Can non-isothermal decomposition measurements be used to assess aging of polymers?

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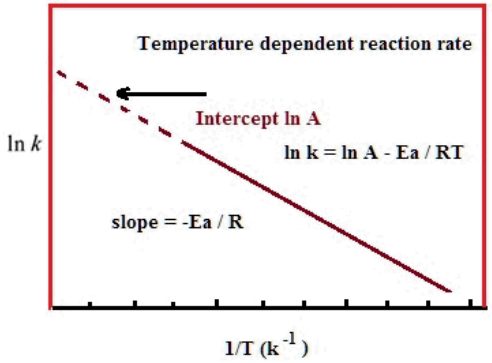
Isothermal Kinetic Measurements

- Traditionally the rate of a reaction is measured at a fixed temperature (isothermal)
  - Multiple measurements at different temperatures (T_n) can be used to determine rate constants (k) and calculate the activation energy (E_a)
  - Some knowledge of the reaction mechanism is required to fit data and obtain meaningful information about the kinetics
  - Great for homogeneous kinetics
  - Limited by the time it takes sample to reach the reaction temperature—reactions can occur prior to reaction T_n
  - Complicated for heterogeneous kinetic reactions

$$\ln(k) = \ln(A) - \frac{E_a}{R} * (\frac{1}{T})$$

Arrhenius equation



Non-Isothermal Kinetic Measurements

- Non-isothermal techniques can be advantageous because sample changes can be measured as the temperature is changed- no temperature jump required
  - Usually faster to collect data and requires fewer experiments

$$\frac{d\alpha}{dt} = \frac{A}{\beta} * e^{-(\frac{E_a}{RT})} * f(\alpha)$$

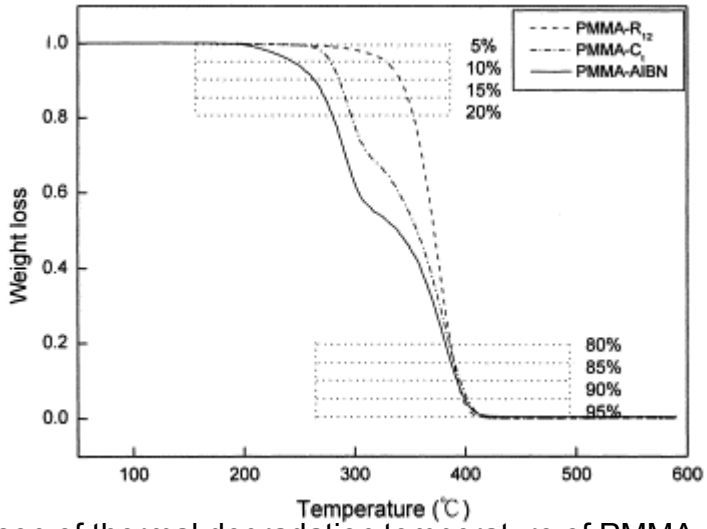
Where α is the extent of conversion at a given time and β is the heating rate; $f(\alpha)$ is the reaction model which can be chosen to fit the data or *a prior* if reasonable information about the mechanism is known

Arrhenius parameters (A and E_a) and reaction model are referred to as the "kinetic triplet"

Vyazovkin, S.; Wight, C. A., *Thermochimica Acta* **1999**, 340–341, 53-68.

Non-Isothermal Degradation Studies via TGA

- Polymer degradation can begin at chain ends
  - Weak links in the polymer chain appear in the initial stages of thermal decomposition
- Thermal gravimetric analyses (TGA) can measure weight loss of sample as a function of temperature



Comparison of thermal degradation temperature of PMMA–R12, PMMA–Ct, and PMMA–AIBN at heating rate 20 °C/min.
From: Hu, Y.-H.; Chen, C.-Y., *Polymer Degradation and Stability* **2003,** *82* (1), 81-88.

- Weight loss for thermal degradation directly related to α
- Therefore, by varying the heating rate β and running a series of TGA experiments, one can mathematically solve for A and E_a
- Still limited by knowledge of $f(\alpha)$

Various Kinetic Models

	Reaction model	$f(\alpha)$	$g(\alpha)$
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	$1/2\alpha^{-1}$	α^{2}
6	Mampel (first-order)	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami–Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$	$[1-(1-\alpha)^{1/3}]^{2}$
11	Contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	Second-order	$(1-\alpha)^{2}$	$(1-\alpha)^{-1}-1$

Drawbacks to nonisothermal model fitting

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- Forced fitting of data to hypothetical kinetic model
  - Since T and α vary simultaneously almost any f(α) can satisfactorily fit data
- Isothermal and nonisothermal experiments are necessarily conducted in different temperature regions
  - Can results in large discrepancies between two measurements
- Multistep decomposition paths are especially problematic
  - Activation energy becomes an average of these steps rather than varying over entire decomposition

Vyazovkin, S.; Wight, C. A., *Thermochimica Acta* **1999**, 340–341, 53-68.

Isoconversional Kinetic Methods

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- Extent of conversion is related to the rate constant reaction mechanism:

$$\frac{d\alpha}{dt} = k(T) * f(\alpha) \qquad (1)$$

- Logarithmic derivative of the rate at constant α:

$$\left[\frac{\partial \ln(\frac{d\alpha}{dt})}{\partial T^{-1}}\right]_{\alpha} = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_{\alpha} + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_{\alpha} \qquad (2)$$

- At constant α and f(α), right term is zero and substituting in Arrhenius equation gives

$$\left[\frac{\partial \ln(\frac{d\alpha}{dt})}{\partial T^{-1}}\right]_{\alpha} = -\frac{E_a}{R} \qquad (3)$$

Developed by Friedman; later Flynn, Wall and Ozawa

Advantages of Isoconversional Kinetic Methods

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- Very simple easy-to-use method for kinetics evaluation, it doesn't require complex mathematics
- It doesn't require any ideas about model structure and initial guess on values of kinetic parameters
- It provides vivid indication of reaction complexity
- It is capable of good approximation of complex experimental data
- It can be successfully used for simulation of reaction course within the temperature interval covered by the experiment
- It has appropriate extrapolation capabilities for single-stage reactions
- It is very suitable for researchers that are not experienced in kinetics

http://www.researchgate.net/publication/253954940_Kinetics-based_simulation_approach_Model-free_versus_Model-based_kinetics_Pros_and_Contras

