Thermal Analysis Application Brief

Application of Time-Temperature Superposition Principles to DMA

Number TA-144

Polymers, because of their viscoelastic nature, exhibit behavior during deformation which is both temperature and time (frequency) dependent. For example, if a polymer is subjected to a constant load, the elastic modulus exhibited by the material will decrease over a period of time. This occurs because the polymer under a load undergoes molecular rearrangement in an attempt to minimize localized stresses. Hence, modulus (stiffness) measurements performed over a short time span result in higher values than longer term measurements. This time dependent behavior would seem to imply that to accurately evaluate material performance for a specific application, one needs to test the material under the actual temperature and time conditions it will see in end-use. Fortunately, that type of tedious testing is not necessary. Using multifrequency or accelerated temperature measurements and theoretical time/temperature superposition treatment of the data, limited lab tests (creep, fixed frequency oscillation, or stress relaxation) are sufficient to project long-term properties under a variety of conditions. Dynamic mechanical analysis (DMA) which

measures the modulus (stiffness) and damping (energy dissipation) properties of a material as the material is deformed under periodic stress is one of the best thermal analysis techniques for using this time/temperature predictive approach.

THEORY

The underlying basis for time/temperature superpositioning is the demonstrated equivalency between time (or frequency) and temperature. It has been demonstrated that viscoelastic data collected at one temperature can be superimposed upon data obtained at a different temperature simply by shifting one of the curves along the time (or frequency) axis (1).

The superposition principle is based upon the premise that the processes involved in molecular relaxation or rearrangements occur at greater rates at higher temperatures. The time over which these processes occur can be reduced by conducting the measurement at elevated temperatures and transposing the data to lower

Figure 1. UNSHIFTED CREEP DATA
(Polycarbonate)
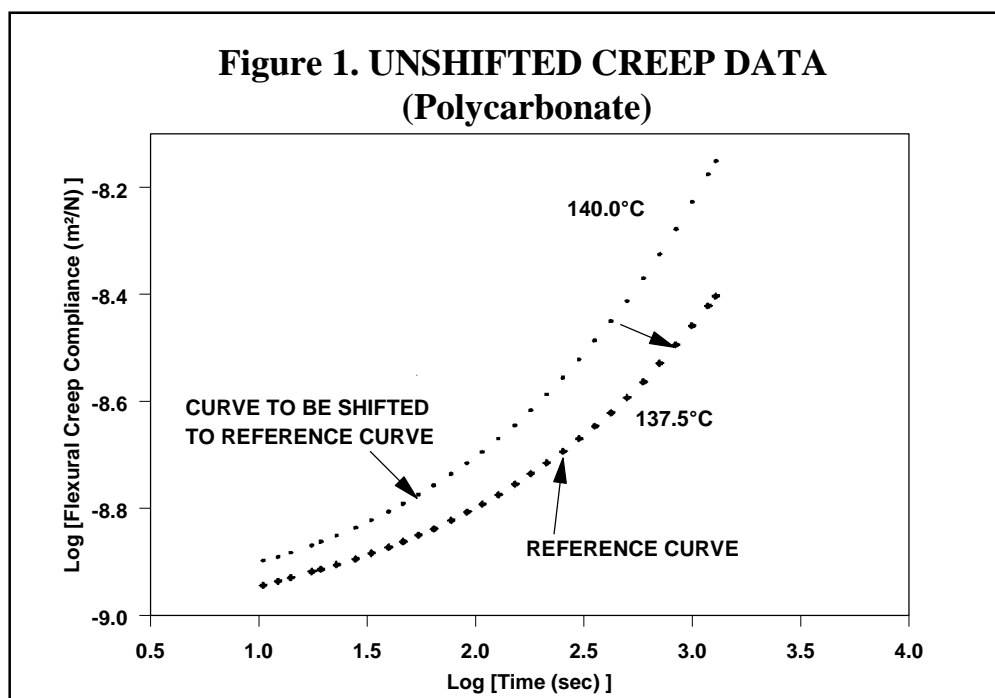
temperatures. Thus, viscoelastic changes which occur relatively quickly at higher temperatures can be made to appear as if they occurred at longer times or lower frequencies simply by shifting the data with respect to time (or frequency).

For example, consider the results of a creep experiment (i.e., constant stress) performed on polycarbonate. Figure 1 shows the log creep compliance (S), where S = [strain (time) / stress], as a function of log time at two different temperatures. The creep compliance curve at 137.5°C is selected as the reference and the data obtained at 140°C can be shifted to the right (i.e., longer times) to superimpose upon the chosen reference, as shown in Figure 2. Shifting the higher temperature data to the lower reference temperature has the effect of making the data appear to have been collected at a lower temperature, which thus increases its corresponding time scale.

Viscoelastic data can be collected by performing static measurements under isothermal conditions (e.g., creep or stress relaxation), or by performing frequency multiplexing experiments where a material is analyzed at a
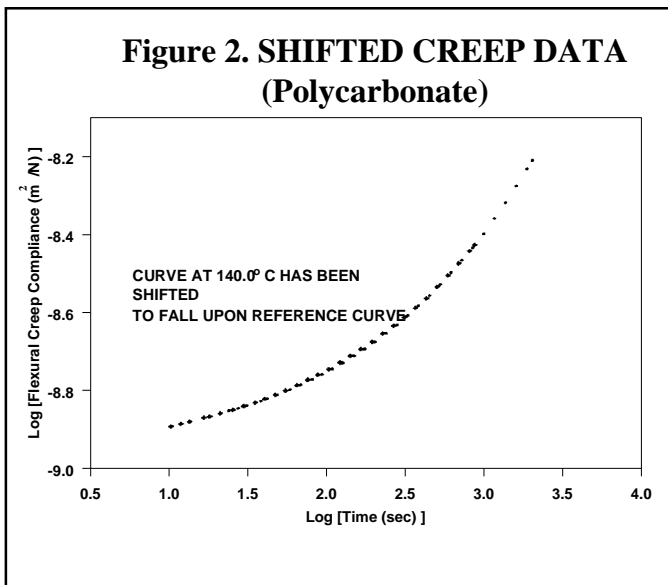
In this equation, T_o, is the reference temperature (typically T_o is taken as the glass transition temperature, Tg), C_1 and C_2 are constants, T is the measurement temperature, and a_T is the shift factor. The temperatures are Kelvin. For many amorphous polymers, it has been found that $C_1 = 17.4$ and $C_2 = 51.6$ (2) when $T_o = Tg$.

The WLF equation is typically used to describe the time/ temperature behavior of polymers in the glass transition region. The equation is based on the assumption that, above the glass transition temperature, the fractional free volume increases linearly with respect to temperature (2). The model also assumes that as the free volume of the material increases, its viscosity rapidly decreases (4).

The other model which is commonly used to relate the shift factors with respect to temperature is the Arrhenius relation:

$$\log a_T = \frac{E}{R(T - T_o)} \tag{2}$$

In this equation, E is the activation energy associated with the relaxation transition, R is the gas constant (R = 8.314

Figure 2. SHIFTED CREEP DATA (Polycarbonate)

CURVE AT 140.0° C HAS BEEN SHIFTED TO FALL UPON REFERENCE CURVE

Figure 3. FREQUENCY MULTIPLEXING (Polycarbonate)

Amplitude (p-p) = 0.50

series of frequencies. By selecting a reference curve and then shifting the other data with respect to time (or frequency), a "master curve" can be generated. A master curve is of great value since it covers times or frequencies outside the range easily accessible by experiment.

The degree of horizontal shifting (i.e., time) required to shift a given set of data upon a reference can be mathematically described with respect to temperature. Two models are commonly used. The first of these relations is the well-known Williams-Landel-Ferry (WLF) equation (2,3):

