ELSEVIER

Polymer 43 (2002) 2117–2120

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Structural development of natural rubber during uniaxial stretching by in situ wide angle X-ray diffraction using a synchrotron radiation

Syozo Murakami[a,*], Kazunobu Senoo[a], Shigeyuki Toki[b], Shinzo Kohjiya[a]

[a]*Laboratory of Polymer Condensed States, Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan*
[b]*Department of Chemistry, State University of New York, Stony Brook, NY 11794, USA*

Received 6 November 2001; received in revised form 4 December 2001; accepted 5 December 2001

Abstract

Structural development of natural rubber during uniaxial stretching was examined by an in situ wide angle X-ray diffraction measurement using a synchrotron. During stretching, the amorphous part showed little change, i.e. an amorphous halo remained clear even at 500% strain. The fraction of induced crystals was very small, though a clear crystalline pattern was observed at 400% strain. Some polymer chains were oriented and crystallized, but most of the chains were not oriented at all in spite of large deformations of the specimen. Only a small amount of polymer chains contributes to the stress and hysteresis loss during elongation. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber; Molecular orientation; In situ X-ray diffraction by a synchrotron

1. Introduction

Natural rubber (NR) is an indispensable elastomeric material because of its ability to crystallize at large deformations resulting in an extraordinary toughness. The induced crystals of NR may arrest the possible crack development where large local strains occur. Recognition of this hypothetical mechanism has given rise to extensive studies on crystal structure and morphological study since the early stage of polymer science development. The NR crystal lattice constants were reported by Mark and von Susich in 1928 [1], Morss in 1938 [2] and Bunn in 1942 [3]. Andrews [4,5] and coworkers [6] examined NR thin film that had been stretched up to a desired strain followed by isothermal crystallization and showed several kinds of morphologies by transmission electron microscopy (TEM) using a staining technique. Recent studies [7–9] by TEM of NR without staining were in accord with the Andrews' and afforded more in detail crystal structure. However, dynamical studies on TEM are extremely difficult. Mitchell [10] studied NR sheet with uniaxial stretching, and calculated crystallinity and orientation ratio based on wide angle X-ray diffraction (WAXD) analysis. Stein and his coworkers [11] evaluated molecular orientations of NR with birefringence. However, the relationship between the structural development during this induced crystallization and details of the stress history during stretching have not been elucidated. This is primarily due to the lack of robust in situ structure measurement technique. Recently, Toki et al. [12] reported the in situ measurement of strain-induced crystallization and stress–strain relation of NR with WAXD. This study suggested that the hysteresis loss observed in stress–strain relation was related to the strain-induced crystallization. However, the intensity of X-ray source has not been powerful enough for the elucidation of dynamic behaviors [13–15]. An in situ birefringence measuring system was fabricated [16,17], but the birefringence measurement detected only the overall molecular orientation of crystalline and amorphous parts.

This communication is reporting in situ WAXD results obtained during the stretching and returning of NR vulcanizates using a powerful synchrotron radiation at SPring-8, Hyogo, Japan. The WAXD patterns obtained are in full agreement with those observed at National Synchrotron Light Source, Brook Heaven National Laboratory, NY, USA, but this point will be separately communicated.

2. Experimental section

2.1. Material

Sulfur vulcanizates of natural rubber were prepared with the recipe shown in Table 1. Ingredients were mixed in an internal mixer. The compounds were vulcanized at 145 °C for 1 h to form 1 mm thick sheets. Dumb-bell shaped

---

[*] Corresponding author. Tel.: +81-774-38-3064; fax: +81-774-38-3067.
E-mail address: murasyo@scl.kyoto-u.ac.jp (S. Murakami).

0032-3861/02/$ - see front matter
PII: S0032-3861(01)00794-7

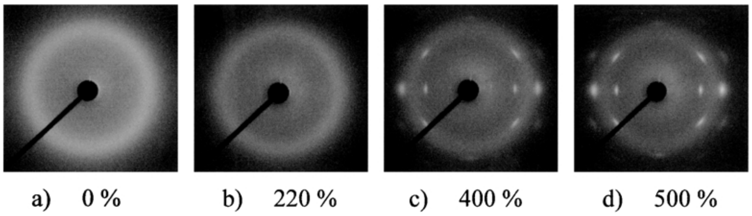

Fig. 1. WAXD pattern of NR upon stretching at room temperature at (a) 0%, (b) 220%, (c) 400% and (d) 500% strain.

