Fatigue Reinforcement in Natural Rubber containing Carbon Black Fillers

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Abstract: Fatigue tests carried out in natural rubber containing carbon black fillers (NR-CB) show a drastic increase of lifetime when the mean fatigue stress is increased. This effect is often attributed to crystallisation which appears at high strain levels.

The main objective of this work is to understand the combined effects of fatigue damage and crystallisation in the case of NR-CB. Crystallisation is characterized using in-situ X-rays diffraction analysis on both fatigue specimens and monotonic tensile specimens. The effect of the fatigue loading history and stress relaxation on crystallisation is studied. Effect of temperature is also investigated. It is shown that crystallisation increases with strain level and relaxation time.

During fatigue, crystallisation tends to decrease but never completely disappears. The presence of crystallites improves the lifetime of the rubber.

1 Introduction

During elongation of natural rubber, the macromolecular chains slip the one on the others and become oriented. This creates an order in the initially amorphous rubber. Chains become increasingly close and crystallisation occurs. Strain-induced crystallites toughen rubber: links between molecular chains limit the intermolecular slip and can stop propagation of cracks nucleated at inclusions (carbon blacks and ZnO). Newly formed crystallites can be characterized using WAXS (Wide Angle X-ray Scattering) and the quantity of crystalline phase can be estimated using crystallisation indexes.

In this study, the role of mechanical loading on crystallisation of NR-CB is investigated. The main objective is to understand the drastic increase of the number of cycles to failure observed when the mean fatigue stress is increased as shown on a Haigh's diagram (Fig. 1). This reinforcement is assumed to be related to the presence of crystallites which act as micro-cracks arrestors.

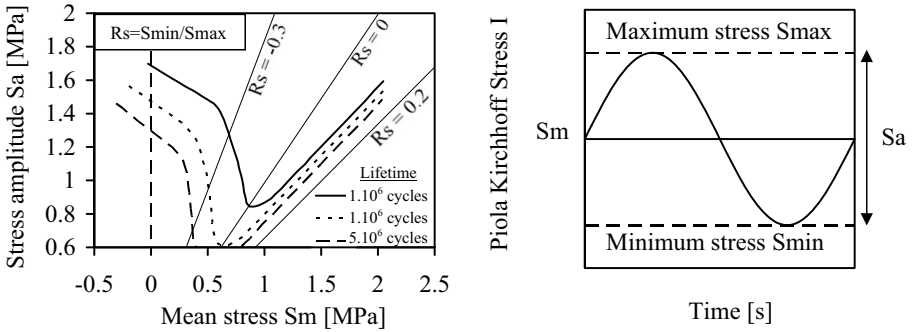

Figure 1: Haigh's diagram in traction for Natural Rubber, [1].

This paper is organized as follows: first the X-rays diffraction technique and the method used to quantify crystallisation are detailed. Second, experiments including monotonic tensile, stress relaxation and fatigue tests with different mean strain are presented. The influence of temperature on crystallisation is also studied by heating pre-strained samples. The evolution of the crystallisation index χ is examined and discussed in each case.

2 Characterization of crystallisation

2.1 Experimental procedure

WAXS gives information in terms of orientation and quantification of crystalline phase and enables to distinguish the amorphous phase from crystallites. Thin straps with a thickness of 2 mm and a width of 10 mm are stretched at a nominal strain rate of $10^{-3}s^{-1}$ then maintained in tension at the maximum deformation. In order to have the same experimental conditions, samples undergo one hour relaxation before using WAXS. Sequential tests in reflexion were performed to study the crystalline phase (see Fig. 2). These tests were carried out using a SIEMENS D500 diffractometer.

