Influence of the loading history on strain induced crystallisation of elastomers with original architecture of crosslinks network

Proposal number:MA-5739
Beamline: D2AM
Shifts: 9
Date(s) of experiment: from: 16/06/2023 to: 19/06/2023
Date of report: 11/09/2023

Warning: this report is a preliminary version, as we did not finished the quantitative analysis of the data. It will be completed after the proposal deadline submission, as we did not yet have access to the corrected data (calibration and background subtraction) The experimental difficulties met during the experiments and the interesting results already deduced from the data obtained during 9 shifts convinced us that additional shifts are necessary to perform complementary experiments. Indeed, we need to confirm our results and to successfully perform the program initially planned in the proposal.

- Objective & expected results (less than 10 lines): **-**

The reinforcement mechanism (i.e. of stress increase) of Natural Rubber (NR) coming from Strain Induced Crystallisation (SIC) is strongly dependent on the mechanical history (strain rate, elongation...). Previous experiments suggested that this reinforcement is not only linked to the crystallinity level, it could also be connected to the morphology and the spatial distribution of the crystallites inside the material. Consequently, we proposed to characterize the in-situ SIC (rate and morphology of the crystals) at various strain rates. The simultaneous use of SAXS and WAXS enable to have information at larger scale than the crystallites but needs the study of rubber without scatterers which masks information about the crystallites, such as fillers, or vulcanization products. For these reasons we studied NR and IR crosslinked with peroxide (instead of sulfur) (IR avoids possible scattering of impurities present in NR).

-Results and the conclusions of the study (main part): **-**

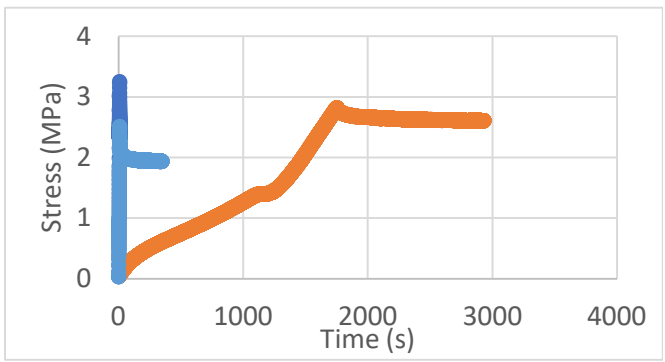


Figure 1 : stress versus time for IR sample stretched at l=6.3 at 0.003 s^{-1} (pink curve) and 0.8s^{-1} and relaxed

A homemade tensile bench was built and adapted for studying fast stretching of isoprene rubber (natural or synthetic) at D2AM with the help of ESRF staff. This setup was completed by a Linkam machine to perform test at lower strain rate (0.002 s-1). Conversely to our homemade machine, this has the advantage to symmetrically stretch the material. With these two machines, we expected to demonstrate the good reproducibility of the results and the absence of consequence of a non symmetrical deformation (which leads to not probe the same volume when the material is stretched). Both machines give indeed consistent result. More importantly, we could obtain SAXS and WAXS data corresponding to

the mechanical stress strain curves measured with the same setup. (see for example figure 2). Rapid observation of the WAXS pattern (we did not yet performed quantitative analysis of the crystallinity, crystallites orientation and dimension) confirm that in spite of a same final elongation, for a same experimental time (which includes a long relaxation step), a different crystalline microstructure is observed. This difference (more and better defined crystallites for low strain rate test, and possibly less oriented), explains different stress levels. However, conversely to what was suggested by previous ESRF experiments, the final stress level seems correlated to the crystallinity. Same conclusion can be done for the NR and IR crosslinked with peroxide. This needs however to be confirmed, given the fact that we suspect that in some cases, in spite of care taken in the choice of the acquisition times, the materials could be damaged by the beam.

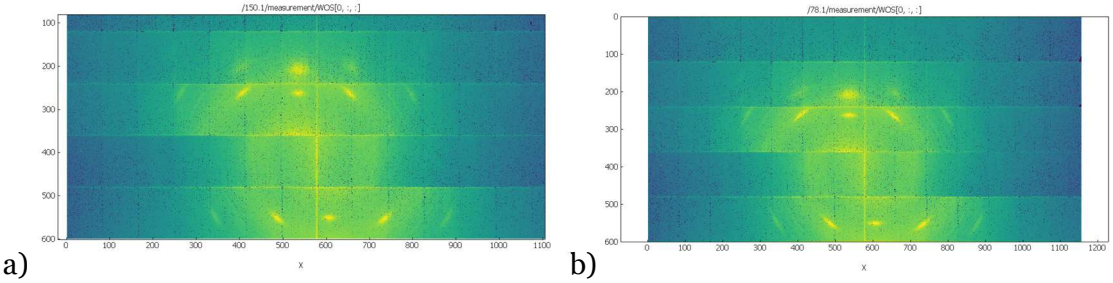


Figure 2 : X ray scattering of NR : pattern obtained with the Linkam machine a) after rapid stretching and relaxation (0.8 s^{-1}) and b) slow stretching and relaxation (0.003 s^{-1}). Data are acquired at the same time after the experiment beginning (2000s).

