Thermokinetic Modeling in an Aerospace Research and Production Environment

Michael W. Lesley, Ph.D.
ATK Aerospace Systems
Research and Development Laboratories
Brigham City, Utah

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Activities and Product Lines We Support

- **Solid propellant rocket motors**
- **Pyrotechnics (flares, etc.)**
- **Energetic material formulation and synthesis**
- **Composite materials**
- **Ammunition**
- **Gas generators**

Why Do We Do Thermokinetic Modeling ?

- **Need mathematical descriptions of reaction rates**
  - Pyrolysis of rocket motor insulators
  - Thermal hazards of energetic systems
  - Curing of thermosetting polymers
  - Aging
- **Models are often used in engineering evaluation**
  - Data must be in a format that engineers can use in their simulation codes
- **Occasionally, models will provide mechanistic information**
  - Presence or absence of autocatalysis

Test Methods We Use

- **Differential Scanning Calorimetry (DSC)**
  - Milligram sized samples; extrapolation to lower temps often required
- **Thermogravimetric Analysis (TGA)**
  - Milligram sized samples; extrapolation to higher heating rates often required
  - In cases where gases react with polymer matrix, mechanism may be different between small and large samples
- **Accelerating Rate Calorimetry (ARC)**
  - Measure bulk exotherms – kinetic analysis may not be valid for solid energetics
- **Isothermal Microcalorimetry (Heat Flow Calorimetry)**
- **Reaction Calorimetry**
- **Dynamic Mechanical Analysis (DMA)**
- **Gas Evolution Methods**
  - Useful for energetic materials

Modeling Tools We Use (or Would Like to Have)

- **Spreadsheet calculations**
- **Custom kinetics codes**
- **Math programs (e.g., Mathematica, Mathcad)**
- **Commercial thermokinetics software**
  - Netzsch Thermokinetics and Thermal Safety Simulations
  - AKTS
  - Other programs available from Mettler, TA Instruments, Perkin-Elmer, etc.
- **IsoKin**
  - Model-free kinetics freeware program from University of Utah (Prof. Charles Wight)
  - Based on Vyazovkin advanced isoconversional method

Caveats

- **Ideally, rates should be measured as closely as possible to experimental temperature conditions**
  - Sometimes extrapolation is necessary
  - It is useful to make an independent measurement at lower temperature to confirm validity of extrapolation
  - Be careful about extrapolating results across a phase transition such as a melt!
- **Measurements at a single heating rate or single isothermal hold temperature cannot be reliably extrapolated outside the experimental conditions**
  - A major conclusion of the ICTAC Kinetics Project!
- **Watch out for autocatalytic reactions**
  - Rate can increase with increasing conversion, meaning material becomes more “unstable” with time – commonly observed with energetic materials!
  - Causes can be true chemical autocatalysis or other phenomena such as nucleation and growth
  - Detect via isothermal experiments or model-free analyses (Friedman plot)

Rate Expressions

General form (α = fractional conversion; 0 ≤ α ≤ 1):

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha)$$

Rate constant (E = activation energy):

$$k(T) = Ae^{-E/RT}$$

Functional form of conversion dependence:

$$f(\alpha) = (1-\alpha)^n$$

Nth Order

$$f(\alpha) = (1-\alpha)^n (1 + K_{cat}\alpha)$$

Autocatalytic (‘Berlin Model’)

$$f(\alpha) = n(1-\alpha)((-\ln(1-\alpha))^{(n-1)/n}$$

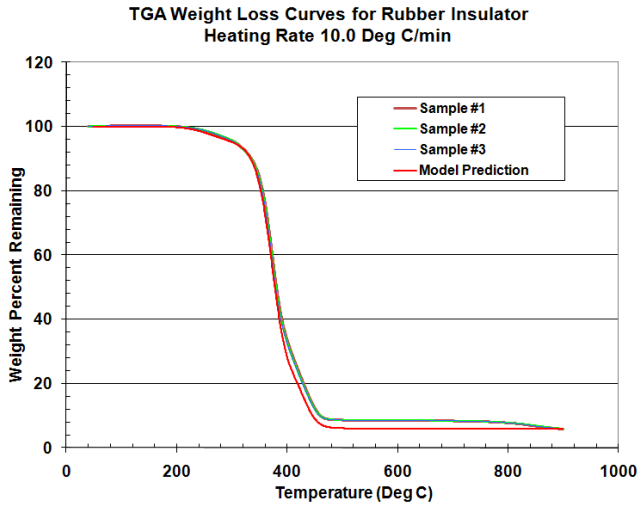
Nucleation/Growth (Avrami-Erofeev)

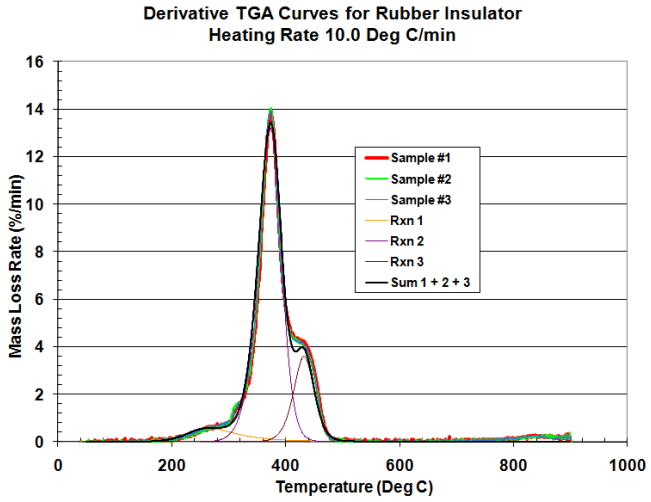
Examples

- **Pyrolysis of rocket motor insulators**
- **Curing model for solid propellant**
- **Cure model and hazard prediction for epoxy composite parts**

