Combined Rheological Methods: From Rheo-Optics to Magneto-Rheology and Beyond

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ABSTRACT

Nowadays a wide variety of different accessories used in combination with rotational rheomters are available. Such techniques range from rheo-optical methods to applying external pressures and electrical or magnetical fields. In addition systems transforming the rotational movement of the rheometer allow investigations on extensional rheology or tribology with a rheometer.

INTRODUCTION

Rheological measurements reveal information on macroscopic material properties as a function of temperatures. The combination of additional techniques with rheological measurements became more popular in recent years. We classify all methods into three main categories.

The first contains all techniques providing additional structural information. Since the mechanical material properties are strongly dependent on the microstructure, information on the microstructure is often valuable for a better understanding of the rheological behavior. The second category includes all systems in which the rheological behavior as a function of an additional parameter is studied. The third category contains techniques transforming the rotational or the axial movements of the rheometer into different types of flow conditions. The geometries or accessories used impose mechanical loads in different geometrical forms onto various types of samples.

The aim of the paper is to give an overview over such widely used combined rheological techniques and to discuss their respective advantages and limitations. However, here we limit ourselves to techniques which can be mounted optionally as special accessories into the MCR rheometer from Anton Paar.

METHODS GIVING ADDITIONAL STRUCTURAL INFORMATION

Establishing a connection between the changes of the microstructure of a fluid in a flow field and their consequences on its macroscopic properties leads to a better understanding of the behavior of complex fluids and allows an optimization of their parameters.

The decision on which technique to choose is based on the size and type of the structure as well as on the general sample properties to be investigated. The proper method for investigating a certain sample depends on the length scale but also on the special requirements needed for the experiment.

For the characterization of materials in the mesoscopic scale, i.e. in the range from one to several hundred nm, techniques like **Small Angle X-ray Scattering (SAXS**) or **Small Angle Neutron Scattering (SANS)**

are often employed[1-3]. Suitable for structure investigations in the micrometer-size range simultaneously with rheological measurements are both, **Microscopy** and **Small Angle Light Scattering (SALS)** since they do not require special preparation of the samples[4]. The density and orientation fluctuations within a sample, averaged over the whole scattering volume, can be well monitored by SALS as intensity distribution in the so-called inverse or momentum space. On the other hand, microscopy images show individual structure elements displayed in the real space. Thus, although both microscopy and SALS result from density (or orientation) fluctuations within a sample, they are complementary methods and together with the information provided by rheological studies contribute to a complete characterization of the samples probed. The simultaneous use of rheo-optical methods has been achieved by developing specialized accessories, for Rheo-SALS and Rheo-Microscopy. Temperature control of these system can be achieved either by Peltier (-20°C to +120°C) or electrical heating devices (RT to +300°C). Other optical techniques are **Birefringence** and **Dichroism** which probe, molecular and structural orientation processes, depending on the exact setup and on the sample. The main advantage of optical methods is relatively easy availability and the possibility to run such experiments in a normal laboratory. However, the limitations are that optical transmission methods require sufficiently transparent samples and the size of the investigated structures should be in the range of micrometers.

SANS and SAXS methods, which are very similar to SALS are overcoming these limitations, however, they require special source for the x-rays (synchrotrons) or the neutrons (reactor or spallation source), which are only available at large research facilities. Nevertheless, special SAXS and SANS accessories have been developed. For SAXS measurements two systems are available. One is temperature controlled by electrical heating elements and employs parallel-plate or a special cone-ring geometry. A typical application is the investigation of shear induced crystallization of polymer melts. In the concentric cylinder geometry the x-ray beam travels through the sample either in tangential or radial direction in order to collect scattering patterns in the planes perpendicular or parallel to the shear gradient direction, respectively. A special temperature control device based on the convection method allows measurements over a broad temperature range (-100°C to +200°C). The SANS cell is similar to the cylinder SAXS system. The main difference is that in case of SAXS the bob and cup are made of Polycarbonate whereas for the SANS system quartz glass is used.

