

Generating master curves for polymeric materials

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Many everyday items are made from thermoplastics. These types of polymers are characterized by the ability to soften on heating and harden on cooling. In their molten state, they can be processed into various shapes using techniques like extrusion, injection molding, or blow molding, among others. One example of a widely used thermoplastic is polymethyl methacrylate (PMMA). Due to its high transparency, it is often used in optical applications like shatterproof glazing.¹

Polymers consist of repetitive units of smaller molecules, so-called monomers, which bond together to form long chains. In a molten state or solution, these polymer chains form random coils with strong intermolecular interactions through entanglements. This results in a complex flow and deformation behavior. Rotational rheometers are widely used to characterize this flow behavior and to evaluate the processability of different types of plastics. Additionally, rheological data can be used to investigate a polymer's molecular mass before and after processing or for recycling purposes.

Due to their structure, polymer melts are characterized by a high elasticity which in many cases prevents rheological measurements in a rotational mode where secondary flows and edge fractures may occur. Hence, frequency-controlled oscillatory tests are used to access information about the

rheological properties at given processing parameters. Cox and Merz found that for linear, unfilled polymers, the dynamic viscosity η as a function of the shear rate $\dot{\gamma}$ can be correlated with the complex $|\eta^*|$ viscosity as a function of the angular frequency ω according to the equation (1).²

However, the so-called Cox-Merz rule does not apply to multiphase liquids like suspensions or chemically crosslinked and gelled systems.³

$$\eta(\dot{\gamma}) = |\eta^*|(\omega) \quad (1)$$

Besides this, certain boundary conditions regarding the measurement technique as well as the rheometer performance must be considered to apply this relation to polymer processing. On the one hand, an oscillatory movement is characterized by the time required to pass through one period at a given deformation amplitude. Therefore, obtaining rheological data in oscillation can take less than a second, minutes, or even up to days or weeks, depending on the chosen frequency. On the other hand, the maximum frequency of commercially available rheometers is usually limited to around 100 Hz (628 rad/s) by the inertia of the measuring system itself.

To overcome this issue, the time-temperature superposition (TTS) principle can be used to obtain master curves that cover a broader frequency range. This application report is intended to provide a guideline for the generation of master curves and to give advice on how to check whether the TTS principle can be applied to a set of data by using the van Gurp-Palmen plot.

Materials and methods

For this study, a Thermo Scientific™ HAAKE™ MARS™ iQ Air Rheometer equipped with temperature chamber TM-CR-O450 was used. The subject of the investigation was a polymethyl methacrylate (PMMA) sample. The measurement routine is shown in Figure 1. All rheological measurements were performed using a parallel-plate geometry with a diameter of 15 mm and a measuring gap of 1 mm. A deformation amplitude γ within the linear viscoelastic range of the sample of 0.5 % was selected. Frequency sweeps from 300 rad/s to 1 rad/s were performed at 180 °C, 200 °C, 220 °C, 240 °C, 260 °C, and 280 °C. To ensure that no thermal degradation occurred, each frequency sweep was carried out with a new sample. For all rheological measurements, matching sample disks were prepared in advance using a HAAKE Minijet Pro Mini Injection Molding System.

Results & discussion

The excitation frequency and the temperature in an oscillatory shear experiment are affecting the viscoelastic properties of polymers in a similar way, meaning that their behavior at increased temperatures equals their behavior at low frequencies and vice versa. Figure 2 shows this phenomenon for the storage modulus G' and loss modulus G'' as a function of the angular frequency at temperatures of 180 °C, 220 °C, and 280 °C for a PMMA melt.

At the selected reference temperature of 220 °C, both G' and G'' intersect each other at an angular frequency of 1.78 rad/s. At 280 °C, PMMA exhibits this crossover at a much higher frequency of 144 rad/s. In contrast to this, at 180 °C, PMMA does not show any crossover of G' and G'' at all. Depending on the temperature, G' and G'' appear to show different parts of the same curve. When applying the TTS principle, this observation is used, and the individual frequency sweep data

sets are shifted horizontally as well as vertically towards a reference temperature T_0 to generate a master curve covering a frequency range significantly larger than the limited range of a single sweep experiment. Hence, frequency measurements at different temperatures can be utilized to obtain information about the viscoelastic properties of a material over a wide range of different time scales.

