to RT Cure epoxy allowed production of up to 10samples/wk with testing, versus 2-3.**
- **Goal is to quickly cycle thru various filler materials at two %Vf values and create a scatter plot survey**
- **Several more materials on order, e.g. graphene and carbon nano-tubes**
- **Some lessons learned fabricating samples…**

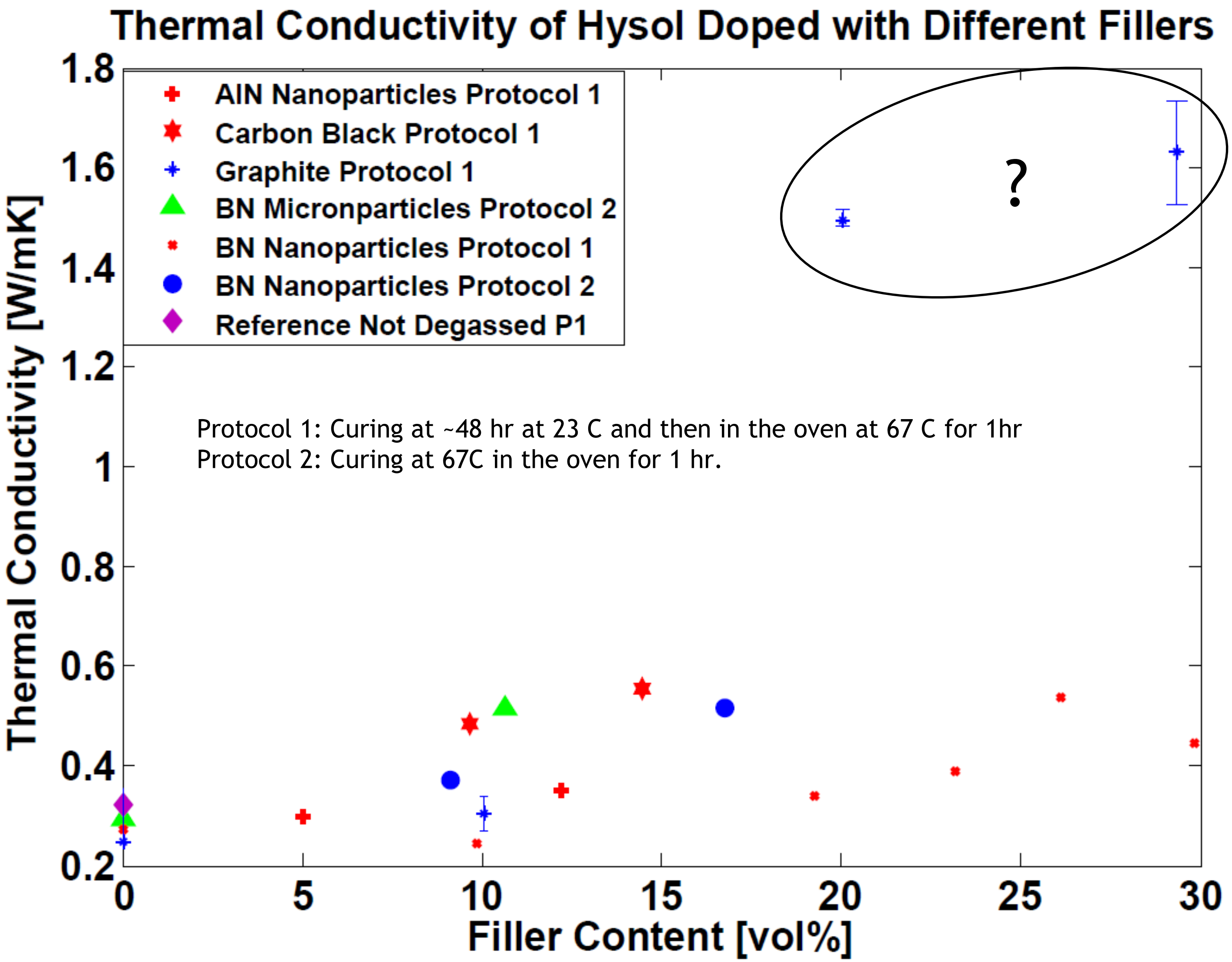
Mixing Equipment is Very important

- We have the "Thinky ARE-310" planetary centrifugal mixer—excellent for incorporating powders
- However we found some bubbles in filled mixes despite 'defoam' cycle (centrifugal action)—required vacuum
- Finer powders, particular nano, adsorb lower viscosity components (Part-B) like cat litter—must pre-mix A/B then add nano-particles
- Unfortunately this limits mix time—mixer mixes by viscosity (shear)—extended shearing may orient plate/fiber like particles in adhesive

