Applications of Photo-DSC and Photo-DMA to Optically Cured Materials

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The Project goals:

- Attempt to understand the effects of curing on sample shape
- Look at changes in geometry of a sample after curing
- Modern instrumentation allows:
  - Curing of photo-initiated samples in DSC and DMA
  - Measurement of residual cure by DSC
  - Measurement of even highly cured samples by HyperDSC
  - Tracking of sample distortion during cure in DMA
Photo-initiated Systems

- Commonly used
  - Dental materials
  - Electronic adhesives
  - Orthopedic applications
  - Coating for low VOC
- Traditionally Studied by Photo-DSC
  - Allows measure of energy of cure
  - Study of cure kinetics
  - Development of cure profiles
Onset = 1.126 min
Light on at 1 minute
Onset = 1.126 - 1.00 = 0.126 minutes

Area = -613.361 mJ
Delta H = -338.8733 J/g

Peak = 1.649 min
Sample rerun under conditions that are known to get complete cure.

Percent cure calculated:

- $\Delta H_{\text{complete cure}} - \Delta H_{\text{second cure}}$
- Divided by $\Delta H_{\text{complete cure}}$
- Times 100
- \[ \left\{ \frac{(-339) - (-37)}{-339} \right\} \times 100 \]
- = 89.1 %
Advantages of UV-DMA

- Measurement of modulus and viscosity as function of cure
- Physical measurements more meaningful for actual production
- Ease of determining gelation and vitrification
- Distortion of the specimen during can be tracked
- Samples can be prepared so DSC can be used afterward to estimate percent of cure
Light on at 5.0 minutes
Experimental concerns

- UV light generates heat. Cooling is a must so that temperature remains fairly constant in run
  - True for both DSC and DMA
  - Advantage of power compensation DSC is it controls temperature and measures energy.
- Light Intensity must be measured in both systems.
  - DSC energy can be measured using graphite targets.
### Calculations

#### Curing:
- Gelation: $E' = E''$
- Virtification – where $E'$ levels off
- Slope of cure used to estimate kinetics
  - See Roller et al for details

![Diagram showing dynamic properties vs time with labels for $E'$, $E''$, $T_{gel}$, and $T_{vif}$]
**Light Sources**

- Hg Lamp
- LEDs
LED System from Digital Light Labs allows programming of cure cycles
Curing and Sample Distortion

- Associated with curing is a shrinkage in the material
- Often exploited in bulk polymerizations by dilatometry to obtain initial rates.
- Shrinkage cause problems in manufacture:
  - Distortion of shapes
  - Gaps and spaces inside parts
  - Bending and twisting
- Known problem in thermal cures
- Also exists in photocures

![Diagram](image-url)
Curing and Sample Distortion

- Samples contract on curing

UV Cure in TMA

- Compression on sample due to settling
- Light on at 30 seconds
- Shrinkage caused by curing

Static Displacement vs Time

- ΔY = 0.028 mm
- Light on at 5 minutes
First Set of Experiments

- A factorial design to look at amount of cure and degree of distortion as a function of light intensity, exposure time, and temperature.

Then develop a cure profile to minimize distort for reasonable curing times.

Finally

- Development of the equivalent of a TTT diagram for time-intensity-transformation relationship.
Crunching the numbers:

- Temperature has minimal affect over the range studied.
- Intensity of the light has the greatest.
- The cure continues after the light is turned off.
- Higher intensities are needed for fuller cures.

<table>
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<tr>
<th>Temperature C</th>
<th>Intensity (w/cm2)</th>
<th>Time min</th>
<th>T gel</th>
<th>T vif</th>
<th>Delta Y</th>
<th>Percent Cure</th>
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Two stage curing by UC

- 15 minutes of UV at low intensity to create gel-glass
- 5 minutes of high intensity UV to finish the cure
- Work is ongoing with a new experimental design for this.
- After a method is developed in the DMA, test specimens will be run.
Mapping curing behavior

- Run a series of isothermal cures at a single intensity.
- Measure the time needed to $T_{gel}$ and $T_{vit}$
- Graph data as done for Gilham-Enns Diagram
Results as a Time-Intensity-Transition Diagram

Time - Intensity - Transformation @ 25 C

Gelation Time
Vitrification Time
The chemistry of curing may not match perfectly with the rheology.

Tracking conversion as the change in absorbance at 6165 cm$^{-1}$ is also used.
Chemical cure versus rheological

BisGMA TEGDMA

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