

Viscoelasticity of Polymers during Heating/Cooling Sweeps

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The well-known interrelation between temperature- and frequency-dependent dynamic mechanical data of thermorheologically simple materials was further investigated to provide useful rheological tools. Applicability of time–temperature superposition to isochronal dynamic mechanical temperature sweeps could be shown. Construction of master curves, $b_T G'(a_T \omega)$ and $b_T G''(a_T \omega)$, was possible from the isochronal data of two polymer samples, a commercial polycarbonate sample with temperature shift factors obeying the WLF equation and a commercial polyethylene sample with temperature shift factors following an Arrhenius expression. If the temperature dependence of the material's relaxation times follows an Arrhenius-type expression, the activation energy can be obtained directly from plots of isochronal loss tangent versus reciprocal temperature. However, in case of a polymer following the WLF equation the shift factors (or parameters of the WLF equation) must be known for this construction to be feasible. Furthermore, it is shown that extension of the experimental temperature window is possible once the frequency master curve is created. An appropriate temperature- and frequency-dependent shift factor c_T is introduced for this extension.

Introduction

The temperature dependence of molecular mobility in polymers can be measured in a small amplitude oscillatory shear experiment with gradually increasing (or decreasing) temperature. This so called “temperature sweep” or “temperature scan” (TS) is a commonly used experiment in polymer rheometry. The frequency ω is held constant during this experiment, and hence, the experiment will be called isochronal TS (although it is only isochronal with respect to the experimental time scale; the probed material time scale changes with temperature). The choice of frequency is quite arbitrary and limits the observation to molecular motions in the vicinity of a single mode instead of covering a wider spectrum of relaxation times. An extension of this common procedure can be easily envisioned: The rheometer could be programmed to probe, while heating a polymer sample, a sequence of frequencies, ω_i , within a frequency window, $\omega_{\min} < \omega_i < \omega_{\max}$. The sequence of frequencies may be repeated cyclically during the temperature scan. The method requires that the sample is in thermal equilibrium at all times which seems to be the case for many polymers even at moderate to high heating rates (Mours and Winter, 1994). In this fashion, a single experiment provides the temperature and frequency dependence of the relaxation spectrum. The problem is that every data point in this experiment (which can be called a “frequency-temperature scan” (FTS)) is taken at a new temperature and data analysis requires interpolation. However, such data interpolation methods and their limits of application are well established (Mours and Winter, 1994). Modern rheometers allow a similar but more time-consuming FTS standard procedure. In this experiment the polymer sample is probed at a cyclically repeated sequence of frequencies. After each frequency sequence, the temperature is increased or decreased in constant programmed steps. With these newly available rheometrical methods, temperature- and frequency-dependent dynamic mechanical data become readily accessible and their properties should be explored further.

Throughout this paper, we will narrowly focus on materials in which time and temperature changes are

equivalent over the entire range of observation, i.e., materials which obey the so called time–temperature superposition principle (Ferry, 1980). This restricts the study to homopolymers (and some miscible blends), but even there time–temperature superposition is limited to finite frequency or time windows. A better understanding of time–temperature superposition behavior in FTS experiments will help to define experimental criteria for measuring the limits where time–temperature superposition starts to break down. In addition, temperature changes may induce transitions in morphology which cause sudden changes in the molecular mobility. These transitions become especially evident when performing FTS in conjunction with calorimetry (DSC) or time-resolved X-ray scattering. In the following, we will *not* address the phenomena of thermally induced transitions. The study is restricted to thermorheologically simple materials.

Because of experimental constraints (e.g., not sufficiently high torque values at low frequencies or slip and inertial effects at high frequencies) it is usually impossible to measure dynamic mechanical data (storage modulus G' and loss modulus G'') with a commercial rheometer directly over more than 3 or 4 decades of frequency. Time–temperature superposition, if applicable, is able to extend the available frequency window. Frequency-dependent data at different temperatures can be superimposed (by simultaneous horizontal and vertical shifting) to yield the desired master curve over an extended frequency window and at a reference temperature T_{ref} within the experimental temperature range. Nowadays, commercial software packages are available that can easily perform this type of shifting (Winter et al., 1993). The superposition typically yields, for example, plots of reduced dynamic moduli $b_T G'$ or $b_T G''$ vs reduced frequency $a_T \omega$ (in the frequency domain) or reduced relaxation modulus $b_T G$ vs reduced time t/a_T (in the time domain). The temperature shift factors a_T and b_T represent the horizontal and vertical shift, respectively, between the experimental temperature and T_{ref} .

