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[Print](#)
(10) » [Improving Thermal Efficiency of Single Screw Extrusion](#) » [Improved Approximations in Thermal Properties for Single Screw Extrusion](#) » [Investigation of Die Drool Phenomenon for Linear HDPE Polymer Melts Having Identical Polydispersity Index but Different \$M_z\$ and \$M_{z+1}\$ Average Molecular Weights](#)

Investigation of Die Drool Phenomenon for Linear HDPE Polymer Melts Having Identical Polydispersity Index but Different M_z and M_{z+1} Average Molecular Weights

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Abstract

In this work, die drool phenomenon, for two linear HDPE polymers having identical 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 increase in linear HDPE chain length promotes the die drool phenomenon.

Introduction

During the extrusion process, there is a tendency for some polymers to adhere at the extrusion die lips. The deposited material builds up into a large mass which frequently breaks away from the die, completely (or partly) encloses the extruded product, adheres perseveringly onto extruded product surface and thus damages it. This effect is in extrusion art defined as undesirable spontaneous accumulation of polymer melt at the die exit face and it is termed like "die drool", "drooling", "die lip build-up", "die bleed", "die plateout", "die deposit", "die drip" or "die moustache" and the accumulated material is generally named "drool". It has been found by Klein [1] in 1981 that there are two different die drool types; the first, which is related to a die (polymer deposit builds up at slow stable rate) and the second, which is related to the screw (die remains clean for a period of time and the polymer deposit rises suddenly). If this phenomenon takes place during the extrusion process for particular polymer system, it is necessary to periodically switch off the extrusion line in order to complete die cleaning which is uneconomical and also time consuming. In 1997, Gander and Giacomini [2] published the overview about the die drool phenomenon. They have concluded that die drool is a complex problem having several minor sources, each of them playing different role according to particular extrusion techniques, processing conditions and polymer materials used. In the open literature, several factors have been found to support the formation of die drool phenomenon. They include pressure fluctuations in screw [1], volatiles, low molecular fractions of the polymer, fillers, poor dispersion of pigments [3], die swell [1, 4], processing near degradation temperature [4-6], dissimilar viscosities in blends [7], improper die design and die material [2, 8-10], negative pressure at the die exit [11], utilization of linear rather than branched polymers [12], high polymer melt elasticity [13], etc. In order to more deeply understand the die drool phenomenon, two carefully prepared linear HDPE polymers having identical polydispersity index (M_w/M_n) but different M_z and M_{z+1} molecular weight averages, have been experimentally investigated.

Experimental

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. The basic characteristics for both samples are summarized in Table 1. As can be seen, polymers having identical polydispersity index (M_w/M_n) but different M_z and M_{z+1} molecular weight averages (see definition below).

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

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 number $[n_i, M_i]$.

Die drool measurements Die drool experiments were performed on a conventional Plasti – Corder 2000 model (Brabender, Germany) single-screw extruder with diameter $D = 30$ 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 $L_3 = 12D$). The extrusion line consists of extruder with four electrically heated zones, transition annular part, specially designed annular extrusion die, which was introduced and used in [5, 11, 12 and 14], photo camera Dimage Z3 model (Konica Minolta, Japan) with resolution of 4 Mpx placed near the die exit for die drool visualization, nitrogen gas vessel with hosepipe supplying N_2 to a die exit vicinity in order to prevent thermal/oxidative degradation of collected die drool samples and finally draw-off mechanism.

Extruder zones (from the hopper to the die) were heated to $T_1 = 150^\circ\text{C}$, $T_2 = 155^\circ\text{C}$, $T_3 = 160^\circ\text{C}$ and $T_4 = 160^\circ\text{C}$, respectively by keeping the annular tube (connecting die and extruder) and die exit temperature constant, $T_5 = T_6 = 160^\circ\text{C}$ ensuring that no sample degradation takes place. Furthermore, total mass flow rate of extruded polymer melt (\dot{m}) was varied from $0.075 \text{ kg}\cdot\text{hr}^{-1}$ up to $0.725 \text{ kg}\cdot\text{hr}^{-1}$ (i.e. from 68 s^{-1} up to 652 s^{-1} in terms of apparent shear rate). After 10 minutes of extrusion at given \dot{m} , the extruder was stopped and the accumulated material (see Figure 1 for the example) was manually removed from the die lip by a tweezer, weighted on a sensitive analytical balance and the procedure was repeated again for the higher \dot{m} . Moreover, this technique was applied three times at each \dot{m} to prove the reproducibility of such testing method. Before each set of three independent 10 minutes tests (at one \dot{m}), barrel, screw and all parts of the die have been perfectly manually cleaned.

