	Experiment title: Ultra Small-Angle X-ray Scattering Study of the Structural Changes of Flowing Conductive Suspensions (Electrofluids) under Shear Deformation	**Experiment number**: sc5382
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Shifts: 9	**Local contact(s)**: William Chevremont	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Lola González-García*, INM – Leibniz-institute for new Materials, Saarbrücken, Germany

Dominik Schmidt*, INM – Leibniz-institute for new Materials, Saarbrücken, Germany

Srishti Arora*, INM – Leibniz-institute for new Materials, Saarbrücken, Germany

Bart-Jan Niebuur*, INM – Leibniz-institute for new Materials, Saarbrücken, Germany
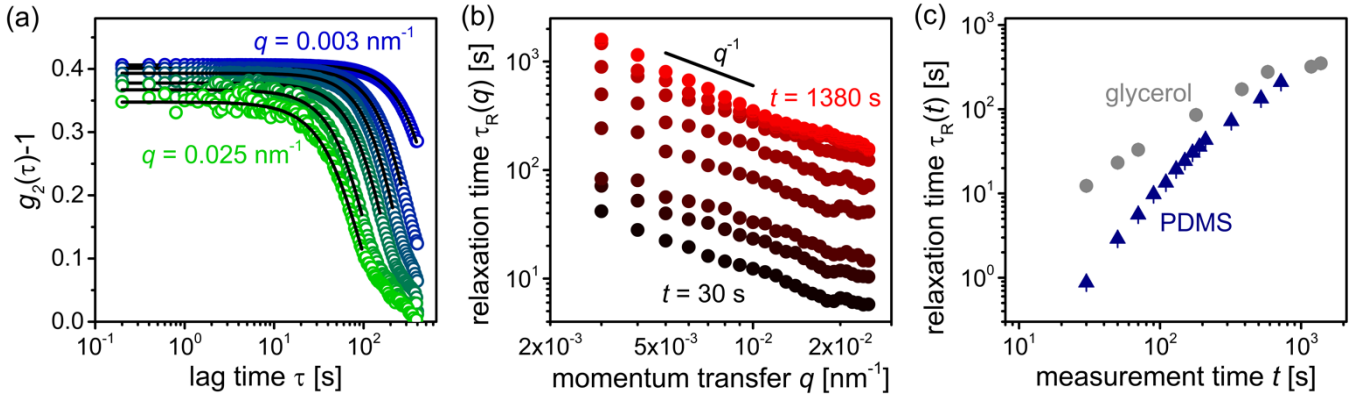
Report:

Soft electrical devices must contain materials that maintain their electrical conductivity under large mechanical strains. A promising approach is using Electrofluids: highly concentrated suspensions of conductive particles that form transient 3D networks. Both their mechanical and electrical properties depend strongly on the network structure, determined by particle-solvent interactions. Understanding the relationship between filler network structure and material properties would help in the design of soft electrical devices based on Electrofluids for targeted applications. Here, we have employed X-ray photocorrelation spectroscopy (XPCS) to explore processes involved in the network recovery after its deformation on samples containing Carbon Black (CB) in two different liquid matrices (polar glycerol and non-polar PDMS).

Electrofluids containing 6 vol% CB in glycerol and in PDMS underwent a rotation shear at 10 s^{-1} for 2 min, after which XPCS was measured to follow the recovery of the CB network structure over time. XPCS provides access to the dynamic structure factor $f(q,\tau)$ via the intensity autocorrelation function $g_2(q,\tau)$ as

