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Nature of Strain-Induced Structures in Natural and Synthetic Rubbers under Stretching

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Introduction. Recently, by the use of synchrotron X-rays, the changes of crystalline and amorphous structures during deformation in natural rubber were studied in real time.[1−3] Some surprising new results were obtained. Perhaps the most interesting finding was that under high strains (>600%) a very large fraction of unoriented amorphous phase (∼75 wt %) still remained in the stretched sample in addition to strain-induced crystals (∼20 wt %) and oriented amorphous chains (∼5 wt %). This indicates that only a small fraction of cross-linked chains are responsible for the entire mechanical performance of the natural rubber, which can be attributed to the nonhomogeneous distribution of the cross-linked network points. In this communication, we have investigated whether the above finding is a universal behavior in synthetic rubbers of different compositions under large uniaxial deformation ratios.

Strain-induced crystallization in vulcanized natural rubber (NR) has been well recognized as the main factor responsible for the toughest mechanical properties among all rubbers (synthetic and natural). The structure of the strain-induced crystals in vulcanized NR has been extensively studied by X-ray diffraction since the 1940s.[4−7] However, the strain-induced crystallization behavior in vulcanized synthetic rubbers was relatively scarce because these materials could not be easily crystallized under normal conditions, except at low temperatures (such as 0 °C).[3]

In this study, three types of synthetic rubbers were studied: polyisoprene rubber (IR), poly(*cis*-1,4-butadiene) rubber (BR) and butyl rubber (poly(isobutylene−isoprene), IIR), which have the following characteristics. (1) IR has the same primary chemical structure as NR, except that NR contains 6 wt % of impurities where IR does not.[8] Since the content of *cis*-1,4 isoprene in NR is 100% and in IR is 98%, the mechanical properties of IR are usually lower than those of NR because the degree of strain-induced crystallization is less in IR. (2) BR was expected to be a rubber of greater ability to crystallize than NR and IR because the *cis*-1,4-butadiene segments are often considered as more crystallizable than the isoprene segments. However, this behavior has never been seen, at least at room temperature; BR is seldom crystallized under large deformation at ambient conditions. The lack of strain-induced crystallization in BR has discouraged its use as a single component rubber. Instead, BR is often used as an additional component in polymer blends. (3) Butyl rubber (poly(isobutylene−isoprene), IIR) is a copolymer containing 97 wt % isobutylene and 3 wt % isoprene. Since isobutylene has no chemical reactive site (unsaturated bond or double bond), the average chain length between the two adjacent reactive points is relatively large. Consequently, the vulcanization network in IIR is expected to be more homogeneous than those in other rubbers. However, IIR also seldom exhibits strain-induced crystallization under deformation. Therefore, the vulcanized synthetic rubbers (IR, BR, and IIR) are considerably weaker than the natural rubber (NR) because of the lacking ability to crystallize under stretching at room temperature. We have successfully crystallized all three synthetic rubbers by uniaxial stretching at 0 °C. The primary objective of this study was to investigate if the nonaffine deformation behavior in NR under strain-induced crystallization conditions also holds true in IR, BR, and IIR. In addition, we wish to develop a universal mechanism for strain-induced crystallization in natural and synthetic rubbers based on the nonhomogeneous network topology.

Table 1. Chemical Compositions and the Cross-Link Recipes for NR, IR, BR, and IIR[a]

	NR	IR	IIR	BR
rubber	100	100	100	100
ZnO		1	5	1
stearic acid	2	2	1	2
MBMTB	1	1		
TBBS	1	1		
Altax			0.5	
ethyl cadmate			2	
CBS				1
sulfur	1.5	1.5	1	1.5

[a] Cure conditions: NR, IR: 60 min at 160 °C; BR: 60 min at 150 °C; IIR: 30 min at 160 °C. NR: SMR-L (Standard Malaysian Rubber light color). IR: Goodyear Natsyn 2200 IR, $M_w = 955\,000$, $M_n = 350\,000$. BR: JSR-BR01 Cis1-4 95%, ML1+4(100 C) = 45. IIR: Bayer Butyl 301 ML1+8(125 C) = 50.

Experiment. Synchrotron measurements were carried out at the X27C beamline in the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The wavelength used was 1.366 Å. The two-dimensional (2D) WAXD patterns were recorded by a MAR-CCD (MAR USA) X-ray detector for quantitative image analysis. The typical image acquisition time for the experiment was 30 s. The diffraction angle was calibrated by the Al_2O_3 standard provided by the National Institute of Standards and Technology (NIST). The tensile machines allowed symmetric deformation of the sample with a deformation rate of 10 mm/min. The original length of the samples was 25 mm. The experiments were carried out at 0 °C using an environmental chamber controlled by liquid nitrogen purging. Four types of rubbers were chosen for this study: NR, IR, BR, and IIR. The chemical compositions as well as the cross-link recipes for these vulcanized rubbers using sulfur as a cross-link agent are listed in Table 1.

