



Influence of strain rate and temperature on the onset of strain induced crystallization in natural rubber

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ABSTRACT

Strain induced crystallization (SIC) of natural rubber (NR) has been studied in a large range of strain rate (from $5.6 \times 10^{-5} \text{ s}^{-1}$ to $2.8 \times 10^1 \text{ s}^{-1}$) and temperature (from $-40 \text{ }^\circ\text{C}$ to $80 \text{ }^\circ\text{C}$) combining mechanical and thermal analysis. Both methods are used to extend the study of SIC from slow strain rates – performed with in situ wide angle X-rays scattering (WAXS) – to high strain rates. Whatever the temperature tested, the stretching ratio at crystallization onset (λ_c) increases when the strain rate increases. This strain rate effect is strong at low temperature (close to T_g) and weak at high temperature (much higher than T_g). A theoretical approach derived from the Hoffman–Lauritzen equation has been developed and provides a good qualitative description of the experimental results. At low temperature, the strong increase of λ_c with strain rate is explained by a too long diffusion time compared to the experimental time. At high temperature, SIC kinetics is rather controlled by the nucleation barrier which mainly depends on the strain energy. When the stretching ratio increases, this nucleation barrier strongly decreases, allowing crystallization even for short experimental time.

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1. Introduction

Most of the studies devoted to strain induced crystallization (SIC) are performed in so-called “quasi-static” conditions: they are carried out at sufficiently low strain rates to lead to a crystallization level which is roughly stable, at a given stretching ratio, over a time range of the order of the experimental time. Such experiments represent the main contribution of the literature to the study of SIC [1–10]. Nevertheless, the dynamic character of SIC in vulcanized natural rubber (NR) [11,12] was evidenced few years after its discovery in 1925 [13]. It was shown

that SIC of NR requires only very short time to occur, as soon as the stretching ratio is high enough. Several studies have also analyzed the stretching ratio at the crystallization onset λ_c as a function of the strain rate. It was shown an increase of this parameter with the strain rate for NR [5], IR (isoprene rubber) [14] or filled NR [15]. Thanks to in situ WAXS measurements [16] or through infra-red analysis [17], the shortest time needed for the appearance of SIC is around several decades of milliseconds for a sample of NR stretched at a stretching ratio of 5, at room temperature (more details on these pioneering works are given in a recent review [18]). This range of induction time was confirmed by recent in situ WAXS experiments using the stroboscopic technique [19,20] or impact tensile test [21,22]. However, in spite of a large number of experimental investigations, a question remains unsolved: what are

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the physical parameters that control SIC kinetics? This question is important in order to properly describe this phenomenon. It is also essential for rubber applications, where the material is submitted to dynamic strain over an extremely large frequency range. Moreover, it is noteworthy that there is no study presenting SIC over a sufficiently large strain rate and temperature ranges allowing a good description of this phenomenon.

Thus, this work presents a SIC study over a strain rates range of around six decades. This is made possible by combining several experimental techniques of detection such as WAXS analysis, mechanical and thermal characterizations. In order to clarify the respective contributions of nucleation and diffusion in the SIC kinetics, the combined effects of temperature (from $-40\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$) and strain rates is also investigated. These contributions are finally quantified through a Hoffman–Lauritzen type description adapted to SIC. This approach is partly based on a thermodynamic development presented in previous papers [23,24]. It is coupled in the present study with the WLF diffusion equation. This approach provides a theoretical frame capable of explaining how temperature and strain influence the appearance of SIC in natural rubber.

