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Description	

**Segregation Behavior of Polyethylene with Broad Molecular  
Weight Distribution by Annealing Procedure  
in Temperature Gradient**

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**ABSTRACT:**

An annealing treatment in a molten state, in which temperature of the top plate is different from that of the bottom one in a compression-molding, leads to molecular weight segregation of high-density polyethylene (HDPE) prepared by mixture of two types of HDPE with different molecular weights ( $M_w = 1.8 \times 10^5$  and  $2.9 \times 10^4$ ). Low molecular weight fraction tends to localize at the surface attached to the higher temperature and vice versa. The segregation behavior is obvious at a large temperature gradient. Although the accuracy and mechanism of the phenomenon have not been clarified yet, this could be applied as a new fractionation method, which does not use a solvent.

**Key Words:** Fractionation, Rheology, Polyethylene, Blend

## INTRODUCTION

It is generally understood that a conventional polymeric material is a kind of a polymer blend having various components with different molecular weight. Therefore, fractionation methods of molecular weight have been studied and developed since the beginning of polymer science. One of the most popular methods of fractionation is a size exclusion chromatography (SEC). A fractional precipitation method is also well known, in which the fractionation is carried out owing to the difference in solubility by adding non-solvent to a dilute solution and/or changing temperature of a solution. Further, a diffusion method and an ultra-centrifugal method are known to be available for fractionation. All of them are introduced in classical textbooks.<sup>[1-5]</sup> In general, however, most methods are carried out using a solution. Further, it takes a very long time to collect a large amount of fractionated samples.

Recently, a new approach to improve the fractional precipitation method was proposed using a supercritical fluid instead of a toxic solvent, which will reduce fractionation time.<sup>[6,7]</sup> Further, a gas anti-solvent technique was also proposed for fractionation, which has a good performance especially to separate low molecular weight materials.<sup>[8,9]</sup> Moreover, flow field fractionation has been focused these days, in which a field is applied to a material in a flow field to cause separation due to different mobilities of various components in the field.<sup>[10-13]</sup> The field can be gravitation, magnetic, thermal, or a cross flow of fluids.

Another interesting research has been performed by Suwa et al.<sup>[14]</sup> They successfully revealed that molecular weight segregation takes place on a surface using polyethylene blends, in which a fraction with low molecular weight tends to localize at a

film surface. Further, they demonstrated that their results correspond to the values calculated following a theory proposed by Kim et al.<sup>[15]</sup> Considering that chain ends have excess free volume, concentration of chain ends is higher in the surface than that in the bulk.<sup>[15,16]</sup> This type of segregation was confirmed for poly(styrene),<sup>[16,17]</sup> styrene-acrylonitrile copolymer,<sup>[15]</sup> and poly(styrene-block-methyl methacrylate).<sup>[18]</sup>

In this research, molecular weight segregation is detected in the temperature gradient. Since this provides a large amount of segregated samples, it could be applied for polymer fractionation. As a preliminary study, the segregation behavior of high-density polyethylene (PE) is investigated by linear viscoelastic properties.

## **EXPERIMENTAL**

### ***Materials and Sample Preparation***

Two types of commercially available high-density polyethylene produced by Ziegler-Natta catalyst, PE-1 (melt flow index = 0.3 g/10min and density = 951 kg/m<sup>3</sup>) and PE-2 (melt flow index = 120 g/10min and density = 950 kg/m<sup>3</sup>), were used in this study.

A binary blend of PE-1/PE-2 (50/50, w/w) was prepared by melt-mixing in an internal batch mixer (Toyoseiki, Labo-plastmil) at 230 °C with pentaerythritol tetrakis (3-3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Ciba, Irganox1010) and tris(2,4-di-tert-butylphenyl)phosphate (Ciba, Irgafos168) as thermal stabilizers and calcium stearate as a neutralizer. The content of each additive was 5000 ppm. The blade rotation speed was 30 rpm and the mixing time was 3 min. The obtained samples were compressed into a flat sheet by a compression-molding machine (Tester Sangyo,

SA303IS) at 230 °C under 10 MPa for 10 min. Then the sample was subsequently cooled down at 30 °C.

