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Shear-induced polarized light imaging as complementary tool to rheology for characterization of complex fluids

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INTRODUCTION

Complex fluids are essential components for different applications of chemical processes, in life science or various industries. In order to optimize their processing as well as their practical applications, detailed knowledge of their rheological properties is essential.

While performing rheological testing, information on the macroscopic material properties is gained as function of experimental conditions. Nevertheless, since the mechanical material properties strongly depend on the microstructure, information on the microstructure is very valuable for a better understanding of the rheological behavior. Thus, the combination of optical techniques with rheological measurements is of interest in order to correlate microstructural properties with the rheological behavior of the material. Different optical methods such as small angle light scattering (SALS), microscopy (polarized, fluorescence, confocal), spectroscopy (NIR, IR, Raman), birefringence and dichroism, as well as pure visualization techniques have been employed.

In this paper, applications of a recently introduced rheo-polarized imaging technique are being discussed[1]. SIPLI (shear induced polarization light imaging) combines a visualization technique with measurements of local stresses through the detection of the birefringence. The shear induced polarized light imaging allows e.g. the observation of flow induced crystallization processes of polymers or the characterization of the orientation of polymer chains in polymer solutions and melts under shear [1-3]. The method is based on the phase difference of light passing through optical active materials and provides information on optical path boundaries between optical isotropic and anisotropic structures.

SETUP

The SIPLI setup is depicted in figure 1, whereas the schematic principle of the SPLI is presented in figure 2. A light source emits light which is transferred by the light guide into the optics. This white light travels through a polarizer to the beam splitter where it is deflected towards the sample so that the sample is illuminated with polarized light. Different polarization states can be generated by rotating the built-in polarizer (analyzer). The image of the illuminated sample is transferred telecentrically to the chip of a color CCD camera, allowing the recording of changes in sample structures induced by the shear forces of the rheometer leading to e.g. birefringence. While parallel-plates and cone-plates systems up to 50 mm in diameter can be used, an area with radius of 25 mm is directly optically monitored by the SIPLI setup.

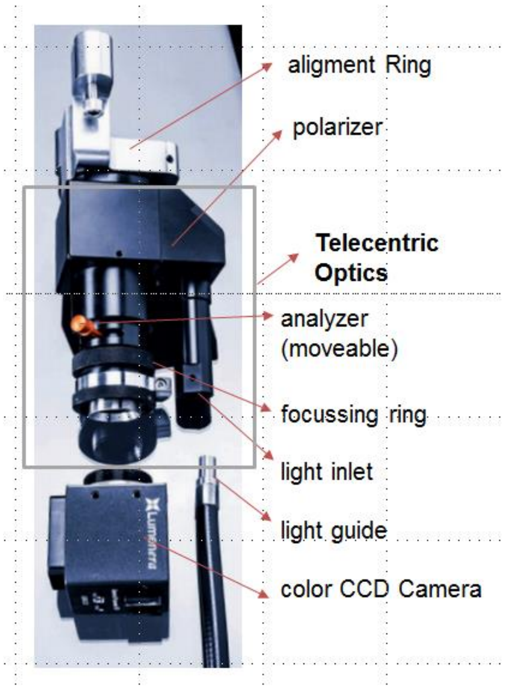

Figure 1. Photo of the SPLI setup

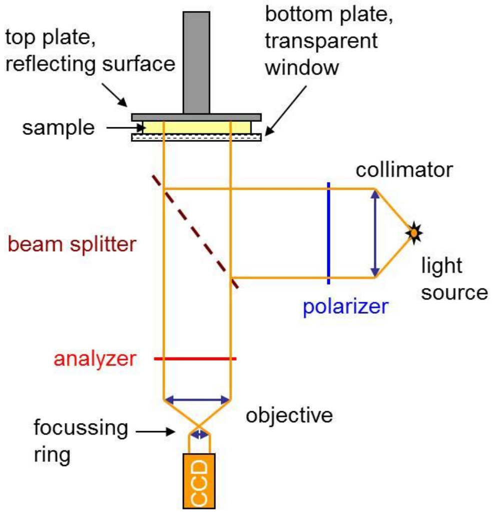

Figure 2. The polarized imaging option enables to monitor the sample using polarized light, a telecentric optics module and a CCD camera.

APPLICATIONS

To emphasize the correlation between the birefringent properties of the materials under shear, their microstructural changes and their rheological behavior simultaneous SIPLI and rheological tests were performed. For all tests shown here cross polarization, i.e. the polarizer oriented perpendicularly to the analyzer, was used.

