DYNAMIC mechanical analysis (DMA)-is a thermal analysis technique that measures the properties of materials as they are deformed under periodic stress. Specifically, in DMA a variable sinusoidal stress is applied, and the resultant sinusoidal strain is measured. If the material being evaluated is purely elastic, the phase difference between the stress and strain sine waves is 0° (i.e., they are in phase). If the material is purely viscous, the phase difference is 90°. However, most real-world materials including polymers are viscoelastic and exhibit a phase difference between those extremes. This phase difference, together with the amplitudes of the stress and strain waves, is used to determine a variety of fundamental material parameters, including storage and loss modulus, tan δ, complex and dynamic viscosity, storage and loss compliance, transition temperatures, creep, and stress relaxation, as well as related performance attributes such as rate and degree of cure, sound absorption and impact resistance, and morphology. The diagram in Figure 1 shows the relationship between several of these parameters.

$$E^* = stress/strain$$
$$E' = E^*\cos\delta$$
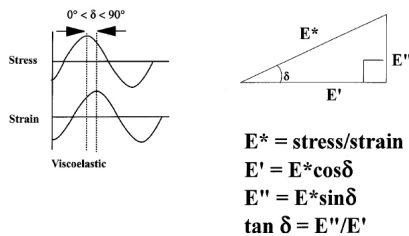$$E'' = E^*\sin\delta$$
$$\tan \delta = E''/E'$$

Figure 1: Viscoelasticity and complex modulus

Most DMA measurements are made using a single frequency and constant deformation (strain) amplitude while varying temperature. Measurements, where the amplitude of deformation is varied or where multiple frequencies are used, provide further information.

INSTRUMENTAL CONSIDERATIONS

There are several components that are critical to the design and resultant performance of a dynamic mechanical analyzer. Those components are the drive motor (which supplies the sinusoidal deformation force to the sample material), the drive shaft support and guidance system (which transfers the force from the drive motor to the clamps that hold the sample), the displacement sensor (which measures the sample deformation that occurs under the applied force), the temperature control system (furnace), and the sample clamps. The DMA 2980 dynamic mechanical analyzer (TA Instruments, Inc., New Castle, DE)

(Figure 2) is based on a patent pending design that optimizes the combination of these critical components. Specifically, the analyzer incorporates a noncontact direct drive motor to deliver reproducible forces (stresses) over a wide dynamic range of 0.001–18 N; an air bearing shaft support and guidance system to provide frictionless continuous travel over 25 mm for evaluating large samples (e.g., fibers as long as 30 mm) or for evaluating polymers at large oscillation amplitudes (±0.5–10,000 μm); an optical encoder displacement sensor to provide high resolution (one part in 25 million) of oscillation amplitude, which results in excellent modulus precision (±1%) and tan δ sensitivity (0.0001); and a bifilar-wound furnace complemented by a gas cooling accessory to allow a broad temperature range (–150 to 600°C) to be covered. The DMA 2980 also features a variety of clamping configurations to accommodate rigid bars, fibers, thin films, and viscous liquids (e.g., thermosets) in bending, compression, shear, and tension modes of deformation.

Figure 2: DMA 2980

APPLICATIONS

Material selection for specific end-use applications

The task of evaluating new materials and projecting their performance for specific applications is a challenging one for engineers and designers. Often, materials are supplied with short-term test information such as deflection temperature under load (DTUL), which is used to project long-term, high-temperature performance. However, because of factors such as polymer structure, filler loading and type, oxidative stability, part geometry, and molded-in stresses, the actual maximum long-term use temperatures may be as much as 150°C below or above the DTUL. DMA, on the other hand, continuously monitors material modulus with temperature and, hence, provides a better indication of long-term,

elevated temperature performance. Figure 3 shows the DMA modulus curves for three resins with nearly identical DTULs but very different moduli at the DTUL and, more importantly, very different modulus trends beyond the DTUL.
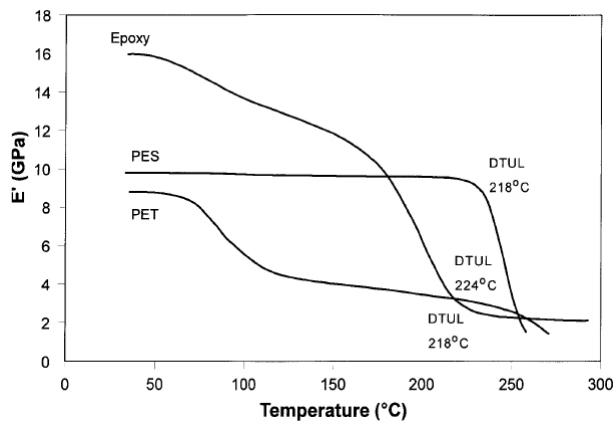

