Thermokinetic Modeling in an Aerospace Research and Production Environment

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

This effort was performed under NASA contract NAS8-97238
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 (\(\alpha = \) fractional conversion; \(0 \leq \alpha \leq 1\)):

\[
\frac{d\alpha}{dt} = k(T) f(\alpha)
\]

Rate constant (\(E = \) activation energy):

\[
k(T) = Ae^{-E/RT}
\]

Functional form of conversion dependence:

\[
f(\alpha) = (1 - \alpha)^n
\]

\(N^{th}\) 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 $\alpha$) 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:
• 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$^{-1}$
  • $n_1 = 2.09$, $n_2 = 1.46$, $n_3 = 0.93$
• 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
• **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):

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

• Conversion versus time under isothermal conditions:

\[
\alpha = 1 - e^{-kt}
\]

• Get predicted heat flow by multiplying \(\frac{d\alpha}{dt}\) by total integrated heat of reaction

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Activation Energy, E (kJ/mole)</th>
<th>Frequency Factor, A (sec(^{-1}))</th>
<th>Heat of Reaction (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBAN #1</td>
<td>66.9502</td>
<td>6.667 x 10(^5)</td>
<td>7.2648</td>
</tr>
<tr>
<td>PBAN #2</td>
<td>67.7556</td>
<td>8.093 x 10(^5)</td>
<td>10.2638</td>
</tr>
</tbody>
</table>
DMA Cure Monitoring of PBAN Propellant

**Determination of Gel Time at 57.4 °C**

- 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

**In (Gel Time) vs. 1/T Plot**

---

**Graph Details**

- **E’ and E”**
- **NModal (Pa)**
- **Time (min)**
- **E’**
- **tan delta**
- **Time to Gel Point**

---

**Equation**

\[ \ln(\text{Gel Time}) = 7468.1/T - 18.854 \]

**Activation Energy**

\[ E = 51.6 \text{ kJ/mole} \]

**Temperature (Deg C) vs. GelTime (hr)**

<table>
<thead>
<tr>
<th>Temp (Deg C)</th>
<th>GelTime (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67.4</td>
<td>33.8</td>
</tr>
<tr>
<td>62.2</td>
<td>27.2</td>
</tr>
<tr>
<td>72.2</td>
<td>12.9</td>
</tr>
<tr>
<td>83.4</td>
<td>6.9</td>
</tr>
</tbody>
</table>
• 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
• **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:

\[
\dot{Q} = \Delta H_{ult} \frac{d\alpha}{dt} = A\Delta H_{ult} e^{-E/R\,T} (1 - \alpha)^n (1 + K_{cat}\alpha)
\]

- \( E = 81.33 \text{ kJ/mole} \), \( A = 2.42 \times 10^6 \text{ sec}^{-1} \),
- \( n = 2.13 \), \( K_{cat} = 239.94 \), \( \Delta H_{ult} = 97.22 \text{ J/g} \)
Validity of Extrapolation of DSC Data

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

- 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 ft$^2$ °F)

Heat Transfer Coefficient = 20 Btu/(hr ft$^2$ °F)

• Should be possible to control exotherm in proposed process
• 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