

Title	長鎖分岐ポリエチレンの溶融弾性を制御する新しい手法に関する研究
Author(s)	Sirirumpoonthum, Monchai
Citation	
Issue Date	2014-09
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/12302
Rights	
Description	Supervisor: 山口 政之, マテリアルサイエンス研究科, 博士

New Methods to Control Melt Elasticity for Long-Chain Branched Polyethylene

1140205 SIRIPRUMPOONTHUM, Monchai
Yamaguchi Laboratory, School of Materials Science

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

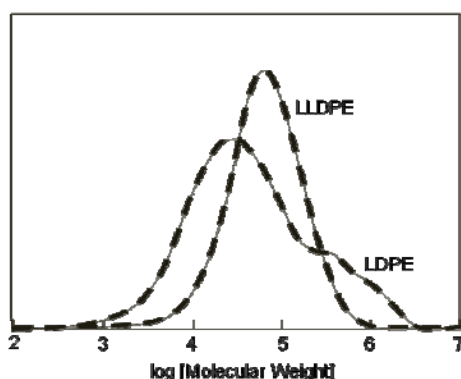


Figure 1. GPC curves of LDPE and LLDPE; (dotted lines) before and (solid lines) after thermal modification (280 °C for 3 min)

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.

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.²⁻⁵ 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 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.

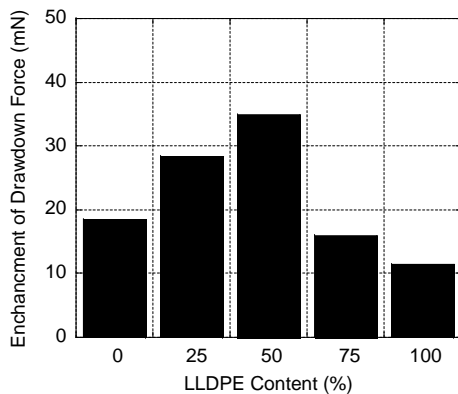


Figure 3. Enhancement of drawdown force at 190 °C for LDPE/LLDPE blends after thermal modification

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.

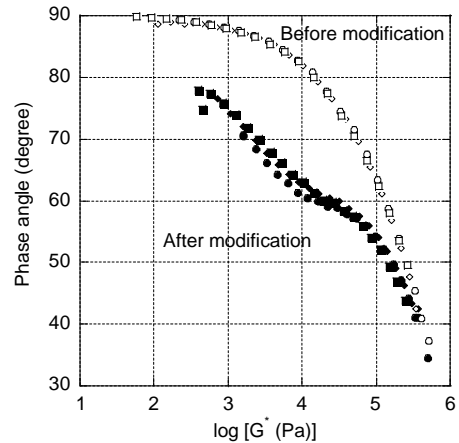


Figure 2. van Gurp-Palmen plots for LLDPE (open symbols) before and (closed symbols) after thermal modification (280 °C for 3 min); (circles) at 130 °C, (diamonds) at 160 °C and (squares) at 190 °C

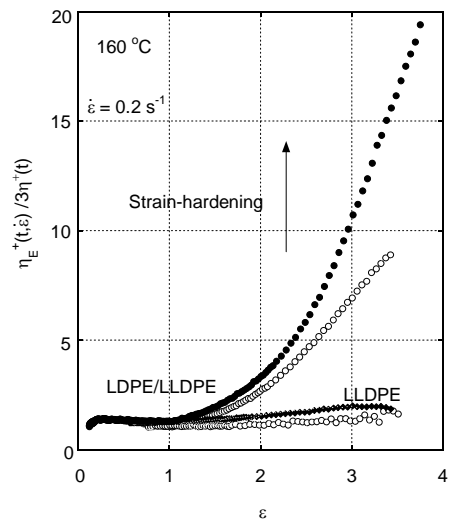


Figure 4. Ratio of uniaxial elongational viscosity $\eta_E^+(t, \varepsilon)$ to that at the low strain rate asymptote $3\eta^+$ as a function of elongational strain ε at a strain rate $\dot{\varepsilon}$ of 0.2 s⁻¹ for (diamonds) LLDPE and (circles) LDPE/LLDPE; (open symbols) before and (closed symbols)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

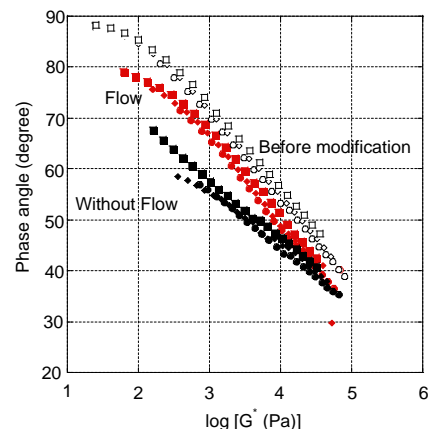


Figure 5. van Gurp-Palmen plots for LDPE (open symbols) before and after modification (closed symbols) with 0.05 wt.% peroxide under flow field and (red symbols) without flow field; at (circles) 130 °C, (diamonds) 160 °C and (squares) 190 °C.

