An Introduction to Dynamic Mechanical Analysis

Jeffrey A. Jansen
June 13, 2019

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Goals

- Become familiar with how DMA can be used to identify the temperature dependency of polymeric materials.
- Gain insight into the use of DMA to evaluate and project the effects of time on polymeric materials.
- Understand how DMA can be used to assess the suitability of a material in the application.

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Outline

- Fundamental Principle
- DMA Method
- Temperature-related Property Evaluation
- Time-related Property Evaluation

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FUNDAMENTALS

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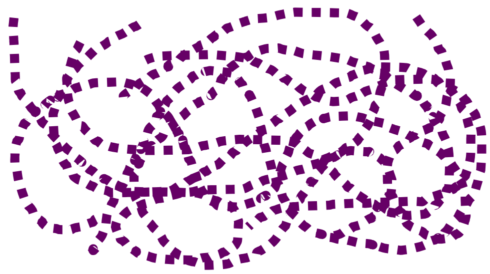
Viscoelasticity

- Because of the molecular structure of the molecules, thermoplastic materials have different properties compared to other materials, like metals.

The polymer molecules consist of very long chains – high molecular weight.

The individual polymer chains are entangled in each other.

The polymer chains are mobile and can slide past each other because they do not share chemical bonds with the other chains around them.



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Viscoelasticity

- Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation.
- Viscous materials, like honey, resist shear flow and strain linearly with time when a stress is applied.
- Elastic materials, like a ~~rubber band~~ **steel rod**, strain when stressed and quickly return to their original state once the stress is removed.
- Viscoelastic materials have elements of both of these properties and, as such, exhibit time-dependent strain.

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Viscoelasticity

- There are three main factors that will affect the viscoelasticity of a plastic part:

Temperature, Time, and Strain Rate

- As the temperature is increased, the polymer chains are further apart, there is more free volume and kinetic energy, and they can slide past one another and disentangle more easily.
- As the strain rate is increased, the polymer chains do not have enough time to undergo yielding and they will disentangle.
- Over time, there is mobility between the polymer chains.

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Viscoelasticity

Elastic Response

- Typical in classical solid materials
- Stress ⟶ Proportional deformation / strain
- $\sigma = \varepsilon \cdot E$ (stress = strain x modulus)
- Response to applied stress: system stores the energy and can return it completely when the stress is removed

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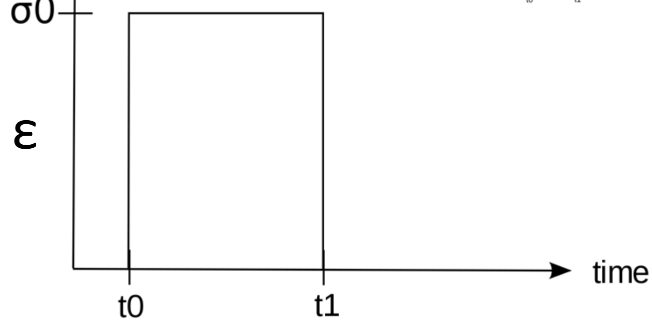
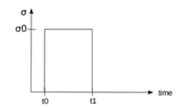
Viscoelasticity

Elastic Response





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Viscoelasticity

Viscous Response

- Typical in classical fluids
- Stress ⟶ strain increases proportionally
- $\tau = \dot{\gamma} \cdot \eta$ (stress = strain rate x viscosity)
- Response to applied stress: energy is lost to the system, strain is not recoverable

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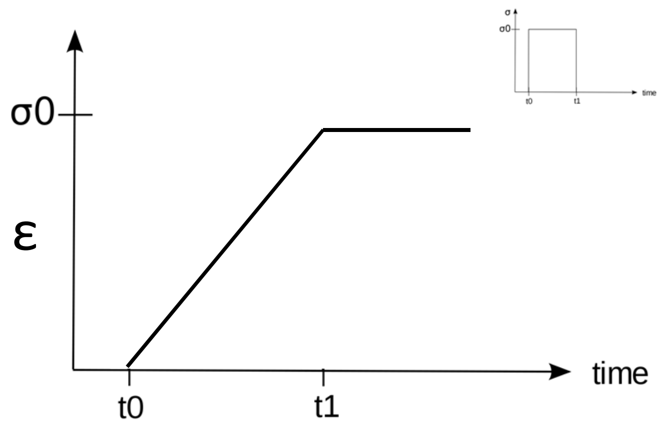
Viscoelasticity

Viscous Response



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Viscoelasticity

Viscoelastic Response

- Thermoplastic materials
- Stress → proportional
- Response to applied stress: system stores energy and returns part of it when the stress is removed - remaining energy is lost to the system, and is not recoverable

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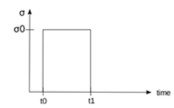
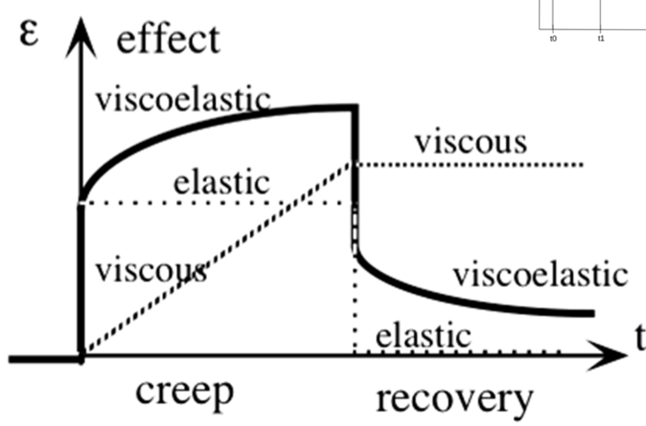
Viscoelasticity

Viscoelastic Response





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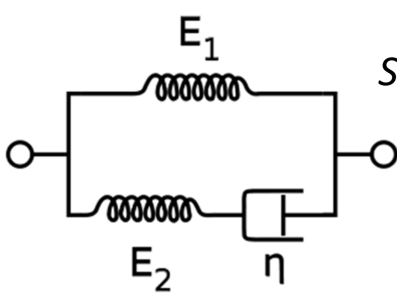
Viscoelasticity



Spring and dashpot model

- Viscoelastic materials have elements of both of these properties and, as such, exhibit time-dependent behavior

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DMA

DMA

- Technique in which a small deformation is applied to a sample in a cyclic manner. This allows the material's response to stress, temperature, frequency and other values to be studied.
- Assesses the proportion of elastic and viscous components in a polymer
- Determines the factors that change this balance
- How will a material perform in a given application environment

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DMA

DMA

Applies a sinusoidal deformation to a sample of known geometry. The sample can be subjected by a controlled stress or a controlled strain. For a known stress, the sample will then deform a certain amount. How much it deforms is related to its stiffness (modulus). A force motor is used to generate the sinusoidal wave and this is transmitted to the sample via a drive shaft.

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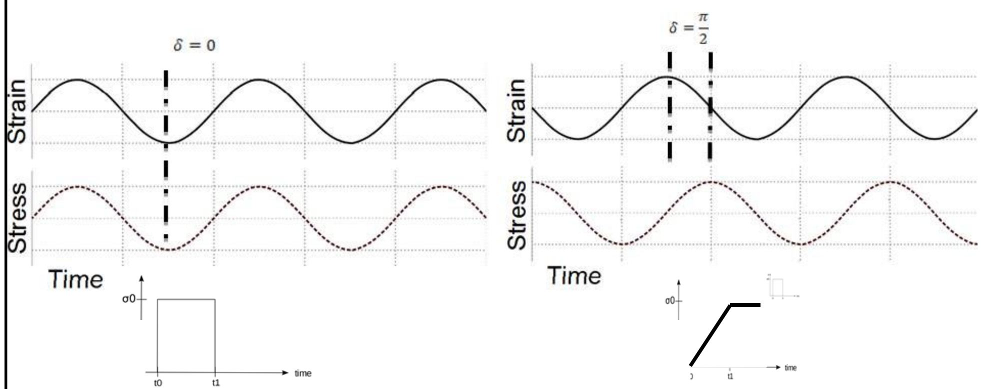
DMA

Elastic System

Viscous System



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DMA

DMA applies an oscillatory load to a sample to evaluate the strain response to stress.

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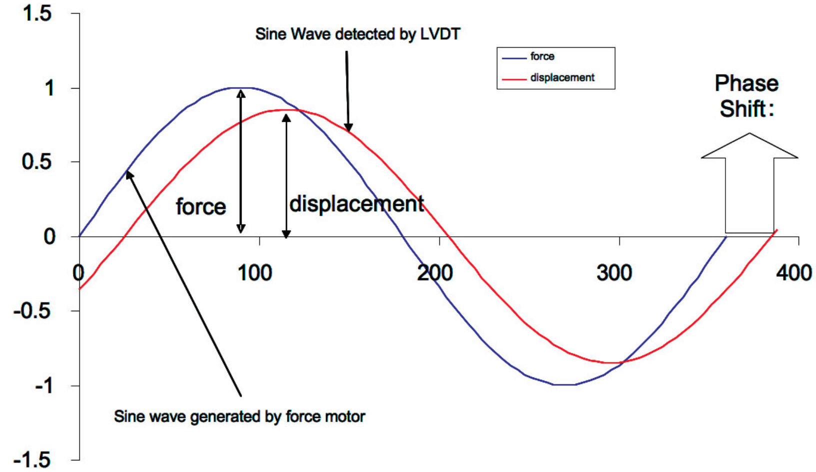
DMA

Viscoelastic System



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DMA

For a viscoelastic material, the stress and strain will be out of phase by some quantity known as the phase angle – common referred to as delta (δ).

Small phase angle – highly elastic
Large phase angle – highly viscous

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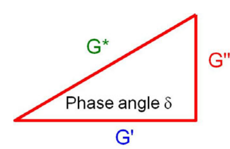
DMA

Complex response of the material is resolved into:

E’ elastic or storage modulus (tensile)
The ability of the material to store energy.

E’’ viscous or loss modulus (tensile)
The ability of the material to dissipate energy.

Tan δ E’’ / E’
Measure of material damping



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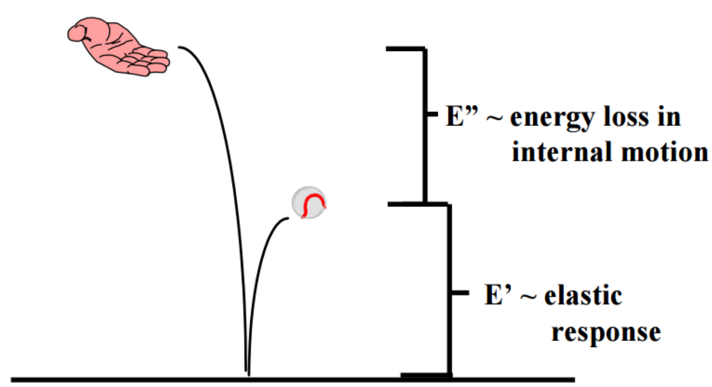
DMA

Why? Let’s bounce a ball.



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TEMPERATURE DEPENDENCY

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DMA Methodology

Temperature Sweep

- ASTM D4065
  - Step Method
  - Continuous Heating Method
- Shear
  - Uncured Crosslinkable Materials
  - Adhesives
  - Pastes
- Flex / Tensile - Consistency
  - Solid-state Performance

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DMA Methodology

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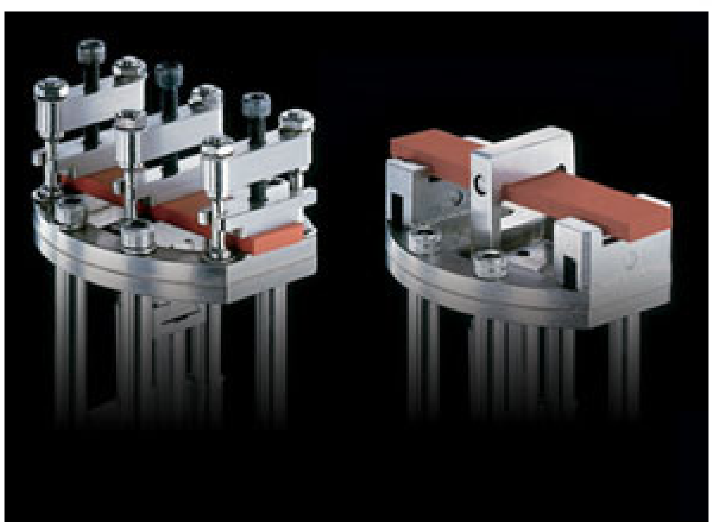
DMA Methodology



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Temperature Sweep

Storage Modulus

- Contribution of the elastic component in the polymer – store energy under conditions of stress
- Stiffness of the material – resistance to strain

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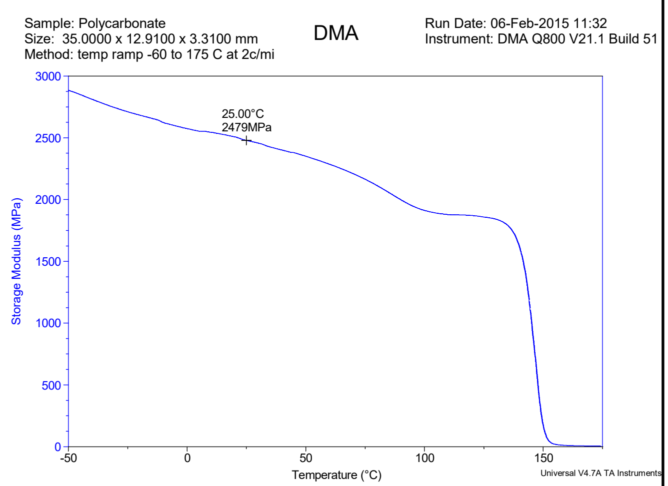
Modulus

- Modulus over a temperature range



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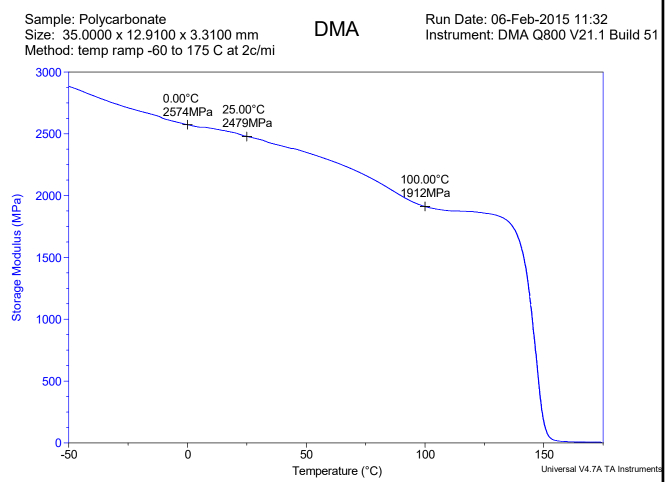
Modulus

- Modulus over a temperature range



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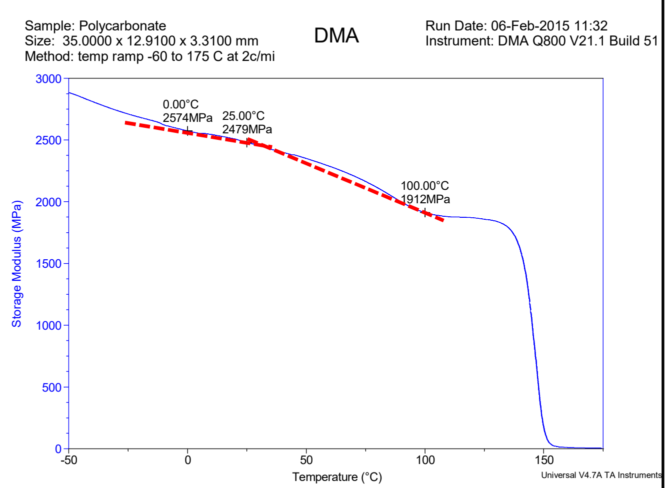
Modulus

- Modulus over a temperature range
- Superior to tensile testing



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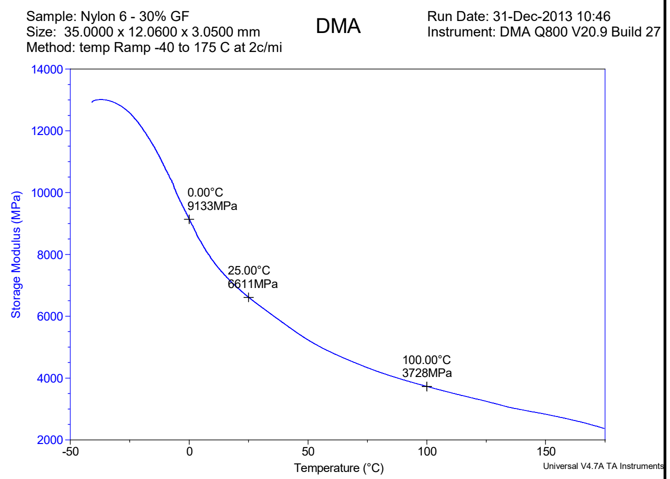
Modulus

- Modulus over a temperature range



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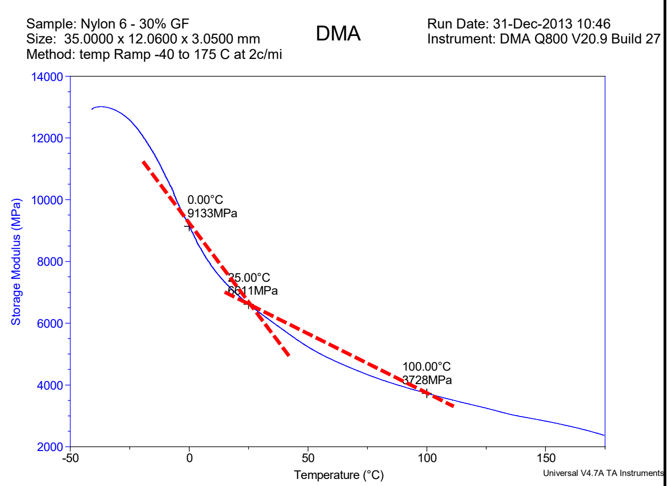
Modulus

- Modulus over a temperature range
- Superior to tensile testing



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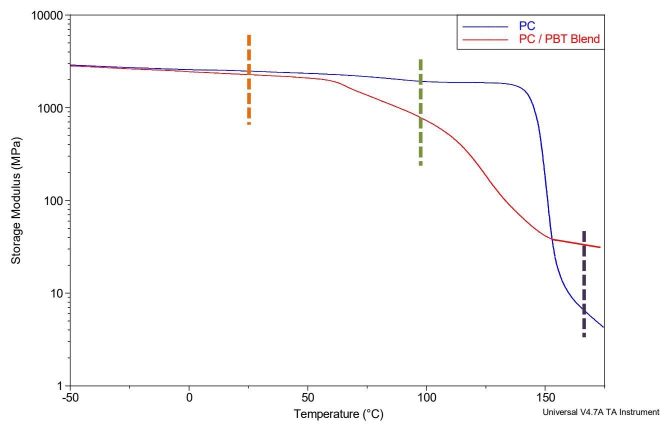
Modulus

- Comparison of two materials
- Modulus cross-over



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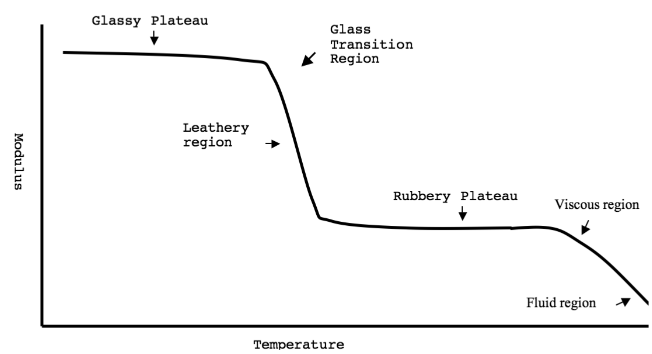
Molecular Structure

- Structural information



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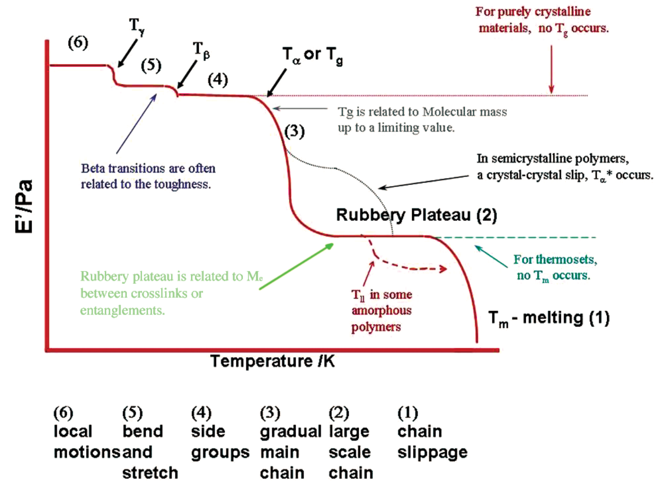
Molecular Structure

- Structural information



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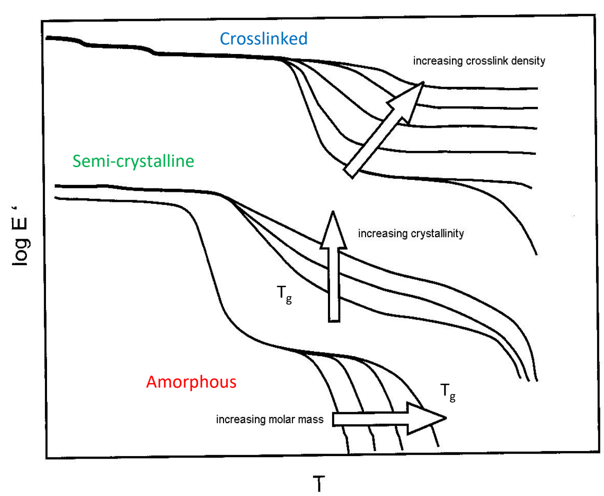
Molecular Structure

- Structural information



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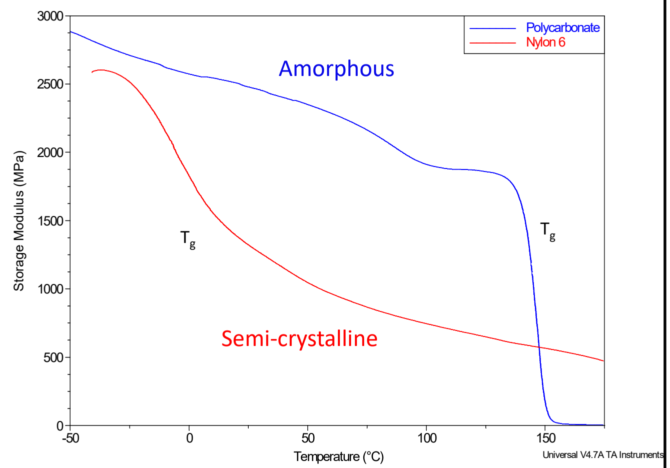
Molecular Structure

- Amorphous vs. Semi-crystalline – structural



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Viscous Properties

Loss Modulus

- Contribution of the viscous component in the polymer – flow under conditions of stress
- Creep / cold flow or stress relaxation
- Not the derivative of the storage modulus

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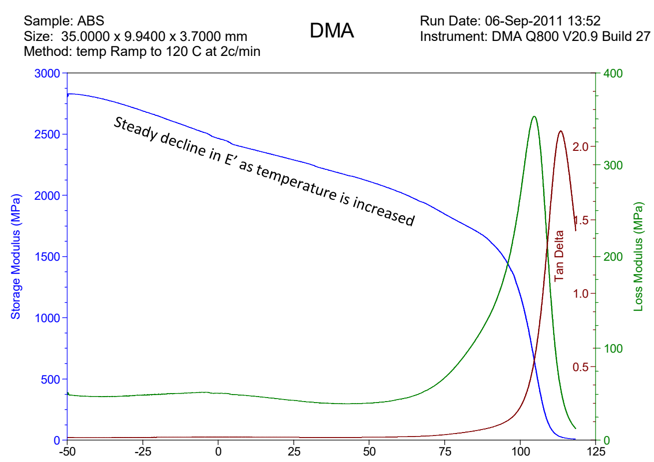
Viscous Properties

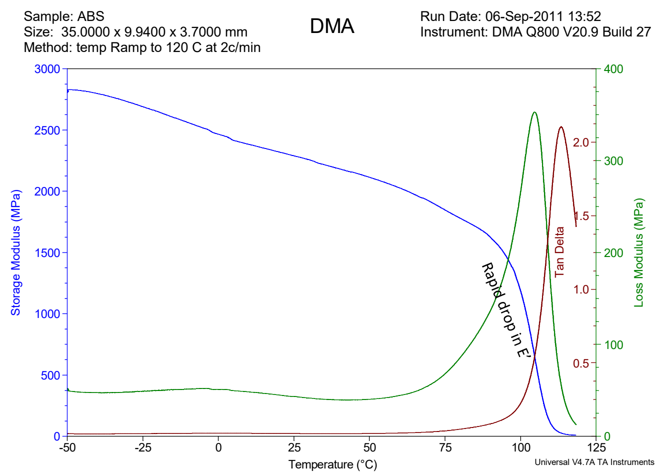
Tan Delta

- Comparison of polymers where storage and loss moduli are subject to change because of alterations on composition, geometry, or processing conditions
- Index of viscoelasticity
- Unitless / dimensionless

Glass Transition



Glass Transition



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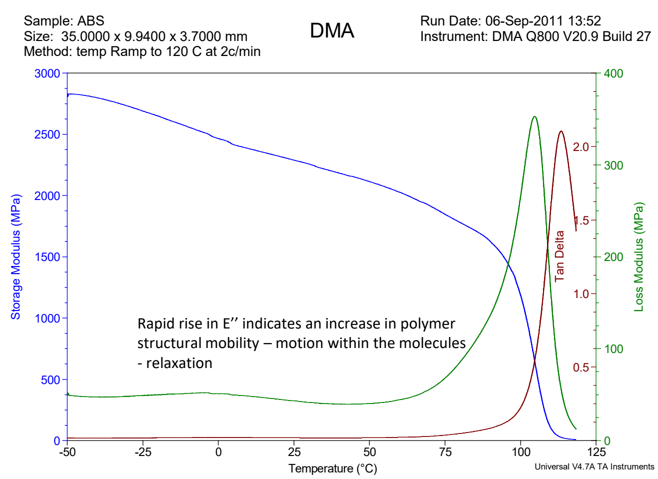
Glass Transition



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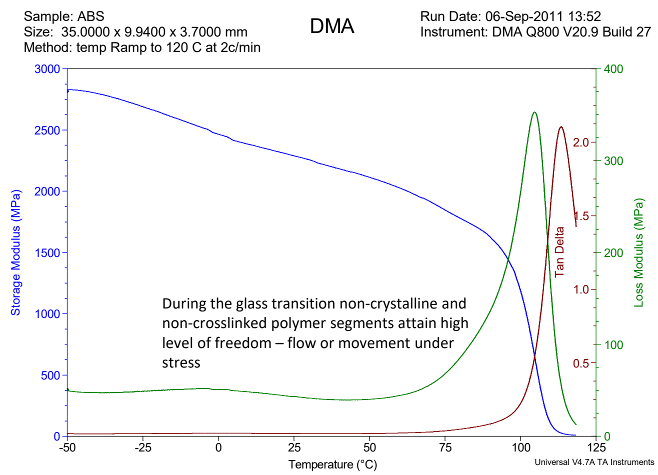
Glass Transition



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Glass Transition Temperature

- DMA provides best measurement technique – direct assessment of molecular changes within the material
- Onset of sharp reduction in storage modulus – practical effect of temperature on load-bearing capabilities
- Loss modulus peak temperature – corresponds well with other thermal analysis techniques, ASTM D 4065
- Tan Delta peak temperature - material has highest ratio of flow to storage – the point of highest realtive viscous contribution

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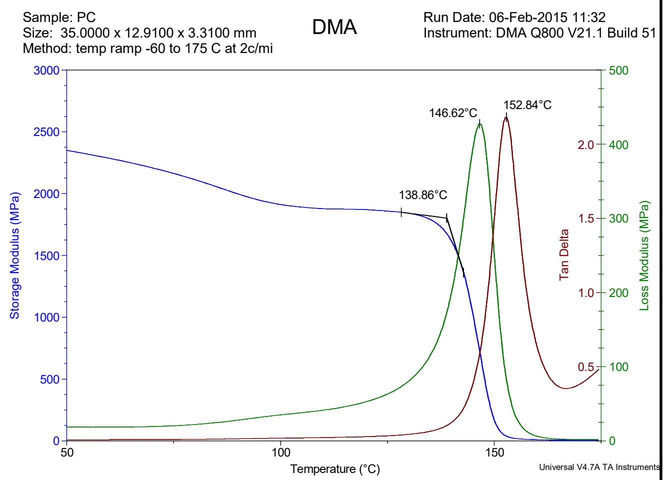
Glass Transition Temperature

- Polycarbonate
- Determining the glass transition temperature (Tg)



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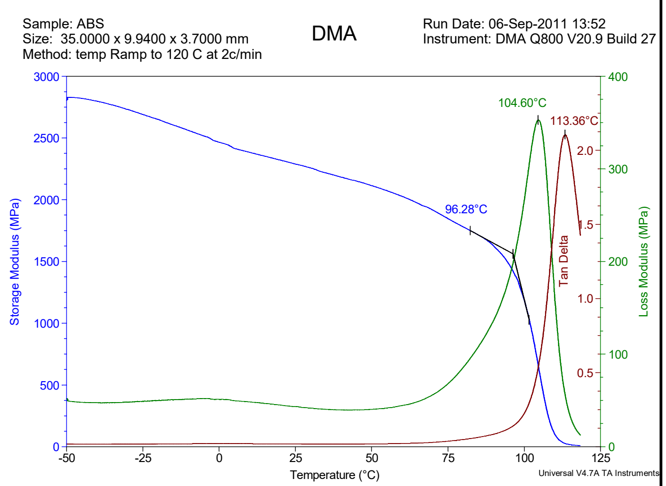
Glass Transition Temperature