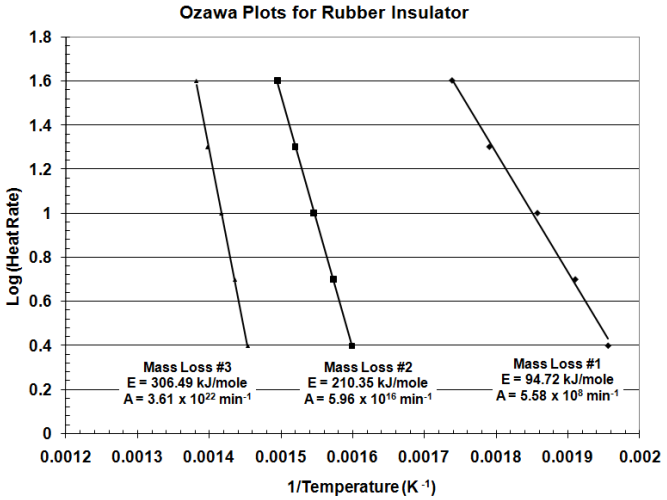
“In-House” Isoconversional Method for Pyrolysis Kinetics

TGA and DTGA of natural rubber flexseal





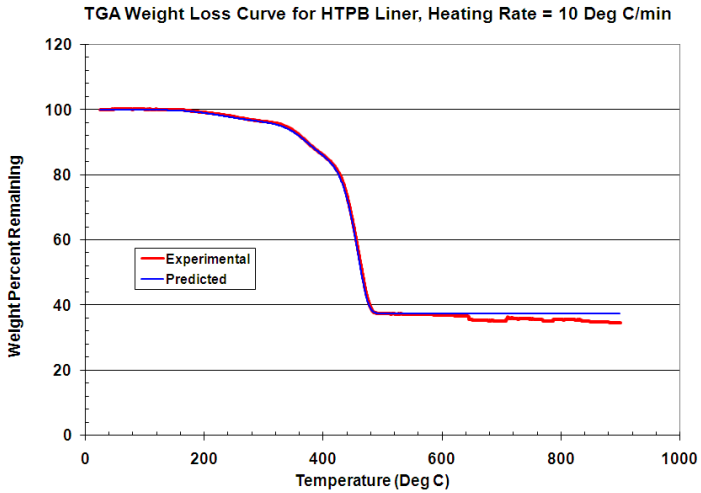
“Ozawa plots” from peaks (or constant α) in multiple heat rate (2.5, 5, 10, 20, 40 °C/min) DTGA data

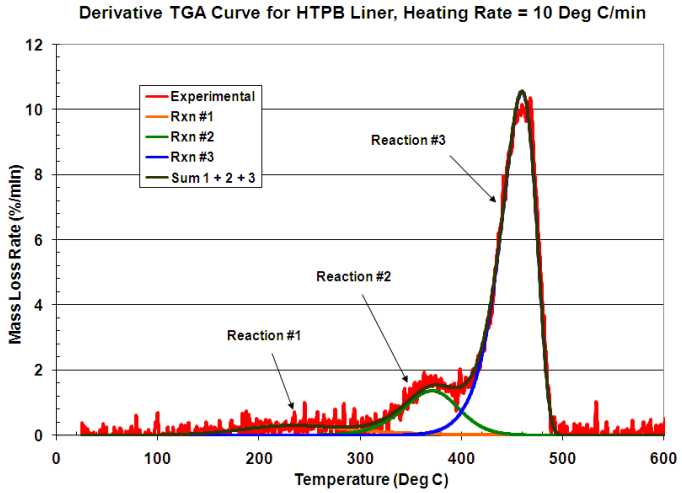


- Get E, A values from Ozawa plots (ASTM E698 method)
- Hold E, A constant throughout analysis
- Model as three independent reactions
- Vary reaction orders and iteratively solve ODEs until a good fit is obtained at all heating rates

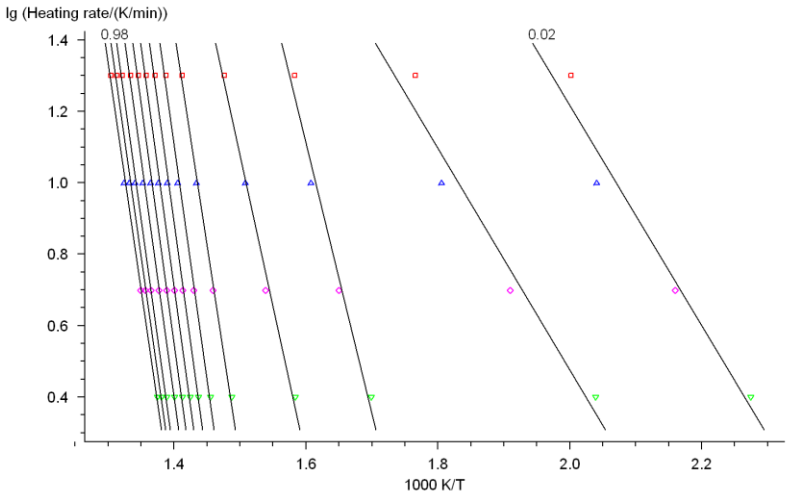
Modeling of Pyrolysis of Hydroxy-Terminated Polybutadiene (HTPB) Rocket Motor Liner with Thermokinetics Software

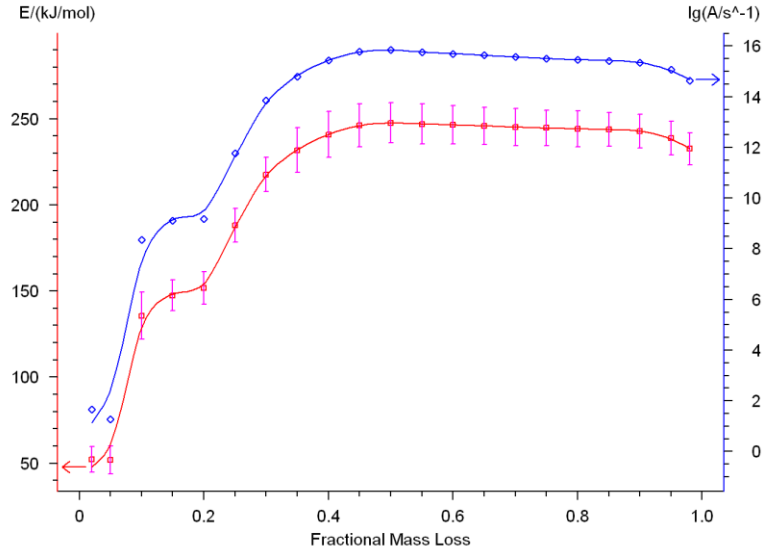
TGA, DTGA of liner:





Model-free estimation of activation energies from multiple heat rate data:

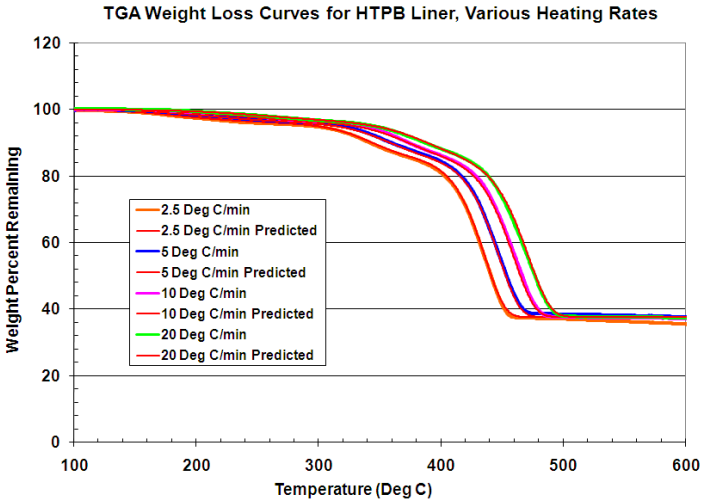


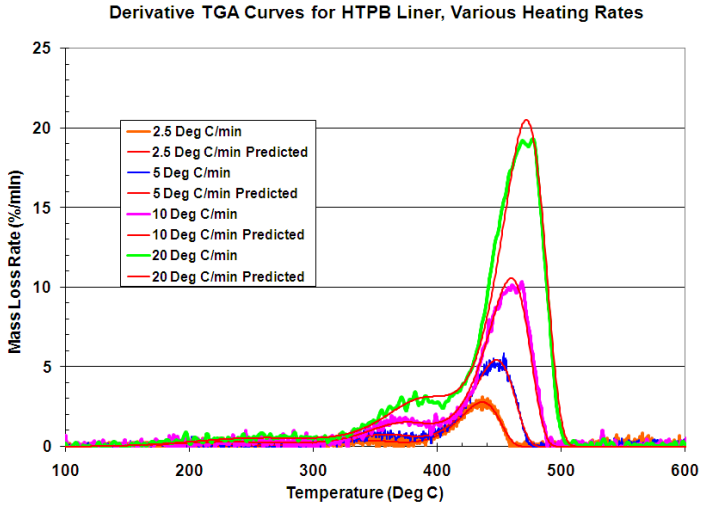


HTPB Liner Pyrolysis (Continued)

- **Modeling approach**
  - Determine number of reactions (3) from DTGA, activation energy vs. conversion plot
  - Get initial estimates of activation energies from model-free analysis
  - Perform multiple nonlinear regression curve fit using model-free values as a starting point
- **Results**
  - Data fit successfully at all heating rates
  - E_1 = 52.67 kJ/mole, E_2 = 149.15 kJ/mole, E_3 = 245.21 kJ/mole
  - $A_1 = 1.01 \times 10^3$ sec^{-1}, $A_2 = 8.79 \times 10^9$ sec^{-1}, $A_3 = 2.80 \times 10^{15}$ sec^{-1}
  - n_1 = 2.09, n_2 = 1.46, n_3 = 0.93

- **Curve fits to 2.5, 5, 10, 20 °C/min data:**





Engineering Use of Pyrolysis Kinetics Data

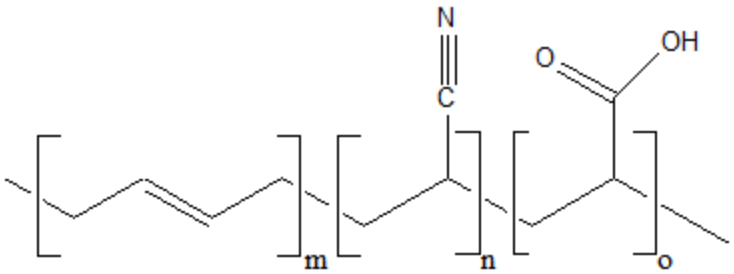
- **Kinetic parameters are used as inputs in rocket motor performance codes**
  - Classical code (Aerotherm Charring Materials Ablation) assumes up to three independent, n^{th} order decomposition reactions
  - More modern codes recently developed by ATK also allow kinetics to be input in alternative formats
    - Advanced isoconversional method – use IsoKin to generate model-free activation energy vs. conversion
    - Discrete reactions with non-n^{th} order rate expressions
  - Other inputs include density, heat capacity, thermal conductivity, elemental composition, and heat of formation
- **Predictions are validated by comparison with data from subscale or full-scale rocket motors/test articles**

Curing of AP-Based Solid Propellants

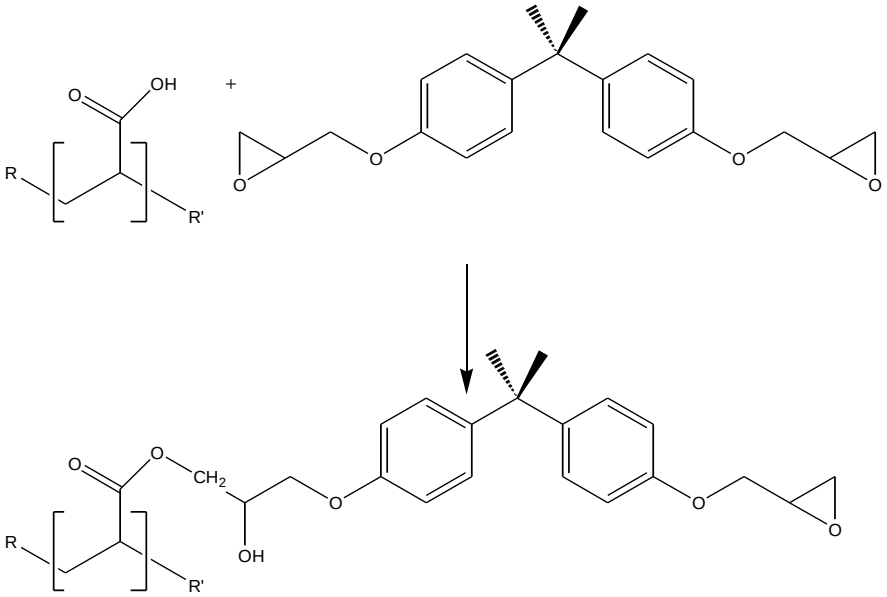
- **Propellant ingredients**:
  - Ammonium perchlorate (AP) oxidizer
  - Aluminum powder fuel
  - Polymeric binder
  - Burn rate modifiers, bonding agents, plasticizers, cure catalysts, etc.
- **Binder systems**:
  - Hydroxy-terminated polybutadiene (HTPB), cured with isocyanate
  - Polybutadiene/acrylonitrile/acrylic acid (PBAN), cured with epoxy
- **Cure reactions are not highly exothermic and cannot be followed by DSC**
  - Use isothermal microcalorimetry to measure heat flow in real time
  - Objective: provide simple rate expressions for use in engineering calculations

PBAN Curing Reaction

- **PBAN polymer (m >> n,o) :**

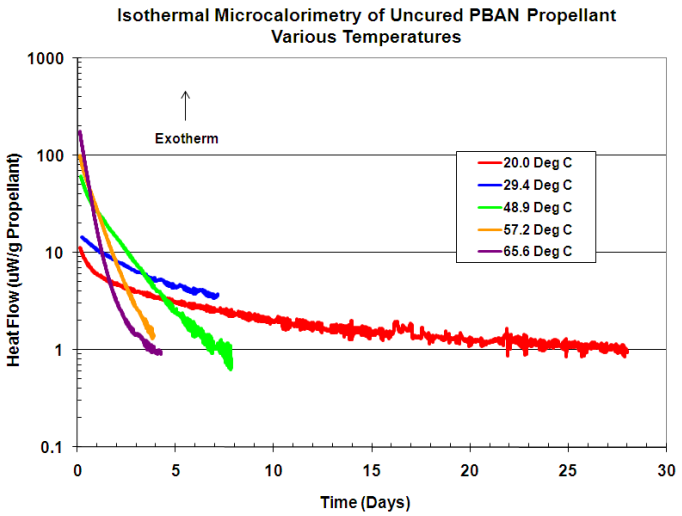


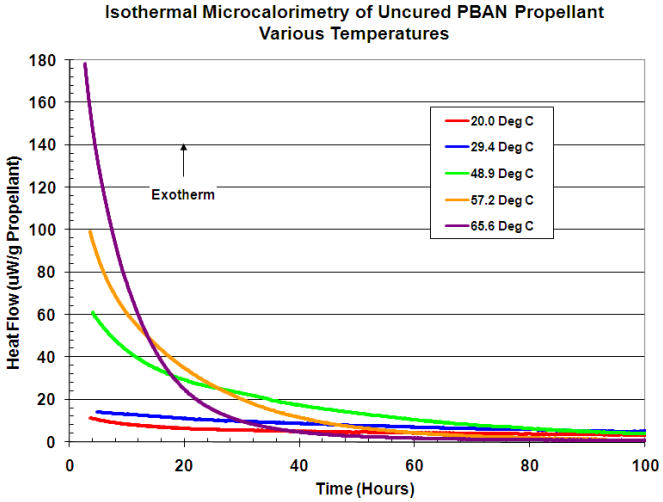
- **Curing of PBAN by epoxy:**



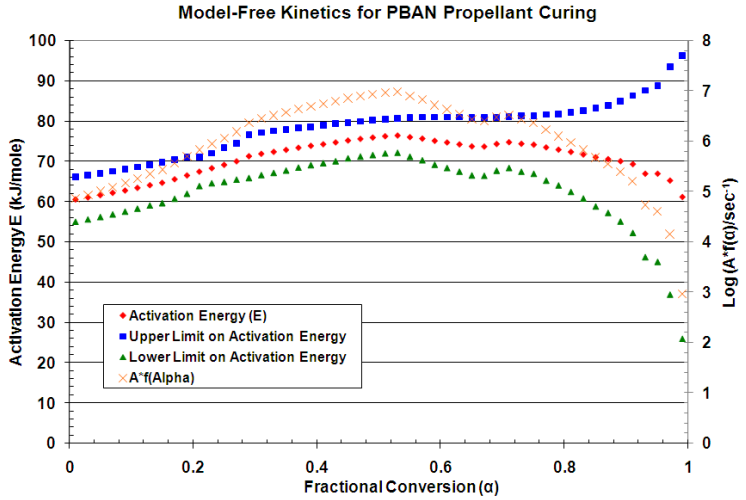
Microcalorimeter Curing Studies of PBAN Propellants

Heat flow vs. time for 20.0 – 65.6 °C:





Model free kinetics:



- Propellant cure times are several days at 50 – 60 °C

- Models were developed from 48.9, 57.2, and 65.6 °C data and extrapolated to lower temperatures

First Order Model from Microcalorimetry

• **Can fit microcal data well with 1st order model (multiple linear regression):**

