Lattice Deformation of Strain-induced Crystallites in Carbon-filled Natural Rubber

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(Received October 23, 2003; CL-031007)

By using a powerful synchrotron X-ray radiation, lattice deformation of strain-induced crystallites in carbon-black-filled natural rubber with nominal stress was clarified. The degree of deformation of the unit cell became smaller by filling with carbon black. This result implies that as some local stress was transferred to carbon black, relatively less stress was apportioned to strain-induced crystallites.

Natural rubber (NR) is an indispensable biomass for modern technology. Its perfectly stereoregular structure has not been imitated even with sophisticated techniques of modern chemical synthesis. Though the strain-induced crystallization of NR has been recognized even before the acceptance of the concept of macromolecules,[1,2] its role on mechanical response of rubbery materials is still under discussion. While the reinforcing effect of strain-induced crystallites has been proposed for the increase in the modulus of highly-stretched NR, the upturn of the modulus can also be explained by the limited extensibility of the network chains.[3] In recent years, we have reported the results of wide-angle X-ray diffraction (WAXD) measurements of strain-induced crystallization in NR samples by using a powerful synchrotron radiation.[4–8] Existence of considerable amount of isotropic amorphous component even at 600% of elongation was revealed in these reports, indicating that the stress is bore only by minor fractions of oriented amorphous and crystalline components. In our latest report,[8] lattice deformation of strain-induced crystallites has been observed, which implies that the crystallites are responsible for the mechanical response. However, these studies dealt with unfilled NR samples. Since carbon-black-filled NR has been used in many applications, clarification of the relationship between the filler and the strain-induced crystallites in terms of mechanical response is desired. In this paper, results of WAXD measurements of strain-induced crystallization in carbon-black-filled NR by using a synchrotron radiation are reported.

Dumbbell-shaped NR specimens of 1-mm thickness were prepared according to the recipe in Table 1. Here, phr stands for parts by weight of hundred part rubber. Synchrotron WAXD experiments and simultaneous tensile measurements were carried out at the X3A2 beamline in National Synchrotron Light Source, Brookhaven National Laboratory, NY, U. S. A. The 2-D WAXD patterns were recorded by a CCD camera with pixel size of 158 μm. The wavelength of the X-ray was 0.1542 nm. The camera length was 93.5 mm (for NR-0 and NR-40H) or 107.0 mm (for NR-20H). These experimental conditions enabled us to detect the change of diffraction angle which corresponds to variation of lattice spacing smaller than 0.04 nm. A tabletop stretching machine from Instron, Inc. that has been modified to allow the symmetric deformation of the sample was used to illuminate the same sample position during stretching with the focused X-ray.[5] The strain rate was 0.4 min^{-1} for all the samples. The WAXD patterns were collected in every 30 s.

Table 1. Formulation of the rubber compounds in phr

Sample code	NR-0	NR-20H	NR-40H
NR (RSS No. 1)	100	100	100
Stearic acid	2.0	2.0	2.0
Active ZnO	1.0	1.0	1.0
CBS[a]	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5
Carbon black[b]	-	20	40

[a] *N*-cyclohexyl-2-benzothiazole sulfenamide
[b] Diablack N339, HS-HAF from Mitsubishi Chemical Co.

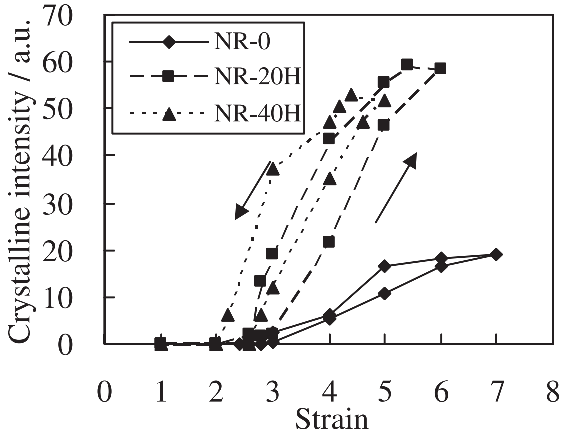

Figure 1. Relationship between crystalline intensity and strain.

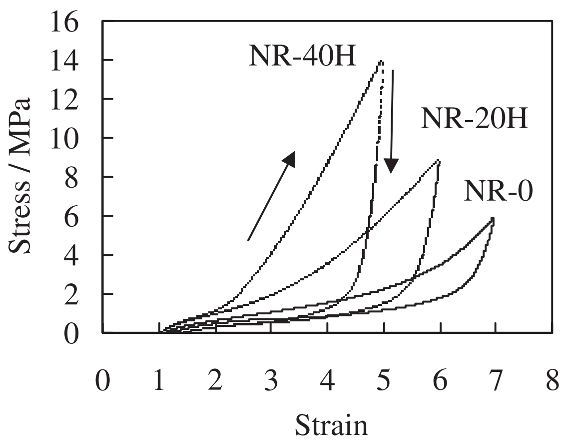

Figure 2. Stress-strain curves of filled and unfilled NR.

