SAND2013-7170C

Understanding Polymer and Composite Aging and Degradation via TGA and DSC Coupled Mass Spectroscopy

PDDG Paris, 2013

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Livermore, CA

SAND 2013-6750

Sandia National Laboratories

Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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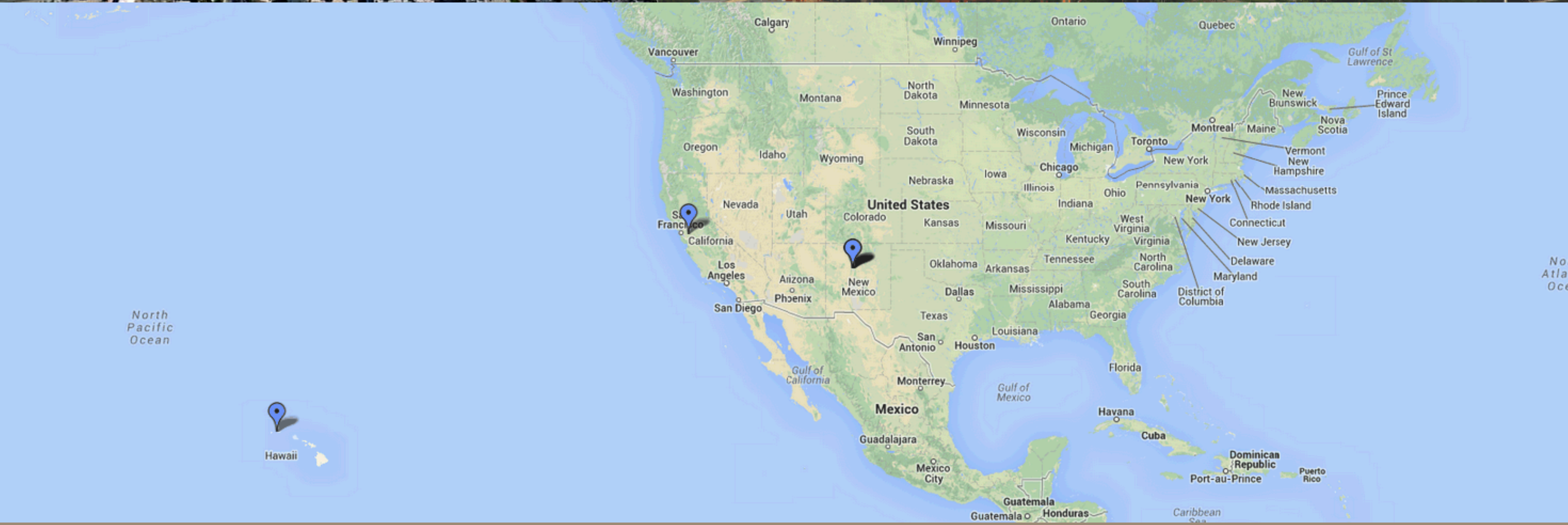
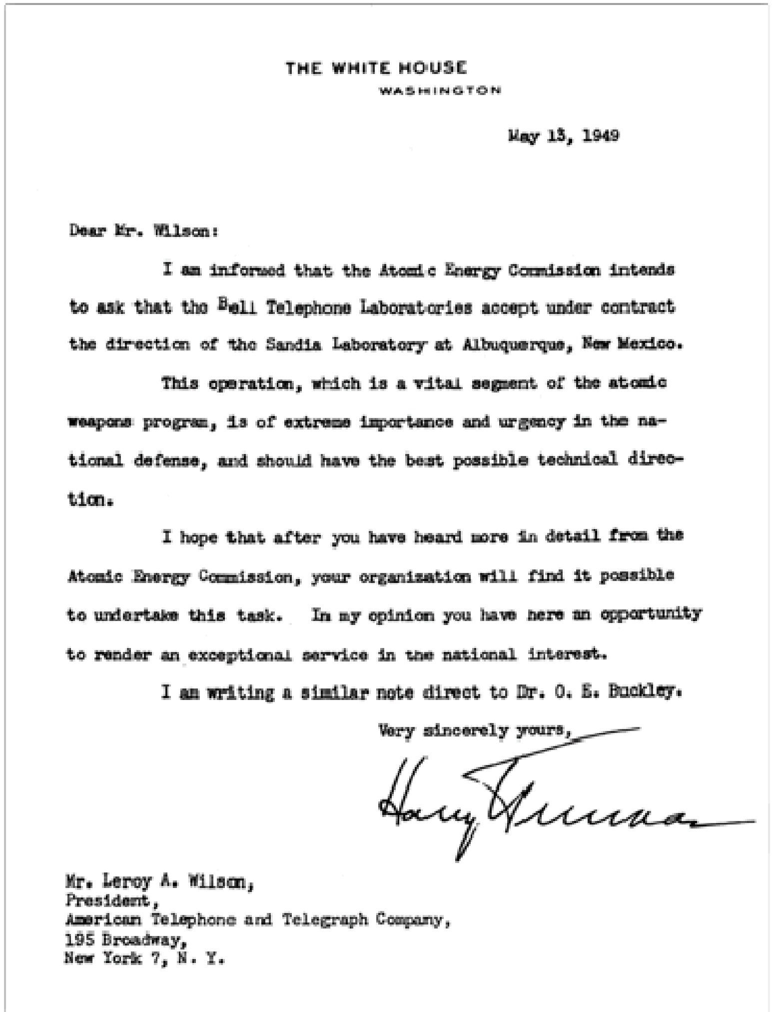
Sandia's Sites

Livermore, California

Albuquerque, New Mexico



Sandia's History



THE WHITE HOUSE
WASHINGTON

May 13, 1949

Dear Mr. Wilson:

I am informed that the Atomic Energy Commission intends to ask that the Bell Telephone Laboratories accept under contract the direction of the Sandia Laboratory at Albuquerque, New Mexico.

This operation, which is a vital segment of the atomic weapons program, is of extreme importance and urgency in the national defense, and should have the best possible technical direction.

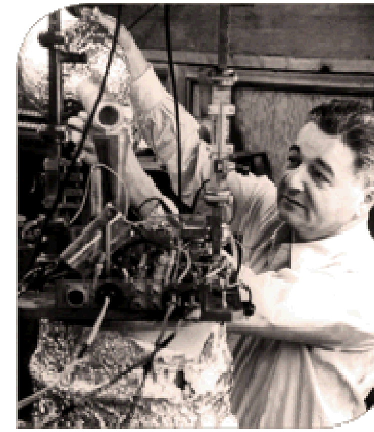
I hope that after you have heard more in detail from the Atomic Energy Commission, your organization will find it possible to undertake this task. In my opinion you have here an opportunity to render an exceptional service in the national interest.

I am writing a similar note direct to Dr. O. E. Buckley.

Very sincerely yours,

Harry Truman

Mr. Leroy A. Wilson,
President,
American Telephone and Telegraph Company,
195 Broadway,
New York 7, N. Y.



Nuclear Weapons

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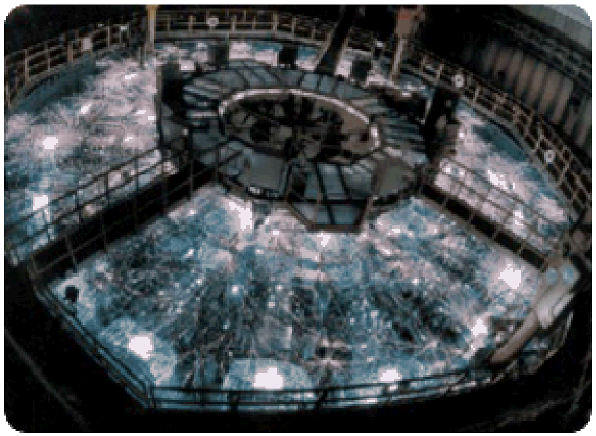
Pulsed power and radiation effects sciences

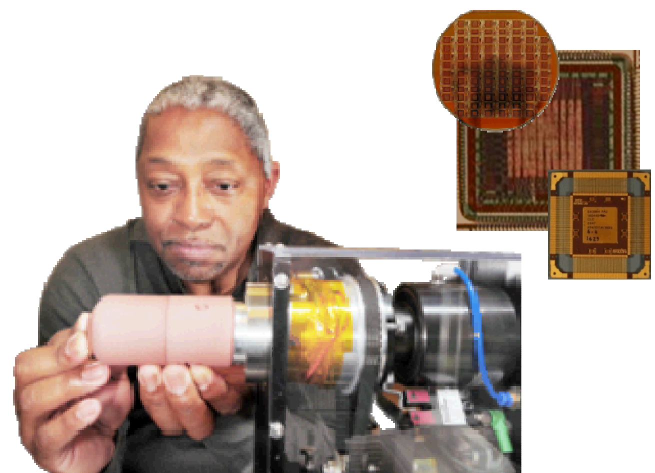


Design agency for nonnuclear components

- Neutron generators
- Arming, fuzing and firing systems
- Safety systems
- Gas transfer systems

