SYNCHROTRON X-RAY STUDIES OF VULCANIZED RUBBERS AND THERMOPLASTIC ELASTOMERS

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Abstract-- Synchrotron X-ray diffraction technique has revealed strain-induced crystallization and molecular orientation in vulcanized rubbers and thermoplastic elastomers (TPE) during deformation in real time. The stress-strain curves and wide angle X-ray diffraction (WAXD) patterns in vulcanized rubbers and TPE were measured simultaneously. In-situ WAXD patterns were taken not only at different strains during uniaxial deformation but also at different temperatures at a constant strain. Results lead to several new insights. (1) Strain-induced crystallization is a common phenomenon in vulcanized rubbers, except SBR (styrene-butadiene rubber), and in TPE (with crystalline hard segments). (2) Strain-induced crystallization decreases the stress and increases the elongation in the strained rubber. (3) The hybrid structure of chemical networks and strain-induced crystallites is responsible to the tensile strength and elongation at break for both systems. (4) Some original crystal fraction (hard segment domain) in TPE is destroyed. During deformation, strain-induced crystallization increases with strain. Upon retraction even to stress zero, the majority of oriented strain-induced crystallites remains in tack with preferred orientation.

Introduction

In the past two decades, intense synchrotron X-rays have made it possible to carry out structural evolution and molecular orientation studies of elastomers in real time or in-situ during deformation. Recently, simultaneous measurements of the stress-strain relationship and synchrotron wide-angle X-ray diffraction (WAXD) data have revealed several new insights into the behavior of strain-induced crystallization in synthetic and natural vulcanized rubbers as well as in thermoplastic elastomer (TPE). These new insights can be summarized as follows.

1. Strain-induced crystallization appears to be a universal behavior in chemically crosslinked rubbers, such as natural rubber (NR), synthetic poly-isoprene (IR), poly-butadiene rubber (BR) and butyl rubber (IIR). The only exception appears to be the styrene butadiene rubber (SBR), which does not crystallize under deformation.
2. Strain-induced crystallites in rubbers or TPE always appear in the form of oriented crystals with the chain axis aligned parallel to the stretching direction.
3. The fraction of un-oriented amorphous molecules remains significantly (i.e., more than 50 % of the whole molecular segments) even at very large strains (e.g. 500-700 %). This can be attributed to the heterogeneity of the cross-link distribution.
4. The initial occurrence of strain-induced crystallization in rubber decreases the stress, which results in a “downturn” prior to a typical “upturn” in the stress curve. The unique stress behavior can be attributed to the competition between the stress increase by stretching and the stress decrease by strain-induced crystallization. The phenomenon is more significant in IR than NR
5. The hybrid network topology, composing a chemical network being reinforced by strain-induced crystallites, appears to dominate the mechanical performance.

6. Thermoplastic poly-olefin (TPO) is composed of small crystallites (hard segments) connected by a large fraction of amorphous chains (soft segments). A large fraction of original crystalline hard segments is destroyed at around strain 1.0. At strains beyond 1.0, strain induces crystallization takes place and the resulting crystalline network behaves similar to crosslinked rubbers.

Experimental Section

Synchrotron X-ray measurements were carried out at the X27C beam line in the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The wavelength of the X-ray used was 1.371 Å. Two dimension (2D) WAXD patterns were recorded by the MAR-CCD X-ray detector (MAR USA) for quantitative image analysis. The typical image acquisition time for each scan was 30 sec. All measured WAXD images were corrected for beam fluctuations and sample absorption prior to data analysis.

The tensile machines allowed symmetric stretching of the sample, permitting the focused X-ray to illuminate the same sample position during deformation. The instrument was based on a modified tabletop stretching machine from the Instron Inc. The chosen deformation rate was 10 mm/min. The original sample length was 25 mm. The initial rate of deformation was 0.007 sec^{-1}. The stress was given by $\sigma = F/(d_0 w_0)$, with F being the force measured by a load cell, d_0 being the original sample thickness and w_0 being the original width. The strain, in terms of the deformation ratio, was given by $\varepsilon = (l-l_0)/ l_0$ with l_0 being the original clamp-clamp distance. The WAXD data analysis was carried out using a software package (POLAR) developed by Stonybrook Technology and Applied Research at Stony Brook, New York.

The stress-strain measurements during uniaxial extension and retraction were carried out at 25^{o}C and 0^{o}C, respectively. In the case of stress relaxation and temperature change experiments, the stretching processes were carried out at 30°C and the rates of temperature increase and decrease were +2°C/min and -2°C/min, respectively. Simultaneous time-resolved WAXD patterns and stress-strain curves were recorded during stretching, retraction, stress relaxation at a constant temperature (30°C) or controlled heating/cooling.

