RHEOLOGY OF THERMOSETTING RESINS DURING CURE FOR PROCESS MODELING OF COMPOSITE MATERIALS

UNIVERSITY OF DELAWARE | CENTER FOR COMPOSITE MATERIALS

Andrew T. Brown, (BME)[2], Dr. Thomas A. Cender[1]

University of Delaware | Center for Composite Materials[1] | Department of Mechanical Engineering[2]

Introduction

- Rheology of resin filled aligned discontinuous fiber materials exhibit complex behavior. In order to decouple the effects of strain rate from the polymer and the composite material, a polymer rheology model is required.
- Viscosity of thermosetting resins change with temperature, strain rate, and cure.
- Strain rate effects are rarely accounted for in composite processing since resin typically flows at low viscosity.
- Composite forming is performed at temperatures closer to the glass transition temperature where the resin is viscoelastic.
- This work develops a cure-viscosity model for staged epoxy resins which accounts for the increase in glass transition temperature.

Methods

Cure Kinetics Measurements

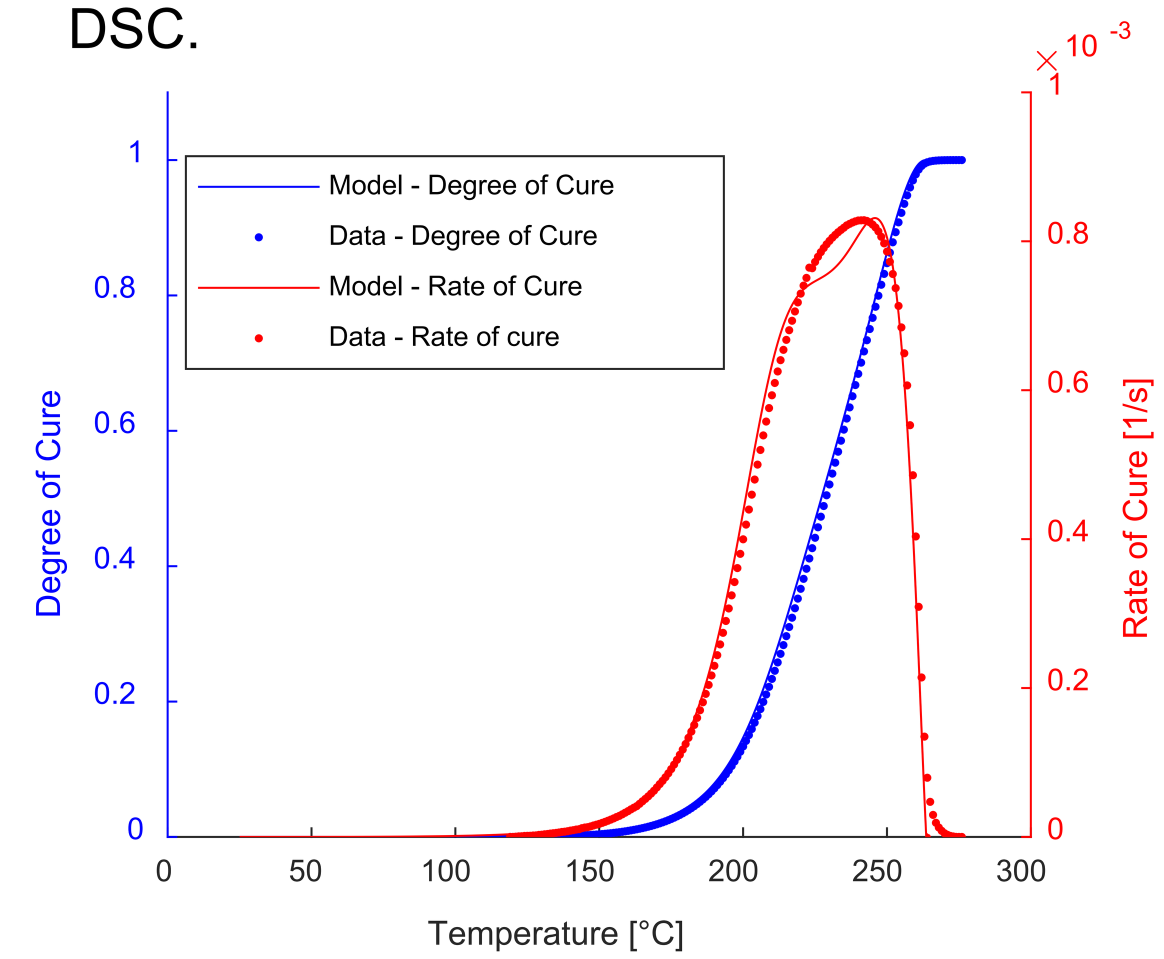
- Rate of reaction and degree of cure were measured using Differential Scanning Calorimetry (DSC) on a Netzsch DSC 214.
- Temperature was ramped at constant rates.

