ESRF	**Experiment title:** **Large scale dynamics in stretched nanocomposites**	**Experiment number**: SC4726
Beamline: ID02	**Date of experiment**: from: 23 to: 26/02/18	**Date of report**: 26/04/18
Shifts: 9	**Local contact(s)**: Lewis Sharpnack	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Banc A*, Philippe A-M*, Chauveau E*, Oberdisse J* and Cipelletti L*

Laboratoire Charles Coulomb, Université de Montpellier

The aim of this experiment was to measure the reorganization dynamics of the filler network in polymer nanocomposites during mechanical sollicitations. Samples were stretched *in-situ*, and ultra small-angle XPCS measurements were performed in order to follow the signal due to the silica filler nanoparticles and their rearrangements under strain in several SBR (Styrene Butadiene Rubber) polymer matrices.

We used the ID02 beamline with an X-ray energy of 12.46 keV. The sample to detector distance was 31m. We installed on the beamline our strain controlled stretching machine equipped with a stress sensor. Several SBR/silica nanocomposites samples with filler volume fraction of Φ=20% were investigated: The filler was kept identical (Zeosil(R) 1165MP) while several parameters of the matrix were changed: the crosslinking (C) and the end-fonctionnalisation (F) of polymer chains that is capable of covalent grafting on the silica nanoparticles. Four samples were investigated: Non-Crosslinked and Non-Functionalised (NCNF), Crosslinked and Non-Functionalised (CNF), Non-Crosslinked and Functionalised (NCF) and, Crosslinked and Functionalised (CF). Firstly the resistance of our samples to beam damage was checked. Then different mechanical tests were performed. Stress relaxations tests were measured for serveral step strains (ε=0.7%, 1.3%, 2.7%, 5.5%,13.5 and 27%) while X-ray spectra were recorded each 5s. In addition, some echoes test measurements were measured after different strain cycles.

Figure 1 (Left) displays the mechanical response of samples NCF and CF after a step strain of 0.7%. The stress decreases with time showing the macroscopic feature of internal relaxation mechanisms. In Fig. 1 (middle) normalized intensity auto-correlation functions $g_2(t,\tau)$-1 at q=0.0063 nm^{-1} for the NCF sample are plotted. Correlation functions start at 0.7 showing that there is a relaxation process faster than the frame acquisition rate used for these experiments. Thus, this kind of experiments would clearly benefit from the fast acquisition procedure (kHz frame rate) enabled on ID02. Correlation functions plotted are obtained for waiting times t such that 0<t<520s, 0 being the beginning of the stress relaxation phase. While the macroscopic stress relaxes, the dynamics of nano-fillers slows down monotoneously (from blue to red). Similar data are plotted on Fig.1 (Right) for the CF sample. In this case the measured correlation functions display a much more complicated "shape". Indeed, at early times of the stress relaxation phase, $g_2(t,\tau)$-1 first decreases before bouncing up to high correlation level, this latter depending on the waiting time. However, at longer waiting time (t>100s, inset), $g_2(t,\tau)$-1 recovers a more conventionnal behaviour characterized by a single decrease down to the noise level.
In order to be more quantitative, we fitted the correlation functions with a single exponential:

$$g_2(\mathrm{t},\tau) - 1 = A * e^{-2\left(\frac{\tau}{\tau_c}\right)^{\beta}} + B \quad (1)$$

where A and B are respectively the intercept and the baseline, τ_c is the characteristic time and β is the stretching exponent.

