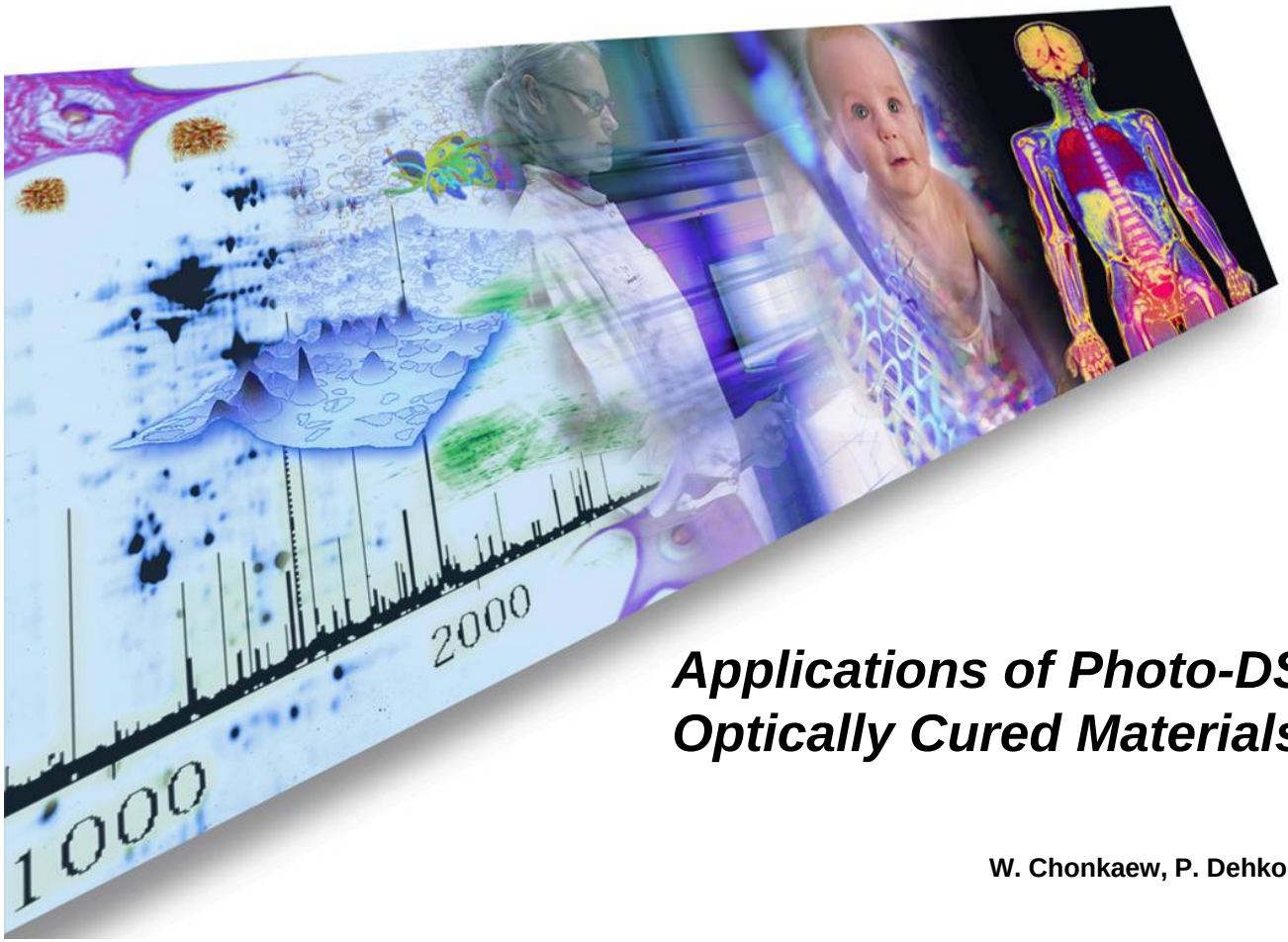
PerkinElmer®
precisely.



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

W. Chonkaew, P. Dehkordi, J. Lang, K. Menard, and N. Menard

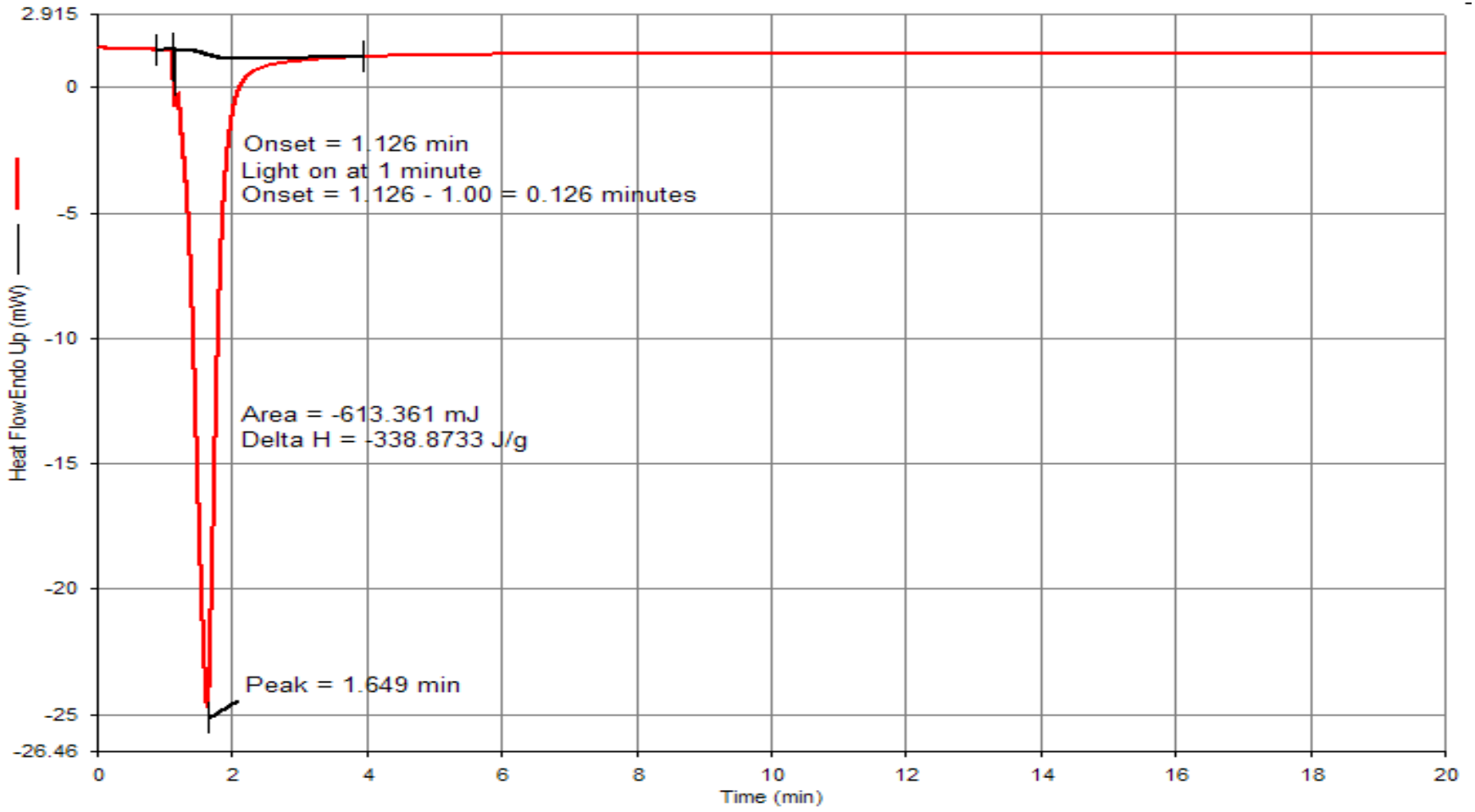
The Project goals:

- **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

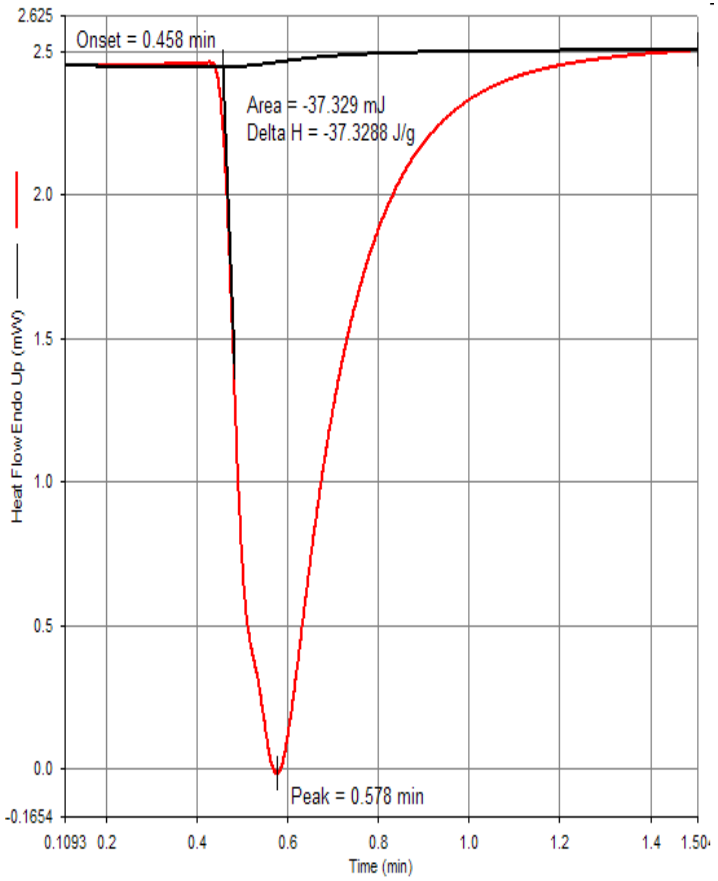
- **Commonly used**
  - **Dental materials**
  - **Electronic adhesives**
  - **Orthopedic applications**
  - **Coating for low VOC**
- **Traditionally Studied by Photo-DSC**
  - **Allows measure of energy of cure**
  - **Study of cure kinetics**
  - **Development of cure profiles**

UV-DSC Data – Curing Studies



UV-DSC Data – Residual Cure

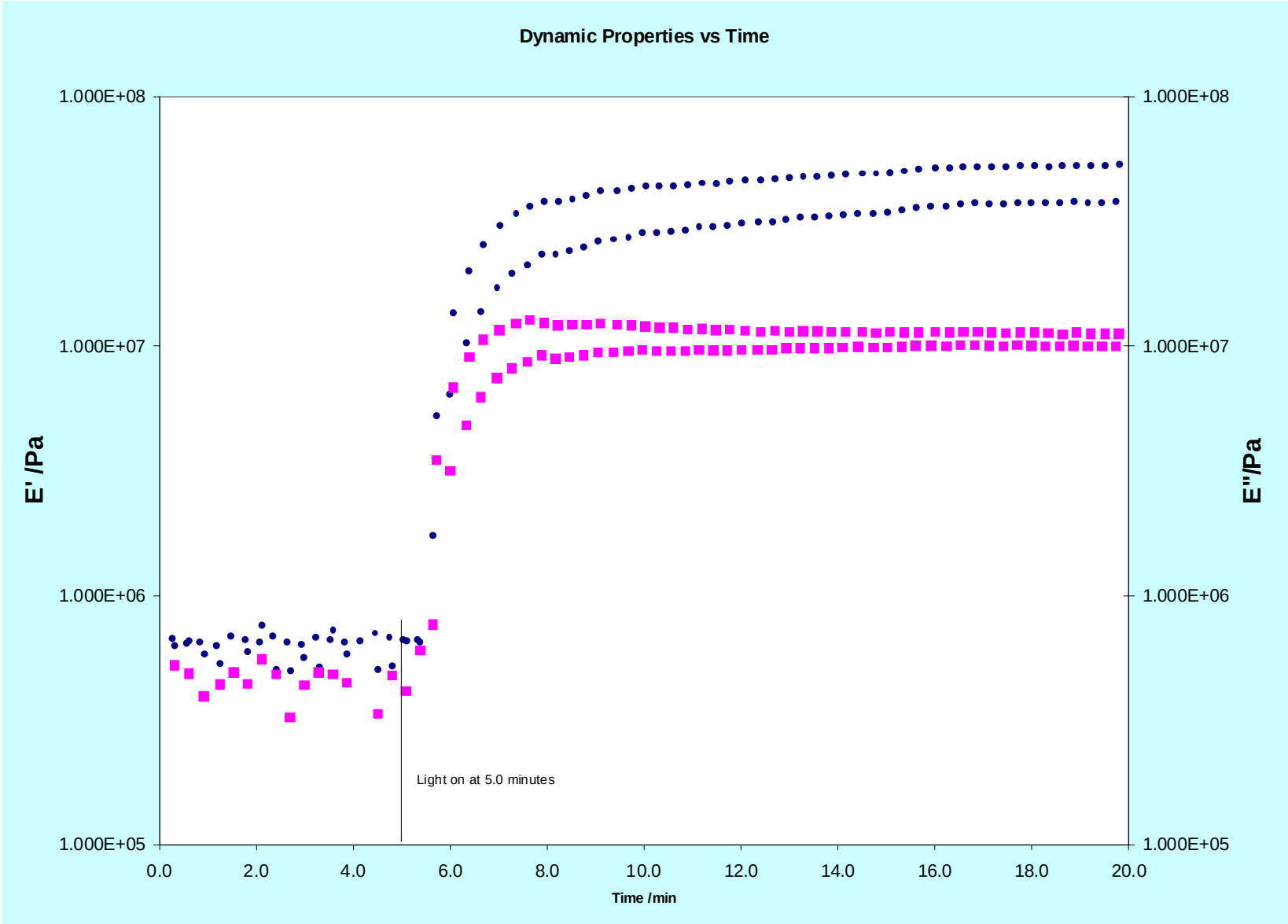
- **Sample rerun under conditions that are known to get complete cure.**
- **Percent cure calculated:**
  - $\Delta H_{complete\ cure} - \Delta H_{second\ cure}$
  - **Divided by** $\Delta H_{complete\ cure}$
  - **Times 100**
  - **{(-339) – (-37)/(-339)} * 100**
  - **= 89.1 %**