$$\log a_T = \frac{-C_1 (T - T_o)}{C_2 + (T - T_o)} \tag{1}$$
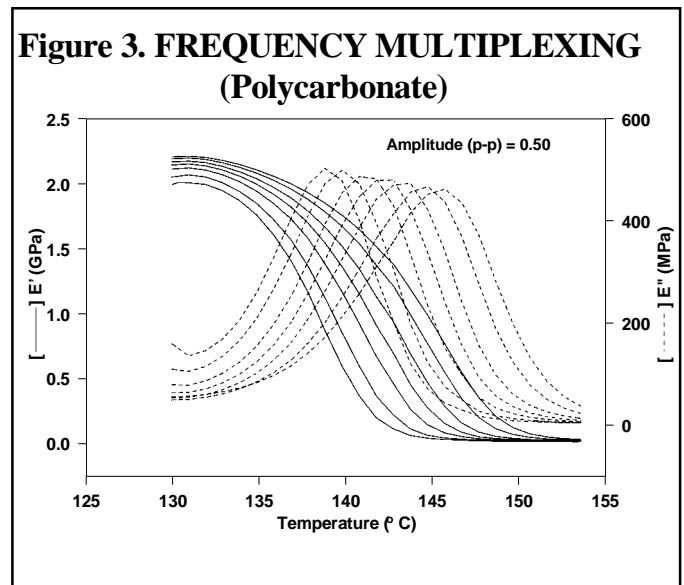
J/mole °C), T is the measurement temperature, T_o is the reference temperature and a_T is the time-based shift factor. The Arrhenius equation is typically used to describe the viscoelastic events associated with β and γ relaxation transitions or for the glass transitions associated with semi-crystalline polymers. Frequently, it is used to obtain the activation energy associated with the glass transition event.

Fitting the experimentally determined shift factors to a mathematical model permits the master curve to be shifted to any desired temperature. Thus, data that was collected and referenced to a high temperature can be shifted, within reason, to low temperatures and vice-versa.

RESULTS & DISCUSSION

To demonstrate the application of time/temperature superpositioning techniques, master curves were generated for polycarbonate, using both frequency multiplexing and creep techniques. The data was generated using the TA Instruments DMA 983 and the master curves were produced using the TA Instruments DMA Superposition software.

The polycarbonate data was obtained in the glass transition region (i.e. 130 to 160°C). It is recommended that, when attempting to generate a master curve on a given material, the experiment be set up to ensure that data is collected as the sample passes completely through the desired relaxation transition.

Displayed in Figure 3 are the DMA results for polycarbonate obtained using frequency multiplexing

