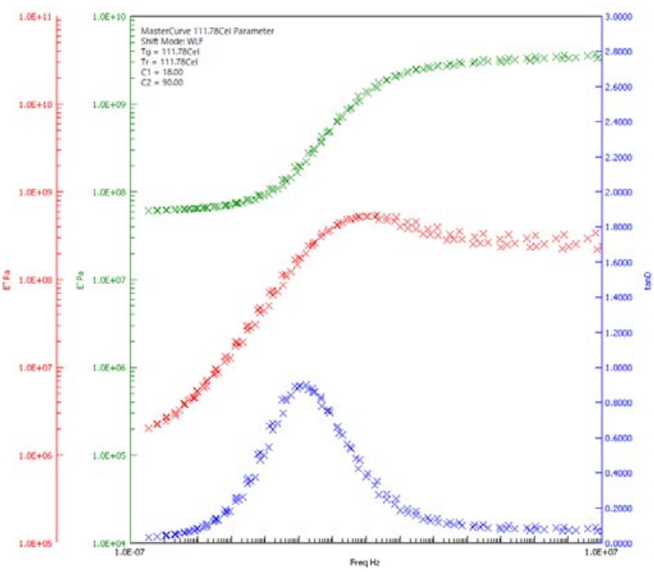
APPLICATION NOTE

DMA7100



Preparation of master curves by dynamic viscoelastic measurements

INTRODUCTION

The elasticity and viscosity of polymers are dependent upon the frequency of an applied force. To evaluate whether a polymer will withstand all operational conditions, it's useful to verify the viscoelastic properties over many potential frequency ranges. Rather than run hundreds of tests, a much more feasible approach is to generate a set of master curves that predicts viscoelastic properties over a wide range of frequencies.

Dynamic viscoelastic measurements help establish how your polymer will behave under specific operating frequencies and temperatures. Properties that are essential to the performance of the finished product, like glass transition temperature, are dependent upon environmental factors such as frequency. However, in real-world applications, applied frequency is not static, and the challenge is to make sure that the final component will not disintegrate or perform poorly because the user has turned up the speed of the motor, for example.

Generating a 'master curve' allows you to predict the viscoelastic properties of a material beyond the range where it's usually possible (or practical) to carry out a measurement. This exercise is based on the time-temperature superposition – where you take advantage of the close relationship between frequency and temperature when a material is subjected to an oscillating force. In essence, you can convert measured temperature changes at a given frequency to frequency changes at a given temperature.

In this application note, we're following the method developed by Williams, Landel, and Ferry (WLF) to generate master curves. It should be noted that this principle only applies to homogeneous amorphous polymers and the WLF equation is only to be used from the glass transition temperature, T_g , plus 100ºC.

Dynamic viscoelastic analysis of polymers is carried out using a dynamic mechanical analyzer (DMA). These measurements give you elasticity and viscosity results at specific frequencies. In order to use these results to generate master curves, you'll need to use a DMA instrument that has this functionality. The Hitachi DMA7100 comes with this capability as standard and is engineered for ultra-low noise and high sensitivity for reliable results, essential when extrapolating measured data.

Hitachi High-Tech Analytical Science's family of thermal analyzers have been employed in the field for more than 45 years, delivering world-class performance for precise materials characterization measurements, such as epoxy adhesive analysis.

HITACHI INSTRUMENTS FOR THE GENERATION OF MASTER CURVES

DMA7100

The Hitachi DMA7100 (dynamic mechanical analyzer) is versatile, high-performance instrument that's ideal for dynamic viscoelastic analysis within production, applied research and R&D for many kinds of materials, including polymers. The instrument includes Hitachi's easy to use software that simplifies understanding and interpreting DMA results, and the DMA7100 is delivered with a complete range of software modules, including master curve generation and activation energy calculations.

The DMA7100 has been designed with advanced signal processing software that delivers a noise-free signal of viscoelastic measurements. This increases the sensitivity of the instrument and makes the results much easier to interpret. Plus, the hardware to control the instrument has superior performance to increase the measurement data point count which increases the accuracy of the results.

Wide frequency and modulus ranges, plus high resolution and customizable fixtures, makes the DMA7100 an extremely versatile instrument, capable of many different applications on a wide range of materials. And automated liquid nitrogen cooling with optimized liquid nitrogen consumption helps to reduce operating costs.

