Study of the cross-linking structure of slide-ring polymer and clay nanocomposite systems by contrast variation SANS

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Nanocomposite gels consisting of polymers and clay particles form a network structure and are known to exhibit properties such as high structural uniformity, excellent elongation and recovery properties. To understand the mechanism of mechanical property of nanocomposite system, it is necessary to investigate the adsorption property between polymers and clay, and the network structure they form. One of the mechanisms for the toughening of polymer gels is using slide-ring polymer that are cross-linked with ring molecules (Cyclodextrin). The ring molecules penetrate a chain polymer (Polyethylene glycol; PEG) and can move freely on the axial chain, resulting in high strength without stress concentration during stretching.

We investigated the structure of nanocomposite solution of clay particles (Laponite XLG (BYK)) and a slide-ring polymer (Polyrotaxane; PR). PR is composed of Cyclodextrin and PEG. The molecular weight of PEG was 35,000. For the structure analysis of such multi components system, we employed contrast variation small angle neutron scattering (CV-SANS) by changing D_2O/H_2O fraction of the solvent. The samples are PEG2.5%/clay2%, PR 10%/clay2%, PEG 2.5%, PR 10% and clay 2% solutions. The prepared SLDs of the solvent are listed in Table 1. (φ denotes D_2O fraction of the solvent). The experiment was performed at SANS-U at JRR-3. The sample to detector distance of 8 m and 1 m were used. The incident neutron beam had a diameter of 10 mm and a wavelength of 7.0 Å.

Table 1. Contrast variations

φ	SLD ($\times 10^{-6}$ Å^{-2})	Description
1.0	6.39	100% D_2O
0.73	4.51	Clay matching
0.16	0.55	PEG matching
0.0	-0.56	100% H_2O

Results: Figure 1 (a) and (b) shows the SANS results of PEG/Clay, PR/Clay and Clay solutions at the contrast of φ = 1 and 0.73, respectively. Regarding the pure clay solution, at the clay-contrast matching point, φ = 0.73 we observed a flat I(Q) profile, while a clear disc-like form factor originated from the shape of clay particle at φ = 1. For PEG/Clay solution, the disc-like form factor was observed even in clay-matching point φ = 0.73. This indicates that PEG polymer is adsorbed around the clay particles to form a disc shape. The PR/Clay solution shows a different I(Q) profile from PEG/Clay, suggesting that PR does not adsorb to the clay as much as PEG and forms a network structure that bridges between clay particles. These microscopic pictures will explain the differences in the viscoelastic properties of these nanocomposite materials.

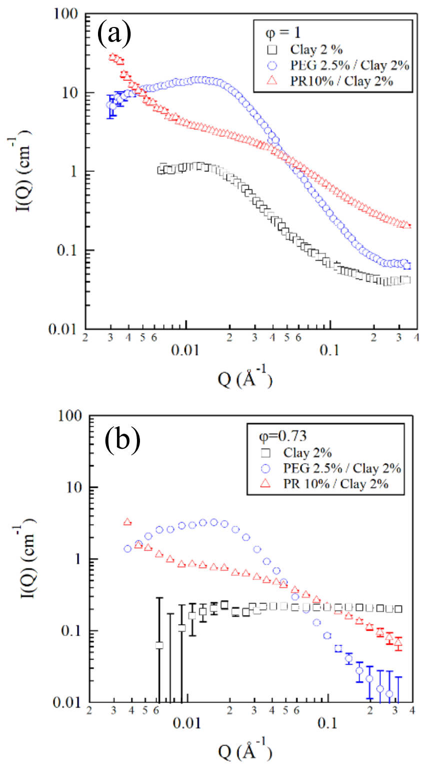

Fig. 1. SANS data of PEG/Clay, PR/Clay and Clay solutions at (a) φ = 1 and (b) 0.73.