Is it done yet? Comparison of Methods to Monitor Degree of UV Cure

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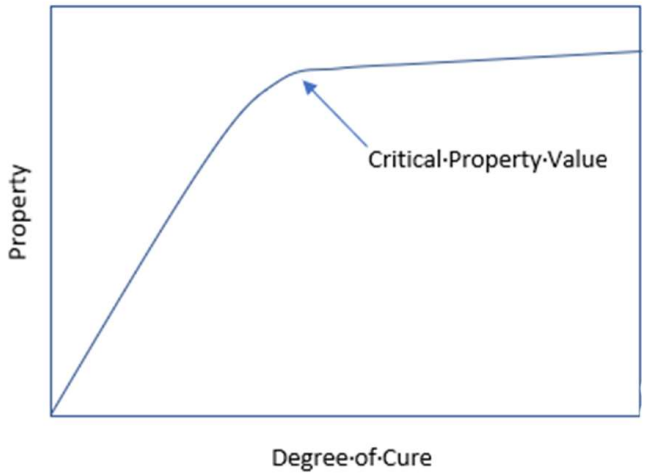
Agenda

- Properties and Degree of Cure
- Differences in Results
- Methods
  - FTIR
  - DSC
  - Rheological (DMA and Rheometer)
  - TMA
- Summary

Properties versus Degree of Cure

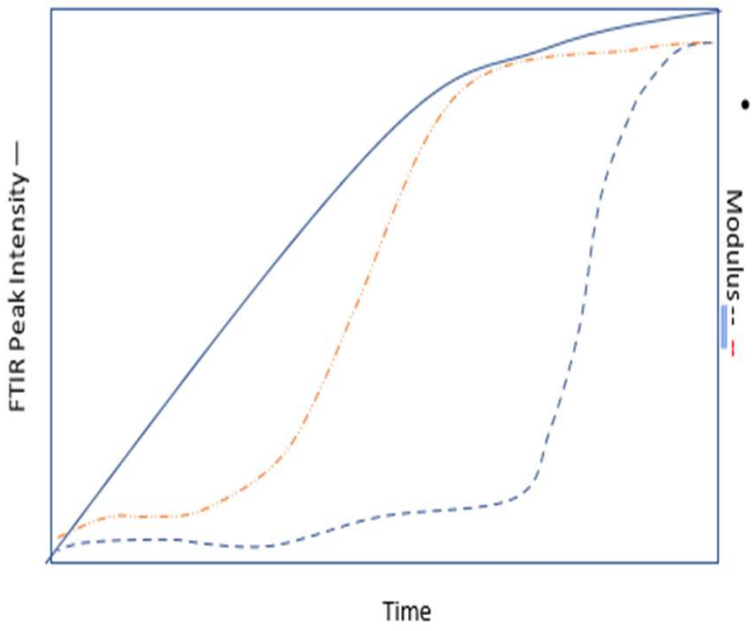


Polymer chains need to reach a certain value to have what we could call “plastic” properties.

How fast the high molecular weight species appear is mechanism dependent.

The “dog-leg” curves applies to most if not all polymer properties.

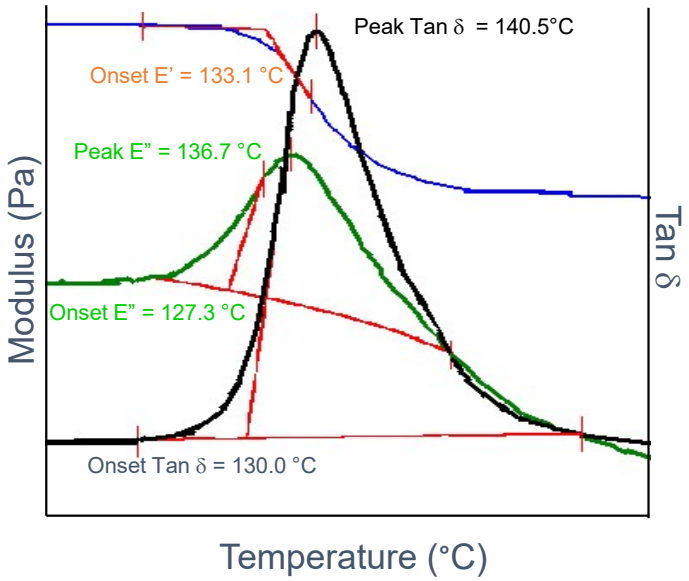
Methods give different results

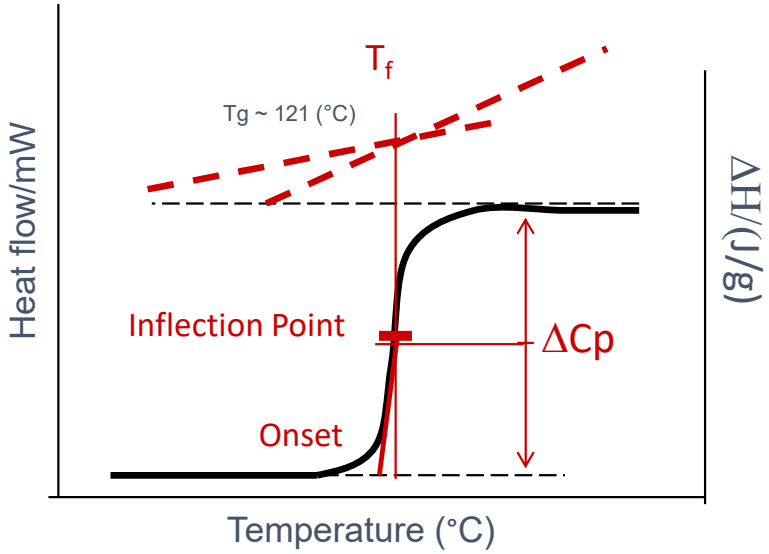


- FTIR, NIR, or Raman measure chemical presence.
- DSC measure energy released and heat capacity changes.
- DMA and Rheology measure modulus and viscosity.
- Depending on the mechanism of polymerization, high molecular weight appears at different degrees of cure.
- “Gelation” and “vitrification” are easier to detect in some methods than others.
- Sample thickness is of interest and how it may affect the above.

Even just measuring the Tg varies

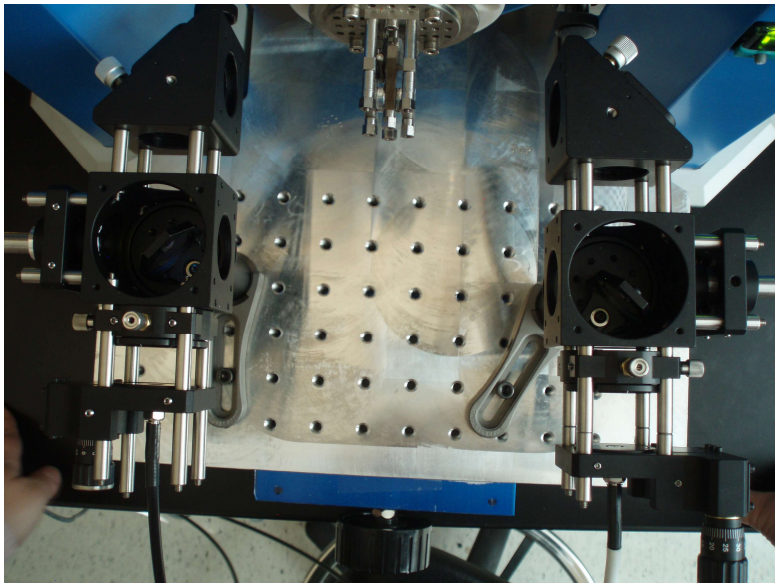
Because Tg is not a temperature, but a region of behavior.

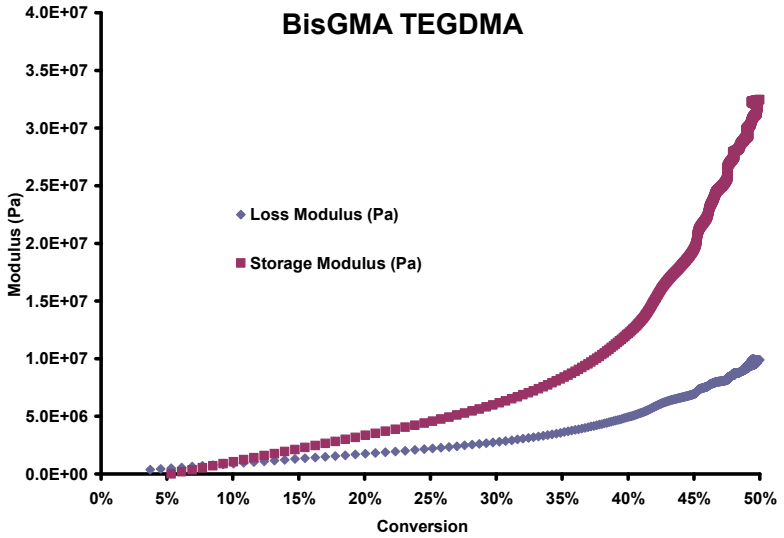




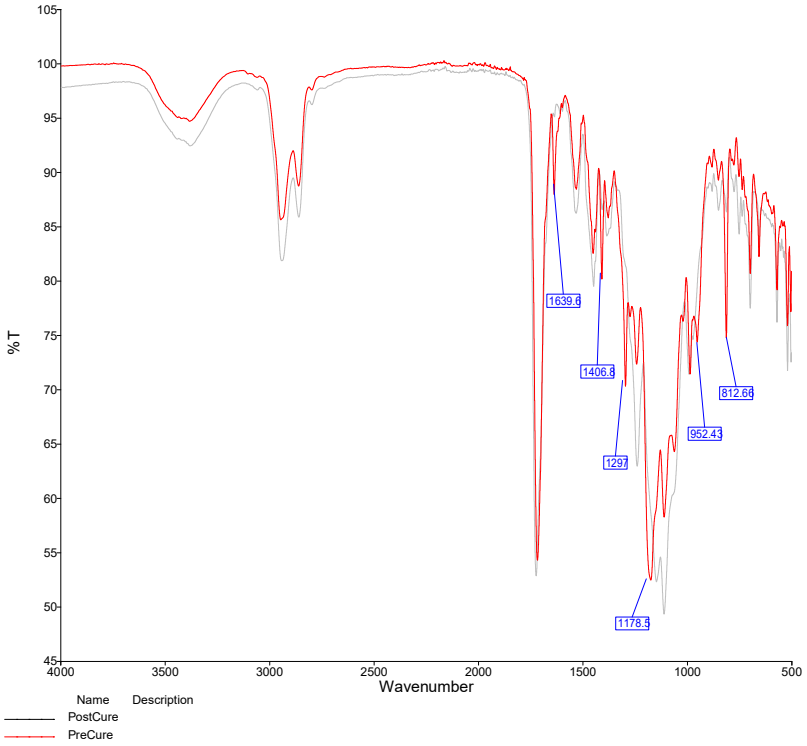
And the less symmetric or wider the Tg is, the worst the agreement is.

Classic Work by Stansbury's group: UV-NIR-DMA system





FTIR

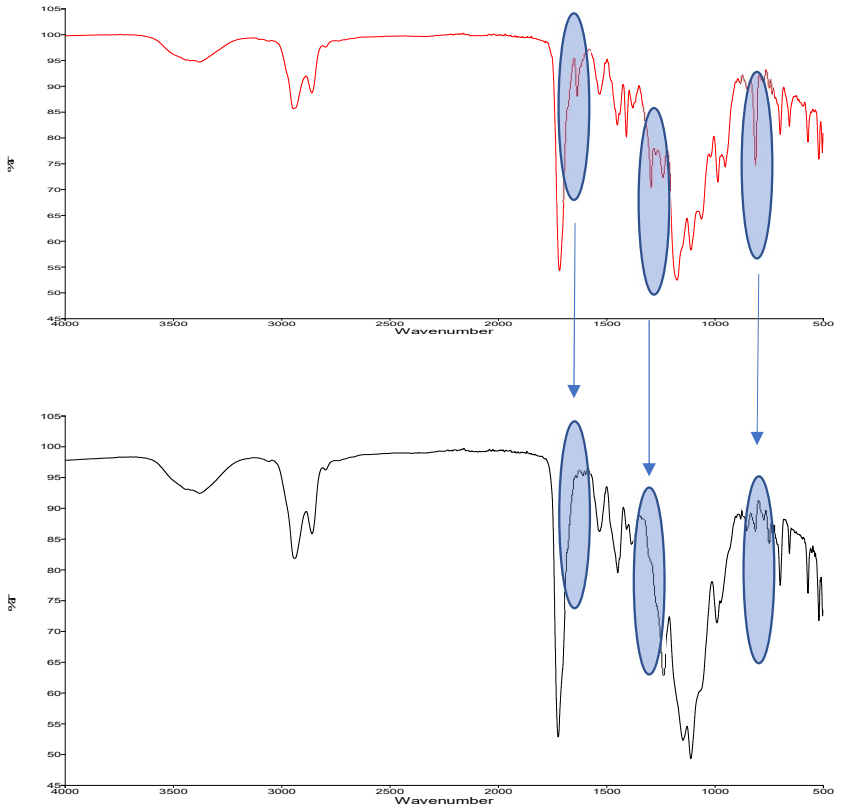


- Overlay of uncured and fully cured nail polish* showing peaks that change over time.
- Peaks at 1639 and 812 cm^{-1} are only present in uncured and partially samples.
- Other peaks are only present in the cured samples.
- The peaks are used to determine degree of chemical cure.

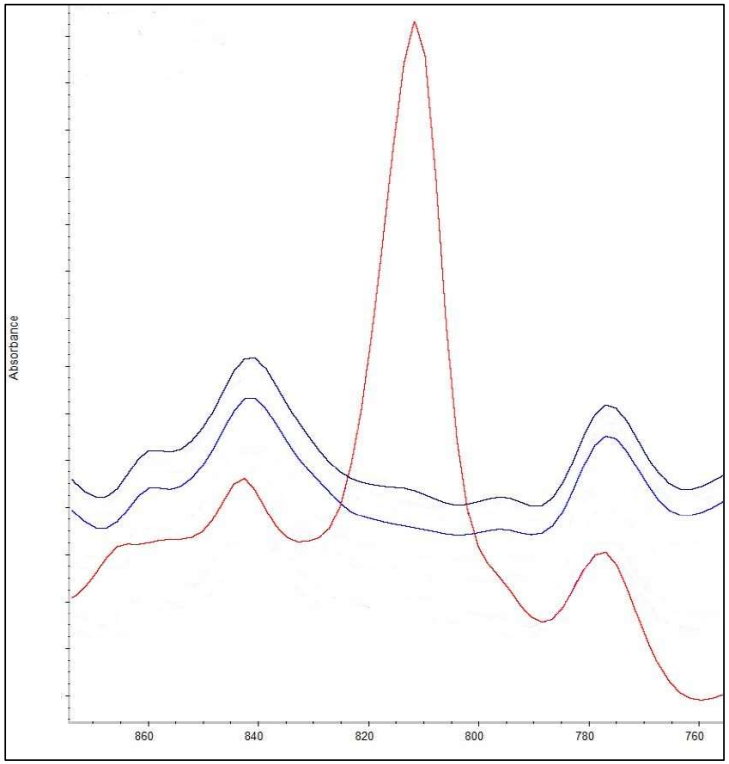
* Samples were an OTC UV curing nail polish used as an example

FTIR -2

- Select peaks vanish over time.
- In a time-based software, we can track the disappearance of a peak.
- The Diamond ATR is simple covered and cured in place.
- Samples can be removed from the ATR as a disc and checked against DSC methods.



