Tomas Bata University in Zlín
Faculty of Technology

Doctoral Thesis

Investigation of Die Drool Phenomenon during HDPE Melt Extrusion

Výzkum jevu die drool během vytlačování taveniny HDPE

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"When the wind fills the sky the clouds will move aside
there will be the road to all our dreams
for any day that stings two better days it brings.
Nothing is as bad as it seem.
Close your eyes, look into the dreams
winds of change will winds of fortune bring."

…from Manowar's ballad
"Master of the Wind"
written by
Joey deMaio

To My Girlfriend Maruška

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Even the small Muse and life fortune deserve my great thanks…

"I do not know what I may appear to the world, but to myself I seem to have been only like a boy playing on the sea-shore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of thruth lay all undiscovered before me."

SIR ISAAC NEWTON (1643 – 1727)

ABSTRACT

In the first part of this work, the current stage of knowledge about *die drool* phenomenon (unwanted spontaneous accumulation of extruded polymer melt at die exit) has been reviewed based on the openly available research literature.

In the second part of this work, the specific experimental set-up, methodology and digital image analysis technique have been proposed and utilized to investigate the effect of processing conditions, polymer melt rheology, molecular characteristics and die design on the *die drool* phenomenon occuring during the extrusion of HDPE melt. It has been found that an increase in HDPE chain branching, and a decrease in its elasticity and shear viscosity significantly reduce the *die drool* phenomenon. It has been demonstrated that molecular weight distribution curves for HDPE extrudate skin, extrudate core and for virgin pellets are practically identical and the *die drool* sample represents their low molecular weight fraction, which suggests that in this case the *die drool* phenomenon can be considered to be the result of the *flow induced molecular weight fractionation* taking place only in a very thin layer near the die wall (within less than 8% of the channel radius for the studied processing conditions) and the extrusion process itself has no effect on the polymer bulk. It has been revealed that the low molecular weight polymer chains start to be fractionated from the main polymer melt stream under the *slip-stick* flow instability regime which consequently then accumulates at the die lips in the form of a low viscosity polymer melt. It has been found that increase in HDPE melt elasticity by thermally induced degradation or by the controlled increase in a small amount of very long linear chains of HDPE polymer (i. e. while keeping the polydispersity index constant), leads to more effective *flow induced fractionation* resulting in narrow molecular weight distribution of the *die drool* sample containing a small amount of long chains. It has been demonstrated that firstly, flared dies are more stabilizing in comparison with chamfered dies and secondly, the effect of die exit angle and flared length on the *internal die drool* intensity during the extrusion of HDPE has a non-monotonic character with an optimum value for the die exit angle of 15° and a flared length to capillary length ratio of 2/15. It has been suggested that the *internal die drool* phenomenon suppresion mechanism through die exit modification can be understood throught the melt pressure/normal stresses at the die exit, adhesion to the metal wall/flowing melt interface and extensional stress induced by the extrudate draw off, which can promote effective and continuous release of low molecular weight species from the die exit region by the moving extrudate.

KEYWORDS: *die drool, die lip buildup, flow instabilities, flow induced molecular weight fractionation, slip-stick, extrusion, shear viscosity, extensional viscosity.*

ABSTRAKT

První část této práce shrnuje současný stav poznání jevu *die drool* definovaného jako nežádoucí spontánní akumulace polymerní taveniny na hraně výstupní štěrbiny při vytlačování.

Druhá část této práce se zabývá výzkumem vlivu zpracovatelských podmínek, reologie, molekulárních charakteristik polymerů a designu vytlačovací hlavy na jev *die drool* při vytlačování HDPE, a to s využitím specifického uspořádání experimentální vytlačovací linky, nových experimentálních postupů a metod obrazové analýzy. Bylo zjištěno, že intenzita jevu *die drool* výrazně klesá s rostoucím stupněm větvení polymerního řetězce a(nebo) klesající elasticitou a smykovou viskozitou dané taveniny. Na základě hodnocení distribuce molárních hmotností povrchové i vnitřní části extrudátu, původního nezpracovaného polymerního granulátu a polymerního stěru z hrany výstupní štěrbiny bylo prokázáno, že při vytlačování taveniny HDPE kruhovou kapilárou je příčinou jevu *die drool* tokem indukovaná frakcionace nízkomolekulárních podílů polymeru (probíhající u stěny, ve vzdálenosti menší než je 8% poloměru kapiláry pro studované procesní podmínky), které se následně akumulují na konci vytlačovací hlavy. Dále bylo zjištěno, že *tokem indukovaná frakcionace* je iniciovaná periodicky se opakujícím ulpíváním a následným sklouzáváním polymerní taveniny u stěny vytlačovací hlavy (jev *slip-stick*) přičemž její efektivita roste s rostoucí elasticitou taveniny HDPE. Experimentální analýza vlivu designu konce vytlačovací hlavy na intenzitu jevu *die drool* prokázala, že zvonovitý charakter tokového kanálu je více stabilizující než prosté sražení hran výstupní štěrbiny, přičemž překvapivě, vliv velikosti úhlu sražení a délky zvonovité části na intenzitu tohoto jevu má nemonotónní charakter s optimálními hodnotami 15° pro výstupní úhel a 2/15 pro délku zvonovité části vztažené k celkové délce výstupní štěrbiny. S cílem porozumět stabilizujícímu vlivu modifikace designu výstupní štěrbiny na jev *die drool* byla navržena hypotéza založená na posouzení vzájemného spolupůsobení tlaku, normálových napětí, adhezivních sil, odtahem indukovaných tahových napětí vznikajících v této oblasti, a to s ohledem na dosažení podmínek intenzivního kontinuálního unášení nízkomolekulárních složek z prostoru výstupní štěrbiny odtahovaným extrudátem.

Kʟíčová slova: *die drool, die lip buildup, nestability toku, tokem indukovaná frakcionace molekulových hmotností, slip-stick, vytlačování, smyková viskozita, tahová viskozita.*

LIST OF PAPERS

The following research papers are included in the present doctoral thesis:

PAPER I

Investigation of Die Drool Phenomenon for HDPE Polymer Melt

Jan Musil and Martin Zatloukal

Chemical Engineering Science 2010, vol. 65, no. 23, pp. 6128-6133.

PAPER II

Experimental Investigation of Flow Induced Molecular Weight Fractionation during Extrusion of HDPE Polymer Melts

Jan Musil and Martin Zatloukal

Chemical Engineering Science 2011, vol. 66, no. 20, pp. 4814-4823.

PAPER III

Experimental Investigation of Flow Induced Molecular Weight Fractionation for Two Linear HDPE Polymer Melts Having Identical M_n and M_w but Different M_z and M_{z+1} Average Molecular Weights

Jan Musil and Martin Zatloukal

Submitted for publication in *Chemical Engineering Science* in 2012

PAPER IV

Effect of Die Exit Geometry on Internal Die Drool Phenomenon during Linear HDPE Melt Extrusion

Jan Musil and Martin Zatloukal

Submitted for publication in *Chemical Engineering Science* in 2012

CONTENT

STATE OF THE ART

"ALTHOUGH TO PENETRATE INTO THE INTIMATE MYSTERIES OF NATURE
AND THENCE TO LEARN THE TRUE CAUSES OF PHENOMENA IS NOT
ALLOWED TO US, NEVERTHELESS IT CAN HAPPEN THAT A CERTAIN FICTIVE
HYPHOTHESIS MAY SUFFICE FOR EXPLAINING MANY PHENOMENA."

LEONHARD PAUL EULER (1707 − 1783)

Nature of polymer melts flow is more complex than their Newtonian counterparts by reason of their viscoelasticity and high stresses occurring in large, rapid deformations during polymer processing. Both, the elasticity and the high stresses arise from high molecular weight (i.e. from enormous length of molecules) of commonly used polymers. Thus, unstable polymer melts flow phenomena are usually *hydroelastic* rather than *hydrodynamic* instabilities. If occur during processing, they significantly complicate or totally destroy the production process. Number of *hydroelastic* instabilities termed as *neck-in, draw resonance, die swell, shark skin, gross melt fracture, vortices, encapsulation* and *interface instabilities during coextrusion* etc. [1-6] is known however, they are still not fully understood yet. Especially, during HDPE polymer melt extrusion, three other unstable phenomena, *slip-stick, flow induced molecular weight fractionation* and *die drool*, can occur.

1. Slip-stick Phenomenon

"WHENCE IS IT THAT NATURE DOES NOTHING IN VAIN: AND WHENCE
ARISED ALL THAT ORDER AND BEAUTY WHICH WE SEE IN THE WORLD?"

SIR ISSAC NEWTON (1643 − 1727)

Among the class of polymer extrusion instabilities, collectively known as *melt fracture* (*slip-stick, shark skin, gross melt fracture*), the *slip-stick* instability is the only one that is associated with pressure/stress and extrudate flow rate oscillations. This instability appears at very narrow processing window (depending on temperature and

mass flow rate for given polymer melt) and in polymer science is defined as periodical oscillations of pressure/stress inside extrusion die between two extreme values, although the imposed flow rate is kept constant. These oscillations result in extrudate that is characterized by alternating rough and relatively smooth regions. *Slip-stick* phenomenon appears primarily at low processing temperatures and on shear stress vs. shear rate dependence creates discontinuity representing transition between stable flow and pseudo-stable flow with *wall slip* (so-called *"superflow"* or *"superextrusion"*).

From historical point of view, probably the first work in which *slip-stick* was experimentally observed was published in 1956 by Tordella [7]. He used several polymer melts (including polyethylene, polymethyl metacrylate, 66 nylon and polytetrafluorethylene) and revealed that "...piston velocity, and thereby flow rate, was uniform with time a short time after startup at stresses below which the products were irregular. At and above the critical stress, the flow rates were irregular and the degree of irregularity increased with increasing shear stress." Further, he observed that "...the extent of the irregularity of the extruded sections increased with decreasing temperature". Nevertheless, it should be mentioned here that in the early years of polymer extrusion *surface* as well as *volume melt fracture* instabilities were considered as one only with different appearance of final extrudate. As lately as, Tordella [8] in 1963 with the aid of flow birefringence technique [9] distinguished *slip-stick* and *gross melt fracture* instabilities and named them as *land fracture* and *inlet fracture*, respectively.

In 1958, Bagley at al. [10] published the first note about discontinuity in the shear stress vs. shear rate dependence measured on capillary viscometer. Authors used linear polyethylene melt and they described a novel phenomenon as "…there is a pressure region in which the output is double-valued, and the extruded filaments can be either smooth or rough depending on the output value." The explanation of this unusual behavior they saw in existence of "…major disturbances in the flow pattern above the capillary entrance."

Since the first *slip-stick* instability experimental observation at the beginning of 1950s, this phenomenon has been the subject of many experimental studies and has been given many different names by researchers studying polymer extrusion

instabilities. For example, *main flow instability* [11], *cyclic melt fracture* [12], *cork flow* [13] or *spurt flow* [14]. Later, many research papers focused on *slip-stick* instability have been published [15-25] and the main ideas and conclusions about it are summarized in the book of Hatzikiriakos and Migler [1] and also in few review papers [6, 26, 27 and 28].

Through the years, several theories about *slip-stick* (and also *wall slip*) formation mechanism in flowing polymer melts have been established. Three main of them are summarized for example in [6]. The first is based on idea of disentanglement/entanglement mechanism of polymer chains in a very thin layer near die wall (cohesive failure). The second assumes that polymer chains periodically loss their adhesion at metal die/flowing polymer interface (adhesive failure). Finally, the third supposes periodical appearance/disappearance of lubrication layer with very low shear viscosity near the die wall consisted of low molecular weight species fractionated from the main polymer melt stream inside extrusion die due to presence of highly inhomogeneous stress field profile.

Despite a lot of works focused on this phenomenon have been already published none of above mentioned theories has been fully validated or rejected.

2. Flow Induced Molecular Weight Fractionation

"NO PHENOMENON IS A REAL PHENOMENON UNTIL IT IS AN OBSERVED PHENOMENON."

JOHN ARCHIBALD WHEELER (1911 – 2008)

Historically, the first notice about polymer melt spontaneously fractionating during flow under inhomogeneous stresses in capillary was presented in 1964 by Busse [29]. 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."

One year later, Schreiber and Storey [30] experimentally tested this energy based theory on three different polyethylene samples. First was low density polyethylene, second and third were blends of linear polyethylenes with broad and narrow molecular weight distribution, respectively. Static light scattering showed significant reduction of molecular weight in a surface layer for the first sample and, more pronounced, for the second one. On the other hand, the third sample showed no marked fractionation. They also tested dies with different length to diameter (*L/D*) ratios and found that magnitude of the fractionation effect increasing with increasing *L/D* ratio. With these results, authors consequently developed a simple mathematical model for *flow induced molecular weight fractionation* [31].

With the assumption that *molecular weight fractionation* during shear flow is thermodynamical phenomenon, Schreiber [32] investigated extruded parts in different layers (from the centerline to the skin) by calorimetry as well as extrudate swelling method. Again, the conclusion was that "the molecular redistribution which we have observed is a feature of crystallizable polymers with very wide molecular weight distributions."

In 1972, Whitlock and Porter [33] performed similar tests with broad distribution polystyrene melt. However, even under widely varying conditions of shear rate, shear stress, and temperature, they observed no significant *molecular weight fractionation*. In order to explain this anomaly, Tirrel and Malone [34] developed stress-induced diffusion mathematical model. Based on their modelling results, they believed that the flow conditions in previous experimental work were not optimal for appearance of a measurable fractionation degree, but that fractionation could be significant under proper flow conditions. Unfortunately, after this little failure, no more research papers focused on *flow induced molecular weight fractionation* in polymer melts in the next more than quarter-century have been published.

Nevertheless, idea of this *molecular fractionation* has been recently rediscovered [35]. Authors extruded poly(ethylene terephthalate) (PET) and poly(ethylene-co-cyclohexylenedimethylene terephthalate) (PETG) materials as a thin films and then, the films milled down in small increments and collected the shavings at each single step for later GPC analysis. The results showed a gradient in the concentration of molecular weight across the film thickness. Again, the trend was the same as in the former Schreiber's work. Thus, molecular weight decreased from centreline towards to the wall. Moreover, authors speculated that "if the hypothesis that shear fields can serve to fractionate polymer melts is true, it could help to explain a number of common polymer processing problems…as…plateout of low molecular weight oligomer on metal surfaces or *drooling* of low molecular weight material from die lips."

3. Die Drool Phenomenon

"An expert is a man who has made all the mistakes, which can be made, in a very narrow field."

Niels Bohr (1885 – 1962)

During extrusion process, there is a tendency for some of the extruded polymer material to adhere to exit edges or open faces of extrusion die from which the extruded material emerges. The material so deposited on the die exit, can build up into a large compact usually degraded mass or can form drips, flakes or powder which frequently break away from the die, adhere onto extruded product surface and thus damage 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 buildup*, *die bleed*, *die plate-out*, *die deposit*, *die drip* or *die moustache* and the accumulated material is generally named *drool*.

Die drool phenomenon can appear in all common extrusion techniques like pipe and profile extrusion, film casting, fibre spinning, film blowing, or cable sheathing. In some of these techniques, *drool* can adhere not only to the outside faces but also to the inside ones which makes simple cleaning procedure based on manual removing of *drool* mass from the die exit face virtually impossible. Then, only one way consisting in periodic stops the extrusion line, disassembling of all extrusion die parts and mechanically cleaning them remains. Clearly, this procedure is time and also money consuming.

Nowadays, two different die drool types called as external die drool (caused by extrudate free surface rupture and suction effect due to presence of negative pressure at the die exit region) and internal die drool (presumably caused by flow induced molecular weight fractionation inside extrusion die) are known.

On the following pages, large detailed literature overview focused on *die drool* phenomenon in historical order is provided. Moreover, this overview is dedicated to all extrusion experts who have contributed to understanding and also suppression of this unwanted phenomenon.

4. Published Milestones Focused on Die Drool Phenomenon

"SCIENCE PROCEEDS BY SUCCESSIVE ANSWERS TO QUESTIONS MORE AND MORE SUBTLE, COMING NEARER AND NEARER TO THE VERY ESSENCE OF PHENOMENA."

LOUIS PASTEUR (1822 − 1895)

From the beginning of polymer extrusion, *die drool* has represented real processing problem as can be seen from wide range of patented solutions and ideas to suppression it broadly introduced below. The basic milestones in research and elimination of this unwanted polymer melt flow phenomenon are following.

One of the original remarks about "…difficulty in the extrusion of thermoplastic resins because of adhesion of hot thermoplastic resin to the extrusion die and, occasionally, because of die corrosion from small amounts of heat decomposition products from the resins" can be found in US Patent from 1946 [36]. It is really difficult to search out who used the term *drooling* in writing form as the first, but probably it could be Foster in 1958 [37]. Further, it should be mentioned that until 1980s all available published works about *die drool* were strictly limited on patents where on the one hand, experimentalists found a large number of more or less successful solutions for *die drool* suppression, however, on the other hand, they did not focus on searching for and understanding of the fundamental formation mechanism of this phenomenon. Only in some exceptions, they speculated that *drooling* can be caused by "...incompatibility of polymer with certain other substances mixed with it before extrusion" (1960, [38]), "...the sudden release of pressure on the polymer material as it emerges from the die into the atmosphere" (1964, [39]) or "…part of the fillers, such as clay, which…may be forced out of the matrix at the point of highest extrusion pressure which is a point along the extruder die area" (1971, [40]).

Klein [41] in 1981 seems to be the first researcher who tried to find fundamental *die drool* formation mechanism. He claimed that the main influence on *die drool* is *die swell* and he also recognized two different *die drool* types. First, *die drool* when polymer deposit builds up at slow stable rate he related with a die. Second, on the

other hand, if the die remains clean for a period of time and the polymer deposit rises suddenly, he saw the problem in the screw.

In 1997, Gander and Giacomin [42] published the first work summarizing the *die drool* problem. They concluded that *die drool* is a complex problem with not only one initiating mechanism but there are several minor sources and each of them can play an important role in different extrusion techniques and also in processing of different polymer materials. They also made a dimensional analysis which provides a unified approach for solving *die drool* problems.

Chaloupková and Zatloukal [43] in 2007 mathematically modelled polymer melt flow in die outlet zone and they disclosed area of *negative pressure* (*suction*) near the die exit edge contributing to material separation from the matrix. This *negative pressure* is caused by melt elasticity and streamline curvature which lead to normal stress generation that consequently causes local pressure decrease at the die exit. Further, they concluded that *negative pressure* is crucial variable for *die drool* phenomenon.

Recently, in 2009 Hogan et al. [44] experimentally investigated possible relationship between *die swell* and *die drool* (as Klein [41] earlier speculated). They concluded that "*die swell* is not a root cause of DBU" (*die buildup*, author's remark). However, more interesting finding in their work is that they as the first analysed *die drool* sample collected from die lip by GPC (gel permeable chromatography) technique and found that it is consisted of low molecular weight/oligomeric material. Nevertheless, they simultaneously admitted that "this very low molecular weight/oligomeric material present in the DBU sample was not observed in the starting resin indicating that it was formed from degradation of the resin."

5. Die Drool Suppression Methods

"N̲o great discovery was ever made without a bold guess."

<div align="right">

Sir Issac Newton (1643 – 1727)

</div>

Although, the fundamental *drooling* formation mechanism is still not fully understood yet; wide range of solutions and ideas suppressing this unwanted phenomenon published in open literature can be found. Generally, they can be divided into three groups. First, design changes inside or outside of extrusion die second, extruded polymer material changes and the last, much smaller group, includes changes of inside or outside processing conditions. Many examples of these ideas are introduced in the following subchapters.

5.1 Die Design Modifications

From historical point of view, suppression of *die drool* was originally solved by die design changes. In above-mentioned US patent from 1946 [36] is proposed polytetrafluoroethylene (PTFE) coating of the die exit surfaces or creating all die parts from this well-slipping polymer. Nevertheless, main disadvantage of this idea consists in extremely rapid wear-out of such polymer. In Figure 5.1.1 is shown further solution presented by Foster [37]. It is based on a shape modification of die exit surface including frusto-conical face with plurality of rubbed grooves creating number of points at the die exit. Toroidal *drool* is then broken into small harmless drips.
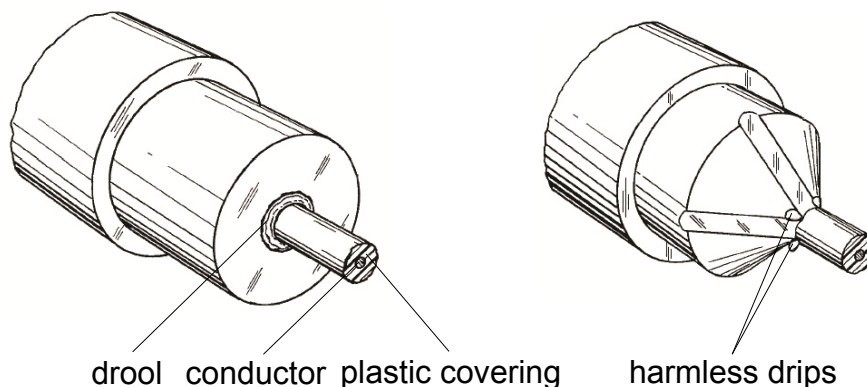

drool conductor plastic covering   harmless drips

Figure 5.1.1: Original (left) and modified (right) die exit surface (adapted from [37]).

Another idea [45] is focused on modification of channel shape between die and wire guiding tip inside a cable coextrusion die. Figure 5.1.2 depicts Budenbender's [39] modification suppressing *die drool* in core tubes extruding by polished chromium outer and inner surfaces facilitating flow and creating unpolished V-shape at the exit end of core tube which together evoke curling *drool* around edges and facilitate breaking off it. Therefore, the *drool* is not continual toroid but it creates again only harmless flakes.
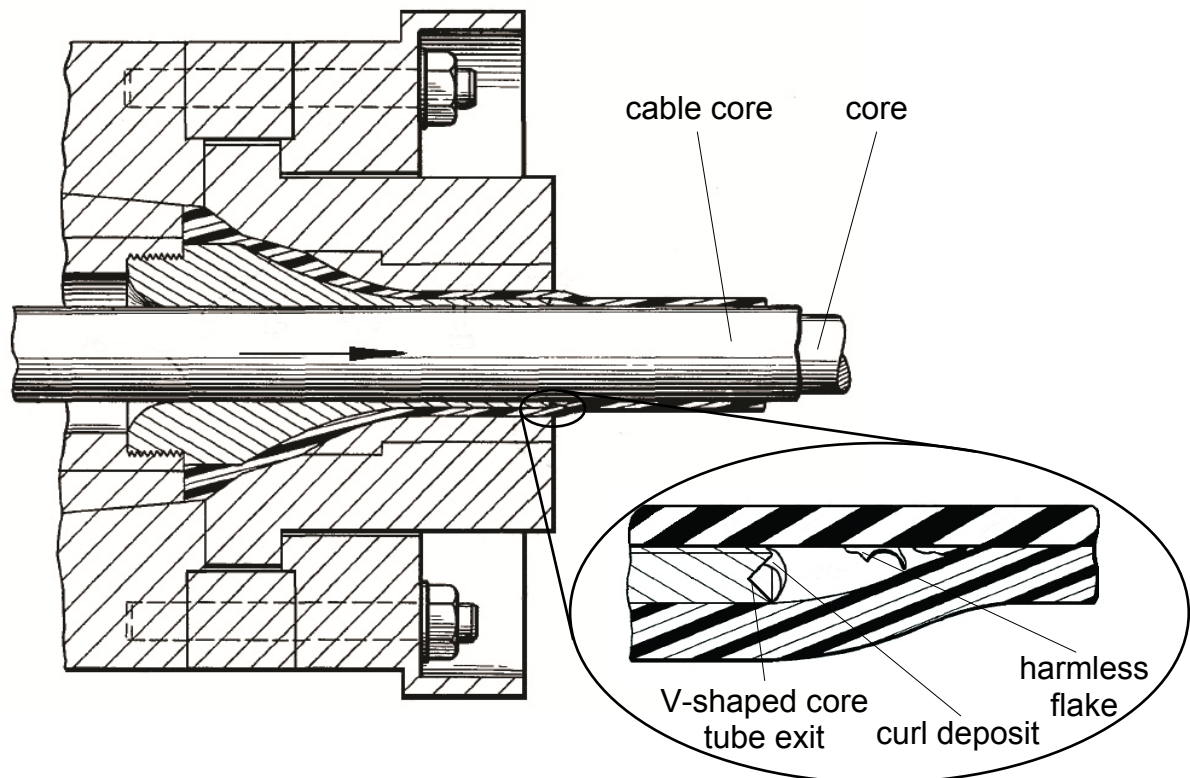
Figure 5.1.2: Budenbender's modification of core tube exit design (adapted from [39]).

Interesting way for *die drool* suppression is using surface-modified dies as presented by Kurtz and Szaniszlo [46]. In their invention, cleaned steel die surface is electroplated with nickel alloy forming a porous layer. The pores are then enlarged and then infused with sub-micron sized particles of well-slipping fluorocarbon polymers. The die is subsequently heat treated to create a smooth, slippery (friction coefficient is 0.08) surface with sufficient hardness. Similar attempt using different die materials is signposted in [47]. Next successful invention proposing flared die exit was

independently patented by Ohhata et al. [48] and Rakestraw et al. [49] (see Figure 5.1.3). Moreover, in both patents suitable dimensions of flared end section are proposed.
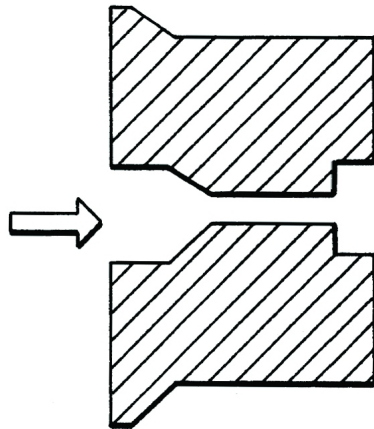

Figure 5.1.3: Flared die exit (adapted from [48]).

The explanation why flared dies are so effective was searched by Ding et al. [50]. They believed that wall shear stress undershoot initiated in flared section can help to reduce material separation from the matrix and they also pointed out on the importance of stress upstream history not only its instantaneous value at the die lip for *die drool* reduction.

Other very interesting solution for suppression not only *die drool* but also other polymer melt flow instabilities is suggested in [51]. It is based on silicon rubber coating of the inside die exit wall. The authors also investigated other die wall materials (e.g. glass, stainless steel, brass, teflon or boron nitride) with conclusion that none of these materials markedly shifts critical shear rates region of well known *slip-stick, shark-skin* and also *gross melt fracture* instabilities. On the other hand, in the case of rubber-coated dies this critical shear rates region is at least 10 times higher in comparison with previously mentioned die wall materials. Further, in this work is also shown, to author's knowledge for the first time in open literature, that *die drool* appears only if *slip-stick* or *shark-skin* regions are overrun.