The obtained sheets were annealed in a molten state in the compression-molding machine for 0.5, 1, and 2 hrs, in which the temperatures of top and bottom plates were controlled separately. The gap between the molds was controlled to be either 1.5 or 3.0 mm. After annealing treatment, the sheets were quenched at 30 °C. Then, both surfaces of the annealed sheet were sliced in the thickness of approximately 300  $\mu\text{m}$  by a knife. The sliced samples were compressed into a flat sheet by the compression-molding machine at 230 °C of both plates and then quenched at 30 °C.

### ***Measurements***

The frequency dependence of oscillatory shear modulus was measured in a molten state by a cone-and-plate rheometer (TA instruments, AR2000) at various temperatures such as 160, 190, and 230 °C under a nitrogen atmosphere.

## **RESULTS AND DISCUSSION**

### ***Rheological Properties of Blends***

Figure 1 shows the master curves of frequency dependence of oscillatory shear moduli such as storage modulus  $G'$  and loss modulus  $G''$  for PE-1, PE-2, and the blend. The reference temperature is 160 °C. As well known, the time-temperature superposition principle is applicable to not only pure samples but also the blend. The apparent flow activation energy is calculated from the slope of the logarithm of the shift factors plotted against the reciprocal of absolute temperature, *i.e.*, Arrhenius plot, following the

well-known Andrade equation,<sup>[19]</sup> and found to be approximately 20 kJ/mol for all samples including the blend, which is a typical value for high-density polyethylene.<sup>[20-23]</sup> The modulus of the blend is located between those of the individual pure components. Further, there is no shoulder peak ascribed to phase separation for the blend. This is reasonable because both components are high-density polyethylene, i.e., a miscible blend. Moreover, it is found from the figure that the zero-shear viscosities of PE-1, PE-2 and the blend are 35000, 80, and 6300 Pa s, respectively.

[Fig.1]

### ***Rheological Properties of Blend after Annealing***

Figure 1 also shows the oscillatory shear moduli for the samples obtained from each surface of the sheet annealed at (top) 300 °C / (bottom) 150 °C for 2 hrs. As seen in the figure, both moduli for the samples collected from the top surface controlled at high temperature are lower than those of the blend prior to annealing in the wide range of frequency, whereas the samples from the bottom surface at low temperature exhibit higher moduli than the blend. The result suggests that low molecular weight fraction is segregated at the surface at high temperature and vice versa. Further, the slopes of  $G'$  and  $G''$  for the top surface are almost similar to those for the bottom, indicating that molecular weight distribution of both samples is not so different.

The weight-average molecular weight  $M_w$  of high-density polyethylene is calculated from the zero-shear viscosity. According to Garcia-Franco, the zero-shear viscosity at 190 °C is expressed as follows;<sup>[24]</sup>

$$\eta_0 = 4.743 \times 10^{-10} \left( \frac{M_w}{14} \right)^{3.33} \quad (1)$$

Following the equation, Mw of pure PE-1 ( $\eta_0 = 2.4 \times 10^4$  Pa s at 190 °C) is  $1.8 \times 10^5$  and that of pure PE-2 ( $\eta_0 = 5.5 \times 10^1$  Pa s) is  $2.9 \times 10^4$ .

Figure 2 shows the calculated values of zero-shear viscosities for the surface samples annealed at various temperature conditions. It is found that a large temperature gap leads to pronounced segregation. Since the thickness of the sample sheets is a constant (1.5 mm for the experiments), it can be concluded that large temperature gradient enhances the molecular weight segregation. Further, low molecular weight fraction is segregated at the high temperature side even when the bottom plate of the compression-molding machine is controlled at higher temperature than the top. It suggests that the gravitational force has no influence on the segregation.

