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Characteristic time of strain induced crystallization of crosslinked natural rubber

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Real time Wide-Angle X-ray Scattering (WAXS) measurements during cyclic tensile tests at high strain rates (from 8 s^{-1} – 280 s^{-1}) and at room temperature on crosslinked Natural Rubber (NR) are performed thanks to a specific homemade device. From the observed influence of the frequency on the crystallization index at the maximum sample elongation, a characteristic crystallization time is deduced. This is done taking into account the material self-heating during such unusually high strain rates. Two regimes for the dynamic process of strain induced crystallization are evidenced. For the NR tested, the obtained characteristic time is around 20 ms when the material average elongation during the cyclic test is above a critical elongation value λ_c . λ_c is the minimum elongation needed to induce crystallization during low strain rate tensile tests. Moreover, a rapid increase of this characteristic time is found when the average elongation decreases below this critical value.

1. Introduction

In tire applications, the ability of natural rubber (NR) to crystallize under strain is one of the reasons for its supremacy over any other synthetic substitutes. Such an ability explains its good crack growth resistance [1–4]. However crystallization is a dynamic process, which can be *a priori* inhibited if the material is submitted to very high strain rates. All the previous studies on strain induced crystallization (SIC) of natural rubber based systems were carried out in quasi-static conditions or low frequency cyclic tests (1 Hz–10 Hz). However, these testing conditions are not representative of a material use in real conditions and may be misleading for the very basic understanding of the link between crack growth resistance and strain induced crystallization.

From thermal measurements after a rapid loading of the sample, Mitchell [5] has estimated that 50 ms are necessary to promote SIC at 400% elongation. It means that if the rate of deformation is high

enough, even at a deformation ratio above 400%, SIC can be avoided. More recently, crystallization kinetics were studied by WAXS also performed after a rapid loading of the material [6]. However, in such experimental conditions, the lowest measurable characteristic time is limited by the acquisition time of the diffraction pattern. To decrease this time, currently around a few tens of ms, the only experimental solution is to perform stroboscopic WAXS measurement during a cyclic test. Such experiments have already been performed in a pioneering study [7], but at frequencies lower than 10 Hz, which are still too low.

2. Experimental

A new device has been built in our laboratory which enables us to obtain diffraction patterns of samples submitted to cyclic tensile tests with large amplitude and at higher frequency (up to 70 Hz). Thanks to this device (cf. Fig. 1), the diffraction pattern is not averaged over the whole cycle, but is acquired at a chosen elongation ratio. In addition the temperature increase of the material, which can be significant at high frequencies, is also estimated during the test thanks to the measurement of the sample surface temperature with an Infra-Red pyrometer (Microepsilon, CTF3-CF3-C3).

The material of the study is a crosslinked unfilled NR, obtained by sulphur vulcanization of NR gum according to the following recipe: rubber (100 phr), stearic acid (2 phr), ZnO (1.5 phr), 6PPD (3

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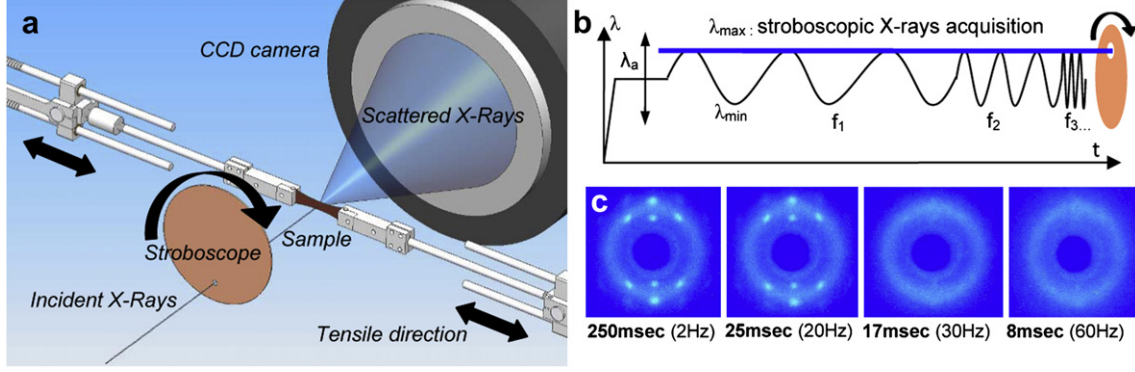


Fig. 1. a. General principle of the in-situ WAXS measurements, b. Schematic representation of the acquisition history, c. WAXS patterns obtained at $\lambda_{\max} = 6.5$ ($\lambda_a = 5.5$).

phr), CBS (1.9 phr), sulphur (1.2 phr). Sample sheets of 0.8 mm thickness were processed by hot pressing at 170 °C during 13 min. The network chain density (ν) estimated from the swelling ratio in toluene and from the Flory–Rehner equation [8] is around 1.4×10^{-4} mol/cm³. In order to avoid microstructure modification during the different mechanical tests, i.e. an uncontrolled Mullins effect, all the samples were stretched four times at the maximum elongation ratio expected during the in-situ cyclic tests ($\lambda = 7$).