The TTS involves the utilization of temperature-dependent horizontal and vertical shift factors a_T and b_T , respectively.⁵ In the case of data sets derived from frequency sweep experiments, the horizontal shift factor a_T defines the shift of the measured moduli data along the x (frequency)-axis towards the data set obtained at the reference temperature T_0 .

Depending on the polymer's glass transition, the temperature dependency of a_T is most commonly described either by the empirical Arrhenius or the William–Landel–Ferry (WLF) models.⁴ Utilizing these two models, measurement data can also be shifted towards reference temperatures for which no experimental data were obtained.

The shift factor b_T allows for a vertical shift and is defined by the density $\rho(T)$ of the polymeric material at a certain temperature in contrast to the reference $\rho_0(T_0)$, as shown in equation (2).⁵

$$b_T = \frac{T_0 \cdot \rho_0(T_0)}{T \cdot \rho(T)} \quad (2)$$

For entangled polymers, the temperature-density dependency is rather small. Hence, values for vertical shift factors are usually around 1. Nevertheless, data sets can be fitted using b_T in such a way that the optical appearance of the master curve can be influenced, and possible experimental errors can be concealed.⁵

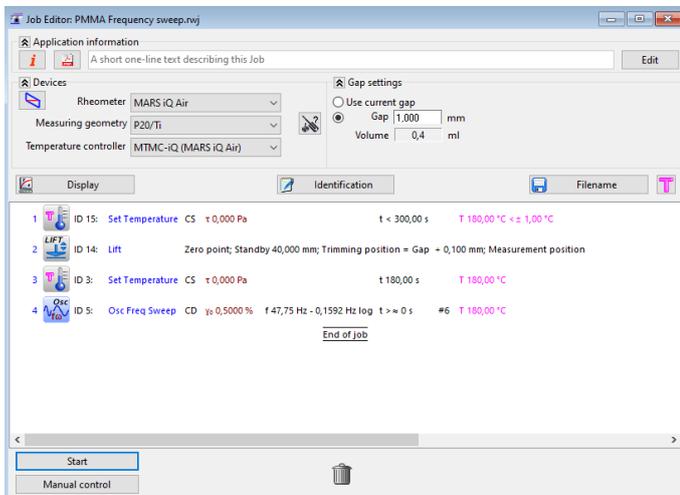


Figure 1: Measurement routine for performing a frequency sweep measurement in the HAAKE RheoWin Software.

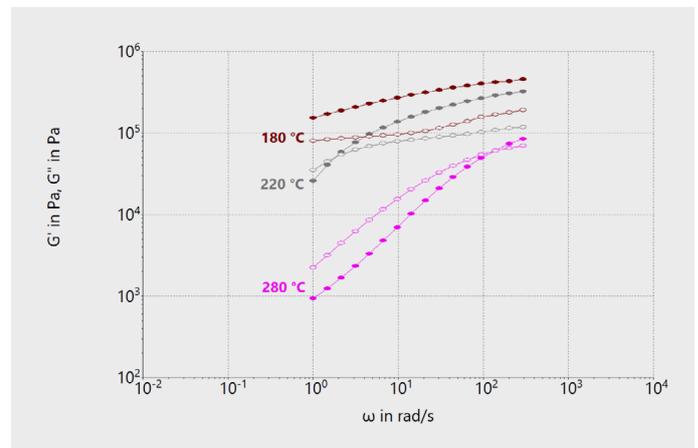


Figure 2: Rheological frequency sweep data at temperatures of 180 °C, 220 °C, and 280 °C for PMMA.

Modern rheometer software, like the HAAKE RheoWin™ Rheometer Control Software, uses advanced mathematical algorithms to shift rheological data and generate master curves in order to obtain information about the viscoelastic properties over an extended frequency range. Please note that the TTS principle cannot be applied to thermorheological complex materials where two or more relaxation mechanisms do not have the same temperature dependency.⁵

The PMMA master curve in Figure 3 was generated from the rheological data displayed in Figure 2. To allow for more overlap and higher precision, additional measurement data was collected at 200 °C, 240 °C, and 260 °C. 220 °C was chosen as the reference temperature.

