

Orientation and Crystallization of Natural Rubber Network as Revealed by WAXD Using Synchrotron Radiation

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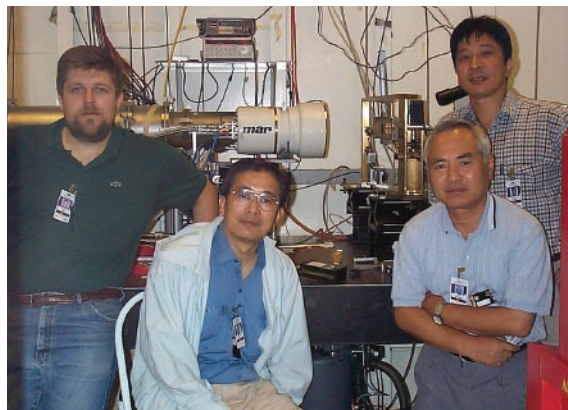
The tough elastic properties of natural rubber (NR) are thought to originate from its ability to crystallize rapidly upon stretching, which has been known since the 1920s. However, the growth mechanism of the strain-induced crystallites for cross-linked NR has only been revealed by our recent in-situ x-ray study of NR under uniaxial deformation. On the basis of these results, a new mechanism for strain-induced crystallization has been proposed.

Natural rubber (NR) is a biomass produced from *Hevea* trees. It is an indispensable material for many industrial and household applications, due to its outstanding tensile strength and crack growth resistance, which can be attributed to its ability to rapidly crystallize upon elongation. The main constituent of NR is cis-1,4-polyisoprene, which has a near-perfect sequence of cis structures – only one or two trans structures are found at both ends of a molecular chain (where cis and trans are the two types of polymer configurations). On the other hand, synthetic cis-1,4-polyisoprene (IR) always contains a few percent of trans structures, which are randomly positioned along the molecular chains. As a result, IR is not as strong as NR.

The x-ray diffraction pattern of stretched NR was reported in the 1920s, prior to the acknowledgment of “macromolecules” or polymers. Though the knowledge of NR strain-induced crystallization was recognized long ago, the crystal growth mechanism in NR that is cross-linked (i.e. includes an additive that bridges the NR chains, giving the material the ability to retrieve its original shape after large deformation) has not been clear for the past eight decades.

In our study, the morphological features of strain-induced crystallites in NR were studied in real time. A series of NR samples with different crosslinking densities were continuously deformed using a custom-made stretching machine. We recorded two-dimensional wide-angle x-ray diffraction (WAXD) patterns during the deformation process with a MAR-CCD camera at beamline X27C.

By analyzing the WAXD patterns along with the tensile response of the NR samples, we recognized several interesting new features. First, even at the onset of crystallization, the NR crystallites were highly oriented. On the other hand, a strong isotropic amorphous halo persisted even when the sample was elongated up to eight times the initial



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length. The onset strain of crystallization upon elongation was almost independent of the cross-linking density. We also observed that the sample with the higher cross-linking density showed the smaller lateral crystallite size and that the crystal lattice was almost linearly deformed in response to nominal stress.

Based on these results, we proposed a model for the strain-induced crystallization (**Figure 1**). When the rubber sample is stretched, some molecular chains are highly extended, while most of the chains remain in the almost randomly coiled state. Upon further elongation, the melting temperature of the sample increases due to entropic changes, and is independent of the cross-linking density. When the melting temperature exceeds the ambient temperature, the system enters a supercooled state and oriented crystallites form immediately on the stretched chains. The molecular chains that are consumed by the crystal growth are supplied by the surrounding coiled chains. In this way, the higher the cross-linking density, which results in dense crystallites, the smaller the lateral crystallite size. As a result of crystallization, an elongated macromolecule coil would be converted into a series of crystalline portions comprised of straight chain segments, and an amorphous portion comprised of coiled chain segments. The entropy of the amorphous portion will increase, while the degree of supercooling (the difference between the ambient temperature and the melting temperature) will decrease. However, further crystallization would be hindered without increasing the supercooling by additionally elongating the sample. The persistence of an almost isotropic amorphous halo in the WAXD pattern of highly strained NR samples can be explained by this model.

The deformation of the crystal lattice indicates that the crystalline portion can bear the stress and act as a nanometer-sized reinforcing filler. As the crystallites appear in response to the mechanical load on NR, the strain-induced crystallization can be regarded as “smart *in-situ* nanocompounding.”



Figure 1. A model of the strain-induced crystallization in vulcanized NR. Relatively short chains are drawn as blue lines. Filled circles represent crosslinks. (a) Before deformation. (b) After deformation: Short chains are fully stretched. (c) Crystallites are grown from the stretched chains (green parts).