ESRF	**Experiment title:** RHEO-SAXS IN-SITU INVESTIGATION OF FLOCCULATION MECHANISM OF CELLULOSE	**Experiment number**: 26-02-778
Beamline: BM26B	**Date of experiment**: from: 09/05/2016 to: 13/05/2016	**Date of report**: 27.05.2016
Shifts: 9	**Local contact(s)**: Hermida Merino Daniel	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists): **W.G. Bouwman* (Delft University of Technology), E.V. Velichko* (Delft University of Technology), T.N. Nikolaeva* (Wageningen University).**

Scientific background. The experiment aimed to spatially and time resolve structural changes of cellulose microfibrils (CMFs) under shear conditions. Dispersions of cellulose microfibrils have received considerable attention as sustainable and natural materials with applications ranging from coatings and packaging materials to food and cosmetics. Their long, anisotropic shape allows the microfibrils to be used as scaffolds in polymer nanocomposites. For such composite gels, emphasis lies on their elastic properties, although their flow properties are also relevant, for instance for industrial processing and behavior during consumer use. A major obstacle in understanding the flow is the compositional and structural heterogeneous nature of these dispersions. Recent studies [1] have shown nonlocal flow behaviour of microfibrillar cellulose suspensions. Based on Rheo-MRI data two different hypotheses to explain such nonlocality were suggested: floccullation of cellulose microfibrils and formation of liquid-cristal like phase in these suspensions.

Samples and experimental techniques. In the experiments we used Rheo-SAXS to study structural changes of cellulose microfibrills in static and under shear conditions. The experimental setup allowed to probe length scales in the order of 4-210 nm. This length region covers well the cross-sectional dimension of microfibrills which are in the order of 60 nm in diameter and would allow to observe presence of microscopic alignment and liquid-crystal structure if such should appear. A special shear-cell was designed for this experiment, which allowed to point the X-ray beam along vorticity direction of the flow as well as probing the mesostructure at different positions across the gap between the moving and the static surface of the cell. In order to have homogeneous flow profile across the gap, a gap of only 1 mm was used with a 38 mm outer radius. Shear rates were varied in a wide range from 1 to 300 s^{-1}. The beam cross section at the sample position was about 120 μm, which allowed to measure five different positions across the gap without overlap. We used the Pilatus detector with the pixel size 172x172 microns square positioned at distance of 6500mm away from sample for the SAXS measurements.

We used two sources of cellulose for sample preparation: cubes of bacterial cellulose in syrup nata de coco dessert (Kara Santan Pertama, Bogor 16964, Indonesia) and Herbacel AQ Plus citrus fibre powder. For preparation of microfibrillated cellulose from bacterial cellulose we used the protocol described in [2]. Cubes of bacterial cellulose were crashed by blender, washed from colorants and flavour agents and redispersed in water in concentration 0.2 wt%. Mixtures of BC and carboxymethil cellulose(CMC) were prepared by adding different amounts of CMC [Ashland Blanose Aqualon, 99.5% pure, 9M31XF, Mw ≈ 250 000 g/mol, degree of polymerization of 1100, degree of substitution (DS) of the carboxymethyl groups of 0.8−0.95] and nanopure water and mixing with a Sylverson mixer (L4RTA) for 5 min at 3600 rpm. Citrus fibre powder was just dispersed in water with a concentration of 2%. These samples were passed once through a Micro-fluidizer (M110S, Microfluidics) with a z chamber of 87 μmat a pressure of 1200 bar. Dilutions were made from the obtained stock solutions by dilution with nanopure water.

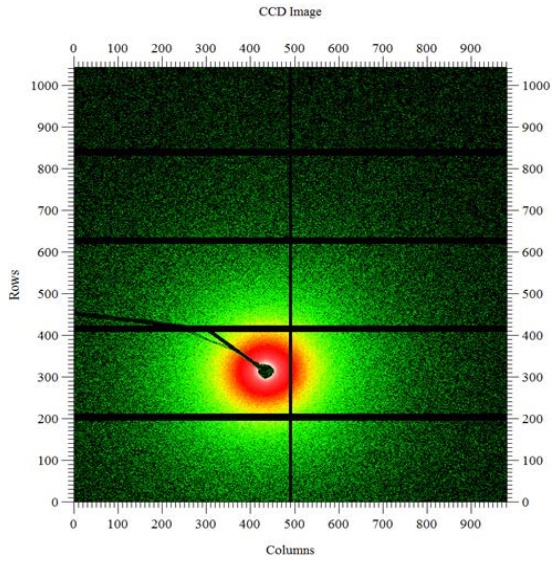

Figure 1. 2D SAXS pattern for sample containing 0.2wt% of BC and 0.05 wt% of CMC at static mode.

