Dynamic mechanical analysis (DMA) can provide insightful information regarding the structure and mechanical properties of a polymeric material. However, this technique is often overlooked, and its capabilities are generally not fully understood.

Because of their molecular structure, polymeric materials such as plastics have different properties compared with other materials, like metals. Specifically, these unique characteristics arise from the fact that:

- Polymers are made up of relatively long chains of repeating structural units, resulting in relatively high molecular weight.
- This chainlike arrangement results in entanglement of the individual polymer molecules.
- These polymer chains do not share chemical bonds with the other chains around them, resulting in mobility. Polymeric materials fail predominately through the disentanglement of the molecular chains.

**Viscoelasticity**

These attributes are tied to the phenomenon of viscoelasticity. Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Elastic materials, like a steel rod, strain when stressed and quickly return to their original state once the stress is removed. Viscous materials, like honey, resist shear flow and strain linearly with time when the stress is applied. When the stress is removed, viscous materials do not exhibit recovery.

Viscoelastic materials have elements of both these properties. When a stress is applied, polymeric materials will exhibit an immediate response, together with continued deformation if that stress is continued. When the stress is released, they will undergo some recovery, although usually gradual and often incomplete.

The performance implications of the viscoelastic nature of polymeric materials are that plastics exhibit temperature, time, and strain rate dependency. It is important to understand the viscoelastic nature of plastic materials so that their behavior in an intended application can be understood.

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. This is evident in a reduced modulus and a lower strength.

As the strain rate is increased, the polymer chains do not have enough time to undergo yielding and they will disentangle. This results in apparent brittle behavior, even within normally ductile materials.

Over time, applied stress results in strain through rearrangement of the polymer chains, known as creep. At stresses below the yield point, this molecular reorganization includes disentanglement as there is no opportunity for yielding. This is often evident as brittle creep rupture. Thus, the long-term strength of a material is often significantly lower than the short-term strength.

**Gaining insights through DMA**

Dynamic mechanical analysis is a thermoanalytical technique that assesses the viscoelastic properties of materials, and can provide insight into the temperature and time dependencies of polymeric materials. DMA evaluates a material’s stiffness, as measured by modulus, as a function of temperature, time, or frequency.

The results obtained as part of a DMA experiment include the storage or elastic modulus (E'), the loss or viscous modulus (E''), and the tangent of the phase angle delta or tan delta (E''/E'). As part of the analysis, a small deformation is applied to a sample in a periodic manner.
For a viscoelastic material, the stress and strain will be out of phase by some quantity, the phase angle delta. A small phase angle corresponds to a highly elastic material, while a large phase angle represents a highly viscous material. The storage modulus is associated with the ability of the material to store energy (the elastic response), while the loss modulus represents the ability to dissipate energy (the viscous response).

The results of DMA experiments allow an assessment of the proportion of the elastic and viscous components within a material. DMA experiments can be conducted in several modes, including tension, shear, compression, torsion, and flexure.

**Temperature-dependent behavior**

The measurement of modulus across a temperature range is referred to as a temperature sweep. Dynamic mechanical analysis offers an advantage over traditional tensile or flexural testing in that the obtained modulus is continuous over the temperature range of interest.

In a standard temperature sweep evaluation, the results show the storage modulus, loss modulus, and the tan delta as a function of temperature (Figure 1). The storage modulus indicates the ability of the material to accommodate stress over a temperature range. The loss modulus and tan delta provide data on temperatures where molecular changes produce property changes, such as the glass transition (Figure 2) and other secondary transitions not detectable by other thermal analysis techniques.

The superiority of DMA over differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) for assessing the glass transition is well documented. Secondary transitions of lesser magnitude are also important, because they can relate to material properties such as impact resistance (Figure 3).

**Figure 1:** DMA thermogram of an ABS resin showing the response of storage modulus, loss modulus, and tan delta to temperature.

