Experimental report

13/10/2020

Proposal: EASY-477 **Council:** 4/2019

Title: Filler size effect in an attractive fibrillated network

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: Vincenzo CALABRESE

Experimental team:

Local contacts: Lionel PORCAR

Samples: (C6H10O5)n

Instrument	Requested days	Allocated days	From	To
D22	5	5	28/07/2019	29/07/2019

Abstract:

In this study we investigated the effect of the silica size (filler) on the mechanical and structural properties of an attractive fibrillated network composed by cellulose nanofibrils (CNF). Oscillatory rheology has been successfully employed to deconvolute mechanical properties arising from both network and filler as well as reconstruct structural information of the gel. Our rheological findings let us hypothesis that the presence of the smaller filler into the CNF network leave the network unaltered, whilst, the larger filler being able to strongly affect the structural properties of the network. These results were associated to the filler-to-mesh size ratio being < 1 and > 1 for the small and the large filler, respectively. Since reconstruction of structural information from rheological measurements is indirect, we would like to test our hypothesis using SANS, where the filler could be matched out (60 vol% D2O), whilst the CNF network still detectable (47 vol% D2O contract match point). Therefore we propose to measure the following samples in 60 wt% D2O.
i) 1 wt% CNF ii) 1 wt% CNF + 1 wt% and 2.5wt% of small and large filler iii) 60% D2O background.
For a total of 6 samples.

Introduction

The effect of the filler size on the structural and mechanical properties of an attractive fibrillated network composed of oxidised cellulose nanofibrils (OCNF) in water was investigated. Silica nanoparticles with different size populations were chosen as colloidal fillers. The focus of the SANS experiment was to highlight structural changes of the OCNF network upon addition of the fillers. For this, contrast matched SANS were performed at a specific H_2O/D_2O ratio to achieve a dominant scattering intensity rising from the OCNF network.

Experiment

To perform a satisfactory contrast match experiments, we begun with the estimation of the H_2O/D_2O ratio where the scattering contribution from the silica nanoparticles is minimal. Silica nanoparticles at an experimentally representative concentration (2.5 wt%) were dispersed in different H_2O/D_2O ratios. In Fig. 1 the scattering intensity ($I(q_o)$) at the lowest accessible scattering vector, q, are plotted as function of the D_2Ovol%. From the linear relationship between $\sqrt{I(q_o)}$ and $\%D_2O$ it was possible to estimate the point where $\sqrt{I(q_o)} \cong 0$, corresponding to *ca*. 60% D_2O.

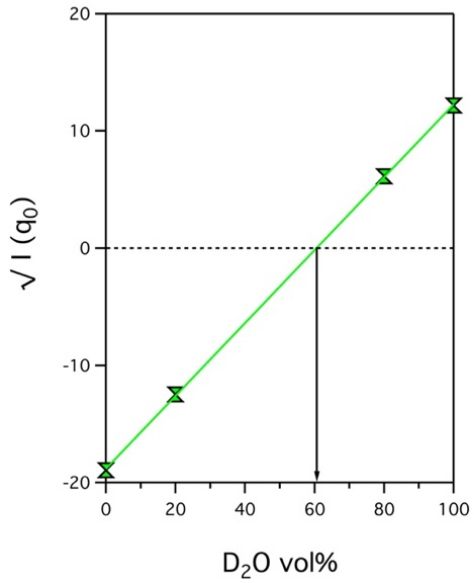

Fig. 1 Contrast match experiment performed for 2.5 wt% silica nanoparticles at different H_2O/D_2O ratios. A linear fit, indicated by the green line, was used to determine the point where $\sqrt{I(q_o)} \cong 0$.

The contrast match experiment was performed using 1 wt% OCNF (Fig. 2, in black) with 1 and 2.5 wt% silica nanoparticles with a mean dimension of 158 nm (SiNp158, in red) and 5 nm (SiNp5, in blue) at a D_2O concentration of 60vol%. The scattering patterns displayed that the OCNF structure is undisturbed by the presence of the fillers. As such, all the curves were satisfactorily fitted using a model of non-interacting flexible cylinders with an elliptical cross-section with constrained parameters of Kuhn length, major and minor radii, as for the 1 wt% OCNF.

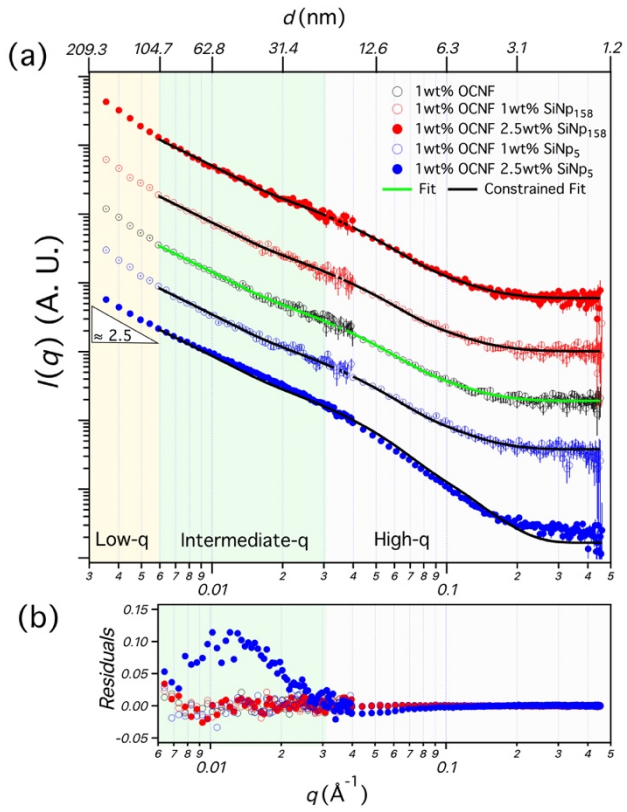

Fig. 2 (a) SANS patterns of the 1 wt% OCNF-based gels (in 100 mM NaCl). For all the samples, the continuous aqueous phase is composed of 60 vol% D2O and 40 vol% H2O. The green line describes the fitting from a model of non-interacting flexible cylinders with an elliptical cross-section. The black lines display the fitting for constrained values of Kuhn length, major and minor radii as found from the fitting of 1 wt% OCNF. The error bars are the standard error in the data points calculated during radial averaging of the initial 2D images. (b) Residual plot from the fits in (a).

Conclusion

The outcome of this experiment has been highly positive and resulted in a prompt publication in Soft Matter (RSC).[1] The contrast match experiment has been vital to understand the network structure at the nm-length scale and complementary to the rheological findings. Moreover, the data obtained from the D22 have been of high quality with a good signal to noise ratio.

Reference

[1] Vincenzo Calabrese, Marcelo A. da Silva, Lionel Porcar, Saffron J. Bryant, Kazi M. Zakir Hossain, Janet L. Scott, Karen J. Edler. Filler size effect in an attractive fibrillated network: a structural and rheological perspective. *Soft Matter*, **2020**, 16, 3303-3310.