High-throughput Measurements of Viscoelastic Properties Using Surface Indentation

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NCMC-14

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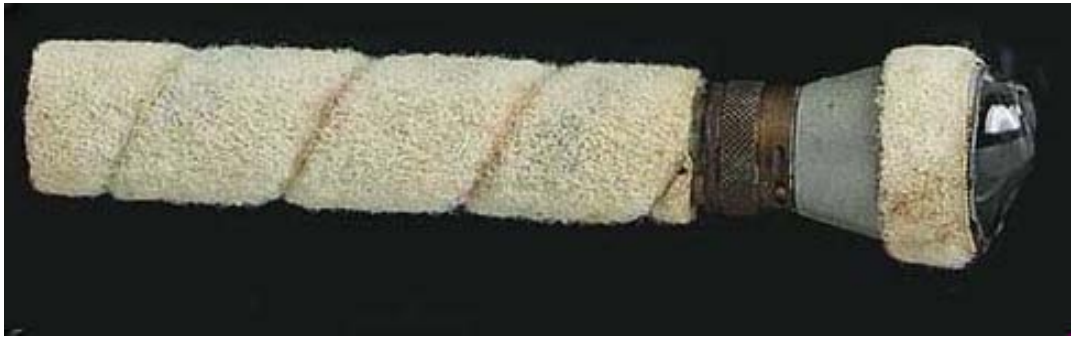
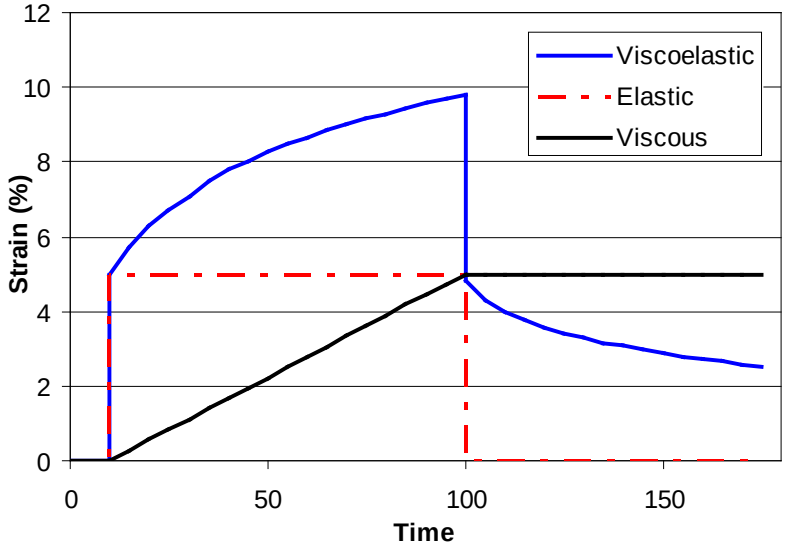
Buzz Aldrin's Flashlight

- Flashlight used in the Gemini 12 spacewalk, auctioned by Christie's in 1999
- Lens material deformed while in space
  - 1999 NY Times: "Offering persuasive testimony that glass really is a very slow-flowing liquid, not a solid, the flashlight's thick lens was blistered and warped by the powerful sucking force of the vacuum of space."
  - Gemini 12 report states it is actually PMMA
- Deformation stresses on the lens from the pressure differential and solar heating



Nonrecoverable Creep

- Jet Engines
  - 1300 to 1500 C operating temperature
  - Higher T_M than most superalloys
  - Single crystal blades eliminate grain defects and improve resistance to creep
- Structural Metals/Polymers
  - Metals and ceramics at high temperatures (30-40% of T_M) exhibit creep behavior under load
  - Grain defects cause permanent dislocations, leading to failure
  - Polymers applications show initial creep – failure occurs under specific conditions



Polymer Creep

Creep in polymers is a permanent deformation of the polymer network under a static or dynamic load

- PMMA bone cement in hip replacements
- Structural adhesives (permanent bonding)
- Pressure Sensitive Adhesives (temporary/permanent bonding)
- Degradation of polymer networks
- Solvated systems, drug release networks, nanostructured polymers

Creep analysis requires significant experimental time to produce creep compliance curves

ASTM Creep Standard

- D2990 Standard
- Parallel testing
- Dead weight apparatus
- 10,000 hour duration
  - 416 days

From D2990
To obtain design data, the test temperatures and environment shall be the same as those of the intended end-use application

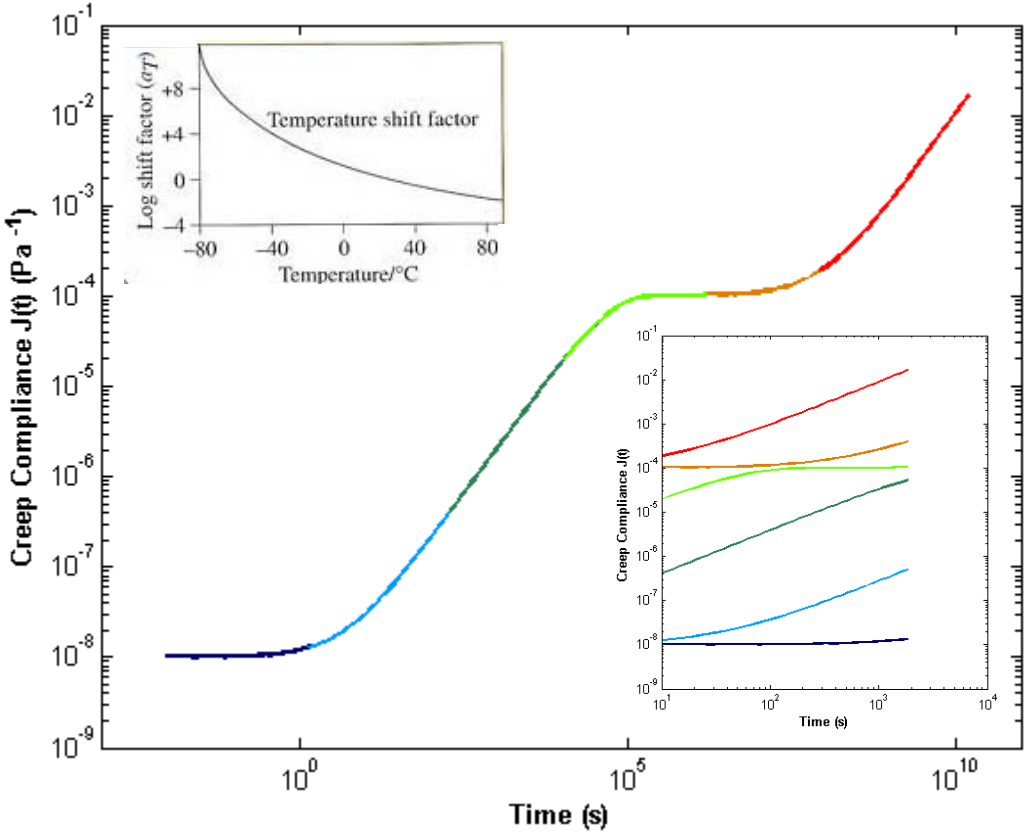
Strain load is constant and chosen by the design engineer