The horizontal shift factor a_T incorporates the influence of temperature on the relaxation time spectrum, i.e., on the relaxation times. This spectrum $H(\lambda)$ is

related to the relaxation modulus $G(t)$ by the following integral equation (Ferry, 1980):

$$G(t) = \int_0^\infty H(\lambda) \exp\left(-\frac{t}{\lambda}\right) \frac{d\lambda}{\lambda} \quad (1)$$

For practical reasons, the relaxation modulus is often represented as a sum of discrete Maxwell modes (exponential decay functions):

$$G(t) = \sum_{i=1}^N g_i \exp\left(-\frac{t}{\lambda_i}\right) \quad (2)$$

It is usually assumed that all relaxation times λ_i exhibit the same temperature dependence. The horizontal shift factor a_T defines the ratio of relaxation times $\lambda(T)$ and $\lambda(T_{\text{ref}})$ for a transformation of the material functions G' , G'' , and G from the reference temperature T_{ref} to a new temperature T :

$$a_T = \frac{\lambda(T)}{\lambda(T_{\text{ref}})} = a_T(T, T_{\text{ref}}) \quad (3)$$

Factorization is possible if one uses another reference temperature T_0 instead of T_{ref} :

$$a_T = \frac{\lambda(T)}{\lambda(T_0)} \frac{\lambda(T_0)}{\lambda(T_{\text{ref}})} = \frac{\lambda(T)}{\lambda(T_0)} a_{T_0} = a_T(T, T_0) a_T(T_0, T_{\text{ref}}) \quad (4)$$

There have been different attempts in the literature to describe the temperature dependence of the horizontal shift factors. Today, the three-parameter Williams-Landel-Ferry equation (WLF) is widely accepted (Ferry, 1980):

$$\ln a_T = \frac{-C_1(T - T_{\text{ref}})}{C_2 + T - T_{\text{ref}}} \quad (5)$$

Its range of validity is approximately $T_g < T < T_g + 200$ K, where T_g is the glass transition temperature of the specific polymer. Williams et al. (1955) proposed universal values of C_1 and C_2 if T_{ref} was chosen somewhat close to T_g . The WLF equation is usually given in terms of the common logarithm of a_T , $\log a_T$; however, for simplicity and comparison with the following equations, we use the natural logarithm, $\ln a_T$, instead. The constant C_1 in eq 5, therefore, equals 2.303 times the value of C_1 commonly found in the literature, e.g., Ferry (1980).

Some researchers prefer the format of the three-parameter Vogel equation (Vogel, 1921; Fulcher, 1925):

$$\ln a_T = \frac{E}{R} \left(\frac{1}{T - T_V} - \frac{1}{T_{\text{ref}} - T_V} \right) \quad (6)$$

It is equivalent to the WLF equation where the equivalent WLF parameters C_1 and C_2 can be expressed as

$$C_1 = \frac{E}{R(T_{\text{ref}} - T_V)} \quad \text{and} \quad C_2 = T_{\text{ref}} - T_V \quad (7a,b)$$

Far above the Vogel temperature, $T \gg T_V$, a simpler two-parameter Arrhenius-type expression yields good agreement with experimental data:

$$\ln a_T = \frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \quad (8)$$

The Arrhenius parameter E/R is usually extracted from a plot of $\log a_T$ vs reciprocal temperature. If the Arrhenius-type dependence is a valid approximation,

this plot shows a straight line with a slope of $E/(2.303R)$. In case of WLF behavior the temperature dependence of a_T deviates from this straight line.

The vertical shift factor basically incorporates the density changes of the material (Ferry, 1980)

$$b_T = \frac{\rho(T_{\text{ref}})T_{\text{ref}}}{\rho(T)T} \quad (9)$$

and its value is usually close to unity for moderate temperature differences.

