An Introduction to Dynamic Mechanical Analysis

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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.
Outline

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

FUNDAMENTALS
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.

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.
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.

Elastic Response

• Typical in classical solid materials
• Stress $\rightarrow$ 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
Viscoelasticity

Elastic Response

- Stress \( \sigma \)
- Strain \( \varepsilon \)
- \( \tau = \gamma \cdot \eta \) (stress = strain rate x viscosity)
- Response to applied stress: energy is lost to the system, strain is not recoverable

Viscous Response

- Typical in classical fluids
- Stress \( \gamma \rightarrow \) 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
Viscoelasticity

Viscous Response

\[ \sigma(t) \quad \varepsilon(t) \quad t \]

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
Viscoelasticity

Viscoelastic Response

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

Spring and dashpot model

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

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

$\tan \delta \quad E'' / E'$

Measure of material damping

Why? Let’s bounce a ball.

$E'' \sim$ energy loss in internal motion

$E' \sim$ elastic response
TEMPERATURE DEPENDENCY

DMA Methodology

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

Sample: Polycarbonate
Size: 35.0000 x 12.9100 x 3.3100 mm
Method: temp ramp -60 to 175 C at 2c/mi
DMA
Run Date: 06-Feb-2015 11:32
Instrument: DMA Q800 V21.1 Build 51

Universal V4.7A TA Instruments
Modulus

- Modulus over a temperature range
- Superior to tensile testing
Modulus

• Modulus over a temperature range

• Superior to tensile testing
• Comparison of two materials
• Modulus cross-over

Modulus

- Storage Modulus (MPa)
- Temperature (°C)

PC vs. PC / PBT Blend

Molecular Structure

- Structural information

Glassy Plateau
Glass Transition Region
Leathery region
Rubbery Plateau
Viscous region
Fluid region
Temperature
Molecular Structure

**Structural information**

For purely amorphous materials, no $T_g$ occurs.

For semicrystalline polymers, a crystal-crystal slip, $T_{c^*}$ occurs.

For thermosets, no $T_g$ occurs.

In semicrystalline polymers, $a_{cr}$ occurs.

$T_g$ is related to Molecular mass up to a limiting value.

$T_m$ - melting

- Local motions and stretch
- Side groups
- Gradual main chain
- Large scale chain
- Slippage

- Bend
- Torsion
- Traction

$log\ E^*$

Crosslinked

Semi-crystalline

Amorphous
Molecular Structure

- Amorphous vs. Semi-crystalline – structural

![Molecular Structure Diagram](Image)

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
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

Sample: ABS
Size: 35.0000 x 9.9400 x 3.7000 mm
Method: temp Ramp to 120°C at 2°C/min

Steady decline in $E'$ as temperature is increased
Glass Transition

Rapid rise in $E''$ indicates an increase in polymer structural mobility – motion within the molecules - relaxation.
Glass Transition

During the glass transition non-crystalline and non-crosslinked polymer segments attain high level of freedom – flow or movement under stress.

- 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 relative viscous contribution
Glass Transition Temperature

- Polycarbonate
- Determining the glass transition temperature (Tg)

Sample: PC
Size: 35.0000 x 12.9100 x 3.3100 mm
Method: temp ramp -60 to 175 C at 2c/mi

DMA
Run Date: 06-Feb-2015 11:32
Instrument: DMA Q800 V21.1 Build 51

Tan Delta

Loss Modulus (MPa)

Storage Modulus (MPa)

Temperature (°C)

Sample: ABS
Size: 35.0000 x 9.9400 x 3.7000 mm
Method: temp Ramp to 120 C at 2c/min

DMA
Run Date: 06-Sep-2011 13:52
Instrument: DMA Q800 V20.9 Build 27

Tan Delta

Loss Modulus (MPa)

Storage Modulus (MPa)

Temperature (°C)
Alloy or Blend

- PPO / PS Resin Blend
  - Tg 215°C
  - Tg 100°C

Resin Alloy: Single Tg 144 °C
Resin Blend: Two Tg

Impact Resistance

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

Impact Modifier Effectiveness

Aromatic Nylon Resin

Use Temperature 55 °C
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.

