

Rheology

9.6 The "WLF"-time-temperature superposition

When testing fluids dynamically in CS-rotational rheometers equipped with parallel-plate-, cone-and-plate-, and coaxial cylinder-sensor systems, stresses will be imposed in a sinusoidal time pattern. The measured strain and phase shift data can then be transformed to the storage modulus G' , the loss modulus G'' , the complex viscosity η^* etc. all as functions of frequency ω . Modern rheometers are designed to cover within reasonable time spans with one particular sensor system - one particular sensor geometry - a frequency range that rarely exceeds much more than 3 decades: i.e. $\omega=0.01$ to 10 1/s. (Technically the min/max values for rheometers are normally $\omega= 0.001/100$ 1/s).

Limitations in practical rheometry normally come from the fact that "super-long" test times will not even be acceptable in basic research applications. Another limitation can be that samples at low temperatures become so highly viscous that their viscosity can no longer be measured with an existing rheometer.

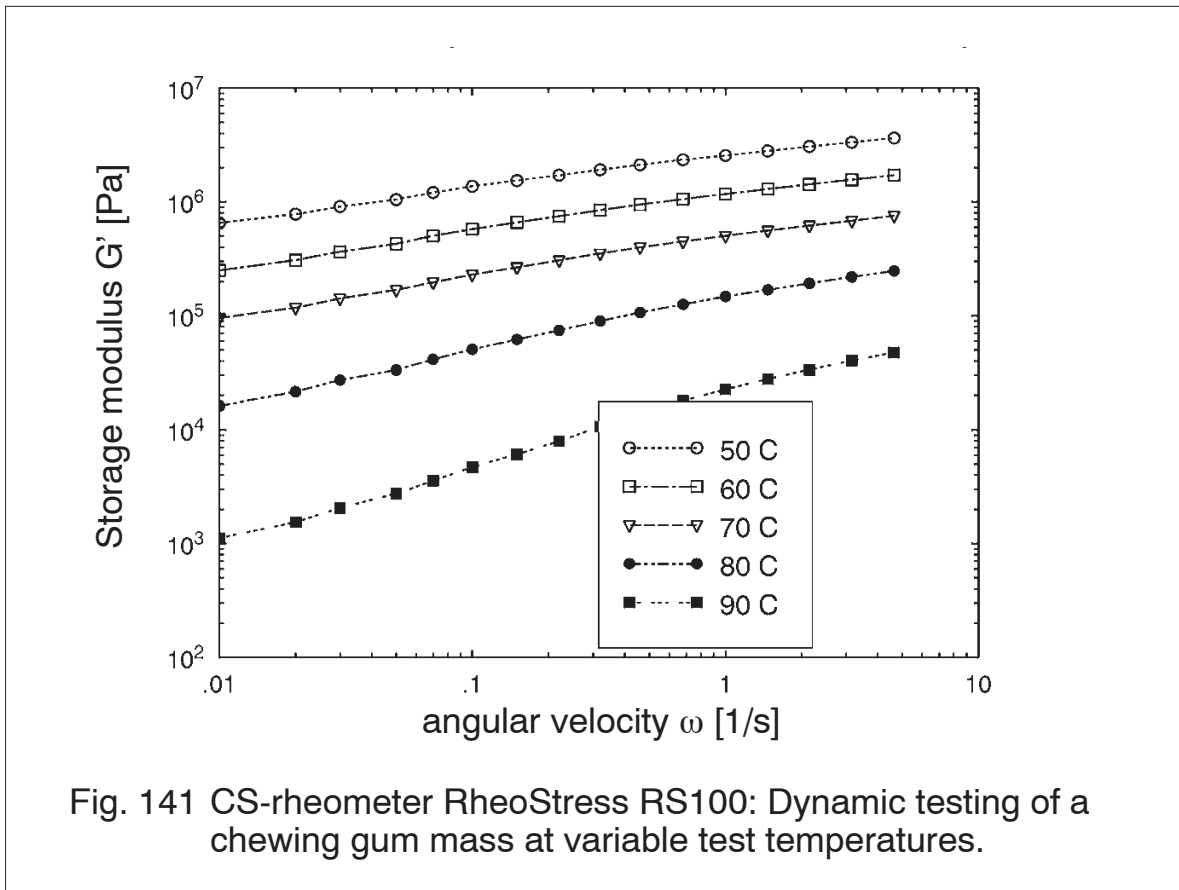
Those who need test data to explore the rheological influence of fillers in gum-type pastes at shear rates as low as 10^{-4} 1/s have to wait some 3 hours. Those who require data at $\omega = 10^{-5}$ 1/s will get the first measurement point after some 24 hours and complete G' and G'' /frequency curves not before the end of two days. It is safe to assume that testing times of this length are not practical.