Limitations of Isoconversional (MFK)

- Overlapping endo and exothermic signals (melting and curing at the same time)
- Competing reaction pathways resulting in different end points
- Reactions with partial diffusion control
- Processes with back reactions
- Variations of reaction stoichiometry

While the activation energies obtained from model-free methods are independent of the heating rate, E_a shows a very strong dependency on the range of betas β's. Different E_a with α is caused by overlapping processes with different individual activation energies

1) "Model-Free Analysis of Thermoanalytical Data-Advantages and Limitations," Opfermann, J. R., Kaisersberger, E., and Flammersheim, H. J., **2002**, Thermo. Acta, 391 (1–2), pp. 119-127
2) "Critical study of the isoconversional methods of kinetic analysis," Criado, J. M.; Sánchez-Jiménez, P. E.; Pérez-Maqueda, L. A., J. Therm. Anal. Cal., **2008**, 92 (1), 199-203.

Weak Links and Polymer Aging

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- Polymer degradation can begin at chain ends
  - Weak links in the polymer chain appear in the initial stages of thermal decomposition
- Late stage mechanisms tend to be associated with normal polymer scissions along the backbone and an increase in the activation energy
  - More regular bonds are broken and the activation energy becomes more reflective of a single step
- Changes in polymer stability related to compositional changes are measurable using isoconversional kinetic methods to calculated changes in the activation energy
- Can this approach be extended to polymer aging or are the changes too subtle?

Isoconversional Kinetics Shows two Stages with Different E_a

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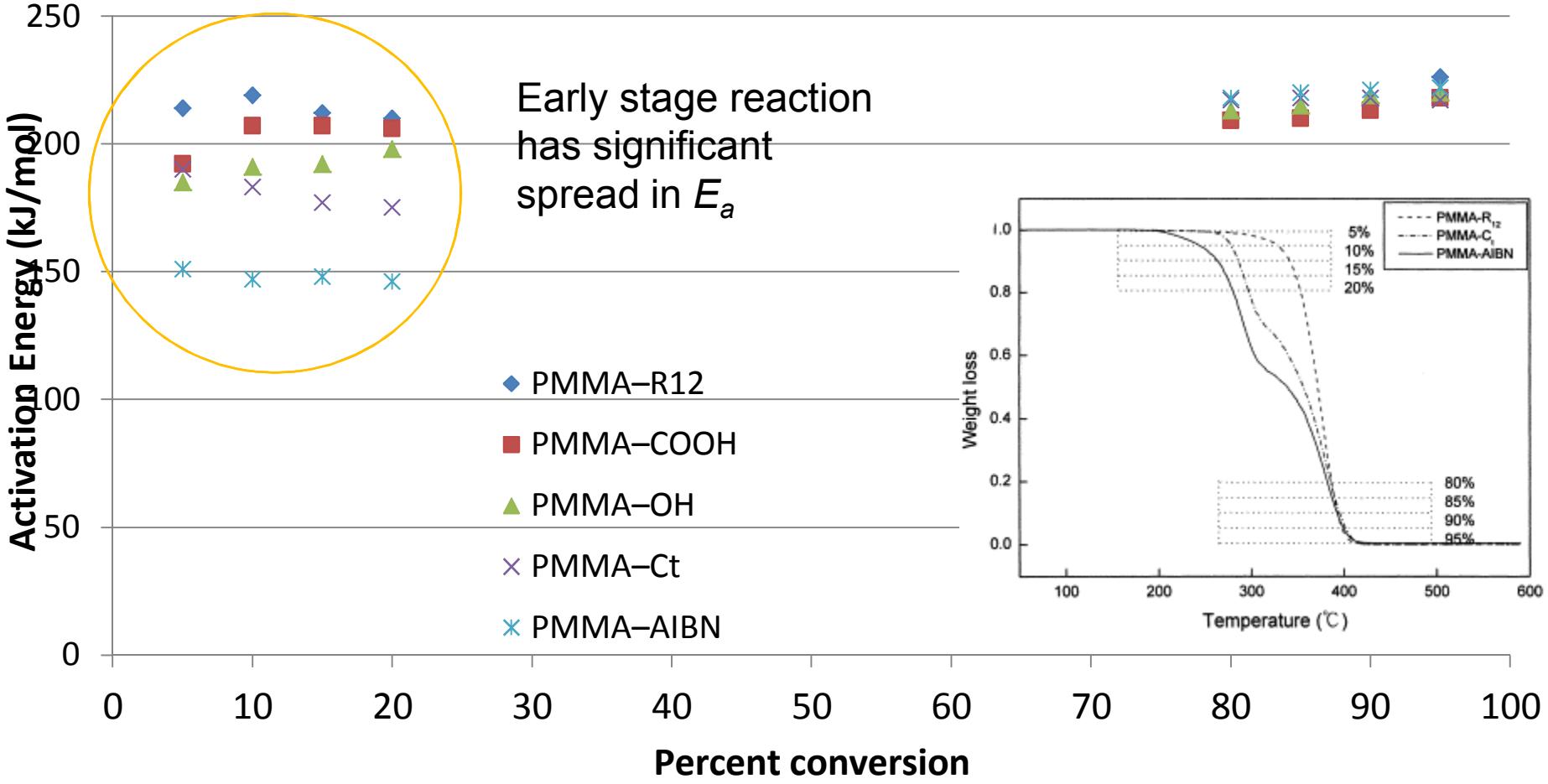

From: Hu, Y.-H.; Chen, C.-Y., *Polymer Degradation and Stability* **2003,** *82* (1), 81-88.

