

Thermal Analysis & Rheology

THERMAL SOLUTIONS

Effect of Frequency on the Modulus and Glass Transition Temperature of PET



In dynamic mechanical analysis, DMA, the viscoelastic properties of a material are characterized by applying a sinusoidal deformation to the material at a single or at multiple frequencies, and monitoring the response of the material. Since polymers are viscoelastic materials, i.e. they simultaneously exhibit solid-like and liquid-like properties, they are by definition time-dependent. This means that the response of a viscoelastic material to an imposed deformation will depend on how fast or slow the deformation was applied to the sample. When characterizing a material by DMA, the time of the deformation is the frequency(ies) as frequency is the inverse of time (frequency = 1/time). Therefore, high frequencies are analogous to short times and low frequencies to long times. The plot above shows the temperature dependence of the storage modulus and tan delta for a piece of PET film at frequencies of 0.1 Hz and 10 Hz. Note in the plot above that the storage modulus is higher for the higher frequency scan then for the lower frequency scan.

The plot above shows an isothermal step and hold scan for a polyethylene terapthalate PET sample scanned at frequencies of 0.1 and 10 Hz. It can be seen in the plot above that at higher frequencies, the storage modulus demonstrates higher values and the glass transition temperature shifts to a higher temperature. Many polymeric materials may experience a range of temperatures and frequencies in their end use application, such as a polymer used in an automobile. It is therefore important to understand the temperature and frequency dependence of polymer materials. Because the glass transition is a kinetic transition, it is strongly influenced by the frequency (rate) of testing. The glass transition is a molecular relaxation that involves cooperative segmental motion whose rate will depend on temperature. Therefore, as the frequency of the test increases, the molecular relaxations can only occur at higher temperatures and, as a consequence, the T_g will increase with increasing frequency. In general, as the frequency increases, there will be a decrease in the intensity of the tan δ , a broadening of the tan $\delta\epsilon\lambda\tau\alpha$ peak, and a decrease o the slope of the storage modulus curve in the region of the transition. ¹

In addition, DMA is most widely used to measure the glass transition temperature of polymers. Because the frequency can have such a significant effect on the temperature at which the glass transition is detected, it is important to report the frequency along with the glass transition temperature. For additional information see TS-64 Measurement of the Glass transition Using Dynamic Mechanical Analysis.

1.Reference: Turi, Edith A., Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, 1997, P. 529.