ESRF	**Experiment title:** **XPCS investigation of filled elastomers**	**Experiment number**: 02-01-614
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Shifts: 9	**Local contact(s)**: Françoise Bley	*Received at ESRF:*

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Report:

The aim of this XPCS experiment was to investigate the stress softening effect (also named Mullins effect) observed for any filled elastomer. At low deformation, the stress softening effect has probably the same origin as the strongly non-linear dynamical-mechanical response (also named Payne effect) [1]. Both effects involve local relaxation times for rearrangement of the aggregates or aggregate network, which is precisely the information expected from XPCS experiments. For this purpose, USAXS using coherent X-rays was combined with mechanical measurements that allowed us to control the deformation rate and to obtain the true deformation as well as the kinetics of relaxation at constant deformation.

1) <u>USAXS-XPCS measurements</u>
The experimental conditions were similar to that used previously [3].
- typical USAXS arrangement: polished tantalum guard slits and a cross-hair beamstop (300µm platinum wire), 7.9 keV and sample to detector distance close to 220 cm
- 10 µm circular pinhole to obtain coherent X-rays
- direct illumination CCD camera

Each run consisted of 700 frames measured each during 5 seconds. Thus, the relaxation process was investigated during about 1 hour at constant deformation.

2) <u>Mechanical measurements</u>
The miniature stretching device developped for measurements under vacuum on D2AM was used. The initial length of the samples was close to 10 mm and the speed of elongation was 5mm/min. The decrease of the stress measured by the force gauge, was monitored simultaneously with the USAXS measurements.

3) <u>Samples</u>
The 0.8 mm thick samples investigated consisted of an elastomer matrix (EPR) filled with carbon black N330 at two different volume fractions ϕ, below the percolation threshold (ϕ=0.10, sample T3) and above (ϕ=0.20, samples T4 and T5). Sample T4 was uncross-linked while T3 and T5 were crosslinked (dicumyl peroxide).

4) <u>Results</u>
The stability of the beam which is mandatory for XPCS measurements, was checked by means of the analysis of the speckle patterns obtained for a static sample (compressed fume silica). In contrast to a previous

precluded any significant information about the dynamics of relaxation.
Nevertheless, the static analysis of the data obtained in this experiment [4] yields information that are new and/or complementary to the previous ones [5].
- for the uncross-linked sample T4, this experiment confirms (Fig. 1, *left*) the formation of an anisotropic SAXS pattern when the deformation becomes larger than that corresponding to the maximum of the stress-strain curve [4, 5]; interestingly, the relaxation of the sample at constant elongation does not involve a structural modification (Fig. 1, *right*) over more than 1 hours;
- for the cross-linked sample T5, containing the same amount of carbon black as T4, Fig. 2 (*left*) shows that the structure of the carbon black network remains nearly the same, at least below about 1 µm, whatever the deformation; it should be noted that the curves measured in all other sectors are completely superimposed; as for T4, relaxation of the sample does not involve a structural modification (Fig. 2, *right*).

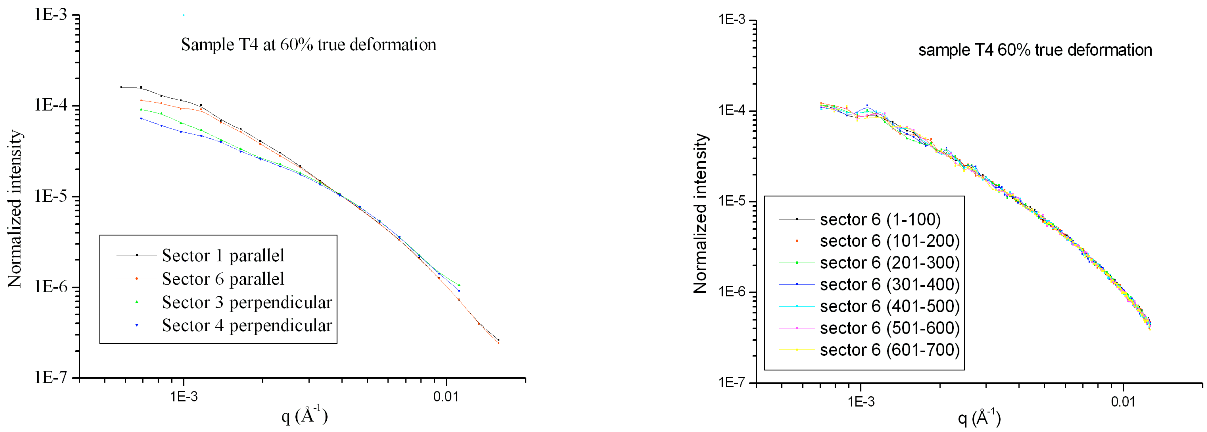

Figure 1. Variation of the scattered intensity *versus* q measured for the uncross-linked carbon black - EPR sample (sample T4) at 60% true deformation: (*left*), total intensity (700 frames) measured during the relaxation (about 1 hour) in the directions parralel and perpendicular to the stretch; (*right*), evolution of the I(q) curves cumulated over 100 frames as a function of time during the relaxation process.

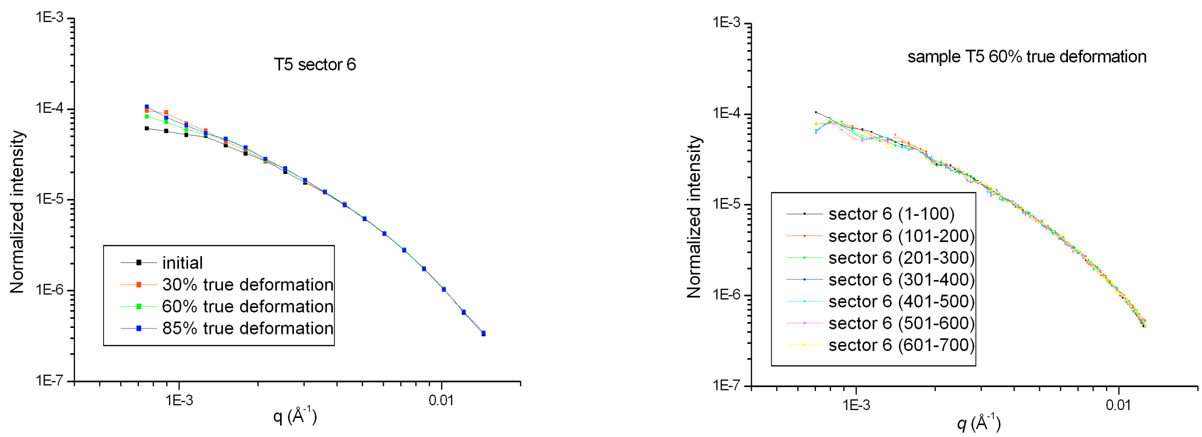

Figure 2. Variation of the scattered intensity *versus* q measured for the cross-linked carbon black - EPR sample (sample T5): (*left*) evolution of the I(q) curves cumulated over 700 frames as a function of the true deformation; (*right*), evolution of the I(q) curves cumulated over 100 frames as a function of time at 60% true deformation.

References

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