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# Molecular weight between physical entanglements in natural rubber: A critical parameter during strain-induced crystallization

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## Abstract

The purpose of this paper is to clarify the role of crosslink density of natural rubber on its strain-induced crystallization. A series of new in situ synchrotron X-ray diffraction experiments were performed during the stretching process of weakly and highly vulcanized natural rubber samples. The experimental data have been analysed in terms of both crystallite size and crystallization rate. Moreover, a careful treatment of previously published data that might appear contradictory has been done. The comparison between all these data, coming from NR of different origins and with different crosslinking states, demonstrates that the molecular weight between physical entanglements in natural rubber appears as a key parameter for strain-induced crystallization (SIC).

*Keywords:* Natural rubber; Deformation; In situ X-ray diffraction

## 1. Introduction

The use of natural rubber (NR) is widespread in everyday life through many household or industrial applications, thanks to its outstanding physical properties such as high stress at break and good crack growth resistance [1]. Natural rubber is essentially constituted of *cis*-1,4 polyisoprene whose stereoregularity allows its rapid crystallization when it is stretched more than 300% of its original length. This peculiarity, named strain-induced crystallization (so called hereafter SIC), gives NR a self-reinforcement character, which has been recognized as the main factor responsible for the toughest mechanical properties. It is worth noting that this phenomenon is interesting both from an academic and industrial point of views [2–5].

In the past, primarily due to the lack of in situ measurement technique, only static SIC of natural rubber has been carried out. In order to clarify questions such as the crystal structure, onset of crystallization, and the maximum crystallinity of stretched natural rubber, several techniques of investigation such as X-ray scattering [6,7], stress relaxation [3,4,8], transmission electron microscopy [9,10], infrared spectroscopy [11], birefringence [12], NMR [13], dilatometry [3,14], have been used.

In recent years, a lot of dynamic studies have extensively focused on natural rubber SIC. The semicrystalline morphology development and the stress–strain relationships have been correlated in real time by using synchrotron X-ray diffraction combined with a stretching technique [15–23]. From experiments performed during cyclic deformations, Trabelsi et al. [21] and Toki et al. [17] concluded that mechanical hysteresis is mainly due to the formation and melting of strain-induced crystallites. Moreover, Toki et al. [17,19,23] revealed that under uniaxial deformation the strain-induced

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crystallites are highly oriented with excellent alignment along the stretching direction. It also showed that up to 75% of polymer chains remain unoriented at large strains. On the other hand, there remain controversies on the relationship between the crystallization kinetics, crystallinity, crystallite dimensions and the decrease in the number of monomers between crosslinks (in other words the increase of network chain density). In particular, Tosaka et al. [20] showed that the crystallization kinetic slowed down with the decrease of network chain density, while Trabelsi et al. [21] claimed the opposite from the experiments performed during dynamic strain-induced crystallization at room temperature. Note that both did not establish a relation between the crystallite volume and the network chain density since Tosaka et al. [20] only measured the crystallite dimensions perpendicular ($L_{200}$ and $L_{120}$) to the stretching direction while Trabelsi et al. only determined the one parallel ($L_{002}$) to it.

The aim of the present article is therefore to clarify these questions. To do so, weakly and highly vulcanized NR samples are prepared and are tested by SAXS under tensile tests. Moreover, the crystallite size evolution during stretching deduced from our experimental results is compared to that described in literature. In particular, the definition of the molecular weight as a key parameter of this evolution is proposed.

## 2. Experimental section

### 2.1. Materials

The materials (supplied by *Rhodia Recherches et Technologie*) have been obtained by sulfur vulcanization of natural rubber according to the recipes given in Table 1. The only difference between the samples is the accelerator (CBS) concentration. Prior to curing (150 °C), each cure time was determined from torque measurement as a function of temperature performed with a Monsanto analyser. Network chain densities ($\nu$) presented in Table 1, have been determined from swelling ratio in toluene and the Flory–Rehner equation [24]:

$$-\left[\ln\left(1-v_2\right)+v_2+\chi_1 v_2^2\right]=V_1\nu\left[v_2^{1/3}-\frac{v_2}{2}\right] \tag{1}$$

where $v_2$ is the volume fraction of polymer in the swollen mass, $V_1$ (106.3 cm$^3$/mol) is the molar volume of the solvent (toluene), and $\chi_1$ is the Flory–Huggins polymer–solvent dimensionless interaction term ($\chi_1$ is equal to 0.39 for the system NR–toluene).

