Biaxial Orientation in Triple Centrifuged Natural Rubber

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Summary: Natural rubber (NR) latex was purified through triple centrifugation process and film samples were prepared. The strain-induced crystallization was studied during the uniaxial elongation of the NR samples at room temperature. Crystalline orientation was detected by wide angle x-ray diffraction (WAXD) measuring the intensity of 200 and 120 reflections. The WAXD patterns were compared with the aspect ratio (width/length) of the original NR films. The results indicate that the induced crystals have a biaxial orientation (BO), where the c-axis is parallel to the draw direction and the a-axis is parallel to the film surface. Using the WAXD through patterns, we distinguish the highly oriented BO region in the samples. In order to analyze the structure and properties of the NR, the effect of BO is an essential factor.

Keywords: aspect ratio; biaxial orientation; natural rubber latex; uniaxial drawing; wide angle x-ray diffraction

Introduction

Crystalline morphologies of natural rubber (NR) were introduced by Andrews using transmission electron microscopy. The thin NR films were crystallized isothermally at $-26\,^{\circ}C$ in the unstrained state. [1] The crystallization was developed into semi-crystalline spherulites. Later, Andrews reported the crystalline morphologies under strain (ε).[2,3] The resulting crystalline morphologies of NR were classified into five groups: (i) At $\varepsilon = 0\%$, spherulitic structure where the α-filaments (named by Andrews[2]) are arranged radially. (ii) At $\varepsilon = 50\%$ sheaf-like structure is developed. (iii) At $\varepsilon = 100\%$, the α-filaments are stacked perpendicular to the stretching direction due to raw nucleation.[3,4] (iv) At $\varepsilon = 200\%$, the length of the α-filaments becomes shorter. Therefore, the morphology for $\varepsilon = 100$–200% is developed by the row (or shish-kebab) crystallization. (v) The morphology for $\varepsilon > 300\%$ is expressed by different structure in which filaments of another type ("γ-filaments" by Andrews) can be observed to orient parallel to the stretching direction.[2,5] The γ-filaments and row nuclei are speculated to the same species.[6] An almost similar classification was given by Reed. [7]

The behavior of the strain-induced crystallization under deformation of NR was also studied by wide angle x-ray diffraction (WAXD).[8,9] However, most of the above works are based on the consideration of uniaxial orientation, where the molecular c-axis is oriented parallel to the draw direction and the orientation of a- and b-axes are random. Recently, we have found the biaxial orientation (BO) in bulk NR film using WAXD. [10] In the present work, we investigate the effects of an aspect ratio (AR = width/length) on BO of the triple centrifuged NR film.

Experimental Procedure

NR latex was collected from Bangladesh Forest Industries Development Corporation. The field latex was purified through triple centrifugation using a facility manufactured by Saito Separator Ltd., Japan. [11]

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The triple centrifuged latex (TCL) was prepared into sheet by the leveled glass dish. The thickness of the TCL sheet was kept 1.0 mm. For experiments, four samples having the different gauge length and width were prepared as listed in Table 1.

All the samples were drawn uniaxially at 25 °C. The apparatus for simultaneous drawing and WAXD measurements is shown in Fig. 1. The draw ratio, λ, is defined as L/L_o, where L_o and L are the overall length of the initial and drawn sample, respectively. We define here coordinates for the drawn sample as the Z-axis parallel to the draw direction. The X- and Y-axes are perpendicular and parallel to the film surface, respectively. We named the WAXD patterns as "through" and "edge" with the incident x-ray beam parallel to the X- and Y-axis, respectively.

The shapes of the original sample and the drawn one at $\lambda = 6.0$ are presented in Fig. 2. The morphologies of the samples were studied by WAXD, performed by a high-intensity x-ray generator (Rigaku RU300). The incident x-ray was monochromatized by a graphite single crystal, having the wavelength of 1.54 Å. The x-ray beam was passed through a point collimation of 100 μm diameter. Standardizing of the WAXD measurements, the camera length and exposure time was kept at 20.5 mm and 10 min, respectively in every case. The WAXD results were recorded by an imaging plate (IP).