Table 1
Recipe of compounds

NR	100	(SMR-5)[a]
Stearic acid	2.0	
Anti-oxidant	1.0	(MBMTB)
Active ZnO	1.0	
Accelerator	1.0	(TBBS)
Sulfur	1.5	

[a] Standard Malaysian rubber number 5.

specimens were cut from the sheet samples. The width of the parallel part of the sample is 3 mm, the gauge length (length of the parallel part) is 10 mm and the distance of clamp–clamp is 24 mm.

2.2. Instruments

A stretching machine was fabricated in order to stretch the sample horizontally by both right and left clamps in the heat chamber. This system allows constant monitoring of the sample at the stationary mid point by X-ray during stretching and retraction. The details of the stretching machine were reported previously [18,19]. The X-ray beam line (BL40XU) of the synchrotron, SPring-8, Hyogo, Japan was used. The wavelength of the X-ray is 0.10 nm. The CCD camera was used as an X-ray detector. The WAXD patterns and their intensities were continuously detected during stretching and returning. The irradiation time of the X-ray in one shot was 10 s.

3. Results and discussion

3.1. Change of the WAXD pattern during stretching

WAXD patterns of NR during stretching at speed of 10 mm/min are shown in Fig. 1. At the initial undeformed point (Fig. 1(a)), only a halo due to an amorphous phase was observed. Even at strain 220% (Fig. 1(b)), the same halo was recognized indicating the sample was still before crystallization. However, small seeds of crystalline diffraction peaks were observed at around 230% strain. At 400% strain (Fig. 1(c)), clear crystalline diffraction peaks and a coexisting halo were observed. At 500% strain, the crystalline diffraction pattern became much clearer but the halo still remained as seen in Fig. 1(d). The crystal structure of natural rubber was determined by Bunn [3], and its crystal system is monoclinic (space group = $P2_1/a$): $a = 1.246$ nm, $b = 0.889$ nm, c (chain axis) = 0.810 nm, $\beta = 92°$. The width in the equatorial direction and in the azimuthal direction of the 120 crystalline reflection remained constant during stretching, but the intensity of peaks increased. The width of crystalline reflection in the azimuthal direction, α, is defined as an angle at the central point in Fig. 2. The fluctuation of the angle of 120 crystalline reflections from the stretching direction, Θ, is evaluated by Eq. (1)

$$\Theta = (180 - \alpha)/180 \quad (1)$$

Because 120 crystalline reflections were on the equator and α was about 12.5°, $\Theta = 0.93$ was obtained. The fluctuation Θ did not depend on the strain, since α remained constant during stretching. This result suggests that the molecular chains in the induced crystals are oriented almost parallel to the stretching direction as when $\Theta = 1$, the chains are perfectly parallel to the stretching direction. The constant width of the intensity profiles in the equatorial direction suggests that the induced crystallites are well packed and of almost the same size.

The ratio of unoriented amorphous and oriented amorphous can be evaluated with the peak scattering intensities of amorphous phases at the equator and meridian directions against the stretching direction shown in Fig. 3. The amorphous scattering intensities at meridian and at equator are defined as I_a(meridian) and I_a(equator), respectively. Both the intensities decreased with the strain, since the thickness of the sample decreased, and the differences of I_a(meridian) and I_a(equator) at each strain were very small, which

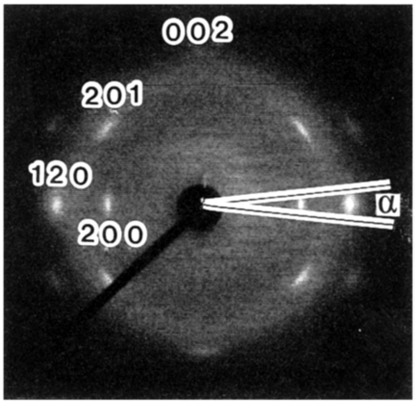

Fig. 2. Crystalline reflection of crystalline plane of NR and the orientation angle of crystallites α.

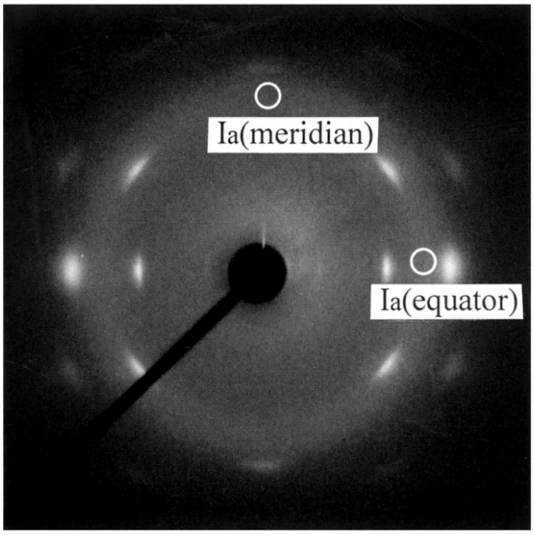

Fig. 3. Definition of I_a(meridian) and I_a(equator).