Advantages of UV-DMA

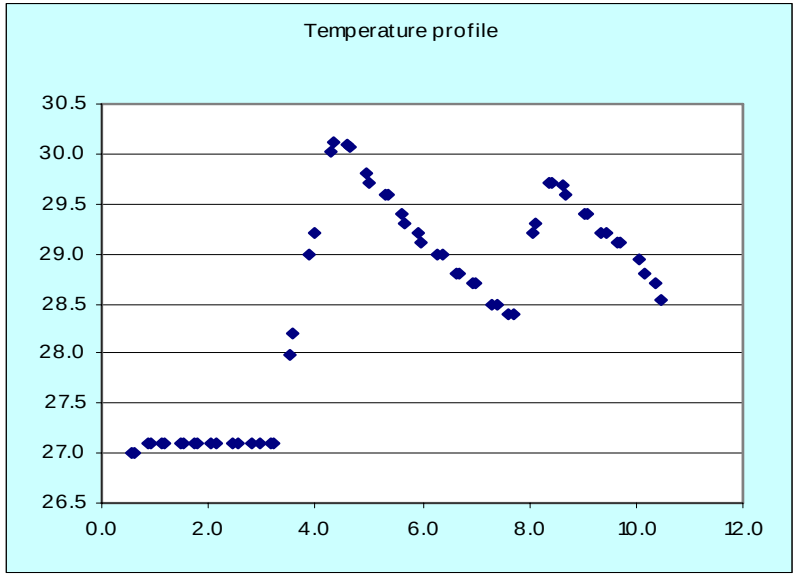
- **Measurement of modulus and viscosity as function of cure**
- **Physical measurements more meaningful for actual production**
- **Ease of determining gelation and vitrification**
- **Distortation of the specimen during can be tracked**
- **Samples can be prepared so DSC can be used afterward to estimate percent of cure**

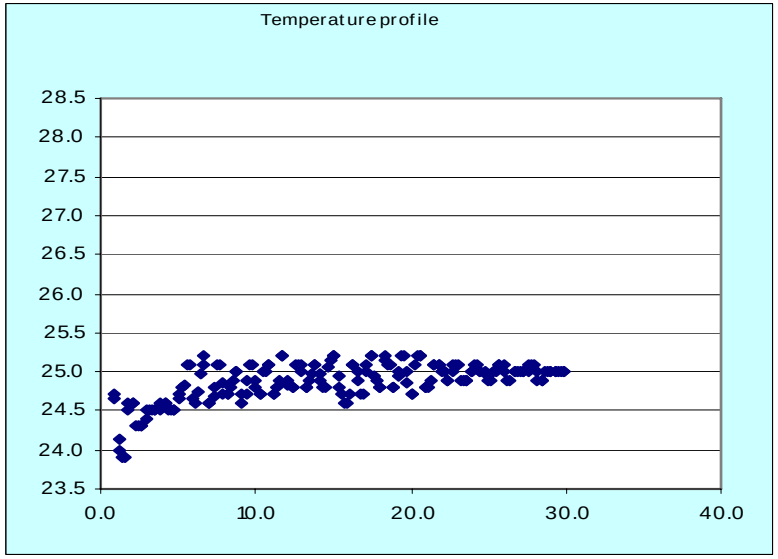
UV-DMA Data


Dynamic Properties vs Time
1.000E+08
1.000E+07
1.000E+06
1.000E+05
E' /Pa
E''/Pa
Light on at 5.0 minutes
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
Time /min