Results and Discussion. WAXD patterns of the stretched NR, IR, BR, and IIR samples near their maximum strains at 0 °C are shown in Figure 1. All four rubbers exhibited distinct diffraction patterns, indicating the occurrence of strain-induced crystallization. Although vulcanized synthetic rubbers are often considered to be very difficult to crystallize by deformation at room temperature, they were fully crystallized at 0 °C under high strains. However, the observed WAXD patterns indicated that these rubbers exhibited

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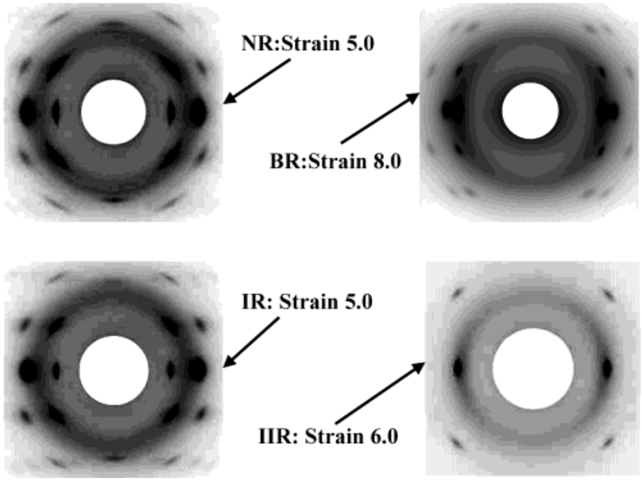

Figure 1. WAXD patterns of stretched NR, IR, BR, and IIR at their maximum strains at 0 °C.

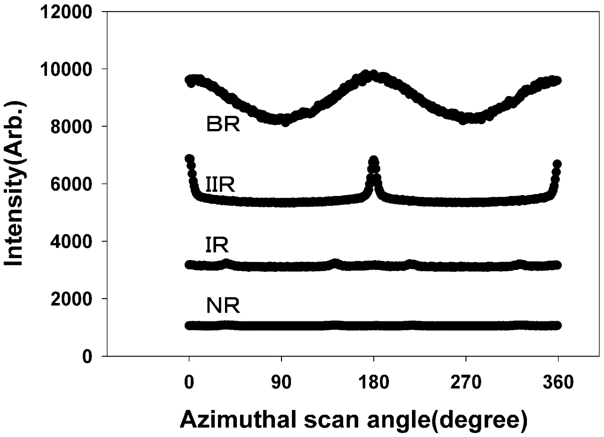

Figure 2. Azimuthal profiles at the amorphous peak position extracted from the WAXD patterns from NR, IR, BR, and IIR at their maximum strain at 0 °C.

somewhat different crystallization behavior from each other, which could be correlated with its cross-link topology.

In Figure 1, the stretched NR and IR samples (strain = 500%) exhibited a similar diffraction pattern, consisting of distinct crystalline reflections from highly oriented polyisoprene crystals[3] and a large fraction of isotropic scattering halo from random amorphous chains. This behavior has been reported by us recently.[2,3] The stretched BR (strain = 800%) also exhibited a fully developed crystalline diffraction pattern with reflections from poly(*cis*-1,4-butadiene) crystals.[9] The BR pattern showed a much smaller fraction of the random amorphous phase and a larger fraction of the oriented amorphous phase than NR and IR. The stretched IIR sample (strain = 600%) exhibited a clear crystalline diffraction pattern from the polyisobutylene crystals[10] but with the least amount of crystalline fraction.

The degree of oriented amorphous fraction in the stretched rubber can be evaluated by the azimuthal scan of the diffraction pattern at the amorphous peak position. Azimuthal profiles of the amorphous phase for the four chosen rubbers are shown in Figure 2. It is seen that NR and IR profiles exhibited almost no azimuthal dependence except for the appearance of four small crystalline reflections. This indicated that the contribution of oriented amorphous phase was quite small in the total amorphous fraction. In contrast, azimuthal profiles of BR and IR samples showed a very strong angular dependence (minimum values at 0° and 180°), indicating the existence of a large fraction of oriented amorphous phase. The breadth of the azimuthal profile in IIR was smaller than that in BR, suggesting that the degree of orientation in the amorphous chains for IIR was higher than that for BR.

Table 2. Fractions of Unoriented Amorphous Phase (ϕ_{UA}), Oriented Amorphous Phase (ϕ_{OA}), and Oriented Crystalline Phase (ϕ_{OC}) of NR, IR, BR, and IIR at Their Maximum Strains at 0 °C

