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## 論文の内容の要旨

### 1. Introduction

Polyethylene (PE) is available for various polymer processing operations because of its widest variety of molecular structure, such as short- and/or long-chain branches and molecular weight distribution. The variety of chain architectures greatly affects the rheological behavior, especially strain-hardening in elongational viscosity. The rheology control is, however, still required to widen the processing window. Therefore, the study on rheological properties of PE is very important. Up to now, several techniques have been proposed, such as shear history, thermal history, and addition of specific processing aids. These techniques have a strong impact on the elongational viscosity which is one of the most important rheological properties at polymer processing. In this study, rheological modification techniques by applying thermal history were proposed.

### 2. Aim of Research

The main objective of this research is to propose new techniques to control the rheological properties of PE. In particular, the rheological modification by the following two methods is studied; (1) The rheological changes of long-chain branched low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and their blends after thermal history at high temperature without thermal stabilizers; (2) Molecular weight segregation of PE under temperature gradient.

### 3. Experimental Results

#### 3.1 Rheological Modification by Thermal history at High Temperature

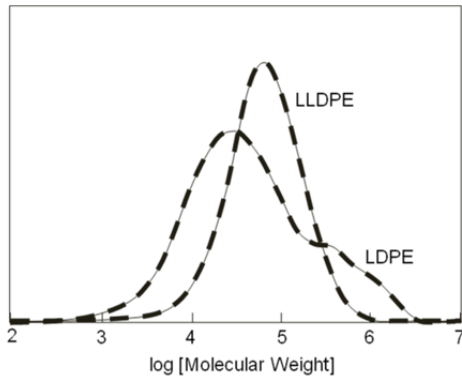


Figure 1. GPC curves of LDPE and LLDPE; (dotted lines) before and (solid lines) after thermal modification (280 °C for 3 min)

However, the thermal history has a strong impact on the linear viscoelastic properties especially for LLDPE as shown in Figure 2. Moreover, the values of phase angle evaluated at various temperatures are not superposed onto each other after thermal modification, demonstrating that long-chain branches are generated during the thermal modification. The result indicates that the cross-linking occurs slightly, leading to a small amount of X-type branch points in LLDPE.<sup>2-5</sup> This structure change greatly affects the drawdown force, a force needed to stretch a molten sample uniaxially. Since the drawdown force has a close relation with elongational viscosity, it should be comprehended exactly. Figure 3 shows the enhancement of drawdown force by thermal history, *i.e.*, the difference in the drawdown force between the virgin sample and the thermally-modified one for LLDPE/LDPE blends. As seen in the figure, the drawdown enhancement is marked for the blends. The enhanced drawdown force is attributed to the

Exposure to high temperature, *e.g.*, 280 °C, which is a typical temperature at extrusion-coating, leads to cross-linking reaction for LDPE, LLDPE and their blends without thermal stabilizers. Although it has been believed to change the molecular structure greatly by the applied thermal history, the molecular weight and its distribution are found to be barely changed as shown in Figure 1.

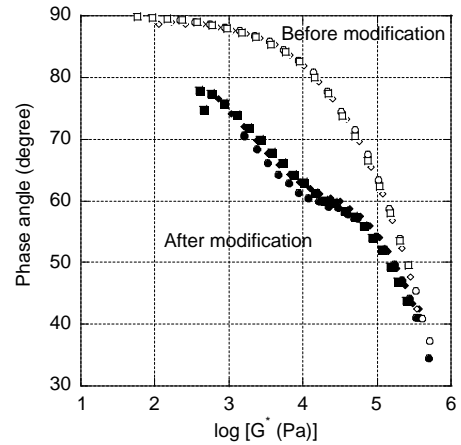


Figure 2. van Gorp-Palmen plots for LLDPE (open symbols) before and (closed symbols) after thermal modification (280 °C for 3 min); (circles) at 130 °C, (diamonds) at 160 °C and (squares) at 190 °C

