INTRIGUING MELTING BEHAVIOR OF THE NATURAL RUBBER CRYSTAL FORMED BY STRAIN-INDUCED CRYSTALLIZATION

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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. It is indeed important to recognize the melting behavior of the crystal as formed by the SIC when heating, since temperature of the tires of aircrafts is suddenly elevated upon landing. Since the initiation of the studies on SIC of NR by two-dimensional wide-angle X-ray diffraction (2d-WAXD) 100 years ago [1], temperature dependence of the SIC behavior has been studied. However, few report can be found for the melting behaviors of the SIC crystal upon heating [2]. It was reported that the degree of crystallinity started to decrease gradually at temperature far below the melting temperature. The former behavior is strange as compared to the case of the general crystalline polymers, and hard to be reasonably explained. Furthermore, the changes of the lattice parameters as a function of temperature have never been reported. Therefore, in this study we thoroughly analyzed the quantitative changes of the orthorhombic lattice parameters of NR, the volume of the unit cell, its thermal expansivity, the crystallite size and its volume, the degree of crystallinity, and the degree of orientation of the crystalline lattice as a function of temperature. Then, the detailed and reliable mechanism of the melting of the NR crystal formed upon the SIC can be given based on such quantitative data.

EXPERIMENTAL

The vulcanized NR rubber sheet (vulcanized with 1.4 phr of sulfur; no carbon black included; 0.25 mm thickness) with 10 mm length and 4 mm width was utilized for this study. At room temperature, the sheet specimen was uniaxially stretched 7 fold by slowly elongation with 0.2 mm/sec to form the SIC crystal. Then, temperature of the stretched specimen (keeping the length constant throughout the heating process) was gradually increased up to 380 K with the constant heating rate of 2 K/min. The WAXD measurements during the heating process were performed simultaneously
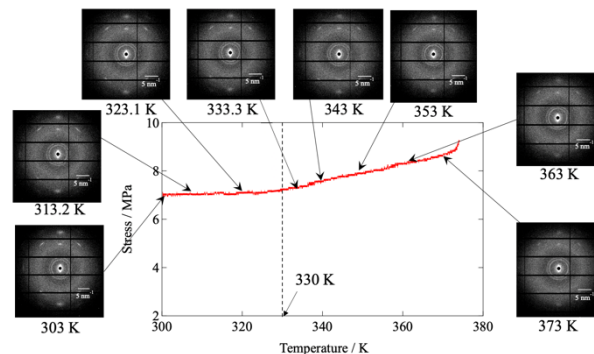

Figure 1: Change in the stress during heating of the stretched and fixed NR specimen at 7 fold elongation. Selected 2d-WAXD patterns are shown together. The elongation direction is horizontal.

with the stress measurements at BL-15A2 of Photon Factory, High Energy Accelerator Research Organization, Japan. The exposure time of the X-ray beam was 5 s for each 2d-WAXD pattern measurement. PILATUS 2M (DECTRIS, Switzerland) was used as a two-dimensional detector. The distance from the specimen to the detector was set to 25 cm.

