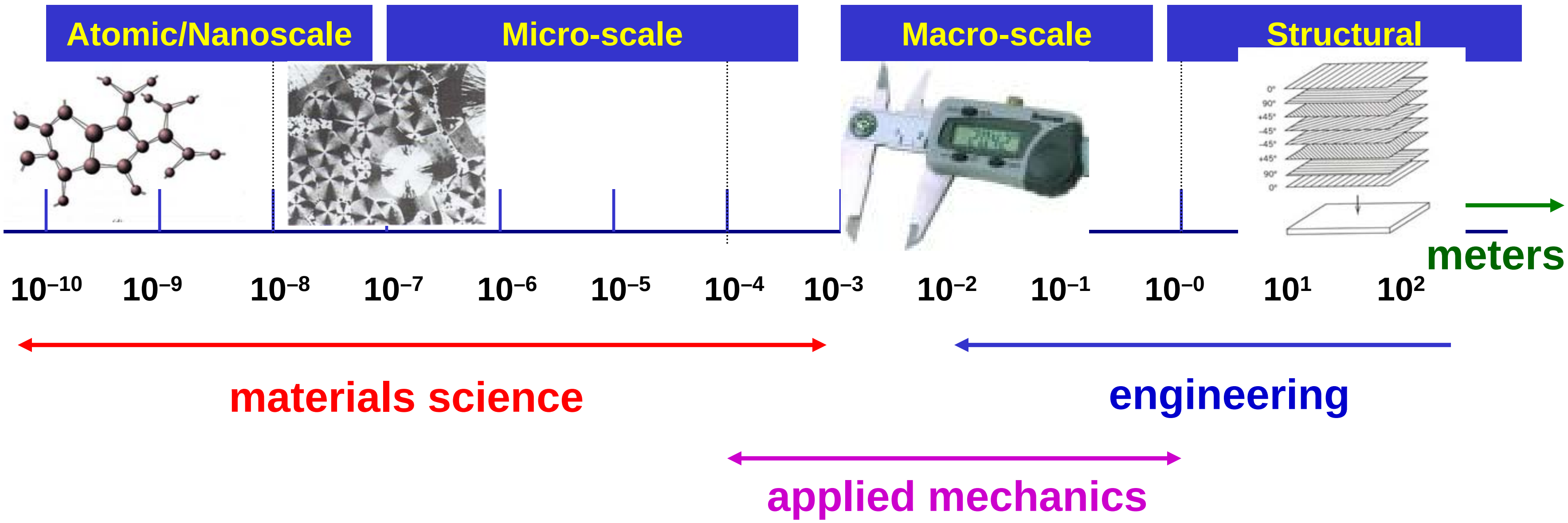
THE MATRIX: EVOLUTIONS II

Pearl Sullivan
Composites and Adhesives Group
Department of Mechanical Engineering
University of Waterloo

IPR 28th Annual Symposium, 16 May 2006

Scope: Multi-scale Analyses



[Adapted from Broek, 1974]

Structure + mechanics are critically linked to function at all scale lengths.

Performance depends on :

- **Inherent polymer structure (materials selection)**
- **Processing**
- **Mechanical/thermal loading on part design**
- **Environmental effects**

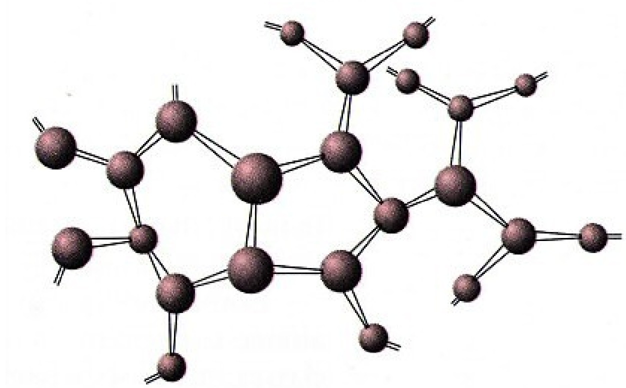
Polymeric Materials Program

THERMOSETS

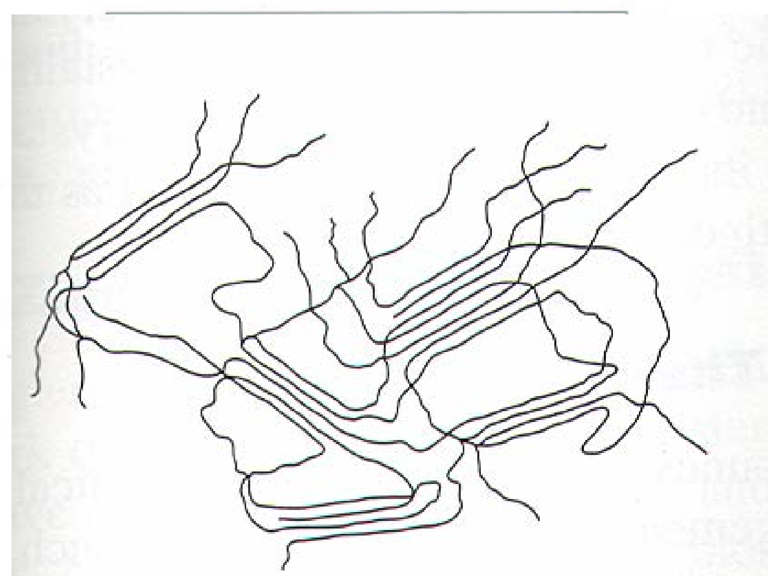
Advanced Composites
Adhesives

THERMOPLASTICS

Amorphous
Semi-crystalline



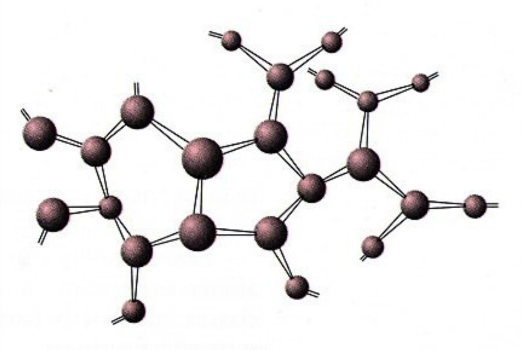
Network 3-D Structure



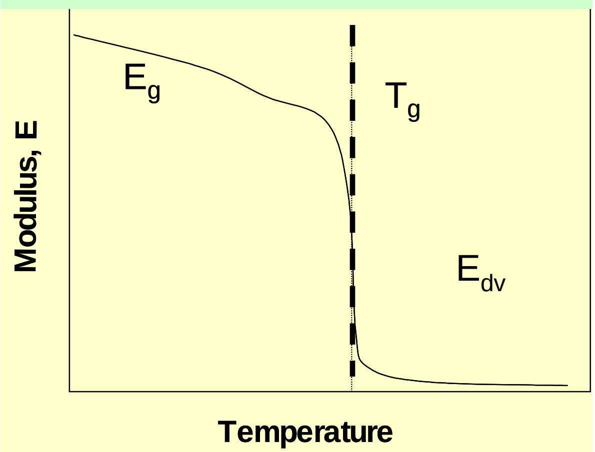
Semi-crystalline – ordered packing in amorphous matrix

