![ESRF logo]	**Experiment title: Effect of shear-flow on the structure and rheology of model concentrated suspension**	**Experiment number**: SC-617
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Report:

In these experiments we have investigated the flow-induced structure of three different types of colloidal systems. The Couette flow cell at the ESRF was used for this purpose and installed on beamline ID02. By translating the Couette geometry with respect to the beam, both the flow-vorticity and the vorticity-gradient plane could be accessed, hence providing an insight into the 3D structure of the dispersions under flow. A wavelength of 1 Å was used in all experiments and a 2D XRII CCD detector was used. The spot size on the sample was 0.3x0.3 mm^2. The experiments were carried out at an ambient temperature of 20°C.

1. Stable colloidal systems – Newtonian Medium

In a first set of experiments the structure of polybutylacrylate latex suspensions, sterically stabilized by adsorbed polymer layers, has been investigated as a function of volume fraction, shear rate and particle size (Sample A1, d_c=127 nm with δ_h = 10nm and Sample A2, d_c = 254 nm and δ_h=17nm). In these systems large-scale bundle structures have been recently observed by means of 2D-SALS experiments under flow [1], an example of a SALS pattern is shown in Fig. 1. It has been suggested that these bundles are due to either a shear-banding instability [2], or by a coexistence of an ordered and disordered structure during flow as obtained from Stokesian dynamics simulations [3]. The SAXS data compare favorably with the latter interpretation. To illustrate this aspect more clearly, a flow curve for one of the dispersions is shown in Fig. 1 together with a SALS patterns and three typical SAXS patterns obtained at the ESRF. At low stress levels the structure is polycrystalline, subsequently the order increases with shear stress to melt away at still higher ones. A detailed analysis of the degree of crystallinity as a function of shear rate and volume fraction and the formation and melting of the ordered structures is being performed.
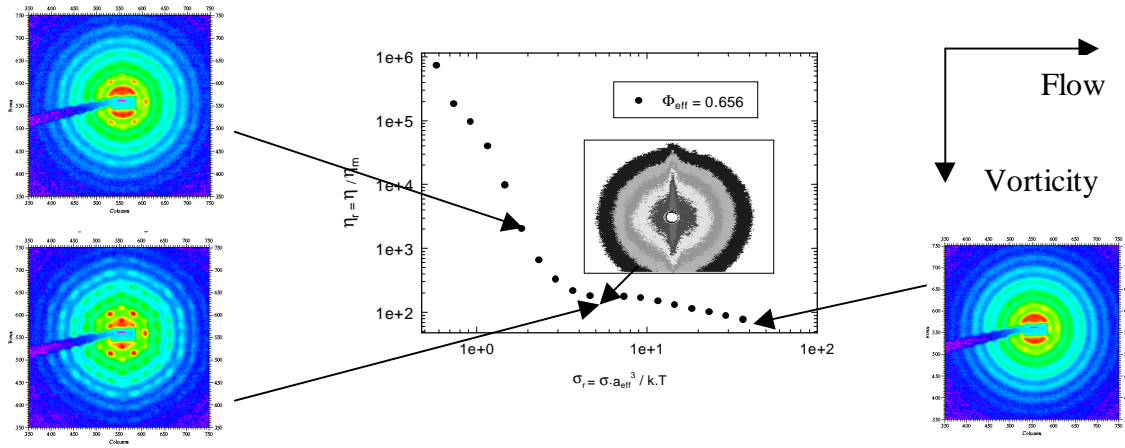
Fig. 1 : Reduced viscosity as a function of reduced stress for an aqeous latex A2 at a core volume fraction of 0.48, the inset shows a typical SALS pattern [1]. SAXS patterns obtained at different stress levels, as indicated by the arrows, during steady state flow are shown as well.

From the SAXS experiments the following conclusions could be obtained:

1. The detail structure of the recently observed flow-induced bundles reveals a coexistence crystalline and amorphous material.

2. A flow-induced order-disorder (OD) transition takes place without the ocurrence of shear-thickening of the viscosity. This demonstrates that an OD transition is not a necessary condition for shear thickening, thus confirming simulation results [4] and supporting other experimental evidence [5] that the dominant mechanism for shear thickening is the formation of hydrodynamic clusters.

