Real-time Observation of Filler Aggregate Structure using Two-dimensional Ultra-small-angle X-ray Scattering

The addition of fillers such as carbon black and silica to an elastomer shows reinforcement effects, which increase modulus of elasticity, tear strength, tensile strength, cracking resistance, and fatigue resistance [1]. The reinforcement effects have been extensively investigated since 1904, when S.C. Mote discovered the effect with carbon black. However, the mechanism of the reinforcement has not yet been understood. A filler composes a hierarchical structure in rubber, where *primary particles form aggregates*, and the aggregates form *agglomerates*, as shown in Fig. 1. The structures of the aggregate and agglomerate, on a size scale of 100 nm - 10 µm, are considered to be the origins of the reinforcement. However, conventional methods of studying the structure on such a size scale, such as light scattering and transmission electron microscopy (TEM), are inappropriate for the study of aggregate structure: the light scattering method is not suitable for an opaque specimen such as filled rubbers, and TEM is not suited to the study of three-dimensional (3D) structures under elongation because it requires thin samples.

Two-dimensional ultra-small-angle X-ray scattering (2D-USAXS) is a promising tool for the observation of structural change on a size scale of 100 nm - 10 µm and is now available at the "medium-length" beamline **BL20XU**. The combination of the high brilliance and long sample-to-detector distance used makes it possible to observe *in situ* 2D-USAXS patterns, which is not possible by conventional USAXS using a Bonse-Hart camera [2]. In the present study, we performed 2D-USAXS of filled rubber under elongation and investigated the change of the aggregate structure.

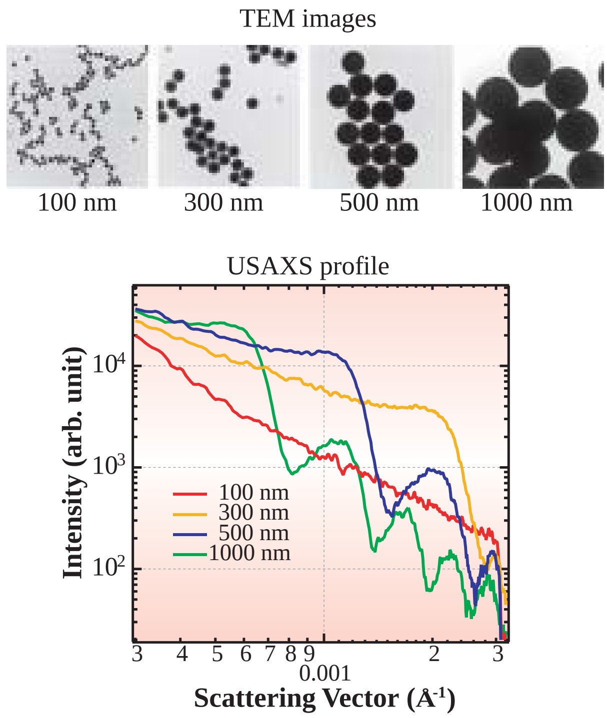

Fig. 2. USAXS profiles and TEM images of silica particles with monodisperse size distribution.

The sample used is styrene-butadiene rubber (SBR) filled with spherical silica particles with a volume fraction of 20% (Seahoster, Nippon Shokubai, Osaka, Japan), which have a monodispersed size distribution. This enables us to separate the structure factor (scattering from aggregates) and the form factor (scattering from a primary particle). A schematic view of the experimental setup at BL20XU is shown in Fig. 1. The X-ray energy is 23 keV and the camera

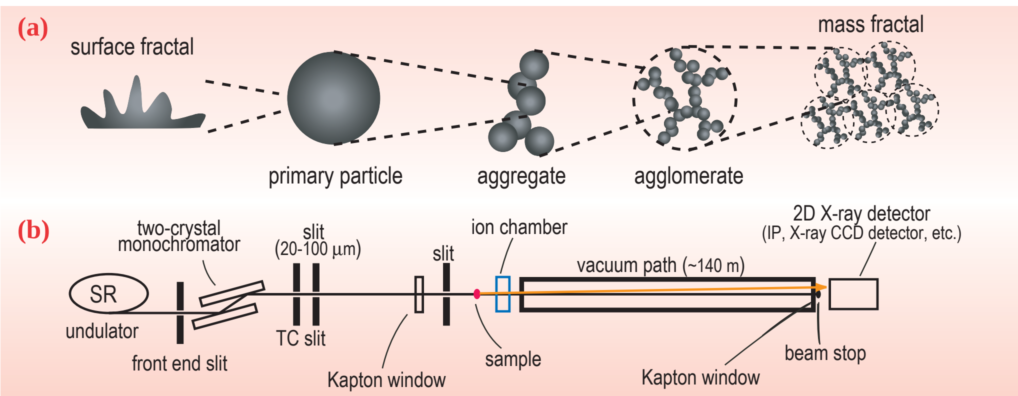

Fig. 1. **(a)** Hierarchical structure of filler in rubber. **(b)** Schematic view of experimental setup. The sample is set at the first experimental hutch in the experimental hall of the storage ring building. The detectors are set at the second hutch in the Biomedical Imaging Center. The sample-to-detector distance is 160.5 m.