Figure 5. PARTIALLY COMPLETED MASTER CURVE
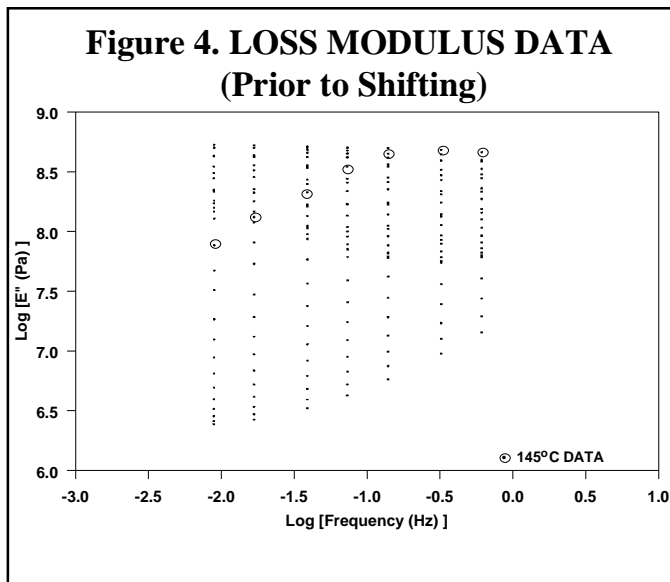
techniques. The specimen was analyzed at frequencies of 0.01, 0.02, 0.05. 0.1, 0.2, 0.5, and 1.0 Hz. It is recommended that a minimum of four frequencies over two decades be used when generating a master curve. The plot shows the flexural storage modulus (E') and loss modulus (E") as a function of temperature at the various analysis frequencies. The loss modulus peak temperatures show that the glass transition moves to higher temperatures as the analysis frequency increases. The loss modulus data can be used to generate a master curve. Displayed in Figure 4 is a plot which represents all of the individual E" data points as a function of log frequency. The data column on the extreme left represents data collected at 0.01 Hz, while that on the extreme right represents data collected at 1.00 Hz.
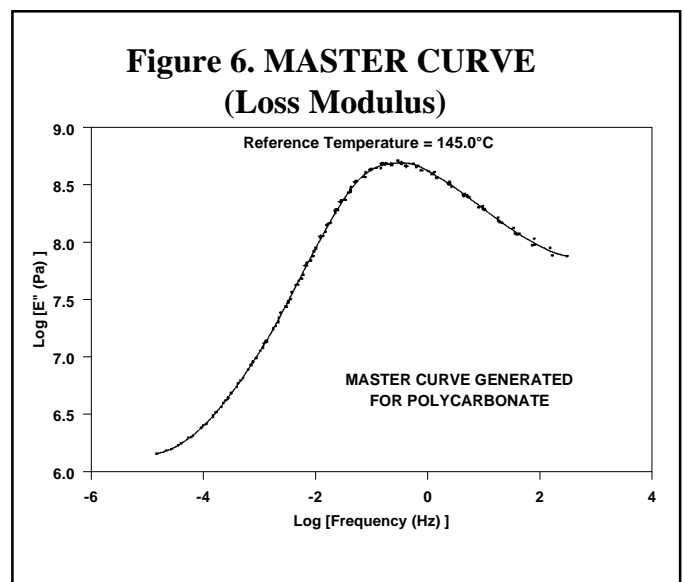
In the generation of the master curve, a reference set of data is chosen. For this experiment, 145°C was selected,
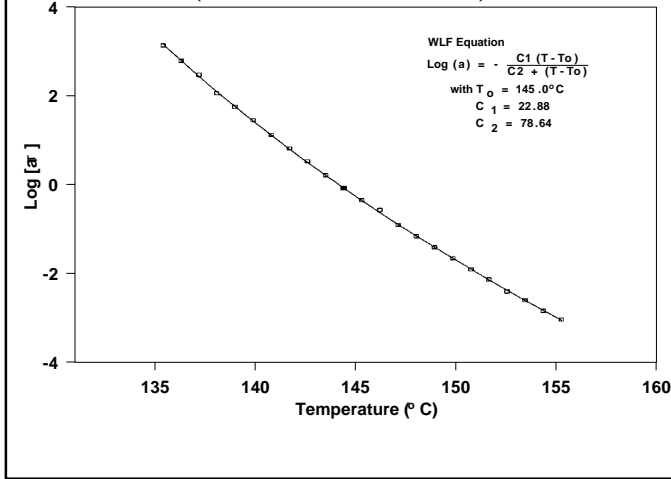
Figure 4. LOSS MODULUS DATA (Prior to Shifting)
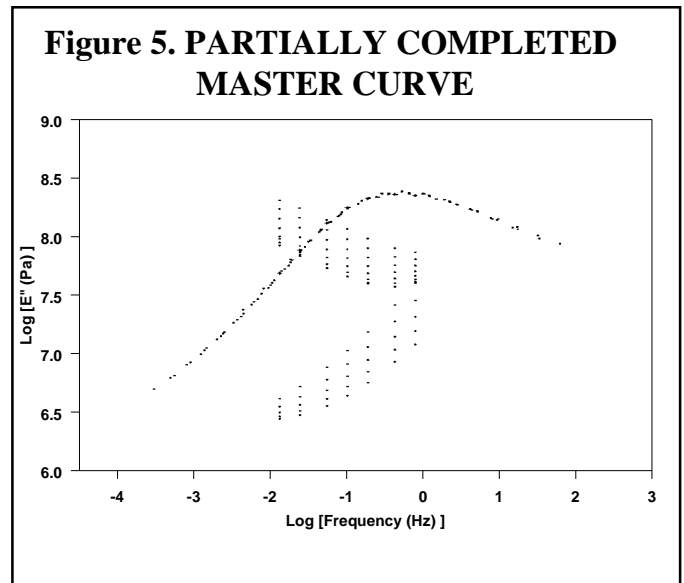
as shown in Figure 4. The remaining sets of data are shifted either to higher or lower frequencies to fall upon the chosen reference. The partially completed master curve is shown in Figure 5. The data sets (from higher temperature experiments) in the lower portion of the plot will be shifted to the left (to lower frequencies), while those in the upper portion will be shifted to the right (to higher frequencies) to cause them to fall upon the intermediate master curve. During the shifting, the computer stores the shift factors, a_T, for later use.

After all of the individual data points are shifted, the complete master curve is obtained for polycarbonate as shown in Figure 6. This curve shows the change in the loss properties with respect to frequency. The maximum energy dissipation occurs at a frequency of 0.31 Hz at 145°C, represented by the peak maximum.

