Simulation of Thermoset Polymer Composite Curing

James Gilbert

Kristof Vanclooster, Stepan Lomov
Outline

• Motivation

• Numerical simulation technique overview
  o Thermal simulation models and parameters
  o Mechanical simulation models and parameters

• Assessment : Comparison to literature

• Assessment : Fast-curing resin
Production & Challenges

**Autoclave**
- Pressure (1-10 bars)
- Vacuum bag
- Prepreg
- Mold

**(Vacuum assisted) resin infusion**
- Atmospheric pressure
- Resin
- Dry fabric
- Lower mold
- Vacuum

**Spring-in**
- Change of corner angle

**Warpage**
- Deformation of flat plane

[1] Reference source 1
[2] Reference source 2
Mitigation of challenges

- Mould Adaptation
- Production process (temperature profile)
- Mould-tool interface (friction)

How to evaluate methods
- Trial and error – large cost/time
- Numerical simulations
Numerical Models
Simulation Procedure

Thermal Properties Simulations Conditions

Thermal Solver

Degree of Cure Glass Transition Temperature

Mechanical Properties Simulation Conditions

Mechanical Solver

Residual Stresses Deformations
Glass Transition Temperature ($T_g$)

- Rubbery to glassy transition
- 2 material parameters $T_{g0}$, $T_{g\infty}$
- 1 curvature parameter $\lambda$

\[
T_g(\alpha) = T_{g0} + \frac{\lambda \alpha \cdot (T_{g\infty} - T_{g0})}{1 - \alpha(1 - \lambda)}
\]

DiBenedetto\textsuperscript{[3]}
Degree of Cure ($\alpha$)

$$\alpha(t) = \frac{1}{H_{\text{tot}}} \int_0^t \frac{dH}{dt} dt$$

Lee et al. \cite{7} (Default Samcef model)

$$\frac{d\alpha}{dt} = k_1 (1 - \alpha)^{n_1} + k_2 \cdot \alpha^m (1 - \alpha)^{n_2}$$

Autocatalytic \cite{5}

N-order \cite{5}
Reaction Limiting Mechanisms

T < \( T_g \) – reaction slows (glassy state)

- Nothing
- Maximum Degree of Cure \(^{[8]}\)
- Glass Transition Temperature \(^{[9]}\)

\[
\frac{1}{T_{g\infty}} \quad \frac{1}{T_{g0}}
\]

Cure Temperature

\( T_g \)

Original Rate – \( k \)

Modified Rate – \( k' \)

Fractional Conversion

\( \alpha_{\text{MAX}} \)

Time (min)

Reaction Rate (s)

Temperature (°C)

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Limiting Mechanisms: $T_g$

The diagram illustrates the relationship between reaction rate and temperature over time. The cure temperature ($T_g$) is marked as a critical point where the reaction rate changes significantly.

- **Cure Temperature**: A line representing the cure temperature ($T_g$) is observed throughout the process.
- **Original Rate**: A curve indicating the reaction rate without modification.
- **Modified Rate**: Another curve showing the reaction rate after modification, showing a notable change after $T_g$.

The x-axis represents time in minutes, and the y-axis represents reaction rate and temperature in degrees Celsius. The diagram highlights the transition points and the impact of $T_g$ on the reaction rate.
Custom Cure Model

- Epilog definition
- Variations:
  - Cure model
  - Reaction limiting mechanism

\[
\frac{d\alpha}{dt} = k_1(\alpha_{max} - \alpha)^{n_1} + k_2\alpha^m(\alpha_{max} - \alpha)^{n_2}
\]

- Notes:
  - Limited line length
  - Imaginary numbers
  - Brackets
RTM-6 Models and Parameters