The last contribution in this section contains chamfer of the die exit edge [52]. Surprisingly, if the chamfer angle is 45°, accumulated *drool* mass is then dramatically reduced. However, it is necessary to remark that such reduction for this chamfer angle

was found only for certain polymers embodying *external die drool* (e.g. metallocene based LLDPE polymer melts). Just note that this *drool* type is related only to die exit region not to full flow channel in the extrusion die (*internal die drool*). Interestingly, they also discuss the possibility of Newtonian liquid (e.g. water) *drooling* with conclusion that during flow of such liquid *drooling* effect can occur however, due to low viscosity of such liquid the die exit face is only wetted.

As can be seen, wide range of die design modifications has been discovered and tested, however, it should be mentioned that no die design change fully eliminates *die drool* phenomenon. Each modification is more or less successful only for narrow range of polymer melts extruded at specific processing conditions.

5.2 Polymer Material Modifications

With slight delay in comparison with die design changes, extrusion experts began to investigate also polymer material modifications. Historically, Havens at el. [53] in 1960 can be considered as the first ones who were interested in finding suitable composition of polyvinylchloride (PVC) showing no *drooling* capability. They found that several types of stearyl phosphates (disodium, aluminium, calcium or barium) in range of 0.5 to 2 weight percent significantly inhibiting *die drool*. In the same year, Henning [38] discovered that diethylene glycol (DEG) as low molecular substance added to the polyethylene prior extrusion in range between 0.5 up to 1 parts by weight, to approximately 100 parts of polyethylene by weight, has significant *die drool* reducing effect. In further patent from 1971 [40] very efficient additive in the form of polytetrafluorethylene (PTFE) granular powder having average particle size of at least 0.5 microns and being effective in an amount of 0.05 to 0.45 parts per 100 parts of rubber or plastic elastomer can be found. Furthermore, in this work other solid lubricants like graphite, mica or molybdenum disulfide were also investigated with conclusion that they are unsatisfactory because of their ineffectiveness, expensiveness, and undesirable changes in physical or electrical properties of final extruded product.

In searching of suitable anti-*drooling* agents continued Yanagisawa et al. [54]. They investigated large number of such agents based on low molecular substances like ethylene glycol, glycerin propyl alcohol etc. and found that materials with solubility

parameter more than 12 are good anti-*drooling* agent candidates for foamed polyolefin resin. In recent patent from 2007 [55] *die drool* problem is solved for white (or opaque) filled polyolefin composition compares three different antioxidants (zinc 2-mercaptotolylimidazole, 2-mercaptotolylimidazole and Irganox 1010). The results showed that at the same processing conditions the first two antioxidant types generate approximately half *drool* amount in comparison with the last one.

Generally, from commercial point of view the most used additive is PTFE in many forms depending on manufacturer because this material is "universal anti polymer melt flow instabilities agent". However, there are some disadvantages connected with its using. For example, high price of such polymer additives or problem with printing of polymer semi-products produced by herewith manner.

5.3 Effect of Processing Conditions

As the last methods solving *die drool* problem were investigated effects of inside and outside processing conditions. For instance, if the *drooling* collar is cooled before it detaches from the die exit face, it may be more easily detached from the profile. This surprising disclosure inspired Bild [56] to equip extrusion die vicinity with plurality of "air-knifes" providing a blast of cold air (or nitrogen) on the collar. His solution is depicted in Figure 5.3.1.

drooling collar   "air-knife"   knife-edge
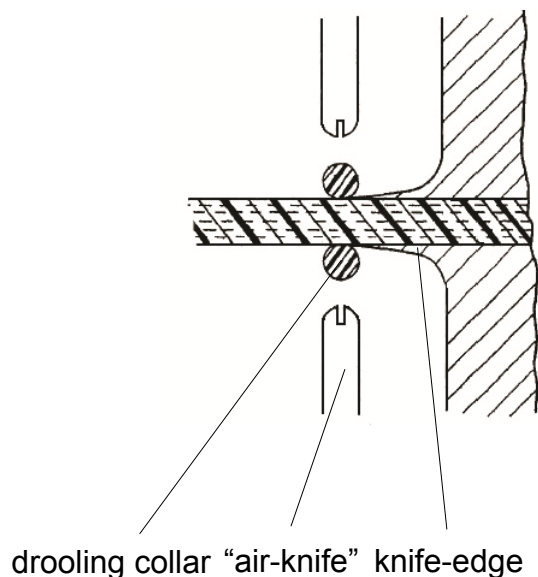
Figure 5.3.1: Bild's imagination of die exit shape and its vicinity suppressing die drool (adapted from [56]).

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In the case of polymer thermoplastics including polyamides, polycarbonates, and polyesters, and more particularly, polyethylene terephtalate (PET), vaporous and low molecular constituents contaminate the die exit. Spencer [57] discovered that if a contaminated air in the immediate vicinity of the extrusion orifice is replaced by a clean hot air, the *drool* is drastically reduced, and in many cases is eliminated fully. His solution with clean hot filtered air distribution plenum is shown in Figure 5.3.2. He also found, quite surprisingly, that *drooling* in thermoplastic sheet casting occurs two or three times more rapidly on the front edge of the die exit than on the rear one (edge on the casting wheel side).

clean hot filtered air distribution plenum
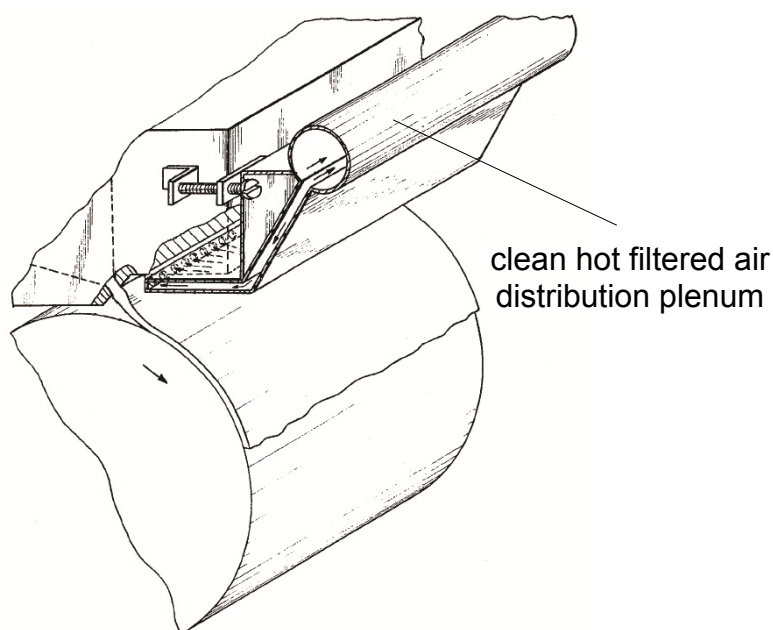
Figure 5.3.2: Sheet casting die exit supplied by clean filtered air (adapted from [57]).

A small notice in [58] suggests that also circulation of hot water around the extrusion die exit reduces *drooling*. Furthermore, two different extruders at the same processing conditions were investigated in [59]. It was found that extruder with single oil-heated control zone barrel shows significantly higher *drooling* than electrically heated barrel with three control zones. This conclusion indicates that thermal history of the extruded compound is also crucial *die drool* formation factor.

From the large above-introduced overview, it is clear that *die drool* is complex phenomenon that occurs in the majority of polymer extrusion techniques. Quite surprisingly, many patents have been focused on cable manufacturing however, also

technology of melt blowing, film blowing, fibre spinning, pipe or profile extrusion and others are negatively affected by *drooling* problem. Further, wide range of polymer materials (polyolefins, PVC, PET, polycarbonates, polystyrenes, thermoplasic elastomers, rubber, or filled compounds) has tendency to form *die drool* at the die exit faces.

6. Quantification of Die Drool Amount

"Error is all around us and creeps in at the least opportunity. Every method is imperfect."

Charles Nicolle (1866 – 1936)

Quantification of *drool* amount is extremely problematic task. It is caused by several types of *drool* (toroidal shape, flakes, drips or powder) and also usually nonuniform time-covering of die exit surface. In spite of these difficulties, several more or less successful methods have been developed.

Probably, the first attempt was published in 1960 [53], where "…dieface buildups of polymer was rated as to amount: 0=none, 3=moderate, and 7=much." Thus, the *drool* amount was evaluated only subjectively. In 1991, Kurtz and Szaniszlo [46] utilized more sophisticated method based on graven lines on the die exit surface where each line represented a 25% *drool* growth based on the die diameter. The time required to cover various fractions of the die exit surface was used as a measure of *drooling* rate. Further, this method was employed by Lee [60].

Chan [47] seems to be the first experimentalist who measured *drool* amount directly. The principle was based on collecting of *drool* material from the extrudate surface and consequently its weighting. Clearly, this method is not actual measurement of *drooling* rate, and also the amount of material remaining on the die exit surface was not quantified. Simple method that utilizes record of *drool* width in given times was suggested by Rakestraw and Waggoner [49] and further used in [55].

The most precise method for *drool* amount evaluating, presented by Horwatt and Hattrich [59], is based on shut-off the extruder after chosen time period and careful direct collecting of the accumulated material from the die exit face. This direct determination of *drool* mass is more objective than the assessing of overlapping time and also takes into account three-dimensional nature of the deposit. Nevertheless, in the case of experiments where the *drool* amount is very small, *drool* deposit must be rigorously collected and also reliable analytical balance is essential. This method was also used by Chai et al. [61].

Last method [62] which partially reduces latter case errors (i.e. smaller *drool* weight = lower accuracy) comprises two-steps indirect *drool* amount determination simply called Digital Image Analysis (DIA). The steps are following. Firstly, digital image of *drool* mass is taken by video or photo camera placed near the die exit, and secondly, *drool* amount evaluation as covered area of die exit surface by suitable software is performed. Furthermore, this analysis is very useful for determination of *drool* accumulation rate (images taken in different times during one test are subsequently compared from die exit face covered area point of view). This method is also described and used in [43].

As can be seen from above introduced overview, last two methods are the best candidates for *drool* amount evaluation. Generally, in the case of polymer melts showing excessive *drooling* is suitable to use direct collection from die exit surface. On the other hand, for assessment of polymer melts with weak *drool* tendency is proper indirect DIA method.

7. Composition Analysis of Drooled Material

"AN EXPERIMENT IS A QUESTION WHICH SCIENCE POSES TO NATURE, AND A MEASUREMENT IS THE RECORDING OF NATURE'S ANSWER."

MAX PLANCK (1858 − 1947)

In order to deeper understanding of *die drool* phenomenon, it is necessary to know also its chemical/structural composition. However, the number of published research works interested in chemical/structural composition analysis of *drooled* material is much lower than in the case of its quantification.

Probably the first harbinger was published in US patent from 1971 [40] where devisers claim that "…deposit contained clay which was forced away from the butyl polymer so that a clay/rubber ratio was deposited which was considerably different than the basic compound." This finding indicates that clay was forced away from the matrix during flow in the extrusion die and subsequently adheres to the die exit face. Nevertheless, first more detailed and more sophisticated analyses have been performed and published more than 30 years later.

The first researcher seems to be Lee [60] in 2002 who presented IR spectrum of collected *drool* deposit (LDPE as a matrix with filler and antioxidants) and he found carbonyl (-C=O) stretching vibration band indicating oxidative degradation of *drool* at the die exit. Further, other two analytic techniques including thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) for *drooled* material analysis of cable sheath consist of EVA/LLDPE matrix can be found in [63]. In this case, both, TGA and DSC methods, indicated that EVA as a material with higher stickiness and lower melting temperature has higher percentage volume in *drool* sample than LLDPE. In recent contribution [64] *die drool* phenomenon study for recycled LDPE can be found. For *drool* analysis authors used not only DSC method, but also, probably as the first, they also measured complex viscosity of *die drool* samples. Last, Hogan et al. [44] published previously-mentioned research work including gel permeable chromatography (GPC) analysis of *drool deposit*.

8. Outline of Die Drool Sources

"WHEN WE SAY THAT SCIENTIFIC KNOWLEDGE IS UNLIMITED, WE MEAN, THERE IS NO QUESTION WHOSE ANSWER IS IN PRINCIPLE UNATTAINABLE BY SCIENCE."

RUDOLF CARNAP (1891 – 1970)

Several possible factors, usually in combination, inducing *die drool* phenomenon have been independently revealed. These factors can be classified into three main groups including effects of *extrusion equipment* (screw, die, transition parts etc.) *design, polymer material,* and *processing conditions* (detailed overview is presented in [42]).

Into the first group we can include *abrupt corners at the die lips* [49, 52], *short land length* [41], *pressure fluctuations in screw* [41], and *dirty die at start-up* [44]. The second group contains *low molecular weight fractions of the polymer, volatiles, fillers, poor dispersion of pigments* [46], *die swell* [41, 44], *dissimilar viscosities in blends* [65], *shark skin* [43, 52], and *slip-stick* [51]. The last group is represented by *high melt temperature* [66], *processing near degradation temperature* [67], and *draw down* [46].

AIMS OF THE DOCTORAL STUDY

"MY GOAL IS SIMPLE. IT IS A COMPLETE UNDERSTANDING OF THE UNIVERSE, WHY IT IS AS IT IS AND WHY IT EXIST AT ALL."

STEPHEN WILLIAM HAWKING (1942)

The main aim of this doctoral thesis work is to develope and utilize specific experimental set-up, methodology and digital image analysis technique in order to investigate the effect of processing conditions, polymer melt rheology, molecular architecture characteristics of polymer chains and die design on *die drool* phenomenon occuring during the extrusion of HDPE melt. The individual aims are provided below:

- Investigation the effect of mass flow rate, temperature, thermally induced degradation, shear viscosity, first normal stress coefficient, uniaxial extensional viscosity, chain branching, presence of small amount of very long linear chains, die exit angle (0°, 15°, 30°, 45°) and flared length to die length ratio (0/15, 1/15, 2/15, 5/15, 8/15) on the *die drool* phenomenon.

- Development of plausible theory allowing to explain the *die drool* phenomenon.

SUMMARY OF THE PAPERS

"THE PROFESSION I'M PART OF HAS AS ITS WHOLE PURPOSE, THE RENDERING OF THE PHYSICAL WORLD UNDERSTANDABLE AND BEAUTIFUL. WITHOUT THIS YOU HAVE ONLY TABLES AND STATISTICS."

ROBERT OPPENHEIMER (1904 – 1967)

This doctoral thesis is written as mono-thematic study focused on experimental investigation of *die drool* phenomenon occuring during HDPE melt extrusion and the most important findings are summarized and discussed in following four original research papers which have already been published (or they are submitted for publication) in *Chemical Engineering Science* journal (publisher *Elsevier*). The main attention has been paid to investigate the effect of processing conditions, polymer melt rheology, molecular characteristics (Papers I, II and III) and extrusion die design (Paper IV) on the *die drool* phenomenon.

PAPER I

Investigation of Die Drool Phenomenon for HDPE Polymer Melt

Jan Musil and Martin Zatloukal

Chemical Engineering Science 2010, vol. 65, no. 23, pp. 6128-6133.

In this work, the *die drool* phenomenon analysis has been performed for HDPE polymer melt by using a specific type of experimental set-up, digital image analysis technique and rheological tools. It has been revealed that the thermally induced degradation occurring inside the processing equipment may lead to HDPE melt elasticity enhancement, which promotes unwanted material accumulation at the end of the extrusion die.

PAPER II

Experimental Investigation of Flow Induced Molecular Weight Fractionation during Extrusion of HDPE Polymer Melts

Jan Musil and Martin Zatloukal

Chemical Engineering Science 2011, vol. 66, no. 20, pp. 4814-4823.

In this work, two different HDPEs with virtually identical number, M_n, and weight, M_w, average molecular weights were investigated from rheological as well as *die drool* phenomenon point of view. It has been revealed that long-chain branching, low polymer melt elasticity and shear viscosity significantly reduce *die drool* phenomenon at the die exit region. It has been concluded that *die drool* phenomenon of HDPE polymer melts can be explained by the *flow induced molecular weight fractionation*.

PAPER III

Experimental Investigation of Flow Induced Molecular Weight Fractionation for Two Linear HDPE Polymer Melts Having Identical M_n and M_w but Different M_z and M_{z+1} Average Molecular Weights

Jan Musil and Martin Zatloukal

Submitted for publication in *Chemical Engineering Science* journal in 2012

In this work, *flow induced molecular weight fractionation* 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 *molecular weight fractionation* is promoted by increase in linear HDPE chain length, it takes place only in a very thin layer near the die wall and its onset and intensity are in direct relationship with *slip-stick* flow instability.

PAPER IV

Effect of Die Exit Geometry on Internal Die Drool Phenomenon during Linear HDPE Melt Extrusion

Jan Musil and Martin Zatloukal

In this work, the effect of die exit design on the *internal die drool* phenomenon occuring during extrusion of HDPE has been experimentaly investigated. It has been revealed, that firstly, the effect of flared length and die exit angle on the *internal die drool* intensity during extrusion of HDPE has non-monotonic character and secondly, flared dies are more stabilizing in comparison with chamfered dies. It has been suggested that suppresion mechanism of the *internal die drool* phenomenon through die exit modification can be understood throught the balance between the melt pressure/normal stresses at the die exit, adhesion at metal wall/flowing melt interface and extensional stress induced by the extrudate draw off, which can leads to flow situation at which low molecular weight species are effectively removed from the die exit region by the moving extrudate and only small portion of it remains at the die exit face.

CONCLUSIONS

In this work, specific experimental set-up and digital image analysis technique have been proposed and utilized to investigate the effect of processing conditions, polymer melt rheology, molecular characteristics and die design on *die drool* phenomenon occurring during the extrusion of HDPE melt and the following findings have been discovered:

- the *die drool* material represents low molecular weight fraction of HDPE, suggesting that *die drool* phenomenon occurring during the extrusion of HDPE polymer melts can be considered as a result of the *flow induced molecular weight fractionation*,

- 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,

- 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 *die drool* intensity to increase due to the thermally induced HDPE degradation enhancing melt elasticity promoting *flow induced molecular weight fractionation*,

- increase in HDPE chain branching, decrease in their very long linear chains content, elasticity, shear viscosity and M_w significantly reduce *die drool* phenomenon,

- due to enhanced melt elasticity (by the presence of long linear chains of linear HDPE polymer), the *flow induced fractionation* is more effective which results in narrow molecular weight distribution of *die drool* sample containing small amount of long chains,

- 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,

- 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),

- flared dies are more stabilizing in comparison with chamfered dies,

- the effect of die exit angle and flared length on the *die drool* intensity during extrusion of HDPE has non-monotonic character with optimum value for the die exit angle 15° and flared length to die length ratio 2/15,

- suppression mechanism of the *die drool* phenomenon through die exit modification can be understood throught the melt pressure/normal stresses at the die exit, adhesion at metal wall/flowing melt interface and extensional stress induced by the extrudate draw off, which can promote effective and continuous release of low molecular weight species from the die exit region by the moving extrudate.

REFERENCES

"To understand a science it is necessary to know its history."

Auguste Comte (1798 – 1857)

1.   HATZIKIRIAKOS, S. G., MIGLER, K. B. *Polymer Processing Instabilities: Control and Understanding*. 1st ed. New York: Marcel Dekker, 2005. 470 p. Chemical Industries: A Series of Reference Books and Textbooks. ISBN 0-8247-5386-0

2.   BIRD, R. B., ARMSTRONG, C., HASSAGER, O. *Dynamics of Polymeric Liquids Volume 1 (Fluid Mechanics)*. 2nd ed. New York: John Wiley & Sons, 1997. 485 p. ISBN 0-471-80245-X

3.   TANNER, R. I. *Engineering Rheology*. 2nd ed. New York: Oxford University Press, 2000. 559 p. Oxford Engineering Science Series. ISBN 0-19-856473-2

4.   TADMOR, Z., GOGOS, C. G. *Principles of Polymer Processing*. 2nd ed. New Jersey: John Willey & Sons, 2006. 961 p. ISBN 0-471-38770-3

5.   MACOSCO, C. W. *Rheology: Principles, Measurements, and Applications*. 1st ed. New York: John Willey & Sons, 1994. 550 p. Advances in Interfacial Engineering Series. ISBN 0-471-18575-2

6.   DENN, M. M. Extrusion Instabilities and Wall Slip. *Annu. Rev. Fluid Mech.* 2001, vol. 33, pp. 265-287.

7.   TORDELLA, J. P. Fracture in the Extrusion of Amorphous Polymers through Capillaries. *J. App. Phys.* 1956, vol. 27, no. 5, pp. 454-459.

8.   TORDELLA, J. P. Unstable Flow of Molten Polymers: A Second Site of Melt Fracture. *J. App. Polym. Sci.* 1963, vol. 7, no. 1, pp. 215-229.

9.   JANESCHITZ-KRIEGL H. *Polymer Melt Rheology and Flow Birefringence*. 1st ed. New York: Springer-Verlag, 1983. 524 p. Polymers/Properties and Applications Series. ISBN 0-387-11928-0

10. BAGLEY, E. B., CABOTT, I. M., WEST, D. C. Discontinuity in the Flow Curve of Polyethylene. *J. App. Phys.* 1958, vol. 29, no. 1, pp. 109-110.

11. WEILL, A. About the Origin of Sharskin. *Rheol. Acta* 1980, vol. 19, no. 5, pp. 623-632.

12. HATZIKIRIAKOS, S. G., DEALY, J. M. Role of Slip and Fracture in the Oscillating Flow of HDPE in a Capillary. *J. Rheol.* 1992, vol. 36, no. 5, pp. 845-884.

13. PIAU, J. -M., EL KISSI, N., TOUSSAINT, F., MEZGHANI, A. Distortions of Polymer Melt Extrudates and their Elimination using Slippery Surfaces. *Rheol. Acta* 1995, vol. 34, no. 1, pp. 40-57.

14. VINOGRADOV, G. V., PROTASOV, V. P., DREVAL, V. E. The Rheological Behavior of Flexible-Chain Polymers in the Region of High Shear Rates and Stresses, the Critical Process of Spurting, and Supercritical Conditions of their Movement at T > Tg. *Rheol. Acta* 1984, vol. 23, no. 1, pp. 46-61.

15. WANG, S. -Q., DRDA, P. A. Superfluid-Like Stick-Slip Transition in Capillary Flow of Linear Polyethylene Melts. 1. General Features. *Macromolecules* 1996, vol. 29, no. 7, pp. 2627-2632.

16. WANG, S. -Q., DRDA, P. A. Stick-Slip Transition in Capillary Flow of Polyethylene. 2. Molecular Weight Dependence and Low-Temperature Anomaly. *Macromolecules*, 1996, vol. 29, no. 11, pp. 4115-4119.

17. WANG, S. -Q., DRDA, P. A. Stick-Slip Transition in Capillary Flow of Linear Polyethylene: 3. Surface Conditions. *Rheol. Acta* 1997, vol. 36, no. 2, pp. 128-134.

18. DURAND, V., VERGNES, B., AGASSANT, J. F., BENOIT, E., KOOPMANS, R. J. Experimental Study and Modeling of Oscillating Flow of High Density Polyethylenes, *J. Rheol.* 1996, vol. 40, no. 3, pp. 383-394.

19. MÜNSTEDT, H., SCHMIDT, M., WASSER, E. Stick and Slip Phenomena during Extrusion of Polyethylene Melts as Investigated by Laser-Doppler Velocimetry. *J. Rheol.* 2000, vol. 44, no. 2, pp. 413-427.

20. ROBERT, L., VERGNES, B., DEMAY, Y. Flow Birefringence Study of the Stick-Slip Instability during Extrusion of High-Density Polyethylenes. *J. Non-Newtonian Fluid Mech.* 2003, vol. 112, no. 1, pp. 27-42.

21. KAY, D., CARREAU, J. P., LEFLEUR, P. G., ROBERT, L., VERGNES, B. A Study of the Stick-Slip Phenomenon in Single-Screw Extrusion of Linear Polyethylene. *Polym. Eng. Sci.* 2003, vol. 43, no. 1, pp. 78-90.

22. AGASSANT, J. -F., ARDA, D. R., COMBEAUD, C., MERTEN, A., MÜNSTEDT, H., MACKLEY, M. R., ROBERT, L., VERGNES, B. Polymer Processing Extrusion Instabilities and Method for their Elimination or Minimisation, *Int. Polym. Proc.* 2006, vol. 21, no. 3, pp. 239-255.

23. TALIADOROU, E., GEORGIOU, G. C., ALEXANDROU, A. N. A Two-Dimensional Numerical Study of the Stick-Slip Extrusion Instability. *J. Non-Newtonian Fluid Mech.* 2007, vol. 146, no. 1-3, pp. 30-44.

24. RODRÍGUEZ-GONZÁLEZ, F., PÉREZ-GONZÁLEZ, J., MARÍN-SANTIBÁÑEZ, B. M., DE VARGAS, L. Kinematics of the Stick-Slip Capillary Flow of High-Density Polyethylene. *Chem. Eng. Sci.* 2009, vol. 64, no. 22, pp. 4675-4683.

25. ALLAL, A., VERGNES, B. Molecular Interpretation of the "Stick-Slip" Defect of Linear Polymers. *J. Non-Newtonian Fluid Mech.* 2009, vol. 164, no. 1-3, pp. 1-8.

26. DENN, M. M. Issues in Viscoelastic Fluid Mechanics. *Annu. Rev. Fluid Mech.* 1990, vol. 22, no. 1, pp. 13-34.

27. LARSON, R. G. Instabilities in Viscoelastic Flows. *Rheol. Acta* 1992, vol. 31, no. 3, pp. 213-263.

28. HATZIKIRIAKOS, S. G. Wall Slip of Molten Polymers. *Progress in Polym. Sci.* 2012, vol. 37, no. 4, pp. 624-643.

29. BUSSE, W. F. Two Decades of High-Polymer Physics: A Survey and Forecast. *Physics Today* 1964, vol. 17, no. 9, pp. 32-41.

30. SCHREIBER, H. P., STOREY, S. H. Molecular Fractionation in Capillary Flow of Polymer Fluids. *Polymer Letters* 1965, vol. 3, no. 9, pp. 723-727.

31. SCHREIBER, S. H., STOREY, S. H., BAGLEY, E. B. Molecular Fractionation in the Flow of Polymer Fluids. *Trans. Soc. Rheol.* 1966, vol. 10, no. 1, pp. 275-297.