The materials used included four crosslinked rubbers (NR, IR, BR, IIR) and one kind of TPE: ethylene-propylene copolymer (Vistamaxx^{TM} specialty elastomer provided by the ExxonMobil Chemical Company).. The TPE was melt-pressed at 160^{o}C into film with a thickness about 1 mm, and was then quenched to room temperature.

Results and Discussion

I. Strain-Induced Crystallization in Vulcanized Rubber

Strain-induced crystallization in NR has been studied quite extensively since the 1940 [1-5]. However, simultaneous measurements of stress-strain relationship and *in-situ* wide-angle X-ray diffraction (WAXD) have only been made recently. The stress-strain relationships and selected WAXD patterns in NR at 25 ^{o}C during uniaxial deformation are shown in Figure 1.

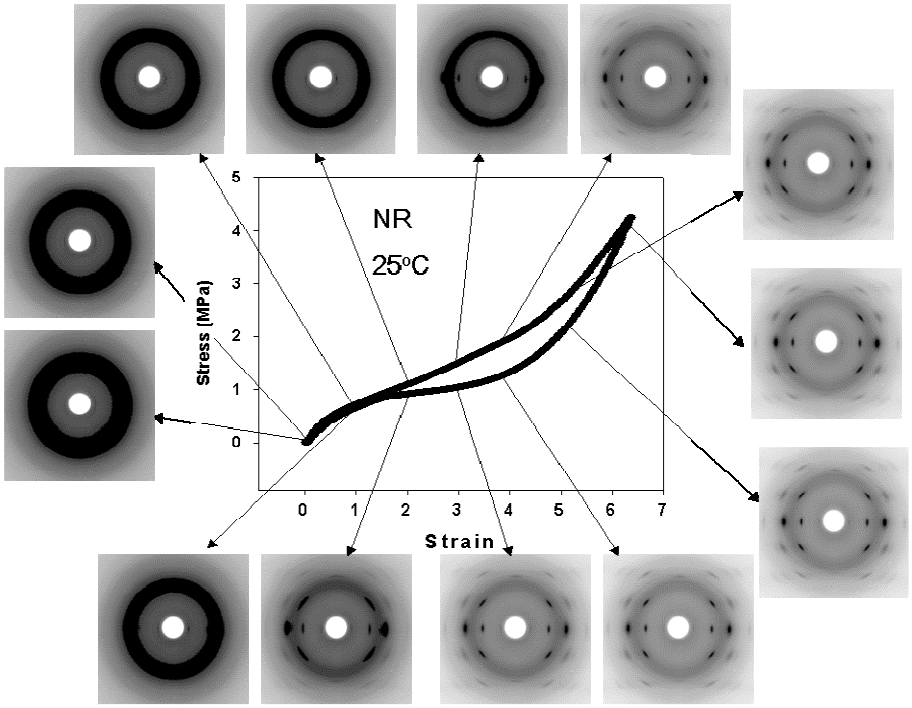

Figure 1. The stress-strain curve and selected WAXD patterns collected during extension and retraction of sulfur vulcanized natural rubber at 25°C. Each image was taken at the average strain indicated by the arrows

NR, Synthetic poly-isoprene (IR), poly-butadiene (BR) isoprene-isobutylene rubber (IIR, Butyl rubber) and Chloroprene rubber (CR) are compared in Fig.2

