Crystallinity and multiaxiality around a crack tip in natural rubber investigated by synchrotron wide-angle x-ray diffraction during fatigue tests

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ABSTRACT. *In tire industry, fatigue crack propagation in elastomers is studied to improve the service life of products. Natural rubber (NR) is a key compound in tires, because of its remarkable mechanical properties and more particularly its excellent resistance to fatigue crack growth as compared to synthetic rubbers. To explain these good properties, the literature often mentions the strain-induced crystallization (SIC) phenomenon that takes place at the tip of fatigue cracks in NR. In this study, an original experimental set-up that couples synchrotron radiation with a homemade fatigue machine has been developed to study SIC and multiaxiality around fatigue cracks in NR. During uninterrupted fatigue tests, recording of wide-angle X-ray diffraction patterns is performed in the crack tip region. It provides a 2D spatial distribution of either crystallinity or principal strain directions. The influence of loading conditions (maximum elongation and non-relaxing loading conditions) on the size of the crystallized zone is particularly investigated, in order to relate it to the fatigue crack propagation rates. Finally, the multiaxiality results, in terms of principal strain directions, give good correlation with results obtained by digital image correlation and finite element analysis.*

INTRODUCTION

The outstanding mechanical behaviour of natural rubber (NR), notably in the case of fatigue loading conditions [1-3] makes this material an ideal choice to meet the demands of many practical applications such as tires. Its ability to crystallize when stretched (strain-induced crystallization, SIC), in particular at the crack tip because of large strain in this region, can explain these good properties in fatigue: the crystallized area in front of the crack act as an obstacle for crack advance.

In this study, classical fatigue crack growth rates were first performed on a filled NR using "pure shear" specimens, and corroborate the results obtained in the past [4,5]: the very good resistance to fatigue crack growth of NR as compared with polyisoprene synthetic rubber (IR), especially for large strain and in the case of non-relaxing loading conditions. Simultaneously, original in-situ fatigue tests where conducted with almost the same loading conditions at the French national synchrotron facility SOLEIL, to determine the crystallized zone in real time by "mapping" the region of the crack tip with wide-angle X-ray diffraction (WAXD) measurements. This experimental method allows to determine the distribution of crystallinity and principal strain directions around a fatigue crack tip during uninterrupted fatigue tests.

The aim of the study is to relate fatigue crack propagation rates in NR to the characteristics of the crystallized zone around the crack tip, during in-situ experiments, in order to explain the good macroscopic fatigue behaviour of this material.

EXPERIMENTAL METHOD

Material and sample

The material is a natural rubber (NR) filled with 50 parts per hundred rubber (phr) of N347 carbon black (CB N347). Vulcanization is carried out with 1.6 phr of sulfur, where CBS acts as an accelerator. Each blend also contains 2.5 phr of ZnO and stearic acid. 6PPD is used as an antioxidant. As a comparison, we used a synthetic polyispoprene rubber (IR) - filled with the same amounts of CB N347, sulfur and additives – in which the strain-induced crystallization is considerably reduced compared to NR. The samples are "pure shear" specimens, prepared and cured by Michelin; this type of samples, also referred to as "planar tension" specimens, is commonly used for fatigue crack growth measurements. They are 157 mm long, 13 mm high and 2 mm thick.

Crack growth rate experiments

Theories applicable to the analysis of fatigue crack propagation measurements are based on the Rivlin and Thomas energy balance approach [7]. These authors showed that the criterion for crack growth is satisfied when the energy release rate G in the sample exceeds the fracture energy, which is an intrinsic parameter of the material. They demonstrated that for a pure shear test specimen, the following equation can be written:

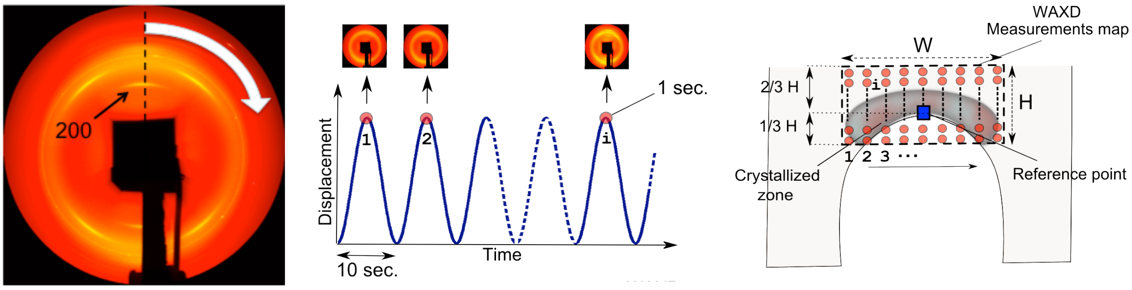
$$G = W_0 l_0 \tag{1}$$

where G is the energy release rate, W_0 is the strain energy density (determined experimentally by the area under the stress-strain curve of an uncracked pure shear specimen) and l_0 the initial height of the specimen (13 mm here).

The tests are performed at Michelin (Clermont-Ferrand, France) on a MTS servo-hydraulic tensile machine. Once clamped, the sample is first cycled during 300 cycles at a global stretch ratio ($\lambda = l / l_0$) of 1.92 and at a frequency of 2 Hz in order to lower the residual stretch due to viscous and Mullins effects. Experiments with uncracked samples are conducted at different global stretch ratios from 1.08 to 1.92 to obtain the strain energy density W_0 at each strain level. Then, we insert three notches into the sample: two at edges (2 cm-long) and one in the middle of the test piece (3 cm-long). A short preliminary cyclic test is then performed to blunt the crack tips and to transform the cutter incisions into fatigue cracks. This procedure is applied before each fatigue crack growth test. Finally, fatigue crack growth experiments are conducted at 2 Hz and for different global stretch ratios, during which we measure the fatigue crack growth rate per cycle (dc/dn in m/cycle), mean of the values measured for the four crack tips, as a function of the energy release rate; the conventional way to represent the results is a log-log (dc/dn) vs. G plot.

In-situ WAXD experiments

The in-situ WAXD experiments are conducted with a homemade fatigue machine where two electrical actuators supply a sinusoidal waveform to impose prescribed displacement to the sample. Their loading capacity is 500 N and their stroke is 60 mm. This apparatus is mounted on the DiffAbs beamline at the French national synchrotron facility SOLEIL (proposal 20110204). The wavelength is 0.1305 nm and the beam size is approximately 300 µm × 200 µm (full width at half maximum height). The two-dimensional WAXD patterns are recorded by a MAR CCD X-ray detector with an exposure time of 1 s (see the typical pattern in Figure 1a). The intense transmitted beam is blocked by a Pb beamstop; a PIN photodiode measures the transmitted intensity through the sample in order to accurately estimate the thickness of the sample in the area exposed to the X-ray beam and also to be able to locate the crack tip. The synchronization of fatigue cycles and WAXD measurements is illustrated in Figures 1b and 1c.



(a) (b) (c)

Figure 1: WAXD measurements during fatigue tests: (a) typical WAXD pattern, the rotation of the reflections (symbolized by the arrow) can be related to a rotation of the principal strain directions, (b) each diffraction pattern is acquired at the maximum displacement of each cycle, (c) between two measurements, the sample moves with respect to the beam to reach the next measurement point on the prescribed map.

After almost the same sample preparation as the one described previously for the fatigue crack propagation rates measurements (except that we introduce only one notch on the edge of the sample), the experiment starts. It consists in mapping the neighbourhood of the crack tip with WAXD measurements without stopping cyclic loading. During data recording, cyclic loading continues. Each diffraction pattern is recorded at the maximum displacement of each cycle as shown in Fig. 1b. Considering that the exposure time is 1 s, a trigger is sent by the stretching machine to the beamline 0.5 s before each maximum displacement. Between two cycles, the sample moves to another position to acquire the next WAXD pattern defined in the map (see Fig. 1c). In order to permit the 1 s recording at the maximum stretch of each cycle and the displacement of the sample between two successive measurements, it is necessary to impose a low loading frequency, i.e. 0.1 Hz. Each map contains 90 diffraction patterns (9×10 points). It was considered that during those 90 cycles, the growth of the crack is negligible as compared to the map size in the fatigue crack propagation direction; this assumption has been verified *a posteriori* from the measurement of the crack length after each loading sequence. More details about the set-up are given in Rublon *et al.* [8].

