

Comparison of the Supercooled Uniaxial Elongational Behavior and Flow-induced Crystal Structure of PE/UHMW-PE Blends

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1. Introduction:

It is known that when semi-crystalline polymers in melts are crystallized under flows the so-called shish-kebab structure is often formed. It is believed that the long chain plays an important role to form the shish-kebab structure. Recently, many researchers report about the effect of ultra-high molecular weight (UHMW) component on the shish-kebab formation process under shear flow [ref. 1-3]. They reported that entanglements of UHMW chain have a significant influence on the shish-kebab structural formation. Generally, the strain-hardening under an elongational flow is often observed for polymer melts with a long relaxation time component. In homopolymer system, the strain-hardening is believed to be arisen from the stretching of the polymer chain to the direction of flow. Minegishi et al. [ref. 4] reported that the enhancement of strain-hardening was greatly affected by entanglements among a small amount of UHMW chains which were added to standard molecular weight distribution analogue.

Generally, the uniaxial elongational flow behavior has conspicuous difference to the shear flow behavior. It is thought that this difference will affect the flow-induced crystallization behavior. However, the most of study about the flow-induced crystallization were investigated under shear flow. Therefore, the aim of this study is to evaluate the effect of UHMW component on the uniaxial elongational behavior under supercooled condition and the crystal structure.

2. Experimental:

We used two types of linear polyethylene that the molecular weights are $M_w = 9.0 \times 10^4$ and $M_v = 1.5 \times 10^6$, respectively. We prepared the blend samples in which UHMW-PE of 0, 0.5, 1, 3, 5, and 10wt% is added, respectively (*e.g.* $C_{\text{UHMW-PE}} = 3\text{wt\%}$ is labeled as PE3). The uniaxial elongational measurement was measured by Meissner-type rheometer (Toyo Seiki Seisaku-sho Co, Melten Rheometer). The temperature protocol for the uniaxial elongational viscosity measurements is shown in Fig. 1. We obtained the crystal structure of the extended samples after the supercooled elongational measurements for SAXS measurements (Rigaku, Micro Max-007HF).

3. Results and discussions:

Fig. 2(a) depicts the uniaxial elongational viscosity $\eta_E^+(t, \dot{\epsilon})$ of PE0, PE3, and PE10 at various elongational strain rates $\dot{\epsilon}$ and 130 °C. The strain-rate-independent linear elongational viscosity increases with increase of $C_{\text{UHMW-PE}}$. The strain-hardening starts to appear above a critical strain ($\epsilon^{(\text{sh})} \cong 0.7$). The critical strain was found to be independent of the strain rates. To compare the strain-hardening behavior among PE0-10, we defined the strain-hardening parameter $\lambda_n (= \eta_{\text{non-linear}}/\eta_{\text{linear}})$. Fig. 2(b) depicts $\ln \lambda_n$ as function of ϵ for PE0-10 at $\dot{\epsilon} \approx 0.1\text{s}^{-1}$ and $T=130$ °C. As seen from Fig. 2(b), $\epsilon^{(\text{sh})}$ is found to be almost independent of $C_{\text{UHMW-PE}}$. The slope of $\ln \lambda_n$ versus ϵ are enhanced with increase of $C_{\text{UHMW-PE}}$ because of the increase of long relaxation time component. To analyze quantitatively, we defined the strain-hardening intensity α (the slope of $\ln \lambda_n$ versus ϵ). α as function of $C_{\text{UHMW-PE}}$ is shown in Fig. 2(c). α starts to increase between $C_{\text{UHMW-PE}} \cong 0.1 \sim 0.5\text{wt\%}$. These

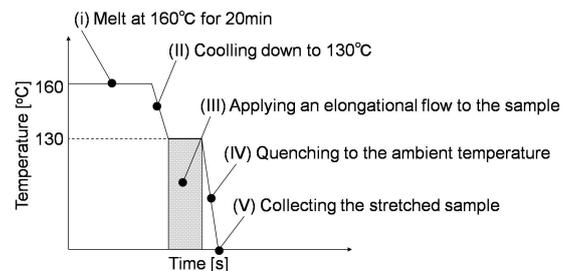


Fig. 1 Temperature protocol for the supercooled uniaxial elongational measurements