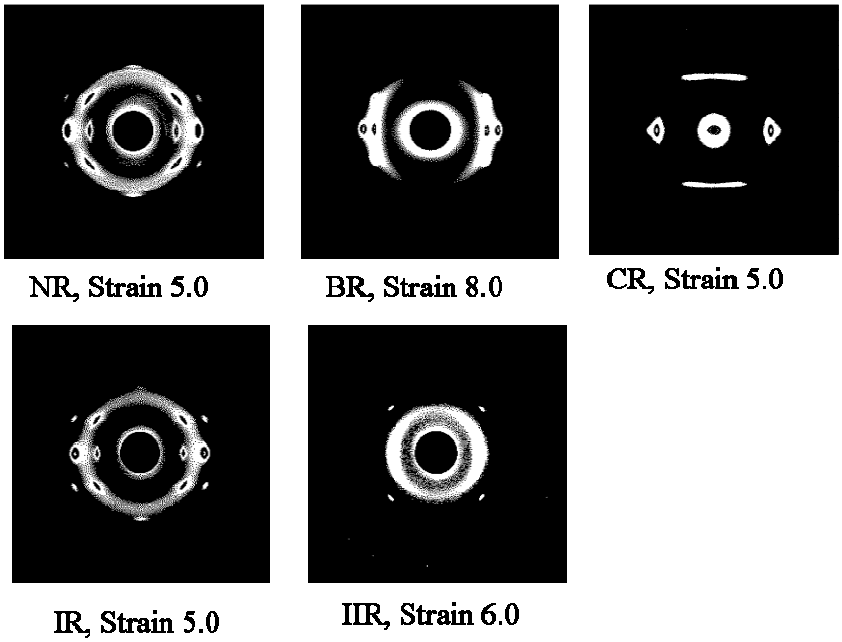

Figure 2. The WAXD patterns of NR, IR, BR, IIR and CR

II. Strain-Induced Crystallization in TPE (Propylene Based Ethylene-Propylene Copolymer)

The chosen TPE is composed of propylene crystals (hard segments) and ethylene-propylene amorphous chains (soft segments). The thermo-mechanical measurements of TPE showed that T_g of the material is –50ºC and T_m of its crystal component is 50ºC.

The *in-situ* stress-strain relationships and selected WAXD patterns during extension to strain 5.0 and subsequent retraction to 1.7 at the zero stress (1st cycle), of this TPE are shown in Figure 3**.** Each image was taken at the strain indicated by the arrow.

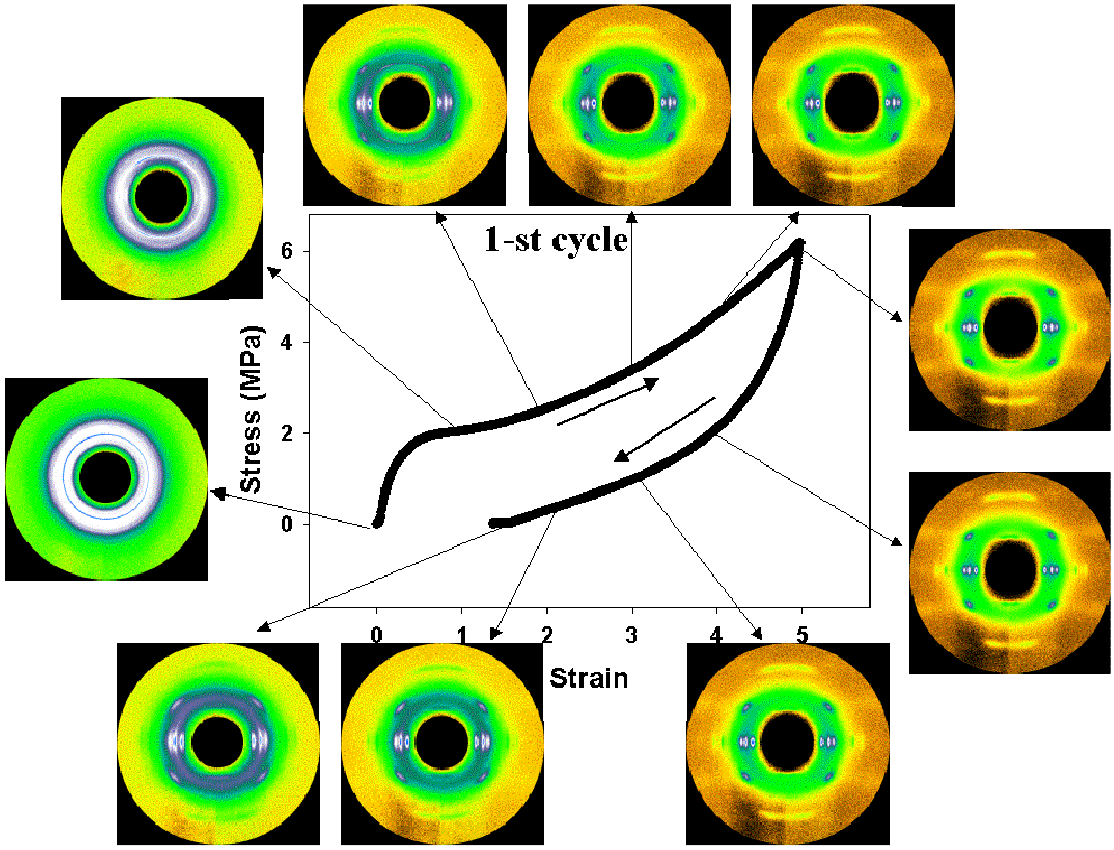

Figure 3. Stress-strain relationship and selected WAXD patterns collected during extension and retraction of the TPE in the first cycle. Each image was taken at the strain indicated by the arrows.

