ESRF	**Experiment title:** Cavity formation upon loading and unloading in cross-linked rubber nanocomposites	**Experiment number**: SC5250
Beamline: ID02 / ID13	**Date of experiment**: **ID02:** 06/05/2022 – 09/05/2022 **ID13:** 21/07/2022 – 25/07/2022	**Date of report**: 27/09/2022
Shifts: 9 + 6	**Local contact(s)**: Michael Sztucki	*Received at ESRF:*

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Report Summary:

The goal of our proposal was to study the effect of polymer blend morphology on cavity formation by varying the type of polymers in a blend and also the blend ratio. Cavities were induced both in the bulk of the material by fatigue at the Continental AG facilities (Hannover, Germany) and locally by tensile deformation using the ID02 custom-made stretcher device and the ID13 3D-printed sample holder with a manual elongation mechanism. We recorded complementary data with high reciprocal space resolution in USAXS and high spatial resolution using a micron-sized beam

At ID02, high reciprocal space resolution Ultra-Small Angle X-Ray Scattering (USAXS) measurements on 1 mm thick dumbbell-shaped rubber samples were performed. Measurements were done on samples both fixed statically and under progressively rising levels of strain to observe structural changes in samples with different blend configurations. Data from both static and dynamic measurements at ID02 allowed us to observe previously not yet systematically studied structural changes of the rubber compounds in the USAXS range: Figure 1 demonstrates this horizontal intensity streak (signifying the presence of cavities) on top of the butterfly-shaped scattering pattern of aligned silica clusters under a (vertical) strain of 269%.
At the ID13 micro-focus beamline SAXS scanning measurements on 10-micron thick stretched rubber films were performed. Scans showed pinpoint differences in the elongated samples, directly connected to the previously found at the ID02 SAXS pattern regions, showing cavitation phenomena. Therefore, cavity nucleation can be located using the scanning technique.

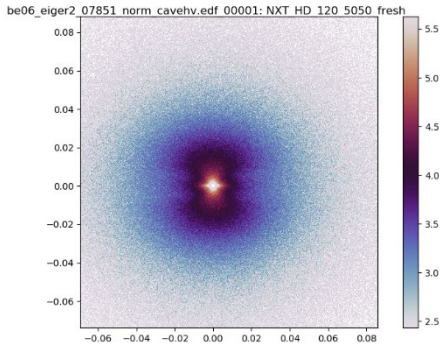

Figure 1: 2D USAXS scattering pattern of a sample made out of 2 different polymers (Natural Rubber [NR] and Solution Styrene-Butadiene Rubber [SSBR]), containing 3-Octanoylthio-1-propyltriethoxysilane and Zeosil® 1165MP silica particles strained to 269%.

ID02 experiment: USAXS of rubber composites

During the first part of our proposal at the ID02 TRUSAXS beamline we performed 2 types of experiments: In the first step, we characterized the undeformed rubber specimens at sample-to-detector distances between 1m and 31m to get full structure information. The empty background was measured to subtract the scattering of the air. Main filler of rubber composites - Zeosil® 1165MP silica particles - was separately measured.
The second type of experiment was performed using a custom-made stretcher device made on the ID02 beamline: 6 samples were attached to the top and bottom clamps of the stretcher. Light-reflecting dots were applied on the surface of samples at a 10mm distance and were detected with a monochrome camera to measure strain levels of installed samples. Clamps were opened up to 450% of the original length until full opening or sample failure.