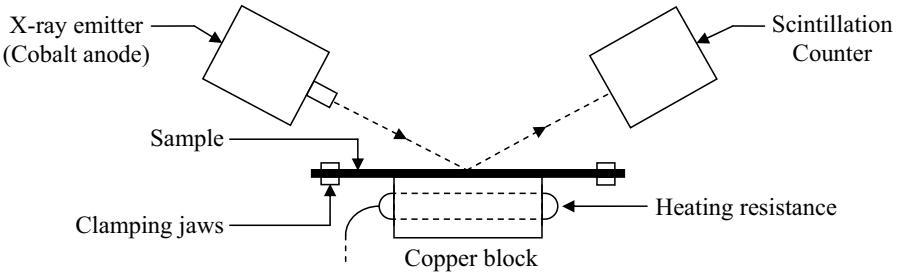

Figure 2: Experimental devices, characterization WAXS.

X-rays are emitted from a cobalt anode tube ($\lambda(Co\text{-}K\alpha)=1,789Å$) on the sample in the direction of stretching (Fig. 2). The reflected rays from the sample are detected by a scintillation counter. The sample is exposed during 45 min to X-rays with a scattering angle 2θ between 14° and 45°. Each test is carried out with a voltage of 40kV and an intensity of 25 mA.

To characterize the effect of temperature, samples are maintained at constant stretch and heated progressively by conduction. The strap remains in contact with a copper block in which a heating resistance is inserted. Temperature is monitored at the surface of the sample and regulated. The prescribed temperature is reached after 15 min.

2.2 Crystallisation index calculation

The diffractogram of a stretched sample in NR-CB shows two peaks, at around 16° and 24°, due to the presence of crystallites together with a halo (larger peak) corresponding to amorphous phase which is always observed (Fig. 3). Crystallisation peaks correspond to a monoclinic structure. Additional peaks related to the presence of ZnO (Zinc Oxide) are also observed.

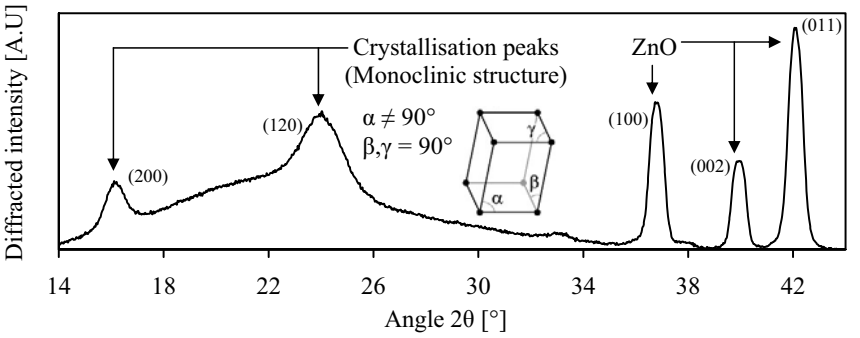

Figure 3: Diffractogram of a stretched sample in NR-CB.

The crystallisation index is calculated determining the intensity of crystallite peaks which is defined as the area under the peak profile. This profile is fitted assuming a split PEARSON VII function (Fig. 3). Once the areas are evaluated, the crystallisation index is calculated as follows:

$$\chi = \frac{I_{Crystalline}^{\lambda(Co(K\alpha))}}{I_{Crystalline}^{\lambda(Co(K\alpha))} + I_{Amorphous}^{\lambda(Co(K\alpha))} + I_{ZnO}^{\lambda(Co(K\alpha))}} \times 100 \ [\%] \qquad \text{(Eq. 1)}$$

where $I_{Crystalline}^{\lambda(Co(K\alpha))}$, $I_{Amorphous}^{\lambda(Co(K\alpha))}$ and $I_{ZnO}^{\lambda(Co(K\alpha))}$ are respectively the areas of crystallites peaks, amorphous peak and ZnO peaks in deformed state.

3 Results and discussion

3.1 Strain-induced crystallisation

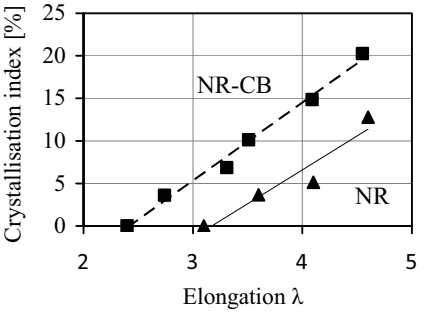

Figure 4: Strain-induced crystallisation for NR and NR-CB.