Assessing Aging via Nonisothermal TGA Measurements

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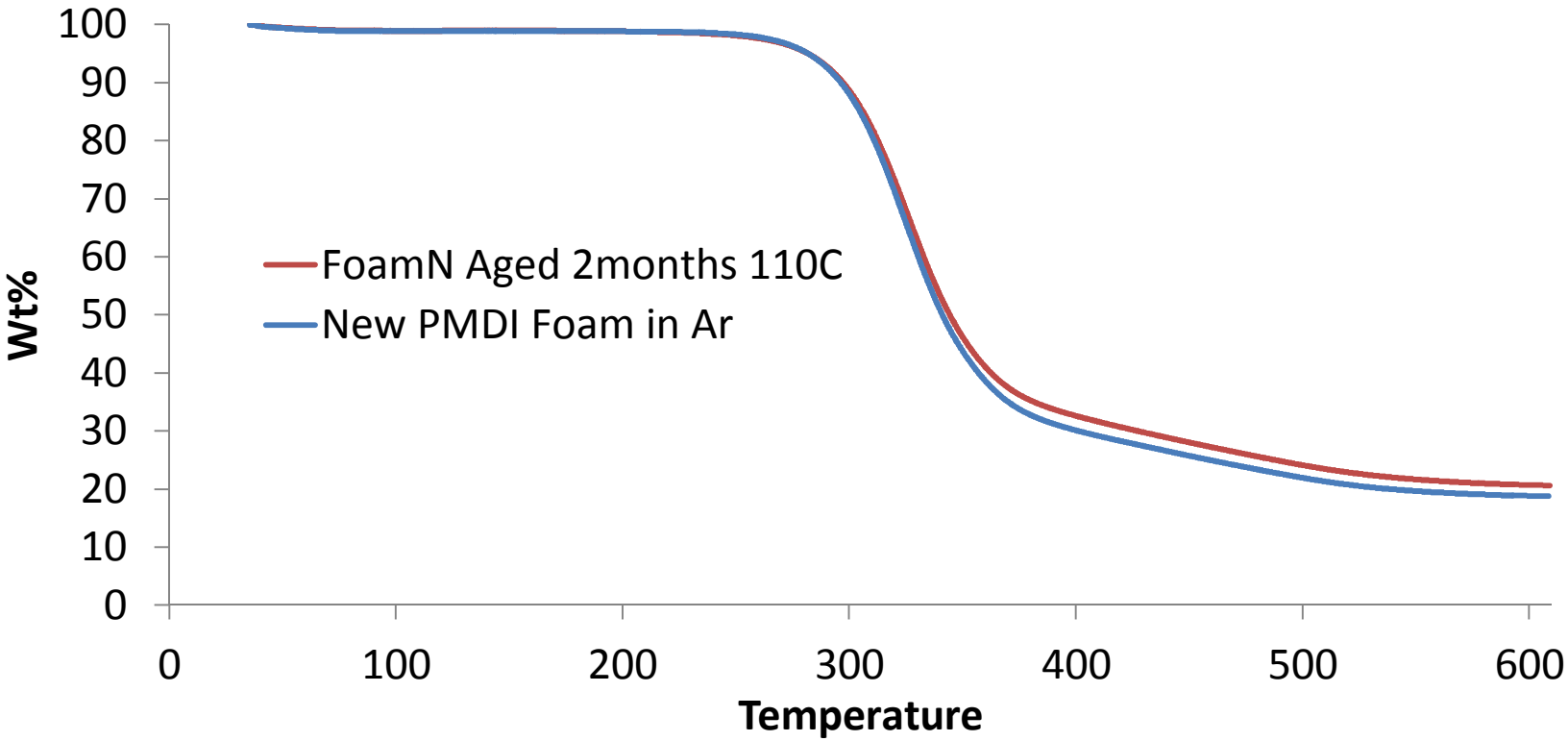
- Do weak links in polymers change with aging?
  - Can we detect these changes using nonisothermal TGA measurements and isoconversional kinetic methods?
- Assumptions
  - Upon thermal decomposition, complex reaction mechanisms occur
  - With aging these mechanisms might change
  - Isoconversional (model free) kinetics cannot deconvolution the different mechanisms but might be able to identify differences
- Applications
  - Surveillance of organic materials used in potting and O-rings with desired long life spans
  - Systems models of abnormal environments where kinetic parameters are needed to predict accident scenarios

Materials List

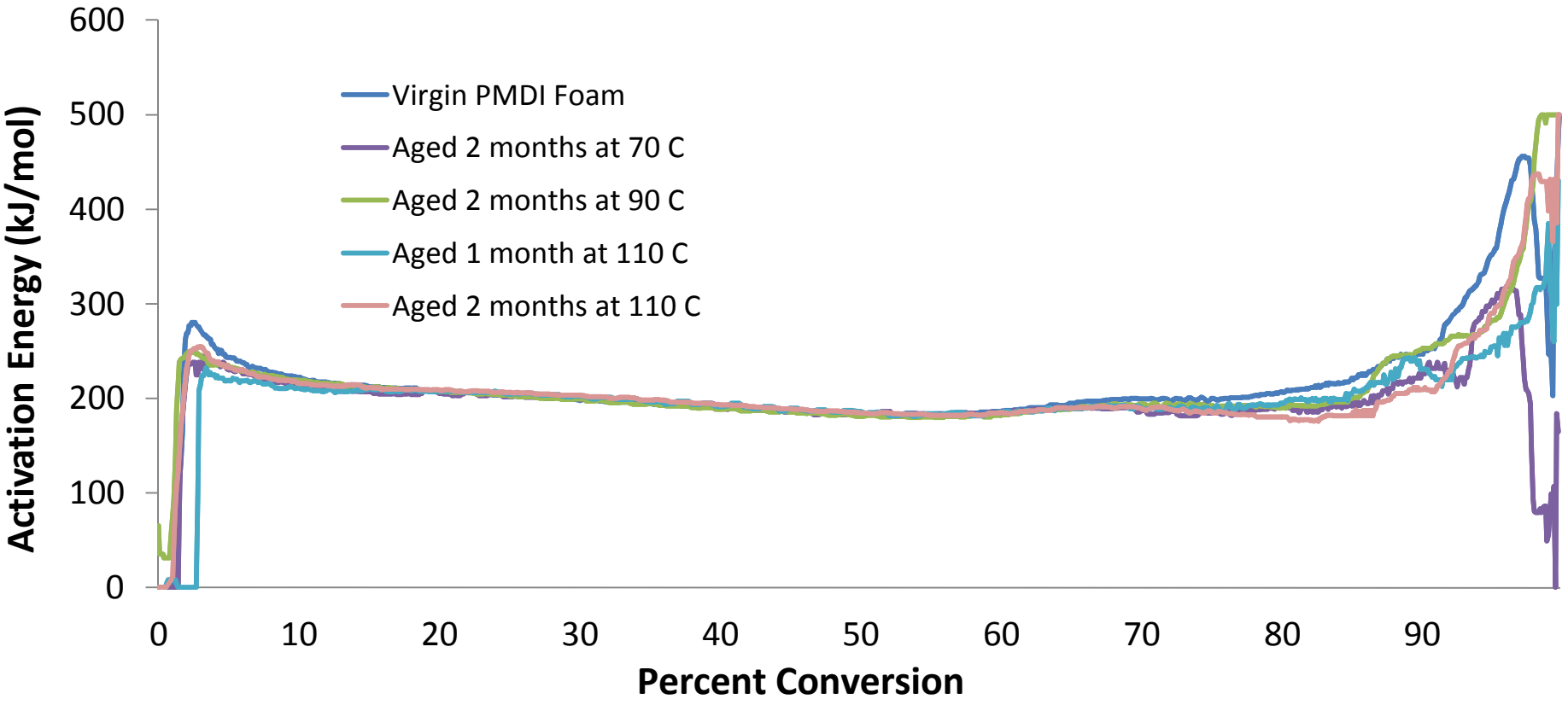
- Poly(dimethyl diphenyl isocyanate) (PMDI)
  - 30 year old foam (FoamP)
  - Newly synthesized foam (FoamN)
- Epoxy materials (Epon™ 826 and Curing Agent Z)
  - 30 year old epoxy with fiber glass (EpoxyP)
  - Newly synthesized epoxy resin (EpoxyN)
- Butyl O-rings
  - Virgin –RB-XV-119 (ASM-01-003)
  - Aged to 16% remaining sealing force –RB-XV-124; Jig #12 124C (ASM 01-005)
  - Aged to 29% remaining sealing force –RB-XIV-44; Jig #22 109C (ASM 01-044)
- Removal Epoxy Foams (REFs)
  - Not aged but done for baselining

