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Strain-induced crystallization around a crack tip in natural rubber under dynamic load

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ABSTRACT

The local degree of crystallinity around a crack tip in natural rubber under dynamic load was measured by time-resolved scanning wide-angle X-ray diffraction (WAXD). Using a high-flux synchrotron microbeam, WAXD patterns with less than 20 ms exposure time were acquired while the notched rubber sample was subjected to cyclic dynamic stretching at a frequency of 1 Hz, similar to the loading conditions in tear fatigue experiments. By scanning the continuously cycling sample, a complete crystallinity map at any given strain phase angle was obtained. The crystallinity at the crack tip is considerably reduced compared to static crack tip scans. Further investigations revealed the underlying structural reasons for the well-known relation between *R*-ratio and crack growth resistance. By performing static crack tip scans on increasingly stretched rubber samples, the mechanisms behind crack deflection and branching were studied.

1. Introduction

Strain-induced crystallization (SIC) in natural rubber (NR) is a fascinating phenomenon, that is not only of academic interest, but also economically important, given that the majority of the natural rubber production goes into the tire industry. Here, natural rubber is preferred over synthetic rubbers due to its unique ability to crystallize under strain. The reinforcing properties of the crystallites provide for an elevation of the tensile strength and a tremendous enhancement of the crack growth resistance [11,19]. The crack growth resistance is the lifetime-limiting factor in rubber products, since despite the presence of an initial crack the material can withstand significant loads [25]. SIC is the main factor governing the crack growth behavior in strain-crystallizing elastomers. The *R*-ratio (ratio between the minimum and maximum strain in a tear fatigue test) dependence of crack growth can be traced back to the finite SIC kinetics. Also the crack topography (e.g. branching, crack deflection, striations) is influenced by SIC, since the crack does not necessarily propagate at the point of highest stress, because the rupture stress varies locally and depends on the crystallinity [8,15,25]. SIC in NR has been studied in numerous papers and its dependency on strain, crosslinking density, fillers and temperature has been established [5,13,21,27,29,33,34]. Most of these experiments were performed on unnotched tensile samples under quasistatic load. Due to the time-dependence of SIC, no model relating SIC to crack growth is currently available and the description of fatigue crack growth is purely phenomenological [18,20,37].

In order to gain new insight into structure–property relationships with respect to fatigue crack growth, it is desirable to perform the structural characterization under loading conditions that more closely represent the loading conditions encountered in tear fatigue analysis and thus are closer to real-life loading cases. For instance, crack growth experiments are typically carried out under dynamic conditions at around 1 Hz. Few structural investigations have been done in this field. Acken reported an SIC onset at higher strains under dynamic loading as compared to static loading [1]. Other works used the stroboscopic technique to resolve the crystallinity evolution under dynamic loading [4,12,14]. Also instructive are the outcomes of strain jump experiments, giving an impression of the SIC kinetics, even though currently no model is available to physically describe the kinetic mechanism of SIC [2,28,30,31]. Recently, the authors reported a reduction of crystallinity under dynamic cyclic load as compared to quasistatic load due to the finite crystallization kinetics, such that the material is unable to reach the steady state under dynamic conditions [2]. The tensile impact experiments suggest that kinetic effects become significant at frequencies above roughly 0.1 Hz.

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Table 1
Rubber recipes. Ingredients are listed in units of phr (parts per hundred rubber by weight).

	NR40	NR50	NR60
NR	100	100	100
Carbon black	40	50	60
CBS	1.5		1.5
Stearic acid	1	5	1
Sulfur	1	1.5	1
Zinc oxide	3	5	3
t_{90} [min]	3.5	13	3.5

The fact that fatigue crack propagation is not only dynamic, but also governed by highly localized processes around the crack tip, further complicates a structural investigation. In the past, researchers reported about static crack tip scans by wide-angle X-ray diffraction (WAXD), scanning the sample with a micron-size X-ray beam and thus obtaining spatially resolved information about the crystallinity in the vicinity of the crack tip [16,32,35]. Due to the stress concentration around the crack tip, the material directly in front of the crack tip was found to be crystalline, whereas the remainder of the sample appeared amorphous or less crystalline. The size of the crystalline zone was found to be dependent on the global strain, the sample geometry and material parameters such as filler content. Lee and Donovan were the first to perform a one-dimensional WAXD crack tip scan [16]. They reported a size of 2 mm–3 mm for the crystalline zone, depending on the carbon black content of the rubber compound. In filled rubbers, the crystalline zone was found to be larger than in gum rubber due to the strain amplification effect of reinforcing fillers. Later, the advent of more powerful synchrotron radiation sources reduced the acquisition time and thus made two-dimensional scans feasible. Trabelsi reported crystalline zones of similar size as Lee and Donovan [32,35].