Time-Temperature Superposition

$$\log a_T = \frac{E_a}{R}\frac{1}{(T - T_0)}$$

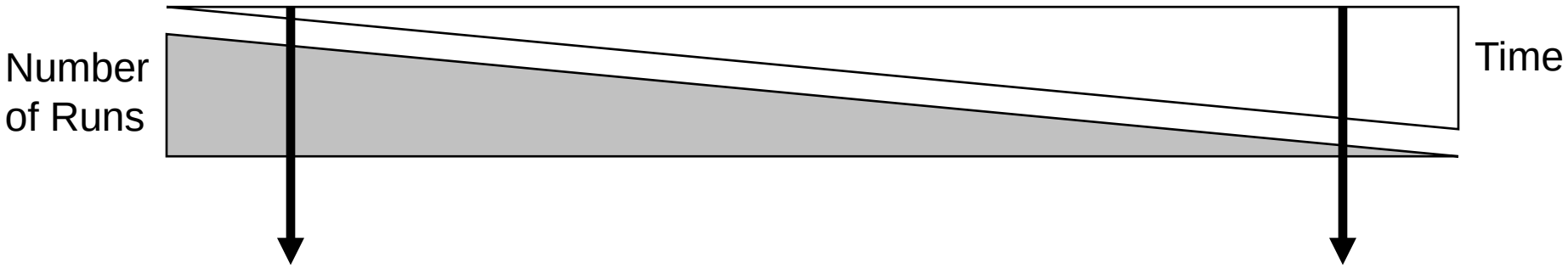
$$\log a_T = \frac{C_1(T - T_0)}{C_2 + (T - T_0)}$$

$$\log a_T = a\frac{1 - e^{-(b(T_{ref} - T))^c}}{d + e^{-(b(T_{ref} - T))^c}}$$



- Multiple temperature creep scans are combined into a single master curve (rheometer, DMA)
- WLF: free volume and temperature are linearly related
- Shift factor relationships become more empirical when WLF fails

