Introduction to Dynamic Mechanical Testing for Rubbers and Elastomers

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Is DMA Thermal Analysis or Rheology?

Definitions

- **Thermal Analysis**
  - measurement as a *function of temperature or time*.

- **Rheology**
  - the science of *stress* and *deformation* of matter.

- **DMA** is the general name given to an instrument that mechanically *deforms a sample* and measures the sample response. The response to the deformation can be monitored as a *function of temperature or time*. 
What can be Studied with DMA?

• Composition
  ▪ Degree of cross-linking
  ▪ Comparison of crystallinity levels
  ▪ Molecular Orientation
  ▪ Effect of Filler

• Physical Properties
  ▪ Prediction of impact resistance
  ▪ Testing of creep or cold flow
  ▪ Stress relaxation behavior
  ▪ Cure behavior

• Viscoelastic Properties
  ▪ Storage Modulus
  ▪ Loss Modulus
  ▪ Tan Delta
  ▪ Glass Transition (T_g)
  ▪ Sub-T_g molecular motions (beta and gamma relaxations)

• Lifetime predictions using Time Temperature Superpositioning
What does a DMA do?

Measures the mechanical properties of a sample as it is deformed over a range of **stress, strain, time and temperature**

- Can either apply **Stress** (Force) and measure **Strain** (Displacement), or apply **Strain** and measure **Stress**

- Determines the **Modulus** of the material (**Stress / Strain**)  

- Controls the **Frequency** (Time) of the deformation to measure viscoelastic properties (**Storage Modulus, Loss Modulus, Tan Delta**)  

- **Temperature** controlled in heating, cooling, or isothermal modes  

- Modes of Deformation: Tension, Bending, Compression and Shear
DMA – Modes of Deformation

- Film/Fiber
- 3-Pt Bending
- Shear Sandwich
- Compression
- Cantilever
- Contact Lens
How does a DMA work?

• The DMA measures raw instrument signals
  ▪ Force, Displacement, Stiffness

• Dimensions of the sample are recorded
  ▪ Length, Width, Thickness

• Software calculates mechanical parameters
  ▪ Stress, Strain, Modulus

Stress (Pa) = \( \frac{\text{Force (N)}}{\text{Area (m}^2\text{)}} \)

Strain = \( \frac{\text{Deformation (m)}}{\text{Length (m)}} \)

Modulus (Pa) = \( \frac{\text{Stress (Pa)}}{\text{Strain}} \)
DMA Viscoelastic Parameters

The Modulus: Measure of materials overall resistance to deformation.

The Elastic (Storage) Modulus:
Measure of elasticity of material. The ability of the material to store energy.

The Viscous (loss) Modulus:
The ability of the material to dissipate energy. Energy lost as heat.

Tan Delta:
Measure of material damping - such as vibration or sound damping.

\[ E^* = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \]

\[ E' = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \cos \delta \]

\[ E'' = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \sin \delta \]

\[ \tan \delta = \left( \frac{E''}{E'} \right) \]
DMA Measurements

- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment.

\[ E = 2G(1 + \nu) \]

\( \nu \): Poisson’s ratio

Modulus: \( G', G'', G^* \)

Rectangular and cylindrical torsion

Modulus: \( E', E'', E^* \)

DMA 3-point bending and tension (Cantilever not shown)
Typical DMA Data

- Glassy Region: Very hard and rigid solid
- Transition Region: Stiff to Soft rubber
- Rubbery Plateau Region
- Terminal Region: Viscoelastic liquid

Log $E'$ and $E''$

Temperature/Time/Frequency$^{-1}$

Storage Modulus ($E'$ or $G'$)
Loss Modulus ($E''$ or $G''$)
Applications of DMA

• Understanding the Glass Transition
• Measuring Transitions in DMA
  ▪ Viscoelastic properties and the Glass Transition
  ▪ Testing considerations
  ▪ Secondary Transitions
• Material properties and the Glass Transition
  ▪ Molecular Structure, Composition, Environmental Effects
• Other Applications
The Glass Transition

• A transition over a range of temperature from a glassy state to a rubber state in an amorphous material

• Mechanical:
  ▪ Below the Glass Transition, the material is in a brittle, glassy state
  ▪ Above the Glass Transition, the material becomes soft and flexible, and a modulus decrease.

• Molecular:
  ▪ Below the Glass Transition, polymer chains are locked in place, without sufficient thermal energy to overcome the barrier for rotational or translational motion.
  ▪ At temperatures above the Glass Transition, there is molecular mobility, and chains can slide past each other
The Glass Transition

- “The glass transition is associated with the onset of long-range cooperative segmental mobility in the amorphous phase, in either an amorphous or semi-crystalline polymer.”
- Any factor that affects segmental mobility will affect $T_g$, including...
  - the nature of the *moving segment*,
  - chain stiffness or steric hindrance
  - the free volume available for segmental motion

Glass Transition $E'$ Onset, $E''$ Peak, and Tan $\delta$ Peak

- **Storage Modulus $E'$ Onset:**
  - Occurs at lowest temperature, relates to mechanical failure

- **Loss Modulus $E''$ Peak:**
  - Occurs at middle temperature
  - Related to the physical property changes
  - Reflects molecular processes - the temperature at the onset of segmental motion

- **Tan $\delta$ Peak:**
  - Occurs at highest temperature; Used historically in literature
  - Measure of the "leatherlike" midpoint between the glassy and rubbery states
  - Height and shape change systematically with amorphous content.

