



Kinetics of strain-induced crystallization in natural rubber: A diffusion-controlled rate law



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ABSTRACT

The kinetics of strain-induced crystallization in natural rubber were studied by synchrotron wide-angle X-ray diffraction (WAXD) in a strain jump setup over a broad temperature range. The increase of crystallinity after a strain jump was observed on a millisecond time scale, until a steady state plateau was approached. A novel model, based on chain dynamics scaling laws for diffusion in polymer networks was developed to interpret the time and temperature dependence of the strain-induced crystallization. In contrast to established thermal crystallization models, this model for the strain-induced crystallization proposes that the formation of stretched crystallizable chain segments takes place before the attachment to a growing crystallite.

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1. Introduction

Strain-induced crystallization (SIC) is a unique phenomenon, which occurs to this extent only in natural rubber (NR), making this biopolymer a very popular choice for high demanding applications like truck tires, which benefit from the outstanding mechanical strength and tear resistance of NR, related to SIC [1,2]. While temperature and strain are the main parameters governing the degree of crystallinity, its time-dependence is especially critical in dynamic loading scenarios. On time scales shorter than a few seconds, due to the finite crystallization kinetics the crystalline microstructure in NR significantly deviates from what is suggested by quasistatic tensile experiments [3].

A short review of SIC studies under dynamic load is given in our previous paper [3]. Using a stroboscopic technique, several studies showed that the crystallinity under cyclic dynamic conditions is lower in comparison to the same strain under static conditions [4–8]. In our previous works, we followed the strain-induced crystallization under dynamic cyclic loading in real time and showed that the crystallinity at a crack tip is reduced under

dynamic load [3,9]. While cyclic dynamic experiments resemble the loading conditions encountered in industrial rubber products, strain jump experiments are more suitable to study the SIC kinetics. In analogy to temperature jump or pressure jump experiments performed to analyze chemical reaction kinetics, the sample is subjected to a step-like strain and the crystallization after the strain step is observed. The first experiments of this kind were performed by Dunning in 1967 [10]. Within the last decade, Tosaka reported a two-step crystallization mechanism, occurring on time scales of 0.1s and 4s [11,12]. In our previous work, we proposed a two step mechanism consisting of a nucleation step and a growth step, the latter of which is dominated by the mobility of crystallizable chain segments. This resulted in a simple power-law relationship between the crystallization rate and the number of crystallizable chain segments. However, no physical interpretation of the fitting parameters was given [3].

While recently models have been proposed for the strain and temperature dependence of SIC [13,14], currently no model for the description of the SIC kinetics is available [15]. Models established for spherulitic growth in thermally induced crystallization, such as the Avrami equation, are not applicable due to the different crystal morphologies. While quiescent crystallization from an isotropic melt typically results in micron-sized three-dimensional spherulites, strain-induced crystallization forms nano-sized crystallites

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from an oriented crosslinked melt. The mass average crystallite size was reported to be on the order of 10 nm [2], which implies a significant crystallite population being smaller than the *nuclei* typically observed in thermal crystallization in semicrystalline polymers.

On the other hand, crystallization theories addressing crystallite growth on smaller length scales, like Hoffman–Lauritzen [16,17], are in principle applicable to SIC, with the limitation that creation and dissolution of thermodynamically stable nuclei should be reconsidered for SIC, taking into account the stabilizing effect of the tension exerted on the chains. In this sense, our proposed model is broadly in line with the Hoffman–Lauritzen approach, which also includes the drafting of chains from the melt by reptation as one of the factors contributing to the crystallite growth rate. Owing to the limited knowledge of the crystalline structure in strain-crystallized NR (crystallite/granule size, growth surfaces, superstructure), we do not attempt to identify the various parameters. Instead, we propose a simple model, which is independent of the morphological details.

This limited knowledge also makes it impossible to make a judgment whether SIC goes through a mesophase or not. While in TIC, experimental data for the temperature-dependence of the crystallite size gives strong evidence for the mesophase model [18], no comparable data (crystallite size vs. strain) exists for SIC in NR. In the context of the mesophase model, the rate determining step would be the transition from the amorphous phase to the mesophase, governed by chain dynamics, while the measured crystallization rates represent the transition from the amorphous to the crystalline phase via the mesophase.

The objective of this paper is to present experimental data, showing the temperature dependency of the SIC kinetics of NR, and to propose a physically sound model for the interpretation of the SIC kinetics. This model takes the diffusion of chain segments to be the rate-determining step. Finally, the model is compared to strain jump experiments over a broad temperature range.