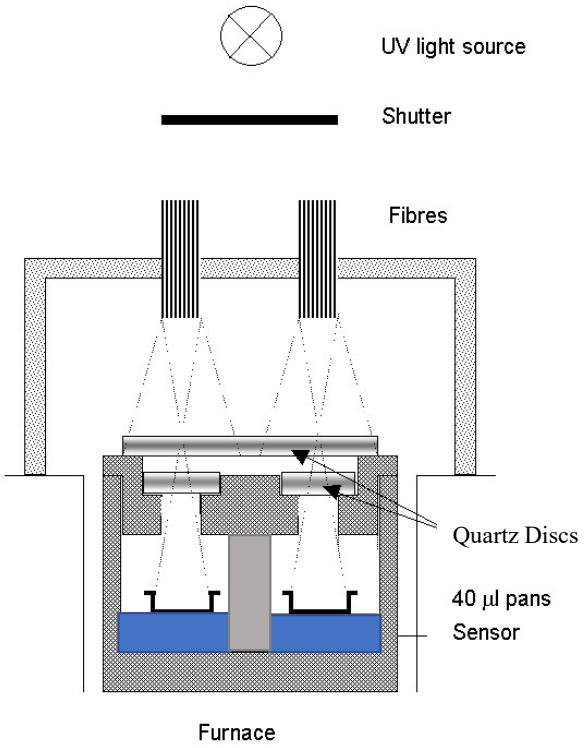
FTIR-3



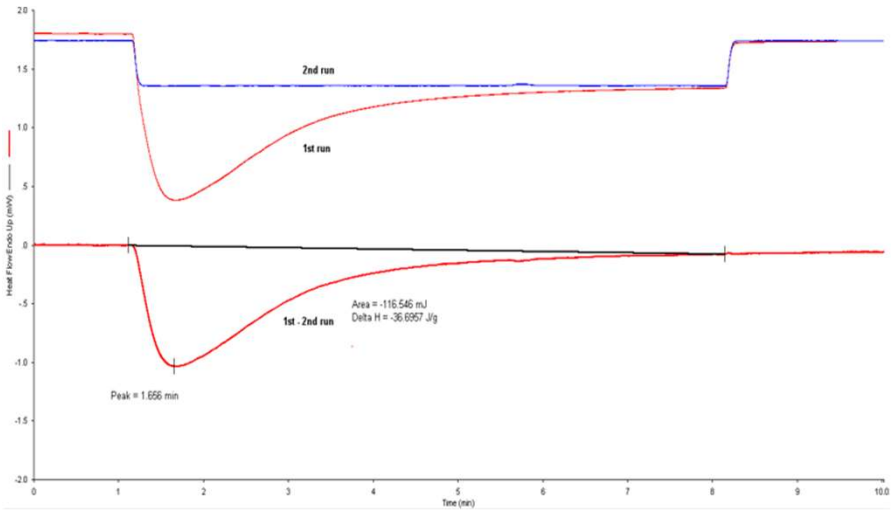
- Difficulties:
  - Small/weak peaks.
  - Highly complex materials with peak masking.
- Often need to consider other techniques?

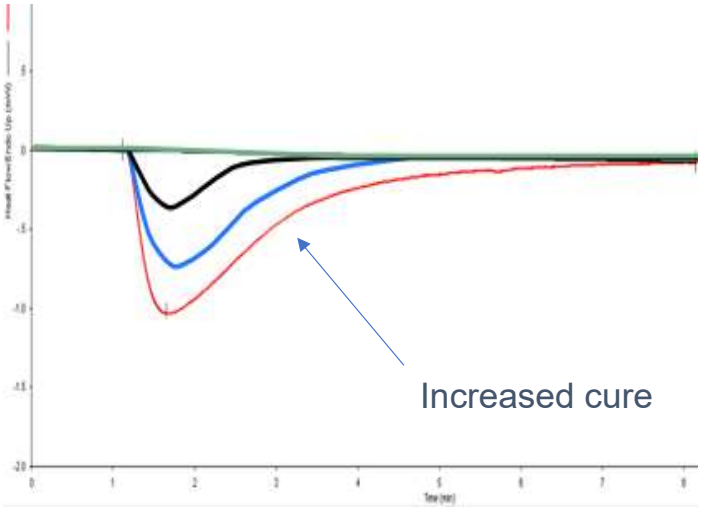
DSC - Differential Scanning Calorimeter

- DSC measures the heat flow associated with a transition.
- For curing, two approaches
  - Changes in the enthalpy of the reaction on heating.
  - Changes in the glass transition temperature on the second heat.
- Environmental isolation and control.