Glass Transition of Polycarbonate: $E'$, $E''$, Tan $\delta$

Sample: Polycarbonate

DMA File: C:\TA\Data\DMA\DMA-PC.001

Storage Modulus (MPa)

Loss Modulus (MPa)

Temperature (°C)

153°C
154°C
159°C

Tan Delta

Universal V4.5A
Elastomer Sample in Bending on DMA Q800

-34.36°C

Sample: Black Rubber
Size: 17.5000 x 12.9700 x 1.0700 mm
Method: Temperature Ramp
Comment: ULSP chiller, screen

File: BlackRubber_03_ULSP_screen_11Jul2013.001
Operator: EP
Run Date: 12-Jul-2013 06:39
Instrument: DMA Q800 V20.30 Build 50

Universal V4.5A TA Instruments
# Air Chiller System (ACS)

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Environmental System</th>
<th>Minimum Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMA Q800</td>
<td>Standard Furnace</td>
<td>ACS-2: -50°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ACS-3: -100 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ACS-3: -100 °C</td>
</tr>
<tr>
<td>DHR-1, 2 or 3</td>
<td>Environmental Test Chamber, ETC</td>
<td>ACS-2: -50 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ACS-3: -85 °C</td>
</tr>
</tbody>
</table>
Characterization of EPDM Rubber by DSC & DMA

DSC Conditions:
-100°C to 40°C
β=10°C/min.
Nitrogen Purge

DMA Conditions:
Single Cantilever Mode
-100°C to 50°C
β=5°C/min.
Freq=1Hz.
Amp=50μm
Frequency Sweep

The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude and temperature.

USES

- High and Low Rate (short and long time) modulus properties.
- Polymer melt processing (shear sandwich).
- Extend range with TTS
Frequency Sweep: Material Response

Terminal Region

Rubbery Plateau Region

Transition Region

Glassy Region

Log $E' (G')$ and $E'' (G'')$

Log Frequency (rad/s or Hz)

Storage Modulus ($E'$ or $G'$)

Loss Modulus ($E''$ or $G''$)
Molecular Structure - Crosslinking

- Linear polymers can be chemically or physically joined at points to other chains along their length to create a crosslinked structure.

- Chemically crosslinked systems are typically known as thermosetting polymers because the crosslinking agent is heat activated.

DMA Cure of Rubber

Rubber Vulcanization
Shear Sandwich Clamp
Frequency: 1 Hz
Amplitude: 20 mm

Full cure
Sheet Molding Compound Cure in Shear Sandwich

Frequency = 1Hz
Amplitude = 20 microns
Tire Compound: Effect of Curing Temperature

![Graph showing the effect of curing temperature on G' (MPa) over time. The graph includes curves for different curing temperatures: 145°C, 140°C, 135°C, 130°C, and 125°C. The time (min) axis is on the x-axis, and G' (MPa) is on the y-axis.](image-url)
Effect of Crosslinking

$M_c = MW$ between crosslinks

Temperature

$\log E'(G')$
Effect of Crosslinking on $T_g$

Increasing Crosslinking

$\downarrow$

Higher Density

$\downarrow$

Less Free Volume

$\downarrow$

Restricted molecular motion

$\downarrow$

More Energy needed

$\downarrow$

Higher Glass Transition Temperature

For low values of crosslink density, $T_g$ can be found to increase linearly with the number of crosslinks.

For high crosslink density, the $T_g$ is broad and not well defined.

Crystallinity, Molecular Weight, and Crosslinking

**Amorphous**
- 3 decade drop in modulus at $T_g$

**Crystalline**
- Increasing MW
- Increasing Crystallinity

**Cross-linked**

Temperature vs. Log Modulus graph:
- $T_m$
- $T_g$

Increasing MW and Crystallinity affect the modulus and temperature behavior.
Effect of Molecular Weight

- Molecular Weight has practically no effect on the modulus below $T_g$.
- $T_g$ and the drop in modulus are also nearly independent of MW if the MW is high enough to form entanglements.
- The rubbery plateau region above $T_g$ is strongly dependent on MW. In the absence of true crosslinks, the behavior is determined by entanglements.
- The length of the rubbery plateau ($T_g \leftrightarrow T_m$) is a function of the number of entanglements per molecule.

“The major effect of the crystallite in a sample is to act as a crosslink in the polymer matrix. This makes the polymer behave as though it was a crosslinked network, but as the crystallite anchoring points are thermally labile, they disintegrate as the temperature approaches the melting temperature, and the material undergoes a progressive change in structure until beyond $T_m$, when it is molten”

Summary

- DMA allows users to obtain mechanical properties over a wide range of temperatures
  - Example: Tires in a variety of environmental conditions

- Resolve weak glass transitions that may otherwise go undetected in other techniques

- Tan $\delta$ as a means to explain energy dissipation of rubbers and elastomers
Thank You

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