高分子のせん断流動結晶化における in-situ X線散乱法をもちいたナノ構造観察

Study of Structure Formation Process of Polymers under Shear Flow with in-situ X-ray Scattering Methods

松葉　豪
Go Matsuba

Institute for Chemical Research, Kyoto University, Kyoto-fu, 611-0011 Japan.

*e-mail: gmatsuba@scl.kyoto-u.ac.jp

Introduction

Crystallization of polymers under flows have been extensively investigated because during most polymer processing the polymers are exposed to various flows such as elongational, shear and mixed flows. On crystallization under shear flow, 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. In this work, we have investigated crystallization process of polyethylene (PE) blends of ultra high molecular weight (UHMW) and low molecular weight components under shear flow, focusing on the effects of UHMW PE on crystallization process and final morphology using the time resolved SAXS technique.

Experimental

In this experiment we used two PEs with molecular weight M_w = 58,600 and ultra-high molecular weight (UHMW) M_w = 2,000,000 and the polydispersities were M_w / M_n = 8 and 12, respectively, where M_w and M_n are the weight-average and number-average molecular weights, respectively. The fraction of the UHMW PE C_{HMPE} was in a range of 0 to 2 wt %.

A Linkam CSS-450 shear cell was used to control shear field and thermal history of the polymer samples. The blend sample with thickness of 300 μm was placed between two stainless parallel plates with windows of Kapton 50 μm thick for SAXS measurements.

Time resolved SAXS measurements were performed with apparatus at the beam line BL-15A in Photon Factory, KEK, Tsukuba. A CCD camera (C4880: Hamamatsu Photonics K.K.) with an image intensifier was used as a detector system for the SAXS measurements. In the measurements we covered a Q range of 6 x 10^{-3} to 2 x 10^{-1} Å^{-1}, where Q is given by $Q = 4\pi\sin\theta/n\lambda$ (2θ and n being scattering angle and the refractive index, respectively).

Results and Discussion

Figure 1 shows 2D SAXS patterns at 116 ºC after a pulse shear with a rate of 32 s^{-1} and strain 3200 % for various C_{HMPE}. The scattering pattern was isotropic for C_{HMPE} < 0.1 wt%, while the spot-like scattering patterns were observed parallel to the shear flow direction for $C_{HMPE} \geq 0.2$ wt%, which must be correspond to the lamella stacks parallel to the shear direction, that is the so-called kebab structure. It should be noted that no equatorial scattering was observed for all UHMW PE concentrations in the SAXS measurements. Does the present result mean that no shish structure was formed during the crystallization process? This result suggests that there should be shish-like structure even though streak-like scattering normal to the flow was not observed in the SAXS measurements.

Furthermore, we showed the crystallization temperature dependence of 2D SAXS patterns of C_{HMPE} = 0.2 wt% in Figure 2. In low crystallization temperature condition such as 116 ºC, 123 ºC and 127 ºC, the kebab structure was observed, however not observed in crystallization at 132 ºC.
The kebab structure formation processes depend on both crystallization temperature

and UHMW PE concentration. This is due to the increase in degree of super-cooling (or quenching depth), which is a driving force of crystallization in this temperature region. On the other hand the meridional spots parallel to the shear direction were not observed in crystallization above 129 °C, at least during the annealing period of 1 h. Note that the meridional spots were observed even above ~129 °C for the concentrations of UHMW PE higher than 0.2 wt%, showing that the critical UHMW PE concentration for the anisotropy exists and depends on the crystallization temperature.

These results suggest that the shish-kebab formation process is much affected by crystal nucleation and relaxation processes of UHMW PE oriented by shear flow. It was found that the critical UHMW PE concentration for anisotropic structural formation exists in crystallization under shear flow. Above fully high concentration, the shish-kebab formation process could be observed in SAXS measurements. Below the critical concentration, the isotropic crystal growth was observed because the UHMW PE chains were not oriented by shear flow. Near the critical concentration, the structural formation under shear flow has a strong dependence on the crystallization temperature. At low crystallization temperature, the crystallization occurs immediately after initial orientation by the shear flow before the chain orientation. However, in high crystallization temperature case, the oriented UHMW PE chains become isotropic because orientated chains relax before beginning crystal nucleation. We will discuss about the effects of UHMW PE chains on the higher-ordered structure formation.

Conclusions

From SAXS measurements, the critical UHMW PE concentration is almost independent of the low crystallization temperature below 127 °C, while it increases with the crystallization temperature above 127 ºC under the same shear condition. Hence, in order to prevent the chain relaxation and form anisotropic structure at the high temperature, the critical concentration of UHMW PE must be higher than that at the low temperature to increase the number of entanglements.

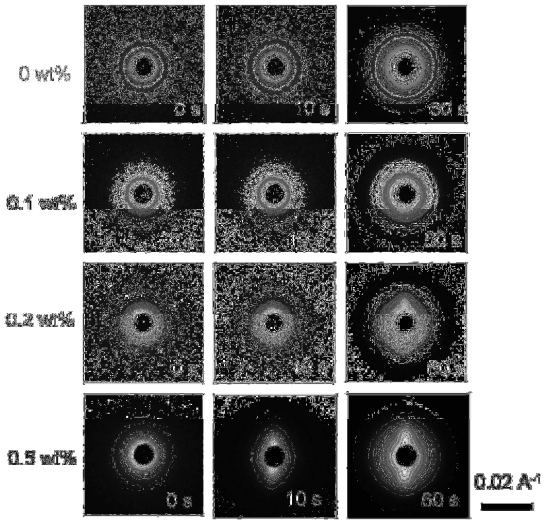

Figure 1 – 2D SAXS patterns of the PE blends with various concentrations of UHMW PE from 0 to 0.5 wt % crystallized at 116 ºC. The shear rate and the strain were 32 s^{-1} and 3200%, respectively.

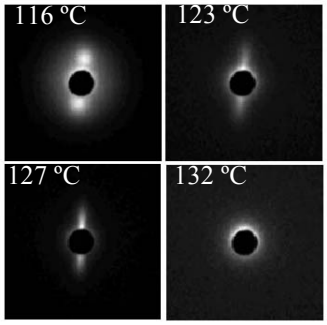

Figure 2 – 2D SAXS patterns of the PE blends with 0.2 wt% concentration of UHMW PE at various crystallization temperatures. The shear rate and the strain were 32 s^{-1} and 3200%, respectively.