Viscoelastic Property Measurements

- Viscosity was measured with a TA Instruments Discovery Hybrid Rheometer using 25mm parallel plates
- Temperature was ramped at constant rates of 1- 4 °C/min until gelation.
- Strain amplitude was set to 0.1 oscillating at 1 Hz. Strain amplitude was adjusted to 0.2 at low viscosity to increase resolution.

Results

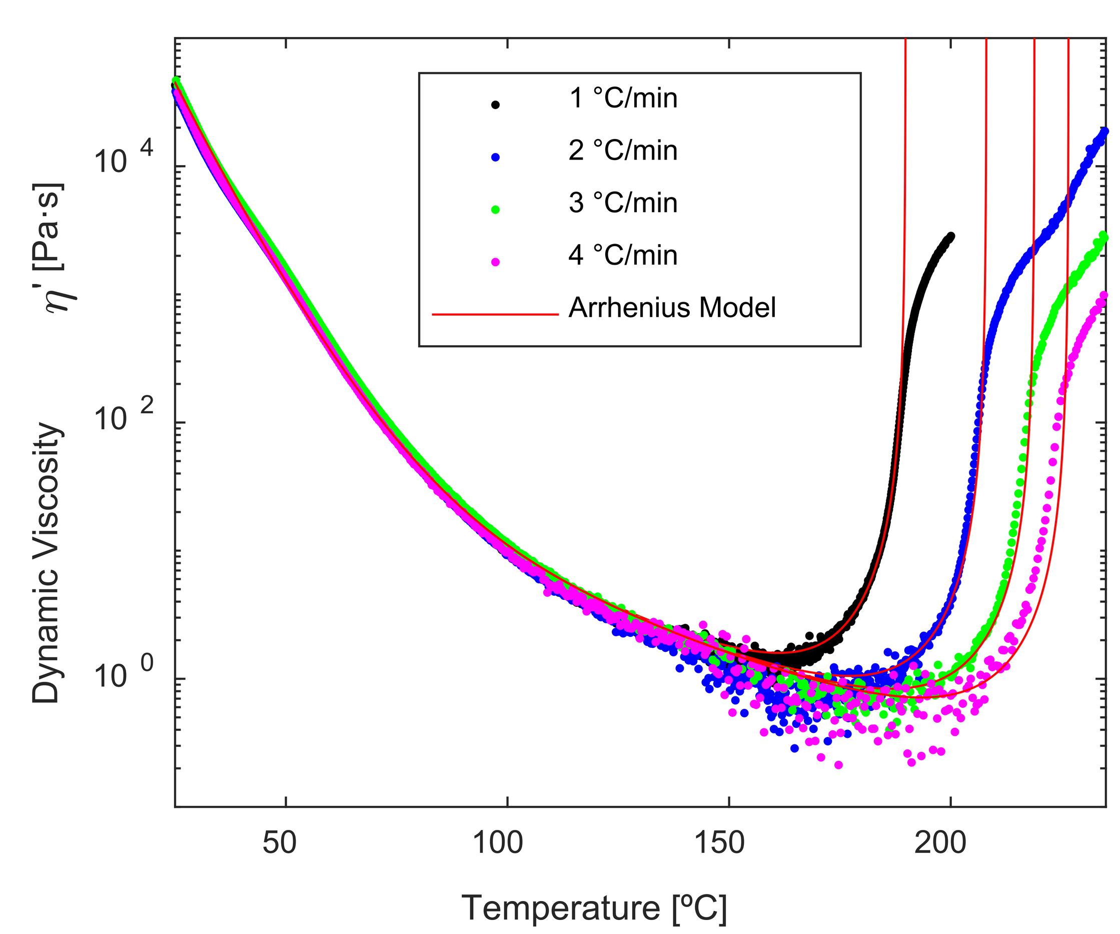
- A cure kinetics model was fit to the rate of reaction and degree of cure data from the DSC.



- The resin cure kinetics model is required to describe the increase in viscosity as degree of cure, α, approaches gelation.
- The standard Arrhenius viscosity model was constructed to predict the increase in viscosity near the gelation point α_g.

$$\eta = \eta_1 e^{\frac{E_1}{RT}} + \eta_2 e^{\frac{E_2}{RT}} \left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^A$$

- The Arrhenius model was fit to viscosity data from the rheometer.