Time-Sampling Continuum



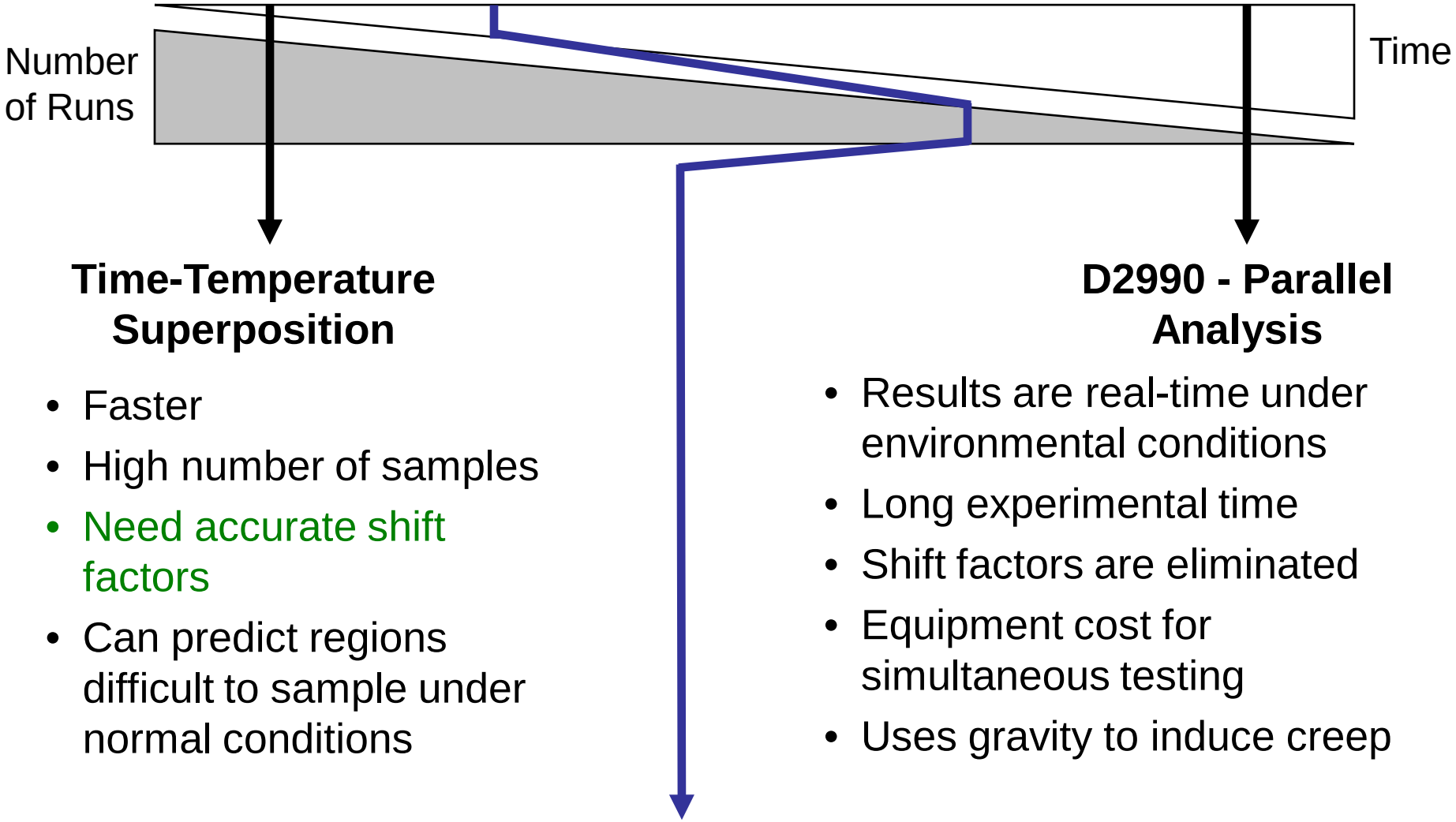
Time-Temperature Superposition

- Faster
- High number of samples
- Need accurate shift factors
- Can predict regions difficult to sample under normal conditions

D2990 - Parallel Analysis

- Results are real-time with the correct conditions
- Long experimental time
- Shift factors are eliminated
- Equipment cost for simultaneous testing
- Uses gravity to induce creep

The Middle Ground



Time-Temperature Superposition

- Faster
- High number of samples
- Need accurate shift factors
- Can predict regions difficult to sample under normal conditions

D2990 - Parallel Analysis

- Results are real-time under environmental conditions
- Long experimental time
- Shift factors are eliminated
- Equipment cost for simultaneous testing
- Uses gravity to induce creep

Reduce the number of runs required through simultaneous measurements

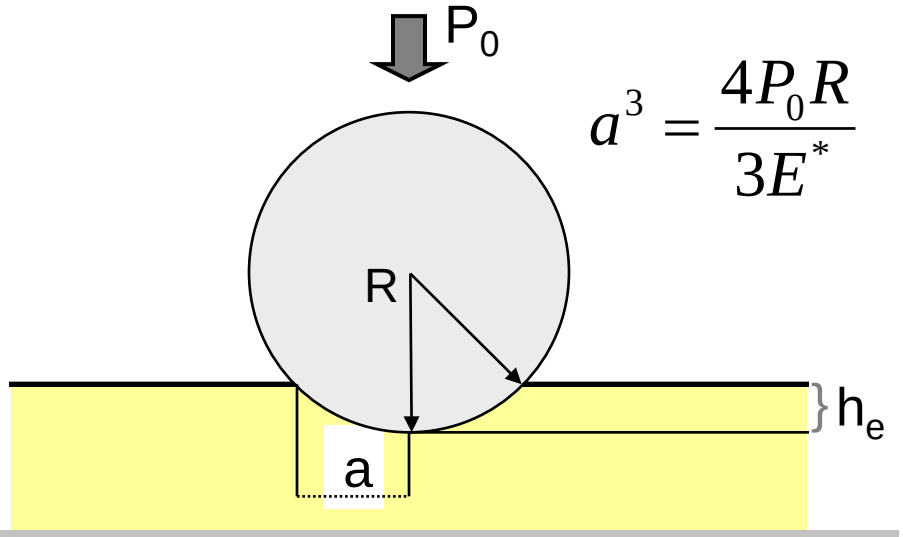
Contact Area of Sphere During Creep

Positives

- Known step load from gravity (static force)
- No temperature effect on measurement mechanisms
- Imaging sequence is expandable
- Radius expansion measures a smaller depth indentation
- Spherical nanoindentation

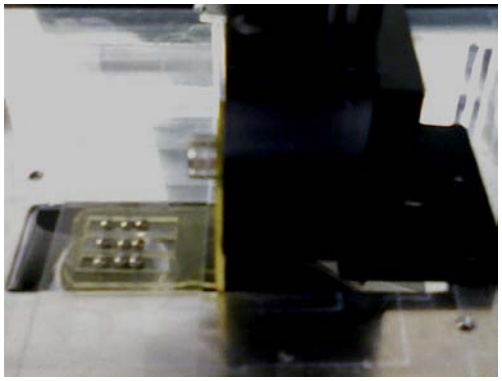
Negatives

- Measuring visual contact area
- Simple compliance calculations fail for thin films
- Substrate confinement effects depend on adhesion and Poisson's ratio



$$a^3 = \frac{4P_0R}{3E^*}$$

Nanoindentation $$J_C(t) = \frac{8\sqrt{R}h_e^{3/2}(t)}{3(1-\nu)P_0}$$



Lee, E. H.; Radok, J. R. M. *J Appl Mech.* **1960**, 27, 438.