<u>Liquid crystals</u>

In figure 3 a rotational test performed for a Cholesteryl oleyl carbonate (COC) is shown. The COC sample forms a chiral nematic liquid crystal between 21°C and 31°C; above 31°C it should be isotropic and no liquid crystal domains should be found.

The shear rate was logarithmical varied between 0.001 and 1000 s^{-1} for the tests performed at 60°C, 40°C and 25°C. A cone-and-plate geometry was used. At all temperatures, the sample shows shear thinning, i.e. with increasing the shear rate the viscosity decreases. The SIPLI images show that at 60 and 40°C the sample is completely isotropic, no orientation effects can be observed. Only when cooled down to 25°C a shear induced crystal-like structure can be observed, see figure 3. At this temperature, dark sectors disposed perpendicularly, the so called birefringent Maltese cross zone, can be observed. The Maltese cross, a set of four symmetrically disposed sectors, corresponds to the transparent area of the sample. The liquid crystals are anisotropic, optically active materials. Thus, the refractive indexes of such materials are not constant, as they depend on the orientation of the domains. The orientations and magnitudes of the refractive indices are depicted by an index ellipsoid, called also optical indicatrix.

The appearance of the Maltese cross indicates a parallel orientation of one of the main axes of the optical indicatrices of a birefringent structure in the plane of polarization of the incident light. Thus, the linearly polarized light passing through will not change its polarization, resulting in dark regions. If the nematic director is not aligned with either one of the polarizing filters, polarized light passing through the first filter becomes partially polarized along the nematic director.

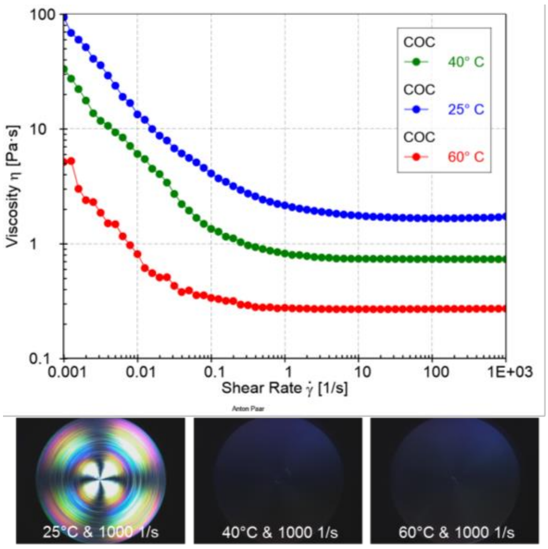

Figure 3. Viscosity curves of the COC liquid crystal at different temperatures.

Cellulose solution

Further, a high concentrated gel-like cellulose solution was measured. In order to visualize the stress distribution as experienced by the sample during the flow the shear rate was logarithmically increased from $1 s^{-1}$ to $1000 s^{-1}$ by using a cone-and-plate geometry (Figure 4) as well as a parallel-plate system (Figure 5). The tests were performed at room temperature.

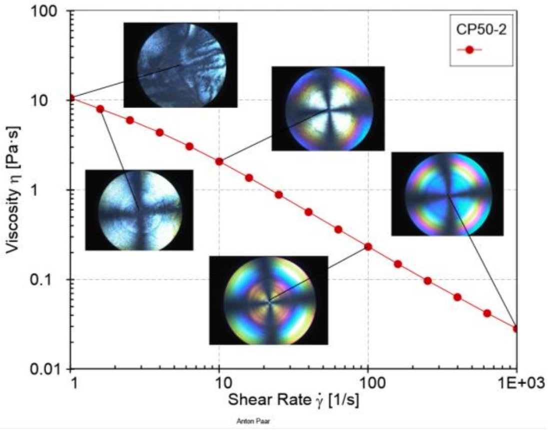

Figure 4. Viscosity curve of the cellulose solution with SIPLI images indicating orientation of the chains in the flow. Measurement performed with a cone-and-plate geometry.

In the beginning of the test the cellulose chains are non-oriented within the flow; increasing the shear rate leads to a decrease of the viscosity due to increasing orientation of the cellulose chains.

This is confirmed optically by the appearance of the Maltese cross which becomes more pronounced with increasing shear rate.

While in a cone-and-plate geometry the shear rate is constant, in the parallel-plate system the sample experiences a radial distribution of the shear rates, from a maximum shear rate at edge of the sample to a zero shear rate in the center of the plate. Thus, the parallel-plate system has the advantage that the birefringence can be displayed over the full range of shear rates within one single experiment.