The stroboscopic acquisition of the WAXS pattern at the chosen elongation is made so that the time of exposure is 1/44th of the time for a complete cycle. This means that the exposure time needed for an acquisition is 44 times longer than the one needed in quasi-static conditions. The sample's gauge length is 6 mm. The device enables us to dynamically stretch the samples over a fixed amplitude $\Delta\lambda$ ranging from 0 to several hundred per cent, around an average pre-elongation λ_a fixed at the beginning of the experiment. The testing procedure is the following: at first, the sample is stretched (in 1 s) at a fixed pre-elongation λ_a , then, after 5 min, dynamic deformation of amplitude $\Delta\lambda$ is started at a given frequency, acquisition (at λ_{\max} thanks to the stroboscope) is then performed after 1 min, during 220 s.

The WAXS study is carried out on the D2AM beam-line of the European Synchrotron Radiation Facility (ESRF). The X-ray wavelength is 1.54 Å. The two-dimensional (2D) WAXS patterns are recorded by a CCD Camera (Princeton Instrument). The in-situ measurements of the absorption by photomultipliers located ahead and behind the sample, are used to normalize the scattered intensities. Each scattering pattern is then azimuthally integrated over 180°. To extract the total intensity of the phase (amorphous or crystalline), peaks are then integrated over the 2θ Bragg-angle domain [5°, 30°]. The crystallinity index CI is calculated from the following formula [9]:

$$CI = \frac{I_c}{I_c + I_a} \quad (1)$$

where I_c is the diffracted intensity of the crystalline part and I_a the amorphous one.

3. Results and discussion

Prior to high velocity experiments, it is necessary to choose the most relevant λ_a values for the study. This is done thanks to WAXS quasi-static experiment as a function of the elongation (10^{-3} s⁻¹ strain rate). Fig. 2 presents the evolution of the crystallinity index as a function of elongation, at room temperature, which is consistent with literature [10]. The critical elongation λ_c above which crystallization occurs can be estimated around 4.

Hence, the chosen pre-elongation values for the dynamic tests are 4, 4.5, 5, 5.5 and 6. $\Delta\lambda$ is equal to 2, chosen so that it can promote a significant change of crystallinity. With such a value, the maximal available frequency of 70 Hz corresponds to a slewing rate of 280 s⁻¹, much higher than the maximum strain rate reached in previously published works [5–7]. Depending on the pre-elongation value λ_a , the sample will always or partly be in the crystallization domain defined in quasi-static conditions. It must be emphasized that if a cycle is performed at very low frequency, CI should vary between its static values at $\lambda_{\min} = \lambda_a - \Delta\lambda/2$, and $\lambda_{\max} = \lambda_a + \Delta\lambda/2$ respectively.

The experiments are successively performed at frequencies ranging from 2 Hz to 70 Hz. The results presented in Fig. 3 evidence a decrease of the crystallinity index (CI) with the frequency increase, whatever the pre-elongation value. For all λ_a , except $\lambda_a = 4$, the crystallinity index (CI) decreases following two regimes: at first, a slow decrease is observed from a value which is consistent with the one measured in quasi-static conditions; then at a critical frequency, CI rapidly drops to reach a zero or a very low value. This critical frequency increases with λ_a . A residual crystallinity is observed for the highest pre-elongation values ($\lambda_a = 5.5$ and $\lambda_a = 6$).

To address the influence of self-heating under such cyclic conditions, surface temperature of the sample is measured. As shown on Fig. 4, the sample temperature increases with frequency. Moreover, from 40 Hz to 70 Hz, the higher the pre-elongation, the higher the heat dissipated. The crystallinity has been previously measured as a function of temperature under quasi-static conditions, for different fixed elongation values. It was found that CI varies almost linearly with temperature (in the temperature and elongation ranges tested). A negative slope of around $-0.0015/^\circ\text{C}$

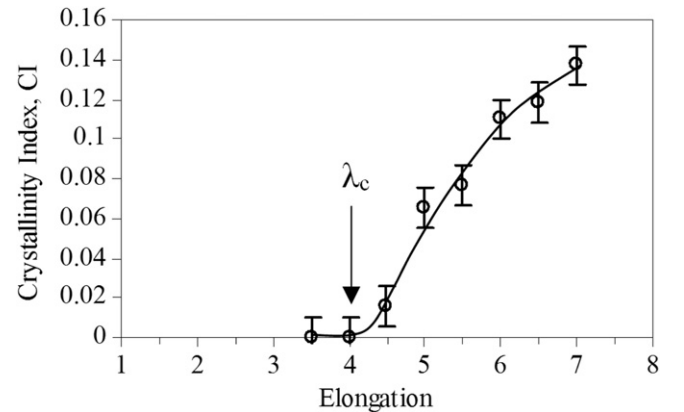


Fig. 2. Crystallinity index versus elongation under quasi-static conditions and at room temperature.