32. SCHREIBER, H. P. Component Redistribution in Extrusion of Polyethylene Compounds. *J. App. Polym. Sci.* 1974, vol. 18, no. 8, pp. 2501-2508.

33. WHITLOCK, L. R., PORTER, R. S. Experimental Investigation of the Concept of Molecular Migration within Sheared Polystyrene. *J. Polym. Sci. Polym. Chem. Ed.* 1972, vol. 10, no. 5, pp. 877-886.

34. TIRRELL, M., MALONE, M. F. Stress-Induced Diffusion of Macromolecules. *J. Polym. Sci. Phys. Ed.* 1977, vol. 15, no. 9, pp. 1569-1583.

35. SHELBY, M. D., CAFLISCH, G. B. Shear Field Induced Diffusion and Molecular Weight Fractionation during Polymer Processing. *Polym. Eng. Sci.* 2004, vol. 44, no. 7, pp. 1283-1294.

36. E. I. DU PONT DE NEMOURS & COMPANY. *Extrusion Apparatus*. Devisers: BERRY, K. L., DOWNING, J. R. *United States Patent Office*, No. 2,403,476, 1946-07-09.

37. WESTERN ELECTRIC COMPANY. *Extruding Dies*. Deviser: FOSTER, A. G. *United States Patent Office*, No. 2,863,169, 1958-12-09.

38. WESTERN ELECTRIC COMPANY. *Method of Making Plastic Articles*. Deviser: HENNING, G. E. *United States Patent Office*, No. 2,960,482, 1960-11-15.

39. WESTERN ELECTRIC COMPANY. *Extruder Core Tubes*. Deviser: BUDENBENDER, H. W. *United States Patent Office*, No. 3,151,357, 1964-10-06.

40.   WYROUGH & LOSER. *Solid Lubricant for Reducing Die-Plating and Die Drag During the Extrusion of Viscous Rubber and Elastomeric Plastic Compositions*. Devisers: LOSER, T. N., JONES, T. *United States Patent Office*, No. 3,600,309, 1971-08-17.

41.   KLEIN, I. Die drool: What Causes It, How to Avoid It. *Plastics World* 1981, vol. 39, no. 5, pp. 112-113.

42.   GANDER, J. D., GIACOMIN, A. J. Review of Die Lip Buildup in Plastics Extrusion. *Polym. Eng. Sci.* 1997, vol. 37, no. 7, pp. 1113-1126.

43.   CHALOUPKOVÁ, K., ZATLOUKAL, M. Theoretical and Experimental Analysis of the Die Drool Phenomenon for Metallocene LLDPE. *Polym. Eng. Sci.* 2007, vol. 47, no. 6, pp. 871-881.

44.   HOGAN, T. A., WALIA, P., DEMS, B. C. Investigation of the Relationships Between Die Build up and Die Swell. *Polym. Eng. Sci.* 2009, vol. 49, no. 2, pp. 333-343.

45.   WESTERN ELECTRIC COMPANY. *Apparatus for Extruding Plastic Compounds*. Devisers: HENNING, G. E., RICHTER, M. W. *United States Patent Office*, No. 3,121,255, 1964-02-18.

46.   UNION CARBIDE CHEMICALS AND PLASTICS TECHNOLOGY CORPORATION. *Reduction in Die Drool in Filled Resins and Product Improvement*. Devisers: KURTZ, S. J., SZANISZLO, S. R. *United States Patent Office,* No. 5,008,056, 1991-04-16.

47.   CHAN, C. -M. Viscosity and the Formation of Die Drool at the Polymer-Metal Interfaces. *Int. Polym. Proc.* 1995, vol. 10, no. 3, pp. 200-203.

48.   GENERAL ELECTRIC COMPANY. *Die Plate for Plastics Extruder*. Devisers: OHHATA, T. et al. *United States Patent Office*, No. 5,417,907, 1995-05-23.

49.   E. I. DU PONT DE NEMOURS & COMPANY. *Polymer Extrusion Die and Use Thereof*. Devisers: RAKESTRAW, J. A., WAGGONER, M. G. *United States Patent Office*, No. 5,458,836, 1995-10-17.

50. DING, F., ZHAO, L., GIACOMIN, A. J., GANDER, J. D. Flaring Dies for Suppress Die Drool. *Polym. Eng. Sci.* 2000, vol. 40, no. 10, pp. 2113-2123.

51. KULIKOV, O., HORNUNG, K. A Simple Way to Suppress Surface Defects in the Processing of Polyethylene. *J. Non-Newtonian Fluid Mech.* 2004, vol. 124, no. 1-3, pp. 103-114.

52. CHALOUPKOVÁ, K., ZATLOUKAL, M. Effect of Die Design on Die Drool Phenomenon for Metallocene Based LLDPE: Theoretical and Experimental Investigation. *J. App. Polym. Sci.* 2009, vol. 111, no. 4, pp. 1728-1737.

53. THE DOW CHEMICAL COMPANY. *Composition Comprising a Vinylidene Chloride Polymer and an Organic Phosphate*. Devisers: HAVENS, C. B., MASON, A. J., WIDIGER, A. T. *United States Patent Office*, No. 2,935,490, 1960-05-03.

54. THE FURUKAWA ELECTRIC COMPANY. *Method for Extrusion Coating Electric Wires with a Foamed Polyolefin Resin Involving Reduced Die-Plateout*. Devisers: YANAGISAWA, K., KOBAYASHI, H., TAYAMA, Y. *United States Patent Office*, No. 3,882,209, 1975-05-06.

55. EQUISTAR CHEMICALS. *White Polyolefin Compositions Having Reduced Die Drool*. Deviser: LEE, C. D. United States Patent Office, No. 2007/0037905, 2007-02-15.

56. IMPERIAL CHEMICAL INDUSTRIES. *Extrusion Process and Apparatus Therefor*. Deviser: BILD, F. United States Patent Office, No. 3,244,786, 1966-04-05.

57. EASTMAN KODAK COMPANY. *Method of Controlling Contaminant Buildup on Extrusion Dies Used in Casting Thermoplastic Sheeting*. Deviser: SPENCER, A. W. United States Patent Office, No. 3,502,757, 1970-03-24.

58. ITZKOFF, M. L., WOODDELL, G. L. Crosslinkable Polyethylene for Wire and Cable: An Update. *Wire Journal International* 1982, vol. 15, no. 5, pp. 60-71.

59. HORWATT, S. W., HATTRICH, G. A. Die Drool in Chemically Crosslinkable Polyolefin Compounds. *Internal publication of Equistar Chemicals company*, 1996.

60. LEE, C. D. Die Lip Build-up in the Extrusion of Highly Filled Low Density Polyethylene. *Annual Technical Conference – ANTEC, Conference Proceedings* 2002, vol. 1, pp. 117-121.

61. CHAI, C. K., ADAMS, G., FRAME, J. Polyethylene Die Deposit – Measurement, Formation Mechanism and Routes to Reduction. *Annual Technical Conference – ANTEC, Conference Proceedings* 2001, vol. 1, pp. 401-405.

62. BOSSCHE, L. Van den, et al. Die Build-up During Polyolefin Processing: A Matter of Polymer Design and Fluoropolymer-Based Processing Additives. *Internal publication of Dyneon company*, 2000.

63. HWANG, S. J., NAM, G. J. The Effect of Ingredients and Processing Conditions on the Extrusion Processability of Halogen-Free Flame Retardant Thermoplastics. *Annual Technical Conference – ANTEC, Conference Proceedings* 2005, vol. 1, pp. 192-196.

64. BRACHET, P., et al. The Problem of Die Drool in the Extrusion of Recycled Polyethylene. *Progress in Rubber, Plastics and Recycling Technology* 2009, vol. 25, no. 4, pp. 199-211.

65. PRIESTER, D. E. Effect of Die Surface Characteristics on Processing Additive Performance. *Annual Technical Conference – ANTEC, Conference Proceedings* 1994, vol. 2, pp. 2059-2061.

66. REYNOLDS METALS COMPANY. *Method of Making Tubular Plastic Film*. Deviser: HINRICHS, D. R. United States Patent Office, No. 3,933,958, 1976-01-20.

67. HOLTZEN, D. A., MUSIANO, J. A. Die Lip Plate-Out: A Proposed Mechanism, *Technical Papers, Regional Technical Conference – Society of Plastics Engineers*, 1996.

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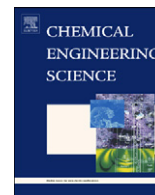
Investigation of die drool phenomenon for HDPE polymer melt

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ABSTRACT

In this work, the die drool phenomenon analysis has been performed for HDPE polymer melt by using a specific type of experimental set-up, digital image analysis technique and rheological tools. It has been revealed that the thermally induced degradation occurring inside the processing equipment may lead to HDPE melt elasticity enhancement, which promotes unwanted material accumulation at the end of the extrusion die.

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1. Introduction

Due to the viscoelastic nature of the polymer melts, unwanted flow phenomena such as *die swell, shark skin, die drool, interfacial instabilities*, etc. (Bird et al., 1987; Tanner, 1985; Hatzikiriakos and Migler, 2005; Klein, 1981; Kurtz and Szaniszlo, 1991; Hogan et al., 2009; Holtzen and Musiano, 1996; Priester, 1994; Gander and Giacomin, 1997; Ding et al., 2000; Dhori et al., 1997; Chaloupkova and Zatloukal, 2007, 2009; Pivokonsky et al., 2008; Zatloukal et al., 2002, 2005, 2005, 2004, 2002, 2001; Martyn et al., 2004, 2009; Zatloukal and Witte, 2006; Shelby and Caflisch, 2004) can occur. The stabilization of these flow phenomena during polymer processing is usually difficult because the relationship between the polymer rheology, equipment design, processing conditions and the flow instabilities is not fully understood yet.

Die drool, also called die build-up, die bleed or plate-out, is the undesirable spontaneous accumulation of polymer melt at the exit edges or open faces of extrusion die during melt extrusion of polyolefins, PVC or filled polymers. This unwanted phenomenon can occur in all common extrusion processes (film blowing, pipe or profile extrusion, fiber spinning, film casting, etc.) and after it arises, the productivity of extrusion line rapidly decreases for the following basic reasons. Firstly, a small amount of accumulated and usually degradated material sticks to the extrudate at the die exit region, which causes depreciation of the final product. In the case of film casting or extrusion of solid profiles it is possible to solve this problem only by stripping of the accumulated material

from the die exit region. However, in the case of film blowing, pipe, cored profile extrusion or wire sheathing the die drool arises not only at the outer exit region but also at the inner one, thereby the first clean opportunity is impossible. Therefore, in these cases, the extrusion line is necessary to periodically switch off to clean the die, which is uneconomical and time consuming.

The fundamental problem of die drool phenomenon is to understand and describe the formation principle of this phenomenon. In the open literature, several factors have been found to support the formation of this instability. They include pressure fluctuations in screw (Klein, 1981), volatiles, low molecular fractions of the polymer, fillers, poor dispersion of pigments (Kurtz and Szaniszlo, 1991), die swell (Klein, 1981; Hogan et al., 2009), processing near degradation temperature (Holtzen and Musiano, 1996), dissimilar viscosities in blends (Priester, 1994), die design (Gander and Giacomin, 1997; Ding et al., 2000; Dhori et al., 1997), etc.

Currently, two basic types of die drool phenomenon are known: external and internal. It has been recently found that the external type of die drool phenomenon for metallocene type of LLDPE polymer is predominantly driven by the extrudate free surface rupture and suction effect due to the negative pressure generated at the die exit region (Chaloupkova and Zatloukal, 2007, 2009), which can be suppressed by the die exit angle modification (Chaloupkova and Zatloukal, 2007, 2009). On the other hand, the internal type of die drool phenomenon can be caused by the flow induced fractionation that occurred before the polymer melt leaves the extrusion die, which is not fully understood yet (Shelby and Caflisch, 2004). Thus, the effect of processing conditions on this unwanted flow phenomenon has been investigated in this work for unfiled HDPE extrusion through annular extrusion die by using a specific type of digital image analysis technique.

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2. Material characterization

In this work, HDPE Tipelin FS 450-26 (TVK, Hungary) polymer, widely used in film extrusion, was chosen for the experimental research. The basic material characteristics are provided in Table 1 (Pivokonsky et al., 2008). In order to evaluate the HDPE polymer

Table 1
Basic properties of chosen polymers.

Property	HDPE Tipelin FS 450-26
Density ($g\,cm^{-3}$)	0.945
M_w ($g\,mol^{-1}$)	212,300
M_n ($g\,mol^{-1}$)	22,430
M_z ($g\,mol^{-1}$)	1,045,000
M_w/M_n (dimensionless)	9.465
DSC peak melting point (°C)	130.3
DSC heat of fusion ($J\,g^{-1}$)	190.3
Crystallinity (%)	64.9
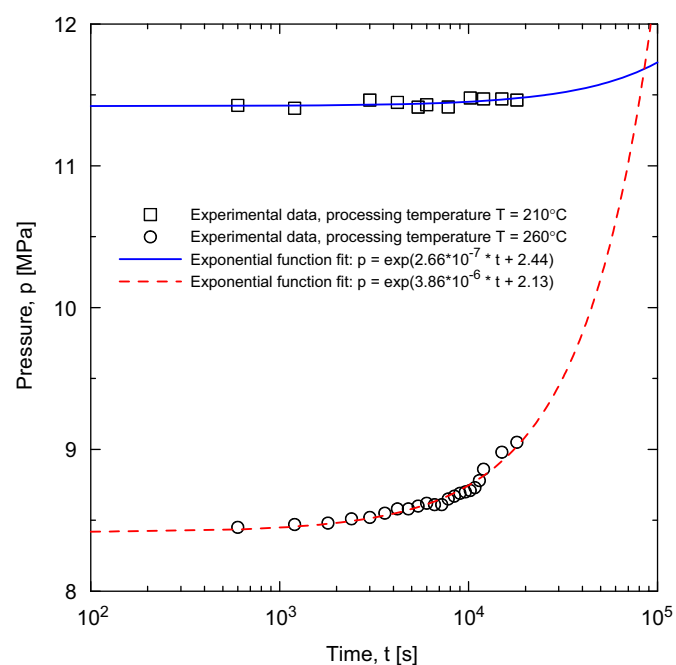
Fig. 1. Effect of processing temperature on the time dependent extrusion pressure for tested HDPE Tipelin FS 450-26 sample.

thermal stability, firstly, polymer pellets were added and melted in the Rosand RH7-2 control speed capillary rheometer equipped by a capillary die having 16 mm length and 1 mm radius. After each 10 min of rest, the constant shear rate ($80\,s^{-1}$) has been applied and the equilibrium capillary pressure drop has been measured. This procedure was repeated 30 times to cover 5 h degradation time period after which the extruded polymer has been collected. This procedure was applied for two different melt temperatures $T = 210$ and 260 °C. Effect of processing temperature and time on the extrusion pressure for the tested HDPE sample is provided in Fig. 1. It is clearly visible that the extrusion pressure rise occurs during the time suggesting that temperature induced degradation leads to molecular weight increase of the tested polymer and the effect is much more pronounced for the higher temperature. In order to understand sample degradation in more detail, frequency dependent complex viscosity/recoverable shear and transient uniaxial extensional viscosity were determined for not degraded as well as degraded HDPE samples (5 h at 210 °C/ 260 °C) by using the rotational rheometer from Advanced Rheometric Expansion System (ARES 2000, Rheometrics Scientific, USA) in parallel-plate mode and the Sentmanat Extensional Rheometer (SER-HV-A01, Xpansion Instruments, USA (Sentmanat et al., 2005, 2004; Sentmanat, 2003), see Fig. 2), respectively. These rheological characteristics are shown in Figs. 3–5. Based on the rheological data depicted in these figures, it can be concluded that thermally induced degradation of HDPE sample leads to increase of complex viscosity/shear elasticity (recoverable shear)/ uniaxial extensional viscosity and the effect is much more pronounced for the highest processing temperature ($T = 260$ °C).

It should be mentioned that the recoverable shear, Sr, is the measure of the shear elasticity, which is given by the following equation:

$$Sr = \frac{N_1}{2\tau_{xy}} \tag{1}$$

where N_1 is the first normal stress difference and τ_{xy} is the shear stress. Considering the Cox–Merz rule (Cox and Merz, 1958) and the similarity between $N_1/2$ and storage modulus G' (Bird et al., 1987), Eq. (1) can be rewritten into the following form:

$$Sr = \frac{G'}{\eta^*\omega} \tag{2}$$

where η^* is the complex viscosity and ω is the frequency. In this work, the recoverable shear shown in Fig. 4 was calculated by using rotational rheometry data according to Eq. (2).
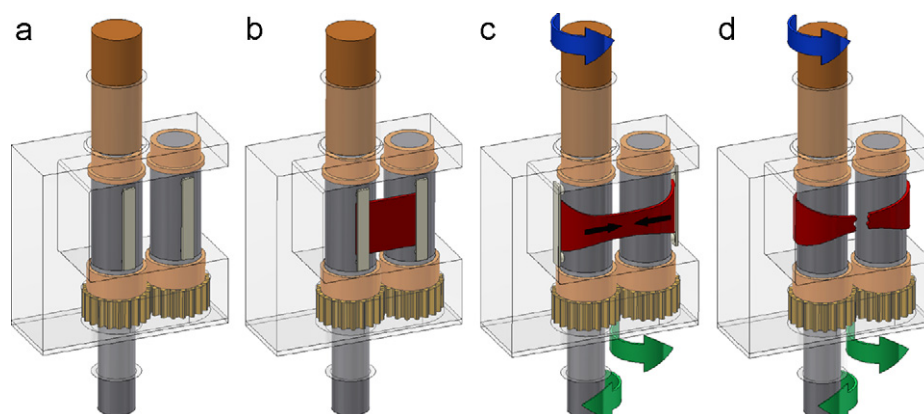
Fig. 2. Visualization methodology for the extensional viscosity measurements of the HDPE polymer melt by using a Sentmanat Extensional Rheometer (SER): (a) SER unit, (b) deposition of the polymer sample on the SER unit, (c), sample stretching and (d) sample at break.
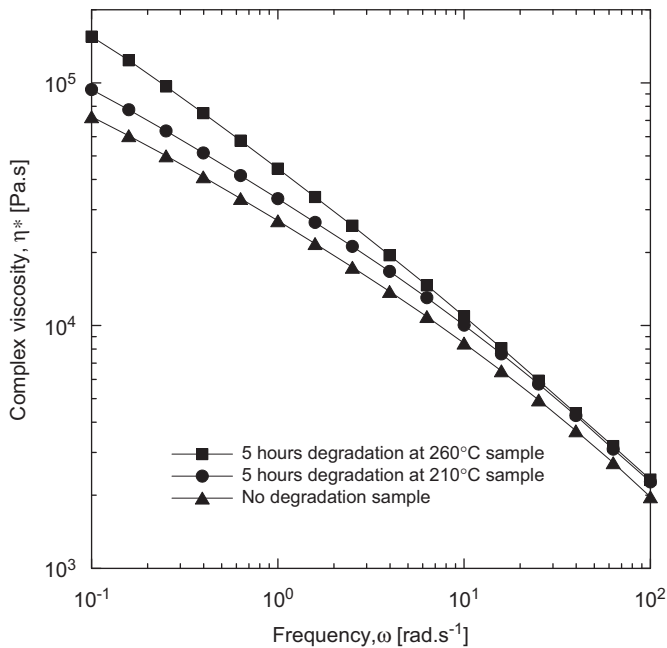
Fig. 3. The frequency dependent complex viscosity for two HDPE Tipelin FS 450–26 samples degraded 5 h at two different processing temperatures (210 and 260 °C). Measurements have been carried out at 180 °C.
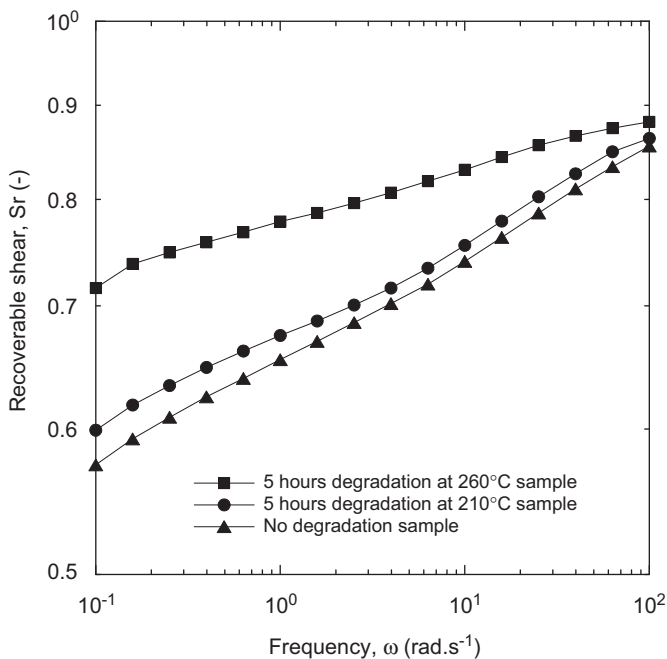
Fig. 4. The frequency dependent recoverable shear for two HDPE Tipelin FS 450–26 samples degraded 5 h at two different processing temperatures (210 and 260 °C). Measurements have been carried out at 180 °C.

3. Die drool experiments

The die drool experiments were carried out on a conventional Brabender Plasti—Corder 2000 single-screw extruder with diameter $D=30$ mm and length $L=25D$ (standard single-thread screw with compression ratio 4:1, and lengths of zones: *feed* $L_1=10D$, *compression* $L_2=3D$, *metering* $L_3=12D$), which was included in the laboratory extrusion line. The schematic view of
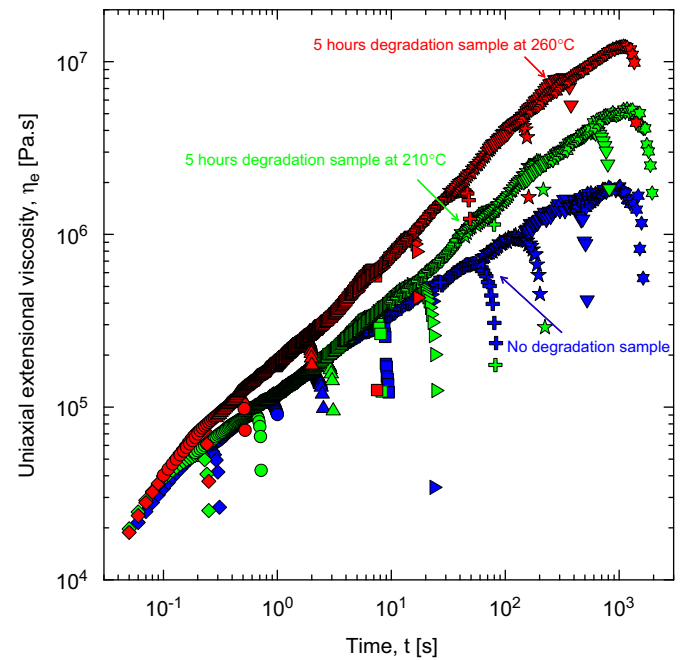
Fig. 5. The transient uniaxial extensional viscosity for two HDPE Tipelin FS 450–26 samples degraded 5 h at two different processing temperatures (210 and 260 °C) and different extensional strain rates $\dot{\varepsilon}$. $\diamond$—$\dot{\varepsilon}=10$ s^{-1}, $\circ$—$\dot{\varepsilon}=3.16$ s^{-1}, $\triangle$—$\dot{\varepsilon}=1$ s^{-1}, $\square$—$\dot{\varepsilon}=0.316$ s^{-1}, $\triangleright$—$\dot{\varepsilon}=0.1$ s^{-1}, $\oplus$—$\dot{\varepsilon}=0.0316$ s^{-1}, $\star$—$\dot{\varepsilon}=0.01$ s^{-1}, ∇—$\dot{\varepsilon}=0.00316$ s^{-1} and $\star$—$\dot{\varepsilon}=0.001$ s^{-1}. Measurements have been done at 180 °C.

laboratory extrusion line is shown in Fig. 6. This line consists of an extruder with four heating zones, transition annular part, specially designed extrusion die, which is introduced in (Chaloupkova and Zatloukal, 2007, 2009), photo camera placed near the die exit, and draw-off mechanism. In our experiments, two different processing conditions are used. In the first case, the extruder zones (from the hopper to the die) are heated to $T_1=80$ °C, $T_2=200$ °C, $T_3=240$ °C and $T_4=260$ °C whereas in the second case, third and fourth extruder zone temperatures are decreased to $T_3=T_4=210$ °C by keeping the annular tube (connecting die and extruder) and die exit temperature in both cases constant, $T_5=T_6=150$ °C. Die drool accumulation has been investigated for both temperature profiles along the screw, two different mass flow rates (0.5 and 1.1 kg h^{-1}) after 30 s (first 15 min), after 1 min (another 15 min) and 5 min (last 30 min) of the 60 min long tests. For each individual test, barrel, screw and all parts of the die have been perfectly cleaned to ensure the reproducibility of the performed measurements.

During the experiments, a digital camera has been used for die drool quantification at the die exit through Normalized Die Drool Area, NDDA, according to the following equation:

$$NDDA = \frac{A_D}{A_{Die}} \tag{3}$$

where A_D and A_{Die} are the area for the accumulated die drool material and the used capillary die cross-section, respectively. This indirect method is very useful for the die drool intensity evaluation because it allows quantification of small die drool amounts (where direct measurements are very difficult or impossible) and it reduces possible errors arising from the careless collection of accumulated material from the die lip. On the other hand, the use of a single camera based digital image analysis is limited only to the processing conditions where 3D effects can be neglected (such as drool thickness or its
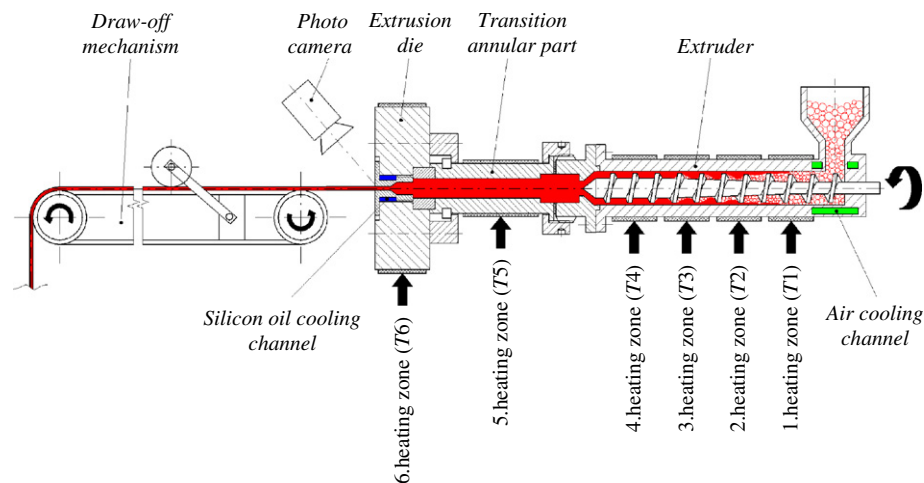
Fig. 6. Schematic 2D cross-sectional view of laboratory extrusion line (not in the scale).
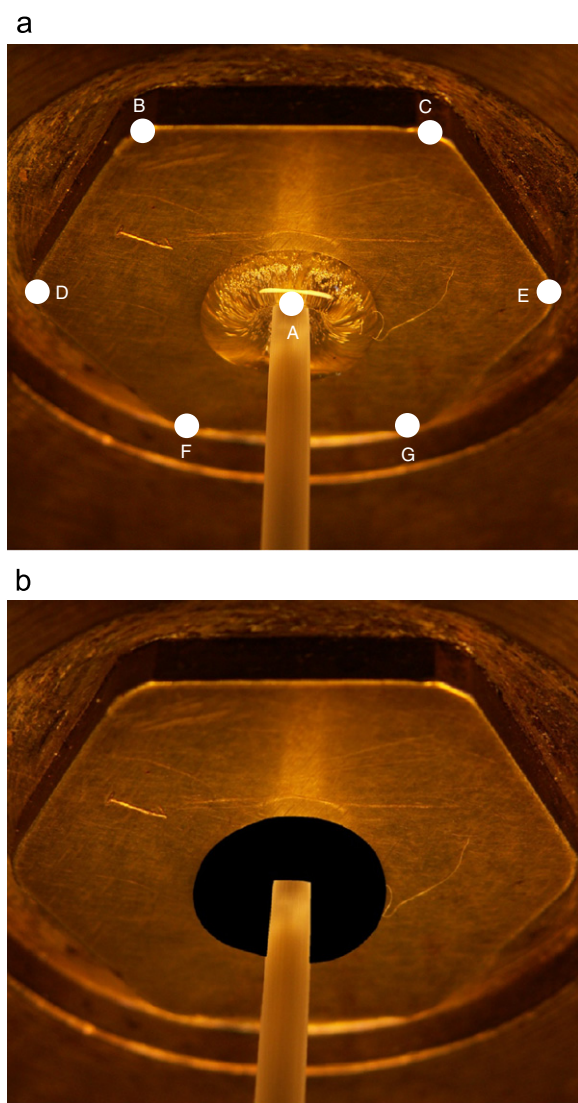
Fig. 7. Digital image analysis technique applied for quantification of die drool amount at the end of the extrusion die: (a) image calibration and (b) determination of die exit area occupied by the accumulated polymer melt (the die drool area). Temperature profile along the screw: $T_1 = 80\,°C$, $T_2 = 200\,°C$, $T_3 = 240\,°C$, $T_4 = 260\,°C$; annular tube (connecting die and extruder) and die exit temperature $T_5 = T_6 = 150\,°C$; extrusion time $= 10$ min.
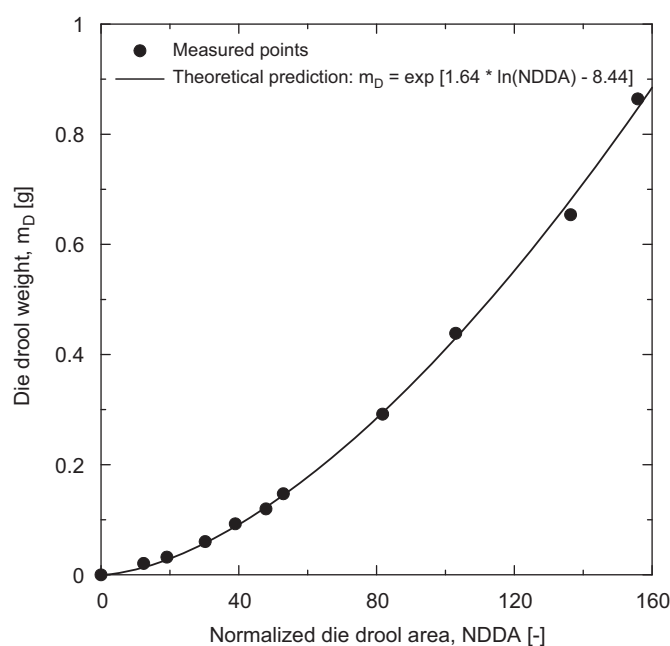
Fig. 8. Normalized die drool area as a function of die drool weight for the tested HDPE sample. Temperature profile along the screw: $T_1 = 80\,°C$, $T_2 = 200\,°C$, $T_3 = 240\,°C$, $T_4 = 260\,°C$; annular tube (connecting die and extruder) and die exit temperature $T_5 = T_6 = 150\,°C$; mass flow rate $= 1.1$ kg h^{-1}.

deformation/rotation in 3D space leading to 'different' 2D surface area for identical drool amount) (Chaloupkova and Zatloukal, 2009). Another complication is given by the impossibility of locating the camera in front of the experimental die (in the perpendicular direction) due to the extrudate drawn off. In order to overcome the above mentioned difficulties, the following strategy has been proposed and applied.

In the first step, the die drool experiment was performed at one set of chosen processing conditions (at which the speed of die drool accumulation was the highest) in order to collect die drooled material after 1, 2, 4, 6, 8, 10, 20, 30, 45 and 60 min. The extruder was stopped after a given extrusion time and the accumulated material (captured by the camera at this moment) was manually removed from the die lip, weighted and the procedure was repeated again for a longer time period. In the second step, the area of the accumulated material at the die exit was determined by using commercially available Didger^{TM} 4

programme; see Fig. 7 for one specific case where 7 calibration points were used to take 45° camera angle view of die drool into account. In the final step, the calibration curve for digital image analysis relating die drool weight and its surface can be constructed as depicted in Fig. 8. It is clearly visible that the relationship between the die drool weight and its surface is exponential, which can be explained by the highly 3D character of the accumulated material shape. In other words, the digital image analysis of die drool phenomenon through its surface determination can be highly erroneous (if the calibration curve is unknown) because the weight vs. surface is not linearly proportional in this case. Due to this, further die drool weight quantification for particular processing conditions was performed through digital image analysis considering such types of the calibration curve.

4. Results and discussion

The characteristics of the die drool phenomenon for HDPE within the time have been investigated for the following processing conditions at which the die drool intensity was found to be the highest: temperature profile along the screw: $T_1=80$ °C, $T_2=200$ °C, $T_3=240$ °C, $T_4=260$ °C; annular tube (connecting die and extruder) and die exit temperature $T_5=T_6=150$ °C; mass flow rate=1.1 kg h^{-1}. The obtained results are shown in Fig. 9. It is clearly visible that the accumulated material takes a torus shape
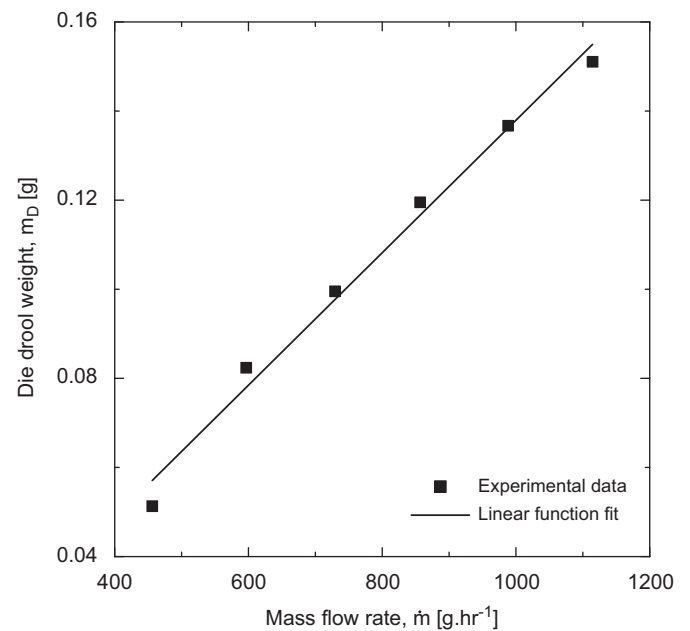
Fig. 10. The effect of mass flow rate on the level of die drool for tested HDPE sample. Temperature profile along the screw: $T_1=80$ °C, $T_2=200$ °C, $T_3=240$ °C, $T_4=260$ °C; annular tube (connecting die and extruder) and die exit temperature $T_5=T_6=150$ °C; mass flow rate=1.1 kg h^{-1}.

Fig. 9. Die drool visualization at the die exit for the tested HDPE sample as a function of extrusion time (temperature profile along the screw: $T_1=80$ °C, $T_2=200$ °C, $T_3=240$ °C, $T_4=260$ °C; annular tube (connecting die and extruder) and die exit temperature $T_5=T_6=150$ °C; mass flow rate=1.1 kg h^{-1}): (a) extrusion time=30 s, (b) extrusion time=15 min and (c) extrusion time=60 min.
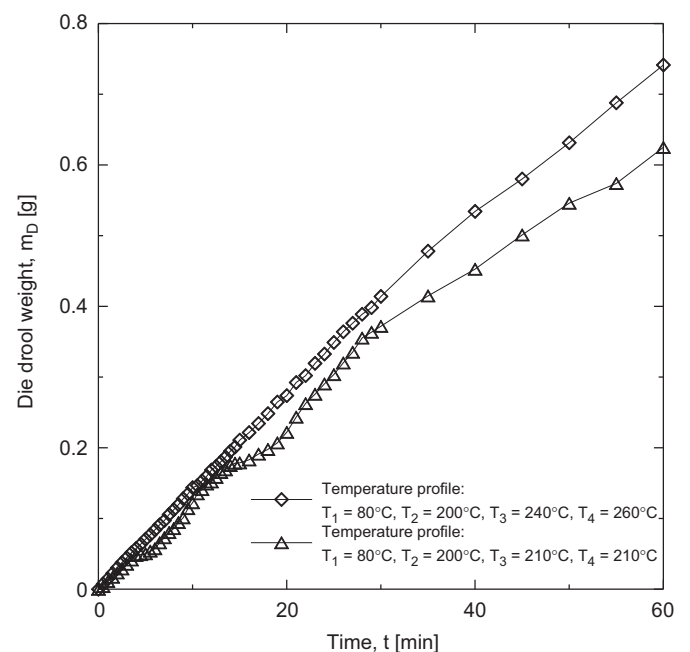
Fig. 11. Die drool amount as a function of time for two different temperature profiles along the screw; mass flow rate=1.1 kg h^{-1}, annular tube (connecting die and extruder) and die exit temperature $T_5=T_6=150$ °C.
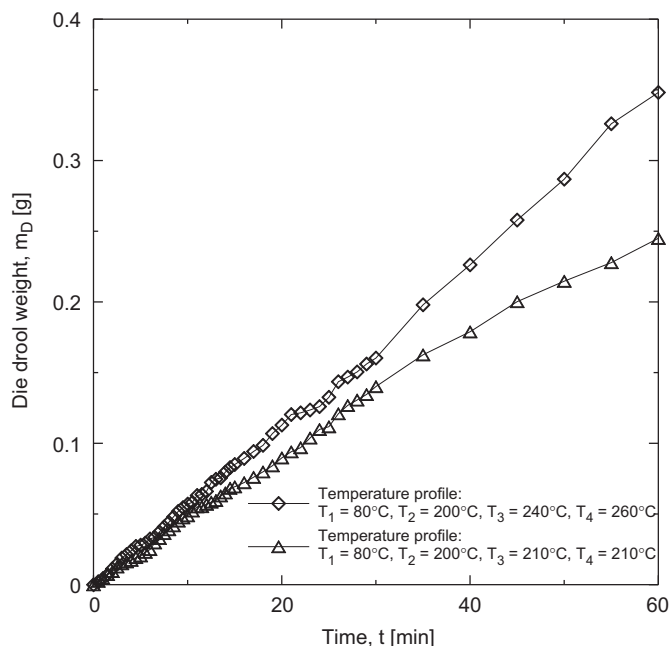
Fig. 12. Die drool amount as a function of time for two different temperature profiles along the screw; mass flow rate=0.5 kg h^{-1}, annular tube (connecting die and extruder) and die exit temperature $T_5=T_6=150\,°C$.

along the exrudate surface rather than flakes or powder as in the case of the external mLLDPE die drool phenomenon (Chaloupkova and Zatloukal, 2009). Moreover, no surface defects occur during HDPE die drool accumulation, which leads us to the conclusion that rupture of the extrudate free surface at the die exit is not the driving factor in this case (unlike for mLLDPE (Chaloupkova and Zatloukal, 2009)).

The effect of mass flow rate on the die drool intensity (for the above mentioned temperature profile) is shown in Fig. 10. It can be seen, that within the investigated mass flow rate range, the mass flow rate increase leads to linear die drool weight increase, which means that the material accumulation speed is much higher than the speed in which the moving extrudate removes the accumulated material from the die lip.

The effect of temperature profile along the screw channel on the die drool intensity is visualized in Figs. 11 and 12 for two different mass flow rates. It is clearly visible that the last two screw zone temperatures increase from 210 to 260 °C causes significant die drool intensity increase even if the annular tube (connecting die and extruder) and die exit temperatures remain unchanged, equal to 150 °C. This behavior can be explained by the increased HDPE melt elasticity due to thermally induced degradation (as shown in the performed rheological analysis) promoting flow induced fractionation of low molecular weight component of HDPE, which is in good correspondence with recent work on molecular weight fractionation during polymer processing (Shelby and Caflisch, 2004) and theoretical study of internal die drool phenomenon (Chaloupkova and Zatloukal, 2009). In more detail, the studied die drool phenomenon can be understood through the original Busse hypothesis (Busse, 1964), stating that during the flow, larger (highly elastic) chains acquire more elastic energy near the wall than small molecules, which generates thermodynamic force tending to increase the concentration of

small molecules at the wall (area of the high stress), and of the larger chains at the centerline (area of the low stress). In the light of this hypothesis (where die drooled material can be viewed as the low molecular weight component of HDPE), increased die drool phenomenon through melt elasticity enhancement can be explained by the increased thermodynamic force driving molecular weight fractionation intensity during the flow.

5. Conclusion

In this work, specific type of digital image analysis technique has been proposed and tested for HDPE die drool investigation. It has been revealed that the temperature increases at the end of the extruder, by keeping the annular tube (connecting die and extruder) and the die exit temperature unchanged, leading the die drool intensity to increase. It has been proved that this type of internal die drool phenomenon is caused by the thermally induced HDPE degradation enhancing melt elasticity and thus promoting the flow induced fractionation of the HDPE melt.

References

Bird, R.B., Armstrong, R.C., Hassager, O., 1987. Dynamics of Polymer Liquids, vol. 1. Wiley, New York.
Busse, W.F., 1964. Phys. Today 17, 32–41 (September).
Chaloupkova, K., Zatloukal, M., 2007. Polym. Eng. Sci. 47, 871–881.
Chaloupkova, K., Zatloukal, M., 2009. J. Appl. Polym. Sci. 111, 1728–1737.
Cox, W.P., Merz, E.H., 1958. J. Polym. Sci. 28, 619–622.
Ding, F., Zhao, L., Giacomin, A.J., Gander, J.D., 2000. Polym. Eng. 40, 2113–2123.
Dhori, P.K., Jeyaseelan, R.S., Giacomin, A.J., Slattery, J.C., 1997. J. Non-Newtonian Fluid Mech. 71, 231–243.
Gander, J.D., Giacomin, J., 1997. Polym. Eng. Sci. 37, 1113–1126.
Hatzikiriakos, S.V., Migler, K.B., 2005. Polymer Processing Instabilities: Control and Understanding. Marcel Dekker, New York.
Hogan, T.A., Walia, P., Dems, B.C., 2009. Polym. Eng. Sci. 49, 333–343.
Holtzen, D.A., Musiano, J.A., 1996. SPE RETEC, St. Louis.
Klein, I., 1981. Plastics World, 112–113.
Kurtz, S.J., Szaniszlo, S.R., 1991. US Patent 5,008,056.
Martyn, M.T., Spares, R., Coates, P.D., Zatloukal, M., 2004. Plast. Rubber Compos. 33 (1), 27–35.
Martyn, M.T., Spares, R., Coates, P.D., Zatloukal, M., 2009. J. Non-Newtonian Fluid Mech. 156 (3), 150–164.
Priester, D.E., 1994. SPE ANTEC Technical Papers, No. 40, p. 2059.
Pivokonsky, R., Zatloukal, M., Filip, P., 2008. J. Non-Newtonian Fluid Mech. 150 (1), 56–64.
Shelby, M.D., Caflisch, G.B., 2004. Polym. Eng. Sci. 44 (7), 1283–1294.
Sentmanat, M.L., Wang, B.N., McKinley, G.H., 2005. J. Rheol. 49, 585–606.
Sentmanat, M.L., 2004. Rheol. Acta 43, 657–669.
Sentmanat, M.L., 2003. US Patent No. 6,578,413.
Tanner, R.I., 1985. Engineering Rheology. Clarendon, Oxford.
Zatloukal, M., Vlcek, J., Slanik, A., Lengalova, A., Simonik, J., 2002. Appl. Rheol. 12 (3), 126–132.
Zatloukal, M., De Witte, J., 2006. Plast. Rubber Compos. 35 (4), 149–154.
Zatloukal, M., Kopytko, W., Saha, P., Martyn, M., Coates, P.D., 2005. Plast. Rubber Compos. 34 (9), 403–409.
Zatloukal, M., Kopytko, W., Lengalova, A., Vlcek, J., 2005. J. Appl. Polym. Sci. 98 (1), 153–162.
Zatloukal, M., Martyn, M.T., Coates, P.D., Vlcek, J., 2004. Plast. Rubber Compos. 33 (7), 305–309.
Zatloukal, M., Vlcek, J., Tzoganakis, C., Saha, P., 2002. Polym. Eng. Sci. 42 (7), 1520–1533.
Zatloukal, M., Vlcek, J., Tzoganakis, C., Saha, P., 2001. Int. Polym. Process 16 (2), 198–207.

PAPER II
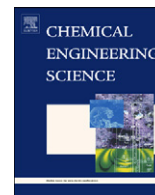
Experimental investigation of flow induced molecular weight fractionation during extrusion of HDPE polymer melts

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ABSTRACT

In this work, two different HDPEs with virtually identical number, M_n, and weight, M_w, average molecular weights were investigated from rheological as well as die drool phenomenon point of view. It has been revealed that long-chain branching, low polymer melt elasticity and shear viscosity significantly reduce die drool phenomenon at the die exit region. It has been concluded that die drool phenomenon of HDPE polymer melts can be explained by the flow induced molecular weight fractionation.

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1. Introduction

The first notice about polymer melt fractionating during flow under inhomogeneous stresses in capillary was presented by Busse (1964). He claimed that "capillary viscometer should tend to fractionate polymer molecules with respect to molecular weight along the capillary radius." His original imagination assumed that near the wall, molecules of high molecular weight acquire large amount of free energy of elastic deformation, while very small molecules do not. Because of thermodynamic force, then, these small molecules tend to increase the concentration near the wall, and, on the other hand, the rest of longer molecules goes close to the centreline. Schreiber and Storey (1965) experimentally tested Busse's hypothesis on three different polyethylene samples. First was low density polyethylene, whereas second and third were blends of linear polyethylenes with broad and narrow molecular weight distribution, respectively. Static light scattering showed significant reduction of molecular weight in surface layer for the first sample and, more pronounced, for the second one. On the other hand, in the third sample no marked fractionation was detected. With the assumption that molecular weight fractionation during shear flow is a thermodynamical

phenomenon, Schreiber (1974) investigated extruded parts in different layers (from the centerline to the skin) by calorimetry. He has concluded that the observed molecular redistribution is a feature of crystallizable polymers with very wide molecular weight distributions. Recently, Shelby and Caflisch (2004) speculated that fractionation of polymer melts in the shear flow could explain 'drooling' of low molecular weight material from die lips, i.e. die drool phenomenon widely discussed in the open literature (Chan, 1995; Gander and Giacomin, 1997; Dhori et al., 1997; Ding et al., 2000; Chaloupkova and Zatloukal, 2006, 2007, 2009; Musil and Zatloukal, 2009, 2010; Zatloukal and Musil, 2010; Zatloukal et al., 2008, 2009; Zatloukal and Chaloupkova, 2007; Brachet et al., 2009).

The main aim of this work is to test this hypothesis using two different high density polyethylenes with virtually identical polydispersity index.

2. Experimental

2.1. Material characterization

Two different types of stabilized HDPE polymers (HDPE Tipelin 6300B KEZ 830795, extrusion grade, TVK, Hungary, and HDPE Liten FB 29 2961, extrusion grade, Chemopetrol, Czech Republic—basic characteristics are summarized in Table 1) were chosen for the experimental research.

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Table 1
Basic characterization of chosen polymers.

	HDPE Liten FB 29 2961	HDPE Tipelin 6300B KEZ 830795
Density[a] (g cm^{-3})	0.950	0.954
M_n (g mol^{-1})	17,175	16,695
M_w (g mol^{-1})	194,950	194,450
M_z (g mol^{-1})	1,045,500	892,350
M_{z+1} (g mol^{-1})	2,342,000	1,815,000
M_w/M_n (–)	11.35	11.65
Melt flow index (2.16 kg/190 °C)[a] (g/10 min)	0.15	0.3
Zero-shear rate viscosity (Pa s)	420,000	123,000
Activation energy (kJ mol^{-1})	17.063	17.039
DSC peak melting point (°C)	132.9	132.7
DSC heat of fusion (J g^{-1})	216.1	245.8
Crystallinity (%)	73.76	83.91

[a] Taken from the original material data sheets.

Advanced Rheometric Expansion System ARES 2000 (Rheometrics Scientific, USA) in parallel plates geometry mode was used to measure linear viscoelastic properties (storage modulus G′, loss modulus G″, complex viscosity η^*) as well as steady state shear viscosity and first normal stress coefficient at low shear rates. In order to capture the Newtonian plateau for both tested HDPE samples, the linear viscoelastic properties were determined through 13 measurements performed at temperature step of 20 °C within 130–370 °C temperature range (all measurements over 210 °C were done under inert N_2 gas atmosphere to prevent polymer sample degradation). Time temperature superposition principle was used to create mastercurve at one reference temperature 190 °C.

Transient uniaxial extensional viscosity η_E was determined by Sentmanat Extensional Rheometer SER-HV-A01 model (Xpansion Instruments, USA (Sentmanat, 2003, 2004; Sentmanat et al., 2005)) attached to ARES 2000. The 'steady state' extensional viscosity data were taken from the peaks appearing on the transient viscosity curves for corresponding extensional strain rates.
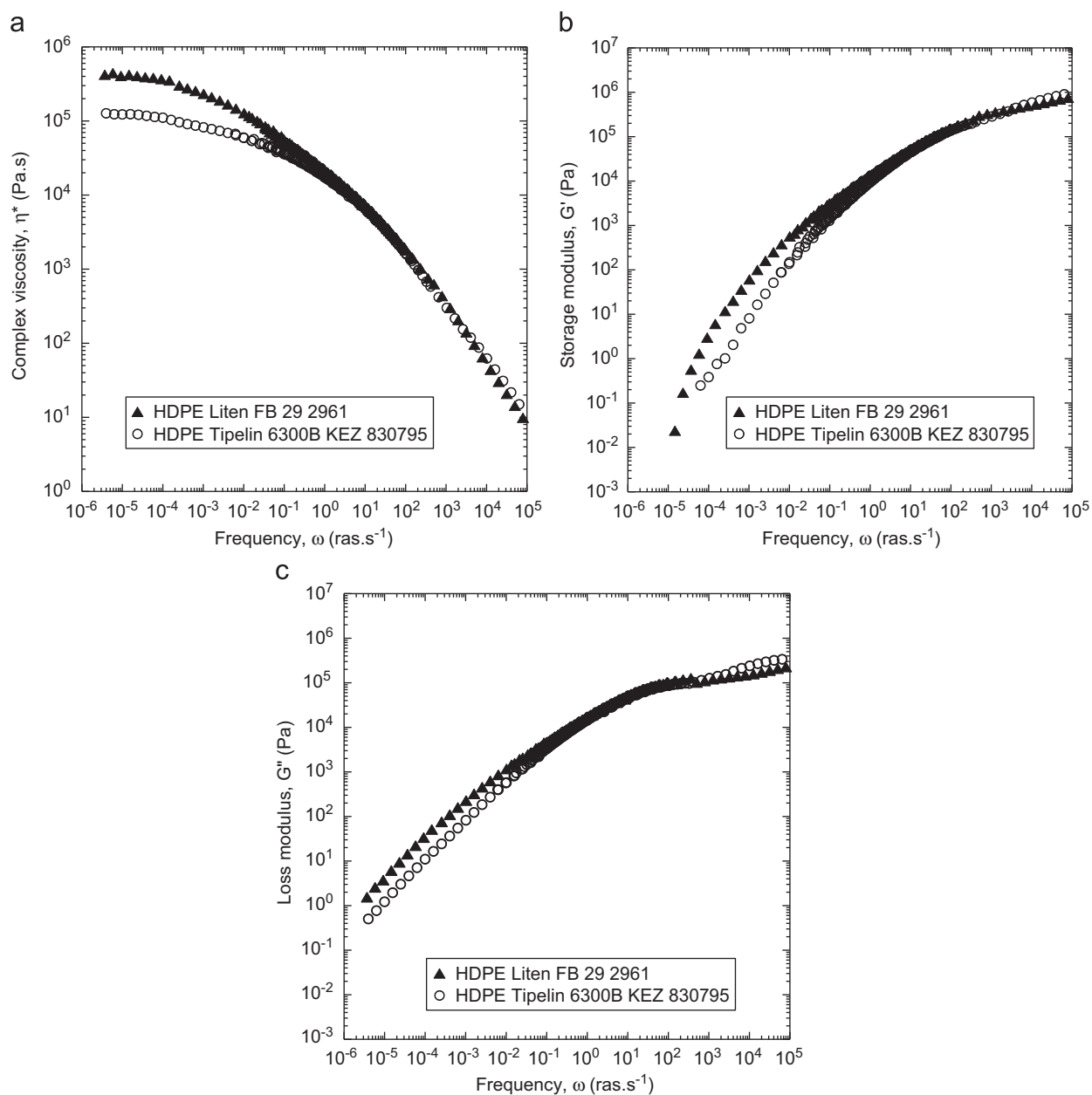
Fig. 1. Linear viscoelastic properties for both tested HDPE polymers measured at 190 °C. (a) Complex viscosity η^*, (b) storage modulus G′ and (c) loss modulus G″.

The steady state shear viscosity and first normal stress coefficient ψ_1 (determined according to Han's exit pressure drop method (Han, 1976, 1998)) were measured at high shear rates using a twin bore capillary rheometer Rosand RH7-2 (Rosand Precision, UK).

All measurements were performed at 190 °C and they are provided in Figs. 1–5. Even if both tested samples have comparable steady state shear and uniaxial extensional viscosities at high deformation rates (due to similarities in number, M_n, and weight, M_w, average molecular weights, see Table 1 and Fig. 5),
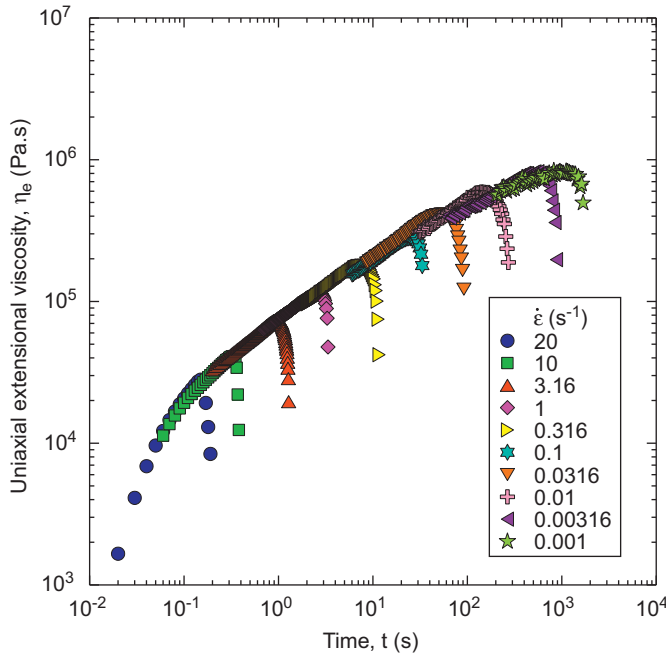
Fig. 2. Transient uniaxial extensional viscosity for HDPE Liten FB 29 2961 at 190 °C.
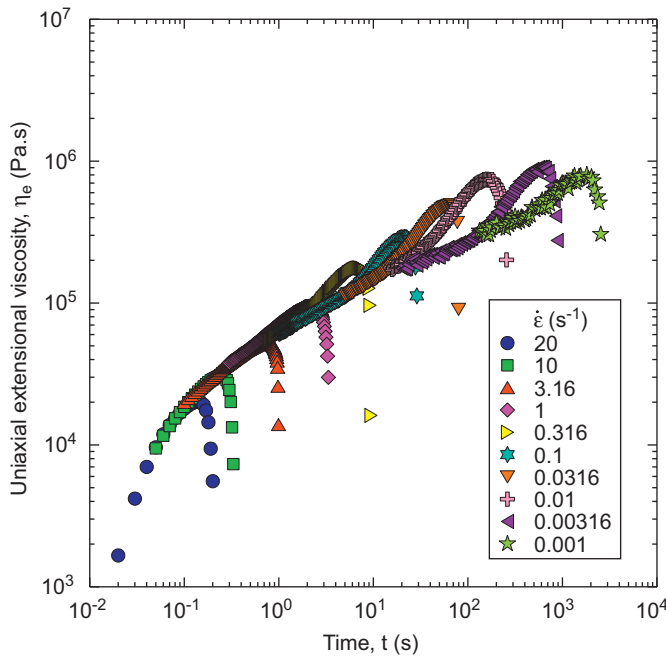
Fig. 3. Transient uniaxial extensional viscosity for HDPE Tipelin 6300B KEZ 830795 at 190 °C.
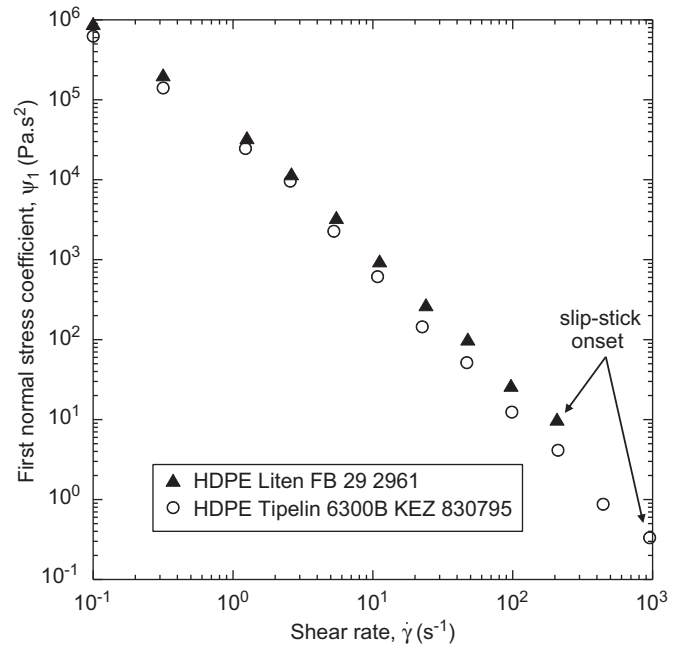
Fig. 4. First normal stress coefficient for both tested HDPE samples measured at 190 °C.
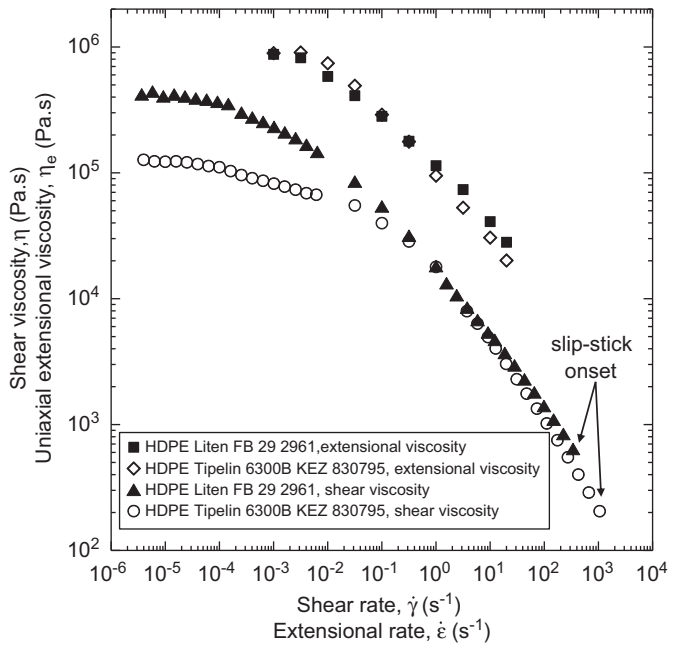
Fig. 5. Steady shear and uniaxial extensional viscosities for both tested HDPE samples measured at 190 °C.

the following differences have been found. First, HDPE Tipelin 6300B KEZ 830795 has lower Newtonian viscosity as well as elasticity than HDPE Liten FB 29 2961. Second, HDPE Tipelin 6300B KEZ 830795 is slightly branched due to the presence of extensional strain hardening in transient uniaxial extensional viscosity curves, which is not the case of HDPE Liten FB 29 2961, therefore it can be considered as the linear polymer (compare Figs. 2 and 3). Finally, the HDPE Liten FB 29 2961 is more sensitive to slip-stick flow instabilities, which are typical for HDPE polymer melts (Hatzikiriakos and Migler, 2005), than HDPE Tipelin 6300B KEZ 830795 as visible in Fig. 5 (more details are provided in the Results and discussion section).

2.2. Die drool measurements

The die drool experiments were carried out 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 $L_3=12D$), which was included in the laboratory extrusion line. The schematic 3D transparent section view of the laboratory extrusion line is depicted in Fig. 6. This line consists of extruder with four heating zones, transition annular part, specially designed annular extrusion die, which was introduced in (Chaloupkova and Zatloukal, 2007, 2009), photo camera Dimage Z3 model (Konica Minolta, Japan) with resolution of 4 Mpx placed near the die exit, and draw-off mechanism.

In all our experiments, the extruder zones (from the hopper to the die) were heated to $T_1=160\,^\circ$C, $T_2=165\,^\circ$C, $T_3=170\,^\circ$C and $T_4=170\,^\circ$C by keeping the annular tube (connecting die and extruder) and die exit temperature constant, $T_5=T_6=170\,^\circ$C, ensuring that no sample degradation takes place. Furthermore, one pressure transducer DYNA-4-1M-15/46 model (Dynisco, USA) in the range of 1000 bar (100 MPa) was placed at the end of the extruder and sampled pressure data during all experiments were directly recorded into PC by special software (Control Web 6 Runtime). Die drool accumulation has been investigated at fixed above-mentioned temperature profile along the screw and ten different mass flow rates ranging from 0.163 up to 1.577 kg h^{-1} (i.e. from 148 up to 1240 s^{-1} in terms of apparent wall shear rate).
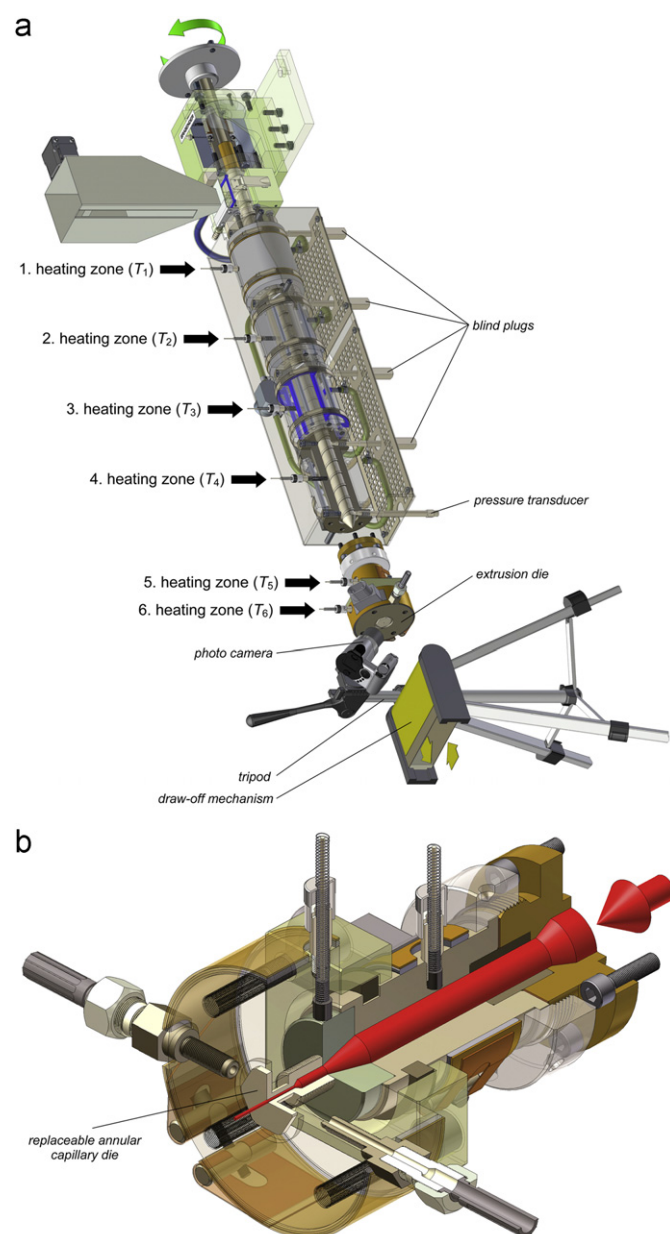
The procedure of die drool mass evaluation was following. The extruder was stopped after 10 min of extrusion and the accumulated material was carefully manually removed from the die lip by a tweezer, weighted on sensitive analytical balance and the procedure was repeated again for the higher mass flow rate. For each individual test, barrel, screw and all parts of the die have been perfectly manually cleaned to ensure the reproducibility of all performed measurements. Die drool intensity has been expressed in dimensionless form through buildup ratio BR, which is defined as the ratio of the mass flow rate of the die drool divided by the total mass flow rate of the extrudate [see the first row of Table 3 in Gander and Giacomin (1997)].

In order to eliminate any possible thermo-oxidative degradation of the polymer sample inside the die as well as at the die lip, the following steps have been done.

- The extrusion time and temperature for each single test was adjusted to be very low, i.e. equal to 10 min and 170 $^\circ$C, respectively. Fig. 7 clearly shows that the complex viscosity, loss and storage moduli measured by Advanced Rheometric Expansion System ARES 2000 remain unchanged even for 300 min at 170 $^\circ$C, proving that no degradation takes place inside the die for the chosen processing conditions.
- Nitrogen N$_2$ has been used as the inert gas atmosphere at the die lip to suppress thermo-oxidative degradation of the accumulated polymer for all the performed experiments.

In Figs. 8 and 9, FTIR spectra measured on Nicolet 380 FTIR Spectrometer (Thermo Scientific, USA) for original polymer pellets, extrudate sample and drooled sample (collected without and with

Fig. 6. Schematic 3D transparent section view of laboratory extrusion line in experimental configuration (a) together with 3D transparent quarter section view of the extrusion die (b).
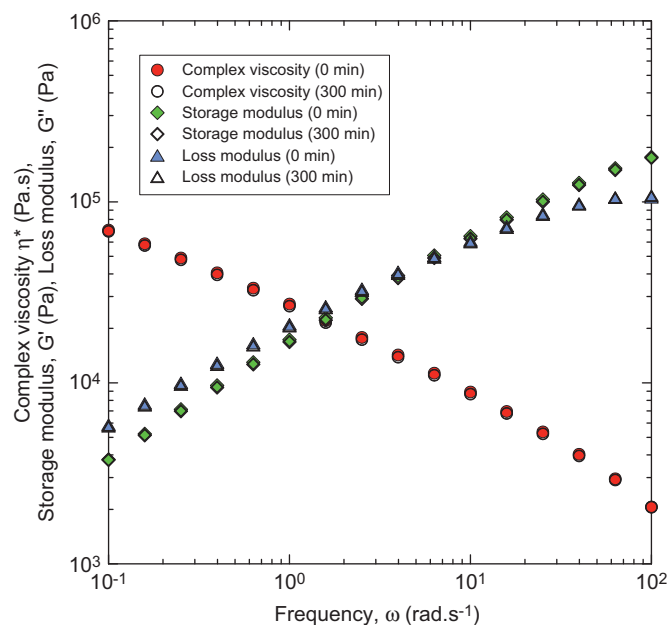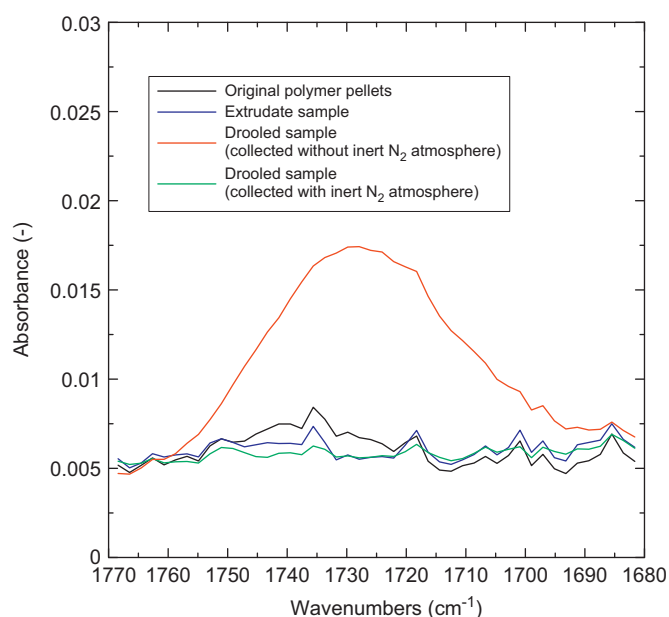

Fig. 7. Complex viscosities, storage and loss moduli for HDPE Liten FB 29 2961 at the zero time (close symbols) and after 300 min test (open symbols).
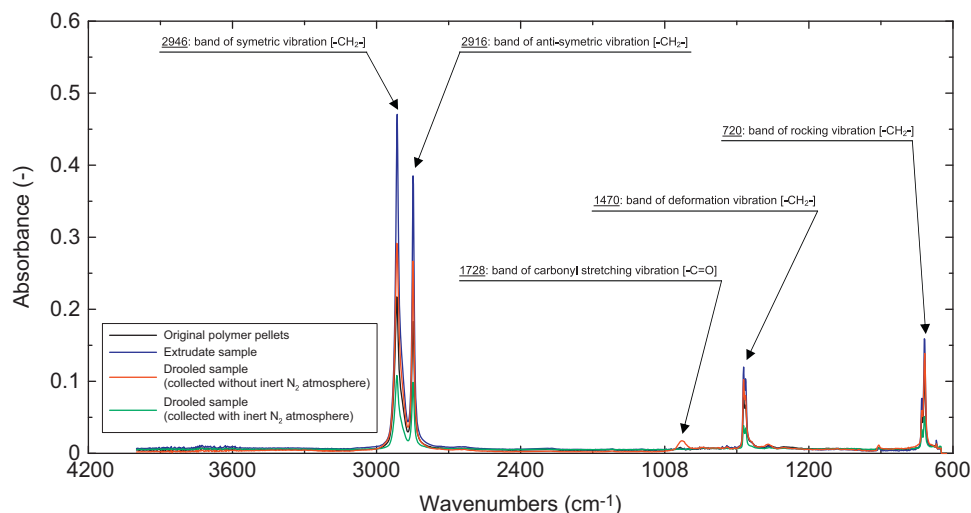
Fig. 8. FTIR spectra of original polymer pellets, extrudate sample and drooled sample (collected without and with inert N_2 gas atmosphere) for HDPE Liten FB 29 2961 samples.

Fig. 9. Detail of the vicinity of wavenumber 1730 cm^{-1} (band of carbonyl –C=O– stretching vibration) for HDPE Liten FB 29 2961 samples.

inert N_2 gas atmosphere at one reference apparent shear rate 1016 s^{-1}) are provided in order to check whether thermo-oxidative degradation takes place during chosen processing conditions.

It is clearly visible that no thermo-oxidative degradation takes place for all tested samples (except of drooled sample collected without inert N_2 gas atmosphere). Just note that thermo-oxidative degradation takes place if a peak at 1730 cm^{-1} wavenumber (band of carbonyl –C=O– stretching vibration) is detected on FTIR spectrum for particular sample. Clearly, the use of the inert N_2 gas atmosphere at the die exit is necessary to suppress degradation at the die exit for the drooled material at the die lips.

3. Results and discussion

The apparent shear rate evolution of die drool phenomenon for both tested HDPE samples, at the identical processing conditions described above, is depicted in Supplemental material Videos S1

and S2. It is clearly seen that more viscous, more elastic and linear HDPE Liten FB 29 2961 generates much higher level of die drool phenomenon (BR varies between 10^{-5} and 10^{-4} depending on the applied apparent shear rate) in contrary to less viscous, less elastic and branched HDPE Tipelin 6300B KEZ 830795 (BR is not measurable within the chosen processing conditions), which is consistent with the theoretical conclusion reported in Chaloupkova and Zatloukal (2009) stating that increase in elasticity promotes die drool phenomenon. In order to more deeply understand flow induced molecular weight fractionation (for the polymer sample with measurable BR), the Molecular Weight Distribution (MWD) as well as M_n, M_w, M_z and M_{z+1} molecular weight averages have been determined by GPC technique (PL-GPC 220 model, Polymer Laboratories, UK) for all drooled samples (each produced and collected at a given apparent shear rate), which are compared with the MWD for original HDPE polymer (see Fig. 10). Clearly, the die drool material represents low molecular weight fraction of HDPE. In more detail, Figs. 11–14 show the effect of flow intensity (expressed by the apparent shear rate) on the M_n, M_w, M_z and M_{z+1} molecular weight averages of drooled samples. As the apparent shear rate increases, M_n (characterizing the fraction of very small molecules) and M_{z+1} (characterizing the fraction of very long molecules) decrease whereas the M_w and M_z averages remain unchanged. This simply means that as the flow intensity increases, the amount of the short molecules in the fractionated polymer is increased too.