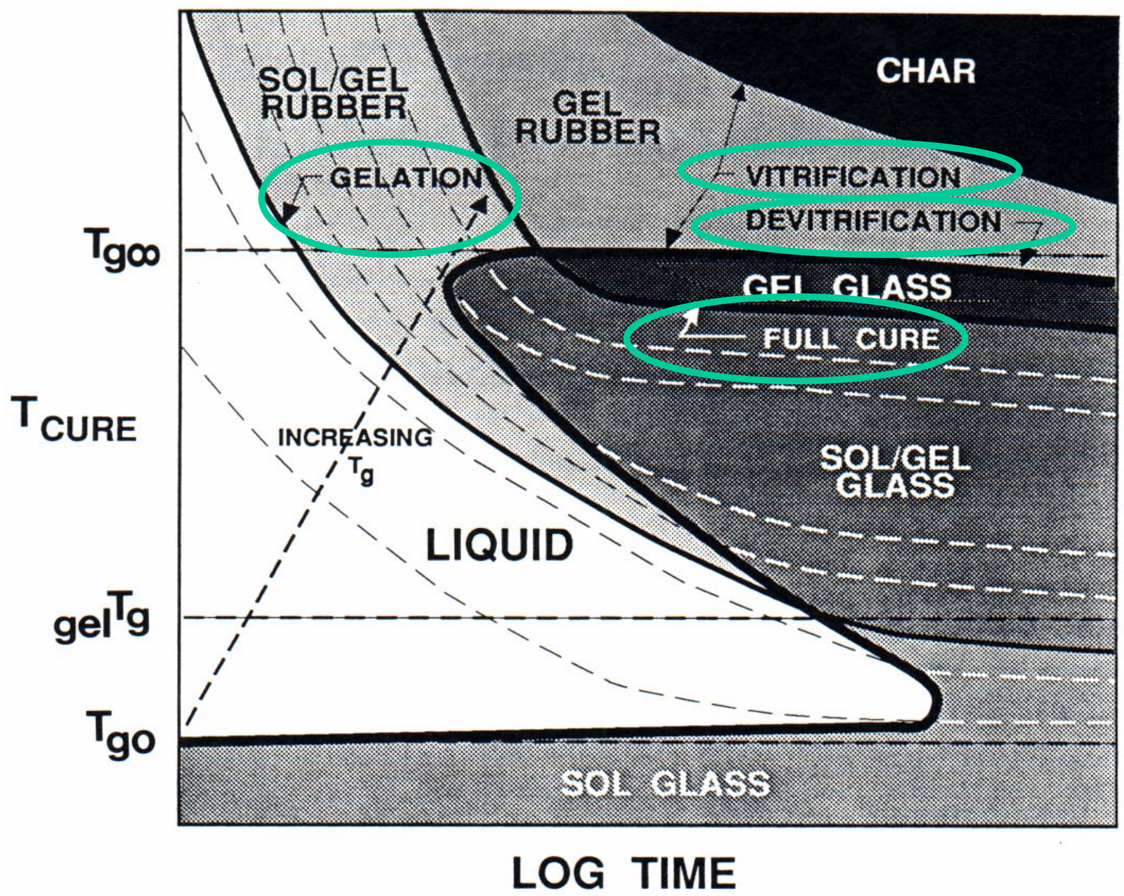
PART I: Thermoset Program

Transitions During Cure of a Thermoset

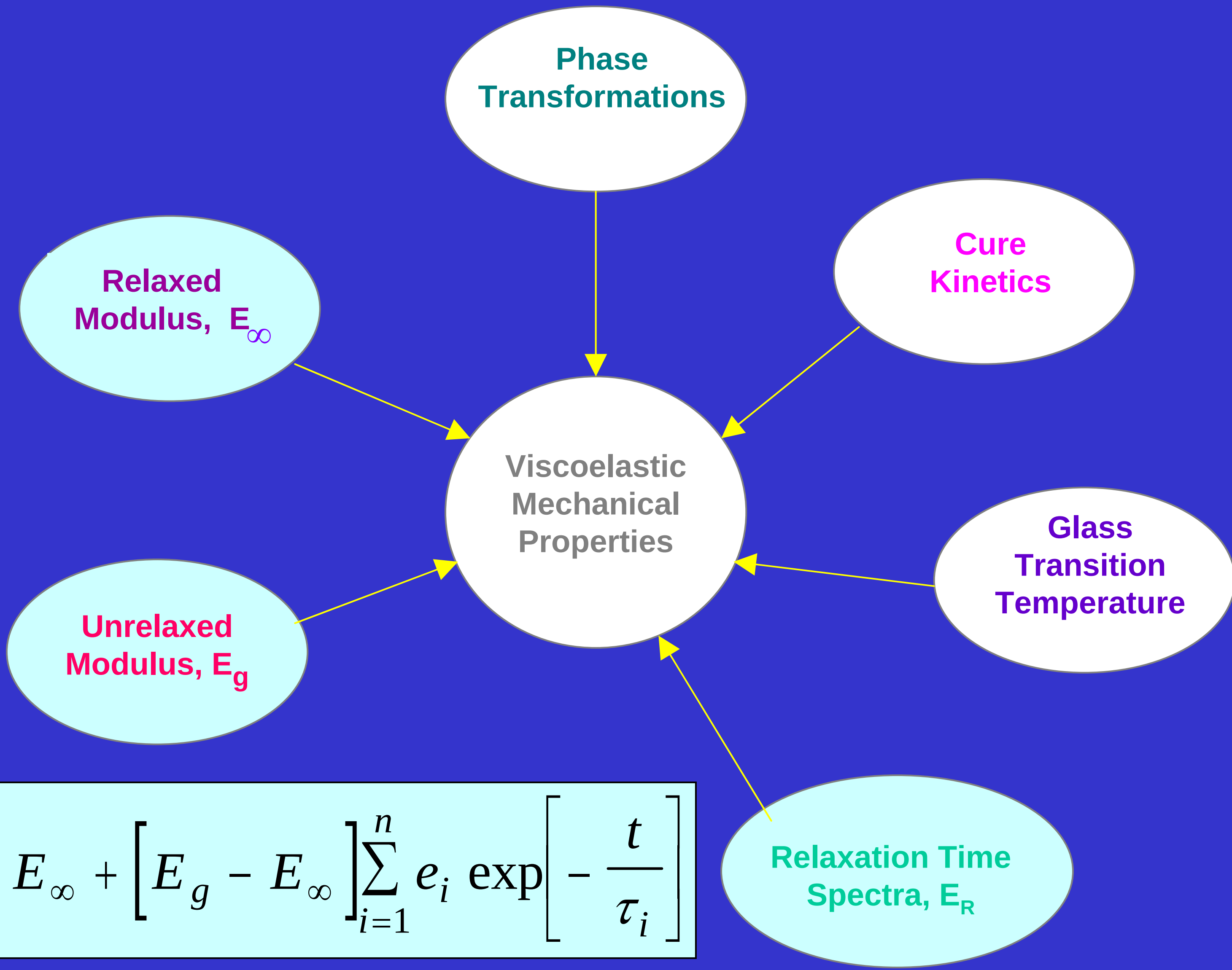


- Polymerization
- Cross-linking
- 3-D Network



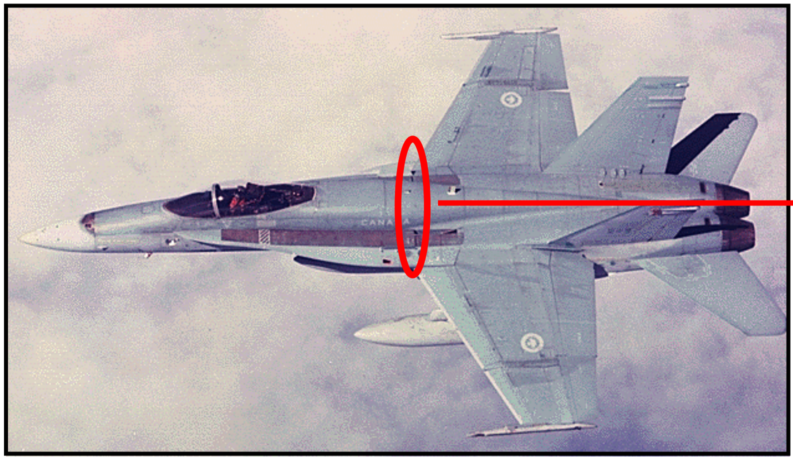


GOAL: A Unified Model for Modulus Development during Thermoset Cure

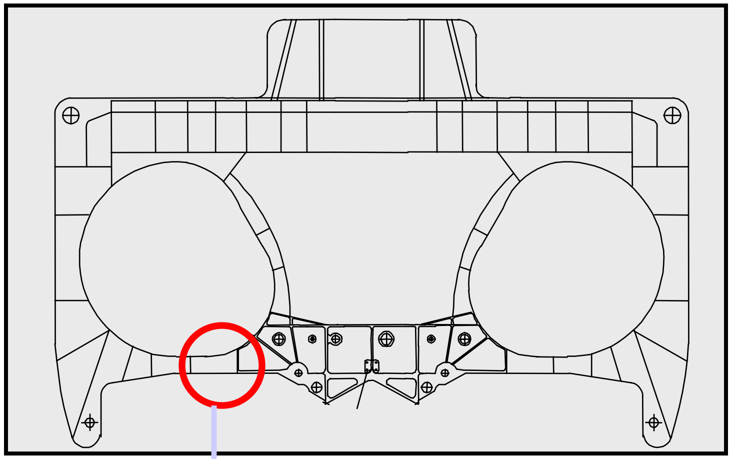


$$E_R(t) = E_\infty + \left[E_g - E_\infty\right]\sum_{i=1}^{n} e_i \exp\left[-\frac{t}{\tau_i}\right]$$

Case I. Composite Patch Repair of Metallic Structures

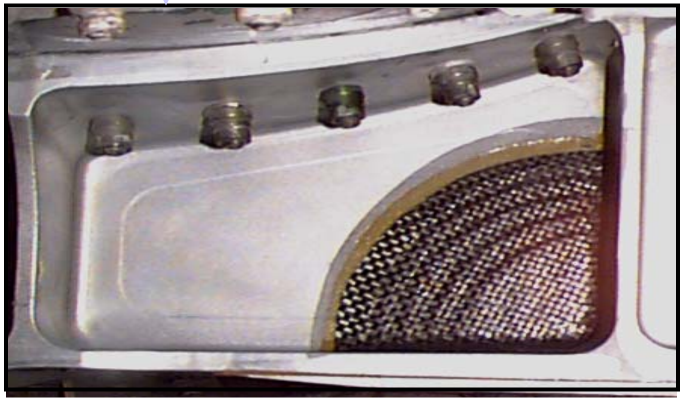


CF-18



Y470.5 Bulkhead

X-19 Repair Patch



Thermoset Adhesives Program

Team:

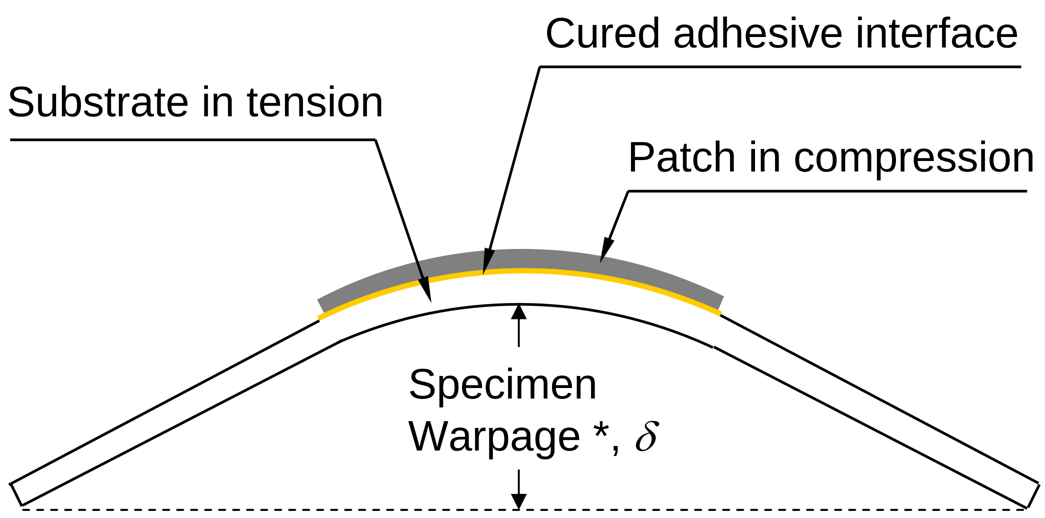
- **Drazen Djokic (MScE)**
- **Angela Rogers (PhD)**
- **Pearl Sullivan**

In collaboration with Dr. Andrew Johnston
The Institute of Aerospace Research, Ottawa

NRC · CNRC
Aerospace/Aérospatial

Project Objectives

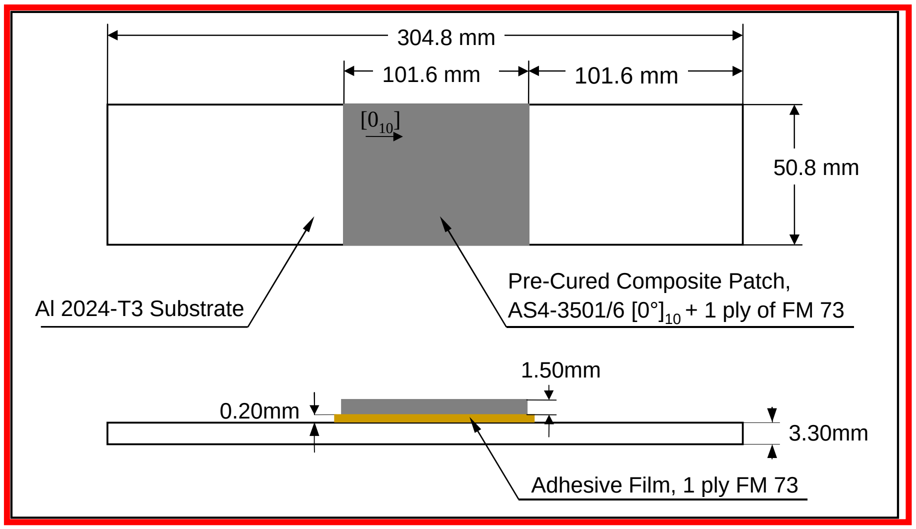
- Investigate residual stress development during patch repair
- Characterize adhesive cure kinetics during cure process
- Develop simulation model (viscous-elastic) for predicting:
  - **Specimen deformation**

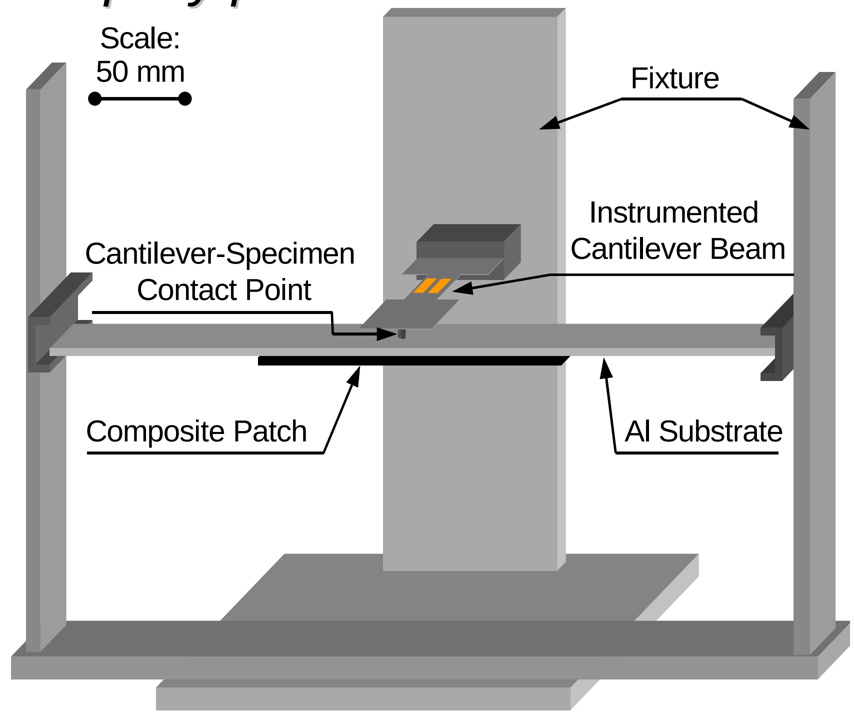


*exaggerated deformation

WARPAGE MEASUREMENT

- *Single-sided repair*
- *Pre-cured unidirectional carbon fibre/epoxy patch*
- *Aluminum substrate*
- *FM 73 film adhesive*





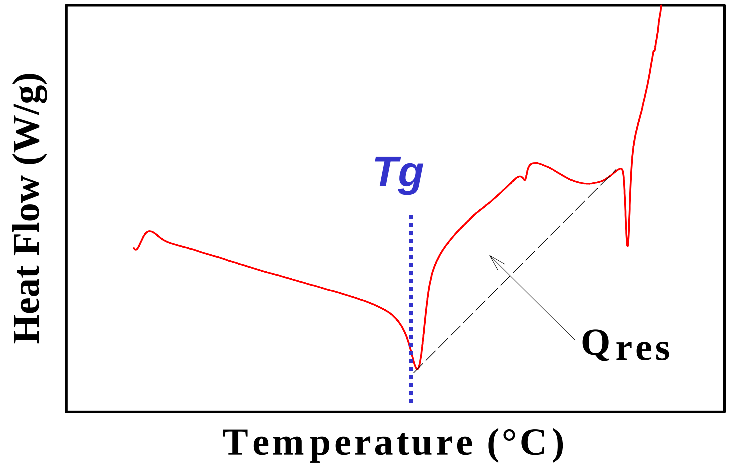
Djokic, D. et. al.
American Society for Composites Annual Meeting, Austin, Texas, Sept 2000, 12 pgs.

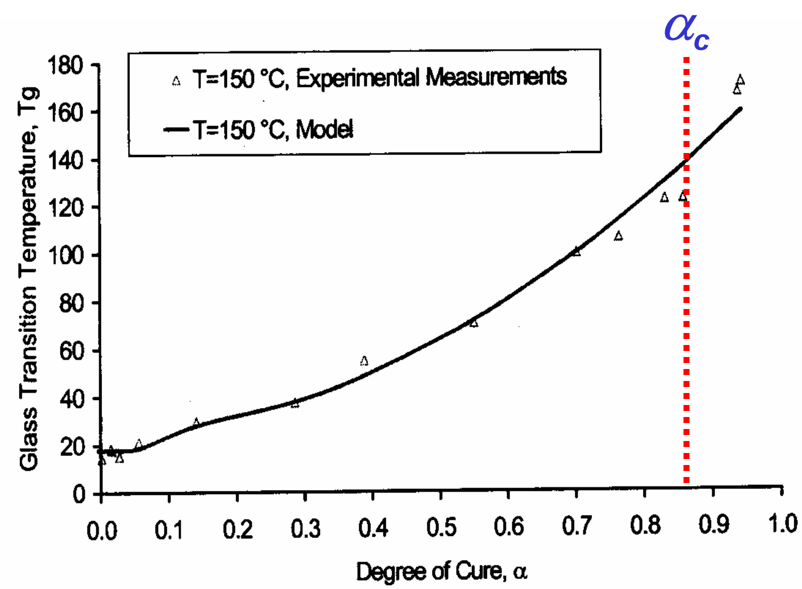
DSC for Cure Kinetics Determination

- Perform a dynamic temperature scan on uncured and partially cured specimens with DSC.
- Calculate T_g from the heat flow data for each sample.
- Calculate the degree of conversion for each specimen.

