Effect of stress relaxation on mechanically induced crystallization in natural rubber

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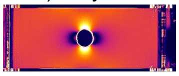
EFFECT OF STRESS RELAXATION ON MECHANICALLY INDUCED CRYSTALLIZATION IN NATURAL RUBBER

A. Le Bihan[a], Y. Marco[a], V. Le Saux[a], L. Chazeau[b], J.-M. Chenal[b], I. Warneboldt[c]

Context & Objectives

Mechanically induced crystallization (MiC) is a widely studied phenomenon. Its characteristics are often determined by wide-angle X-ray diffraction (WAXD) at synchrotrons, ESRF, SOLEIL, DESY…

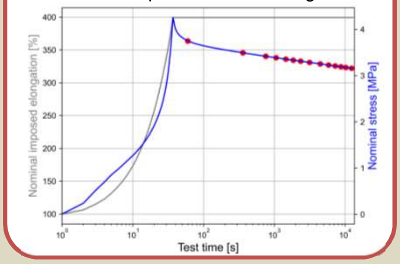


$\Delta\theta, \underline{\sigma}, \underline{\varepsilon}, \ldots ? \longleftrightarrow \underline{\chi_c}$

The main objective is to be able to measure crystallization by a less consequential way : infrared thermography. It is necessary to generate data and better understand MiC in order to realize an infrared-crystallization conversion model.

Performed Tests

WAXD measures during stress relaxation for different temperatures and elongations :

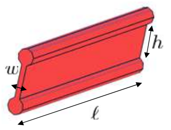


Studied Materials

- Formulation :

	NR05	NR42	IR42
Matrix	cis-polyisoprene	cis-polyisoprene	trans-polyisoprene
CB	5 phr	42 phr	42 phr
Other	processing agent, accelerator activator, vulcanization agent, antioxidant …		

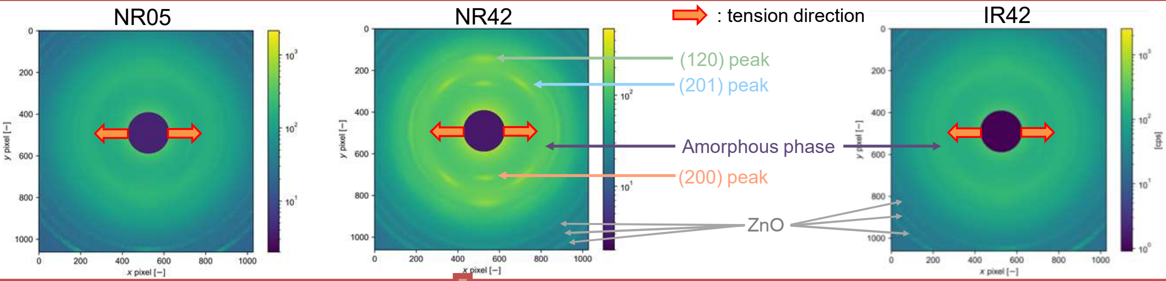
- Samples :



mini pure shear
$w = 1$ mm
$h = 6$ mm
$\ell = 10$ mm

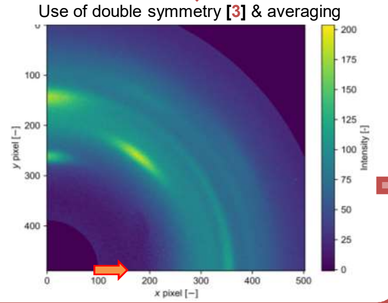
0 Raw images

- Wavelength : λ =1,54 Å
- Exposure time : 240s
- Tests performed at INSA Lyon
- Significant MiC for filled natural rubber
- Indentification of (d_{hkl}) peaks and all different components from litterature [1], [2].



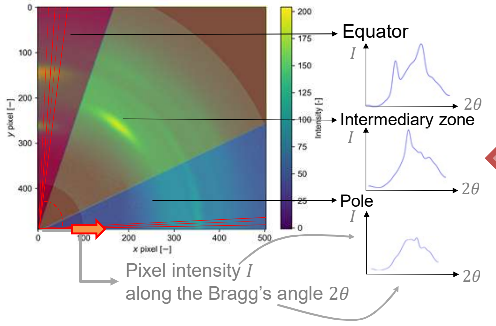
1 Data reduction

Use of double symmetry [3] & averaging



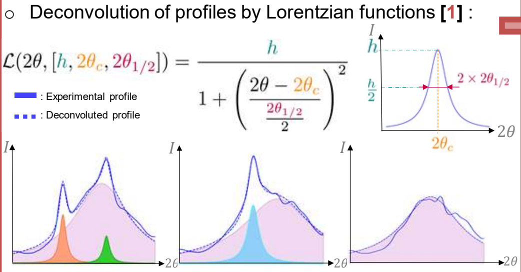
2 Bragg's profiles & deconvolutions

- Definition of 3 sectors & addition of profiles per sector :



- Deconvolution of profiles by Lorentzian functions [1] :

