Physical aging during cure of thermosets: effect of temperature

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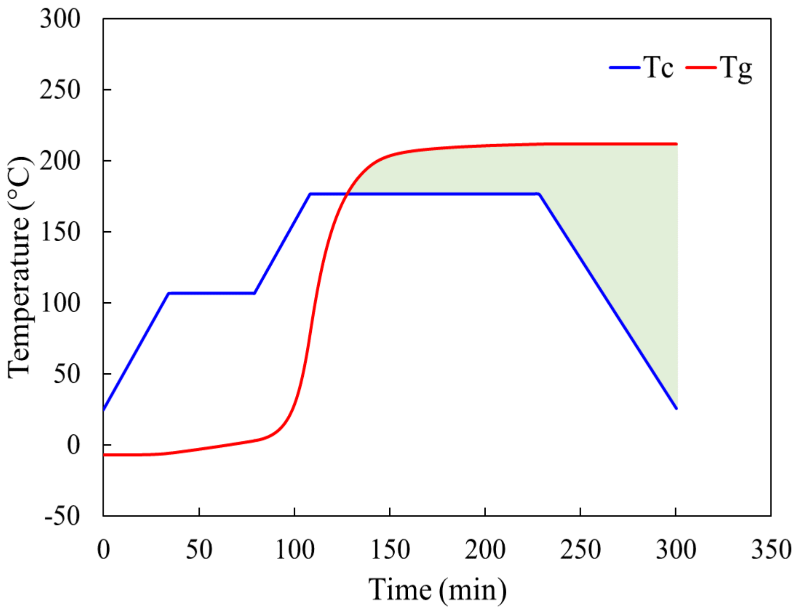
Introduction

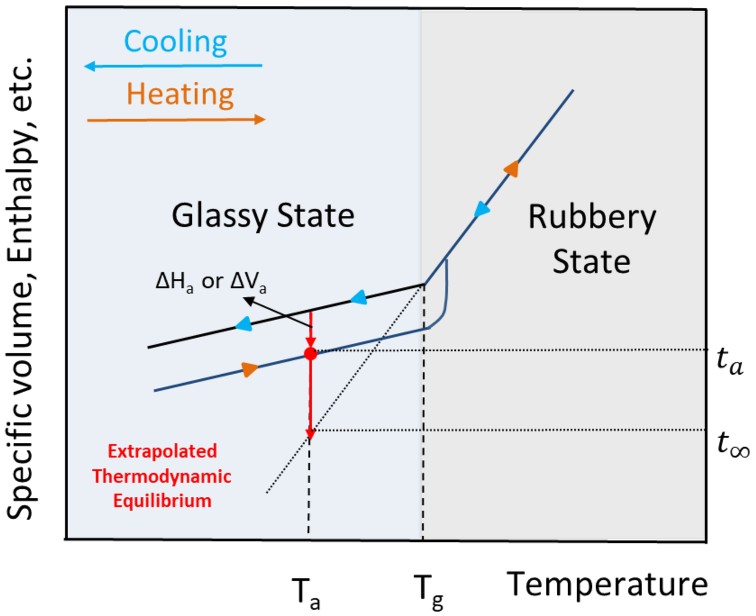
Isothermal cure reaction in thermoset polymers:

- Shift from reaction kinetics-controlled rate to diffusion-controlled reaction rate, upon vitrification during cure
- This transition is well captured by current cure kinetics models

The missing piece:

- In the glassy state, the phenomena of physical aging is expected to occur, as well as diffusion effects
- Thorough understanding of this phenomenon and its incorporation into next generation of cure kinetics models is required





Experimental method and results

Experimental method

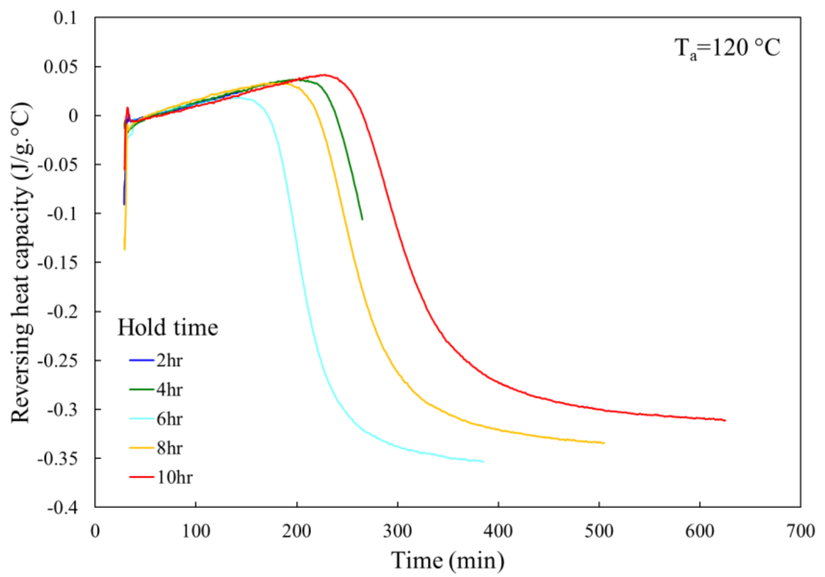
Material system
- Hexcel 8552 - Form: Resin Film
- Degassed at 60°C in Vacuum oven for 2 hrs
- Material model shows that cure advancement is negligible

