

Small-Angle Neutron Scattering Study on Strain-Induced Crystallization and Nonuniformity of Natural Rubber

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It is well known that natural rubber (NR) contains non-rubber components such as proteins, phospholipids and fatty acids, carbohydrates and inorganic substances. However, no reports on the direct morphological evidence of non-rubber components in solid have been published as far as we know. Thus, the microscopic structure of NR was investigated by SANS in this study. It was compared with those of deproteinized NR (DPNR) and isoprene rubber (IR). The results of small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM) were also discussed in order to elucidate the structural characteristics of NR. Peroxide-cross-linked NR and IR samples were prepared by milling and heat-pressing. SANS experiments were carried out at SANS-U (C1-2), JRR-3M in JAEA (Tokai). The wavelength was 7.0 Å. The sample-to-detector distances were chosen to be 2.00 and 8.00 m. The scattered intensity were collected with an area detector and then circularly averaged. Dry and swollen samples with deuterated toluene were subjected to SANS.

The following conclusions were obtained. (i) Both SANS and SAXS intensities, $I_{\text{SANS}}(q)$ and $I_{\text{SAXS}}(q)$, of NR have a strong q -dependence as shown in Figure 1, indicating presence of large scale inhomogeneities. Here, q is the magnitude of the scattering vector. This strong q -dependence disappears by deproteination (DNPR). The inhomogeneities were assigned to protein aggregates, which was supported by AFM. These aggregates were found to be larger in size as well as in volume fraction than those of cross-link inhomogeneities introduced by cross-linking since cross-linking did not produce any significant increase in scattering. (ii) IR does

not show such inhomogeneities. (iii) The microscopic structures of swollen cross-linked NR by deuterated toluene are successfully reproduced by SANS intensity functions consisting of squared-Lorentz and Lorentz functions. The size of protein aggregates was evaluated to be of the order of 200 Å or larger. (iv) Swelling of both cross-linked NR and cross-linked IR introduces gel-like concentration fluctuations whose mesh size is of the order of 20 Å. These results indicate that NR possesses inherent inhomogeneities in bulk and additional thermal concentration fluctuations in swollen state, respectively.[1, 2]

References

- [1] M. Shibayama: *Macromol. Sci. Phys.* **199** (1998)1.
- [2] T. Karino *et al.*: *Biomacromolecules*, in press.

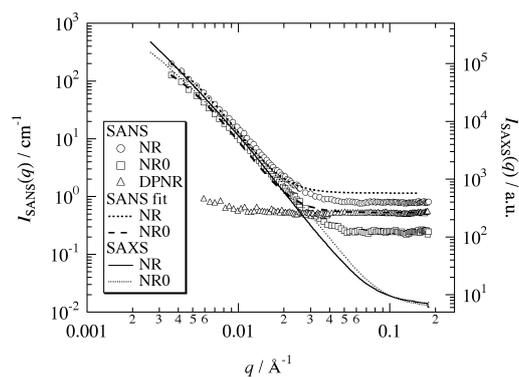


Fig. 1. SANS (symbols) and SAXS curves (thin lines) of NR rubbers (a) before (NR) and (b) after milling (NR0) without cross-linker. The thick dotted and dashed lines denote the fit with SL-function.