Structure analyses of rubber-filler systems by using contrast variation SANS

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Abstract

Rubber-filler systems have been one of the most successful composite materials and have been widely used in industry such as tire and belts so on. We need to explore the adsorption of rubber in filler particles point in terms of structure analyses to clarify the correlation between the mechanical properties and the structures for rubber-filler systems In this study, The polymer layers absorbed on silica particles in rubber-silica systems have investigated with contrast variation small-angle neutron scattering (SANS) method. The scattering intensities of specimens swollen by the solvents having various scattering length densities were measured.

We used Poly(styrene-*ran*-butadiene) (SBR) as rubber. The Silica particles were compounded into SBR by using Banbury mixer, and the samples were swollen by mixture of deutarated hexane (d-hex) and hexane (h-hex) with various composition. We conducted SANS measurements with SANS-J-II spectrometer at JRR-3 (Japan Research Reactor-3) in JAEA (Japan Atomic Energy Agency), Tokai, Japan.

Figure 1 shows the change in the scattering profiles $I(q)$ of the swollen rubber-silica system with the scattering length density of solvent. The scattering intensity decreases with h-hex. The q-dependence of $I(q)$ changes with the scattering length density, suggesting that the swelling ratio of solvent to rubber is spatially inhomogeneous and that the network density has spatial fluctuations. As shown in Figure 2, we estimated the partial scattering functions by using singular value decomposition: the scattering function for polymer-polymer correlation $S_{PP}(q)$, the scattering function for silica- silica correlation $S_{SS}(q)$, and the scattering function for polymer- silica correlation $S_{PS}(q)$.

The analyses of $S_{PS}(q)$ and $S_{SS}(q)$ explored the existence of dense polymer layers around silica aggregates. $S_{SS}(q)$ reflects hierarchical structures formed by silica particles. To characterize the adsorption layer quantitatively, we calculated the scattering functions for the model consisting of the aggregation of Silica particles, the adsorption layers on the silica particles and the matrix region. The model can well express the experimental partial scattering functions as shown in Figure 2 (solid line) and several characteristic parameters are estimated from the analyses, such as the size of aggregates, the thickness of layers, the volume fractions of polymer of layers and matrix, and the correlation length of the matrix network. The contrast variation SANS is found to be a powerful tool of the analyses of the structures of the rubber-filler systems.

Keywords: Contrast variation SANS, Hierarchical structure, Silica aggregation

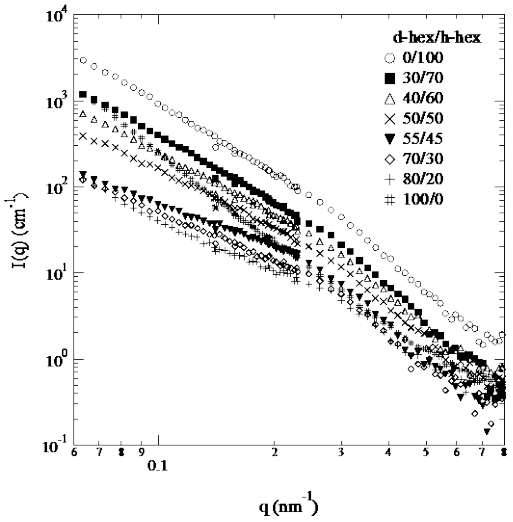

Fig.1 Scattering profiles for rubber-filler system swollen by d-hex/h-hex.

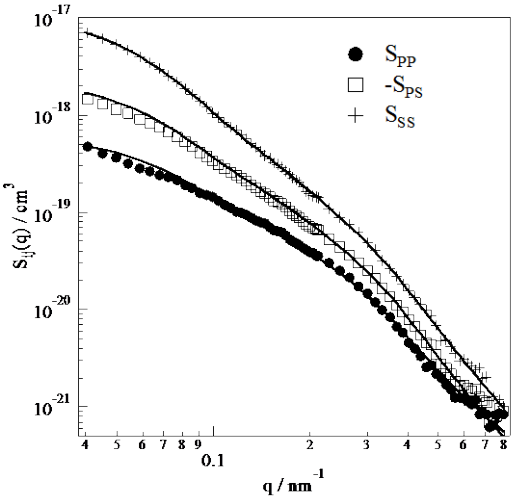

Fig.2 Partial scattering functions of rubber - filler systems

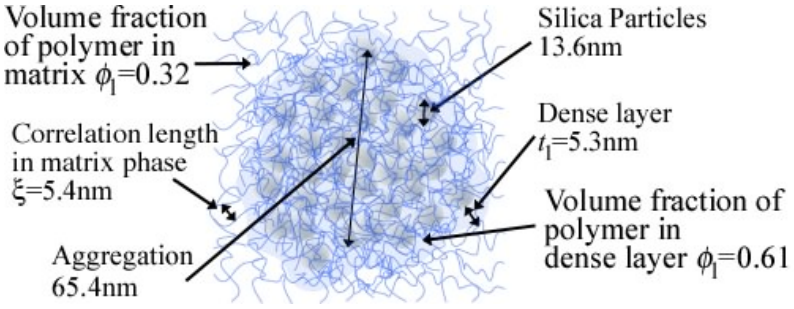

Fig.3 Characteristic parameters yielded by analyses.