Study on two-dimensional small-angle X-ray scattering of *in situ* silica filled nanocomposite elastomer during deformation

Yuko Ikeda,[a]* Yoritaka Yasuda,[a] Shinya Yamamoto[b] and Yuiti Morita[a]

[a]Kyoto Institute of Technology, Graduate School of Science and Technology, Japan, and [b]Kyoto Institute of Technology, Faculty of Engineering and Design, Japan. Correspondence e-mail: yuko@kit.ac.jp

Morphological change of *in situ* generated silica particles was investigated by a time-resolved two-dimensional small-angle X-ray scattering technique and a simultaneous tensile measurement. The *in situ* silica particles with diameter *ca* 34 nm were homogeneously dispersed in a rubbery matrix and the morphological change of the particles was followed up to the elongation ratio $\alpha = 2$ during stretching and from $\alpha = 2.5$ during retracting. The observed two-dimensional small-angle X-ray scattering patterns agreed with the simulation results by Rharbi *et al.* [*Europhys. Lett.* (1999), **46**, 472–478] where a shear displacement model was proposed for the deformation mode of their soft nanocomposite.

1. Introduction

Most of the particulate filler-filled rubber products are soft nanocomposites, although the concept of nanocomposites has been significantly expanded in this century. Reinforcement of rubber by inclusion of fillers such as carbon black and silica is very common in rubber technology (Kraus, 1965). Carbon black has been utilized in the rubber industry for about 100 years. The mechanism of reinforcement, however, is not yet fully understood. Not only the geometric factors such as size and shape and the content, but also the interfacial interaction between the particle and rubbery matrix must be taken into account in order to elucidate the reinforcement effect. One of the difficulties for the clarification of the role of nanofiller in the reinforcement is the aggregation of nanoparticles in the rubbery matrix, which was recognized in rubber products prepared by the conventional mechanical mixing technique. Therefore, a model nanocomposite with well dispersed nanoparticles in a rubbery matrix should be of much value for analyzing the reinforcement effect.

For the preparation of such a model, *in situ* silica filling is useful. The silica formation is based on the sol–gel reaction of tetraethoxysilane (TEOS) in a rubber matrix. The reaction of TEOS takes place in two steps, the hydrolysis and the condensation reactions, to produce SiO_2. This sol–gel process has been originally noted for the preparation of inorganic glasses at lower temperatures (Brinker & Scherer, 1982). In the field of rubber science, crosslinked rubbers have been subjected to this *in situ* silica filling (Mark & Pan, 1982; Mark, 1985; Kohjiya *et al.*, 1994; Kohjiya & Ikeda, 2000). This method produces homogeneously dispersed nano-silica particles in the rubbery matrix.

In this paper, a morphological change of primary *in situ* silica particles in a rubbery matrix is reported by a simultaneous tensile and two-dimensional small-angle X-ray scattering (two-dimensional SAXS) measurement at the length scale of *ca* 10–220 nm.

Up to now, several studies on the deformation of soft nanocomposites have been reported. For examples, one of the pioneering works is a study on the deformation behavior of nanocomposites composed of Nanolatex and silica of *ca* 20 nm diameter by small-angle neutron scattering (SANS) under a slow elongation, where the obtained scattering patterns were compared with those by a computer simulation (Rharbi *et al.*, 1999). Together with several experimental studies (Rharbi *et al.*, 1996; Clement *et al.*, 2001; Kishimoto *et al.*, 2006; Morfin *et al.*, 2006; Harrak *et al.*, 2006), active simulations (Oberdisse *et al.*, 2000) were also conducted by changing the geometry, phase hardness and degree of aggregation of nanoparticles in the composites, where the experimental results by SANS, small-angle X-ray scattering (SAXS), ultra-small-angle neutron scattering (USANS), ultra-small-angle X-ray scattering (USAXS) and atomic force microscopy (AFM) were utilized. Several of the samples in these studies, however, were the nanocomposites in which the nanoparticles seem to be aggregated in the matrixes. Thus, our study is to conduct time-resolved experiments under the fast deformation of the soft nanocomposites in which there was well dispersed *in situ* generated particulate silica.