length is 160.5 m. In this setup, the USAXS in a q-range of 4×10^{-4} - 2.5×10^{-3} Å^{-1} is recorded, where q is the scattering vector defined as $q = 4\pi \sin\theta / \lambda$, λ is the X-ray wavelength and 2θ is the scattering angle. As area detectors, an imaging plate and an X-ray CCD detector coupled with X-ray image intensifier (XRII) [3] are used. Figure 2 shows the USAXS profiles of the particles and the corresponding TEM images. The exposure time for each 2D-USAXS image is around 100 ms.

Figure 3(a) shows the 2D-USAXS images of rubber filled with silica particles (diameter: D = 540 nm) under elongation. The structural information on a size scale of 250 nm - 1500 nm is available from the images. It corresponds to that on the distribution of the silica particles inside the aggregates in this sample. When the samples are stretched, four spots appear and then change their positions, while the scattering angle is kept constant. This indicates that the distance between neighboring silica particles remains constant in stretched rubber (approximately 860 nm). A sample filled with small particles (D = 100 nm) shows different scattering patterns, as shown in Fig. 3(b). In this case, the USAXS patterns have information on the distances between the aggregates rather than on those between the particles. When the sample is stretched, the distance between the aggregates increases in the direction of the elongation. This suggests that the rubber between the aggregates is mainly stretched.

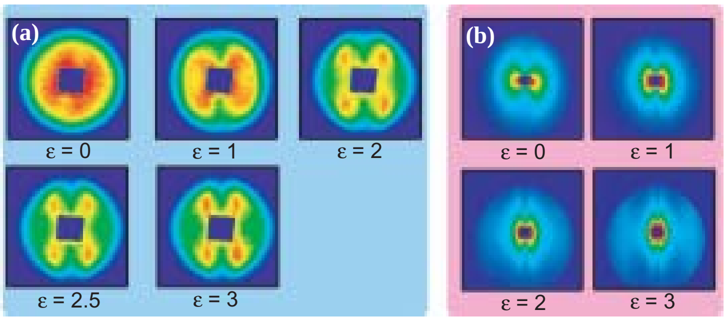

Fig. 3. **(a)** 2D-USAXS images of stretched rubber filled with silica particles (diameter = 540 nm). e is the elongation ratio defined as $\varepsilon = \Delta L/L$, where L is the initial length of the sample and ΔL is the elongation length of the sample. The sample is stretched in the horizontal direction. **(b)** 2D-USAXS images of stretched rubber filled with silica particles (diameter = 100 nm). The sample is stretched in the horizontal direction.

The combination of 2D-USAXS and viscoelastic measurements reveals the relationship between the aggregate structure and reinforcement, as shown in Fig. 4, which records the stress-strain curve of rubber filled with silica particles (D = 300 nm) and corresponding 2D-USAXS images. The images showed the hysteresis corresponding to that of the stress-strain curve. Therefore, the morphology of the aggregation is found to affect the hysteresis of stress-strain curve.

In summary, by *in situ* 2D-USAXS, the structural change of aggregates in stretched rubber has been observed for the first time, which, previously, had only been speculated on the basis of viscoelastic experiments. Further study by 2D-USAXS will elucidate the long-time unresolved mechanism of the reinforcement in filled rubber.

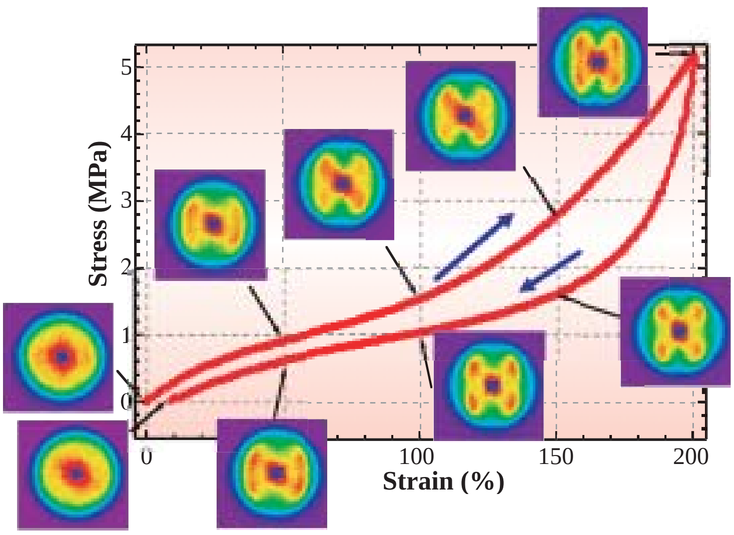

Fig. 4. 2D-USAXS images and stress-strain curve of rubber filled with silica particles (diameter = 300 nm). The sample is stretched in the horizontal direction.

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