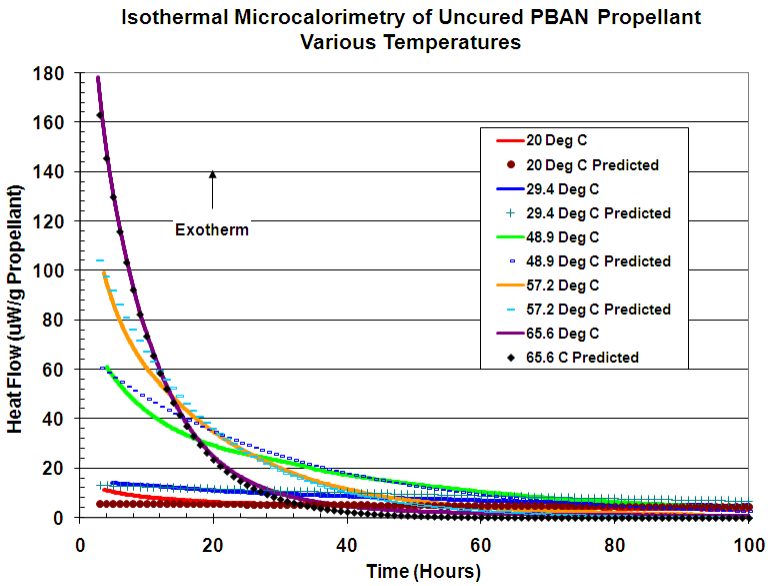
$$\frac{d\alpha}{dt} = k(1-\alpha) = Ae^{-E/RT}(1-\alpha)$$

Propellant	Activation Energy, E (kJ/mole)	Frequency Factor, A (sec^{-1})	Heat of Reaction (J/g)
PBAN #1	66.9502	6.667×10^5	7.2648
PBAN #2	67.7556	8.093×10^5	10.2638

• **Conversion versus time under isothermal conditions:**

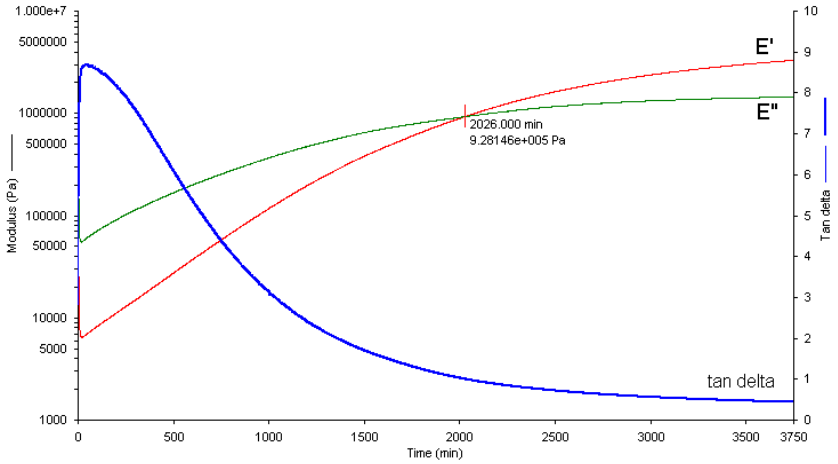
$$\alpha = 1 - e^{-kt}$$

• **Get predicted heat flow by multiplying dα/dt by total integrated heat of reaction**

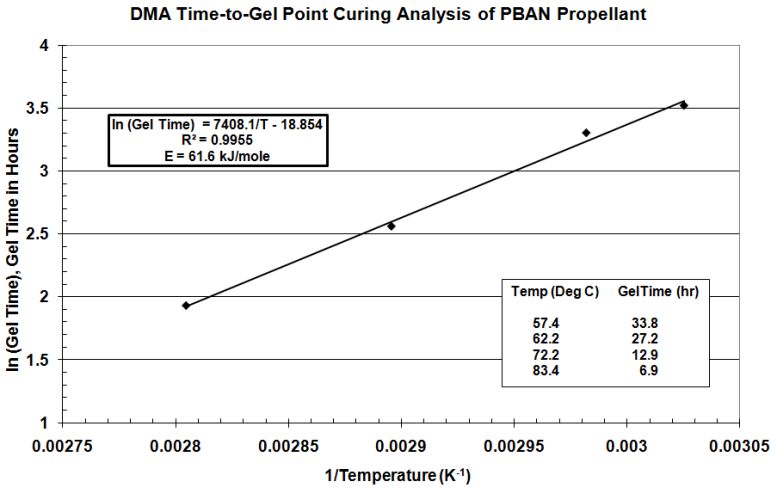


DMA Cure Monitoring of PBAN Propellant

Determination of Gel Time at 57.4 °C



ln (Gel Time) vs. 1/T Plot



- DMA gel point time agrees with times determined by other methods (FTIR, solid state NMR, sol/gel)

- Activation energy is within the range determined by model-free kinetics

PBAN Propellant Curing Study Summary

- **Curing of propellant is observable in real time with a microcalorimeter**
  - No heat flow signal in DSC, even with a ~ 20 milligram sample
  - Measurements are made in the actual temperature range where curing occurs, so extrapolation is not required
  - Can easily measure rates of cure beyond the gel point (~ 34 hours at 57 °C), which is not possible with many other techniques (FTIR, solid state NMR, sol/gel, etc.)

- **Cure data were fit by a simple first-order model in the 50 – 65 °C range**
  - Model-free kinetics will be more accurate, but this approach provides a simple algebraic formula for engineering evaluation
  - Extrapolation of data to ambient temperature range was also successful