Time-temperature superposition of experimental data as described above yields shift factors a_T and b_T at different temperatures so that the necessary parameters of eqs 5, 6, or 8 can be evaluated by regression techniques. If the parameters are known, the constructed master curve can be shifted to any temperature within the experimental range. Extrapolation of shift factors to temperatures outside the experimental window is possible but should be viewed with caution.

Since time-temperature superposition is a common technique, master curves of the type $b_T G'(a_T \omega)$, $b_T G''(a_T \omega)$ are abundant in the literature. Because of the method of constructing those master curves they are mostly viewed as plots of G' or G'' vs frequency at a certain reference temperature with some factor a_T depending on this reference temperature. The importance of this factor is usually not fully appreciated.

It is, however, obvious for linear viscoelastic reasons that frequency-dependent data at a set of constant temperatures (frequency sweep (FS)) and temperature-dependent data at a set of constant frequencies (TS) are equivalent regarding their amount of information. Construction of G' and G'' master curves is generally possible from TS data as well, and master curves could be viewed as a plot of G' or G'' vs temperature shift factors (i.e., replacing the temperature by the temperature shift factor) at some reference frequency. This was first proposed by Onogi and Ui (1956) and again later by Yannas and Tobolsky (1966). They realized that frequency-dependent data (at a constant temperature T_0) can be derived from temperature-dependent measurements (at a constant frequency ω_0) if the temperature shift factors are known. The temperature-dependent data at ω_0 were plotted versus a reduced frequency $a_{T_0} \omega$ where

$$a_{T_0} \omega = a_T \omega_0 \quad (10)$$

with $a_{T_0} = a_T(T_0, T_{\text{ref}})$ and $a_T = a_T(T, T_{\text{ref}})$. From this equation the equivalence of temperature- and frequency-dependent data is evident (either data at fixed T_0 and variable ω or at variable T and fixed ω_0).

This idea was also discussed by Ferry (1980) who, however, stated that a superposition of temperature-dependent data at different frequencies is not possible because of the nonlinear dependence of a_T on temperature.

Engel and Sacher (1975) proposed a computer program of frequency-temperature superposition that implemented Onogi's and Ui's idea in a so-called double shift procedure. They used the "universal" constants of the WLF equation at $T_{\text{ref}} = T_g + 50$ K originally proposed by Williams et al. (1955) to perform the above-mentioned transformation from temperature-dependent to frequency-dependent data. Subsequently, the data was shifted back to the desired reference temperature. However, it seems that this very useful characterization

method has been forgotten since. No further literature could be found by the authors. Also, it is not very satisfying that the transformation depends on the universality of C_1 and C_2 and might fail if a material does not belong to this universality group.

From a fundamental point of view it is interesting to investigate whether a master curve can be easily created from measurements of temperature-dependent data at several frequencies (FTS data) (as proposed by Onogi and Ui, 1956), whether the temperature window can be extended as well as the frequency or time window in case of materials which obey ordinary time-temperature superposition, what format the shift factors take, and whether it is necessary to assume universality for C_1 and C_2 . This study combines experimental observations with a detailed analysis of temperature-frequency shifting.

Experimental Section

A partially cross-linked polycarbonate (PC Lot 150 as supplied by GE Plastics) was chosen because of its high temperature sensitivity. The material characteristics and sample preparation were already published elsewhere (Mours and Winter, 1994). A Rheometrics Mechanical Spectrometer, RMS 800, with parallel plate geometry was used for the dynamic mechanical measurements. Temperature sweeps from 170 to 280 °C were performed at several frequencies between 0.1 and 100 rad/s.

The second polymer is a commercial polyethylene (supplied by Exxon) which is much less temperature sensitive. Samples for the rheological measurements were pressed in an evacuated molding device. Temperature sweeps in the range from 120 to 250 °C were performed on a Rheometrics Dynamic Spectrometer, RDS 7700, with parallel plate geometry in a nitrogen atmosphere. Several values for the T_g of polyethylene can be found in the literature (Brandrup and Immergut, 1975): From DSC measurements a value of -125 °C was obtained, and WLF fits of volume relaxation resulted in values ranging between -51 and -33 °C. These differences are pronounced, but the experimental temperature window in our experiments was much higher than any of the reported values of T_g . Therefore, the Arrhenius-type expression for the horizontal shift factors, eq 8, holds for this material.