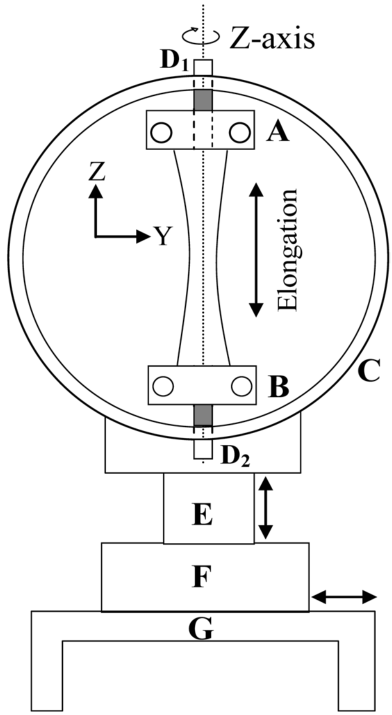

Figure 1.
Schematic diagram of the drawing apparatus. The two clamps (A and B) were attached to the frame C by the screws D_1 and D_2. The sample was drawn uniaxially by manual displacement of them. Sample position was adjusted by the movement of C which was finely controlled by the displacements of manipulators E and F. For measurements of the edge pattern, the sample is rotated by 90° around the Z-axis. The apparatus was connected to the x-ray diffraction facility by G.

Results

Intensity Distribution

The crystal structure of NR, namely *cis*-1,4-polyisoprene, was determined by Bunn [12] and reported as monoclinic; a = 1.246 nm, b = 0.889 nm, c (chain axis) = 0.810 nm and $\beta = 92°$. Four molecular chains are passing through the unit cell. In the present measurement, we used the similar crystal structure as

Table 1.
The gauge length, width and thickness of the experimental samples.

Sample	Length (L)	Width (W)	Thickness (T)	*Aspect ratio (W/L)
TCL- 1	8	1	1	0.125
TCL- 2	8	8	1	1.0
TCL- 3	6	8	1	1.33
TCL- 4	4	8	1	2.0

* The aspect ratio (AR) is the ratio between width and length of the initial sample.

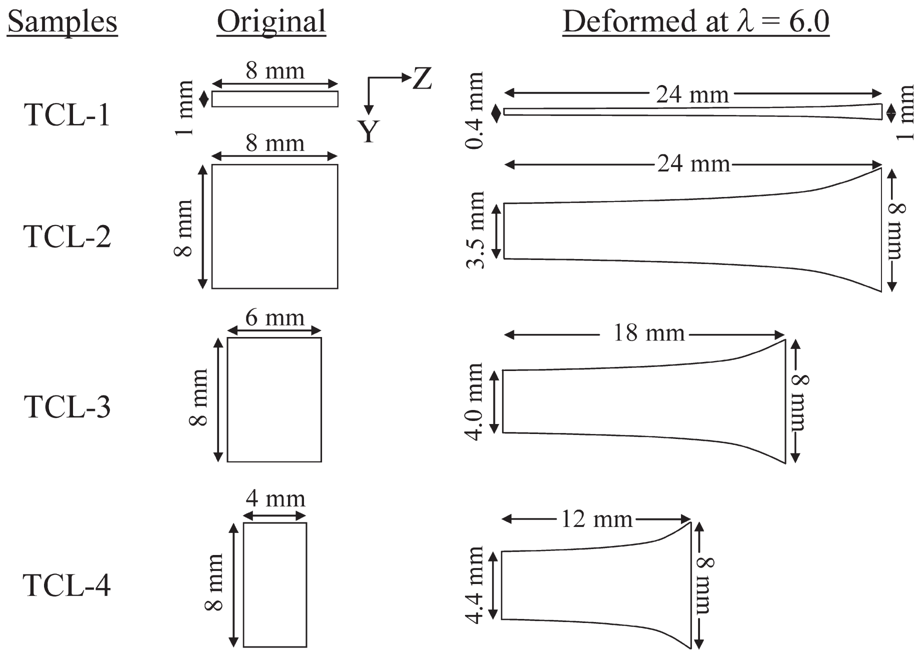

Figure 2.
Shapes of original samples (left side) having different gauge lengths. For clamping, 4 mm space was added on both sides of the original sample. The deformed shapes (a half of the symmetrical parts) of the samples at $\lambda = 6.0$ are shown in the right side. The value of the draw ratio ($\lambda = 6.0$) corresponds to $\varepsilon = 500\%$ followed by Andrews.