- ABS
- Determining the glass transition temperature (Tg)



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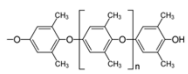
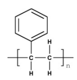
Alloy or Blend

- PPO / PS Resin Blend



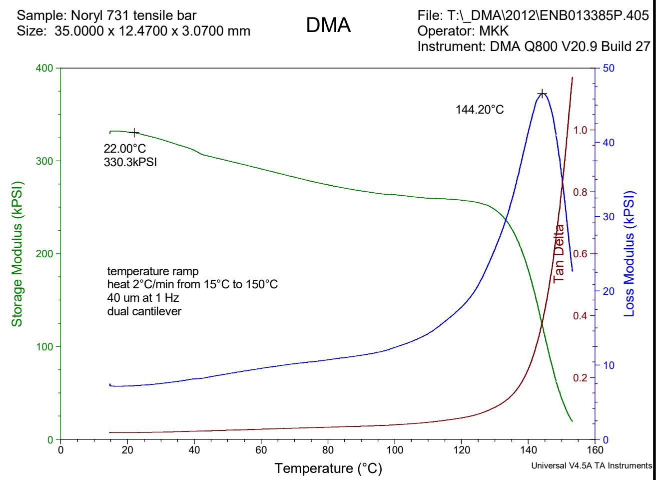
Tg 215°C



Tg 100°C

Resin Alloy: Single Tg 144 °C

Resin Blend: Two Tg



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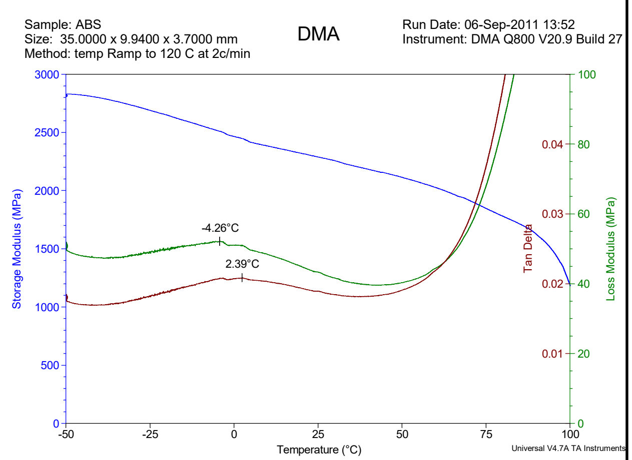
Impact Resistance

- Secondary transition – short range molecular mobility
- Energy absorption – impact properties



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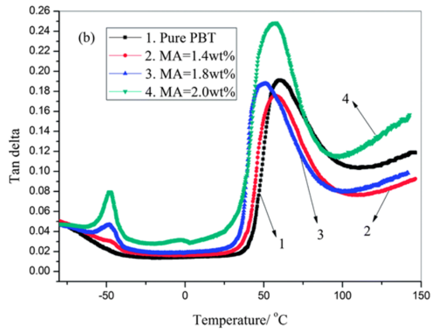
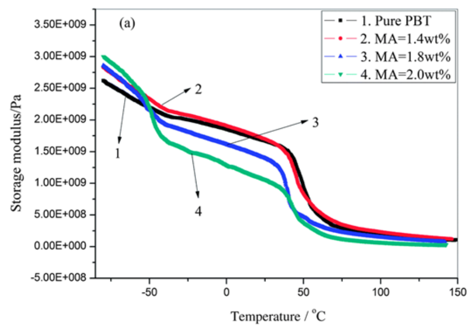
Impact Resistance

Impact Modifier Effectiveness





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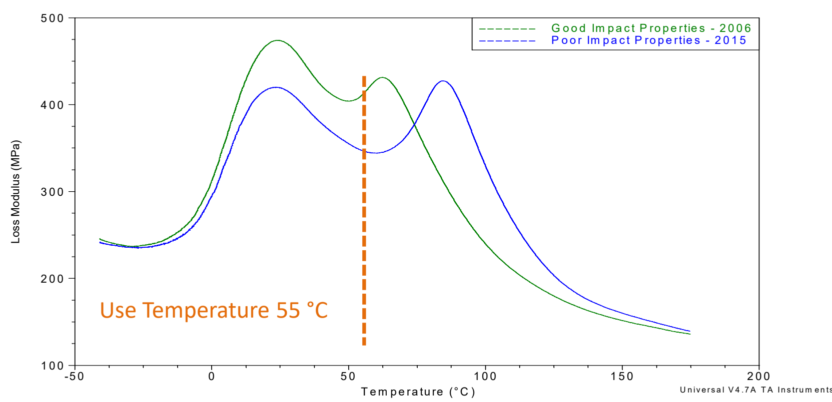
Impact Resistance

Aromatic Nylon Resin



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Solvent-induced Rearrangement

- Figure 4: As-molded PC – typical results. Rom Modulus at 25 °C - 340 kpsi.
- Figure 5: Altered behavior after the PC has been exposed to cyclohexanone – major ingredient in adhesive bonding agent. Modulus at 25 °C reduced to 315 kpsi. More importantly, the presence of a preliminary relaxation that occurs between 40°C and 80°C with a peak near 60°C. The elastic modulus reduction associated with this transition represents a 40% decline and is associated with a greater degree of molecular mobility within the polymer matrix as a result of contact with the cyclohexanone.

Figure 4. DMA scan for as-molded polycarbonate

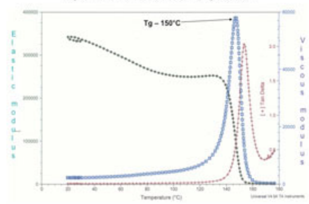
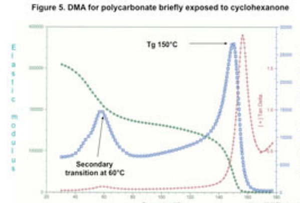


Figure 5. DMA for polycarbonate briefly exposed to cyclohexanone



Plastic Today
The Materials Analyst, Part 114: The challenge of bonding plastic components in medical devices
By Michael Sepe
Published: February 17th, 2010

TIME DEPENDENCY

Creep

Creep is…..

the tendency of a solid material to deform permanently under the influence of constant stress (tensile, compressive, shear, or flexural). It occurs as a function of time through extended exposure to levels of stress that are below the yield strength of the material.

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Creep

- Low to moderate forces exerted over an extended time → lower ductility. Can result in brittle fracture in normally ductile plastics
- Inherent viscoelastic nature of polymers leads to time dependency
- Prolonged static stresses lead to a decay in apparent modulus through localized molecular reorganization of polymer chains
- At stresses below the yield point molecular reorganization includes disentanglement as there is no opportunity for yielding

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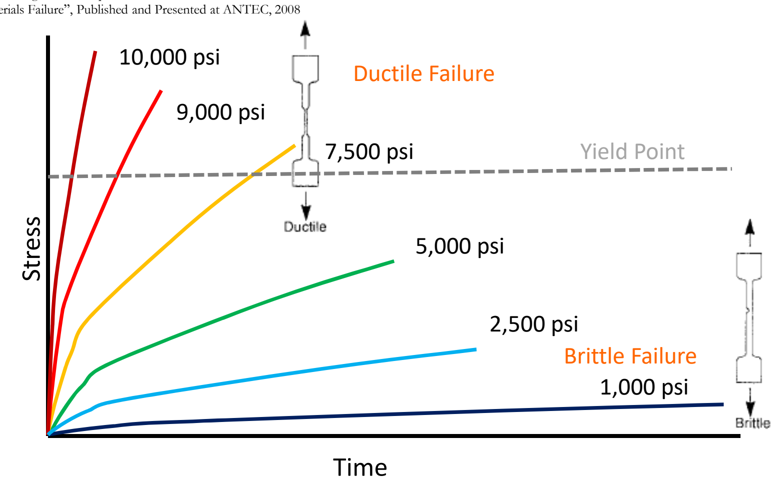
Creep

Source: "Understanding the Consequence of Ductile-to-Brittle Transitions in a Plastics Materials Failure", Published and Presented at ANTEC, 2008



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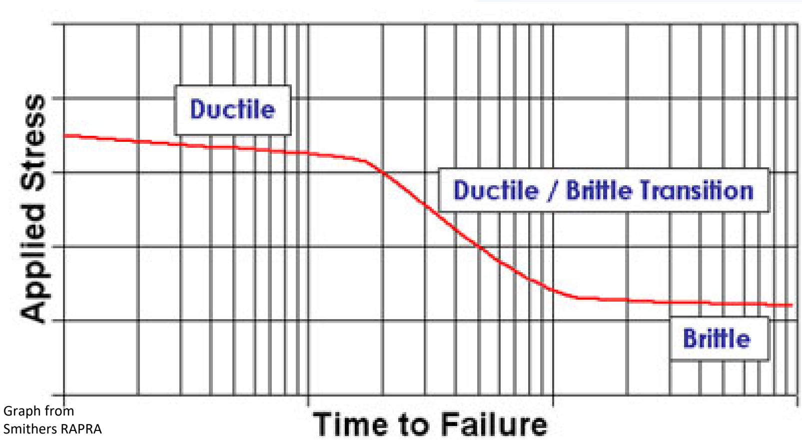
Creep



Graph from
Smithers RAPRA
http://www.rapra.net

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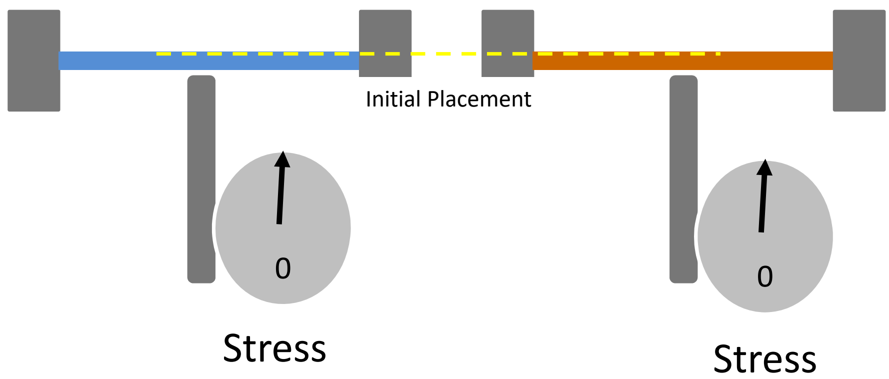
Creep