DSC Method 1 - ΔH Changes

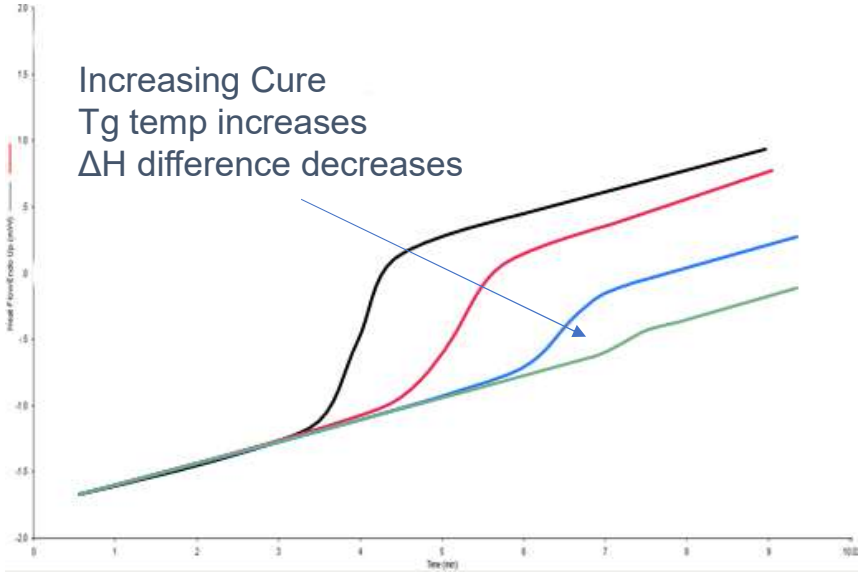




Allows control at various temperatures and to measure enthalpy if a thermal component is required post-UV.

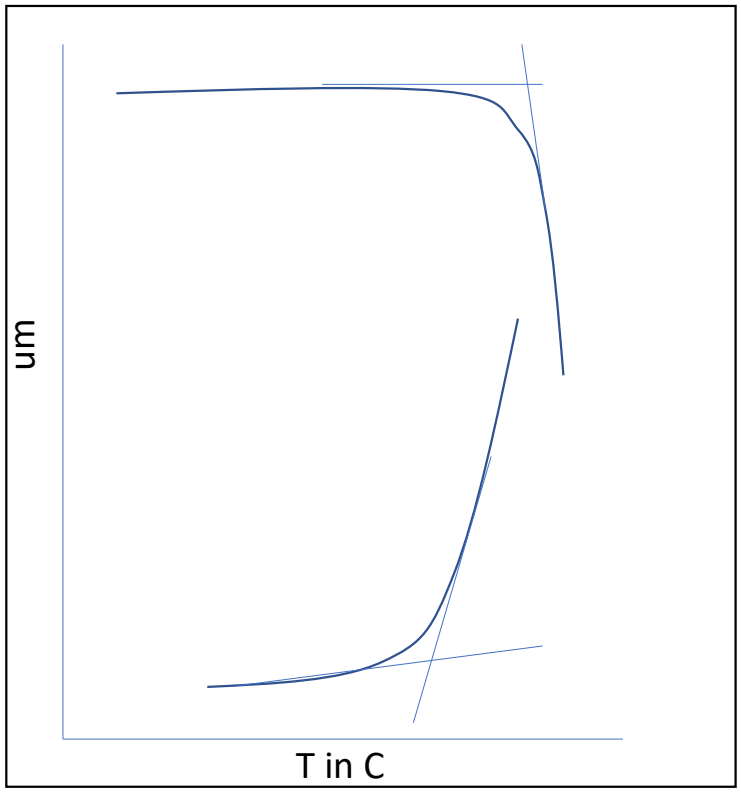
Method 2 - Tg

- Requires a temperature scan following the UV cure scan.
- On production sample, a small area of material or flashing is sacrificed.
- As heating is often 20°C/min, runs are short. Higher speeds may increase sensitivity.
- Very high degree of cure may be undetectable.

