A new integrated Rheo Small Angle Light Scattering (Rheo-SALS) device

Jörg Läuger, Patrick Heyer, Gerhard Pfeifer

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

ABSTRACT

A new Rheo-Small-Angle-Light-Scattering (Rheo-SALS) device is introduced. It consists of a SALS module, which can be easily adapted as a modular accessory to a commercially available rheometer. Both concentric-cylinder or parallel-plate geometries can be used. Details of the new Rheo-SALS device and experimental results are presented.

INTRODUCTION

Small Angle Light Scattering (SALS) is a widely used technique for investigations of micrometer-sized structures. SALS has been used in combination with applied flow fields for many years. However, a combination of a SALS setup with a research rheometer (Rheo-SALS) would be more suitable for detailed investigations on structure-property relationships of complex fluids. Such devices have been designed at several university laboratories. However, to make Rheo-SALS methods more commonly available a new device has been developed.

The Physica Rheo-Small-Angle-Light-Scattering (Rheo-SALS) setup allows getting structural information simultaneous to the rheological data. Purely rheological methods provide information on the macroscopic behavior of the samples. That means with a rheometer it is possible to determine macroscopic material functions. On the other hand the macroscopic behavior of a substance is strongly dependent on its microscopic structure parameters. Information on the microstructure is often helpful for a better understanding of the rheological behavior. SALS is one of the most widely used techniques for getting structural information simultaneous to the rheological data[1-3].

The Physica Rheo-SALS setup features a complete SALS system directly attachable to a standard research rheometer. Thus allowing SALS investigations simultaneously to all rheological test modes the rheometer offers.

PRINCIPLE OF SALS

In light scattering the angular distribution of the scattered light, which is induced by an 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 intensity distribution.

The elastically scattered light intensity is generally dependent on fluctuations in the polarizabillity and fluctuations in the anisotropy of the polarizabillity, which themselves are a result of differences in the concentration and in the orientation between the components of a multiphase system, respectively.

If unpolarized light or no polarizer and analyzer are used the scattering is so-called unpolarized and the scattering is sensitive on concentration fluctuations.

If polarization elements are used, two configurations are possible:

1. Polarizer and analyzer are perpendicular (crossed polarizers). This so-called depolarized scattering is sensitive on orientation fluctuations.
2. Polarizer and analyzer are parallel (parallel polarizers). This so-called polarized scattering is sensitive on concentration and orientation fluctuations.

Fig. 1 shows the principles of an unpolarized and a polarized SALS scattering experiment, respectively.

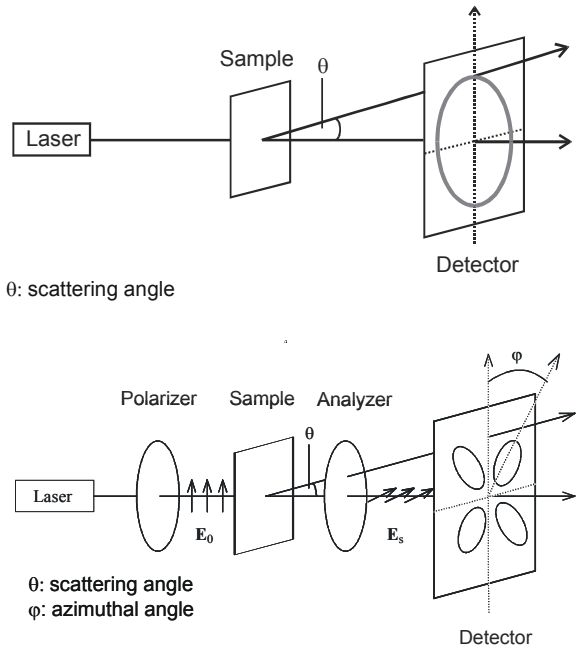

Figure 1. Different experimental setups for a SALS experiment. Top: unpolarized scattering, Bottom: polarized scattering.

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.

As depicted in Fig. 2 in combination with a shear flow device, like in a Rheo-SALS setup, four different configurations for the polarizer (P) and the analyzer (A) with respect to the shear flow direction are possible.

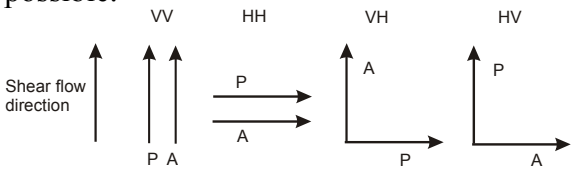

Figure 2. Four different positions of polarizer (P) and analyzer (A) with respect to the shear flow direction.