2. Experimental

2.1. Materials

Peroxide-crosslinked isoprene rubber was prepared as follows: 100 g of isoprene rubber (IR, JSR IR-2200) was mixed with one gram of dicumyl peroxide (*i.e.* 1 phr in terms of parts per hundred rubber by weight) on a two-roll mill. The mix was cured under a heat-pressing at 428 K for 30 min in a mold to give a crosslinked IR sheet of 1 mm thickness. *In situ* silica filling was carried out by the sol–gel reaction of TEOS in the crosslinked IR matrix. The crosslinked IR sheet was immersed in TEOS for 24 h at 313 K. The swollen IR sheet was then immersed in 2 wt% aqueous solution of *n*-butylamine at 323 K for 48 h to conduct the sol–gel reaction of TEOS. The sample was dried under vacuum at 323 K for 48 h. The *in situ* silica content was 9.7 vol% (22 phr), which was determined by thermogravimetric analysis (Rigaku TG). The network-chain density of the sample was 1.0×10^{-4} mol cm^{-3} which was determined by a microcompression method (Flory, 1953; Smith, 1969) using a Thermo-Mechanical Analyzer (TG-50TMA of Shimadzu Co.). Ring-shaped specimens

were cut out from the *in situ* silica filled sample, with inner and outer diameters of 11.7 and 13.7 mm, respectively.

2.2. Transmission electron microscopy

Ultra-thin film of the sample was prepared using a microtome (MT-XL Ultramicrotome, Boeckeler Instrument, Inc.) in liquid nitrogen. The specimen was placed on a copper grid which was coated in advance with Folmvar and evaporated carbon. Then, a transmission electron microscopy (TEM) observation was carried out with a transmission electron microscope (Jeol TEM-100U). The accelerating voltage was 80 kV.

2.3. Simultaneous small-angle X-ray scattering and tensile measurement

Synchrotron SAXS measurements were carried out on the BL-40B2 beamline at SPring-8, Harima, Japan (http://www.spring8.or.jp/j/). A special-made tensile tester (with cooperation of Aiesu Giken Co., Kyoto) was placed on the beamline. During the tensile measurement at room temperature (*ca* 298 K), SAXS patterns were recorded simultaneously. The wavelength of the X-ray was 0.15 nm and the camera length was 3 m. Two-dimensional SAXS patterns were recorded using CCD camera (Hamamatsu C4880-00). The incident beam was exposed at every 6 s for 50 ms in order to avoid radiation damage of the specimen. Using the tensile tester, the specimen could be stretched symmetrically to be irradiated at almost the same position of the specimen by X-ray. The ring-shaped sample was used to correctly measure the elongation ratio (α) of the deformed sample. Here, α is defined as $\alpha = l/l_0$, in which l_0 is the initial length and l is the length after deformation. The stretching and retracting speeds were 100 mm min^{-1}, *i.e.* strain speed was 5 s^{-1}.

3. Results and discussion

Fig. 1 shows a TEM photograph of the *in situ* silica filled soft nanocomposite, the silica content of which was 9.7 vol%. *In situ* generated silica particles in the peroxide-crosslinked IR matrix were spherical. The average diameter of the *in situ* silica particles was *ca* 34 nm and its distribution was very narrow. Also, the dispersion of the particles in the rubber matrix was random, *i.e.* very homogeneous. The distance between the silica particles was calculated to be *ca* 72 nm. The sol–gel reaction of TEOS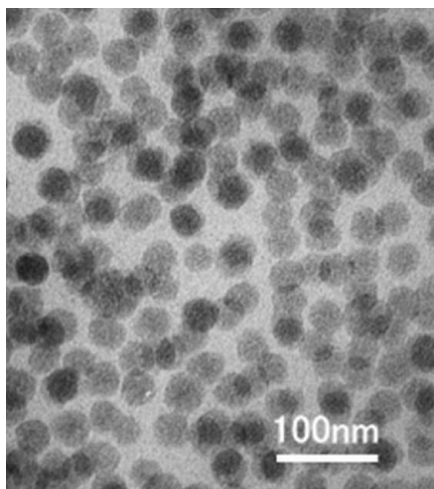 was found to produce very fine and homogeneous silica particles in the IR network. Therefore, this nanocomposite is most preferable as a model for investigating the deformation behavior of nanofillers in soft materials.

