

	Experiment title: Investigation of hierarchical structure of dispersion of carbon nanotubes in a solution of flexible-chain polymers under shear flow	Experiment number: SC-4482
Beamline: ID02	Date of experiment: from: 7 July 2017 to: 8 July 2017	Date of report: September 10, 2016
Shifts: 6	Local contact(s): Mariani Alessandro	<i>Received at ESRF:</i>
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Experiments with polyacrylonitrile (PAN) – carbon nanotubes (CNT) – DMSO systems

Finalizing the studies started in scope of the previous experiment (SC4167), we measured the scattering from solutions of PAN in DMSO and the dispersions of CNT on their basis. We observed that the scattering profiles from the PAN solutions were independent of the polymer molecular weight (80 to 150 kDa) or the shear rate (0 to 300 s⁻¹).

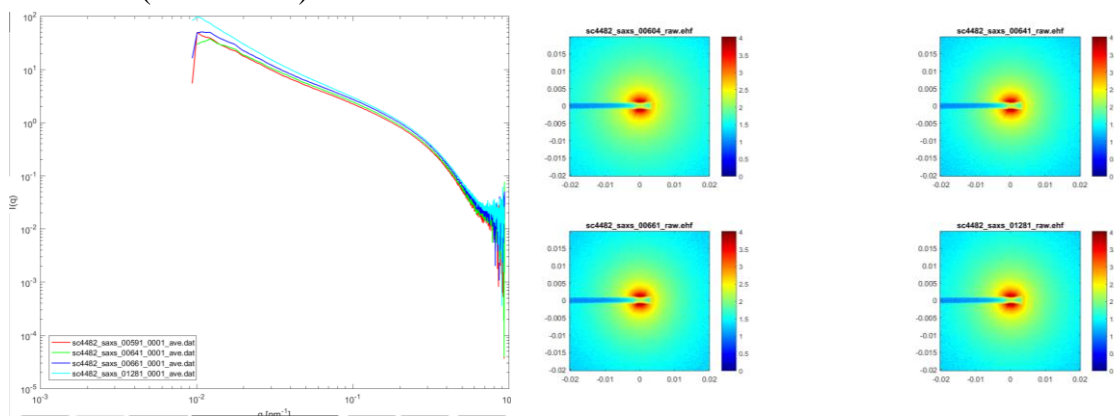


Fig. 1. SAXS data of CNT–PAN–DMSO dispersion (10 wt% PAN, 4 mg/mL CNT, shear rate 0–300 s⁻¹).

Shear of a CNT–PAN–DMSO dispersion led to slight increase in the scattering intensity. As an example, Fig. 1, shows the SAXS data for the CNT-filled system containing 10 wt% of PAN and 4 mg/mL of CNT (scattering from DMSO was subtracted). Yet, the result cannot be unambiguously attributed to a structural change of the filler in the dispersion, since the 2D scattering profiles did not mark any significant orientation of the scattering particles (Fig 1, *right*). The data quality was likely strongly worsened by the scattering from the solvent (DMSO); therefore, we concentrated our efforts on the investigation of aqueous dispersions.

Experiments with poly-N-vinylpyrrolidone (PVP) – carbon nanotubes (CNT) – water systems

The integrated scattering curves (Fig. 2, *left*) for the CNT-filled solution of PVP (360 kDa, 15 wt%) in water were slightly different depending on the shear rate (0–500 s⁻¹), especially at the low q range, which can mark the aggregation-deaggregation processes. However, the shape of the 2D scattering profiles remained the same independently of the shear rate. Hence, we conclude that no prominent orientation of the CNTs could be observed in the applied measuring geometry. Probably, the orientation would be observed in the tangential

position of the beam with respect to the cell, yet due to the limited experiment duration we could only measure the system in the radial position.