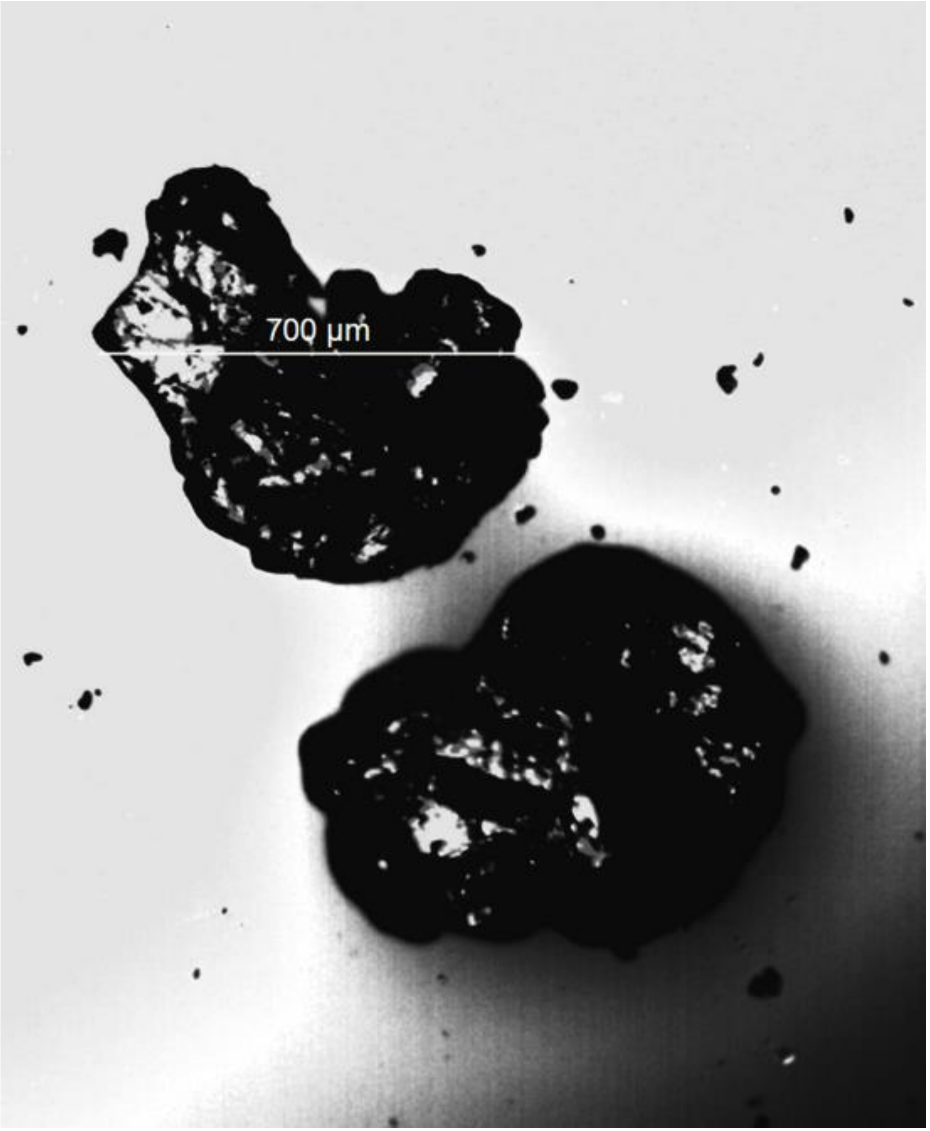
Mixing problems

- Part A 3-6kp viscosity—not great to mix into
- Mixed epoxy falls to a few hundred poise, but mixing adds energy that limits pot life
- References of nano-particles hastening cure exist
- Some nano-particles (graphene) come as suspensions in solvents
  - To mix into epoxy, would need to evaporate solvent
  - OTOH, graphene is created by exfoliating (shearing) graphite in a liquid with appropriate viscosity and surface energy (perhaps an epoxy candidate exists)
- CE might be a good candidate for this ~100poise mixed and unmixed.