Tensile stress-elongation ratio curve of the nanocomposite is illustrated in Fig. 2 and simultaneously obtained two-dimensional SAXS patterns are shown in Fig. 3. In each SAXS pattern, the number inside shows the elongation ratio and 're' means the retracting process. The SAXS patterns beyond $\alpha = 2.5$ and $\alpha = $ re3 under the stretching and retracting processes, respectively, were not subjected to the analysis due to the over-running of detectable range of scattering peaks under the present experimental conditions. As shown in Fig. 3(*a*), an isotropic pattern was observed before stretching, which may imply that the silica particles were randomly dispersed in the rubber matrix before stretching. This was fully in accord with the TEM result in Fig. 1. The estimated average spacing between the silica particles, d, was *ca* 73 nm, where d was calculated by $d = 2\pi/q$. This equation is derived from $q = 4\pi\sin(\theta/2)/\lambda$ and the Bragg equation. q is the magnitude of scattering vector, θ is the scattering angle and λ is the wavelength of the X-rays. The obtained value was in good agreement with that obtained by TEM.

By stretching the sample to $\alpha = 1.5$, the ring-shaped two-dimensional SAXS pattern was changed to the pattern shown in Fig. 3(*b*), where the meridional scattering increased and equatorial scattering significantly decreased. It was not a butterfly pattern, which was detected by stretching of carbon black filled styrene–butadiene vulcanizate by Morfin *et al.* (2006), for example. It is worth noting that a similar two-dimensional SAXS pattern with our result was obtained by a computer simulation for a soft nanocomposite by Rharbi *et al.* (1999). The simulation was conducted as follows: hard sphere particles were placed at random in a box that represented the polymer matrix, then the box was stretched in the parallel direction and compressed in the perpendicular direction and the centers of mass of the particles were displaced affinely in accord with the macroscopic deformation. Applying these mechanisms to our nanocomposite, we can deduce that upon deformation the internal stress forces the silica particles to come close together in the perpendicular direction and to separate in the parallel direction against the stretching direction, respectively. Consequently, the morphology shown in Fig. 4(*b*) of *in situ* silica particles is speculated to be formed at $\alpha = 1.5$. Recently, we clarified that the network structure of peroxide-crosslinked natural rubber was more homogeneous compared with that of the sulfur-
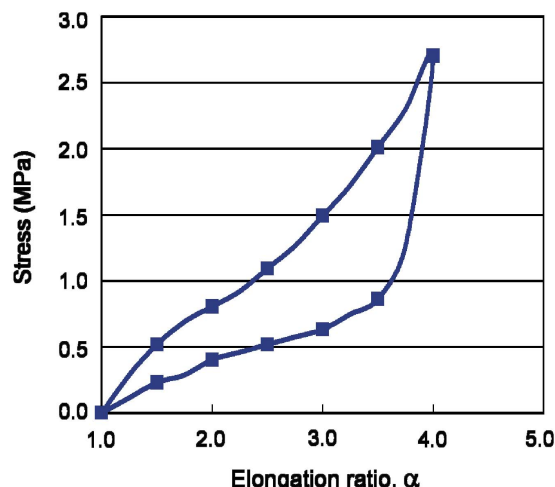

Figure 1
TEM photograph of the *in situ* silica filled IR nanocomposite.

Figure 2
Stress–elongation ratio curve of the *in situ* silica filled IR nanocomposite.

