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Strain-induced crystallization of peroxide-crosslinked natural rubber

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Abstract

Effect of network-chain density (ν) on the strain-induced crystallization of peroxide-crosslinked natural rubber was studied by fast time-resolved synchrotron wide-angle X-ray diffraction. It was observed that the elongation ratio at the onset of strain-induced crystallization (α_c) became smaller with the increase of ν. The difference of the entropy between the undeformed and deformed states at each α_c was nearly equal in spite of the variation of ν. The calculated melting temperature at α_c of the samples was also almost the same regardless of their ν. These observations mean that the strain-induced crystallization occurred when the deformation brought about a definite entropic state for peroxide-crosslinked natural rubber. They agreed with the prediction by Flory and were consistent with the classical theory of rubber elasticity.

Keywords: Peroxide-crosslinked natural rubber; Strain-induced crystallization; Network-chain density

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1. Introduction

Recently, the studies on the strain-induced crystallization (SIC) of crosslinked rubber have been extensively conducted by synchrotron wide-angle X-ray diffraction (WAXD) [1–14]. The synchrotron radiation system combined with a stretching machine becomes a powerful tool for studying dynamics of deformation behavior of soft materials, because the effect of relaxation of macromolecules can be minimized by setting the irradiation time shorter. Thus, several interesting results on SIC of natural rubber (NR) and synthetic rubber have been reported and the observed phenomena have been discussed by comparing with theoretical models. For example, we found that the rate of SIC of sulfur-crosslinked NR was faster for the samples with higher network-chain density (ν) [14], which was the opposite trend in the former works conducted for the stretched samples during relatively long-time under small strain [5,15]. The difference would be ascribed to the speed of each WAXD measurement. Thus, the importance of direct observation of structure in real time during deformation of rubber is clear.

Among general-purpose rubbers, NR is necessary to prepare the high performance pneumatic tires used under severe conditions. One reason for the excellent mechanical properties of NR has been assumed due to its SIC ability. Thus, most of the NR products, so far, have been produced using a sulfur-cure system, and consequently many studies on the SIC of sulfur-crosslinked NR have been conducted [1–12,14,16–23]. However, only a few reports [3,9,13,19] have partially described the crystallization of peroxide-crosslinked NR upon stretching. Peroxide-crosslinked NR is nowadays utilized more and more owing to their high transparency, lower compression set and improved heat resistance. Therefore, it is important for practical applications to reveal characteristics of SIC for peroxide-crosslinked NR in situ during deformation.

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In this study, experimental results on SIC for peroxide-crosslinked NR with different ν are reported, which were obtained by fast time-resolved synchrotron WAXD measurements at SPring-8 during uniaxial stretching. As mentioned above, the relationship between stress and SIC of crosslinked rubber under deformation has been extensively investigated. However, we can hardly find the studies on the dependence of ν on the SIC of crosslinked rubber, although it can be predicted by Flory's theory [16,24]. This scientific background also forms the motivation for this work.

2. Experimental

Peroxide-crosslinked NR samples were prepared as follows: NR was mixed with dicumyl peroxide (DCP) on a two-roll mill. The mixes were cured under a heat-pressing at 155 °C in a mold to give crosslinked NR sheets of ca. 1 mm thickness. The optimal pressing time of each compound was determined on the basis of the result of cure characteristics from a JSR Curelastmeter III, which was used to monitor the progress of curing. The recipes of NR mixes and processing conditions are shown in Table 1. Ring-shaped specimens were cut out from the sheet, the inner and outer diameters of which being 11.7 and 13.7 mm, respectively.

Synchrotron WAXD measurements were carried out at BL-40XU beam line in SPring-8, Harima, Japan [25]. A custom-made tensile tester was situated on the beam line and WAXD patterns were recorded simultaneously during tensile measurement at r.t. (ca. 25 °C). The wavelength of the X-ray was 0.08322 nm and the camera length was 213 mm. The two-dimensional WAXD patterns were recorded using a CCD camera (Hamamatsu C4880-50). Intensity of the incident X-ray was attenuated using a rotating slit equipped by the beam line and the incident beam was exposed at every 6 s for 200 ms in order to avoid radiation damage of the specimens. The absorption correction for thinning of the samples was carried out by calculating the correction coefficient, which was obtained by using absorption coefficients per density [26] and weight fractions for each element in the samples, assuming the affine deformation. Here, the Poisson ratio of the samples was assumed to be 0.5. Intensities of the incident beam and transmitted beam through air were measured by using ion chambers.