If the molecular axes are parallel to the shear flow direction the so-called VV-scattering is more sensitive on orientation fluctuations, whereas HH-scattering is more sensitive on concentration fluctuations. VH- and HV-scattering are only dependent on orientation fluctuations. If the sample has no strong optical rotational force the VH-scattering equals the HV-scattering.

THE RHEO-SALS DEVICE

Figs. 3 and 4 show the setup of the Rheo-SALS system. Polarized light of a laser diode with a wavelength of 658 nm is deflected into the measuring geometry by a prism. If there are concentration or orientation fluctuations existing in the sample, the incoming light is scattered at the sample. After passing the analyzer the scattered light from a certain point along the gap in a concentric-cylinder geometry is collected by a focusing optics and directed onto a screen. A CCD camera records the scattering patterns from the screen. The camera can be synchronized directly from the rheometer software. The geometry can be changed easily to a parallel-plate setup without any further realignment. The accessible scattering angle covers a range from 2° up to 12°, which gives a range for the scattering vector q from 0.3 μm^{-1} up to 2 μm^{-1}.

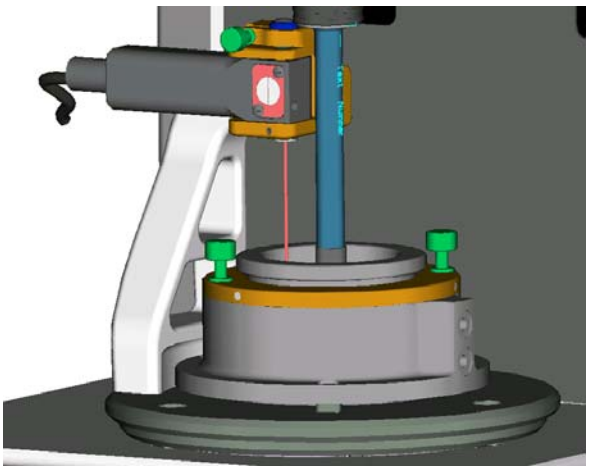

Figure 3. Drawing of the laser system and the measurement geometry attached to the Rheometer.

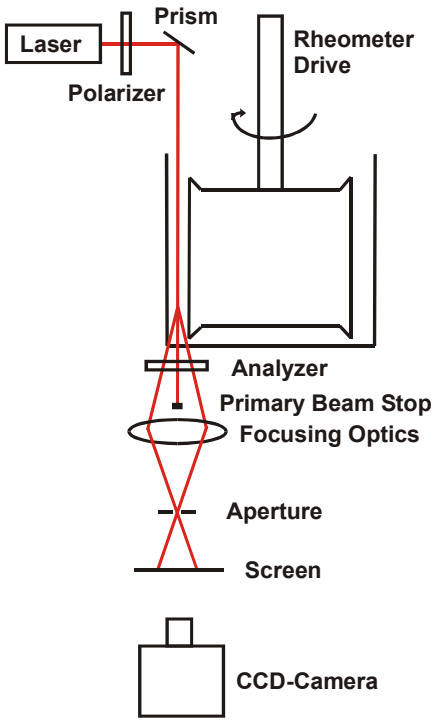

Figure 4. Schematic presentation of the Physica Rheo-SALS System.

Depending if parallel-plate or concentric-cylinder geometries are used, the scattered light is detected in a different plane with respect to the shear flow field as indicated in Fig. 5.

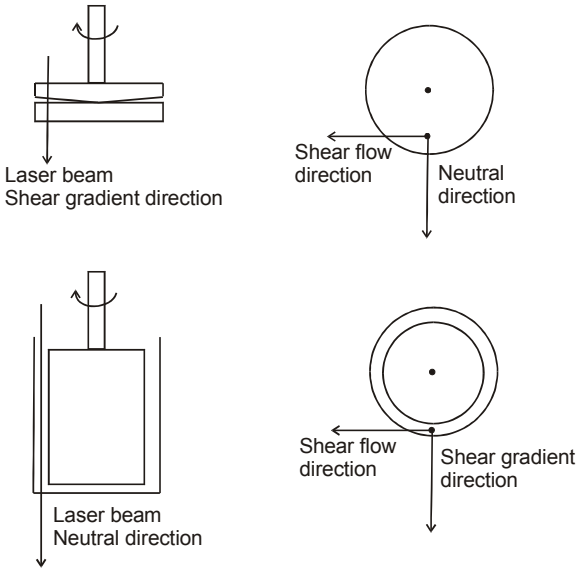

Figure 5. Different measurements planes for parallel-plate and concentric-cylinder geometries.

