DIVERCITY IN STRAIN-INDUCED CRYSTALLIZATION OF NATURAL RUBBER BY BIAXIAL ELONGATION

Ruito Tanaka[1], Tomohiro Yasui[1], Yuji Kitamura[2], Katsuhiko Tsunoda[2], Hideaki Takagi[3], Nobutaka Shimizu[3], Noriyuki Igarashi[3], Kenji Urayama[4] and Shinichi Sakurai[1,*]

[1]Department of Biobased Materials Science, Kyoto Institute of Technology, Kyoto, Japan
[2]Bridgestone, Kodaira, Tokyo, Japan
[3]High Energy Accelerator Research Organization, Tsukuba, Ibaraki, Japan
[4]Department of Material Chemistry, Kyoto University, Kyoto, Japan

INTRODUCTION

Natural rubber (NR) is soft and simultaneously robust to meet requirements for exclusive safety of tires of aircrafts. Namely, they should not be broken when momentary stress is applied. Strain-induced crystallization (SIC) is considered to play an important role for the toughening of NR. To check the significance of SIC behaviors experimentally, we have thoroughly conducted wide-angle X-ray scattering (WAXS) measurements on NR specimens under the biaxially elongated states using some beamlines at Japanese synchrotron radiation facilities such as SPring-8 and Photon Factory of KEK. For this purpose, we have developed the specially-designed apparatus (**Fig. 1**), which enables biaxial elongation of the sheet specimen of vulcanized NR. The studies on SIC of NR by WAXS have an extremely long history since 100 years ago [1], and reliable crystalline lattice parameters have been reported by Nyburg as the orthorhombic lattice with a = 1.246, b = 0.889, and c = 0.81 nm [2]. Then, comparatively recently, have actively reported such studies by using the X-ray scattering technique [3-7]. In this presentation, we will show the diversity of the strain-induced crystallization (SIC) behaviors by conducting biaxial extension of NR in several manners including the planar deformation (equibiaxial and non-equibiaxial, as well as the hysteresis of the crystallization behaviors depending upon the ways of deformation of the specimen).

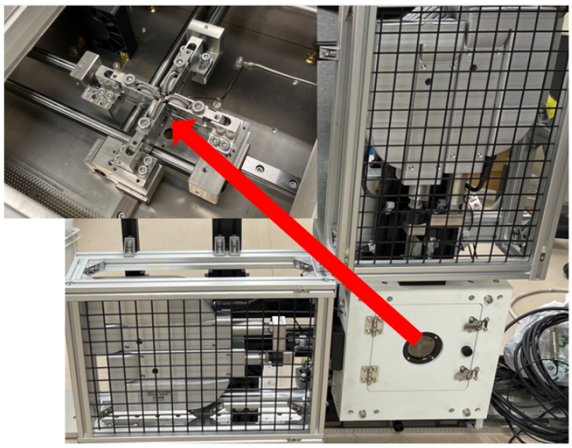

Figure 1: Apparatus for the measurement of the X-ray scattering of the NR sheet specimen subjected to the biaxial deformation. The stress measurement is simultaneously possible. Also, temperature-control up to 130˚C is possible.

EXPERIMENTAL

The elongation apparatus is compact and bears the thermally isolated chamber which enables temperature control of the specimen subjected for the biaxial elongation from room temperature up to about 130˚C (**Fig. 1**). The chamber contains four crossheads to grip the sheet specimen with 90˚ crossed angles. The minimum length between two crossheads is 1 cm, and its maximum stroke is 10 cm, resulting

in the 10-fold elongation ratio at most. Unfortunately for the vulcanized NR sheet specimens, we have encountered the problem of slippage at the gripping jaws. To avoid this unfavorable slippage during elongation, we utilized the cross shape of the NR sheet specimen, taking after the idea by Beurrot et al. [8].

Fig. 2 shows the images of the specially prepared specimen used for the experiment. The specimen is cross-shaped with a cylindrical protrusion at each end to avoid slippage of the specimen sheet out from the jaw during elongation, bearing a round-shaped dimple with thinner thickness in its central portion. This was designed to be more easily deformed under a given strain, as compared to the remained four arm portions (limbs) of the specimen. It was required to calibrate the real strain of the dimpled portion by video-recording the deformation process of the mesh lattice (with 1 mm spacing of the lattice pattern) during the deformation of the specimen. Note that the lattice pattern was stamped on the surface of the dimpled portion in prior to installing the specimen. Then, it was found that the dimpled portion can be elongated up to 4-flod of the elongation ratio for the condition of the apparatus operation with maximum stroke between the two crossheads. The incident X-ray beam was introduced at the center of the dimple of this sheet specimen for the WAXS measurements during the biaxial elongation.