Photopolymerization

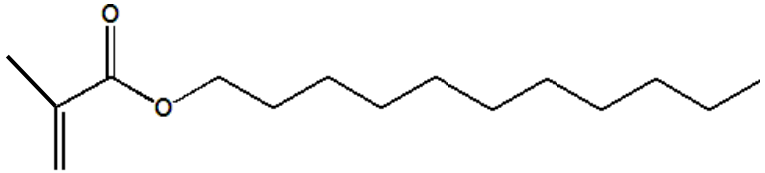
$$R \xrightarrow{h\nu} 2I\cdot$$

$$I\cdot + M \xrightarrow{h\nu} M\cdot$$

$$M_i\cdot + M \xrightarrow{h\nu} P_{i+1}\cdot$$

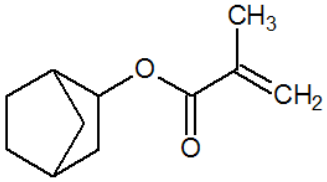
$$P_i\cdot + P_j\cdot \xrightarrow{h\nu} P_{i+j}$$

- Solvent-free Processing
- Thick Polymer Samples
- Wide Range of Material Properties
- Broad use in adhesives, automotive materials
- Broad PDI
- **Can tailor to produce high rates of creep**



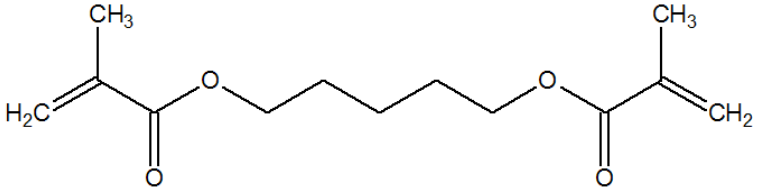
Lauryl Methacrylate (LMA)

Low T_G



Isobornyl Methacrylate (IBoMA)

High T_G

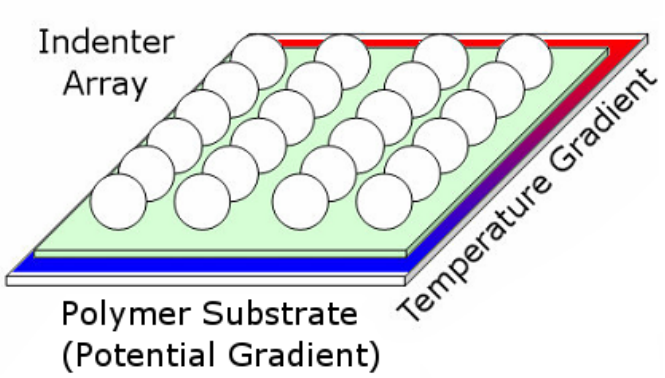


Hexanediol dimethacrylate (HDDMA)

Crosslinker

Multiple Indentations

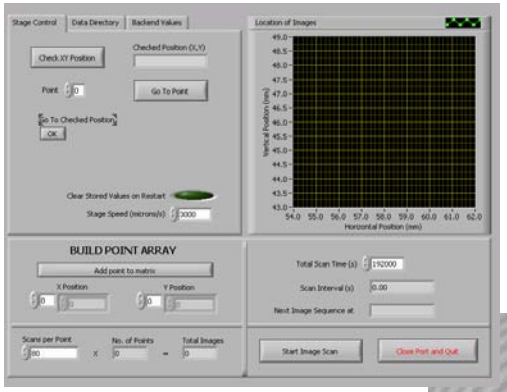
- Temperature gradients for simultaneous time-temperature scans
- Polymer gradients for compositional studies
- Single spheres allow for inexpensive additional measurements on the same substrate

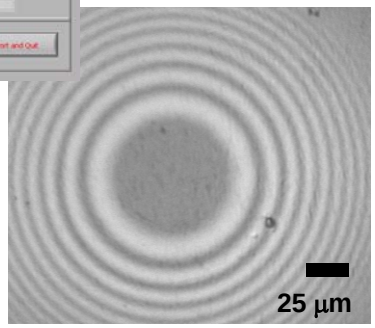


Microscope

Multiple Sample Process

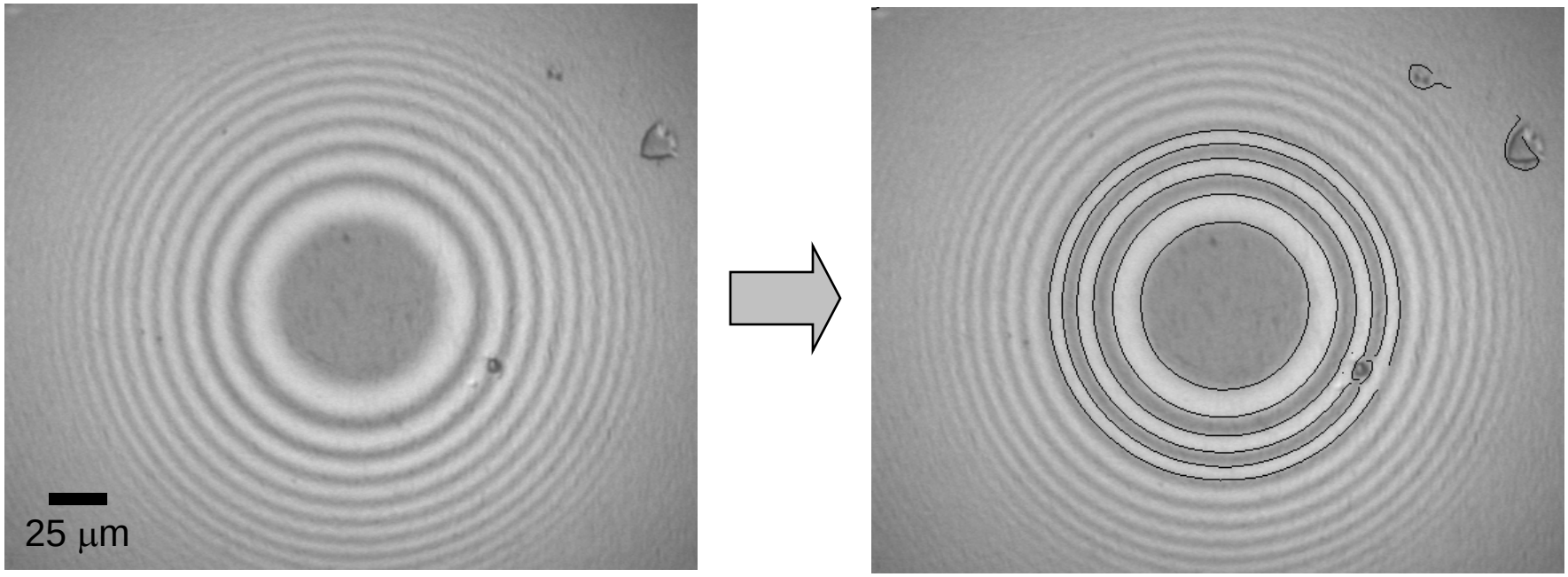
- Raster to each sphere in the array, take an image of the contact point (controlled by LABVIEW)
- Performed for creep greater 100 s because of raster time
- Image processing locates contact area in every image





