ESRF	**Experiment title:** Large scale dynamics in nanocomposites during and after tensile strain cycles: Towards a microscopic approach of the Mullins effect?	**Experiment number:** SC-4859
Beamline: ID02	**Date of experiment:** from: 19/10/2018 to: 22/10/2018	**Date of report:** 09/09/2021
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Report: The general objective of our experiment was to investigate the filler dynamics during tensile stress relaxation of silica-SBR nanocomposites. The present experiment was a follow-up of a preceding USA-XPCS experiment at ID02 (SC4726, 23-26 Feb 2018).

The scientific background of our studies is to investigate and provide microscopic understanding for the striking mechanical behavior of polymer nanocomposites. There are several strong effects, in particular the Payne (low deformation) and the Mullins effect (large deformation), and their combination leads to complex material properties. The precise nature of the microscopic mechanisms involved in these macroscopic properties are still under debate. In these experiments, we have focused on the Mullins strain softening which is measured in cycles of stretching experiments. It results in weaker stress after a first elongation-retraction cycle. Structural rearrangements of nanoparticles and rupture of the filler network are usually invoked to explain this effect but no microscopic evidence exists. Our aim was thus to access the multiscale (and thus q-dependent, unlike DWS) dynamics in mechanically solicited nanocomposites.

Simplified industrial nanocomposites relevant for the car tire industry, made of Styrene-Butadiene Rubber (SBR) filled with strongly aggregated industrial silica (Si) nanoparticles (R=9 nm) have been studied [1]. Nanocomposite samples were chosen above the percolation threshold (ca. 12%v) such that samples possess a filler network which can then be probed (and eventually broken) by mechanical strain. Several SBR/silica nanocomposite samples with filler volume fraction of ca. 20%v were investigated. Technically, we used the ID02 beamline with an X-ray energy of 12.46 keV. The sample to detector distance was 31 m. Our own strain controlled stretching machine equipped with a stress sensor was installed on the beamline, allowing us to perform oscillatory uni-axial strain experiments simultaneously with SAXS/XPCS.

The static structure of our samples had to be characterized first. SAXS pattern of typical samples displays aggregates with a size of R_{agg} = 30 nm [2] and a percolated network at larger scale, see Figure 1 for illustration. We have developed experiments to study the dynamics of opaque samples using Diffusing Wave Spectroscopy (DWS, a dynamic light scattering method for optically turbid samples) combined with uniaxial tensile stretching

[3]. The length-scale range accessible by DWS ranges from 10 nm to 200 nm and experiments probe the dynamics of individual nanoparticles. However, a percolated network of particles is formed in our nanocomposite samples and the study of the dynamics at larger scales is of great interest and complementary to the DWS analysis, which does not possess q-resolution.

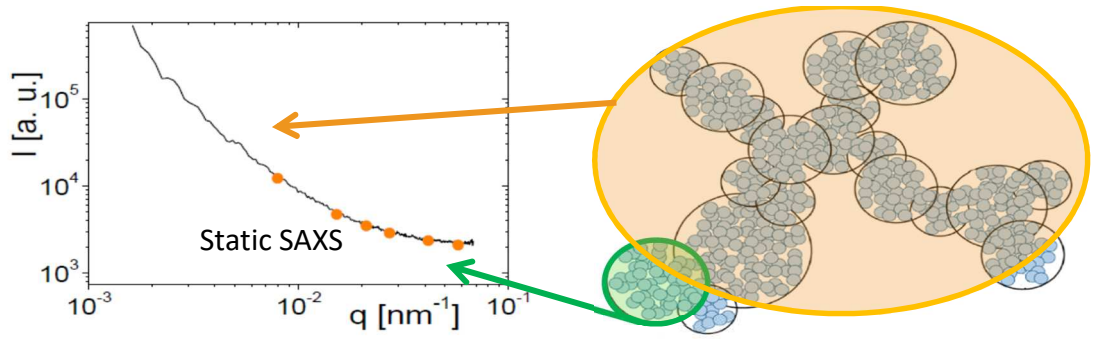

Figure 1: (left) SAXS isotropically averaged intensity for a typical SBR-silica simplified industrial nanocomposite. Orange dots indicate dynamic measurements. (right) Schematic view of multi-scale aggregation in theses samples.

As we aimed at the mechanical behavior (Mullins effect), it is shown below that the subsequent stress-strain isotherm superimposes during the stretching phase (Figure 2, left) for the pure matrix, whereas in presence of NPs (PNCs), a softening effect sets in. This is the kind of deformation studied during our XPCS experiments.