Warhead systems engineering and integration

Production agency

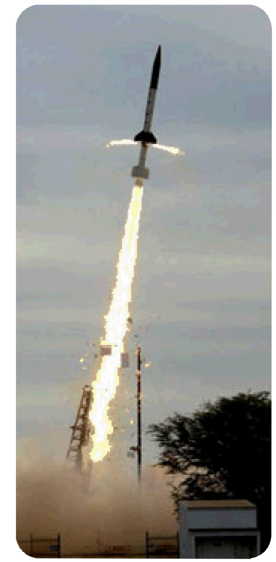


Defense Systems and Assessments

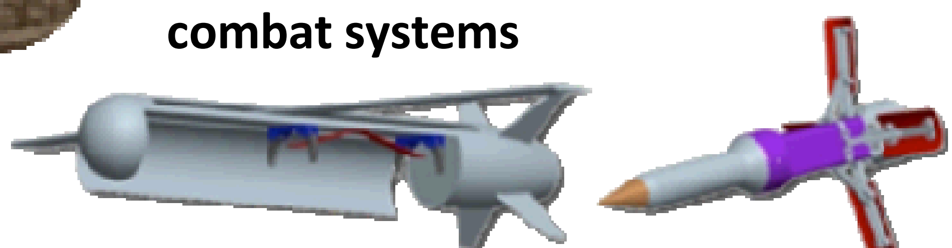
Synthetic aperture radar

Support for NASA

Support for ballistic missile defense

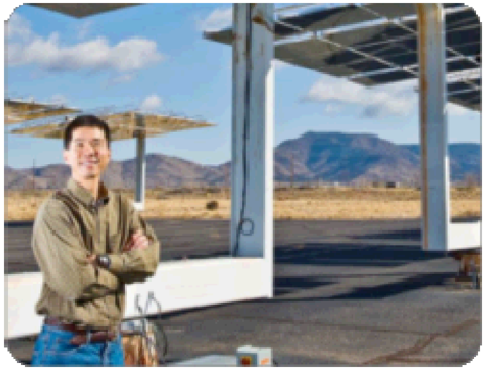


Ground sensors for future combat systems

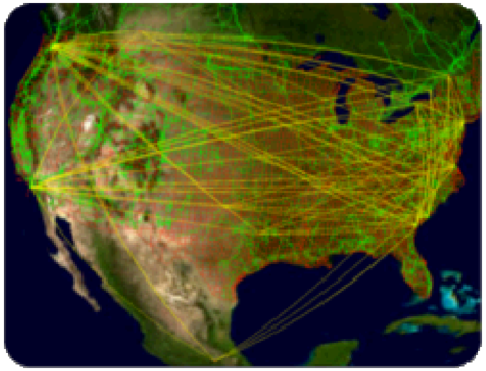


Energy, Climate, and Infrastructure Security

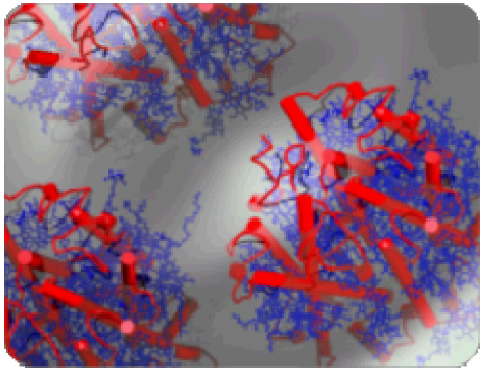
Energy



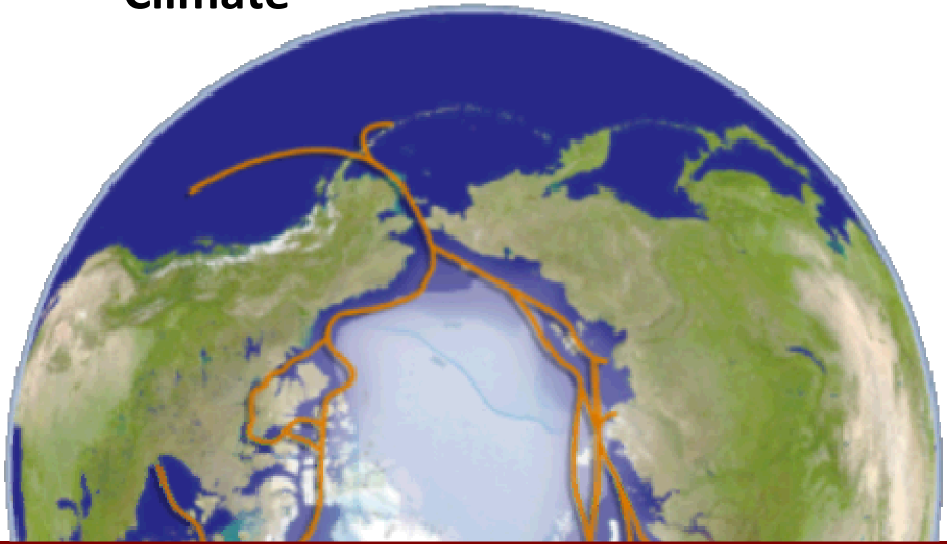
Infrastructure



Crosscuts and enablers



Climate



jbei
Joint BioEnergy Institute

International, Homeland, and Nuclear Security

Critical asset protection

Homeland defense and force protection

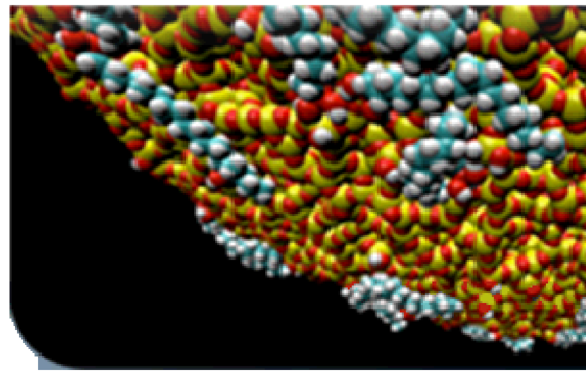
Homeland security programs

Global security

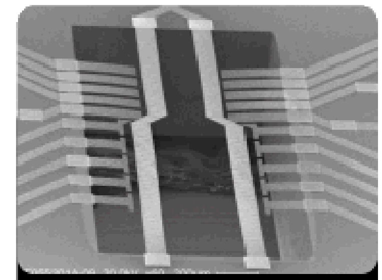
Science and Engineering Foundations

Computing and information science

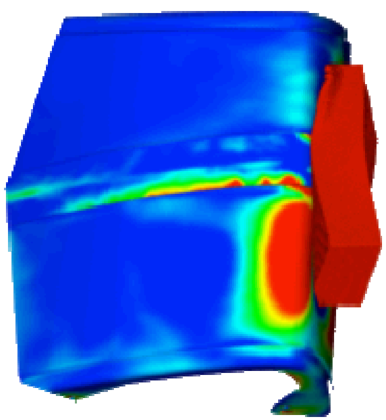
Materials science



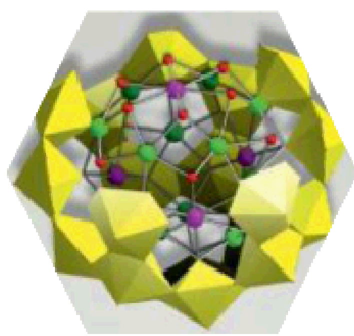
Nanodevices and microsystems



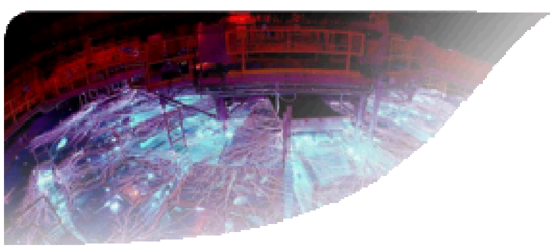
Engineering sciences



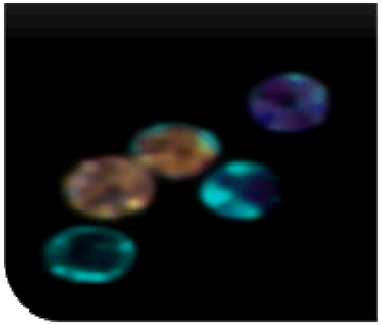
Geoscience



Radiation effects and high-energy density science

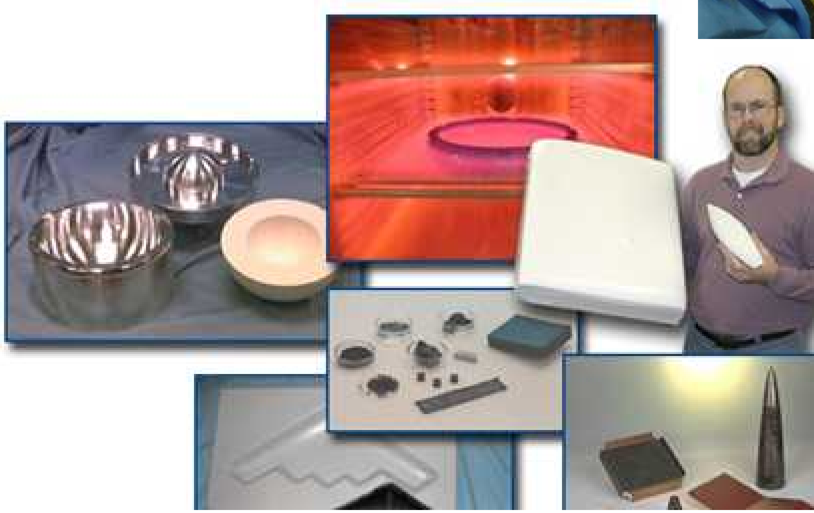


Bioscience



Materials Chemistry at SNL/CA

Cover a variety of area from composites to electroplating to small molecule synthesis to foams and epoxies



Understanding Polymer Aging and Handling

- Nine-month program to investigate mechanical and materials properties of stockpile foam and epoxy resins
- What, if any "aging" effects could be detected?
- Do we anticipate future aging assuming the same conditions?
- How do we handle these materials for continual use?

- Can we use thermal gravimetric analysis (TGA) or differential scanning calorimetry (DSC) to address these questions?

Materials of Interest

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- Poly(dimethyl diphenyl isocyanate) (PMDI)
  - 30 year old foam (FoamP)
  - Newly synthesized foam (FoamN)
- Epoxy materials (Epon™ 826 and Curing Agent Z)
  - 30 year old epoxy with fiber glass (EpoxyP)
  - Newly synthesized epoxy resin (EpoxyN)

- All four materials subjected to bake-out/accelerated aging in argon for one or two months

Bake-Out and Accelerated Aging

- *Bake-out:* This term refers to heating a sample at a specified temperature in order to induce a specific change. For example, a bake-out might drive out water from a sample. A bake-out is ideally performed at a temperature and for a time period which does not alter the inherent physical or chemical properties of the material and can be considered to drive reversible processes.
- *Accelerated aging (or ageing in the UK):* This term refers to heating a specimen above ambient conditions for a specified time period to mimic the aging of a sample held at ambient temperatures for a much longer duration. Aging is typically considered an irreversible process due to physical or chemical changes in the material.

Experimental Objective

- Can we distinguish between bake-out and accelerated aging by looking at the thermal decomposition properties of a material?
  - If a material undergoes an irreversible chemical change during a bake-out process, this change may be detectable in subsequent thermal decomposition measurements
  - By using variable heating rate TGA, we can measure the onset temperature of decomposition and the activation energy

Materials Investigated by TGA and DSC

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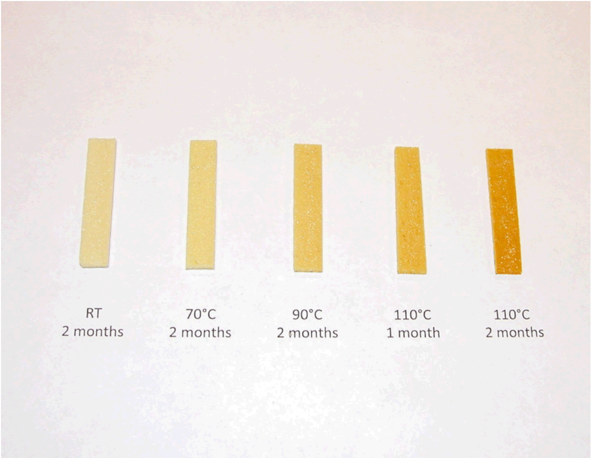
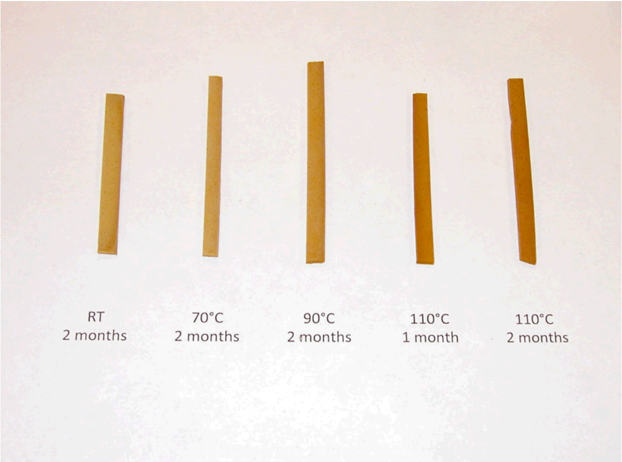
Description and code of materials used in this study.	
Sample Code	Sample Description
FoamP	Foam from stockpile (> 20 years old)
FoamP@70C	Foam from stockpile heated to 70 °C for two month
FoamP@90C	Foam from stockpile heated to 90 °C for two month
FoamP@110C-1month	Foam from stockpile heated to 110 °C for one month
FoamP@110C-1month	Foam from stockpile heated to 110 °C for two month
FoamN	New foam made in 2012
FoamN@70C	New foam heated to 70 °C for two month
FoamN@90C	New foam heated to 90 °C for two month
FoamN@110C-1month	New foam heated to 110 °C for one month
FoamN@110C-1month	New foam heated to 110 °C for two month
EpoxyP	Epoxy with glass from stockpile (> 20 years old)
EpoxyP @70C	Epoxy from stockpile heated to 70 °C for two month
EpoxyP @90C	Epoxy from stockpile heated to 90 °C for two month
EpoxyP @110C-1month	Epoxy from stockpile heated to 110 °C for one month
EpoxyP @110C-1month	Epoxy from stockpile heated to 110 °C for two month
EpoxyN	New epoxy without glass made in 2012
EpoxyN@70C	New epoxy heated to 70 °C for two month
EpoxyN @90C	New epoxy heated to 90 °C for two month
EpoxyN @110C-1month	New epoxy heated to 110 °C for one month
EpoxyN @110C-1month	New epoxy heated to 110 °C for two month

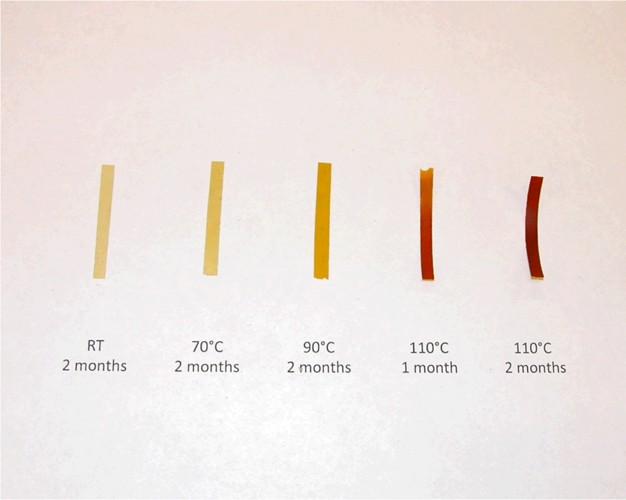
Visual Comparison of Aged Materials



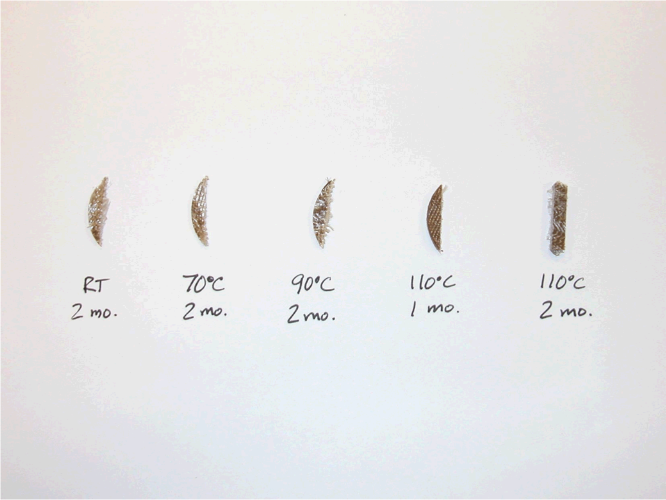
FoamN



FoamP



EpoxyN

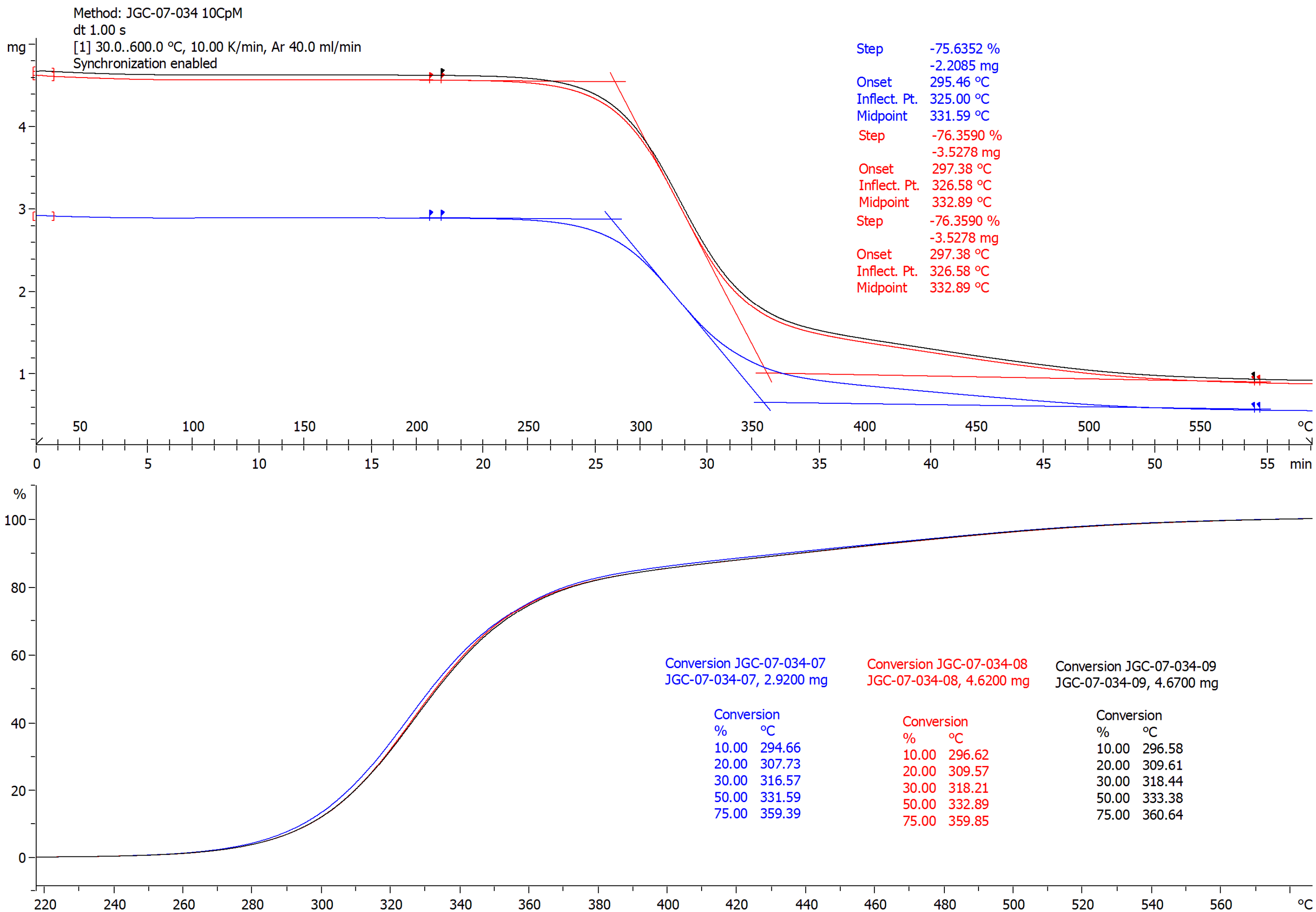


EpoxyP

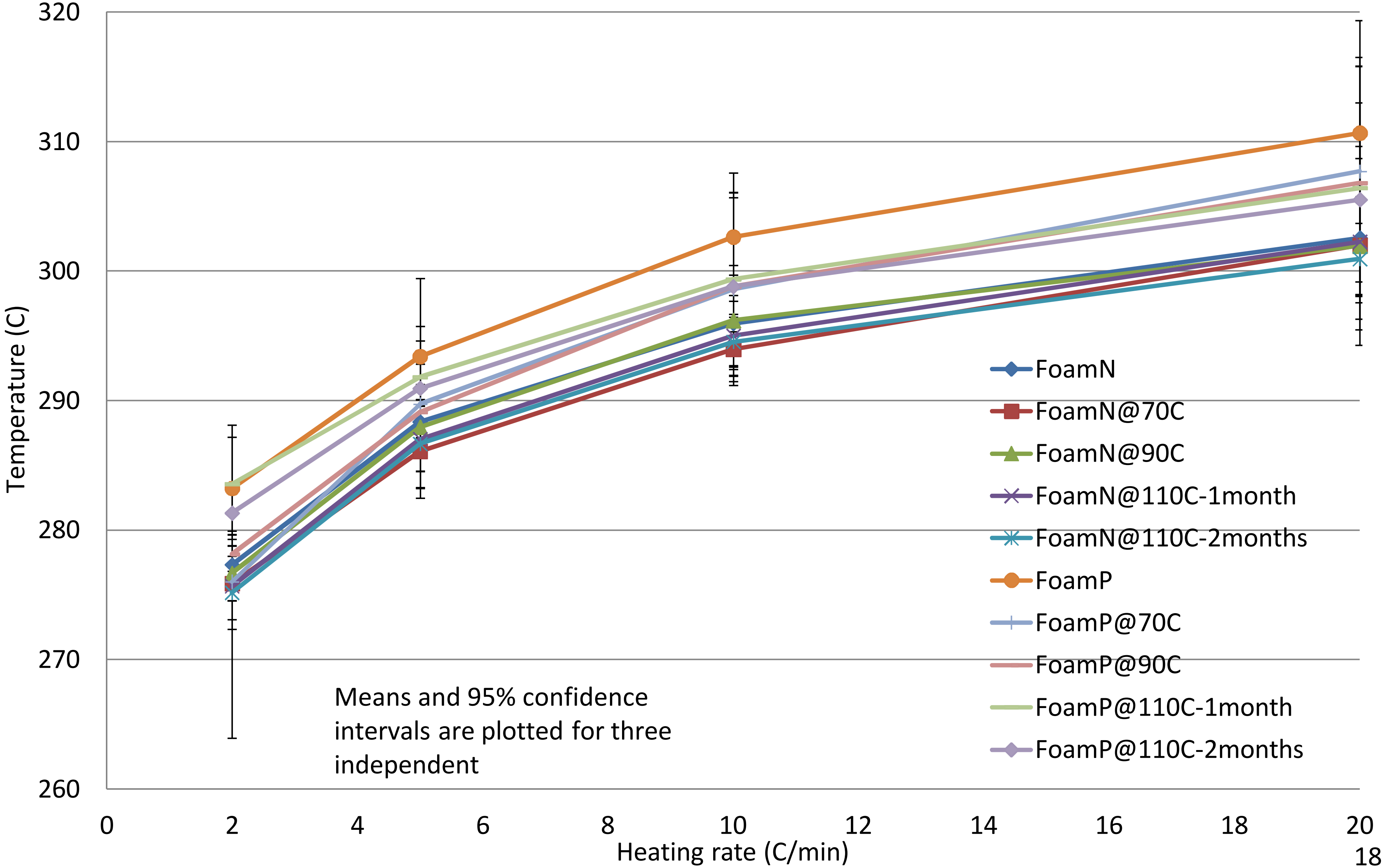
Experimental Procedure and Data Processing

- Standard data collection and analysis
  - Heated from 30 – 600 C under argon and measured weight loss (TGA) and heat flow (DSC)
  - Varied heating rate (α) 2, 5, 10 and 20 C/min
  - Repeated three times
  - Compared % conversion (β) at different heating rates for each material
  - Also (attempted) analyzes of 1st derivative of heat-flow from DSC to confirm methodology
- Model-Free Kinetics Approach
  - Calculate the apparent activation energy (E_a) of decomposition reaction using variable heating rate data
  - Plot E_a as a function of α and compare to un-aged materials