The studies by Lee & Donovan and Trabelsi were done under static conditions. However, in a tear fatigue experiment, the rubber is subjected to dynamic stretching [11,26]. In the vicinity of the crack tip, the strain rates are even higher due to the stress and strain concentration. Thus, the time dependence of SIC may not be neglected. For a more thorough understanding of the processes in front of the crack tip, it is necessary to combine the spatial resolution of WAXD scans with the time resolution of dynamic experiments. This has now become possible owing to new brilliant light sources such as the MiNaXS beamline at DESY (Deutsches Elektronen-Synchrotron) [3,23].

2. Experimental

2.1. Specimen preparation

Pale crepe natural rubber (Weber und Schaer, Germany) was mixed with carbon black N234 (Orion Engineered Carbons Corax), stearic acid (Fisher Scientific), CBS (n-cyclohexyl-2-benzothiazole sulfenamide, Lanxess) and zinc oxide (Fisher Scientific) in an internal mixer, as listed in Table 1. Afterwards sulfur (Fisher Scientific) was added on a two-roll mill. Vulcanization was carried out at 160 °C according to the optimum vulcanization time t_{90} obtained from a vulcameter test. The recipe for the dynamic crack tip scans was optimized for the study of strain-induced crystallization: A medium carbon black loading shifts the SIC onset to lower strains, without excessively increasing the high strain moduli. A low crosslinking density keeps the stresses low, allowing larger amplitudes without crack growth. Tensile samples with beaded ends for better clamping were obtained by die-punching for the use at the synchrotron as well as in the SEM. A notch of .5 mm depth was made with a scalpel (inset in Fig. 1).

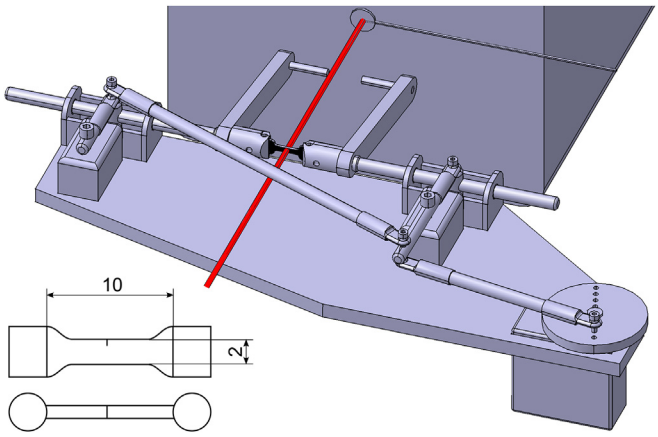

Fig. 1. Dynamic miniature tensile machine set up in the beamline, along with detector and beamstop. The beam (red) is not drawn to scale. Inset: Geometry of the single edge notched tensile (SENT) sample. Sample thickness is 1 mm and notch depth is 0.5 mm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Dynamic tensile experiments

A miniature tensile machine was specifically built for the use in synchrotron beamlines (Fig. 1). A cyclic harmonic strain of a frequency of approximately 1 Hz acts on the tensile sample. The tensile direction is horizontal. A lever mechanism ensures that the sample center remains aligned with the X-ray beam at all times, since both clamps move synchronously in opposite directions. Thus, the motion rate with respect to the beam is minimized at the crack tip, giving a better spatial resolution at a given exposure time. The strain amplitude is adjustable by varying the stroke of the eccentric. The prestrain is also adjustable.

The strain field was measured using the digital image correlation (DIC) software GOM Aramis (GOM mbH, Germany). A white speckle pattern was applied to the sample surface with airbrush paint. The photos were taken during static experiments in the beamline, but not directly during exposure. Afterwards, the strain field data was exported and transformed to the same coordinate system as the WAXD scans, using PV-Wave (Rogue Wave, CO).

2.3. Wide-angle X-ray diffraction

The WAXD experiments were performed at the MiNaXS-beamline at DESY (Deutsches Elektronen-Synchrotron, Germany). The wavelength was 0.107 nm and the beam size was around 25 μm × 35 μm. The photon rate was around 5×10^{11} photons/s. A PSI Pilatus 300K pixel detector with a dead time of 3 ms was installed at a sample distance of 100 mm. The sample and the detector were aligned perpendicular to the beam. Fiber symmetry is assumed to hold. This assumption is justified, as the stress field in the vicinity of the crack tip is predominantly uniaxial [9]. All crack tip scans were performed with a spatial resolution of 100 μm in vertical and horizontal direction (in the laboratory reference system), i.e. the tensile machine was mounted on two linear stages that were moved perpendicular to the beam in steps of 100 μm. Each two-dimensional scan consists of a number of horizontal line scans. A Perl script allows to perform a complete two-dimensional scan without any further user interaction required.

For a static scan, one diffraction pattern for each scanning point was collected, with an exposure time of 0.5 s. The stages would halt