Time-temperature superposition: Turning hours of work into years of information

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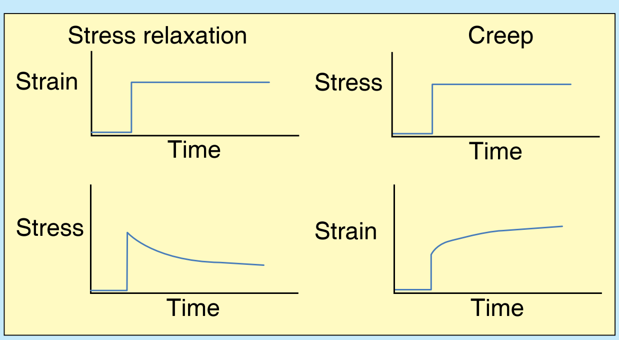
Rubbers and other elastomeric materials have time-dependent mechanical properties at ambient conditions. This phenomenon is called viscoelasticity, and engineers need to understand viscoelasticity and take it into account when designing new products. However, the relevant time scales to a particular product may not be accessible to conventional mechanical testing techniques. For example, parts may be in service for years, but conducting a mechanical test that takes years to finish is not often feasible. In contrast, some applications subject elastomer parts to high frequency vibrations that are not accessible with conventional measurement techniques. Time-temperature superposition (TTS) is an advanced thermomechanical analysis method that allows rubber scientists and engineers to extrapolate the mechanical properties of polymeric materials to long times or high frequencies using tests that last less than a day. TTS exploits the unique equivalence of time and temperature in soft materials to allow engineers to characterize materials rapidly and accelerate the design cycle.

Viscoelasticity and the dynamic mechanical analyzer

Before delving into the principles and application of time-temperature superposition, it is beneficial to first understand the fundamentals of viscoelasticity and dynamic mechanical analysis.

Time-temperature superposition testing of elastomeric materials is almost always performed on a test instrument called a dynamic mechanical analyzer (DMA). The DMA is a specialized thermo-mechanical test instrument that shares some similarities with conventional load frame based mechanical test equipment. A sample of the material is deformed by an actuator or motor, while the force required to deform the sample is measured by a load cell. Based on the geometry of the test fixture, the measured force and deformation are used to calculate the modulus of the test material. Common test geometries include tension, compression, three-point bending and cantilever bending.

Figure 1 - stress relaxation and creep tests



In contrast to conventional load frames, DMAs are generally engineered for precise temperature and heating rate control at the expense of having a low maximum force. Even small and moderately sized conventional load frames are designed with maximum capacities in the kN range, while DMAs typically have a maximum force of only 10-20 N.

DMAs are also designed for oscillatory measurements. The load train and test fixtures are designed to minimize their mass (and therefore inertia), which also provides minimal thermal mass when heating or cooling a sample. Oscillatory measurements at low strain amplitudes are a great way to measure the viscoelastic properties of elastomers.

Measuring the viscoelastic properties of polymers is generally performed in three different measurement modes: stress relaxation, creep and oscillatory. In a stress relaxation test, a constant strain is applied to the sample, and the decay is measured in stress as a function of time to calculate the relaxation modulus, $E(t) = \sigma(t)/\varepsilon_0$. In a creep test, a constant stress is applied to the sample, and the strain is measured as a function of time to calculate the creep modulus $D(t) = \varepsilon(t)/\sigma_0$. The processes of stress relaxation and creep tests are illustrated in figure 1. In an oscillatory test, a sinusoidal strain is applied to the sample and the stress is measured. For viscoelastic materials, the stress signal is a sinusoid with the same frequency as the strain, but phase shifted by an amount δ. The storage modulus is calculated $E' = \sigma_0/\varepsilon_0 \cos(\delta)$ and loss modulus $E'' = \sigma_0/\varepsilon_0 \sin(\delta)$, as shown in figure 2. The storage modulus is proportional to the elastic energy stored during one loading cycle, while the loss modulus is proportional to the viscous energy dissipated during one loading cycle.