The reaction of visco-elastic fluids to sinusoidally imposed shear stresses is related to the mobility of molecules and volume elements within such a sample. This mobility, also characterized by the relaxation time spectrum, is related to the type of the major fluid component but also to the type and percentage of all other ingredients of a particular material. At low temperatures this mobility is small so that the reaction of such a fluid is slow. If one raises the temperature, the molecular mobility is increased so that one can explore the effect of enclosed filler aggregates or rubbery volume elements in a thermoplastic melt by means of higher and faster responses in the visco-elastic fluid. A strong, fluid specific correlation between the time of response related to the material functions at the measured frequencies and the temperature, at which samples are rheologically measured, exists.

This interdependence was explored as early as 1955 by M. L. Williams, R.F. Landel and J.D. Ferry who provided a theoretical understanding of the temperature dependence of the physical structure of the fluids. They tested polymer samples at temperatures 50 to 100°C above their glass transition temperature T_g in steady shear and in dynamic tests. This leads for each temperature value to a set of curves of i.e. G' , G'' or the phase-shift-angle δ as a function of angular velocity. These material functions can span 2 to 3 decades for a given temperature range of some 50°C - Fig. 141. The resulting

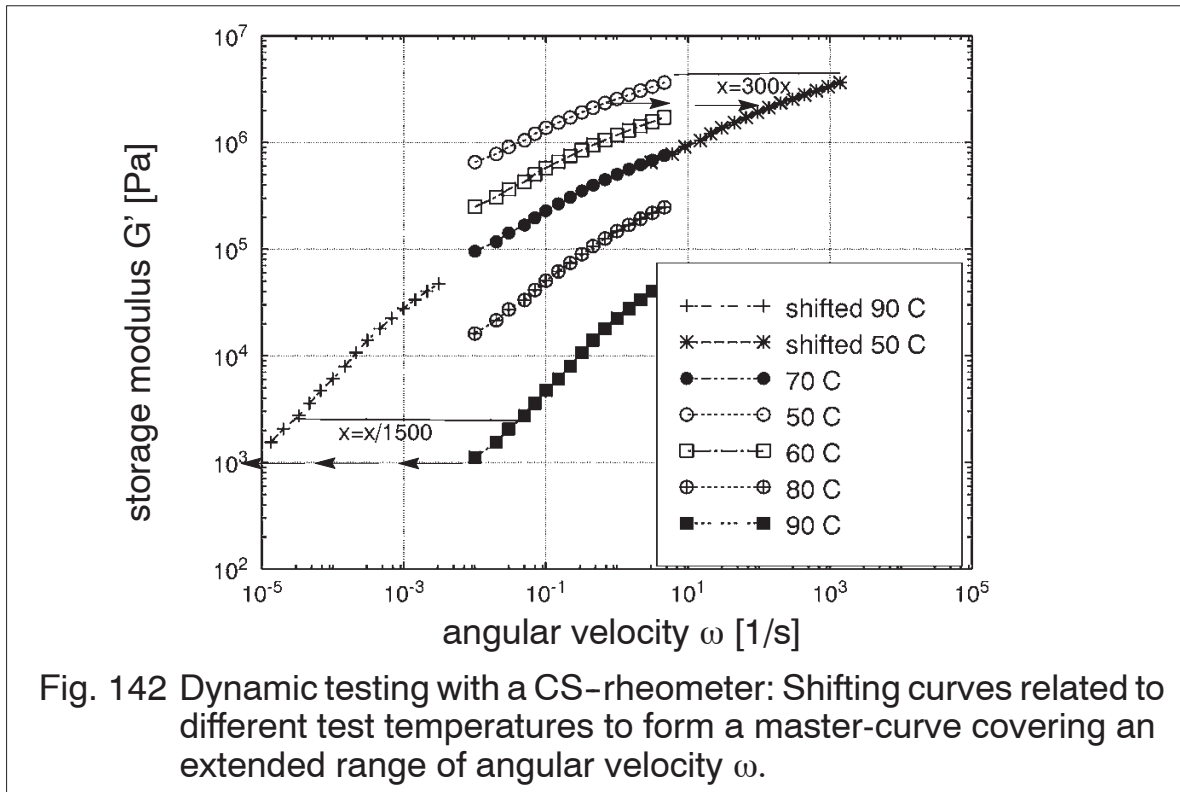
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curves of a particular rheological material function such as the storage modulus G' will form a temperature-related set of curves within a G' /frequency diagram with the curve at lowest temperature being positioned highest. These curves differ not only in their vertical position but also in their shapes which gradually change with temperature.