Results and Analysis

Figure 1 shows the dynamic moduli, G' and G'' , of the polycarbonate sample as a function of temperature for three different frequencies. The shift factors for this material were obtained previously (Mours and Winter, 1994). Their temperature dependence can be well described by the WLF equation, eq 5, with $C_1 = 13.84$, $C_2 = 89.38$ K, and $T_{ref} = 463$ K (190 °C). The vertical shift factors, b_T , were found to be close to unity. These values are similar to those obtained by others on polycarbonate samples; e.g., Mercier et al. (1965) found that their material (polycarbonate of bisphenol A) exhibited a WLF-type temperature dependence with $C_1 = 9.93$ and $C_2 = 91$ K at $T_{ref} = 190$ °C.

A plot of G' or G'' vs horizontal shift factor could be easily generated with the above values of C_1 , C_2 , and T_{ref} , see Figure 2. Shifting with respect to frequency ($\omega_0 = 1$ rad/s) was readily performed and yielded the desired master curve (Figure 3). The "normal" master curve (from superposition of isothermal frequency sweeps)

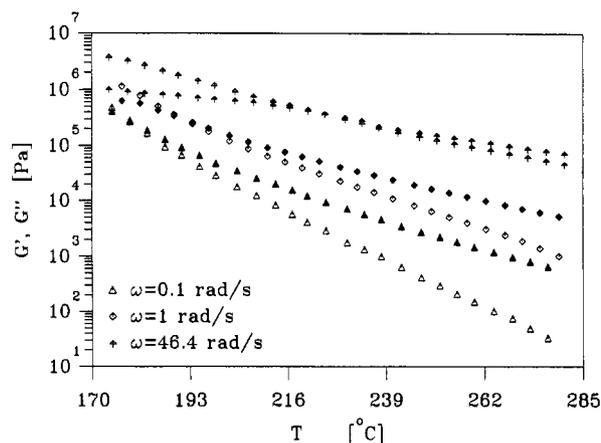


Figure 1. Temperature dependence of dynamic moduli $G'(T, \omega_i)$ (open symbols) and $G''(T, \omega_i)$ (filled symbols) for PC Lot 150 at three different frequencies ω_i .

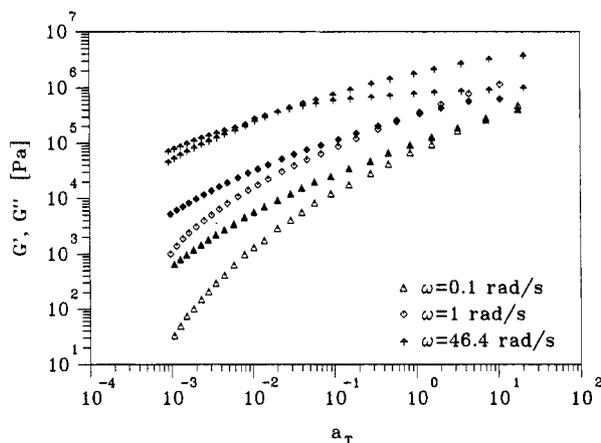


Figure 2. Same G' and G'' data as in Figure 1, but temperature T was replaced by a_T . The a_T data were calculated from eq 5 using $T_{ref} = 150$ °C, $C_1 = 13.84$, and $C_2 = 89.38$ K.

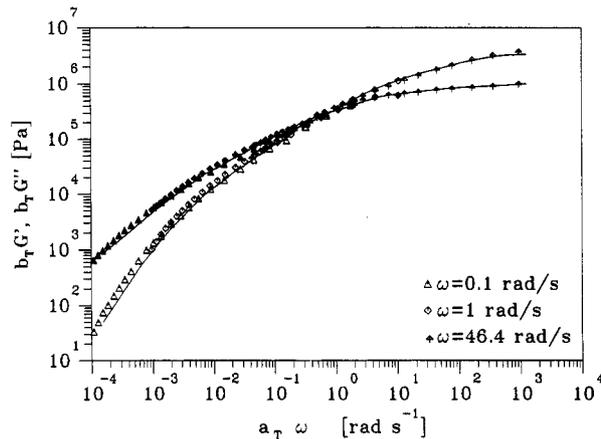


Figure 3. G' and G'' master curves for PC Lot 150. The data points (symbols) were obtained by shifting of the data in Figure 2 while the lines represent master curves from superposition of isothermal frequency sweeps (conventional method).

is drawn as a continuous line for comparison. Good agreement can be seen.