The molecular weight between crosslinks is deduced from $\nu$ following:

$$M_c=\rho/\nu \tag{2}$$

where $\rho$ is the density and $M_c$ is the molecular weight between crosslinks.

Note that Trabelsi et al. [21] have shown similar results between network chain densities calculation based on the Flory–Rehner equation and Young modulus measurements. Dumbbell shaped specimens were cut from 1 mm thick sheet.

Table 1
Recipe of vulcanized NR samples and network chain density

| Sample code | NR-0 | NR-1 | NR-2 | NR-3 | NR-4 | NR-5 |
|---|---|---|---|---|---|---|
| SMR 10,[a] phr[b] | 100 | 100 | 100 | 100 | 100 | 100 |
| Stearic acid, phr | 2 | 2 | 2 | 2 | 2 | 2 |
| ZnO, phr | 4 | 4 | 4 | 4 | 4 | 4 |
| 6PPD, phr | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| CBS,[c] phr | 0 | 1.5 | 1.75 | 2.25 | 2.5 | 3 |
| Sulfur, phr | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| $\nu$[d] | 0.23 | 1.61 | 1.71 | 1.80 | 1.91 | 1.95 |

[a] Standard Malaysian rubber number 10.

[b] Parts by weight for hundred parts of rubber.

[c] *N*-Cyclohexyl-2-benzothiazole sulfenamide.

[d] Network chain density ($\times 10^4$ mol cm$^{-3}$): $\nu=\rho/M_c$ ($M_c$ is the average molecular weight between the network crosslinks determined by swelling and $\rho$, equal to 0.93 kg/m$^3$, is the NR density).

### 2.2. Instruments

A homemade stretching machine allowing the symmetric deformation of the sample was used to probe by X-ray the same sample position during stretching at 0.25 min$^{-1}$ strain rate. High resolution is necessary for real-time measurements; thus our in situ wide-angle X-ray scattering (WAXS) study was carried out on the D2AM beam-line of the European Synchrotron Radiation Facility (ESRF). The wavelength of the X-ray is 0.54 Å. The two-dimensional (2D) WAXS patterns were recorded every 10 s by a CCD Camera (Princeton Instrument). During stretching, the thickness and then the absorption of the sample decrease. The in situ measurements of the absorption by photomultiplicators, located ahead and behind the sample, are used to normalize the scattered intensities. It is important to recall that all the measurements have been performed at room temperature. The SIC at low temperature and at fixed draw ratio is not under the scope of this paper.

## 3. Results and discussion

The recipes and cure conditions of vulcanized samples prepared in others studies are different from ours. Therefore network structure could be very different, which could modify their behavior of crystallization under uniaxial deformation and the corresponding mechanical properties. Thus, it is necessary to show that characteristic parameters (crystallite sizes and orientation) of our samples are comparable to those of the literature samples, in order to demonstrate that the effect of physical entanglements in vulcanized natural rubber during strain-induced crystallization is a universal insight.

### 3.1. Change of crystallite parameters depending on network chain density

The crystal structure of natural rubber is orthorhombic and its space group is *Pbca* [25]. Thus, the crystallite orientation along the draw axis is deduced from the intensity distribution of the 002 reflection, which is obtained by the azimuthal scan of the peak. Experimental reflection profile is fitted with

Gaussian function and can be fully characterized by its half-width at half-height ($\psi_{1/2}$). The variation of the azimuthal half-width with draw ratio during the stretching process is shown in Fig. 1. When the crystallites appear, the higher the network chain density, the higher the $\psi_{1/2}$. Upon further elongation, the value of $\psi_{1/2}$ ($\sim 5°$) becomes independent on $\nu$, and indicates an excellent alignment of the crystallites along the stretching direction. Thus, the increase in crosslink density reduces the NR matrix mobility and delays the orientation of the crystallites during the stretching process.

