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The goal of my PhD is to study colloidal particle dispersion in liquid crystals (LCs) under flow. After characterizing the colloids in nematic LCs without application of shear stress, the next step was to characterize the system under flow for a range of concentrations. Preliminary rheoimaging measurements showed that interesting structures [1], such as cylindrical structures of colloids, appeared at intermediate shear rates, which then broke up to form dispersed clusters at high shear rates.

Taking this further, I have performed oscillatory rheology on an SDS-Decanol based lyotropic liquid crystal system [2]. There are two main reasons for choosing this as our model system. Firstly, it is a similar system to that used by our partner company, The Mentholatum Company and secondly, a lot is known about how colloids behave in thermotropic nematic LCs but very little is known about how they behave in lyotropic nematic LCs. It will be interesting to study this system and compare the results with thermotropic system. I explored two phases of the system;

- (a) the nematic calamatic phase (NC1) in which the concentration of Sodium Dodecyl Sulphate (SDS) is 24.8%, Decanol is 4.8% and the rest 70.4% is water and,
- (b) the isotropic phase in which the concentration of SDS is 23%, Decanol is 2% and 75% is water.

The PMMA-PHSA (poly (methyl methacrylate) stabilized with hairs of poly (12-hydroxy stearic acid)) particles of (1.131±0.025) µm in diameter are dispersed in these two phases. After comparing the rheology results for isotropic and NC1 phase of the SDS-Decanol system, I performed rheometry measurements with anionic polystyrene-block-poly (N-vinyl-2-pyrrolidone) PS-b-PVP (1.253±0.034) µm dispersed in NC1 LCs. The surface charge of anionic PS-b-PVP is calculated from the zeta potential measurement using Malvern Zetasizer Nano Z. The surface charge is then calculated using Gouy-Chapman model [3] and is found to be -  $(0.3128 \pm 0.0008) \frac{C}{m^2}$ . Lastly, I will discuss the microfluidics set up used to image colloids and LCs mixture under flow using fast confocal microscope.

From Figure 1a, it can be seen that as the  $\phi$ % of PMMA in NC1 LCs (black) increases the value of G' and G'' also increases. But there are two regimes, for  $\phi \le 20$  % the viscous property of the sample dominates i.e. G''> G' and the sample behaves more fluid like, whereas for  $\phi >$ 20 % the value of G' > G'' i.e. the material begins to flow after a certain critical value of strain. Figure 2b, shows the director configuration of NC1 LCs around the PMMA particles (quadrupolar symmetry). It was shown in my first year report, that when PMMA particles are dispersed in nematic LCs their directors tend to align perpendicular to the colloid surface showing quadrupole defect. For dilute emulsions,  $\phi \le 20$  % the population of these quadrupolar defects or isolated Saturn rings are higher. This is because independent Saturn rings do not require disclination lines to connect them and without disclination lines there is no line tension. But for a more concentrated suspension these isolated Saturn ring defects become entangled. The rheology plot in figure 1c, suggests that the maximum storage modulus (G') for PMMA in NC1 LCs increases linearly up to  $\phi = 45\%$  (linear fit - red). The inter particle distance at  $\phi = 50\%$  is **1.086** considering random close packing fraction at  $\phi = 64\%$ . The distance between disclination lines between two entangled Saturn ring defects is found to be 1.1 [5] which is greater than the inter-particle distance at  $\phi = 50\%$ . The value of  $\phi$  for which the inter-particle distance is 1.1 is at  $\phi = 48\%$ . So for  $\phi > 48\%$ , we presume particles start forming aggregates with particle-particle contacts.



Figure 1. (a) Graph showing maximum value of storage modulus (solid symbol) and loss modulus (open symbol) for different volume fraction  $\varphi = (5 - 50)$  % of PMMA in NC1 LCs mixture (black) and PMMA particles in isotropic phase of SDS-Decanol system (blue). (b) Graph showing maximum value of storage (solid symbol) and loss modulus (open symbol) for different volume fraction  $\varphi = (5 - 50)$  % of PMMA in NC1 LCs mixture (black) and PS-b-PVP particles in NC1 LCs mixture (green). (c) Graph showing linear fit on maximum storage modulus for different volume fraction  $\varphi = (5 - 50)$  % of PMMA particles dispersed in NC1 LCs mixture (black) and PMMA particles in isotropic phase of SDS-Decanol system (blue). (d) Graph showing linear fit on maximum storage modulus for different volume fraction  $\varphi = (5 - 50)$  % of PMMA in NC1 LCs mixture (black) and PS-b-PVP particles in NC1 LCs (green).

For the second sample of PMMA particles in isotropic phase (blue), the value of G' and G'' also increases with  $\phi$  with G'' always greater than G' implying that samples are always fluid like as they are in isotropic liquid. But it can be seen that the magnitude of G'(PMMA in NC1) is 3

orders of magnitude greater than that of G'(PMMA in iso) and G'' (PMMA in NC1) is 2 orders of magnitude greater than that of G'' (PMMA in iso).



Figure 2. a. Schematic of director configuration of PMMA particles around NC1 LCs, b. Schematic of director configuration of PS-b-PVP particles around NC1 LCs.

After comparing the results of PMMA particles in isotropic liquid and in NC1 LCs, we compared the rheological behavior of two different particles - PMMA and PS-b-PVP dispersed in NC1 LCs. Figure 1b, shows that the value of G' and G'' for PS-b-PVP in NC1 LCs also increases with  $\phi$  with G'' always greater than G'. But it can be seen that the G'(PMMA) is one order of magnitude greater than G'(PS) and the value of G'' (PMMA) is also one order of magnitude greater than G'(PS). Thus concluding that the surface charge on PS-b-PVP is affecting the structure of the system hence its rheological behavior. We argue that there is different alignment around PMMA (normal) and styrene (surrounded by liquid layer). This is confirmed by the fact that imaging showed clusters in the PMMA case (similar to that in thermotropic system) and crystallites in the polystyrene case. Clusters lead to gel formation at lower volume fraction and therefore higher G'. Chain formation or aggregation would not lead to this. I have also sketched the director configuration for polystyrene in NC1 LCs (Figure 2b).