Thermo-analytical technique: Enthalpy relaxation
- Dynamic Scanning Calorimetry (DSC)
- Inert gas purge flow (N_2): 50 ml/min
- Modulation Parameters: Period: 60s - Amplitude: ± 1°C

Temperature cycle
- Temperature cycle: isothermal hold following by ramp to 270 °C at 2 °C/min
- Aging temperature (T_a) = 100 to 150 °C
- Aging time (t_a) = 2 to 10 hours

Image courtesy of TA Instruments

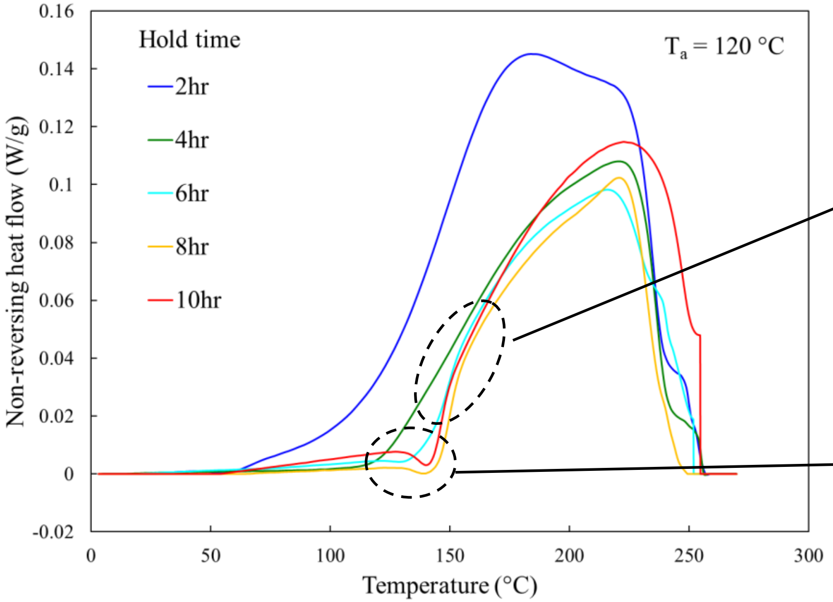
Results



Isothermal hold at T_a= 120 °C
Vitrification time ≈ 4 hours
Vitrification DoC ≈ 0.64

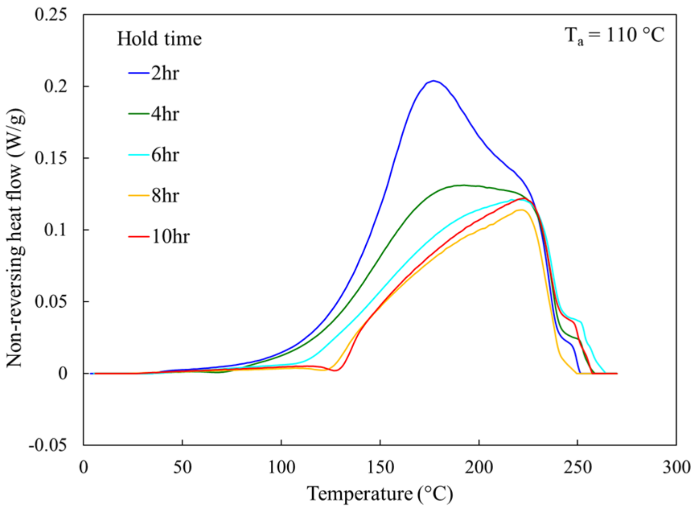
✓ Physical aging is expected to develop past this time