The shift factors can now be fitted to one of the mathematical models. Displayed in Figure 7 is a plot of
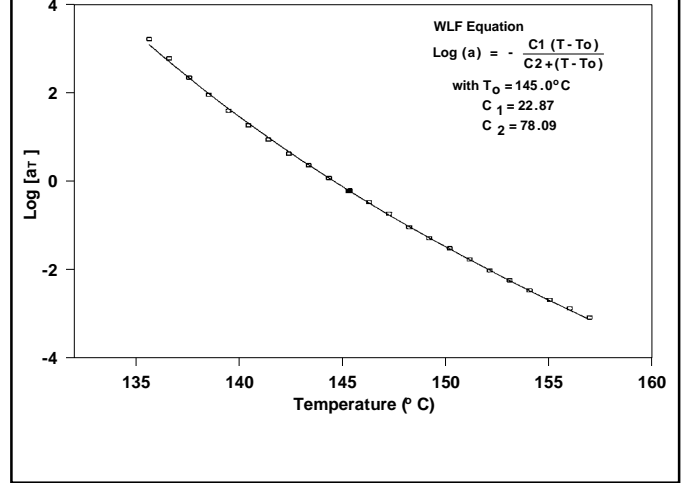
Figure 6. MASTER CURVE (Loss Modulus)

Figure 7. WLF EQUATION
(E" Shift Factor Fit)

WLF Equation

$$\text{Log}\,(a) = -\frac{C1\,(T - To)}{C2 + (T - To)}$$

with $T_O = 145.0°C$
$C_1 = 22.88$
$C_2 = 78.64$

Y-axis: Log [aт]
X-axis: Temperature (° C)

Figure 9. WLF EQUATION
(E' Shift Factor Kit)

WLF Equation

$$\text{Log}\,(a) = -\frac{C1\,(T - To)}{C2 + (T - To)}$$

with $T_O = 145.0°C$
$C_1 = 22.87$
$C_2 = 78.09$

Y-axis: Log [aт]
X-axis: Temperature (° C)

the experimentally determined shift factors as a function of temperature. The shift factor plot is slightly curved, reflecting WLF-type behavior. The WLF equation was thus selected to relate the shift factors to temperature. The solid line represents the WLF model while the boxes represent the experimentally determined shift factors. An excellent fit is obtained with the software-based assessments of the constants: $C_1 = 22.9$ and $C_2 = 78.8$. Once the shift factors have been described by the model, the master curve can be transposed to any desired temperature by the software. It is recommended, though, that the master curve be shifted only to temperatures in the range in which the data was collected. This ensures a valid extrapolation of data.

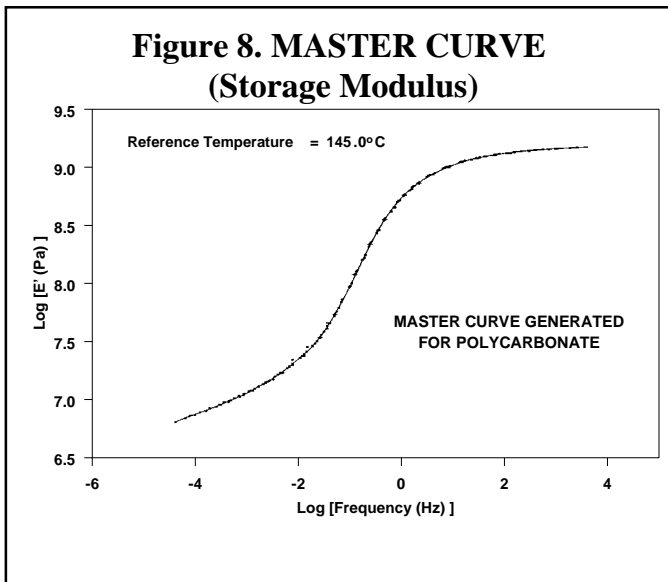A master curve for any of the other viscoelastic quantities (i.e. flexural storage modulus [E'], flexural storage compliance [S'], flexural loss compliance [S"], and tan delta [δ]) can be generated from the polycarbonate data using the DMA Superposition software.

Figure 8 displays the master curve generated from the storage modulus data for polycarbonate. The curve has been referenced to a temperature of 145°C. This curve shows the effects of frequency on the modulus of polycarbonate at this temperature. At very low frequencies (or long times) the material exhibits a low modulus and behaves similar to a rubber. At high frequencies (or short times) the polycarbonate behaves like an elastic solid and has a high modulus. This master curve demonstrates that data collected over only two decades of frequency can be transformed to cover nine decades.

The shift factor plot obtained from the generation of the E' master curve is displayed in Figure 9. The WLF equation again was selected to model the time-temperature behavior. Best-fit values of the constants $C_1 = 22.9$ and $C_2 = 78.1$, were obtained by the software. These constants are in very good agreement with those obtained previously from shifting the loss modulus data. These results are not surprising since, in theory, equivalent WLF constants should be obtained for any of the viscoelastic quantities for a given material.
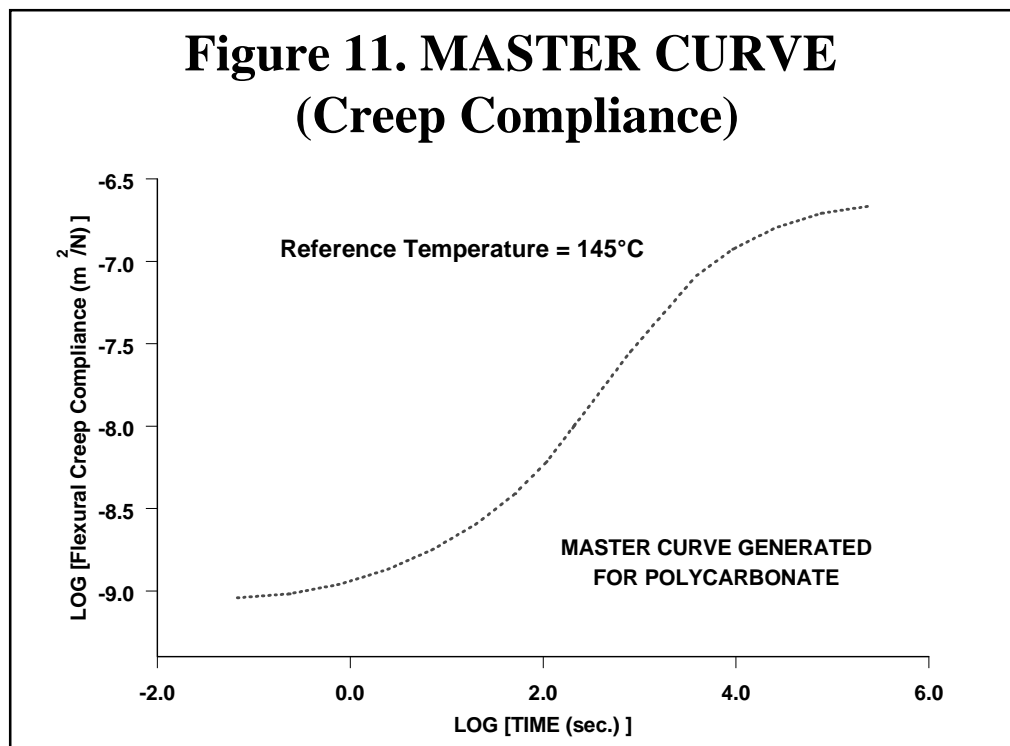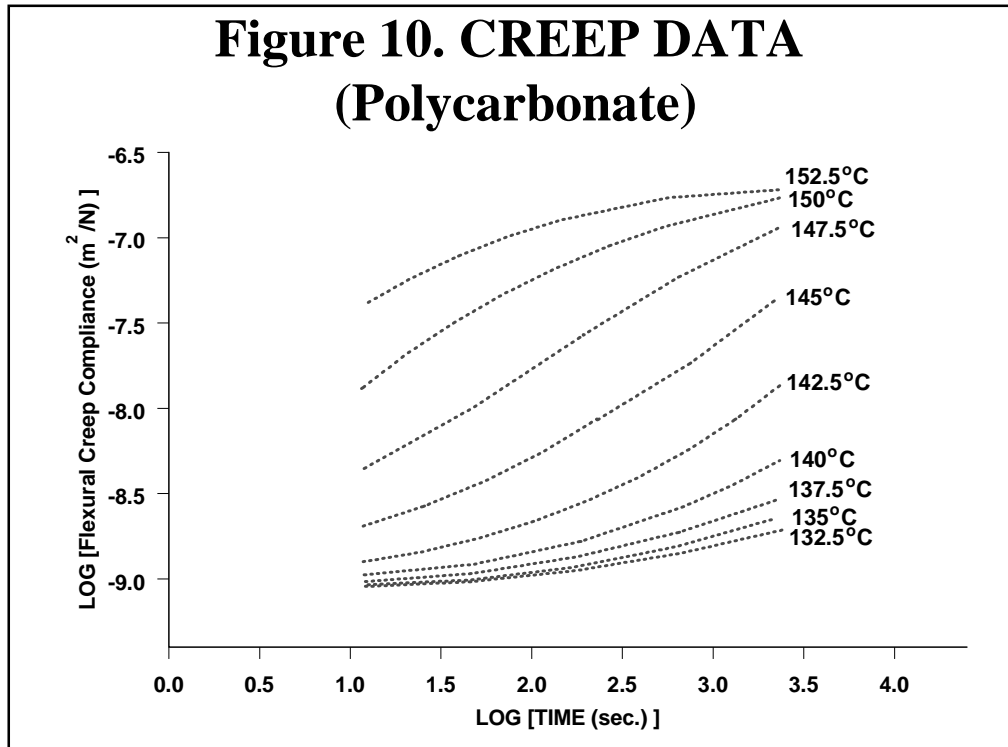
Figure 8. MASTER CURVE
(Storage Modulus)