This master curve can also be regarded as a plot of dynamic moduli vs modified temperature as stated previously. Therefore, it can be used to extend the experimental temperature window for a certain reference frequency ω_0 . A new shift factor (denoted by c_T) that includes the frequency dependence has to be introduced. It will be shown that this shift factor

depends on temperature as well. The new temperature T can be defined as shifted temperature

$$T = c_T T_0 \quad (11)$$

where T_0 is the temperature at which the frequency-dependent data is measured. Introducing eqs 5 and 11 into eq 10 by simultaneously dropping the now unnecessary temperature index 0 results in

$$\ln\left(a_T \frac{\omega}{\omega_0}\right) = \frac{-C_1(c_T T - T_{\text{ref}})}{C_2 + c_T T - T_{\text{ref}}} \quad (12a)$$

Similar equations can be derived if the Vogel (eq 6) or Arrhenius-type (eq 8) expressions for the horizontal shift factor a_T are used:

$$\ln\left(a_T \frac{\omega}{\omega_0}\right) = \frac{E}{R} \left(\frac{1}{c_T T - T_V} - \frac{1}{T_{\text{ref}} - T_V} \right) \quad (12b)$$

$$\ln\left(a_T \frac{\omega}{\omega_0}\right) = \frac{E}{R} \left(\frac{1}{c_T T} - \frac{1}{T_{\text{ref}}} \right) \quad (12c)$$

Obviously, these equations can be solved for c_T or $c_T T$:

$$c_T T = T_{\text{ref}} - C_2 \frac{1}{1 - \frac{C_1}{C_2 + T - T_{\text{ref}} - \ln \frac{\omega}{\omega_0}}} \quad (13a)$$

$$c_T T = T_V + \frac{1}{\frac{1}{T - T_V} + \frac{R}{E} \ln \frac{\omega}{\omega_0}} \quad (13b)$$

$$c_T T = \frac{1}{\frac{1}{T} + \frac{R}{E} \ln \frac{\omega}{\omega_0}} \quad (13c)$$

Hence, the dynamic moduli, G' and G'' (from TS at a set of constant frequencies) can be superimposed onto a "temperature master curve", i.e., the specific data sets are plotted versus $c_T T$. The results of such a superposition for the investigated polycarbonate and polyethylene samples are shown in Figure 4a,b. An extension of the experimental temperature window (170–280 °C in the case of polycarbonate, 120–250 °C in the case of polyethylene) is therefore possible.

Discussion

An important aspect of experiments with changing temperature is thermal equilibrium. The material in the rheometer does not instantaneously reach the temperature of the surrounding medium due to thermal inertia, i.e., the heating or cooling rate in temperature sweeps is inherently limited. Commercial instruments therefore usually allow the user to program a "soak time" between temperature change and actual start of the dynamic mechanical experiment. In our experiments this time was set to 2 min.

The characteristic time for unsteady state heat conduction can be estimated from (Schlünder, 1989)