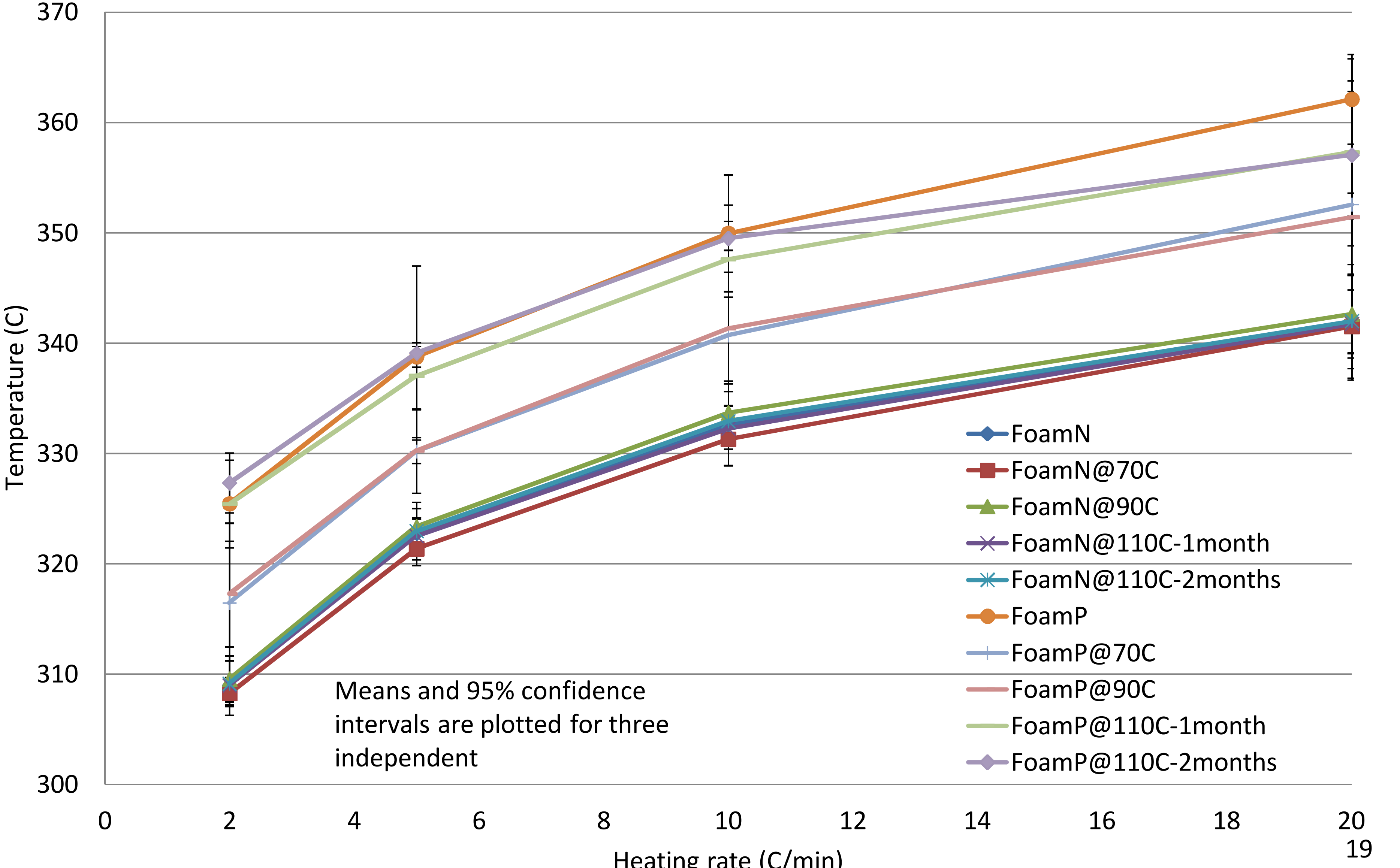
Typical TGA Data for FoamN



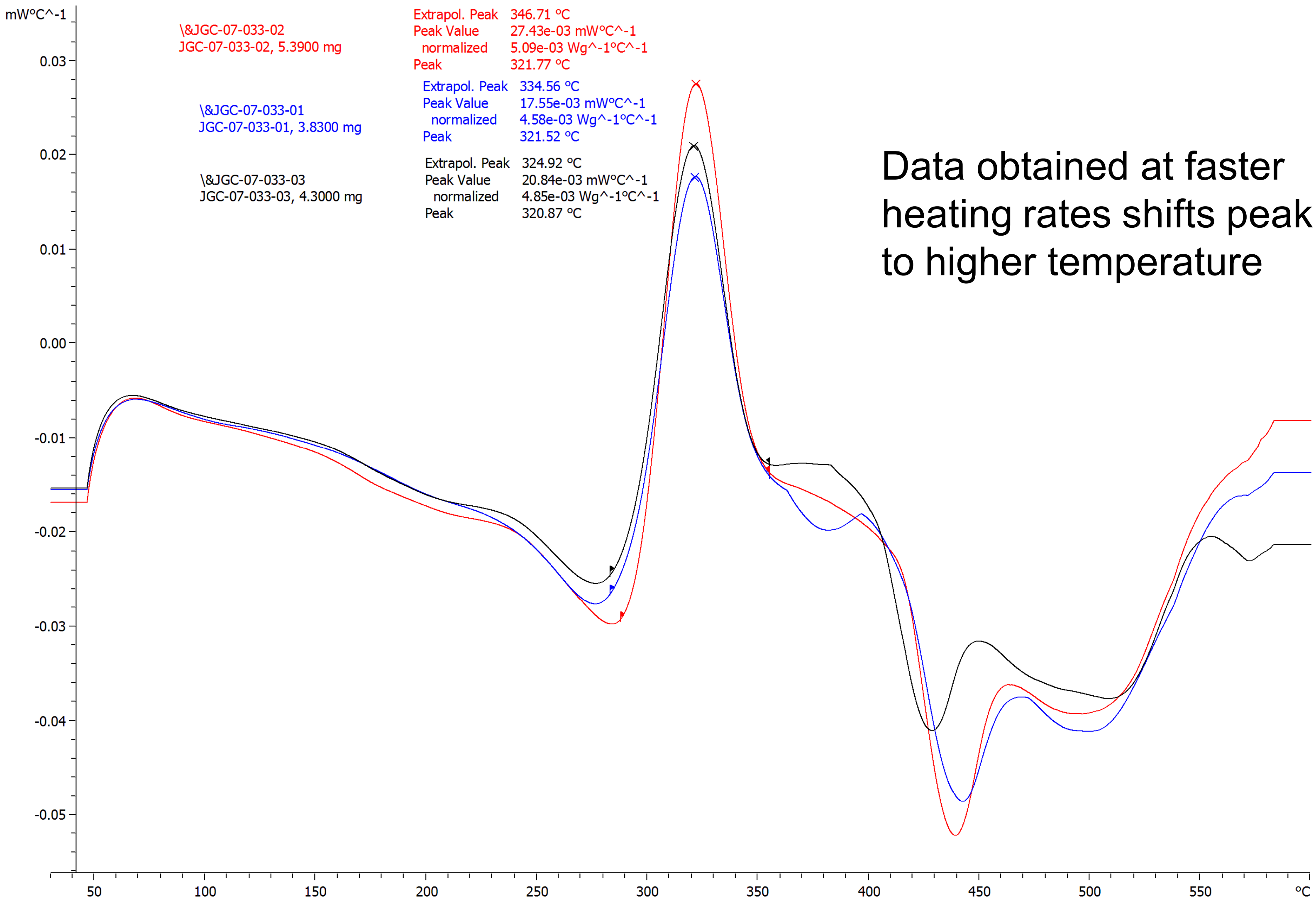
Foams: T vs. Heating Rate: α=10%



Foams: T vs. Heating Rate: α=50%

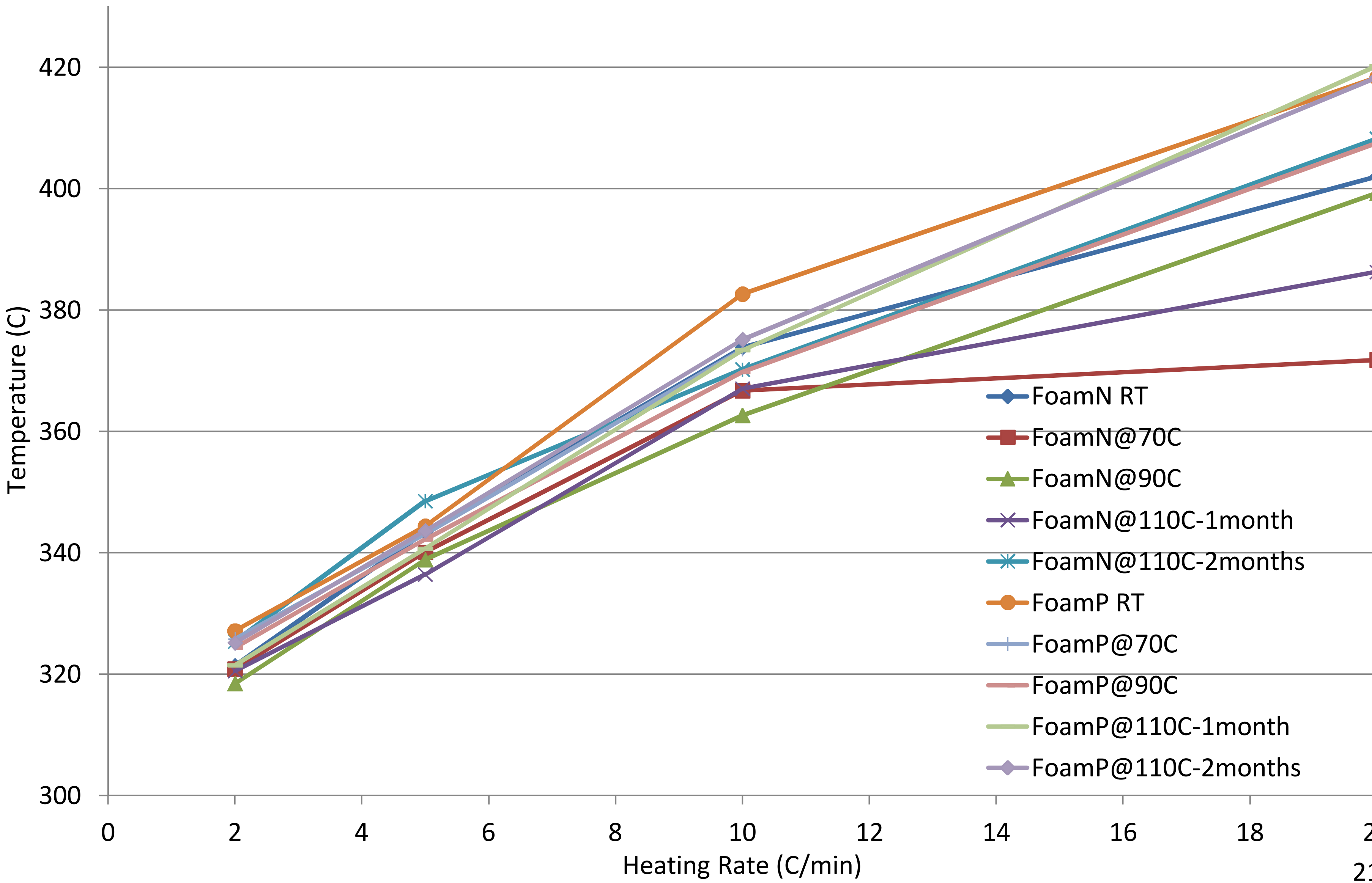


1st Derivative of DSC Data FoamN



Data obtained at faster heating rates shifts peak to higher temperature

Foams: Plots of 1st Derivative DSC Data

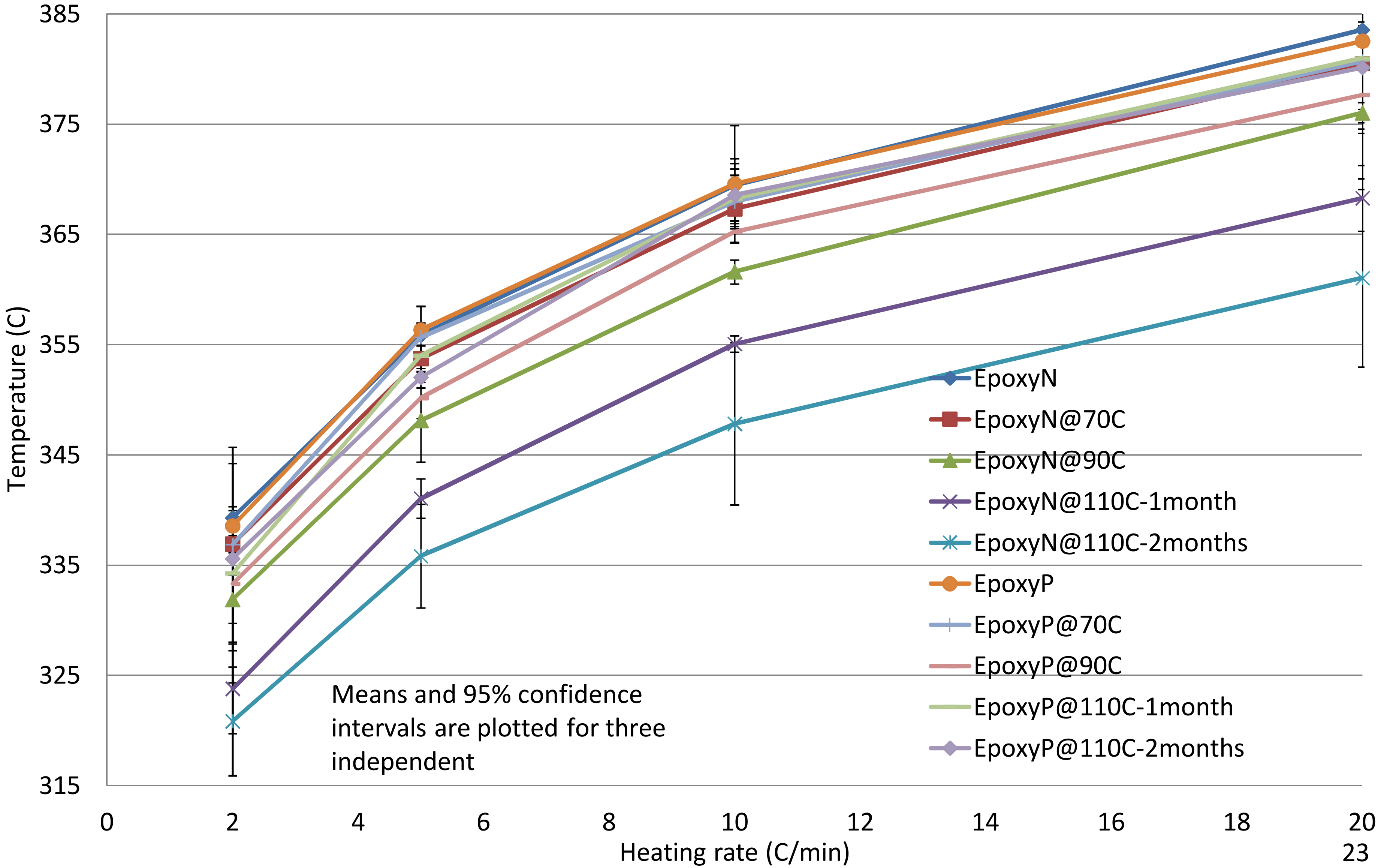


Foam Summary of 10 and 50% Conversion

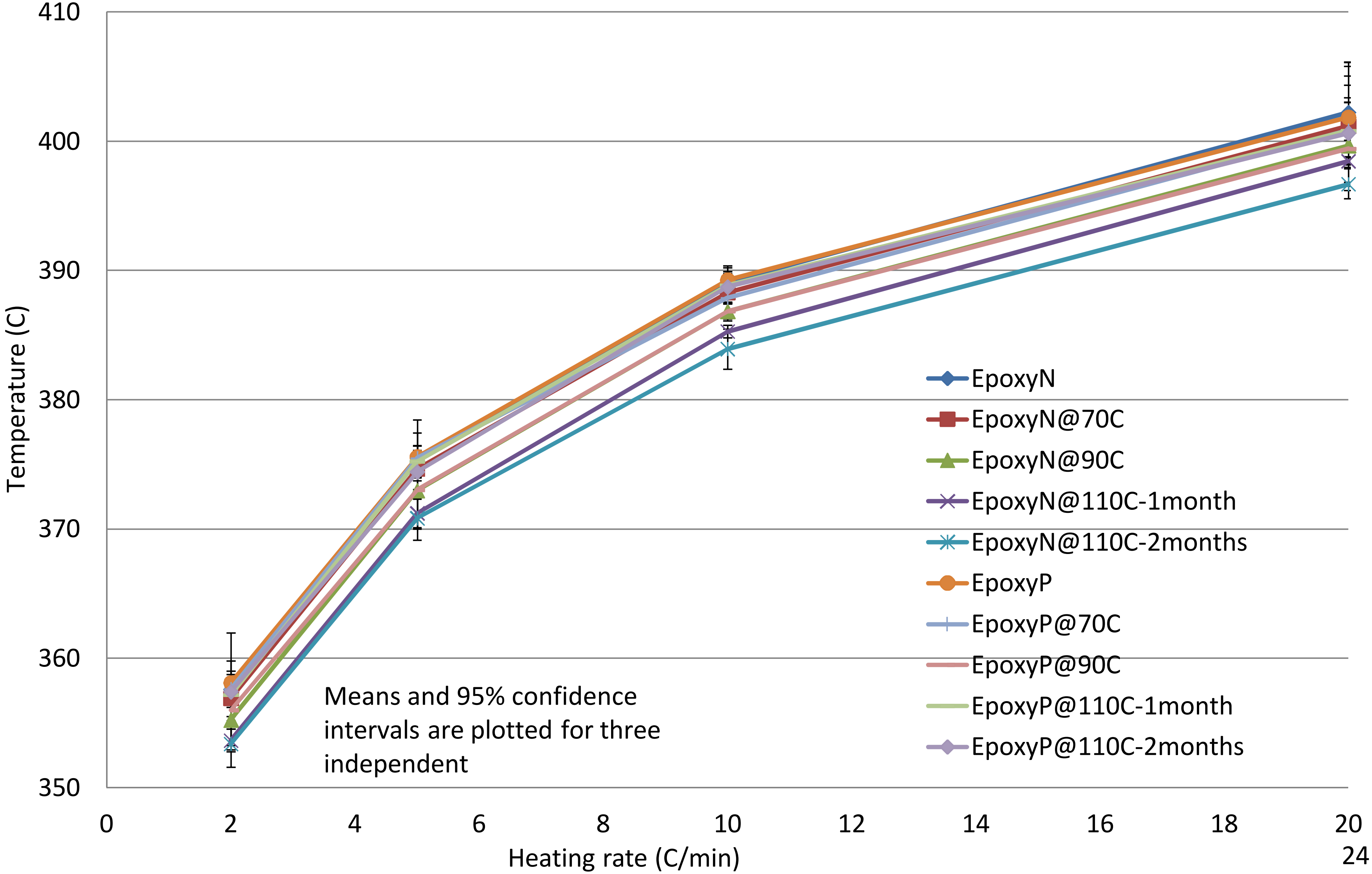
- FoamP consistently has the highest temperature versus β compared to the aged parts but the difference is within experimental error.
- From these data, it appears that FoamN has a slightly lower thermal stability compared to FoamP, which could be due to a difference in polymer density