Figure 2 - oscillatory viscoelastic test

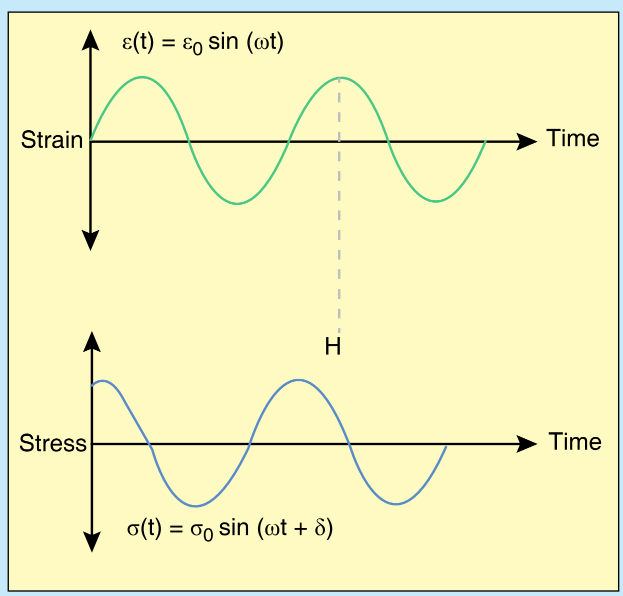
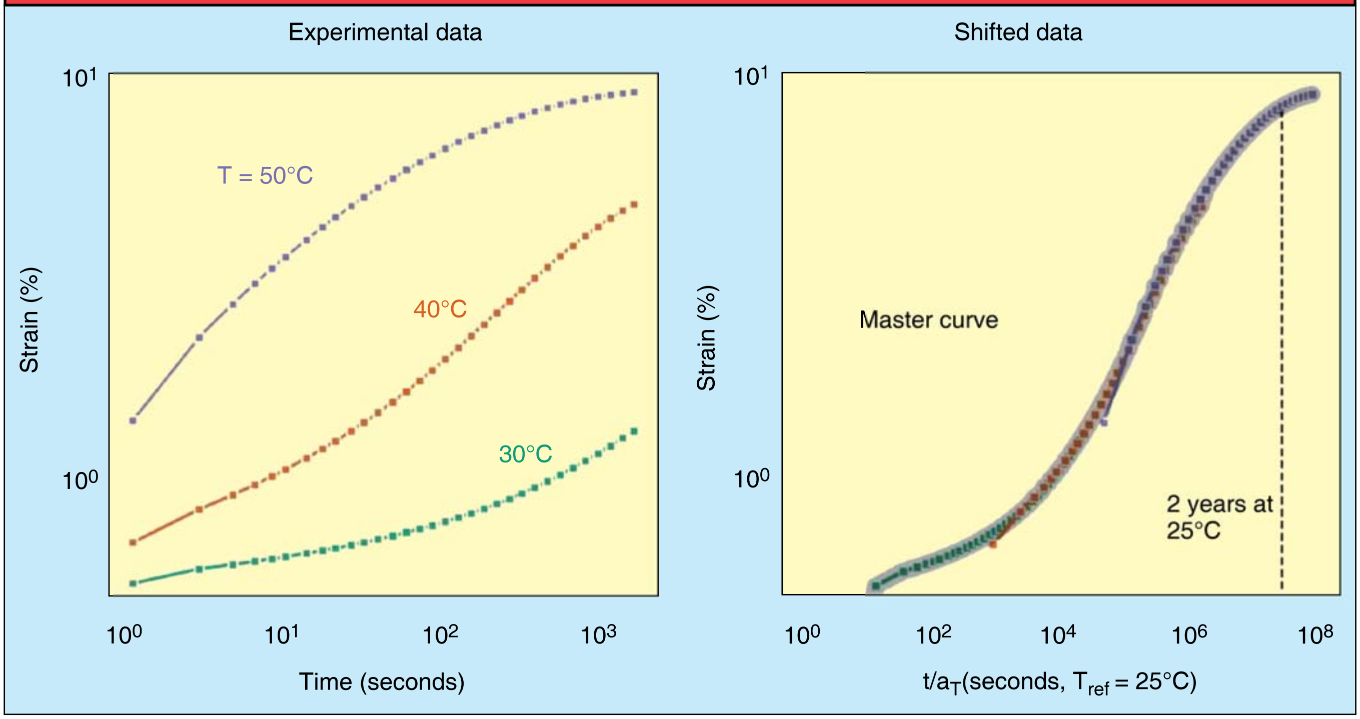


Figure 3 - creep test data at three different temperatures (left); master curve at 25°C generated by applying TTS analysis to the creep data at 30, 40 and 50°C (right); creep performance for this material was predicted up to approximately 2 years at room temperature using tests that lasted less than 2 hours



Time-temperature superposition

Now that viscoelasticity is understood, advantageous use of the thermomechanical properties of polymers can be discussed. The general theory behind time-temperature superposition is that testing a material for a short time at a high temperature is equivalent to testing for a long time at a lower temperature. The time-temperature equivalence can be understood as follows: The viscoelastic properties of polymers are caused by the kinetics of sliding polymer chains. Those kinetic events are accelerated at elevated temperature, but otherwise cause similar effects (ref. 1). If the time-temperature equivalence relationship for a material of interest can be measured, then measurements of its mechanical properties to time scales that are beyond the equipment's capabilities can be extrapolated.