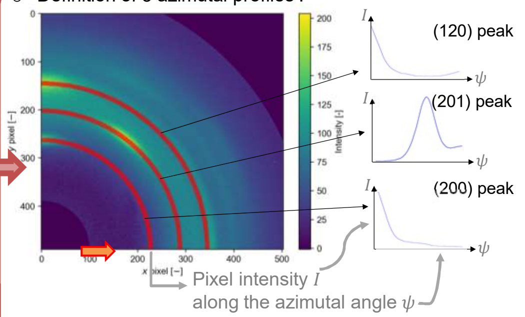
$$\mathcal{L}(2\theta, [h, 2\theta_c, 2\theta_{1/2}]) = \frac{h}{1 + \left(\frac{2\theta - 2\theta_c}{\frac{2\theta_{1/2}}{2}}\right)^2}$$



→ crystalline / amorphous split : crystallites dimensional parameters

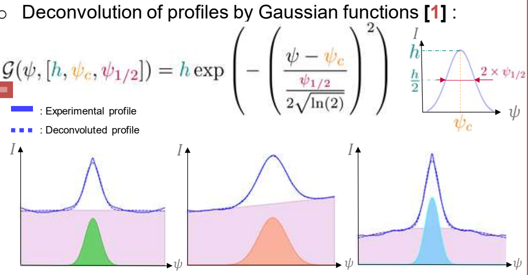
3 Azimutal profiles & deconvolutions

- Definition of 3 azimutal profiles :



- Deconvolution of profiles by Gaussian functions [1] :

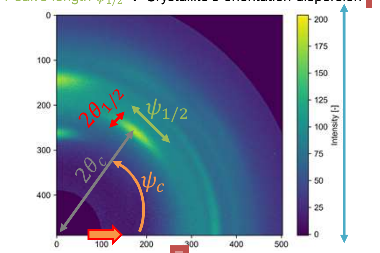
$$\mathcal{G}(\psi, [h, \psi_c, \psi_{1/2}]) = h \exp\left(-\left(\frac{\psi - \psi_c}{\frac{\psi_{1/2}}{2\sqrt{\ln(2)}}}\right)^2\right)$$



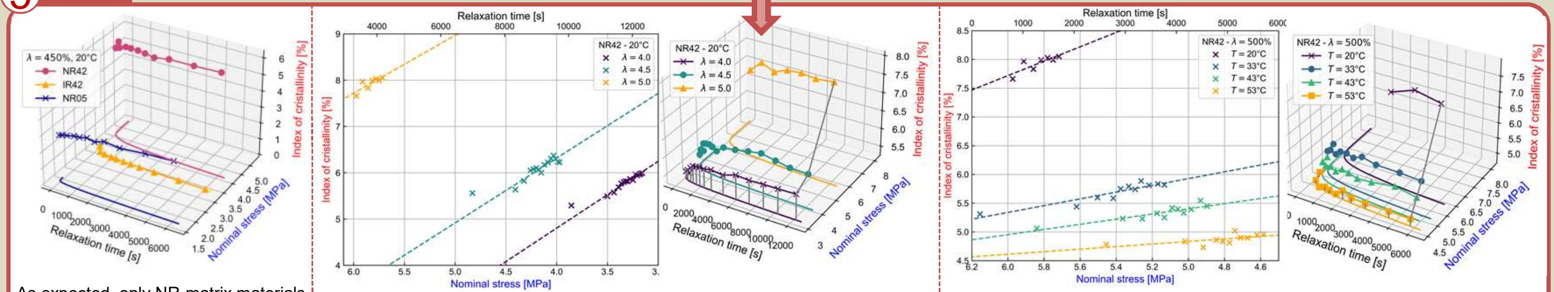
→ crystalline / amorphous split : crystallites orientation data

4 Obtainable information

- Bragg's angle $2\theta_c$ → Lattice parameter
- Peak's width $2\theta_{1/2}$ → Crystallites' size
- Peak's intensity I → Index of cristallinity
- Azimuthal angle ψ_c → Crystallite's mean orientation
- Peak's length $\psi_{1/2}$ → Crystallite's orientation dispersion



5 Results



As expected, only NR-matrix materials crystallize. Fillers permit to increase the MiC phenomenon.

During stress relaxation, the index of crystallinity χ varies linearly with stress σ. The $\frac{\partial \chi}{\partial \sigma}$ coefficient remains the same whatever the value of the imposed elongation.

During stress relaxation, temperature has two effects : it leads to lower indexes of cristallinity χ and it reduces the $\frac{\partial \chi}{\partial \sigma}$ coefficient (i.e. MiC kinetics).

References

[1] N. Candau, « Compréhension des mécanismes de cristallisation sous tension des élastomères en conditions quasi-statiques et dynamiques », Thesis, INSA Lyon, 2014
[2] P.-A. Albouy, J. Marchal, et J. Rault, « Chain orientation in natural rubber, Part I: The inverse yielding effect », *Eur. Phys. J. E*, vol. 17, nº 3, p. 247-259, 2005.
[3] S. Beurrot, « Cristallisation sous contrainte du caoutchouc naturel en fatigue et sous sollicitation multiaxiale », Thesis, Ecole Centrale de Nantes, 2012

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