A different technique used in combination with rheology is dielectric spectroscopy. Based on the study of the material response to an applied electric field, the **Dielectric Spectroscopy** can be used as a complementary technique to rheology and gives additional information about the material in ranges that are less accessible to mechanical analysis.

METHODS APPLYING AND CHANGING AN ADDITIONAL PARAMETER

Rheological parameters are always dependent on temperature. Different device for an accurate and reliable temperature control have been described earlier. Therefore, in this paper we want to focus on additional parameters for which it is often of large interest to apply them simultaneously to a rheological measurement. One such parameter is the **Pressure**. Many applications like oil recovery or food processing require rheological measurements at elevated pressures. Different pressure cells with concentric cylinders, double gap or parallel-plate geometries cover different ranges in pressure, temperature, and viscosity range.

So-called smart fluids change their rheological properties dramatically after

application of an external magnetic or electrical field. Special rheometer accessories have been developed in order to apply a magnetic or an electric field to a sample simultaneous to the rheological measurements. In a **Magneto-Rheological Device** (MRD) the magneto rheological fluid (MRF) is located in a parallel plate geometry or a new twin gap configuration in which the MRF is below and above the plate-geometry[5-8]. Magnetic filed strengths of more than 1Tesla can be applied and the influence of the magnetic field on the MRF can be studied. For electro-rheological fluids (ERF) **Electro-Rheological Devices** (ERD) based on concentric cylinders and parallel plates are available allowing the application of fields strength of up to 12.5kV [9].

UV-light triggering a chemical reaction is often used for curing adhesives, glues, or printing inks. A rheometer allows to follow the large mechanical changes during this reaction.

METHODS TRANSFORMING THE TRADITIONAL RHEOMETER INTO A NEW INSTRUMENT

A modern research rheometer employs a highly dynamic motor and an extremely sensitive torque sensor. Moreover, it has a sophisticated axial drive and a corresponding normal force sensor. It offers tremendous ranges in speed and torque with the advantage that both the movement, i.e. rotational speed or angle, and the force, i.e. the torque can be set and controlled and the respective property is measured. This makes a rotational rheometer the ideal platform for a lot of new applications.

One example is the use of an bi-cone geometry to measure interfacial shear rheology properties of thin films at the liquid/liquid or the liquid/air interface[10,11]. These types of measurements are only possible due to the low torque capability of the rheometer. Using the **Interfacial Rheology System (IRS)** has the advantage that now all kinds of rheological testing modes are easily possible on interfacial films, which was not possible with existing devices.

Another example is extensional rheology of polymer melts by the use of a special **Extensional Fixture (SER)**, which transforms the rotation of the rheometer into extensional stretching of the sample by two counter rotating drums. However, only the fast dynamical control of the rotational movement of the rheometer allows the fast application of the extensional strain rate, which is needed for the measurement of the transient extensional viscosity[12].

Tribology embraces the study of friction, wear and lubrication. A tribometer requires speed and normal force control as well as a torque measurement to acquire tribological data. This and the intension to measure so-called Stribeck curves as well as the static friction with one single instrument led to the idea to design an accessory turning the rheometer into a high resolution **Tribometer** based on a ball on pyramid principle. Friction coefficients under dry and lubricated condition between different materials can be measured in a wide temperature range[13,14].

Other techniques in this category, which include **Tack Testing** or **Penetration Tests** are tests using the axial movement and normal force measurements.

CONCLUSIONS

Methods used in combination with a rotational rheometer have been described and categorized into three main classes. Rheological testing on its own is a powerful tool for characterizing complex fluids and for solving all kinds of application problems related to the handling of liquids. However, the large variety of the different methods, which were already available show that nowadays a rheometer offers much more than standard rheological testing at certain temperatures. With the ever increasing need for a better understanding of fundamental processes it is believed that this trend is very likely to continue. Rotational rheometer which are basically the most sophisticated

devices for measuring and controlling rotational speed, angle and torque are more and more used not just in situations where an additional technique is adapted simultaneous to the rheological measurements but also for applications outside traditional rheological testing in which the measurement and control capabilities of the rheometer is used by its own.

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