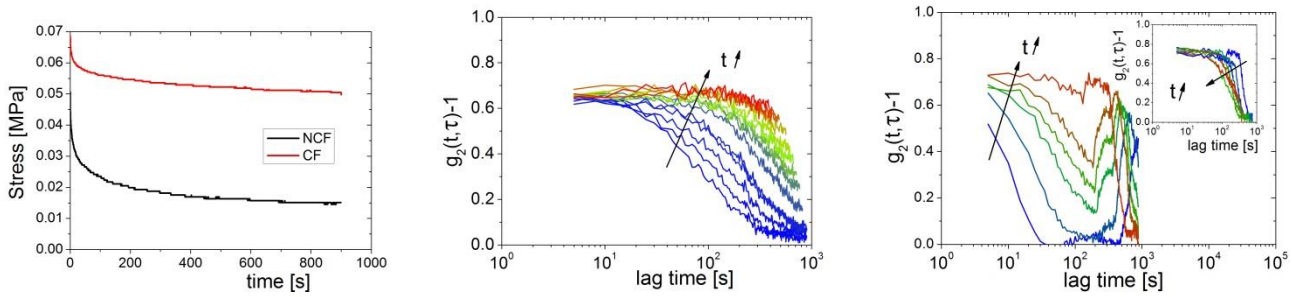

Figure1. *(Left) Stress relaxation after a step strain of 0.7% as a function of time. (Middle) Normalized intensity auto-correlation functions $g_2(t,\tau)$-1 for different times t versus lag time τ measured for the NCF sample. (Right) Same as (Middle) but for the CF sample. Main plot:Auto-correlation functions for short relaxation times (t<100s). Inset: long relaxation times t>100s.*

In Fig.2 (Left) both the characteristic time and the stretching exponent obtained by fitting the correlation functions with eq.1 are plotted. The dynamics of the NCF sample slows down through the whole relaxation phase with a characteristic time going from 400s to 1000s following a $t^{1/2}$ power law, and an almost constant stretching exponent roughly equal to 1. In the case of the CF sample, we splitted the fitting procedure into two steps. We first fit the fast relaxation occuring at the beginning of the stress relaxation phase (red symbols on Fig.2 (Left)). The sample shows a faster dynamics than the NCF sample. In addition the slowing down of the dynamics is also faster, following a t^2 power law. Then, the long time relaxation is fitted and results are plotted in Fig.2 (Right). This slow relaxation seems to be steady, or slightly accelerating, with a characteristic time comprised between 200 and 500s. The main feature of this slow relaxation process is its morphology (see inset of Fig.2 (Left)) that goes from a highly compressed (β=4.5) to a moderately compressed (β=1.5-2) exponential decrease.

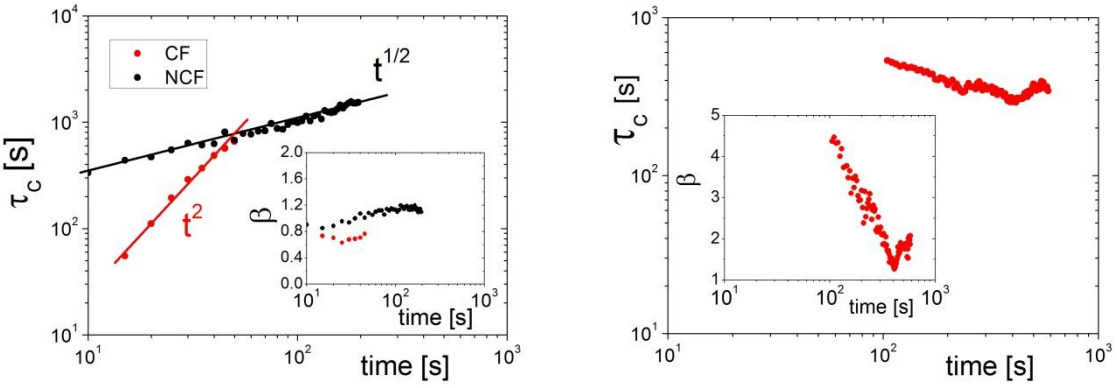

Figure2. *(Left) Characteristic relaxation time τ_c as a function of time t for both CF (red) and NCF (black) samples. Inset: stretching exponent β versus time t for both samples. (Right) Fitting parameters obtained for t>100s on the CF sample (corresponding correlation functions are in inset of Fig.1 Right).*

This quick overview shows the rich dynamic behavior of these nanocomposite samples during a stress relaxation. Especially, it is shown that the chemical nature of the polymer matrix modifies in depth the nature of the dynamics of the nano-fillers. It is striking to see that, whereas both presented samples display the same qualitative macroscopic response after a step strain, the microscopic path to relax the stress in each of them is different and thus call for a deep experimental investigation. It is worth saying that this study will largely benefit from the scattering vector resolution offered by the beamline. Indeed, we already observed (not shown in the present report) that the dynamics of the fillers depends on q and also that the nanocomposite samples do not behave the same way in the directions parallel and perpendicular to the stretching.