[Fig.2]

Figure 3 shows the effect of annealing time on the segregation at the annealing condition of (top) 300 °C / (bottom) 150 °C. It is obvious that the molecular weight increases with the duration time of annealing for the low temperature side, and vice versa.

[Fig.3]

In order to understand the effect of thermal decomposition on the segregation behavior, the sample sheet having the annealing history at 300/150 °C for 2 hrs is kneaded again in the internal mixer at 230 °C for 5 min and compressed into a flat sheet at 230 °C of both plates of the compression-molding machine. The oscillatory shear modulus of the obtained sample is shown in Figure 4. The moduli of the re-mixed sample is completely the same as those of the original blend sample prior to annealing, demonstrating that the



current experimental results shown in Figs.1-3 are not attributed to the thermal decomposition.

[Fig.4]

The segregation behavior is obvious at a narrow gap between both plates of the compression-molding machine. Figure 5 shows the loss modulus for the segregated samples annealed at (top) 200 °C / (bottom) 150 °C for 30 min employing two samples with different thickness. As seen in the figure, there is only little difference between them when the gap between the molds is 3 mm, suggesting that no segregation occurs in the blend sample. This result indicates again that temperature gradient is important for the segregation.

[Fig.5]

Although the detailed mechanism is unknown for the phenomenon, it is completely different from the surface segregation of low molecular weight fraction as already demonstrated in various papers.<sup>14-18</sup> The experimental results presented in this paper, however, could be explained using the concept of free volume. Because the free volume fraction of a polymer melt increases with temperature, chain ends having a large free volume would prefer to a high temperature region.

Finally, the technique could be applied as a new fractionation method, although more characterization should be carried out quantitatively. Since the method does not require any solvent, it will be worth for studying more to be applicable for the fractionation. At least, the phenomenon should be understood in detail, because most conventional polymers have broad distribution of molecular weight.

## CONCLUSION

Thermal history in a compression-molding machine, in which the temperature of one mold is higher than the other, leads to molecular weight segregation of high-density polyethylene in a molten state. High molecular weight fraction is localized at the surface attached to the mold with low temperature and vice versa. The segregated behavior becomes obvious with the annealing time and temperature gradient. Since the method is free from toxic solvent, it could be applicable to a fractionation method of polymers based on more experimental results.

## Acknowledgement

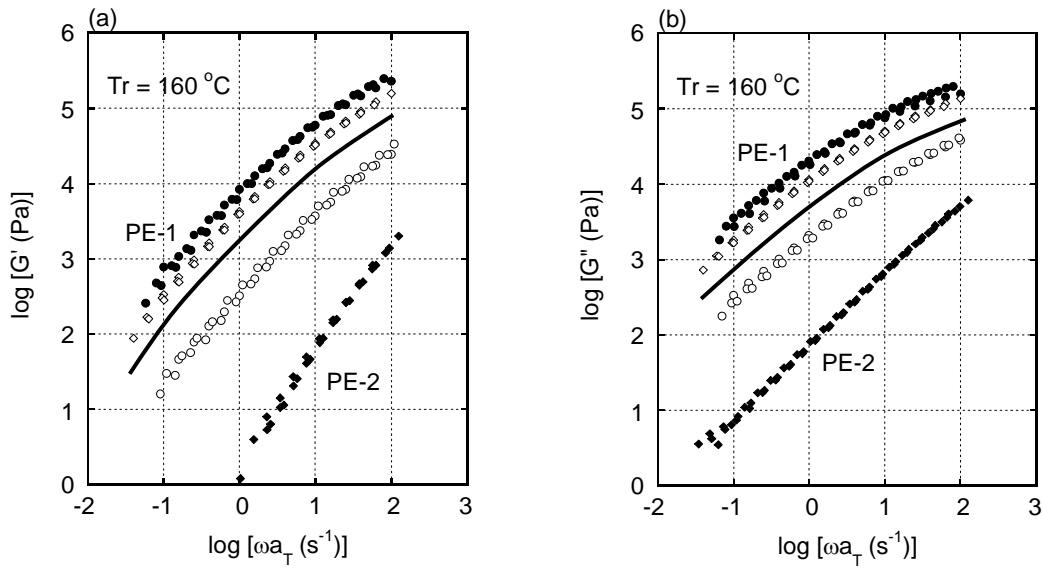
The authors would like to express their gratitude to Messrs. Yasuo Satoh and Keita Mihira of Prime Polymer Co., Ltd. for their valuable advice and the kind supply of the samples employed in this study. Further, the authors gratefully acknowledge Dr. Takaaki Hattori of Japan Polyethylene for his advice of the experimental technique.

