

Dynamic Mechanical Analysis Basics: Part 1 How DMA Works



Introduction and history

Dynamic Mechanical Analysis (DMA) is a very important tool in the modern polymer laboratory despite the fact that only a few books have concentrated on this technique.¹ The first attempts at conducting oscillatory experiments to measure the elasticity of a material were performed by Poynting² in 1909. Other early work used methods to apply oscillatory deformations by various means to study metals³. These experimental techniques were reviewed by te Nijenhuis⁴ in

1978. In early discussion, Miller's book on polymer properties⁵ referred to dynamic measurements of molecular structure and stiffness. Commercial instruments at this time included the Weissenberg Rheogoniometer (~1950) and the Rheovibron (~1958). The Weissenberg Rheogoniometer, which dominated cone-and-plate measurements for over 20 years, was the first commercial version of the instrument to measure normal forces.⁶ By the time Ferry wrote the "*Viscoelastic Properties of Polymers*"⁷ in 1961, dynamic

Key Features

- ▶ The basic mathematics of DMA
- ▶ DMA operating principles and how they apply to various materials

measurements were an integral part of polymer science. Ferry summarized the work to date and remains a major reference. In 1967, McCrum *et al.*⁸ collected the current information on DMA and Dielectric Analysis (DEA) into his landmark textbook.

The technique remained fairly specialized until the late sixties when commercial instruments became more user-friendly. Near the beginning, instruments were difficult to use, slow, and limited in their ability to process data. In the late seventies, Murayani⁹ and Read¹⁰ wrote books on the uses of DMA for material characterization. PerkinElmer[®] developed a controlled stress analyzer based on their Thermo-mechanical Analyzer (TMA) technology, which was designed for increased low-end sensitivity.

In 2007, PerkinElmer acquired the DMA 8000 from Triton Technologies. The DMA 8000 has a novel design that makes it unique in the marketplace.

Operating principles

If a constant load applied to a sample begins to oscillate sinusoidally, as shown in Figure 1, the sample will deform sinusoidally. This will be reproducible if the material is deformed within its linear viscoelastic region. For any one point on the curve, the stress applied is described as:

$$\sigma = \sigma_0 \sin \omega t$$

σ is the stress at time t , σ_0 is the maximum stress, ω is the frequency of oscillation, and t is the time. The resulting strain wave shape is dependent on how much viscous and elastic

behavior the sample has. In addition, the rate of stress can be determined by taking the derivative of the above equation in terms of time:

$$d\sigma/dt = \omega\sigma_0 \cos \omega t$$

The two extremes of the material's behavior, elastic and viscous, provide the limiting extremes that will sum to give the strain wave. The behavior can be understood by evaluating each of the two extremes. The material at the spring-like, or Hookean limit, will respond elastically with the oscillating stress. The strain at any time can be written as:

$$\epsilon(t) = E \sigma_0 \sin(\omega t)$$

$\epsilon(t)$ is the strain at anytime (t), E is the modulus, σ_0 is the maximum stress at the peak of the sine wave, and ω is the frequency. Since in the linear region σ and ϵ are linearly related by E , the relationship is:

$$\epsilon(t) = \epsilon_0 \sin(\omega t)$$

ϵ_0 is the strain at the maximum stress. This curve, shown in Figure 1b, has no phase lag, nor time difference from the stress curve, and is called the in-phase portion of the curve.

The viscous limit is expressed as the stress being proportional to the strain rate. This is the first derivative of the strain. This is best modeled by a dashpot and for that element the viscous response in terms of strain rate is described as:

$$\epsilon(t) = \eta d\sigma_0/dt = \eta\omega\sigma_0 \cos(\omega t)$$

or

$$\epsilon(t) = \eta\omega\sigma_0 \sin(\omega t + \pi/2)$$

η is the viscosity. Substituting terms makes the equation:

$$\begin{aligned} \epsilon(t) &= \omega\sigma_0 \cos(\omega t) \\ &= \omega\sigma_0 \sin(\omega t + \pi/2) \end{aligned}$$