The three authors realized that one may shift the curves of this family horizontally – along the frequency/angular velocity abscissa – and perhaps also vertically so that all curves form a single master curve for a reference temperature. If the reference temperature is chosen to be in the middle of the chosen measuring temperatures then the curves at test temperatures below the reference temperature are shifted to the right, i.e. to higher frequencies until the ends of adjacent temperature curves just meet or partially overlap. Similarly test curves of higher than the reference temperature are shifted to the left. This “master curve” formed by this combination or “superposition” then covers a frequency range that significantly increases the range of the actually measured, temperature related curves. An example of such a diagram with “manually” shifted curves is presented in Fig. 142, while Fig. 143 shows an example of a computerized evaluation of 3 master curves.

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Providing test data for a given material function within a limited frequency range at variable temperatures and the curve shift that follows leads to extended ranges of reaction times or frequencies. This data transformation is known as the "time-temperature superposition" and it is linked to the names of those scientists Williams, Landel and Ferry who backed the empirical curve shift procedure by a scientifically based theory: WLF.

When measuring at different temperatures within a range not exceeding 50°C the shift of measured curves - in the example of Fig. 143 of $G'/\text{frequency}$ - will lead to rheological data by means of the master curves that can easily cover an 8 decade frequency range which otherwise cannot be explored.

The actual testing, that can lead to such a master curve, will require normally not more than a single hour for both the warming-up-phases to 5 increasing test temperatures and the subsequent tests at each temperature level. The computerized shift procedure with the HAAKE WLF-software and a modern computer requires only a minute or two. The total test and evaluation time for this time-temperature superposition is then about a 1/10 to 1/20 of the time that an actually measured, wide frequency master curve would require - if an actual testing was at all possible.

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The computer software for the WLF superposition works in two steps.

1). It determines automatically how much the temperature related curve segments must be shifted horizontally – shift factor $a(T)$ – and/or vertically – shift factor $b(T)$ – to form a continuous master curve at the reference temperature.

$$\omega(T) = a(T) \cdot \omega(T_0)$$

$a(T)$ = horizontal shift factor

$\omega(T)$ = frequency at a freely chosen temperature T

$\omega(T_0)$ = frequency at the reference temperature T_0 .

Since the frequency ω is linked to the relaxation time λ of the fluid, the above equation can be rewritten:

$$1/\lambda(T) = a(T) \cdot 1/\lambda(T_0)$$

It indicates what the deformation-time-response is with respect to the complex modulus G^* . The phase shift angle that marks the response or relaxation times of fluids is related to temperature changes.

For samples that show large density differences it may be required to shift individual measured curves not only horizontally but also vertically by means of the shift factor $b(T)$.

Having measured G' -data one can write:

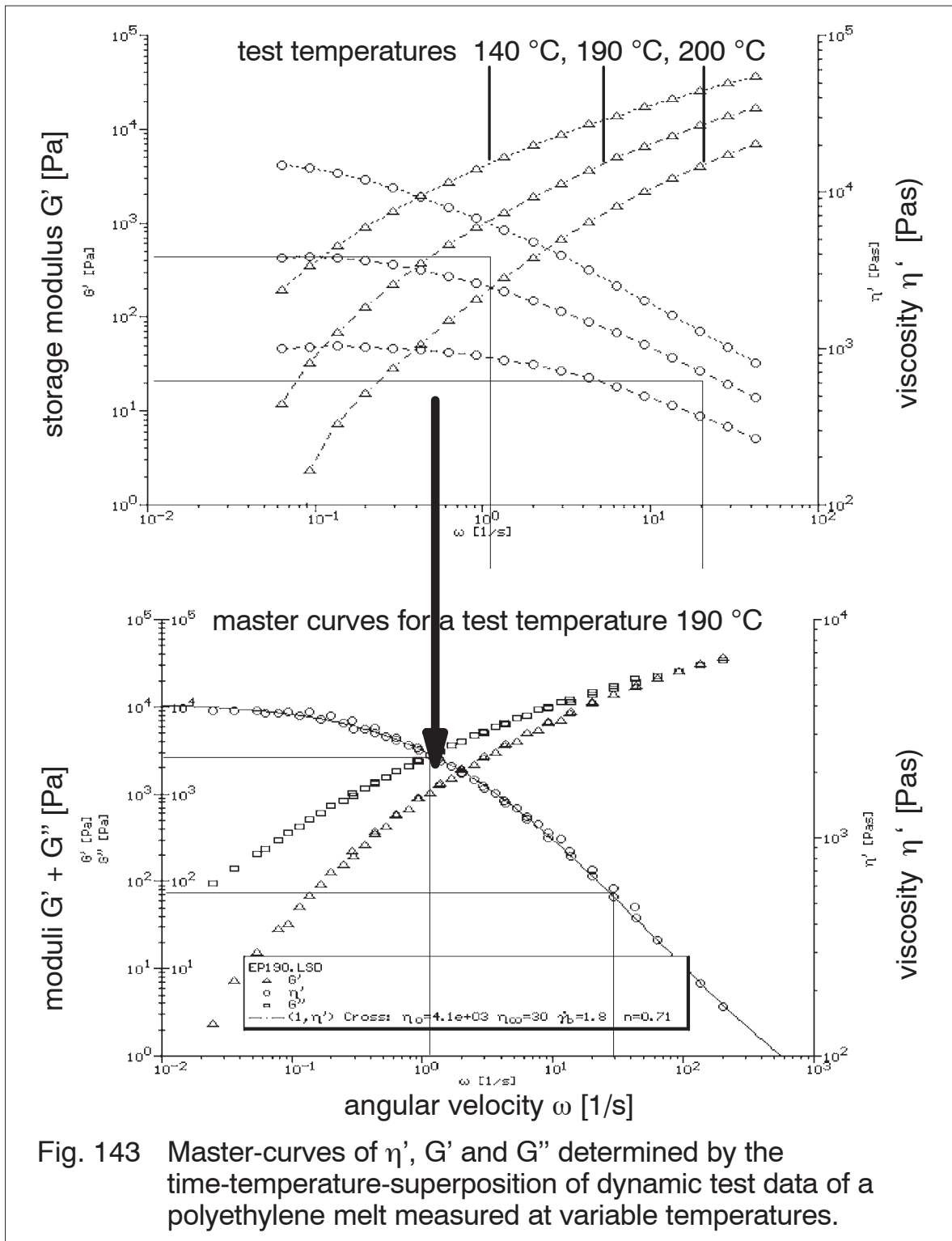
$$G'(T) = b(T) \cdot G'(T_0)$$

T being again the freely chosen temperature and T_0 the reference temperature. The shift factor $b(T)$ of most fluids is close to “1”. It is therefore decades apart from the value $a(T)$ and it may then be neglected.

2.) Plotting the actually determined shift factors $a(T)$ and $b(T)$ as a function of temperature provides curves for which a regression calculation will lead to a fitting mathematical equation. It can then be used to determine the shift factors for any intermediate temperature and for the master curves of the material functions such as G' , G'' , η^* or η' at that reference temperature.

This time-temperature superposition allows one to explore fluids rheologically in frequency ranges which are otherwise not possible, neither technically nor time-wise. But one has to keep in mind that the measured curves within the whole temperature range only gradually change with temperature, i.e. the rheological behavior does not change abruptly as is the case close to the glass-transition temperature. At T_g the mobility of molecules changes drastically. It therefore would not make sense to “extrapolate” from curves below T_g to those above. The shift factor $a(T)$ found for a particular fluid will relate mainly to the response time – “internal clock” – of the dominant matrix material of the fluid. In polymer blends the major blend polymers should have similar response times in order to determine one meaningful $a(T)$. Shift factors of compounds with a high percentage of filler basically different from the matrix material should be critically checked.

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When discussing master curves, one must not neglect the fact that at the ends of the extended frequency ranges, the level of tolerance or the significance of the mathematically determined data is reduced in comparison to actually measured data.