The high oriented amorphous fraction means that non-Gaussian chains between network points are extended and increase the entropy stress. During retraction, the fraction of oriented amorphous decreases to zero and oriented crystal decreases only slightly. It is suggested that the orientation of amorphous molecules are mainly responsible for the observed stress because the zero-orientation of amorphous coincides with the zero-stress. In order to investigate the existence and its transformation of the higher order structure than crystallites, small angle X-ray scattering (SAXS) analysis was applied to the TPE. During the extension and retraction processes in the 1st cycle, the stress-strain relationships and selected SAXS patterns are shown in Figure 4. Each image was taken at the strain indicated by the arrow.

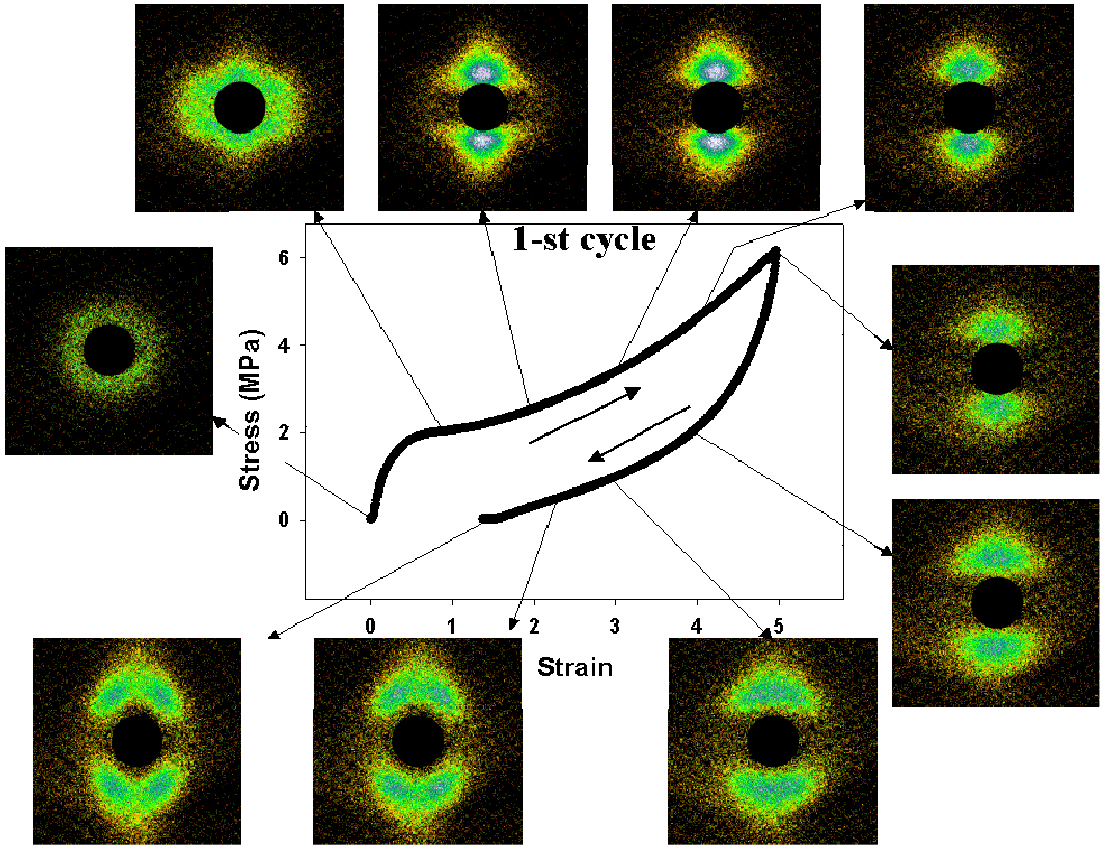

Figure 10. Stress-strain relationship and selected SAXS patterns collected during extension and retraction of the TPE in 1-st cycles. Each image was taken at the strain indicated by the arrows.

Conclusions

Synchrotron X-ray studies using WAXD and SAXS with varying thermo-mechanical deformation conditions in vulcanized rubber and thermo-plastic elastomers revealed several new insights into the subject of strain-induced crystallization, molecular orientation and the stress-strain relationships.

Acknowledgement

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