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Silicone Quality Control with a Rubber Process Analyzer (RPA)

Jessica Gialamas

Application Engineer

- 2+ years in polymer industry
- BS in Chemical Engineering from Cleveland State University
- MBA from John Carroll University

AGENDA

1. Introduction to Alpha Technologies
2. Introduction to the RPA
3. Rheology, Viscoelasticity, and Viscosity
4. Testing Silicones with an RPA

Alpha Technologies At-A-Glance

150+	50+	25+	7	ISO	
GLOBAL DIRECT ASSOCIATES	FIELD SERVICE TECHNICIANS	CUSTOMER & TECH SUPPORT	DEGREED APPLICATION ENGINEERS	17025 CERTIFIED	$5.5B PUBLICLY TRADED PARENT

Sales / Demo Office   Direct Sales / Field Service Associates

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What is an RPA

Sample prep for LSR’s

INTRODUCTION TO THE RPA

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Premier RPA is Four Instruments in One

- Process Simulator
- Cure-meter
- DMA
- Rheometer

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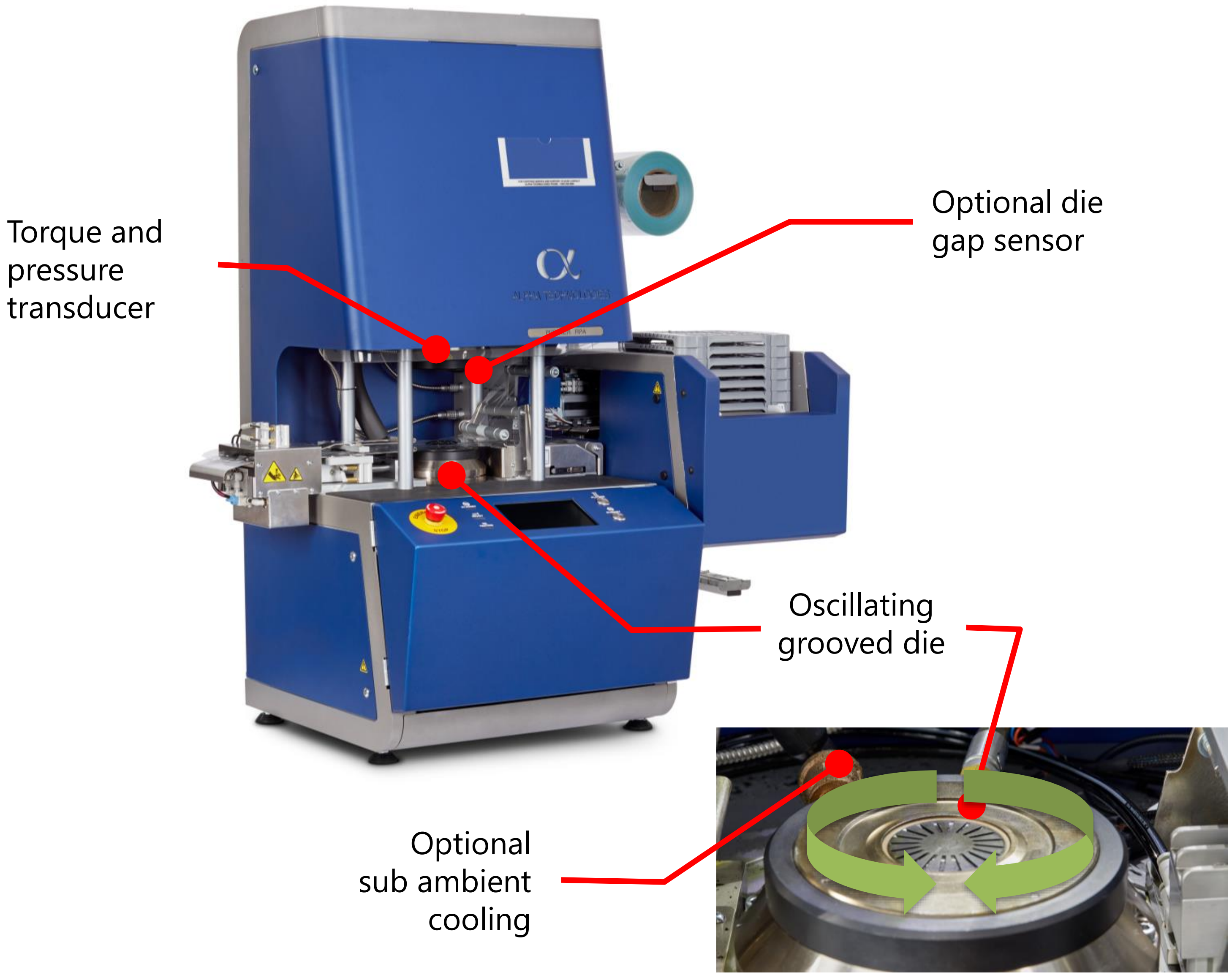
DEFINITION

WHAT IS A RUBBER PROCESS ANALYZER (RPA)?

- Introduced by Alpha Technologies (Monsanto) in 1992 to advance beyond simple cure testing with the Moving Die Rheometer (MDR)
- Measures dynamic rheological properties of rubber, compounds and polymer melts as well as stress relaxation tests.
- Several pre-defined tests are used to gain deep insights to material behavior
- Measurements can be taken at a range of strains, strain rates and temperatures
- Captures properties before, during and after cure with one sample

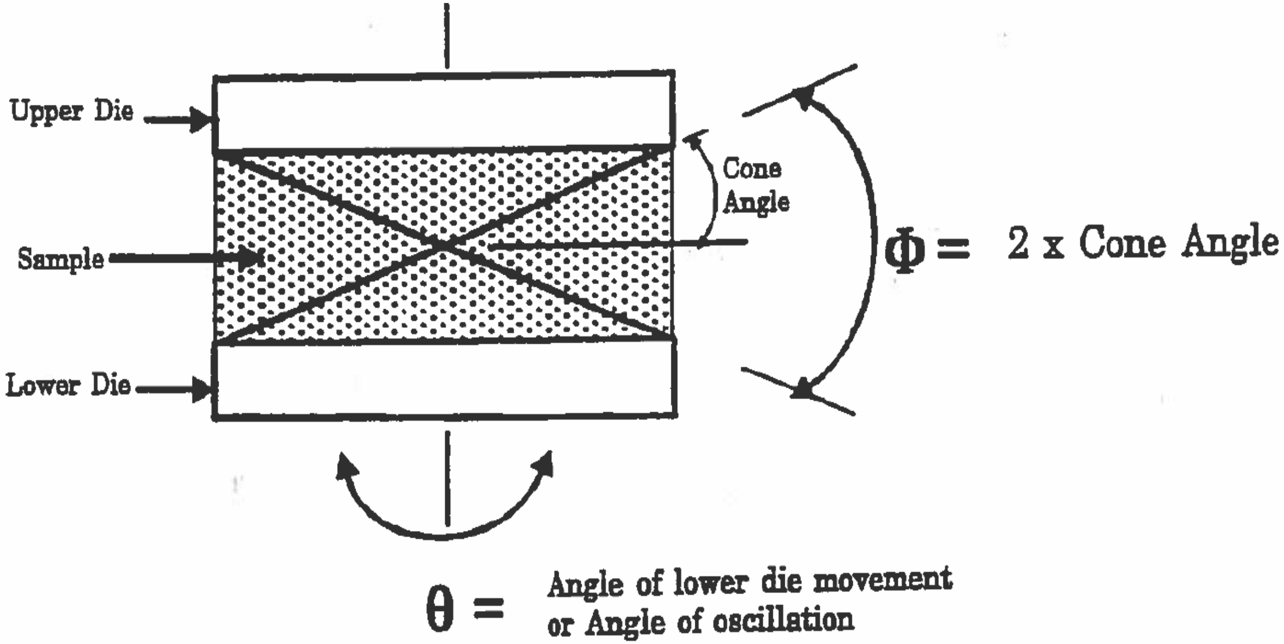


Biconical Dies are Important to Normalize Forces

Φ = 2 X Cone Angle

If θ = Angle of Movement

Then strain = $\dfrac{\theta}{\Phi}$



What are Applications of the RPA?