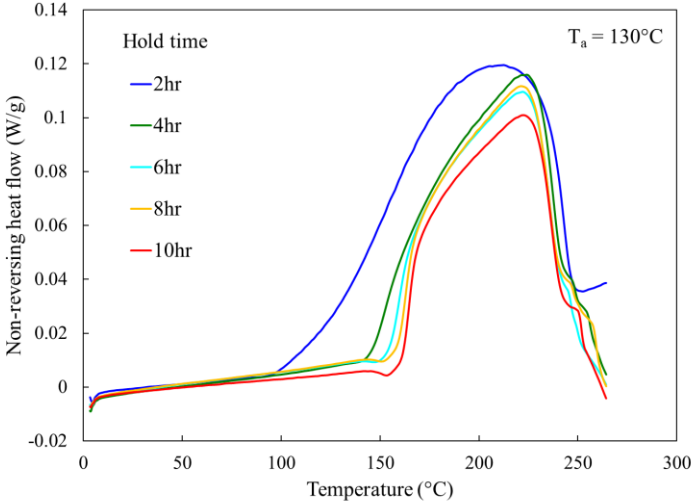
Results: heating ramp after isothermal cure



Change in the shape of cure reaction exotherm

Endothermic peak associated with physical aging





- Endothermic peak → fingerprint of physical aging
- Increase in the area under the curve of the endothermic peak.

- Delay in residual cure reaction with increasing aging time.
- Progressive change in the shape of residual heat flow with increasing aging time

- Consistent trends at different aging temperatures

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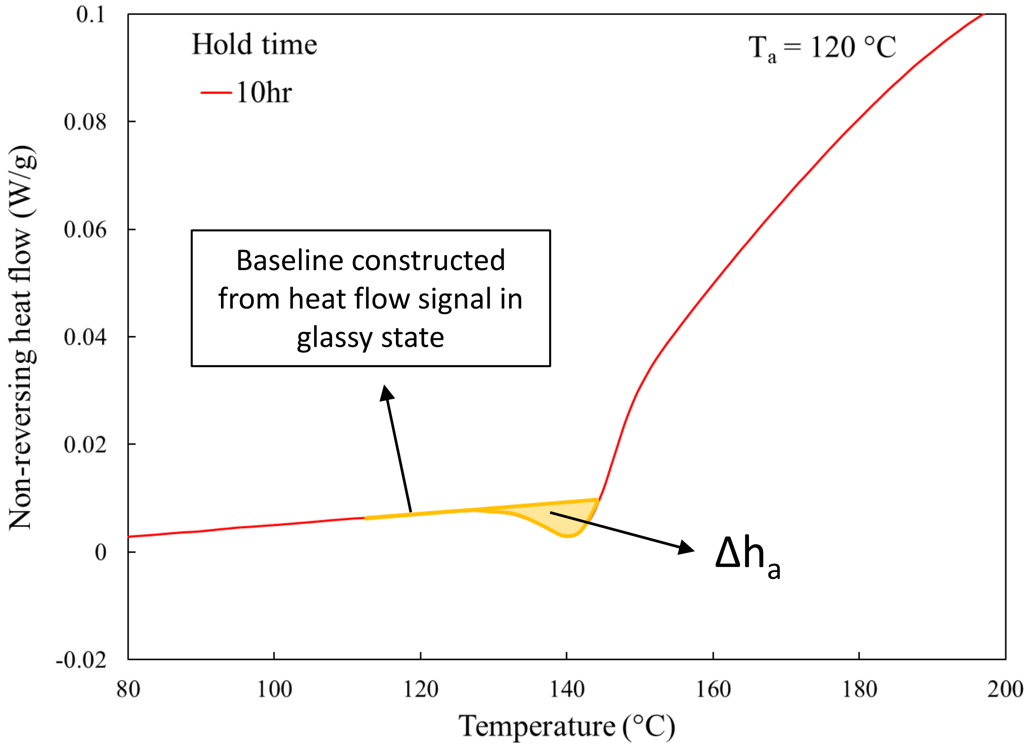
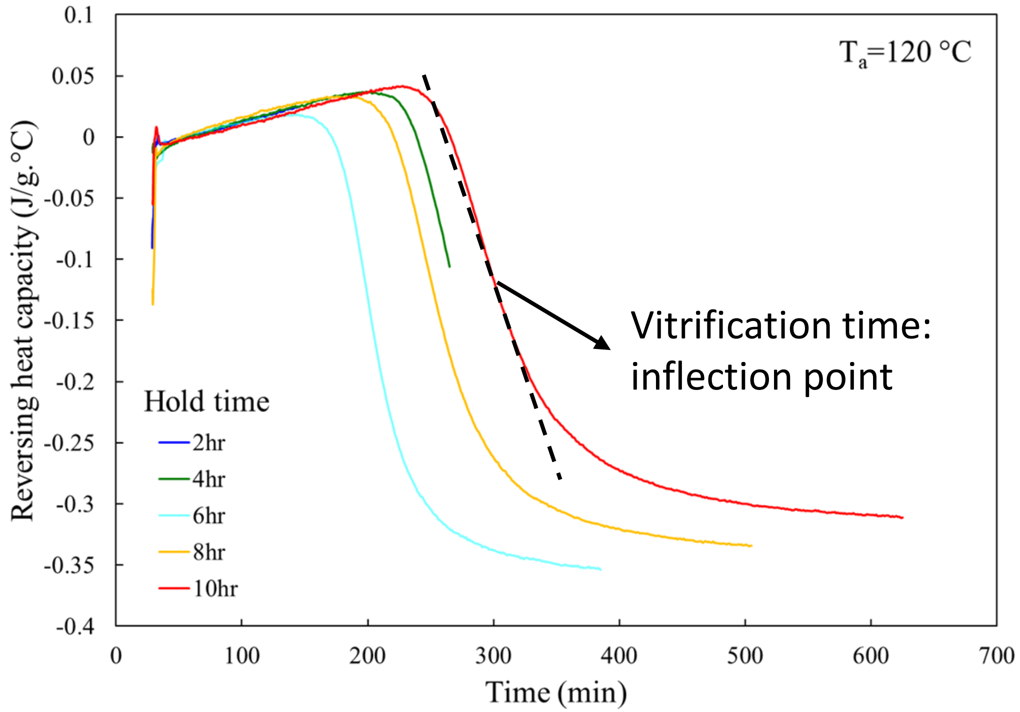
Enthalpy of aging