In practice, the process of TTS testing involves measuring the viscoelastic properties of the material; either the creep modulus, stress relaxation modulus, or storage and loss modulus over a range of temperatures that include the intended use temperature (called the reference temperature T_{ref}). TTS analysis generates two outputs: (1) a master curve, and (2) shift factors, typically denoted a_T. The master curve is the viscoelastic modulus of the material at the reference temperature. The shift factors quantify the time-temperature relationship for the material in question, and allow the master curve to be shifted to different temperatures.

As an example, consider the creep test data in figure 3. The creep modulus of this thermoset polymer was measured at three temperatures: 30°C, 40°C and 50°C. To create the master curve, the curves along the time axis are shifted until they overlap. Creating the master curve determines the shift factors a_T through the relationship:

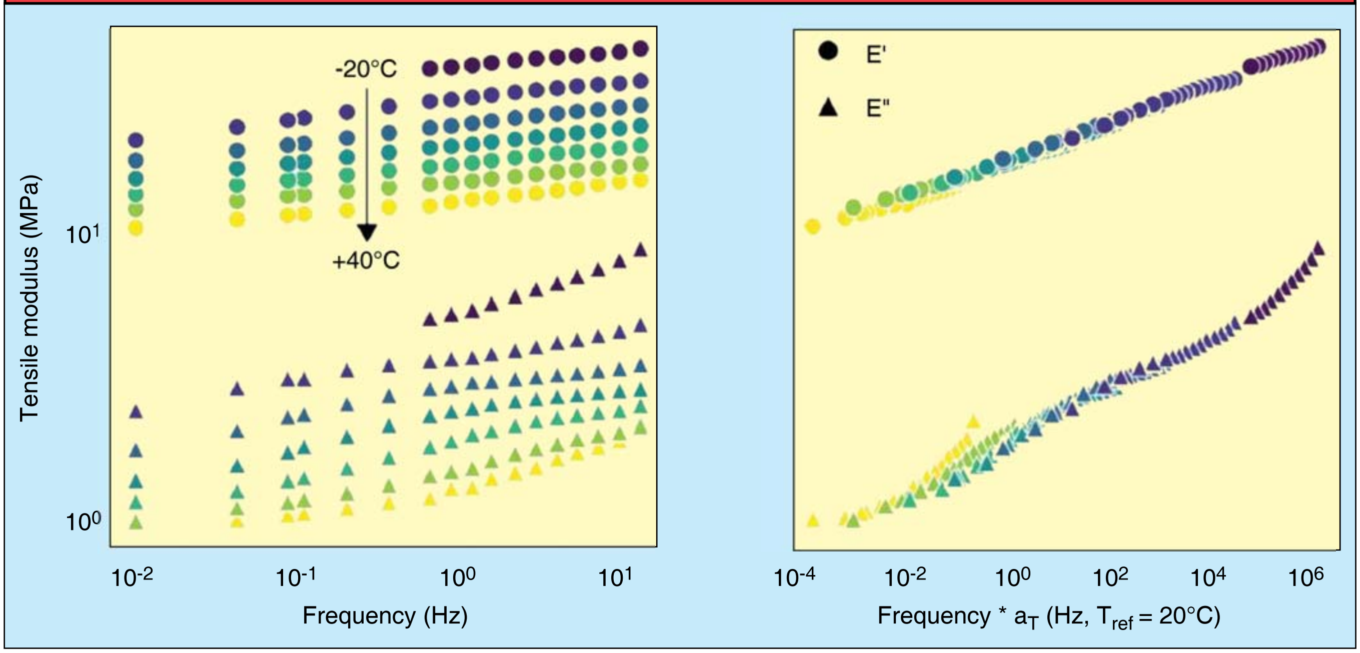
$$a_T\,(T_{test}) = t\,(T_{test})/t(T_{ref})$$

Notice the time axis of the master curve in figure 3: The maximum time is about 10^8 seconds, or close to three years. This is a typical result for materials when using TTS analysis in creep; a reasonable expectation for most materials is to be able to forecast the creep performance for approximately one to 10 years by testing at temperatures from 50°C to 100°C above the reference temperature.

