Rheo Small Angle Light Scattering (Rheo-SALS) and Rheo-Microscopy as tools for investigations of structure-property relations in complex fluids.

Jörg Läuger, Patrick Heyer

Anton Paar Germany GmbH,
Helmuth-Hirth-Str. 6, D-73760 Ostfildern / Germany
Phone: +49-711-72091-0, info@anton-paar.com, www.anton-paar.com

ABSTRACT

Microscopy and Small-Angle-Light-Scattering (SALS) devices, which can be attached to a standard research rheometer, are described. Combining optical with rheological measurements is valuable to gain a better understanding of the dependencies between the microstructure and the mechanical properties of complex fluids.

INTRODUCTION

Rheological methods reveal information on macroscopic material properties. However, the mechanical material properties are strongly dependent on the underlying microstructure. Therefore information on the microstructure is often valuable for a better understanding of the rheological behavior. Microscopy and Small Angle Light Scattering (SALS) are widely used optical techniques for investigations of micrometer-sized structures. SALS gives information on the structure averaged over the whole scattering volume, whereas a microcopy image shows individual structure elements. On the other hand microscopy displays the structure in the real space, whereas light scattering, like other scattering methods, measures an intensity distribution in the so-called inverse or momentum space. Although both microscopy and SALS result from density (or orientation) fluctuations they are complementary methods.

However, a combination of such setups with a standard rotational research rheometer would allow to perform all rheological tests the rheometer can do simultaneously to the optical measurements. To achieve this goal accessories for both Rheo-SALS and Rheo-Microscopy have been developed, which can be easily adapted onto the MCR rheometer platform from Anton Paar.

RHEO-SALS

SALS is one of the most widely used techniques for getting structural information simultaneous to the rheological data.

In light scattering the angular distribution of the scattered light, which is induced by a incoming primary laser beam, is measured and analyzed with respect to angle and intensity. Under certain assumptions structural information can be obtained from the scattered light distribution.

The elastically scattered light intensity is generally dependent on fluctuations in the polarizabillity and fluctuations in the anisotropy of the polarizabillity, respectively, which themselves are a result of differences in the concentration and in the orientation between the components of a multiphase system. The use of polarizer and analyzer before and after the sample allow to distinguish between scattering arising from concentration and orientation fluctuations.

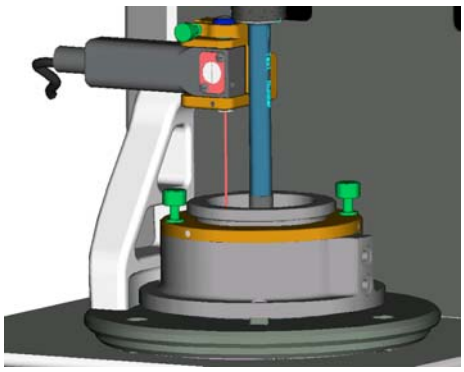

Figure 1. Drawing of the laser system and the measurement geometry attached to the Rheometer.

Fig. 1 depicts the top part of the Rheo-SALS system, whereas in Fig. 2 a schematic diagram of the concentric cylinder setup is shown. Polarized light of a laser diode with a wavelength of 658 nm is deflected into the measuring geometry by a prism. After passing the sample and the analyzer a focusing optics collects the scattered light from a certain point in order to prevent multiple scattering, which is critical in concentric cylinder measurements. Nevertheless the geometry is exchangeable from concentric cylinders to parallel-plate geometry without any further realignment. The light scattering patterns are recorded by a CCD camera located below the screen on which the scattered light is directed.

The absolute value of the scattering vector is defined by the following equation:

$$q = \frac{4\pi}{\lambda} \cdot \sin(\theta/2) \qquad (1)$$

with λ being the wavelength of the light beam and θ representing the scattering angle, respectively.

The accessible scattering angle of the SALS system covers a range from 2° up to 12°, which represents a range for the scattering vector q from 0.3 μm^{-1} up to 2 μm^{-1}.

Temperature control is done by a liquid thermobath. For measurements on polymer melts a special high temperature version of the SALS device is available, which offers a temperature range up to 300°C. The high temperature system works for plate-plate geometries in a range of scattering angles from 2° up to 24°, i.e. in a q-range from 0.3 μm^{-1} up to 4 μm^{-1}.