Bunn. The BO is observed by comparing the intensity of 200 and 120 reflections in the WAXD patterns. In Fig. 3, WAXD patterns at the central position of the drawn samples are compared as a function of AR in both through and edge directions. The intensities of 200 and 120 reflections are measured along the equator with respect to the scattering angle (2θ). Due to the difference of the structure factor [12], the intensity of 200 reflection is lower than that of 120 in Fig. 3 (a). The intensity distribution is almost same in Fig. 3 (b) and (d). This fact indicates that TCL-1 has the uniaxial orientation.

Intensity of 200 reflection is increased in Fig. 3 (f). On the other hand, intensity of 200 decreases in Fig. 3 (h). The results show the appearance of the biaxial orientation (BO) in TCL-2. Due to the volume effect, as an x-ray beam passed a longer distance in the edge measurement, the WAXD edge patterns become intense in Fig. 3 (g), (k) and (o). Increasing the AR values, a large difference is observed in the through {Fig. 3 (j)} and edge {Fig. 3 (l)} patterns. Finally in TCL-4, the 120 and 200 reflections are separately distributed in Fig. 3 (n) and (p). The results demonstrate that the degree of BO increases with AR.

Qualitative Degree of BO Measured by the WAXD through Pattern

Using the WAXD through patterns, BO is distinguished by the intensity of 200 and 120 reflections. For classification of BO, we judged by the WAXD through patterns. We named (200 + 120) region when the through pattern has both 200 and 120 reflections such as Fig. 3 (a), (e) and (i). We named (200) region when the pattern has almost 200 reflection such as Fig. 3 (m). The degree of BO is higher in the (200) region. In order