New PMDI Foam TGA at 10 K/min



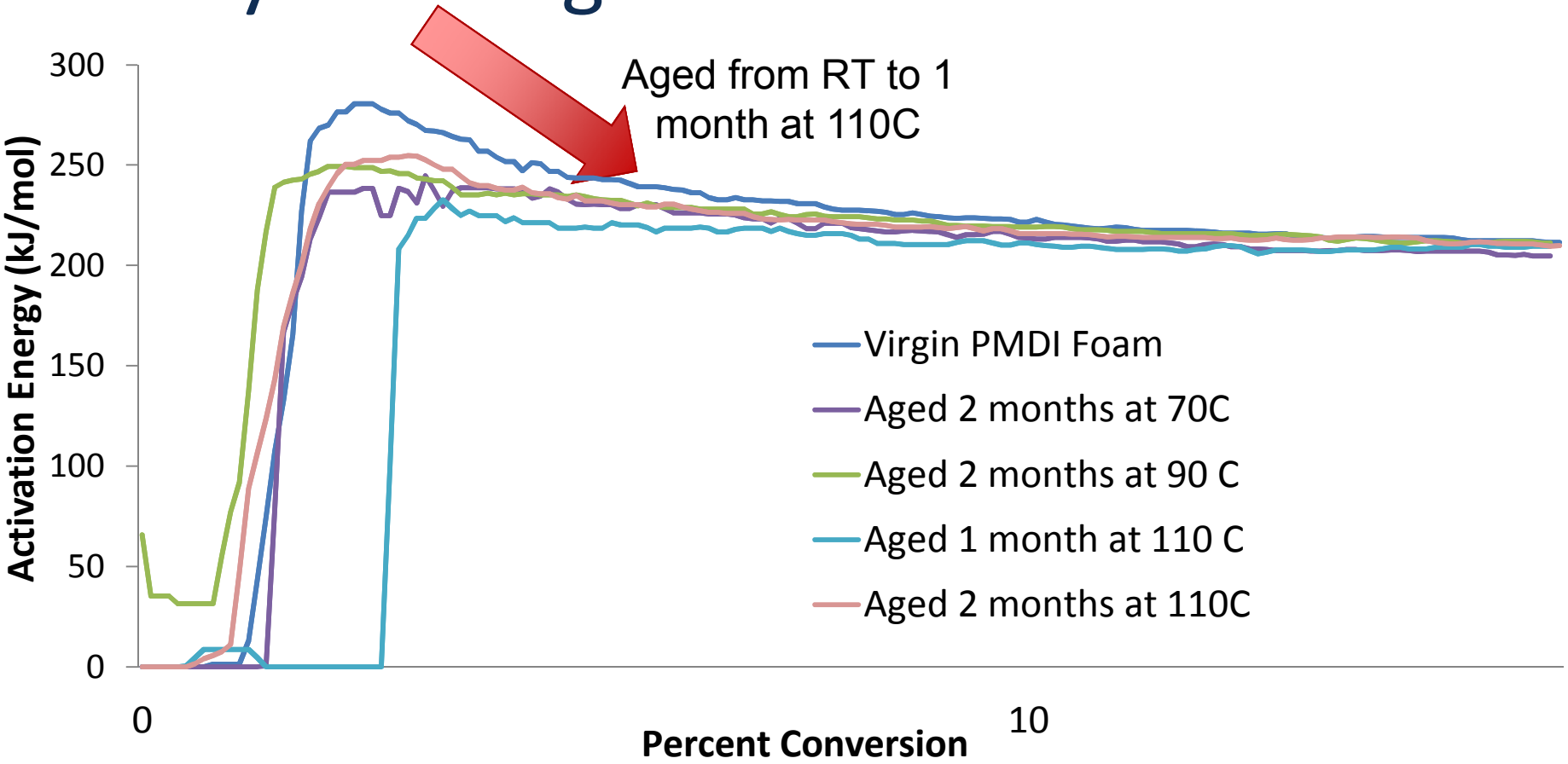
- Representative TGA curves for new foam
  - Overall traces are fairly similar
  - Collected data at 2, 5, 10 and 20 K/min for isoconversional kinetic analyses