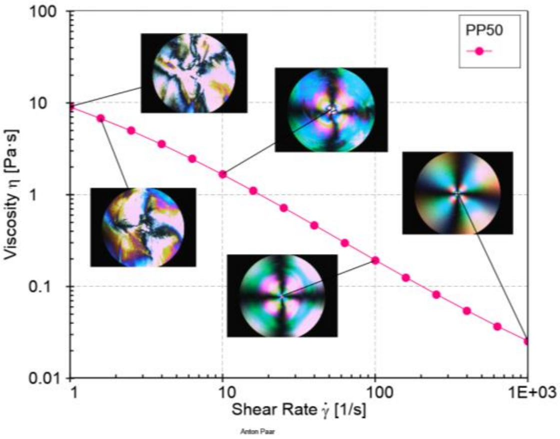

Figure 4. Viscosity curve of the cellulose solution with SIPLI images indicating orientation of the chains in the flow. Measurement performed with a parallel-plate geometry.

DNA solution (salmon DNA)

The figure 6 shows as an application a strain sweep on a gel like DNA-solution. As the strain exceeds the limit of the linear region the molecules are stretched leading to a birefringence which can be detected by the SIPLI technique.

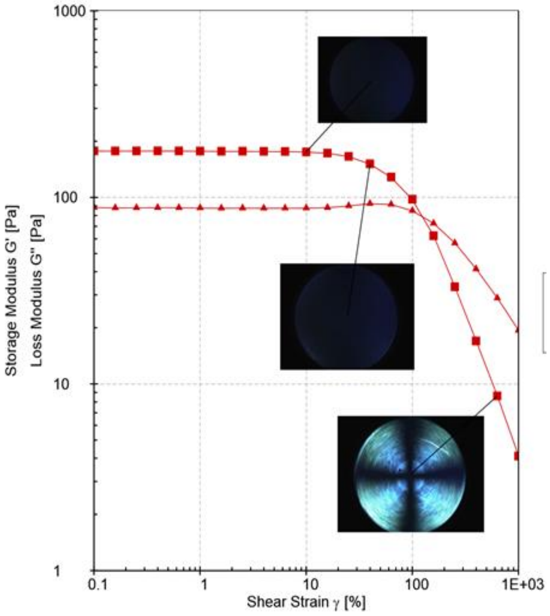

Figure 6. Strain sweep on a gel like DNA-solution with the corresponding SIPLI images.

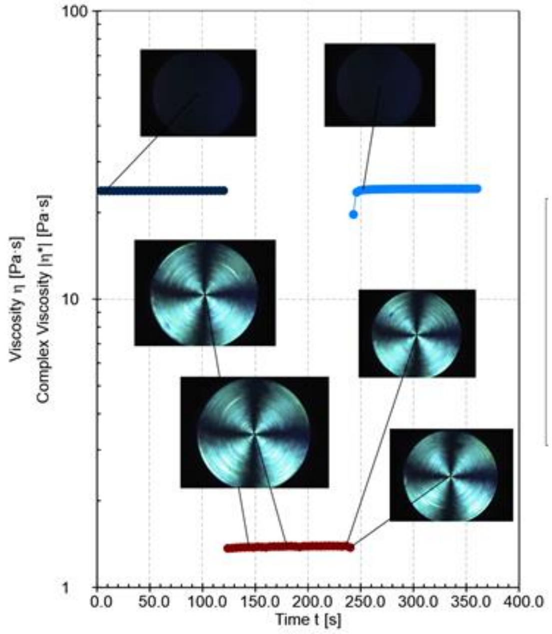

Figure 7. Three interval test on a gel like DNA-solution. Fast orientation of molecules at high shear rate and fast relaxation after cessation of the flow is observed.

In order to monitor the orientation and relaxation of molecules, a so called “three interval test” was conducted. In the first and third interval a small amplitude oscillation was performed, in order to simulate the rest situation. The second interval (120 s) was a high shear interval (1000 s^{-1}). At rest, no molecule orientation could be observed resulting in black SIPLI images. At high shear rates, the sample experiences large stress, the molecules become oriented in the flow, leading to sample birefringence. As it can be seen in figure 7 the molecules orient very fast under large shear rate and relax very fast after cessation of shear.

CONLUSIONS

In all these applications emphasized the correlation between the birefringence properties of the materials under shear, their microstructural changes and their rheological behavior. While at rest, the viscoelastic liquids at rest are optically isotropic, under shear flow the refractive indices can become uniaxially anisotropic due to stretching, deformation and/or orientation of the molecules along the direction of flow, the samples become birefringent.

Thus, it can be concluded that the SIPLI (shear induced polarization light imaging) can be used as complementary method to rheology in order to monitor shear induced structural changes in complex fluids.

REFERENCES

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