Experimental report

05/10/2018

Proposal: 9-12-531 **Council:** 4/2017

Title: Formation of cellulose-starch gelsand the effect of surfactant

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Julien SCHMITT**

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Julien SCHMITT
Vincenzo CALABRESE

Local contacts: Isabelle GRILLO

Samples: Cellulose/Starch
cellulose/starch + SDS
cellulose/starch + SDS/DTAB

Instrument	Requested days	Allocated days	From	To
D11	3	1	10/04/2018	11/04/2018
D22	3	0		
D33	3	0		

Abstract:

Our group has been working on functionalised cellulose nanofibrils which form gels in aqueous formulations. Previously we have studied the gels formation upon addition of SDS, allowing gelation of the sample due to depletion flocculation between the SDS micelles and the anionic cellulose. Here, we aim at forming starch/cellulose gels and study their structural properties, and the effect of different kind of surfactant micelles to the gel structure. Selective deuteration of either the cellulose (via deuterated bacterial cellulose growth) or surfactant (SDS and DTAB) will allow us the study the gels structural properties and the micellar shapes in the mixtures.

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Details of experiment:

Experiment number: 9-12-531
Title: Formation of cellulose-starch gels and effect of surfactant
Instrument: D11 Local Contact: Ralf Schweins
Date of measurement: 10th of April 2018. 1 day allocated
Principal investigator: Prof. Karen Edler, University of Bath
Team: Dr Julien Schmitt, Dr Marcelo Alves da Silva, Vincenzo Calabrese

Objectives:

This proposal is part of an ongoing project focused on the formation of an interpenetrating starch-cellulose network to form gels with possible applications in personal care and agrochemicals, in collaboration with several universities (UEA, Bristol, Bath) and industrial partners (Croda, Unilever). Addition of soluble starch polymers to partially oxidized cellulose (OCNF, oxidized cellulose nanofibrils) suspensions creates gels with increased viscosities over single component suspensions. In this one day experiment, we aimed to study the effect of surfactant (sodium dodecylsulfate, SDS, dodecyltrimethylammonium bromide, DTAB) on the gelation properties of partially TEMPO-oxidized cellulose nanofibril (OCNF) suspensions, without and with soluble starch polymer. The goal was to study the possibility to highlight an element in the mixtures by selected deuteration; and probe new gel systems to help prepare future neutron experiments.

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Firstly, we have studied the diverse methods to produce deuterated cellulose nanofibrils: either via the production of deuterated bacterial cellulose, or by exchange of hydrogen atom within the nanofibrils by reaction with NaOD at high temperature, following a protocol proposed by Nishiyama et al.[1] The first method gives very low yield of bacterial cellulose, which is extremely sensitive to TEMPO oxidation, which does not allow recovery of sufficient material for further studies. The second method proved to modify the fibrils cross-section and increase fibril-fibril attraction as can be seen from the patterns in Fig 1. This material was therefore not taken forward further in this experiment but will be considered for future work.

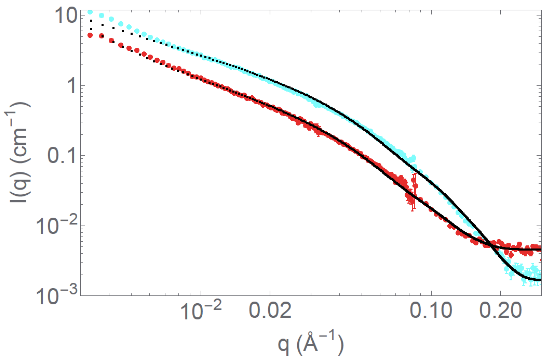

Figure 1: SANS patterns of hOCNF at 1wt% in D_2O (cyan) and dOCNF at 1wt% in D_2O (red). Signals were fitted using the model for rigid cylinders with an elliptical cross-section.

We then studied OCNF in presence of surfactant (SDS or DTAB). By contrast variation techniques (OCNF and hSDS in D_2O to probe everything, OCNF and dSDS in 50%D_2O to focus on SDS only, OCNF and dSDS in D_2O to focus only on OCNF), we showed that in OCNF-SDS mixtures, OCNF experience a fibril-fibril attraction, while SDS micelles observe a decrease of the volume fraction of interaction (modelled by a hard-sphere potential), compared to the signal of the isolated components. These results are consistent with a depletion-flocculation mechanism for the gelation in presence of SDS. With DTAB, OCNF experience an aggregation modelled by larger fibrils (Figure 2).