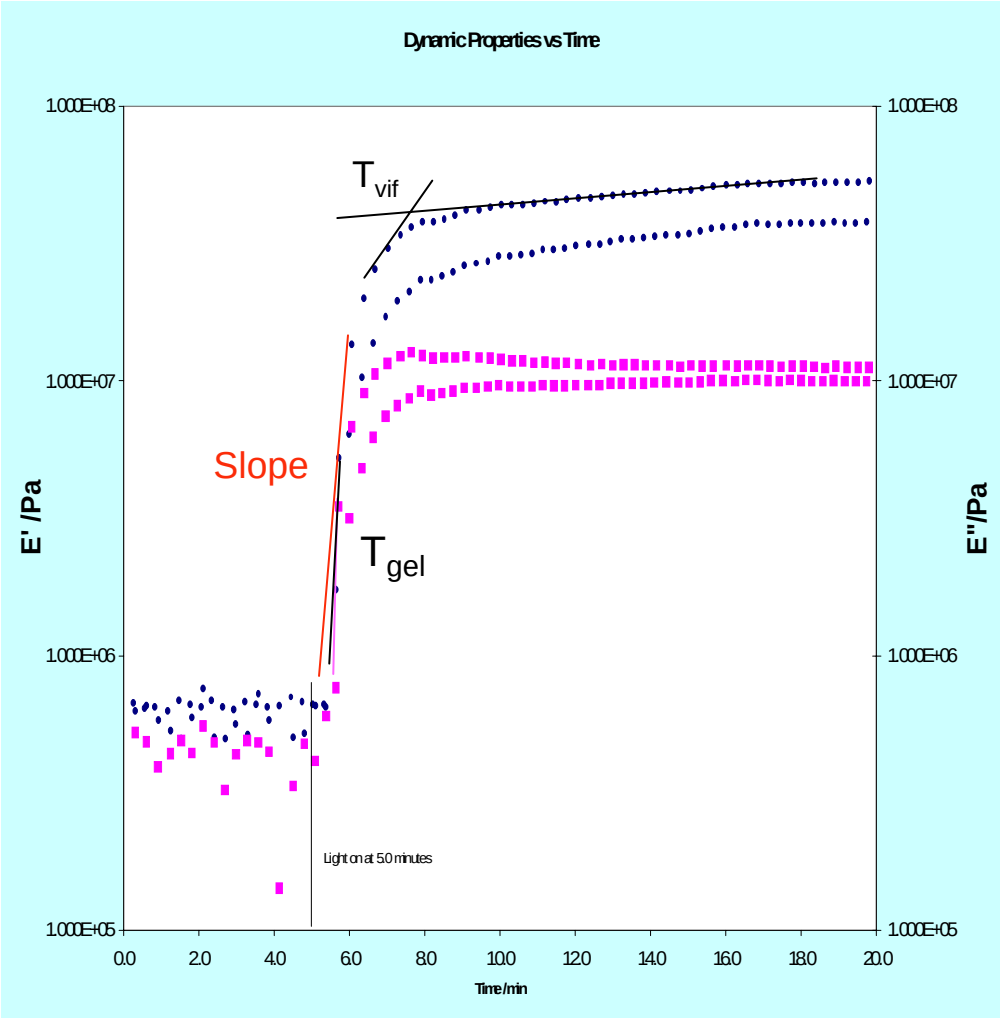
Experimental concerns

- **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.**



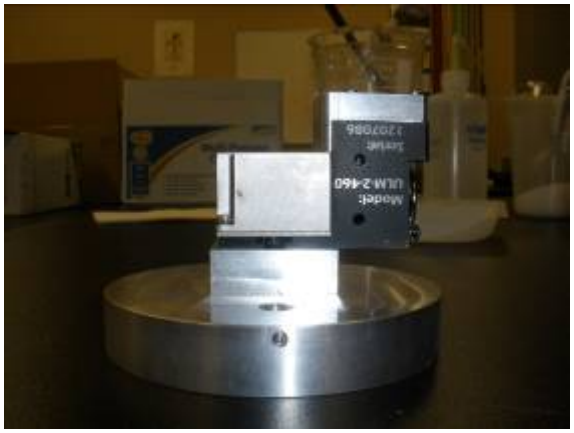


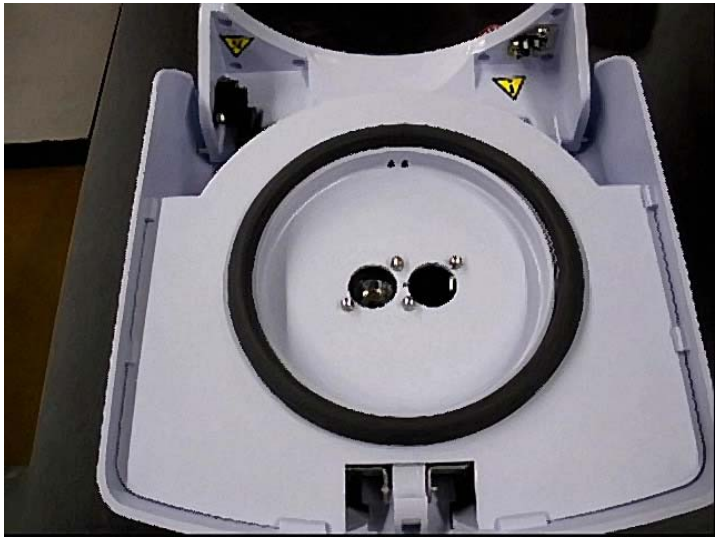
- **Curing:**
  - **Gelation E' = E"**
  - **Virtification – where E' levels off**
  - **Slope of cure used to estimate kinetics**
    - **See Roller et al for details**