The average crystallite sizes $L_{hkl}$ in the direction normal to the ($hkl$) planes are estimated from the Scherrer equation:

$$L_{hkl} = K\lambda_{\mathrm{w}}/\left(\beta_{1/2}\cos\theta\right) \tag{3}$$

where $\lambda_{\mathrm{w}}$ is the wavelength and $\theta$ is the Bragg angle.

In this study, each peak (200, 120 and 002) is fitted with a Lorentzian function in which the half-width at half-height is $\beta_{1/2}$. According to the parameters chosen for the simulation of experimental peaks, the value selected for $K$ is 0.64. It is worth noting that these variations of the three crystallite dimensions (Fig. 2a–c) are simultaneously measured during the stretching while in literature only one or two crystallite sizes have been recorded during SIC. In the Trabelsi's paper [20], let us recall that only the $L_{002}$ length is measured, while in Tosaka's paper [21], the $L_{200}$ and the $L_{120}$ lengths are measured. It clearly appears that transversal lengths and longitudinal length display different trends. The crystallite dimension $L_{002}$ reaches rapidly a steady value like in Ref. [21]. This is not the case for both $L_{200}$ and $L_{120}$ during stretching that shows an increase with the stretching ratio up to a draw ratio of 5, where they stabilize. Moreover, the sample with the highest crosslink density has always the smallest crystallite dimensions. A possible scenario in agreement with these results is proposed by Tosaka et al. [20]: the crystallites are initiated from oriented nuclei (short chains fully stretched) of length $L_{002}$ and the lateral crystal growth is supplied from the surrounding coiled chains via chain folding. This lateral growth is made more difficult in the case of the most vulcanized samples due to the topological constraints induced by the more numerous crosslinks.

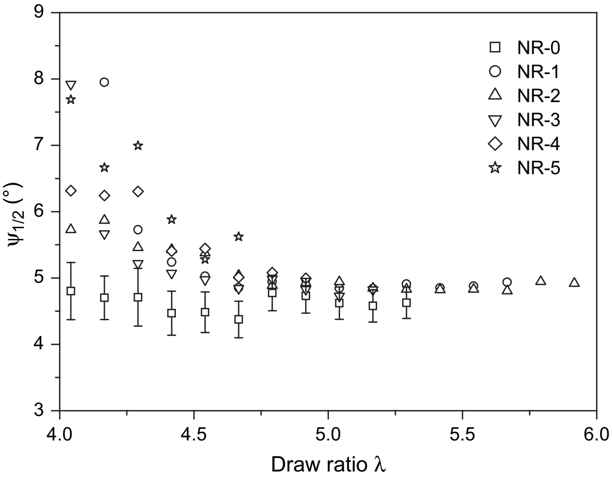

Fig. 1. Crystallite orientation along the stretching direction at $T = 20$ °C, strain rate 0.25 min$^{-1}$ for the six different crosslinked samples.

