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Strain-induced crystallization of carbon black-filled natural rubber during fatigue measured by in situ synchrotron X-ray diffraction

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ABSTRACT

Natural rubber (NR) exhibits great fatigue properties which are usually explained by its ability to crystallize under strain. Nevertheless, strain-induced crystallization of NR in fatigue has never been investigated. We perform original in situ fatigue tests during which the degree of crystallinity, and the number and volume of crystallites are measured by synchrotron wide angle X-ray diffraction. For all loading conditions, the number of crystallites is constant. The evolution of their volume depends on the minimum stretch ratio achieved at each cycle. The results show that cyclic loading conditions modify the macromolecular structure of the material, in particular of its amorphous phase.

1. Introduction

Natural rubber (NR, cis-1,4-polyisoprene) vulcanizates have the ability to crystallize under strain at room temperature. Strain-induced crystallization (SIC) of NR has been discovered by Katz in 1925 with the help of X-ray diffraction [1]. This technique has since permitted to obtain the crystallographic data of NR [2,3], to exhibit the existence of stretch ratio thresholds of crystallization and melting of the crystallites [4,5], to relate SIC to the mechanical hysteresis of the stress–strain response [6,4], and to put into light the effect of fillers such as carbon black [7]. For more details on the use of X-ray diffraction for SIC in NR, the reader can refer to the recent review of Huneau [8].

The great majority of the studies on SIC of NR focus on uniaxial quasi-static cycles and relaxation tests. Here, the expression "quasi-static" stands for low strain rates compared to crystallization rate. But NR is often used in engineering applications for its great properties in fatigue such as long fatigue life, even at large strain [9–11]. The mechanical properties of NR have been thoroughly studied [12–14]; but studies on the evolution of SIC during fatigue testing of NR are very rare, though it is often accepted that the remarkable fatigue properties are closely related to SIC. This is mainly because the typical frequencies of fatigue tests (1 Hz or more) are not compatible with the long time acquisition required by X-ray diffraction measurements (from a few seconds to an hour). Nevertheless, Kawai succeeded in measuring SIC during fatigue by using a stroboscopic technique to accumulate the weak intensity of the diffracted beam over a large number of cycles [15]. He studied only one set of loading conditions for which both minimum and maximum stretch ratios achieved are 3.5 and 4.5, respectively. In this case, he observed an increase in the degree of crystallinity with the number of cycles. Furthermore, Rouvière et al. recently measured the evolution of crystallinity along fatigue life for different uniaxial loading conditions by performing interrupted fatigue tests [16]. Nevertheless, this method does not allow to separate SIC induced by fatigue from SIC induced by constant stretching during the 45-min acquisition of the X-ray diffractogram.

The aim of the present study is to measure the evolution of the strain-induced crystallinity during fatigue of carbon black-filled NR and to determine the mechanisms that drive this evolution. For this purpose, we developed an innovative experimental method which allows to measure SIC in real time during a fatigue experiment. In-situ wide angle X-ray diffraction (WAXD) measurements are performed with a very short exposure time achieved thanks to synchrotron radiation. Thanks to the results obtained, we highlight the key role of the melting stretch ratio and we propose two mechanisms of SIC in NR fatigue depending on loading conditions.

2. Experimental method

2.1. Material and samples

The material used in this study is a carbon black-filled natural rubber, cross-linked with 1.2 phr (per hundred of rubber) of sulphur and CBS accelerator. It also contains ZnO (5 phr) and stearic acid (2 phr) and is filled with 50 phr of N330 carbon black. The

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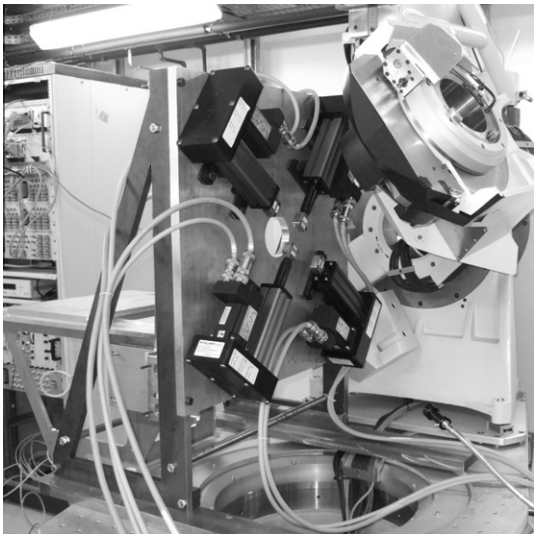

Fig. 1. Uniaxial fatigue machine in DiffAbs beamline.

samples are classical flat dumbbell specimen with a 10 mm gauge length and a 2×4 mm^2 section.