In order to evaluate the development of crystallinity, the integrated intensity of 200 and 120 reflections was estimated and the value was normalized by the beam fluctuation, the Lorentz factor and the volume fraction of rubber component in the sample. The

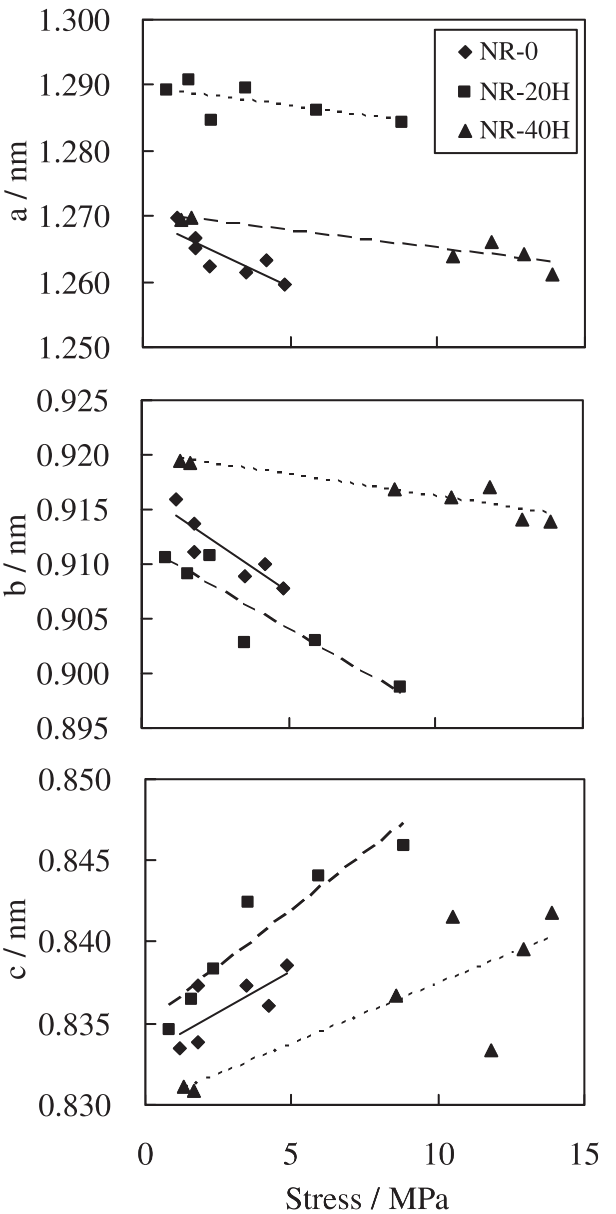

Figure 3. Relationship between stress and lattice constants.

estimated value, which is related to the net crystallinity in the rubber component, is referred as the "crystalline intensity" in this report. Figure 1 shows the development of crystalline intensity for filled and unfilled samples. Figure 2 illustrates the corresponding stress-strain curves. Enhancement of crystallization and upturn of modulus by filling with carbon black is apparent. It should be noted that the onset strain of crystallization was shifted to a smaller strain value by filling with carbon black, as shown in Figure 1. In the case of unfilled samples, the onset strain was independent of the crosslinking density.[8] The shift of the onset strain and the enhancement of crystallization by filling of carbon black was thought to be due to the increase in true strain of rubber component in the filled sample.

Lattice constants of the strain-induced crystallites were estimated from each WAXD pattern by using the least-square regression method. A rectangular unit cell was assumed.[9,10] Figure 3

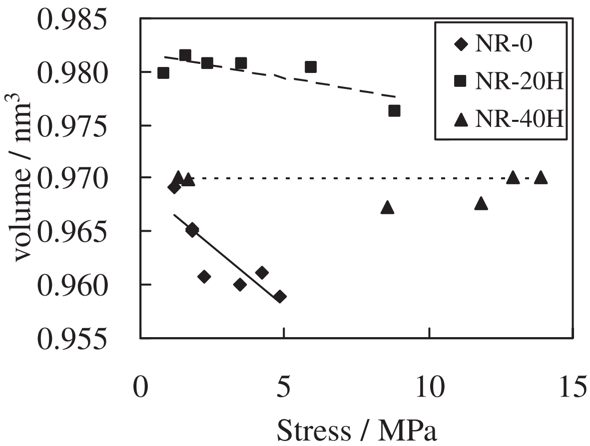

Figure 4. Relationship between stress and volume of unit cell.

shows the dependence of lattice constants on the nominal tensile stress. It was found that absolute values of lattice constants were shifted among the samples because the relative intensity of the amorphous halo, which slightly affects estimation of peak positions of crystalline reflections on the halo, was different from sample to sample. However, the relative change of lattice constants in the chosen samples showed an interesting trend. The contractions of the unit cell parameters in the *a* and *b* directions (perpendicular to the stretching direction), and the elongation of the *c* axis parameter (parallel to the stretching direction) are illustrated in Figure 3. The volume of the unit cell was calculated from the lattice constants, which is plotted against stress in Figure 4. The volume of the unit cell decreased with the increase in tensile stress.

An important finding is that the absolute values of the gradients in the plots became smaller with the increase in carbon black content, as shown in Figures 3 and 4. These results indicate that the stress to the crystallites was decreased by carbon black. It is conceivable that as some local stress was transferred to carbon black, relatively less stress was apportioned to strain-induced crystallites. This is a good contrast to the effect of increase in crosslinking for unfilled NR; the degree of lattice deformation with stress was almost independent of crosslinking density,[8] though the increase in crosslinking density has also lead to the enhancement of strain-induced crystallization. These results imply that not only the strain-induced crystallites but also the carbon black particles are responsible for the mechanical response of the carbon-black-filled NR. More detailed analysis of the effect of carbon black is in progress.

This work was partly supported by a Grant-in-Aid for Scientific Research (B)(2), No. 15404011, from Japan Society for the Promotion of Science. B. Hsiao thanks the support of National Science Foundation (DMR-0098194) in the U. S. A.

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Published on the web (Advance View) January 26, 2004; DOI 10.1246/cl.2004.220