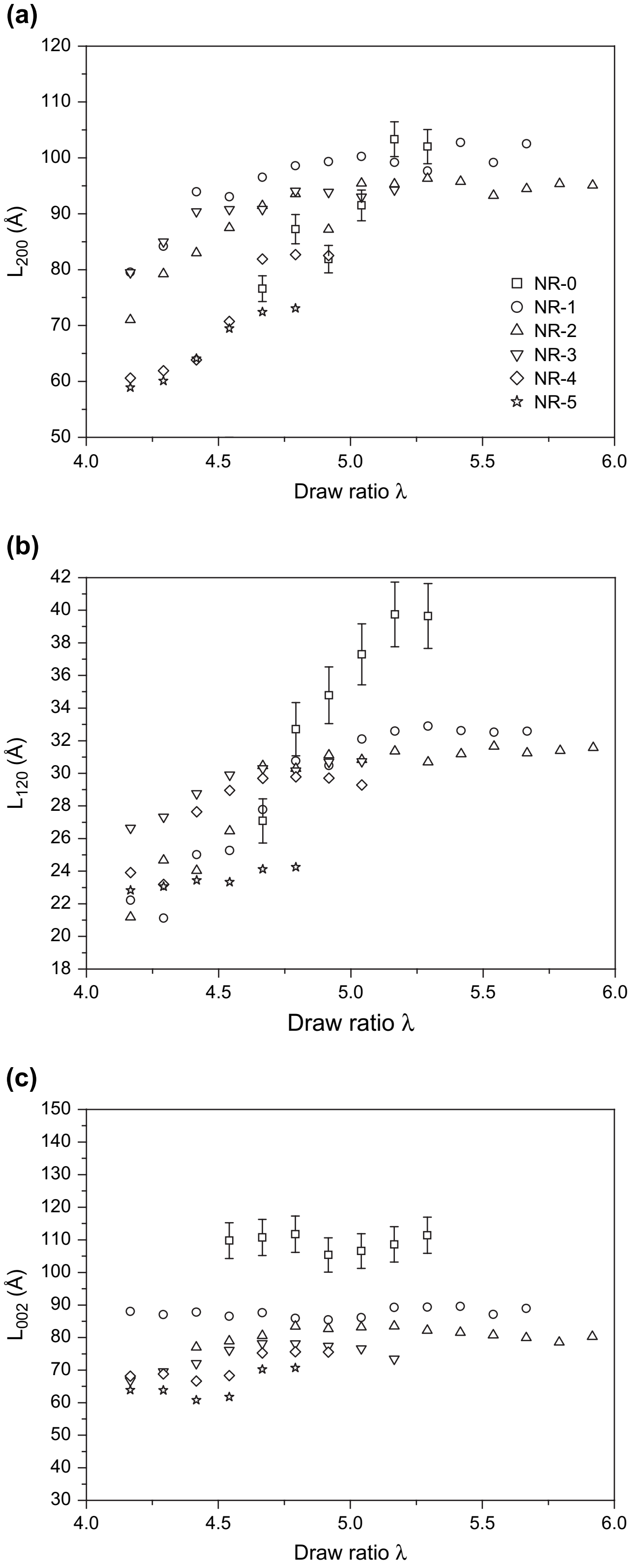

Fig. 2. Variation of crystallite sizes: (a) $L_{200}$, (b) $L_{120}$, and (c) $L_{002}$ during the stretching process for each crosslinked sample.

To go further, we have plotted for all samples (Fig. 3a) the average molecular weight between the network crosslinks ($M_c$) versus the crystallite volume ($V_c$) calculated from the higher crystallite sizes. The $V_c$ evolution as a function of $M_c$ can be divided in two regimes. At high crosslink density ($M_c < 6000\ \mathrm{g\,mol^{-1}}$), a decrease in $M_c$ leads to decrease in the crystallite growth while at weak crosslink density ($M_c > 6000\ \mathrm{g\,mol^{-1}}$) $V_c$ is quasi-independent on $M_c$.

To corroborate these results, data extracted from Tosaka et al. [20] are also plotted in Fig. 3b. Thus, the same behavior is observed. It is interesting to remark that the critical value of $M_c$ ($\sim 6000\ \mathrm{g\,mol^{-1}}$), which separates both regimes of $V_c$ growth, is close to the molecular weight between physical entanglements in natural rubber [26] ($M_e \sim 7000\ \mathrm{g\,mol^{-1}}$). Therefore, $M_e$ appears as a key parameter of the NR SIC. Moreover, this suggests that physical entanglements contribute substantially to the properties of natural rubber when they are weakly crosslinked, this can be explained by the fact that the crosslinking process traps the entanglements.

### 3.2. Singular kinetic crystallization of vulcanized natural rubber

In this work, the crystallinity ($X_c$) is evaluated using the simplified method of Mitchell [7], which has been applied in several studies [21]. The crystallinity values are plotted in Fig. 4a for all samples. Unfortunately our stretching machine does not enable to reach the maximum crystallinity for each sample. However, it is clearly shown that the higher the elongation, the higher the degree of crystallization. Moreover, the onset draw ratio of crystallization is almost independent of the crosslink density.