Very Preliminary Results



Can't use *this* graphite…

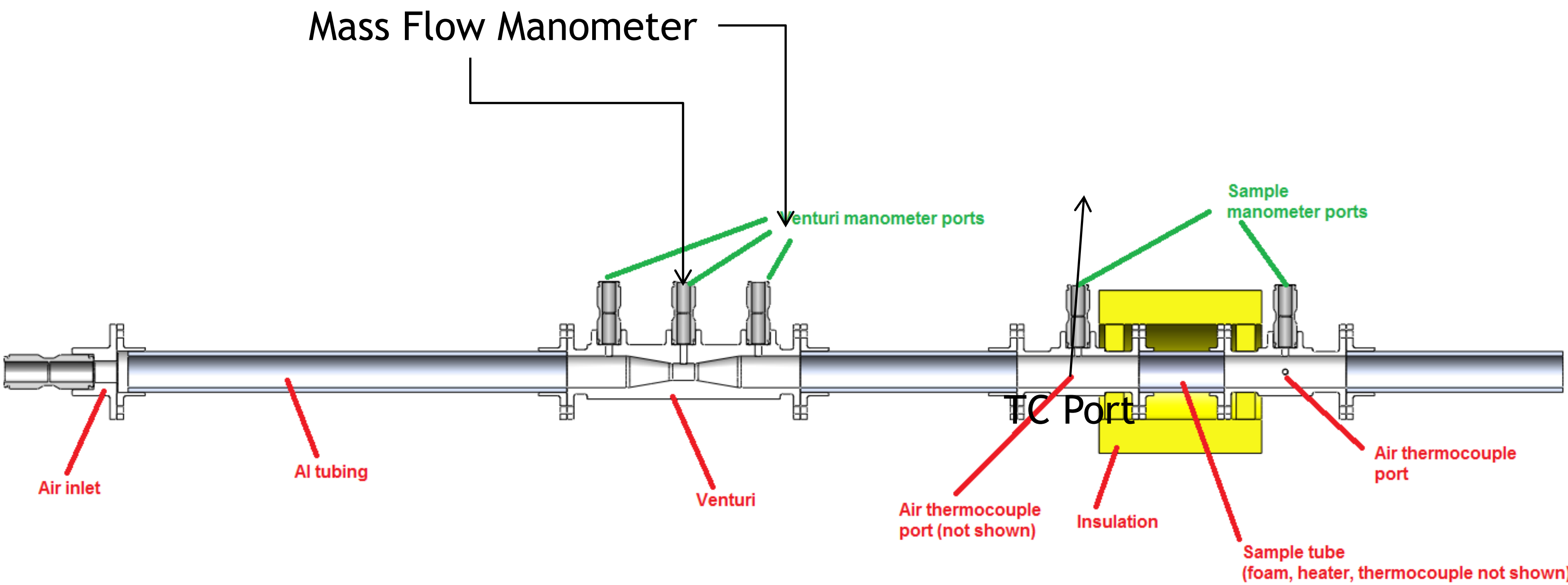


- Graphite flakes range from 0.5--0.7mm (9mm sample)
- Picture is pre-mixed—some evidence of break-up in samples
- Probing graphite particle releases graphite flakes
- Stuff to try:
  - Ball mill smaller
  - Mix longer
- Not usable as adhesive with this particle size, but interesting result…

