Dynamic Mechanical Analysis (DMA) Basics and Beyond

\[ \varepsilon^*_\omega = \sum \frac{\Delta \varepsilon_\beta}{1 + \mathbf{i} \omega \tau_\beta} \]

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Thermal Analysis
PerkinElmer Inc.
April 2000
The DMA lets you relate:

- Molecular structure
- Processing conditions
- Material behavior
- Product properties
DMA Structure in general

How the DMA works:

- Constant inputs and outputs function as in the TMA
- A sine wave current is added to the force coil
- The resultant sine wave voltage of the LVDT is compared to the sine wave force
- The amplitude of the LVDT is related to the storage modulus, $E'$ via the spring constant, $k$.
- The phase lag, $\delta$, is related to the $E''$ via the damping constant, $D$. 
Outstanding Flexibility 1: Multiple Geometries

- Compressive
- Extension
- Shear
- Flexure
- Parallel Plate
- Cup & Plate
- Tray & Plate
- Sintered Plates
- 3 pt. Bending
- 4 pt. Bending
- ASTM Flexure
- Dual Cantilever
- Single Cantilever
- Extension
- Shear Sandwich
- Coaxial Cylinder
- Paper Fold
Stress Causes Strain...

Cauchy or Engineering Strain

\[ \varepsilon = \frac{\Delta L}{L_o} \]

Henchy or True Strain

\[ \varepsilon = \ln \left( \frac{\Delta L}{L_o} \right) \]

Kinetic Theory of Rubber Strain

\[ \varepsilon = \frac{1}{3} \{ \frac{L}{L_o} - \left( \frac{L_o}{L} \right)^2 \} \]

Kirchhoff Strain

\[ \varepsilon = \frac{1}{2} \{ \left( \frac{L}{L_o} \right)^2 - 1 \} \]

Murnaghan Strain

\[ \varepsilon = \frac{1}{2} \{ 1 - \left( \frac{L_o}{L} \right)^2 \} \]

The different definitions of tensile strain become equivalent at very small deformations.
The Elastic Limit: Hooke’s Law

\[ \text{Strain increases with increasing Stress} \]

\[ \sigma = k \epsilon \]
Real vs... Hookean Stress-Strain Curves

Curve 1: DM&Creep Recovering Parallel Plate
File info: Dress90R Thu Apr 14 15:16:52 1994
Sample Height: 359 mm Creep Stress: 2600.0 mN
Recovery Stress: 1.0 mN
Dresser 90 Durameter

Limiting Modulus

Hookean

Behavior

Real behavior

σ
ε

Slope 164296.5 Pa/%
Slope 359171.32 Pa/%

Temp: 20.0 C
Time: 5.3 min

KPM
PERKIN-ELMER
7 Series Thermal Analysis System
Thu Apr 14 16:34:38 1994
The Viscous Limit: Newtonian Behavior

The speed at which the fluid flows through the holes (the strain rate) increases with stress!!!
Viscosity Effects

- Newtonian behavior is linear and the viscosity is independent of rate.
- Pseudoplastic fluids get thinner as shear increases.
- Dilatant Fluids increase their viscosity as shear rates increase.
- Plastic Fluids have a yield point with pseudoplastic behavior.
- Thixotropic and rheopectic fluids show viscosity-time nonlinear behavior. For example, the former shear thin and then reform its gel structure.
Polymers are Non-Newtonian Fluids!!!

- At low shear rates, the viscosity is controlled by MW. The material shows Newtonian behavior.
- Viscosity shows a linear dependence on rate above the $\eta_0$ region.
- At high rates, the material can no longer shear thin and a second plateau is reached.
Analyzing a Stress-Strain Curve

- Linear region
- Nonlinear region
- Yield point $(\varepsilon_y, \sigma_y)$
- Young's modulus $(E)$
- Failure $(\varepsilon_B, \sigma_B)$

The area under the curve to this line is the energy needed to break the material.

$$E = \frac{d\sigma}{d\varepsilon} = \frac{\sigma_L}{\varepsilon_L}$$
Under Continuous Loads: Creep Recovery

- Applying a constant load for long times and removing it from a sample.
- Allows one to see the distortion under constant load **and** also how well it recovers.
Creep is a fundamental engineering test.

- Creep is used as a basic test for design.
- By looking at both the creep and recovery parts of the curve, we can begin to examine how polymers relax.
Dynamic Stress

\[ \text{Force (dynamic)} \]

\[ \text{Stress} = FA \]

\[ \text{Phase angle} = \delta \]

\[ \text{Material response} \]

\[ \text{Amplitude} = k \]

\[ \text{Strain} = \frac{y}{y^0} \]
Why? Let’s bounce a ball.