2.2. Testing machine

Experiments have been conducted with the homemade stretching machine shown in Fig. 1. It is composed of four electrical actuators, but only two opposite ones were used in this study. Their movements are synchronized, in order to keep the centre of the specimen fixed during the fatigue tests. Their loading capacity is ±500 N and their stroke is 75 mm each.

2.3. Procedures

2.3.1. Accommodation

In order to lower the residual stretch ratio of the sample due to Mullins effect and viscoelasticity, all the samples are pre-cycled just before testing: 5 cycles at a higher strain level than during fatigue tests for Mullins effect (maximum displacement of the clamps is 45 mm, except for fatigue test No. 4 described hereafter, before which the maximum displacement is 50 mm); additional 50 cycles for viscous effect (at the same displacements of the clamps than during the fatigue tests).

2.3.2. Preliminary quasi-static experiment

A quasi-static test is beforehand conducted to determine (i) the relation between the stretch ratio λ and the displacements of clamps which will be used in all other experiments and (ii) the stretch ratio thresholds of crystallization λ_C and melting λ_M of the material at room temperature and low strain rate (similarly as in [17]). During these experiments, the sample is elongated of 90 mm at the speed 0.012 mm s^{-1}, the total duration of the cycle being about 2 h. A scattering pattern is recorded every 98 s. The local stretch ratio λ at the centre of the sample is *a posteriori* measured continuously by video extensometry. Finally, this experiment is a quasi-static test from $\lambda = 1$ to $\lambda = 4$ at $\dot{\lambda} = 1.1 \times 10^{-3}$ s^{-1}, and it leads to $\lambda_C = 2.36$ on the loading path and $\lambda_M = 1.80$ on the unloading path.

2.3.3. Fatigue experiments

The fatigue tests are conducted by prescribing triangular displacements of the clamps. They are performed at conventional frequencies for rubber, i.e. around 1 Hz, which limit self-heating to about 3° only [18]. As the minimum exposure time to record a diffraction pattern is 1 s (about the duration of a full cycle), it is not possible to record the diffraction patterns while the actuators are in motion. Therefore, to measure the evolution of SIC during fatigue testing, the tests are paused at maximum displacement every 250 cycles to record a complete diffraction pattern. As the fatigue machine is triggered by the monitoring system of the X-ray beam, the duration of the pause is less than 1.5 s. The first scattering pattern is recorded during the first cycle of the test.

Four different fatigue tests have been performed. Table 1 presents the corresponding minimum and maximum displacements of the clamps d_{min} and d_{max}, the corresponding minimum and maximum stretch ratios λ_{min} and λ_{max} and the loading frequency f. To summarize the fatigue tests, Fig. 2 presents the loading conditions in terms of stretch ratios, and compares them to the thresholds of crystallization λ_C and melting λ_M (measured during the preliminary experiment).

Table 1
Fatigue loading conditions.

Test No.	d_{min} (mm)	d_{max} (mm)	λ_{min}	λ_{max}	f (Hz)
1	0	20	1.00	2.90	2.5
2	4	33.2	1.44	3.66	0.8
3	9.3	33.2	1.98	3.66	1
4	25	45	3.18	4.02	1.5

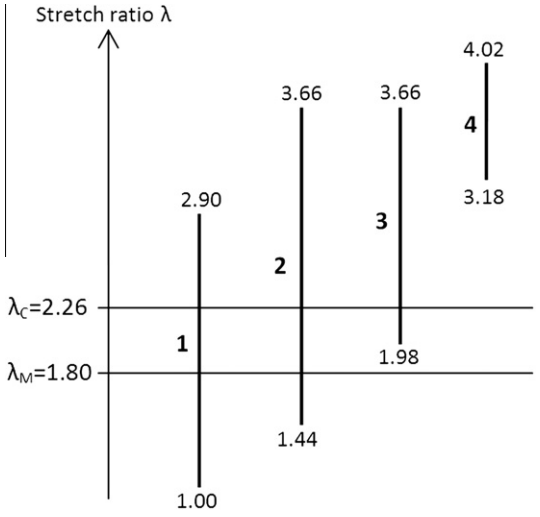

Fig. 2. Minimum and maximum stretch ratios reached during fatigue tests and threshold stretch ratios for crystallization λ_C and melting λ_M. Bold numbers stand for the fatigue tests numbers.

2.3.4. Relaxation experiments

The relaxation tests consist in quickly stretching a sample to a given stretch ratio and then maintaining the same stretch level. They last 28 min and scattering patterns are recorded every 2 min. Table 2 presents the stretch ratios at which the three relaxation experiments are conducted. The stretch rate $\dot{\lambda}$ of the loading path is between 5.6 and 6.0 for the three tests.

Table 2
Relaxation loading conditions.

Test No.	λ
5	2.41
6	2.90
7	3.66