Figure 3: DMA comparison of materials with similar DTULs

The polyethylene terephthalate (PET) in this example represents a semicrystalline material, and its modulus begins to decrease rapidly at 60°C as the material enters its glass transition. The amorphous component in the polymer achieves an increased degree of freedom, and at the end of the glass transition, the modulus of the material has declined by about 50% from room temperature values. Because of its crystalline component, the material then exhibits a region of relative stability before the modulus again drops rapidly as the crystalline structure approaches the melting point. The actual modulus of a resin of this type at the DTUL is only 10–30% of the room temperature value. The DTULs of highly filled systems based on this resin are more closely related to the melting point than to the significant structural changes associated with the glass transition temperature (Tg).

The polyethersulfone (PES) in Figure 3 is a high-performance amorphous resin. Amorphous materials exhibit higher Tgs than their semicrystalline counterparts and maintain a high percentage of their room temperature properties up to that point. However, with the onset of the glass transition, the loss in properties is sudden and complete, even for highly reinforced grades. The DTULs of these systems are closely associated with the Tg, but almost always fall on the steeply sloped part of the modulus curve. Thus, the DTUL occurs in a region of great structural instability, and the actual maximum temperature for reliable performance under load is 15–30°C below the DTUL. Finally, the epoxy is a cross-linked system with a well-defined Tg. The temperature dependency of the modulus in such materials is related to the cross-link density. The relationship of the DTUL modulus is similar to that observed for PET. However, in this case, the cross-linked system provides an extended region of stability well beyond the Tg and the DTUL. Thus, while both thermoplastic systems are no longer solid above 250°C, the epoxy has structural integrity and virtually the same modulus at 300°C as it has at 250°C. It is therefore still serviceable for short-term excursions above

the DTUL and may prove useful for extended periods under reduced loads, providing that it possesses good thermal and oxidative stability.

Projection of material behavior using superpositioning

Polymeric materials, because of their viscoelastic nature, exhibit behavior during deformation and flow that is both temperature and time (frequency) dependent. For example, if a polymer is subjected to a constant load, the deformation or strain (compliance) exhibited by the material will increase over a period of time. This occurs because the material under a load undergoes molecular rearrangement in an attempt to minimize localized stresses. Hence, compliance and modulus measurements performed over a short time span result in lower and higher values, respectively, than longer-term measurements. This time-dependent behavior would seem to imply that the only way to accurately evaluate material performance for a specific application is to test the material under the actual temperature and time conditions the material will see in the application. This implication, if true, would present real difficulties for the material scientist because the range of temperature and/or frequencies covered by a specific instrument might not be adequate or, at best, might result in extremely long and tedious experiments.

Fortunately, however, there is a treatment of the data, designated as the method of reduced variables or time–temperature superposition (TTS), which overcomes the difficulty of extrapolating limited laboratory tests at shorter times to longer-term, more real-world conditions. This TTS-treatment is well grounded in theory and can be applied to the data obtained from DMA multi-frequency experiments.

The underlying bases for TTS are that the processes involved in molecular relaxation or rearrangements in viscoelastic materials occur at accelerated rates at higher temperatures and that there is a direct equivalency between time (the frequency of measurement) and temperature. Hence, the time over which these processes occur can be reduced by conducting the measurement at elevated temperatures and transposing (shifting) the resultant data to lower temperatures. The result of this shifting is a master curve where the material property of interest at a specific end-use temperature can be predicted over a broad time scale.

