Flow Induced Molecular Weight Fractionation during Capillary Flow of Linear Polymer Melt

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Abstract: In this work, one linear high density polyethylene melt is experimentally investigated from flow induced molecular weight fractionation point of view. It has been revealed that redistribution of polymer macromolecules takes place just in a very thin layer near the capillary wall where shear stress is the highest.

Key-Words: Flow induced molecular weight fractionation, Die drool, Wall Slip, Flow instabilities, Elasticity, Extrusion, Polymer melt.

1 Introduction

Linear polymer melts consist of different long macromolecules which are entangled to each together. During flow of such system through a narrow capillary (or through different inside shapes of extrusion dies in common polymer processing) at given temperature and high shear rates (i.e. high shear stresses), wall slip can occur. Different theories about its formation mechanism have been hitherto developed and they are summarized for example in [1]. One of them assumes formation of lubrication layer with low-enough shear viscosity consisting of low molecular weight species (i.e. short macromolecules) which are forced away from the main stream towards to the wall at and beyond critical wall shear stress.

Historically, the first notice about possibility of polymer melt spontaneous fractionation during flow under inhomogeneous stresses in capillary was presented in 1964 by Busse [2]. On the theoretical level, he claimed that “capillary viscometer should tend to fractionate polymer molecules with respect to molecular weight along the radius of the capillary.” His original imagination assumed that “near the wall, molecules of high molecular weight acquire relatively large amounts of free energy of elastic deformation, while very small molecules do not. Hence, there is a thermodynamic force that tends to increase the concentration of very small molecules at the wall, and of the larger molecules nearer the axis.”

This theory was soon tested experimentally on different polyethylene melts [3-5] and authors really found that skin layer contains low molecular weight species. However, are the polymer macromolecules fractionated through full flow channel cross-section as assumed Busse in his original imagination or the redistribution takes place just in a very thin layer near the wall where shear stress is maximum? Finding the answer to this question is the main motivation for this contribution.

2 Experimental

For our research, one commercially available stabilized unfilled virtually linear high density polyethylene polymer melt having broad molecular weight distribution was chosen (HDPE Liten FB 29 E2009 5498 7937, extrusion grade, Unipetrol RPA, Czech Republic, basic characteristics are summarized in Table 1).

2.1 Rheological Characterization

As the first, shear and extensional viscosities for the chosen polymer melt have been measured. In more detail, the shear viscosity at low shear rates was measured on rotational rheometer Advanced Rheometric Expansion System ARES 2000 (Rheometrics Scientific, USA) and for high shear rates capillary rheometer Rosand RH7-2 (Rosand Precision, United Kingdom) was used.
Further, uniaxial extensional viscosity was determined by Sentmanat Extensional Rheometer SER-HV-A01 model (Xpansion Instruments, USA [6]) attached to ARES 2000.

Table 1. Basic characterization of chosen linear HDPE polymer melt.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g.cm⁻³)</td>
<td>0.950</td>
</tr>
<tr>
<td>( M_n ) (g.mol⁻¹)</td>
<td>16,115</td>
</tr>
<tr>
<td>( M_w ) (g.mol⁻¹)</td>
<td>228,350</td>
</tr>
<tr>
<td>( M_z ) (g.mol⁻¹)</td>
<td>1,412,000</td>
</tr>
<tr>
<td>( M_{z+1} ) (g.mol⁻¹)</td>
<td>2,826,000</td>
</tr>
<tr>
<td>( M_w/M_n ) (-)</td>
<td>13.94</td>
</tr>
<tr>
<td>Melt flow index (g/10min)</td>
<td>0.15</td>
</tr>
<tr>
<td>Zero-shear rate viscosity (Pa.s)</td>
<td>380,000</td>
</tr>
<tr>
<td>Flow activation energy (kJ.mol⁻¹)</td>
<td>14.031</td>
</tr>
<tr>
<td>DSC peak melting point (°C)</td>
<td>130.7</td>
</tr>
<tr>
<td>DSC heat of fusion (J.g⁻¹)</td>
<td>242.6</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td>82.81</td>
</tr>
</tbody>
</table>

*Taken from the original material data sheet for basic polymer HDPE Liten FB 29.

Used detachable fixture also with the sample behaviour during one test is depicted in Fig. 1.

Fig. 1. Scheme of SER-HV-A01 detachable extensional rheometer (left) and polymer melt sample behavior during one test (right): (a) sample loading, (b) sample stretching, (c) sample at break.

The rheological properties were determined at 190°C and the results are shown in Fig. 2.