- **Characterize materials to predict good processing.**
  - Molecular weight (Mw)
  - Molecular weight distribution (MwD)
  - Identify Non-Newtonian flow properties
- **Determine quality of materials.**
  - Homogeneity
  - Dispersion
  - Scorch
  - Cure rate
  - **Dynamic Viscosity:** In terms of Shear Rate, Temperature, and State of Cure

Resin Sample Preparation

- Liquid resins
- Designed to prevent loss of sample during a test
- Helps increase sample cavity pressure
- Reduces slippage

*Patented test method

Another method is to dispense a fixed volume using a syringe.

Rheology Overview

Viscoelasticity Overview

Viscosity Overview

RHEOLOGY, VISCOELASTICITY, AND VISCOSITY

What is Rheology?

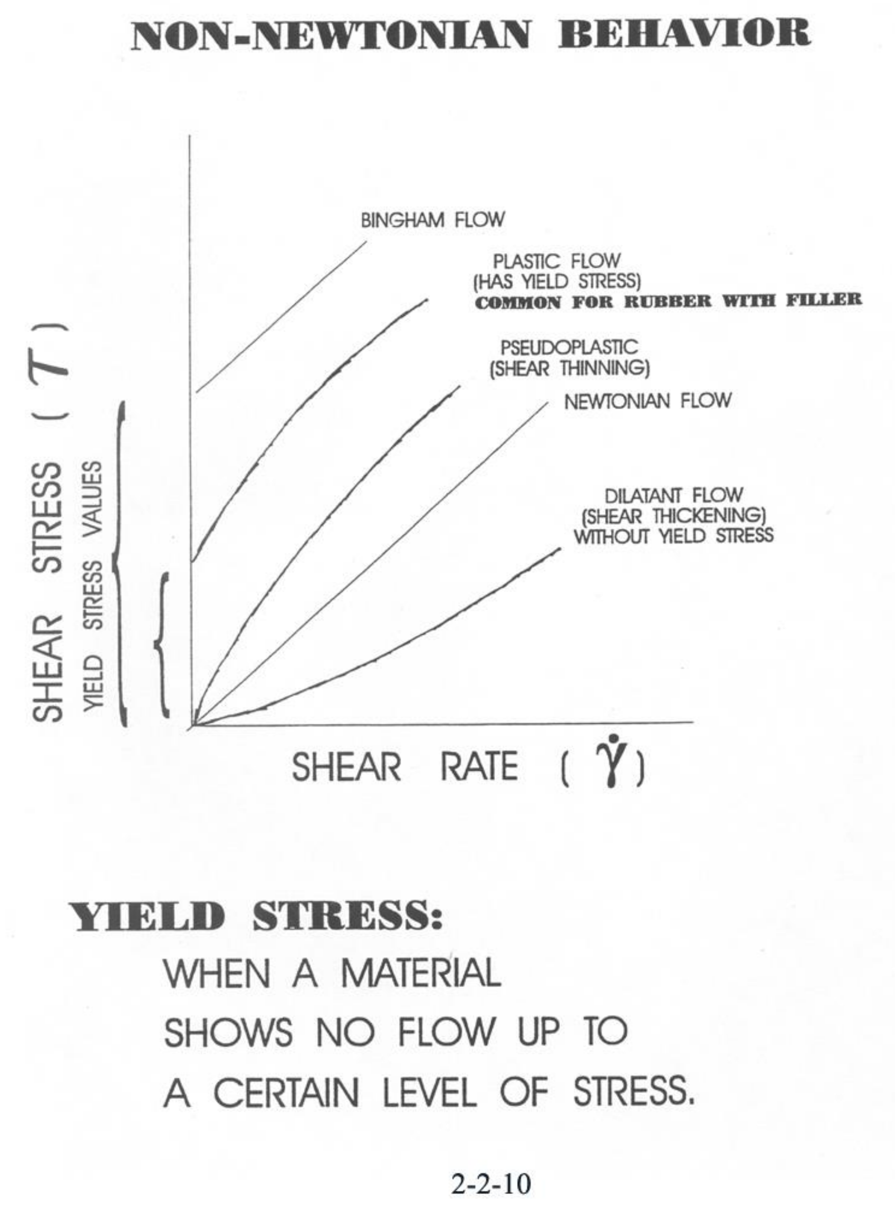
The measurements made by the Premier RPA are rheological measurements. In order to understand these measurements, it is important to understand Rheology.

Rheology is defined as the science of the deformation & flow of materials in terms of stress, strain and time.*

*Hawley's Condensed Chemical Dictionary, Eleventh Edition

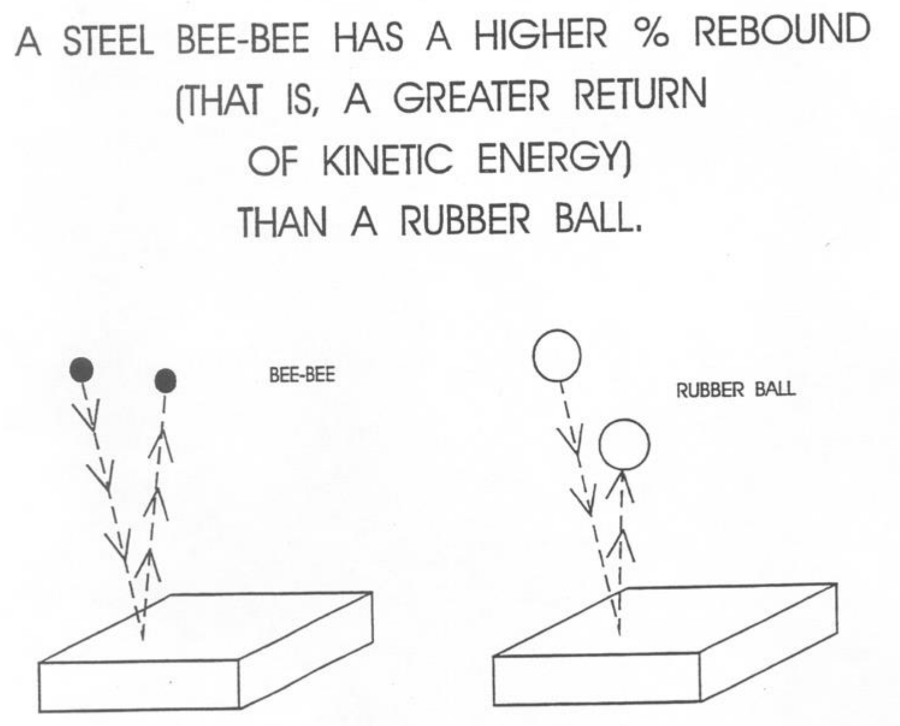
Viscoelastic

All polymers have some characteristics of a liquid and some characteristics of a solid. Therefore, polymers are called **VISCOELASTIC** materials



Example of the Elastic Quality

- A perfectly Elastic material will bounce back to the same height
- The higher (magnitude) it is dropped from, the higher it will bounce in response
- Materials that have a viscous component will not bounce all the way back (Hysteresis)



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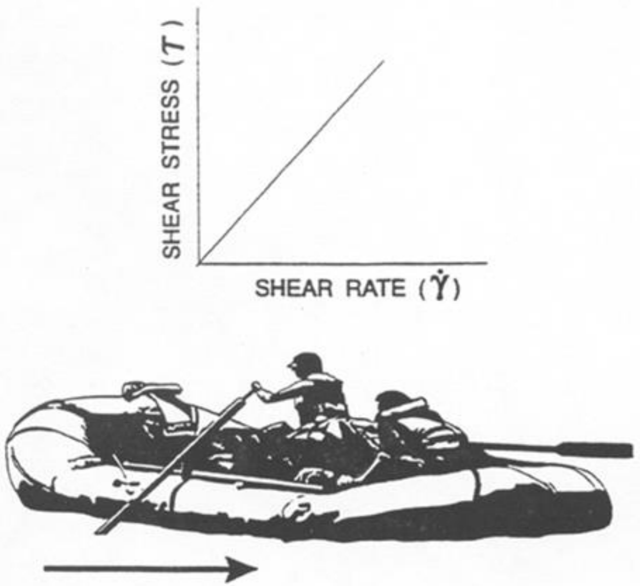
Example of the Viscous Quality

- Rate Dependent

If you are paddling a raft, the faster you push the paddle through the water the more resistance you feel

NEWTONIAN FLUID

WITH A **NEWTONIAN FLUID** SUCH AS WATER, THE SHEAR STRESS IS PROPORTIONAL TO THE SHEAR RATE.

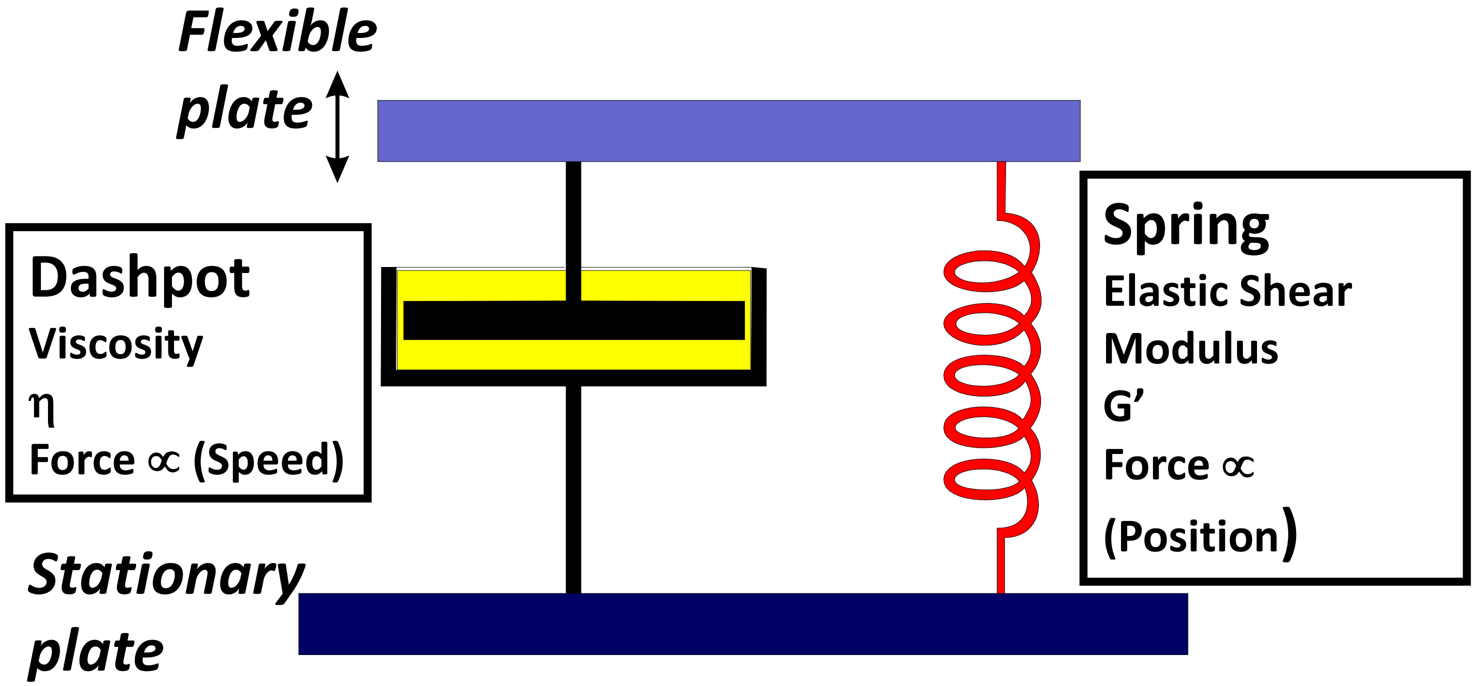


Put it All Together… Makes Viscoelasticity

- The liquid response depends on speed of deformation while
- the solid response depends on the amount of deformation.

*Assume the Flexible Plate is moving sinusoidally.

Voigt model of viscoelastic behavior



Dynamic Viscosity η^*

- A quantity that measures the force needed to overcome internal friction in a fluid

Empirical Relationship discovered by Cox-Merz: $\eta_\gamma = \eta_\omega^*$

"The **shear rate dependence** of the **steady-state viscosity** equals the **frequency dependence** of the **complex viscosity**"

Dynamic viscosity is calculated by: $\eta_\omega^* = G^*/\omega$

Where… $\omega = 2\pi f$ (units are in radians/sec)

f = Oscillation Frequency in Hz

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Processing Concerns for Silicones

Viscosity Dependance

Curing with Silicones

TESTING SILICONES WITH AN RPA

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What are some problems that silicone manufacturers face?

Supplier quality

Shelf life

Verification of mix (A:B ratio)

Injection mold flow

Verify mold/cure

Final product properties

Premier RPA Subtests That Can Measure Viscosity

- **Frequency Sweeps**
  - 0.1-3000 CPM
- **Strain Sweeps**
  - 0.07%-1255%
- **Temperature Sweeps**
  - Can mimic mold cure
  - Room Temperature – 230C

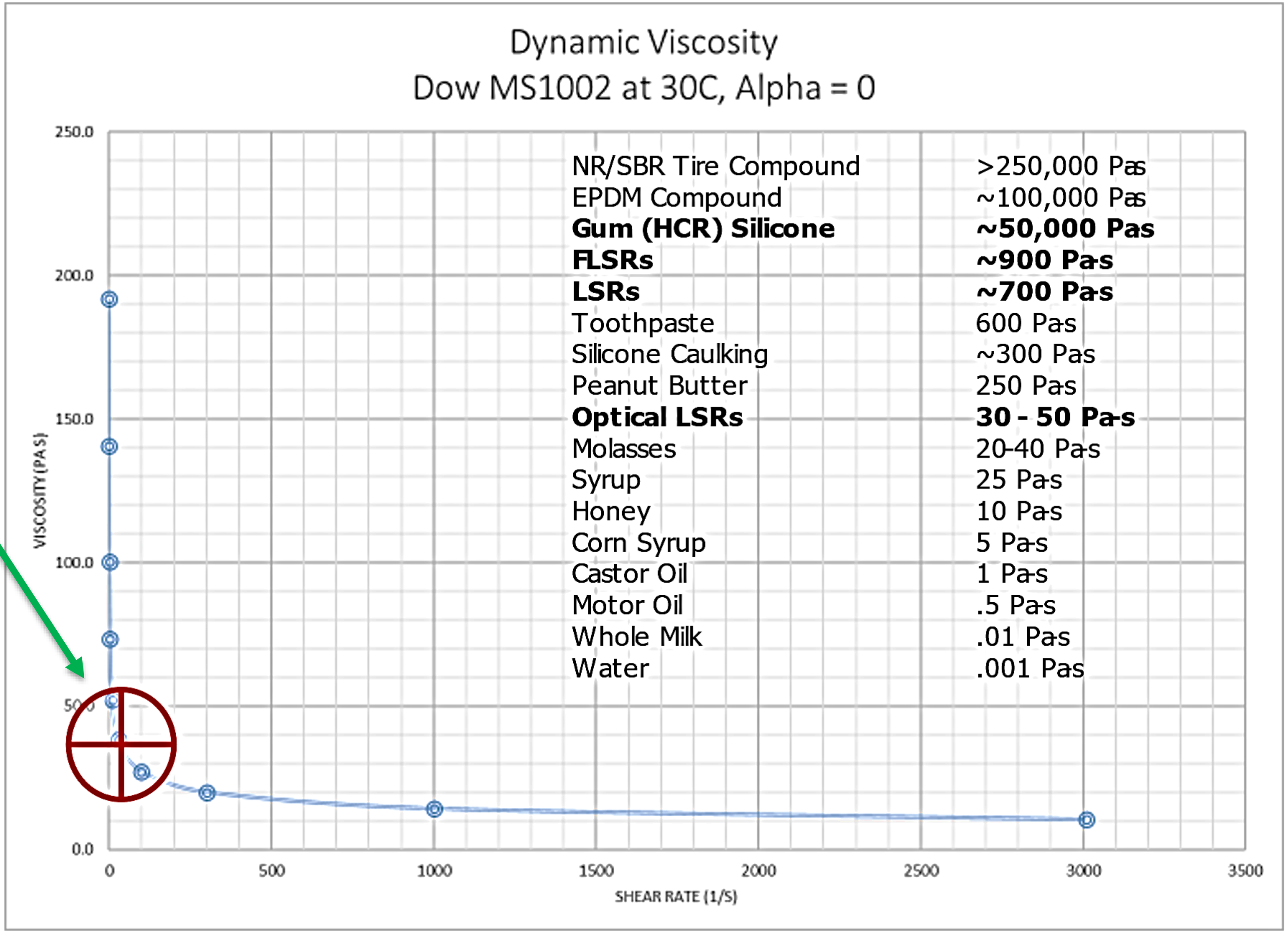
Viscosity is Shear Rate Dependent

FAQ: "What is the Viscosity of this Silicone?"

Answer: It depends…

**Most data sheets give Viscosity at 10 S^{-1}, Room temperature, α=0*

- During production, the silicone will experience a wide range of these conditions
- Shear rate has a **MAJOR** impact on viscosity
- The RPA with use of the power law can predict behavior through this range



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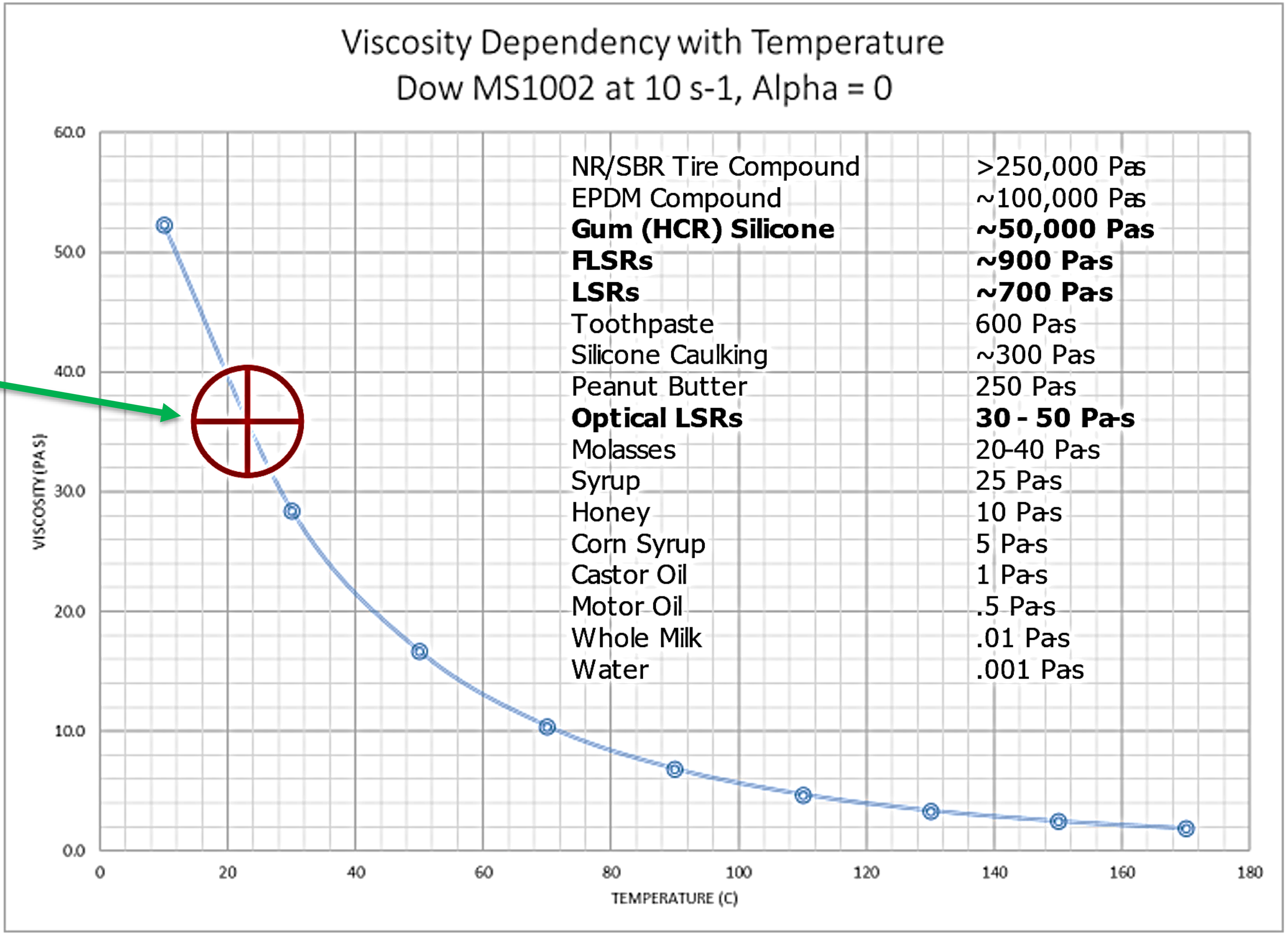
Viscosity is Temperature Dependent

*Temperature has a **MODERATE** impact on viscosity

- Typical processing conditions occur well above room temperature
- At a given shear rate viscosity **decreases** temperature **increases**



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Viscosity is State of Cure Dependent

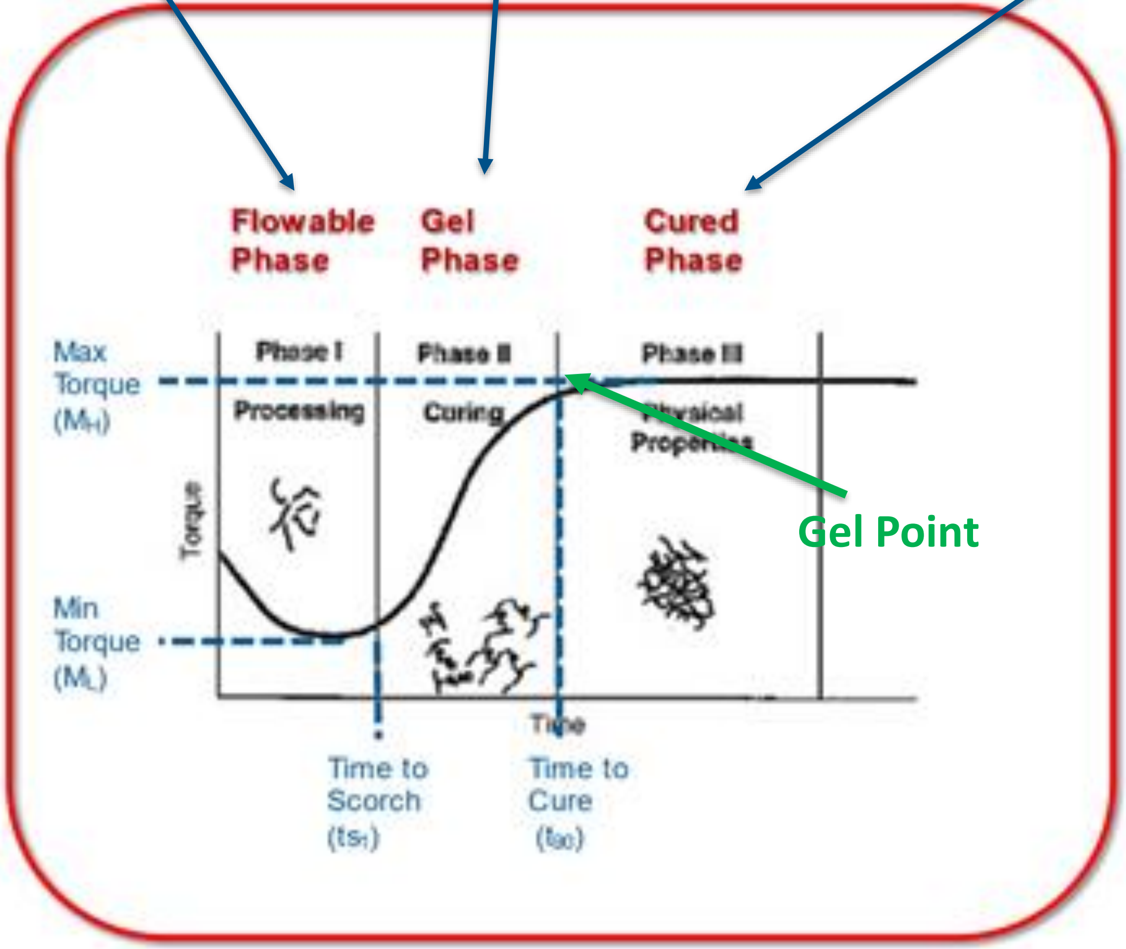
*α=0 indicates no cure has taken place (Raw Polymer)