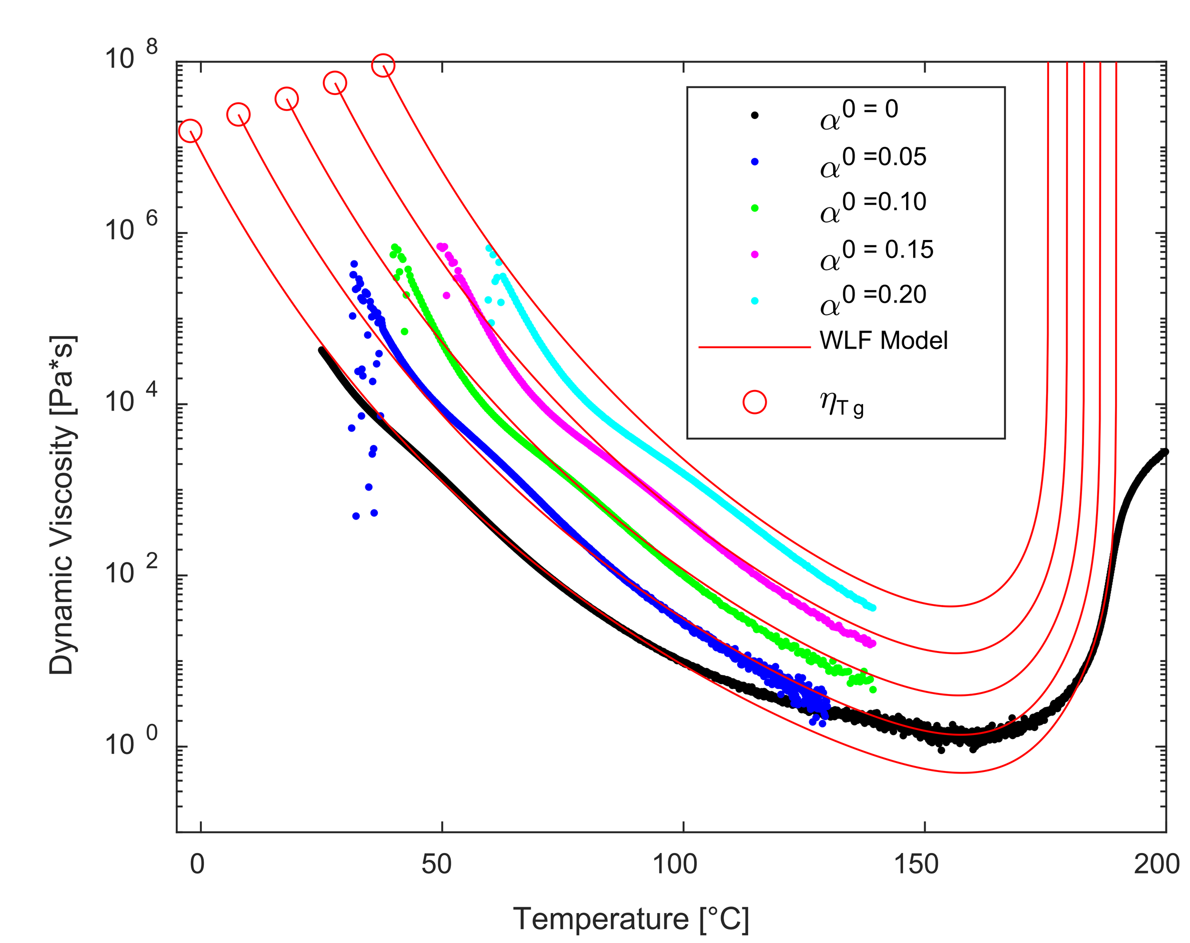
- The Arrhenius model does not work when the resin is staged to a non-zero initial cure.
- To account for the initial cure, the cure dependent glass transition temperature T_g is used as a reference.

