How to Obtain Shear Viscosity of a Polymer Melt with an Oscillation Measurement: The Cox-Merz Rule

Claire Strasser and Senol Gezgin

Introduction

 A rotational rheometer can make measurements under defined shear rates or stresses in both viscometry (where the upper plate rotates) and in oscillation (where the upper plates oscillates at a specified frequency). While shear viscosity is often the most commonly desired result from a rotational experiment, the oscillation test delivers information about the visco-elastic properties of the sample, particularly its complex viscosity (η*) obtained from its complex stiffness (G*)[1].

In the following, polypropylene was measured using both viscometry and oscillation and the shear viscosity (η) was compared with its complex viscosity (η*).

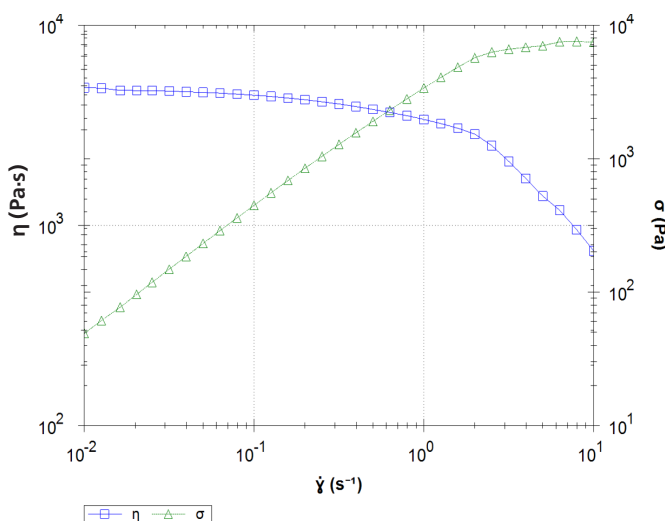## Rotational Measurement on Polypropylene

A rotational measurement was carried out on polypropylene pellets using the NETZSCH Kinexus ultra+ rheometer. Table 1 details the measurement conditions.

Figure 1 displays the resulting curves of the shear stress (σ ,green) and the shear viscosity (η, blue) for the programmed shear rates. In the low shear rate range, the increase in shear stress with increasing shear rates is linear and the shear viscosity is almost constant: This is the Newtonian plateau of the material.

Around 0.1 s^{-1}, the shear viscosity begins to decrease with increasing shear rates. The slope changes; this is an

Table 1. Test parameters of the rotational measurement

Device	Kinexus ultra+ mit HTC Prime
Geometry	CP2/20 (Cone-Plate, angle: 2°, diameter: 20 mm)
Temperature	190°C (approx. 30°C above the melting temperature)
Measurement gap	66 µm
Shear rates ($\dot{\gamma}$)	0.01 to 10 s^{-1}

Rotational Measurement

The upper plate rotates with a defined shear rate $\dot{\gamma}$ [s^{-1}].

The shear stress σ [Pa] required for this rotation is determined.

Result: The shear viscosity η [Pa·s] (i.e., the resistance to the flow) is calculated:

$$\eta = \frac{\sigma}{\dot{\gamma}}$$

1 Shear viscosity (η, blue) and shear stress (σ, green) during the rotational measurement on molten polypropylene

NETZSCH

indication of more pronounced shear-thinning behavior. However, a look at the steady-state curve (which is an indication for time-independent flow within the sample, Figure 2, black) shows that above this shear rate, the flow is no longer time-independent. It is ensured that the measurement leads to correct shear viscosity values by checking the steady-flow values: They amount to 1 for a laminar, time-independent flow. Here, the curve increase proves that the shear viscosity values displayed are no longer reliable in the last decade.

