

Evaluation of Structural Change in Nanoclay/Polymer Suspensions Studied by Small-Angle Neutron Scattering

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Suspensions composed of nanoclay (with widths of tens to hundreds of nm) and polymers dispersed/dissolved in liquids are known to exhibit characteristic rheological responses such as shear-thickening (i.e., steady-state viscosity increases with increasing shear rate) [1]. Recently, we found that the addition of 2.5 wt% poly(ethylene oxide) (PEO) with a molecular weight of 4 Mg/mol to a bentonite (BNT; with a thickness of ca. 1 nm and a width of ca. 500 nm)/water suspension (at the weight fraction of BNT as $\phi_{\text{BNT}} = 10$ wt%) exhibits a remarkable temperature dependence of rheological responses, in addition to exhibiting shear-thickening. We speculated that the temperature dependence of the system described above was due to the change in structures formed by BNT and PEO in water, and expected that these changes could be evaluated by small-angle neutron scattering (SANS) by tuning the scattering contrast.

10 wt% of BNT was dispersed in water with different D₂O/H₂O ratio (i.e., 100/0, 90/10, 80/20 and 70/30), and then 2.5 wt% of 4M-PEO was dissolved. The samples were poured into an assembly cell with a thickness of 2 mm, provided at the beamline. SANS measurements were performed at the SANS-U beamline with the sample-to-detector length of 12 and 2 m, and the wavelength of neutron beam of 7 Å. The samples are mounted on a sample changer, and measured at 25 and 40 °C.

Figure 1 shows the 1D-averaged SANS profiles of BNT/4M-PEO/water suspensions at different D₂O/H₂O ratio measured at 25 °C. As a comparison, the data for 4M-PEO/D₂O solution, and H₂O and D₂O solvents are also shown. Note that two-dimensional scattering patterns of the samples measured in this study are all essentially isotropic, and thus can be discussed without arbitrariness from 1D-profiles. In Figure 1, as the D₂O/H₂O ratio changes, the SANS profiles of the BNT/4M-PEO suspensions also change. That is, the scattering intensity $I(q)$ becomes

weaker as the H₂O ratio increases. This result is because the scattering length density of the solvent (i.e., H₂O/D₂O mixture) and BNT becomes closer and the scattering ability weakens as the H₂O fraction increases, as reported previously [2,3]. If some characteristic scattering patterns were observed in the BNT/PEO suspension with D₂O/H₂O = 70/30, where the contrast between BNT and solvent is almost identical, then further discussion would be possible, but in the q range measured it is difficult.

When the 1D-SANS profiles of BNT/4M-PEO suspensions measured at 25 and 40 °C are compared, almost no difference is appeared in the scattering profiles irrespective of H₂O/D₂O ratio (although the data do not show), which is different from the results of the rheological measurements. This result suggests that there is little change in the structure formed by BNT/PEO, or that such a change has not been detected within the present observation q range.

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- [2] A. Nelson, et al., *Langmuir* **20**, 2298 (2004).
- [3] T. Matsunaga, et al., *Macromolecules* **43**, 5075 (2010).

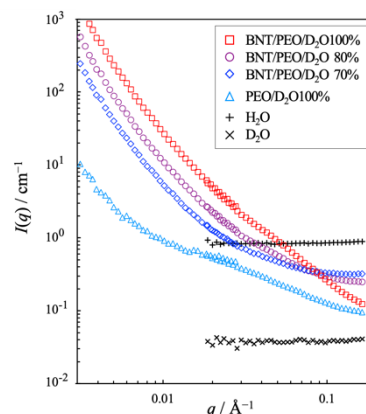


Fig. 1. 1D-averaged SANS profiles of BNT/4M-PEO/water suspensions with different D₂O/H₂O ratio, as well as 4M-PEO/D₂O, D₂O and H₂O measured at 25 °C.