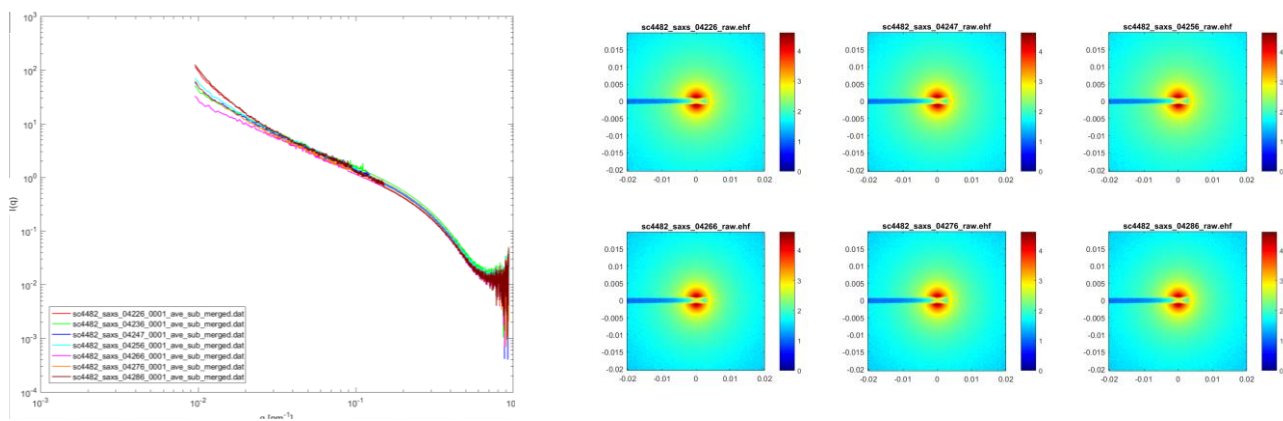


Fig. 2. SAXS data of CNT–PVP–water dispersion (15 wt% PVP360, 4 mg/mL CNT, shear rate 0–500 s⁻¹).

Experiments with poly-N-vinylpyrrolidone (PVP) – graphene (AO3) – water systems

We performed similar rheo-SAXS experiments with dispersions containing graphene oxide (AO3 grade) nanoparticles. The sample data for one of the dispersions (15 wt% of PVP360 and 1 mg/mL of AO3) are shown in Fig. 3. It should be noted that despite lower concentration than that of CNT in a similar system (cf. Fig. 2), the scattering from the AO3 dispersion was about an order of magnitude stronger. That masked the effects of scattering from the solvent and the polymer and gave more reliable data.

We observed significant asymmetry of the 2D scattering profiles depending on the shear rate (Fig. 3, *right*). In detail, the initially round profile (0–0.1 s⁻¹ shear rate, top-left picture) became stretched along the vertical axis at some point (1 s⁻¹, top-middle picture), and then turned stretched along the horizontal axis (100–500 s⁻¹, bottom row). The variation of the scattering intensity followed the 2D profile shape: stretching along the vertical axis led to the increase in the integrated scattering intensity, and vice versa. It should be noted that the structural changes were completely reversible: both the integrated intensity and the 2D profile shape returned to the initial state within 20–30 min after the shear was stopped.

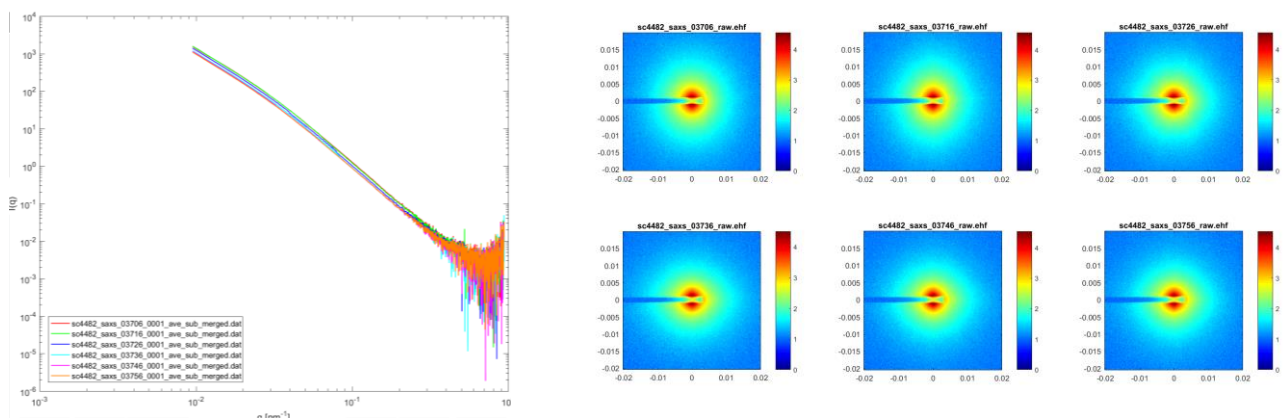


Fig. 3. SAXS data of AO3–PVP–water dispersion (15 wt% PVP360, 1 mg/mL AO3, shear rate 0–500 s⁻¹).

It should be noted that the behavior of the AO3 dispersions was different depending on the molecular weight of the PVP in the solution. This will be discussed in detail in the paper that is under preparation now. Further processing of the scattering data is currently in progress.

Major conclusions

- Study of the dispersions in DMSO was strongly limited by the scattering from the solvent. We conclude that such measurements are hardly possible at the so low concentration of the filler.
- CNT–PVP–water dispersion revealed slight variation in the integrated scattering intensity depending on the shear rate. Analysis of the 2D profile showed no orientation of the filler particles.
- AO3–PVP– water dispersions revealed shear-induced reversible orientation of the filler particles marked in both the integrated profiles and in 2D images. On top of the shear rate, the orientation behavior was found dependent on the concentration of the filler and molecular weight of PVP in the solution.