In creep testing, material performance was measured over a long period of time. In contrast, in certain applications, the concern is with high frequency material behavior, equivalent to short periods of time. In the automotive industry, noise, vibration and harshness (NVH) describe the process of designing a vehicle to minimize noise transmitted to the passengers. The human-audible range of frequencies is 20 Hz to 20 kHz. Engineers designing components that are supposed to reduce audible noise transmission need to know how their materials behave over this frequency band. However, most DMAs have a maximum measuring frequency of 100 Hz. How can one measure at frequencies up to 20 kHz?

Enter time-temperature superposition. In contrast to creep testing, the material properties will be measured at temperatures below the expected use temperature (reference temperature). The lower temperature will slow down the kinetic processes that underpin viscoelasticity, and TTS can be used to extrapolate

Figure 4 - storage moduli (circles) and loss moduli (triangles) measured at temperatures down to -20°C (left); master curves generated using TTS (right); material properties near 10^6 Hz, well above the limit of the DMA, were measured



measurements to the high frequency range.

In figure 4, the storage modulus and loss modulus of a rubber sample was measured at temperatures between -20°C and +40°C, and frequencies between 0.01 and 10 Hz. In the right-hand figure, the curves have been shifted along the frequency axis until they overlap, creating the master curve. Creating the master curve determines the shift factors a_T through the relationship:

$$a_T\,(T_{test}) = f\,(T_{ref})/f\,(T_{test})$$

Note that the relationship is inverted from the equation for creep, because frequency has units of 1/second. The results shown in figure 4 allow for the measurement of the viscoelastic properties of this material at frequencies close to 106 Hz.

Once the shift factors for a given material have been determined, the master curve can then be shifted to other temperatures of interest. Products are generally expected to perform well across a range of temperatures. With a TTS master curve and shift factors in hand, the master curve can be shifted along the time or frequency axis to see how the material will behave at those other temperatures.

Often, choosing a new reference temperature requires interpolating or extrapolating the shift factors. They are fitted to an Arrhenius model or, more commonly, the Williams-Landel-Ferry (WLF) equation:

$$\log_{10} a_T = (-C_1\,(T - T_{ref})/C_2 + (T - T_{ref})$$

C_1 and C_2 are empirical constants that must be determined by fitting the experimental data. Figure 5 shows the shift factors determined during the creation of the master curve in figure 4. The dashed line is a fit to the WLF model.

Using the WLF fit, the master curve can be shifted to any number of different temperatures. This is shown in figure 6 for three temperatures: -20°C, 20°C and 40°C. Note that the frequency range for each reference temperature is different. This is because the frequency range at the reference temperature is determined by the difference between the measurement temperatures and the reference temperature.

Put another way, if one is interested in the high frequency behavior of their material, one needs to include tests at tempera-

Figure 5 - shift factors from the TTS analysis (the red dashed line is a fit to the WLF model); the model can be used to interpolate or extrapolate the master curve to new temperatures, as shown in figure 6

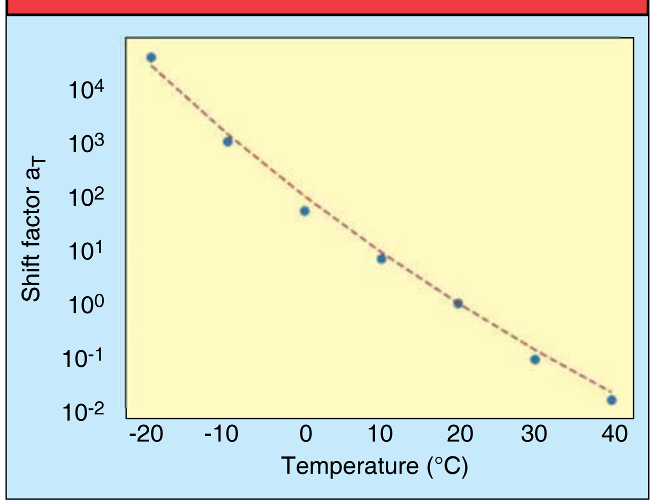
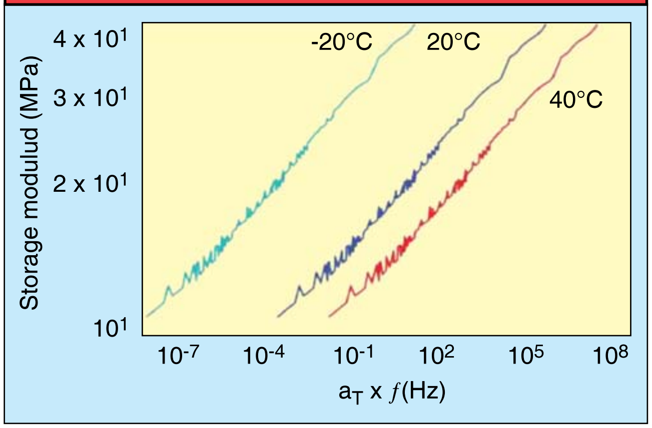