- DSC data are inconclusive due to scatter

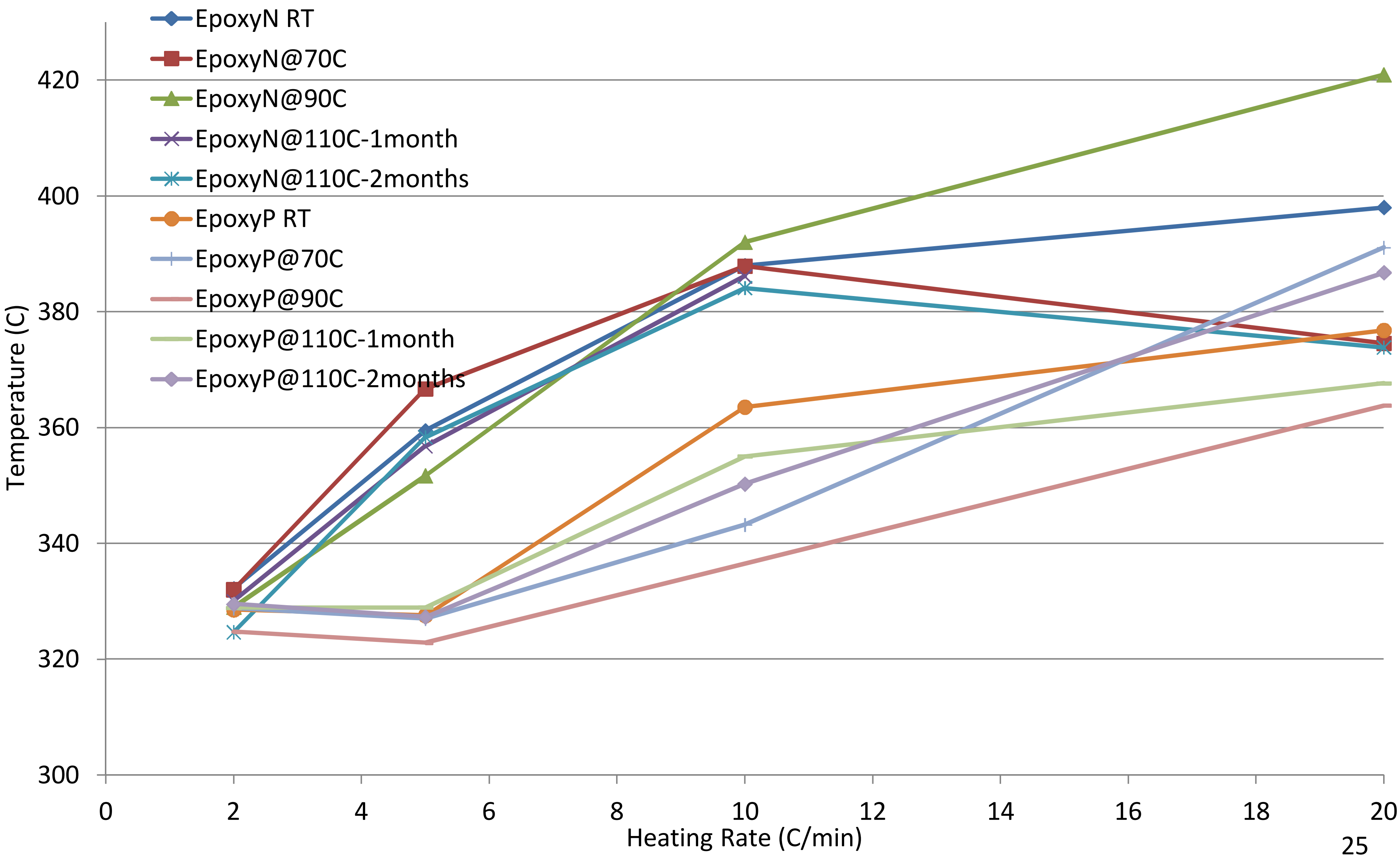
Epoxies: T vs. Heating Rate: α=10%



Epoxies: T vs. Heating Rate: α=50%



Epoxy: Plots of 1st Derivative DSC Data



Epoxy Summary of 10 and 50% Conversion

- EpoxyP and EpoxyN have nearly identical T versus β curves despite EpoxyP containing a glass filler and being a decades-old part
- The effects of aging on EpoxyN are more pronounced compared to EpoxyP
- EpoxyN@110-2months drops nearly 20 degrees whereas EpoxyP@110-2months shows <5 °C decrease in temperature for 10% conversion at all β values
- At α = 50% the differences between all 10 materials decreases significantly compared to α = 10%.

Model-Free Kinetics

- Assumes Arrhenius-type temperature dependency for the chemical reaction
- No knowledge of the reaction mechanism is required
- Apparent activation energy (E_a) is a function of reaction conversion (α) and not heating rate (β)

- Allows for prediction of a chemical conversion at any other isothermal temperature or heating rate (almost)

Apparent Activation Energy FoamN

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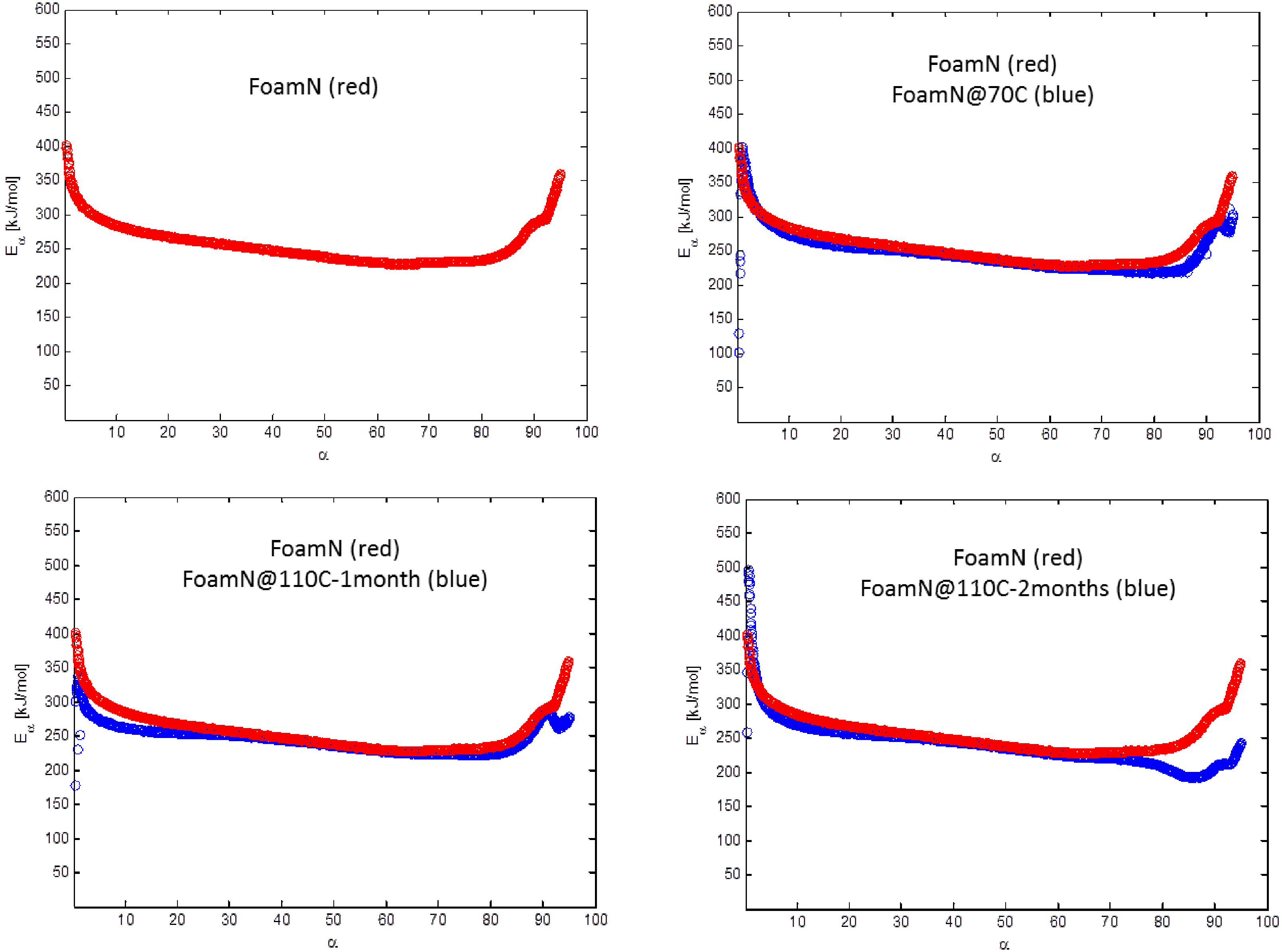
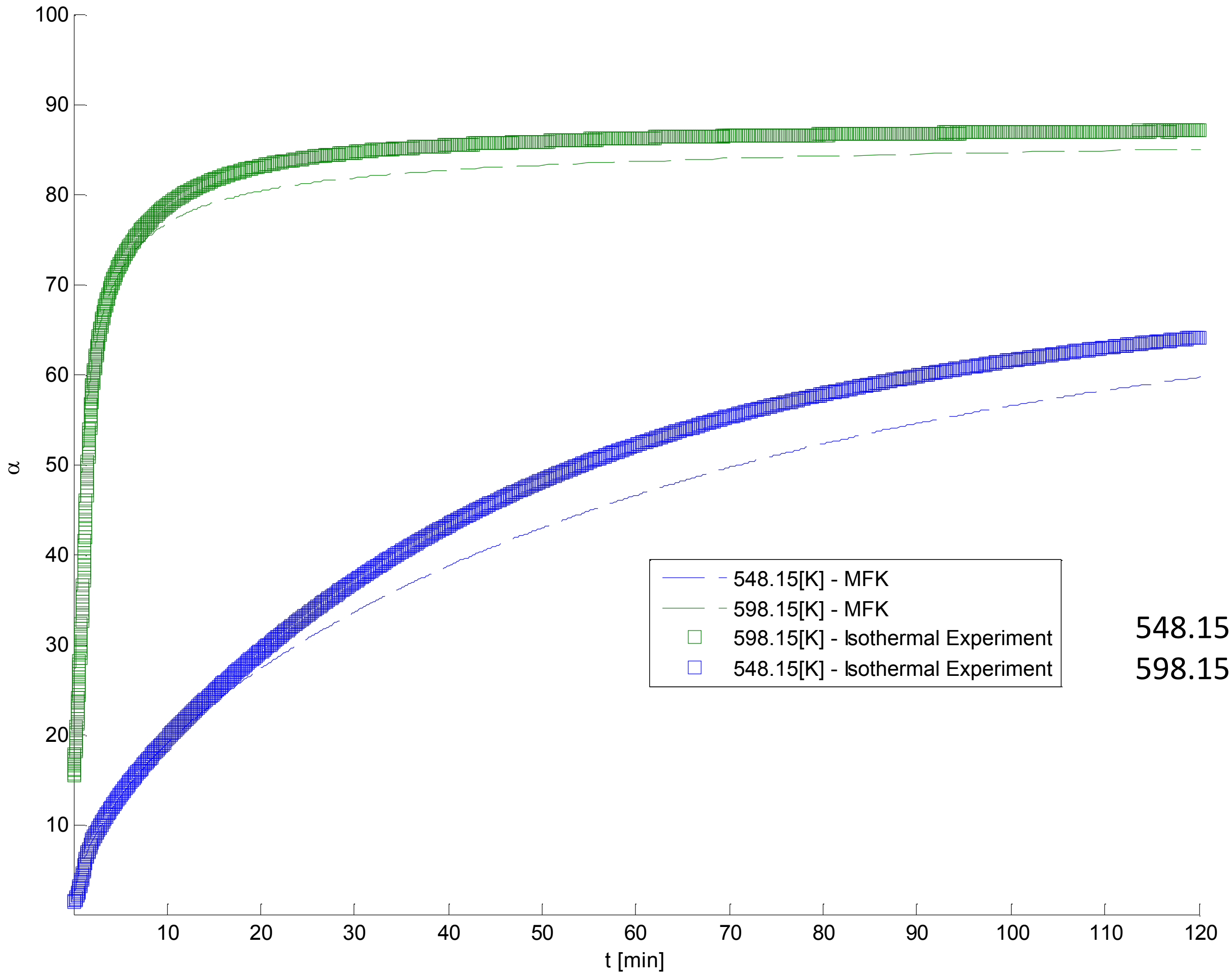
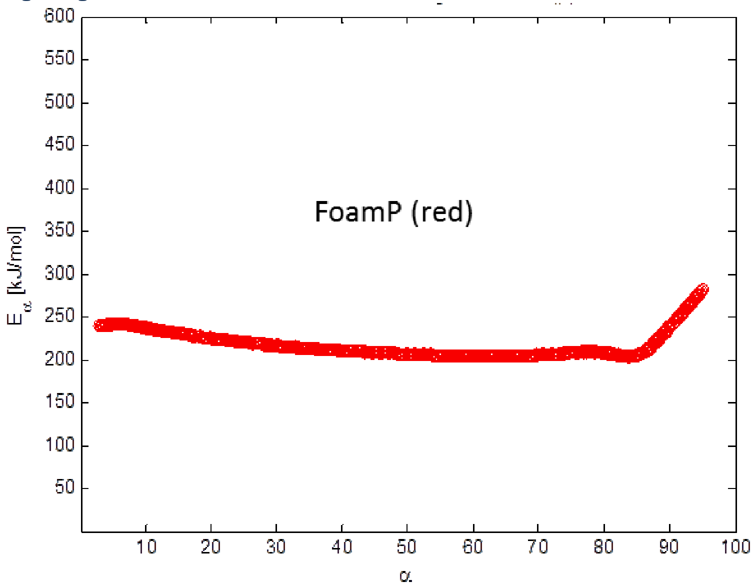