suggests that the amorphous halo has remained almost constant up to very high strains. This result means that molecules in the amorphous part did not orient much and most of polymer chains remained random in direction. The degree of scattering intensity of parallel molecules for perpendicular molecules of the amorphous region in the stretching direction (the orientation ratio of the amorphous part), χ, is defined as in Eq. (2)

$$\chi(\%) = \{[I_a(\text{equator}) - I_a(\text{meridian})]/I_a(\text{equator})\} \times 100 \tag{2}$$

χ was 4.7% at 500 strain. The crystallinity which was evaluated from the intensity profile at equator by the CCD camera detector was 13.7% at 500% strain. But, it may still be lower than this value by the other detector. The oriented amorphous phases may be easily transformed into the induced-crystal phase. Although the transformation results in the decrease of the oriented amorphous parts and increase of the induced crystalline parts, the amount of crystalline parts may be very small. The result suggests that only less number of molecules are oriented and crystallized by stretching and most of the molecules are not oriented even under high strains.

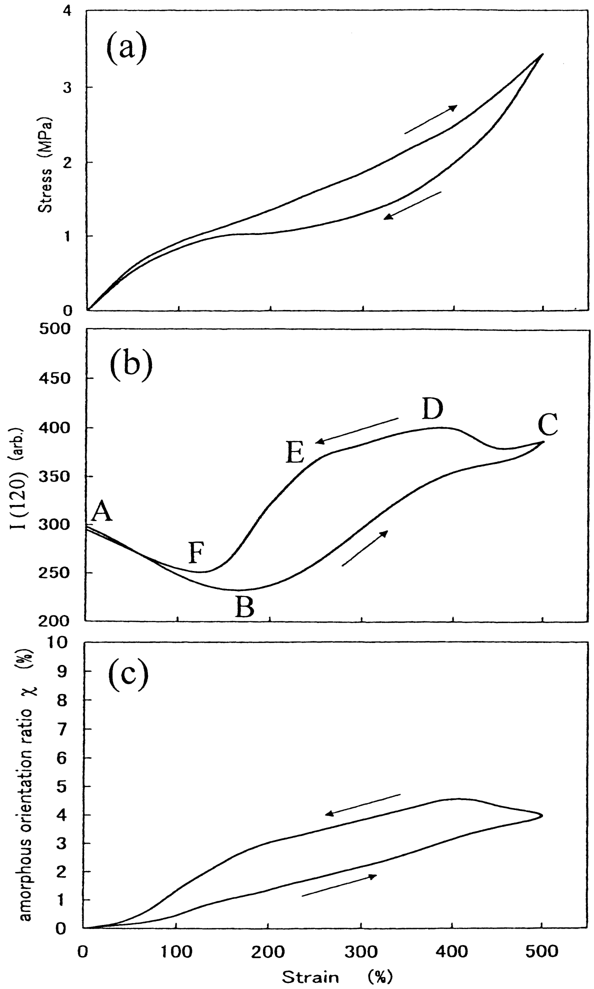

Fig. 4. (a) Hysteresis of stress, (b) $I(120)$ and (c) amorphous orientation ratio χ against strain.

3.2. Hysteresis of stress, the diffraction intensity of 120 crystalline reflections and the orientation of amorphous phases against strain

NR shows significant hysteresis loss as revealed by the stress–strain relation shown in Fig. 4(a). The stress during retraction was lower than the one during stretching. The peak intensity at the position of (120) plane of crystallites, $I(120)$, also showed hysteresis against strain as shown in Fig. 4(b). However, it is in the opposite direction, i.e. $I(120)$ during retraction is higher than the one during stretching. In Fig. 4(b), A to B is amorphous intensity which decrease as the specimen becomes thin. The intensity increased by stretching due to amorphous orientation over B point. At about 230% strain, 120 crystalline reflection starts to appear. This crystalline intensity showed a rapid increase until 400% strain and a gentle increase until 500% strain at C point. While retracting from C, the intensity decreased a little, and then increased up to D than the one at C. The intensity decreased slowly from D to E and decreased suddenly over at E point. From E to F, it is thought that crystal structure disappears rapidly. The point which 120 crystalline reflection disappeared perfectly was at 142% strain. The X-ray intensity at F point is that of the amorphous phases in the specimen.