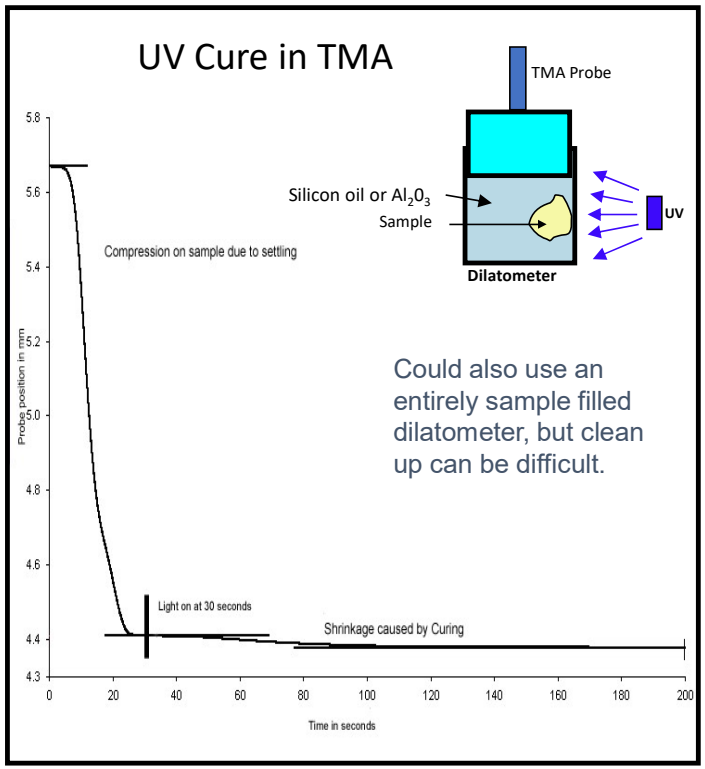


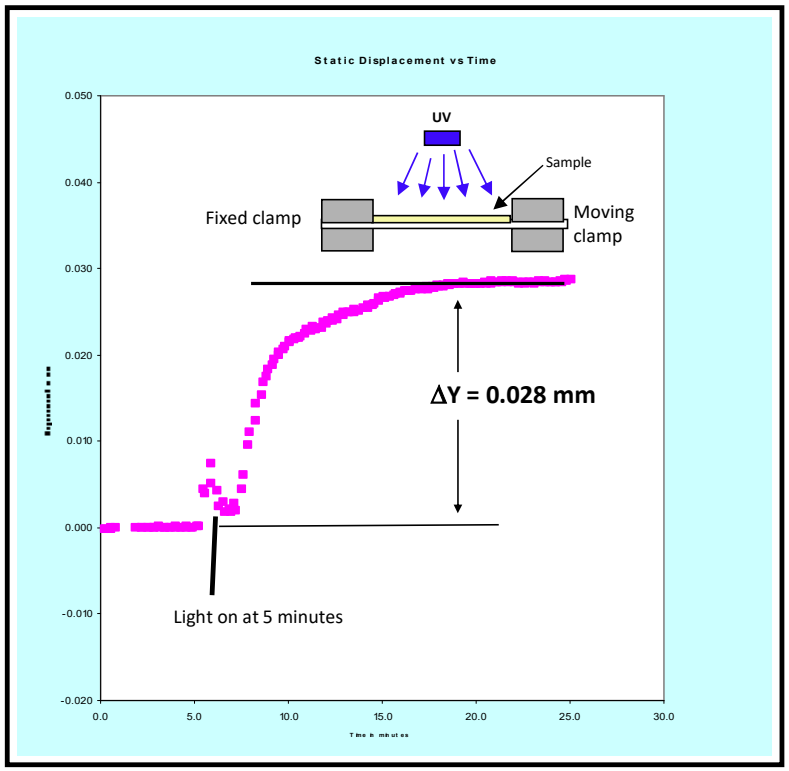
TMA – Thermomechanical Analysis

- Measures size changes in materials.
- At Tg, the rate of expansion changes.
- The intersection of the baselines gives the Tg temperature.
- A slower method but allows measure of CTE and shrinkage.



Tracking dimensional changes

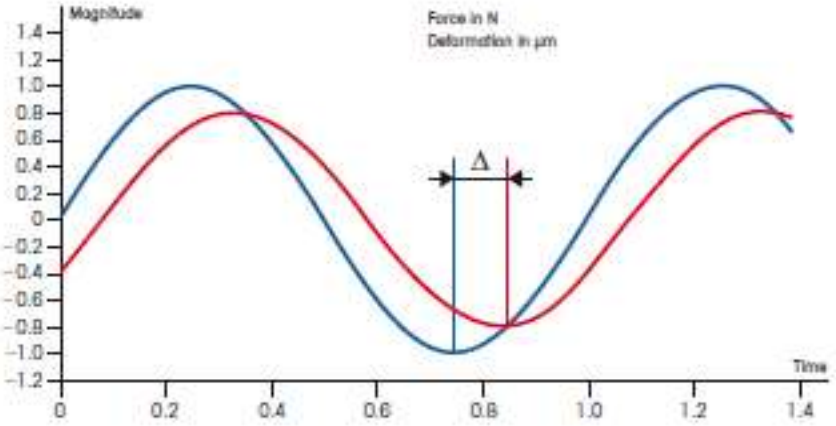




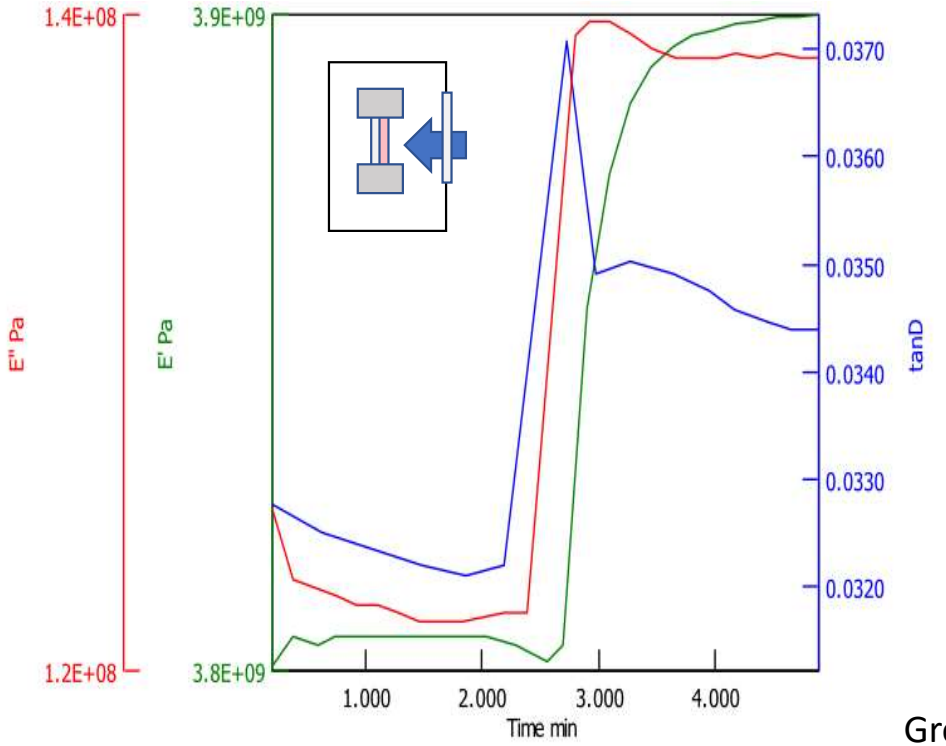
Rheological approaches – DMA and Rheometer