The custom-made tensile tester (ISUT-2201, Aiesu Giken, Co., Kyoto) could stretch the specimen symmetrically to examine almost the same position of the specimen by X-ray diffraction/scattering. Ring-shaped samples were subjected to the tensile measurement in order to give a constant stretching speed and to correctly measure the elongation ratio (α) of deformed samples. Here, α is defined as $\alpha = l/l_0$, in which l_0 is the initial length and l is the length after deformation. The stretching speed was 100 mm/min, i.e., strain speed was 5/min.

The obtained WAXD images were processed using a software "POLAR" (Stony Brook Technology & Applied Research, Inc.) [2,8,10]. The WAXD patterns of stretched samples were decomposed into three components, i.e., isotropic, oriented amorphous and crystalline components. All components were azimuthally integrated in the range of ±75° from the equator, and the analytical method described in our previous paper [10] was utilized to determine "crystallinity index (CI)" and "oriented amorphous index (OAI)" by the following equations. "Un-oriented amorphous index (UAI)" was calculated by "UAI = 1 − (CI + OAI)".

$$\mathrm{CI} = \frac{\sum_{\text{crystal}} 2\pi \int \sin\phi \, \mathrm{d}\phi \int I(s) s^2 \mathrm{d}s}{\sum_{\text{total}} 2\pi \int \sin\phi \, \mathrm{d}\phi \int I(s) s^2 \mathrm{d}s} \tag{1}$$

$$\mathrm{OAI} = \frac{\sum_{\text{oriented amorphous}} 2\pi \int \sin\phi \, \mathrm{d}\phi \int I(s) s^2 \mathrm{d}s}{\sum_{\text{total}} 2\pi \int \sin\phi \, \mathrm{d}\phi \int I(s) s^2 \mathrm{d}s} \tag{2}$$

In Eqs. (1) and (2), $I(s)$ represents the intensity distribution of each peak that is read out from the WAXD pattern, s is the radial coordinate in reciprocal space in nm^{-1} unit ($s = 2(\sin\theta/\lambda)$, where λ is the wavelength and 2θ is the scattering angle), and ϕ is the angle between the scattering vector of the peak and the fiber direction.

The ν of samples was estimated on the basis of the classical theory of rubber elasticity [17].

$$\sigma = \nu kT\left(\alpha - 1/\alpha^2\right) \tag{3}$$

where σ is stress, k is the Boltzmann constant and T is absolute temperature.

3. Results and discussions

Fig. 1(a) shows the stress–strain curves of peroxide-crosslinked NR samples, where symbols show the irradiation points of WAXD. The larger the ν, at the earlier strain the upturn of stress occurred. The slope of the upturn tended to become larger with the increase of ν. It is ascribable to the SIC of NR. Variations of UAI, OAI and CI are plotted against α in Fig. 1(b)–(d), respectively. By stretching, NR chains immediately started to orient to the stretching direction and UAI decreased as shown in Fig. 1(b). The decrease of UAI for each sample was small at the beginning and became larger after a certain elongation ratio, which shifted to the smaller strain with the increase of ν. Namely, the orientation of NR

Table 1
Preparation of the samples

Sample code	P-NR-1	P-NR-2	P-NR-3	P-NR-4
NR (RSS#1) (phr[a])	100	100	100	100
DCP[b] (phr[a])	1.0	2.0	2.5	3.0
Time of heat-pressing[c] (min)	21	27	30	30
$\nu \times 10^4$ (mol/cm^3)	0.76	1.38	1.70	1.93

[a] Parts per one hundred rubber by weight.

[b] Dicumyl peroxide.

[c] At 155 °C.