After a preliminary correction taking into account the change in both sample thickness due to extension and intensity of the incident beam, we determine the total diffracted intensity along one radius of the pattern, I_{total} at the azimuthal angle corresponding to the (200) reflection arc, from which we can identify an amorphous phase and a crystallized phase. Then, these data are fitted by a series of Pearson VII functions. Finally, we define a coarse index of crystallinity as follow:

$$\chi = \frac{I_{200}}{I_{200} + I_{amorphous}} \tag{2}$$

where I_{200} is the maximum intensity of the (200) Bragg reflection and $I_{\text{amorphous}}$ is the intensity of the amorphous peak.

Once the mapping is recorded, a post-processing analysis leads to the plot of “iso-χ” curves around the crack tip, which permits to determine the size and the shape of the crystallized zone. Taking into account the value of the transmitted intensity as a measurement of thickness, we can also calculate the crystallized volume at crack tip.

These maps also allow the investigation of multiaxiality around the crack tip. Indeed, the rotation of WAXD reflections can be directly linked to the rotation of the principal strain directions (see Fig. 1a). Moreover, in a previous study [9] we have shown that the disorientation of the crystallites (given by the half width at half maximum of the peak on the azimuthal profile of the reflection) can be related to the stretch biaxiality factor B ($B = \varepsilon_2 / \varepsilon_1$, where ε_1 and ε_2 are the two principal true strains).

Digital Image Correlation (DIC)

Thanks to DIC, it is possible to obtain the displacement fields and the strain fields around fatigue crack tips in the stretched state. It also provides the principal strain directions. In the present study, the commercial DIC software DaVis (edited by LaVision) is used. In order to get a sufficient contrast on the surface of the samples, a speckle pattern was created by using a white talcum powder. The pixel size was approximately 4 microns.

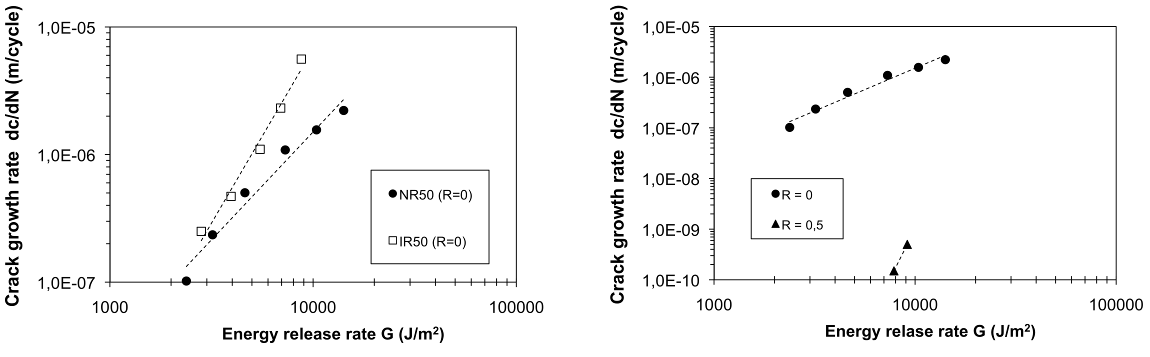
Finite Element Analysis

FEA is used to compute the map of principal strain directions that can be compared to WAXD and DIC results. The ABAQUS implicit software is used for that purpose. The constitutive equation for the material is the incompressible hyperelastic neo-Hookean model. Accounting for symmetries of the problem and in order to reduce calculation time, only one half of the crack tip was considered. Approximately 10.000 linear Q4 elements were used for the simulation.

RESULTS AND DISCUSSION

Fatigue crack growth rates

First, the fatigue crack growth behaviour of the natural rubber (NR) filled with 50 phr of carbon black is compared with the one of the synthetic isoprene rubber (IR) filled with the same amount of carbon black. The crack growth rates results are presented in Figure 2a. We can notice that for a given energy release rate, the crack growth rate is lower for the filled NR, and this is especially emphasized for high values of energy release rate. Those results are consistent with the literature: as an example, Lake [4] obtained similar results by comparing a NR with a SBR (styrene-butadiene rubber), which is completely amorphous, even at large stretch ratios.