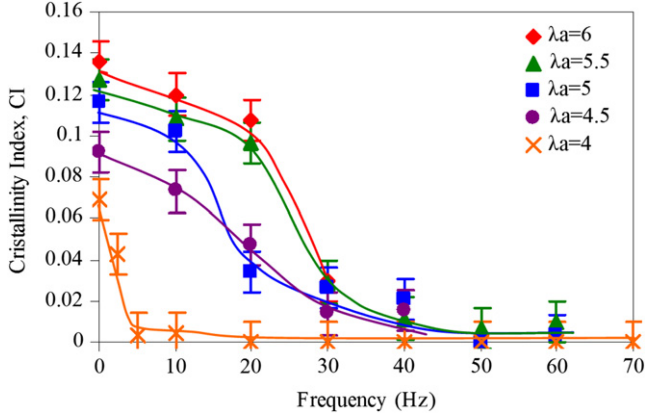


Fig. 3. Crystallinity index during cyclic tensile measured at λ_{\max} , for various pre-elongations and frequencies. Data obtained in quasi-static conditions are added at the corresponding frequency of 0 Hz. Solid lines are included to aid with the readability of the graph.

was estimated, regardless of the elongation value. Such a dependence has already been reported in the literature for very similar materials and experimental conditions [9]. Following the assumption of an equivalence between the heat brought by an external source and the heat brought by the sample self-heating, we can estimate the CI variation associated to temperature changes in our system. For the highest frequency value (70 Hz), the temperature increase could be at the origin of a CI decrease of around 0.04 for cyclic tests at $\lambda_a = 6$ and 0.015 for cyclic tests at $\lambda_a = 4$. Clearly, this cannot explain the abrupt CI drop observed on Fig. 3. This drop must be the consequence of a crystallization process that is slow compared to the strain rate of the test. Thus, a characteristic time for this process can be extracted from our data.

As evidenced by the data of Rault et al. [11], under static conditions, the decrease of CI with an increase of temperature can be seen as the result of an increase of λ_c with temperature. For the same NR, they have found that λ_c increases with a $0.036/^\circ\text{C}$ slope. A consequence of such an increase is that the elongation domain, in which SIC can occur, decreases. Thus, in Fig. 5, the CI values are re-plotted as a function of a normalized time ($t(\lambda_{\max}) - t(\lambda_c)$, the time during which the sample is elongated from λ_c (deduced from Rault's data) up to λ_{\max} , within one cycle. The SIC data previously obtained under quasi-static conditions are added to the graph. They confirm that the CI values at low frequency, i.e. long time, tend

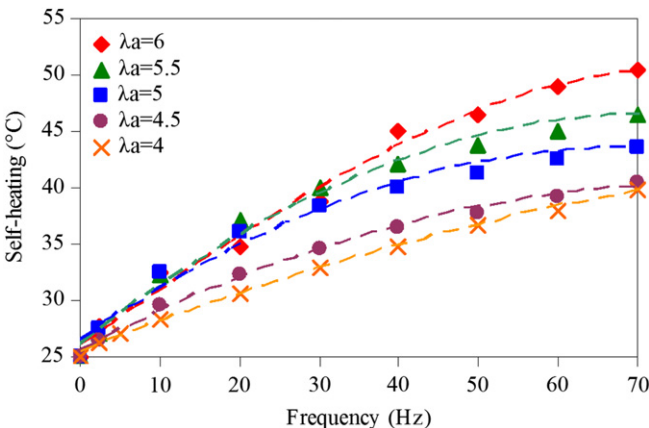


Fig. 4. Surface temperature of the sample as a function of the frequency.