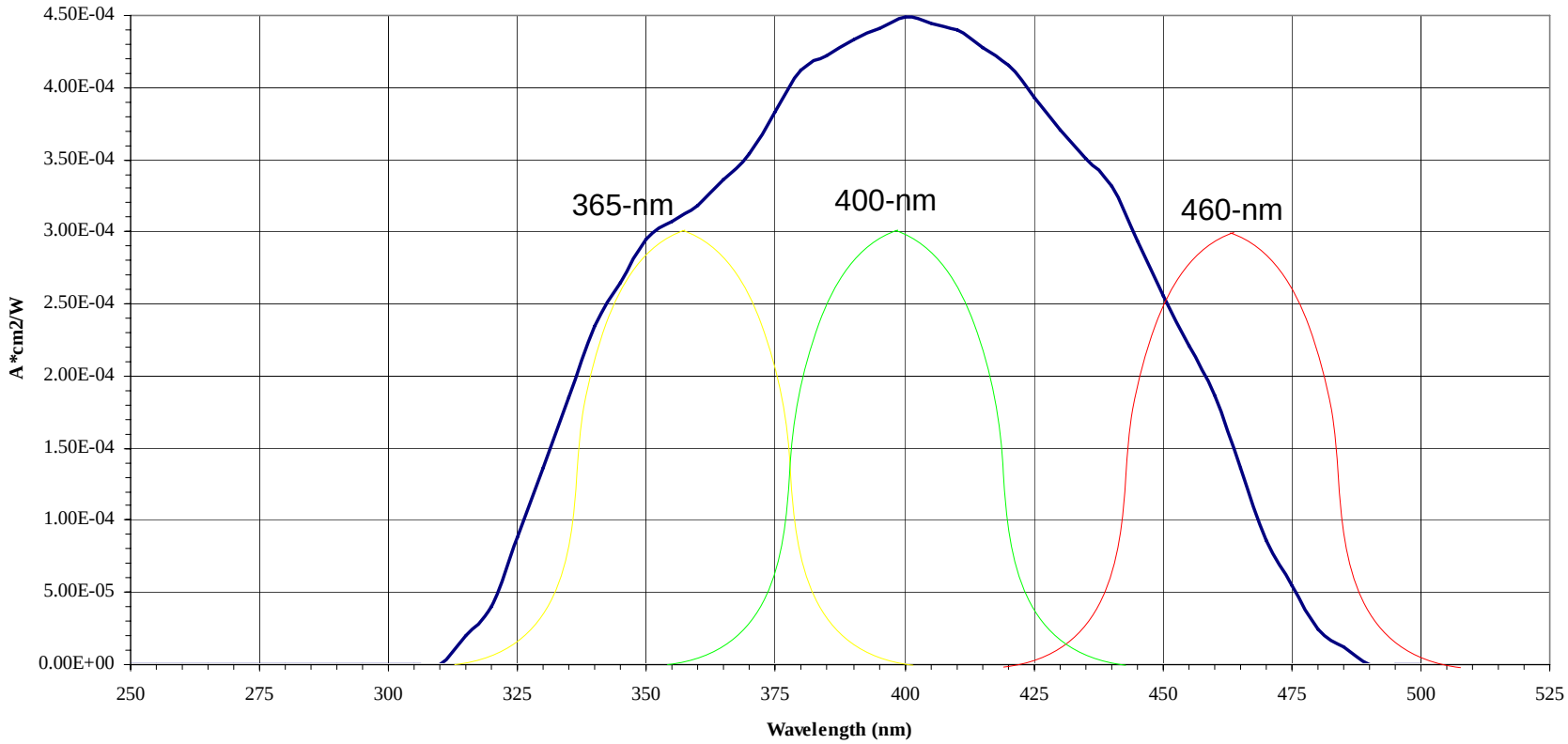
Light Sources

- **Hg Lamp**
- **LEDs**



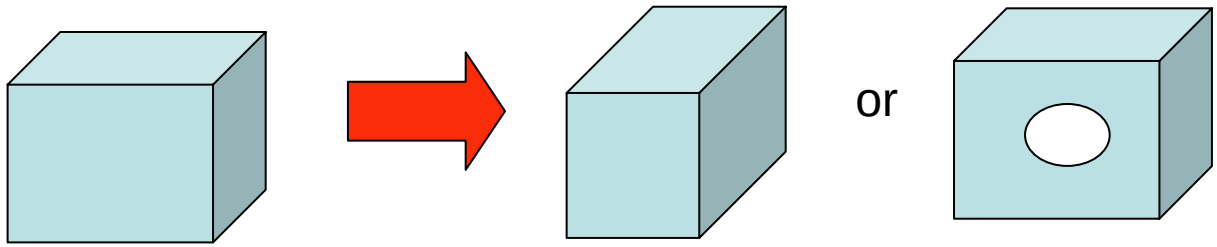


Light Intensity and Bandwidth



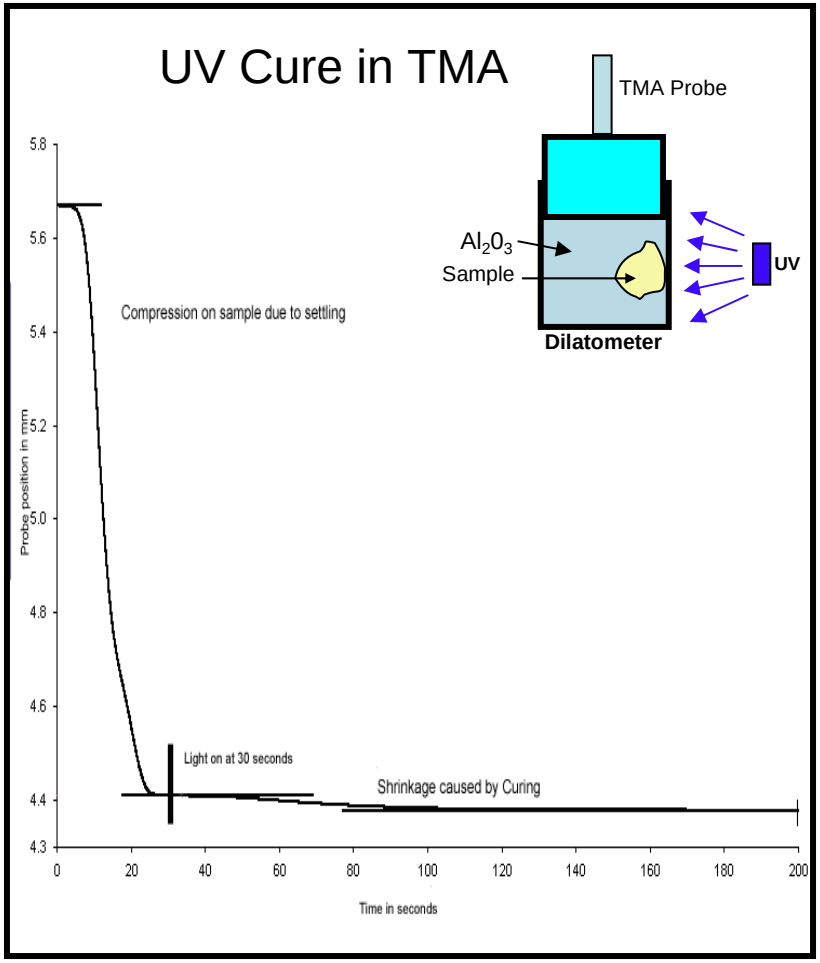
LED System from Digital Light Labs allows programming of cure cycles