$$t_{\text{char}} = \frac{L^2}{\kappa} \quad (14)$$

where L is a characteristic length of the sample and κ

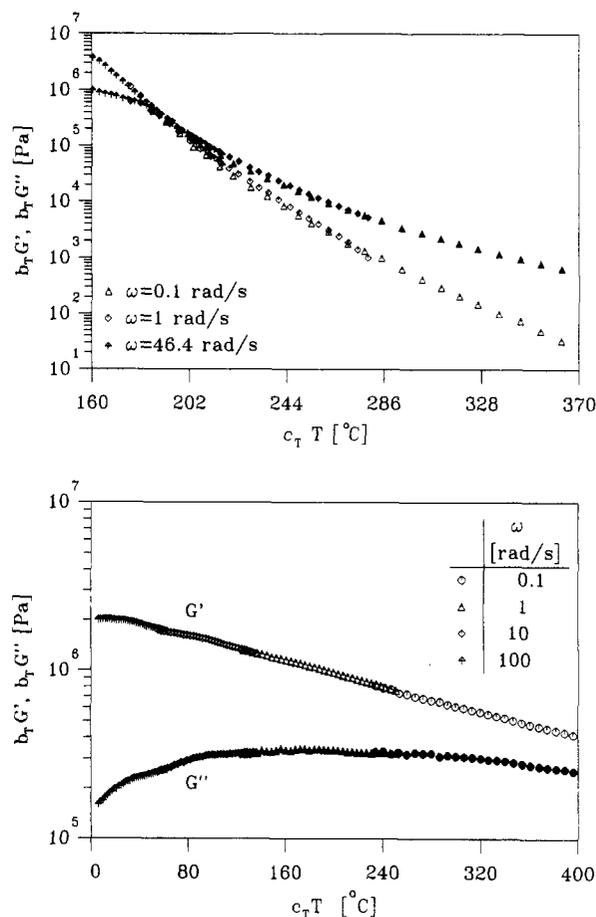


Figure 4. (a) "Temperature master curve" for PC Lot 150 at a reference frequency of 1 rad/s. (b) "Temperature master curve" for PE at a reference frequency of 1 rad/s.

is the thermal diffusivity. A valid assumption is that the rheometer fixtures reach the temperature of the environmental chamber much faster than the polymer sample. Therefore, the characteristic length in eq 14 is the sample thickness. Typical values for the thermal diffusivity of PC and PE are 1.1×10^{-7} and 10^{-7} m²/s, respectively (Birley, 1974). Using a sample thickness of approximately 1 mm this results in characteristic times for heat conduction of 9.1 s for PC and 10 s for PE. These values are short compared to the soak time of 2 min. Hence, it can be safely assumed that the samples were nearly in thermal equilibrium during the actual dynamic mechanical experiments.

As pointed out in the analysis section, the new shift factors c_T are not a sole function of frequency (as the temperature shift factors a_T are a function of temperature only) so that the superposition of temperature-dependent data is not a purely horizontal shifting (with b_T close to unity) as in the frequency case. An exception to this is obviously $c_T(\omega=\omega_0)$ which is equal to 1 by definition. Shift factors c_T of the polycarbonate sample for several frequencies as a function of temperature are shown in Figure 5.

Because of this simultaneous dependence on temperature and frequency and the nonlinear form of eqs 13a–13c, evaluation of these shift factors seems impossible. The necessary parameters for the WLF (C_1 and C_2) or the Vogel equation (E/R , T_V) cannot be deduced from sole temperature sweep data (see also Ferry, 1980). However, in the limiting case of the Arrhenius-type dependence of the temperature shift factor a_T (eqs 8 and 13c), the parameter E/R can be evaluated from temperature sweep data at different frequencies. From eq 13c

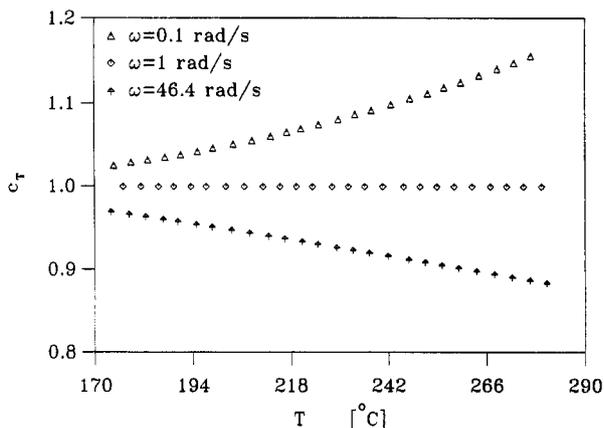


Figure 5. Frequency-temperature shift factors $c_T(T)$ for PC Lot 150 at three different frequencies ($\omega_0 = 1$ rad/s).