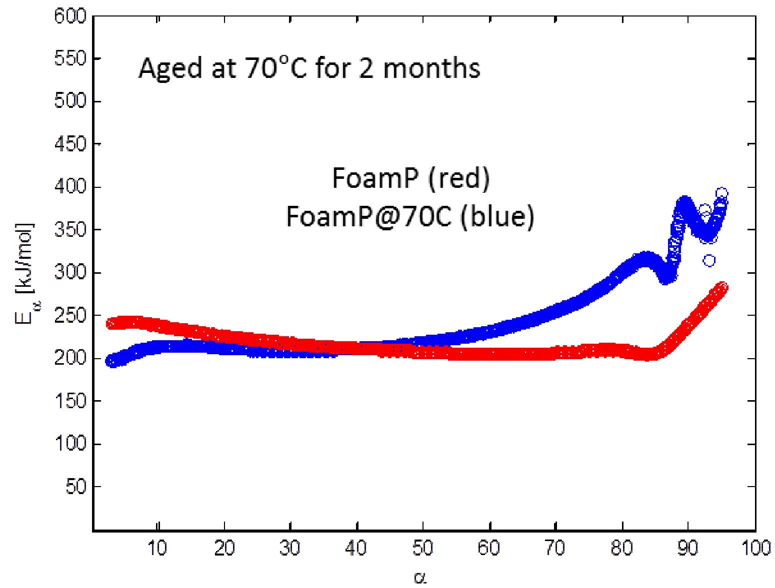
Comparing MFK to Isothermal Experiments: FoamN

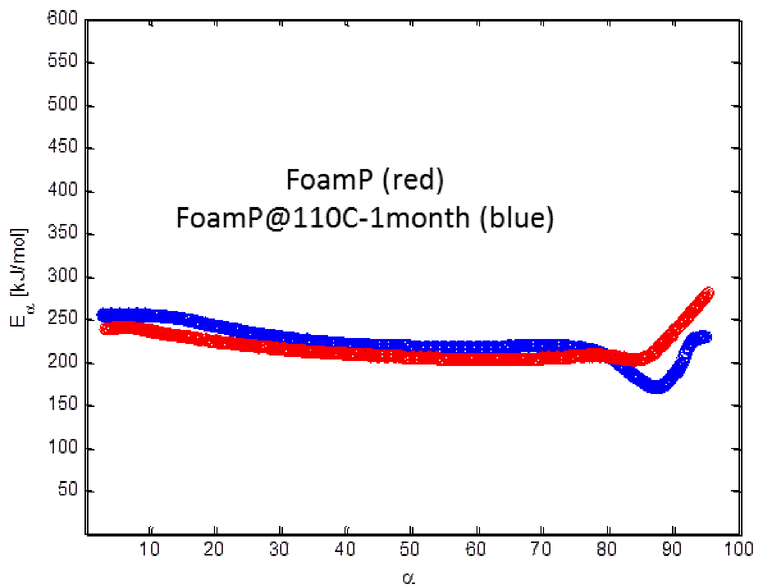


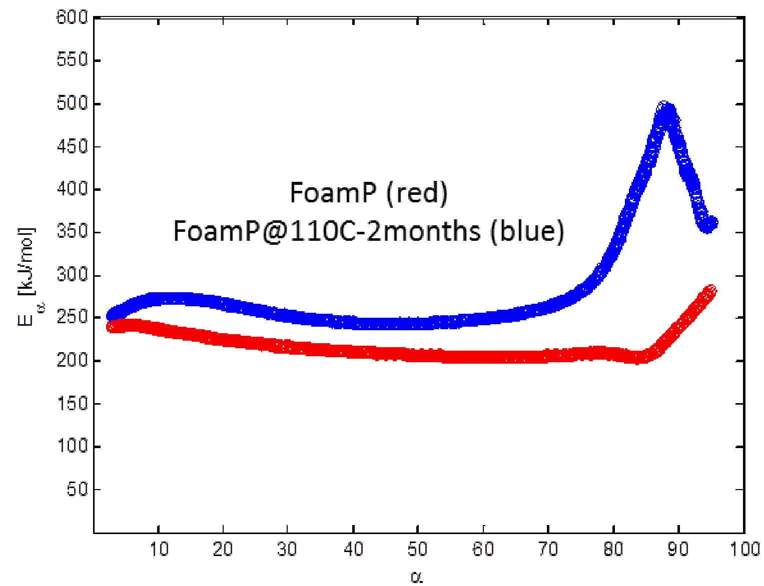
548.15[K]=275°C
598.15[K]=325°C

Apparent Activation Energy: FoamP

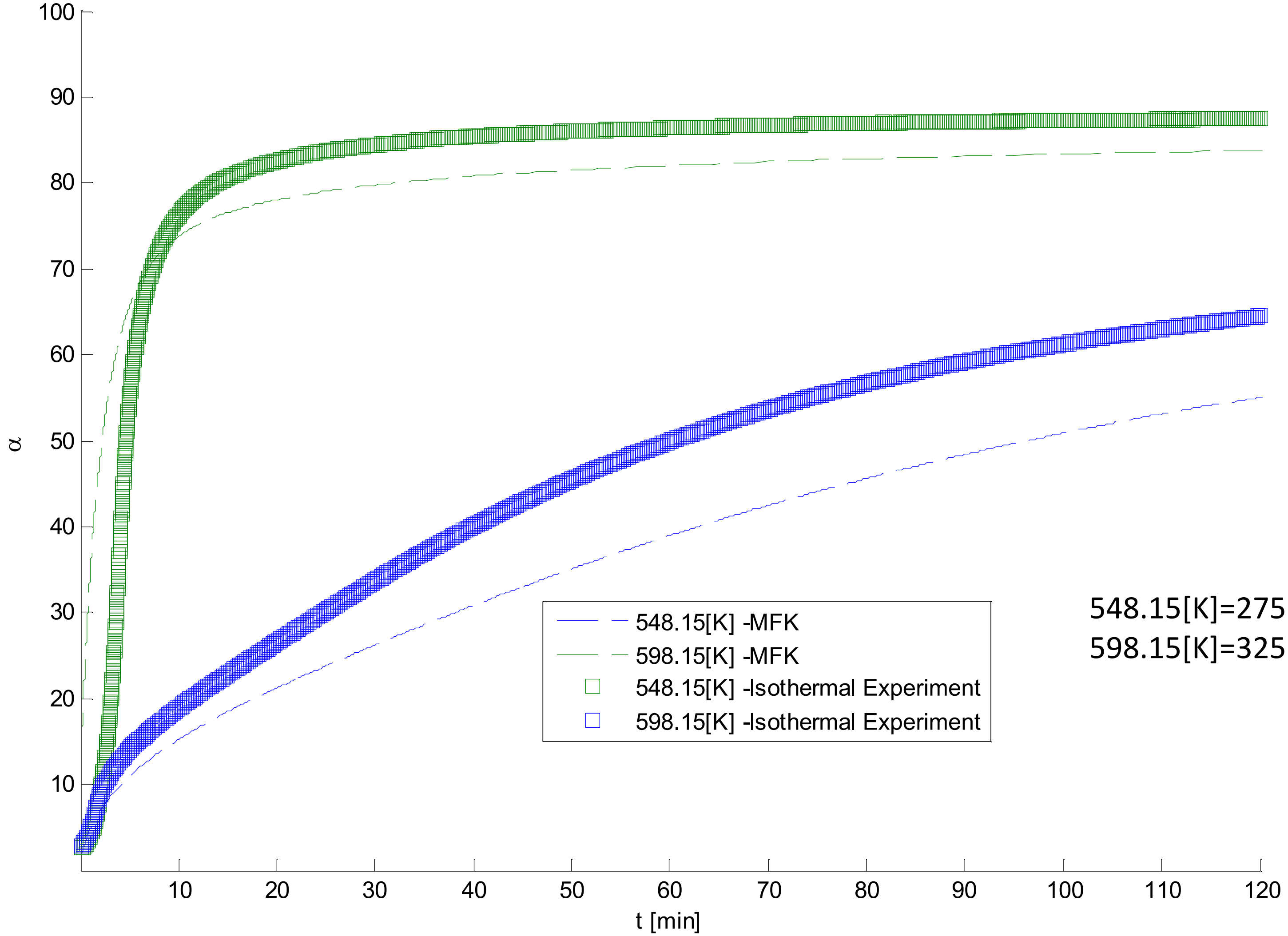








Comparing MFK to Isothermal Experiments: FoamP



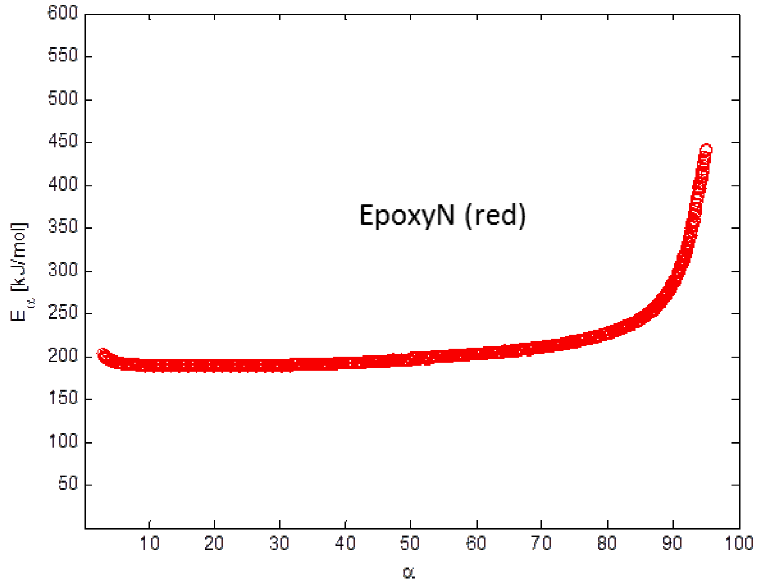
548.15[K]=275°C
598.15[K]=325°C

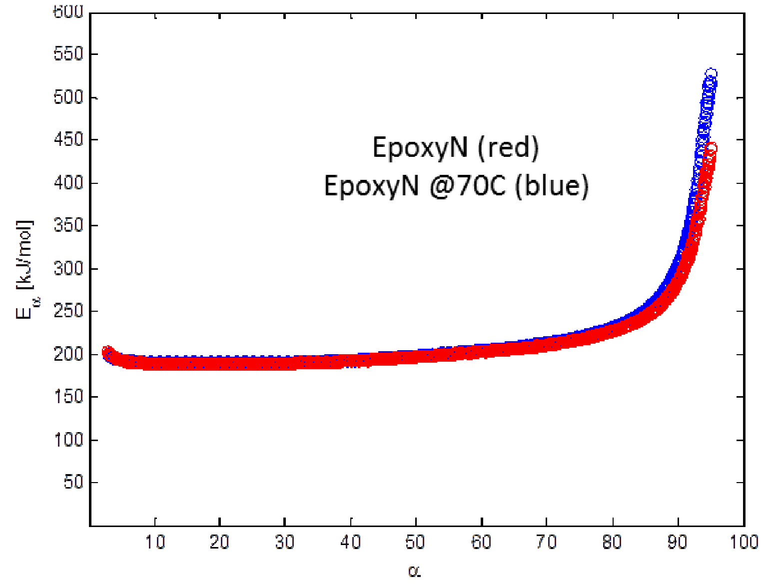
Foam Summary of MFK Analyses

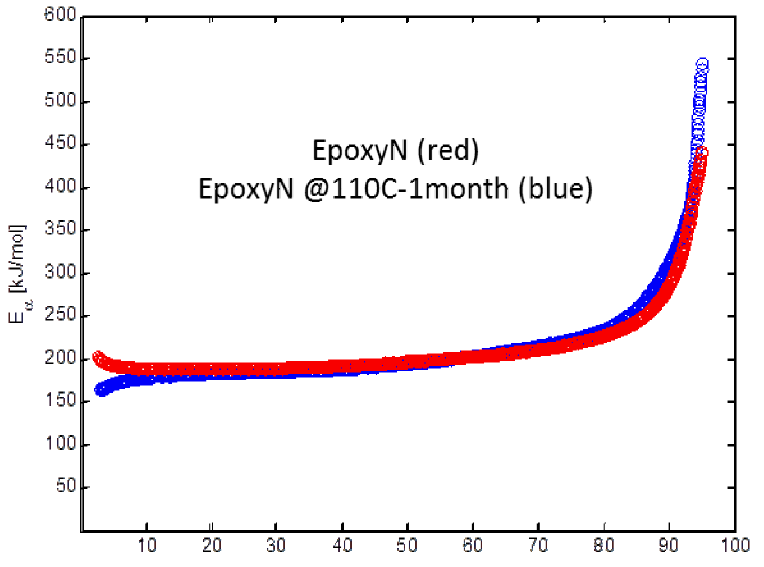
- For FoamN, the E_a is nearly identical for α = 30 – 70% but some modest deviations are observed at α < 10%. Specifically, FoamN@110C-1month shows a lower apparent activation energy than FoamN, which could be attributed to aging. However, this difference is lost for FoamN@110C-2month