Die drool intensity has been expressed in dimensionless form through buildup ratio BR (firstly introduced by Gander and Giacomini in [2]):

$$BR = \frac{\dot{B}}{\dot{m}} \quad (2)$$

where \dot{m} is defined above and B means buildup rate:

$$\dot{B} = \frac{B}{t_e} \quad (3)$$

where B is the mass of accumulated *die drool* material at the die exit face and t_e is the total extrusion time of each test (10 minutes in this case).

Results and Discussion

As can be seen in Figures 2 and 3, transient uniaxial extensional viscosity curves (measured by Sentmanat Extensional Rheometer SER-HV-A01 model attached to Advanced Rheometric Expansion System ARES 2000) for both HDPEs show no strain hardening peaks indicating presence of linear chains only for both polymers. Moreover, as can be seen in Figures 4 and 5, HDPE 1 has slightly higher steady shear viscosity (determined by twin-bore capillary rheometer Rosand RH7-2 and rotational rheometer ARES 2000 in parallel plates configuration), uniaxial extensional viscosity and shear elasticity (determined according to Han's methodology [15]) than HDPE 2.

Apparent shear rate dependent die drool intensity in the form of dimensionless buildup ratio, BR and real die exit face visualization are provided in Figures 6 and 7, respectively. It is clearly seen that the die drool phenomenon is more pronounced for HDPE 1 sample in comparison with HDPE 2 sample and its onset occurs at lower apparent shear rates for HDPE 1 in comparison with HDPE 2 sample. Due to the fact that these two linear HDPE polymers having identical

polydispersity index (M_w/M_n) but HDPE 1 sample has higher M_z and M_{z+1} molecular weight averages (indicating the presence of very long chains) in comparison with HDPE 2 sample (see Table 1 and Figure 8a), it can be concluded that an increase in linear HDPE chain length promotes the die drool phenomenon. Interestingly, the die drool material created during HDPE 1 sample extrusion has slightly narrower MWD than die drool sample created during HDPE 2 extrusion (see Table 2 for the M_w/M_n ratio). Moreover, the content of long chains in the HDPE 1 die drool sample is smaller (low M_z and M_{z+1} averages) in comparison with HDPE 2 die drool sample (high M_z and M_{z+1} averages) as can be seen in Figure 8b and Table 2. This indicates that more elastic HDPE 1 sample is able to more effectively push shorter chains toward the die wall in comparison with less elastic HDPE 2 sample which is in good agreement with our previous work [12, 16] and the original Busse's flow induced molecular weight fractionation theory [17].

Conclusion

It has been found that small amount of very long linear chains in the linear HDPE polymers promotes die drool phenomenon. It has also been found that due to enhanced melt elasticity by the presence of long linear chains of linear HDPE polymer, the flow induced fractionation (causing die drool phenomenon) is more effective which results in narrow MWD of die drool sample containing small amount of long chains (low M_z and M_{z+1} averages).

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	HDPE 1	HDPE 2
Density (g.cm^{-3})	0.950	0.950
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 (-)	14.05	13.94
Melt flow index (g/10min)	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 ($^{\circ}\text{C}$)	130.8	130.7
DSC heat of fusion (J.g^{-1})	234.9	242.6
Crystallinity (%)	80.16	82.81

Table 1: Basic characterization of chosen HDPE polymers.