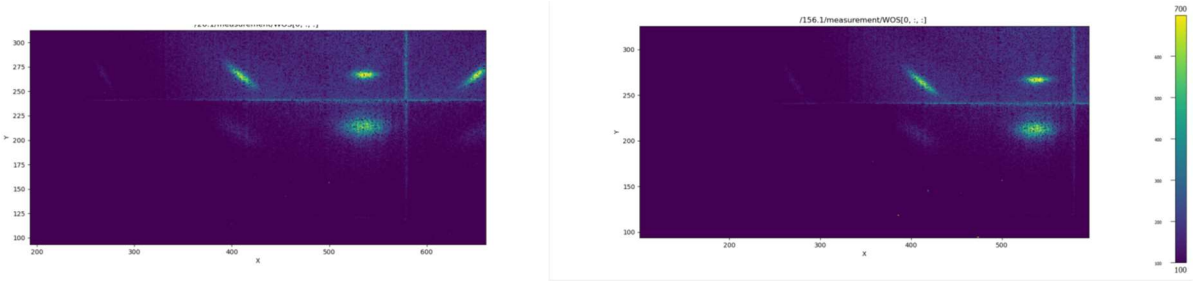
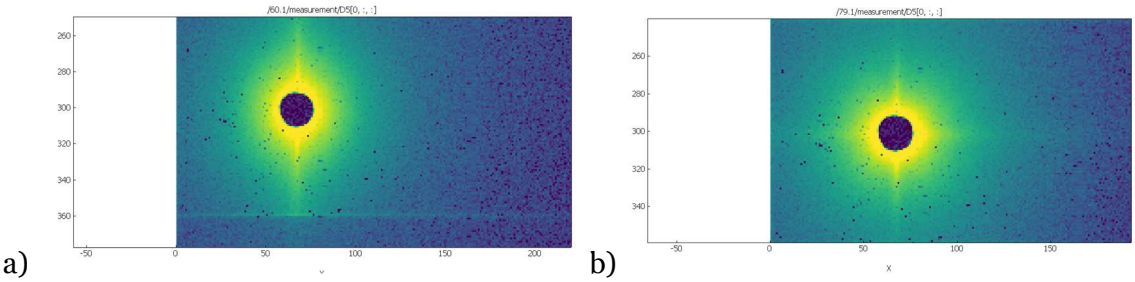


Figure 2 : X ray scattering of vulcanized IR: pattern obtained with the Homemade ultrafast machine a) after rapid stretching and relaxation (10 s^{-1}) and b) slow stretching and relaxation (0.003 s^{-1}). Data acquired at the same time after the experiment beginning (2000s).

The difference of the observed stress can be explained by a different degree of orientation in the remaining amorphous chains or a structure formed at a scale longer than the one studied (more than 5 nm). Additional multistep loading with intermediate relaxations are required to better understand the formation of this microstructure.

SAXS pattern were simultaneously acquired. Note that, to the author knowledge, such SAXS data on stretched polyisoprene are very original. Their preliminary analysis unexpectedly suggests the development of a very anisotropic structure which may actually correspond to the formation of cavities inside the stretched materials. These cavities, oriented in the tensile direction, seem to exist only when the sample have been previously stretched up to the crystallisation onset. Actually their shape may be closer that of microcracks, and they appear, once created, as soon as the samples are stretched. They are, after their formation, not directly related to the crystallinity level. It is therefore necessary to subtract this signal to conclude on the scattering of the crystalline microstructure. In addition IR sample show at all stretching

values (therefore neither correlated to the crystallites) a different pattern with an elliptical pattern in the tensile direction. Careful data treatment is ongoing to identify its origin.



a) b)

Figure 3: SAXS pattern of NR and IR crosslinked with peroxide and stretched at slow strain rate (0.003 s^{-1}) at λ=6.3

To conclude, the preliminary results (as we did not get yet the treated data), are encouraging but ask questions on the one hand on the origin of the SAXS pattern, and on the other hand on the anisotropy of the crystallite microstructure generated at large strain, and on the scale of this anisotropy.

- Justification and comments about the use of beam time (5 lines max.): **-**

We strongly thank the D2AM beamline staff for their help in conducting our experiments. Installation of both tensile machines took more time than expected, this limited the time available. The low strain rate experiments at large strain with relaxation require more than 1h, which limited the possibility to study reproducibility. or to perform more complex loading history (multistep relaxations). Moreover, we did not studied all the samples planned in the proposal (samples crosslinked in two steps and crosslinked by irradiation). We therefore demand additional shifts (cf. Proposal submitted).

- Publication(s): **-**

To early to be done. Undoubtedly, the results described in this report will be the source of publications after a complete data treatment of the SAXS and WAXS data.