cured one, by studying their strain-induced crystallization behavior using simultaneous tensile and synchrotron wide-angle X-ray diffraction measurements (Ikeda *et al.*, 2007). Therefore, the *in situ* silica particles generated in the peroxide-crosslinked IR network must be placed at random without a maldistribution in the rubber matrix. This characteristic is considered to give the two-dimensional
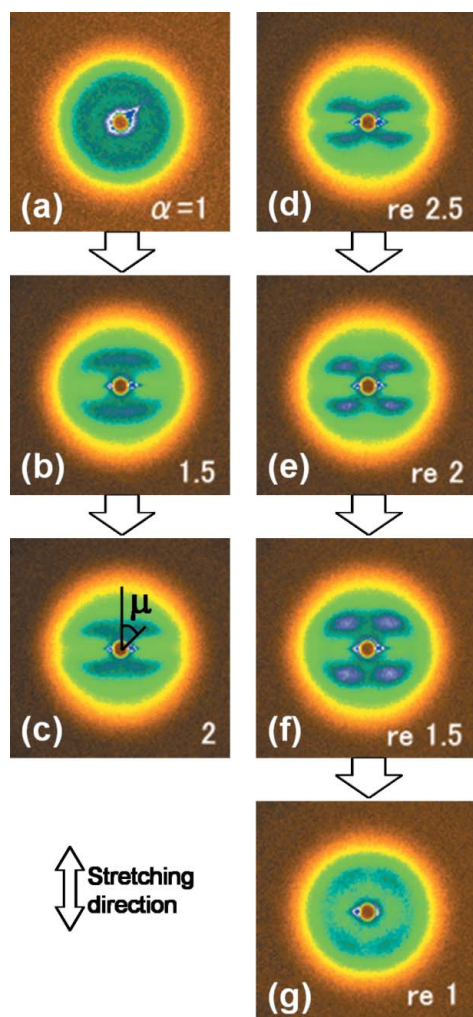
SAXS pattern shown in Fig. 3(*b*) in agreement with the simulation result.

By further stretching to $\alpha = 2$, the two-dimensional SAXS pattern evolved into a set of four maxima as shown in Fig. 3(*c*), although the intensity scale makes it difficult to see the maxima. This observation is considered to suggest the formation of a buckling structure of silica particles by stretching. Our AFM observation supported this consideration (not shown here). This morphological change of *in situ* silica particles is ascribable to the elongation in the stretching direction and the compression from the lateral directions occurring simultaneously during uniaxial stretching. On the appearance of a four-spot pattern, Rharbi *et al.* (1999) proposed two processes; either some long aggregates buckle under the lateral compression, or the space in the perpendicular direction to the stretching between two aggregates is filled up by another aggregate that forced between them. For the moment, we can not clarify the mechanism of buckling for our nanocomposite. However, the four-spot pattern obtained was very similar to the computer simulated one on the basis of the shear displacement model by Rharbi *et al.* (1999). Thus, the latter phenomenon can be ascribed to the deformation mechanism for our *in situ* silica filled nanocomposite. From the consideration mentioned above, the estimated morphological change of *in situ* silica particles in the IR network is illustrated in Fig. 4. It is a very simplified image to understand and the real model may be less organized. Further time-resolved SAXS measurement is necessary for clarifying the phenomenon.

In this study, the four-spot pattern to show the buckling structure of *in situ* silica particles was clearly detected during the retracting process as shown in Fig. 3(*d*)–(*g*). The spacing between the silica layers decreased upon retracting. Moreover, the degree of buckling to the stretching direction in the retracting process became smaller with the decrease of strain, which was ascribed to the releasing the compression from the lateral directions. The buckling structure was also found to partially remain when the sample was retracted to $\alpha = 1$ at the retracting speeds of 100 mm min^{-1}.

The distance between the silica layers along the stretching direction (D) was calculated by using an equation of $D = d/\cos \mu$, where μ is the azimuthal angle of the four-spot pattern as shown in Fig. 3. Using the D values at each deformation, the microscopic elongation ratio was calculated and plotted against the macroscopic elongation ratio measured by the simultaneous tensile measurement in Fig. 5. Interestingly, a good linearity was observed between them, which suggests the affine deformation of the *in situ* silica filled soft nanocomposite. It should be kept in mind, however, that the silica particles are undeformable and consequently the crosslinked IR matrix of the nanocomposite must be deformed non-affinely to the macroscopic deformation.

Figure 3
Two-dimensional SAXS patterns of the *in situ* silica filled IR nanocomposite during tensile deformation.

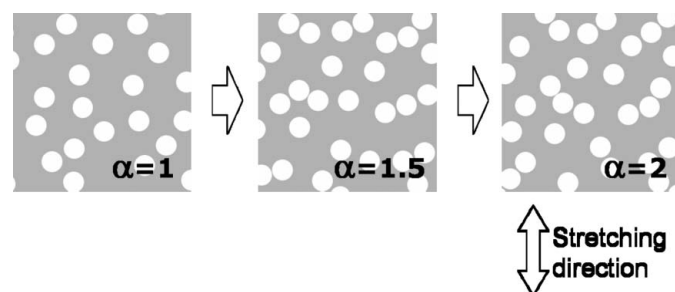**Figure 4**
Speculated morphological change of silica particles in the *in situ* silica filled IR nanocomposite upon deformation.