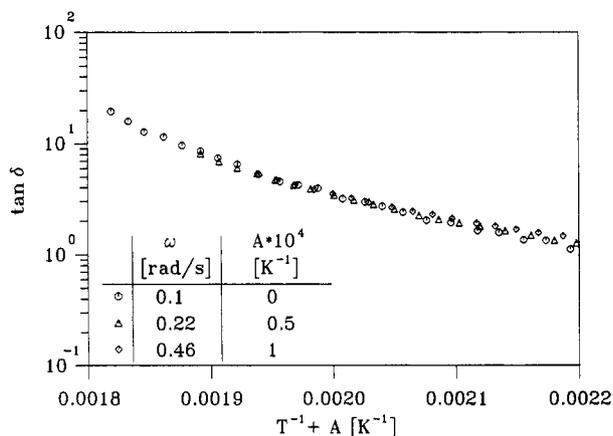


Figure 6. Loss tangent, $\tan \delta(1/T)$, for PC Lot 150. The data from temperature sweeps at different frequencies were shifted horizontally onto the reference frequency ($\omega_0 = 0.1$ rad/s) data set. The horizontal shift A equals $R/E \ln \omega/\omega_0$ according to eq 15.

follows

$$\frac{1}{c_T T} = \frac{1}{T} + \frac{R}{E} \ln \frac{\omega}{\omega_0} \quad (15)$$

Since a plot of $b_T G'$ or $b_T G''$ vs $c_T T$ yields a "temperature master curve", a plot over reciprocal temperature on a linear scale of the different temperature sweeps and subsequent horizontal shifting of these data onto a reference frequency should give shift factors $R/E \ln \omega/\omega_0$ and a value for E/R as needed in the Arrhenius-type expression. To avoid influences of the vertical shift factors, b_T , horizontal shifting of $\tan \delta$ vs $1/T$ is to be preferred as in the case of superposition of frequency-dependent data. This was performed for both polycarbonate and polyethylene data. For the polycarbonate data, a sufficiently good superposition can be seen only at high temperatures (Figure 6). This is not surprising since the Arrhenius-type expression is only valid far away from the glass transition temperature. A plot of shift factors a_T vs reciprocal temperature for this material shows a linear region at the same high temperatures (Figure 7). The polyethylene shift factors follow an Arrhenius-type expression over the entire experimental temperature window (Figure 8). The superposition of loss tangent in a plot versus reciprocal temperature is therefore good for all temperatures (Figure 9).

The values of E/R deduced from the shifting of temperature sweep data (Figures 6 and 9) are 15 500

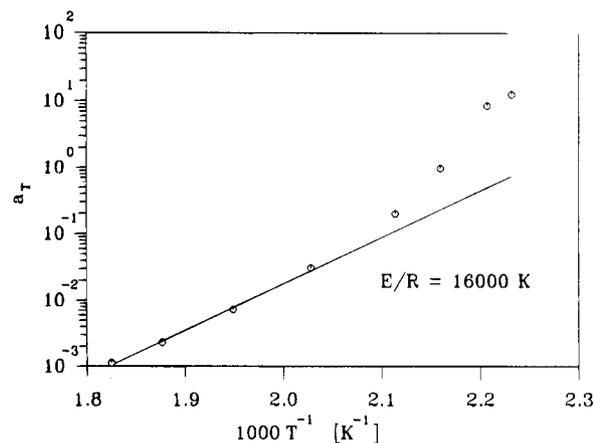


Figure 7. Temperature shift factors a_T of PC Lot 150 versus reciprocal temperature (Arrhenius plot). The slope equals the parameter $E/(2.303R)$ (see eq 8).

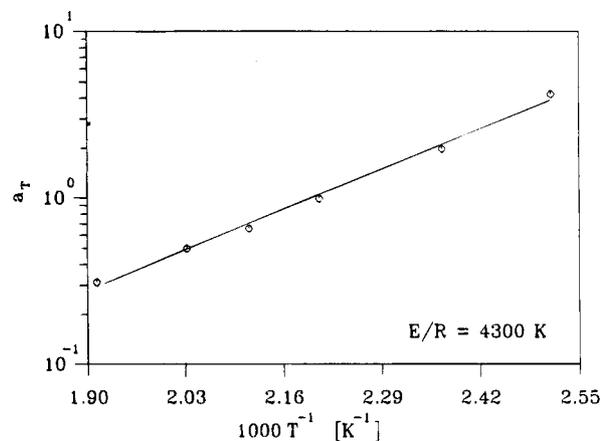


Figure 8. Temperature shift factors a_T of PE versus reciprocal temperature (Arrhenius plot). The slope equals the parameter $E/(2.303R)$ (see eq 8).