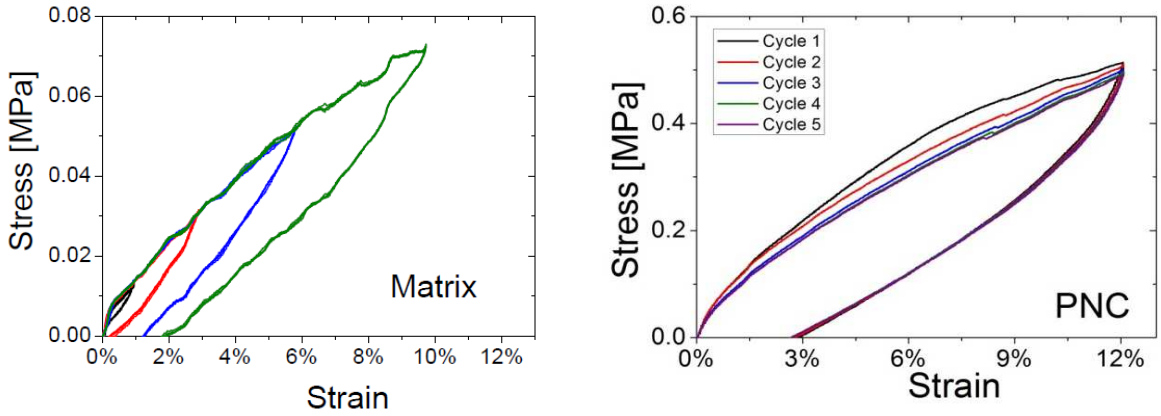

Figure 2: (left) Pure matrix (without NPs) showing no Mullins softening, (right) In PNC (matrix with NPs), softening is observed after different cycles.

The XPCS experiments were performed on the multispeckle UltraSmall-Angle X-ray Photon Correlation Spectroscopy (USA-XPCS) set up [4] to measure the dynamics of silica nanoparticles and aggregates in SBR nanocomposites during and after tensile stress. The corresponding echo measurements are illustrated below, giving access to the change in dynamics after repeated deformation. The length- and time-scale characteristics of the set-up, 2.10^{-3} nm^{-1} < q < 7.10^{-2} nm^{-1} and 10^{-4} < t < 10^{3} s, were chosen to follow the dynamics of supramolecular structures such as percolated silica aggregates in elastomer nanocomposites. The sample dynamics has been measured during and after tensile stress for different tensile elongations to cover elastic and plastic regimes, see Figure 2 for illustration of the mechanical behavior. Correlation functions were described by the following formalism giving access to the decay of the correlations, and to its translation in mean-square-displacement of nanoparticles:

$$g_2(t, \tau, q) - 1 = \frac{\langle I_p(t,q) I_p(t+\tau,q) \rangle_p}{\langle I_p(t,q) \rangle_p \langle I_p(t+\tau,q) \rangle_p} - 1$$

$$g_2(t, \tau, q) - 1 = b \exp\left(\frac{-q^2 \langle \Delta r^2 \rangle}{3}\right)$$

A typical result is shown in Figure 3 for the mean displacement deduced from the decay of the correlation functions:

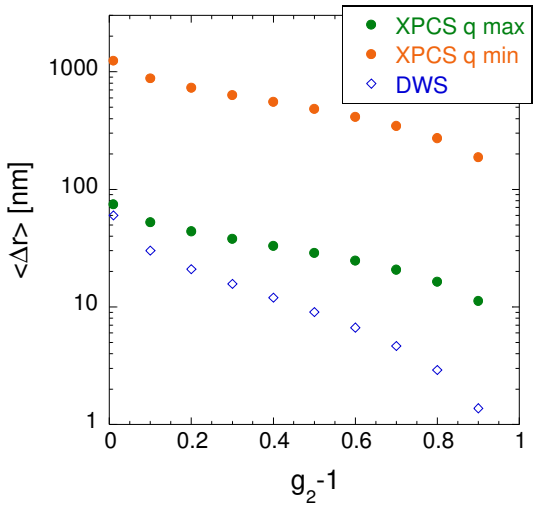

Figure 3: Mean displacement of nanoparticles at different q-values compared to the DWS-measurements (which does not allow measurement at fixed q), as a function of the correlation. At low q, the displacements are larger, corresponding to the larger spatial environment probed. Also, DWS measures more local displacements only.

Figure 3 illustrates that the overall behavior of the samples is sound: larger zones are subject to larger deformations (q-dependence), and the displacements increase with increasing loss of correlation. It was therefore possible to follow the dynamics of polymer nanocomposites under cyclic strain, as shown in Figure 4:

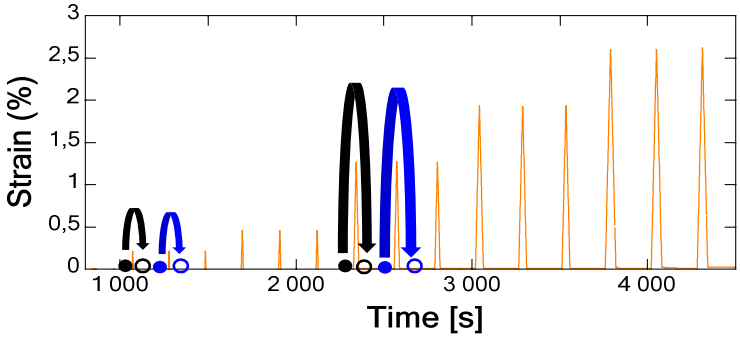

Figure 4: Sequence of increasing strains as a function of experimental time. XPCS spectra are continuously monitored. It is then possible to study the impact of a single/second/etc strain cycle on the decorrelation of the nanocomposite structure.