With a parallel-plate geometry the incoming primary beam travels along the shear gradient direction and the scattering pattern is detected in the plane of the shear flow and the neutral direction. With a concentric-cylinder geometry the incoming primary beam travels along the neutral direction and the scattering pattern is detected in the plane of the shear flow and the shear gradient direction.

EXPERIMENTAL

As an example a sample consisting of 1% polyisobutylene (PIB) in poly-dimethylsyloxane (PDMS) has been used for measurements. This sample represents a model system for an immiscible polymer blend with domains of PIB in a PDMS matrix.

The measurements described have been performed employing the Physica Rheo-SALS system with a parallel-plate geometry in combination with a Physica MCR rheometer.

RESULTS AND DISCUSSION

Fig. 6 shows a flow curve of the PIB / PDMS sample. Observable is a viscosity

plateau with a zero shear viscosity in the shear rate range between 1 s^{-1} and 20 s^{-1}. The viscosity starts to decrease at shear rates above 20 s^{-1}. Fig. 7 displays scattering patterns taken at various shear rates simultaneously with the measurement of the flow curve.

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 as the sample starts to flow (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 and the more stretched the scattering patterns are.

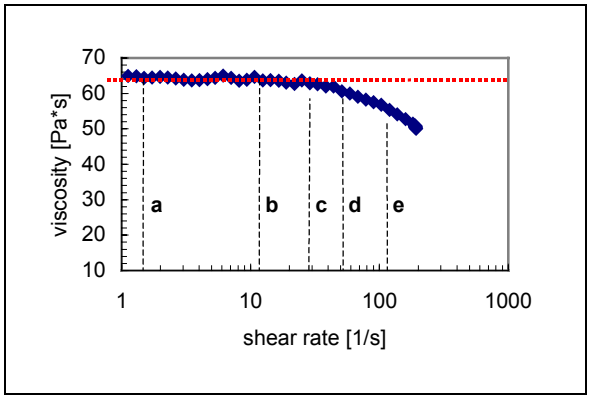

Figure 6. Flow curve of PIB/PDSM polymer blend. The shear rates at which scattering patterns of Fig. 7 are taken are indicated.

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. Generally the light scattering shows an inverse reproduction of the structure present. After removal of the shear flow the structure and thus the light scattering pattern relax back to circular shape.

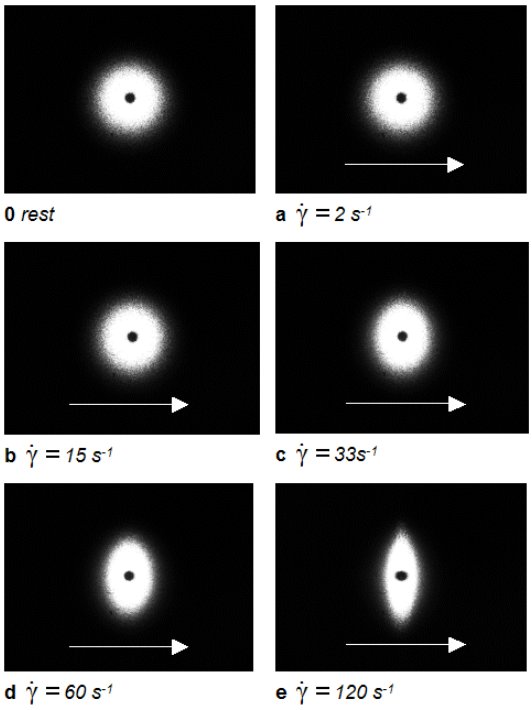

Fig. 7. Light scattering images at different shear rates. The arrow represents the shear flow direction.

CONCLUSIONS

A new integrated Rheo-SALS system is presented which can be adapted modularly to a standard research rheometer. Both parallel-plate and concentric cylinder geometries are possible and easy to switch. The system allows a simultaneous determination of rheological properties by the rheometer and structural information by the SALS setup.

REFERENCES

1. Nakatani A.I., Waldow D.A., and Han C.C., *Rev. Sci Instr.*, **63** 3590 (1992).
2. Fuller G.G., *Optical Rheometry of Complex Fluids* (Oxford University Press, New York, 1995) pp177, and references therein.
3. Läuger J. and Gronski W., *Rheologica Acta*, **34**, 70 (1995).