	HDPE 1	HDPE 2
	<i>Die drool sample</i>	<i>Die drool sample</i>
M_n (g.mol ⁻¹)	14,475	13,720
M_w (g.mol ⁻¹)	72,555	81,150
M_z (g.mol ⁻¹)	243,500	276,800
M_{z+1} (g.mol ⁻¹)	613,900	663,350
M_w/M_n (-)	5.012	5.915

Table 2: Basic characteristics of die drool samples collected after 10 minutes of extrusion at apparent shear rate 348 s⁻¹.

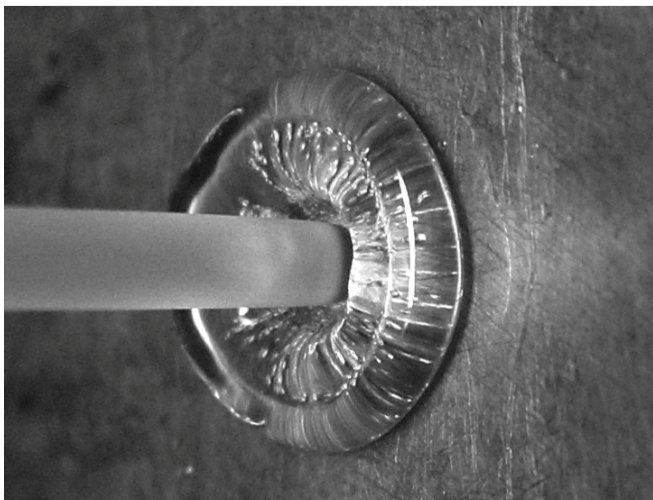


Figure 1: Typical appearance of HDPE die drool phenomenon after 10 minutes of extrusion by using the proposed experimental set-up and chosen processing conditions (HDPE 1 at 160°C and apparent shear rate 652 s⁻¹).

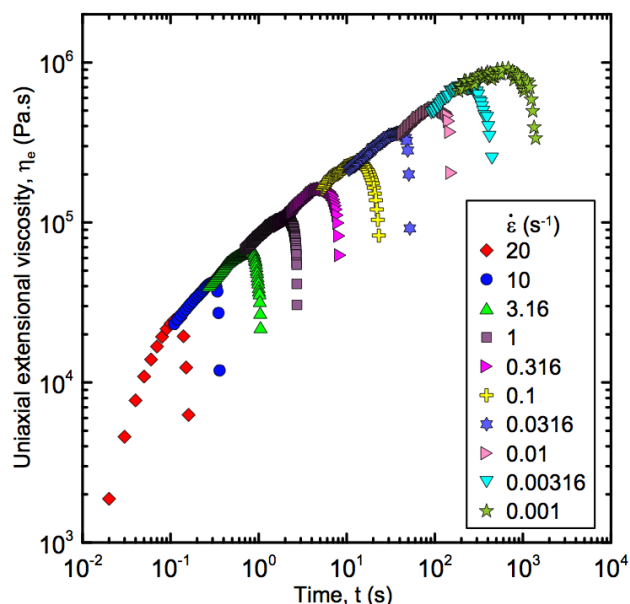


Figure 2: Transient uniaxial extensional viscosity for HDPE 1 at 190°C.

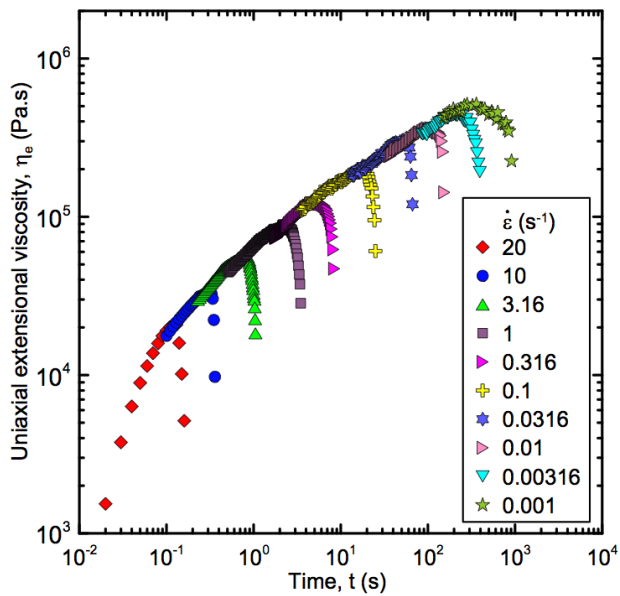


Figure 3: Transient uniaxial extensional viscosity for HDPE 2 at 190°C.

