Structural study on the impact of strain rate and heat transfer on mechanical reinforcement of natural rubber

Proposal number:20201186
Beamline: D2AM
Shifts: 9
Date(s) of experiment: from: 09/04/2021 to: 11/04/2021
Date of report: 20/01/2022

- 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...). Our 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 characterise the in-situ SIC (rate and morphology of the crystals) of NR elongated at various strain rates. Besides, the increase of the strain rate induces a temperature variation of the sample coming from the latent heat of crystallization which could delay the kinetic of crystallization. In order to investigate the impact of heat transfer on both mechanics and structure, we studied SIC of samples having different thicknesses and correlate those results with temperature measurements already performed in our laboratory.

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

A homemade tensile bench was built and adapted for studying fast stretching of natural rubber (NR) at D2AM with the help of ESRF staff. **The first type of experiment consisted in stretching NR at fast ($16s^{-1}$) and slow ($0.05s^{-1}$) strain rates and following the kinetics of crystallization and stress relaxation simultaneaously at constant elongation (λ=6)**. After 100s, the stress level is 30% higher for sample stretched at low strain rate (Figure.1a)). The difference in terms of crystallite size and degree of crystallinity is too small to be considered as significant (Figure 1.b)). With the obtained data, we failed to explain the difference observed in the mechanical behavior of NR induced by the strain rate. However, this experiment confirms that for a same elongation and a same crystallinity, the stress can be significantly different.The difference of the oberved stress should 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). The presence of sulphur and zinc oxide in our samples and the holes present on the xray detector inhibit an in depth study of the degree of orientation of the chains and of the superstructure of crystals. Therefore, it could be interesting to study polyisoprene crosslinked with peroxyde to obtain relevant Xray scattering data without zinc oxide scattering.

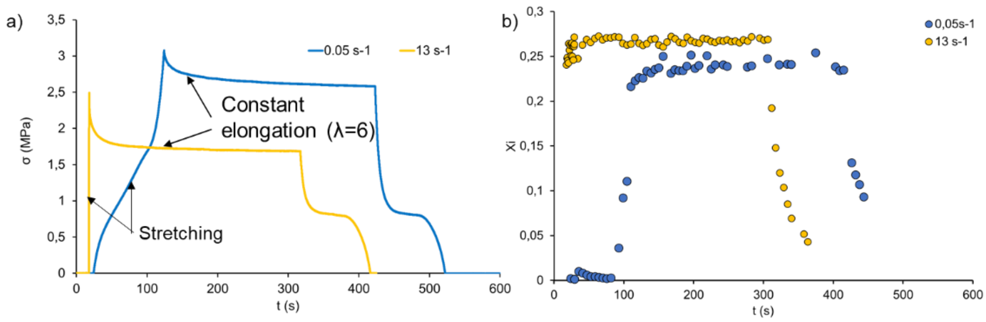

Figure.1 a) Stress versus time for sample streched at 0.05 s^{-1} and 16 s^{-1} b) crystallinity as a function of time

The second type of experiment consist in following simultenaously the stress relaxation of samples of different thicknesses (with different heat transfer time constants) and their kinetics of crystallization. The stress relaxation as a function of time is presented on figures 1.a) and 1.b), it is shown that the stress relaxation is faster for the thinner sample. The stress relaxation is usually attributed to the crystallization of NR because the fraction of crystalline parts limits the elongation of the remaining amorphous one. Therefore, this results suggest that decreasing the sample thickness speed up the NR crystallization kinetics. This results is confirmed by in situ waxs measurement, in which the intensity of the peak associated to the (002) diffracting plane increases faster for the thinner sample. Finally, the stress and intensity variations seem to be correlated as it is shown on Figure 1.d). It proves that the heat transfer has an impact on both strain induced crystallization kinetics and stress relaxation. An oral communication has been made on DEPOS 30, and the writing of a publication is ongoing. This result could be taken into account in experiments involving specific heat transfer, such as in crack propagation studies, or fatigue tests in marine environment.

