2.10: Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA), also known as forced oscillatory measurements and dynamic rheology, is a basic tool used to measure the viscoelastic properties of materials (particularly polymers). To do so, DMA instrument applies an oscillating force to a material and measures its response; from such experiments, the viscosity (the tendency to flow) and stiffness of the sample can be calculated. These viscoelastic properties can be related to temperature, time, or frequency. As a result, DMA can also provide information on the transitions of materials and characterize bulk properties that are important to material performance. DMA can be applied to determine the glass transition of polymers or the response of a material to application and removal of a load, as a few common examples. The usefulness of DMA comes from its ability to mimic operating conditions of the material, which allows researchers to predict how the material will perform.

A Brief History

Oscillatory experiments have appeared in published literature since the early 1900s and began with rudimentary experimental setups to analyze the deformation of metals. In an initial study, the material in question was hung from a support, and torsional strain was applied using a turntable. Early instruments of the 1950s from manufacturers Weissenberg and Rheovibron exclusively measured torsional stress, where force is applied in a twisting motion.

Due to its usefulness in determining polymer molecular structure and stiffness, DMA became more popular in parallel with the increasing research on polymers. The method became integral in the analysis of polymer properties by 1961. In 1966, the revolutionary torsional braid analysis was developed; because this technique used a fine glass substrate imbued with the material of analysis, scientists were no longer limited to materials that could provide their own support. Using torsional braid analysis, the transition temperatures of polymers could be determined through temperature programming. Within two decades, commercial instruments became more accessible, and the technique became less specialized. In the early 1980s, one of the first DMAs using axial geometries (linear rather than torsional force) was introduced.

Since the 1980s, DMA has become much more user-friendly, faster, and less costly due to competition between vendors. Additionally, the developments in computer technology have allowed easier and more efficient data processing. Today, DMA is offered by most vendors, and the modern instrument is detailed in the *Instrumentation*section.

Basic Principles of DMA

DMA is based on two important concepts of stress and strain. Stress (σ) provides a measure of force (*F*) applied to area (*A*), 2.10.1 .

$$\sigma = F/A \tag{2.10.1}$$

Stress to a material causes strain (γ), the deformation of the sample. Strain can be calculated by dividing the change in sample dimensions (Δ*Y*) by the sample's original dimensions (*Y*) (2.10.2). This value is often given as a percentage of strain.

$$\gamma = \Delta Y/Y \tag{2.10.2}$$

The modulus (*E*), a measure of stiffness, can be calculated from the slope of the stress-strain plot, Figure 2.10.1, as displayed in \label{3} . This modulus is dependent on temperature and applied stress. The change of this modulus as a function of a specified variable is key to DMA and determination of viscoelastic properties. Viscoelastic materials such as polymers display both elastic properties characteristic of solid materials and viscous properties characteristic of liquids; as a result, the viscoelastic properties are often a compromise between the two extremes. Ideal elastic properties can be related to Hooke's spring, while viscous behavior is often modeled using a dashpot, or a motion-resisting damper.

$$E = \sigma/y \tag{2.10.3}$$

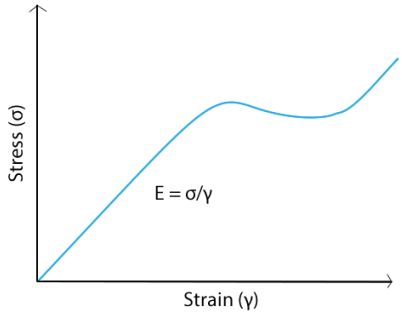

Figure 2.10.1 An example of a typical stress versus strain plot.

Creep-recovery

Creep-recovery testing is not a true dynamic analysis because the applied stress or strain is held constant; however, most modern DMA instruments have the ability to run this analysis. Creep-recovery tests the deformation of a material that occurs when load applied and removed. In the "creep" portion of this analysis, the material is placed under immediate, constant stress until the sample equilibrates. "Recovery" then measures the stress relaxation after the stress is removed. The stress and strain are measured as functions of time. From this method of analysis, equilibrium values for viscosity, modulus, and compliance (willingness of materials to deform; inverse of modulus) can be determined; however, such calculations are beyond the scope of this review.