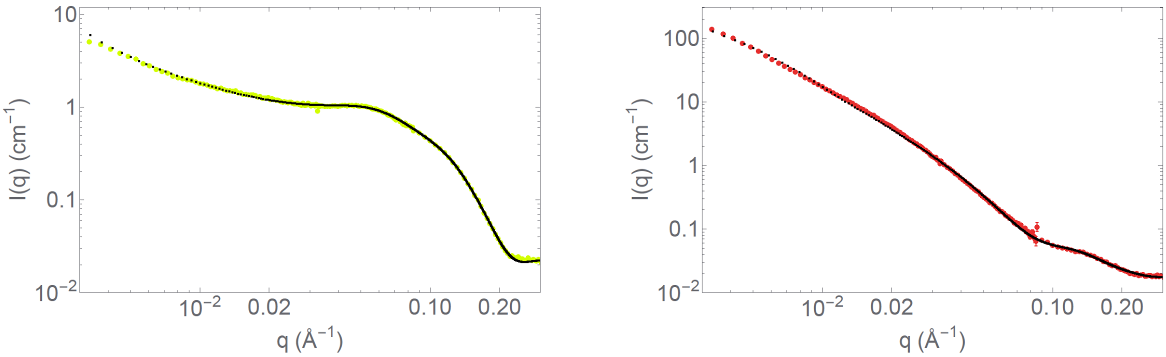

Figure 2: SANS patterns of OCNF at 1wt% in D_2O with (left) hSDS at 40 mM and (right) DTAB at 5mM. OCNF+SDS was fitted by the combination of attractive OCNF and SDS micelles in interactions. Other contrasts provided study of OCNF or SDS only. OCNF+DTAB was fitted with a signal from micelles plus large bundle formed by aggregating OCNF.

Preliminary tests of OCNF suspensions with mixtures of SDS and DTAB as the surfactant component were also conducted (molar ratio [SDS]/[DTAB]=80/20). Results showed, as for SDS, a combination of the signal from micelles and attractive OCNF. Micelles formed by mixtures of SDS and DTAB were found to be much more anisotropic than SDS micelles (aspect ratio of 5.3 for SDS/DTAB versus 1.7 for SDS at the same concentration of 40 mM of surfactant). Further studies of the effect of this variation on the rheology of the suspensions as well as further scattering studies are currently underway.

Another system that we probed was the modification of OCNF to graft onto the surface hydrophobic octyl-chains in order to modify its properties in solution (referred to as HM-OCNF, for hydrophobically-modified OCNF). We demonstrated that HM-OCNF scattering also could be fitted using nanorods with similar dimensions but more attractive interactions than the scattering from pure OCNF suspensions in water. Also, it was shown that, contrarily to OCNF, HM-OCNF does not gel in presence of alcohol, with little change in fibril-fibril interactions.

Finally, mixtures of different types of cellulose fibrils (OCNF or OBCNF for oxidised bacterial cellulose nanofibrils and CCNF for cationised cellulose nanofibrils) or mixtures of cellulose nanofibrils with cationised starch were studied, to enhance interactions using electrostatic attraction between the objects. Results of mixtures of different cellulose fibrils showed that opposite charges results in increased rheological properties only if the two types of fibrils present differences in their sizes (OBCNF being ten times longer and thicker than OCNF or CCNF). Small portion of cationised starch change drastically the rheological properties and the SANS pattern in OCNF dispersions. Data treatment is still underway, and this gives the first bricks for future studies on the addition of small charged polymers in OCNF suspensions.

Likely outcomes

The study of OCNF with SDS will be used in a publication that is currently in preparation. The characterisation of HM-OCNF will probably also be used in an upcoming paper. Finally, studies of mixtures of cellulose fibrils or OCNF and starch will be used as preliminary results for future beamtime applications.

References:

1. Nishiyama et al, Macromolecules 1999, 32, 2078-2081