RESULTS AND DISCUSSSION

Fig. 1 shows the change in the stress as a function of time with selected 2d-WAXD patterns. It is noteworthy that the stress started to increase around 330 K, which can be ascribed to the effect of the entropy elasticity. The reflection peaks were clearly observed for (200), (120), (201), and (002) planes in all 2d-WAXD pattern. To obtain the 1d-WAXD profile, we conducted sector average of the pattern with respect to the scattering vector (q vector) direction where the diffraction spots were observed (within $\pm 5°$ sector range). Thus-obtained 1d-WAXD profiles are shown in **Fig. 2** where the intensity was plotted against the magnitude of the scattering vector (q) as defined by $q = (4\pi/\lambda) \sin\theta$ with λ and θ being the wavelength of X-ray ($\lambda = 0.9232$ nm) and half the diffraction angle, respectively. The (200) and (120) reflection peaks continuously shifted towards lower q range, while the (002) reflection peak shifted towards higher q range. The (201) reflection peak more or less stayed at constant q position with $q = 0.497 \sim 0.500$ nm^{-1}. By assuming the orthorhombic lattice, the lattice constants a, b, c values can be evaluated, and evaluated values were plotted in **Fig. 3(a)**. As compared to the reported values $a = 1.246$, $b = 0.889$, $c = 0.81$ nm by Nyburg [3], our results for a and c reasonably coincide but the result of b values are about 28% smaller. The reason is unknown at present. It is noteworthy that the c value decreases as a function of temperature, which suggests the shrinkage of the main chain of NR due to the increased vibration at higher temperature, while the a and b values exhibit the thermal expansion. Note however that the lattice volume ($V = a \cdot b \cdot c$) itself exhibits thermal expansion, as shown in **Fig. 3(b)**. Based on this set of data, temperature dependence of the thermal expansivity, $\alpha = (\partial \ln V / \partial T)_P$, was evaluated and shown together in **Fig. 3(b)**. Here, interestingly it is found to start increasing at 330 K, which coincides with the onset temperature of the change in the stress as shown in **Fig. 1**.
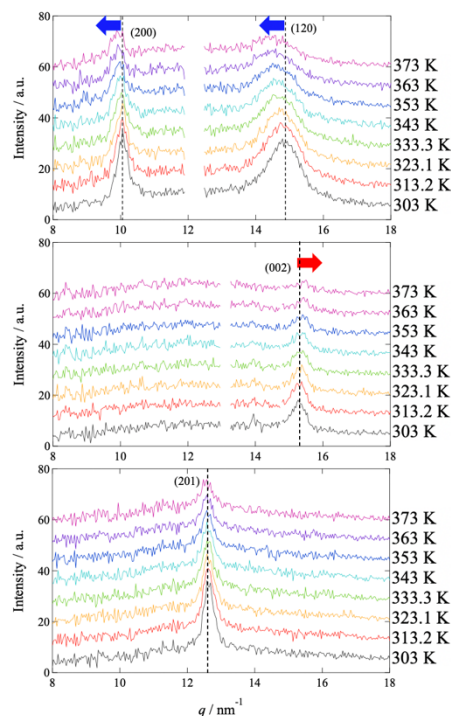

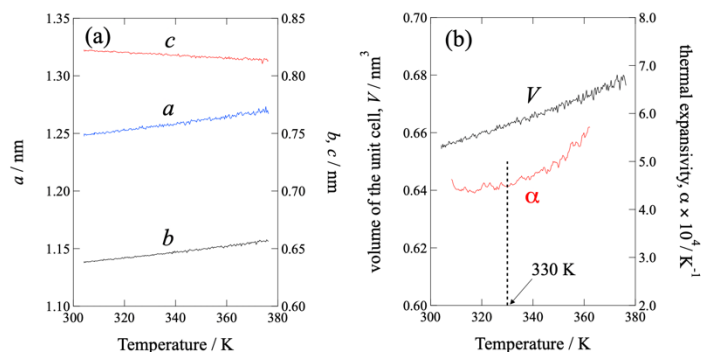**Figure 2:** 1d-WAXD to highlight the crystalline reflection peaks.

Figure 3: Temperature dependencies of (a) lattice constants, and (b) the volume of the unit cell and the thermal expansivity.
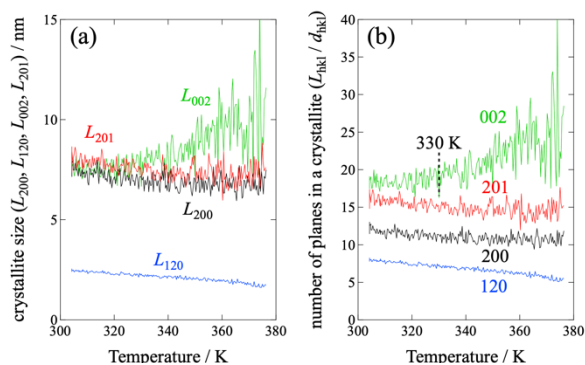

Figure 4: Temperature dependencies of (a) crystallite size, and (b) the number of planes included in a crystallite.