$$T_g = A_1 + B_1\alpha + C_1\alpha^2 \qquad \alpha < \alpha_c$$

$$T_g = A_2 + B_2(\alpha - \alpha_c) + C_2(\alpha - \alpha_c)^2$$
$$\text{for } \alpha > \alpha_c$$



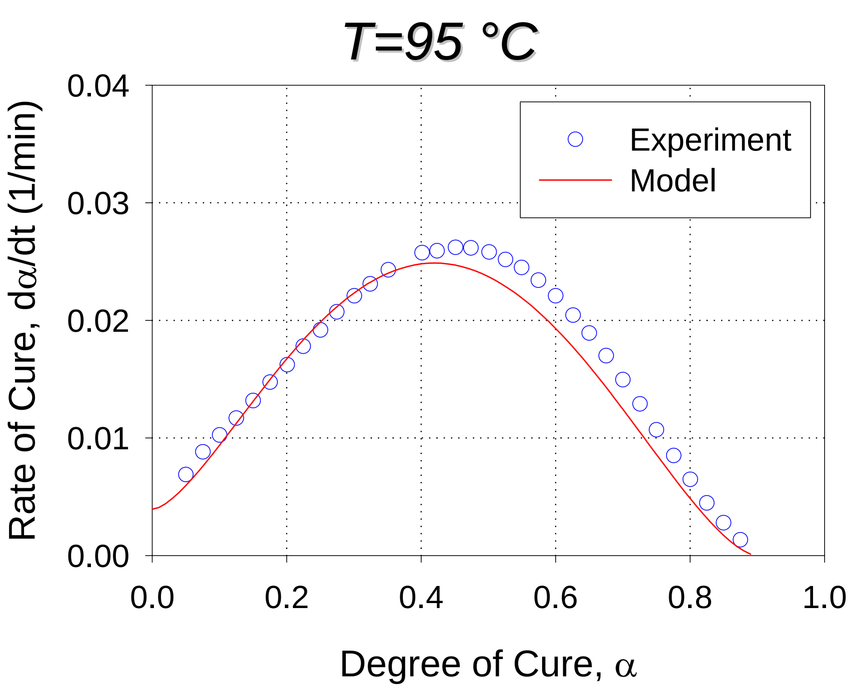


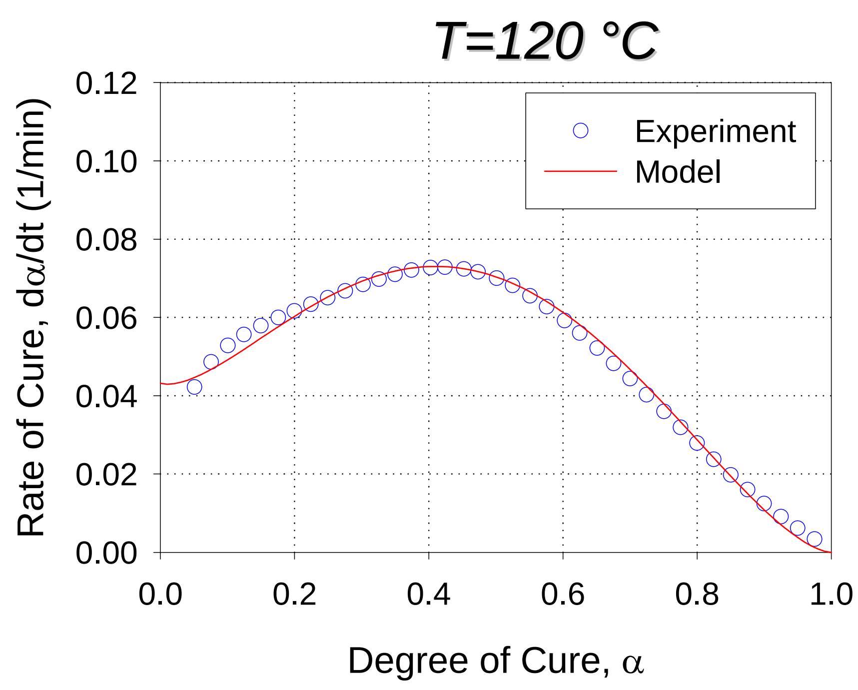
Analytical Models: Cure Kinetics Equation

An existing semi-empirical model (Kamal and Sourour,1973)

$$\frac{d\alpha}{dt} = \left(K_1 + K_2 \alpha^{1.8}\right)\left(\alpha_f - \alpha\right)^{1.85}$$

Model Predictions and Experimental Measurements





Analytical Models: Viscoelastic Response

Relaxation Modulus:

$$E(T,t,\alpha)=E^{\infty}(\alpha)+\left(E^{u}(\alpha)-E^{\infty}(\alpha)\right)\exp\left[-\left(\frac{t}{a_T(T,\alpha)\,\tau(\alpha)}\right)^{0.19}\right]$$

Shift Function:

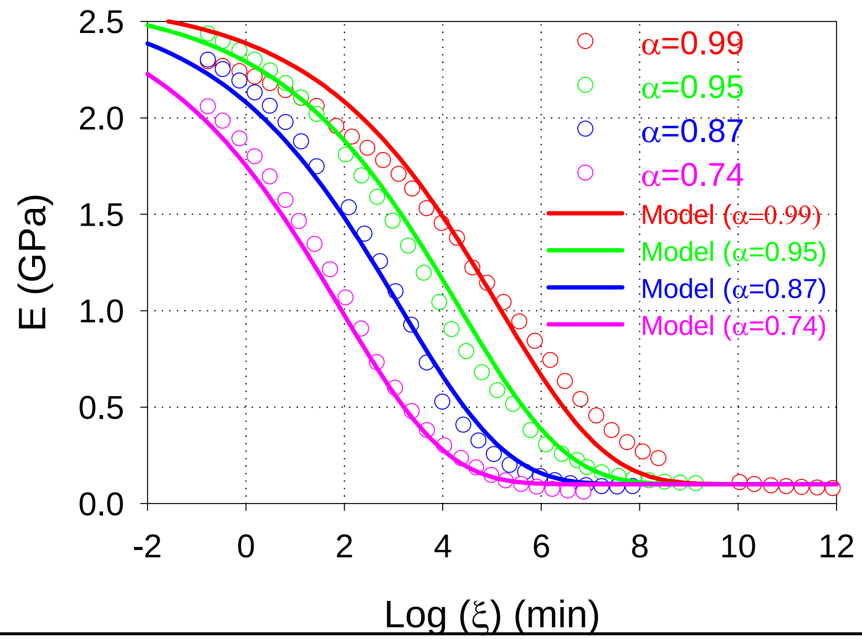
$$\log(a_T)=C_1(\alpha)+\frac{C_2(\alpha)}{T}$$

Relaxation Time:

$$\log(\tau)=\frac{1.333\alpha^2}{1-0.735\alpha}+3.512\alpha-3.073$$

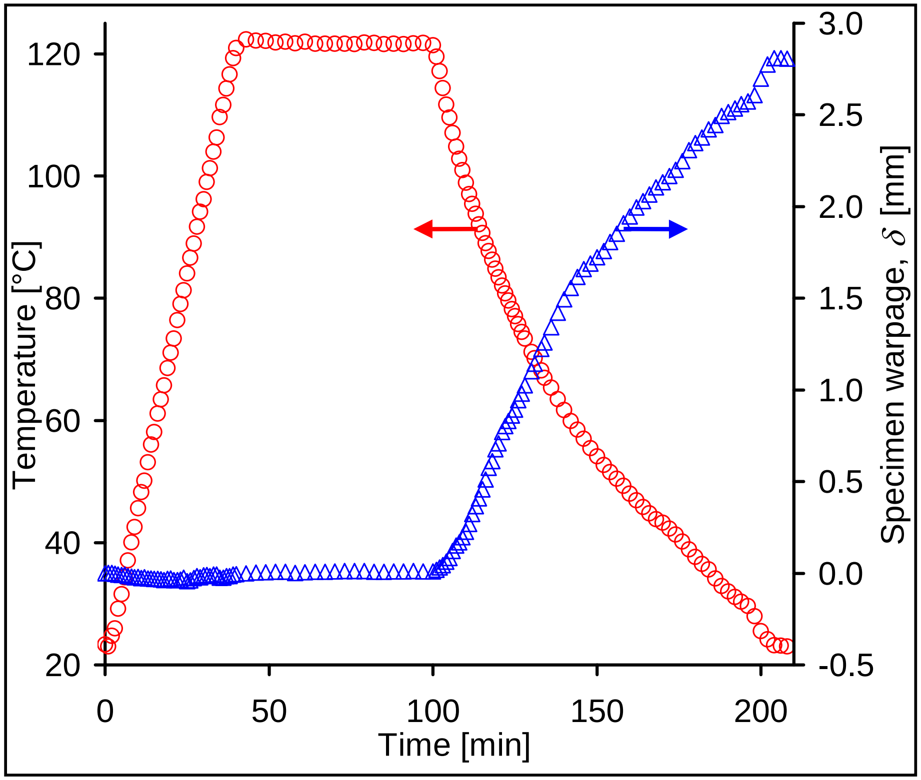
Master Curves,

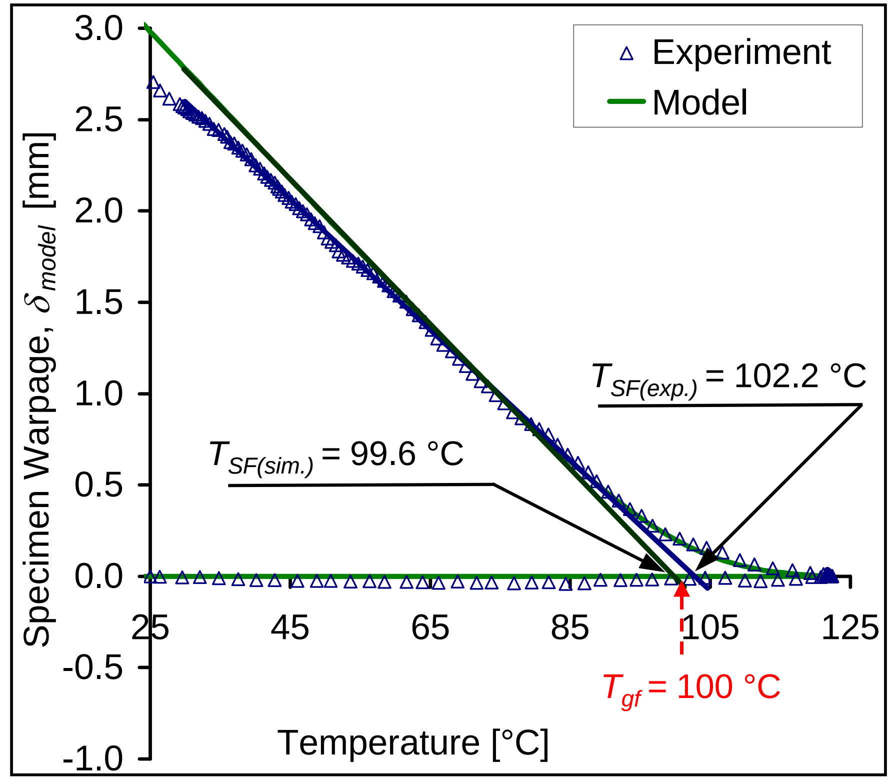
Model and Experimental Results:



Results: Single-Step Cure Cycles

Test 1: T_{cure}=121 °C, t_{hold}=60 min



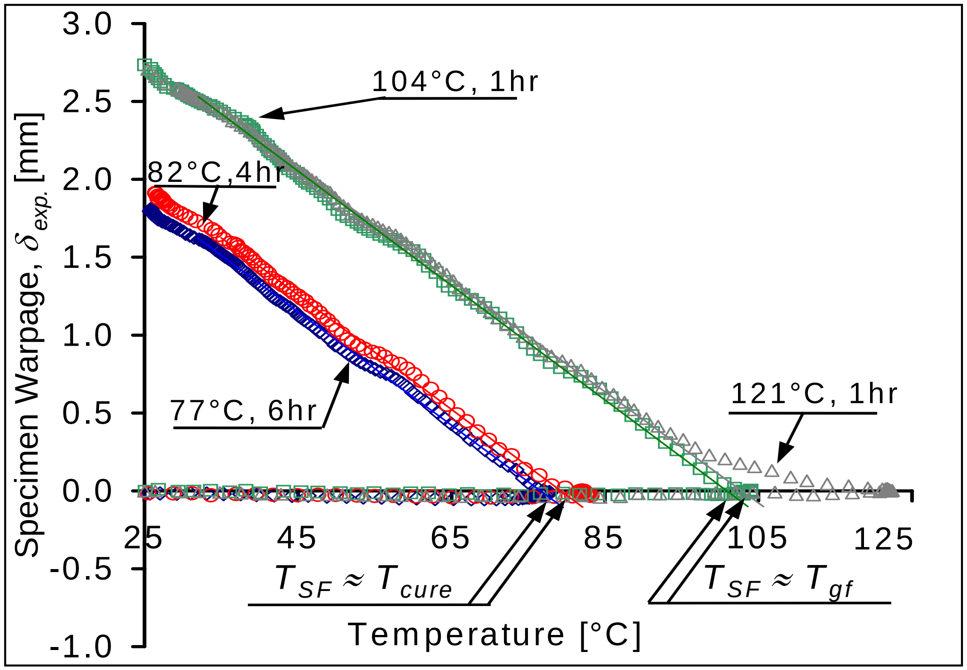


- *Negligible warpage during heating and isothermal hold*
- *Non-linear warpage until 100 °C (T_{gf})*

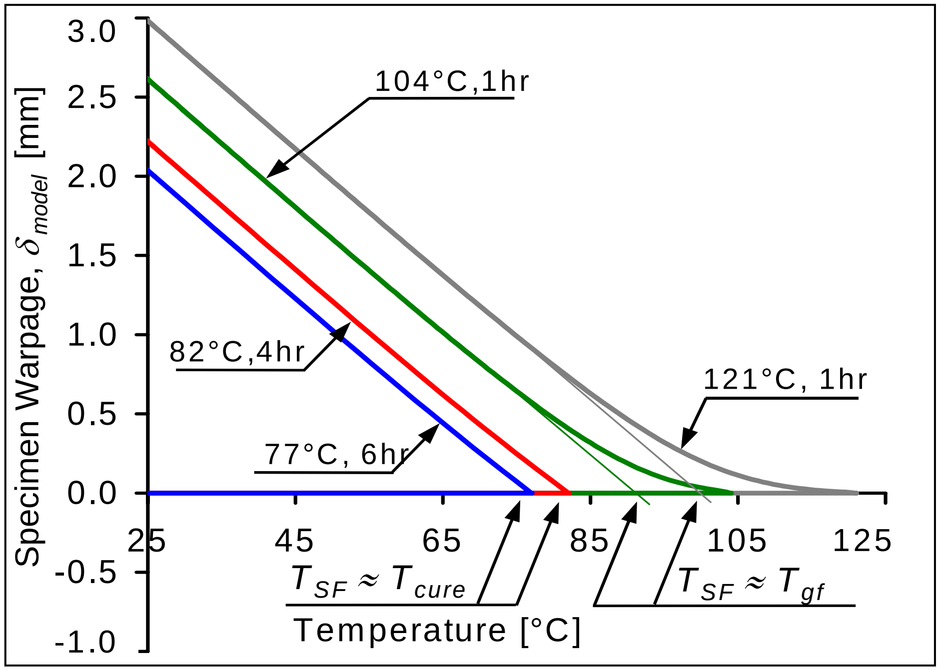
Djokic, D. et. al.
Composites A:Applied Sci and Manuf.
Vol 33(2), 2001, pp. 277-288.