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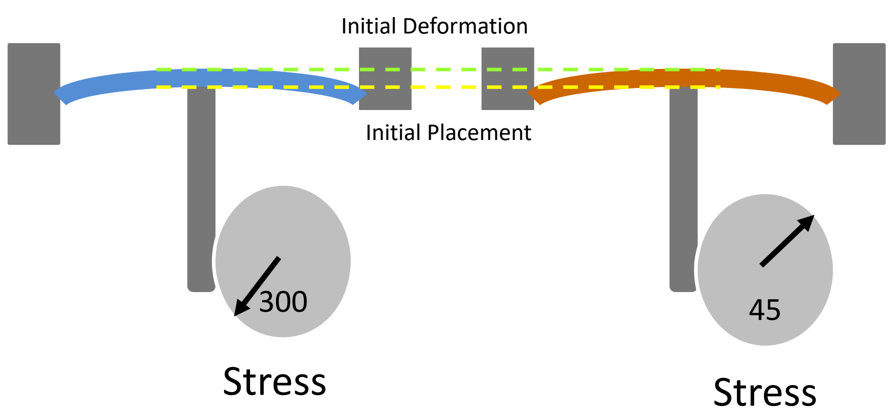
Creep



Day 1

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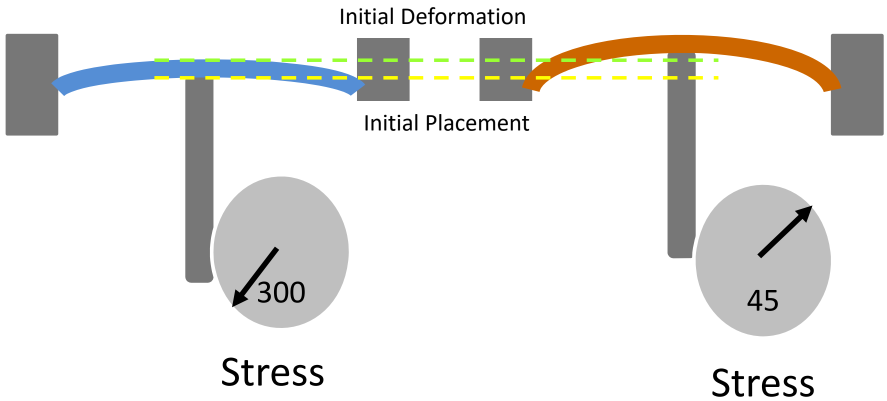
Creep



Day 10

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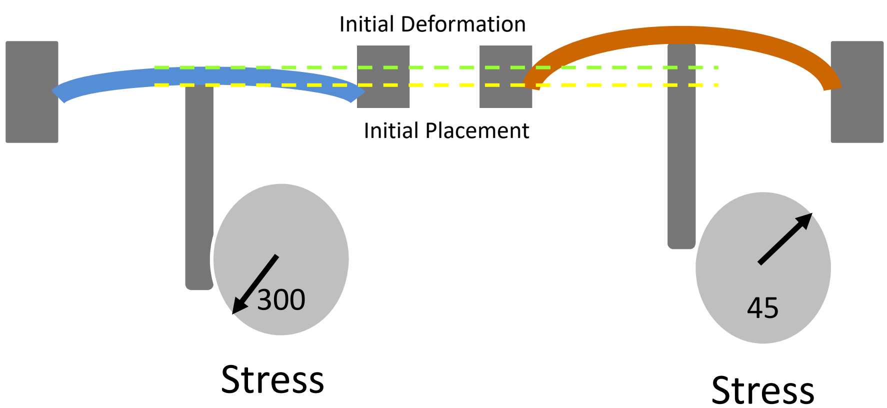
Creep



Day 100

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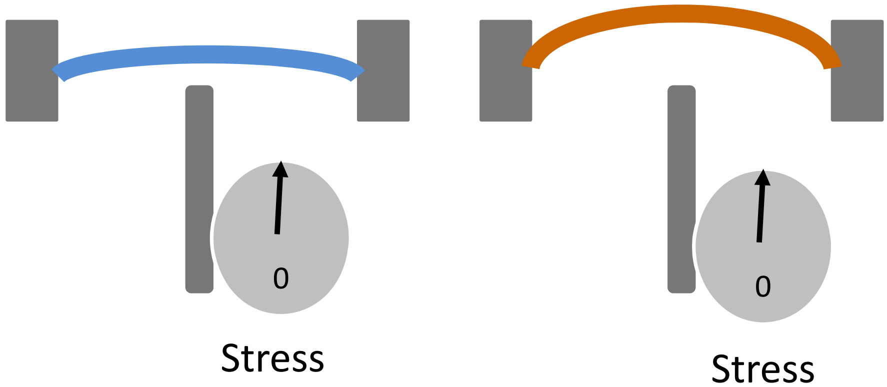
Creep



Day 100

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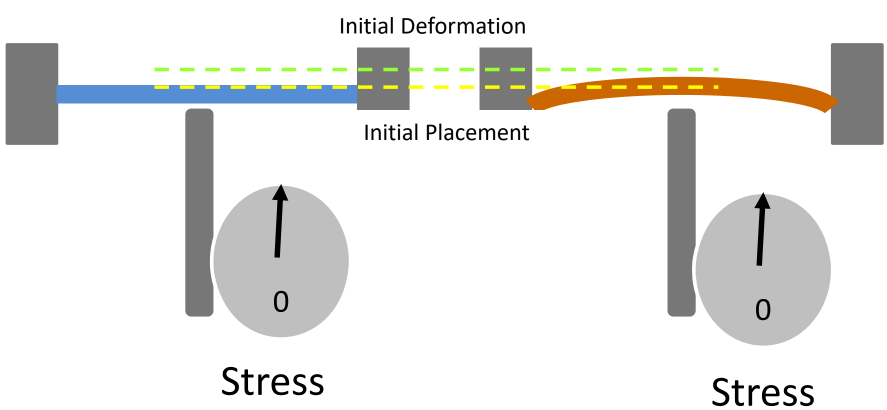
Creep



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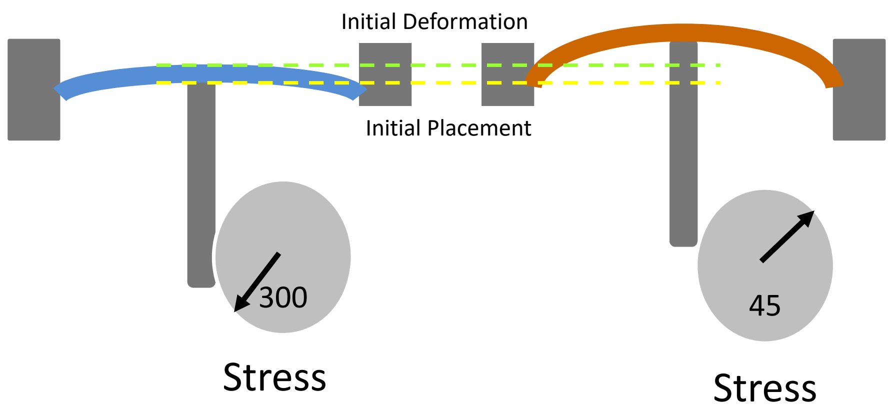
Creep Rupture



Day 100

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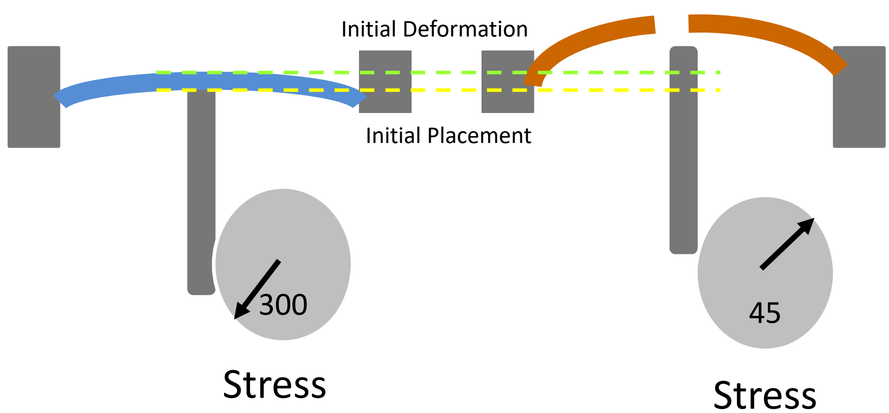
Creep Rupture



Day 1000 ??

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Viscoelasticity

- If a polymeric material is under constant stress or strain, a continual change in the apparent modulus is observed.
- The modulus (tangent modulus or Young's modulus) of a material is expressed as the applied stress divided by the resulting strain.

$$E \equiv \frac{\text{tensile stress}}{\text{tensile strain}} = \frac{\sigma}{\varepsilon}$$

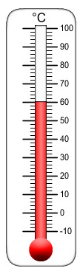
- The modulus value is the slope of the stress/strain curve in the linear region of the curve.
- Under constant stress this is observed in the form of an increasing level of strain, known as creep.
- Under constant strain this is observed in the form of an decreasing level of apparent stress, known as stress relaxation.

Viscoelasticity

- When a material is placed under a constant stress or strain, the response observed initially will be a function of the modulus of the material.
- If stress is continuously applied, strain will continually increase. Therefore, the calculated modulus at a point later in time will appear to have decreased. However, the stiffness of the material is not actually decreasing.
- Apparent modulus is the apparent stiffness of the material and is a mathematical artifact for describing the effect of a constant stress on the manner and the corresponding increase in strain over time.