(a) (b)

Figure 2: Fatigue crack growth rates results: (a) NR50 and IR50, (b) NR50 for $R = 0$ and $R = 0.5$.

The influence of the mechanical loading and in particular non-relaxing conditions (when the rubber sample is not fully unstretched during the fatigue cycle) is also studied. We can define a load ratio R as follows:

$$R = \frac{\lambda_{\min} - 1}{\lambda_{\max} - 1} \quad (3)$$

where λ_{min} and λ_{max} are respectively the minimum and the maximum stretch ratios reached during the fatigue cycle. Then, non-fully unloading cyclic tension leads to a positive load ratio $R > 0$. Figure 2b provides the crack growth rates results on a filled NR (50 phr of CB) for $R = 0$ and $R = 0.5$. For $R = 0.5$, the fatigue crack growth rate is considerably reduced (0.15 nm/cycle for $G = 7850$ J/m^2), similarly to the results found by other authors [10,11].

In-situ WAXD experiments results

Figure 3 presents "iso-χ" curves at crack tip of the filled NR, for four different values of energy release rate. It demonstrates that the global energy release rate during cyclic loading has a noteworthy influence on the size of the crystallized zone at crack tip. Figure 4 quantifies this result, with a plot of the volume of the crystallized zone as a function of energy release rate.

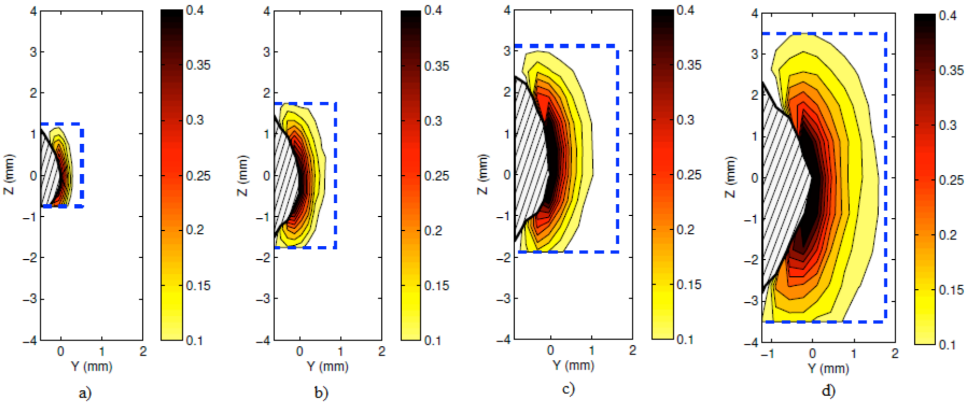


Figure 3: Iso-crystallinity curves at crack tip in NR50 samples for four different values of energy release rate: a) $G = 4620$ J/m^2, b) $G = 7290$ J/m^2, c) $G = 10390$ J/m^2, d) $G = 14140$ J/m^2.