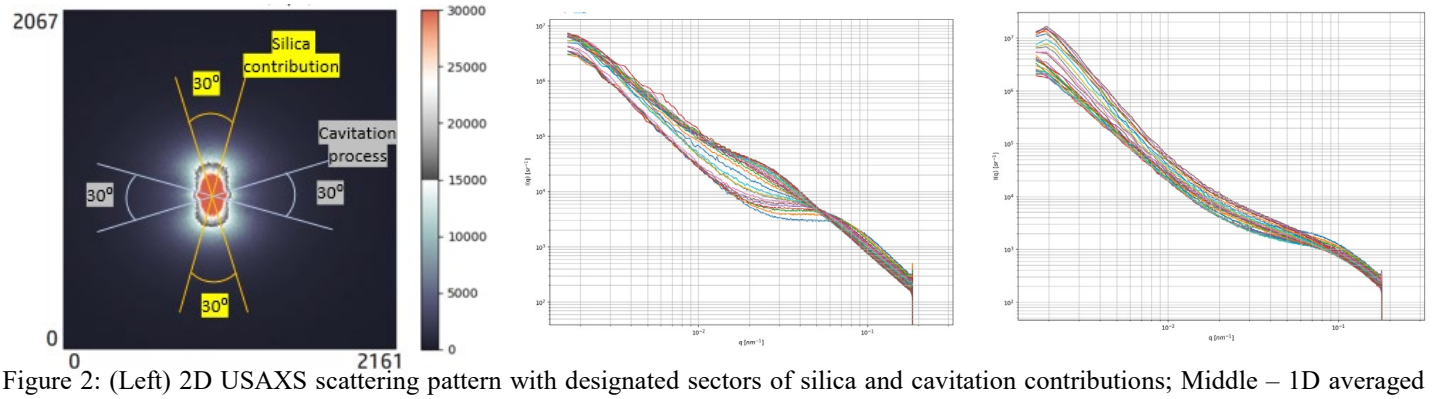

Figure 2: (Left) 2D USAXS scattering pattern with designated sectors of silica and cavitation contributions; Middle – 1D averaged scattering pattern of aligned silica clusters in strain direction; (Right) 1D averaged scattering pattern of aligned silica clusters perpendicular to strain direction; superimposed by of cavitation contributions at higher strain levels.

We measured 156 samples in different states (fresh samples without defects; samples cyclically fatigued to 89%/136% in room temperature/60ºC). 3 main sample batches consisted of 36 unfatigued untreated rubber samples. Each batch consists of 12 samples: each series has samples with 4 different silica concentrations, 1 type of organosilane, and 3 different polymer blend ratios. For most undeformed samples, we observed an inhomogeneous "butterfly"-shaped scattering pattern, an indicator of the initial orientation of silica clusters and aggregates inside the rubber.
At strain levels >150%, we detected a pronounced rise of intensity in the direction perpendicular to the elongation direction (Figure 1) which is reported in the literature as an indicator of cavitation mechanism in rubber composite. However, this phenomenon was never systematically studied in the USAXS low-q regime.

In our further quantitative analysis, we will extensively work on the explanation of its appearance with information from detailed structural information extracted from partial integration of the SAXS patterns in the direction parallel and perpendicular to the applied strain (Figure 2).

ID13 experiment: Small Angle X-ray Scattering scanning of highly elongated rubber composites

During the experiment on the ID13 beamline, we stretched our samples up to 2.5 times of original length and performed the SAXS raster scanning technique on multiple rubber samples using a highly collimated 2x2 µm beam. We looked into areas, which visibly showed the highest strain levels. Limiting our observations to the SAXS regions where the streak is expected and unexpected (Figure 3B, red – streak regions, green – regions without streak) we saw differences in performed scans (Figure 3A, red and green). Of particular interest are spots in the scans (Figure 3C) which appear only in streak regions and are related to the cavitation process.

Thanks to the micron resolution of the beam at ID13 we can observe this effect over a big area of our sample (Figure 4), however, to get more precise information on cavitation we realized that higher resolution SAXS scanning using a beam with 200nm size would be required.

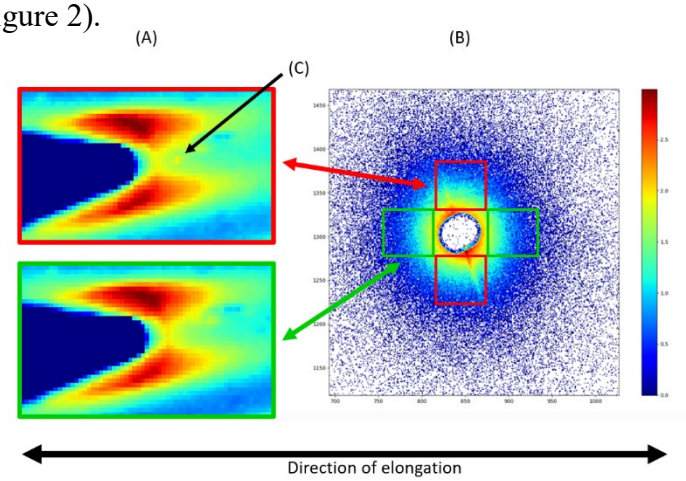

Figure 3: (A) integrated intensity of SAXS raster scan of the rubber sample stretched in horizontal direction: each pixel represents a single SAXS measurement; (B) 2D SAXS scattering pattern. Cavities are expected in the regions marked in red (C) spot indicating cavitation.

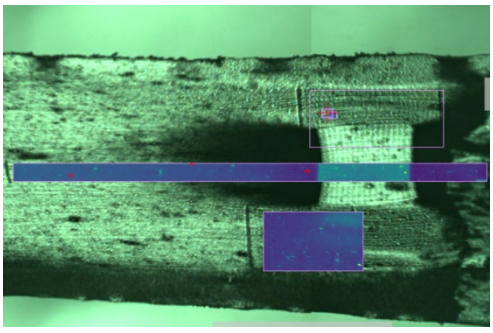

Figure 4: Top - microscopy image of horizontally strained sample with superimosed microbeam scans on top of it