It seems that intensity of the slip-stick flow instabilities (and slip intensity at high shear rates) is in direct relation with the level of HDPE molecular weight fractionation occurring during the flow as indicated in Figs. 15 and 16 (where measured wall shear stress is plotted as a function of the apparent shear rate), i.e. first, the die drool onset occurs at transition slip-stick and slip flow regime, and, second, the sample (linear HDPE) with higher slip-stick intensity shows higher die drool intensity and vice versa. It seems that chain branching significantly reduces flow induced molecular weight fractionation (die drool phenomenon) by reduced chain mobility through increased level of entanglements between the chains, which works against the forces driving flow induced molecular weight fractionation processes. The obtained experimental data can be interpreted in the following way. Under slip-stick region (at a given apparent shear rate range), low molecular weight polymer chains start to be fractionated from the main polymer melt stream, which results in low viscosity layer formation at the die wall. When the certain amount of low
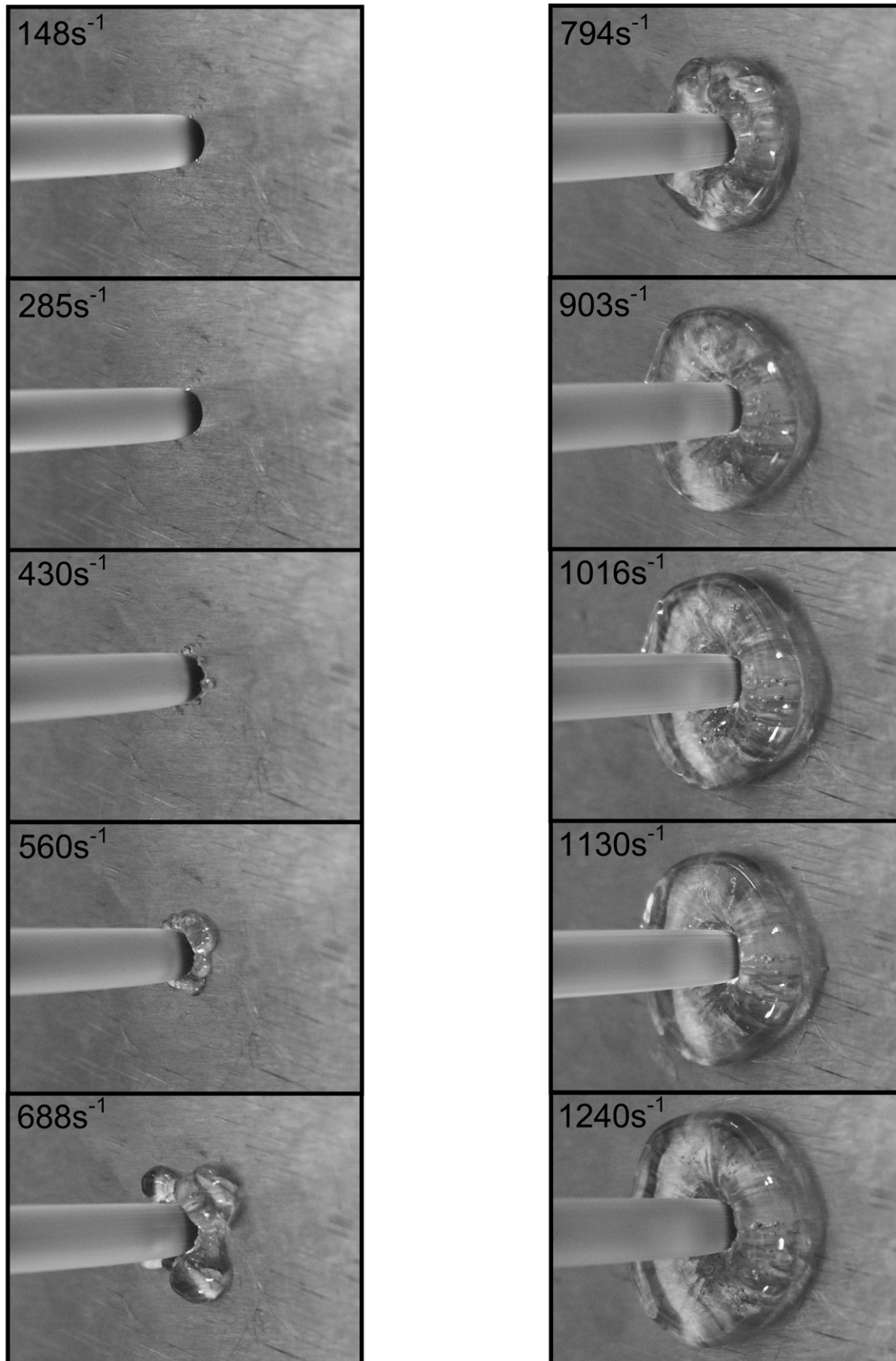
Video S1. Die exit visualization after 10 min of extrusion of HDPE Liten FB 29 2961 at different apparent shear rates, $T=170$ °C. Die drool time development for apparent shear rate 1016 s^{-1} is provided here in the form of supplementary material as the video. A video clip is available online. Supplementary material related to this article can be found online at doi:10.1016/j.ces.2010.06.047.
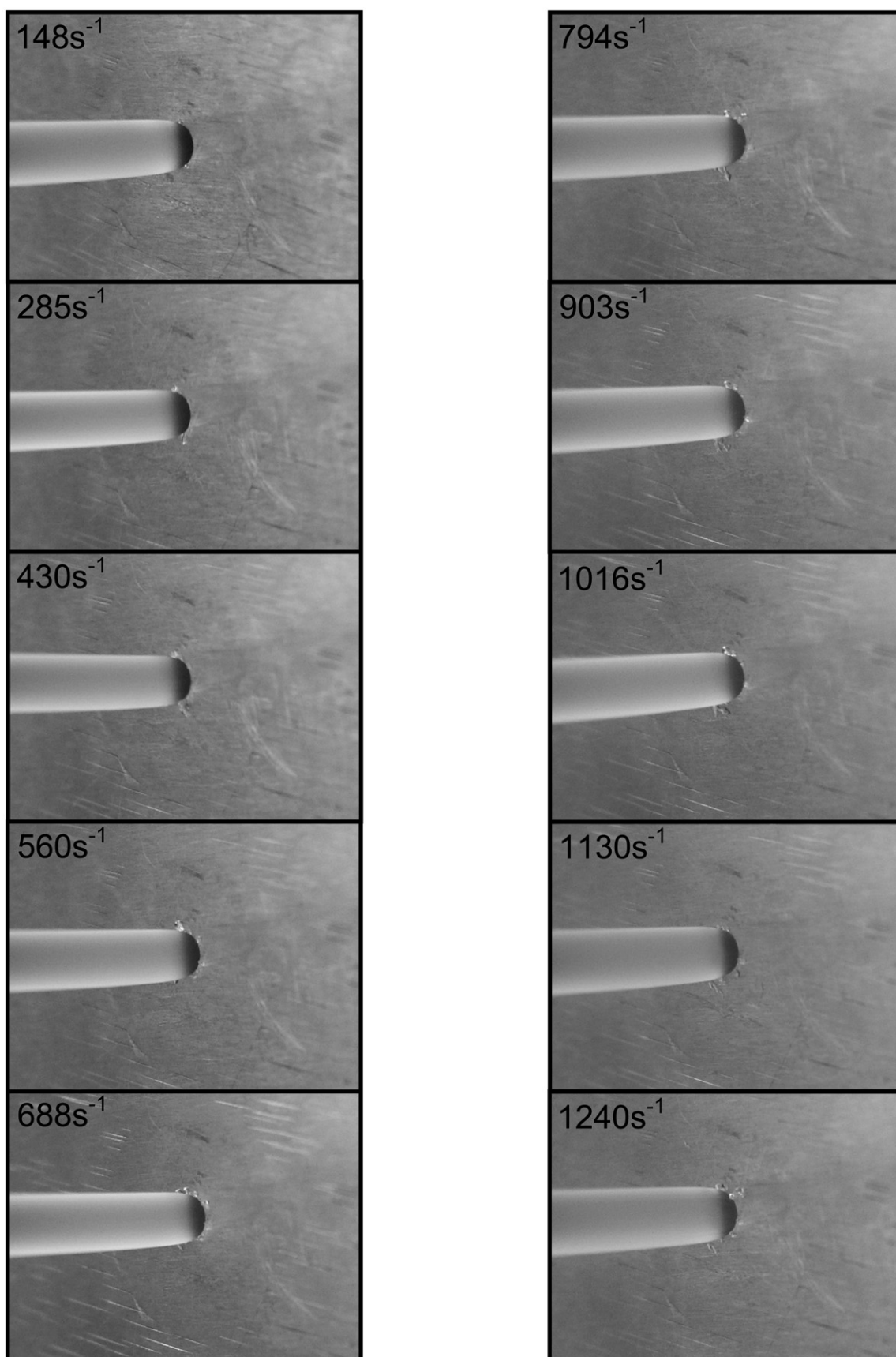
Video S2. Die exit visualization after 10 min of extrusion of HDPE Tipelin 6300B KEZ 830795 at different apparent shear rates, $T=170$ °C. Die drool time development for apparent shear rate 1016 s^{-1} is provided here in the form of supplementary material as the video. A video clip is available online. Supplementary material related to this article can be found online at doi:10.1016/j.ces.2010.06.047.
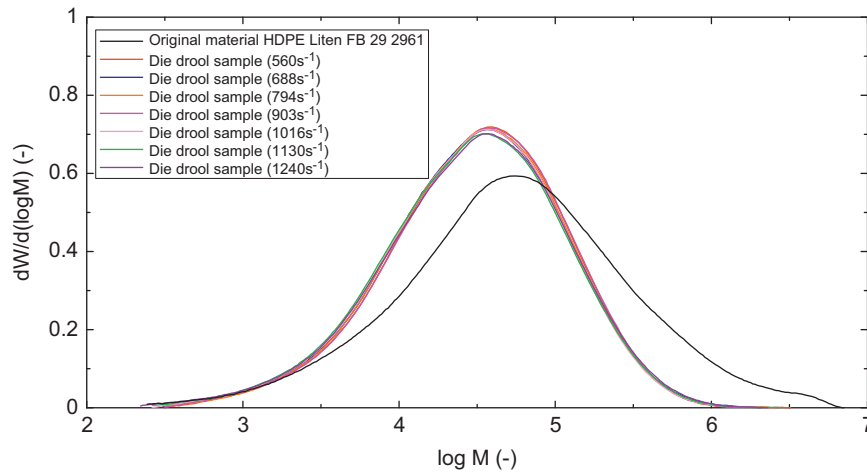
Fig. 10. Comparison between Molecular Weight Distribution (MWD) for original HDPE Liten FB 29 2961 and drooled samples collected under inert N_2 gas atmosphere from the die lip at different apparent shear rates.
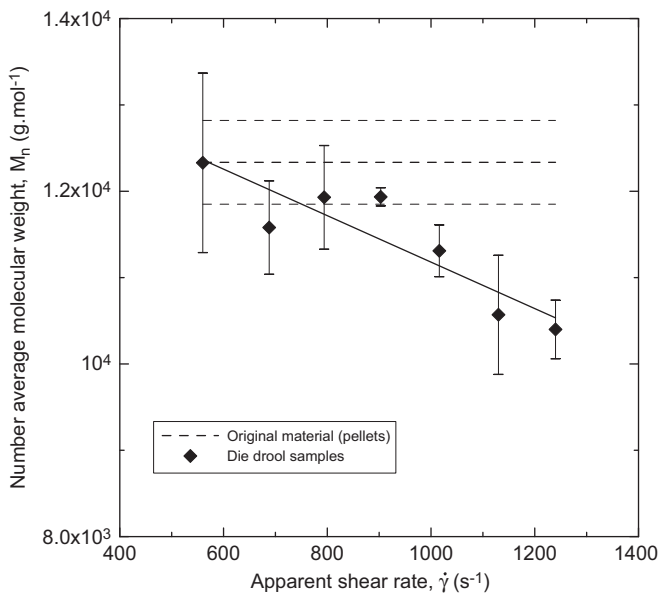
Fig. 11. Effect of apparent shear rate on the number average molecular weight (M_n) of the drooled sample. The original HDPE Liten FB 29 2961 sample is taken as the reference.
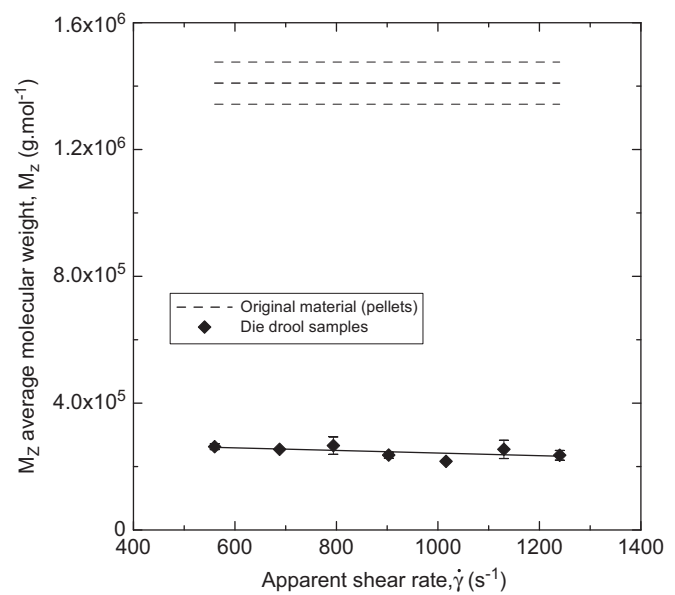
Fig. 13. Effect of apparent shear rate on M_z average molecular weight of the drooled sample. The original HDPE Liten FB 29 2961 sample is taken as the reference.
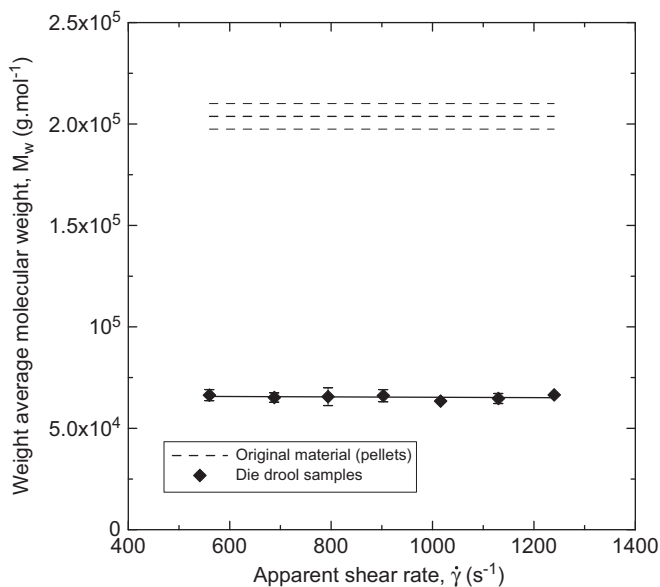
Fig. 12. Effect of apparent shear rate on weight average molecular weight (M_w) of the drooled sample. The original HDPE Liten FB 29 2961 sample is taken as the reference.
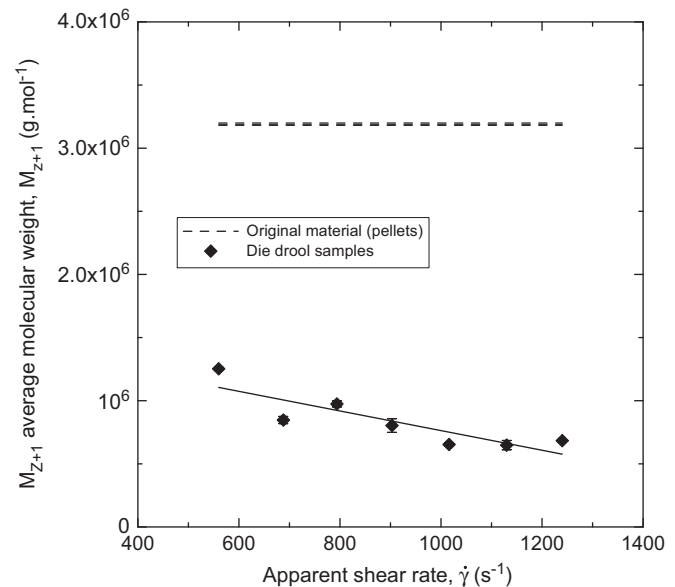
Fig. 14. Effect of apparent shear rate on M_{z+1} average molecular weight of the drooled sample. The original HDPE Liten FB 29 2961 sample is taken as the reference.
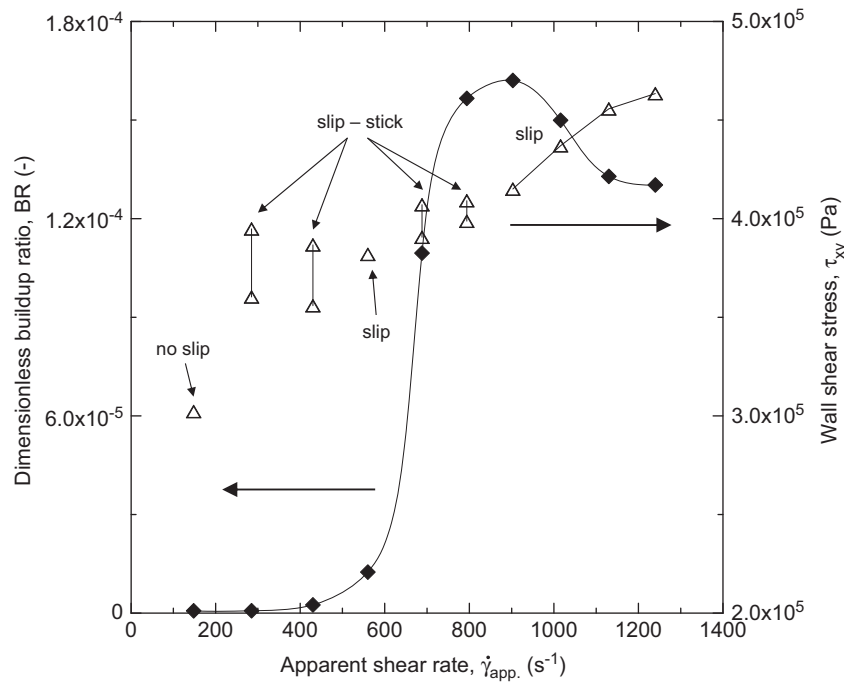
Fig. 15. Dimensionless buildup ratio (10 min of extrusion)/wall shear stress as a function of apparent shear rate for HDPE Liten FB 29 2961, $T = 170\,°C$.
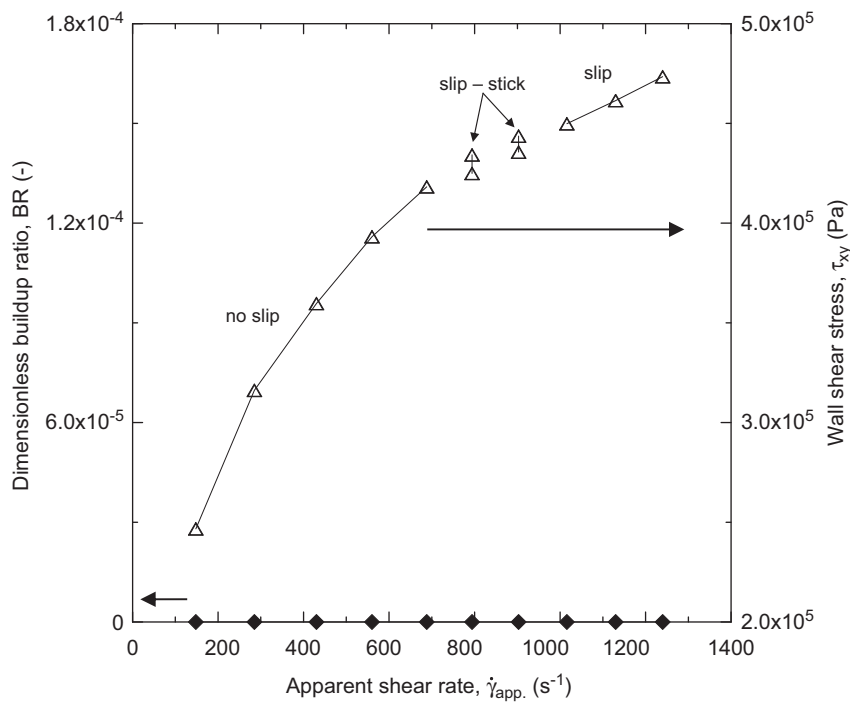
Fig. 16. Dimensionless buildup ratio (10 min of extrusion)/wall shear stress as a function of apparent shear rate for HDPE Tipelin 6300B KEZ 830795, $T = 170\,°C$.

enough viscosity layer is created at sufficiently high apparent shear rates, full slip starts to occur at the die wall. This however results in accumulation of created low viscosity polymer at the die lips.

It is crucially important to mention that drool rate has been significantly reduced for HDPE sample when the processing temperature has been increased. In more detail, buildup ratio BR for HDPE Liten FB 29 2961 (at low apparent shear rates) has been reduced in order of magnitudes when the processing temperature has been changed from 170 to 210 °C, i.e. from

10^{-5} down to 10^{-9}. This is consistent with the proposed explanation for the die drool phenomenon for HDPE polymers. For increased temperature, HDPE melt viscosity as well as elasticity decrease, slip-stick instabilities are shifted to much higher apparent shear rates and most importantly, they become less intensive (i.e. intensity of flow induced fractionation is reduced). On the other hand, it has been shown in our recent work (Musil and Zatloukal, 2010) that the extrusion at very high temperatures (260 °C) may lead to HDPE melt viscosity and elasticity increase (due to thermally induced degradation

followed by recombination of polymer chains) causing more intensive die drool phenomenon in comparison with low temperature extrusion (210 °C).

In fact, the adjustment of 170 °C as the processing temperature in the performed die drool experiments for HDPE polymer melts was the key factor to accelerate the die drool rate in this work.

At the end of this section, let us compare the nature of die drool phenomenon for the investigated HDPE melt with the metallocene based LLDPE melt reported in the open literature (Ding et al., 2000; Chaloupkova and Zatloukal, 2006, 2007, 2009; Zatloukal et al., 2008; Zatloukal and Chaloupkova, 2007). In the case of the mLLDPE, the flow induced molecular weight fractionation has been found to be connected with the die exit only (external die drool) whereas for HDPE melt, the flow induced molecular weight fractionation seems to take place predominantly inside the die (internal die drool), i.e. nature of the die drool phenomenon for both samples seems to be different.

4. Conclusion

For the two grades of HDPE studied, results suggest that increase in HDPE chain branching, decrease in their elasticity (ψ_1), shear viscosity and M_w significantly reduce die drool phenomenon occurring during the extrusion process. It has been demonstrated that the die drool material represents low molecular weight fraction of HDPE, suggesting that die drool phenomenon occurring during the extrusion of HDPE polymer melts can be considered as a result of the flow induced molecular weight fractionation.

References

Brachet, P., Hinrichsen, E.L., Larsen, A., Bjorndal, L.K., Brendryen, F., Lia, T., 2009. The problem of die drool in the extrusion of recycled polyethylene. Prog. Rubber Plast. Recycl. Technol. 25, 199–211.

Busse, W.F., 1964. Two decades of high-polymer physics: a survey and forecast. Phys. Today 17, 32–41.

Chaloupkova, K., Zatloukal, M., 2006. Analysis of die drool phenomenon for metallocene based linear polyolefins. In: Proceedings of the Annual Technical Conference, ANTEC, vol. 2, pp. 956–960.

Chaloupkova, K., Zatloukal, M., 2007. Theoretical and experimental analysis of the die drool phenomenon for metallocene LLDPE. Polym. Eng. Sci. 47, 871–881.

Chaloupkova, K., Zatloukal, M., 2009. Effect of die design on die drool phenomenon for metallocene based LLDPE: theoretical and experimental investigation. J. Appl. Polym. Sci. 111, 1728–1737.

Chan, C.M., 1995. Viscosity and the formation of die drool at the polymer-metal interfaces—effects of surface-coatings. Int. Polym. Process. 10, 200–203.

Dhori, P.K., Jeyaseelan, R.S., Giacomin, A.J., Slattery, J.C., 1997. Common line motion. III. Implications in polymer extrusion. J. Non-Newtonian Fluid Mech. 71, 231–243.

Ding, F., Zhao, L., Giacomin, A.J., Gander, J.D., 2000. Flaring dies to suppress die drool. Polym. Eng. Sci. 40, 2113–2123.

Gander, J.D., Giacomin, A.J., 1997. A Review of die lip buildup in plastics extrusion. Polym. Eng. Sci. 37, 1113–1126.

Han, C.D., 1976. Rheology in Polymer Processing. Academic Press, New York (Chapter 5).

Han, C.D., 1998. In: Collyer, A.A., Clegg, D.W. (Eds.), Techniques in Rheological Measurements. Chapman and Hall, London (Chapter 6).

Hatzikiriakos, S.G., Migler, K.B., 2005. Polymer Processing Instabilities, Control and Understanding. Marcel Dekker, New York.

Musil, J., Zatloukal, M., 2009. Investigation of internal die drool phenomenon for different HDPEs. In: Proceedings of the AIP Conference, vol. 1152, pp. 69–74.

Musil, J., Zatloukal, M., 2010. Investigation of die drool phenomenon for HDPE polymer melt. Chem. Eng. Sci. 65 (23), 6128–6133.

Schreiber, H.P., 1974. Component redistribution in extrusion of polyethylene compounds. J. Appl. Polym. Sci. 18, 2501–2508.

Schreiber, H.P., Storey, S.H., 1965. Molecular fractionation in capillary flow of polymer fluids. Polym. Lett. 3, 723–727.

Sentmanat, M.L., 2003. Dual Wind-up Extensional Rheometer. US Patent 6,578,413.

Sentmanat, M.L., 2004. Miniature universal testing platform: from extensional melt rheology to solid-state deformation behavior. Rheol. Acta 43, 657–669.

Sentmanat, M.L., Wang, B.N., McKinley, G.H., 2005. Measuring the transient extensional rheology of polyethylene melts using the SER universal testing platform. J. Rheol. 49, 585–606.

Shelby, M.D., Caflisch, G.B., 2004. Shear field induced diffusion and molecular weight fractionation during polymer processing. Polym. Eng. Sci. 44, 1283–1294.

Zatloukal, M., Chaloupkova, K., 2007. Effect of die design and wall slip on die drool phenomenon for metallocene based LLDPE: theoretical and experimental investigation. In: Proceedings of the Annual Technical Conference, ANTEC, vol. 4, pp. 2379–2383.

Zatloukal, M., Musil, J., 2010. Applied rheology for HDPE die drool phenomenon. In: Proceedings of the Annual Technical Conference, ANTEC, vol. 1, pp. 748–751.

Zatloukal, M., Chaloupkova, K., Martyn, M., Coates, P., 2008. Analysis of metallocene based LLDPE flow with respect to die drool phenomenon by using FEM and flow visualization experiment, Technical Papers. Reg. Tech. Conf.—Soc. Plastic. Eng. 1, 192–196.

Zatloukal, M., Sambaer, W., Libotte, A., 2009. Understanding and quantification of die drool phenomenon during polypropylene extrusion process. In: Proceedings of the Annual Technical Conference, ANTEC, vol. 3, pp. 1572–1577.

PAPER III

Experimental Investigation of Flow Induced Molecular Weight Fractionation Phenomenon for Two Linear HDPE Polymer Melts Having Identical M_n and M_w but Different M_z and M_{z+1} Average Molecular Weights

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ABSTRACT

In this work, *flow induced molecular weight fractionation* 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 *molecular weight fractionation* is promoted by increase in linear HDPE chain length, it takes place just in a very thin layer near the die wall and its onset and intensity are in direct relationship with *slip-stick* flow instability.

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 [1] in 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 [2] for broad Molecular Weight Distribution (MWD) linear high density polyethylene melts by using static laser light scattering, Schreiber [3] for broad MWD crystallizable polymers by applying calorimetry technique, Shelby and Caflisch [4] for poly(ethylene terephthalate) and poly(ethylene-co-cyclohexylenedimethylene terephthalate) utilizing gel permeation chromatography (GPC), Musil and Zatloukal [5, 6] for linear and branched high density polyethylenes by gel permeation chromatography and flow visualization technique. It has been shown that first, *flow induced fractionation* is promoted by broadening MWD [5, 7] and chain branching decrease [5], second, its onset and intensity well correlates with the *slip-stick* instability [5, 6] and finally, it can result in unwanted accumulation of low molecular weight components at the die exit [5], i.e. *die drool* phenomenon which is widely discussed in the open literature [4-20]. In order to understand the complicated link 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 experimentally investigated in this work.

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.

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 Figures 1-2. As can be seen, even if both polymers have identical polydispersity index (M_w/M_n), i.e. the same MWD, and contain practically the same amount of short and intermediate chains, they slightly differ in amount of long chains because their M_z and M_{z+1} molecular weight averages are different (see definition bellow).

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

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].

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 (25 mm plates diameter) within 0.1 up to 100s^{-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 determined through 13 single measurements performed at temperature step of 20°C within 130°C-370°C temperature range (all measurements over 190°C were done under inert N$_2$ gas atmosphere to prevent polymer sample thermo/oxidative degradation). Finally, time temperature

superposition principle was used to create mastercurve at one reference temperature 190°C.

Thermal stability was investigated at 160°C (flow fractionation test temperature) in air atmosphere within 300 minutes time interval through variation intensity evaluation in all above mentioned linear viscoelastic properties.

Shear Viscosity

Rotational rheometer *ARES 2000* and twin-bore capillary rheometer *Rosand RH7-2* (Rosand Precision, United Kingdom) in circular capillaries mode (diameter of 1 mm, *L/D* of 0 and 16) were used for determination of steady-state shear viscosity, η, at low and high shear rates, respectively.

Slip-stick instability quantification

Slip-stick phenomenon represents the flow condition at which time dependent pressure/stress oscillation occurs at particular apparent shear rate. Its onset and intensity were determined by *Rosand RH7-2* capillary rheometer equipped with capillary with diameter 0.5 mm, and *L/D* ratio 16 utilizing apparent wall shear stress difference variable defined as:

$$\Delta\tau_{\mathrm{w}}(\dot{\gamma}) = \tau_{\mathrm{w,MAX}}(\dot{\gamma}) - \tau_{\mathrm{w,MIN}}(\dot{\gamma}) \tag{2}$$

where $\tau_{\mathrm{w,MAX}}(\dot{\gamma})$ and $\tau_{\mathrm{w,MIN}}(\dot{\gamma})$ represent the maximum and minimum wall shear stress, respectively, at the given apparent shear rate.

Extensional Viscosity

Transient uniaxial extensional viscosity, η_{E}, was determined on *Sentmanat Extensional Rheometer SER-HV-A01 model* (Xpansion Instruments, USA [21-24]) attached to *ARES 2000* rotational rheometer which is depicted in Figure 3. The sample width was fixed to be 12.7 mm (done by calibrated dual blade cutter) and the thickness about 0.65 mm (measured precisely before each test by a micrometer). Note that the 'steady state' extensional viscosity data were taken from the peaks appearing on the transient viscosity curves for corresponding extensional strain rates.

First Normal Stress Coefficient Measurements

The steady state first normal stress coefficient, ψ_1, was determined at high shear rate range according to Han's exit pressure drop method [25, 26] on *Rosand RH7-2* capillary rheometer with attached slit die (see Figure 4) having channel length, $l = 100$ mm, width, $w = 10$ mm and gap size, $g = 1$ mm, and utilizing three pressure transducers placed along the channel length (expressed here as distance from the die entry): 31 mm (10,000 PSI), 60 mm (10,000 PSI) and 89 mm (1,500 PSI). All measurements have been done in a constant piston speed mode at apparent shear rates for which the wall shear stress was higher than 25 kPa in all experiments as suggested in [26]. This justifies the extrapolation procedure for exit pressure determination and thus validating the exit pressure method for reliable determination of ψ_1.

Flow Induced Molecular Weight Fractionation Intensity Measurements

Flow induced molecular weight fractionation intensity measurements 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 $L_3 = 12D$*) which was included in specially designed laboratory extrusion line. At the end of the extruder, pressure transducer *DYNA-4-1M-15/46* model (Dynisco, USA) in range of 1,000 bar (100 MPa) was placed and sampled pressure data during all experiments were directly recorded into PC by special software (Control Web 6 Runtime). The overall 3D view of laboratory extrusion line is depicted in Figure 5 (detail views of the extruder and the die are introduced in our previous work [5]). Section view of used replaceable capillary also with dimensions (*L/D* ratio is 9.375) is shown in Figure 6. The line consists of extruder with four electrically heated zones, transition annular part, specially designed annular extrusion die, which was introduced and used in [5, 6 and 15, 16], 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.