Figure 3. (a) Mean square displacement (msd) curve for PMMA in water (blue), PMMA in NC1 LCs (black) and PS-b-PVP in NC1 LCs (green). (b) Linear fitted msd curve for PMMA in NC1 LCs (black) and PS-b-PVP in NC1 LCs (green).

Using the microfluidics set-up, I have imaged the above three systems;

(a) PMMA in water (isotropic liquid)  $\phi = (1 \%)$ ,

- (b) PMMA in NC1 LCs phase  $\phi$  = (0.1 %) and
- (c) PS-b-PVP in NC1 LCs phase  $\phi = (0.1 \%)$

The pressure pump was used to let sample flow through the channel slides, imaging was done using fast confocal microscope at 14 frames/s. The flow direction of the sample was considered to be in y direction. Particle tracking was done using standard tracking algorithm developed by Eric Weeks group [4].

Mean square displacement (msd) ( $\Delta X^2$ ) in x direction was calculated for all the three samples and the plots are shown in figure 3. Sample (a) with PMMA in water will show Brownian motion in x direction whereas for samples (b) and (c), the elastic interactions between colloids and LCs may cause behavior that deviates from, or restrains, Brownian motion. From Figure 3a, it can be seen that the ( $\Delta X^2$ ) for PMMA in water is greater than that in NC1 LCs system. From Brownian motion equation in 2D, we get a relation between msd ( $\Delta X^2$ ) and lag time ( $\delta t$ ) is given by  $\Delta X^2 = 4.D.\delta t$ . After linear fitting the curve of PMMA in isotropic phase, we get, y = 0.2058 + 0.0757x, which implies 4D = 0.0757, D= 0.019, D is the diffusion coefficient. From D we can calculate the viscosity of the system using,  $D = \frac{k_BT}{3\pi\eta a'}$ , where k is the Boltzmann constant, T is absolute temperature in Kelvin,  $\eta$  is the viscosity of the system and a is the radius of the particles.

The value of  $\eta$  (PMMA in water) was found to be **(0.0184 ± 0.0002)** Pa.s. The ratio of  $\eta$  (PMMA in water) and  $\eta$  (water) is 23. This increase in viscosity as compared to water can be attributed to the sedimentation of particles in the channel leading to increase in their concentration. The concentration calculated from the image is found to 16 % by vol fraction. Using the same method I calculated the value of  $\eta$  (PMMA in NC1) and  $\eta$  (PS in NC1). Figure 3b shows the linearly fitted plot for both the cases, from which the value of  $\eta$  (PMMA in NC1) is **(0.261 ±0.005)** Pa.s and  $\eta$  (PS in NC1) is **(0.337 ± 0.007)** Pa.s. The value of viscosity of NC1 LCs found from our rheology measurement is  $\eta$  (NC1) = **(0.24 ±0.03)** Pa.s, it matches well with the literature value of  $\eta$  (NC1) = **0.27 Pa.s** [1].

# **Future Work**

The microfluidics work has just begun, and we have identified a few variety of flow channels best suited for our experiments. We will be carrying out more detailed measurements with charged and uncharged colloids in nematic phase of LCs to explore whether elastic interactions affect the flow behaviour. After characterizing the flow behaviour of colloids in lyotropic nematic LCs, next step would be to characterize lamellar phase under flow as it is similar to the system being used in our partner company, The Mentholatum Company. I will also investigate imaging of colloid and LC mixtures for various concentrations starting from a dilute suspension  $\phi = 0.1$  % up to 20 %. The flow rate will also be varied from flow velocity **v** = 0 µm/s, 10 µm/s and 100 µm/s. This will give us an insight of how the micro-structure changes with the flow rate. We will compare the channel flow experiments results with our in house simulation of colloids and LCs done by Oliver Henrich.

### **References:**

1. T.A.Wood, A Self-Quenched Defect Glass in a Colloid-Nematic Liquid Crystal Composite, Science Vol. 334, Issue 6052, 2011, pp 79-83.

- 2. T.Thiele, Rheology and nuclear magnetic resonance measurements under shear of sodium Dodecyl sulfate/decanol/water nematics. Journal of Rheology 45, 29, 2001.
- 3. https://www.chem.uci.edu/~ardo/echem/UCI-CHEM248-2017W\_lecture14.pdf.
- 4. http://www.physics.emory.edu/faculty/weeks//idl/
- 5. T. Araki, Colloidal Aggregation in a Nematic Liquid Crystal: Topological Arrest of Particles by a Single-Stroke Disclination Line, PRL 97, 127801, 2006.

# **Conference and Schools:**

- I have attended a joint conference of the British Liquid Crystal Society (BLCS) and German Liquid Crystal Society (DFKG), held from 21-23 March 2016 at Edinburgh.
- I gave a presentation on the behaviour of colloidal dispersion in the lyotropic liquid crystal at an International Conference on Soft Matter (ICSM 2016) held from 11 17 Dec 2016 at Jaipur, India. Since this is an industry inspired PhD.
- I also gave a presentation on different kinds of defects induced by spherical particles in nematic LC at the Mentholatum Company during our annual visit. The presentation was based on how surface alignment changes the behaviour of colloids in the nematic liquid crystal.
- I have presented a poster at Advanced School in Soft Condensed Matter, held in Durham University from 9-12 April 2017.