Air Flow thru conductive Foam

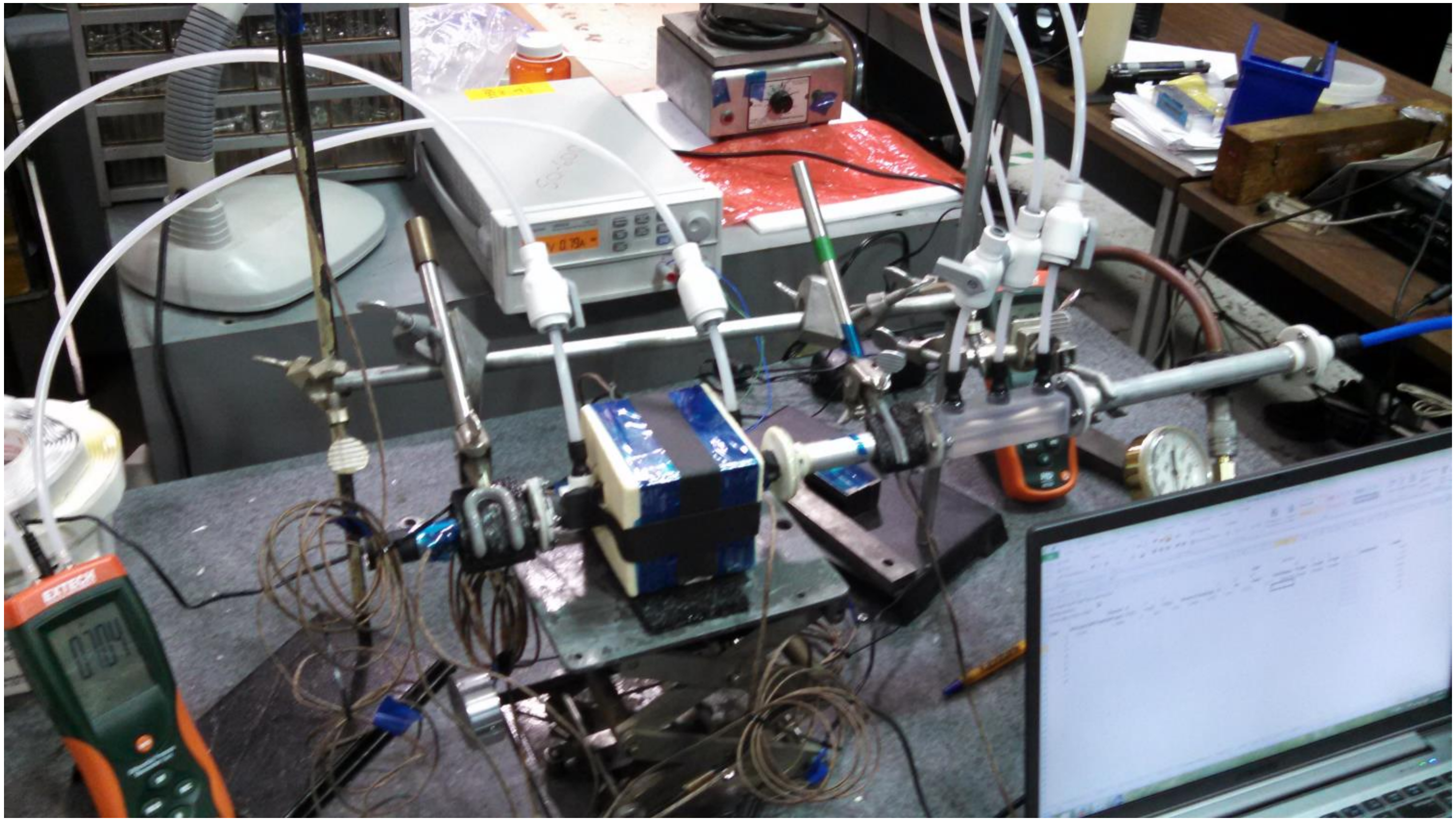
- Adding conductive foam to the flow has two benefits to heat exchange
  - It increases the area of exchange
  - It increases the effective volumetric conductivity of the flow
- Foam is specified by Density, Pore Size, and Conductivity
  - Given those as inputs; we should be able to predict effective heat transfer enhancement
  - Density or Void fraction and Pore size should predict pressure drop characteristics
- Several papers propose models relating the above but are very sensitive the inputs
  - Need data to start correlating models.

Test setup



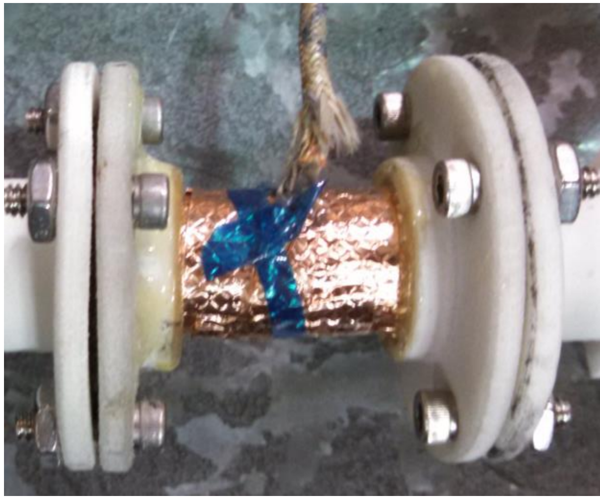
- Schematic of test setup.
- Venturi measures air flow
- Additional modifications required to improve accuracy

