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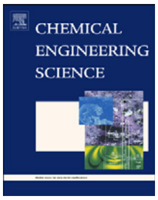

Experimental investigation of flow induced molecular weight fractionation phenomenon for two linear HDPE polymer melts having same M_n and M_w but different M_z and M_{z+1} average molecular weights

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HIGHLIGHTS

- ▸ Flow induced molecular weight fractionation was investigated for HDPE polymers.
- ▸ Increase in linear HDPE chain length promotes molecular weight fractionation.
- ▸ Slip–stick flow instability is in direct relationship with molecular weight fractionation.
- ▸ Molecular weight fractionation takes place only in very thin layer near die wall.
- ▸ Formed low viscosity slip layer accumulates at the die lips and causing die drool.

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ABSTRACT

In this work, flow induced molecular weight fractionation for two linear HDPE polymers having the same polydispersity index (M_w/M_n) but different M_z and M_{z+1} molecular weight averages, has been experimentally investigated. It has been revealed that first, onset as well as intensity of slip–stick instability and flow induced molecular weight fractionation are in direct relationship, i.e., low molecular weight polymer chains start to fractionate from the main polymer melt stream at the onset of slip–stick flow regime initiating formation of low viscosity layer at the die wall, which leads to its consequent unwanted accumulation at the die lips–die drool phenomenon. Second, due to enhanced melt elasticity (by the presence of long linear chains of linear HDPE polymer), the flow induced molecular weight fractionation is more effective which results in narrow molecular weight distribution of die drool sample containing small amount of long chains. Third, buildup ratio sensitivity to apparent shear rate is the highest in the slip–stick regime and its value increases with increased content of very long chains. Finally, the flow induced molecular weight fractionation takes place only in a very thin layer near the die wall (i.e., within less than 8% of the channel radius for the studied processing conditions and HDPE polymer samples).

1. Introduction

During flow of viscoelastic polymer melts, flow induced molecular weight fractionation (redistribution of macromolecules according to their molecular weights) can occur inside a flow channel due to presence of highly inhomogeneous stress field profile. Historically, the first notice about this phenomenon was presented by Busse (1964). He speculated that "near flow channel wall, macromolecules of high molecular weight acquire large amount of free energy of elastic deformation, while very small macromolecules do not. Because of thermodynamic force, then, these small macromolecules tend to increase the concentration near the wall, and, on the other hand, the rest of longer macromolecules goes close to the centerline". This theory has consequently been supported experimentally by Schreiber and Storey (1965) for broad Molecular Weight Distribution (MWD) linear high density polyethylene melts by using static laser light scattering, Schreiber (1974) for broad MWD crystallizable polymers by applying calorimetry technique, Shelby and Caflisch (2004) for poly(ethylene terephthalate) and poly(ethylene-*co*-cyclohexylenedimethylene terephthalate) utilizing gel permeation chromatography (GPC), Musil and Zatloukal (2011),

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Zatloukal and Musil (2011) for linear and branched high density polyethylenes by gel permeation chromatography and flow visualization technique. It has been found that first, mass flow rate and temperature increase at the end of the extruder, by keeping the annular tube (connecting die and extruder) and the die exit temperature unchanged, leading the flow induced molecular weight fractionation intensity to increase due to the thermally induced HDPE degradation enhancing melt elasticity (Musil and Zatloukal, 2010). Second, flow induced fractionation is promoted by broadening MWD (Musil and Zatloukal, 2011; Chai et al., 2001) and chain branching decrease (Musil and Zatloukal, 2011), and finally, it can result in unwanted accumulation of low molecular weight components at the die exit (Musil and Zatloukal, 2011), i.e., die drool phenomenon which is widely discussed in the open literature (Shelby and Caflisch, 2004; Musil and Zatloukal, 2011, 2010; Zatloukal and Musil, 2011; Chai et al., 2001; Klein, 1981; Kurtz and Szaniszlo, 1991; Rakestraw and Waggoner, 1995; Chan, 1995; Gander and Giacomin, 1997; Lee, 2002; Hwang and Nam, 2005; Chaloupkova and Zatloukal, 2007, 2009; Brachet et al., 2009; Hogan et al., 2009; Zatloukal et al., 2009). However, it is still not fully understood yet what is the effect of very small amount of very long linear chains in the polymer on the flow induced molecular weight fractionation onset, intensity and efficiency as well as in what part of the flow channel it predominantly takes place. In order to understand such complicated relationship between the molecular structure of polymer chains and flow induced molecular weight fractionation in more detail, two linear HDPE polymer melts with same polydispersity index (M_w/M_n) but different M_z and M_{z+1} molecular weight averages have been investigated by specific experimental set-up and methodology, which is described in the next section.