Creep-recovery tests are useful in testing materials under anticipated operation conditions and long test times. As an example, multiple creep-recovery cycles can be applied to a sample to determine the behavior and change in properties of a material after several cycles of stress.

Dynamic Testing

DMA instruments apply sinusoidally oscillating stress to samples and causes sinusoidal deformation. The relationship between the oscillating stress and strain becomes important in determining viscoelastic properties of the material. To begin, the stress applied can be described by a sine function where σ_o is the maximum stress applied, ω is the frequency of applied stress, and t is time. Stress and strain can be expressed with the following 2.10.4.

$$\sigma = \sigma_0 sin(\omega t + \delta);\ y = y_0 cos(\omega t) \tag{2.10.4}$$

The strain of a system undergoing sinusoidally oscillating stress is also sinuisoidal, but the phase difference between strain and stress is entirely dependent on the balance between viscous and elastic properties of the material in question. For ideal elastic systems, the strain and stress are completely in phase, and the phase angle (δ) is equal to 0. For viscous systems, the applied stress leads the strain by 90°. The phase angle of viscoelastic materials is somewhere in between (Figure 2.10.2).

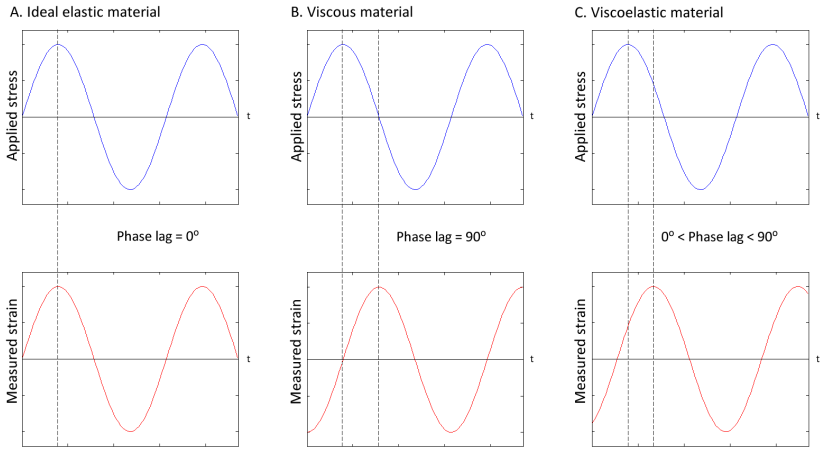

Figure 2.10.2 Applied sinusoidal stress versus time (above) aligned with measured stress versus time (below). (a) The applied stress and measured strain are in phase for an ideal elastic material. (b) The stress and strain are 90° out of phase for a purely viscous material. (c) Viscoelastic materials have a phase lag less than 90°. Image adapted from M. Sepe, *Dynamic Mechanical Analysis for Plastics Engineering*, Plastics Design Library: Norwich, NY (1998).

In essence, the phase angle between the stress and strain tells us a great deal about the viscoelasticity of the material. For one, a small phase angle indicates that the material is highly elastic; a large phase angle indicates the material is highly viscous. Furthermore, separating the properties of modulus, viscosity, compliance, or strain into two separate terms allows the analysis of the elasticity or the viscosity of a material. The elastic response of the material is analogous to storage of energy in a spring, while the viscosity of material can be thought of as the source of energy loss.

A few key viscoelastic terms can be calculated from dynamic analysis; their equations and significance are detailed in Table 2.10.1.

Table 2.10.1 Key viscoelastic terms that can be calculated with DMA.

Term	Equation	Significance
Complex modulus (E^*)	$E^* = E' + iE''$	Overall modulus representing stiffness of material; combined elastic and viscous components
Elastic modulus (E')	$E' = (\sigma_o/\gamma_o)cos\delta$	Storage modulus; measures stored energy and represents elastic portion
Viscous modulus (E'')	$E'' = (\sigma_o/\gamma_o)sin\delta$	Loss modulus; contribution of viscous component on polymer that flows under stress
Loss tangent ($tan\delta$)	$Tan\delta = E''/E'$	Damping or index of viscoelasticity; compares viscous and elastic moduli

Types of Dynamic Experiments

A temperature sweep is the most common DMA test used on solid materials. In this experiment, the frequency and amplitude of oscillating stress is held constant while the temperature is increased. The temperature can be raised in a stepwise fashion, where the sample temperature is increased by larger intervals (e.g., 5 ^oC) and allowed to equilibrate before measurements are taken. Continuous heating routines can also be used (1-2 ^oC/minute). Typically, the results of temperature sweeps are displayed as storage and loss moduli as well as tan delta as a function of temperature. For polymers, these results are highly indicative of polymer structure. An example of a thermal sweep of a polymer is detailed later in this module.

In time scans, the temperature of the sample is held constant, and properties are measured as functions of time, gas changes, or other parameters. This experiment is commonly used when studying curing of thermosets, materials that change chemically upon heating. Data is presented graphically using modulus as a function of time; curing profiles can be derived from this information.

Frequency scans test a range of frequencies at a constant temperature to analyze the effect of change in frequency on temperature-driven changes in material. This type of experiment is typically run on fluids or polymer melts. The results of frequency scans are displayed as modulus and viscosity as functions of log frequency.

Instrumentation

The most common instrument for DMA is the forced resonance analyzer, which is ideal for measuring material response to temperature sweeps. The analyzer controls deformation, temperature, sample geometry, and sample environment.

Figure 2.10.3 displays the important components of the DMA, including the motor and driveshaft used to apply torsional stress as well as the linear variable differential transformer (LVDT) used to measure linear displacement. The carriage contains the sample and is typically enveloped by a furnace and heat sink.

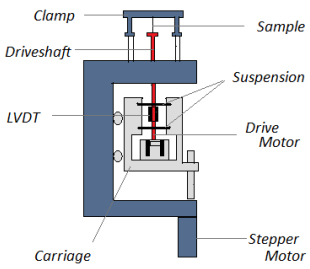

Figure 2.10.3 General schematic of DMA analyzer.

The DMA should be ideally selected to analyze the material at hand. The DMA can be either stress or strain controlled: strain-controlled analyzers move the probe a certain distance and measure the stress applied; strain-controlled analyzers provide a constant deformation of the sample (Figure 2.10.4) Although the two techniques are nearly equivalent when the stress-strain plot (Figure 2.10.1) is linear, stress-controlled analyzers provide more accurate results.

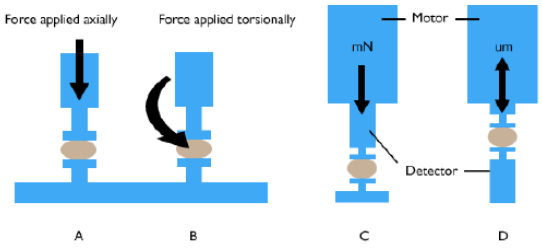

Figure adapted from M. Sepe, *Dynamic Mechanical Analysis for Plastics Engineering*, Plastics Design Library: Norwich, NY (1998).

DMA analyzers can also apply stress or strain in two manners—axial and torsional deformation (Figure 2.10.5) Axial deformation applies a linear force to the sample and is typically used for solid and semisolid materials to test flex, tensile strength, and compression. Torsional analyzers apply force in a twisting motion; this type of analysis is used for liquids and polymer melts but can also be applied to solids. Although both types of analyzers have wide analysis range and can be used for similar samples, the axial instrument should not be used for fluid samples with viscosities below 500 Pa-s, and torsional analyzers cannot handle materials with high modulus.

Different fixtures can be used to hold the samples in place and should be chosen according to the type of samples analyzed. The sample geometry affects both stress and strain and must be factored into the modulus calculations through a geometry factor. The fixture systems are specific to the type of stress application. Axial analyzers have a greater number of fixture options; one of the most commonly used fixtures is extension/tensile geometry used for thin films or fibers. In this method, the sample is held both vertically and lengthwise by top and bottom clamps, and stress is applied upwards

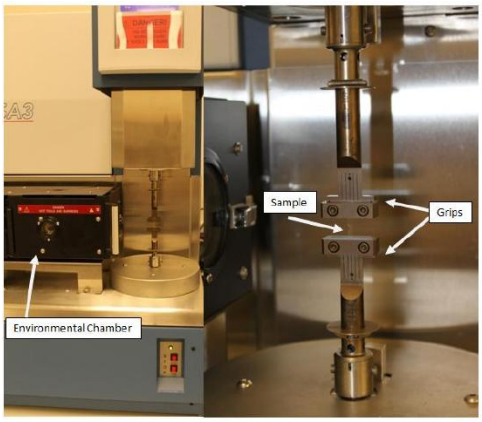

Figure 2.10.5 Axial analyzer with DMA instrument (left) and axial analyzer with extension/tensile geometry (right).