Figure 6 - using the shift factors and the WLF equation, how the material will respond at many different temperatures can be predicted; the master curve has been shifted to reference temperatures of -20°C, 20°C and 40°C



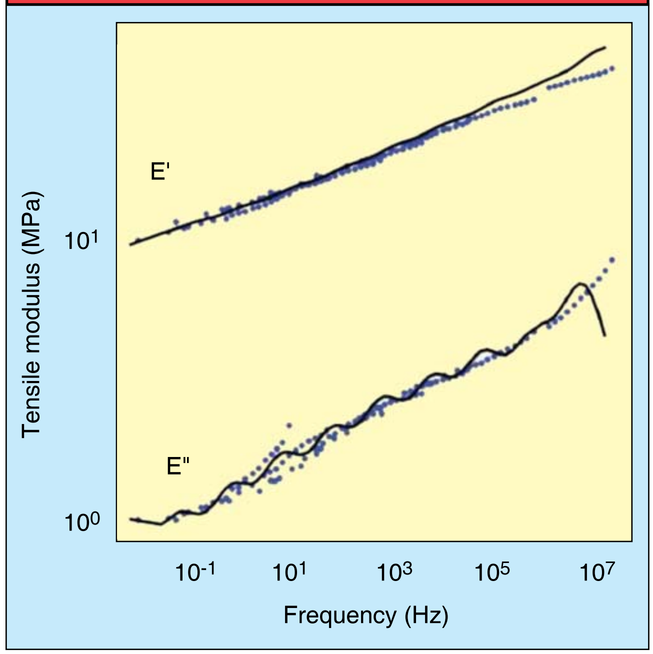
tures below the expected use temperature to measure the high-frequency behavior at low temperatures. This often requires DMAs that are capable of testing at very low temperatures, even below -100°C. Such low temperature testing often requires specialized equipment using liquid nitrogen for maintaining such low temperatures.

Using TTS data in finite element analysis simulations

Finite element analysis (FEA) is an advanced simulation methodology that powers much of modern engineering design. Understanding the high frequency or long time behavior of one elastomeric material is important, but that material likely forms just one part of an assembly or part. FEA can shape the material into a part and simulate how it interacts with the other components of the assembly. To do so, a material model needs to be calibrated to use as an input for the FEA software. Material models can be thought of as a system of mathematical equations that approximate the material's response to applied stresses, strains and changes in temperature.

Linear viscoelastic material models are most often used to describe test results from TTS. Figure 7 shows a linear viscoelastic model calibrated to the test data from figure 4. This model is called a Prony Series model, and conceptually consists of a series of parallel Maxwell elements (a spring in series with a dashpot). The particular model in figure 7 consists of six parallel Maxwell elements and one spring. The spring represents the material's long-time elastic modulus.

Figure 7 - a linear viscoelastic material model calibrated to the master curves; the blue lines are the master curves from figure 4, and the black lines show the model predictions, which match the master curves well



The model then has seven constants that need to be fitted to the experimental data. The black lines in figure 7 are the predictions of the model, which match the master curve quite well.

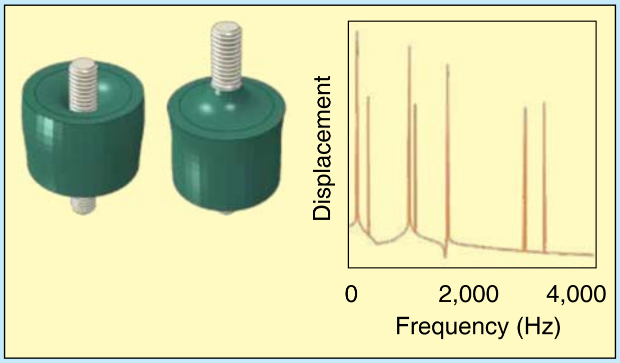
Table 1 shows the input file format for this linear viscoelastic model in the FEA program Abaqus. Linear viscoelastic models are available in most commercial FEA codes, though each has its own specification for how the parameters are calculated and