This curve is shown in Figure 1c. Now, take the behavior of the material that lies between these two limits. The difference between the applied stress and the resultant strain is an angle, δ . This must be added to equations. So the elastic response at anytime can now be written as:

$$\epsilon(t) = \epsilon_0 \sin(\omega t + \delta)$$

Using trigonometry this can be rewritten as:

$$\begin{aligned} \epsilon(t) &= \epsilon_0 [\sin(\omega t) \cos \delta \\ &\quad + \cos(\omega t) \sin \delta] \end{aligned}$$

This equation, corresponding to the curve in Figure 1d, can be separated into the in-phase and out-of-phase strains that correspond to curves like those in Figure 1b and 1c respectively. These are the in and out phase moduli and are:

$$\epsilon' = \epsilon_0 \sin(\delta)$$

$$\epsilon'' = \epsilon_0 \cos(\delta)$$

The vector sum of these two components gives the overall or complex strain on the sample:

$$\epsilon^* = \epsilon' + i\epsilon''$$

These terms are often written with E instead of the ϵ used here and referred to as E' (E prime) and E'' (E double prime).

Applications

What does all this mean to the working laboratory? If we take the Young's modulus of a material, we get one data point about its behavior. Real materials are more complex. For example, if we drop a super ball, the ball doesn't bounce back exactly to our hand because of losses to internal motions and friction. The

amount of bounce can be related to the storage modulus, E' , a measure of how elastic the material acts under these conditions of temperature, load, and frequency. The lost height can be related to the loss modulus, E'' . This is illustrated in Figure 2. The ratio of the loss modulus to the storage modulus is also the tan of the phase angle and is called damping:

$$\text{Damping} = \tan \delta = E''/E'$$

Damping is a dimensionless property and is a measure of how well the material can disperse energy. Damping lets us compare how well a material will absorb or lose energy.

Applied to real materials, the DMA 8000 can give the temperature and intensity of transitions as a function of temperature and frequency. This can be done very quickly, allowing one to collect the modulus of a material from $-150\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ in under a half hour, while also seeing the transitions that occur in the material and its frequency dependence.¹¹ Using the DMA 8000 with its 100 frequencies per run, one can collect an incredible amount of data in one pass. The frequency data can then be used to generate a master-curve to calculate frequency dependent activation energy, as shown in Figure 3, or to study the frequency dependence of transitions. This large amount of information available from one scan in the DMA 8000 is why it is one of the most basic tools needed in the modern material laboratory. More detailed discussions of how these are applied to specific materials are available in other application notes.