As an exemplary key result of our study, the impact of the first and second strain cycle is shown in Figure 5. On the left, the decorrelation is plotted, and on the right the corresponding mean displacement.

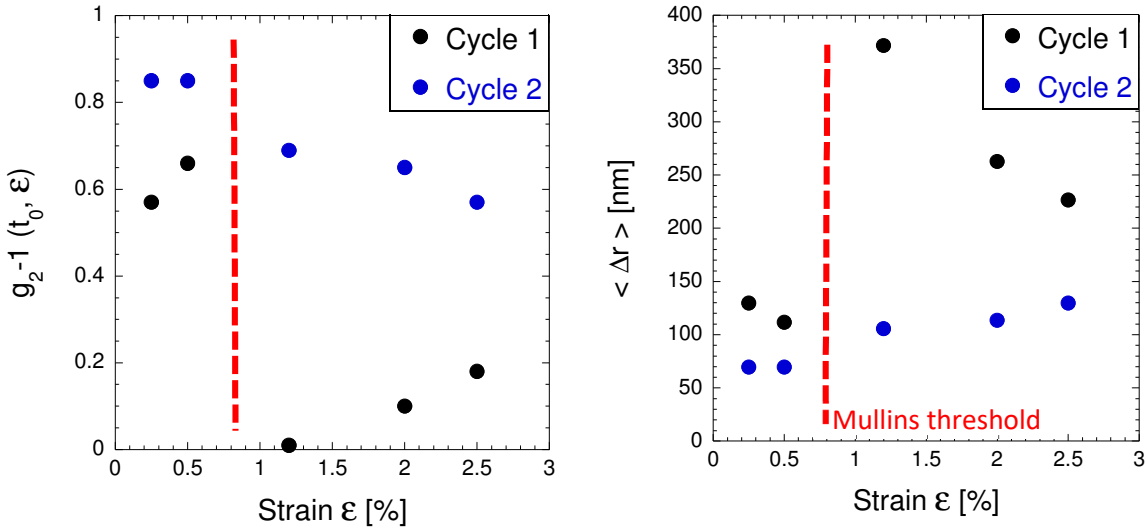

Figure 5: (left) Decorrelation observed as a function of strain for the first and second cycle. (right) Corresponding mean displacement. The vertical line indicates the strain above which the Mullins effect is observed in these samples.

The results summarized in Figure 5 illustrate that the strain-dependent Mullins effect as shown in Figure 2 takes its microscopic origin in the displacement and loss of correlation (i.e. particles not returning to their original positions). The stronger the strain, the higher the displacements, and the more important the loss of correlation. The Mullins effect, with its strain softening in successive strain cycles is reflected by the fact that the first cycle has a strong effect, i.e. the filler network is broken or strongly and irreversibly deformed, whereas the second cycle does not have this impact – our interpretation is that the already broken network is not broken any further by strain of the same amplitude. Higher strains, however, are then seen to induce again additional decorrelation in Figure 5, while the second deformation (Figure 4) does not have this effect.

In conclusion, we have investigated the relationship between the Mullins strain softening effect and the measurement of echoes in speckle pattern associated with different strain cycles amplitudes. We have found evidence for a microscopic signature of the Mullins effect in terms of decorrelation in particle positions induced by strain and highlighted by XPCS. This implies network remodeling at the scale of a few 100 nm, the strongest remodeling occurring at the Mullins strain threshold indicated in Figure 5. We hope to have a more detailed view on spatial rearrangement occurring under oscillatory shear strain as studied by SAXS after our new measurement campaign (proposals submitted). To this end, we have now developed a combined SAXS-reverse Monte Carlo approach [5] capable of identifying large-scale aggregation and in particular, percolation effects.

References:

[1] Musino *et al. Macromolecules* **50**, 5138-5145 (2017). "Synergistic Effect of Small Molecules on Large-Scale Structure of Simplified Industrial Nanocomposites".

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[4] Moller *et al. Journal of Synchrotron Radiation* **23**, 929-936 (2016). "Multi-speckle X-ray photon correlation spectroscopy in the ultra-small-angle X-ray scattering range".

[5] Musino *et al. Nanoscale*, **12**, 3907-3915 (2020).