Guidelines for using TTS

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BACKGROUND

It is well known that there is an equivalence of the effects of time and temperature on the rheological properties of viscoelastic materials[1]. At low temperatures a material will behave in the same fashion as at high frequency, and at high temperature the material will behave as it would at low frequency.   Data in a range of temperatures over modest frequency ranges(see figure 1) can be collected and arranged to predict the behavior over a wider frequency range than possible in practical testing. Bear in mind that very low frequencies can take days or weeks for measurements, and ultra high frequencies cannot be measured by existing instruments. The modulus data can then be shifted horizontally along the abscissa to overlap forming a smooth curve. This approach allows the generation of master curves of modulus data spanning considerably wider ranges of time (frequency) and/or temperature than the range of the original data (see figure 2).

Master curves can be constructed also, using shift factors derived from the Williams, Landel, Ferry (WLF) equation according to:

$$\log a_T = -c_1(T - T_o)/c_2 + (T - T_o)$$

Here a_T is the temperature shift factor, T_o is an arbitrary reference temperature and c_1 and c_2 are constants derived from curve fitting and are generally accepted at 17.44 and 51.60 respectively when To=Tg.

The manual calculation process of generating shift factors is extremely tedious. Fortunately, the extensive work required to produce a master curve is reduced to the push of a button by using TAI-Orchestrator TTS curve shifting software.

Master curves can be particularly helpful in understanding the rheological behavior of a polymer. The superposition process separates the two principle variables—time and temperature—upon which the viscoelastic properties depend, expressing the properties in terms of a single function for each.

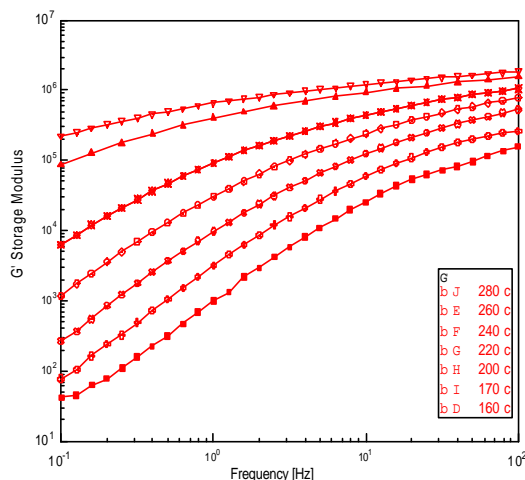The master curve shows the frequency dependence of the material at a constant reference

Fig. 1: TTS overlays of Frequency/ Temperature Sweep data.

temperature, T_o ; the effect of temperature on the viscoelastic properties is shown by the variation of the shift factor a_T with temperature.

One can see very clearly from Figures 1 and 2 that data taken over only 3 decades of frequency (Figure 1) can be shifted to generate a master curve which spans 7 decades of frequency (Figure 2).

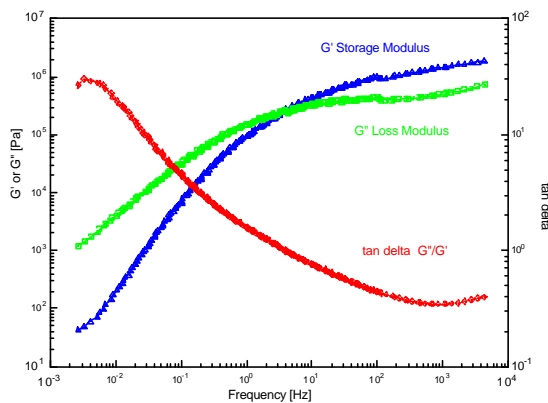Nonetheless, caution must be exercised in the use of the WLF equation and TTS. The various

Fig. 2: Master Curve for ReferenceTemperature of 200 C

equations and methods employed to calculate shift factors have limits, and these must be respected if reliable information is to be derived from their use.

J. D. Ferry[2] has developed some guidelines (1989) concerning the limits of the WLF equation, which are presented in the following sections:

TESTS OF APPLICABILITY OF TTS FOR A NEW POLYMER

Before attempting to employ the WLF equation for time-temperature superposition of rheological data, the following aspects should be considered:

- Are temperatures spaced closely enough to provide substantial overlap of logarithmic curves of *G(t)*, *G'*, *G"*, etc., and do their shapes match exactly?

- Is the same a_T obtained from shifting G' and

G" or J' and J*" ?*

- Is the empirical plot of log a_T against T a smooth curve with no zigzags?

- If the temperature dependence of a_T fits the WLF equation, do the coefficients c_1 and c_2 have reasonable values? (the product of c_1 and c_2 should be independent of the choice of T_o and be of the order of 400 to 900).

If these criteria are not fulfilled, the WLF method may not work. However, generation of a master curve may be possible using a more complicated analysis.

WHEN NOT TO USE TTS

Simple time-temperature superpositioning (shifting of curves with or without the WLF equation) should not be used if:

- Any crystallinity is present, especially if partial melting occurs in the temperature range concerned.

- The actual structure changes with temperature; e.g., labile cross-links dissociate.

- The material is a block copolymer (TTS may work within a limited temperature range. However, a more complicated analysis is usually required.)
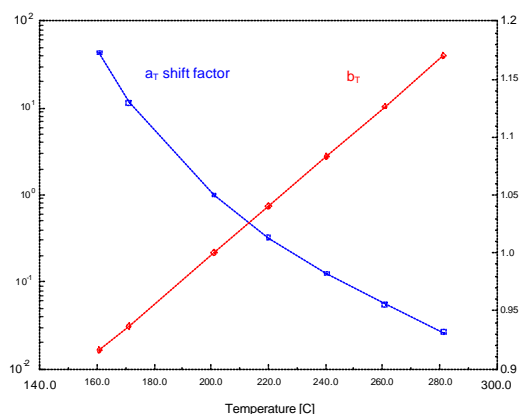
- The material is a composite of different

Fig 3: Shift factors for Mastercurve in Figure 2.

polymers.

- Viscoelastic mechanisms other than configurational changes of the polymer backbone occur; e.g., side-group motions, especially near Tg.

WHEN NOT TO USE THE WLF EQUATION (EVEN IF TTS APPEARS TO WORK)

The WLF equation should not be used for TTS in the following circumstances:

- If $T > Tg + 100°$, or if T < Tg and the polymer is not elastomeric, the Arrhenius form (see below) is usually better.

- If the temperature range is small, then c_1 and c_2 cannot be calculated precisely and the Arrhenius form is a satisfactory approximation. The Arrhenius form is:

$$\ln a_T = (Ea/R)(1/T - 1/T_o)$$

where *Ea* is the apparent activation energy.

By following these simple guidelines, the master curves generated by TAI-Orchestrator's TTS curve shifting software will offer an excellent representation of material behavior over a wide range of times and frequencies within the confines of standard laboratory testing.

REFERENCES

1. AN005 Generating mastercurves; TAI productn note
2. Ferry, J.D., Viscoelastic Properties of Polymers