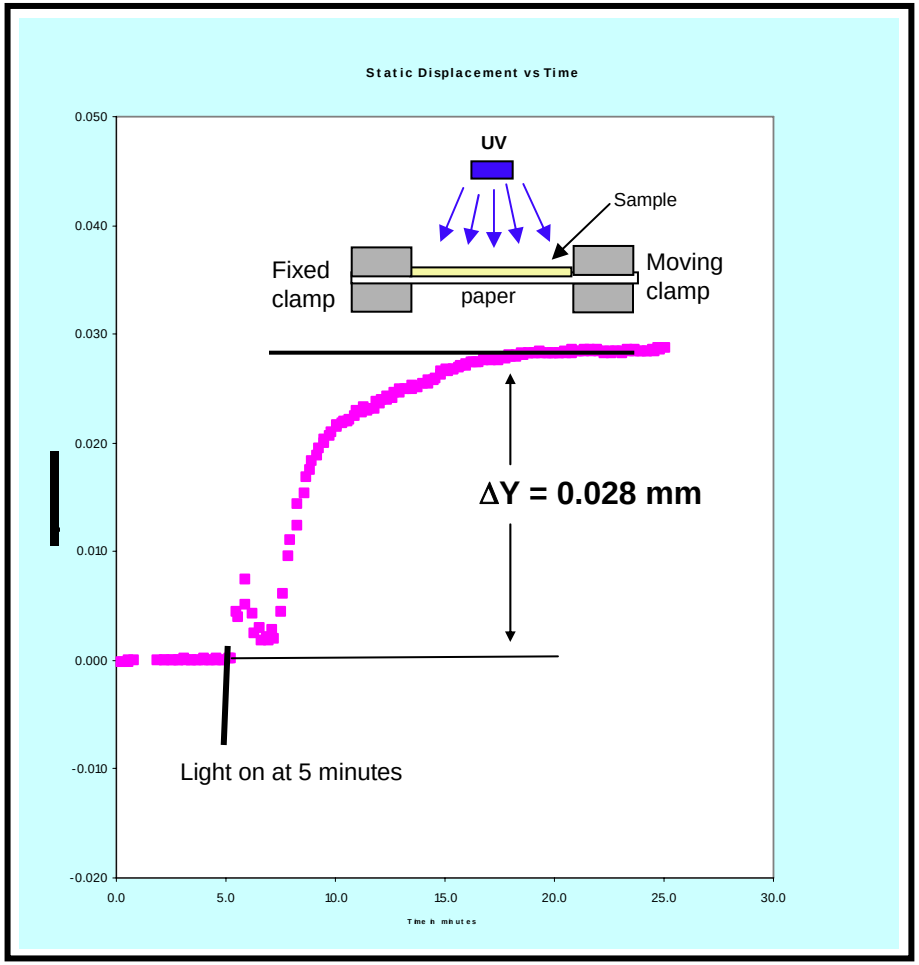
- **Associated with curing is a shrinkage in the material**
- **Often exploited in bulk polymerizations by dilatometry to obtain initial rates.**
- **Shrinkage cause problems in manufacture:**
  - **Distortion of shapes**
  - **Gaps and spaces inside parts**
  - **Bending and twisting**
- **Known problem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



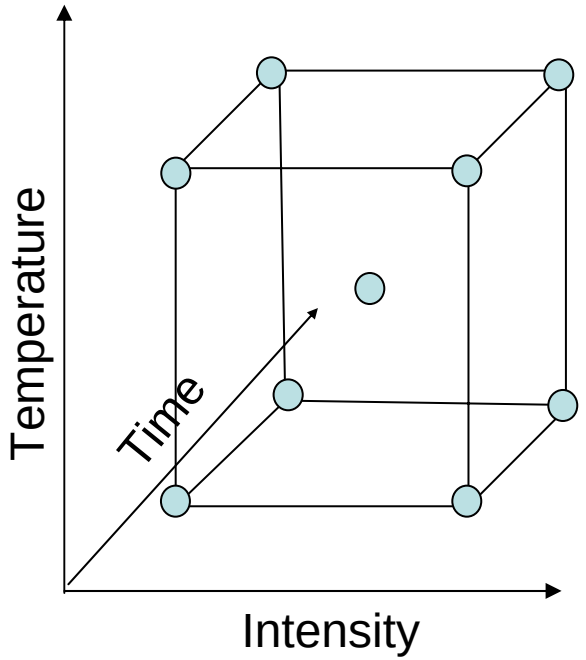
Curing and Sample Distortion

- **Samples contract on curing**





- **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**



Experimental Design results

Temperature C	Intensity (w/cm2)	Time min	T gel	T vif	Delta Y	Percent Cure
25	110	30	0.1	11	0.019	95.4
50	110	30	0.1	10	0.016	96.3
25	40	30	0.4	14	0.003	89.1
50	40	30	0.4	13	0.004	90.3
50	40	10	0.4	13	0.004	90.8
25	40	10	0.5	15	0.003	90.1
25	110	10	0.1	15	0.013	96.7
50	110	10	0.1	10	0.015	97
37.5	75	20	0.3	12	0.006	94.6

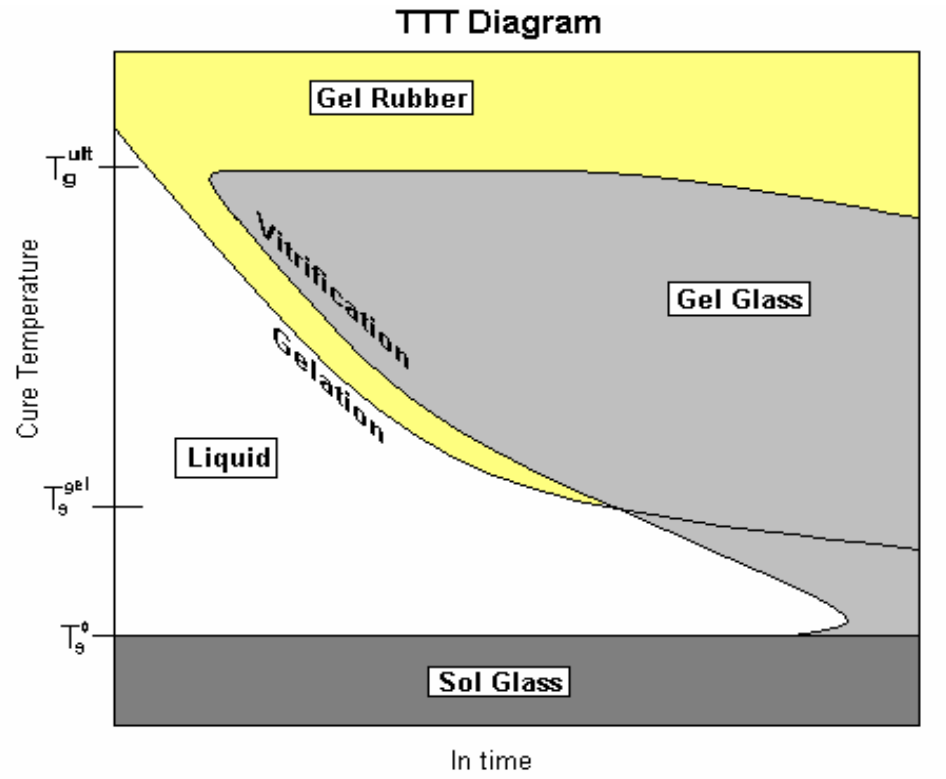
- **Crunching the numbers:**
  - **Temperature has minimal affect over the range studied**
  - **Intensity of the light has the greatest**
  - **The cure continues after the light is turned off**
  - **Higher intensities are needed for fuller cures.**