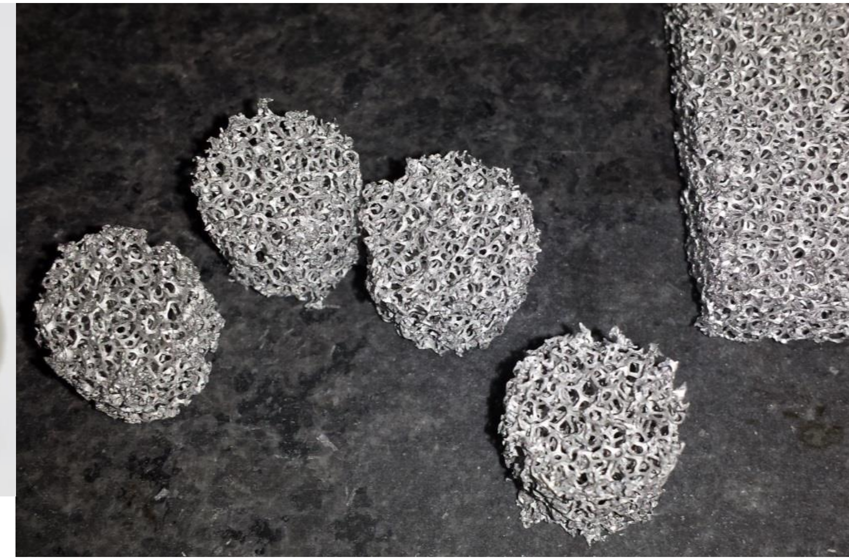
Initial Setup



- *Heat input in sample section with foam*
- *Study how foam affects transfer of heat to air flow*
- *Tests guided modification of setup to improve it*

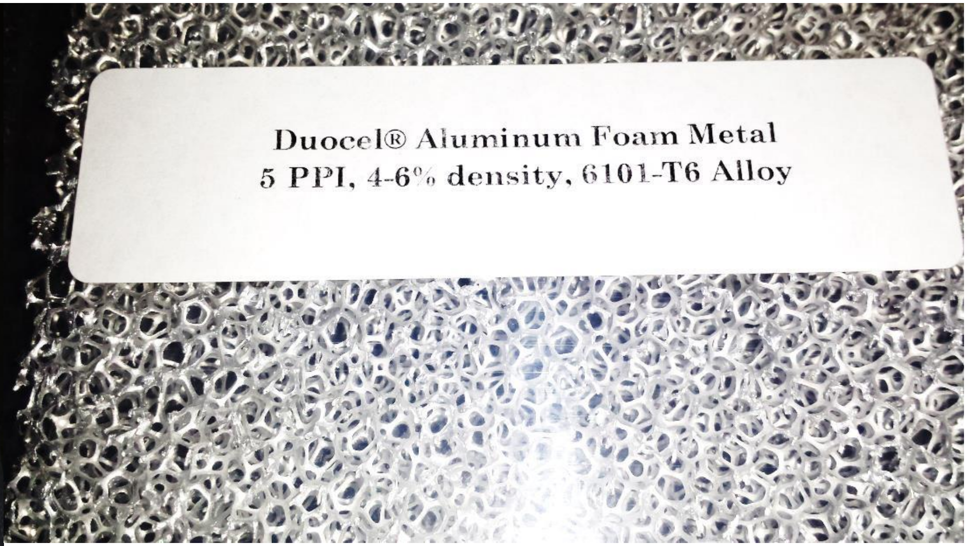
Samples





- Started with Aluminum Foam
  - Length diameter set by sample range 5ppi – 15mm dia.
- 5 proved difficult to fabricate (ligands bend, don't cut)
- EDM (Wire discharge machining) works—also works on 'glassy' carbon foam, and graphitic foam (slowly)
- EDM improves consistency of sample preparation