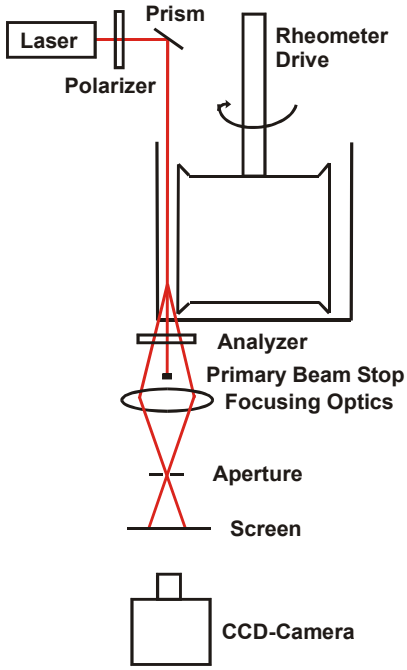

Figure 2. Schematic presentation of the Rheo-SALS System.

As example a model polymer blend consisting of 1% polyisobutylene (PIB) in polydimethylsyloxane (PDMS) has been used for measurements.

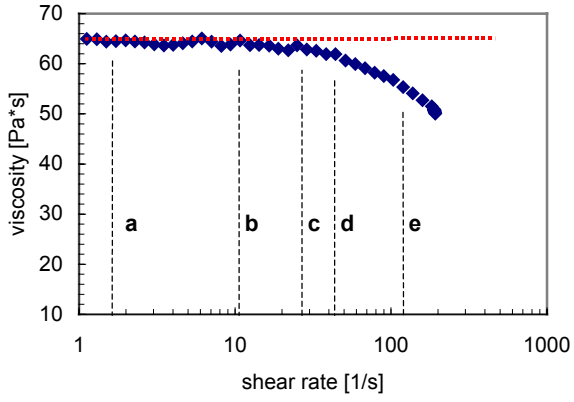

Figure 3. Flow curve of a PIB/PDSM polymer blend. The shear rates at which scattering patterns of Fig. 4 are taken are indicated.

Fig. 3 shows a viscosity curve of the PIB/PDMS sample. At small shear rates between 1 s^{-1} and 20 s^{-1} a zero shear viscosity can be observed. The viscosity starts to decrease at shear rates above 20 s^{-1}. Fig. 4 displays scattering patterns taken at various shear rates simultaneously with the measurement of the flow curve.

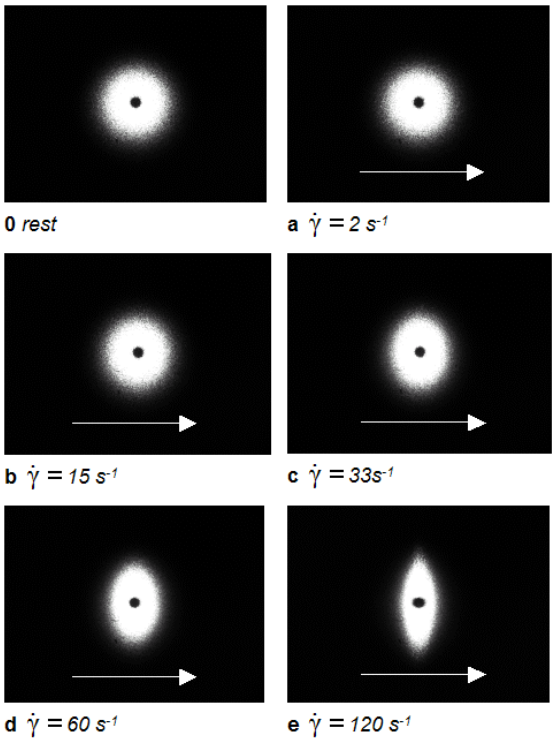

Figure 4. Light scattering images at different shear rates. The arrow represents the shear flow direction.

The comparison between the light scattering images and the flow curve shows, that there is no difference visible between the image recorded in rest and in the zero viscosity range (a, b). As soon the viscosity starts to decrease (c) the scattering images begin to change from a circular to an elliptical shape (d, e). This change represents the orientation and deformation of the PIB domains. The higher the shear rate, the more oriented and deformed these domains are leading to more stretched scattering patterns. Light scattering on large dimensions cause small scattering angles. Conversely small structures in the sample lead to large scattering angles. Therefore the deformation of the PIB domains in shear flow direction results in scattering patterns, which are elliptically shaped and oriented perpendicular to the shear flow direction.

RHEO-MICROSCOPY

The microscopy setup as shwon in Fig. 5 and Fig. 6 consists of a CCD camera, a microscopy tube and a long working distance objective. The illumination is integrated in the microscopy tube and illuminates the sample from the bottom side (incident light). Due to the modular design the light sorce as well as the CCD camera and the objectives can be exchanged.