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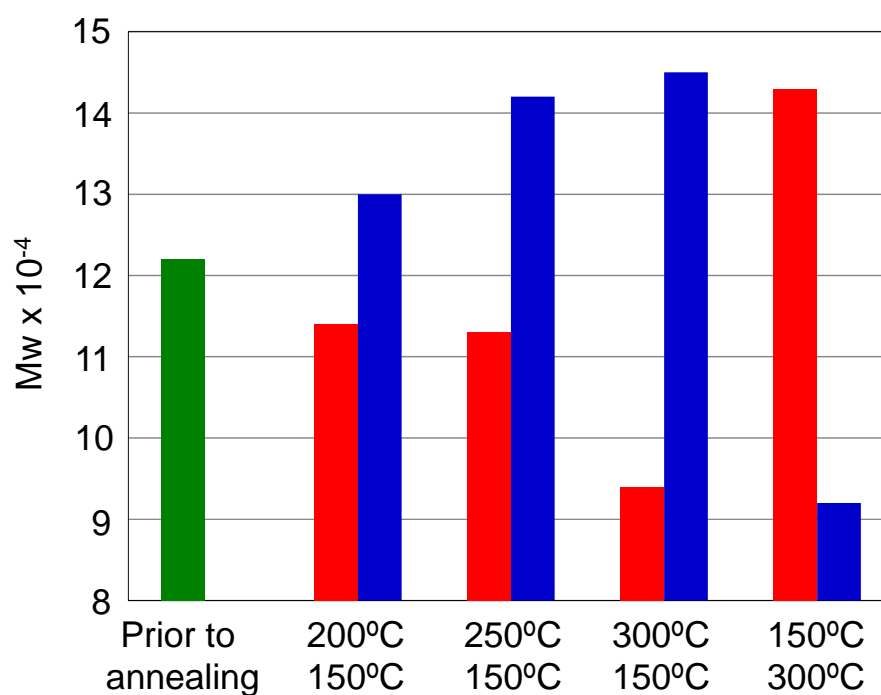
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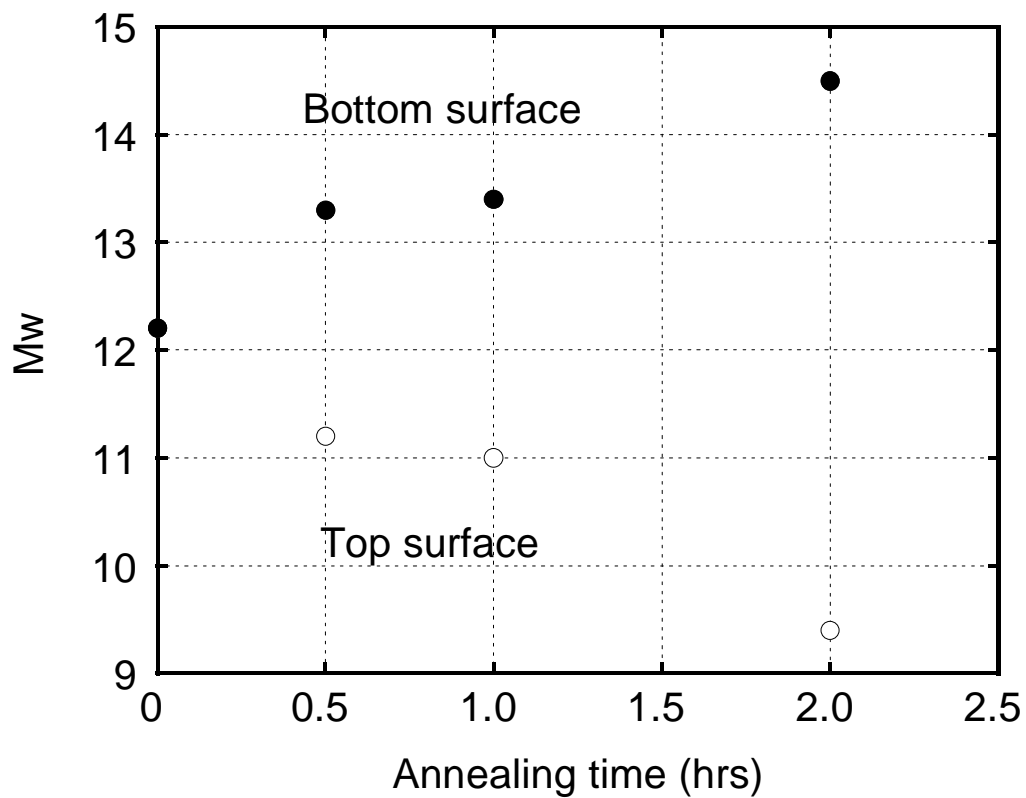
## Figures