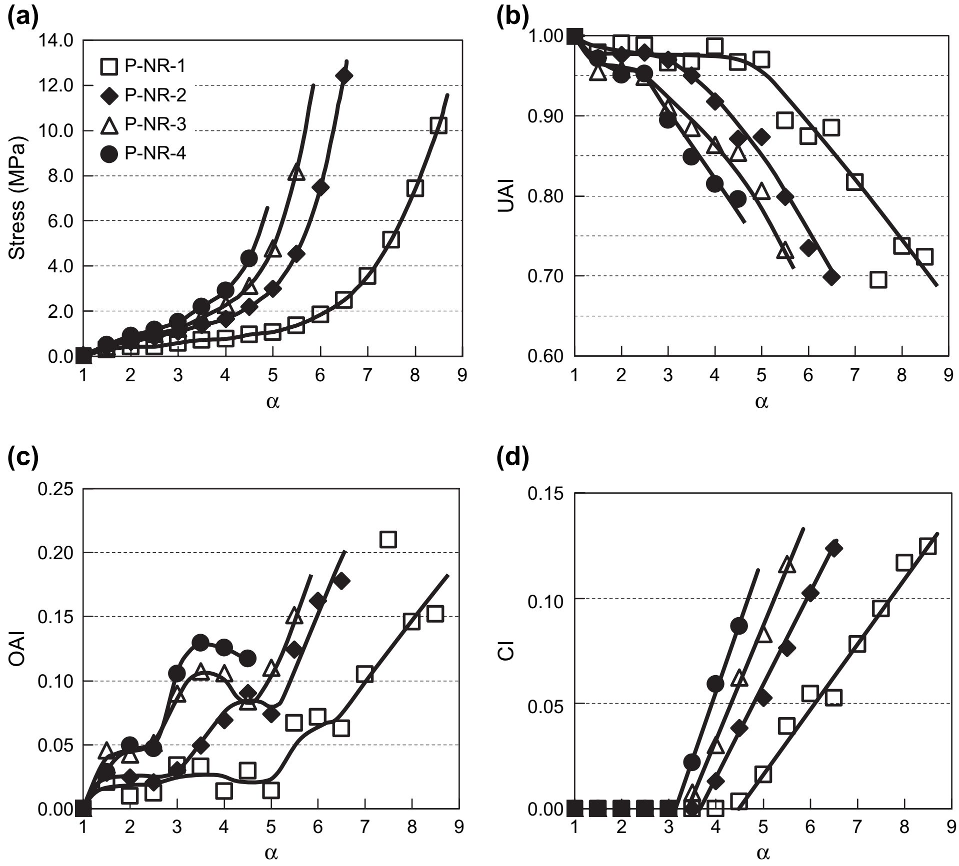

Fig. 1. Stress–strain curves (a) and elongation ratio dependence on UAI (b), OAI (c) and CI (d) of P-NR samples. The lines of UAI, OAI and CI are guides for eyes.

by stretching tended to become larger in the smaller strain with the increase of ν. There were a lot of un-oriented amorphous chains even at high strain for all samples, i.e., UAI comprising more than ca. 70% was detected at their highest strain in all the peroxide-crosslinked NR samples with different ν. This observation was same with that of the sulfur-crosslinked NR samples with different ν values [14].

In Fig. 1(c), it was observed that the OAI of each sample immediately increased by stretching and it abruptly rose via a gradual increase of OAI. After that, a small drop of OAI was detected for all samples and their OAI increased again with strain except P-NR-4. Comparing the changes of OAI with those of CI in Fig. 1(d), the abrupt increase of OAI was found to bring the onset of SIC. The increase of OAI became larger and the peak top of OAI tended to shift to the lower elongation ratio with the increase of ν when the definite strain for each sample was compared.

It is worth noting that an elongation ratio at which the crystallization started (α_c) shifted to the smaller α with the increase of ν as shown in Fig. 1(d). The clear dependence of α_c on ν is shown in Fig. 2. Here, the difference of entropy between the undeformed and the deformed states at α_c (ΔS_{def}) was elucidated on the basis of the classical theory of rubber elasticity [17] as follows: assuming the affine deformation, ΔS_{def} is formulated as Eq. (4)

$$\Delta S_{\mathrm{def}} = -(1/2)\nu k\left(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - 3\right) \tag{4}$$

where α_1, α_2, and α_3 are elongation ratios in the direction distinguished by the subscripts. When the Poisson ratio of the samples is assumed to be 0.5, Eq. (4) becomes

$$\Delta S_{\mathrm{def}} = -(1/2)\nu k\left(\alpha^2 + 2/\alpha - 3\right) \tag{5}$$

ΔS_{def} at each α_c of the samples was calculated and plotted against ν in Fig. 3. It is clear that ΔS_{def} at α_c of the samples was almost equal among the samples in spite of the variation of ν value. It is consistent with the fact that whether or not a given chain is lengthened by the deformation depends only

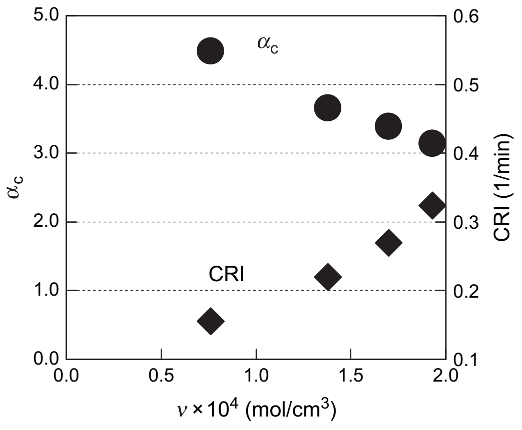

Fig. 2. Effect of network-chain density on α_c and CRI of P-NR samples.