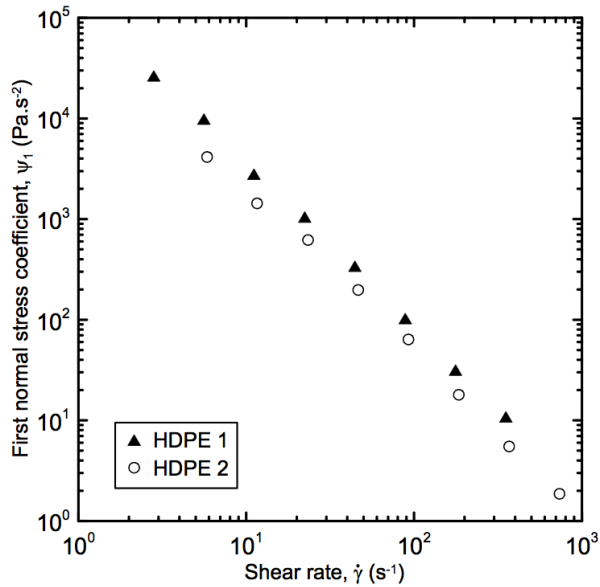


Figure 4: Stable-state first normal stress coefficient for both investigated HDPE polymer melts measured at 190°C.

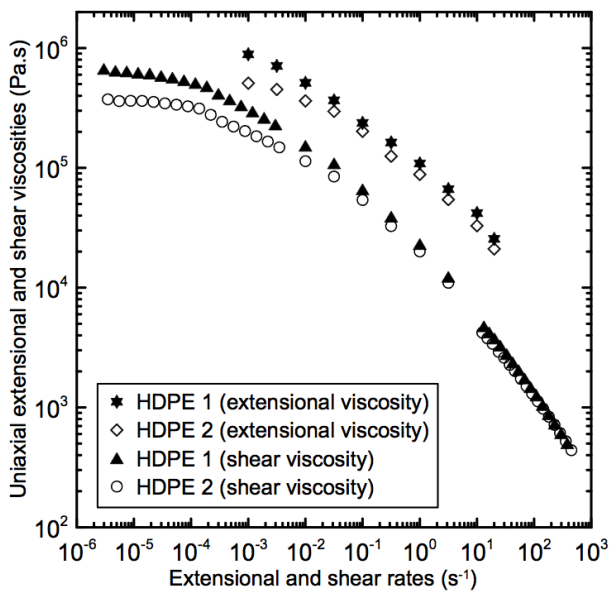


Figure 5: Stable-state shear and uniaxial extensional viscosities for both investigated HDPE polymer melts measured at

190°C.

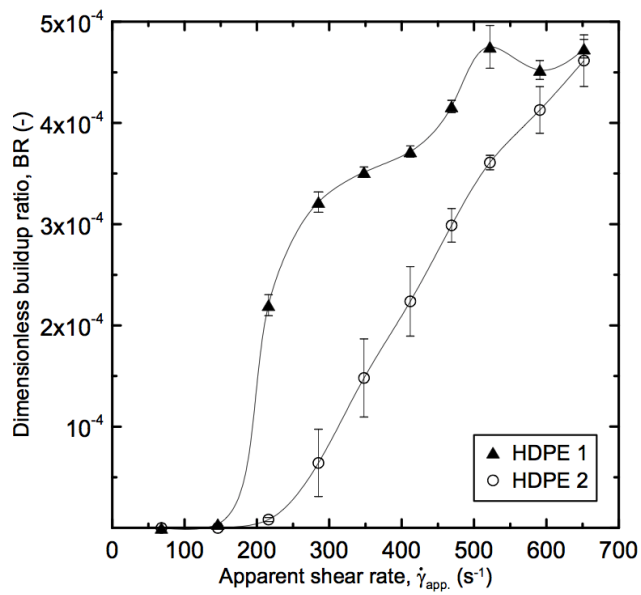


Figure 6: Dimensionless buildup ratio (10 minutes of extrusion) as a function of apparent shear rate for both investigated HDPE polymer melts determined at 160°C.