Processing Results

- Find edges of sphere indentation image
- Calculate Hough Transform to find circles
- Report Radius and Circle Position



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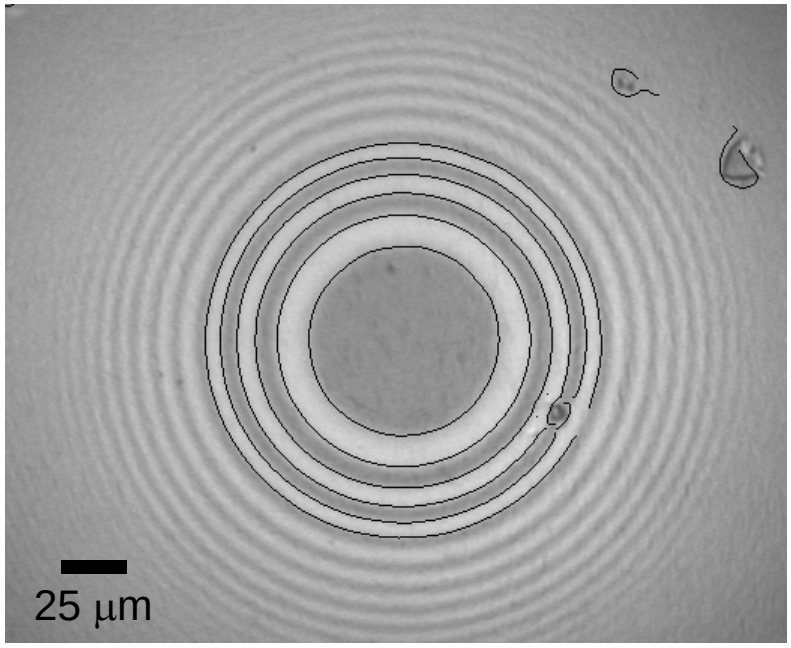