- As alpha increases viscosity also increases
- All processing must be done and the LSR set into mold before the **GEL POINT** occurs
- At the Gel point Molecular weight goes to infinity and the material will no longer flow

Phase 1. loose individual polymer chains that can flow easily

Phase 2. Entanglements start to occur

Phase 3. Full 3D Polymer Matrix is locked into place



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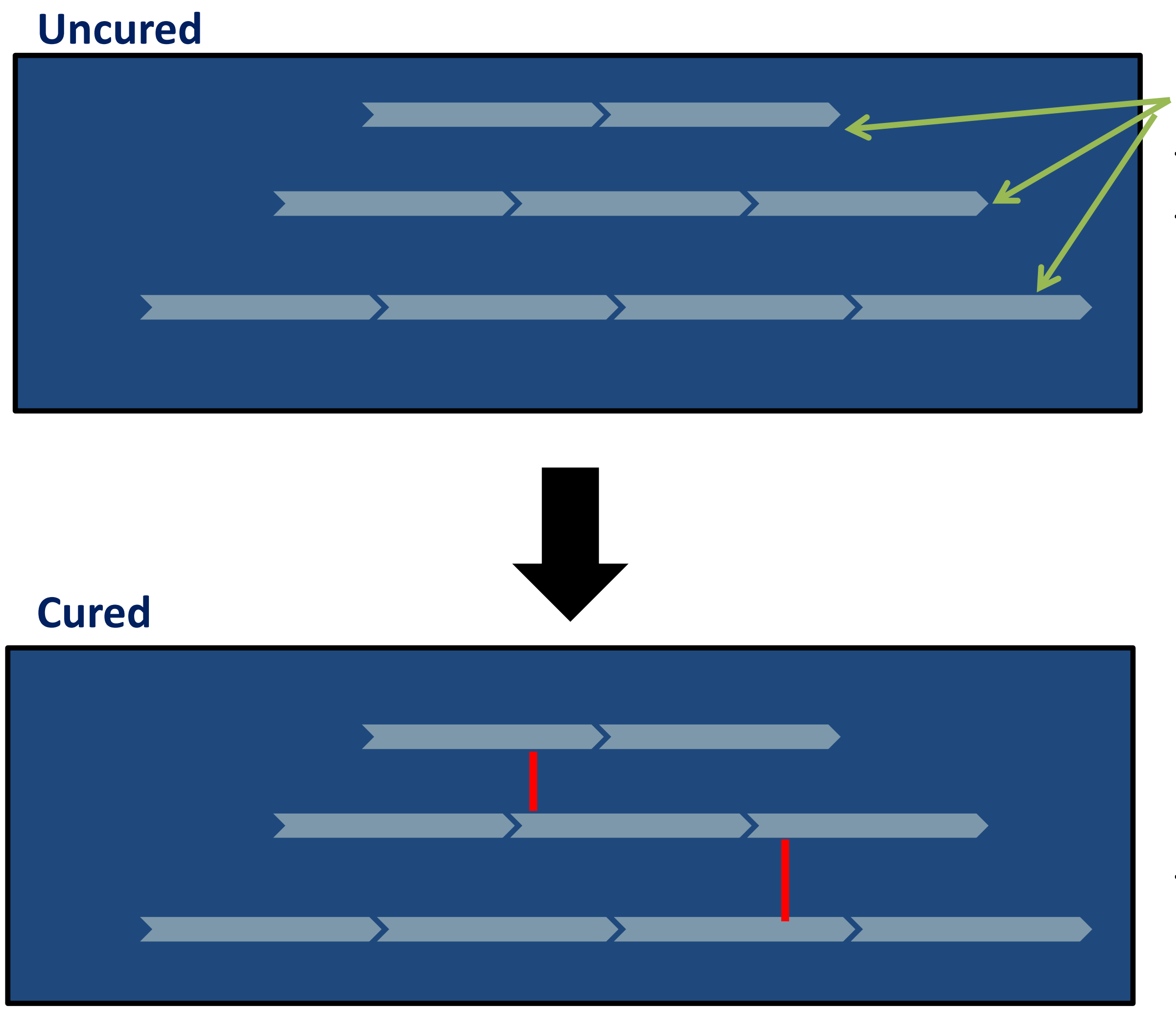
Crosslinking Reaction



Polymer molecules above the glass transition temperature can move around.

Example: LSR

Crosslinking significantly increases the size of an elastomer molecule with a few reactions and prevents movement.

