Experimental Report template

Proposal title: Rheological properties of lamellar and fibrillar hydrogels formed from microbial glycolipidsglycolipids		**Proposal number:** SC-4778
Beamline: BM26B	**Date(s) of experiment:** from: 13/04/2018 to: 16/04/2018	**Date of report:** 06/11/2018
Shifts: 9	**Local contact(s):** Daniel Hermida-Merino	*Date of submission:* 06/11/2018

Objective & expected results:

Lamellar hydrogels, discovered in 1996 by Safinya and composed of a DMPC (dimyristoyl phosphatidyl choline) Lα phase stabilized by less than 1 wt% of a polymer-grafted lipid and addressed as Lα,g (the g subscript stands for gel), were the first example of self-assembled lipids providing an elastic 2D soft material at low volume fractions. Since then, polymer-stabilized lipid phases have become the standard to obtain lamellar hydrogels, and it is only very recently that the possibility to prepare polymer-free lamellar hydrogels was reported. In the work by Niu et al., a mixture of hexadecyl- glyceryl maleate (HGM) with sodium dodecyl sulphonate (SDS) provide iridescent lamellar gels. Since then, surfactant mixtures or lipid/surfactants systems have also become a standard in the preparation of hydrogels. Both from a fundamental and technological point of view one could wander how to control the formation of lamellar hydrogels and whether there are ways to both simplify even further and add functionality to the development of lamellar hydrogels at high water content (> 90 wt%).

In a recent work, we have shown that a biobased (microbially-derived) glucolipid undergoes a reversible micelle-to-lamellar phase transition when going from basic to neutral pH (transition pH is in the vicinity of pH 7.8) at room temperature. The lamellae spontaneously form a lamellar hydrogel and in this run we characterize the rheological properties of this coupound, GC18:0, as a function of pH, probing the lamellar structure at the same time.

Results and conclusion

The structural analysis of a GC18:0 hydrogel (5 wt%) obtained through hydrolysis of GDL is performed by time-resolved rheo-SAXS experiments, performed at the BM26B beamline. Fig. 1a shows the G´, G´´ curve recorded during rheo-SAXS and the corresponding time-dependent pH profile. As expected, the viscoelastic properties can be divided into three regions: sharp increase of the moduli, lag-time and stabilization after G´> G´´. The corresponding SAXS patterns recorded before (t_0, pH 8.1) and after GDL addition (t_0 through t_{214}) show an evolution from a micellar solution (the broad hump at 0.7 nm^{-1} is due to micellar interactions) to a lamellar system, the latter characterized by a broad Bragg reflection below 0.1 nm^{-1}. A similar evolution of the SAXS data was recorded before on a more diluted GC18:0 system.

The analysis of the SAXS profiles was done through fitting the curves with a lamellar form factor and a Lorentzian peak. We could extract the first order Bragg peak position, q_0, the full width at half maximum, FWHM, related to the spatial correlation between the lamellar domains, and the thickness (T_h) and length (L) of, respective, the hydrophilic and hydrophobic layers. We find that all parameters oscillate during the sharp increase and lag time of the moduli, and in particular during the Tanδ< 1 (G´> G´´, below ~40 min) to Tanδ> 1 (G´< G´´, above ~40 min) transition. q_0 increases, then decreases and finally increases to a plateau (Fig. 1c), indicating that the repeating distance, d, shrinks after going through a maximum at ~60 min. T_h and L also oscillate in the same time domain (Fig. 1d) but the amplitude of the variation of d prevails over the

oscillation of the bilayer thickness ($2T_h$+L), quantified to few Ångstrom between 0 and 300 min. The evolution of d_w (d-$2T_h$-L) (Fig. 1d) clearly show that its increase between 50 min and 100 nm is significative (Δd~ 4 nm) and much more important than the oscillation of the bilayer thickness, although towards equilibrium d_w has an exponential decrease.