Curing Model and Hazard Prediction for a Carbon/Epoxy Composite Part

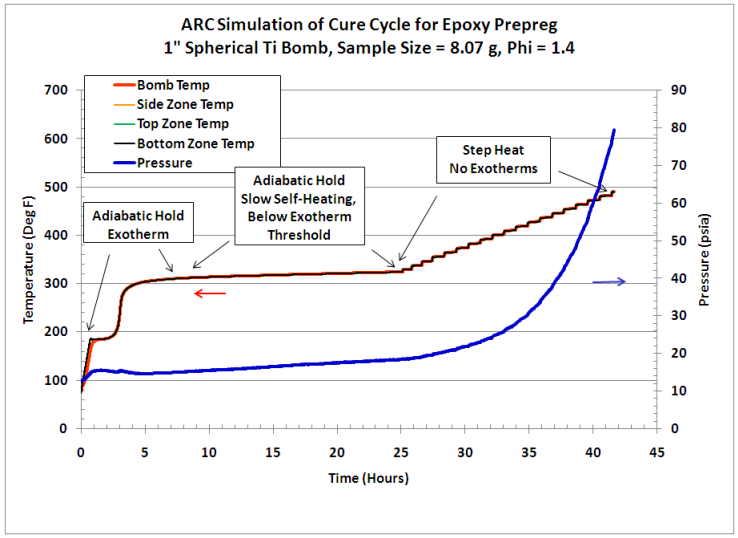
- **Proposal – cure a composite part using the following:**
  - Hold at 185 °F (85 °C) for approximately 6 hours
  - Hold at 285 °F (140 °C) for approximately 14 hours
  - Ramp heat at 2.5 °F/minute (1.4 °C/minute) between steps

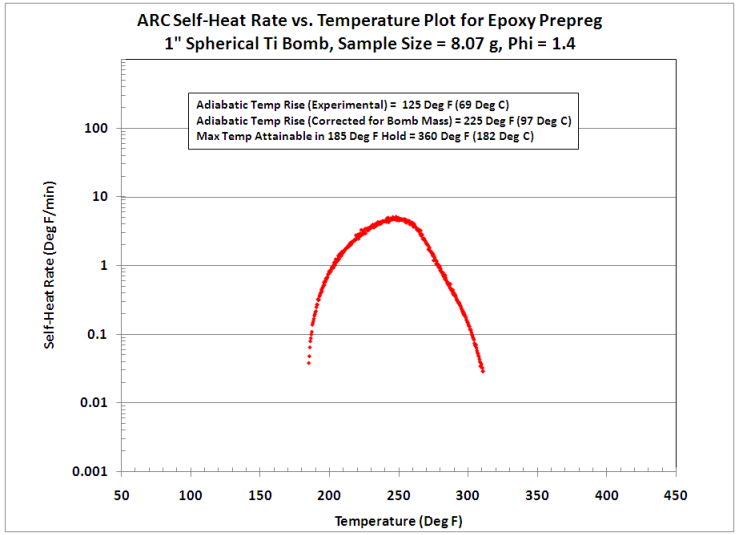
- **Concern: can this cure cycle result in a catastrophic thermal runaway event?**
  - Avoid “smoke-off” and/or damage to equipment by exposure to extreme temperature

- **Approach:**
  - Characterize bulk exotherms using adiabatic calorimetry (ARC) – worst case
  - Develop kinetic model from DSC data and couple with heat transfer code to predict temperature and cure profiles

Accelerating Rate Calorimetry of Epoxy Prepreg

ARC temperature/pressure vs. time and self-heat rate vs. temperature plots:

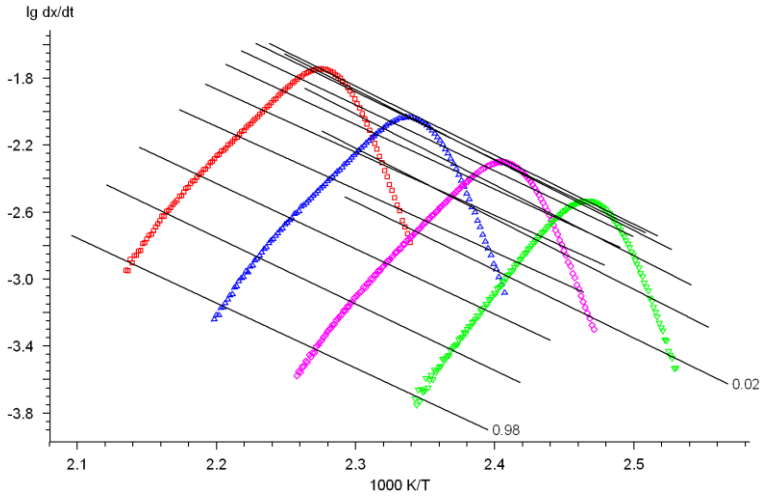


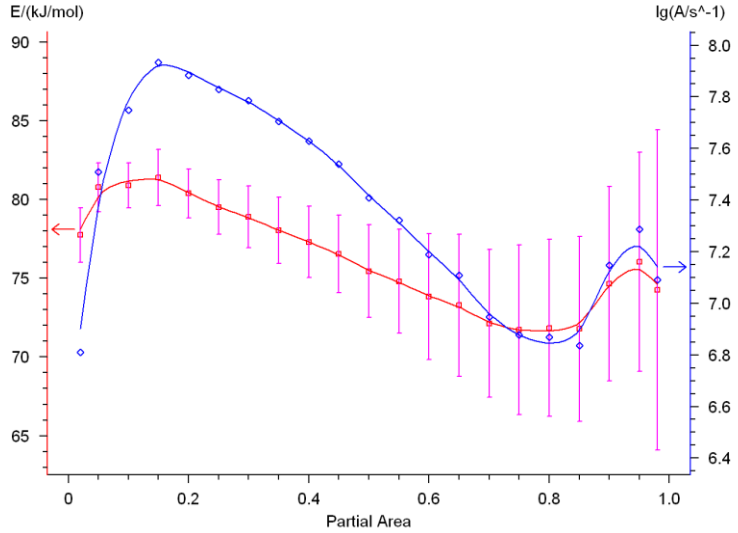


- **"Thermal runaway" can occur during 6 hour/185 °F hold**
- **Worst-case temperature increase from this adiabatic runaway presents no credible risk of smoke-off**
- **But, if the part does not come up to temperature until well into the hold and/or heat transfer is efficient, the cure energy may not be dissipated**
- **If a substantial amount of cure energy remains, this could cause a problem during a second (285 °F) hold**
- **Therefore, a kinetic model was constructed from DSC data and inserted into a thermal simulation code to better understand the behavior**