TIME DEPENDENCY
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.

- 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
Creep

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

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

Creep

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

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Creep

Initial Placement

Stress

0

0

Metal Plastic Initial Placement Stress

Day 1

300

45

Stress

Creep

Initial Deformation

Initial Placement

Metal Plastic Initial Placement Stress

Day 1

300

45

Stress
Creep

**Initial Placement**

**Initial Deformation**

Stress

**Day 10**

**Initial Placement**

**Initial Deformation**

Stress

**Day 100**

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6/13/2019
Creep

Day 100

Stress

Initial Placement

Initial Deformation

6/13/2019
Creep Rupture

Initial Deformation

Initial Placement

Day 100

Stress

300

45

Creep Rupture

Initial Deformation

Initial Placement

Day 1000 ??

Stress

300

45

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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.

\[ E = \frac{\text{tensile stress}}{\text{tensile strain}} = \frac{\sigma}{\varepsilon} \]

- 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.

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
have the same effect
on Plastics

Time and Temperature

Universal V.7A TA Instruments

Storage Modulus (MPa)

Loss Modulus (MPa)

Temperature (°C)
**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
DMA-TTS

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

DMA-TTS

- Build master curve by shifting individual plots
- Extends time
DMA-TTS

- Build master curve by shifting individual plots
- Extends time

Master curve represents apparent modulus over time
Creep Projection

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

**Apparent Modulus v. Time**

Polyacetal Creep at 25 °C

- DMA temperature sweep matches well with master curve

Sample: Polyacetal
Size: 35.0000 x 12.4800 x 3.1200 mm
Method: temp ramp -40 to 165 °C at 2°C/min

**Sample Polyacetal**

**DMA**

Run Date: 18-Aug-2015 10:13
Instrument: DMA Q800 V21.1 Build 51

Universal V4.7A TA Instruments
Creep Projection

- Master curve as semi-log plot

Apparent Modulus v. Time
Polyacetal
Creep at 25 °C

• Tensile properties to establish modeling parameters

Polyacetal
Tensile Stress - Strain at 25 °C
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

- Able to model and compare multiple temperatures

![Apparent Modulus v. Time](image)

Time and Temperature

- Sample: Polyacetal
- Size: 35.0000 x 12.4800 x 3.1200 mm
- Method: temp ramp -40 to 165°C at 2°C/min

![Storage Modulus](image)
**Time and Temperature**

![Graph showing Apparent Modulus v. Time for Polyacetal creep at 25 °C.](image)

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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
Failure Example – Part 1

• Partial cracking at design corner – adequate radius

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

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
DMA-Creep Experiment

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

**Tensile Stress - Strain at 23 °C**
Nylon 6/6 30% Glass Fiber

- Stress / Strain

Intended Safety Margin

- Applied Stress
- Part Strength
- Safety Margin: 112 MPa
  - SF 2.9

Stress
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Actual Safety Margin – Time Zero

Applied Stress | Part Strength
---|---
Safety Margin
112 MPa
SF 2.9

Reduction of Apparent Strength over Time

Applied Stress | Part Strength
---|---
Time
Proposed Material Substitution

• Replacement of 30% glass fiber reinforced nylon 6/6 with 30% glass fiber reinforced polyarylamide (PARA)

DMA-Nylon 6/6 30% Glass Fiber

• Modulus as expected
• Tg: 67 °C
• Looming loss of modulus
DMA-Polyarylamide 30% Glass Fiber

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

DMA-Comparison of Temperature Effects

- Higher initial modulus - structure
- Higher Tg - structure
DMA-Creep Experiments

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

Apparent Modulus vs. Time Creep at 25 °C

- Polyarylamide 30% Glass Fiber
- Nylon 6/6 30% Glass Fiber

Strain vs. Time Creep at 25 °C

- 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)
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.
Questions?

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