By applying TTS, the original angular frequency range of each set of measurement data (1 to 300 rad/s) was extended to 0.03 to 2600 rad/s. This range is wide enough to cover the shear rates that occur in many typical polymer processing techniques like extrusion (1...1.000 s⁻¹) and even reaches shear rates present during injection molding (10...10.000 s⁻¹).⁶ With additional frequency sweeps performed at temperatures below 180 °C, the master curve could be extended to even higher frequencies/shear rates.

To verify the applicability of the TTS principle for a given polymer fluid, van Gorp-Palmen reported that the phase angle δ , as a function of complex shear modulus $|G^*|$ for each isothermal frequency sweep used to generate a master curve, must superpose into a single continuous curve.⁷ The so-called van Gorp-Palmen plot of the individual PMMA frequency sweep measurements is shown in Figure 4.

This way, the van Gorp-Palmen plot can be used to understand whether a polymer sample can be considered as thermorheological simple, like in the case of the PMMA grade used for this study.

Based on the G' and G'' master curve, information on the complex viscosity $|\eta^*|$ of the sample is automatically obtained by the rheometer software using equation (3).

$$|\eta^*| = \frac{\sqrt{G'^2 + G''^2}}{\omega} \quad (3)$$

By applying a suitable model fitting, like the Carreau-Yasuda curve fit according to equation (4), several material-dependent parameters can be obtained out of a master curve for complex viscosity.⁸

$$|\eta^*|(\omega) = \frac{\eta_\infty + (\eta_0 - \eta_\infty)}{(1 + (\lambda\omega)^a)^{\frac{1-n}{a}}} \quad (4)$$

In Equation 4 η_0 is the zero-shear viscosity, η_∞ the viscosity at infinite shear rate and λ a time constant which represents a characteristic relaxation time of the sample. The power law index n describes the shear thinning behavior at high shear rates, while the transition factor a describes the process of polymer chain disentangling within the polymer network and hence the transition from the Newtonian plateau to the shear thinning behavior of the material.

Figure 5 illustrates the different Carreau-Yasuda curve fit parameters shown on an example master curve.

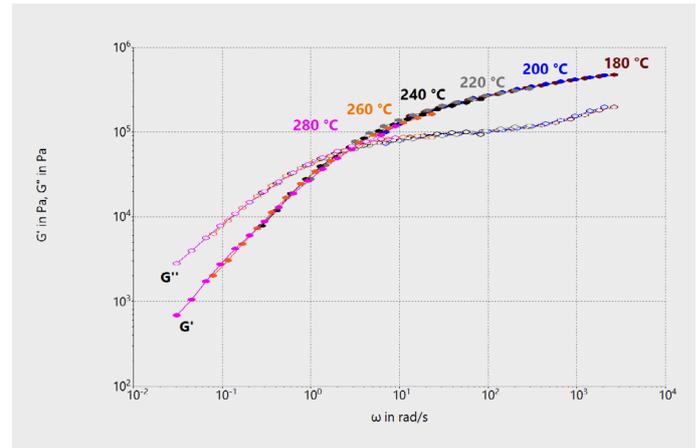


Figure 3: G' and G'' master curve at a reference temperature of 220 °C obtained from frequency sweep data at 180 °C, 200 °C, 220 °C, 240 °C, 260 °C and 280 °C for a PMMA melt.

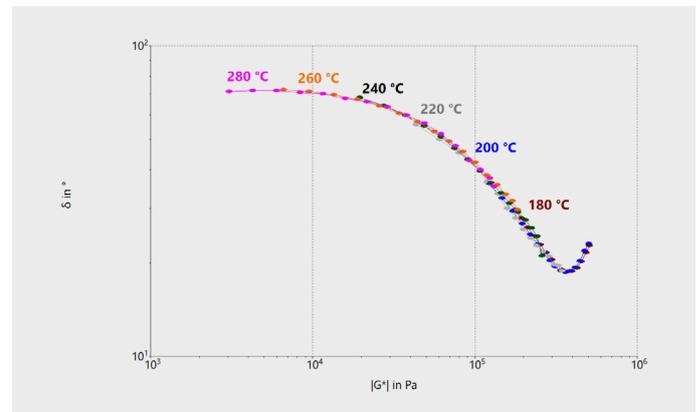


Figure 4: van Gorp-Palmen plot for the single PMMA frequency sweep tests performed at different temperatures.

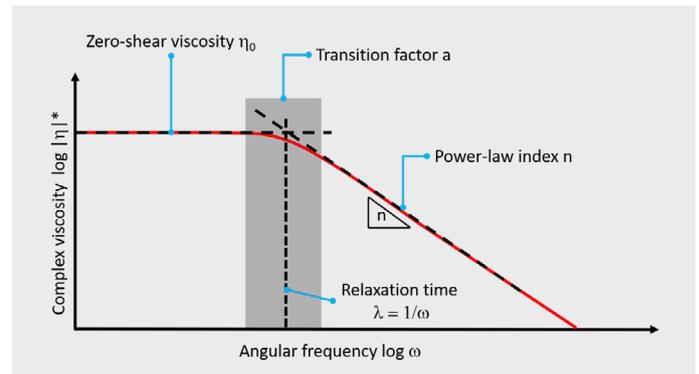


Figure 5: Carreau-Yasuda curve fit parameters illustrated at an example master curve.

To obtain these material-specific parameters for the investigated PMMA sample, a Carreau-Yasuda curve fitting was performed on the complex viscosity data of the master curve. Both the generation of the master curve as well as the curve fitting was carried out using the respective HAAKE RheoWin Software functionalities.

The Carreau-Yasuda parameter for the PMMA master curve at 220 °C has been calculated by the HAAKE RheoWin Software, as shown in Table 1.

| Parameter | Value |
|-----------|-------------|
| η_0 | 100.200 Pas |
| λ | 0.81 |
| a | 0.74 |
| n | 0.20 |

Table 1: Carreau-Yasuda curve fit parameter for a PMMA master curve at a reference temperature of 220 °C.

Parameters of high practical relevance for polymer processing are the zero-shear viscosity η_0 as well as the transition factor a. It is well known that η_0 is proportional to the average chain length of a polymer. The transition factor corresponds to the distribution of different chain lengths. Hence, changes in the zero-shear viscosity after processing or recycling can directly be correlated with the molecular mass or the polydispersity of a polymer.

Conclusion

In this application note, the generation of a master curve from frequency sweep data acquired at different temperatures and using the TTS principle was described for a PMMA sample. The van Gorp-Palmen plot was introduced as a quick and easy way to verify whether a set of frequency sweep data is suitable for performing TTS shifting. Furthermore, the Carreau-Yasuda curve fitting model was discussed as a method to obtain various polymer-specific parameters from master curves, which can be used to characterize the effect of various processing techniques or recycling steps on the average molecular mass or the molecular mass distribution of a polymer material.

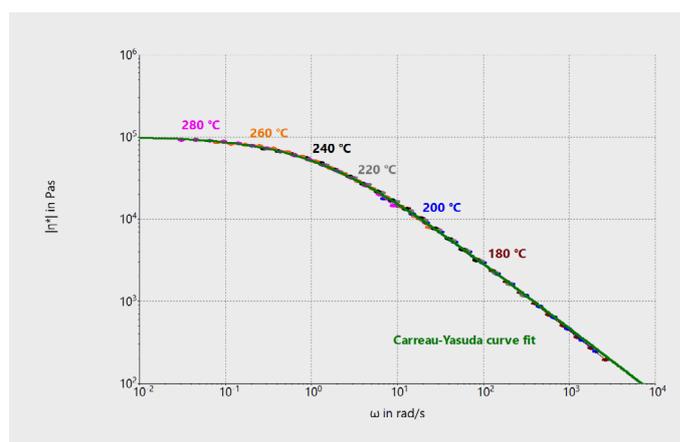


Figure 6: Complex viscosity master curve at a reference temperature of 220 °C obtained out of frequency sweep data at 180 °C, 200 °C, 220 °C, 240 °C, 260 °C and 280 °C for a PMMA melt including Carreau-Yasuda curve fit.

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