Experimental report

22/09/2015

Proposal: **9-10-1392** **Council:** 4/2014

Title: SANS study of the reformation of an engine oil gel after shear

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Magnesium carbonate nanoparticles with magneisum alkyl salicylate sheath in dodecane

Instrument	Requested days	Allocated days	From	To
D33	2	0		
D22	2	0		
D11	2	1	15/10/2014	16/10/2014

Abstract:

We would like to observe the change in neutron scattering observed after applying shear stress to gel samples. Complete gelation of samples of dodecane containing an engine oil additive on the addition of water and acetic acid has been observed. After shear the recovery of structure in the gel has been measured using a rheometer; initially there is a period of rapid recovery of mechanical strength (indicated by increasing values of the elastic modulus, G'), which decays to a gradual recovery over time. This recovery is dependent on temperature. The additive is an overbased detergent: colloidal magnesium carbonate particles stabilised by a sheath of magnesium alkyl salicylate surfactant molecules. Using SANS we would like to further our understanding of the gel reformation, using isotopic contrast variation, comparing the scattering data with rheological data.

Experiment proposal number 9-10-1392

SANS study of the reformation of an engine oil gel after shear

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D11, Isabelle Grillo, 15-16/10/14

Introduction

Nanoparticles of metal carbonate are added to engine oil to neutralise acids. Surfactants are adsorbed to the surface of these particles during their preparation and are essential to ensuring stability, acting as a steric barrier to aggregation. Contamination of the lubricant with water and other polar molecules can negatively affect the stability and effectiveness of this class of additive.[1,2] Increased use of biodeisel is exacerbating this issue, making the study of these additives ever more important.

Gelling of dodecane solutions of an overbased detergent additive consisting of magnesium alkyl salicylate surfactant adsorbed to magnesium carbonate particles can occur on the addition of water. The time taken for the solutions to completely gel is dependent on many factors, including the additive concentration, volume of water added and the temperature. Rheology data and SANS experiments have found that the magnesium carbonate particles form a fractal network with a fractal dimension of 2.2. This suggests that the network is formed by reaction limited cluster aggregation,[3] which is thought to be due to some residual steric hindrance of particles approaching from remaining adsorbed surfactant.

It was hoped that study of the gels using SANS after shear would allow us to better understand both the liquid like state observed immediately on application of a high shear stress, and the mechanism for rebuilding strength which occurs over the following minutes to hours on cessation of shearing.

Materials and method

The overbased detergent samples studied were kindly provided by Infineum UK and were used without further purification. High purity n-dodecane was dried using molecular sieves and filtered through PTFE 0.45 µm syringe filters before use. Deuterated *n*-dodecane and water were purchased to prepare samples of different contrasts and were used without purification.

Gels were prepared at 3.5 wt% additive in dodecane before contamination with water at an oil solution:water ratio of 10:1 (the most studied system) one month before the experiment. Samples were prepared and stored at ILL to minimise shear disruption to the gels before loading into the rheometer for measurements.

The mechanical and neutron scattering properties of the gels were measured simultaneously, using an Anton Paar Physica rheometer installed on the beam line. A titanium cup and bob geometry were used, with the neutron beam passed through the centre of the cup and bob. Three detector positions were used to access a large Q range: 1 m, 8 m and 40 m. SasView software was used to fit the scattering data to known models.

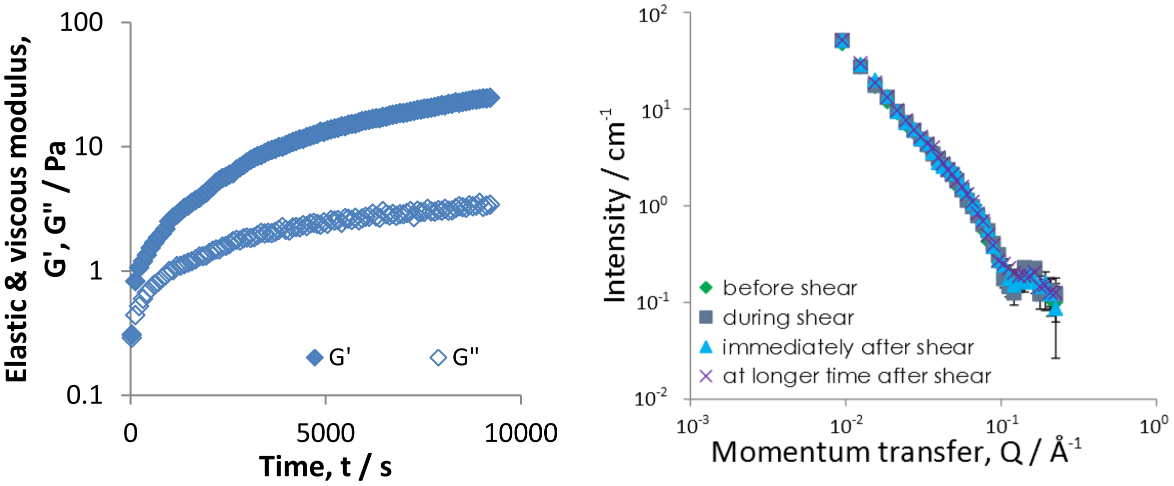

Figure 1. Left: Change in elastic and viscous modulus with time after shear. Right: Scattered intensity as a function of momentum transfer before, during and after shear for a gel sample.

Results and analysis

On application of a steady shear stress of 20 Pa there was a clear decrease in the viscosity of the sample, as expected. The recovery of the elastic and viscous moduli were followed using a single frequency oscillation test (Figure 1). However, no change in the scattering profiles of any of the different contrast gels was observed either on shearing or when the shearing was stopped.

This lack of change in the scattering pattern suggests that a vast difference in the mechanical properties of these systems can be observed with only a subtle change in the structure on the length scales being examined. Indeed, any change in the scattering must occur to lower Q than was measured on D11. Similar results have been reported for other gelled colloidal systems on shearing.[4]

It is thought that, on shearing, only a few links in the network are broken. Thus, the large fractal aggregates remain mostly intact, reflected in the lack of change in the SANS data. The slow reformation is due to the low volume fraction of particles in the system. A schematic of the proposed change in structure on shearing is shown in Figure 2.

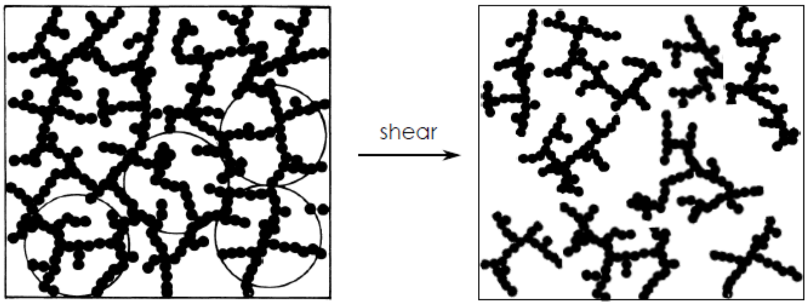

Figure 2. Schematic of the proposed change to structure of the fractal network on shearing, image adapted from reference 5.

References

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(2) Tavacoli, J.; Dowding, P.; Steytler D.; Barnes, D.; Routh, A. *Langmuir*, **2008**, *24*, 3807-3813.
(3) Sorensen, C. M. *Aerosol Sci. Technol.* **2001**, *35*, 648.
(4) Rueb, C.; Zukoski, C. *J. Rheol.,* **1997**, *41*, 197.
(5) Shih, W.; Shih, W.;Kim, S., Liu, J.; Aksay, I. *Phys. Rev. A*, **1990**, *42*, 4772-4779.