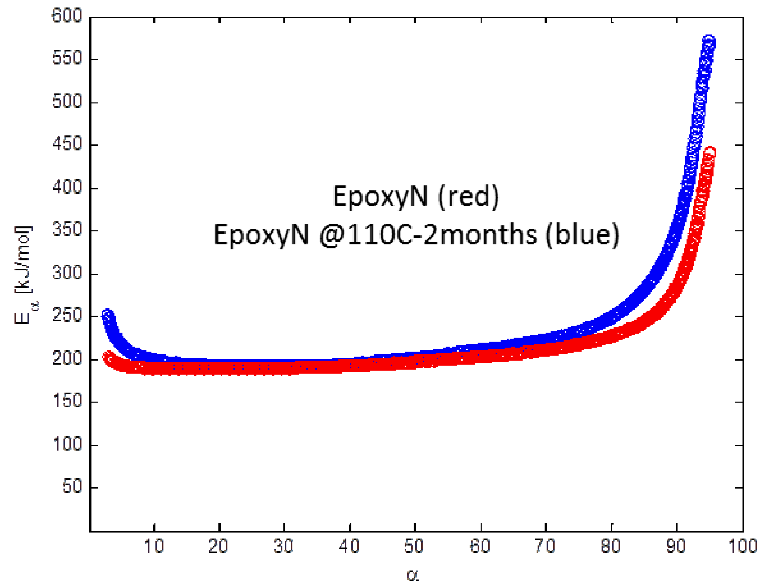
- Differences in E_a for FoamP are more notable. Compared to the un-aged sample in red, the aged samples have a higher apparent activation energy except for FoamP@70C, which crosses at α = 45%

Apparent Activation Energy: EpoxyN

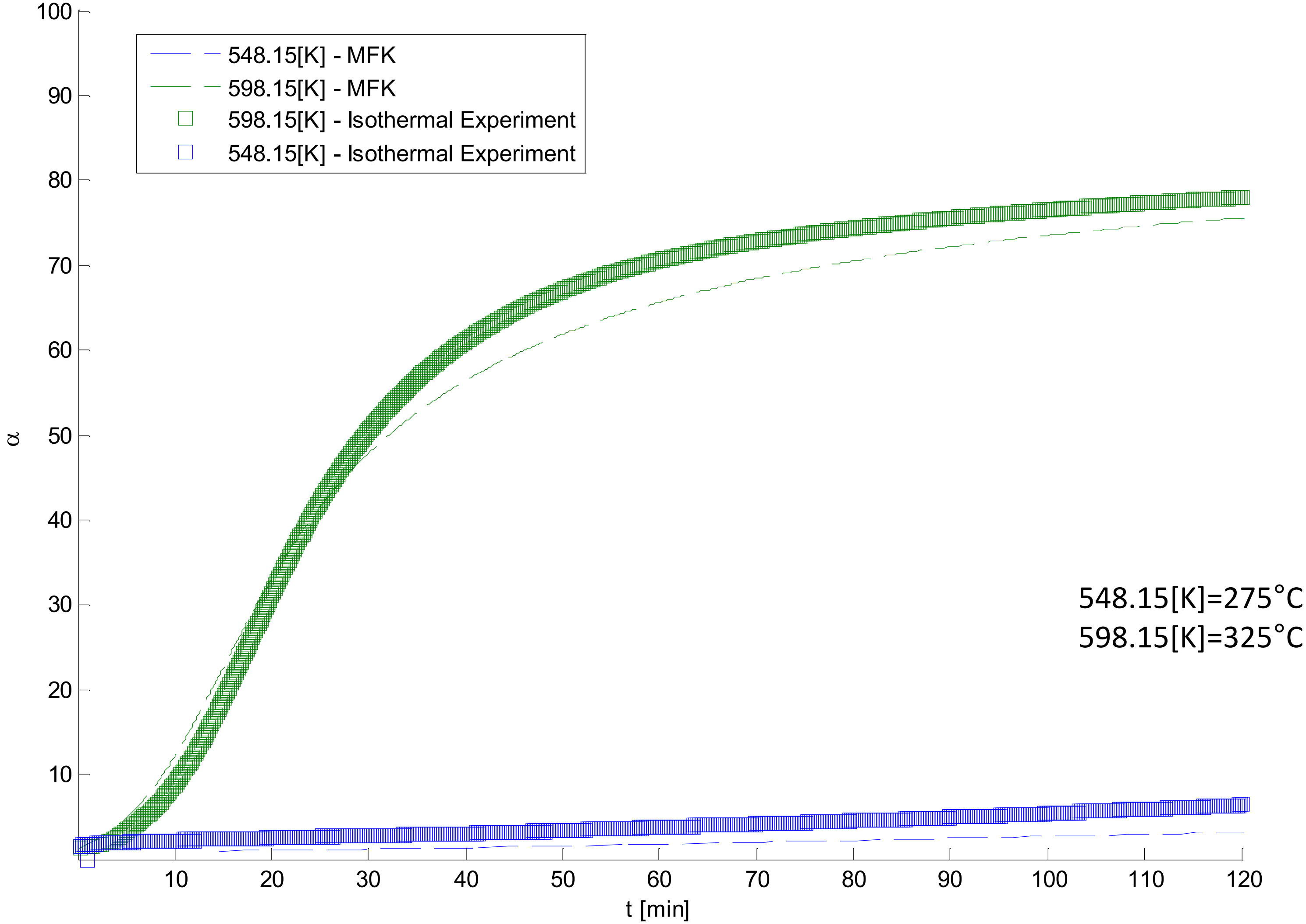




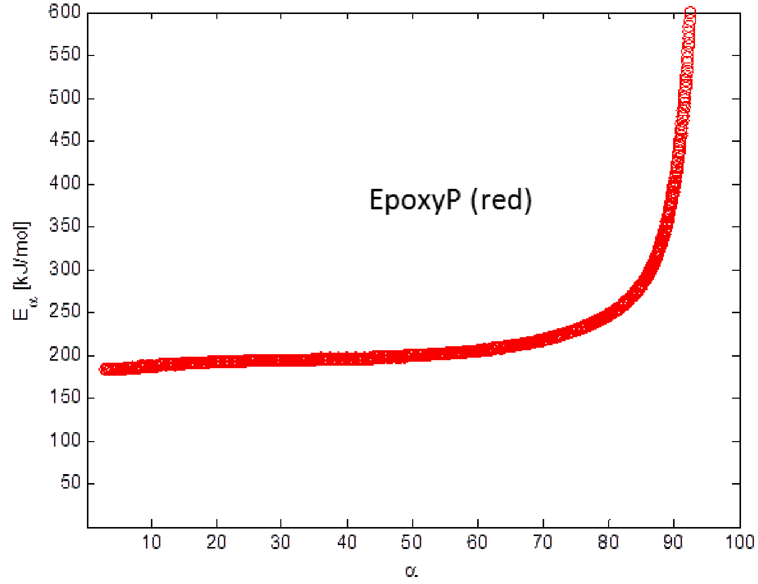


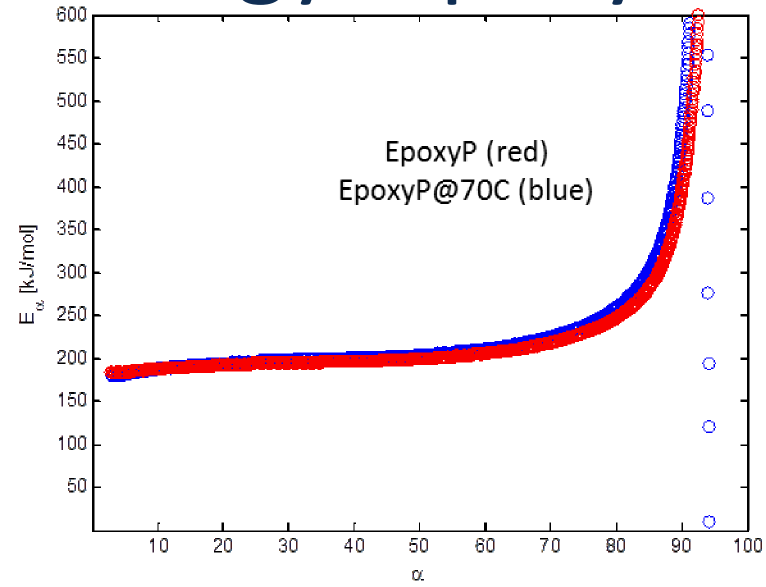


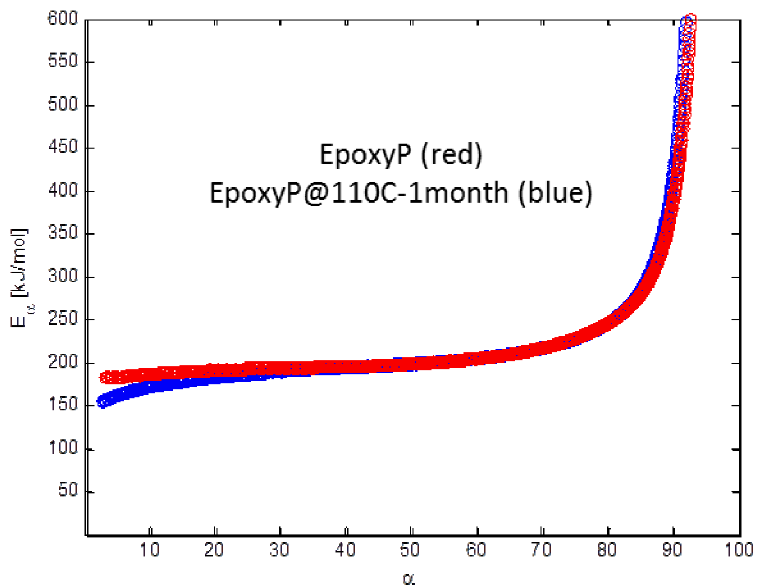
Comparing MFK to Isothermal Experiments: EpoxyN