2. Material and experiments

2.1. Materials

The studied material is a vulcanized unfilled natural rubber. The material recipe is the following: rubber gum (100 phr) which is a Technically Specified Rubber (TSR20) provided by Michelin Tire Company, stearic acid (2 phr), ZnO (1.5 phr), 6PPD (3 phr), CBS (1.9 phr) and sulfur (1.2 phr) (where phr means g per 100 g of rubber). The material has been processed following the Rauline patent [25]. First, the gum is introduced in an internal mixer and sheared for 2 min at $60\text{ }^{\circ}\text{C}$. Then, the vulcanization recipe is added and the mix is sheared for 5 min. Afterward, the material is sheared in an open mill for five minutes at $60\text{ }^{\circ}\text{C}$. Sample sheets are then obtained by hot pressing at $170\text{ }^{\circ}\text{C}$ during 13 min. Dumbbell-shaped samples, with a 6 mm gauge length (l_0) and 0.8 mm thickness, are machined. The number density of the elastically effective sub-chains (so-called hereafter average network chain density ν) was estimated from the swelling ratio in toluene and from the Flory–Rehner equation [26] and found equal to $1.4 \times 10^{-4}\text{ mol cm}^{-3}$. This density is tuned so that (i) it promotes the development of strain induced crystallization [4] and (ii) it is high enough to avoid an inverse yield effect [27]. In order to avoid microstructure modification during the different mechanical tests, i.e. an uncontrolled Mullins effect, the samples are stretched four times up to stretching ratio ($\lambda = 7$) higher than the maximum stretching ratio reached during the in situ cyclic tests ($\lambda = 6$). A similar procedure is proposed in the work of Chenal et al. [4].

2.2. In situ WAXS

The in situ WAXS experiments are carried out on the D2AM beamline of the European Synchrotron Radiation Facility (ESRF). The X-ray wavelength is 1.54 \AA . Because

of a limitation due to the relatively long detection times (several seconds) of the CCD camera, in situ WAXS are only performed at low strain rates ($4.2 \times 10^{-3}\text{ s}^{-1}$ and $1.7 \times 10^{-2}\text{ s}^{-1}$). For the lowest speed, the sample is tested through a monotonic loading–unloading cycle. For the highest ones, the sample is only stretched and then relaxed in the deformed state.

The two-dimensional (2D) WAXS patterns are recorded by a CCD camera (Princeton Instrument). The beam size is small enough ($300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$) to avoid superimposition with the scattered signal. The background, (i.e. air scattering and direct beam intensities) is properly measured in absence of any sample. It can then be subtracted to the total intensity scattered in the presence of the rubber sample. The corrected scattering intensity is finally normalized by the thickness and the absorption of the sample. Each scattering pattern is integrated azimuthally. The deconvolution of the curve $I = f(2\theta)$ enables the extraction of the intensity at the peak top and the width at half height of each crystalline peak and the intensity at the peak top of the amorphous phase. The crystallinity index CI is then calculated as follows [28]:

$$\frac{I_{a0} - I_{a\lambda}}{I_{a0}} \quad (1)$$

where I_{a0} and $I_{a\lambda}$ are the intensity of the amorphous phase at the peak top in the unstretched state and the stretched state, respectively.

2.3. Mechanical characterization

The EPLEXOR[®] 500 N of Gabo Qualimeter society (Ahlden, Germany) is used in order to carry out mechanical characterization at different temperatures. Mechanical tests consist of a monotonic stretching at various strain rates, from $5.6 \times 10^{-5}\text{ s}^{-1}$ to $1.1 \times 10^{-1}\text{ s}^{-1}$ and from the relaxed state up to the maximum stretching ratio $\lambda = 6$. Before each tensile test, a soak time of five minutes guarantees that the desired temperature (from $-40\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$), obtained by air circulation, is homogeneous in the oven. The test carried out at the lowest strain rate is stopped at an early stage (λ around 5) because the time reaches the limitations of the experimental set up. To perform experiments at highest strain rates, ranging from $1.1 \times 10^{-1}\text{ s}^{-1}$ to $2.8 \times 10^1\text{ s}^{-1}$, mechanical characterization is carried out thanks to an MTS tensile test machine. For all the mechanical tests, the tensile force is converted into nominal stress $\sigma = F/S_0$. Stress is then plotted as a function of the nominal stretching ratio $\lambda = l/l_0$. λ is accurately measured by videoextensometry.

2.4. Infrared thermography coupled with mechanical tests

For the highest strain rates, ranging from $1.1 \times 10^{-1}\text{ s}^{-1}$ to $2.8 \times 10^1\text{ s}^{-1}$, coupled mechanical and thermal characterization is carried out thanks to an MTS tensile test machine. Two types of mechanical tests are performed: (i) stretching/unstretching, (ii) stretching and relaxation in the deformed state. The temperature increase on the samples surface during such tests is measured thanks to

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