Results: Single-Step Cure Cycles

Experiment



Model



Next Steps

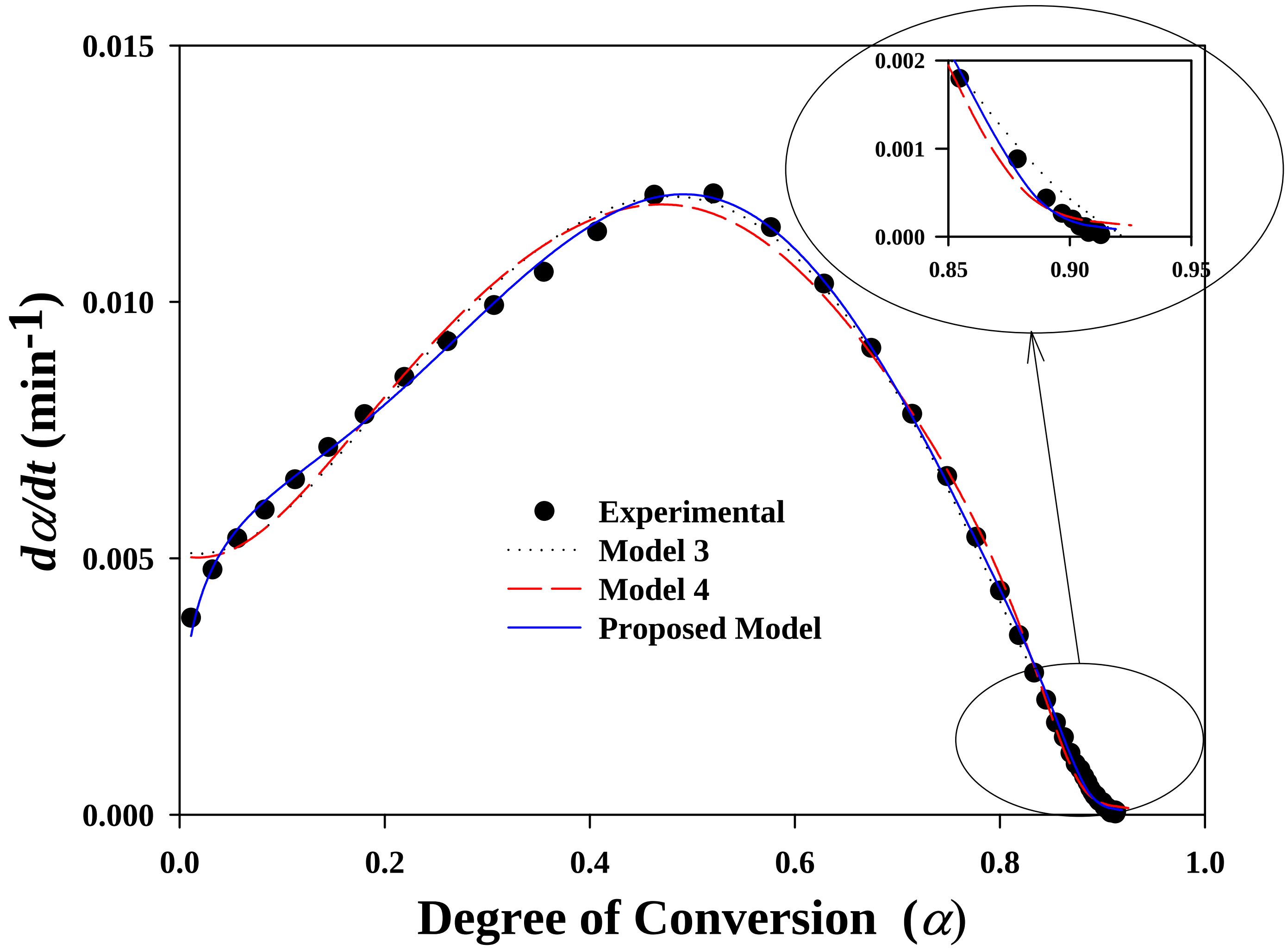
1. *Patch repair model for multi-step cure can be improved by:*

- *Including diffusion effects in cure kinetics model*
- *Including viscoelastic response within gelation-vitrification range*

2. *Modulus development needed:*

- *Integrate models into FE code*

Comparison of Models



Refined Cure Kinetics Model

$$\frac{d\alpha}{dt} = \frac{k_1 \alpha^{m1} (1 - \alpha)^{n1} + k_2 \alpha^{m2} (1 - a)^{n2}}{1 + exp\left[C\left(\alpha - \alpha_c\right)\right]}$$

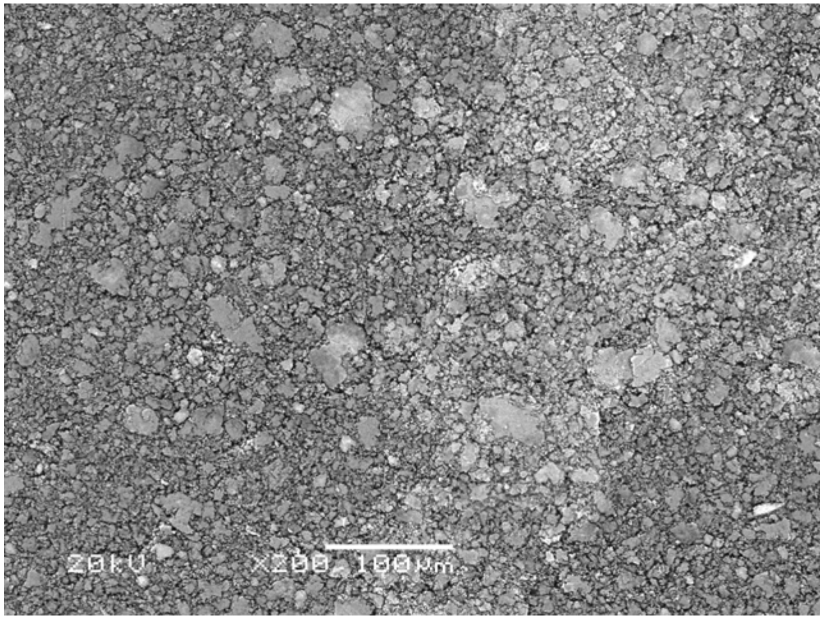
This model:

- **Suggests that chemical curing is primarily the result of a combination of two autocatalytic reactions;**
- **Includes a diffusion factor in the denominator.**

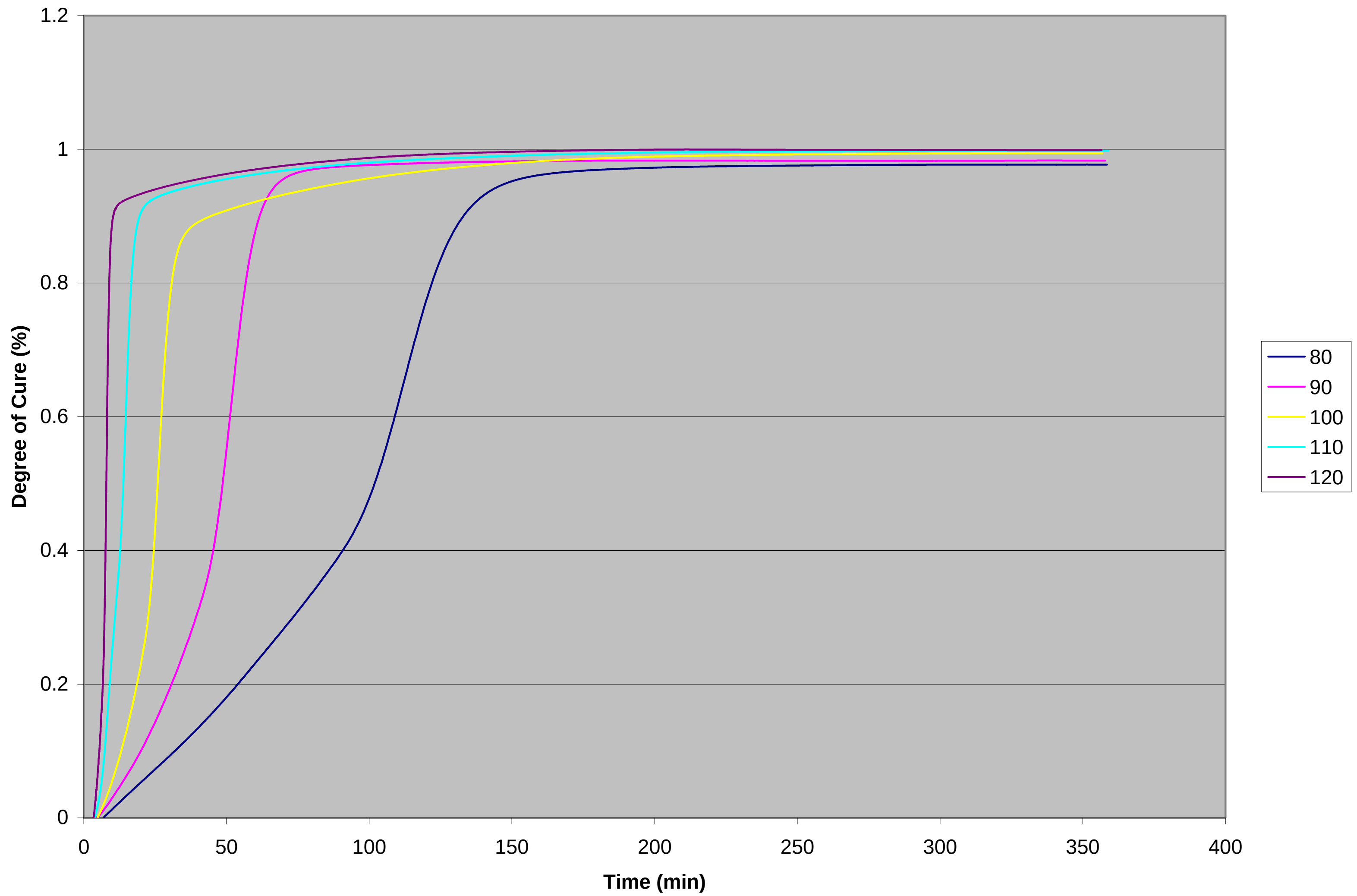
Rogers, A. and Lee-Sullivan, P., Polymer Engineering and Science Vol. 43(1), Jan 2003, pp 14-25

