ESRF	**Experiment title: Cellulose nanofibrils with clays as aqueous rheology modifiers**	**Experiment number**: SC-3111
Beamline: ID02	**Date of experiment**: from: 15-07-2011 to: 18-07-2011	**Date of report**:
Shifts: 9	**Local contact(s)**: Dr. Jeremie Gummel	*Received at ESRF:*

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Report:

Personal care products frequently contain polymers and surfactants that are only used to give the product its desired structure. Because fossil fuels are becoming scarce, it has been suggested that oxidised cellulose could instead be used as a rheology modifier in these products. It has been found that C6-partially oxidised cellulose[1] forms gels with salt,[2] clays and anionic surfactants. Our aim is to find out why these gels form.

This experiment consisted of two parts: static samples in 1.5 mm capillaries and rheology using the HAAKE Mars II rheometer with a couette geometry. Measurements were made at 12.5 keV and a detector distance of 1.46 m with the FReLoN Kodak CCD detector. For the static samples we measured samples consisting of cellulose + non-ionic surfactants with and without salt. Previously we have studied gel formation of negatively charged oxidised cellulose with anionic surfactants. Our results suggest these mixtures form gels due to the amount of salt (counterions) present in the samples. Cellulose with non-ionic surfactants alone doesn't gel, but when equimolar amounts of salt are added, above 20 mM salt and surfactant, gels are formed. Here therefore we measured the structure of these nonionic surfactant, salt and cellulose gels to determine how the surfactant micelles interact with the cellulose fibrils in the gel structure.

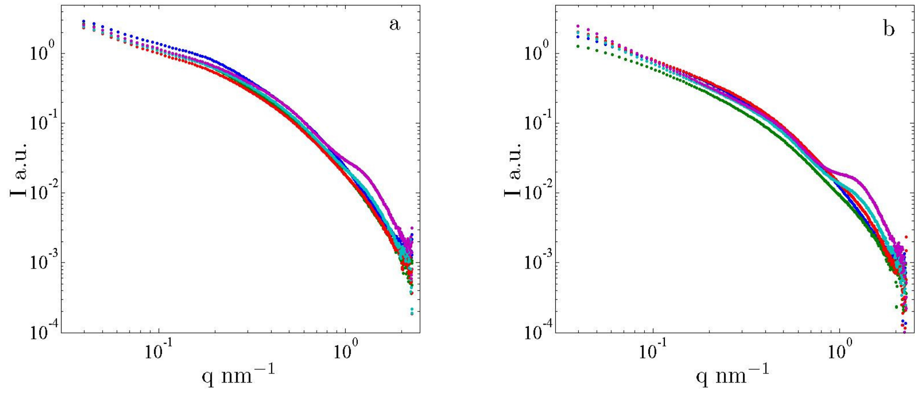

Figure1. Scattering of 8 g/L cellulose with (a) Brij58 and (b) Brij58 and equimolar amounts of NaCl. Brij58, NaCl concentrations: 5 mM (dark blue), 10 mM (green), 20 mM (red), 40 mM (light blue), 80 mM (purple).

In figure 1 the SAXS patterns of cellulose with non-ionic surfactant Brij 58 (fig 1a) and cellulose, Brij58 and salt (fig 1b) are shown. Especially at the higher surfactant concentrations the shapes of the curves both at high q and at low q differs. The higher scattering at low q for the systems with salt is probably an indication of larger, network structures, responsible for the gel formation.

In the static part of the experiment we also studied cellulose/clay mixtures (fig 2). In figure 2a the small angle X-ray scattering curves of montmorillonite with different amounts of cellulose are shown. The lowest scattering intensity is observed for the clay sample on its own. The scattering intensity of 10%

montmorillonite 90% oxcell is slightly higher and increases when there is more clay present in the samples. The scattering curves of the 50% montmorillonite 50% oxcell and 60% montmorillonite 40% oxcell are very similar. The shape of the curves also changes for the two different clay systems.