Where does this behavior come from? A look at Figure 3 provides the answer. Additional to the shear viscosity (blue), the shear stress (green) is plotted along with the first normal stress difference (N1, red). The strong increase in the first normal stress difference, N1, most probably results from the Weissenberg effect: The elastic properties of the sample dominate the viscous properties. The sample attempts to push up the upper geometry (this is not possible because the measurement gap remains constant during the measurement). This effect is highlighted by the N1 curve exceeding the shear stress curve.
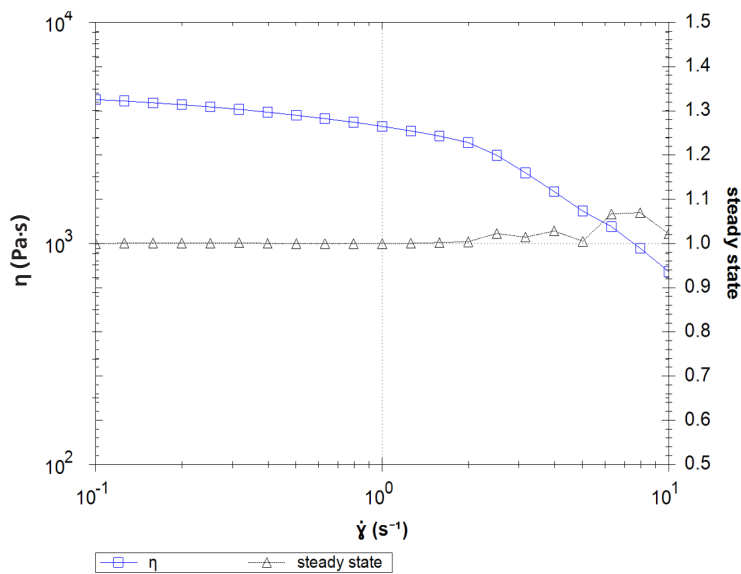
2 Shear viscosity (η, blue) and steady state (black) during the rotational measurement on a polypropylene melt
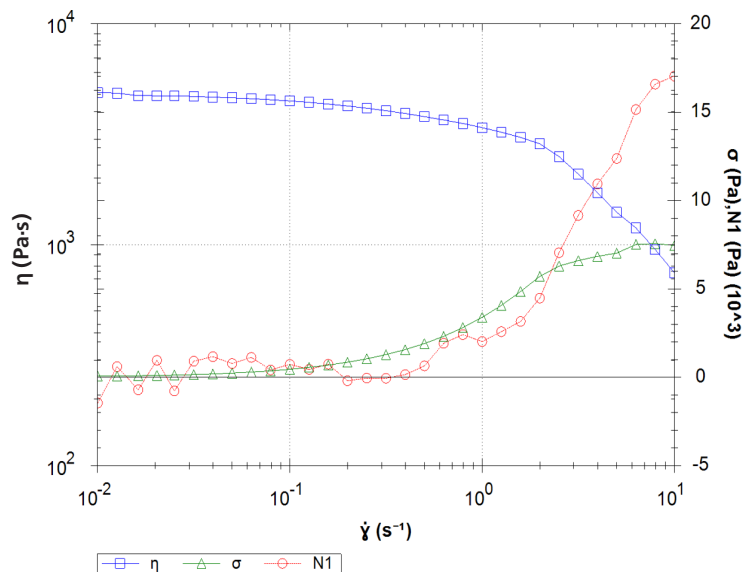
3 Shear viscosity (η, blue), shear stress (σ, green) and first normal stress difference (N1, red) during the rotational measurement on a polypropylene melt

NGB · Application Note 236 · EN · 1022 · Technical specifications are subject to change.

2|4

NETZSCH

How to Obtain Shear Viscosity Values: The Cox-Merz Rule

In such cases, where the shear viscosity curve cannot be evaluated properly, the Cox-Merz rule [2] is very useful. It is an empirical relationship stating that for most polymer melts, the shear viscosity (η) as a function of the shear rate ($\dot{\gamma}$ [s^{-1}]) is equal to the complex viscosity (η^* [Pa·s]) as a function of the angular frequency (ω [rad/s]). This second curve is obtained by an oscillation measurement in which the frequency is varied (frequency sweep).

Oscillation Measurement

The upper plate oscillates with a defined frequency f [Hz] or ω [rad/s] and amplitude [%] or complex shear strain γ [%].

The complex shear stress σ^* [Pa] required for this oscillation is determined.

Result: The viscoelastic properties of the sample are determined, in particular its complex stiffness G' and its complex shear viscosity η^* [Pa·s]:

$$\eta^* = \frac{G^*}{\omega}$$

First, an amplitude sweep is performed in order to determine the strain to be used during the frequency sweep. The deformation applied on the polymer has to be low enough not to lead to a breakdown of the sample structure. In other words, the strain selected must be in the linear viscoelastic range (LVER) of the sample, where strain and stress are related by a linear relationship.

Table 2 details the conditions of the oscillation measurements performed on polypropylene.

Figure 4 displays the resulting curves of the elastic, loss moduli and phase angle as a function of deformation (Figure 4A) and the corresponding shear stress (Figure 4B). At the beginning of the measurement, the elastic and viscous moduli remain constant: This indicates that the applied deformation does not destroy the sample structure. However, from a shear strain of 20%, an increase in amplitude leads to a decrease in both moduli, while the phase angle increases. In accordance with ISO 6721-10, the end of LVER is determined at the amplitude leading to a decrease of 5% in the G´ value. In this case, it corresponds to a value of 32%.