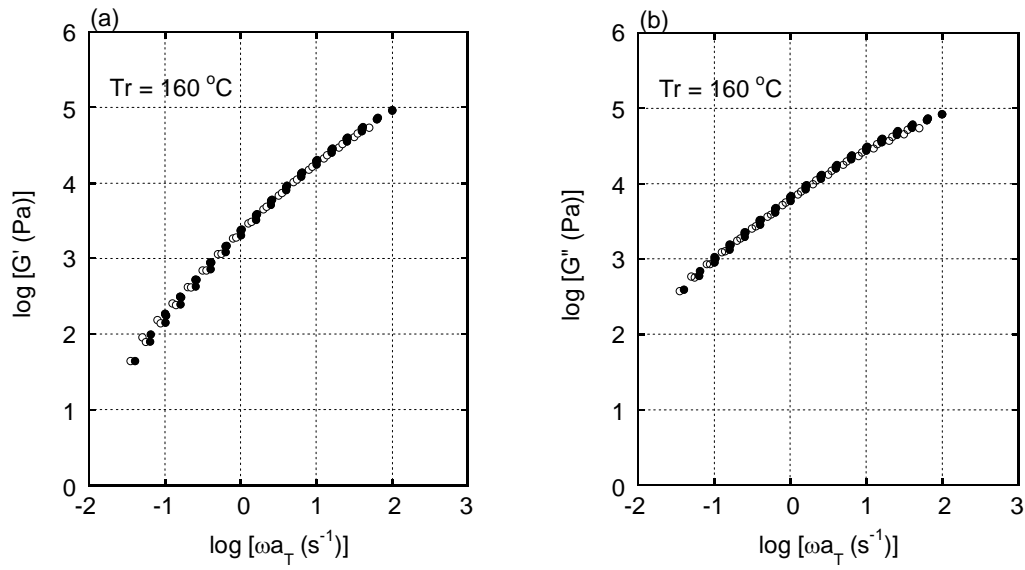
**Figure 1** Master curves of frequency dependence of (a) shear storage modulus  $G'$  and (b) loss modulus  $G''$  at 160 °C; (closed circles) PE-1, (closed diamonds) PE-2, and (solid line) the blend prior to annealing. The master curves of surface parts of the samples after annealing at the condition of (top) 300 °C / (bottom) 150 °C for 2hrs are also plotted; (open diamonds) low temperature side and (open circles) high temperature side.