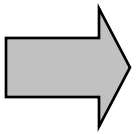

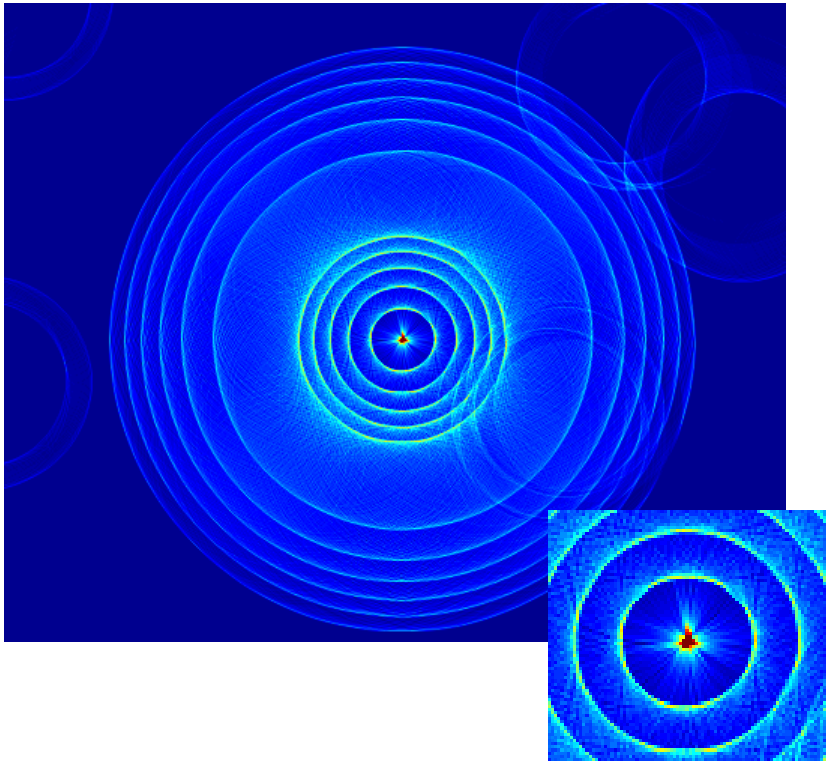

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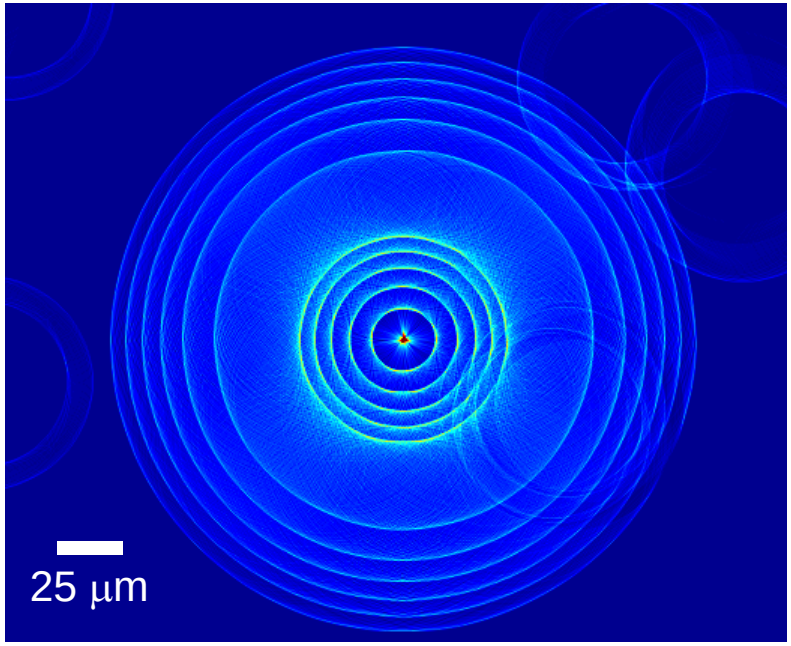
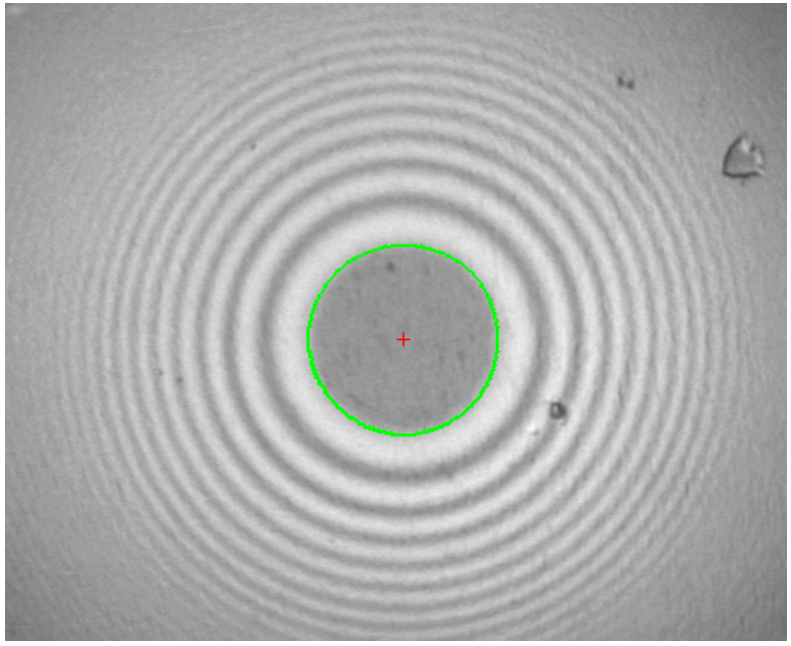
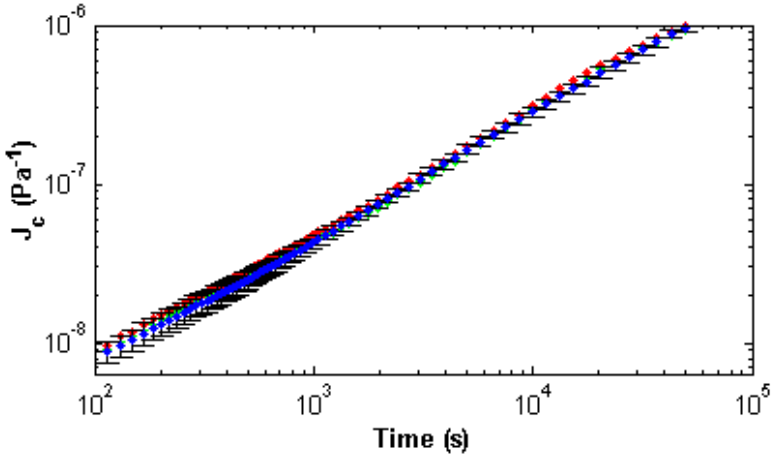


