



Generating Mastercurves

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THE EQUIVALENCE OF TIME AND TEMPERATURE EFFECTS¹

The rheological behavior of viscoelastic materials varies with both time and temperature. Repeating DMA tests with the same material at different temperatures shifts the $\tan \delta$ peaks in the transition region to shorter times (higher frequencies) with increasing temperature. This is evident from figure 1, showing stress relaxation measurements made on a polymer at a series of temperatures over a time span of a minute to a week. Large differences are seen, yet only a small range of the viscoelastic response manifests itself within these time (frequency) spans. A broader picture of the time-related response is needed to understand this behavior fully.

But this is easier said than done, for the information is not equally accessible experimentally. While measurements that span a wide range of pertinent temperatures can be made with relative ease, it is not as easy to achieve measurements outside the range of mentioned times: Changes that occur in less than a second are difficult to measure, and time spans longer than a week are inconveniently long.

A solution arises from the experimental findings that time and temperature of time-dependent processes have equivalent effects on the rheological properties of linear viscoelastic materials. Thus, if the temperature of a flexible polymer is lowered, stress relaxation or creep recovery (as well as dynamic mechanical responses) take longer than they would at a higher temperature, and the extent these processes are slowed is proportional to the temperature reduc-

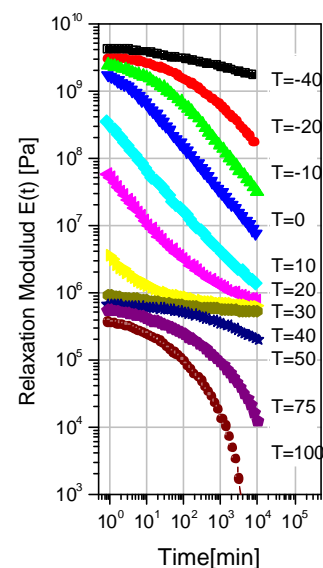


Fig. 1. Stress relaxation data as a function of temperature

tion. Conversely, elevating the temperature speeds these processes in proportion to the temperature increase.

Furthermore, it was observed that the principal effect of changing the temperature is to rescale the time: Temperature changes shift the viscoelastic functions along the modulus and time (or frequency) scales without changing their shapes. A result of the foregoing observation was the finding that a composite curve called a “master curve” could be generated from a series of curves of overlapping data collected at different temperatures.

This procedure is referred to as time-tem-

perature superposition (TTS).

TIME-TEMPERATURE SUPERPOSITION (TTS)

Increasing temperature shifts the transition area, which shows as a drop in the modulus or a

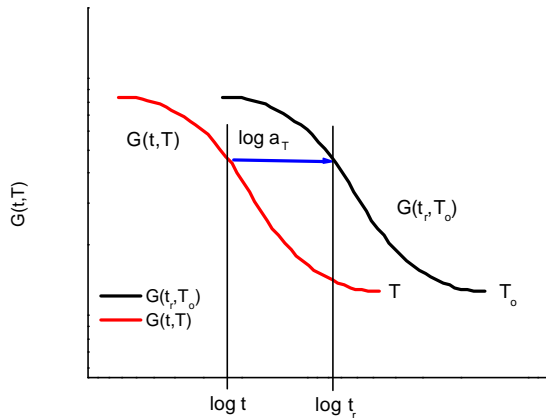


Fig. 2. Experimental determination of the shift factor a_T

damping peak in $\tan d$, to shorter times or higher frequencies. The shape of $G(t)$, G' , G'' and $\tan d$ however are not altered. The superposition is

therefore a parallel shift along the logarithmic time or frequency axes³.

This is shown schematically in figure 2 for the shear modulus $G(t)$. The parallel shift can be expressed as :

$$G(t,T)=G(t_r,T_0) \text{ with } t_r=t/a_T(T,T_0)$$

The factor a_T is the horizontal shift factor and t_r the reduced time. In order to shift the dynamic moduli G' or G'' the reduced angular frequency $\omega_r=a_T(T,T_0)\omega$ has to be used.

The sign of a_T (the direction of the shift) depends on the sign of the temperature difference $(T-T_0)$

For the various material parameters the TTS can be expressed as:

$$G(t,T)=G_{T_0}(t_r)=G_{T_0}(t/a_T)$$

$$G'(w,T)=G'_{T_0}(w_r)=G'_{T_0}(w a_T)$$

$$G''(w,T)=G''_{T_0}(w_r)=G''_{T_0}(w a_T)$$

$$\tan d(w,T)=\tan d_{T_0}(w_r)=\tan d_{T_0}(w a_T)$$

G_{T_0} is the relaxation modulus at the reference temperature T_0 .