Fig. 4(a) exhibits the change in the crystallite size (L_{hkl}) as a function of temperature for all of the peaks observed in the 2d-WAXD patterns, i.e., (200), (120), (201), and (002) planes, according to the Scherrer's equation from the integral breadths of those reflection peaks. Again interestingly, L_{002} exhibits increasing tendency, while the others show the monotonic decrease with an increase in temperature. Although such increasing tendency of L_{002} implies the growth of crystallites in the c-axis direction (namely in the NR main chain direction), the effect of the c-axis increasing tendency as a function of temperature should be ruled out for the sake of the quantitative discussion. For this purpose, the number of the hkl planes included in a crystallite was estimated by L_{hkl} / d_{hkl}, and shown in **Fig. 4(b)**. Then, more clearly it can be seen that the number for the (002) planes is increased while the others are decreased. Therefore, it can be concluded that crystallites grows in the NR main chain direction, while it is melting off in the other perpendicular directions upon heating. Interesting, the onset of the growth in the c-axis direction is consistent with that of stress increase (**Fig. 1**) and thermal expansivity (**Fig. 3(b)**).

Finally, the change in the degree of crystallinity (χ_c) as a function temperature is shown in **Fig. 5**. It was simply evaluated from the 2d-WAXD patterns by the following equation, $\chi_c = (A_{200} + A_{120} + A_{201} + A_{002}) / (A_{200} + A_{120} + A_{201} + A_{002} + A_{amo})$ where A_{hkl} stands for the integrated peak intensity of the (hkl) plane and A_{amo} does that of the amorphous halo peak, based on the peak deconvolution of the circularly averaged 1d-WAXD profile obtained from the 2d-WAXD pattern. In **Fig. 5**, χ_c clearly exhibits monotonic decrease with temperature, which is somewhat strange because the melting temperature is much higher than the temperature range examined here (about 100 K higher). Can crystallites feel that they should be going to melt? To clearly discuss about this matter, it is important to rule out the possibility of apparent decreasing in χ_c by the shrinkage of crystallites, as expected the decreasing tendency of the crystallite size (**Fig. 4(a)**). Although the crystallite volume is needed to estimate for this purpose, it was impossible to do so accurately because of lack of information of the detailed shape of the NR crystallite. Therefore, we decided to approximate it by the triple product $L_{200} \cdot L_{120} \cdot L_{002}$ (assumption of a rectangular parallelepiped of the crystallite) and shown together in **Fig. 5**. It is then found that the volume of the crystallite decreases with temperature up to 330 K and likely stays constant in the higher temperature range. Furthermore, its decreasing tendency coincides with that of χ_c so that the decreasing tendency below 330 K is not ascribed to the real melting of crystallites but to the shrinkage of the crystallites. However, it is noteworthy here to recognize that the decreasing tendency of χ_c higher than 330 K is still observed in such a temperature range much lower than the real melting temperature, being probably due to the gradual melting of the smaller crystallites which should have a lower melting temperature. As a conclusion, to the best of our knowledge, the clear experimental finding of the shrinkage of the c-axis of the NR crystal with an increase of temperature has never reported before.

ACKNOWLEDGEMENTS

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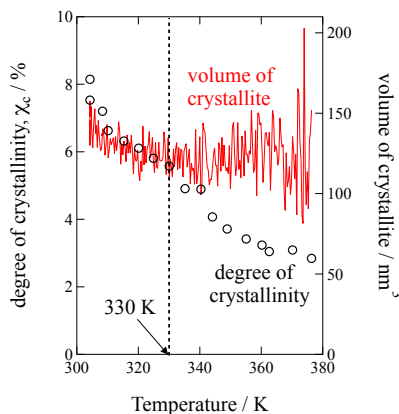
Figure 5: Temperature dependencies of χ_c and the volume of crystallite.