**Figure 2** Weight-average molecular weight  $M_w$  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. The top value of the temperature represents the temperature of the top plate at compression-molding and vice versa.

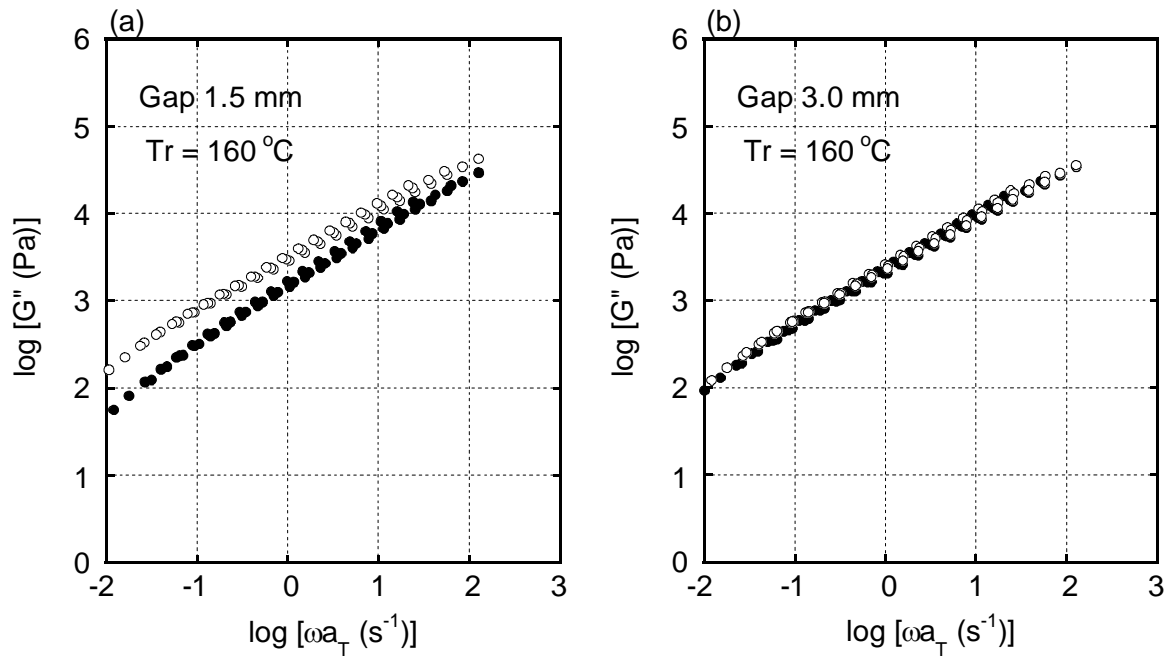


**Figure 3** Weight-average molecular weight  $M_w$  for the surface samples after annealing for various residence times at (top) 300 °C / (bottom) 150 °C; (open symbols) top surface and (closed symbols) bottom surface.



**Figure 4** Master curves of frequency dependence of (a) shear storage modulus  $G'$  and (b) loss modulus  $G''$  for blends at  $160\text{ }^\circ\text{C}$ ; (closed symbols) blend sample prior to annealing and (open symbols) re-mixed sample after annealing at the condition of (top)  $300\text{ }^\circ\text{C}$  / (bottom)  $150\text{ }^\circ\text{C}$  for 2hrs.





**Figure 5** Master curves of frequency dependence of shear loss modulus  $G''$  for surface parts of the samples after annealing at the condition of (top)  $200\text{ }^\circ\text{C}$  / (bottom)  $150\text{ }^\circ\text{C}$  for 30 min. The gap between the molds was (a) 1.5 mm and (b) 3.0 mm. (open circles) bottom surface and (closed circles) top surface.