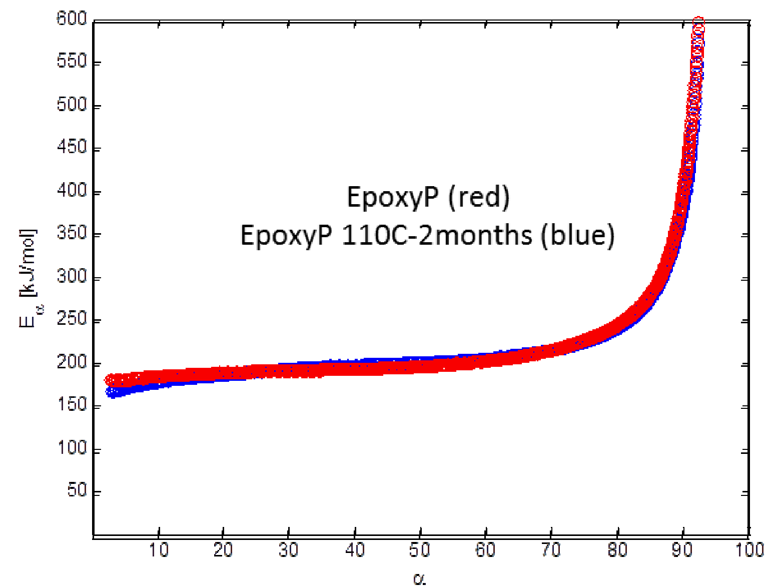


Apparent Activation Energy: EpoxyP

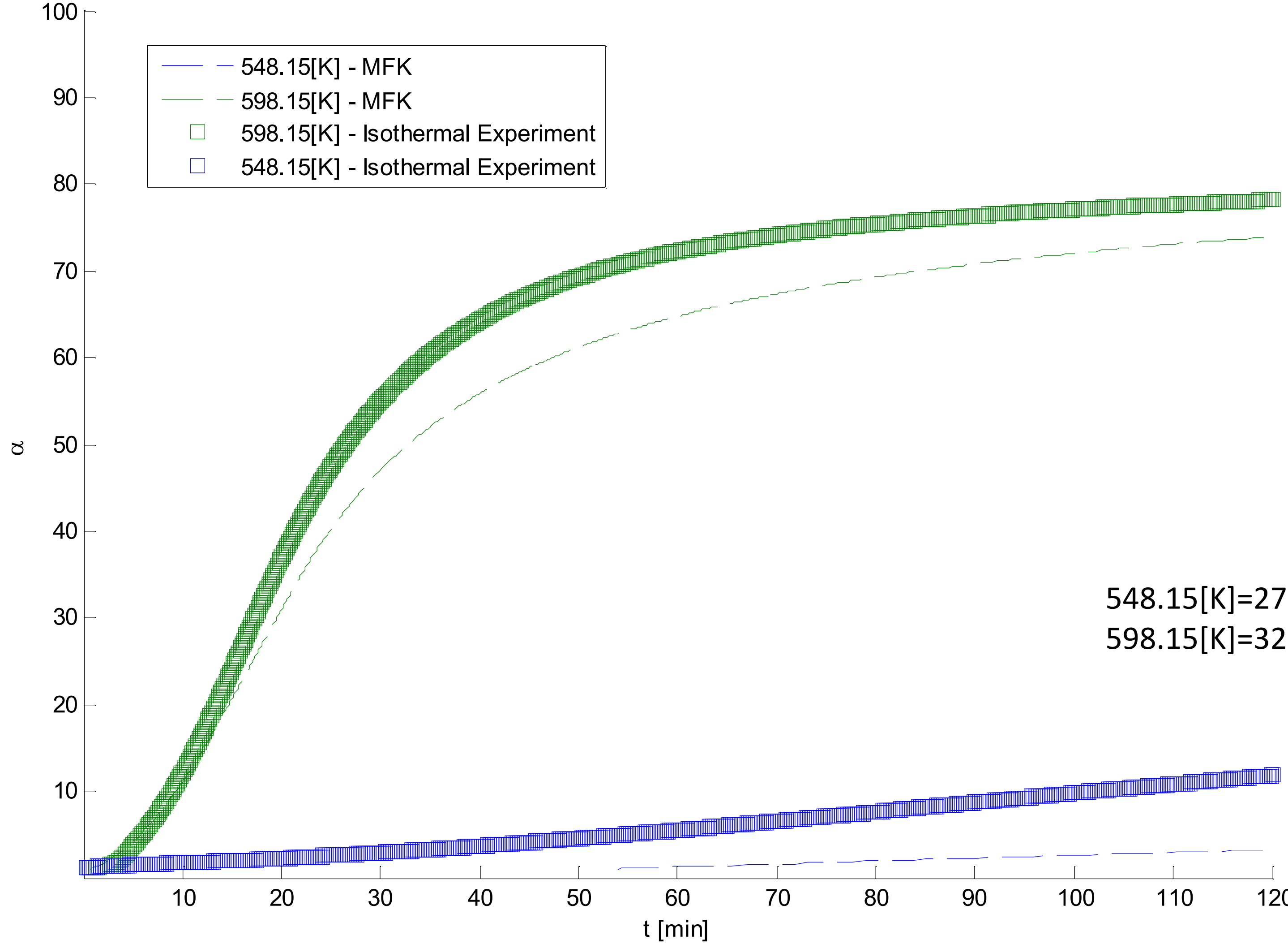








Comparing MFK to Isothermal Experiments: EpoxyP



548.15[K]=275°C
598.15[K]=325°C

Epoxy Summary of MFK Analyses

- Only modest differences are observed for all α except at α < 10%. Where there is deviation, for example EpoxyN, the differences are not consistent; EpoxyN@110C-1month has a lower apparent activation energy than EpoxyN but for EpoxyN@110C-2months it is the opposite.

- EpoxyP@110-1month and 2months at α < 10% both appear to have lower E_a compared to EpoxyP but the differences are modest.

Overall Summary and Conclusions

- Results show temperature spread is larger at lower conversions (10% versus 50%).
- Convergence is seen as the decomposition progresses, suggesting thermal decomposition is nearly independent of aging. This point demonstrates the need to understand *initial rates of reaction at lower temperatures, where differences between materials are most significant.*
- Model-free kinetics can potentially be a powerful tool for predicting thermal stability

Future work:

Continue to use MFK to understand higher temperature environments

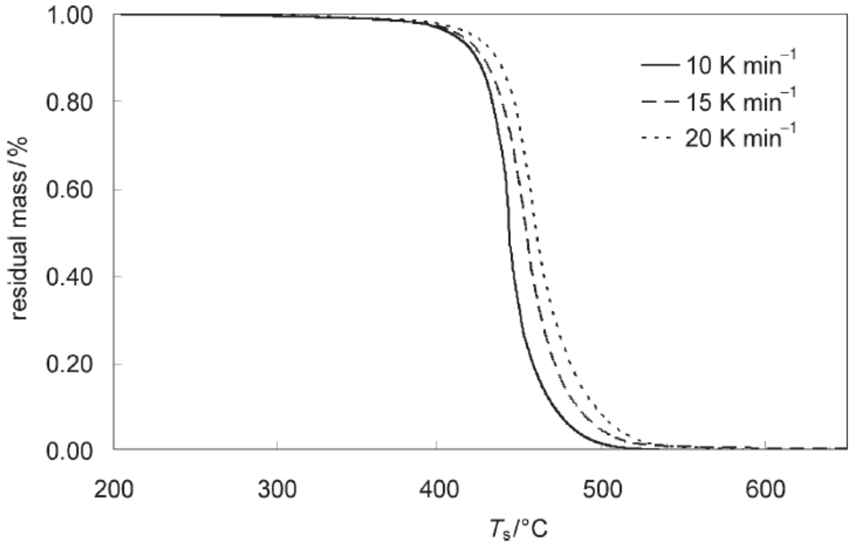
Back-up

Introduction to Model Free Kinetics

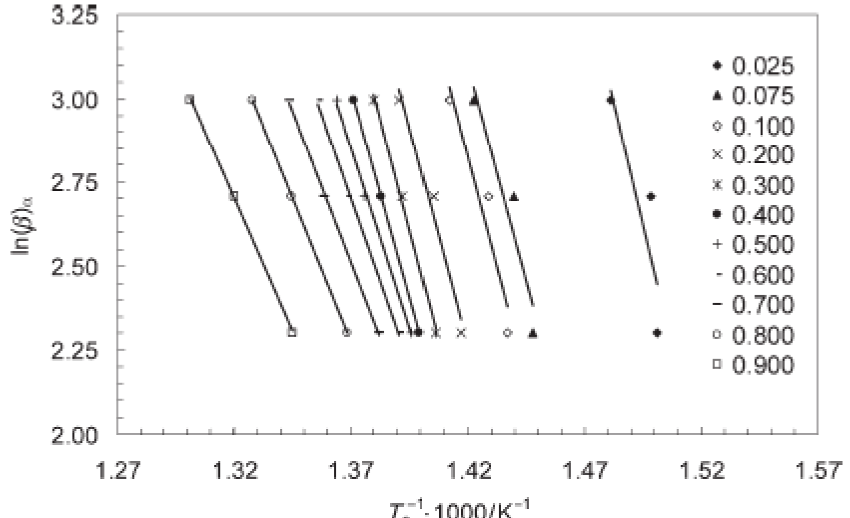
- Problem:
  - Solid-state reactions are difficult to predict because heterogeneous conditions prevent a consistent model from being employed
- Technique Summary:
  - Isothermal reaction rates can be predicted from variable temperature rate conversion experiments
- Desired output:
  - Output: We want to know the isothermal rate of conversion.
    - $\frac{d\alpha}{dt} = k(T)f(\alpha)\,;\; k(T) = A\,exp\left(-\frac{E}{RT}\right); f(\alpha)$ =mechanism changes w/ α
    - Rearranged: $\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\frac{dt}{dT} = \frac{A}{\beta}\,exp\left(-\frac{E}{RT}\right)f(\alpha); \beta = \frac{dT}{dt}$
    - Approximate solution for $\frac{d\alpha}{dT}$:
      - $g(\alpha) = \frac{A}{\beta}\int_0^T exp\left(-\frac{E}{RT}\right)dT = \int_0^\alpha \frac{1}{f(\alpha)}d\alpha$
- Assumptions:
  - Constant extent of conversion only depends upon temperature
    - $ln\left(\beta\frac{d\alpha}{dt}\right)_\alpha = ln(A_\alpha f[\alpha]) - \frac{E_\alpha}{RT}$ (Mathematical result of assumption)

Parameters Needed:

Conversion at different heating rates



Heating rate vs. inverse temp (constant α)



$$Effectively\ \frac{d\alpha}{dT}$$

$$ln\left(\beta\frac{d\alpha}{dt}\right)_\alpha = ln(A_\alpha f[\alpha]) - \frac{E_\alpha}{RT}$$

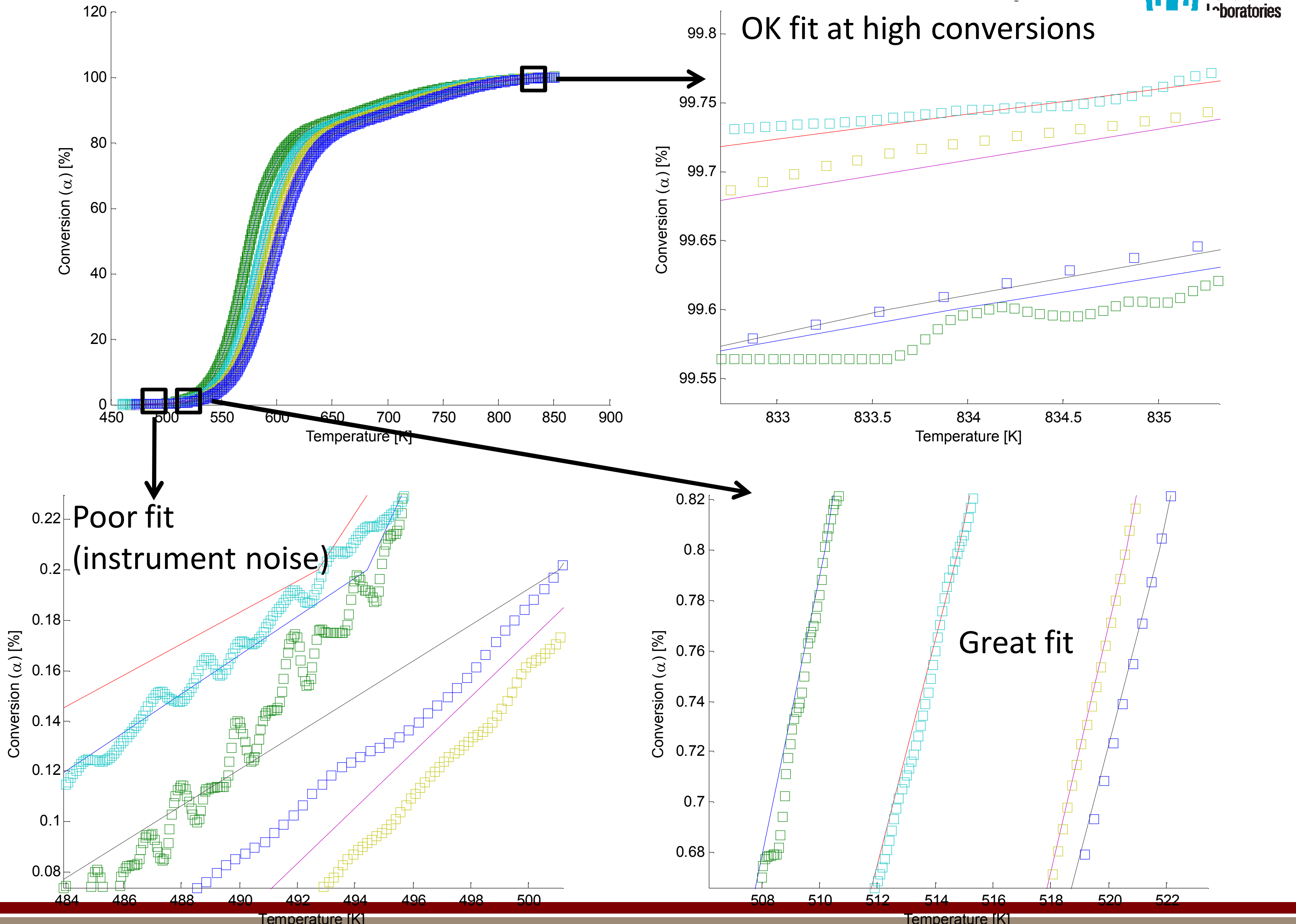
$$ln(\beta)_\alpha = INTERCEPT - \frac{E_\alpha}{R}\left(\frac{1}{T}\right)$$

Slope

Inherent Uncertainties

- Fitting functions
  - General fits: used a cubic spline (piecewise defined polynomial)
  - α vs T: characterize variations and then choose $\Delta\alpha$
- Only three β needed for a line
  - Effect due to using a combination of three or all four
- Noise at very low values of α

Cubic spline fit: with caveat - only evaluate between 0.5<α<99.5



Isothermal Analysis

1. Determine average mass loss / series (i.e. FoamN as made was 76%±1.6)
2. Calculate for time step $\alpha = \frac{M_i - M_t}{M_i - M_f}$;
3. $t_o = T_{iso}[K]$

M_i - initial mass,
M_f- final mass
M_t-mass at each discrete times