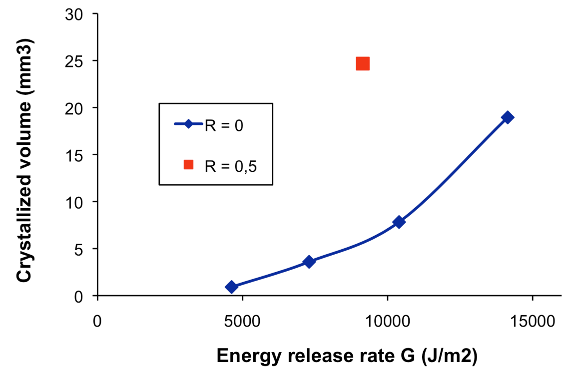
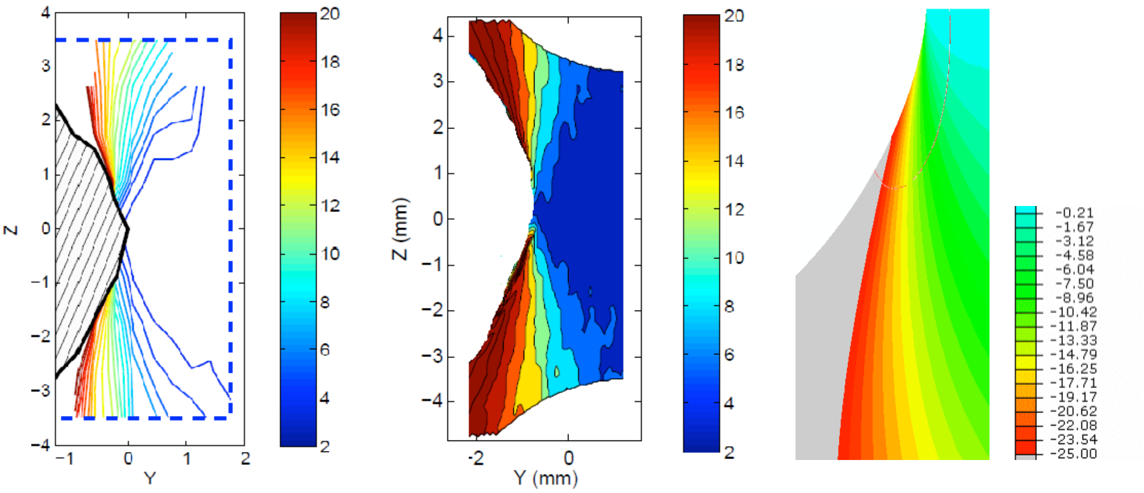


Figure 4: Plot of the volume of the crystallized zone at crack tip as a function of G.

Figure 4 also illustrates the impact of the load ratio R on the volume of this crystallized zone. We notice the outstanding effect of a positive load ratio on SIC: for $R = 0.5$, the crystallized volume is highly increased compared to $R = 0$.

Finally, Figure 5a shows the rotation (in degrees) of the principal strain directions obtained from the WAXD pattern. In the upper and the lower region of the crack tip, this rotation reaches 20°. This result is in a good agreement with those determined by DIC (see Fig. 5b) and FEA (see Fig. 5c).



(a) (b) (c)

Figure 5: rotation of the principal strain directions (in degrees) for G =14140 J/m^2 obtained by: (a) WAXD, (b) DIC, (c) FEA.

Discussion

First, we can draw a parallel between fatigue crack growth measurements and WAXD results to evaluate the impact of the crystallized zone in front of the crack tip on the macroscopic crack propagation rates:

- The results of crack growth measurements shown in Fig. 2a and the evolution of the crystallized volume at crack tip with energy release rate plotted in Fig. 4 are compared. On the one hand, the resistance to fatigue crack growth in NR is greater than the one in IR, especially for high values of G. On the other hand, the volume of the crystallized zone at crack tip increases with G. Recalling that IR almost does not crystallize when stretched, it proves that SIC slows down crack growth. To sum up: the higher the energy release rate, the larger the crystallized zone at crack tip and the lower the crack growth rate.
- An increase of the load ratio R from 0 to 0.5 leads to a high decrease of the crack growth rates (see Fig. 2b), and simultaneously it leads to a larger crystallized volume (see Fig. 4). Once again, the larger the crystallized zone at crack tip and the lower the fatigue crack growth rate.

Second, the WAXD technique appears to be a reliable tool to study multiaxiality in strain-crystallizing polymers such as NR, since it allows to measure the principal strain directions. Beyond the present study, it may be noted that WAXD patterns can also be correlated with the stretch biaxiality factor B in the case of planar biaxial tests in which B has a value between 0 and 1 ($B = 0$ corresponds to planar tension and $B = 1$ corresponds to equibiaxial tension) [9].

CONCLUSIONS

Thanks to an original experimental set-up, which consists in the association of a homemade fatigue machine with synchrotron WAXD, we measured the distribution of crystallinity at fatigue crack tip in a filled natural rubber during fatigue tests. The comparison of these results with fatigue crack growth rates permits to emphasize the influence of the crystallized zone on crack propagation in filled elastomers, and leads to an explanation of the remarkable resistance to fatigue crack growth of natural rubber.

The multiaxiality, in terms of principal strain directions, can also be plotted around the crack tip by using the rotation of the WAXD reflections.

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