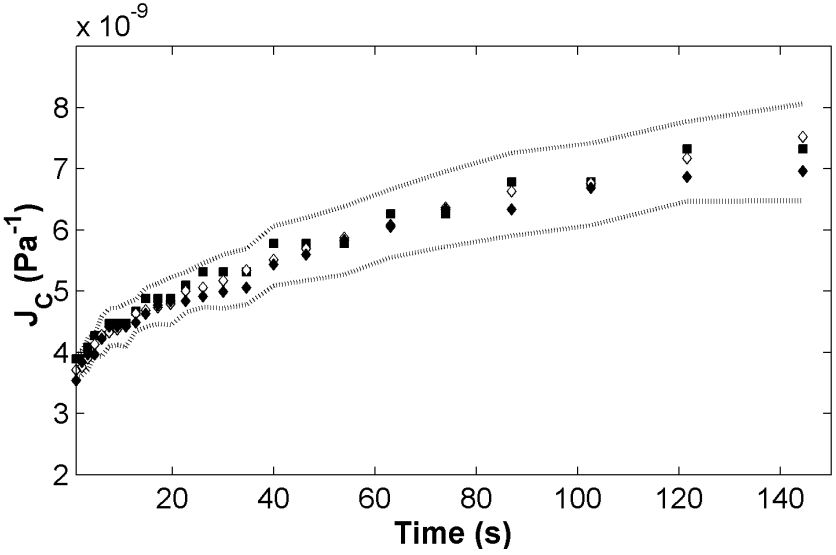


Limitations and Repeatability

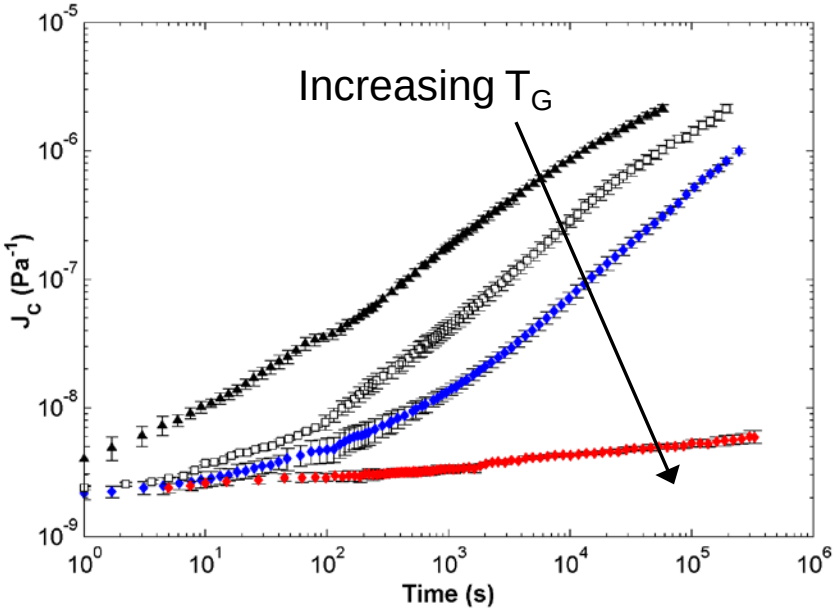
- Statistically equivalent creep compliance over 100000 s (3+ days)
- Load/radius deviation of individual spheres is minuscule in comparison to contact radius error from image analysis

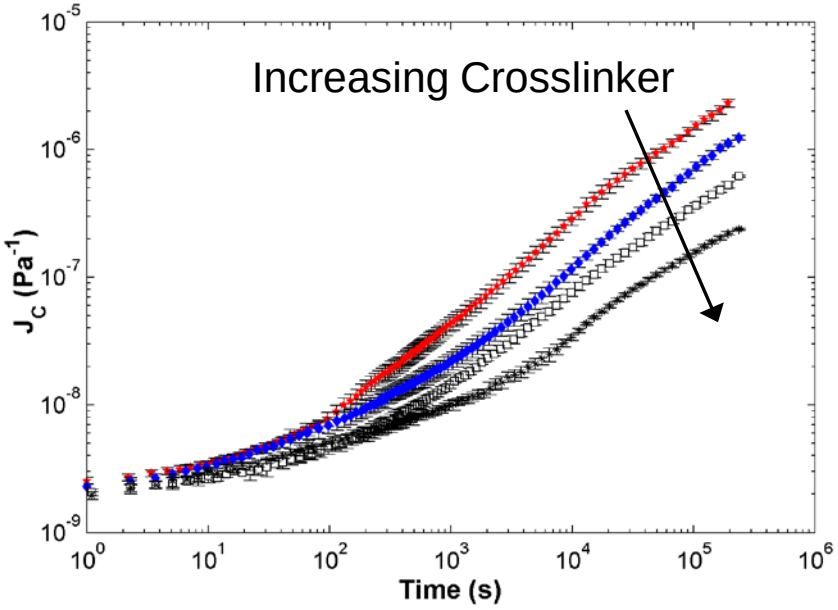


- Small sphere sizes (R < 2.5 mm) produce statistically equivalent results
- Substrate thickness below ~50 μm begin to show polymer-substrate effects, correctable for lower film thickness
- Contact effects in highly adhesive system cause non-circular contact areas and higher standard error



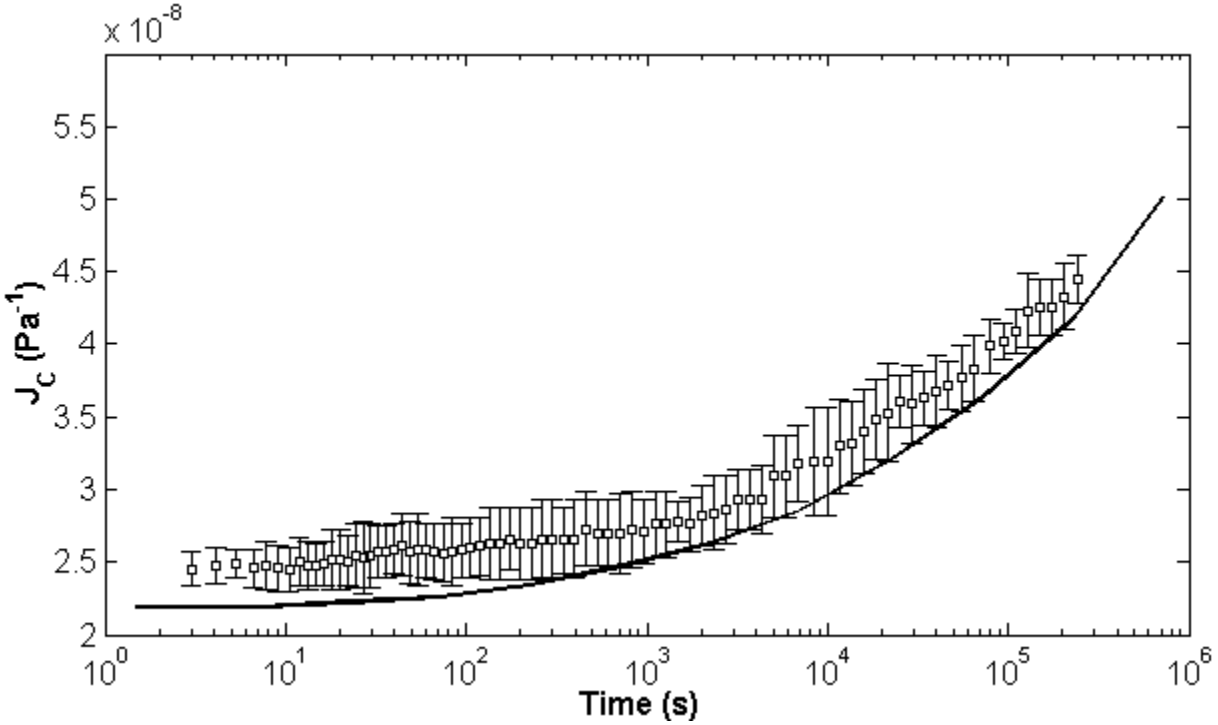
Compositional Effects





- Higher glass transition temperature polymer systems show reduced creep compliance
- Increasing crosslinking density reduces creep while initial creep compliance remains equivalent