Foam Samples

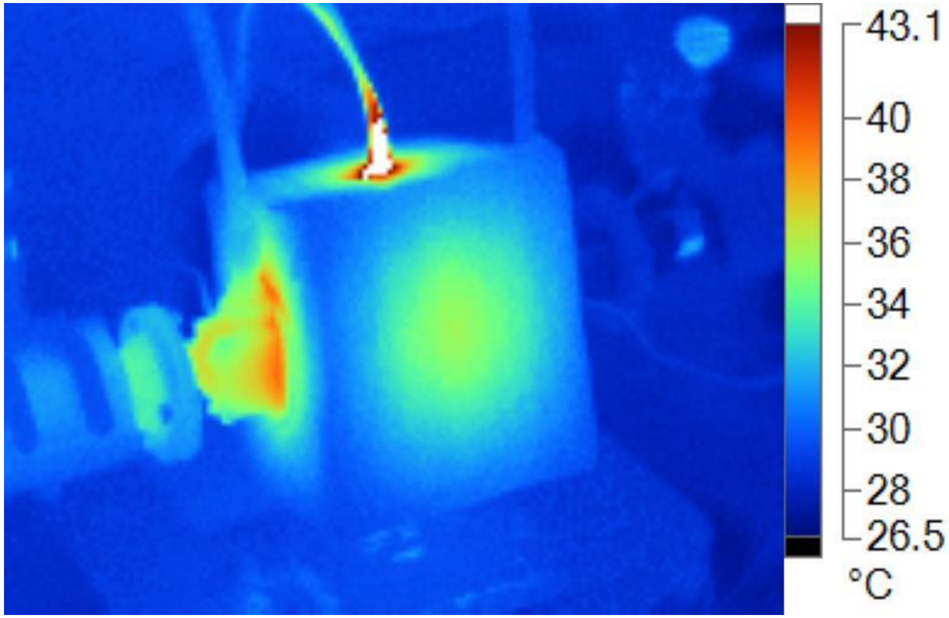


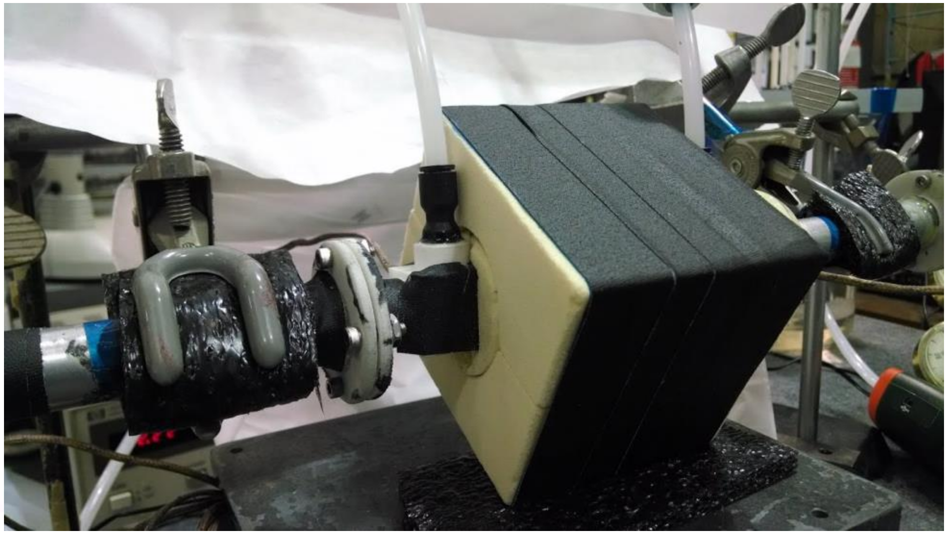
- Using Aluminum as a 'known' K (thermal conductivity)
- Has similar morphology to Carbon Foam
- Interested in developing machine vision tool to quantify 'PPI'
- Void fraction by mechanical weight
- "K" perhaps with TPS500s

Mass Flow and velocity

- Venturi for different mass-flow ranges (orifice size)
- Used similar on STAR, calibrated with large bag
- Good to 2-3% if not choked; had problem when using fan
- Separate Manometer used across sample