Time and Temperature

Time and Temperature have the same effect on Plastics



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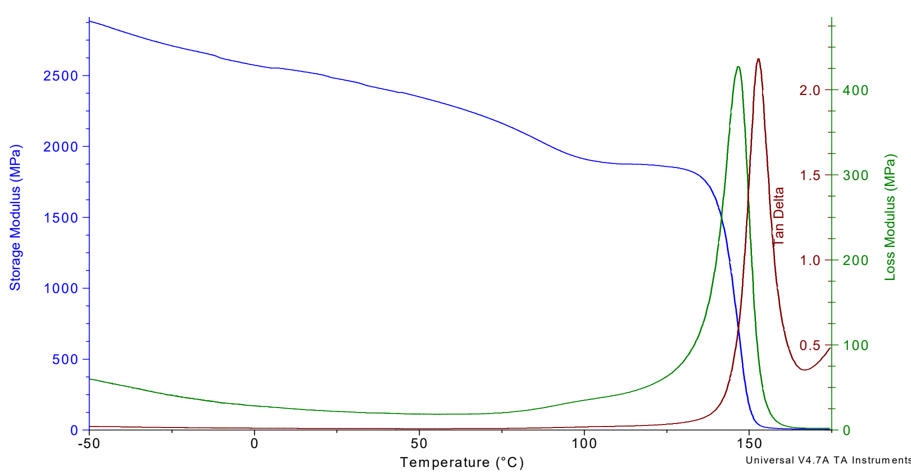
Time and Temperature



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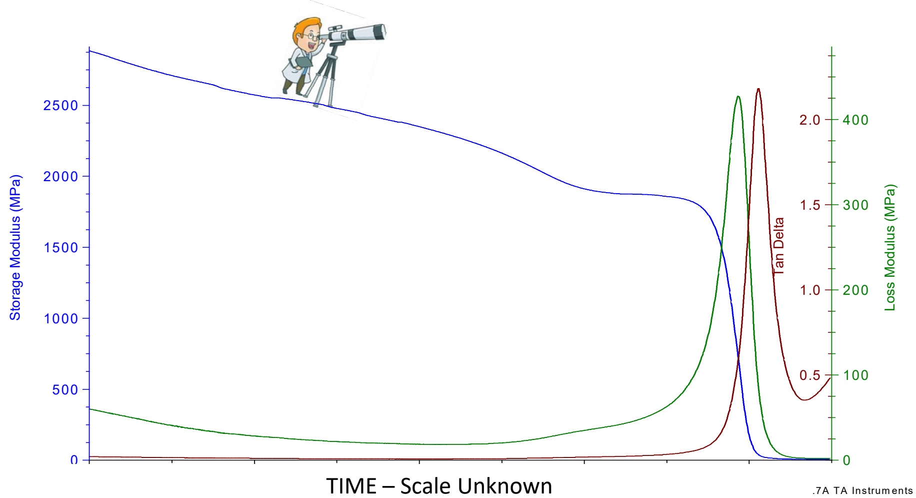
Time and Temperature



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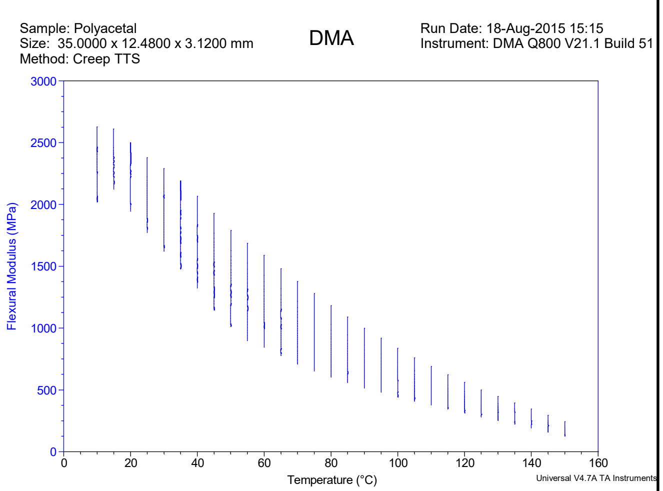
DMA-TTS

Time-Temperature Superposition

- Multiple fifteen-minute determinations for at isothermal conditions
- From 10 to 145°C increments of 5°C
- Evaluations conducted using a dual cantilever configuration
- Stress of 1.9 MPa



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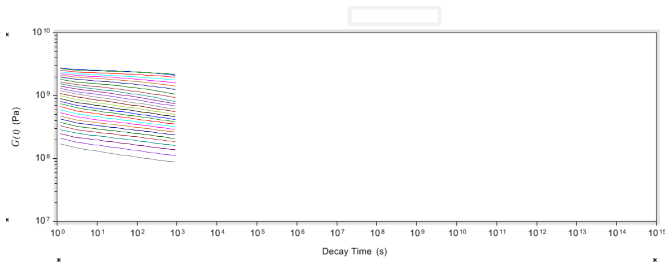
DMA-TTS

- Plots of modulus versus decay time for each temperature
- Select temperature of interest



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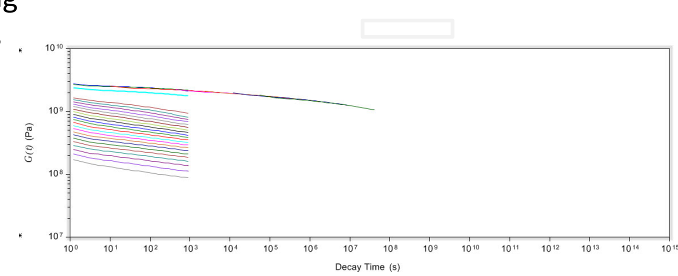
DMA-TTS

- Build master curve by shifting individual plots
- Extends time



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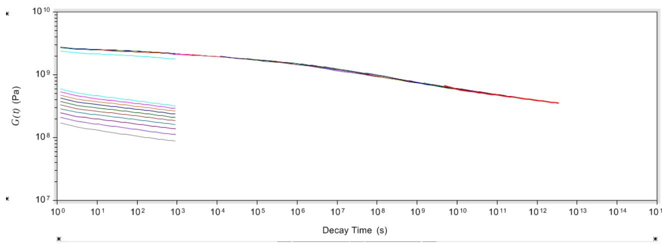
DMA-TTS

- Build master curve by shifting individual plots
- Extends time



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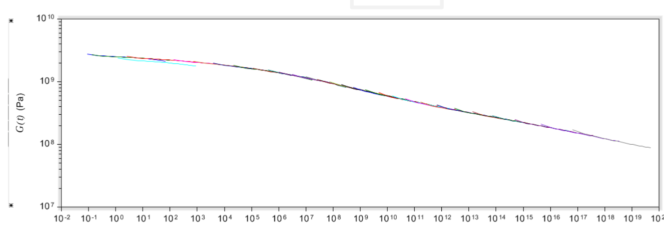
DMA-TTS

- Master curve represents apparent modulus over time



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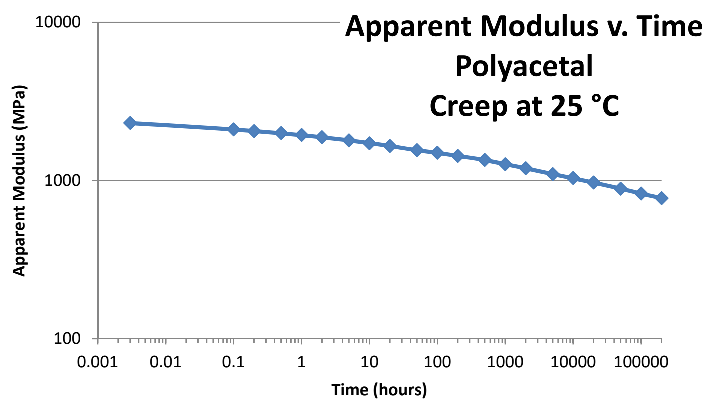
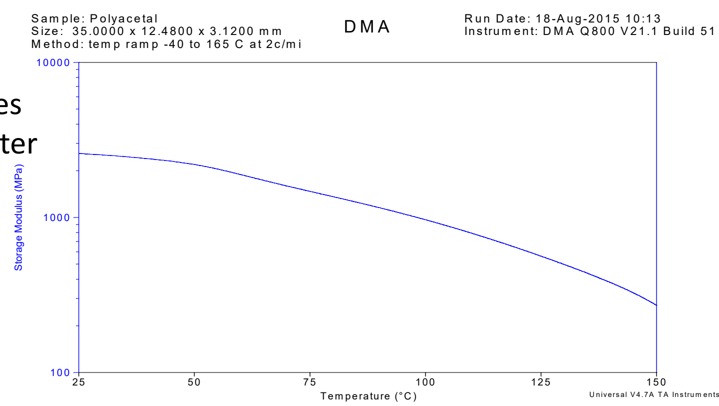
Creep Projection

- Master curve represents apparent modulus over time
- Log / log plot



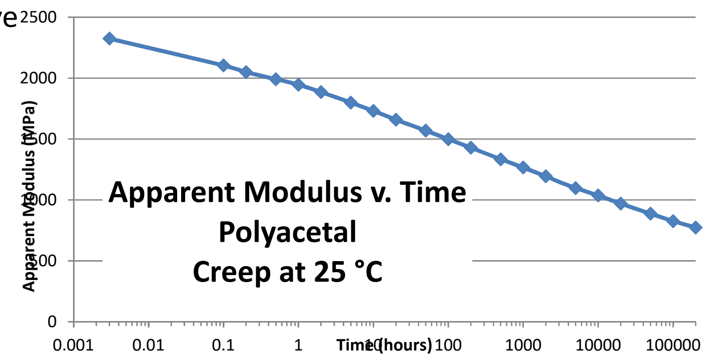
Creep Projection

- DMA temperature sweep matches well with master curve



Creep Projection

- Master curve as semi-log plot



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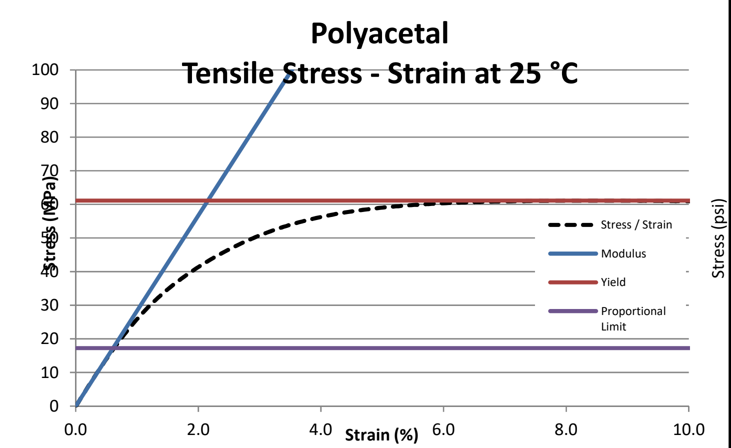
Creep Projection