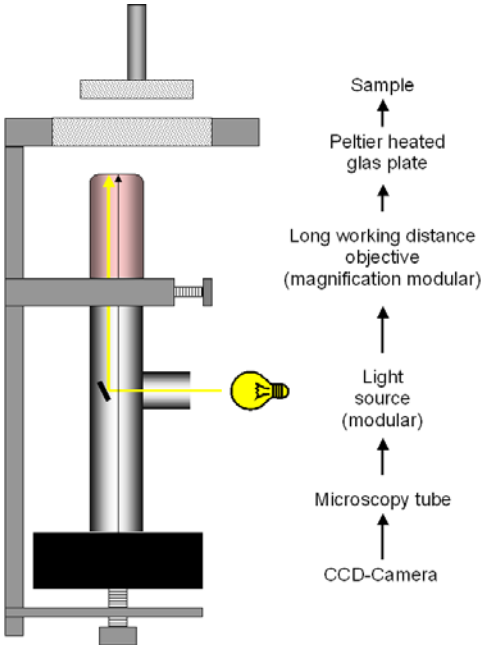

Figure 5. Principle of the Rheo-Microscope setup.

The microscope is movable in y- and z-direction for foccusing and selecting a certain observation area. The rheological measurements take place at the top of a glass plate heated by Peltier elements. An additional Peltier heated hood can be used for assuring an accurate temperature control and an uniform temperature distribution throughout the sample up to 120°C. The

parallel-plate measurement geometry is made of glass as well to prevent reflections.

As for the SALS system a high temperature version of the microscope setup is available, which offers a temperature range up to 300°C

Figure 6. View of the upper and lower measuring plates. The objective with the illumination can be seen underneath the bottom glass plate.

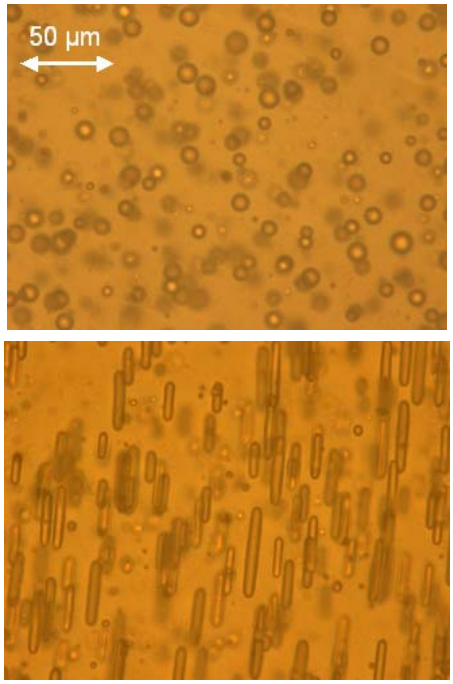

Figure 7. Microscope images at rest (top) and at 50 s^{-1}(bottom)

In Fig. 7 microscopy images on the same PIB/PDMS sample as used for the SALS measurements are shown at rest and at a shear rate of 50 s^{-1}, respectively. The flow direction on the images is in vertical direction. The flow field leads to a stretching of the PIB droplets in the flow direction.

In Fig. 8 the viscosity curve and the corresponding microscopy images at the respective shear rates for a water/oil emulsion are presented. At small shear rates the viscosity is high and the droplets small. With increasing shear rate the viscosity decreases and the droplets are getting bigger due to agglomeration. By increasing the shear rate further the droplets start to be deformed and finally they are breaking and leading to smaller droplets in the emulsion.

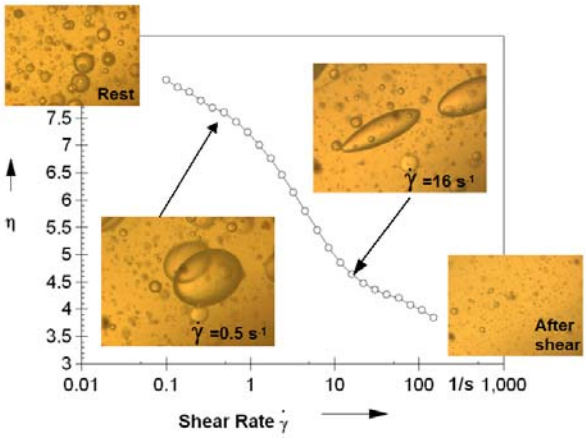

Figure 8. Viscosity curve and microscopy images for a water/oil emulsion.

CONCLUSIONS

Light microscopy is a real space method and the individual structure elements can be seen. In light scattering the scattering from many structure elements is detected at the same time and in case of the droplet structure the scattering pattern are deformed perpendicular to the flow direction, since SALS is giving the information in the inverse space of the scattering vector. However, both techniques reveal the same type of information. Microscopy and SALS are complementary methods. In combination with Rheology both are valuable tools to reveal information on the microstructure of complex fluids subjected to a flow field.