	NR	IR	BR	IIR
ϕ_{UA} (%)	75.3	74.7	56.2	59.3
ϕ_{OA} (%)	9.1	8.7	24.0	28.0
ϕ_{OC} (%)	15.6	16.6	19.8	12.7

Mass fractions of the crystal phase (oriented: ϕ_{OC}; unoriented: ϕ_{UC}) and amorphous phase (oriented: ϕ_{OA}; unoriented: ϕ_{UA}) were determined using a novel two-dimensional diffraction image analysis method, which has been described elsewhere.[1,2,11] Using this method, the contribution of the unoriented crystal (ϕ_{UC}) was found to be nil in all four rubbers. All the strain-induced crystals were highly oriented. Consequently, there were only three components present in the stretched rubbers: unoriented amorphous phase (ϕ_{UA}), oriented amorphous phase (ϕ_{OA}), and oriented crystalline phase (ϕ_{OC}). These values for stretched NR, IR, BR, and IIR at 0 °C are summarized in Table 2. In IR (similar to NR), the relatively small amount of oriented crystal fraction (∼20%) and the very large amount of unoriented amorphous fraction (∼75%) are due to the deformation of a nonhomogeneous cross-linked network, formed during the sulfur vulcanization process in the pseudo-solid state.[1−3] The stretched BR showed relatively high crystalline and oriented amorphous fractions. The higher crystallinity in BR is expected because of the greater crystallizability in *cis*-1,4-butadiene chains (although a high strain is necessary to induce crystallization). The stretched IIR showed the lowest crystalline fraction but also a higher oriented amorphous fraction among the tested rubbers. The observation of relatively high oriented amorphous fraction and low unoriented amorphous fraction (∼50%) in BR and IIR suggests that their cross-link topology may be more homogeneous than that in NR and IR. However, it is apparent that none of the rubbers follow the true affine deformation or the phantom model typically used to describe the deformation of an ideal network elastomer.[12−14]

It is conceivable that the real network in vulcanized rubber is composed of molecules with a broad distribution of chain lengths between the network points, since the practical vulcanization process cannot create a homogeneous network distribution.[3,12] Under stretching, only the molecules of small chain length between the densely packed network points can be oriented and form crystallites, whereas the molecules of much longer chain lengths would remain in the random coil state.[15] A schematic diagram of the strain-induced network structure in vulcanized rubber under large deformation is illustrated in Figure 3. It is hypothesized that all the strain-induced crystallites are in the form of a microfibrillar structure containing extended-chain conformation.[1−3] These crystallites are connected by oriented amorphous tie chains, which form a new network structure that is primarily responsible for the tough mechanical properties. This new network structure is immersed in a large volume of random amorphous

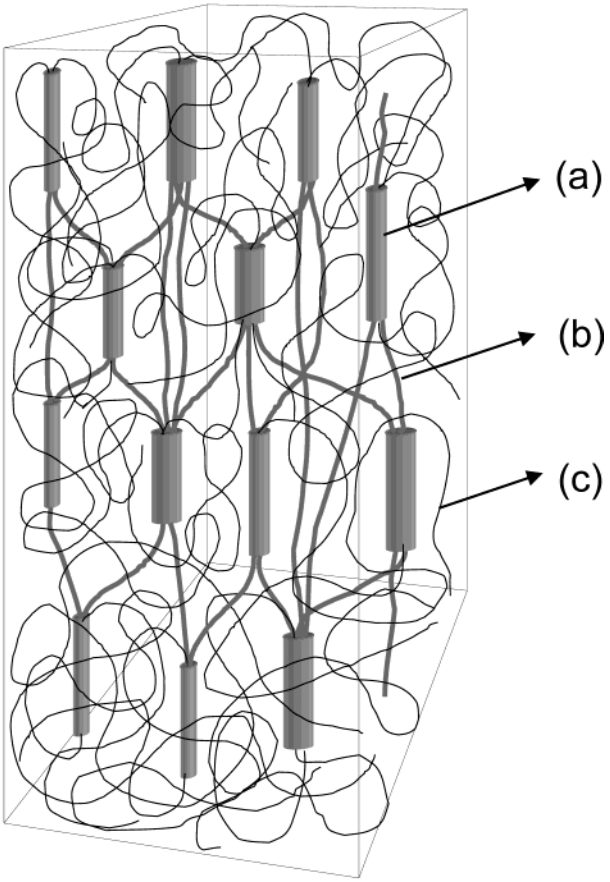

Figure 3. Schematic diagram of the strain-induced structure in stretched rubbers: (a) crystalline fibrils, (b) oriented amorphous chains, (c) unoriented amorphous chains.

chains. As the initial chemical network topology becomes more homogeneous (as in the case of BR and IIR), the strain required to induce the crystallization becomes larger and the fraction of the oriented amorphous tie chains also increases. However, the proposed mechanism in Figure 3 appears to be universal in all vulcanized rubbers.

Conclusion. In-situ synchrotron X-ray diffraction study on vulcanized natural and synthesized rubbers (NR, IR, BR, IIR) at their maximum strains at 0 °C was carried out. All chosen rubbers exhibited a universal mechanism containing the relationship between molecular orientation and crystallization as follows.

1. The majority of the molecules (50−75% in mass) remain in the unoriented amorphous state, even at their maximum strains. The maximum fraction of the strain-induced crystallites at high strains is only about 20%. The rest of the chains are in the oriented amorphous state (5−25%), which may act as tie chains between the strain-induced fibrillar crystallites.

2. The relationship between molecular orientation and strain-induced crystallization depends on the intrinsic characteristics of polymer crystallizability as well as the cross-link topology. The cross-link topology is a direct function of vulcanization agents and the cross-link conditions.

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