



	Experiment title: Relaxation dynamics of filled elastomers	Experiment number: SC-3024
Beamline: ID10A	Date of experiment: from: 08/12/2010 to: 14/12/2010	Date of report: 11/10/2014 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Yuriy Chushkin	
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Report:

The purpose of this experiment was to study by XPCS the relaxation dynamics of silica and carbon black fillers in natural and synthetic rubber, as a function of filler concentration and temperature (down to the glass transition of the material).

Experimental

The small-angle X-ray scattering (SAXS) and XPCS measurements were performed at the TROIKA beam line ID10A of the ESRF with an X-ray energy of 8.06 keV ($\lambda = 1.54 \text{ \AA}$) selected by a single-bounce Si(111) monochromator, in the “16 bunch” filling mode of the storage ring. A (partially) coherent beam is obtained by inserting a 10 μm pinhole aperture a few centimeters upstream of the sample. The sample-to-detector distance was 2180 mm, for an accessible q -range of 2.16 to 25 10^{-3} \AA^{-1} .

We used a 2D Maxipix detector consisting of 256×256 square pixels (55 μm in size) and with acquisition rates of up to 1 kHz. For XPCS, a few thousand images were recorded (at a rate of 1 to 10 Hz) and the intensity autocorrelation functions $g_2(q,t)$ were calculated by ensemble averaging [1] over pixels with the same absolute value of the scattering vector. The SAXS pattern is obtained as the average intensity over all the images in each run.

The main difficulty was the evolution of the system under the X-ray beam. We used freshly prepared samples (in contrast with the aged one used for preliminary measurements during SC-2690, see proposal 24336). At room temperature, the time scale changed from one acquisition to the next, as shown in Figure 1: the characteristic times, defined as the inflection points of the autocorrelation functions increase (shift to the right) for all q values between 2.4 and 12 10^{-3} \AA^{-1} (indicated in the first image) in a sequence of four measurements.

Another unexpected complication was the difference in relaxation behaviour as a function of the sample fixation: we did not obtain the same results for samples that were clamped and those that were simply stuck to the sample holder using vacuum grease.

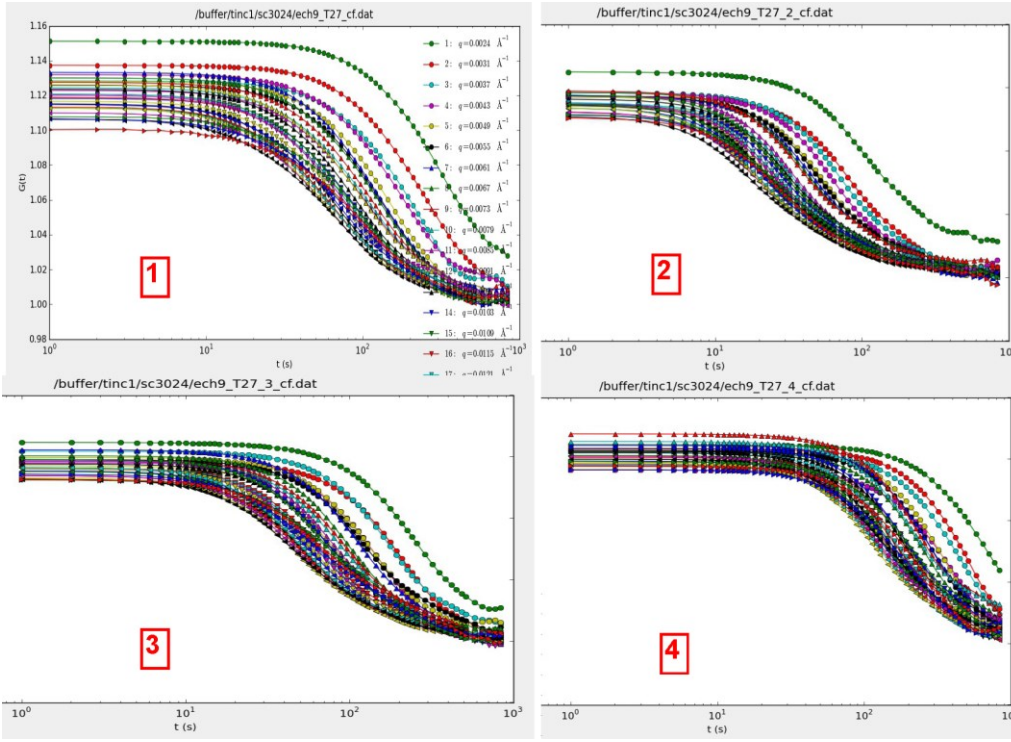


Figure 1: Correlation functions for a carbon-black-loaded sample (the load $Q = 17$ phr) close to room temperature ($T = 27^\circ\text{C}$). The four panels correspond to different acquisitions in immediate sequence, in the order indicated by the labels. The shift of the curves to the right, indicating “aging” (increase of the relaxation time) is clearly visible for all scattering vector values.

At lower temperatures, the aging effect is less marked, but the time behaviour is quite erratic, and likely due to differences between the individual samples more than to the control parameters (load and temperature).

Conclusions

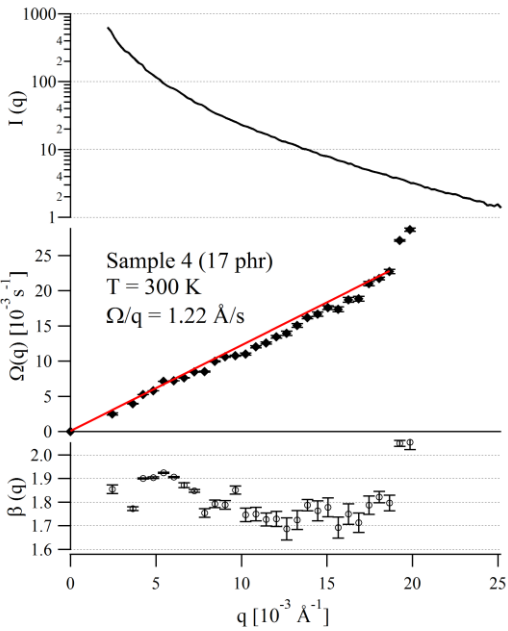


Figure 2: Static intensity $I(q)$, relaxation rate $\Omega(q)$ and stretching parameter $\beta(q)$ for a representative sample at room temperature.

References

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- [3] A. Duri and L. Cipelletti, Length scale dependence of dynamical heterogeneity in a colloidal fractal gel. *Europhys. Lett.* **76**, 972 (2006).