E_a Calculated via Model Free Analyses of Aged Foam



Overlapping traces show Ea very consistent for most of reaction suggesting aging does not affect decomposition

E_a Calculated via Model Free Analyses of Aged Foam



Zooming in < 15% conversion shows an initial decrease in the activation energy; opposite trend of what is expected for "weak link" proposal and not all data are consistent

Old Foam "Part" Isoconversional Kinetic Analyses

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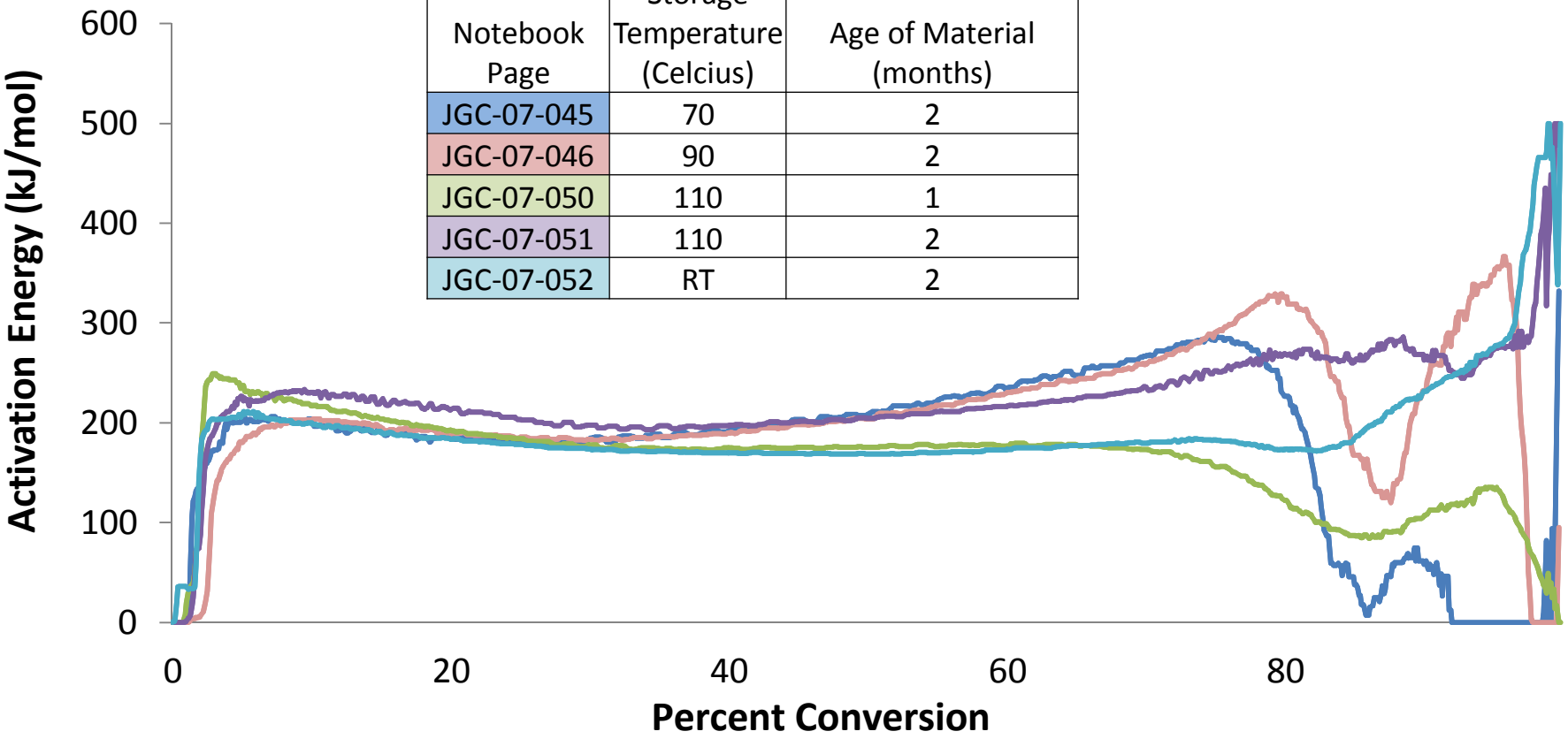
Notebook Page	Storage Temperature (Celcius)	Age of Material (months)
JGC-07-045	70	2
JGC-07-046	90	2
JGC-07-050	110	1
JGC-07-051	110	2
JGC-07-052	RT	2



- Very little observable difference between foam at RT and 2 months at 110C
  - Could be due to no change with artificial aging or that this foam source was from a 30 year old part