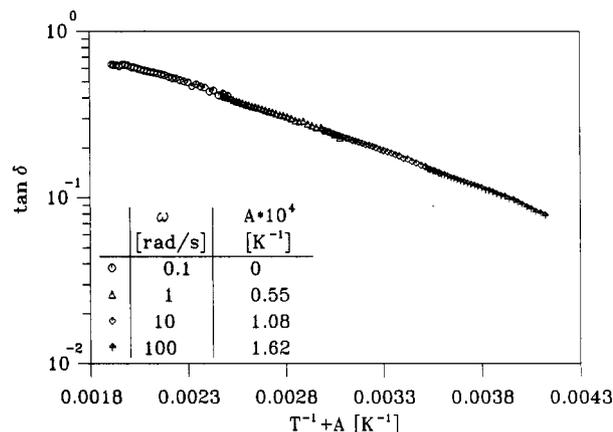


Figure 9. Loss tangent, $\tan \delta(1/T)$, for PE. The temperature sweep data at different frequencies were shifted horizontally onto the reference frequency ($\omega_0 = 0.1$ rad/s) data set. The horizontal shift A equals $R/E \ln \omega/\omega_0$ according to eq 15.

K for polycarbonate and 4230 K for polyethylene. This is in good agreement (within the error margin introduced by the shifting procedure) with the values obtained from fitting the a_T data by an Arrhenius-type expression (Figures 7 and 8) (PC, $E/R = 16\ 000$ K; PE, $E/R = 4300$ K).

Determination of WLF parameters requires frequency sweep data. Instead of several single frequency sweep experiments, frequency-temperature scans (FTS) could be performed. The data can, if analyzed accordingly,

be regarded as single frequency sweeps at several temperatures.

The vertical shift factors, b_T , cannot be easily extracted from TS data. A plot of G' or G'' vs shifted reciprocal temperature, eq 15, with subsequent vertical shifting (as in the conventional time-temperature superposition) does not yield shift factors since the temperature dependence of b_T would require a gradual shift of all data points.

The applicability of time-temperature superposition to extend the experimental temperature window is limited to the temperature regime in which the material exhibits thermorheologically simple behavior. Although technically an extension, e.g., below the crystallization temperature is possible, such an extension does not reveal meaningful data since morphological changes are not accounted for.

Conclusions

A wide range of polymeric materials obey time-temperature superposition. For these materials it could be shown in this study that master curves created in two different ways, from isochronal temperature sweeps or from isothermal frequency sweeps, coincide, but data analysis is more complicated for the isochronal temperature sweep. Only in the case of an Arrhenius-type temperature dependence can horizontal shift factors a_T be deduced directly by shifting of the isochronal temperature sweep data. The Arrhenius-type dependence is normally found at the high-temperature end of the experiment ($T \gg T_g$). Unfortunately, for the more common case of WLF temperature dependence, isochronal temperature sweeps cannot yield the shift factors directly because of their nonlinear T -dependence. It is necessary to perform isochronal temperature sweeps at a set of discrete frequencies (frequency-temperature scan as proposed here) and interpolate to obtain the shift factors. This interpolation procedure will also allow one to distinguish materials which obey time-temperature superposition from those which do not. In summary, the isochronal temperature sweep is one of the most simple experiments, but data analysis requires elaborate methods (which can be assigned to the computer).

A different look at the temperature shift factors and the introduction of a new "frequency shift factor" c_T revealed the possibility of applying time-temperature superposition to extend the accessible temperature window beyond the experimentally investigated one.

Equations for these new shift factors in terms of frequency and temperature are given for three different cases (WLF, Vogel, and Arrhenius-type expressions).

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