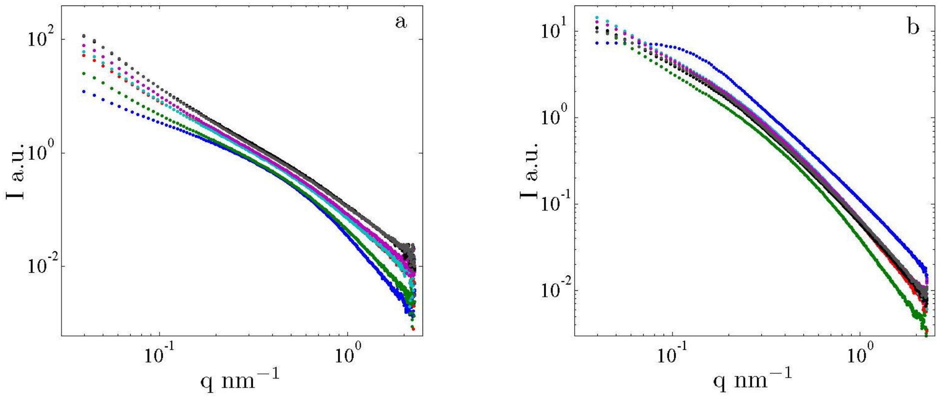

Figure 2. Scattering of cellulose with(a) 3wt% montmorillonite, mixing ratios x clay: y oxcell: 1:0 (dark blue), 1:9(green), 2:8 (red), 3:7(light blue), 4:6 (purple), 5:5 (black) and 6:4(grey), (b) 3 wt% laponite, mixing ratios, x clay: y oxcell: 1:0(dark blue), 2:8 (green), 3:7 (red), 4:6 (light blue), 5:5 (purple), 6:4 (black) and 7:3 (grey).

In the second part of the experiment we studied the change in small angle scattering patterns as function of the shear rate for cellulose-surfactant gels. We studied mixtures of different concentrations of cellulose with 40 mM AOT, 40 mM 1 AOT:1 SDS and 40 mM 1AOT: 1$C_{16}E_8$. All these gels are shear thinning. The aim of these measurements was to study the effect of micelle shape on the gel formation. AOT is a double tailed surfactant and will form lamellar phases, mixing this surfactant with SDS or $C_{16}E_8$ induces formation of more elongated cylindrical micelles with different charge densities on the micelle surface.

Figure 3 shows the radial (a) and tangential (b) scattering of 4 g/L cellulose with 40 mM AOT as function of the shear rate. For the radial scattering, the position of the small peak in the middle of the scattering curve (which gives information about the spacing between the lamellae) is constant. The position of this peak for the tangential scattering at higher shear rates in the tangential case, is shifted to lower q, meaning that the distance between the lamellae is becoming bigger.

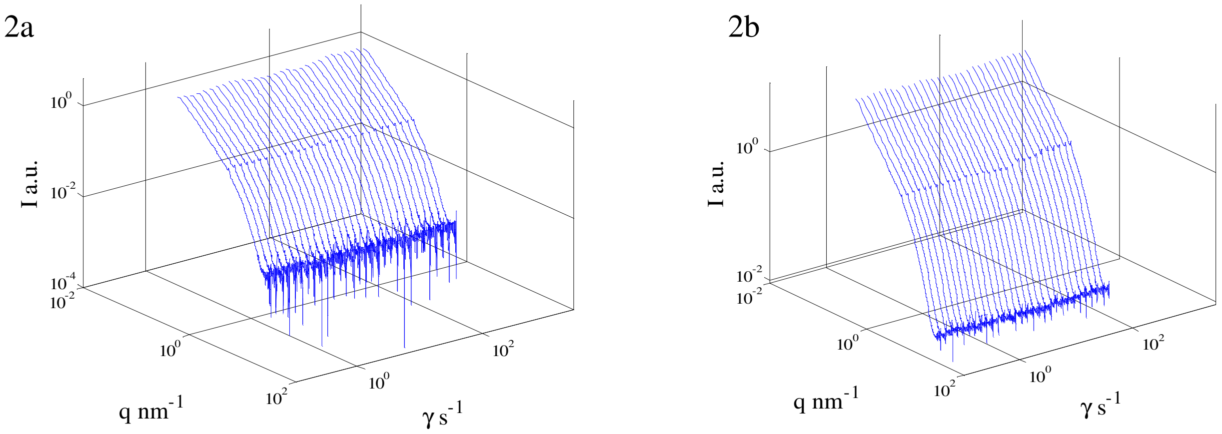

Figure 3. Scattering of 4 g/L cellulose with 40 mM AOT as function of the shear rate (a) radial and (b) tangential scattering

Further analysis of these scattering measurements will assist our understanding of the properties of these gels and so give us new insights for the design of more environmentally friendly personal care products.

References:

1. T. Saito, S. Kimura, Y.Nishiyama, A. Isogai, , Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* **2007,** *8* (8), 2485-2491.
2. S. Lindhoud, P. Colver, J.L. Scott, K.J. Edler, Gel formation of C_6-partially oxidised cellulose with salts, *Biomacromolecules*, **2011**, submitted.