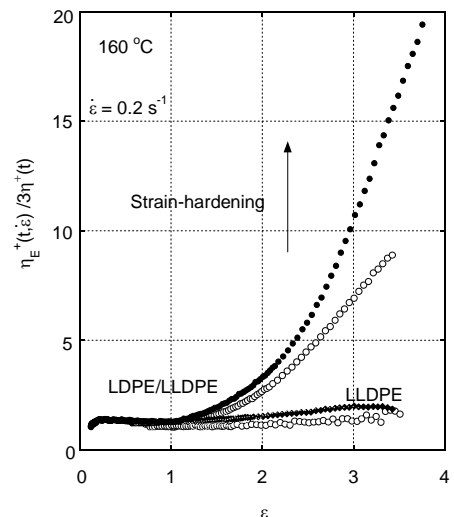


Figure 4. Ratio of uniaxial elongational viscosity  $\eta_E^+(t, \varepsilon)$  to that at the low strain rate asymptote  $3\eta^+$  as a function of elongational strain  $\varepsilon$  at a strain rate  $\dot{\varepsilon}$  of 0.2 s<sup>-1</sup> for (diamonds) LLDPE and (circles) LDPE/LLDPE; (open symbols) before and (closed symbols) after thermal modification.

marked strain-hardening in elongational viscosity as seen in Figure 4. Considering that a comb-shaped branch polymer shows marked strain-hardening behavior, the result suggests that the intermolecular cross-linking reaction occurs between LDPE and LLDPE.

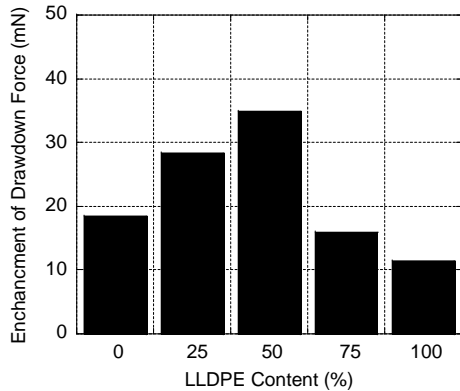


Figure 3. Enhancement of drawdown force at 190 °C for LDPE/LLDPE blends after thermal modification

The cross-linking efficiency is greatly enhanced by the addition of a peroxide compound. Furthermore, flow field during reaction affects the structure of cross-linked PE and thus the rheological properties, as seen in Figure 5.

The phenomenon is explained by the ratio of intermolecular/intramolecular reactions. Once the intramolecular cross-linking occurs, further reaction within the same molecules takes place more frequently because the radius of gyration of a polymer chain is small due to the existence of long-chain branches.

### 3.2 Molecular Weight Segregation of Polyethylene by Annealing Procedure in Temperature Gradient

The rheological modification of HDPE by annealing procedure under temperature gradient was studied. The applied thermal history in a compression-molding machine, in which the temperature of one mold is higher than the other, is firstly found to induce molecular weight segregation in the molten state as shown in Figure 6. In the figure, the weight-average molecular weight  $M_w$  of HDPE is calculated from the zero-shear viscosity at 190 °C.<sup>6</sup> The high molecular weight fraction is localized at the surface attached to the mold with low temperature and vice versa. Even when the bottom plate of the

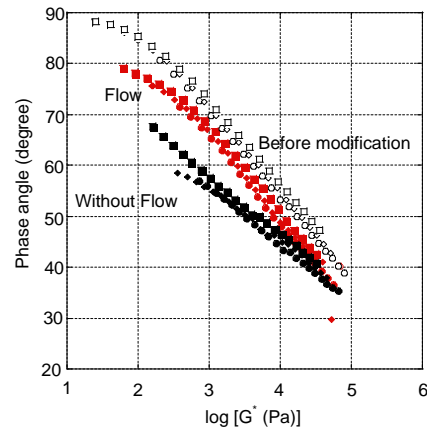


Figure 5. van Gurp-Palmen plots for LDPE (open symbols) before and after modification (closed symbols) with 0.05 wt.% peroxide under flow field and (red symbols) without flow field; at (circles) 130 °C, (diamonds) 160 °C and (squares) 190 °C.

compression-molding machine is controlled at higher temperature than the top, the low molecular weight fraction is still segregated at the high temperature side. The result suggests that there is no effect of gravity force. The segregation behavior becomes obvious with the annealing time and temperature gradient as seen in Figure 7.

