::: Application Report

Anton Paar

MCR 702 Improving the Characterization of Samples Showing Edge Fracture

Keywords: MCR 702, Cone Partitioned Plate, Polymers, LAOS, Start-Up Shear Measurements, Strain Sweep, Frequency Sweep

1 Introduction

When characterizing the rheological properties of a sample, a number of external influences need to be taken into consideration, such as temperature and pressure. Furthermore, sample-specific properties must be taken into account when choosing a suitable measuring geometry and defining a measuring regime, in order to avoid any misinterpretation of the measuring results. For example wall-slip effects and shear banding but also turbulent flow may result in erroneous measuring results.[1]

A main limitation for characterizing polymer melts and concentrated polymer solutions at large deformation and/or high shear rates is known as edge fracture. This kind of sample instability is characterized by a deformation of the sample's surface at the free edges between the upper and lower part of the geometry (Fig. 1).

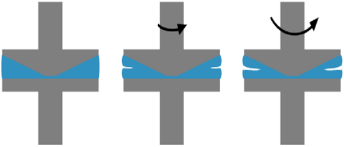

Fig. 1 Illustration of the propagation of edge fracture at increasing shear rates (from left to right) in a cone/plate geometry.

Furthermore, secondary flow effects may develop within the sample at the edge. Deformation of the surface and secondary flow propagate radially as a function of both time and applied deformation. Hence, edge fracture results in increasing measuring errors within standard cone/plate or plate/plate geometries when presetting large deformations and/or high shear rates. Consequently, the accuracy of start-up shear measurements and flow curves at high shear rates as well as for large-amplitude oscillatory shear (LAOS) measurements can be strongly influenced by edge fracture.

In order to reduce the influence of edge fracture in measurements, a specific measuring system has been recommended (e.g.[2]–[5]). This measuring system consists of a cone and a partitioned plate and will be hereafter called cone partitioned plate (CPP).

The aim of the following measurements is to highlight the difference in the measuring performance when using such a CPP in comparison to conventional cone/plate geometries.

2 Experimental

2.1 The Instrument – MCR 702

The measurements were conducted with an MCR 702 TwinDrive consisting of two EC motors. One motor is used as the upper drive and measuring unit, as known from a stress-controlled rheometer. The second motor is mounted in the lower port of the device and can be also used as drive and measuring unit. Because both motors can be separately used as drive units and torque transducers, it is possible to work not only in counter-rotation mode, but also in separate motor-transducer mode, where the lower motor is used as a drive unit and the upper motor is exclusively used as the measuring unit.

The setup of a CPP consists of a cone that is connected to the lower drive and is used to preset a deformation or a shear rate acting on the sample. Furthermore, the CPP consists of a partitioned plate which is mounted on the flange of the upper drive (Fig. 2). The partitioned plate consists of two parts. The inner part is attached directly to the upper measuring drive and the outer ring is fixed to the drive flange and therefore stationary. Hence, only the inner plate is used to transmit the sample's stress while the target of the outer ring is to hold the sample within the gap.

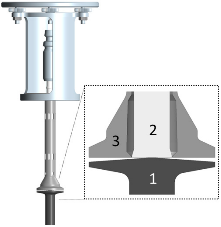

Fig. 2 Setup for a cone partitioned (CPP) plate with lower cone (1) used for stressing the sample, upper inner measuring plate (2) and upper outer stationary ring (3).

Using this setup, the flow instabilities that arise at the edge of the CPP do not have an impact on the sample's properties that are detected in the center of the sample only. Hence, the CPP reduces the effect of trimming, and enables rotational and oscillatory measurements even at deformations which would result in an incomplete filling of the active measuring zone of conventional measuring geometries.

2.2 Measurements

Measurements were performed with a CPP8-4 consisting of an upper inner measuring plate (diameter d = 8 mm), an upper stator (outer diameter d_O = 25 mm) and a lower cone (d = 25 mm; cone angle α = 4°; cone truncation s = 50 µm). Additionally, measurements were carried out with a standard cone/plate geometry (CP25-3; d = 25 mm; cone angle α = 3°; s = 170 µm)

2.2.1 Strain Sweep

Presetting: constant frequency f = 1 Hz; strain sweep = 0.01 % to 1000 % (logarithmic ramp); temperature T = 25 °C; number of measuring points n_{MP} = 26; steady-state mode.

