Structural Formation Process of Polymers under Shear Flow

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Crystallization of polymers under shear flow have been extensively investigated because polymers are exposed to various flows such as elongational, shear and mixed flows during industrial processing. These processes can significantly affect the crystallization kinetics and final morphology. For example, when polymer crystallizes under flows, the so-called shish-kebab structure could be observed. The shish-kebab structure consists of long central fiber core (shish) and lamellar crystals (kebab) periodically attached along the shish structure and surrounded by the shish structure. We showed that the small angle neutron scattering (SANS) with deuterium labeling method was very powerful to study the crystallization kinetics of polymers under shear flow.

In the present experiment, we performed the time-resolved SANS measurements on crystallization processes of blends of deuterated low molecular weight and protonated ultra-high molecular weight polyethylene (PE) with the handmade shear cell specialized for observation of polymer crystallization process with/without shear flow [1]. The blend samples were molten at 190 C and then cooled down to a crystallization temperature of 124.5 C at a rate of about 40 C/min. The sample was subjected to pulse shear just after reaching the crystallization temperature. The shear rate and strain are 90 (1/s) and 1000 %, respectively. The molecular weight of low molecular weight deuterated and protonated ultra-high molecular weight PE (d-PE/h-PE) is 56,500 and 2,000,000, respectively. The time-resolved SANS measurements were carried out on SANS-U spectrometer on JRR-3, JAEA, Tokai, Japan.

Figure 1 shows that the time evolution of 2D SANS profiles for a blend d-PE/h-PE = 3/97 under shear flow. Just after inducing shear flow (0.5 min), the streak-like scattering normal to the shear direction could be observed, and then the strong scattering profiles parallel to the shear direction appeared and became stronger after 2.5 min. The normal streak-like scattering and parallel scattering were assigned to shish and kebab structures, respectively. These results suggest that the shish structure grows before kebab structural formation. Furthermore, the observed shish-structure is in micron ordered and very similar to the shish-like structure observed with time-resolved light scattering measurements. As h-PE concentration decreases the scattering profile became isotropic. This result suggests that the structural formation process depend on the existence of entanglements of high molecular weight components.

Reference:
[1] K. Nishida et al, Activity Reports on Neutron Scattering Research, ISSP, U of Tokyo, 13, 2006.

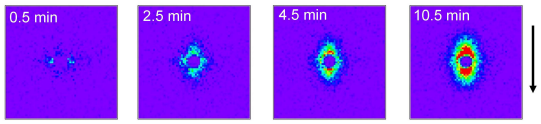

Fig. 1. Figure 1. Time evolution of 2D SANS profiles for deuterated and hydrogenated polyethylene blend.