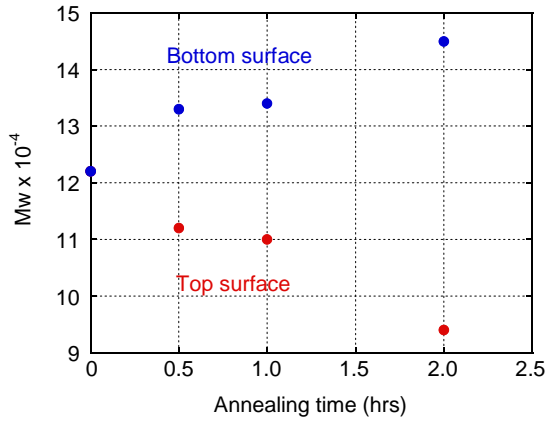


Figure 7. Weight-average molecular weight  $M_w$  of HDPE for the surface samples after annealing for various residence times at (top) 300 °C / (bottom) 150 °C; (red) top surface and (blue) bottom surface.

The molecular weight segregation in temperature gradient is further studied using LDPE. It is found that the strain-hardening behavior of high molecular weight fraction is higher than that of virgin one. The result suggests that the strain-hardening in elongational viscosity can be enhanced by the thermal history with the temperature gradient for LDPE without chemical reaction, as seen in Figure 8.

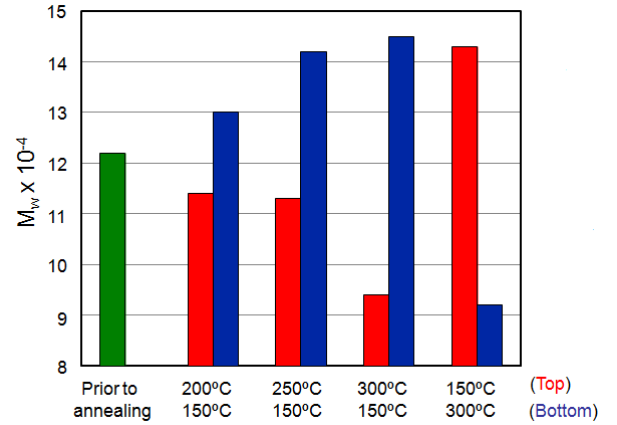


Figure 6. Weight-average molecular weight  $M_w$  of HDPE calculated from  $\eta_0$  for the blend samples annealed at various temperature conditions for 2 hrs; (green) prior to annealing, (red) surface at the bottom, and (blue) surface at the top.

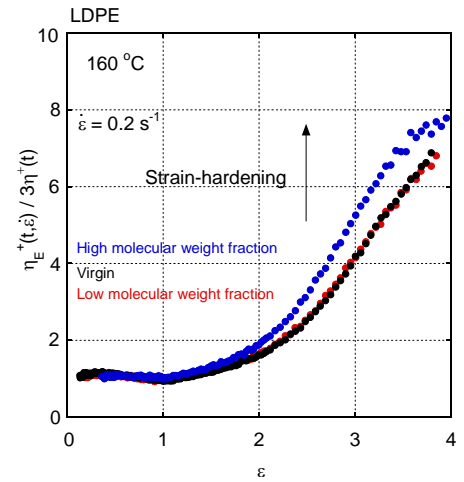


Figure 8. Ratio of uniaxial elongational viscosity  $\eta_E^+(t, \dot{\epsilon})$  to that at the low strain rate asymptote  $3\eta^+(t)$  of LDPE as a function of elongational strain  $\epsilon$  at a strain rate  $\dot{\epsilon}$  of  $0.2 \text{ s}^{-1}$  for (black) virgin, (blue) high molecular weight and (red) low molecular weight fraction.