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

$E' \sim$ elastic response
All this is calculated from $\delta$ and $k$:

- From $k$, we calculate $E'$ (storage modulus)
- From $\delta$, we calculate $E''$ (loss modulus)
- then:

  $\tan \delta = \frac{E''}{E'}$

  $E^* = E' + iE'' = \sqrt{(E')^2 + (E'')^2}$

  $G^* = \frac{E^*}{2(1+\nu)}$

  $\eta = \frac{3G^*}{\omega}$
To apply this to materials...

Dynamic Stress Scan

Since each part of the ramp has a sine wave stress associated with it, we get:

\[ \tan \delta, \quad E^*, \quad E', \quad E'' \]

\[ \eta \]

for each data point!!
For example, DSS Curves
Now, let’s induce temperature as a variable.

- We can heat the material under minimal load at a calibrated rate.
- This allows the material to change with temperature.
- These changes can be described in terms of free volume or relaxation times.
Thermomechanical Analysis as a starting Point.
TMA - It’s all free volume.
And it’s not just Tg.

(The traditional way to do heat set)
Time Temperature Scans at a Fixed Frequency

- hold frequency constant and vary temperature or time at temperature
- allows detection of transitions in material
- allows one to study cures
- most sensitive method for finding Tg
- can also get changes in dimension (TMA) while collecting DMA data
- Best probe of polymer relaxations as function of temperature
Idealized Multi-Event DMA Scan

- **Tm** - melting (1)
- **Rubbery Plateau** (2)
- **Tg** - glass transition (3) α
- **local bend side gradual large chain motions and groups main scale slippage**

Event Numbers:
- (1) Chain slippage
- (2) Large scale chain
- (3) Gradual main chain
- (4) Side groups stretch
- (5) Bend and stretch motions
- (6) Local bend side gradual large chain motions and groups main scale slippage
In more detail...

<table>
<thead>
<tr>
<th>Deformation</th>
<th>Molecular Motion</th>
<th>Unstrained State</th>
<th>Strained State</th>
</tr>
</thead>
<tbody>
<tr>
<td>F: Secondary Dispersion</td>
<td>F: Localized Motion</td>
<td>F: Increasing</td>
<td>F: Increasing</td>
</tr>
<tr>
<td>E: Hookean Behavior (gamma)</td>
<td>E: Bend &amp; Stretch Bonds</td>
<td>E: Main Chain Large Scale Mobility</td>
<td>E: Chain Slipping</td>
</tr>
<tr>
<td>D: Second Transition (beta)</td>
<td>D: Side Groups</td>
<td>D: Main Chain Gradual</td>
<td>D:</td>
</tr>
<tr>
<td>C: Primary Transition (alpha)</td>
<td>C:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B: Highly Visco Elastic (rubbery)</td>
<td>B:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A: Flow (melt)</td>
<td>A:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Crystalline Polymer
Crystal-crystal slip
Cross-linked

R. Seymour, 1971
Common changes show as:

- **MW**: 
- **MWD**: 
- **Crosslink Density**: 
- **Crystallinity**: 

- **$E'$**
- **$\tan \delta$**
Tg are easily seen, as in PET Film

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Storage Modulus (Pa × 10^9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>79.35</td>
<td>C</td>
</tr>
<tr>
<td>83.29</td>
<td>C</td>
</tr>
<tr>
<td>107.82</td>
<td>C</td>
</tr>
</tbody>
</table>

File info: demofilm
Frequency: 1.00 Hz
Amplitude: 21.949 μ
Tension: 110.000%

Curve 1: DMA
Temp/Time Scan in Extension
File info: demofilm
Frequency: 1.00 Hz
Amplitude: 21.949 μ
Tension: 110.000%

# pet film:demofilm
Onset 79.35 C
Onset 83.29 C
Onset 107.82 C

PERKIN-ELMER
7 Series Thermal
Analysis System
Sun Nov 26 21:02:11 1995
or in PP fishing line.

Sample prep can be minimal if only temperatures are needed.
Transitions are clearly seen in highly crosslinked samples

This $T_g$ is undetectable in the DSC !!!!!!
as well as in blends.
It’s not always so simple:

For example, crystal-crystals slips can cause $\alpha^*$ transitions
Higher Order Transitions affect toughness

Impact was good if $T_g/T_\beta$ was 3 or less.
...and also define operating range.
It can get complex...