$g_2(q,\tau) - 1 = A[f(q,\tau)]^2$ where A is the Siegert constant. Figure 1(a) shows the intensity autocorrelation functions, g_2-1, of 6 vol% CB in glycerol obtained after 580 s after deformation as an example. In all cases, $f(q,\tau)$ was modelled using a compressed exponential function given by $f(q,\tau) = \exp[-(\tau/\tau_R)^\beta]$, with τ_R being the relaxation time related to the nanoparticle dynamics. Compression exponents, β, of 1.5-2.0 were obtained. In all the cases, τ_R follows a q^{-1} dependency, as depicted in Figure 1(b) exemplarily, indicating a spatially restricted motion. These results are in good agreement with what observed in the literature for other concentrated colloidal system and colloidal gels. In these cases, both observations have been attributed to the build-up of internal stresses due to jamming of particles in an anisotropic force field [1], i.e., their mobility is reduced due to crowding [2]. The following ballistic motion of the particles leads to the observed properties of $f(q,\tau)$.
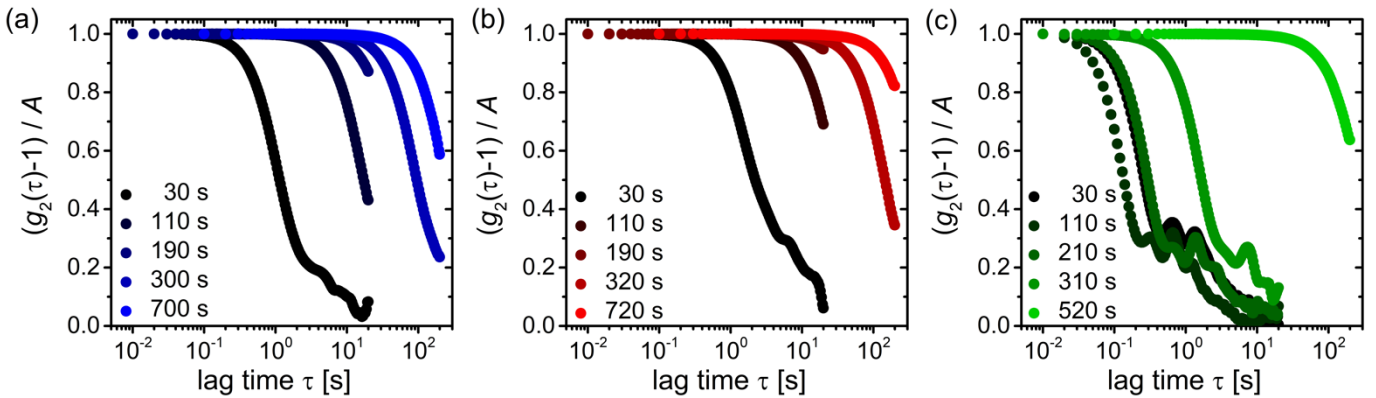
The picture that emerges is the following. During shear, the CB network is disrupted, meaning that CB particles have more freedom to move, which also fits to the strong shear thinning behavior observed for these Electrofluids. As soon as the applied shear stops, the CB particles interact to each other rebuilding the 3D network. As soon as they come closer, a dynamic jamming takes place and the diffusion of CB is strongly reduced. The anisotropic nature of the applied shear leads to a ballistic motion. Over time, the internal stresses relax, as is evident from the increasing τ_R over time shown in Figure 1(c) for 6 vol% CB in both glycerol and PDMS. The comparison of Electrofluids based on polar (glycerol) and non-polar (PDMS) solvents (Figure 1(c)) revealed an effect of the solvent on dynamic jamming of CB: for glycerol, τ_R is generally larger than for PDMS, meaning that less stress is created internally. This may be explained by the differences in interaction strength.

The weaker interaction of CB with glycerol leads to easier rearrangement of the network and, therefore, weaker internal stresses.

Figure 1: (a) Intensity autocorrelation functions $g_2(\tau)$-1 of 6 vol% CB in glycerol at 580 s after network deformation. The colors indicate different q-values, as indicated in the graph. Black lines: fits as described in the text. (b) Relaxation times τ_R in dependence on momentum transfer q at different times after network deformation, as indicated in the graph. (c) τ_R at 0.01 nm^{-1} in dependence on measurement time t of CB in glycerol (grey spheres) and in PDMS (dark blue arrows).

Furthermore, the influence of shear frequency has been investigated. Figure 2 exemplarily shows normalized intensity autocorrelation functions $(g_2(\tau)$-1$)/A$ of 6 vol% CB in PDMS obtained during recovery after rotational shear at 1, 10, and 100 s^{-1} for 2 min. In all cases, the autocorrelation functions show a decay at lag times increasing with time, which implies a significant slow down of the CB dynamics. After rotation shear at 1 and 10 s^{-1}, an equilibrium is approached after ~700 s. It can be concluded that the time scales involved in forming the CB network are similar in these two cases. The situation is qualitatively different after shear at 100 s^{-1}. While after rotation shear at 1 and 10 s^{-1}, the curves show only a single decay, at 100 s^{-1}, an oscillatory behaviour of g_2-1 is visible, which is a strong indication for unidirectional motion of the sample [3]. Therefore, the dynamics are dominated by flow of the sample, presumably in shear direction. After ~500 s, the oscillations have disappeared, as is also evident from autocorrelation functions obtained at larger q-values (not shown here). At this time, flow is expected to have terminated, and the rearrangement of CB follows the processes as described above.

Figure 2: Normalized intensity autocorrelation functions $(g_2(\tau)$-1$)/A$ of 6 vol% CB in PDMS at $q = 0.003$ nm^{-1} after rotational shear for 2 min at 1 s^{-1} (a), 10 s^{-1} (b), and 100 s^{-1} at times as indicated in the graphs.

Future analysis of the data will focus on the direction dependency of the CB network recovery (parallel vs. perpendicular to shear direction) and the kinetics of network formation from ultra small-angle X-ray scattering curves.

[1] L. Cipelletti, L. Ramos, S. Manley, E. Pitard, D. A. Weitz, E. E. Pashkovski and M. Johansson. *Faraday Discuss.*, 2003, **123**, 237-251.
[2] D. Bi, J. Zhang, B. Chakraborty, R. P. Behringer. *Nature*, 2011, **480**, 355-358.
[3] J. Möller, T. Narayanan. *Phys. Rev. Lett.* 2017, **118**, 198001.