- Despite modern terminology these operate on the same principles.
- An oscillatory stress is applied to the sample at a set frequency.
- Multiple frequencies can be used to match applications.
- Difference is sample form geometry.
- DMA refers instruments for solid or supported samples.
- Rheology for liquid samples.
- Possibility of lifetime estimation via Time-Temperature Superposition.
- Can give an idea of molecular weight and molecular weight distribution.
- Stress-strain curves and creep/recovery.

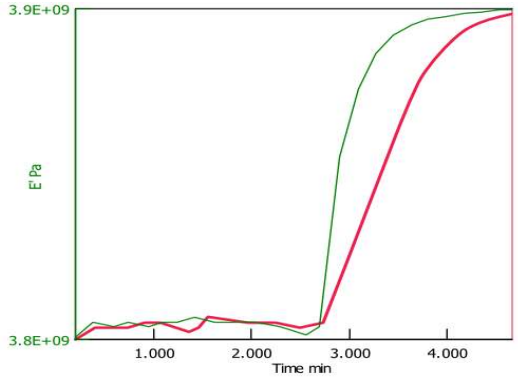
Storage Modulus (E’ or G’): Elastic response
Loss Modulus (E’’ or G’’): Viscous response, dissipation
Tan Delta: Damping, ratio of E’’/E’ or G’’/G’



DMA- Dynamic Mechanic Analyzer



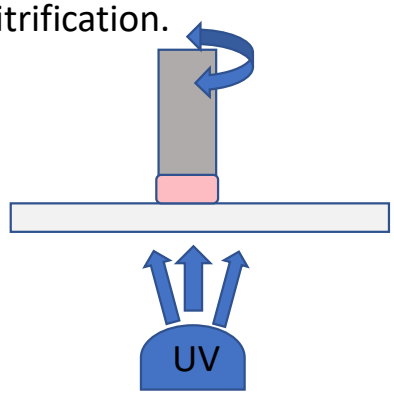
- Paper used as a support in tension. Its modulus can then subtracted out.
- 395 nm light on at 2.5 minutes at 25°C at 1 hertz.
- Because it is supported, modulus values and gelation are not used here.
- You can see substrate and coating interactions.