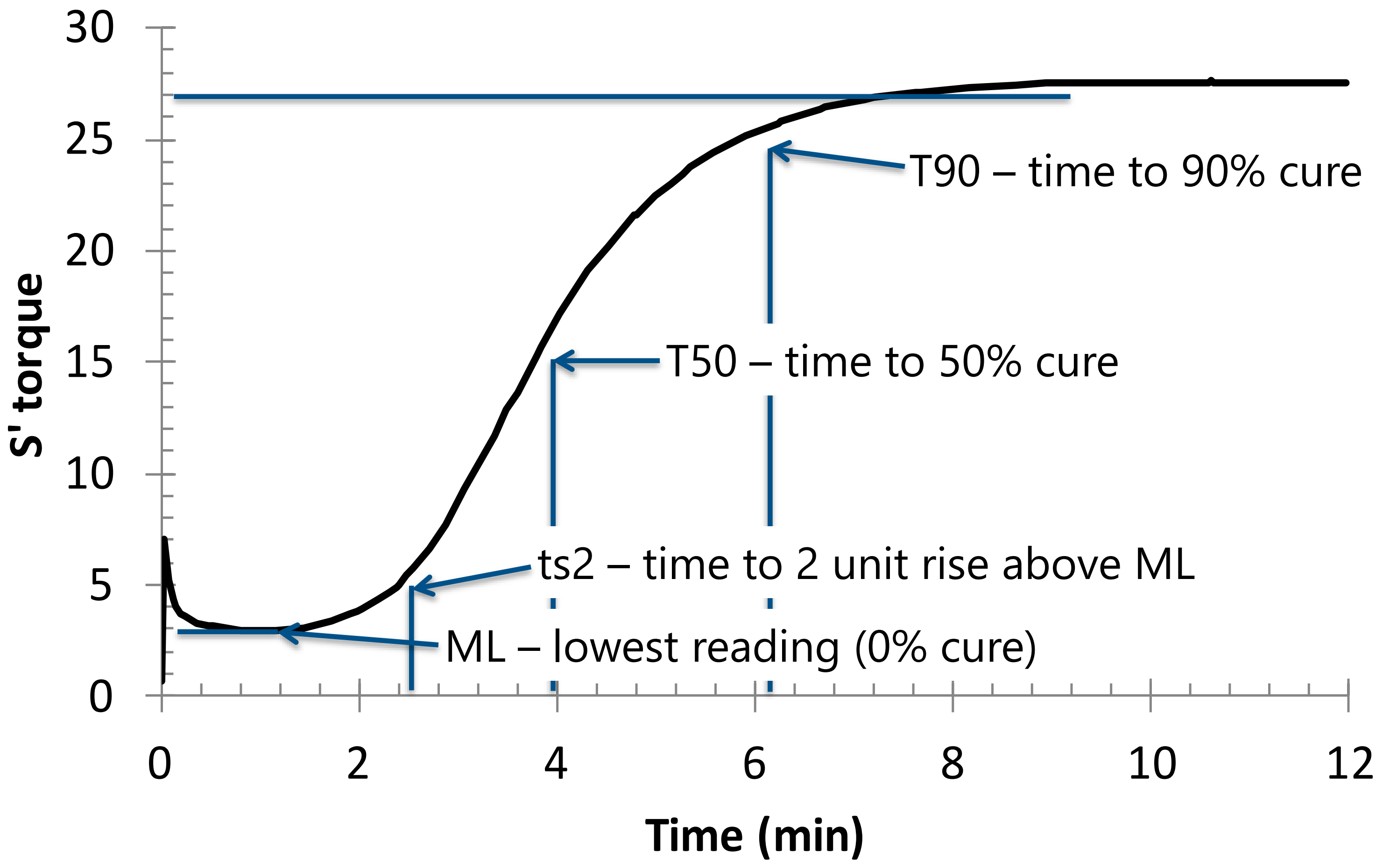
Example: Finished Tube

Each Time Sweep has Specific Goals

- **Isothermal Cure**
  - Measure cure properties of silicone
  - Meets ASTM D5289
- **VTA Cure**
  - Measure cure properties of silicone under non-isothermal conditions
    - Use a simple ramp and hold
    - Use temperature profile from rubber mold

Typical Cure Curve

- T-times; T10, T50, T90 provide the state of cure in %
- This can be used to optimize a process (T90) or for QC
- Scorch Times (Ts2) identify how long a material can be at a given temperature before it starts to cure



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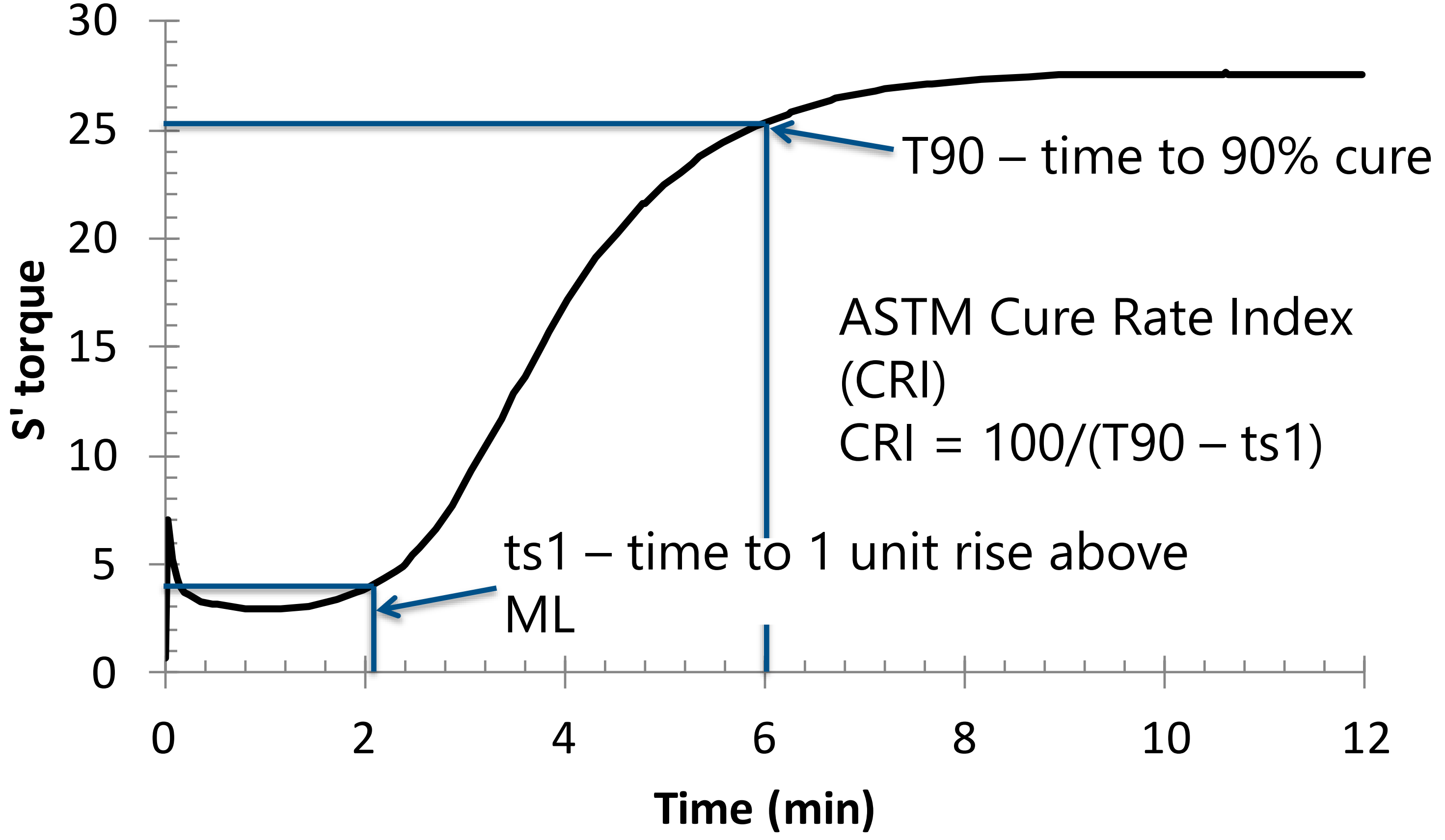
ASTM Cure Rate Index

*Cure rate index lets you know how quickly a material cures compared to others with similar cure packages



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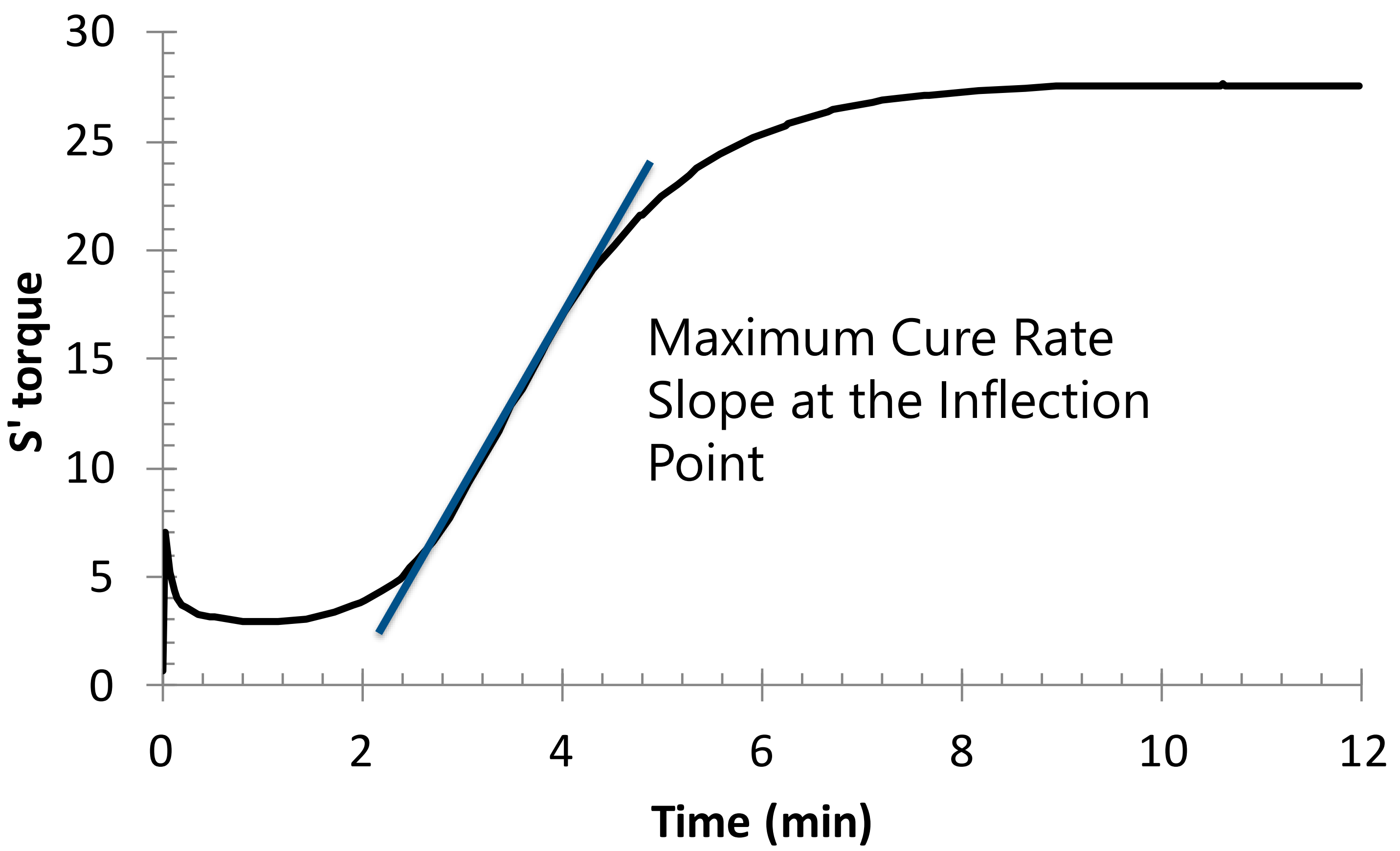
Maximum Cure Rate

