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Strain-Induced Crystallization of Natural Rubber Using Synchrotron Radiation ~ Effects of Difference in the Stretching Mode on SIC ~

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1 Introduction

Natural rubber (NR) exhibits strain-induced crystallization (SIC), in which NR crystallizes and becomes tougher when the sample is subjected to strain. SIC has been studied when the stretching mode is uniaxial stretching. However, considering the environment in which NR is actually used, it is assumed that strain may be applied under conditions similar to multiaxial stretching. Therefore, we measured two-dimensional wide-angle X-ray scattering (2D-WAXS) patterns under biaxial stretching using a biaxial stretching apparatus and discussed SIC behaviors of NR under various stretching modes.

2 Experiment

We prepared a sheet [40 × 40 × 0.284 mm] of vulcanized NR (containing sulfur of 1.40 phr) for 2D-WAXS measurement. The sheet was mounted on the cross head of the biaxial stretching apparatus and stretched at a strain rate of $\dot{\varepsilon_x} : \dot{\varepsilon_y} = 2:1$, $3:1$ and $5:1$. However, the sample could not be stretched at the originally scheduled strain rate because the specimen was gradually slipped out of the chuck of the stretching apparatus as it was being stretched. The initial length of the sample was 22 mm in both the X-axis and Y-axis directions. X-rays were incident from the normal direction of the sheet specimen to simultaneously measure the stress and the WAXS patterns. The X-axis stretching reached the stretching limit first, then the specimen was continued to be stretched in the Y-axis direction with the X-axis being fixed, and the WAXS patterns were also continued to be recorded by using the synchrotron radiation as an X-ray source at the beamline BL-15A2 of Photon Factory at KEK (High-Energy Accelerator Research Organization) in Tsukuba, Japan.

3 Results and Discussion

Figure 1 shows the phase diagram of onsets and disappearing points of SIC in the $\varepsilon_x - \varepsilon_y$ space. Here, ε_x is the strain in the X-axis direction and ε_y is the strain in the Y-axis direction. For uniaxial stretching, planar stretching and 3 : 1 and 5 : 1 of apparent strain rate, SIC was found to take place as the crystalline peaks appeared in the WAXS pattern. By analyzing the temporal changes of the intensity of the peaks in detail, onset of SIC could be accurately determined. And these are indicated by filled circles in Figure 1. Points A, B, C, and D in Figure 1 are onsets of SIC at uniaxial stretching, planar stretching, and 3 : 1 and 5 : 1 of apparent strain rates, respectively. For 2 : 1 of apparent strain rate (orange dashed line), SIC did not take place. Considering that fact, the existence region of SIC (the green region, higher ε_x side than the green dashed line) is shown in Figure 1. Next, as described earlier, the specimen was continuously stretched in the Y-axis direction after reaching the stretching limit in the X-axis direction in order to investigate whether the crystalline peaks disappear. As a result, the crystalline peaks disappeared at point C´ and D´ for 3 : 1 and 5 : 1 of apparent strain rate, respectively (open circles). Based on these results, a blue-colored region is drawn in Figure 1 as the stable existence region of SIC. The blue region is larger than the green region, indicating that once SIC crystals are formed, they do not melt easily even after strain relaxation. Since these two regions are symmetrical about the linear line of $\varepsilon_y = \varepsilon_x$, it is assumed that the same regions also exist in the space of $\varepsilon_y > \varepsilon_x$.

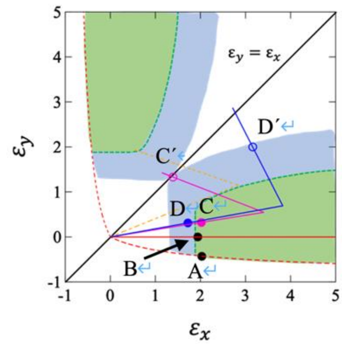

Fig. 1: Onset of SIC (●, ● and ●) shown in the diagram of ε_x-ε_y, where ε_x and ε_y are the strain of the specimen in the X (horizontal) and Y (vertical) axes, respectively. Points A, B, C and D indicate the onsets of SIC for the cases of uniaxial, planar, 3 : 1 of apparent strain rate and 5 : 1 of apparent strain rate, respectively. The points C´ and D´ indicate the disappearing point of the WAXS peaks for 3 : 1 of apparent strain rate and 5 : 1 of apparent strain rate, respectively, when the specimen highly stretched in the X direction was continuously stretched in the Y direction. The region painted with green is for the SIC formed during stretching the specimen, while the region painted with blue is for the stable SIC existence upon releasing the strain.

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