Figure 3 shows the master curve as a result of shifting the curves in Figure 1 along the horizontal axis and superimposing them in regions of modulus overlap. The net effect is a composite curve over a much wider range of time (fre-

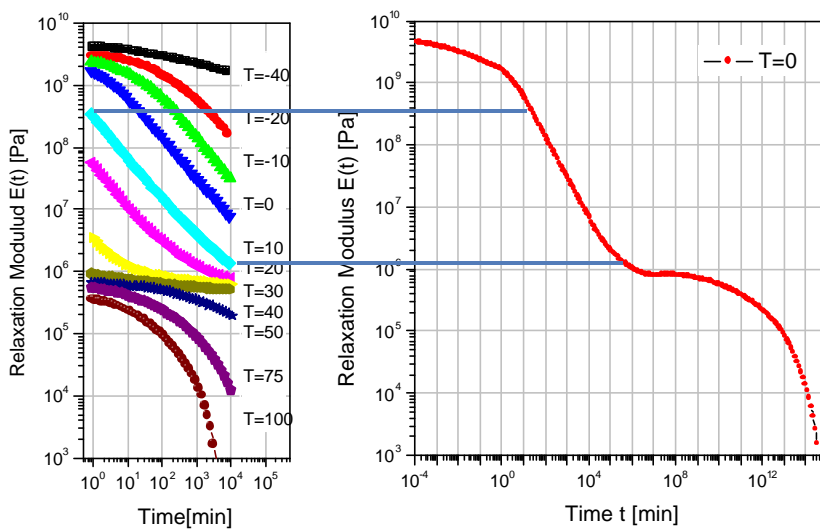


Fig. 3. Master curve generated by horizontally shifting data from fig 1

quency) than was accessible in the original test.

The time-temperature superposition can be applied to amorphous, non modified polymers to obtain modulus and damping information in the frequency range, not accessible through the experiment at a constant temperature. However not all relaxation processes shift in the same way and the t-T superposition cannot be applied across several relaxation processes. A material is referred to as thermo-rheological simple, if all the relaxations times shift with the same shift factor a_T .

If the t-T-shift is known for a process at the reference temperature T_o , it can easily be reduced to another reference temperature T_o' using following conversion:

$$\log a_T(T, T_o') = \log a_T(T, T_o) - \log a_T(T_o', T_o)$$

TIME TEMPERATURE SHIFT THROUGH A TRANSITION (THE WILLIAMS, LANDEL, FERRY EQUATION)

During a glass transition, a small change in temperature goes along with a significant drop in the modulus, sometimes over several decades. However the magnitude of the change (slope on the logarithmic plot $m = d \log G(t) / d \log t$) throughout the the transition is significant and can be described by the following expression:

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

This equation is well known as the Williams, Landel, Ferry (WLF) equation. T_o is the reference temperature, c_1 and c_2 are material constants, which also depend on T_o . Every reference temperature has its associated parameter set c_1 and c_2 . The following parameter combinations however are invariants for the WLF equation:

$$T_o' - c_2' = T_o - c_2 = T_{oo} \quad \text{and}$$

$$c_1' \cdot c_2' = c_1 \cdot c_2$$

For any amorphous material, if the reference temperature T_o is selected to be the mid point of the transition, then T_{oo} is material independent and equal to $T_g - 30^\circ$ with T_g the glass transition. The invariant $c_1 \cdot c_2$ represents the curvature of the $a_T(T, T_o)$ factor.

TIME TEMPERATURE SHIFT IN THE FLOW REGION

The time temperature shift in the flow region of an amorphous uncrosslinked polymers is very different from the shift in the glass transition region. Instead of the modulus $G(t)$, the expression $G(t)/(rT)$ shifts parallel with time i.e frequency. The density-temperature correction can be significant in the flow region (20 to 30% for PS)

The governing equations for the TTS in the flow region change to:

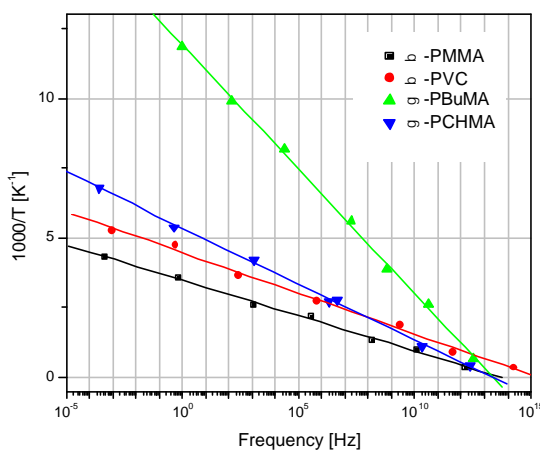


Fig. 4. Arrhenius diagram for different secondary relaxation processes of a variety of materials