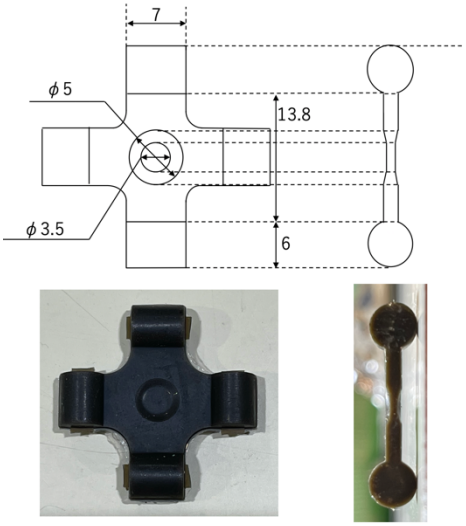

Figure 2: Blue print for the specially prepared NR specimen for the biaxial elongation and (a) images of the real NR specimen (a) the plan view and (b) the side view.

RESULTS AND DISCUSSSION

Fig. 3 compares the 2-dimensional wide-angle X-ray diffraction (2d-WAXD) patterns obtained for the specimens under (a) the uniaxial and (b) the planar extension mode, where in the latter case the specimen was drawn in one direction while its size was kept constant by holding the specimen with the gripping jaws to prevent shrinkage. Although these patterns look similar to each other, closer examination finds the lack of the (120) reflection peaks in the latter case, which appear in the horizontal direction in the former case (as has been already reported by Katz [1]). Our extensive studies ascribed the lack to the planar orientation of the (120) planes parallel to the surface of the sheet specimen [9]. Furthermore, it was revealed that the crystallites melted completely when the drawn specimen was relaxed. However, the strain at the melting of the crystallites was lower than that at the onset of SIC. This clearly indicates that once-formed crystallites by the SIC is stable in the reversing process where the drawn specimen was relaxed. As for the equibiaxial extension, we confirmed SIC at 3.7 strain with the random orientation of the crystal lattice, as has been reported by Beurrot et al. [8], which is very much contrasted

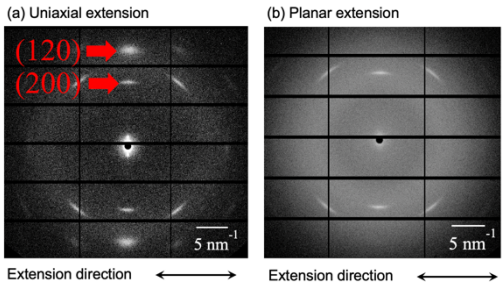

Figure 3: 2d-WAXD patterns for the NR sheet specimens under (a) the uniaxial and (b) the planar extension mode, where in the latter case the specimen was drawn in one direction while its size was kept constant by holding the specimen with the gripping jaws to prevent shrinkage.

to the case of the uniaxial or planar elongation where the *c* axis is parallel to the extension direction (**Fig. 3**).

We also examined the SIC behaviors upon the two-step extension, as the following manner; the specimen was first drawn in one direction (the planar extension) to form crystallites and then the drawn specimen (of which size was fixed at the strain where the 2d-WAXD pattern exhibited the crystalline reflection peaks) was further drawn in the direction perpendicular to the extension direction in the first step of the extension. The 2d-WAXD pattern as shown in **Fig. 3(b)** was obtained in the beginning of the second step of the extension. Then, the arcs of the (200) reflection was diffused with an increase of the strain in the direction perpendicular to the extension direction of the first step, indicating the randomization process of the crystallite orientation. Simultaneously, the reflection became vague, and finally disappeared before reaching the equibiaxial state if the strain of the first step of the extension was much lower than 3.7, which is the onset of SIC for the case of the equibiaxial extension. In case when the strain was closer to 3.7 but even slightly lower than that, the Debye-Scherrer ring of the (200) reflection remained in the 2d-WAXD pattern, suggesting the survival of the crystallites with random orientation. This result indicates that once-formed crystallites by SIC in the first step of the extension is still stable in the final state of the equibiaxial extension, even though the equibiaxial strain is slightly lower than the critical strain value of the onset of SIC for the case of the equibiaxial extension.

As a conclusion, the diversity of the SIC behaviors of NR were found by conducting the biaxial extension, suggesting that the SIC strongly depends upon hysteresis of the applied strain.

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