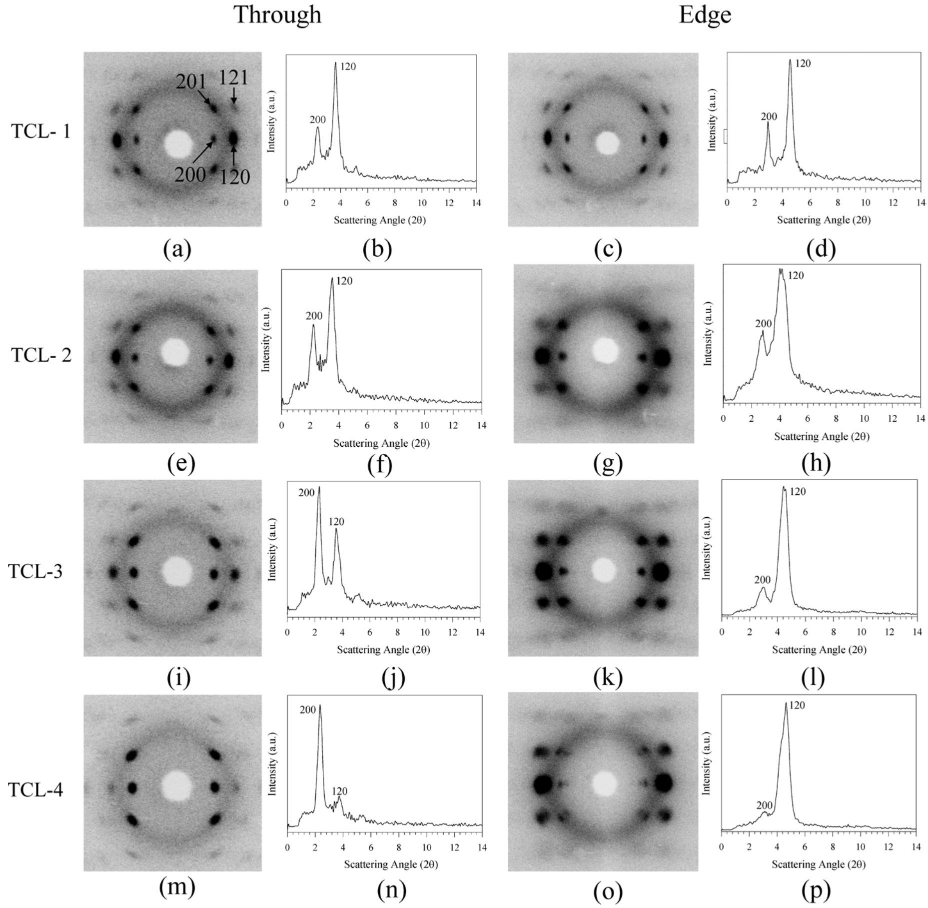

Figure 3.
Comparison of the through and edge WAXD patterns with intensity distribution of 200 and 120 reflections at the central position of samples TCL-1, TCL-2, TCL-3 and TCL-4.

to observe the overall distribution of BO, WAXD through patterns were measured over the entire surface of the drawn film for all samples. Measurements were taken every 0.5 and 1 mm area along the Y- and Z-axes, respectively. The survey results are summarized by mapping as the (200 + 120) and (200) regions on the film surface. The mapping for BO regions in all samples are shown in Fig. 4. TCL-1 sample has no (200) region except (200 + 120). TCL-2 shows clear (200) region near the clamping end. The (200) region is increased for TCL-3. The (200) region is covered most of the area in TCL-4. The BO becomes lower in the periphery for all the samples shown by the (200 + 120) region.

Discussions

Effect of the Aspect Ratio on the Strain-Induced Crystallization

During the uniaxial drawing of the NR film, the strain induced crystal has BO. The degree of BO is changed with AR of the samples. TCL-1 has no BO showing uniaxial orientation. In TCl-2, the different intensity distribution indicates the appear-

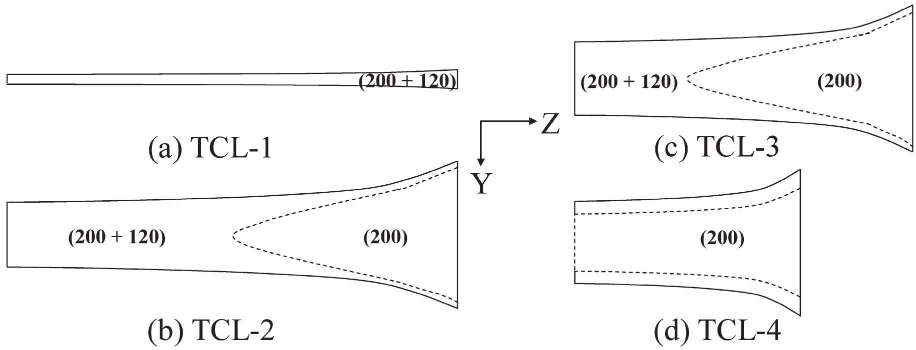

Figure 4.
BO regions of the four samples.

ance of BO. Degree of BO is increased in TCL-3 and TCL-4.

The WAXD results shown in Fig. 3 are possible to explain using a concept of the intensity distribution of 200 and 120 reflections in the reciprocal space. Based on the WAXD results, we propose the distribution model in Fig. 5. The inner and outer rings correspond to the distribution of intensity for 200 and 120 reflections, respectively. Considering the intensity at the cutting position by Ewald sphere, intensity of the through and edge patterns are estimated. In the reciprocal lattice of NR crystal, 200 and 120 reflections exist on the a^*-b^* plane.