- Tensile properties to establish modeling parameters



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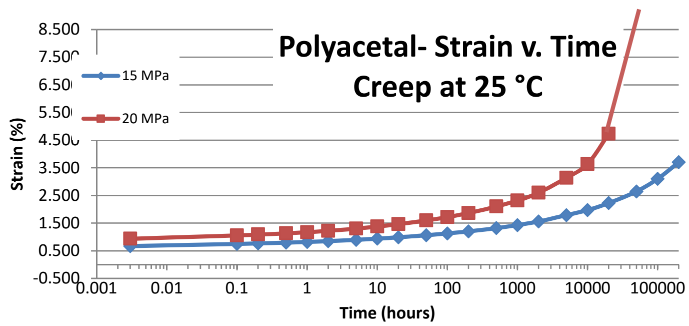
Creep Projection

- Use stress to determine strain over time
- Project time to cracking



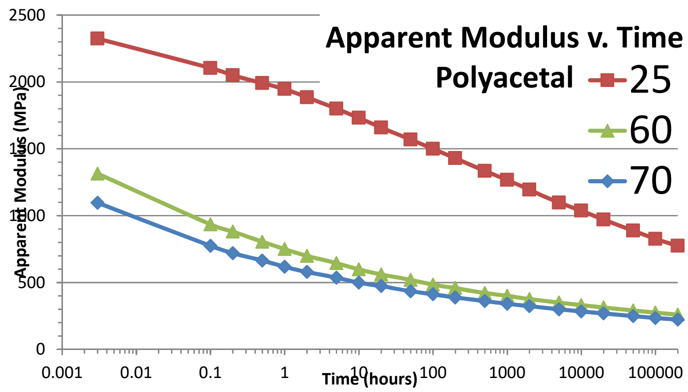
Projected time to cracking:
15 MPa: >200,000 hours (22.8 years)
20 MPa: 45,700 hours (5.2 years)

Creep Projection

Time hours	Max Working Stress Mpa
0.003	50
0.1	45
0.2	44
0.5	43
1	42
2	40
5	39
10	37
20	36
50	34
100	32
200	31
500	29
1000	27
2000	26
5000	24
10000	22
20000	21
50000	19
100000	18
200000	17

Creep Projection

- Able to model and compare multiple temperatures



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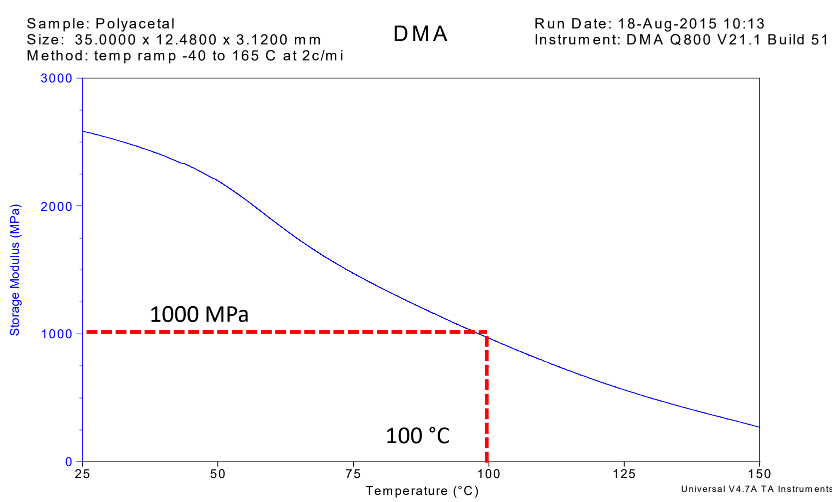
Time and Temperature



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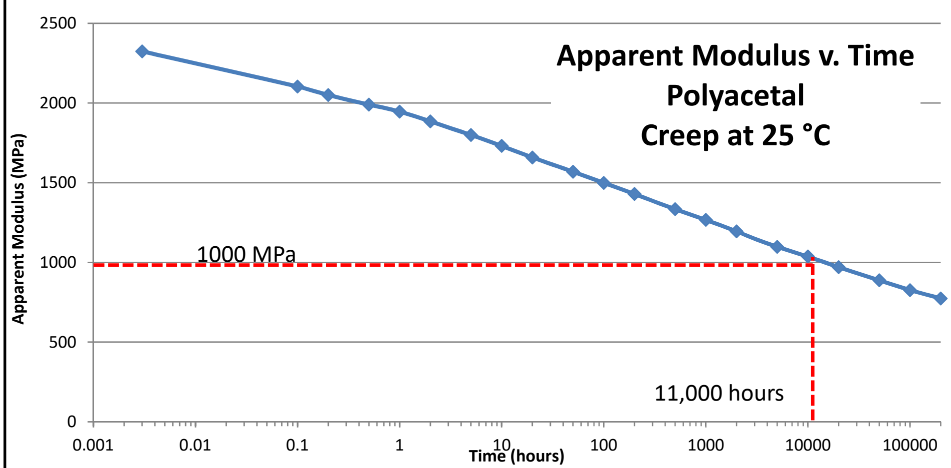
Time and Temperature



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Failure Example

- Failure of automotive aftermarket component
- Cracking observed in some parts after approx. 2 years, some longer
- Nylon 6/6 – 30% glass fiber reinforced
- Load bearing – predicted at 60 MPa, constant load application
- Not an under-hood application

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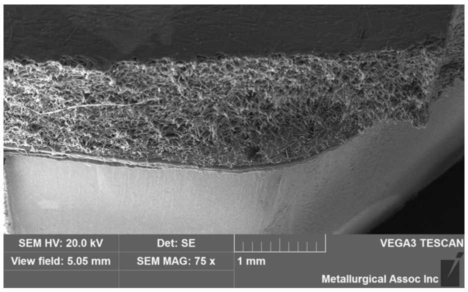
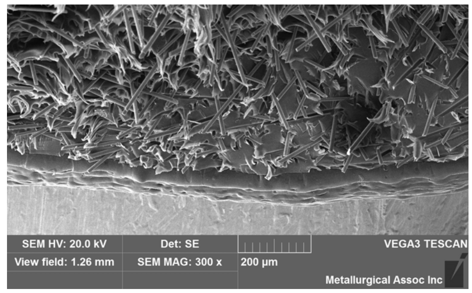
Failure Example – Part 1

- Partial cracking at design corner – adequate radius





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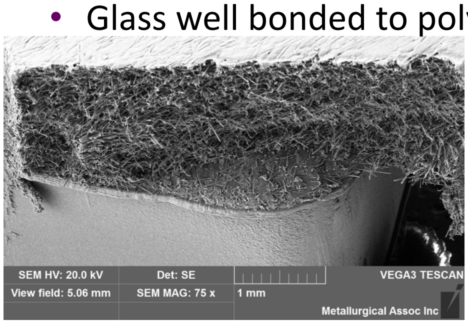
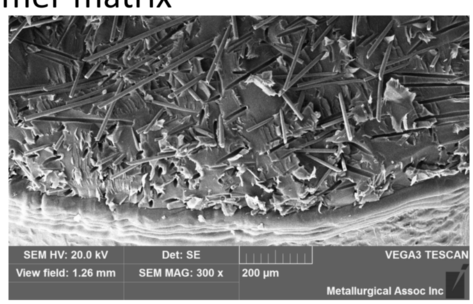
Failure Example – Part 2

- Glass oriented relatively randomly
- Glass well bonded to polymer matrix





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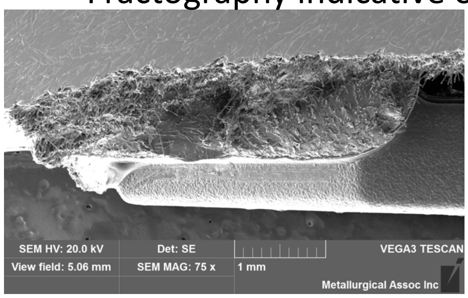
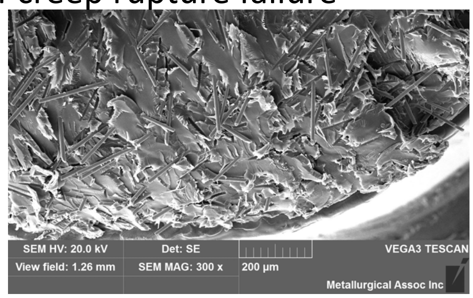
Failure Example – Part 3

- Similar fracture features on all parts examined
- Fractography indicative of creep rupture failure





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Creep Rupture Failure

- Consistent failure mechanism across all parts.
- The cracking lacked significant macro and micro ductility. However, substantial ductility was present within the laboratory fracture and at isolated locations outside of the crack origins. Indicated that the material was not inherently brittle. Ductile-to-brittle transition.
- Multiple individual cracks formed within the component at a design corner – adequate radius. The cracks subsequently coalesced and propagated.
- The fracture characteristics were indicative of stresses that exceeded the long-term strength of the material through a creep rupture mechanism.
- Material analysis as expected - 30% glass fiber reinforced nylon 6/6
  - No molecular degradation
  - No contamination
  - Good crystallinity
  - Proper glass content

