Role of Low Mw Components in Polymer Crystallization under Shear Flow

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It is well known that when polymers in melts and solutions are crystallized under elongational and/or shear flows the so-called shish-kebab structure is formed, which consists of long central fiber core (shish) surrounded by lamellar crystalline structure (kebab) periodically attached along the shish. In the previous research, it was found that high molecular weight component composed mainly shish structure. Now, we carried out the structural formation processes of shish-kebab during drawing was confirmed by in-situ small-angle neutron scattering (SANS) measurements on a polyethylene (PE) blend of low molecular weight deuterated PE and high molecular weight hydrogenated PE(3 wt%). Time-resolved SANS measurements were performed with SANS-U spectrometer at the JRR-3M reactor in JAPAN Atomic Energy Research Institute (JAERI), Tokai.

On drawing process of the blends, it was observed that the isotropic crystal structure gradually formed the anisotropic shish-kebab structure with in-situ SANS measurements in Figure 1. At first 10 min, the isotropic pattern changed horizontally long ellipsoid-like profiles. This suggested that the isotropic lamella was stretched and distorted. Between 20 min and 80 min, the shish-kebab formation processes were observed. In high temperature condition, the long spacing period increased with drawing process, while the long spacing period decreases in low temperature condition. In high temperature, the " tie chain " between lamella could extend and be pulled off from lamella crystal because of high mobility. On the other hand, low mobility in low temperature prevented the " pulled off " process and then the lamella crystal could be broken. After 80 min, we observed the processes of " kebab evaporating ". Such disappear of kebab structure could be caused by " shish-formation process " from kebab structure.

Furthermore, we evaluated the detailed shish-kebab structure from these 2D SANS profiles. The shish kebab structure can be described as core-shell cylinder model. The radius of core cylinder was about 45 nm and the shell cylinder had two core cylinders.

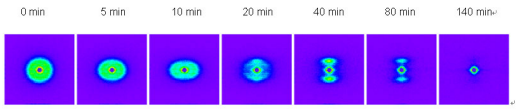

Fig. 1. Time evolution of 2D SANS patterns during crystallization process of PE at 110 C, drawing rate = 6 micron/ s