In Fig. 5 (a), homogenous intensity distribution for TCL-1 demonstrates that (200) and (120) planes are uniformly populated in

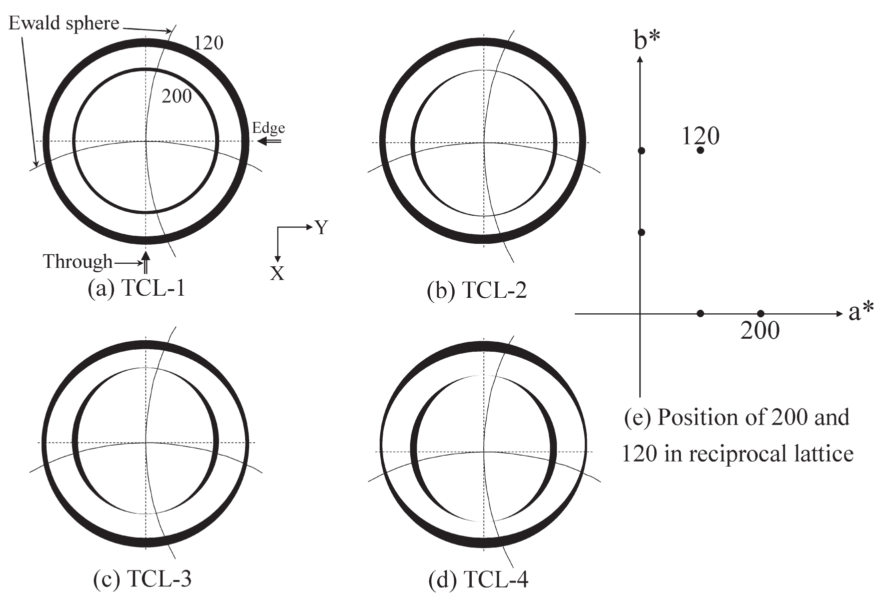

Figure 5.
Intensity distribution model in reciprocal lattices for 200 and 120 reflections. (a) TCL-1 (b) TCL-2 (c) TCL-3 and (d) TCL-4.

all directions. Depending on AR, the features of the distribution become inhomogeneous. In Fig. 5 (d), the 200 reflection is concentrated on the Y-axis showing strong BO. In TCL-4, crystalline a-axis is mostly populated along the Y-axis. The results in the distribution of the (200) region shown in Fig. 4 confirms that the degree of BO increases with AR of the initial sample. The width of the four samples is compared in Fig. 2. From the results, BO is closely related to the sample width at $\lambda = 6.0$. During the strain induced crystallization of the large AR sample, the crystalline a-axis becomes parallel to the film surface. The degree of BO changes continuously all over the film surface depending on AR.

The above results are possible to explain by the following considerations. At $\lambda = 6.0$ ($\varepsilon = 500\%$), highly oriented filaments (γ-filaments) are grown parallel to the draw direction. From the oriented filaments, raw crystallization occurs like a process of the (-filaments named by Andrews. The secondary crystallization ((-filaments) develops along the crystalline a-axis to the inter- space between the γ-filaments. If we suppose the distribution of the γ-filament is widened with the sample width, the a-axis of the (-filament will develop along the Y-axis. As a result, the degree of BO is related to the sample width at $\lambda = 6.0$, determined by AR.

The $(200 + 120)$ region is appeared along the periphery for all samples. As NR is an elastic material, the strain may be relaxed at the free edge of the film. Due to the relaxation of the sample strain, the thickness of both sides of the drawn NR might be increased. The low BO at the periphery of the sample is due to the effect of the thickness relaxation or a disturbance in the strain distribution. From the results of the qualitative analysis using WAXD through patterns, the degree of BO is enhanced by AR of the original NR film. The present results indicate that the crystallization mechanism is closely related to BO.

Conclusion

During the uniaxial elongation of NR film, the effect of AR was measured by WAXD. The inhomogeneous WAXD distribution of the intensity of 200 and 120 reflections is analyzed by the development of BO of the induced crystals, where the c-axis is parallel to the draw direction and the a-axis is parallel to the film surface. The degree of BO increases with AR of the initial sample. By the precise survey using WAXD through patterns, the NR film was distinguished into two regions: (i) $(200 + 120)$ region having low degree of BO, (ii) (200) region with high degree of BO. From qualitative evaluation of the WAXD patterns, the degree of BO is related to the sample width at $\lambda = 6.0$, which arises from AR of the original samples.

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