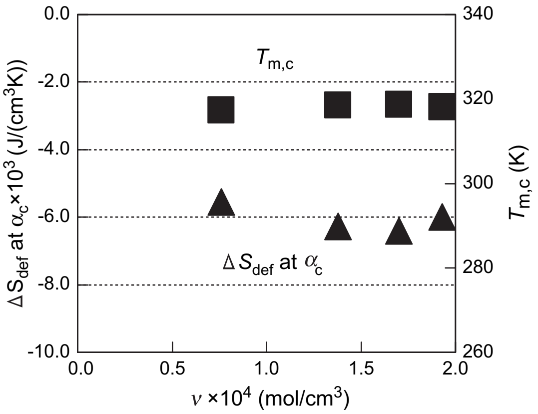

Fig. 3. Effect of network-chain density on ΔS_{def} at α_c and $T_{m,c}$ of P-NR samples.

on the orientation of its end-to-end vector and not on its initial length [16]. The obtained result means that the SIC occurred when the definite ΔS_{def} was reached for peroxide-crosslinked NR samples by stretching, regardless of their ν. In other words, the degree of deformation which brought about the desired decrease of entropy for the crystallization of peroxide-crosslinked NR upon stretching is dependent on ν.

It is also observed that the SIC of peroxide-crosslinked NR samples proceeded linearly with the strain in all the samples as shown in Fig. 1(d). From the slope of the straight line and the strain speed, each relative SIC rate was calculated and its index is plotted in Fig. 2 as "crystallization rate index" (CRI: the product of "slope in the strain dependence of CI" and "strain speed"). It was found that CRI was also clearly dependent on ν, which was interestingly an opposite result with the temperature-induced crystallization of NR networks [27]. In our previous study, we have proposed that a certain fraction of the stretched network chains would play the role of nuclei for SIC [7]. As there should be more nuclei in stretched rubber with the higher ν values, SIC is accelerated under our experimental condition. On the other hand, the crosslinking points cannot be included in crystallites and consequently it is expected for crosslinked rubber with high ν that the necessity to exclude the crosslinking from crystallizing molecules would retard crystallization. These two opposite trends are considered to influence SIC of the crosslinked rubber. In the crystallization speed, the effect of nucleation would be mainly appeared and SIC was more accelerated in the peroxide-crosslinked NR samples with higher ν. This observation was in agreement with the result detected by experiment on the post-stretch crystallization behavior for sulfur-crosslinked NR samples [14].

Using the obtained ΔS_{def}, the melting temperature at α_c ($T_{m,c}$) was also evaluated in this study. After Yamamoto and White [21], the melting temperature in the deformed state ($T_{m,\alpha}$) is increased by an amount

$$T_{m,\alpha} - T_{m,1} = (\Delta H_\alpha/\Delta S_\alpha) - (\Delta H_1/\Delta S_1) \tag{6}$$

or

$$1/T_{m,\alpha} = (1/T_{m,1}) - \Delta S_{def}/\Delta H_1 \tag{7}$$

if the heat of fusion is independent of deformation. Here, ΔH is the heat of fusion, ΔS is the entropy of fusion, and the subscripts α and 1 indicate the elongation ratio. For NR networks, it was reported that the heat of fusion is almost independent of deformation [16]. Therefore, Eq. (7) was utilized for the calculation of $T_{m,c}$, where $T_{m,1}$ and ΔH_1 were cited as 308.5 K and 15.6 cal/g in Refs. [28,29], respectively. As the density of peroxide-crosslinked NR samples was ca. 0.94 g/cm^3, ΔH_1 was estimated to be ca. 6.1×10^7 J/m^3. In Fig. 3, the relationship between the $T_{m,c}$ and ν is shown. They were approximately constant and ca. 318 K, regardless of their ν.

Almost constant ΔS_{def} and $T_{m,c}$ of all samples with different ν studied here mean that the supercooling in the onset of SIC of peroxide-crosslinked NR is also constant regardless of ν. By increasing ν for peroxide-crosslinked NR, their ΔS_{def} for SIC was reached at smaller strain. This result was in accord with the prediction from Flory's theory [16,24] and was consistent with the classical theory of rubber elasticity [17]. It was the first experimental support to Flory's theory done by the fast time-resolved experiments, as far as we know.

The different SIC behavior of peroxide-crosslinked NR comparing with that of sulfur-crosslinked NR may be ascribable to the homogeneity of crystallizable phase and/or network structure of the samples. The more detailed comparative studies are in progress and will be reported in the near future.

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