Two stage curing by UC

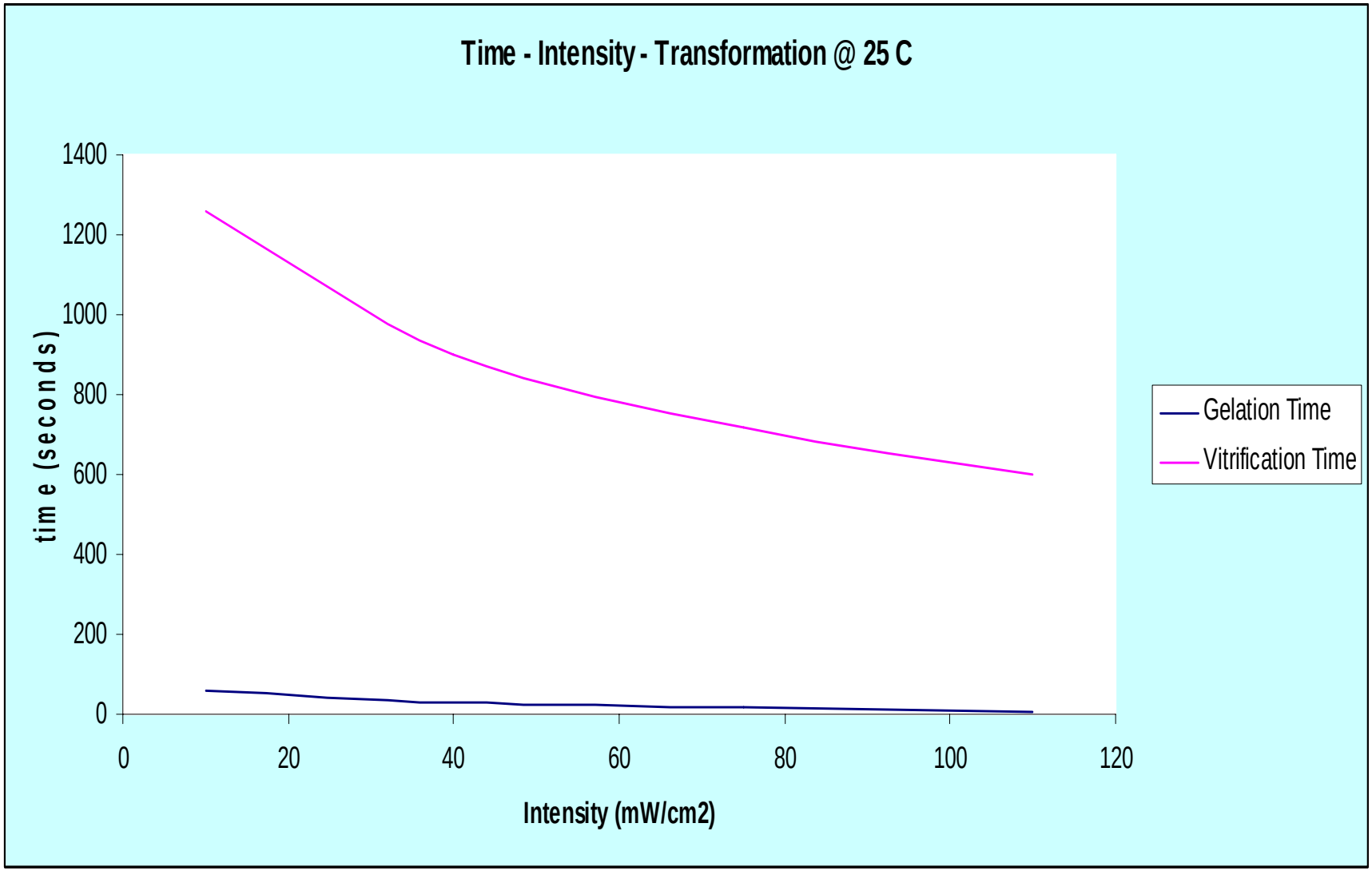
- **15 minutes of UV at low intensity to create gel-glass**
- **5 minutes of high intensity UV to finish the cure**
- **Work is ongoing with a new experimental design for this.**
- **After a method is developed in the DMA, test specimens will be run.**

Mapping curing behavior

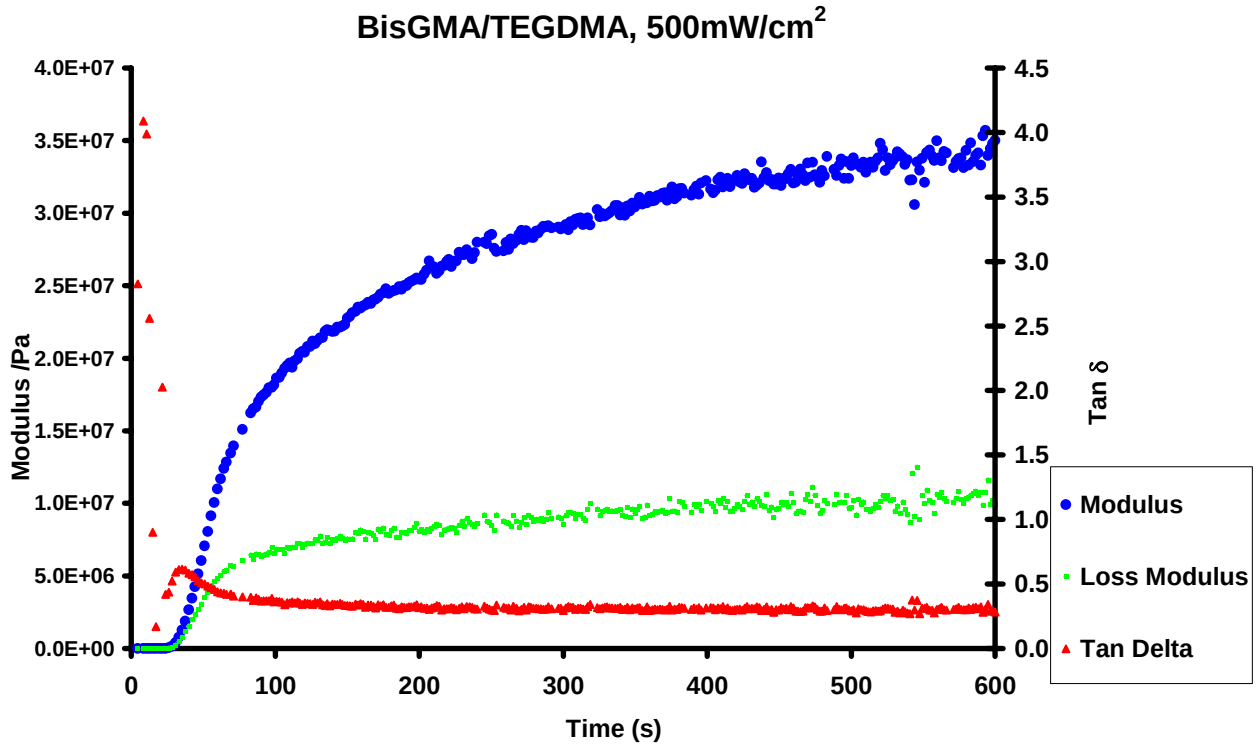
- **Run a series of isothermal cures at a single intensity.**
- **Measure the time needed to T_{gel} and T_{vit}**
- **Graph data as done for Gilham-Enns Diagram**