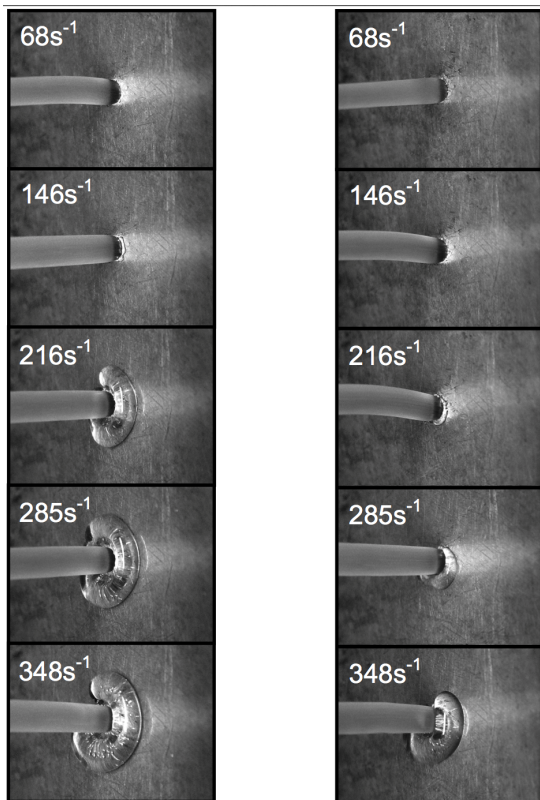


Figure 7: Die exit face visualization after 10 minutes of extrusion of HDPE 1 (left) and HDPE 2 (right) at different apparent shear rates, $T_{die} = 160^{\circ}C$.

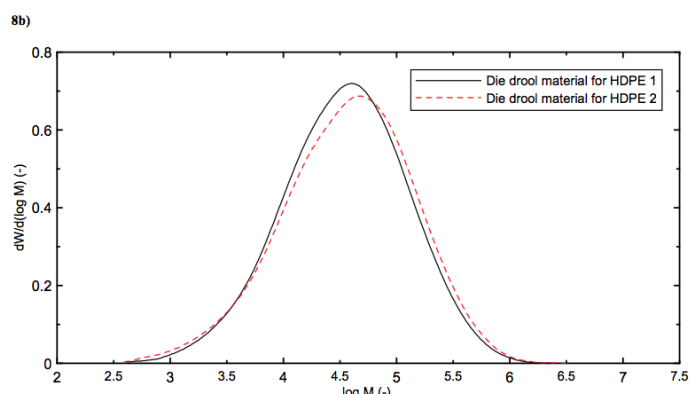
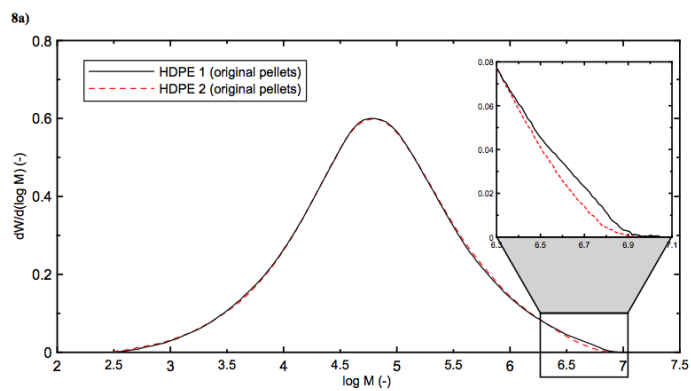


Figure 8: Molecular Weight Distribution (MWD) of the analyzed polymer samples. 8a) MWD for HDPE 1 and HDPE 2 (original pellets). 8b) MWD for die drool materials collected under N_2 inert gas atmosphere at apparent shear rate 348 s^{-1} and $T_{\text{die}} = 160^\circ\text{C}$.

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