Epon™ 826 Epoxy Isoconversional Kinetic Analyses

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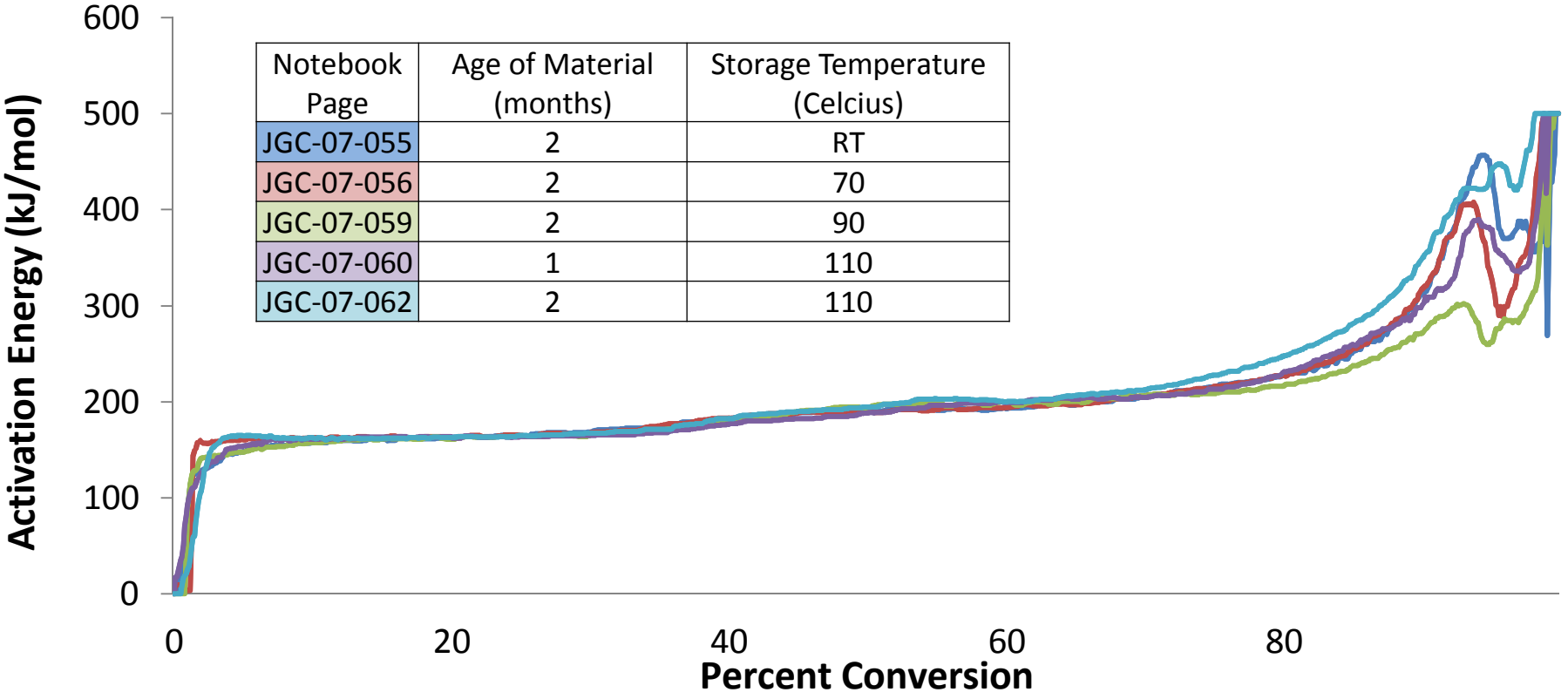
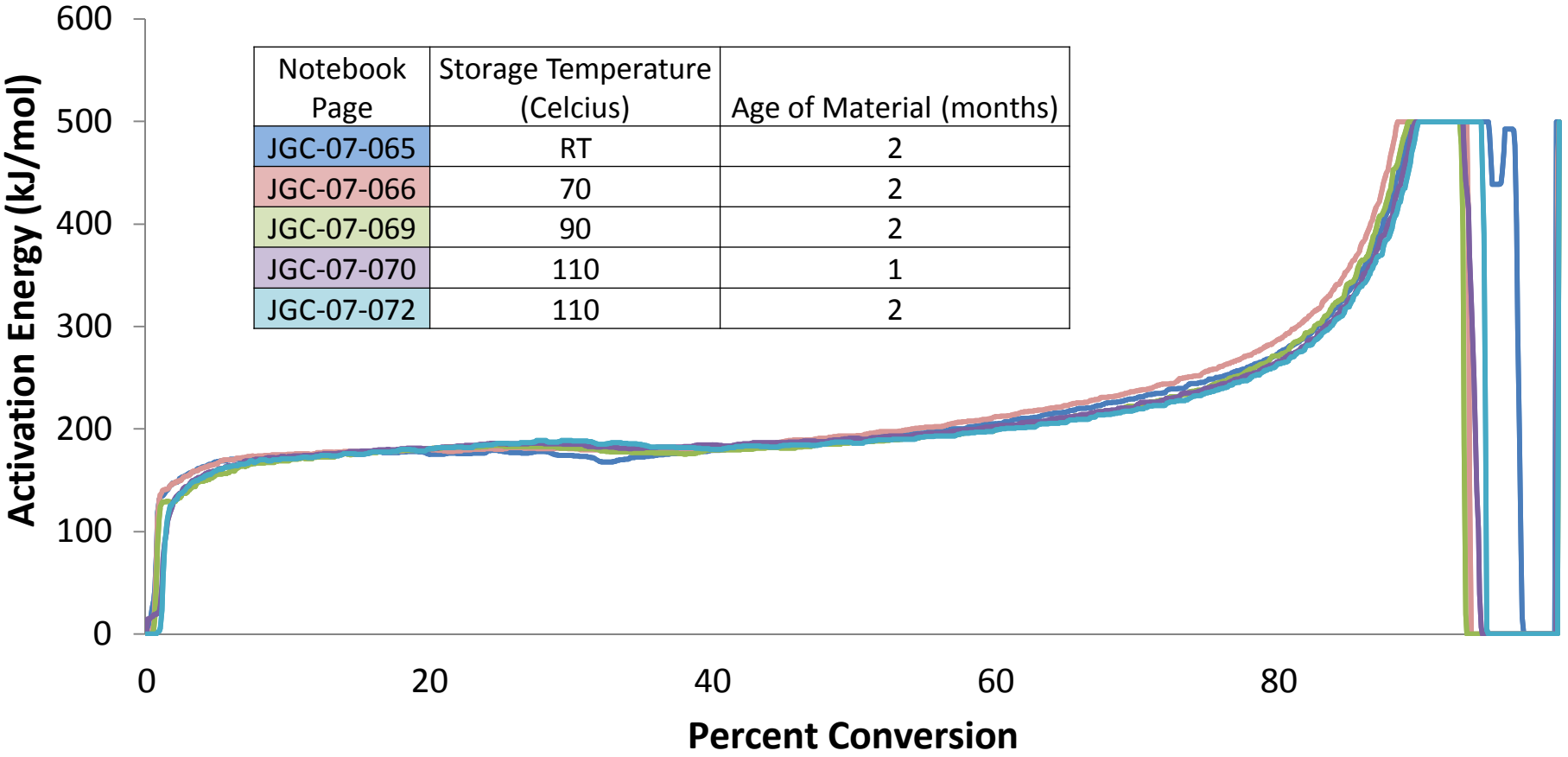
Notebook Page	Age of Material (months)	Storage Temperature (Celcius)
JGC-07-055	2	RT
JGC-07-056	2	70
JGC-07-059	2	90
JGC-07-060	1	110
JGC-07-062	2	110