Figures 4 and 5 show TTS results for an epoxy composite. Figure 4 shows the DMA multi-frequency curves obtained over four decades (0.1–100-Hz). The ability of the DMA 2980 to obtain data at 100 Hz and above shortens the experimental time required to obtain the four decades of frequency required for good TTS extrapolations. Figure 5 shows the master curve obtained by combining the multi-frequency experiments. Note that the behavior of the epoxy (at 148°C) can be projected over 15 decades of frequency, which is well beyond the four decades used in the experiment. Further evaluation of the data indicates that the behavior of this material around the glass transition follows the William-Landel-Ferry (WLF) equation.
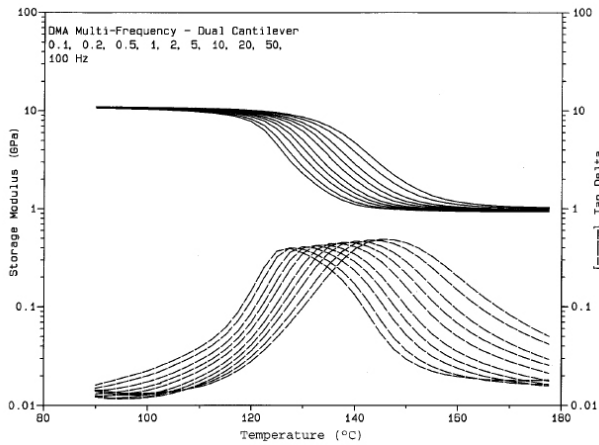
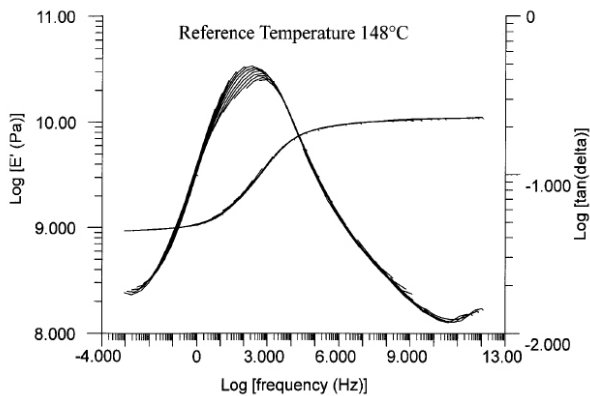Figure 4: Epoxy fiberglass composite—stepwise isothermal frequency sweeps

Figure 5: TTS of epoxy fiberglass results

Determination of curing behavior

Thermosetting liquids such as prepregs, adhesives, and paints/ coatings can be evaluated in DMA (dual-cantilever mode) using a supporting structure such as fiberglass braid. In these experiments, information about the curing properties (e.g., onset of cure, gel point, vitrification) can be obtained as the material progresses from a liquid to a rigid solid. Figure 6 illustrates the results for a latex paint. The large change in modulus at about 12 min reflects the onset of drying and curing. The use of log (time) as the x-axis accentuates the weak tan δ peak associated with final vitrification. Although not shown in this figure, a related plot of E′ and E″ versus time is often used to detect gel point as the point where those curves intersect.
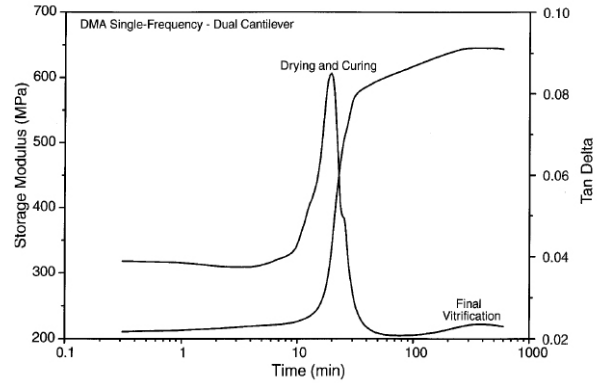

Figure 6: Latex curing on fiberglass braid

Film and fiber stress/strain measurements

Stress/strain measurements are widely used to characterize films and fibers over a broad range of viscoelastic behavior. Although conventional physical testing devices can accommodate thin films and single filament fibers, the results are difficult to obtain, and the accuracy is doubtful since the mass and inertia of the grips are much greater than the tensile strength of the material being evaluated. The clamping arrangements and force range of DMA are more suitable for examining these materials. Curves like that shown in Figure 7 for a polyethylene film can be obtained by ramping the force (stress). In this case, the broad range of travel for the DMA 2980 (25 mm) allows the behavior of this 4-mm long film to be completely characterized through breaking.
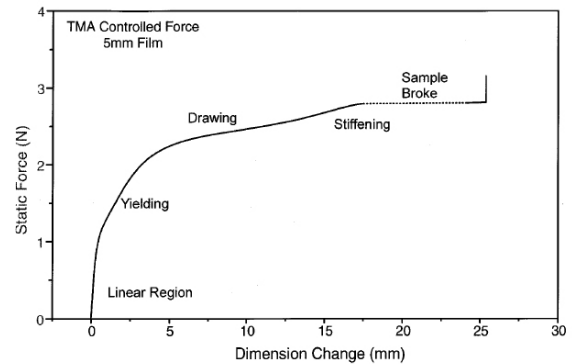

Figure 7: Stress-strain evaluation of polyethylene film

SUMMARY

DMA is a versatile technique that complements the information provided by the more traditional thermal analysis techniques (DSC, TGA [thermogravimetric analysis], and TMA [thermomechanical analysis]). Hence, it is rapidly becoming a necessary component of a laboratory interested in characterizing the properties of polymers.

By Jon Foreman

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