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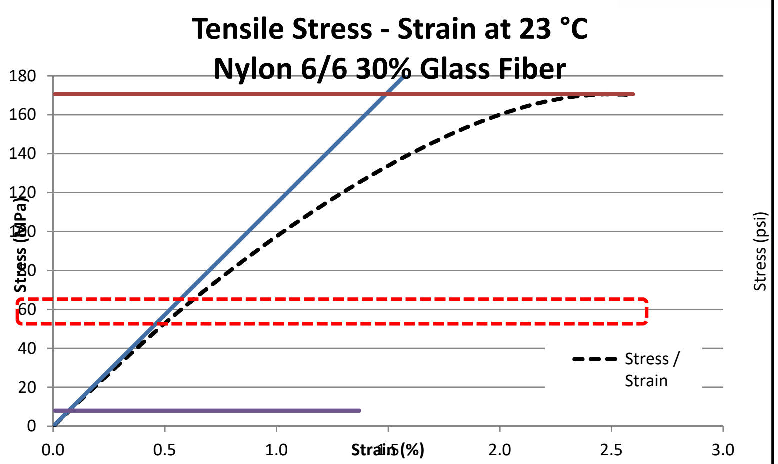
DMA-Creep Experiment

- Tensile strength: 172 MPa
- Predicted stress: 60 MPa



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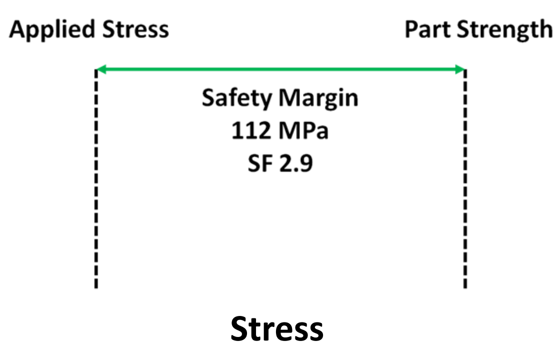
Anticipated Safety Margin



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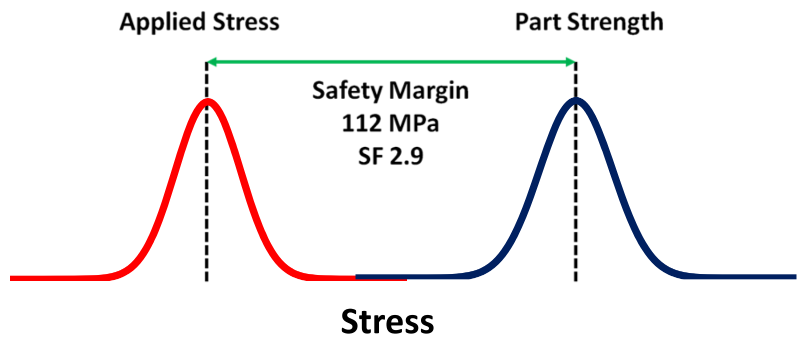
Actual Safety Margin – Time Zero



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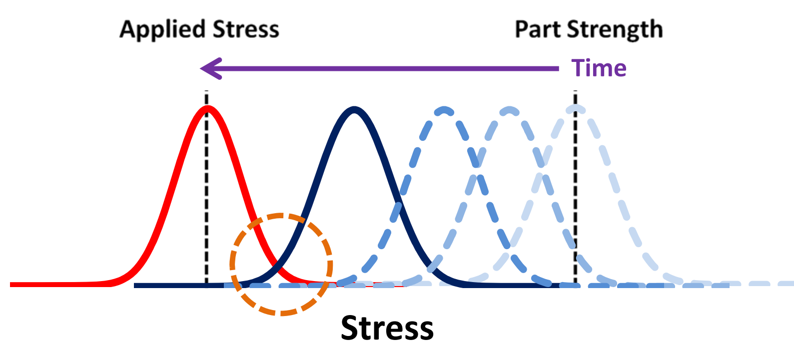
Reduction of Apparent Strength over Time



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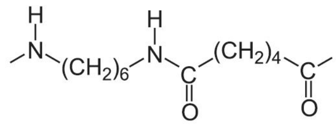
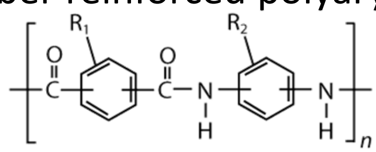
Proposed Material Substitution

- Replacement of 30% glass fiber reinforced nylon 6/6 with



30% glass fiber reinforced polyarylamide (PARA)



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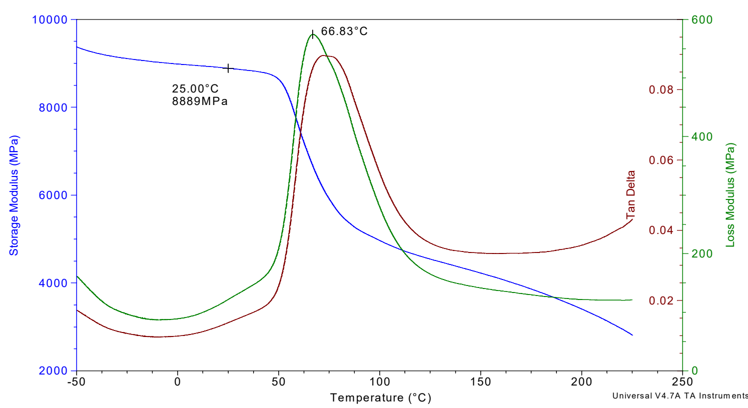
DMA-Nylon 6/6 30% Glass Fiber

- Modulus as expected
- Tg: 67 °C
- Looming loss of modulus



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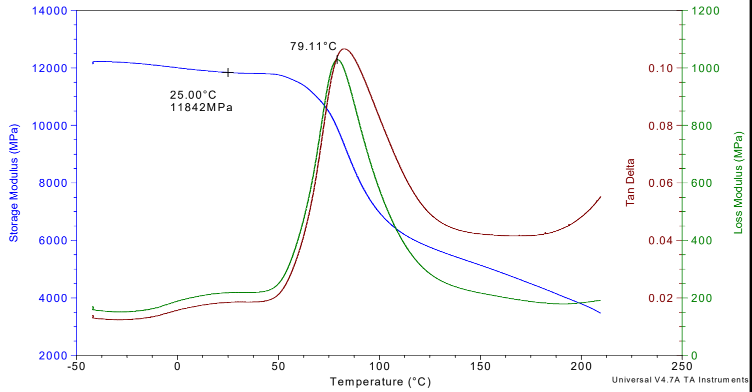
DMA-Polyarylamide 30% Glass Fiber

- Modulus as expected
- Tg: 79 °C (higher)
- Looming loss of modulus



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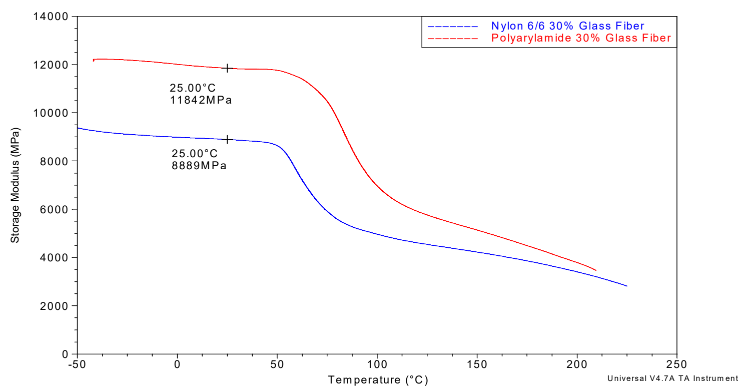
DMA-Comparison of Temperature Effects

- Higher initial modulus - structure
- Higher Tg - structure



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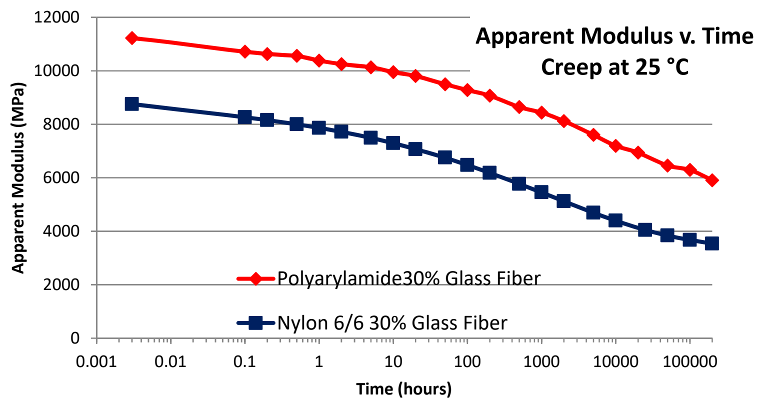
DMA-Creep Experiments

- Master curves of apparent modulus vs. time show differences
- Consistent with relative temperature sweeps



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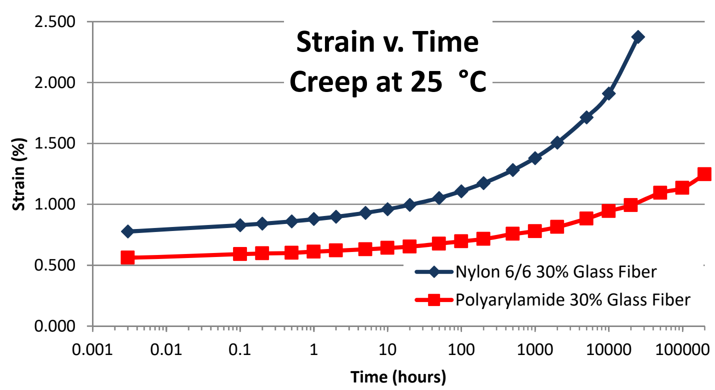
DMA-Creep Experiments

- Strain vs. time at 60MPa
- Cracking in nylon 6/6 projected for 25,000 hours (2.85 years)
- No cracking projected for polyarylamide in 200,000 hours (20+ years)



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Additional Testing

- Additional temperatures - above ambient most critical
- Glass fiber orientation – longitudinal and transverse
- Knit lines
- Moisture content – dry-as-molded and conditioned

Limitations

- Testing performed on "ideal" samples. Factors that decrease material strength will reduce the predicted time or stress to produce failure:
  - Molecular degradation from service or molding - oxidative or ultraviolet (UV) radiation
  - Environmental stress cracking
  - Transverse glass orientation
  - Inadequate molecular fusion from knit lines
- Models time to crack initiation. The actual time to catastrophic failure under the temperature and stress conditions modeled may be somewhat greater than those predicted by the model. for resins that exhibit an ultimate strain limit that is much greater than the yield strain.

THANK YOU

Questions?

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