Case II. Dimensional Stability of Microelectronic Bonds

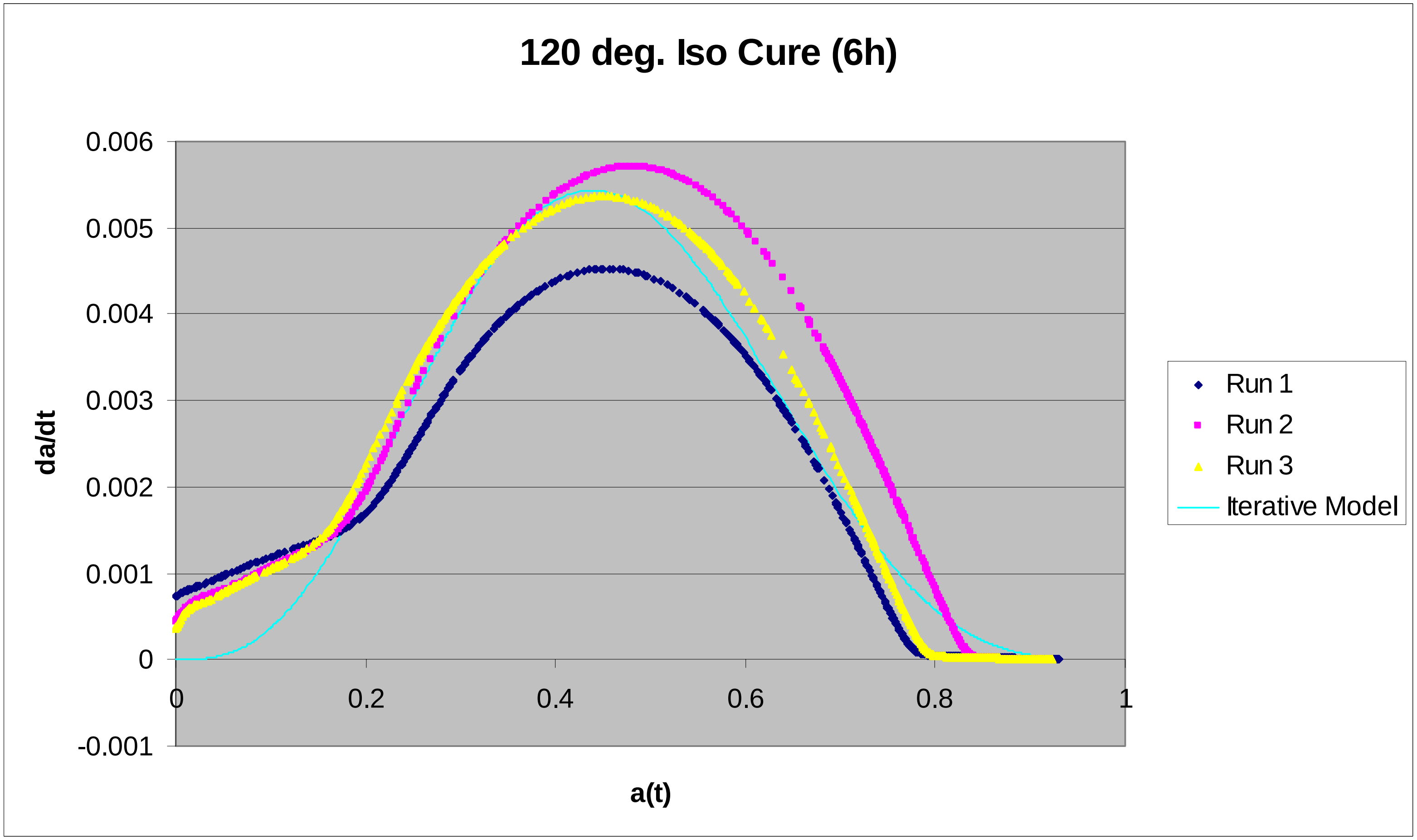
- Epo-tek H20E two-part epoxy
- Silver filled; sub micron-size
- Electrically Conductive Adhesive (ECA)
- Thermally conductive
- Applications:
  - Microelectronics
  - Optoelectronics



Cure Conversion with Time

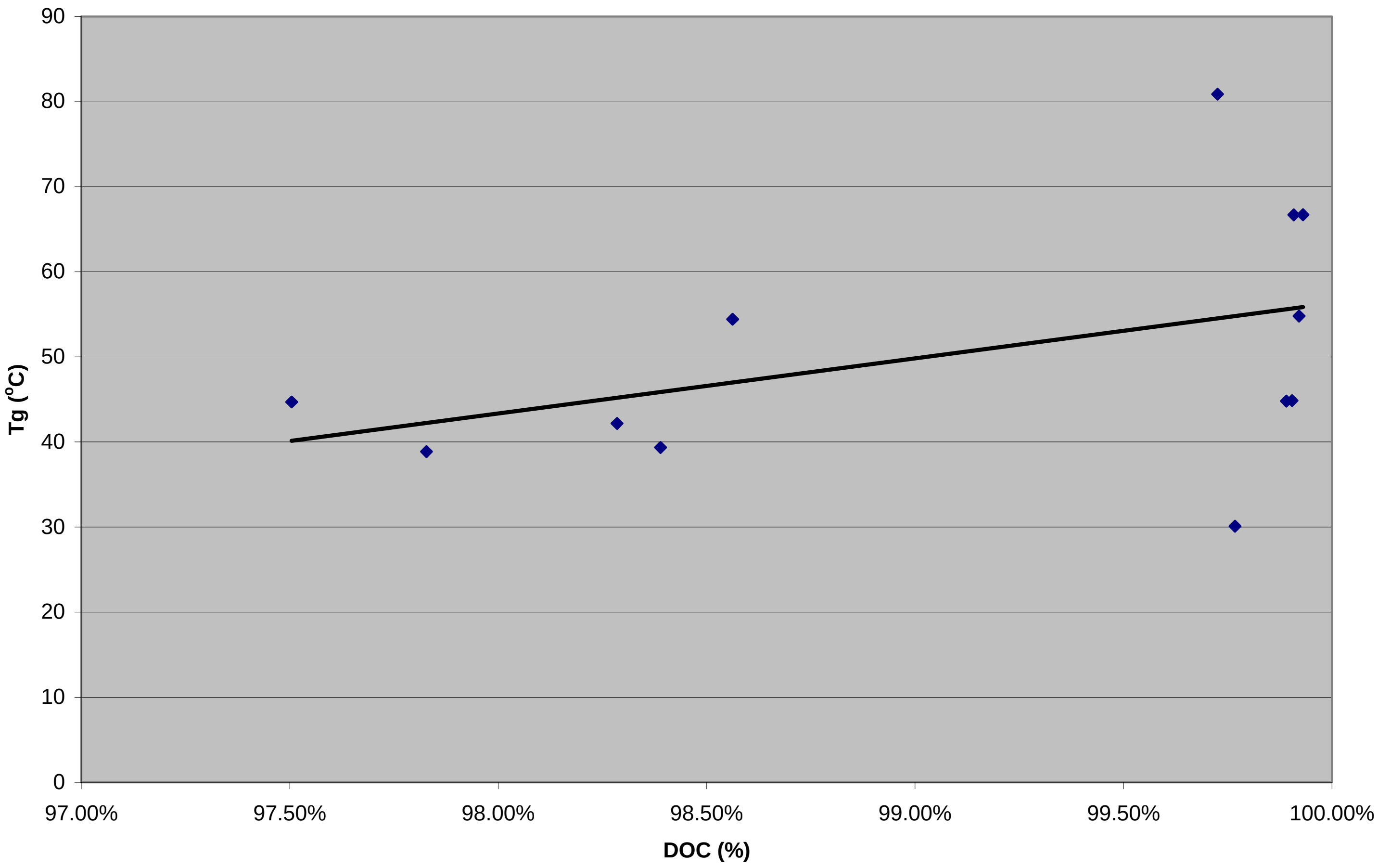


Cure kinetics for Electrically Conductive Adhesive (ECA)



Garvin, M. and Lee-Sullivan, P., Canadian Themal Analysis Meeting, Toronto, May 2006

Tg Advancement with Degree of Cure



Ultimate Goal of Thermoset Cure Modeling Program

$$E_R(t,T,\alpha) = E_\infty(T,\alpha) + \left[E_g(T,\alpha) - E_\infty(T,\alpha)\right] \sum_{i=1}^{n} e_i \exp\left[-\frac{t}{a_{T,\alpha}\,\tau_i(T,\alpha)}\right]$$

For application in computational modeling:

- **adhesive bonding processes**
- **composite processing**
- **microelectronic assembly, e.g. underfill, encapsulation**

Part II : Thermoplastic Program

Goals

- Characterize time-, temperature- and moisture effects on stability of thin-walled moldings
  - Creep and Stress Relaxation

- Develop phenomenological model to predict the intrinsic viscoelastic constitutive behaviour (e.g. time-dependent bulk modulus).

