

Bridge You and Nano

## **Time-Temperature Superposition Using Dynamic Mechanical Analysis**

With their low cost and ease of manufacture, structural polymer components have become increasingly common in consumer products. While switching from metal to polymeric components can decrease the material cost of a product, there are additional design considerations to take into account. One of those considerations is the viscoelastic nature of polymeric materials.

The time and temperature dependent behavior of polymers is due to their molecular structures. As a polymer is stressed, it undergoes molecular rearrangement in an attempt to relieve the stress. This results in an apparent decrease in stiffness (or storage modulus) over time. This would seem to imply that polymers must be evaluated for specific applications by testing under the conditions they will be subjected during use. Fortunately, there is a demonstrated relationship between the time (frequency) and temperature at which a material is tested. In other words, it is possible to determine very low (or high) frequency properties by simply testing the material at a higher (or lower) temperature. This relation is known as 'time-temperature superposition' (TTS).

Dynamic mechanical analysis (DMA) characterizes the viscoelastic behavior of materials by applying a sinusoidal force to a specimen and measuring the material response. It is one of the most sensitive and accurate techniques for applying the time-temperature superposition principle.



Figure 1. Demonstration of time-temperature superposition. The isotherms for 107°C and 99°C are shifted to predict low frequency properties at 91°C.

With TTS, it has been demonstrated that it is possible to determine material properties for very low or high frequencies by performing creep, stress relaxation, or multiple frequency tests at a variety of different temperatures. By shifting the isothermal data along the time (frequency) axis, it is possible to obtain a single isotherm, typically referred to as the 'master curve,' of the modulus for a much broader range of frequencies than was tested. This is illustrated in Figure 1.



The amount of shifting required to obtain the master curve can be mathematically described by the Williams-Landel-Ferry equation, shown in Equation 1.

Equation 1: 
$$log(a_T) = -C_1^o \frac{T-T_0}{C_2^0 + T - T_0}$$

In this equation,  $T_0$  is the reference temperature, i.e. the temperature to which all the isotherms are shifted.  $T_0$  is typically defined as the glass transition temperature, Tg.  $C_1^o$  and  $C_2^0$  are empirical constants (17.4 and 51.6, respectively, for many amorphous polymers), T is the temperature of the isotherm to be shifted, and  $a_T$  is the shift factor

To illustrate the principle of TTS, Ebatco's NAT Lab tested poly(ethylene terapthalate) (PET) ribbon at a variety of temperatures and frequencies. By applying the WLF model, the isotherms are shifted to create a master curve for the storage (E') and loss (E'') moduli at 91°C, the glass transition temperature of the material, presented in Figure 2.



Figure 2. Master curve for PET at 91°C.