Figure 4 shows the evolution of crystallisation index of NR and NR-CB versus the maximum imposed elongation. Results show that crystallisation starts for an elongation equal to λ_c(NR-CB) = 2.4 for NR-CB and λ_c(NR) = 3.1 for NR. Above these thresholds, crystallisation index gradually increases. Performing sequential measurements on NR, Toki et al. [4] reported that crystallisation occurs above $\lambda = 3$ which is consistent with the present investigation. These results indicate that the macroscopic stretch needed to induce crystallisation is lower in the case of NR-CB. This could be related to an amplification of strains caused by the presence of hard fillers as explained in [5, 6] so that local stretches reach the critical crystallisation stretch of NR.

3.2 Crystallisation during relaxation

Stress relaxation tests were conducted for two elongations $\lambda = 3.5$ and $\lambda = 4.5$ for durations between 1 and 72 hours.

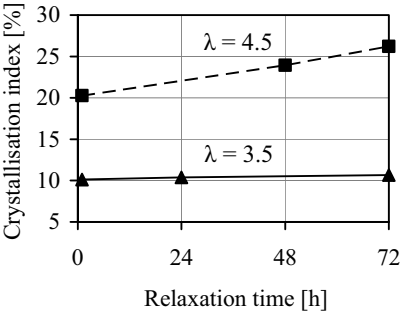

Figure 5: Influence of relaxation on crystallisation index of NR-CB.

Figure 5 shows the variation of the crystallisation index as a function of relaxation time. Crystallisation increases with holding time in particular for high values of pre-stretch ($\lambda = 4.5$). These results are in agreement with Toki's et al. results [4]. Crystallisation during relaxation is interpreted in [4] as the formation of secondary crystallites corresponding to folded-chain lamellae formed from strain induced extended-chain crystallites. Formation of lamellae corresponds to the retraction of a molecular chain and consequently to a decrease of the load (i.e. stress relaxation).

3.3 Influence of temperature on crystallisation

In order to see the influence of temperature, experiments were realized for two elongations $\lambda = 4$ and $\lambda = 4.5$ for which the crystallisation phenomenon is pronounced (Fig. 6). As mentioned before, the same sample is used for all temperatures. This implies that stress relaxation occurs during the test duration (about 5 hours). For that reason, the temperature is gradually increased (and not decreased) as relaxation is probably faster at high temperature.

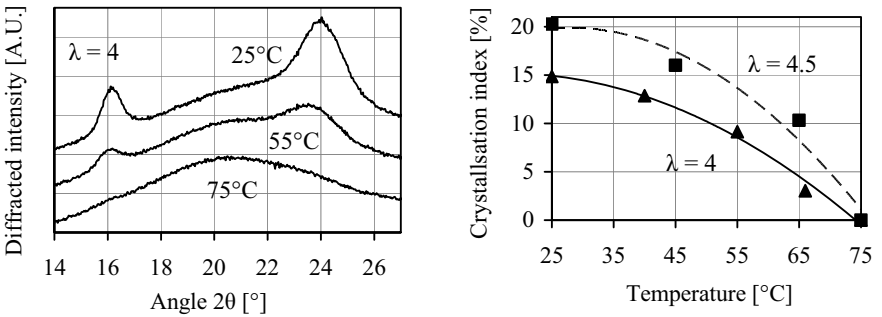

Figure 6: Influence of temperature on crystallisation of NR-CB.

Figure 6 shows the decrease of crystallisation index with increasing temperature. At about 75°C (this would correspond to the crystallites melting point), crystallisation disappears regardless of pre-straining.