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.⁶ 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 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.

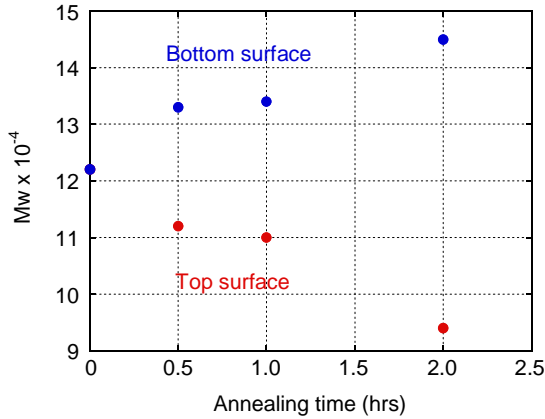


Figure 7. Weight-average molecular weight M_w of HDPE for the surface samples after annealing for various residence times at (top) 300 °C / (bottom) 150 °C; (red) top surface and (blue) bottom surface.

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.

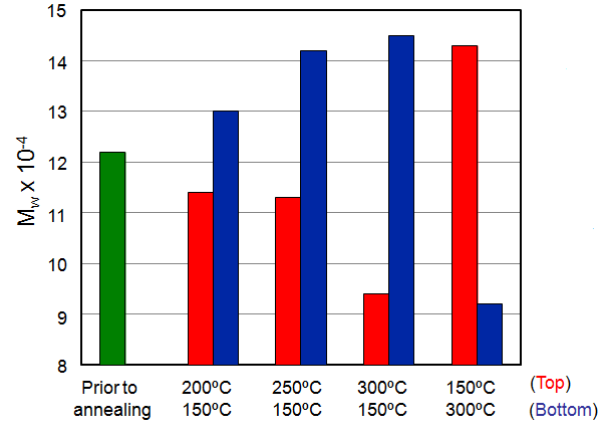


Figure 6. Weight-average molecular weight M_w of HDPE calculated from η_0 for the blend samples annealed at various temperature conditions for 2 hrs; (green) prior to annealing, (red) surface at the bottom, and (blue) surface at the top.

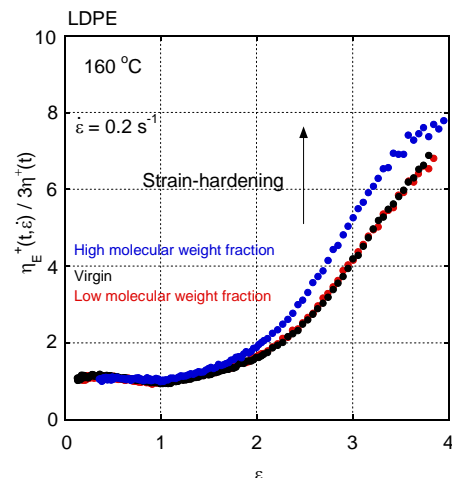


Figure 8. Ratio of uniaxial elongational viscosity $\eta_E^+(t, \varepsilon)$ to that at the low strain rate asymptote $3\eta^+$ of LDPE as a function of elongational strain ε at a strain rate $\dot{\varepsilon}$ of 0.2 s⁻¹ for (black) virgin, (blue) high molecular weight and (red) low molecular weight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

1. Ono, K.; Yamaguchi, M., *J. Appl. Polym. Sci.*, **2009**, *113*, 1462.
2. Stockmayer, W. H., *Chem. Phys.*, **1944**, *12*, 125.
3. Peacock, A. J., *Polym. Commun.*, **1987**, *28*, 259.
4. Rijke, A. M.; Mandelkern, L., *Macromolecules*, **1971**, *4*, 594.
5. Keßner, U.; Münstedt, H., *Polymer*, **2010**, *50*, 507.
6. Garcia-Franco, C. A.; Harrington, B. A.; Lohse, D. J., *Macromolecules*, **2006**, *39*, 2710.

Table of contents

Contents	Page
1. General Introduction	1
2. Rheological Modification by Cross-linking Reaction	45
3. Molecular Weight Segregation of Polyethylene by Annealing Procedure in Temperature Gradient	115
4. General Conclusions	155

List of publications

1. **Monchai Siriprumpoonthum**, 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.
2. **Monchai Siriprumpoonthum**, Naoya Mieda, Vu Anh Doan, Shogo Nobukawa, Masayuki Yamaguchi
Effect of Shear History on Flow Instability at Capillary Extrusion for Long-Chain Branched Polyethylene, *J. Appl. Polym. Sci.*, 2012, *124*, 429-435.
3. **Monchai Siriprumpoonthum**, Shogo Nobukawa, Yasuo Satoh, Hiroko Sasaki, Masayuki Yamaguchi
Effect of Thermal Modification on Rheological Properties of Polyethylene Blends, *J. Rheol.*, 2014, *58*, 449-465.
4. **Monchai Siriprumpoonthum**, 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