The value of $I(120)$ may be inclusive of the contribution from oriented amorphous and unoriented amorphous phases, but their contribution is little since the amorphous intensity peak position is away from the crystalline intensity peak position. As stated before, the amount of oriented amorphous and unoriented amorphous parts kept almost unchanged during stretching. Therefore, the strain dependency of $I(120)$ is due to induced crystals. $I(120)$ shows higher value after the start of retraction than the one at the largest strain during stretching. It may be caused by the transformation from oriented amorphous phases to crystals. Although the hysteresis loss of *I*(120) seems to be significant, the amount of crystalline parts must be very small according to the behavior of amorphous parts as seen in Figs. 3 and 4(c) because it seems to be thought that in the orientation crystallization of ordinary semicrystalline materials, the amorphous chains orient to stretching direction and then the oriented amorphous chains change to crystal [20–22]. The values of the curve in Fig. 4(c) show the difference of the amorphous peak intensity at equator to the one at meridian. The orientation ratio χ of amorphous parts also show hysterisis as shown in Fig. 4(c). The largest value of χ is about 5%. This value suggests that only small number of polymer chains are oriented, while most of polymer chains are not oriented. The small number of polymer chains certainly show hysteresis as well as crystalline parts do. Therefore, the small number of polymer chains contribute to the stress. During retraction these small number of chains may decrease the stress drastically because a part of these polymers are crystallized and do not contribute entropy force during retraction.

4. Conclusions

The in situ WAXD measurements using the synchorotron X-ray reveal the response of amorphous molecules and induced crystals during stretching. Amorphous halo remains even at large strains, which implies that most of the polymer chains are not oriented. In other words, the oriented amorphous parts are very few. Crystallized polymer chains are also very few. The remaining molecules show random orientation, i.e. they remain to be amorphous up to high elongations. Natural rubber may be easily recovered to its original length because the amount of the crystallized parts is very small by stretching. The induced crystals seem to be well packed, parallel to the stretching direction and of almost the same size. The small amount of rubber chains seem to endure whole stress and most of the polymer chains are not oriented at all, which suggests a different picture of deformation from the conventional Affine deformation [23].

Acknowledgements

The synchrotron radiation experiments were performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal no. 2000B0398-ND-np). We appreciate cooperation of Mr Katsuaki Inoue of the SPring-8 and Dr Yukihiro Nishikawa of the RIKEN Harima Institute.

References

[1] Mark H, von Susick G. Kolloid Z 1928;46:11.
[2] Morss HA. J Am Chem Soc 1938;60:2371.
[3] Bunn CW. Proc R Soc Lond A 1942;180:40.
[4] Andrews EH. Proc R Soc Lond A 1962;270:232.
[5] Andrews EH. Proc R Soc Lond A 1964;272:562.
[6] Andrews EH, Owen PJ, Sing A. Proc R Soc Lond A 1971;324:79.
[7] Shimizu T, Tosaka M, Tsuji M, Kohjiya S. Rubb Chem Technol 2000;73:926.
[8] Tsuji M, Shimizu T, Kohjiya S. Polym J 1999;31:784.
[9] Tsuji M, Shimizu T, Kohjiya S. Polym J 2000;32:505.
[10] Mitchell GR. Polymer 1984;25:1562.
[11] Hashiyama M, Gaylord R, Stein S. Die Makromol Chem Suppl 1975;1:579.
[12] Toki S, Fujimaki T, Okuyama M. Polymer 2000;41:5423.
[13] Gehman SD, Field JE. J Appl Phys 1939;10:564.
[14] Luch D, Yeh GSY. J Macromol Sci Phys B 1973;97:121.
[15] Shimomura T, White JL, Spruiell JE. J Appl Polym Sci 1982;27:3553.
[16] Toki S, Sen TZ, Valladares D, Cakmak M. ACS Rubber Div. Spring Meeting, Paper#12, 2001.
[17] Toki S, Sen TZ, Valladares D, Cakmak M. ACS Rubber Div. Fall Meeting, Paper#42, 2001.
[18] Murakami S, Tanno K, Tsuji M, Kohjiya S. Bull Inst Chem Res Kyoto Univ 1995;72:418.
[19] Murakami S. Nippon Kagaku Kaishi 2000;2:142.
[20] Asano T, Seto T. Polym J 1973;5:72.
[21] Murakami S, Nishikawa Y, Tsuji M, Kawaguchi A, Kohjiya S, Cakmak M. Polymer 1995;36:291.
[22] Bedia EL, Murakami S, Kitade T, Kohjiya S. Polymer 2001;42:7299.
[23] Treloar LRG. The physics of rubber elasticity. 3rd ed. London: Clarendon Press, 1975.