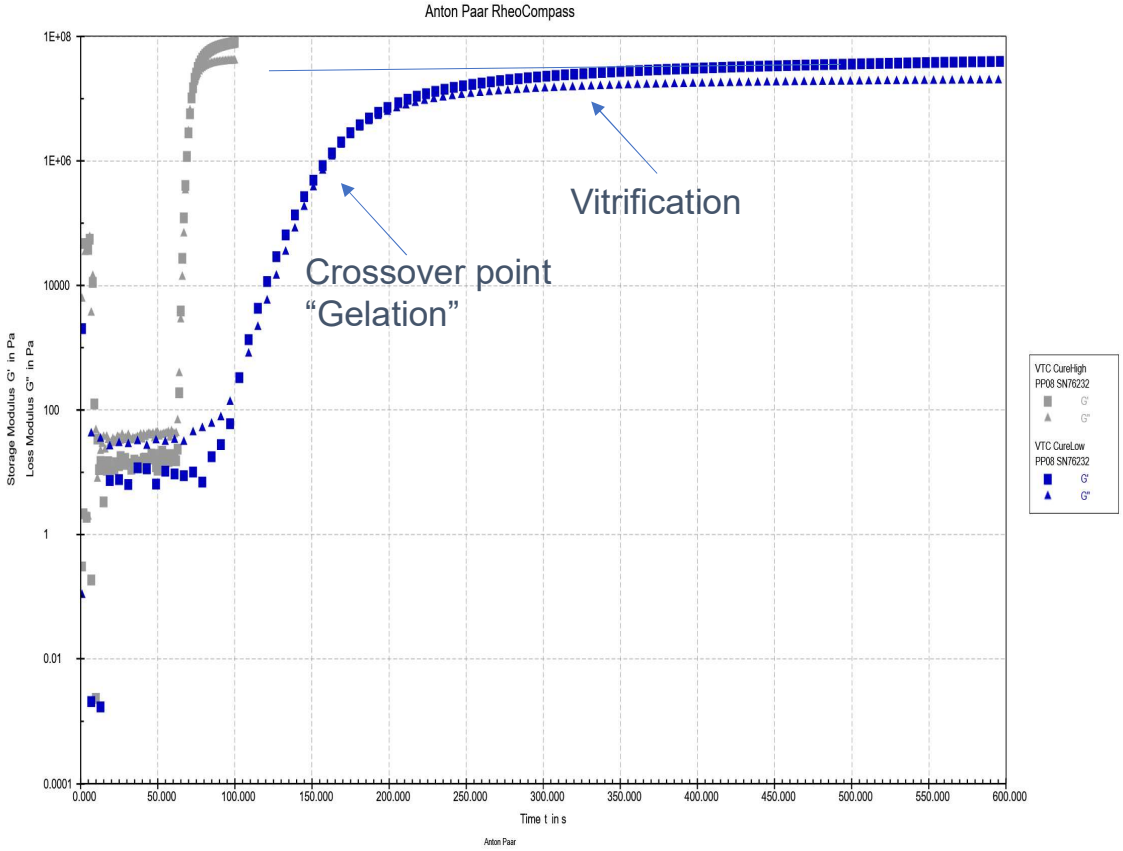


Green line light intensity is four times the red.

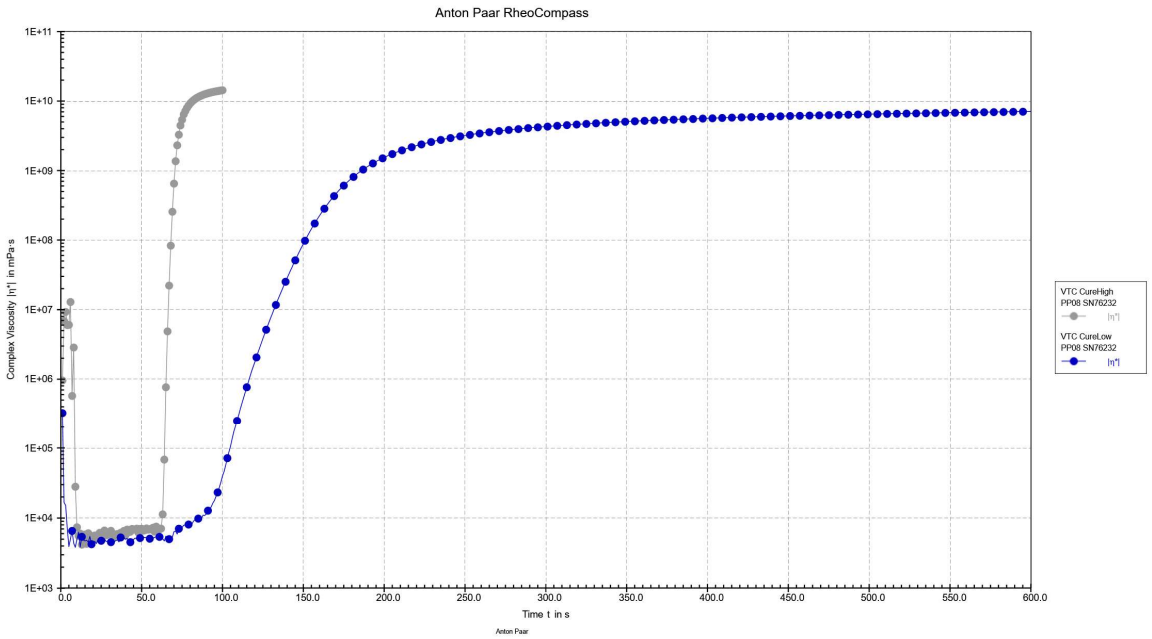
Rheology - Parallel Plate

- Single frequency scan at 1 hertz.
- Frequency can vary or multiple frequencies applied.
- Sample irradiated from bottom via a quartz lower plate with Peltier temperature control and hood.
- Crossover of G’ and G” estimates gelation.
- Leveling off of the G’ estimates vitrification.





Viscosity



- Viscosity (eta*) calculated from data set.
- Does not exactly match other methods.
- If performed in a rheometer, early stages may require different plate sizes.

Summary

Method	Measures	Reports	Get degree of cure from	Pros	Cons
FTIR	Absorbance of key peaks	Peak height and cm-1	Formation/ disappearance of peaks or ratios	• Rapid • Inexpensive	• Not as sensitive, may be distorted depending on if similar bonds are naturally present. • No physical or thermal info.
DSC	Shift in baseline	Tg	Temperature, Delta cp	• Relatively fast, • High temperature accuracy	• Have to know specific temperatures to compare to for DSC. • One result per run. • No mechanical data.
	Energy changes	Delta H	Resulting peak/lack thereof	• Relatively fast, high accuracy	• Need comparative values. • No mechanical info.
TMA	Change in position	Tg	Temperature	• Thin coating in situ • Shrinkage* (different experiment)	• Slow. • Only temp.
DMA/Rheometer	Stiffness	Modulus	Modulus value, Tg location	• Effective mechanical cure	• Slow. • Requires skilled tech.
	Damping	Tan Delta	Peak location		
Rheology	Viscosity	Viscosity	Viscosity increase	• Applies to real world	• Can be slow. • Requires skilled tech.

Finally…

Thank you to

- Mary Kay Corp
- Hitachi High-Tech Analytical
- You for listening

Equipment used

- PerkinElmer DSC8500
- Perkin Elmer Spectrum 2
- Mettler Toledo TMA 2+
- Hitachi DMA7100
- Anton Parr MCR302 Rheometer
- Omnicure S2000