ALL-INCLUSIVE SOFTWARE WITH SIMPLE MEASUREMENT WIZARD

The NEXTA TA software within the DMA7100 gives you options for how you want to operate the analyzer. New users can get reliable and accurate results and experienced operators can use these instruments for more advanced analysis. For generating master curves, the simple measurement wizard can be used which will walk the user through the analysis, from setting up the sample ID to taking the measurement, prompting for key parameters at every stage.

PERFORMANCE AND RESULTS

Background

The WLF equation has the following general formula:

$$\log a_T = -C^0_1 \frac{T - T_0}{C^0_2 + T - T_0} \quad \text{———} \quad (1)$$

For a given reference temperature T_0, this equation determines the amount of horizontal shift (a_T) for data measured at T_0 and T. This horizontal shift quantity, a_T, is called the "shift factor". In this case, C_1 and C_2 are empirical constants that are determined by the reference temperature T_0. Substituting the glass transition temperature, T_g , for the reference temperature, T_0, gives us:

$$\log a_T = -C^g_1 \frac{T - T_g}{C^g_2 + T - T_g} \quad \text{———} \quad (2)$$

For most amorphous polymers C_1 and C_2 have the following values:

$$C^g_1 = 17.44 \qquad C^g_2 = 51.6$$

By substituting these numerical values into Equation (2), we have:

$$\log a_T = -17.44 \frac{T - T_g}{51.6 + T - T_g} \quad \text{—} \quad (3)$$

The shift factor a_T for most amorphous polymers can be approximated by this equation.

Master curve generation with the DMA7100 of PMMA

To illustrate the method of generating master curves we used a sample of poly(methyl methacrylate), PMMA.

Dynamic viscoelastic measurements for frequency range 0.01 Hz to 100 Hz

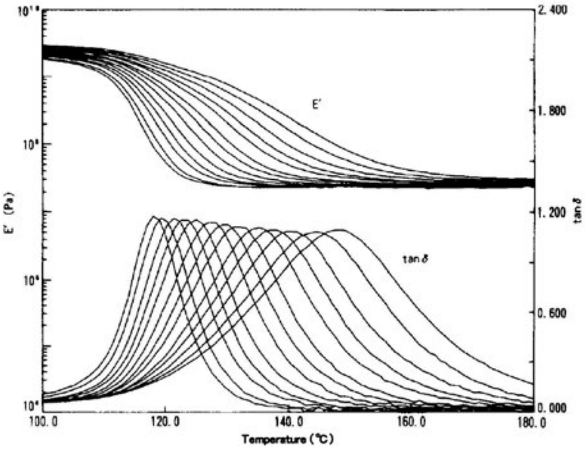


Figure 1 E' and tanδ curves for PMMA

Figure 1 shows the results for DMA measurements over 13 different frequencies, ranging from 0.01 Hz to 100 Hz. The upper curve shows the storage modulus data (E') and the lower one the loss tangent (tanδ) for the main dispersion (glass transition, T_g,) of PMMA. The graph clearly shows that T_g changes for different applied frequencies.

Frequency dispersion data from figure 1

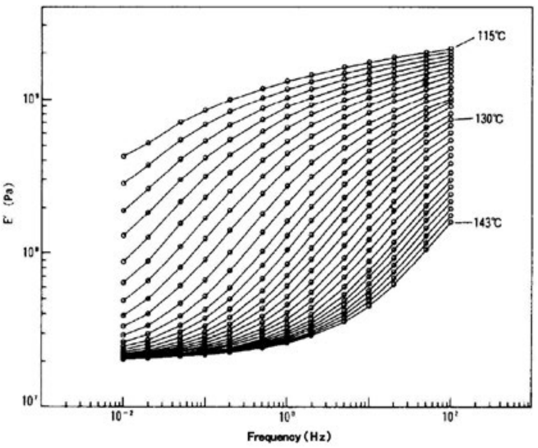


Figure 2 Frequency dispersion data for E' for T_g of PMMA

Figure 2 uses the E' curves measured in figure 1 to generate a series of constant temperature curves showing E' over a range of frequencies.