2.2.2 Frequency Sweep

Presetting: angular frequency sweep ω = 300 rad/s to 0.01 rad/s (logarithmic ramp); strain sweep γ = 0.1 % to 10 %; temperature T = 25 °C; number of measuring points n_{MP} = 25; steady-state mode.

2.2.3 Start-up Shear Measurements

Presetting: shear rate $\dot{\gamma}$ = 0.1/1/5/10/30 s^{-1}; number of measuring points n_{MP} = 264; temperature T = 25 °C; measuring time t_{MP} = 0.001 s to 1 s (logarithmic ramp).

3 Results and Discussion

3.1 Strain Sweep

A strain sweep is the initial measurement performed with an unknown material prior to running further oscillatory measurements, in order to get information about the limit of the linear visco-elastic range (LVE range). The LVE range is defined as the region where the storage and loss moduli both show no significant change in their mechanical response. Within this region, both the standard cone/plate geometry and the CPP show an overlaying response, as shown in Fig. 3.

In the LVE range, the sample undergoes no irreversible deformation and oscillatory measurements are therefore usually performed within this region. On the other hand, in recent years, there has been increasing interest in characterizing the rheological behavior in the non-linear range because deformations in most industrial applications can be large and fast.[6] In this region, the material's structure begins to break down, as observed by the decrease in the moduli curves in Fig. 3. However, when using a standard cone/plate geometry, a decrease in the moduli could also be affected by inhomogeneous filling of the gap and some loss of sample due to edge fracture effects. Hence it is difficult to clearly characterize the material's breakdown and to distinguish between material properties and measuring errors.

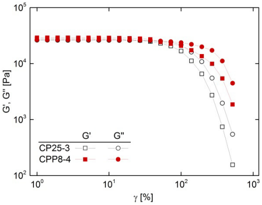

Fig. 3 G' and G'' of PDMS as a function of the strain γ when using a CP25-3 and a CPP8-4.

In contrast, when using the CPP, the reduction of the moduli occurs at higher strains, indicating that the values recorded with the standard cone/plate geometry are lower due to the stronger impact of edge fracture. Because the measuring zone of the CPP is far away from the edge region of the geometry, the results are much less influenced by inhomogeneous filling and sample loss in this region. This can clearly be seen in the differences in the curves measured at higher strains with the two systems, even though inhomogeneous filling was observed for both systems at the outer part of the geometry. In Fig. 4, edge-fracture effects are shown with PDMS as an example for a CP25-3 and a CPP8-4 at 25 °C, f = 1 Hz and γ = 139 %. While inhomogeneities in the sample are detectable for both geometries, the results of the amplitude sweeps are less affected in case of the CPP.

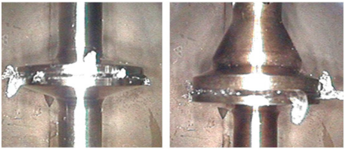

Fig. 4 Visualization of edge fracture effects for PDMS when measuring with a CP25-3 (left) and a CPP8-4 (right) at f = 1 Hz and γ = 139 %.

Hence, working with a CPP increases the accuracy of the measuring results in the transition zone between the linear and non-linear viscoelastic range, extending the range for LAOS measurements to characterize materials in similar conditions to those encountered in industrial applications.

3.2 Frequency Sweep

The visco-elastic response of PDMS as a function of frequency measured in the linear visco-elastic regime is depicted in Fig. 5.

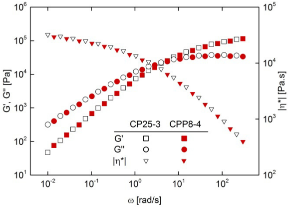

Fig. 5 G', G'' and $|\eta^*|$ of PDMS as a function of the angular frequency ω when using a CP25-3 and a CPP8-4. For better visibility only even or odd numbered measuring points are shown.

With frequency sweeps, higher frequencies relate to shorter time responses, while lower frequencies are related to longer time responses. At higher frequencies, PDMS behaves like a visco-elastic solid (G' > G"), indicating that the sample keeps its shape in the short term. At lower frequencies, however, the behavior of PDMS changes from that of a visco-elastic solid to that of a visco-elastic fluid (G" > G'). This transition is characterized by the presence of a Newtonian plateau of the complex viscosity at lower frequencies, where the material behaves as a fluid showing leveling properties over a longer time scale.

A comparison of the results of the frequency sweep (Fig. 5) indicates that both configurations (standard CP and CPP) show exactly the same mechanical response for the measured PDMS.

3.3 Start-up Shear Measurements

The transient behavior of PDMS at different shear rates is depicted in Fig. 6 using a CP25-3 and a CPP8-4. In general, at lower shear rates, a longer time is required to reach the steady state. Furthermore, the viscosity in the steady-state regime decreases with increasing shear rates, indicating shear thinning behavior. Additionally, with increasing shear rates an overshoot in viscosity is observed due to the elastic response of the material.

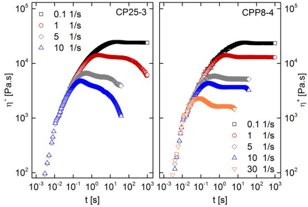

Fig. 6 Start-up shear viscosity η of PDMS as a function of the measuring time at the constant shear rate when using a CP25-3 and a CPP8-4.

The results at the lowest shear rate (shear rate $\dot{\gamma}$ = 0.1 s^{-1}) indicate good agreement between the standard CP and the CPP geometry in terms of the mechanical properties measured.

However, with increasing shear rates and, in the case of the CP25-3, the steady-state plateau becomes shorter and is followed by a distinct decrease in viscosity. This distinct decrease is caused by edge fracture effects, which result in sample being ejected out of the gap and subsequent erroneous calculation of the rheological parameters. Hence, when using a CP geometry, the rheological characterization of the material is limited for the lowest shear rates and it is impossible at higher shear rates, where inhomogeneities may result in misinterpretations.

Even though the sample is ejected from the measuring plate when using the CPP, the impact of inhomogeneities on the measuring results at the outer part of the geometry are less pronounced. With increasing time, however, the edge fracture process propagates to the zone of the measuring area in the center, which can be seen after some time in the decreasing viscosity.

Nevertheless, in case of PDMS, the shear rate suitable for determining the steady-shear behavior is about 30 times higher than for the CP25-3. Hence, with the CPP, visco-elastic samples can be characterized at higher shear rates, which are not achievable with a standard cone/plate configuration.

4 Conclusions

The cone partitioned plate geometry (CPP) minimizes the impact of edge fracture effects when analyzing visco-elastic materials in the non-linear range. This increases the accuracy of the results and broadens the range for performing large-amplitude oscillatory shear (LAOS) tests, start-up shear measurements and flow curves.

5 References

[1] Mezger, T.G. (2014). The Rheology Handbook. 4th Ed., Vincentz Network, Hannover.

[2] Meissner, J., Garbella, R.W., Hostettler, J. (1989). Measuring normal stress differences in polymer melt shear flow. J. Rheol. 33, 843-864.

[3] Schweizer, T. (2002). Measurement of the first and second normal stress differences in a polystyrene melt with a cone and partitioned plate tool. Rheol. Acta 41, 337–344.

[4] Schweizer, T. (2003). Comparing cone partitioned plate and cone standard-plate shear rheometry of a polystyrene melt. J. Rheol. 47, 1071-1085.

[5] Snijkers, F., Vlassopoulos, D. (2011). Cone partitioned plate geometry for the ARES rheometer with temperature control. J. Rheol. 55, 1167-1186.

[6] Hyun, K, Wilhelm, M, Klein, C.O., Cho, K.S., Nam, J.G., Ahn, K.H., Lee, S.J., Ewoldt, R.H., McKinley, G.H. (2011). A review of nonlinear oscillatory shear tests: Analysis and application of large-amplitude oscillatory shear (LAOS). Prog. Polym. Sci. 36, 1697-1753.

Measurements: James Eickhoff
Text: James Eickhoff, Gunther Arnold

Contact: Anton Paar GmbH

Tel: +49 711 72091 600
rheo-applications@anton-paar.com
http://www.anton-paar.com