<table>
<thead>
<tr>
<th>#</th>
<th>Source</th>
<th>Cure Model</th>
<th>Vitrification</th>
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<tr>
<td>1</td>
<td>Balvers #1</td>
<td>Kamal &amp; Sourour</td>
<td>none</td>
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<td>2</td>
<td>Karkan #1</td>
<td>Lee et al.</td>
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<td>3</td>
<td>Brauner</td>
<td>Kamal &amp; Sourour</td>
<td>( k_D = \exp \left( \frac{-b}{T} \right) )</td>
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<td>4</td>
<td>Balvers #2</td>
<td>Kamal &amp; Sourour</td>
<td>( k_D = A_D \exp \left( \frac{-E_D}{RT} \right) \exp \left( \frac{-b}{T} \right) )</td>
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<td>5</td>
<td>Karkan #2</td>
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<td>6</td>
<td>Navabpour #1</td>
<td>Kamal &amp; Sourour</td>
<td>( \alpha_{max} )</td>
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<tr>
<td>7</td>
<td>Navabpour #2</td>
<td>Lee et al.</td>
<td>( \alpha_{max} = \frac{n_2}{m_2} )</td>
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<tr>
<td></td>
<td>El Sawi</td>
<td>Lee et al.</td>
<td>( \alpha_{max} = f(T, T_{g0}, T_{g\infty}) )</td>
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</tbody>
</table>

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<thead>
<tr>
<th></th>
<th>Balvers #1</th>
<th>Karkan #1</th>
<th>Brauner</th>
<th>Balvers #2</th>
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<th>Navabpour #1</th>
<th>Navabpour #2</th>
<th>El Sawi</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_{tot} ) (kJ/kg)</td>
<td>429</td>
<td>436</td>
<td>419</td>
<td>455</td>
<td>436</td>
<td>450</td>
<td>450</td>
<td>430</td>
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<tr>
<td>( A_1 ) (s(^{-1}))</td>
<td>44.62</td>
<td>57.8</td>
<td>4.5 \times 10^6</td>
<td>148.75</td>
<td>75.0</td>
<td>27.612</td>
<td>39.300</td>
<td>34.00</td>
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<tr>
<td>( A_2 ) (s(^{-1}))</td>
<td>17.65</td>
<td>26.0</td>
<td>1.3 \times 10^6</td>
<td>10.438</td>
<td>21.60</td>
<td>15.369</td>
<td>51.334</td>
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<tr>
<td>( E_1 ) (kJ/mol)</td>
<td>74.41</td>
<td>74.69</td>
<td>74.69</td>
<td>76.825</td>
<td>74.69</td>
<td>72.61</td>
<td>74.00</td>
<td>47.00</td>
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<td>( E_2 ) (kJ/mol)</td>
<td>58.16</td>
<td>58.37</td>
<td>58.37</td>
<td>55.329</td>
<td>58.37</td>
<td>57.70</td>
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<td>( n_1 ) (-)</td>
<td>0.449</td>
<td>1.786</td>
<td>1.114</td>
<td>1.15</td>
<td>1.3618</td>
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<td>T dependent</td>
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<tr>
<td>( n_2 ) (-)</td>
<td>1.171</td>
<td>1.217</td>
<td>1.20</td>
<td>1.229</td>
<td>1.216</td>
<td>1.275</td>
<td>1.128</td>
<td>T dependent</td>
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<tr>
<td>( b ) (-)</td>
<td>0.05</td>
<td>0.2267</td>
<td>0.26</td>
<td>1.42 \times 10^28</td>
<td>6.5 \times 10^{18}</td>
<td>21.624</td>
<td>136</td>
<td></td>
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<tr>
<td>( A_D ) (s(^{-1}))</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>( E_D ) (kJ/mol)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>( \lambda ) (-)</td>
<td>0.383</td>
<td>0.435</td>
<td>0.50</td>
<td>0.543</td>
<td>0.435</td>
<td></td>
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<td>0.44</td>
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<tr>
<td>( T_{g0} ) (°C)</td>
<td>-14.58</td>
<td>-11</td>
<td>-15</td>
<td>-13.09</td>
<td>-11</td>
<td></td>
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<td>-27</td>
</tr>
<tr>
<td>( T_{g\infty} ) (°C)</td>
<td>220.51</td>
<td>206</td>
<td>170</td>
<td>217.88</td>
<td>206</td>
<td></td>
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<td>209</td>
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<tr>
<td>( D ) (°C)</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>( F ) (°C)</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>
Literature Model Comparison