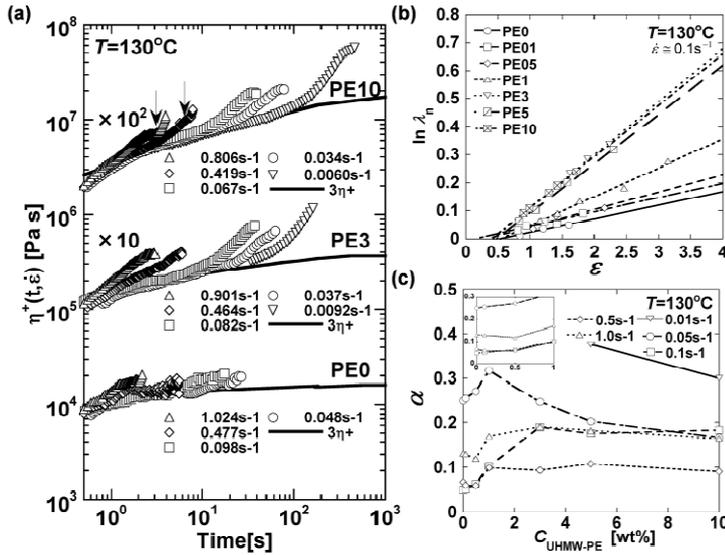


Fig. 2 (a) Uniaxial elongational viscosity of PE0,3,10 at 130 °C under various $\dot{\epsilon}$. (b) λ_n as function of ϵ at $\dot{\epsilon} \approx 0.1 \text{ s}^{-1}$ at 130 °C. (c) α as function of $C_{\text{UHMW-PE}}$ at various $\dot{\epsilon}$.

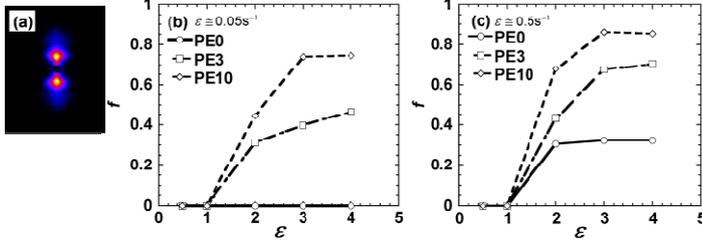


Fig. 3(a) 2D SAXS patterns of the stretched PE10 up to $\epsilon \approx 4$ at 0.81 s^{-1} . f as function of PE0, PE3, and PE10 around (a) 0.05 s^{-1} and (b) 0.5 s^{-1} at various ϵ .

increase of ϵ and $C_{\text{UHMW-PE}}$. From the comparison between the strain-hardening and orientation function f , the critical strain of strain-hardening ($\epsilon^{\text{sh}} \cong 0.7$) and the critical-orientation strain ($\epsilon^{\text{ori}} \cong 1$) exhibited almost same tendency. These results suggest that the forming of shish-kebab structure is necessary to stretch the polymer chain to the flow direction, since the strain-hardening is arose from the stretching of the long polymer chain to the direction of flow. At higher strain region ($\epsilon \geq 3$), the polymer chain is not able to stretch any further, since the polymer chain are sufficiently stretched already. In case of PE0 around 0.05 s^{-1} , since α is very weak, the polymer chain are not sufficiently stretched to the flow direction. From these results, we found that it is necessary to stretch the polymer chain above ϵ^{ori} in order to form of shish-kebab structure.

4. Summary:

We found that the reason for the enhancement of the forming of shish-kebab structure was dominated by the stretching of UHMW-PE chain. In our presentation, we explain more detail.

5. References:

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values which start to show stronger strain-hardening may be related to the entanglement number of UHMW-PE chains N_u . PE01 and PE05 give N_u value of 1.4 and 6.8, respectively. From these results, it is found that the strain-hardening is enhanced by the entanglements among UHMW-PE chains, and the enhancement of strain-hardening are almost zero above the entanglement number of UHMW-PE chains $N_u > 2$. N_u is estimated as follows;

$$N_u = C_{\text{UHMW-PE}} (M_{\text{UHMW-PE}} / M_c) \quad (1)$$

where $M_{\text{UHMW-PE}}$ and M_c are the molecular weight of UHMW-PE and the molecular weight between entanglement ($\cong 1250 \text{ g/mol}$) [ref. 5], respectively.

Fig. 3(a) shows the 2D SAXS patterns of the stretched PE10 up to $\epsilon \approx 4$ at 0.81 s^{-1} . This 2D SAXS pattern clearly showed shish-kebab structure. To analyze quantitatively, the degree of orientation of lamellar in the stretched sample of PE0, PE3, and PE10 around 0.05 s^{-1} and 0.5 s^{-1} at various ϵ was determined by using the Herman's method [ref. 6] in Fig. 3(b)(c). f starts to increase above critical-orientation strain ($\epsilon^{\text{ori}} \cong 1$), and f enhanced with