Master curve for T_g of PMMA at 130ºC

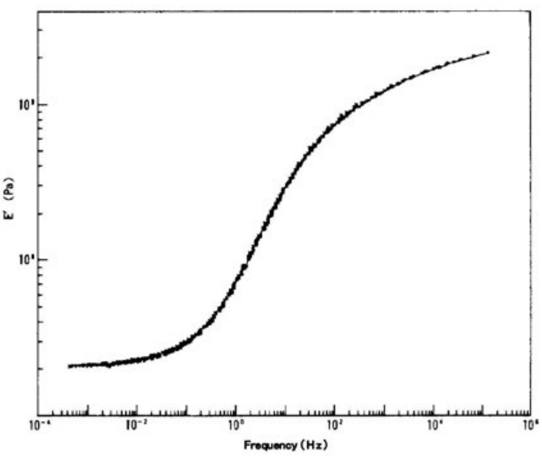


Figure 3 The master curve of the main dispersion of PMMA at 130ºC

Figure 3 is an example of a master curve taken from the data shown in figure 2. This is based on the WLF equation (shown above), from which the reference temperature, T_0, is set to 130ºC. Over the frequency range in the graph, 10^{-3}Hz — 10^{5}Hz, the individual curves merge into a single master curve.

Activation energy of T_g of PMMA

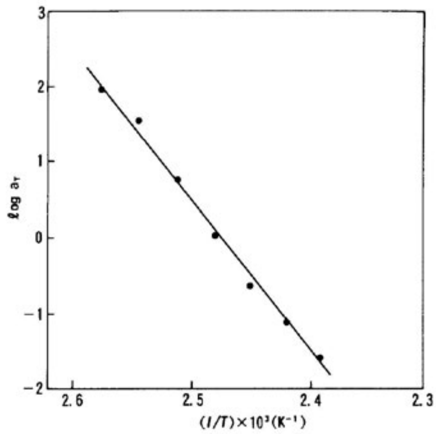


Figure 4 log a_T vs. 1/T plot of the main dispersion of PMMA

Figure 4 shows the relationship between the calculated log of the shift factor (log a_T) for various temperatures and the reciprocal temperature, 1/T. (The shift factor was calculated using equation 3 above.) This is an example of an Arrhenius plot where the gradient is the activation energy of the relaxation event (the glass transition in this case). The activation energy for T_g of PMMA is calculated as 382.9 kJ/mol. Also, in this case there is only one line. This implies that the main dispersion of the PMMA is due to a single event, the glass transition. This is not always the case, as can be seen in figure 5.

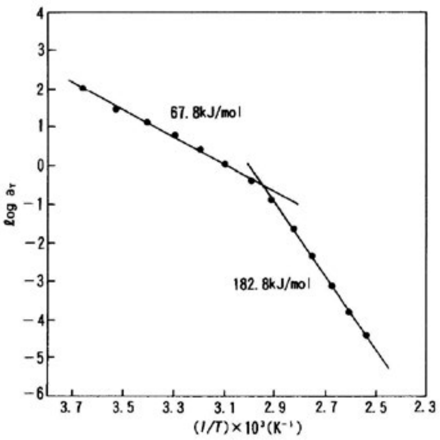


Figure 5 log a_T vs. 1/T plot of the main dispersion of high-density polyethylene

Figure 5 shows the Arrhenius plot for HDPE. We can see two straight lines with different gradients. This implies that the main dispersion of HDPE is due to two different mechanisms of significantly different activation energies.

SUMMARY

The advanced software and high sensitivity of the **DMA7100** make it ideal for generating master curves to predict polymer viscoelastic behavior over a wide frequency range. The instrument also allows for activation energy calculations of different types of polymer, allowing for reliable evaluation of the performance of polymer products under many different operating scenarios.

Many applications have been optimized for Hitachi High-Tech Analytical Science's thermal analyzers. For more information on other applications, please contact our experts at **contact@hitachi-hightech.com**.

DMA7100: ULTRA-SENSITIVE MECHANICAL CHARACTERIZATION

Our dynamic mechanical analyzer range is engineered for ultra-low noise and high sensitivity, making it ideal for precise viscoelastic measurements of polymers, rubbers, thin films and other materials within a production or research environment.

The DMA7100 range offers:

- Ease of use with simple sample clamping mechanism and step by step guidance software
- Low operating costs with auto LN2 cooling unit that reduces nitrogen consumption
- Ability to perform sinusoidal and synthesis wave oscillations, stress-strain, creep/recovery and stress relaxation measurements.
- Ultra-low noise and Lissajous monitoring ensures reliability of the results for every measurement
- Supports a variety of deformation modes: tension, dual-cantilever bending, 3-point bending, shear, film-shear and compression.

Visit **www.hitachi-hightech.com/hha** for more information.