File info: T2n4ptg Fri Jan 18 18:14:51 1991
Frequency: 1.00 Hz Dynamic Stress: 1.00e+07 Pa
Storage Modulus (Pa) L

# 1 NYLON MONOFILAMENT: T2n4ptg
Initial Run

Modulus (Pa)

Temperature (°C)

Stress Relief

Tg or Tα

B. Cassel
PERKIN-ELMER
7 Series Thermal
Sun Nov 26 20:59:14 1995

PerkinElmer instruments.
Curing of Thermosets

• can be studied at constant temperature or by a temperature ramp
• can get minimum viscosity, gelation point (time), vitrification point, and activation energies from DMA curve
• can adapt instrument to do simultaneous DEA-DMA to follow cure to completion
• cure studies are not limited to polymeric systems but include food products like cakes and cookies
Analysis of a Cure by DMA

E’-E” Crossover ~ gelation point
10^6 Pa ~ Solidity

vitrification point

Curing

Minimum Viscosity (time, length, temperature)
QC can often be done by simply fingerprinting the resin.

Note the different slopes and the different curve shapes.
Postcure studies allow process optimization:

Postcure time vs... Tg and E'

Temperature

0 hours 1 hour 2 hours 3 - 8 hours

Tan δ

0.0 0.5 1.0

150 175 200

Property

0 20 40 60 80 100 120 140 160 180 200

0 2 4 6 8

TIME IN HOURS

E'@50 (E9 PA)
E' ONSET
TAN D PEAK
TAN D ONSET

PerkinElmer™ instruments.
Frequency Scans

- hold temperature constant and vary frequency
- allows one to look at trends in material
- can estimate changes in MW and MWD
- looks at both tack-like and peel-like behavior
- can use data for Time Temperature Superposition to extend frequency range or predict age life.
Frequency determines the type of response

More solid like
More liquid like
Flow dominates
Elastic dominates
For example, two hot melt adhesives...

show affect of rate (peel vs.... tack)
Creep can look at distortion under load,
cyclic application of loads,

Differences can be seen in good and bad samples and get more apparent with several cycles. Here the bad material is not flowing enough to fill the pores and form a mechanical bond.
and with varying temperatures.
And you can tabulate this stuff graphically...

- The time to $1/e$ percent recovery is the relaxation.
- This is a measure of how quickly a material recovers.
  (There is a lot more to this subject.)
Stress Relaxation

• By exploiting the special controls of the DMA-7e, we can run stress relaxation experiments.
• These look at how the force change for a sample kept at a set distortion as a function of time or temperature.

Sample would be distorted to y length and held.
Don’t forget the DMA-7e also does **Stress Scans**

- can do either static or dynamic ramps
- static scans calculate Young’s modulus and stress-strain curves
- dynamic scans give material response to increasing oscillatory forces:
  - get complex viscosity and modulus for each data point
  - can look at changes in elasticity (E’) and lag (phase angle) with increasing stress
- Both methods are fast tests for QC applications after the material has been fully characterized by other DMA modes.
Specialized Testing is Possible...

The design of the DMA-7e makes it possible to do:

Time-Temperature Superposition (TTS)
DEA/DMA
Tests in Solution
Microscopic DMA
Photo DMA
DMA-?
PP fibers in solvent

![Graph showing force in mN vs temperature in °C for different solvents: xylene, air, water, and iso-octane.](image-url)
To Review, DMA ties together...

molecular structure
- Molecular weight
- MW Distribution
- Chain Branching
- Cross linking
- Entanglements
- Phases
- Crystallinity
- Free Volume
- Localized motion
- Relaxation Mechanisms

processing conditions
- Stress
- Strain
- Temperature
- Heat History
- Frequency
- Pressure
- Heat set

Material Behavior

product properties
- Dimensional Stability
- Impact properties
- Long term behavior
- Environmental resistance
- Temperature performance
- Adhesion
- Tack
- Peel

Material Behavior
Conclusions

• DMA allows you to preform a wide range of tests from sensitive probes of molecular structure to model studies.
• the DMA-7e allows operation as six different instruments to maximize flexibility.
• Data can be overlayed with DSC, TGA, TMA, and DTA for easier analysis.
References: Books

• Brostow et al., Failure of Plastics, Hanser, 1986.
• Gordon et al., Computer Programs for Rheologists, Hanser, 1995.
• Mascosko, Rheology, VCH, 1993.
• Matsouka, Relaxation Phenomena in Polymers, Hanser, 1993.