3.4 Crystallisation during fatigue

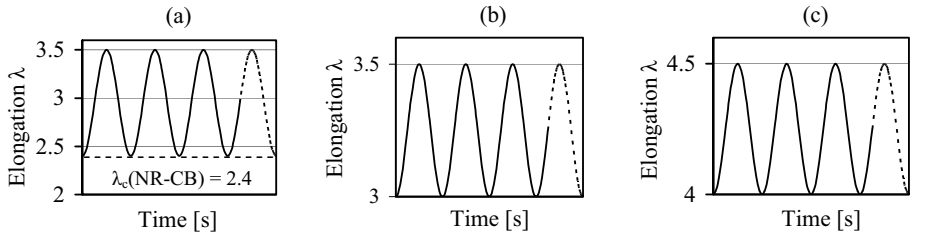

Figure 7: Fatigue loading conditions at frequency of 1 Hz.

Influence of fatigue on the crystallisation index is studied using three loading conditions at a frequency of 1Hz (Fig. 7):

- (a): the sample is subjected to an elongation between $\lambda = 2.4$ and 3.5. The lower elongation is close to the critical stretch λ_c(NR-CB).
- (b): the elongation amplitude is chosen between $\lambda = 3$ and 3.5 so that cycling is performed above λ_c(NR-CB).
- (c): Keeping the same amplitude as (b), the mean stretch level is increased.

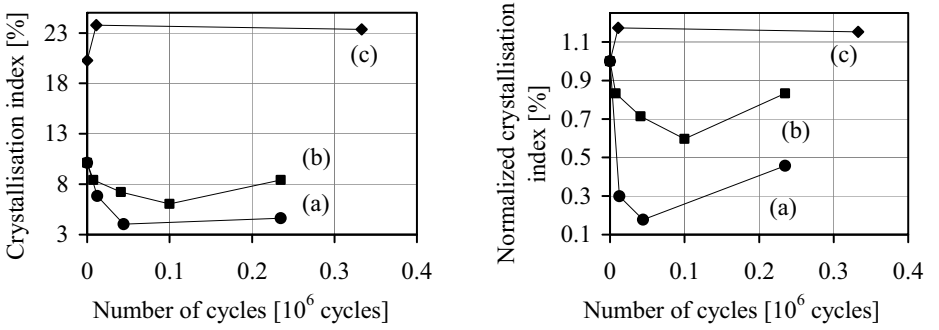

Figure 8: Influence of fatigue on crystallisation index (a), (b) and (c) after 1 h of relaxation.

Measurements are performed on samples maintained at the maximum stretch level of the imposed cyclic loading. The crystallisation index is plotted in figure 8 as a function of the number of imposed fatigue cycles for the three loading conditions. Results show the decrease of crystallisation index with increasing the number of cycles for (a) and (b). The decrease observed for (a) is more important than for (b). Based on the Haigh's diagram, lifetime is smaller for case (a) and maximum for case (c) which qualitatively corroborates well with the amount of crystallites.

Figure 8 indicates an increase of crystallisation index above 200,000 cycles for cases (a) and (b). The same figure shows a slight increase of the crystallisation index with increasing the number of cycles for case (c). These results support a hypothesis of crystallites accumulation during fatigue tests and have to be confirmed. Regardless of the loading conditions, crystallisation does not seem to disappear.

5 Conclusion

Sequential tests performed at several strain levels, showed an increase of crystallisation index with increasing the maximum strain level imposed. Results highlighted the influence of hard fillers which amplify local strain and enable to reach the minimum stretch level required to observe crystallisation.

The study of crystallisation during relaxation is in agreement with the formation of a secondary type of crystallites [4]. Crystallites increase in concentration with decreasing stress.

This study also enabled to define the "melting point" of crystallites at around 75°C regardless of the maximum strain level reached.

The three studied fatigue loading conditions showed that crystallisation index decreases with increasing the number of cycles. The amount of crystallites increases with increasing the minimum strain and improves the lifetime of the material.

Acknowledgments

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