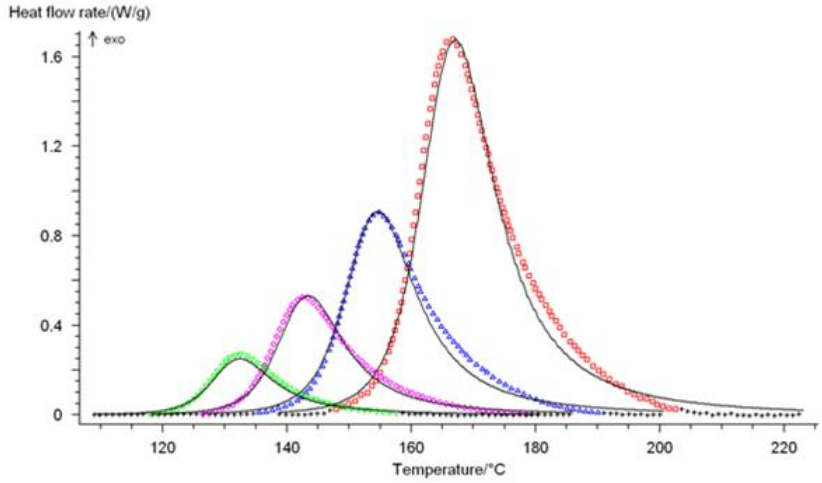
DSC Analysis of Epoxy Prepreg

Model-free (Friedman) analysis:





DSC at 2.5, 5, 10, and 20 °C/minute with curve fits:



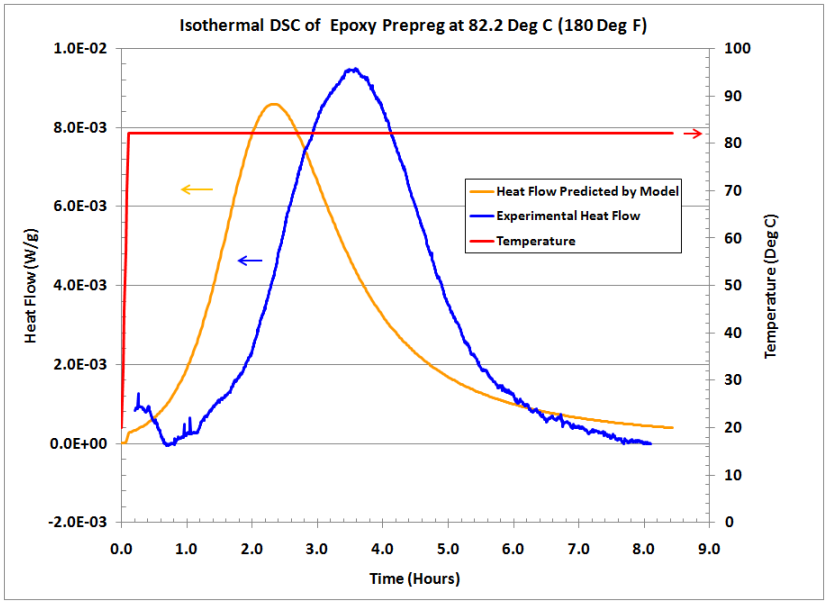
- Friedman plots indicate autocatalytic reaction
- Multiple linear regression curve fit to autocatalytic model:

$$\dot{Q} = \Delta H_{ult}\frac{d\alpha}{dt} = A\Delta H_{ult}e^{-E/RT}(1-\alpha)^{n}(1+K_{cat}\alpha)$$

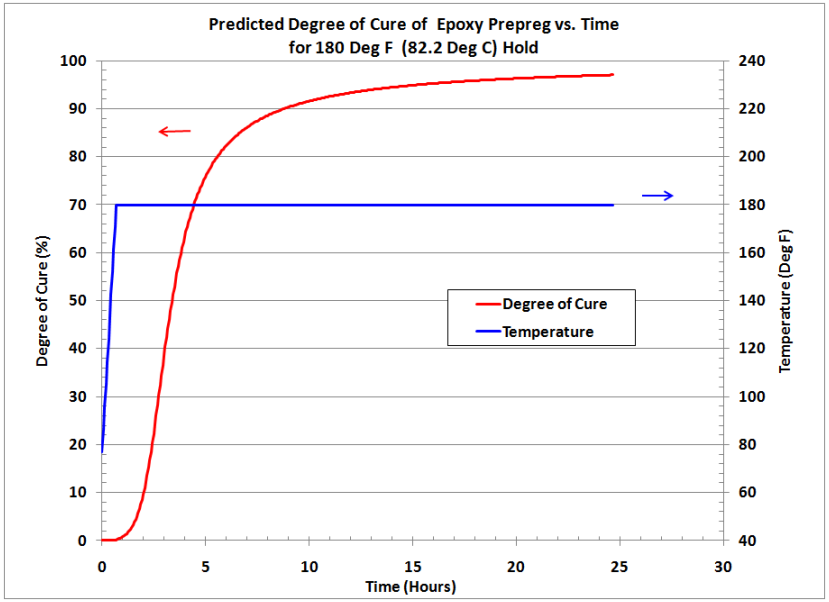
- E = 81.33 kJ/mole, A = 2.42 x 10^{6} sec^{-1}, n = 2.13, K_{cat} = 239.94, ΔH_{ult} = 97.22 J/g

Validity of Extrapolation of DSC Data

Isothermal DSC at 82 °C (180 °F) – predicted vs. actual



Predicted conversion vs. time at 82 °C (180 °F)