- Enthalpy of aging can be quantified from the area under the curve of the aged sample and a baseline.
- Typical baseline is the second heating curve of the same sample, but this is not suitable for partially cured thermosets.



The baseline is constructed as a tangent line to the heat flow signal of the DSC test in the glassy range.



Aging time = hold time – vitrification time

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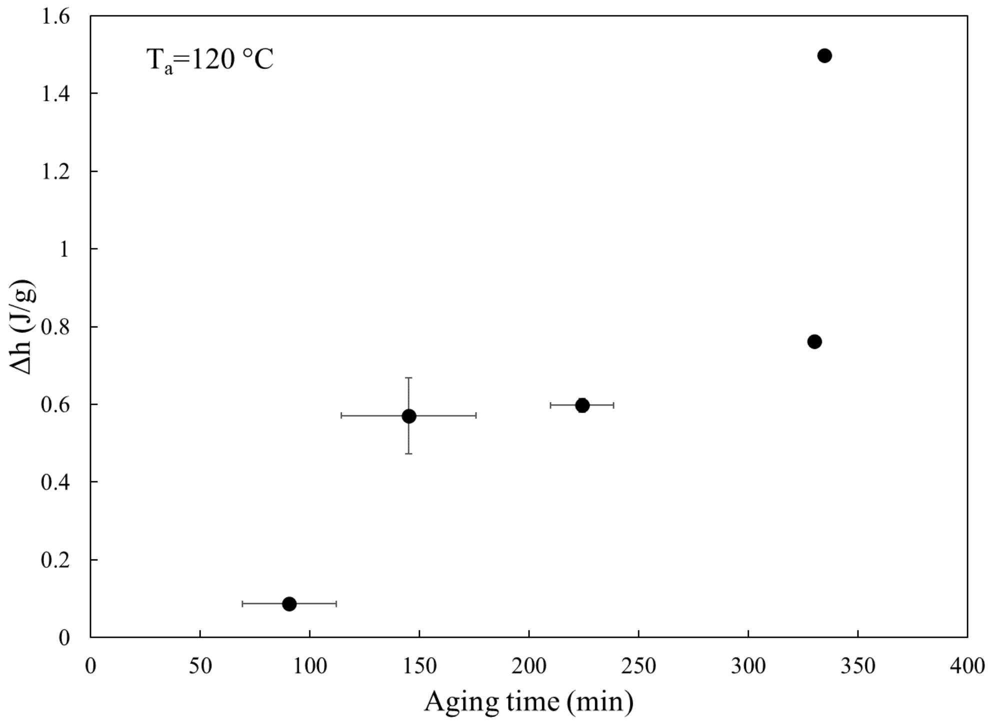
Enthalpy of aging

Cross-plot of the increase in aging enthalpy with true aging time for a hold temperature of 120 °C



✓ the aging enthalpy is seen to measurably increase over timescales relevant to composites processing.

Conclusion and future work

1. In this work, physical aging from the viewpoint of process of advanced carbon fiber reinforced thermoset polymers has been studied.

2. Systematic characterization of physical aging in thermoset resins during cure via DSC has been performed.

3. Aging enthalpy and true aging time are quantified, with the former requiring a modification to the methods used in the literature for thermoplastic polymers and nominally fully cured thermoset resins.

4. It is shown, in a quantifiable manner, that physical aging increases with aging time for a partially cured thermoset resin, and that this affects the residual cure behaviour.

- **Future work:**
- Development of a new experimental protocol to separate physical aging from the cure reaction, and investigation and further quantification of the behavior of physical aging of partially cured thermoset resins at different degrees of cure.