Table 1 - the input file for the material model in figure 7 for the FEA software program Abaqus; the input file contains the parameters for the material model in a text file format that is unique for each FEA program

```
* Material, name = MCal_Mat
** Calibrated with MCalibration
** Units: [length] = millimeter, [force] = Newton, [time] = seconds, [temperature] = Kelvin
** Calibration file name: Rubber.mcal
* Density
1e-09
*Hyperelastic, Yeoh, moduli-instantaneous
**          C10, C20, C30,           D1, D2, D3
4.123744428,     0, 0,0.007602561,    0,    0
*Viscoelastic, time = prony
**           gi,      kappai,           taui

0.0705829,               0,        1,000
  0.057639,              0,          100
0.0769322,               0,           10
0.0965108,               0,            1
  0.123909,              0,          0.1
  0.190715,              0,         0.01
```

Figure 8 - material model calibrated to the TTS master curve allows for prediction of the frequency response of the vibration isolator (green rubber between the two threaded connections); the purpose of the rubber is to decrease vibrations between the two connections; associated images show the axial deformation mode with deformation exxagerated to highlight the response (left); related calculated resonant frequency of the vibration isolator (right)



idiosyncratic input file format.

Once a material model is calibrated and input into the FEA code, the response of a part, assembly or product to external loads or changes in temperature can be simulated. Vibration isolators are rubber parts used to damp vibrations between machine components or connections between them. Incorrectly deploying vibration isolators can lead to excess noise and vibrations that could damage sensitive equipment. Figure 8 shows the frequency response of a rubber vibration isolator that was simulated in Abaqus. The resonant frequencies and mode shapes can help NVH engineers to minimize the transmission of vibrations between parts of their equipment.

Limitations of TTS

TTS is a useful technique for most polymer materials and elastomers. However, it will not work for all materials under all conditions. In general, it is difficult to say if TTS will apply to a particular material without doing some testing to investigate. However, there are a few guidelines that make time-temperature superposition more likely to be successful:

- Stay within the linear viscoelastic range of the material. Each material has its own unique linear viscoelastic limit (a maximum stress in the case of creep tests, or maximum strain amplitude for oscillatory tests) below which the modulus does not depend on the applied stress or strain. Testing at stresses and strains below the linear viscoelastic limit makes TTS more likely to capture the material behavior accurately.
- The simpler the structure and composition of the material, the more likely it is for TTS to apply to the material. Multi-phase materials such as certain blends and composites may have multiple kinetic processes that contribute to viscoelasticity, and each process will have different temperature dependence. For these materials, it will be impossible to create an overlapping master curve as was done in figures 3 and 4. Such materials are called thermorheologically complex.

Figure 9 - three-point bend test fixture for long term creep testing

When both speed and accuracy are important to a design, validation testing alongside creep TTS testing are typically recommended. In those efforts, the first phase of the project will be to generate a creep master curve, as is shown in figure 3. The second phase (often run concurrently) is to perform long term creep testing, without any accelerated testing. The long term testing can last for days, weeks, months or years, depending on the application. Long term creep testing can be performed on dedicated test fixtures, such as the three-point bending fixture in figure 9. At predefined checkpoints, the long term creep behavior can be compared to the TTS master curve, and analyses can be adjusted accordingly.

Combining TTS testing with long term validation testing combines the quick turnaround of TTS testing with the improved accuracy and representativeness of real time testing. The TTS master curve allows designers to make initial designs quickly, and begin the iterative design process. As real time data are combined with the master curves, the designs can be modified to adjust for any differences between the TTS master curve and real time creep test results.

Conclusion

The value of time-temperature superposition is measuring material properties at timescales that are not feasible or are not possible with real-time testing and conventional laboratory equipment. By taking advantage of the viscoelastic nature of rubbers, elastomers and other polymers, one can use reduced temperature to measure high frequency behavior, or elevated temperature to measure long-time behavior. TTS can predict years of behavior with tests that last a few hours, or predict mechanical properties up to the MHz range for high frequency applications. Taking advantage of TTS early in the design process can help engineers iterate and refine designs rapidly and with confidence.

References

1. J.D. Ferry, Viscoelastic Properties of Polymers, John Wiley & Sons, Inc. (1980).