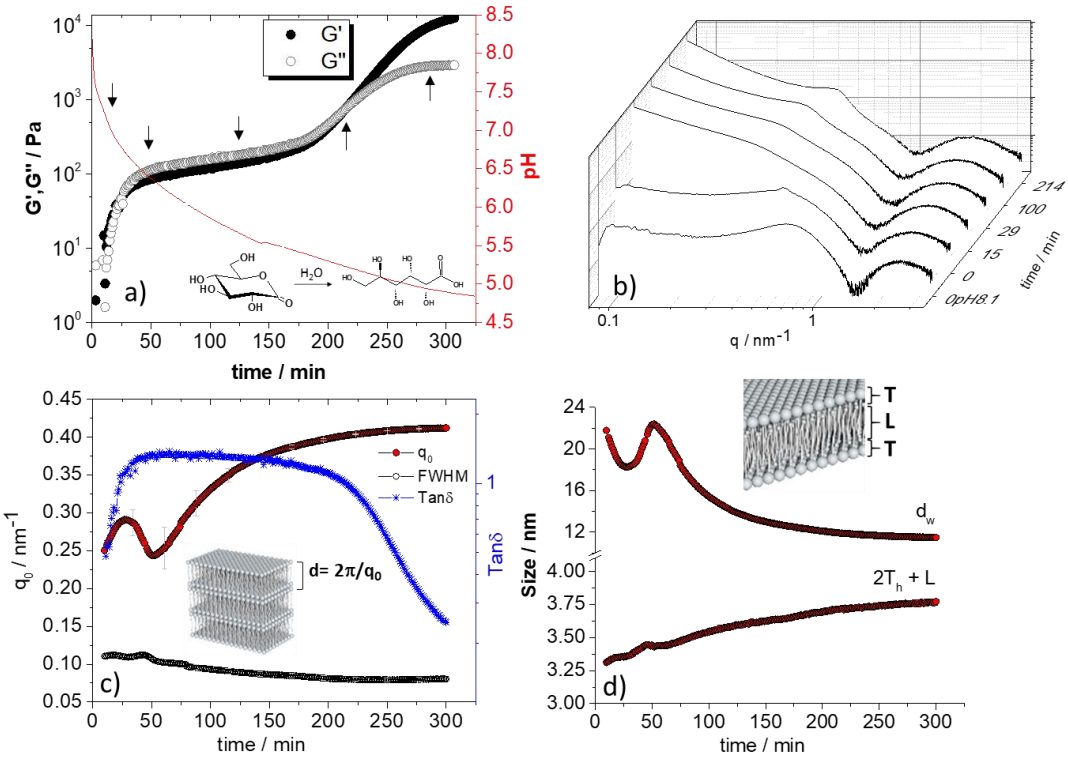

Figure 1 - a) Time-dependent evolution of G´ and G´´ (ω= 6.28 rad.s^{-1} and γ = 0.1 %) for a GC18:0 solution prepared at 5 wt% and initial pH= 8.1 and upon addition of 50 mM GDL. In red, the solution pH during GDL hydrolysis. These experiments are synchronized with SAXS acquisition at BM26B beamline. b) Typical SAXS profiles extracted at different times during the rheo-SAXS experiment shown in a). c-d) Time-dependent evolution of c) peak position q_0, full width at half maximum (FWHM), d) bilayer total thickness ($2T_h$+L) (T_h and L respectively being the thickness of the bilayer hydrophilic and hydrophobic regions) and water layer thickness ($d_w = 2\pi/q_0 - 2T_h + L$).

The experiments done on the BM26B beamline indeniably show that the hydrogel formation is associated to the formation of a swollen lamellar phase with water layer thickness contained between 10 nm and 15 nm after equilibration time if about 5h.
We were able to study the formation of the lamellar hydrogel under various conditions of temperature. Oscillatory and shear rheology SAXS experiments could also be performed.

Data acquisition and treatment

Experiments coupling rheology and SAXS have been performed using a beam energy of 12.65 KeV and a sample-to-detector distance of 3.23 m, where silver behenate is used as q-calibration standard. A MCR 501 rheometer (Anton Paar, Graz, Austria) equipped with a Couette polycarbonate cell (gap 1 mm) was coupled to the beamline and controlled through an external computer in the experimental hutch using the Rheoplus/32 V3.62 software. A radial scattering configuration, where the beam passes the sample along the velocity gradient direction, was used. The rheology and SAXS acquisitions are synchronized manually with an estimated time error of less than 5 s. Due to standard security procedures, the first rheo-SAXS experimental point is systematically acquired with a delay of about 3-4 minutes. SAXS signal acquisition and processing is the same as above. Data are not scaled to absolute intensity. The signal of the Pilatus 1M 2D detector (172 x 172 µm pixel size), used to record the data, is integrated azimuthally with PyFAI to obtain the I(q) vs. q spectrum ($q = {4\pi \sin\theta}/{\lambda}$, where 2θ is the scattering angle) after masking systematically wrong pixels and the beam stop shadow. Silver behenate (dref = 58.38 Å) is used as SAXS standard to calibrate the q-scale. Data are not scaled

to absolute intensity.

Justification and comments about the use of beam time:

The use of the beamline associated to the rheometer was well-adapted to the kinetics of lamellar hydrogel formation for the GC18:0 compound. The acquisition time was sufficient to acquire high-quality data, the rheometer was well-aligned and support from the local contact was very high.

Problems during beamtime:

We did not experience any trouble during the beamtime