![Fig. 2. Stable-state uniaxial extensional and shear viscosities for investigated HDPE polymer melt determined at 190°C.](image)

2.2 Flow Induced Molecular Weight Fractionation Experiments

Conventional Plasti – Corder 2000 model (Brabender, Germany) single-screw extruder with diameter \( D = 30 \text{ mm} \) and \( L = 25D \) (standard single-thread screw with compression ratio 4:1, and lengths of zones: feed \( L_1 = 10D \), compression \( L_2 = 3D \), metering \( L_3 = 12D \)) with specially designed extrusion die with circular replaceable capillary (firstly introduced in [7]) were used for flow induced molecular weight fractionation experiments. Both, experimental configuration and extrusion die are depicted in Figs. 3 and 4, respectively. The extruder heating zones (from the hopper to the die) were heated to \( T_1 = 150°C \), \( T_2 = 155°C \), \( T_3 = 160°C \) and \( T_4 = 160°C \), respectively by keeping the annular tube (connecting die and extruder) and die exit temperature constant, \( T_3 = T_6 = 160°C \). It should be noted that the exiting temperature 160°C was chosen with respect to DSC calorimetry curve to ensure polymer material is totally melted and simultaneously, the fractionation effect is the most pronounced because of the high level of stored elastic energy in the melt [2, 8]. To investigate the fractionation effect, one high-enough mass flow rate (MFR) of 730 g.hr⁻¹ (650 s⁻¹ in term of apparent shear rate) was set up.
2.3 Samples Preparation

In order to investigate flow induced molecular weight fractionation in more detail, following samples were collected, prepared and further analyzed. The original polymer pellets were considered as the first sample. Further, extrudate at above-mentioned processing conditions was taken and samples representing its core and skin, both prepared mechanically by a thin cutter were then made. Skin sample was peeled from the extrudate surface as a small flakes with average thickness of 0.1 mm. Core sample was grinded down to average radius of 0.4 mm. Just note that radius of used replaceable capillary die was 0.8 mm and \( L/D \) ratio was 9.375. For better imagination, non-proportional scheme of prepared extrudate samples across capillary radius in Fig. 5 is illustrated.

The last sample was taken (under inert \( \text{N}_2 \) gas atmosphere to prevent possible thermal/oxidative degradation) from the die face where spontaneous accumulation of the extruded polymer melt (\textit{die drool} phenomenon [7-16]) takes place at sufficiently high shear stresses generated during the flow at the die wall probably due to presence of low viscosity layer at the die wall which is consequently forced away from the die (see Fig. 6, flow direction is from top to bottom).

![Fig. 3. Laboratory experimental setup.](image1)

![Fig. 4. Quarter section view of used specially designed extrusion die with replaceable capillary.](image2)

![Fig. 5. Non-proportional scheme of our extrudate core and skin layout imagination inside capillary.](image3)

![Fig. 6. Die drool formed at capillary exit face.](image4)
2.4 Samples Analysis

All above-mentioned samples were further analysed by gel permeable chromatography (GPC) technique. Molecular weight averages ($M_n$, $M_w$, $M_z$ and $M_{z+1}$) as well as molecular weight distributions (MWD) were determined by PL-GPC 220 model (Polymer Laboratories, United Kingdom) equipped by refractometric detector PL-220 DRI. Mobile phase was 1,2,4-trichlorobenzene HPLC grade (Scharlau, Spain) stabilized by 0.025% Santonox R (flow rate: 1ml.min$^{-1}$). Each polymer sample was prepared as 1mg dissolved in 1 ml of mobile phase and it was measured two times. Finally, testing temperature was 160°C.

3 Results and Discussion

In this section, the most important results are presented and discussed in more details. As the first, in Fig. 7 molecular weight distribution curves of all tested samples are plotted. Original pellets MWD curve is taken as a reference one. Core and more pronounced skin MWD curve are slightly shifted towards to low molecular weights. However, shift in the case of die drool MWD curve is much more significant.

The more detailed analysis is provided in Figs. 8-11 where, number $M_n$, weight $M_w$, $M_z$ and $M_{z+1}$ molecular weight averages are plotted as the functions of position across the capillary radius for all three samples (representing extrudate core/skin and die drooled polymer). Just note that $M_n$, $M_w$ and $M_z$, $M_{z+1}$ molecular averages are sensitive to the presence of short and very long polymer macromolecules, respectively. It can be clearly seen that all averages fall from axis towards to the wall. In more detail, from core to skin sample slightly and from skin to die wall (die drool sample) significantly. This simply means that amount of short macromolecules is significantly increased primarily near the die wall. This suggests that flow induced molecular weight fractionation takes place just in a very thin layer near the die wall where the shear stress is maximum rather than in the bulk.

![Fig. 7. Molecular weight distribution curve for all analysed samples.](image)

![Fig. 8. Decrease of number, $M_n$ molecular weight average across capillary radius.](image)
4 Conclusion

It has been experimentally revealed that for one investigated common linear HDPE polymer melt significant flow induced molecular weight fractionation takes place predominantly in a very thin layer near the die wall where the shear stress is maximum. The decrease of short macromolecules amount in the rest of the capillary cross-section is negligible.

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References:


