Combined Rheo-SAXS Investigations using a Laboratory SAXS System

Relevant for: SAXS, Rheology, Polymers, Surfactants

Rheology deals with the flow and deformation of matter, it relates a material's molecular structure to its mechanical properties. Applying mechanical force, e.g., shear to a material can result in orientation of molecular assemblies or crystallization. Small-angle X-ray scattering (SAXS) determines structural parameters of nanostructured materials: size, shape, inner structure and orientation. Relating the nanostructure of a material to its macroscopic mechanical properties requires in-situ characterization techniques such as rheology combined with SAXS.

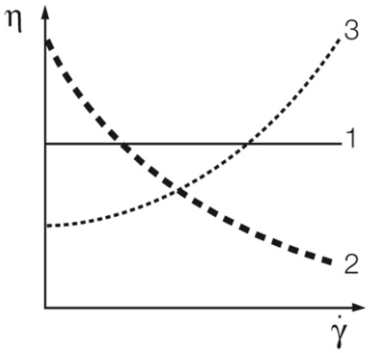

Figure 1: Flow behavior of liquids depending on shear rate. (1) ideally viscous, (2) shear-thinning, (3) shear thickening.

1 Introduction

Understanding the flow behavior and the viscosity of complex fluids is a key factor in many fields of science and technology.[1] The processing of many new materials has to be adapted to these properties to maximize efficiency, e. g., in extrusion processes in polymer production. But also in many other fields, ranging from nanoparticle solutions to medical applications understanding the rheological properties is crucial for both research and production.

Classical rheology can measure both the flow behavior (or deformation behavior in a solid) as well as the viscosity of materials by applying a shear force. In this way it is possible to obtain information on material properties on a macroscopic scale. The flow behavior of liquids can be classified into three different categories:

- Ideally viscous (viscosity independent of shear rate)
- Shear-thinning (viscosity decreasing with shear rate)
- Shear thickening (viscosity increasing with shear rate)

Bulk properties of complex fluids under shear often depend on the structure of the fluid at the nano- or microscopic level. Hence rheology experiments are often combined with other analytical techniques to study the macroscopic and the nano- or microscopic properties at the same time. Depending on the size range that needs to be investigated different methods based on e.g. small-angle scattering can be used. Small-angle light scattering is a standard method used in combination with rheology, however it can only reveal structural insight on a scale larger than approx. 1 µm. Small-angle X-ray scattering (SAXS) can determine a materials' structure on the nanometer scale.[2] Thus it is capable to give insights into structures down to the molecular level, making it the ideal technique for understanding the properties of modern nanomaterials. The combination of rheology and SAXS is often called RheoSAXS. It has been first established a few years back at the SOLEIL synchrotron[3] and subsequently became a standard method used on SAXS beamlines at synchrotrons all over the world.

The current state-of-the-art X-ray sources and the RheoSAXS module for SAXSpoint 2.0 now allow transferring this method to the laboratory for the first time (Figure 2).

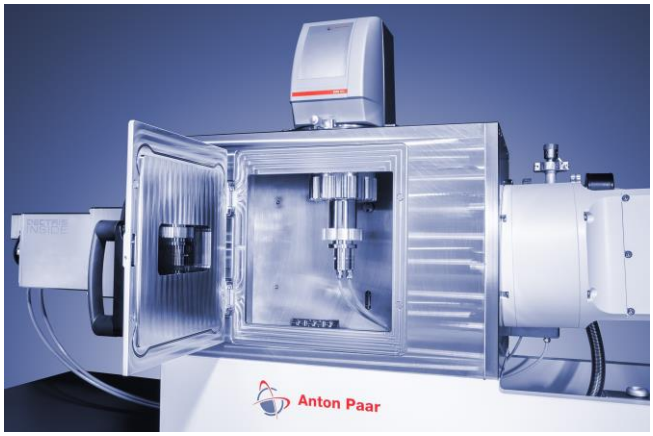

Figure 2: Anton Paar SAXSpoint 2.0 with mounted RheoSAXS module.

Graphene oxide (GO) is the main precursor of graphene-based materials made by solution processing.[4] It is known to be very stiff, having a Young's modulus compareable to that of steel. Using in-situ RheoSAXS measurtments it can be shown that besides its high stiffness graphene oxide is also superflexible.

2 Experimental details and discussion

Here we describe *in situ* measurements on the sample (graphene oxide) under shear by using a laboratory RheoSAXS setup as depicted in Figure 2.

Solutions of graphene oxide flakes in water were kindly provided by Seyed Hamed Aboutalebi (Pasargad Institute of Advanced Innovative Solutions, Teheran) and used as received.

To measure the rheological properties the RheoSAXS module for SAXSpoint 2.0 by Anton Paar was used. It consists of an Anton Paar DSR 502 rheometer head in combination with a measuring cell suitable for *in situ* SAXS measurements. The measuring geometry used for the rheological measurement is that of a concentric cylinder (for details on measurements geometries see e. g., the Applied Rheology handbook[1]).

The measuring cell of the RheoSAXS module is optimized for SAXS measurements, ensuring lowest possible background and highestX-ray transparency. The measuring cell is temperature controlled for reproducible measurement results using a steel enclosure that can be connected to a water bath.

The steel enclosure allows for two different X-ray beam paths through the measuring cell (illustrated in Figure 3) to allow for revealing different structural orientations in the SAXS measurement:

- In the radial beam path the beam passes centered through the measuring cup and the concentric cylinder.
- In the tangential beam path the beam passes the concentric cylinder on the right side.

Experimental Parameters – Rheology	
Instrument	Anton Paar DSR 502
Bearing	Air
Max. Torque	230 mNm
Min. Torque rotation	10 nNm
Min. Torque oscillation	2nNm
Sample volume	8 mL
Sample concentration	2 mg/mL
Sample temperature	20 °C

Table 1: Experimental details for the rheological experiment.

In situ RheoSAXS measurements were carried out using the Anton Paar SAXSpoint 2.0 instrument in combination with the RheoSAXS module. Table 2 lists the experimental details of the SAXSpoint 2.0 instrument used for this experiment.

Experimental Parameters – SAXS	
Instrument	Anton Paar SAXSpoint 2.0
X-ray generator	Anton Paar Primux 100
Power	50 W (50 kV / 1 mA)
Beam collimation	Point collimation
X-ray detector	Dectris Eiger R 1 M
Exposure time	Multiple frames of 10 s
Sample stage	RheoSAXS module

Table 2: Experimental set-up for in-situ RheoSAXS measurements of graphene oxide solutions.

Before starting the measurement, the aqueous solution of GO flakes was filled into the measuring cell Measurements of water were used as the background. The sample was sheared at specific, constant shear rates for a certain time to allow for the SAXS measurements, before increasing the shear rate again. This measuring process can be conveniently programmed using the Rheocompass and SAXSdrive software programs. After finishing the experiment a shear curve as depicted in Figure 4a was obtained. One can clearly distinguish two different regimes: that of a shear-thinning behavior in the beginning of the experiment and that of an ideally viscous behavior at high shear rates.

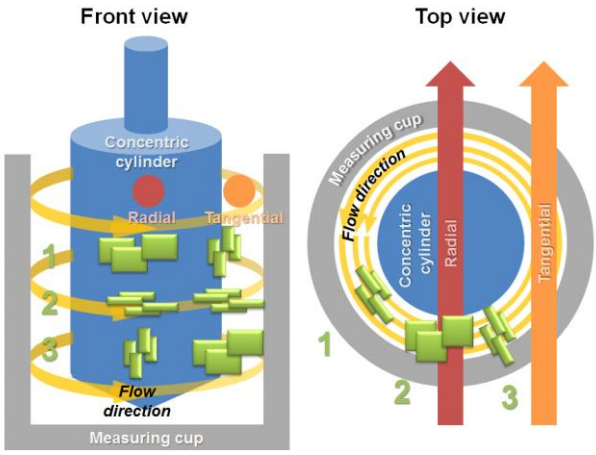

Figure 3: Possible orientations (denoted 1, 2, and 3) of graphene oxide upon shear in both side-view and top-view projection. The two different measurement positions (radial/tangential) of the RheoSAXS module for SAXSpoint 2.0 are also shown.

To understand the switch in flow behavior a deeper insight into the structural/orientational changes of the GO nanosheets is essential. This question cannot be solved by rheology experiments alone but needs insight into the changes in GO flake orientation at the molecular level. Thus, a complementary method that can look *in situ* into the nanostructure of the GO flakes under shear is required. SAXS is ideal for that since it is capable of measuring the sample in its liquid, sheared state. The RheoSAXS module for SAXSpoint 2.0 allows measuring the flow behavior and the changes in nanostructure at the same time. To study the GO flakes under shear measurements at different shear rates along the shear curve displayed in Figure 4a were taken (indicated by the numbers below the shear curve).

The obtained 2-dimensional scattering patterns for each measurement point were then evaluated for the nanostructure by subtracting the background (water) and then integrating the scattering patterns azimuthally. Scattering patterns were taken both in radial and tangential positions (Figure 3).

Since GO is a sheet-like material, the sheets can arrange in different ways. The possibilities for this arrangement are visualized in Figure 3. All of these orientations are easily distinguishable by SAXS measurements, if they are carried out in both radial and tangential position.

From the SAXS measurements 2-dimensional scattering patterns are obtained. These were integrated azimuthally around the primary beam. The resulting curves are displayed in Figure 4b and c. Both scattering curves, obtained in radial and in tangential measuring configuration, show a significant difference between the initial curves (1-9, shear-thinning regime) and the last curve (10, ideally viscous regime. When analyzing the characteristics of the scattering curves 1 to 9 it becomes clear that these can be attributed to an arrangement displayed as orientation 1 in Figure 3. This implies that the GO nanosheets orient parallel to the cylinder walls. In this orientation the excluded volume is minimized and the effect can be understood as an entropic alignment of the flakes.[4] This alignment forms already instantly without applying any shear force and is maintained as the preferential orientation at lower shear rates while the flow behavior of the sample is shear-thinning.

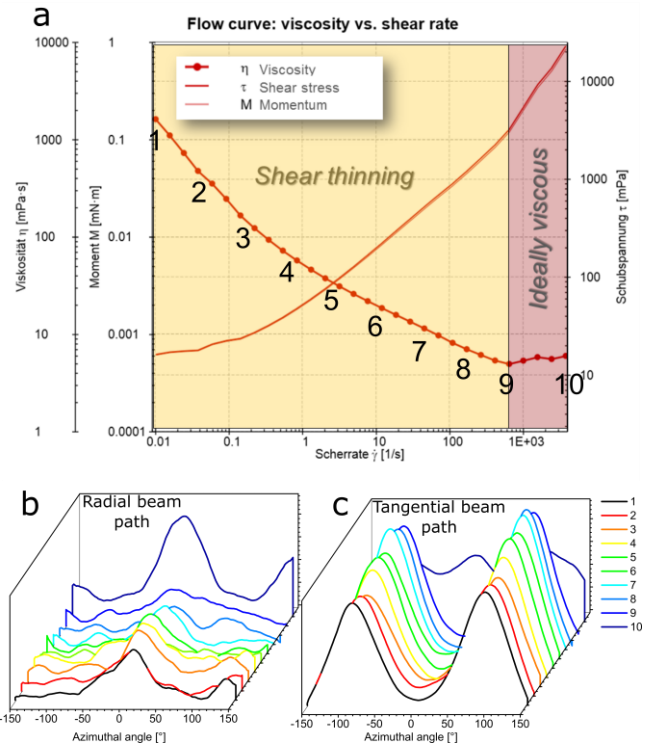

Figure 4a: Shear curve of GO nanosheets in water. The areas of different flow behavior (shear thinning vs ideally viscous) can clearly be distinguished. The numbers given below the viscosity curve correspond to the SAXS measurement points displayed in the graphs b and c. These graphs show results of the azimuthal integration of the 2D scattering patterns in both radial (b) and tangential configuration (c). The change in structure when reaching the ideally viscous state is clearly visible by the change in scattering orientation.

At shear rates higher than about 1000 1/s the flow behavior of the GO solution changes from shear-thinning to ideally viscous. This effect has to be caused by some change in the alignment of the GO flakes. If one looks at the scattering curves in this regime (curves 10 in both the radial and the tangential configuration of Figure 4b and c) it is clearly visible that the shape of the curves is substantially different to the previous curves. In case of the radial X-ray beam path a strong maximum around 0 deg azimuthal angle has evolved. In the tangential measurement mode the maxima at 90 deg. vanish; a new maximum at around 0 deg azimuthal angle is observed. These scattering curves can only be explained with an

alignment in which the flakes orient perpendicular to the walls of the measurement cylinder (orientation 2 in Figure 3). The driving force for this re-arrangement can be intuitively understood when assuming that flakes oriented perpendicular to the flow direction experience large viscous drag forces and thus re-orient along the flow direction to minimize this drag.[4]

3 Conclusion

Combining rheology with small-angle X-ray scattering gives valuable insights into both a material's structure and its macroscopic properties (flow/deformation behavior). Understanding this relationship is of tremendous importance in both scientific and industrial applications.

With the dedicated RheoSAXS module for SAXSpoint 2.0 such studies are for the first time also available in the laboratory, expanding the experimental possibilities for lab-based SAXS instruments to a variety of new applications.

4 References

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Contact Anton Paar GmbH

Tel: +43 316 257-0

support-saxs@anton-paar.com | www.anton-paar.com