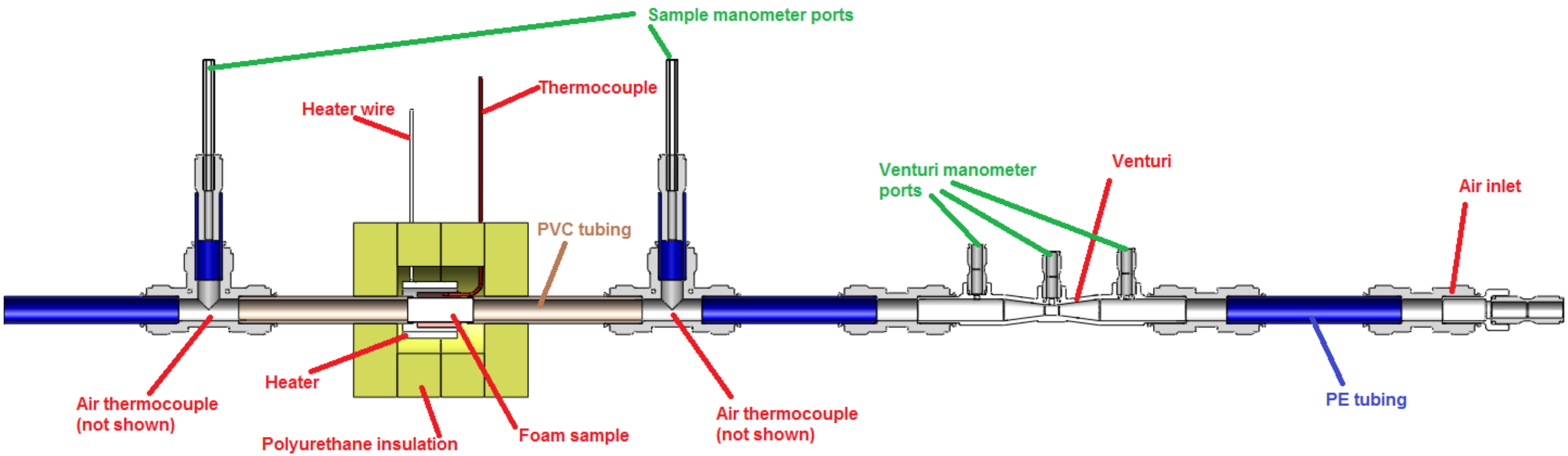
Thermal short circuit

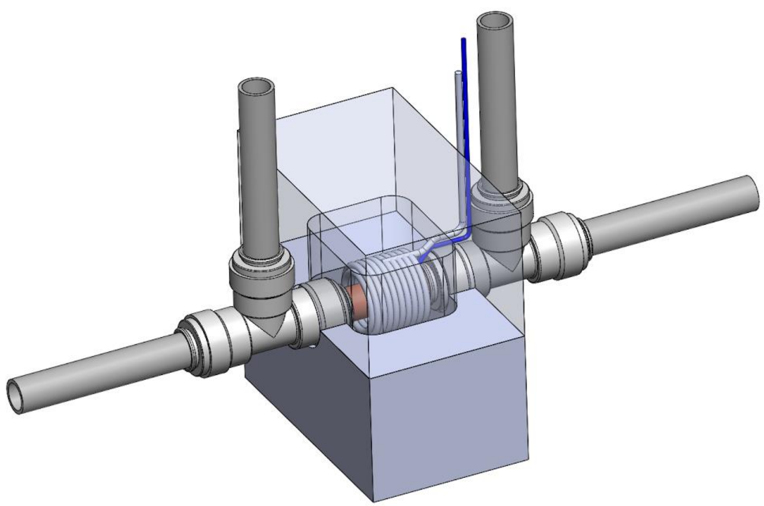


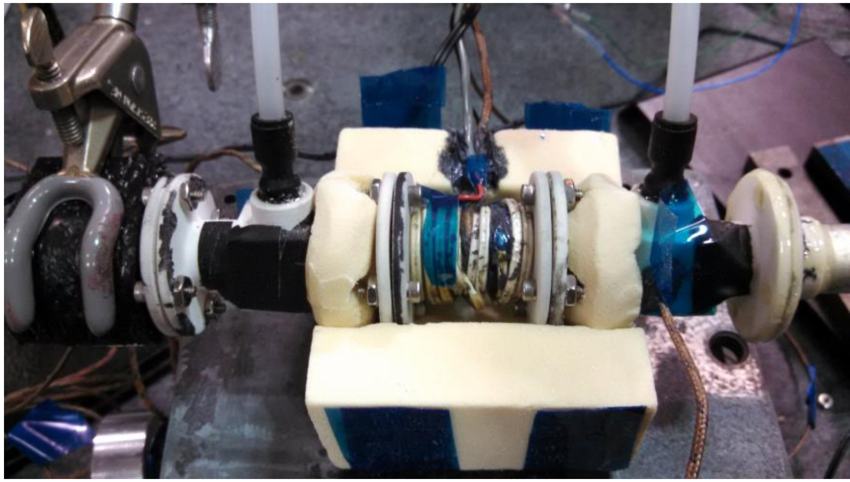


- Heat conduction along aparatus effects TC measurements
- ΔT of air across sample measure of Q
- When dragged together by conduction Q ~ 0
- Improved isolation, both separation and insulating pipes