2. Experimental

The experimental part is divided here into three main stages: rheological characterization of chosen polymer samples, determination of flow induced molecular weight fractionation intensity by using annular extrusion die and GPC characterization of 'drooled' material at the die exit, extrudate skin and core.

2.1. Material characterization

In this work, two linear and well stabilized HDPE extrusion grades (HDPE 1—HDPE Liten FB 29 E2009 3220 4479 and HDPE 2—HDPE Liten FB 29 E2009 5498 7937) from Unipetrol RPA, Czech Republic were used. Their basic characteristics are summarized in Table 1 and Figs. 1 and 2. As can be seen, even if both polymers contain practically the same amount of short and intermediate chains (i.e., M_n and M_w molecular weight averages are equal), they slightly differ in amount of long chains because their M_z and M_{z+1} molecular weight averages are different (see definition below).

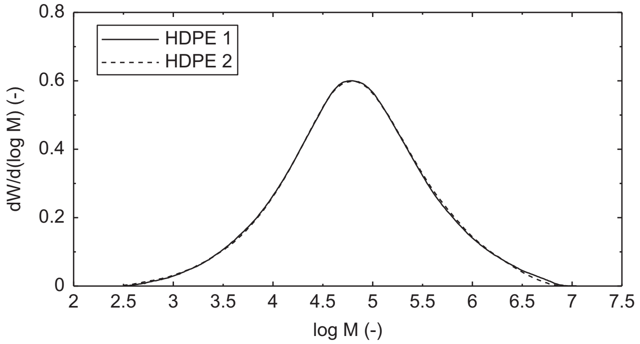

Fig. 1. Molecular weight distribution (MWD) curves for both investigated polymer melts (in the form of virgin pellets).

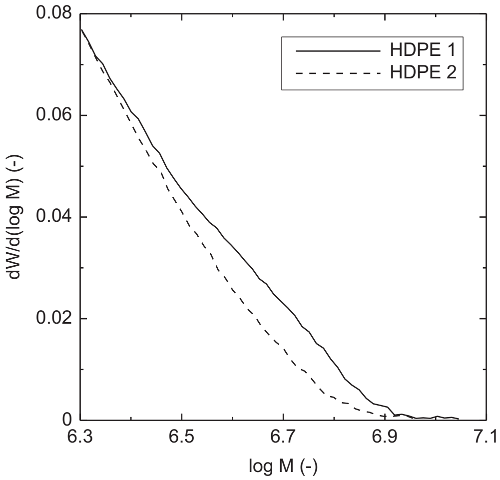

Fig. 2. Detail view of high molecular weight tail in MWD curves for both investigated polymer melts (in the form of virgin pellets).

Table 1
Basic characterization of chosen HDPE polymers.

	HDPE 1	HDPE 2
Density *(g cm^{-3})	0.95	0.95
M_n (g mol^{-1})	17,045	16,115
M_w (g mol^{-1})	239,300	228,350
M_z (g mol^{-1})	1,613,000	1,412,000
M_{z+1} (g mol^{-1})	3,476,000	2,826,000
M_w/M_n (–)	14.04	14.17
Melt flow index (190 °C/2.16 kg) * (g/10 min)	0.15	0.15
Zero-shear rate viscosity (Pa s)	670,000	380,000
Flow activation energy (kJ mol^{-1})	13.817	14.031
DSC peak melting point (°C)	130.8	130.7
DSC heat of fusion (J g^{-1})	234.9	242.6
Crystallinity (%)	80.16	82.81

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

$$M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} \quad M_{z+1} = \frac{\sum n_i M_i^4}{\sum n_i M_i^3} \tag{1}$$

where n_i is the fraction of molecules having the molecular weight M_i, in a blend of monodisperse species described by the set of numbers [n_i, M_i].

2.2. Linear viscoelastic properties

Linear viscoelastic properties (storage modulus G', loss modulus G'', and complex viscosity η^*) were measured on Advanced Rheometric Expansion System ARES 2000 (Rheometrics Scientific, USA) in parallel plates geometry mode (plates diameter of 25 mm) within 0.1 s^{-1} up to 100 s^{-1} frequency range at 1% shear strain to guarantee linear viscoelasticity regime only. In order to capture Newtonian plateau for both tested HDPE samples, linear viscoelastic properties were measured at temperature step of 20 °C within 130–370 °C temperature range, which represents 13 single measurements in total (all measurements over 190 °C were done under inert N_2 gas atmosphere to prevent polymer