For torsional analyzers, the simplest geometry is the use of parallel plates. The plates are separated by a distance determined by the viscosity of the sample. Because the movement of the sample depends on its radius from the center of the plate, the stress applied is uneven; the measured strain is an average value.

DMA of the glass transition polymers

As the temperature of a polymer increases, the material goes through a number of minor transitions ($T\gamma$ and T_β) due to expansion; at these transitions, the modulus also undergoes changes. The glass transition of polymers (T_g) occurs with the abrupt change of physical properties within 140-160 ºC; at some temperature within this range, the storage (elastic) modulus of the polymer drops dramatically. As the temperature rises above the glass transition point, the material loses its structure and becomes rubbery before finally melting. The idealized modulus transition is pictured in Figure 2.10.6

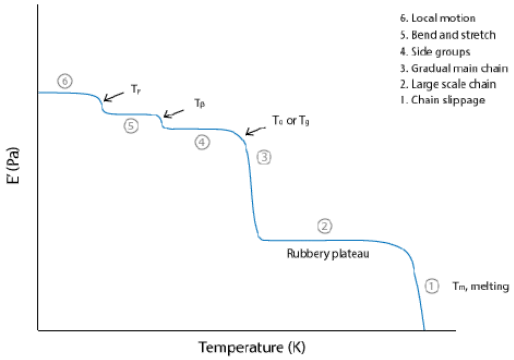

Figure 2.10.6 Ideal storage modulus transitions of viscoelastic polymers. Adapted from K. P. Menard, *Dynamic Mechanical Analysis: A Practical Introduction*, 2nd ed., CRC Press: Boca Raton, FL (2008).

The glass transition temperature can be determined using either the storage modulus, complex modulus, or tan δ (vs temperature) depending on context and instrument; because these methods result in such a range of values (Figure 2.10.6), the method of calculation should be noted. When using the storage modulus, the temperature at which *E'* begins to decline is used as the T_g. Tan δ and loss modulus *E"* show peaks at the glass transition; either onset or peak values can be used in determining *Tg*. These different methods of measurement are depicted graphically in Figure 2.10.7.

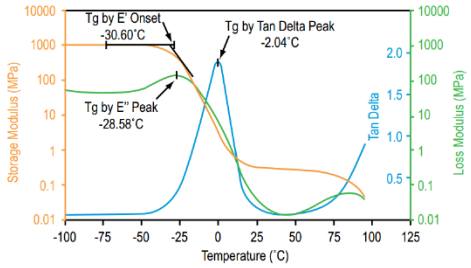

Figure 2.10.7 Different industrial methods of calculating glass transition temperature (*Tg*). Copyright 2014, TA Instruments. Used with permission.

Advantages and limitations of DMA

Dynamic mechanical analysis is an essential analytical technique for determining the viscoelastic properties of polymers. Unlike many comparable methods, DMA can provide information on major and minor transitions of materials; it is also more sensitive to changes after the glass transition temperature of polymers. Due to its use of oscillating stress, this method is able to quickly scan and calculate the modulus for a range of temperatures. As a result, it is the only technique that can determine the basic structure of a polymer system while providing data on the modulus as a function of temperature. Finally, the environment of DMA tests can be controlled to mimic real-world operating conditions, so this analytical method is able to accurately predict the performance of materials in use.

DMA does possess limitations that lead to calculation inaccuracies. The modulus value is very dependent on sample dimensions, which means large inaccuracies are introduced if dimensional measurements of samples are slightly inaccurate. Additionally, overcoming the inertia of the instrument used to apply oscillating stress converts mechanical energy to heat and changes the temperature of the sample. Since maintaining exact temperatures is important in temperature scans, this also introduces inaccuracies. Because data processing of DMA is largely automated, the final source of measurement uncertainty comes from computer error.