$$T_g = 200\alpha - 3\ [°C]$$

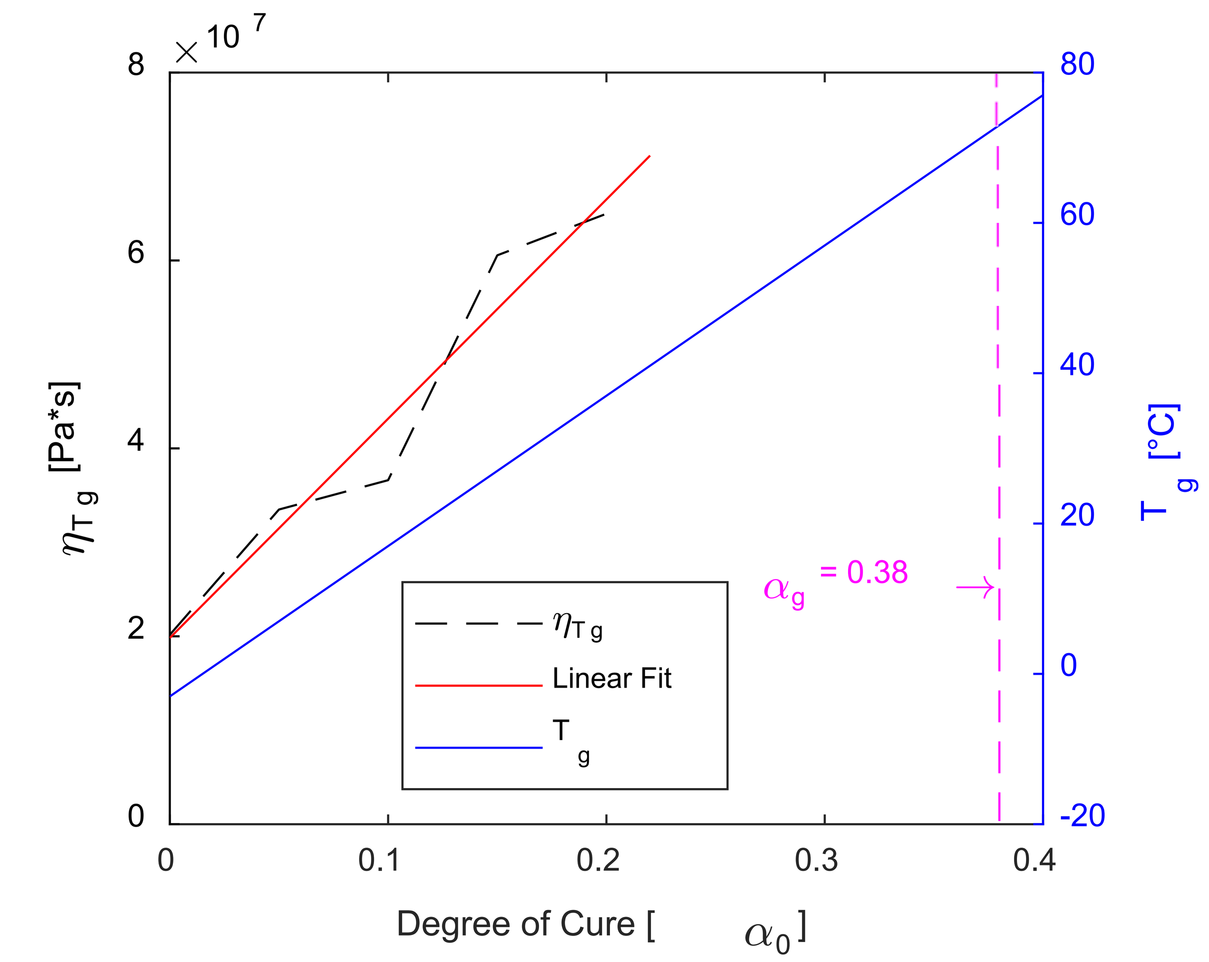
- The William-Landel-Ferry (WLF) viscosity model accounts for changing T_g making it more accurate at higher initial cures.

$$\eta(T) = \eta_{Tg} \exp\left(\frac{C_1\left(T - T_g(\alpha)\right)}{C_2 + T - T_g(\alpha)}\right)\left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^A$$

- To study the effect of initial cure, samples were staged to $\alpha_0 = 5$, 10, 15, 20% cure in the rheometer. Viscosity was measured at a 2 °C/min constant temperature ramp.
- In the WLF model C_1 and C_2 were fixed, $T_g(\alpha_0)$ was used as a reference, and η_{Tg}, the viscosity at the glass transition temperature, was a free parameter.
- Here C_1 =12.9 and C_2 =101.7



- η_{Tg} and $T_g(\alpha_0)$ were plotted against degree of cure. η_{Tg} varies linearly with degree of cure like $T_g(\alpha_0)$.



Conclusion and Path Forward

- The Arrhenius viscosity model only applies to the viscosity of B-staged resins.
- The WLF model accounts for the cure dependent glass transition temperature of the resin and thus more accurately models viscosity at low temperatures.
- Future work will investigate the effect of strain rate and employ the WLF model for time shift factors in the viscoelastic regime.

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