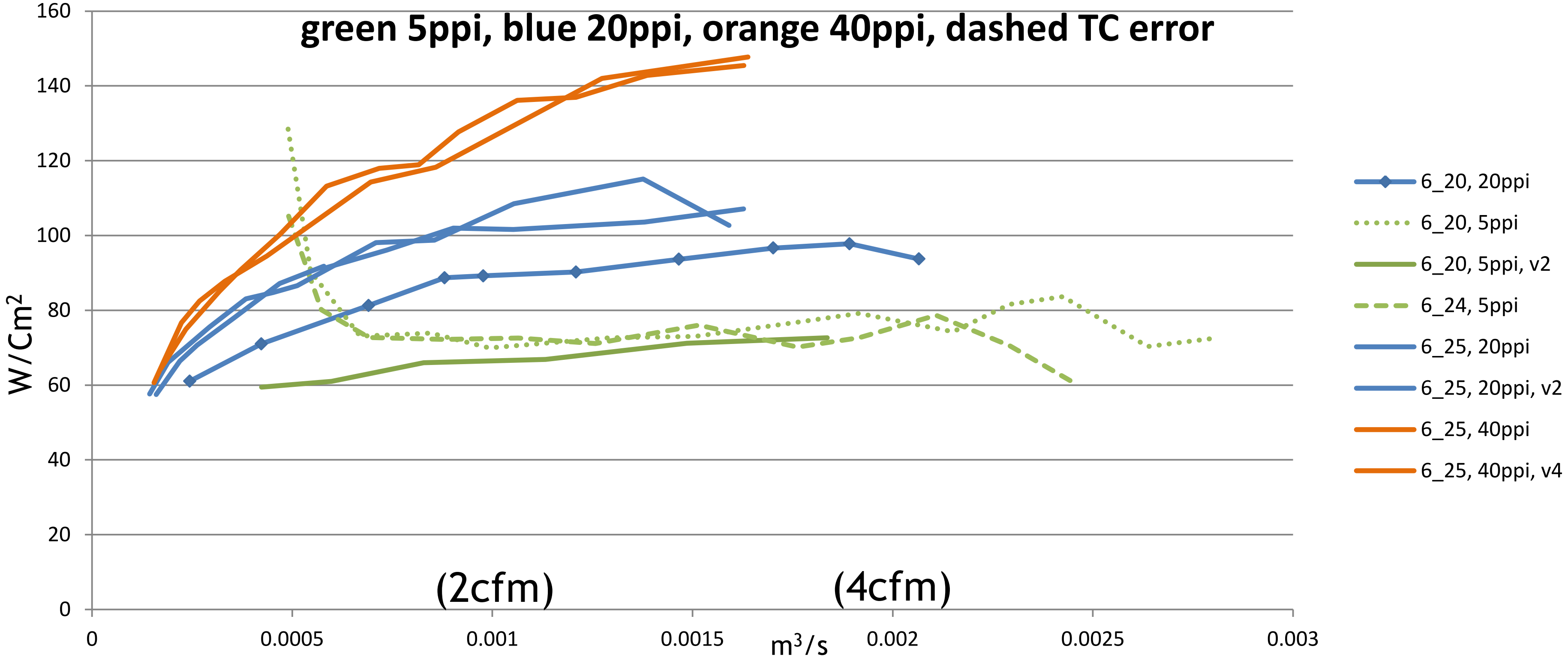
New test bench (arrives this week)







Recent Data original setup



- Consistency is improving, results starting to look as expected
- Effective "H" is normalized to area of outer radius of sample
- These are not results, but they have the functional form of the types of curves we want to fit—more with new setup

Conclusion

- Consistency of practice and repeatability of results are starting to improve for all efforts presented
- Neat CE Resins do exotherm, but not catastrophically, safety is no longer a concern for future testing (can go faster)
- Thermal conductivity results are too preliminary to conclude
- Work can proceed much more rapidly on all fronts