Reference Temperature = 145.0°C

MASTER CURVE GENERATED FOR POLYCARBONATE

Y-axis: Log [E' (Pa)]
X-axis: Log [Frequency (Hz)]

In addition to fixed frequency data, creep or stress relaxation data can be used with the DMA superposition software to generate master curves. Creep data was obtained on polycarbonate in the temperature range of 130 to 155°C using the DMA 983. The log creep compliance (S) is displayed as a function of log decay time in Figure 10. One of the curves is selected as a reference (T_o = 145°C, in this case) and the other curves are shifted along the log time axis to superimpose upon the reference. The final master curve for polycarbonate, based on the creep data, is displayed in Figure 11. The curve shows that, at small time intervals, the material exhibits a relatively low compliance (or high modulus). At longer times, viscous flow occurs and the material exhibits a high compliance (or low modulus). The effects of time on the mechanical properties of polycarbonate are clearly demonstrated in this master curve.

The master curve can be used to determine the time (or frequency) at which a particular viscoelastic quantity reaches some "critical" value. For example, a rubber hose may rupture after months or years of use when the rubber

Figure 10. CREEP DATA (Polycarbonate)

Figure 11. MASTER CURVE (Creep Compliance)

Reference Temperature = 145°C

MASTER CURVE GENERATED FOR POLYCARBONATE

achieves a certain compliance value. The time that it takes to achieve this particular critical compliance at a given temperature can be easily established from the master curve.

DMA Master Curves can be generated in any of the three modes - fixed frequency, stress relaxation, and creep. Other examples applications include:

- *Gaskets* - to measure flow (creep) and stress relaxation effects which reduce seal integrity over time.
- *Force-fit snap parts* - to measure stress relaxation effects, which can lead to joint failure.
- *Structural beams* - to measure modulus drop with time, which leads to increasing beam deflection under load over time.
- *Bolted plates* - to measure creep of the polymer, which reduces the stress applies by the fastener.
- *Hoses* - to measure creep of the polymer, which can lead to premature rupture of the hose.
- *Acoustics* - to aid in the selection of materials which exhibit high damping properties in a specific frequency range.
- *Elastomer mounts* - to assess the long-term creep resistance of mounts used for vibration damping with engines, missiles and other heavy equipment.

SUMMARY

The effects of time and temperature on polymeric materials are important when considering these materials for demanding structural and engineering applications where metals have traditionally been used. Dynamic mechanical analysis (DMA) combined with time/temperature superposition software provides a convenient method for rapidly assessing important performance properties (e.g. strength, impact resistance, creep) of materials as a function of both time and temperature, thereby allowing design engineers to compare material performance with specific applications requirements.

REFERENCES

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