Results as a Time-Intensity-Transition Diagram

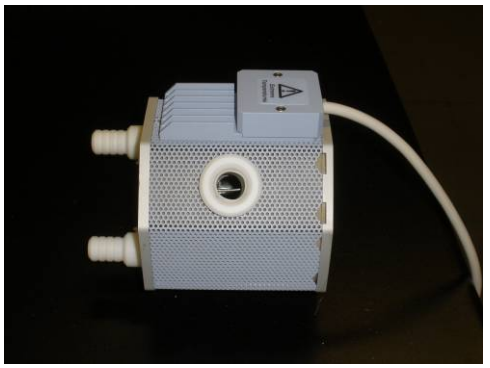


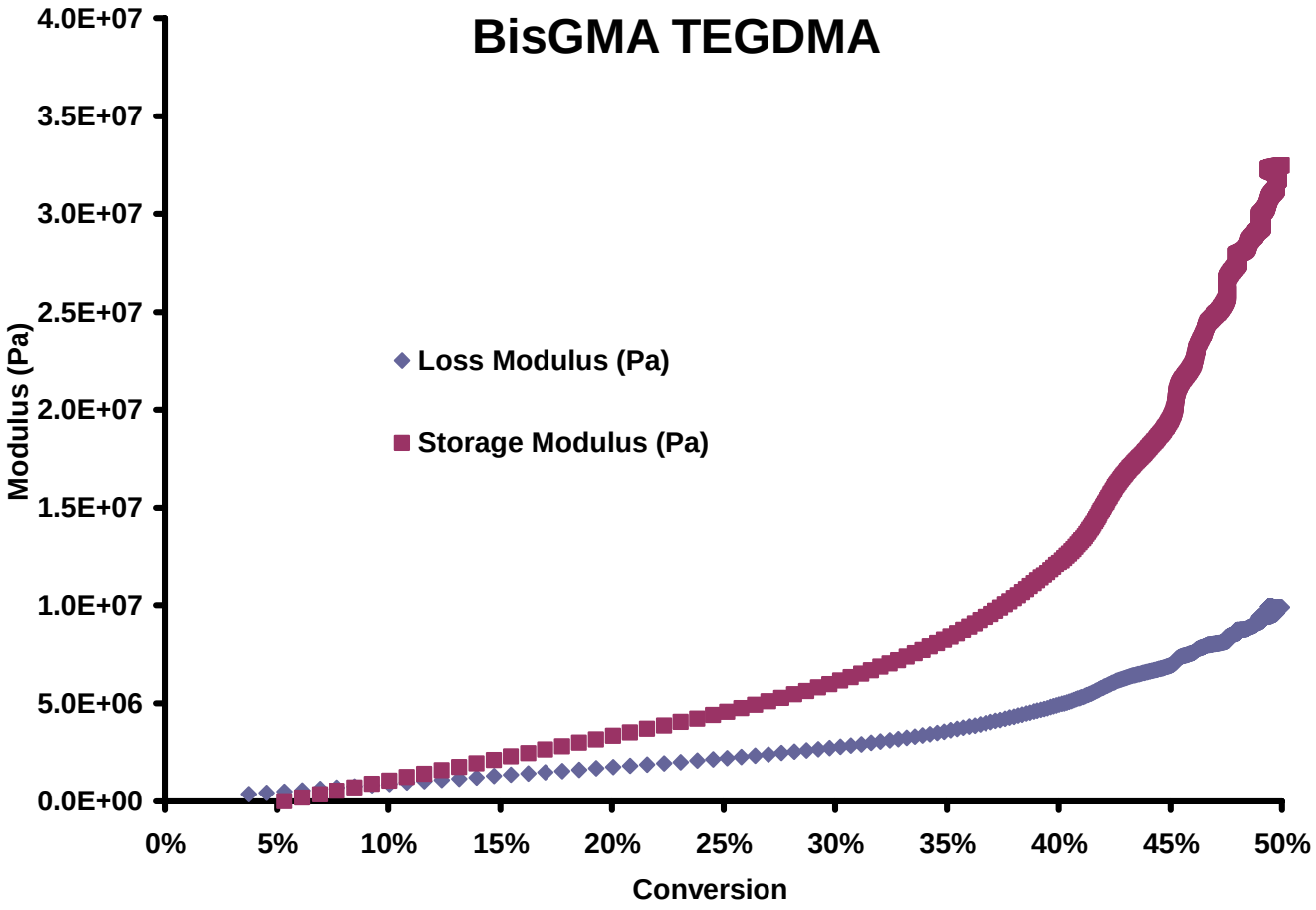
- **The chemistry of curing may not match perfectly with the rheology.**



Tracking conversion as the change in absorbance at 6165 cm^{-1} is also used

Chemical cure versus rheological





Newman et al., Proceeding Acad. Dental Materials., 2008, in prep.

Contacts and Acknowledgements:

Prof. W. Brostow, Matls. Sci. Eng., U. North Texas, Denton, TX
Prof. W. Chonkaew, Department of Chemistry,
King Mongkut's Technical University, Bangkok, Thailand
P. Dehkordi, Digital Light Labs, Knoxville, Tennessee.
Dr. J. Lang, PerkinElmer LAS, Atlanta, Georgia
Dr. K. Menard, PerkinElmer LAS, Shelton, Connecticut
and Matls. Sci. Eng., U. North Texas, Denton, TX.
N. Menard, LAPOM, Matls Sci Eng., U. North Texas, Denton, TX

Special thanks to:
Littman Dental Laboratories for supplying material samples