Gelation Mechanism of Clay-Polymer Nanocomposite Hydrogel using Contrast Variation SANS

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Recently, clay-polymer nanocomposites have been focused much attention because of their excellent physical properties. Haraguchi et al. reported a novel clay-polymer nanocomposite gels (NC gels) consisting of synthetic hectorite (Laponite) and poly(*N*-isopropylacrylamide) (PNIPA)[1]. This NC gel has excellent physical properties, such as toughness, large deformability, large swelling ration, rapid shrinking capability, and high transparency. We carried out structure investigation of NC gels of various concentrations by small-angle neutron scattering using contrast variation technique (contrast-variation SANS) in order to learn the gelation mechanism.

We prepared NC gels of four different concentrations, two dense samples were in gel state and two dilute samples remained sol state. Investigating the microscopic structures of these samples near galation threshold, we can learn the galation mechanisms of NC gels. Since NC gel is a three components system, consisting of clay, PNIPA, and water, the scattering intensity is given by clay-clay, clay-polymer, polymer-polymer correlations. Thus using water of more than three different scattering length densities, we can decompose the scattering intensities into their partial scattering functions. In this case, we used contrast controlled water with different D_2O fraction.

Fig.1(a) shows the scattering intensities of the most dense sample and the partial scattering functions. Scattering intensity of NC gel is minimum in the case of D_2O fraction was 56%. With increasing D_2O fraction, the scattering intensity became large. Fig.1(b) shows the partial scattering functions obtained from the scattering intensities of Fig.1(a) by singular value decomposition. In order to check the validity of decomposition, the reconstructed scattering intensities are added in Fig.1(a) with solid line. Comparing these scattering intensities, the decomposition was successful. The most important result is that the sign of $S_{CP}(q)$, which corresponds to the clay-polymer cross-correlation, is positive. It indicates that there are spatial cross-correlation between clay and polymer. Then we assumed that clay platelets are surrounded by polymer layers and these surrounded clay platelets are tied by polymer network. Thus we calculated the scattering function from this model and we can successfully fit these partial scattering functions. From the fitting, clay platelets are surrounded by polymer layers, whose volumes are about 2.5 times of the clay platelets. Furthermore, this model represented the scattering functions of the other samples, regardless of gel and sol. It indicates that the microscopic structures of NC gel are almost identical regardless of gel and sol.

[1] K. Haraguchi and T. Takehisa, *Adv. Mater.* **14**, 1120 (2002).

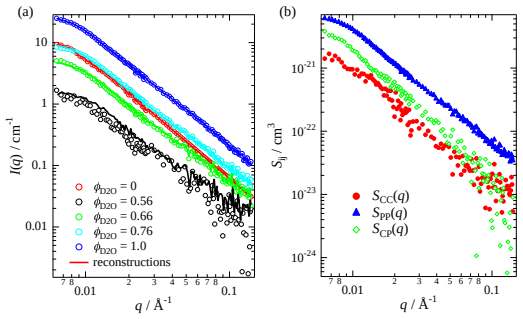

Fig. 1. (a)Scattering intensities and (b)obtained partial scattering functions.