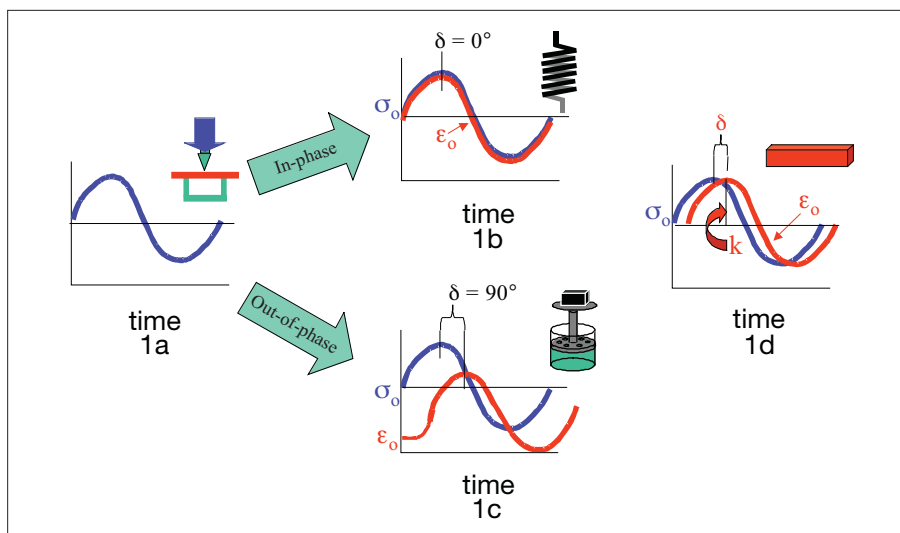


Figure 1. (a) When a sample is subjected to a sinusoidal oscillating stress it responds in a similar strain wave provided the material stays within its elastic limits. When the material responds to the applied wave perfectly elastically, an in-phase storage, or elastic response is seen, (b) while a viscous response gives an out-of-phase loss, or viscous response, (c) Viscoelastic materials fall in between these two extremes (as shown in d). For the real sample in (d), the phase angle, δ , and the amplitude at peak, k , are the values used for the calculation of modulus, viscosity, damping, and other properties.

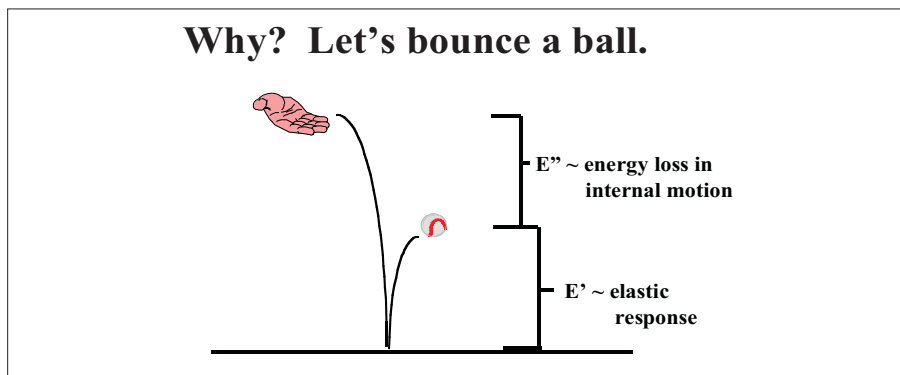


Figure 2. When a super ball is dropped, the bounce can be conceptualized as E' , the stored energy. The amount it doesn't rebound can be described as E'' , the energy lost.

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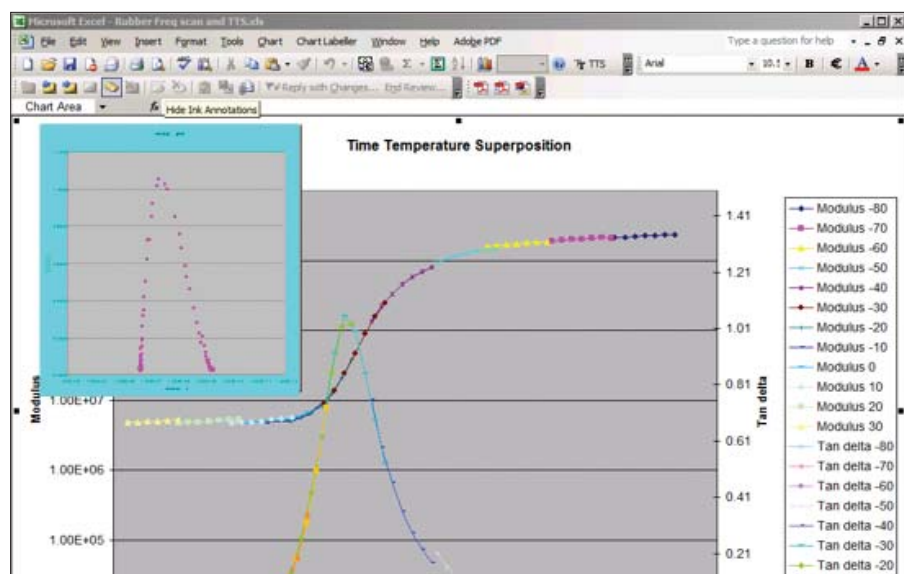


Figure 3. A mastercurve on a filled rubber generated from the DMA 8000 TTS software. The overlay shows the wicket plot.

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