#### 4. Conclusions and Prospect

Rheological modification using thermal history is studied employing various types of PE. The elongational viscosity of LDPE/LLDPE blends is enhanced by structure change caused by intermolecular

cross-linking reaction at high temperature, which is responsible for good processability. The effect of flow field on the structure change by cross-linking reaction is also clarified. Furthermore, it is also found that the elongational viscosity of PE can be enhanced by segregation behavior occurred in the temperature gradient, which could be applied as a novel fractionation method.

## 5. References

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## List of publications

1. **Monchai Siriprumponthum**, Naoya Mieda, Shogo Nobukawa, Masayuki Yamaguchi  
Segregation Behavior of Polyethylene with Broad Molecular Weight Distribution by Annealing Procedure in Temperature Gradient, *J. Polym. Res.*, 2011, *18*, 2449-2453.
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*J. Rheol.*, 2014, *58*, 449-465.
4. **Monchai Siriprumponthum**, Shogo Nobukawa, Masayuki Yamaguchi

## Rheological Modification of Low-density Polyethylene by Segregation Behavior in Temperature Gradient (to be submitted)

**Keywords:** rheology, long-chain branched polyethylene, rheological modification, melt elasticity, polymer processing

### 論文審査の結果の要旨

高分子溶融体はからみ合い相互作用により弾性を示し、その結果、さまざまな成形加工法への適用が可能になる。特に押出ラミネート加工では、溶融弾性が高いほどフィルム幅が狭くなる現象を防ぐことができるため、弾性向上への樹脂改質が主として重合方法の工夫により検討されている。一般的に、溶融弾性は長鎖分岐を導入することにより向上できることが知られているが、本論文では市販の長鎖分岐ポリマーの溶融弾性を、熱履歴によって向上することを目的として研究を進めている。論文は大きく二つの技術から構成されており、いずれも押出ラミネート加工に用いられる長鎖分岐型低密度ポリエチレン (LDPE) を対象として実験を行っている。

まず、押出ラミネート加工が行われる高い温度域でポリエチレンが受ける構造変化と溶融弾性について調べている。基本的な知見を得るために、LDPE のみならず直鎖状低密度ポリエチレン (LLDPE) も用いて検討したところ、LLDPE ではマクロラジカル間の反応により星形の分岐構造が形成されるもののその数はわずかであり、溶融弾性を著しく高めるには至らないことが判明した。一方、LDPE ではマクロラジカル間の反応は LLDPE よりもさらに少ないものの、溶融弾性は顕著な向上を示した。一般に楕形分岐高分子では分岐点間の部分鎖が伸長しやすく、これが溶融弾性に大きく寄与することが知られていることから、熱履歴中に楕形分岐構造が形成されたことが示唆される。さらに、LLDPE と LDPE のブレンドを熱改質すると、LLDPE と LDPE の間で分子間の交差反応が生じ、効率的に楕形分岐構造が形成されることが判明した。その結果、溶融弾性は著しく向上する。

次に、温度勾配下における分子量分別法について検討した。分子量分布の広い市販 LDPE 溶融体を温度勾配が存在する環境下で放置すると、高温側に低分子量成分、低温側に高分子量成分が偏析することが明らかになった。高温側では、多くの自由体積分率を必要とする分子末端が存在しやすいため本現象が生じると推測される。また、本現象を利用することにより、分子量分布の広い LDPE から高分子量成分のみを取り出すことが可能である。LDPE の高分子量成分は長鎖分岐が十分に発達している分子鎖に富むことが知られているが、その結果、顕著な溶融弾性を示す。なお、温度勾配下で分子量分別が可能になれば、溶媒を使うことなく、かつ大量の分別試料を簡単に調製できることから、今後の応用が期

待される。

以上、本論文は、工業的に利用されている長鎖分岐ポリエチレンの溶融弾性をさらに向  
上させ、成形加工性を改良する方法を具体的に示していると共に、そのメカニズムに関し  
てレオロジー特性などをベースに明らかにしており学術的に貢献するところが大きい。よ  
って博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。