Table 2.   Test parameters of the oscillation measurements

|	Amplitude Sweep	Frequency Sweep
Device	Kinexus ultra+ with electrically heated chamber	
Geometry	PP25 (plate-plate, diameter: 25 mm)	PP25
Temperature	190°C (approx. 30°C above the melting temperature)	
Measurement gap	1 mm	1 mm
Frequency	1 Hz	10^{-3} to 10 Hz
Shear strain (γ^*)	1 to 100%	-
Shear stress (σ^*)	-	1,000 Pa
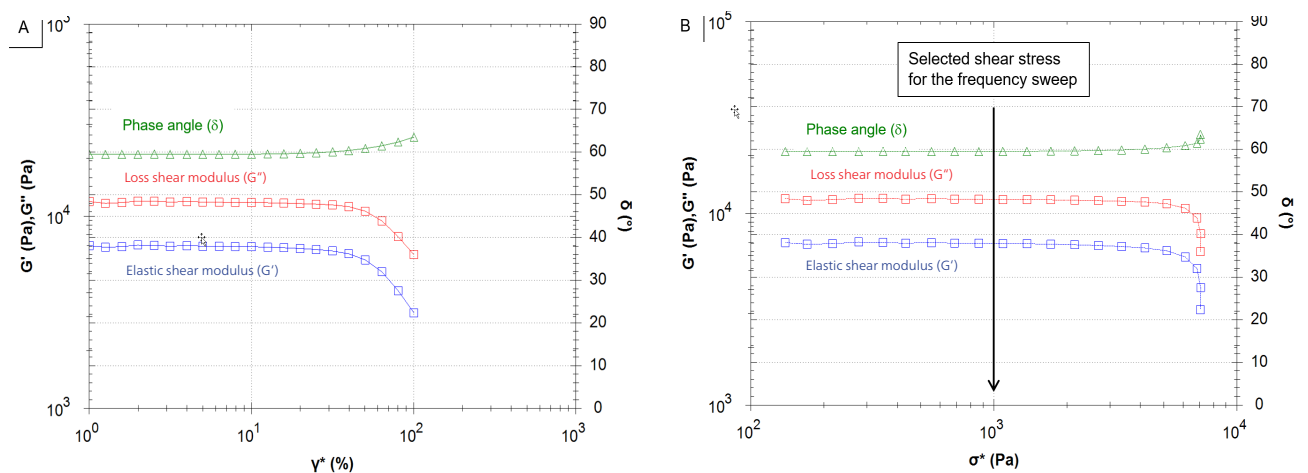
4   Storage (G´, blue) and loss shear modulus (G", red) and phase angle (δ, green) during the oscillation measurement on a polypropylene melt. A: as a function of the shear strain. B: as a function of the shear stress.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

NETZSCH

The curves obtained during the amplitude sweep can also be displayed as a function of shear stress (Figure 4B). For the subsequent frequency sweep, a shear stress of 1000 Pa was applied to the sample.

Figure 5 depicts the shear viscosity from the rotational measurement (blue) along with the complex viscosity from the frequency sweep (orange). Both curves are in good agreement between 10^{-2} and 2 rad/s. This confirms the results discussed above: The flow instabilities occurring at higher shear rates prevent the flow from being time-independent. Consequently, no reliable results can be obtained with the rotational measurement. However, applying Cox-Merz allows for easy determination of the steady-state shear viscosity: One just needs to obtain the complex viscosity as a function of the angular frequency after having carried out an oscillation measurement.
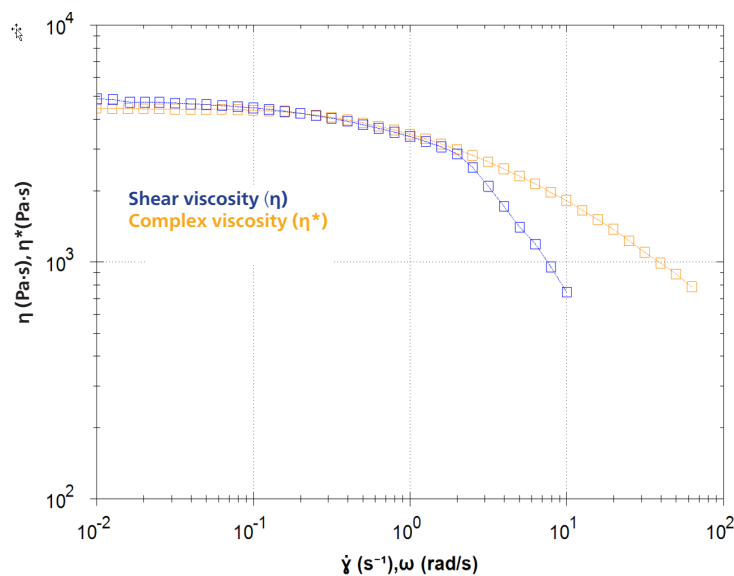
5 Shear viscosity (η, blue) and complex viscosity (η*, orange) during the rotational and oscillation measurements on molten polypropylene melts

Cox-Merz Rule

- Empirical relationship
- Concerns most unfilled polymer melts
- $\eta\,(\dot{\gamma}) = \eta\,^*(\omega)$

Conclusion

The shear viscosity and complex viscosity of a polypropylene melt were compared by means of a rotational and an oscillation measurement. As long as a steady flow can be applied to the polymer, good agreement between the shear viscosity and complex viscosity could be demonstrated. This behavior is expected from the Cox-Merz rule.

For higher shear rates, where flow instabilities occur, a steady flow is no longer reached. Here, the Cox-Merz rule is of great use because it reveals knowledge of the shear viscosity using the complex viscosity.

References

[1] Basic Introduction to Rheology, NETZSCH White Paper
[2] Correlation of dynamic and steady flow viscosities, W. P. Cox, E. H. Merz, Journal of Polymer Science, Volume 28, Issue 118, April 1958, Pages 619-622

NETZSCH