**Figure 2:** Three different ways to assess the glass transition of a polycarbonate resin are illustrated based upon the onset of decrease in storage modulus, the localized maximum within the loss modulus, and the localized maximum within the tan delta. All three methods illustrate changes within the material. However, the maximum within the loss modulus is generally recognized as the glass transition temperature.

**Figure 3:** The glass transition of the butadiene functionality within an ABS resin is shown. The butadiene is responsible for the impact resistance of the material.

**Figure 4:** The storage moduli responses to temperature are shown for a semi-crystalline resin and an amorphous resin. The amorphous resin loses all loadbearing capabilities at the glass transition, while the semi-crystalline material retains some properties above glass transition.
The ability of a plastic component to retain mechanical properties over the service temperature range is essential and is well predicted by DMA.

The data generated through DMA experiments provides important information into the performance and structure of plastic materials. Such data can be very useful when evaluating structure, comparing materials, and assessing suitability for a service application (Figures 4 and 5).

**Time-dependent behavior**

In addition, dynamic mechanical analysis can also be conducted to evaluate creep behavior through the application of constant stress, or stress relaxation by using a constant strain. 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.

Over time, under conditions of constant stress, a plastic material will undergo an increasing level of strain, known as creep. The apparent modulus is a mathematical artifact of this phenomenon. As the strain increases, the apparent modulus will decrease. However, the true stiffness or modulus of the material may remain largely unchanged.

The viscoelastic nature of polymeric materials results in time and temperature equivalency. This means that time and temperature will have the same effect on plastics. Specifically, just as modulus decreases with increasing temperature, the apparent modulus of the material will decrease over time (Figure 6).

**Figure 5:** A comparison of the storage moduli for polycarbonate and PC+PBT resins is presented. Note the differences in modulus between the two materials over the temperature range evaluated. The glass transition within the PBT is responsible for the early onset loss of modulus, while the crystalline structure of the PBT is responsible for the retention of modulus above the glass transition of the polycarbonate in the blend.

**Figure 6:** The upper graph shows the reduction in modulus of a polyacetal resin with increasing temperature. The modulus decreases to 1,000 MPa at approximately 100 °C. The lower graph shows the reduction in apparent modulus over time at 25 °C. Note that the apparent modulus decreases to 1,000 MPa after approximately 11,000 hours.

**Figure 7:** A creep DMA evaluation is conducted through a series of short-term experiments at discrete temperatures. A stress is applied, and the resulting strain is used to calculate the apparent modulus over the time period of the individual experiments.
DMA creep evaluations are carried out by conducting a series of relatively short-term isothermal experiments (Figure 7). The material is exposed to constant stress, and the strain response is measured. Time-temperature superposition is then used to extend the time response at a specific temperature of interest (Figure 8). The result is a master curve of apparent modulus over time (Figure 9).

If the magnitude of the continuous service stress can be determined, the apparent modulus master curve data is combined with tensile test results to calculate the anticipated strain over time (Figure 10). This allows a computation of the projected time to failure, identified as crack initiation.

Dynamic mechanical analysis is a powerful tool that can provide valuable information into the structure and performance properties of plastic materials. This includes both temperature-dependent and time-dependent characteristics of the material.

The applications of DMA exceed those illustrated in this article, and include an understanding of the frequency-dependency of the material, the characterization of polymer blends, the analysis of crystallinity, the assessment of thermoset cross-linking, evaluation of the effects of aging and degradation, and the elucidation of solid – liquid interactions. The wide range of information that can be extracted through dynamic mechanical analysis makes it a valuable tool in the plastics analytical laboratory.

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**ABOUT THE AUTHOR**

Jeffrey A. Jansen is senior managing engineer and a partner with The Madison Group, a Madison, Wis.-based provider of consulting services to the plastics industry. He is an expert in failure analysis; material analysis; identification and selection; and aging studies for plastic and rubber components. A senior member of SPE, Jansen also is a past chairman of SPE’s Failure Analysis & Prevention Special Interest Group. Jansen is hosting an SPE webinar called “An Introduction to Dynamic Mechanical Analysis” on Sept. 21. Contact him at jeff@madisongroup.com.