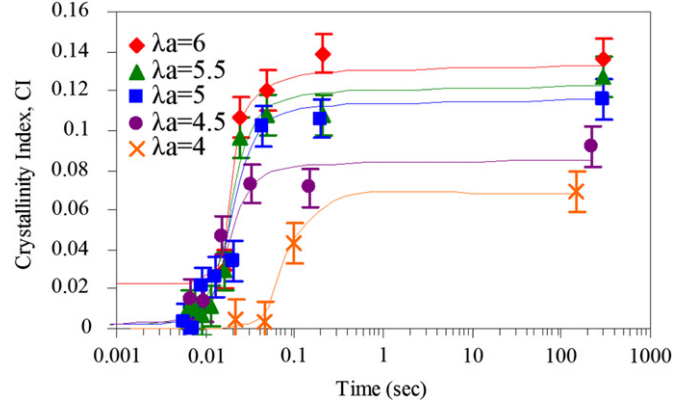


Fig. 5. Crystallinity index versus normalized time for various pre-elongations. Data obtained in quasi-static conditions are added at the corresponding times. Curves fitting (equation (2)) are added in solid lines.

toward the CI values under quasi-static conditions. As shown on the plot, above several hundred milliseconds, the maximum crystallinity is reached, for pre-elongations varying from $\lambda_a = 4.5$ to $\lambda_a = 6$. At $\lambda_a = 4$ a retardation of the induction time of crystallization is observed. A fit of the data with a stretched exponential function is proposed:

$$CI = CI(\lambda_{\min}) + (CI(\lambda_{\max}) - CI(\lambda_{\min})) \left(1 - \exp\left(-\left(\frac{t}{\tau}\right)^n\right) \right) \quad (2)$$

In such an equation, τ corresponds to a characteristic time of the crystallization phenomenon, while n is related to the distribution of this characteristic time. $CI(\lambda_{\min})$ and $CI(\lambda_{\max})$ are deduced from CI measurements under quasi-static conditions, corrected for the temperature effect. n is found equal to $3 (\pm 0.5)$ regardless of the pre-elongation. As shown on Fig. 5, the fitting law is in good agreement with the data. A residual crystallinity should remain at very low times (high frequencies) for the test at $\lambda_a = 6$, as indicated by the fit. Its expected value should be close to the CI found at λ_{\min} during the quasi-static elongation but at a temperature corresponding to the one reached during the cyclic test. However, the experimental value is lower. This might be explained by a slight underestimation of the self-heating phenomenon.

Fig. 6 plots the deduced characteristic time. The characteristic time is found to be almost constant for pre-elongation values above the critical elongation $\lambda_c = 4$. It is around 20 ms. This value is two times lower than the one found by Mitchell [5] measured using

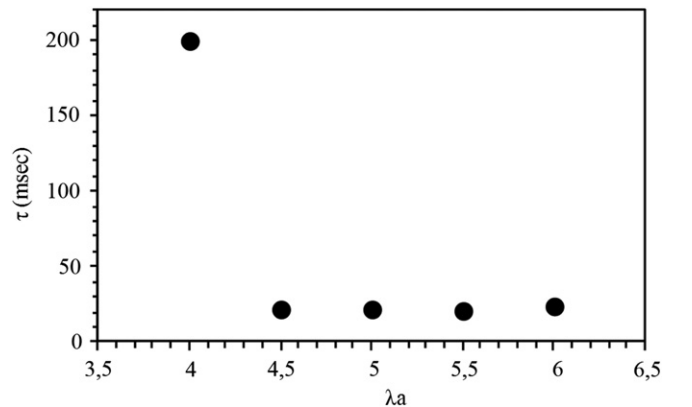


Fig. 6. Crystallization characteristic time versus the average elongation during cyclic tests.

a thermal analysis at an elongation of $\lambda = 6.5$. However, his estimation of 50 ms includes the time needed to deform the sample up to λ_c . Subtracting this time, both values are found to be in good agreement. The corrected characteristic time of crystallization for the unique test at $\lambda_a = 4$ is 10 times larger than the characteristic time found for higher λ_a . Such a result is expected since it is known that below a critical elongation, NR crystallization is a very slow process whose kinetics is related to the one observed without strain. The increase of τ with a decrease of the elongation is due to the transition from the rapid SIC process to the slow thermally induced crystallization process [12].

4. Conclusion

We have presented here a unique set of experiments which provide the crystallinity index of NR at the maximum elongation during high velocity tensile cyclic tests. Results confirm that SIC is a dynamic process with two different regimes depending on the elongation level: one regime with a slow crystallization kinetics, and another one in which molecular orientation induced by the elongation is sufficiently high to promote a fast process. In the second regime, the crystallization characteristic time – defined here as the time needed to crystallize, once the sample is elongated above the critical elongation for SIC under quasi-static conditions – is independent of the average elongation of the cyclic test. It is estimated at around 20 ms for the tested NR.

The existence of the first regime should be confirmed by experiments with different strain amplitudes. Moreover, thanks to work in progress, CI obtained here at the maximum elongation value will be completed by CI along the complete cycle. This will be

done on different materials to study the influence of the network chain density (ν) or the fillers as well [13]. These data will be of a major importance in the construction of a physical model predicting the kinetics of the strain induced crystallization for natural rubber compounds.

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