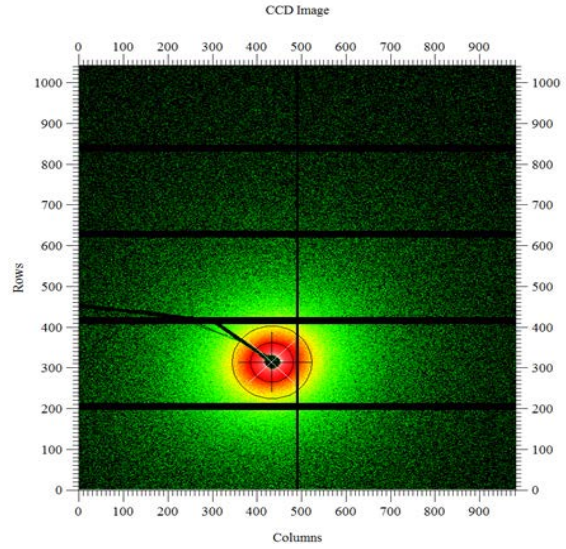

Figure 2. 2D SAXS pattern for sample containing 0.2wt% of BC and 0.05 wt% of CMC at shear-rate of 300 s^{-1}.

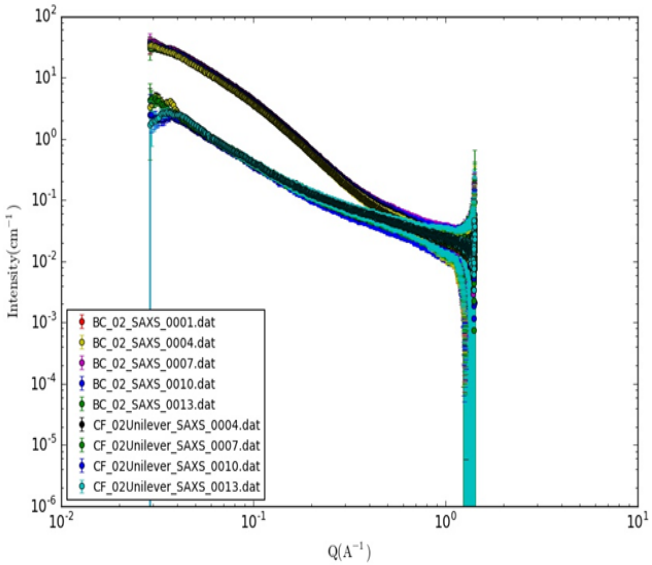

Figure 3. Q-dependencies of the scattered intensity for microfibrillated cellulose samples obtained from bacterial cellulose and from citrus fibre at concentration of 0.2%wt.

Results. The 2D SAXS pattern shown in Figure 1 was taken from a dispersion containing 0.2wt% of BC and 0.05 wt% of CMC at static conditions (without shear applied). Radial averaging of the pattern has not shown any anisotropy for the wide range of shear-rates (0-100 s^{-1}) which indicates that no liquid crystal structure is present in the system. Only the highest applied shear-rate caused a slightly anisotropic SAXS pattern (see Figure 2) which might be explained by a elliptical shape of the cellulose flocks at such a high shear rate. Decreasing shear-rate caused disappearance of such anisotropy. The scattering patterns for each sample taken at static conditions after all the shear manipulations were identical to the ones taken in the beginning of the experiment which indicates reversibility of shear-induced changes in the system.

Figure 1 shows axially averaged Q-dependencies of scattering intensity for dispersions of bacterial cellulose and citrus fiber at concentration of 0.2wt%. These curves were measured for each sample at various positions across the gap in static conditions after all the shear measurements were done. As can be seen for each sample the curves are completely overlapping, which indicates a homogeneous density distribution across the gap. Q-dependencies are considerably different for cellulose suspensions obtained from bacterial and plant sources which is in good agreement with literature [3,4] stating that plant cellulose microfibrills have round cross-section while cross-section of bacterial cellulose microfibrills is rectangular.

Thus, from the experiments we can conclude absence of liquid-crystal structure which leaves only flocculation hypothesis suitable to explain nonlocal flow of the cellulose dispersions. Obtained data suggests that average flock size is bigger than reached in current geometry (200 nm) and needs further investigation by means of Rheo-USAXS and Rheo-SESANS.

References

1. D. W. Kort et al., Soft Matter, **DOI:** 10.1039/c5sm02869h (2016).
2. A. Kuijk et al., Langmuir, **29**, 14356−14360 (2013).
3.I. Siró et al., J. of Applied Polymer Science, **119**(5), 2652–2660 (2011).
4. P.C. Tischer, Biomacromolecules, **11**(5), 1217–1224 (2010).