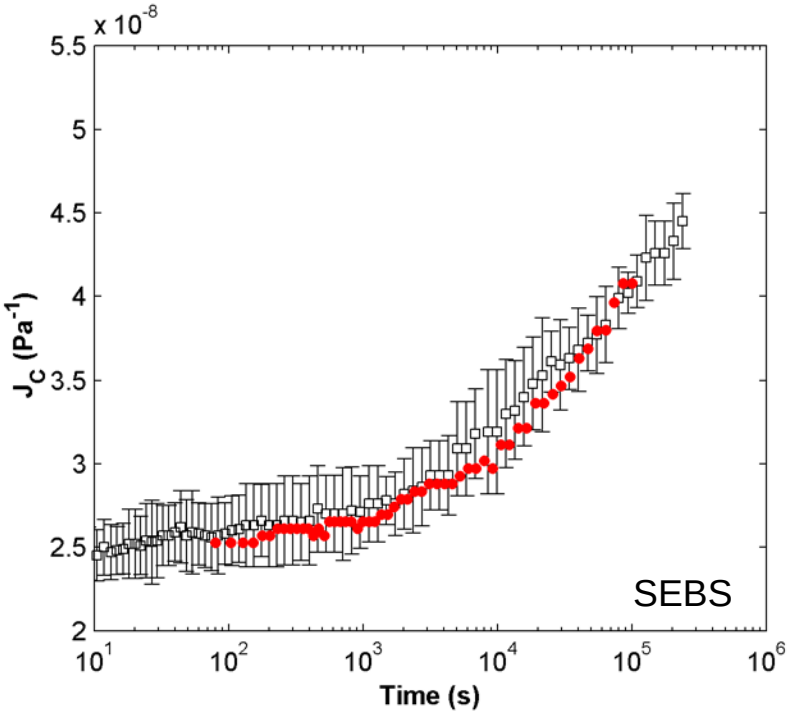
Comparison to Literature

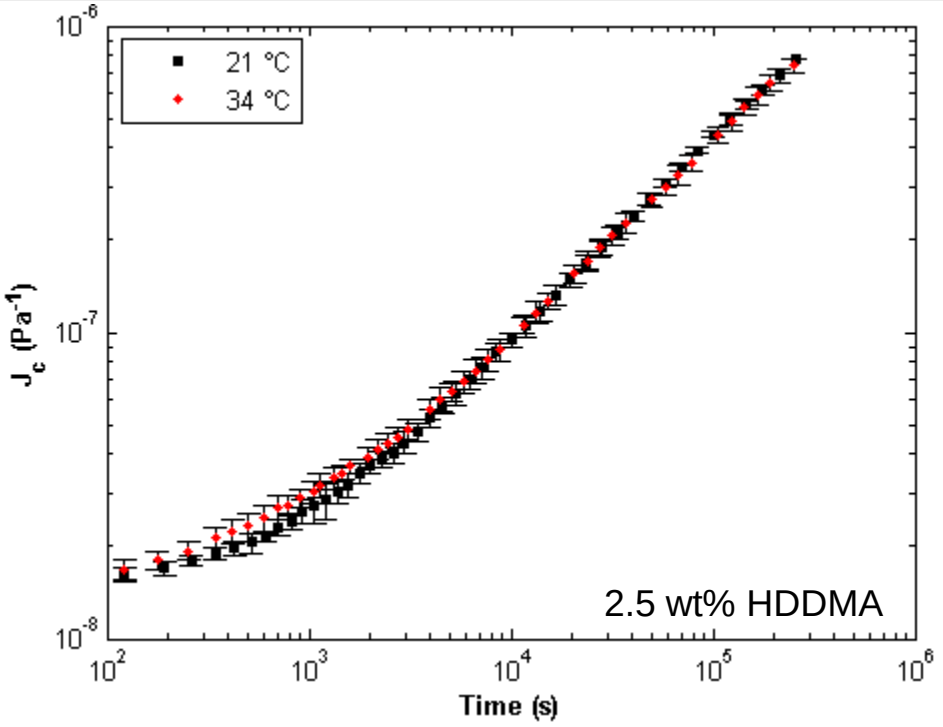


- Creep compliance measurement slightly higher than reference data at all points
- Different geometry was used with reference curve compiled from time temperature superposition (tensile creep)
- PDMS (Slygard 184) samples also have equivalent compliance values to rheometry and DMA creep tests

Rek, *Macromolecular Symposia*, 2003 - Kraton G1650M (SEBS)

Time-Temperature Shifting





- SEBS and photopolymer samples show valid time-temperature superposition
- Comparable creep compliance values throughout the entire experiment

Time (s)	21 °C $J_C(t)$ (Pa^{-1}) x 10^{-8}	34 °C $J_C(t)$ (Pa^{-1}) x 10^{-8}
426	1.97 ± 0.09	2.24 ± 0.21
3975	5.26 ± 0.35	5.61 ± 0.39
11835	10.48 ± 0.82	10.53 ± 0.67
23557	16.84 ± 0.97	17.17 ± 1.11
58026	30.8 ± 1.0	30 ± 2.0
146436	55.4 ± 1.9	54.4 ± 3.5

Conclusions

- Indentation load is constant and can be measured over the range of creep compliance needed for viscoelastic systems ($J_C = 10^{-5}$ to 10^{-9} Pa^{-1})
- Samples show consistent trends expected with theory and demonstrate good agreement when compared to DMA or rheometry experiments from literature
- Temperature gradient analysis enables parallel creep compliance measurements for the determination of shift factors of a polymer sample from a single experiment
- Changes in creep compliance for thin films will allow for confinement effects at the polymer-substrate interface to be studied