The extruder zones (from the hopper to the die) were heated to $T_1 = 150°C$, $T_2 = 155°C$, $T_3 = 160°C$ and $T_4 = 160°C$ by keeping the annular tube (connecting die and extruder) and die exit temperature constant, $T_5 = T_6 = 160°C$ ensuring that no sample degradation takes place. It should be noted that the low exiting temperature 160°C for both melts was chosen to achieve highly pronounced fractionation effect due to high efficiency of both melts to store elastic energy because of their high relaxation times [5, 16, 19, 20] as well as to suppress any thermal/oxidative degradation. Furthermore, mass flow rates (MFRs) were varied from 0.075 kg.hr^{-1} up to 0.725 kg.hr^{-1} (*i.e.* from 68 s^{-1} up to 652s^{-1} in term of apparent shear rates) in order to investigate *flow induced molecular weight fractionation* under stable flow regime, unstable *slip-stick* flow and *"superflow"* (pseudo-stable flow at the highest shear rates at which significant *wall slip* takes place) for both HDPE melts.

In order to measure fractionated (*drooled*) polymer mass accumulated at the die exit, the following direct methodology, originally proposed by Chai *et al.* in 2001 [7], was used. The extruder was stopped after 10 minutes of extrusion and the accumulated material was carefully manually removed from the die lip by a tweezer, weighted on a sensitive analytical balance and the procedure was repeated again for the higher MFR. The procedure has been repeated three times for each MFR to calculate corresponding standard deviation. Before each set of three independent 10 minutes tests (at one apparent shear rate), barrel, screw and all parts of the die have been disassembled and perfectly manually cleaned. Then, *die drool* intensity has been expressed in dimensionless form through buildup ratio *BR* (firstly introduced by Gander and Giacomin in [12]):

$$BR = \frac{\dot{B}}{\dot{m}} \tag{3}$$

where $\dot{m}$ is total mass flow rate of extruded polymer melt and $\dot{B}$ means buildup rate:

$$\dot{B} = \frac{B}{t_e} \tag{4}$$

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

With the aim to directly evaluate the *flow induced fractionation* tendency inside the extrudate (at given apparent shear rate), 0.1 mm thick extrudate skin and 0.8 mm diameter extrudate core samples were mechanically prepared by a thin cutter from each extruded string.

Molecular weight averages (M_n, M_w, M_z and M_{z+1}) as well as molecular weight distributions were determined by *PL-GPC 220* model (Polymer Laboratories, United Kingdom) equipped with refractometric detector *PL-220 DRI* for all samples representing *drooled* material, extrudate core and skin. Mobile phase was 1,2,4-trichlorbenzene HPLC grade (Scharlau, Spain) stabilized by 0.025% Santonox R (flow rate: 1 ml.min^{-1}). Each polymer sample was prepared as 1mg dissolved in 1ml of mobile phase and it was measured two times. Testing temperature was 160°C.

RESULTS AND DISCUSSION

In this section, results of rheological characterization and *flow induced molecular weight fractionation* intensity measurements for both investigated HDPE polymer melts are presented and discussed in more detail.

Rheological Characterization

Rheological characteristics for both HDPE polymer melts were determined at one reference temperature 190°C and the results are depicted in Figures 7-11.

Firstly, both samples can be considered as virtually linear ones because no strain hardening peaks can be detected on their transient uniaxial extensional viscosity, η_e, curves (see Figures 7 and 8).

Secondly, both samples differ only in the content of chains having very long relaxation times (long chains) because both storage G' and loss G'' moduli, complex viscosity η^* and steady shear/uniaxial extensional viscosity difference between both samples can only be detected at very low frequencies (below 10^{-1} rad.s^{-1}, see Figures 9a, 9b and 9c) and deformation rates (below 10^{-1}s^{-1}, see Figure 10), respectively. Clearly, HDPE 1 has higher zero-shear viscosity, zero-extensional viscosity, shear elasticity (expressed by ψ_1, Figure 11) and sensitivity to *slip-stick* flow instabilities (see Figures 10, 11 and especially Figure 12) than HDPE 2 sample, which is in good correspondence with average molecular weights provided in Table 1.

Finally, thermal/oxidative degradation does not take place for both samples during 300 minutes at 160°C (flow fractionation test temperature) because G', G'' and η^* remains unchanged as shown in Figures 13 and 14. This is important finding which justify the statement that 10 minutes long *flow induced molecular weight fractionation* experiments utilized in this work are predominantly driven by the Busse's thermodynamic force and not by the thermal/oxidative polymer melt degradation inside the extruder/extrusion dies, which could (due to chain scission) also cause creation of the low molecular weight components consequently *drooling* at the die exit as shown by Hogan and Walia in 2009 [18].

Flow Induced Molecular Weight Fractionation

First, the effect of shear flow intensity on *flow induced fractionation* is analyzed here through apparent shear rate dependent dimensionless buildup ratio (defined above) and real die exit face visualization, which are provided in Figures 15 and 16-17, respectively. It is clearly seen that the level of *die drool* 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 Figures 1, 2), 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 18 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 [5] and the original Busse's *flow induced molecular weight fractionation* theory [1].

Second, the effect of flow type (i.e. stable flow regime, unstable *slip-stick* flow and pseudo-stable *"superflow"*) on the *flow induced molecular weight fractionation* is investigated here through Figures 19 and 20, where both, apparent wall shear stress and dimensionless buildup ratio are plotted as the functions of apparent shear rate. It is clearly visible that for both HDPE samples, the onset as well as intensity of *slip-stick* instability and *molecular weight fractionation* is in direct relationship. Moreover, dimensionless buildup ratio (*BR*) sensitivity to apparent shear rate, $\dfrac{\partial BR}{\partial \dot{\gamma}_{app}}$, is the highest in the *slip-stick* regime and its value increases with increased M_z and M_{z+1} molecular weight averages. This supports the hypothesis that low viscosity layer starts

to be formed at the die wall under *slip-stick* flow regime due to intensive fractionation of low molecular weight polymer chains from the main polymer melt stream. When the critical apparent shear rate, at which the certain amount of low enough viscosity layer at the die wall is created, full slip (*superflow*) starts to occur which is followed by low viscosity polymer accumulation at the die lips (*die drool*).

Finally, in order to investigate *flow induced molecular weight fractionation* in more detail, MWD curves for 0.1 mm thick extrudate skin and 0.8 mm diameter extrudate core samples (prepared from 2.5 mm diameter extruded string at apparent shear rate $348s^{-1}$) were compared with corresponding *die drool* sample and virgin pellets for both tested HDPEs (see Figure 21). As can be seen, MWD curves for extrudate skin, extrudate core and virgin pellets are practically identical and *die drool* sample represents their low molecular weight fraction, which suggests that 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 given processing conditions) and the extrusion process itself has no effect on the polymer bulk.

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 revealed 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). It has been demonstrated, firstly, that the onset as well as intensity of *slip-stick* instability and *molecular weight fractionation* is in direct relationship, and secondly, buildup ratio sensitivity to apparent shear rate is the highest in the *slip-stick* regime and its value increases with increased M_z and M_{z+1} molecular weight averages. Finally, it has been found that MWD curves for extrudate skin, extrudate core and virgin pellets are practically identical and *die drool* sample represents their low molecular weight fraction, which suggests that 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) and the extrusion process itself has no effect on the polymer bulk.

ACKNOWLEDGEMENT

REFERENCES

1.   Busse, W. F. *Two Decades of High-Polymer Physics: a Survey and Forecast*. Physics Today **19(9)**, 32-41 (1964).

2.   Schreiber, H. P., Storey, S. H. *Molecular Fractionation in Capillary Flow of Polymer Fluids*. Polymer Letters **3(9)**, 723-727 (1965).

3.   Schreiber, H. P. *Component Redistribution in Extrusion of Polyethylene Compounds*. J. App. Polym. Sci. **18(8)**, 501-508 (1974).

4.   Shelby, M. D., Caflisch, G. B. *Shear Field Induced Diffusion and Molecular Weight Fractionation During Polymer Processing*. Polym. Eng. and Sci. **44(7)**, 1283-1294 (2004).

5.   Musil, J., Zatloukal, M. *Experimental Investigation of Flow Induced Molecular Weight Fractionation During Extrusion of HDPE Polymer Melts*. Chem. Eng. Sci. **66(20)**, 4814-4823 (2011).

6.   Musil, J., Zatloukal, M., Gough, T., Martyn, M. *Experimental Investigation of Die Drool and Slip-stick Phenomena during HDPE Polymer Melt Extrusion*. AIP Conference Proceedings **1375**, 26-42 (2011).

7.   Chai, C. K., Adams, G., Frame, J. *Polyethylene Die Deposit – Measurement, Formation Mechanism and Routes to Reduction*. Annual Technical Conference – ANTEC, Conference Proceedings **1**, 401-405 (2001).

8.   Klein, I. *Die drool: What Causes It, How to Avoid It*. Plastics World **39(5)**, 112-113 (1981).

9.   Kurtz, S. J., Szaniszlo, S. R. *Reduction in Die Drool in Filled Resins and Product Improvement*. US Patent 5,008,056 (1991).

10.   Rakestraw, J. A., Waggoner, M. G. *Polymer Extrusion Die and Use of Thereof*. US Patent 5,458,836 (1995).

11.   Chan, C. M. *Viscosity and the Formation of Die Drool at the Polymer-Metal Interfaces*. Intern. Polymer Process. **10(3)**, 200-203 (1995).

12.   Gander, J. D., Giacomin, A. J. *Review of Die Lip Buildup in Plastics Extrusion*. Polym. Eng. and Sci. **37(7)**, 1113-1126 (1997).

13. Lee, C. D. *Die Lip Build-up in the Extrusion of Highly Filled Low Density Polyethylene.* Annual Technical Conference – ANTEC, Conference Proceedings **1**, 117-121 (2002).

14. Hwang, A. J., Nam, G. J. *The Effect of Ingredients and Processing Conditions on the Extrusion Processability of Halogen-Free Flame Retardant Thermoplastics.* Annual Technical Conference – ANTEC, Conference Proceedings **1**, 192-196 (2005).

15. Chaloupkova, K., Zatloukal, M. *Theoretical and Experimental Analysis of the Die Drool Phenomenon for Metallocene LLDPE.* Polym. Eng. Sci. **47(6)**, 871-881 (2007).

16. Chaloupkova, K., Zatloukal, M. *Effect of Die Design on Die Drool Phenomenon for Metallocene Based mLLDPE: Theoretical and Experimental Investigation.* J. App. Polym. Sci. **111(4)**, 1728-1737 (2009).

17. Brachet, P., et al. *The Problem of Die Drool in the Extrusion of Recycled Polyethylene.* Progress in Rubber, Plastics and Recycling Technology **25(4)**, 199-211 (2009).

18. Hogan, T. A., Walia, P., Dems, B. C. *Investigation of the Relationships Between Die Build up and Die Swell.* Polym. Eng. and Sci. **49(2)**, 333-343 (2009).

19. Zatloukal, M., Sambaer, W., Libotte, A. *Understanding and Quantification of Die Drool Phenomenon during Polypropylene Extrusion Process.* Annual Technical Conference – ANTEC, Conference Proceedings **3**, 1572-1577 (2009).

20. Musil, J., Zatloukal, M. *Investigation of Die Drool Phenomenon for HDPE Polymer Melt.* Chem. Eng. Sci. **65(23)**, 6128-6133 (2010).

21. Sentmanat, M. L. *Dual Windup Extensional Rheometer.* US Patent 6,578,413 (2003).

22. Sentmanat, M. L. *Dual Windup Drum Extensional Rheometer.* US Patent 6,691,569 (2004).

23. Sentmanat, M. L. *Miniature Universal Testing Platform: From Extensional Rheology to Solid-State Deformation Behaviour.* Rheol. Acta **43(6)**, 657-669 (2004).

24. Sentmanat, M. L., Wang, G. H., Mckinley, G. H. *Measuring the Transient Extensional Rheology of Polyethylene Melts Using the SER Universal Testing Platform*. J. Rheol. **49(3)**, 585-606 (2005).

25. Han, C. D. *On Slit- and Capillary-Die Rheometry*. Trans. Soc. Rheol. **18(1)**, 163-190 (1974).

26. Han, C. D. in Collyer, A. A., Clegg D. W. (Eds.) *Techniques in Rheological Measurements (Chapter 6)*. London: Chapman and Hall, 1998.

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/2.16kg)* (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 (°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.

Table 2: Basic characteristics of *die drool* samples collected after 10 minutes of extrusion at apparent shear rate 348s^{-1}.

	HDPE 1	HDPE 2
	die drool sample	*die drool sample*
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 (-)	5.01	5.92
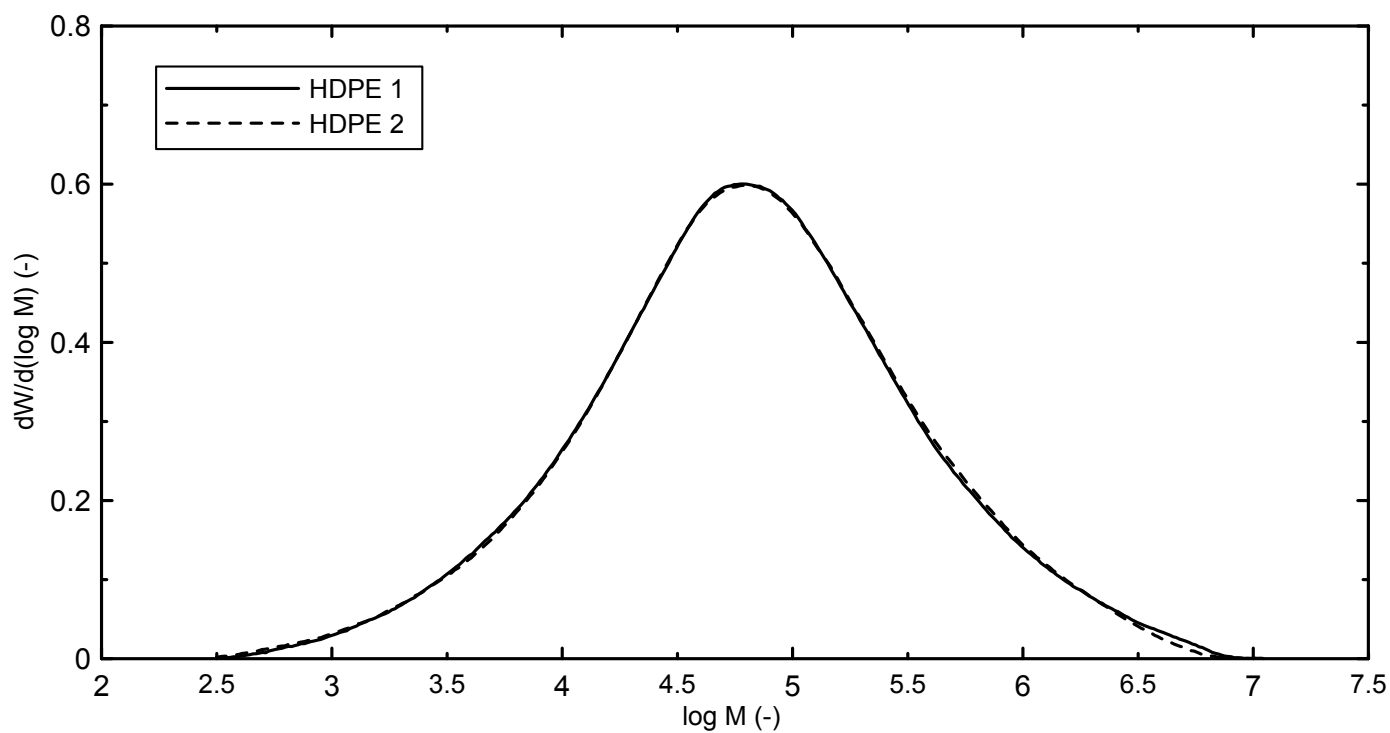
Figure 1 Molecular weight distribution (MWD) curves for both investigated polymer melts (in the form of virgin pellets).
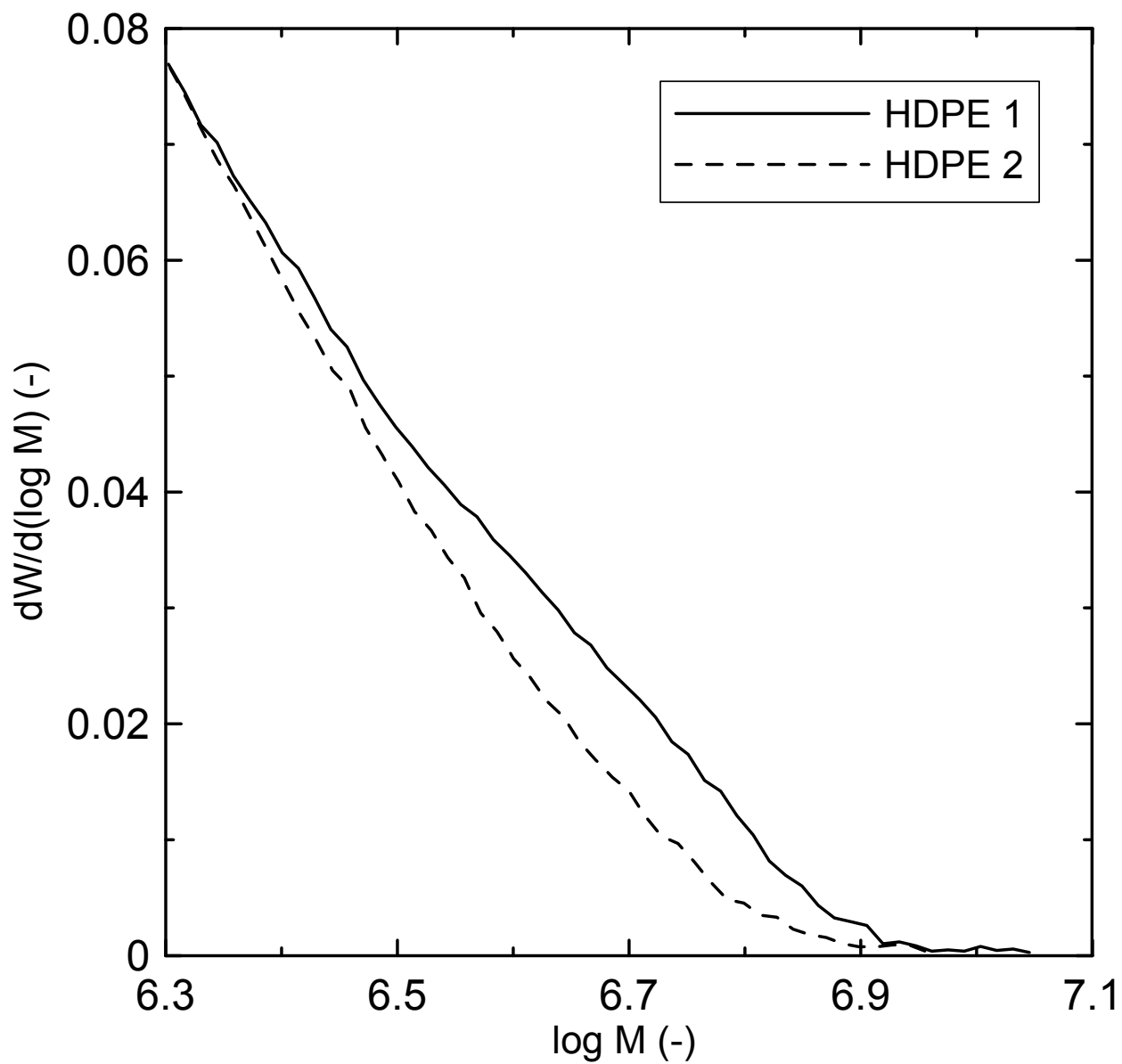
Figure 2 Detail view of high molecular weight tail in MWD curves for both investigated polymer melts (in the form of virgin pellets).
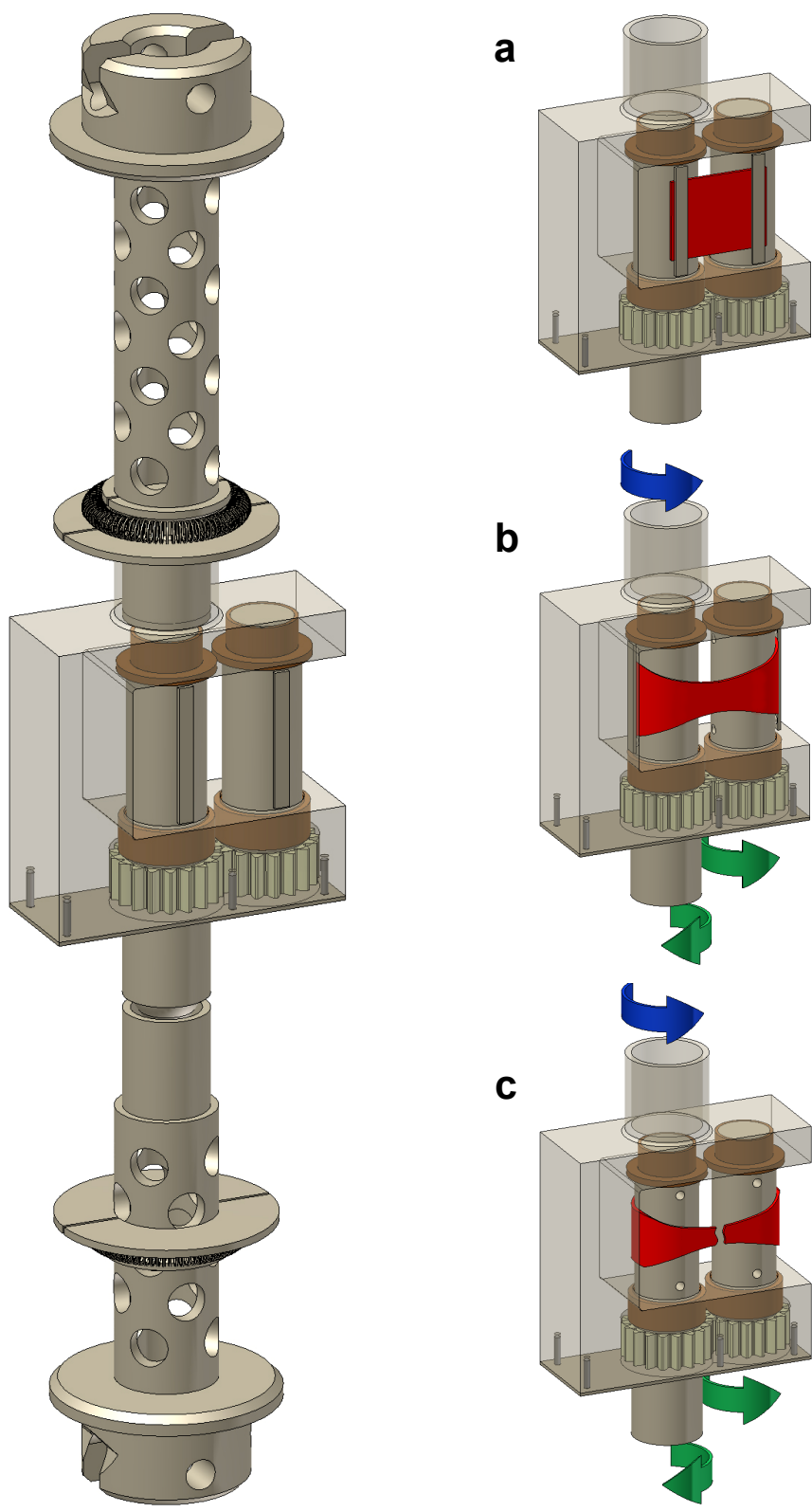
Figure 3 Detachable extensional rheometer *SER-HV-A01* (left) and polymer melt sample behaviour during one test (right): (a) sample loading, (b) sample stretching, (c) sample at break.
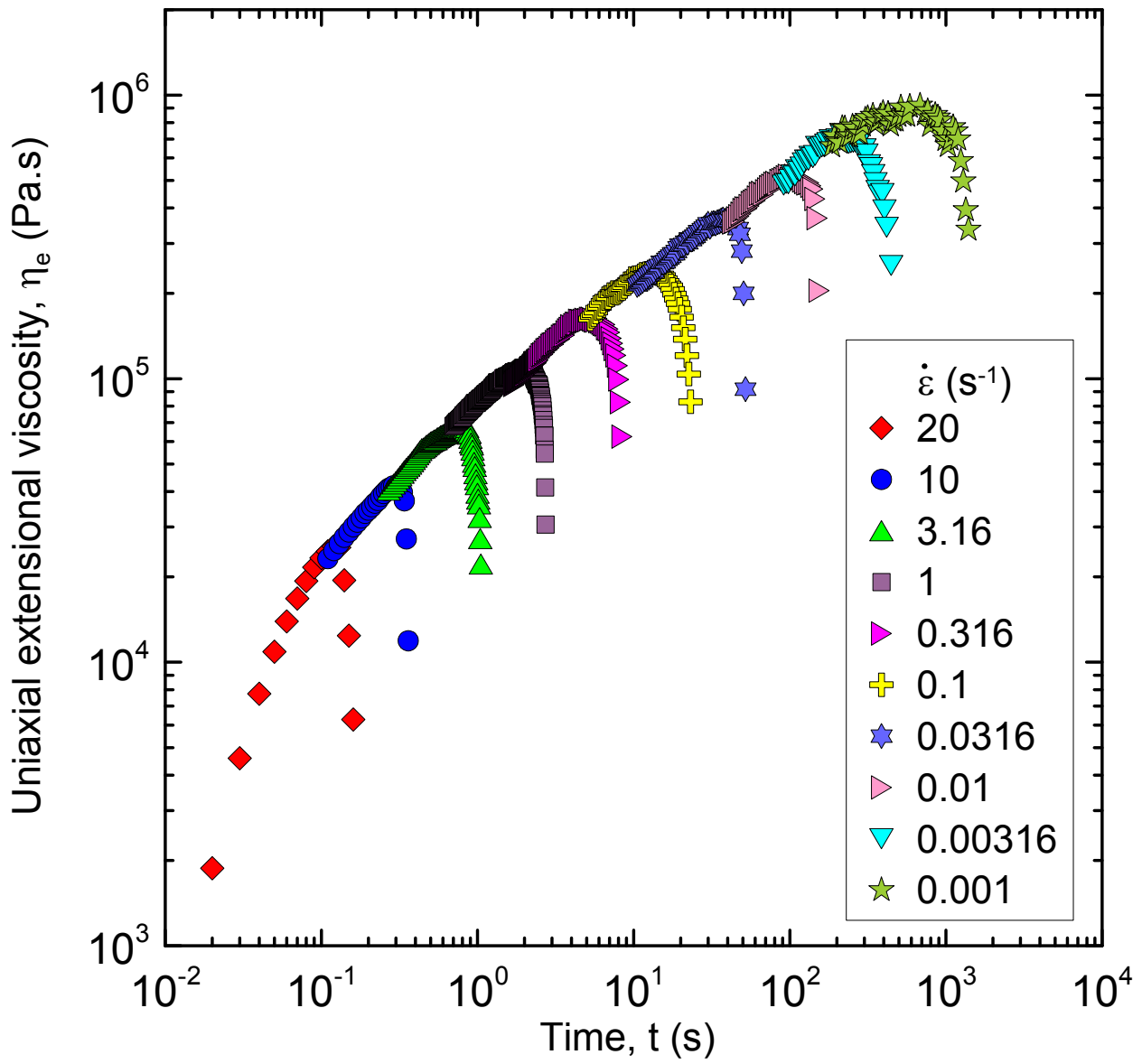
pressure transducer 1
(10,000 PSI)