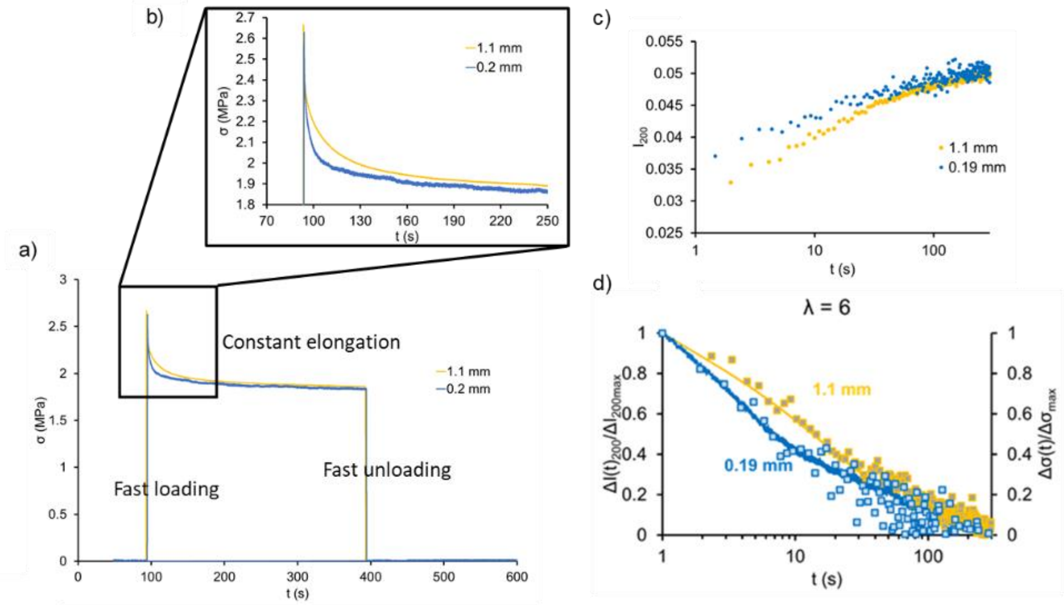

Figure.2 Comparison of sample with two thicknesses a) and b) stress evolution as function of time c) intensity of the 002 plane diffracting peak d) stress (line) and intensity (points) variations as a function of time

Regarding the perspectives, we tried to periodically and partially deform a NR sample with a square sollicitation between an elongation of λ=4 and λ=6. The maximum crystallinity and stress increase from the first cycle to the second.
Interestingly, in addition to crystallization kinetics, it seems that crystal melting is not instantaneous when the minimum elongation value is greater than the melting elongation typically λ>3. The reason could be the viscoelastic response of rubber or the negative temperature variation induced by unloading. Melting kinetics has been mentioned in the literature before (Samaca Martinez et al., polymer, 2013), but to our knowledge it has never been directly demonstrated by structural measurements. We did not have time to reproduce our result during the allocated beam time due to the COVID context (our PhD student was alone with the beam staff). Therefore, this study could be implemented with a new beam time.

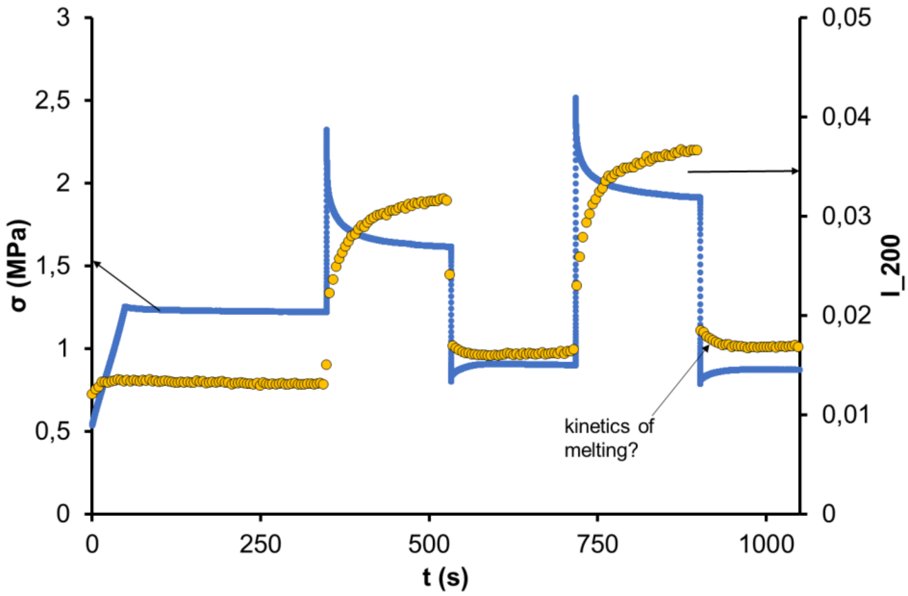

Figure.3 Stress and intensity variations for sample submitted to a square solicitation between λ=4 and λ=6 at a frequency of f=0,0027Hz

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

9 shifts were necessary to perform all the experiments we had planned. Unfortunately, because of the covid-19 pandemic, only the PhD student was allowed to go to ESRF. She therefore worked all day with the local contact, but the night shifts were lost (at least 2 shifts). We would like to strongly thank the D2AM beamline staff for their help in conducting our experiments in this specific context.

- Publication(s): **-**

Conferences H. Haissoune, J-M Chenal , G. Coativy , L.Chazeau,G. Sebald, L. Lebrun, Pour un mode de réfrigération innovant : Effet élastocalorique dans le caoutchouc naturel, 30ème Colloque sur la Déformation des Polymères Solides (Depos30), La Napoule, du 28 September to 1st of October 2021.

Article Impact of heat transfer on strain induced crystallization in natural rubber , Hiba Haissoune[a,c], Jean-Marc Chenal[c] , Gaël Sebald[b], Laurent Chazeau[c], I. Morfin[d], Laurent Lebrun[a], Gildas Coativy[a], Writing in progress