- No aging affects detected for Epoxy, consistent with other analytical tools

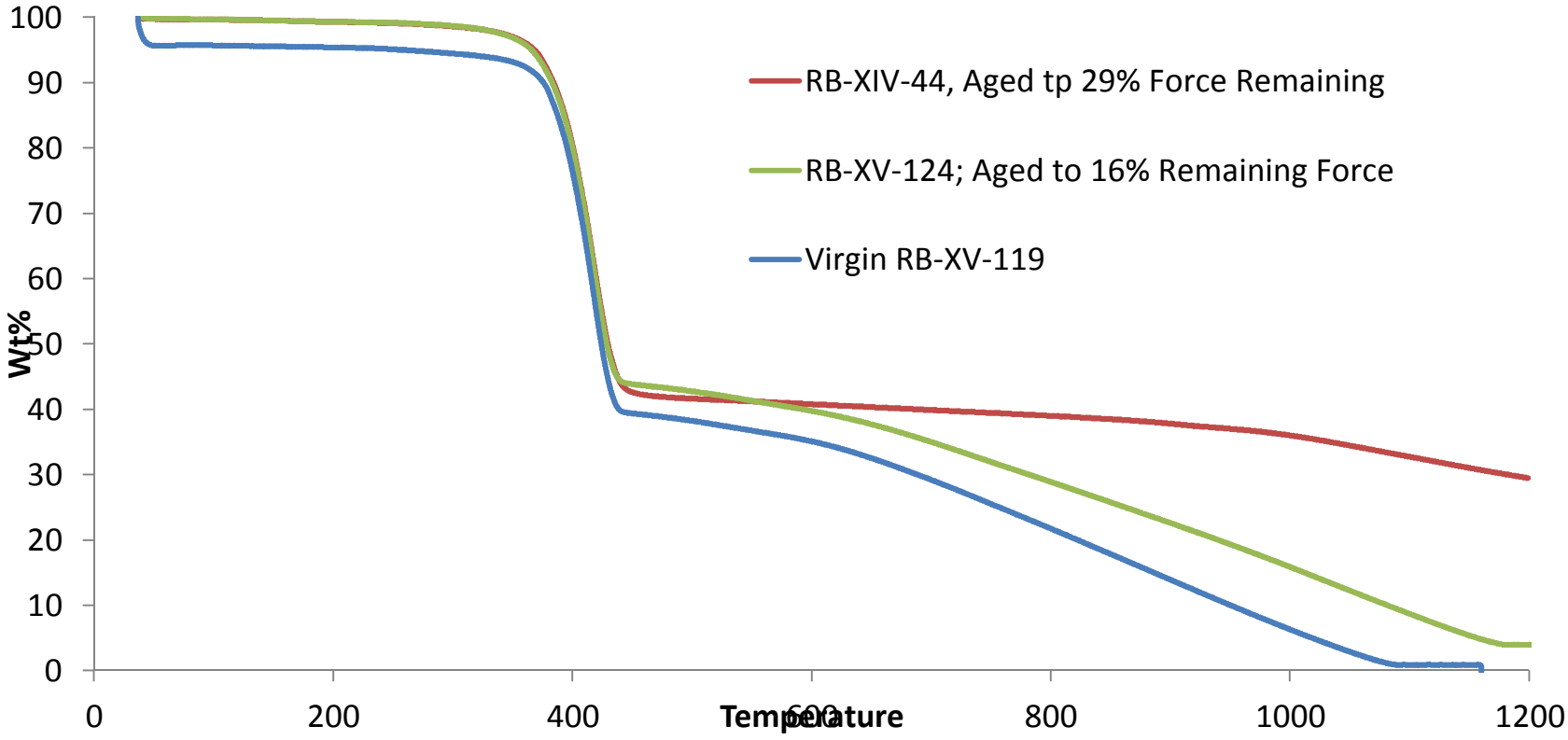
Old Epoxy with Glass Isoconversional Kinetic Analyses

Notebook Page	Storage Temperature (Celcius)	Age of Material (months)
JGC-07-065	RT	2
JGC-07-066	70	2
JGC-07-069	90	2
JGC-07-070	110	1
JGC-07-072	110	2



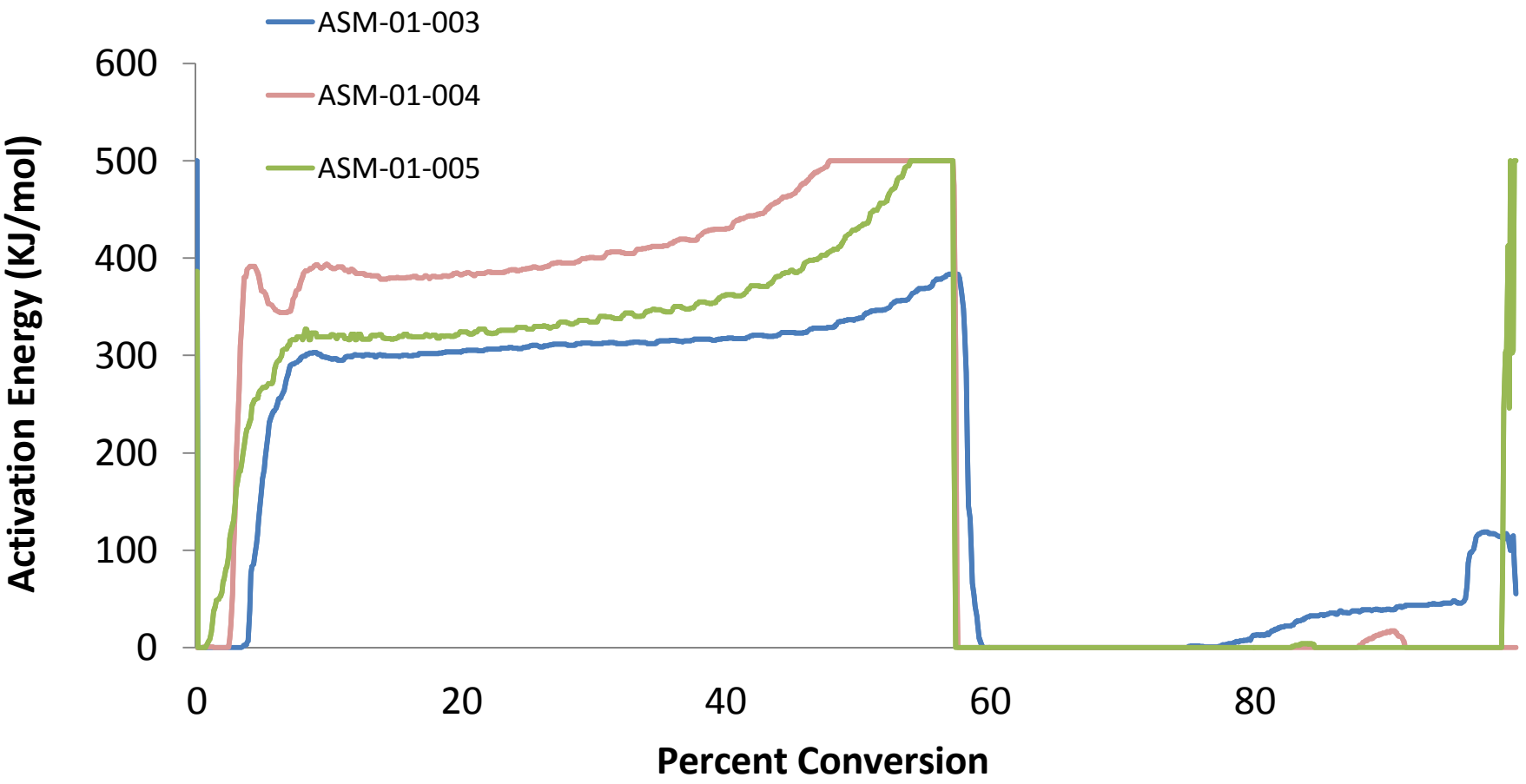
- No aging affects detected for Epoxy, consistent with other analytical tools and high stability of epoxies