All the samples being stretched at the same strain rate, a better view of the kinetic crystallization is achieved by plotting the maximum rate of crystallization for each sample $(dX_c/d\lambda)_{max}$ versus the network chain density ($\nu$) (Fig. 4b). A symmetrical trend curve was arbitrarily plotted but the authors are aware that there is no physical argument for such symmetry. But, again our experimental data are compared with data

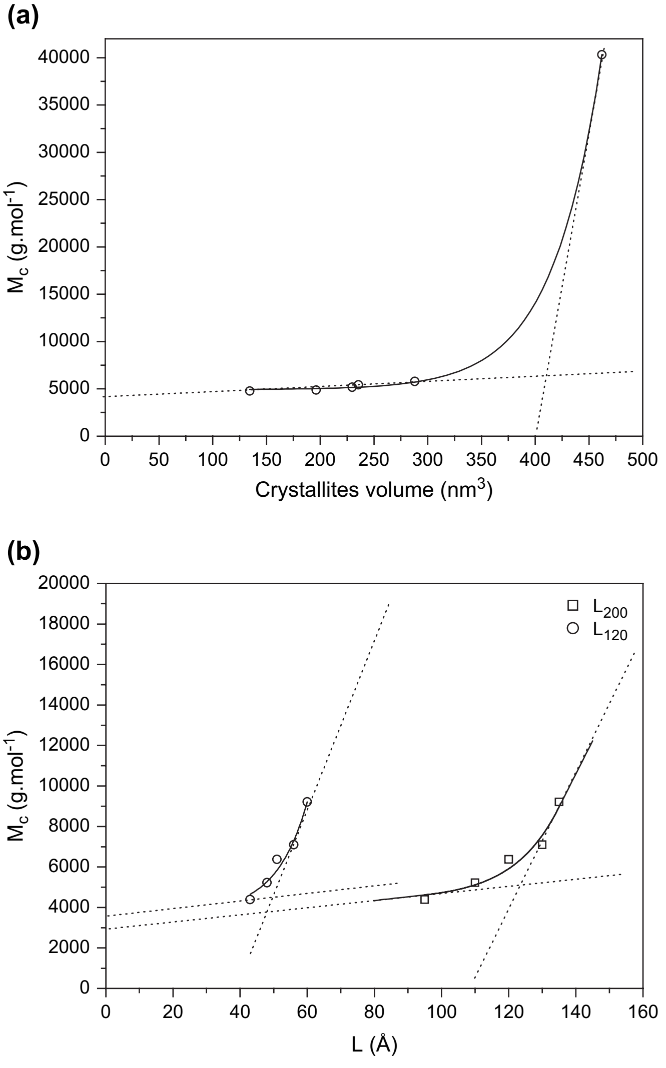

Fig. 3. Variation of average molecular weight between the network crosslinks versus (a) crystallite volume deduced from our experiments, (b) crystallite sizes $L_{200}$ and $L_{120}$ extracted from the data of Tosaka et al. [20].