- The inflection point where there are more products than reactants
- The reaction is moving at its fastest point



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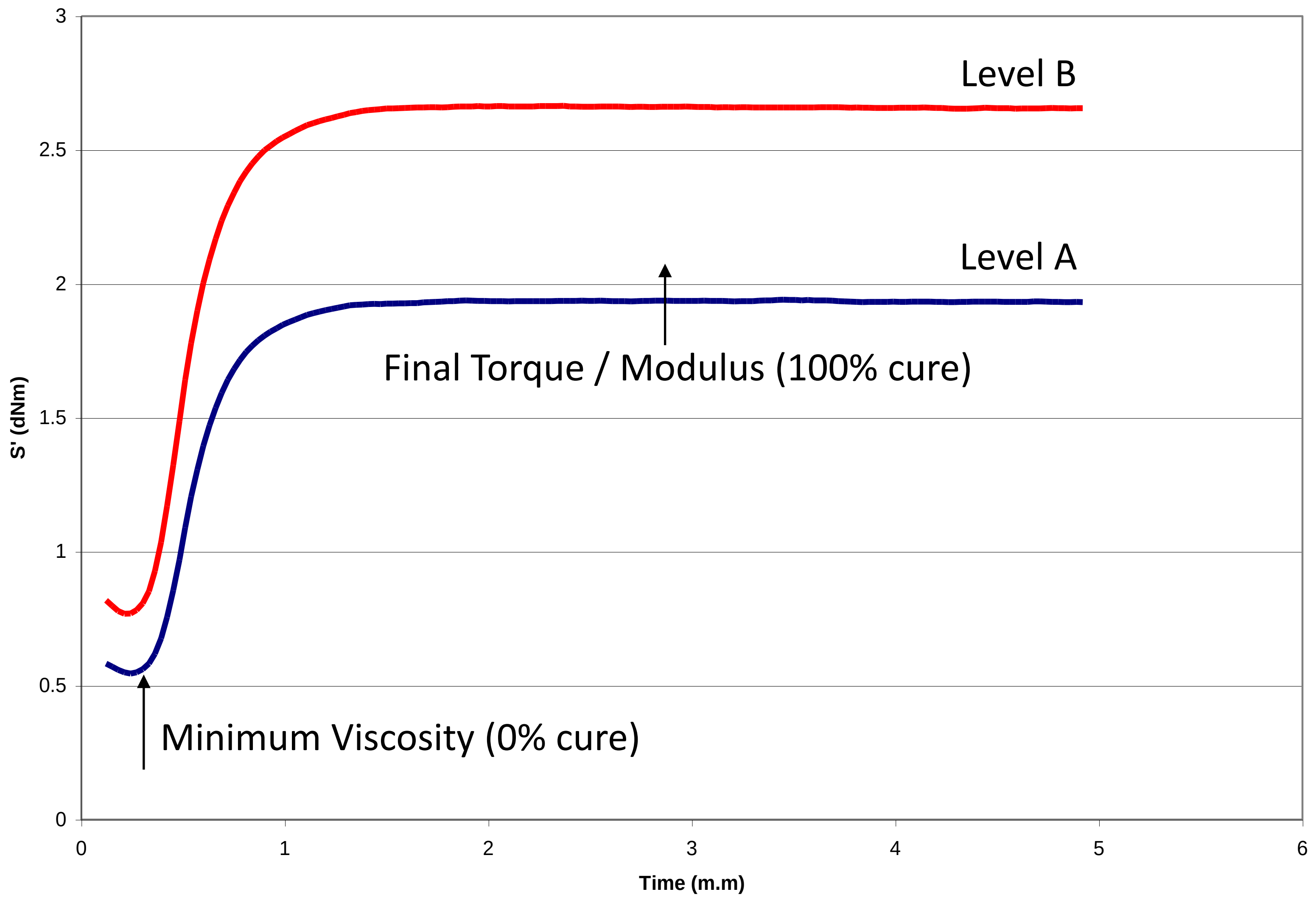
Effect of Curative Level on Silicone Cure Properties

- Additives can have a **MAJOR** impact on cure kinetics and final properties
- Even a small change in loading level of curative can have a huge impact



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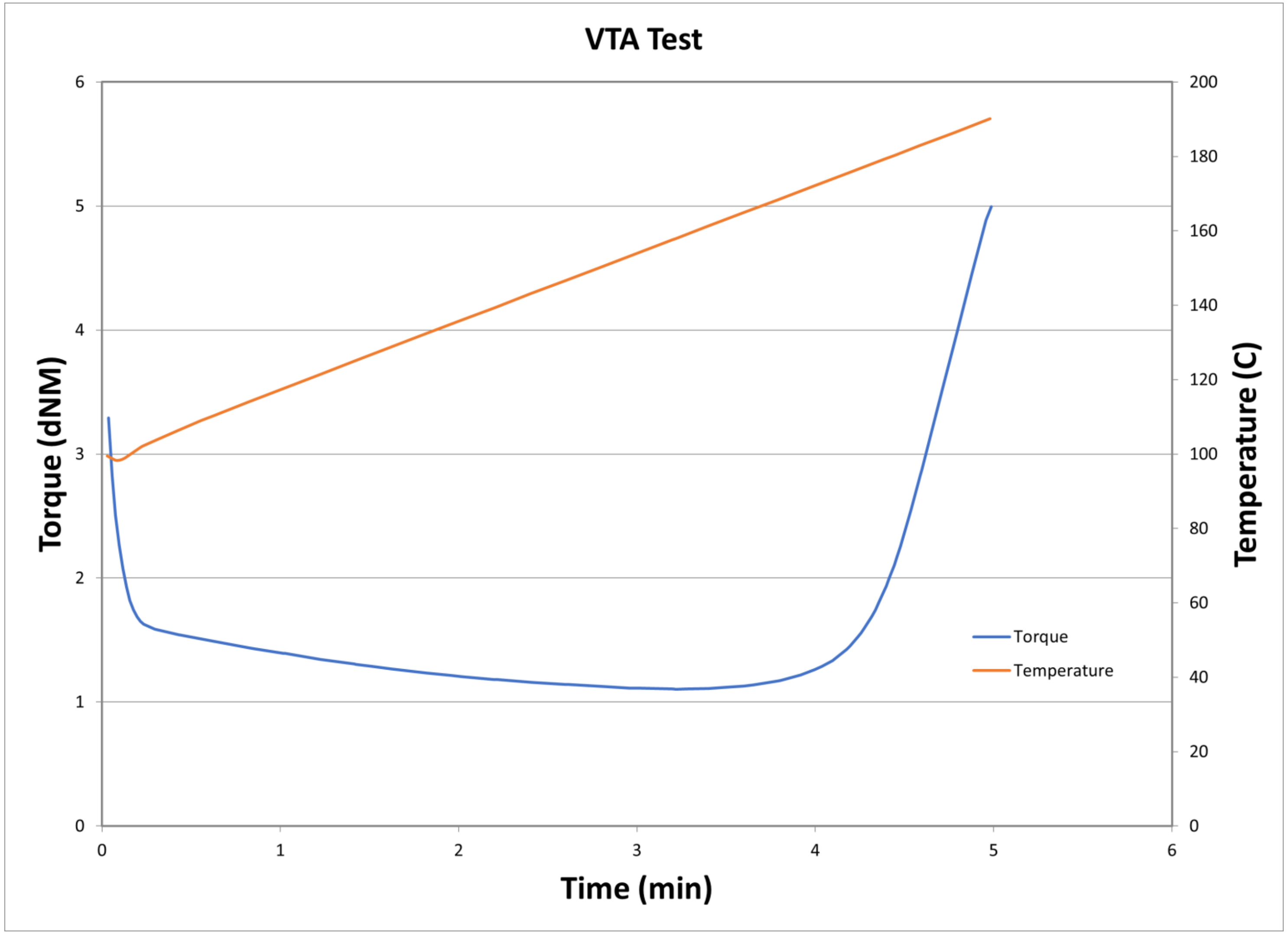
Variable Temperature Analysis