4. Conclusion

The morphological change of the *in situ* silica particles, which were generated in the IR network with a fairly homogeneous dispersion, was investigated during the deformation by two-dimensional SAXS and simultaneous tensile measurements. The morphology of *in situ* silica particles became the buckling structure from the random state by elongating to the stretching direction and compressing from the lateral directions during uniaxial stretching. These observed morphological changes were in good agreement with those of the simulation on the basis of the displacement model by Rharbi *et al.* (1999). The buckling structure of silica particles was clearly observed during the retracting process. The affine deformation of this nano-
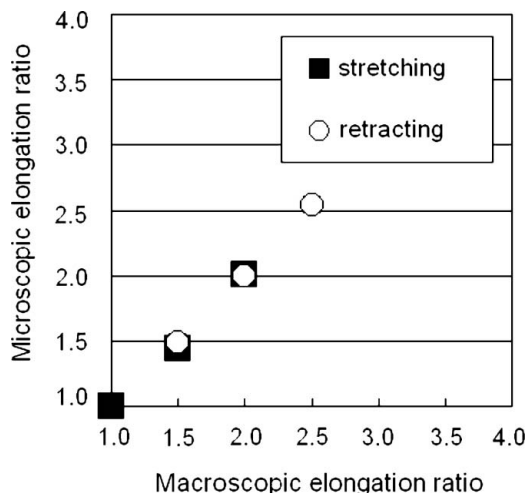
Figure 5
Relationship between the microscopic and macroscopic elongation ratios of the *in situ* silica filled IR nanocomposite.

composite was detected at low strain. USAXS or USANS results are required to elucidate the deformation behavior of *in situ* silica particles further up to the larger deformation.

References

Brinker, C. J. & Scherer, G. W. (1982). *Sol–Gel Science*. New York: Academic Press.
Clement, F., Bokobza, L. & Monnerie, L. (2001). *Rubber Chem. Technol.* **74**, 847–870.
Flory, P. J. (1953). *Principles of Polymer Chemistry*. Ithaca: Cornell University Press.
Harrak, A. E., Carrot, G., Jestin, J., Oberdisse, J. & Boue, F. (2006). XIIIth International Conference on Small-Angle Scattering, 9–13 July, Kyoto, Japan.
Ikeda, Y., Yasuda, Y., Makino, S., Yamamoto, S., Tosaka, M., Senoo, K. & Kohjiya, S. (2007). *Polymer*, **48**, 1171–1175.
Kishimoto, H., Shinohara, Y., Suzuki, Y., Takeuchi, A., Uesugi, K., Yagi, N., Muraoka, K., Mizoguchi, T. & Amemiya, Y. (2006). XIIIth International Conference on Small-Angle Scattering, 9–13 July, Kyoto, Japan.
Kohjiya, S. & Ikeda, Y. (2000). *Rubber Chem. Technol.* **73**, 534–550.
Kohjiya, S., Yajima, A., Yoon, J. R. & Ikeda, Y. (1994). *Nippon Gomu Kyokaishi*, **67**, 859–861.
Kraus, G. (1965). *Reinforcement of Elastomers*. New York: Interscience.
Mark, J. E. (1985). *Science of Ceramic Chemical Processing*, edited by L. L. Hench & R. D. Ulrich, ch. 47. New York: John Wiley & Sons.
Mark, J. E. & Pan, S.-J. (1982). *Macromol. Chem. Rapid Commun.* **3**, 681–685.
Morfin, I., Ehrburger-Dolle, F., Grillo, I., Livet, F. & Bley, F. (2006). *J. Synchrotron Rad.* **13**, 445–452.
Oberdisse, J., Rharbi, Y. & Boue, F. (2000). *Comput. Theor. Polym. Sci.* **10**, 207–217.
Rharbi, Y., Boue, F., Joanicot, M. & Cabane, B. (1996). *Macromolecules*, **29**, 4346–4359.
Rharbi, Y., Cabane, B., Vacher, A., Joanicot, M. & Boue, F. (1999). *Europhys. Lett.* **46**, 472–478.
Smith, D. (1969). *Rubber Chem. Technol.* **42**, 580–588.