RTM-6 cured at 160°C

Virtual DSC

Degree of Cure

Time (min)
Cure-induced deformations

- Develop during cure
- Sources
  - Mismatch in CTE (mould/fibre/matrix)
  - Cure shrinkage of matrix
- Matrix evolving
  - Modulus change
  - Relaxation
Matrix Modulus

Visco-elastic effects: Relaxation
Preliminary Matrix Curing Simulation

Virtual DSC

Temperature (°C) vs. Time (min)

- Heating
- Chemical Cure
- Cooling

Strain

T_g ∝ Degree of Cure

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Assessment:
Comparison to literature
Assessment: Comparison to literature

- Experiment by Albert & Fernlund [17]
- 8 factors tested in fractional factorial

- Factors tested 1 at a time
- Measuring spring-in on final part

<table>
<thead>
<tr>
<th>Reference</th>
<th>Test Value</th>
</tr>
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<tbody>
<tr>
<td>Part shape</td>
<td>C, L</td>
</tr>
<tr>
<td>Layup</td>
<td>Unidirectional $[0]<em>n$, Quasi-isotropic $[0, +45, -45, 90]</em>{ns}$</td>
</tr>
<tr>
<td>Part thickness</td>
<td>8 plies, 16 plies</td>
</tr>
<tr>
<td>Part angle</td>
<td>90°, 45°</td>
</tr>
<tr>
<td>Arm length</td>
<td>Long, Short</td>
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<tr>
<td>Friction</td>
<td>High 0.3, Low 0</td>
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<tr>
<td>Mould material</td>
<td>Steel, Aluminum</td>
</tr>
<tr>
<td>Cure cycle</td>
<td>1-hold, 2-hold</td>
</tr>
</tbody>
</table>

![Diagram of cure cycle](image)

**Cure Cycle**

- Temperature (°C)
- Time (min)
- Gel Point
- 1-hold
- 2-hold
Spring-in angle analysis

- Spring-in
- Secant
- Tangent
- Original shape
- Warpage
- Corner
- Total spring-in
Simulation results

![Simulation Results Graph]

- **Spring-in Angle (°)**

  - Reference
  - L-shape
  - Quasi-isotropic
  - 45° Angle
  - 16 plies
  - Short Arms
  - 2-hold cure
  - Low Friction
  - Aluminium Mould

- **Simulation Results**
  - Corner
  - Warpage
Results: comparison to literature

**Layup**

<table>
<thead>
<tr>
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<th>Literature</th>
<th>Simulation</th>
</tr>
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<tbody>
<tr>
<td>UD</td>
<td>1.0±0.5</td>
<td>2.5±0.5</td>
</tr>
<tr>
<td>QI</td>
<td>1.5±0.5</td>
<td>2.0±0.5</td>
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**Part Angle**

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<thead>
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<th>Simulation</th>
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<tbody>
<tr>
<td>90°</td>
<td>1.5±0.5</td>
<td>2.0±0.5</td>
</tr>
<tr>
<td>45°</td>
<td>1.0±0.5</td>
<td>1.5±0.5</td>
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</tbody>
</table>
Assessment: Fast-curing resin
Assessment: Fast-curing resin
Identification of Cure Parameters

- Fast curing (automotive) resin
  - SR 8500/SZ 8525 from Sicomin
- Using Differential Scanning Calorimetry
  - Dynamic, Isothermal, Interrupted
Glass Transition Temperature