2. Stable colloidal systems – Liquid crystalline medium

A second set of experiments investigated the behaviour of suspended particles in a liquid crystalline polymer (LCP) matrix. Adding particles to LCP's can be expected to interfere with the microstructural features of the polymer during flow, thus inducing complex changes in the rheology [6,7]. The liquid crystalline nature of the matrix could also introduce anisotropic interactions between the particles, which would further complicate the behaviour [8]. As a liquid crystalline polymer matrix a solution of hydroxypropylcellulose (Klucel LF from Aqualon) in twice distilled water. For all samples studied the matrix phase consisted of 55% HPC (by weight) in water. The colloidal particles were electrostatically stabilized silica particles that carry a negative surface charge (Ludox TM-50 from) Dupont with an average diameter of 28 nm. With the setup on beamline ID02 the sample to detector distance could be varied from 1 to 10 m, covering a q-range of approximately 0.025 nm-1 to 5 nm^{-1}. Due to this wide range and the small size of our filler particles the diffuse scattering lobes of the liquid crystalline matrix and the scattering pattern of the particulate fillers could be resolved. In this manner information about the particulate structure as well as the liquid crystalline order in the matrix could be obtained in a single experiment.

To determine the particulate structure factor we used a sample with 10% silica particles. This has a high enough volume fraction to pick up the intra-particle interference. Figure 2 shows the resulting structure factor as a function of the magnitude of the scattering vector. The structure was essentially liquid-like, and somewhat surprisingly, shearing has no effect on the particulate structure. The two results indicate that the coupling between the liquid crystalline matrix and the particulate structure is weak. The molecular order than can be measured in flowing LCPs is a convolution of two contributions [9]. Firstly, there is the molecular order inside the domains, characterized by the molecular order parameter. The molecular order parameter reflects the width of the orientation distribution of the rods around the orientation of the local director. Generally liquid crystalline materials have a polydomain structure, where the orientation of the director can be different in different domains. This gives rise to an orientation distribution of local directors as well. Fig. 3 shows the overal orientation parameter S, obtained by a method according to Picken et al. [10] as a function of shear rate and as a function of filler concentration. The effect of particle size has also been investigated.
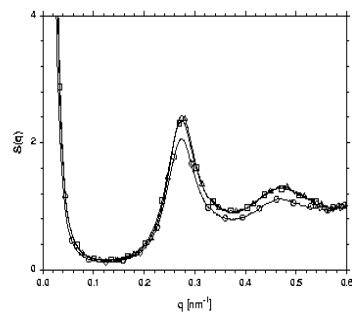
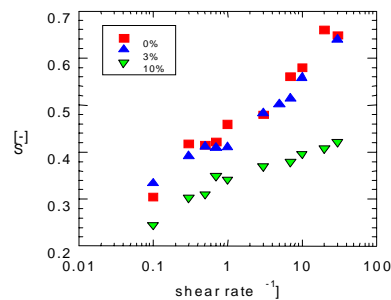*Fig. 3 Structure factor under flow shear rates are 1, 10 and 100 s⁻¹*

Fig. 4 Overall orientation parameter as a function of shear rate for three volume fractions (0,0.03 and 0.1)

From the SAXS experiments the following conclusions could be deduced:

1. The particulate structure is not affected by the presence of a liquid crystalline matrix, indicating a weak coupling between the polymer nematic and the particles. This confirms what had been suggested from rheological measurements [7]
2. Reasonable high particle volume fractions are needed to significantly reduce the overall order of the nematic phase, whereas the first normal stress difference is strongly affected [6,7].

3. Weakly flocculated colloidal systems

Some preliminary experiments have been performed on weakly flocculated dispersions. Two systems were explored. The first system consisted of 5% charged silica particles (30nm) in water and was depletion flocculated by a low molecular weight PEO. Depletion flocculaton allows for a very good control of the degree of flocculation. The second system contained PMMA particles with grafted polymer layers, flocculated by collapse of the polymer layer by adding of non-solvent for the latter. In this system the interaction potential cannot be controlled as well, but by changing the temperature the system can be deflocculated. This enables one to wipe out all effects of the mechanical history. The preliminary results enabled us to fine tune our model systems for further experiments. They should results in a description of the effect of flow on the various length scales in these flocculated systems.

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