- Identify the temperature where the reaction starts to take place
- Learn about temperature dependency of cure rate



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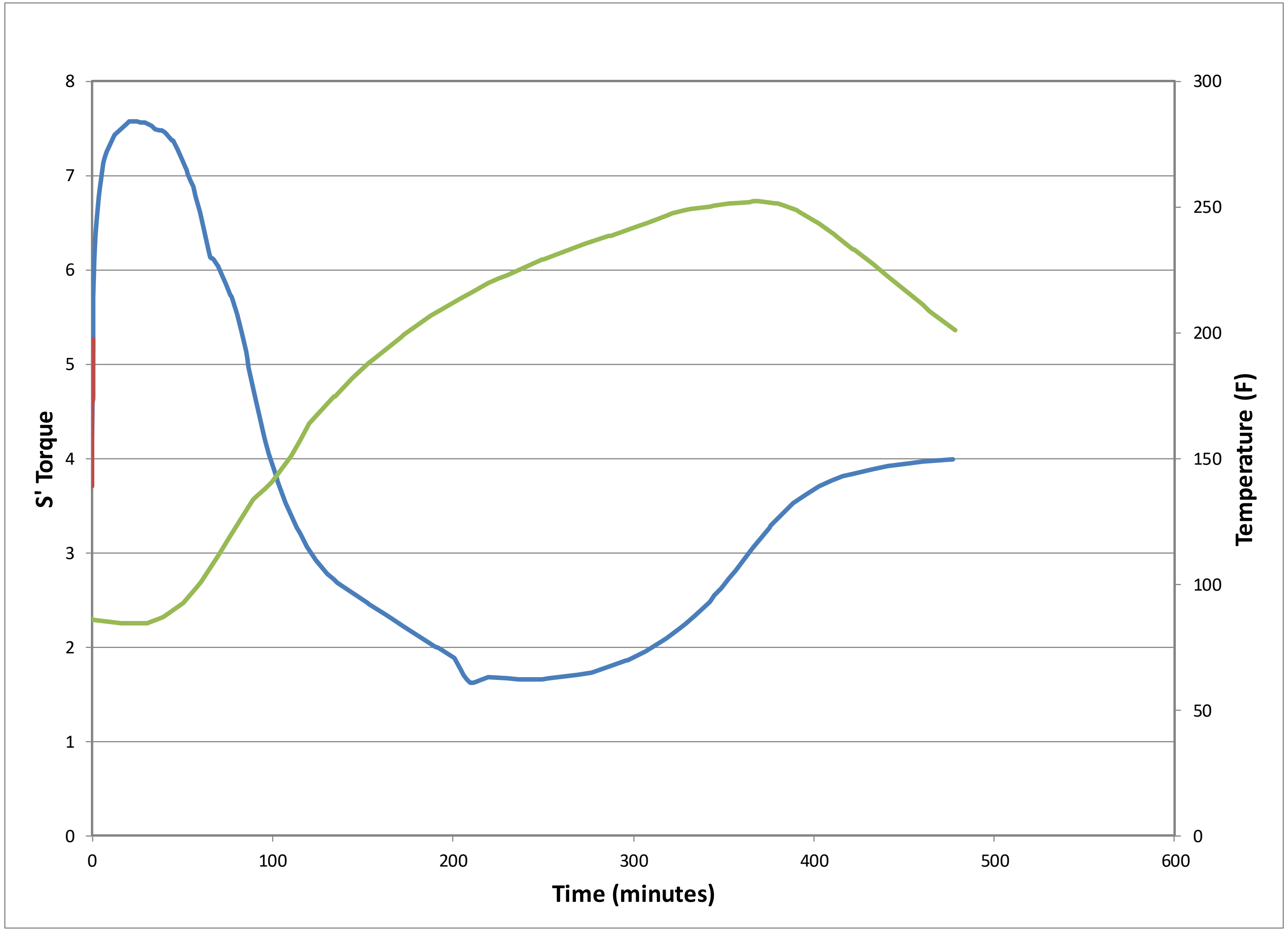
Temperature Profile

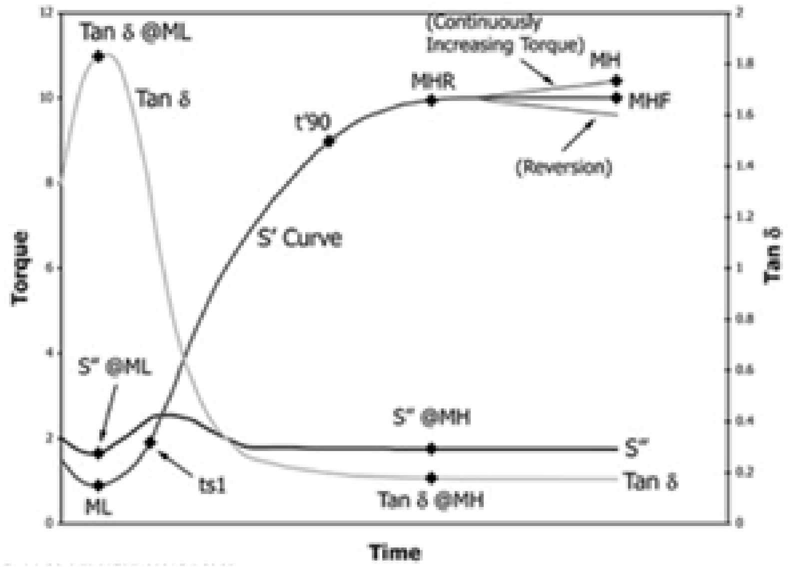
- Using a thermocouple, you can record the molds temperature profile
- It is possible to upload this file into the Premier RPA to simulate the cure



RPA Rheology Test Standards

- ASTM D5289- Cure
- ASTM D6204- Processing
- ASTM D8059- Dispersion
- ASTM D6601- Physicals
- ASTM D6048- Stress Relaxation

- Rheological Terms
  - Viscosity
  - Viscoelasticity
  - Shear Thinning
  - Green Strength
  - Cure



- Rheological Measurements
- ASTM D5289
  - Tan δ (delta)
  - Time to Scorch (ts1)
  - Time to Cure (t'90)
  - Maximum Torque (MH)
  - Minimum Torque (ML)
  - Elastic Torque (S')
  - Viscus Torque (S")
  - Cure Rate or Slope
  - State of Cure
  - Cure Time
  - Ultimate State of Cure
  - Reversion
  - Marching Modulus

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CONCLUSION

- Silicone properties depend on Shear Rate, Temperature, and State of Cure. The RPA can measure all three!

- Testing is important to determine optimum Processing Conditions

- Further testing is important to monitor the batch-to-batch Quality Control of silicone products

- Real world Temperature Simulation can be collected and directly uploaded to the RPA

Questions?

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