Injection molded plastic resin pricing trends, $/lb

	1993	1998	2003	2008*	2013*
Average injection molded plastics	**.47**	**.51**	**.57**	**.63**	**.71**
LDPE, general purpose (GP)	.35	.46	.67	.75	.83
LDPE, lid resin	.37	.45	.66	.75	.84
Polystyrene, GP	.46	.40	.56	.62	.68
Polystyrene, high impact	.48	.42	.58	.64	.71
HDPE, GP	.27	.34	.50	.56	.62
Polypropylene, GP	.29	.31	.45	.50	.55
Polypropylene, random copolymer	.29	.33	.48	.53	.57
PVC	.29	.38	.42	.47	.52
Polycarbonate	1.38	1.59	1.40	1.55	1.70
Nylon 6	1.15	1.44	1.22	1.38	1.54
TP polyester, PET	.93	.99	.99	1.05	1.11
TP polyester, PBT	1.15	1.05	1.03	1.08	1.13
ABS, pipe fittings	.75	.60	.56	.58	.60
ABS, high impact	.87	.77	.71	.70	.68
Melamine	.85	.91	.92	.93	.93
Unsaturated polyester, GP	.57	.88	.81	.87	.92
Phenolics, GP	.74	.79	.80	.81	.82
Urea	.72	.72	.72	.73	.73

Source: The Freedonia Group Inc.

**Forecast*

The accuracy of predictions on resin pricing depends heavily on future prices of petroleum and natural gas. When these figures were published, oil prices were less than $50/bbl. In March 2006, oil prices hovered around $60/bbl.

Post-Molding Dimensional Stability

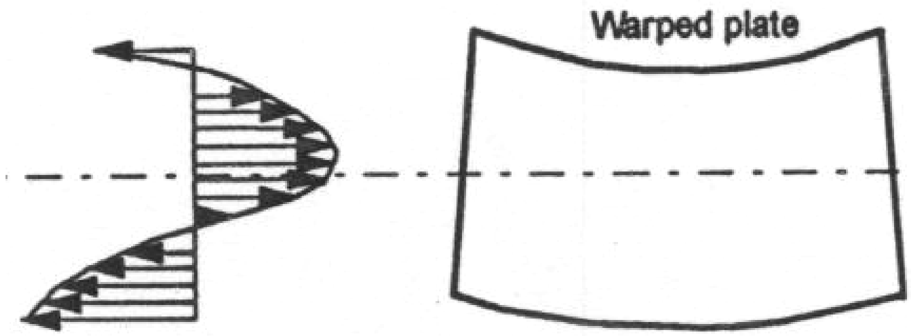
Does your part warp after molding?

- **Case 1: Polypropylene (PP)**

  Cooling rate effects on part warpage during injection molding

Post-molding thin-wall warpage

- Warpage in thin-walled plates due to unsymmetrical residual stress during uneven cooling



- **Can be minimized through part-cavity design and processing conditions**

Measuring Post-Molding Warpage

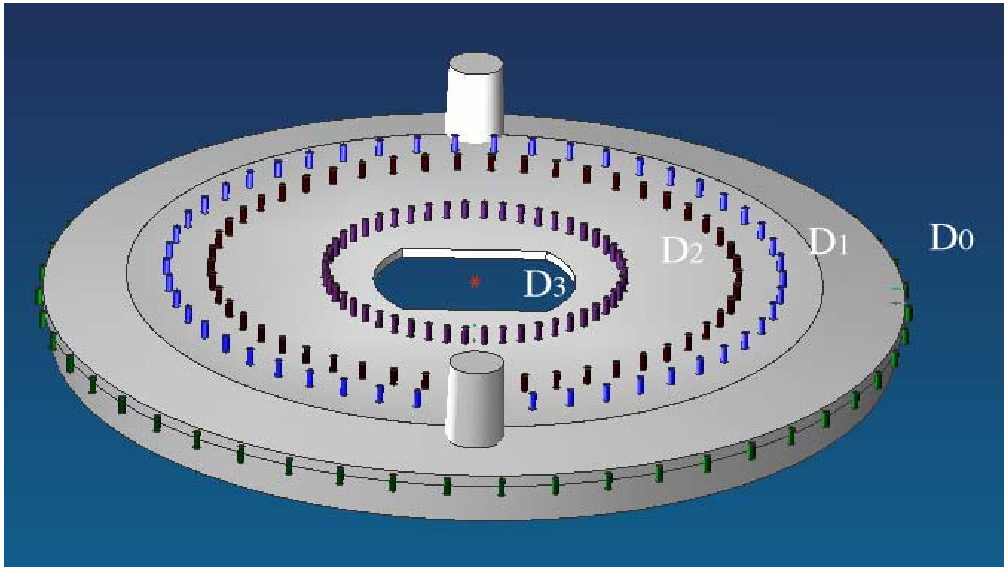
using Coordinate Measuring Machine

- **Circularity was calculated from 50 measurements: *D0***

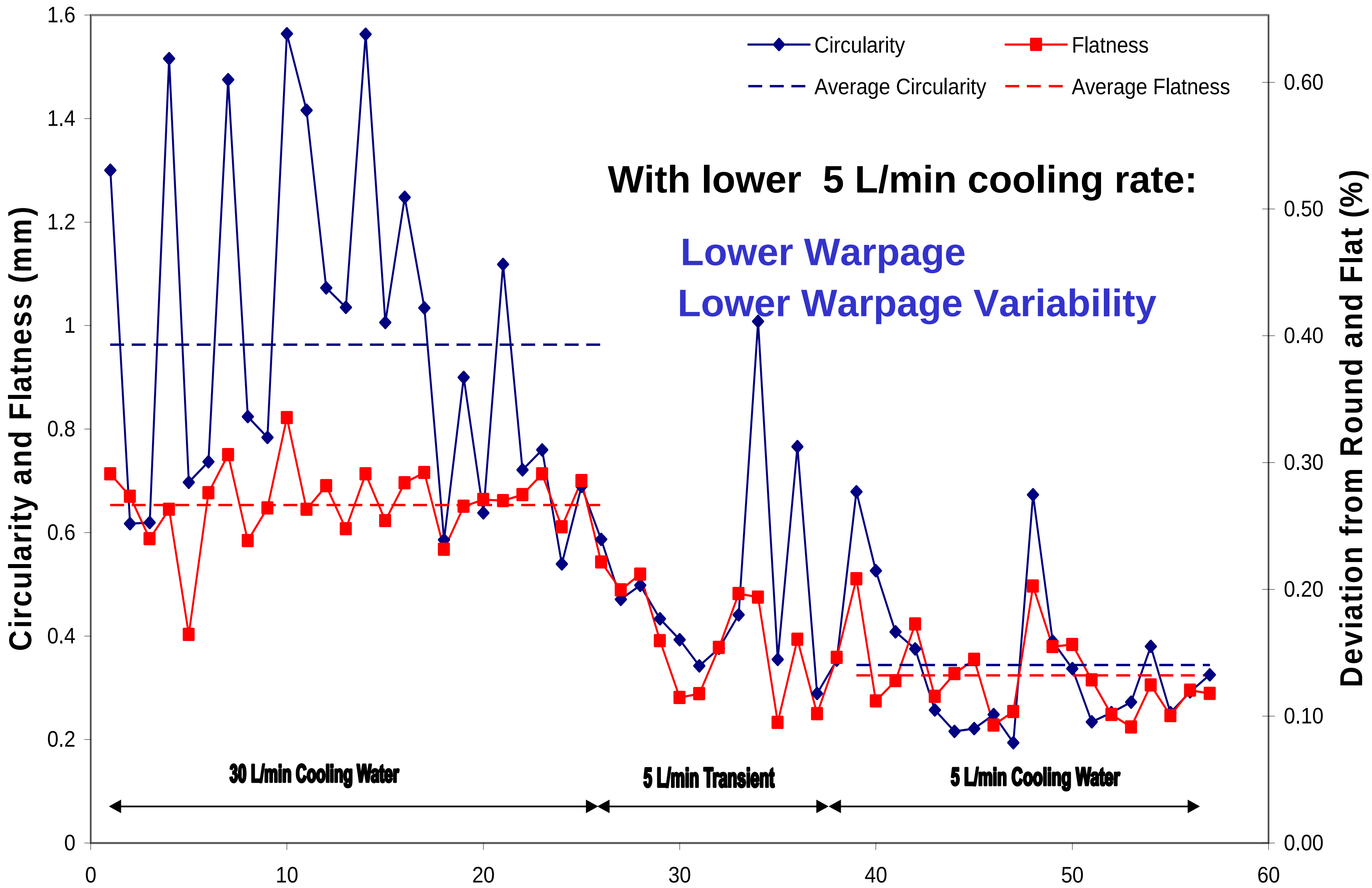
Deviation = ∆ diameter/ d

- **Flatness was calculated from 150 measured points on the surface: *D1, D2, D3***

Deviation = ∆ height/ d



Disk diameter, d ~ 10 in



Warpage after one week after molding

Evolution of Warpage over 1 Week

Increasingly more warpage as the part ages for higher cooling rate