Butyl O-rings TGA at 10 K/min



- Representative TGA curves for new foam
  - Virgin O-ring has a rapid decrease (seen in triplicates too)
  - Collected data at 2, 5, 10 and 20 K/min for isoconversional kinetic analyses

Model Free Analyses of Aged O-Rings



- More significant spread in E_a from Isoconversional analyses for butyl O-rings

Isoconversional Kinetic Summary

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- Data processed from at least four heating rates (β)
- Initial analyses were done in Matlab* and data were interpolated using spline fitting
- Software package from Mettler Toledo treated as a "black box"
  - Can incorporate isothermal measures with nonisothermal TGA
  - Can be used to predict conversion plots at other temperatures assuming the mechanism does not change
  - Unable to extract error bars
  - Unable to import data from other instruments to process and compare
- Problem of cross-over
  - Some TGA measurements showed cross-over of curves for slow versus fast heating rates– competing pathways are not predictable
  - Different end points

Mohoric, I.; Krajnc, M.; Sebenik, U., *Chem. Biochem. Eng. Q.* **2009,** *23* (4), 493-496

Conclusions and Future Work

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- Using an autosampler it is easy to collected a lot of data very quickly
  - Great for statistics but also requires careful tracking and a lot of analyses!
- Nonisothermal measurements mimic some real world environments
  - Abnormal environments where temperature increases
  - Easier to acquire than isothermal measurements
- **Lack of differences could be due to no aging in materials (poor materials choice) or insensitive technique**
- Future work will include incorporating mass spectroscopy measurements and baselining new materials for systems modeling

Acknowledgements

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  - Mat Celina
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  - Alan Moore
  - Ryan Keedy
- Funding
  - Technical Readiness Program

Back-up slides

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Full quote from Vyazovkin

- The first is a result of the prevalent use of kinetic methods that involve force fitting of nonisothermal data to hypothetical reaction models. Following this “model-fitting approach”, Arrhenius parameters are determined by the form of $f(\alpha)$ assumed. Because in a nonisothermal experiment both T and α vary simultaneously, the model-fitting approach generally fails to achieve a clean separation between the temperature dependence, $k(T)$, and the reaction model, $f(\alpha)$. As a result, almost any $f(\alpha)$ can satisfactorily fit data at the cost of drastic variations in the Arrhenius parameters, which compensate for the difference between the assumed form of $f(\alpha)$ and the true but unknown reaction model. For this reason, the model-fitting methods tend to produce highly uncertain values of Arrhenius parameters.
- The second major reason for this disagreement arises from the fact that isothermal and nonisothermal experiments are necessarily conducted in different temperature regions. If decomposition involves several steps with different activation energies, the contributions of these steps to the overall decomposition rate measured in a thermal analysis experiment will vary with both temperature and extent of conversion. This means that the effective activation energy determined from thermal analysis experiments will also be a function of these two variables. However, the usual implementation of model-fitting methods is aimed at extracting a single value of the activation energy for an overall process. The value obtained in such a way is in fact an average that does not reflect changes in the reaction mechanism and kinetics with the temperature and the extent of conversion.

Limitations Continued

- The resultant kinetics doesn't give any information about features of a reaction mechanism, in particular, if a reaction involves several stages it is hard to distinguish between self-accelerating and non-accelerating stages
- Correctness of extrapolation in case of complex multi-stage reactions is questionable due to the concept of the overall conversion used – for complex reactions this conversion may strongly depend on the reaction course due to change of contribution of different stages, that is, overall conversion observed under conditions of experiments can significantly differ form overall conversion under conditions to be simulated, which will result in inapplicability of the kinetics
- The resultant kinetics is inconvenient for handling because the $k_0(\alpha)$, $E(\alpha)$ functions are defined in tabular form, due to this reason transferability of the kinetics is very limited
- The method is principally inapplicable in many practical cases
  - adiabatic data - because it is impossible to get the representative set of cross-sections
  - Combination of signals with opposite signs, e.g. combination of exothermic and endothermic peaks on DSC curves and so forth
  - Processes with branched reaction paths (parallel stages)
  - Processes with partial diffusion control
  - Processes with reversible reactions
  - Distinct variations of the initial compositions of samples for curves belonging to a common data set
- Isoconversional method is principally based on Arrhenius linearization. As it was shown in Newsletter N6, in many cases it may result in obtaining unsafe estimates of parameters

http://www.researchgate.net/publication/253954940_Kinetics-based_simulation_approach_Model-free_versus_Model-based_kinetics_Pros_and_Contras