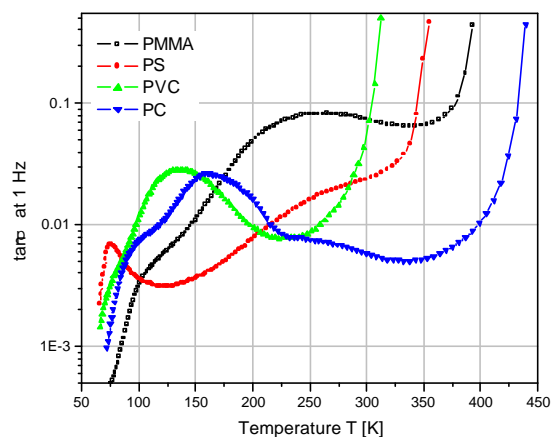


Fig. 5 Damping behaviour of various polymers as a function of temperature

$$(\rho_0 T_0 / \rho T) G(t, T) = G_{T_0}(t/a_T)$$

$$(\rho_0 T_0 / \rho T) G'(\omega, T) = G'_{T_0}(\omega a_T)$$

$$(\rho_0 T_0 / \rho T) G''(\omega, T) = G''_{T_0}(\omega a_T)$$

$$\tan \delta(\omega, T) = \tan \delta_{T_0}(\omega_r) = \tan \delta_{T_0}(\omega a_T)$$

Note, that the equation for $\tan \delta$ does not t
PHASE BEHAVIOUR OF AMORPHOUS
POLYMERS IN A TIME-TEMPERATURE

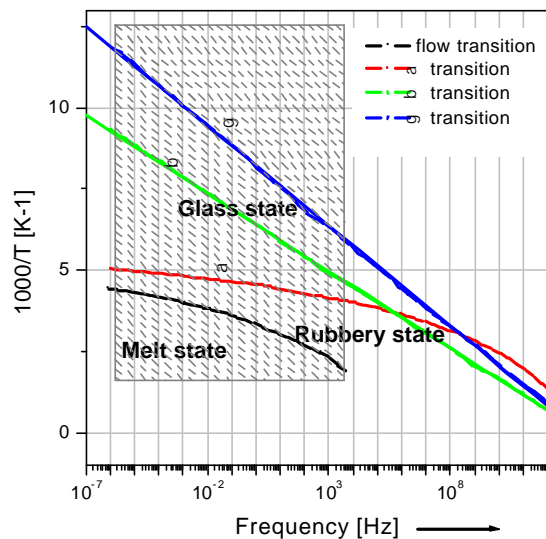
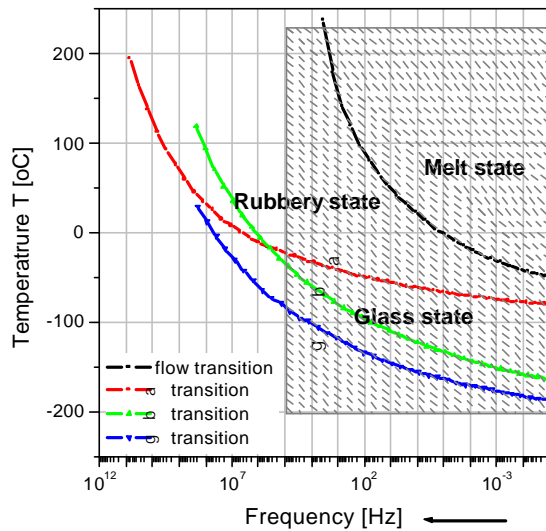


Fig. 6a Phase transitions represented in a frequency-temperature diagram according to WLF

Fig. 6b. Phase transitions represented in a frequency-temperature diagram according to Arrhenius

DIAGRAM

Figure 5 shows the damping function of a series of commercial polymers including PMMA, PVC, PC and PS as a function of temperature. PMMA shows a broad β relaxation which can be attributed to the rotation of the methyl-ester group around the -C-C- bond connecting the side group to the main chain. The β transitions of PC and PVC have to be attributed to local translational displacements of short sections of the main chain. PS has a very low damping in the glassy state. A relaxation, related to the rotation of the phenyl ring can be seen at very low temperature only. The low temperature transitions are directly related to the impact resistance of polymers. The short time damping correlates with the energy absorption during the impact. Materials without significant low temperature damping are brittle. This is the case for PS. Impact resistant PS is a co-polymer of polystyrene and polybutadiene, the polybutadiene adding significant damping to the low temperature transition.

Transitions of amorphous polymers are associated to regions with pronounced damping characteristics. Figure 6 shows the typical transition temperatures as a function of the test frequency in a WLF and Arrhenius representation for an amorphous polymer. Notice, that the secondary transitions in the Arrhenius representation are represented by a straight lines.

The flow transition separates melt and rubbery plateau, the glass transition (α) the rubbery region and the glass.

CONCLUSION

Master curves are helpful for understanding the rheological behavior of a polymer: The superposition process separates the two main 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 time dependence (in terms of frequency) of the material at a constant reference temperature T_0 ; the temperature dependence of the viscoelastic properties is shown by the variation of the shift factor with temperature.

This method of generating master curves is not limited to variations with temperature. Shift factors have been defined in terms of concentration, applied strain, etc.² and the WLF equation has been generalized to yield a shift factor a_{21} for a relaxation time t_1 in state 2 to that in state 1.¹

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