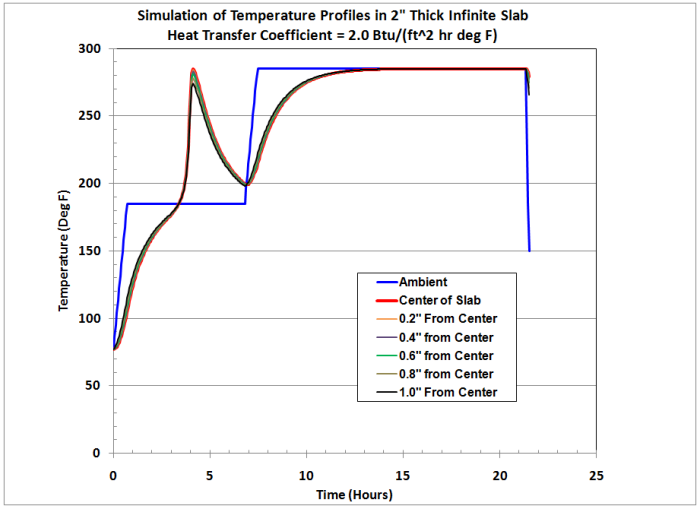


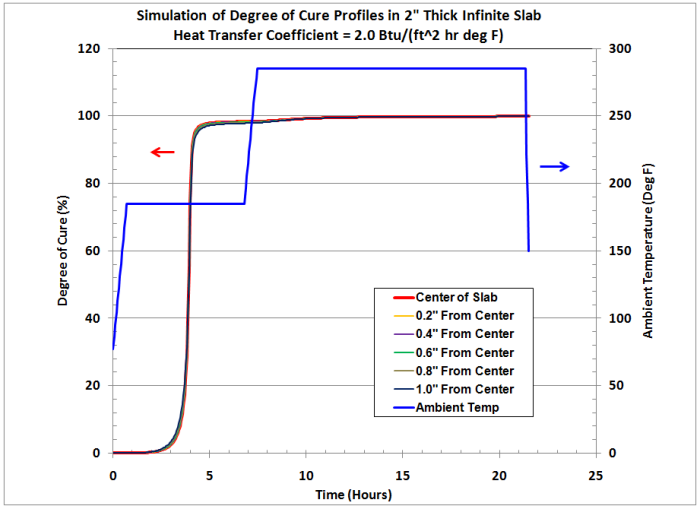
- Isothermal DSC confirms reaction is autocatalytic; extrapolation of model to 185 °F/85 °C is reasonable

- If temperature is held above 180 °F for 8 hours or more, degree of cure should exceed 90 percent

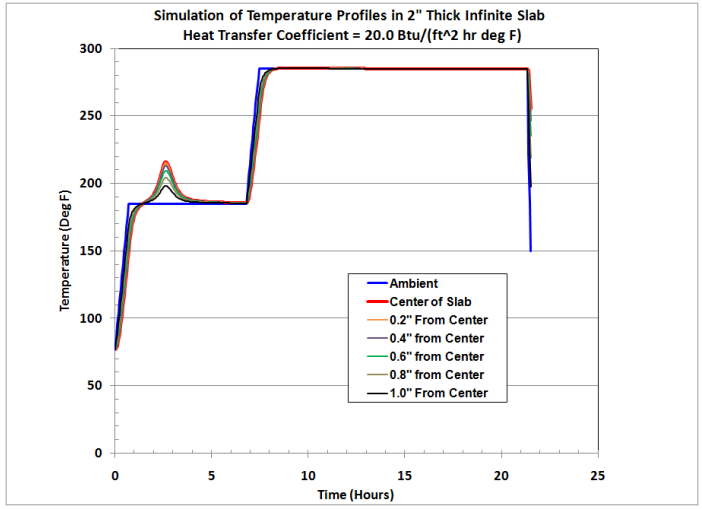
Thermal Simulations Cure Cycle Predictions – 2 Inch Thick Infinite Slab

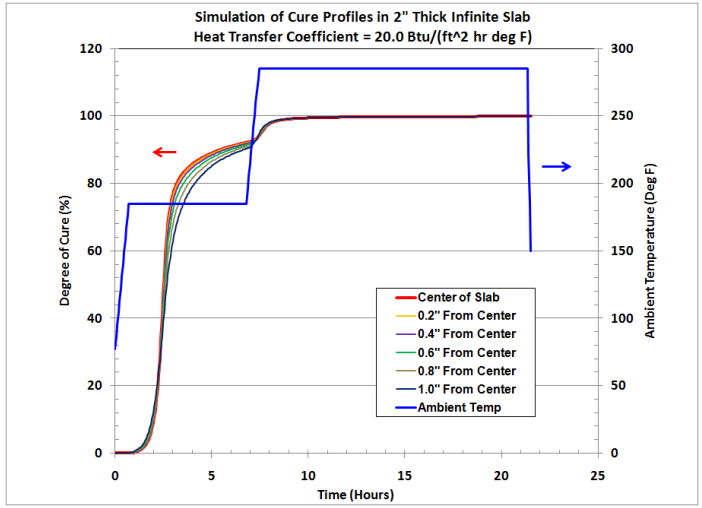
Heat Transfer Coefficient = 2 Btu/(hr ft² °F)





Heat Transfer Coefficient = 20 Btu/(hr ft² °F)





- Should be possible to control exotherm in proposed process

Composite Part Cure Study Summary

- **Proposed cure cycle was approved with the requirement that centerline temperature of the part be above 180 °F for eight hours before heating to 285 °F**
- **Part was successfully cured without undue exotherms**
  - Maximum centerline temperature during 185 °F hold was 211 °F, similar to model prediction
- **If necessary, the heat transfer engineering group can create a model that uses the DSC kinetics and duplicates the actual geometry of a part**
  - This can be used by process engineers for cure cycle optimization

Concluding Remarks

- **Thermokinetic modeling has proven its value for measuring thermal response and reaction rates of a wide variety of aerospace materials**
- **Quantitative predictions, useful for engineering calculations, are routinely made**
- **Extrapolation of results outside the temperature, etc. range where the data are acquired must be done with caution**
  - It is preferable to check the extrapolation against real data in the actual range of operation if possible
- **Often, a complete interpretation of the meaning of the results cannot be made without considering rates of heat transfer within the material and to the surroundings**
  - Partnerships with engineers are crucial
  - Data must be in a format that engineers can actually use
- **Modern thermokinetics software packages are extremely useful and time-saving**
  - But, users must understand the underlying theory and limitations of the programs