2. Experimental

2.1. Materials

In order to reduce potential nucleation effects induced by particulate ingredients, a very simple rubber formulation was used. Pale crepe natural rubber (Weber & Schaefer, Germany) was masticated in an internal mixer and then blended with 1 phr of dicumyl peroxide on a two-roll mill. Vulcanization was carried out in a mold for tensile bars at 160 °C for 16 min according to the vulcanization time t_{90} obtained in a vulcameter test. The molecular weight between crosslinks, measured by NMR, was $M_c = 3696 \text{ g mol}^{-1}$, following the method described by Vieyres et al. [19].

2.2. Tensile experiments

Tensile samples with beaded ends for better clamping were used (length 10 mm between beads, parallel length 6 mm, width 2 mm, thickness 1 mm).

For strain jump experiments, the samples were mounted in a custom-made tensile impact machine. A spring-driven apparatus is released by an electric motor, stretching the sample up to a maximum strain of 550% within less than 10 ms. Afterwards, the strain is held fixed. A shadow on the X-ray detector moves as soon as the spring is released in order to synchronize the scattering data. The strain values given in the following are optical strains measured on reference samples of the same geometry and material in the same tensile machine ex situ.

For quasistatic tensile experiments, a custom-made miniature tensile machine was used, moving both clamps to keep the sample aligned with the beam. The optical strain was recorded in situ. The strain rate was 0.06 s^{-1} .

Nitrogen gas was tempered to the desired temperature and directed at the sample by means of two porous membranes positioned above and below the sample. The gas temperature was measured in direct vicinity (about 3 mm) to the sample, using a small thermocouple, and enough time was allowed for thermal equilibration.

2.3. WAXD setup

WAXD experiments were carried out at the MiNaXS beamline at DESY (Deutsches Elektronen Synchrotron) [20], using a PSI Pilatus 300K detector. Photon flux was around $5 \times 10^{12} \text{ s}^{-1}$ at a wavelength of 0.0954 nm. The scattering patterns were background corrected and normalized to unit sample thickness. The relative degree of crystallinity was computed from the ratio of the volume under the (120) peak compared to the volume under the amorphous halo (cf. Fig. 1 in Supplementary Material) [21]. This approach assumes that either the crystal orientation fulfills fiber symmetry or that the crystal orientation is similar for all samples studied. The relative crystallinity was translated to (approximate) absolute values Φ by comparison with independent methods, like dilatometry.

For the quasistatic experiments, the detector frame rate was 2 s^{-1} . For the strain-jump experiments, the exposure time and dead time were 4 ms each, resulting in a frame rate of 125 s^{-1} . 10^4 diffraction patterns were recorded per strain jump experiment. To improve the signal-to-noise ratio, patterns were averaged over equidistant intervals on a logarithmic time axis, reducing the 10^4 patterns to 100 patterns. This yields relatively high noise at short times.

3. Results and discussion

3.1. Quasistatic tensile experiments

As reference, the evolution of crystallinity, Φ , under quasistatic strain at different temperatures between -25 °C and 50 °C is shown in Fig. 1. Crystallization sets in around $\epsilon_{onset} = 300\%$ strain at 25 °C and develops almost linearly with strain. Here, ϵ_{onset} is defined as

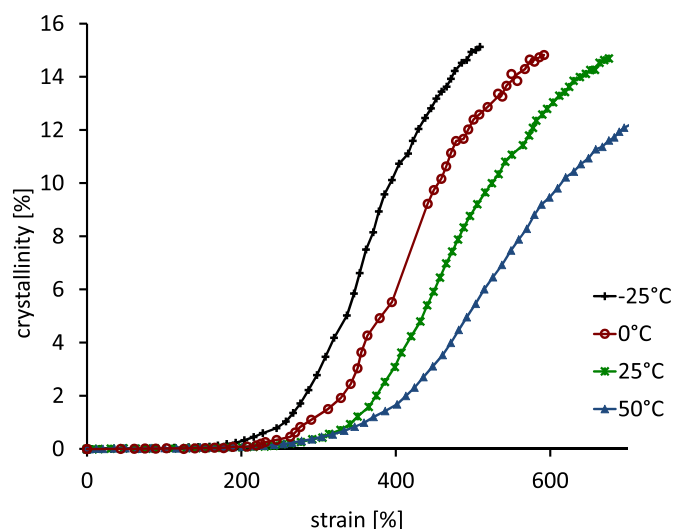


Fig. 1. Crystallinity vs. strain at different temperatures during quasistatic tensile experiments.

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