$T_{g0} - Change over experiments$

$T_{g0}: -12.37 \degree C$
$T_{g\infty}: 124.2 \degree C$
$\lambda: 0.3367$
$\alpha_0: 0.236$

$T_g(\alpha) = T_{g0} + \frac{\lambda \alpha \cdot (T_{g\infty} - T_{g0})}{1 - \alpha (1 - \lambda)}$
Thermal Parameter Fitting

- Minimising residuals in Matlab
  - Explicitly calculate cure evolution

<table>
<thead>
<tr>
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<th>$\lambda$</th>
<th>$T_{g0}$</th>
<th>$T_{g\infty}$</th>
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<tr>
<td>Dynamic</td>
<td>0.056</td>
<td>-20.8</td>
<td>110.9</td>
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<tr>
<td>Isothermal</td>
<td>0.488</td>
<td>-15.8</td>
<td>89.2</td>
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Thermal Parameters

• Minimising residuals in Matlab
  ○ Explicitly calculate cure evolution

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<tr>
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<th>$T_{g0}$</th>
<th>$T_{g\infty}$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$n_1$</th>
<th>$m$</th>
<th>$n_2$</th>
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<td>Dynamic</td>
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<td>-20.8</td>
<td>110.9</td>
<td>0.001</td>
<td>157</td>
<td>22.5</td>
<td>47.3</td>
<td>0.60</td>
<td>2.74</td>
<td>2.36</td>
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<tr>
<td>Isothermal</td>
<td>0.488</td>
<td>-15.8</td>
<td>89.2</td>
<td>80.5</td>
<td>175</td>
<td>52.3</td>
<td>72.7</td>
<td>1.04</td>
<td>0.001</td>
<td>0.001</td>
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</table>
Assessment: Fast-curing resin

- Pressure
- Heat transfer to the environment
- Water flow
- Contact condition

Temperature, °C

Exotherm - curing

- Temperature
- Degree of Cure

Temperature distribution during heating
Results

Produced Part

Simulation Results

Opening Angle, °

Part length, 0 = wide end, mm

Wide End  Transition Zone  Narrow End
Trends in the results

Change in the Opening Angle, °

Spring-out

Spring-in

Produced Parts
Simulated Part

Wide End  Transition Zone  Narrow End
Conclusions & Future Work

• Parameters and model variations are numerous and show similar cure evolution for RTM-6

• Predicted impact of various manufacturing and design parameters and compared to experimental results

• Parameter identification for the cure-model parameters of a fast-curing resin
  ∘ Revisions to the testing procedure should be investigated

• Predicted spring-in on an industrially relevant part followed similar trends to experimental results
  ∘ Additional effects should be investigated (relaxation, mechanical parameters)
Relaxation

- Stiffness reduction over time after a stimulus

\[ E(\xi) = E_0 \left[ 1 - \sum_{m=1}^{M} w_m \left( 1 - e^{-\frac{\xi}{\tau m}} \right) \right] \]
Attempt with Relaxation

- Required parameter identification
- Simulation time (mecano)
  - Reference ~3hr
  - With relaxation ~126hr
Thank you

The authors kindly acknowledge the support of Flanders Make and Flanders Innovation & Entrepreneurship (VLAIO) with this study, which is part of an ICON project entitled "Virtual Design Platform for Sheet Material Products (VIDESPRO icon)"
References


Limiting Mechanisms: $T_g$ (Math)

$$k_D = \exp\left(\frac{-b}{0.00048(T - T_g) + 0.025}\right)$$

$0.00048(T - T_g) + 0.025 = 0$ when $T - T_g = -52.1^\circ C$

During cooling $T - T_g < -52.1^\circ C$

$$k_D = \exp\left(\frac{-b}{-\varepsilon \approx 0}\right)$$

$\frac{1}{k_i'} = \frac{1}{k_i} + \frac{1}{k_D}$

$= \frac{1}{k_i} + \frac{1}{\infty}$

$= \frac{1}{k_i}$