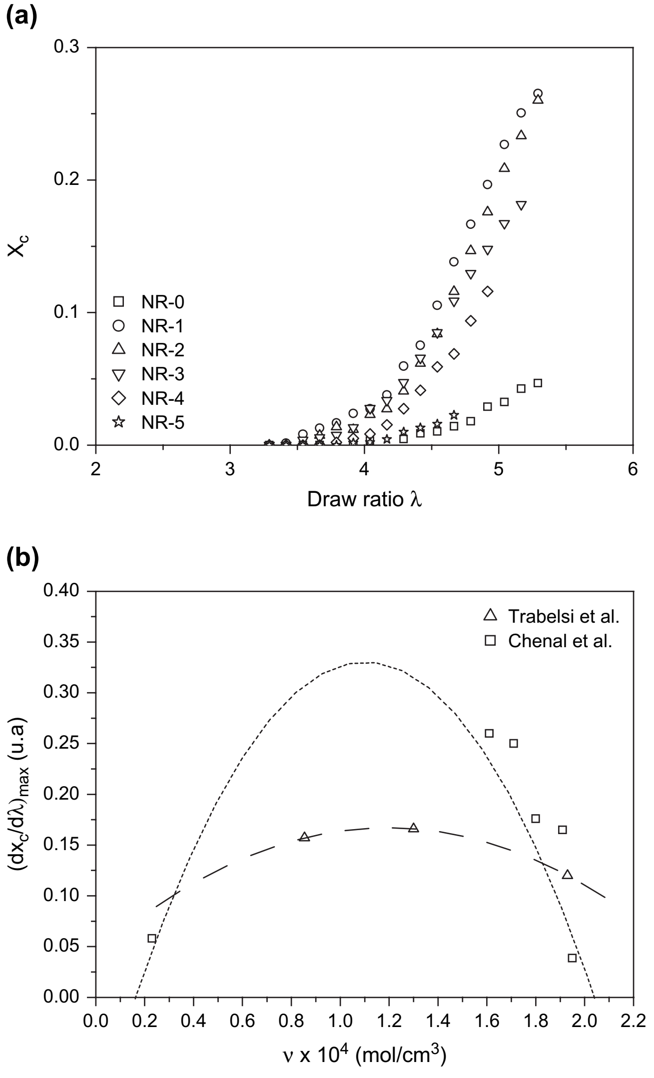

Fig. 4. (a) Effect of network chain densities ($\nu \times 10^4\ \mathrm{mol\,cm^{-3}}$) on crystallization behavior of samples. (b) Variation of $(dX_c/d\lambda)_{max}$ versus $\nu$ deduced from our experiments and extracted from the data of Trabelsi et al. [21].

extracted from the literature: we have calculated the $(dX_c/d\lambda)_{max}$ from the results of Ref. [21]. Like in our experiments, two different regimes, at weak and high crosslink densities, are highlighted: when the crosslink density decreases, the rate of crystallization increases, and then decreases [27]. The maximum crystallization rate seems obtained for an average molecular weight between crosslinks close to $7000\ \mathrm{g\,mol^{-1}}$ ($\nu \sim 1.2 \times 10^{-4}\ \mathrm{mol\,cm^{-3}}$). Thus, the molecular weight between physical entanglements in natural rubber ($M_e$) represents the boundary between both regimes. In addition, this finding is general for NR and seemingly independent on the crosslink network structure of the natural rubber. Indeed, it is supported by the comparison with experimental data of literature obtained with samples for which this structure is likely different from that of our own samples. The nucleation of the crystallite nuclei by stretching and the mechanism of lateral crystal growth previously discussed could explain these two trends. Indeed, when a weakly vulcanized sample is stretched, only few nuclei are created and thicken, consequently the crystallinity cannot quickly increase. On the other hand, when a highly crosslinked sample is stretched, numerous nuclei are formed but, in this case, the degree of vulcanization restricts the chain mobility, which hinders the crystal lateral growth, and explains the slowness of the crystallization rate. To summarise, the crystallization rate of weakly ($M_c < M_e$) and highly crosslinked ($M_c > M_e$) samples are, respectively, governed by the nucleation and the growth of the crystallites during uniaxial deformation.

## 4. Conclusions

The study of crystallite sizes and crystallization rate during stretching of natural rubber as a function of the degree of vulcanization clearly emphasizes the role of physical entanglements in natural rubber of weakly crosslinked samples ($M_c < 7000\ \mathrm{g\,mol^{-1}}$). $M_e$ is therefore a critical parameter to consider when studying SIC. In addition, it appears that the evolution of the crystallite dimensions can be explained by the model of crystal growth during uniaxial deformation proposed by Tosaka.

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[27] Note that similar experiments have been performed on lightly crosslinked filled elastomers and will be published in near future. In that case, the increase of a global crosslink density measured from swelling experiments is due to the fillers. Like with unfilled samples, a maximum in the crystallization kinetic is observed.