pressure transducer 2
(10,000 PSI)

pressure transducer 3
(1,500 PSI)
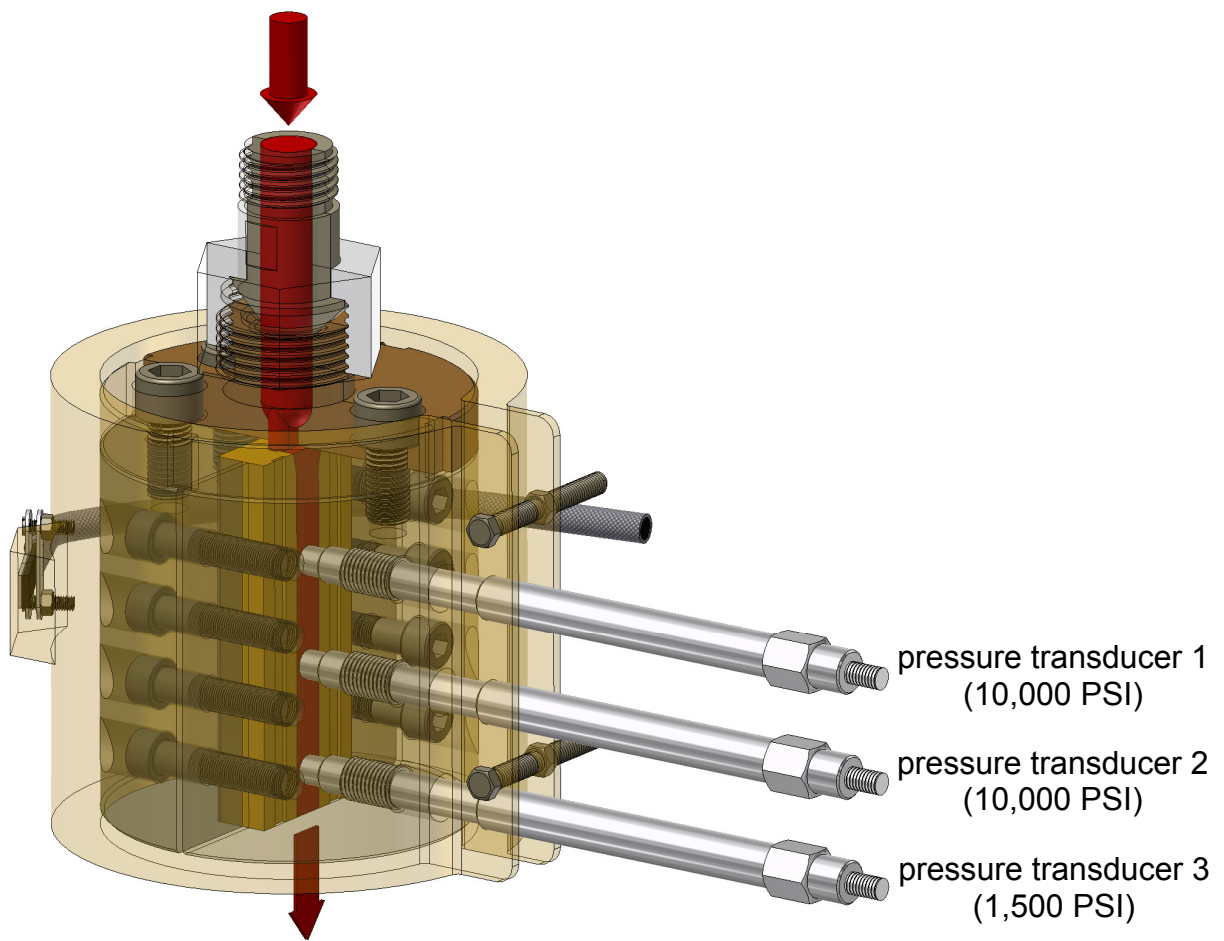
Figure 4 Transparent section view of used slit die.
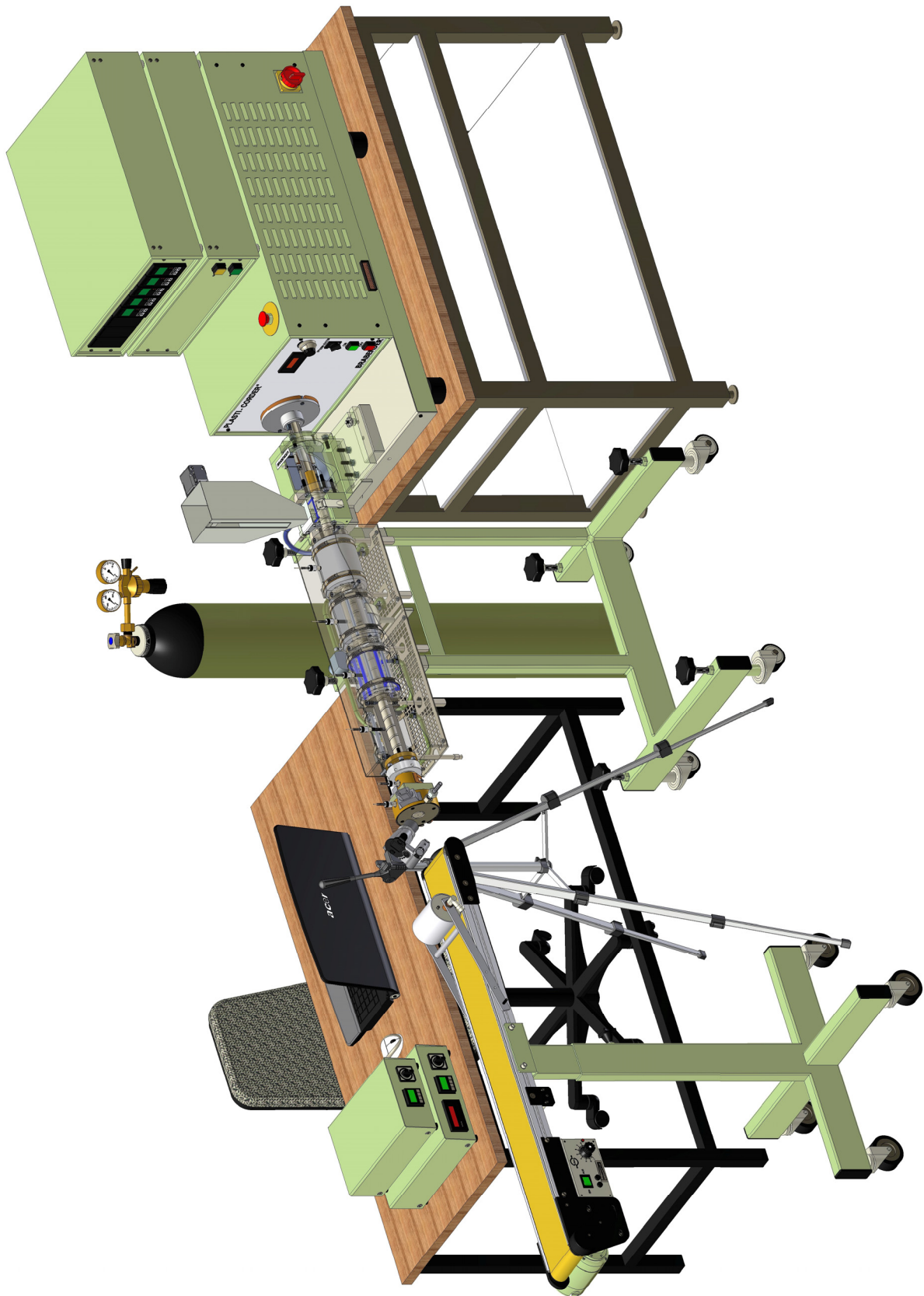
Figure 5 Overall 3D view of special laboratory extrusion line for *die drool* measurements.

A-A

cooling channel

Ø1.6

Ø6
M18

3 10 2 2
33

A

27

A
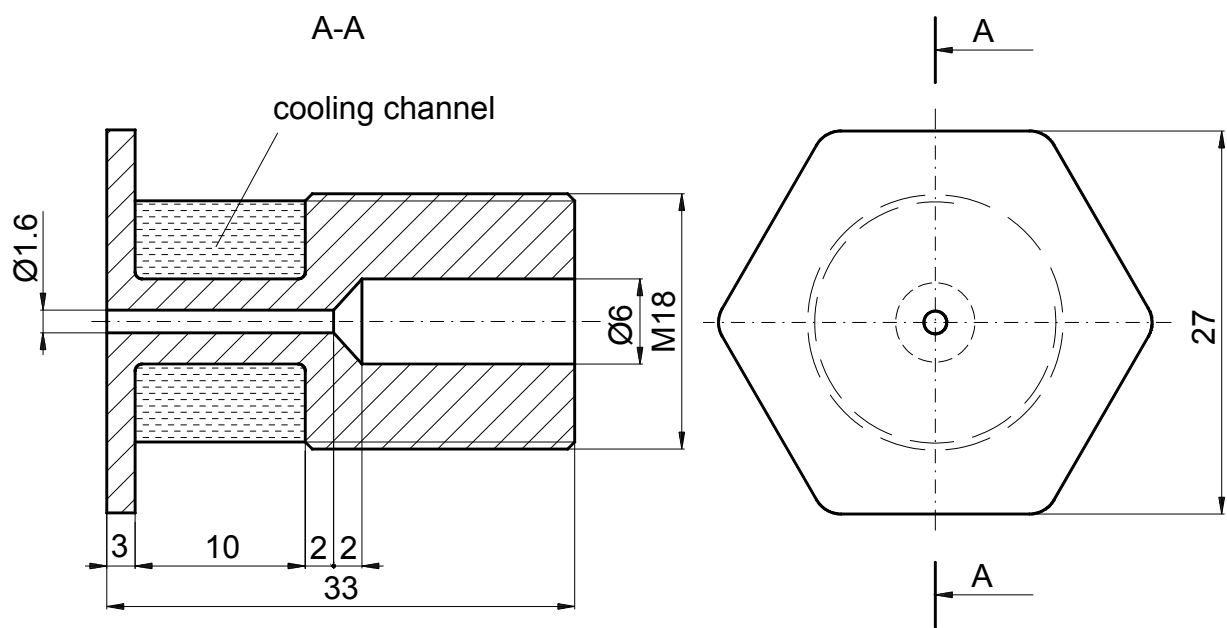
Figure 6 Section view of used replaceable capillary die with dimensions.

Figure 7 Transient uniaxial extensional viscosity for HDPE 1 at 190°C.
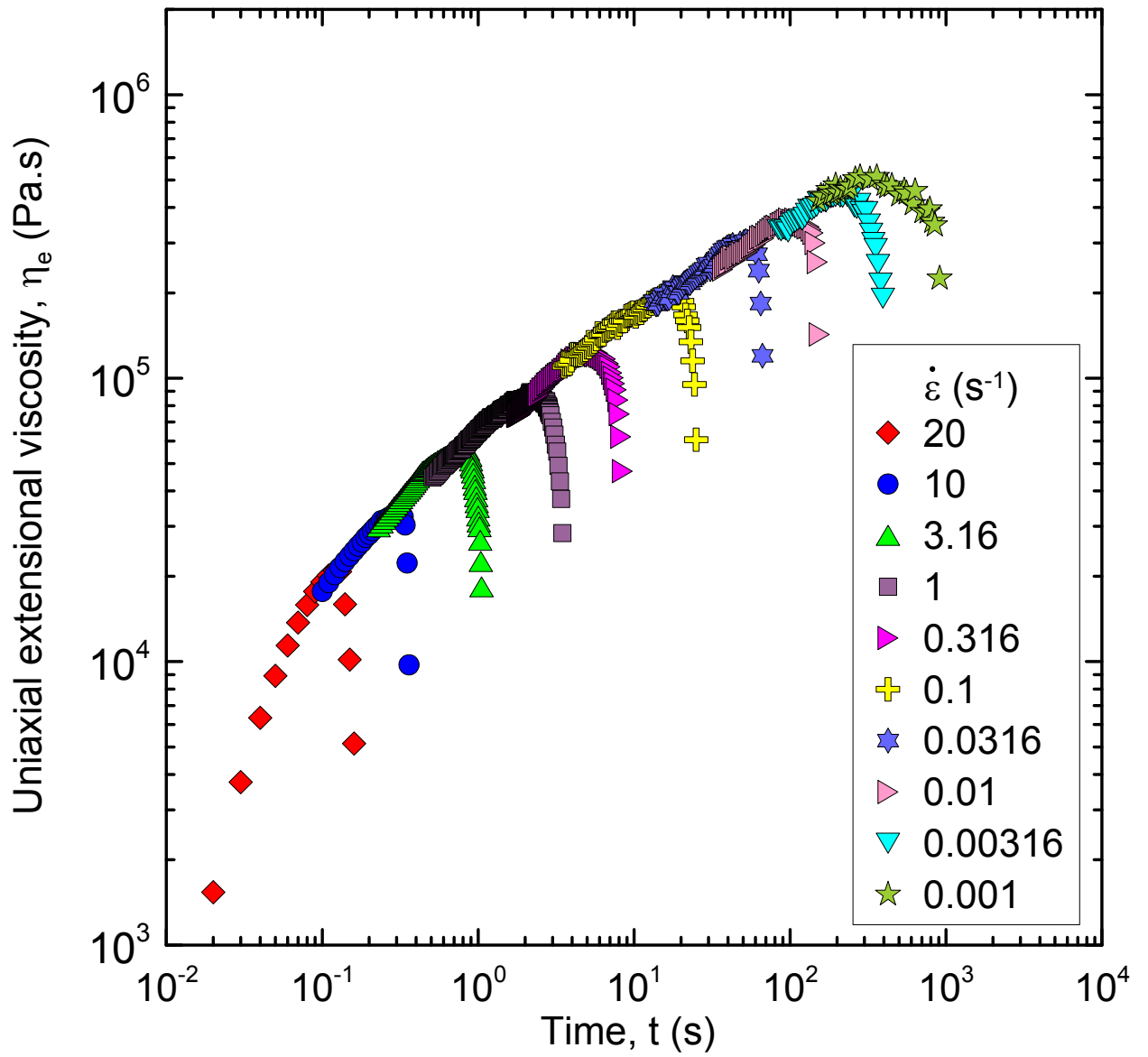
Figure 8 Transient uniaxial extensional viscosity for HDPE 2 at 190°C.
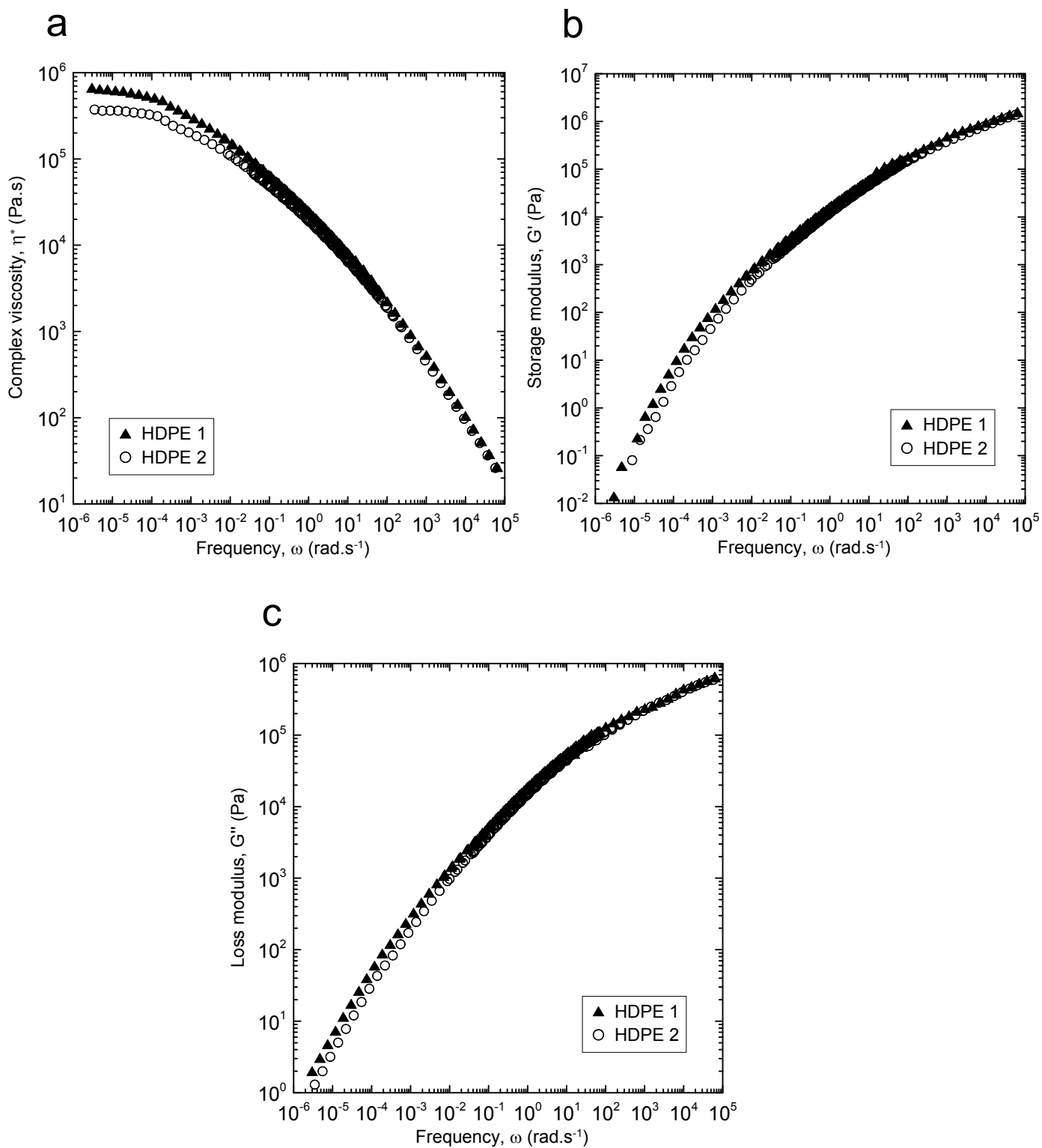
Figure 9 Linear viscoelastic properties for both investigated HDPE polymer melts measured at 190°C. (a) complex viscosity, η^*, (b) storage modulus, G', and (c) loss modulus, G''.
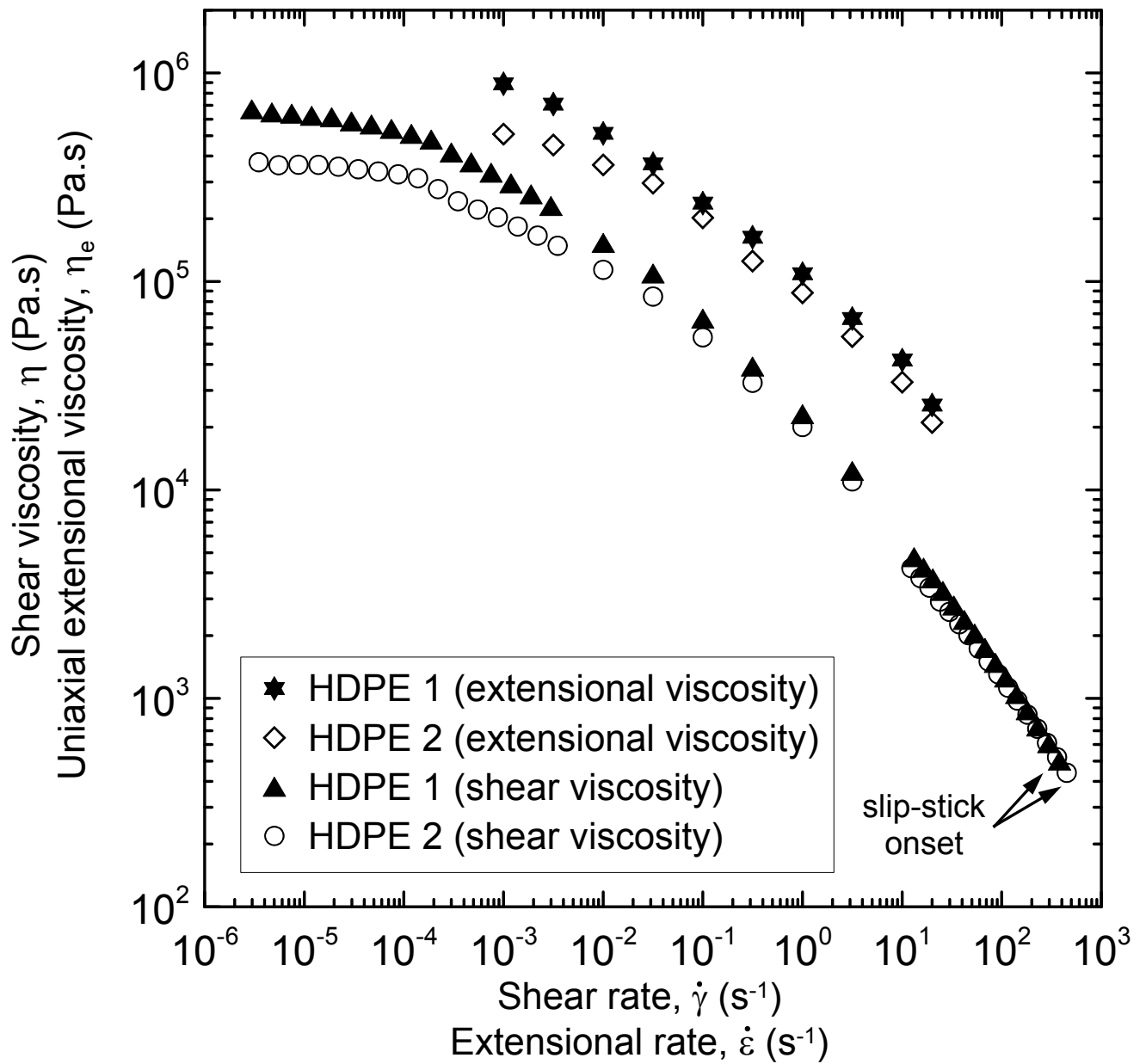
Figure 10 Steady-state shear and uniaxial extensional viscosities for both investigated HDPE polymer melts measured at 190°C.
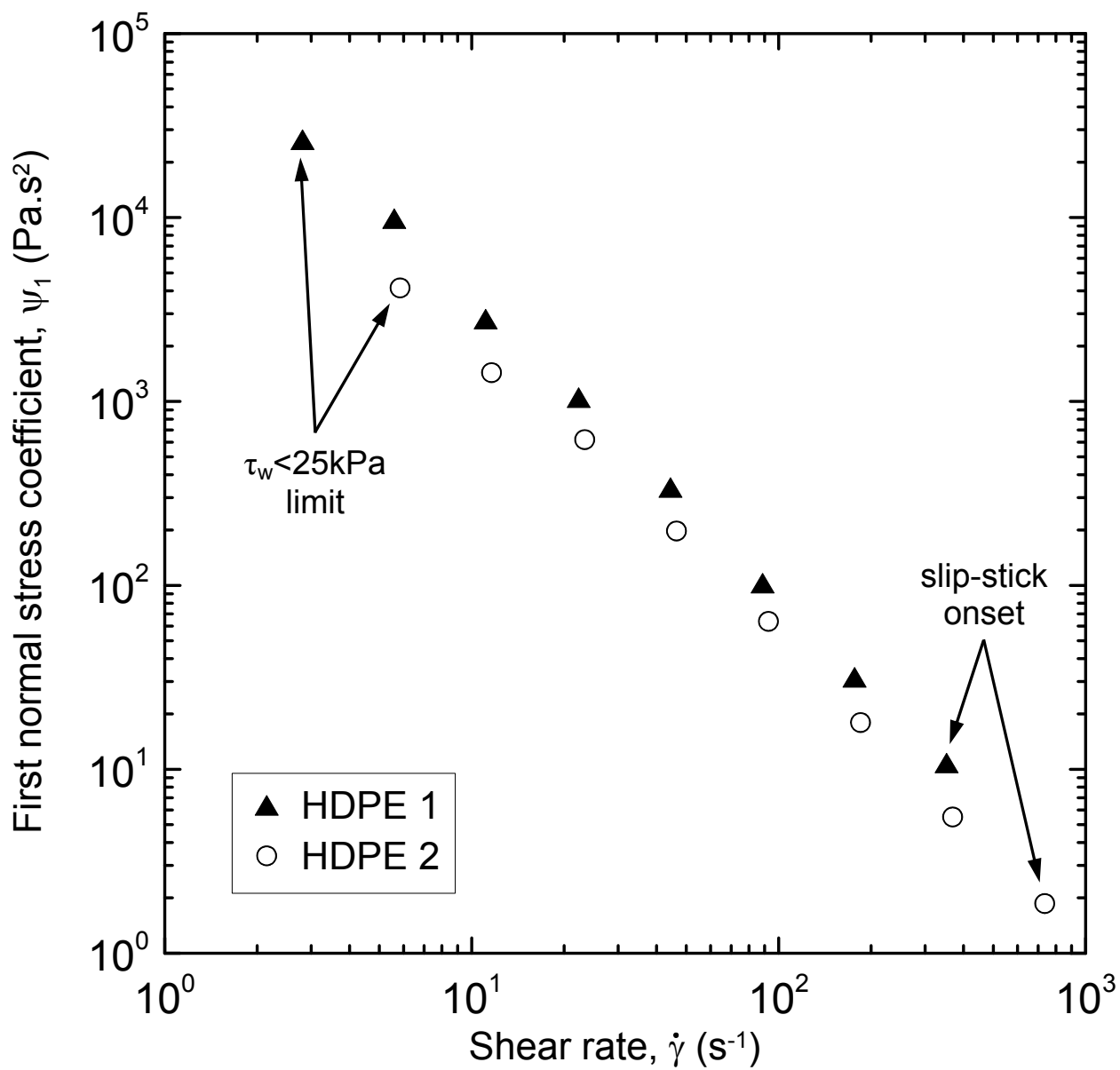
Figure 11 Steady-state first normal stress coefficient for both investigated HDPE polymer melts measured at 190°C.
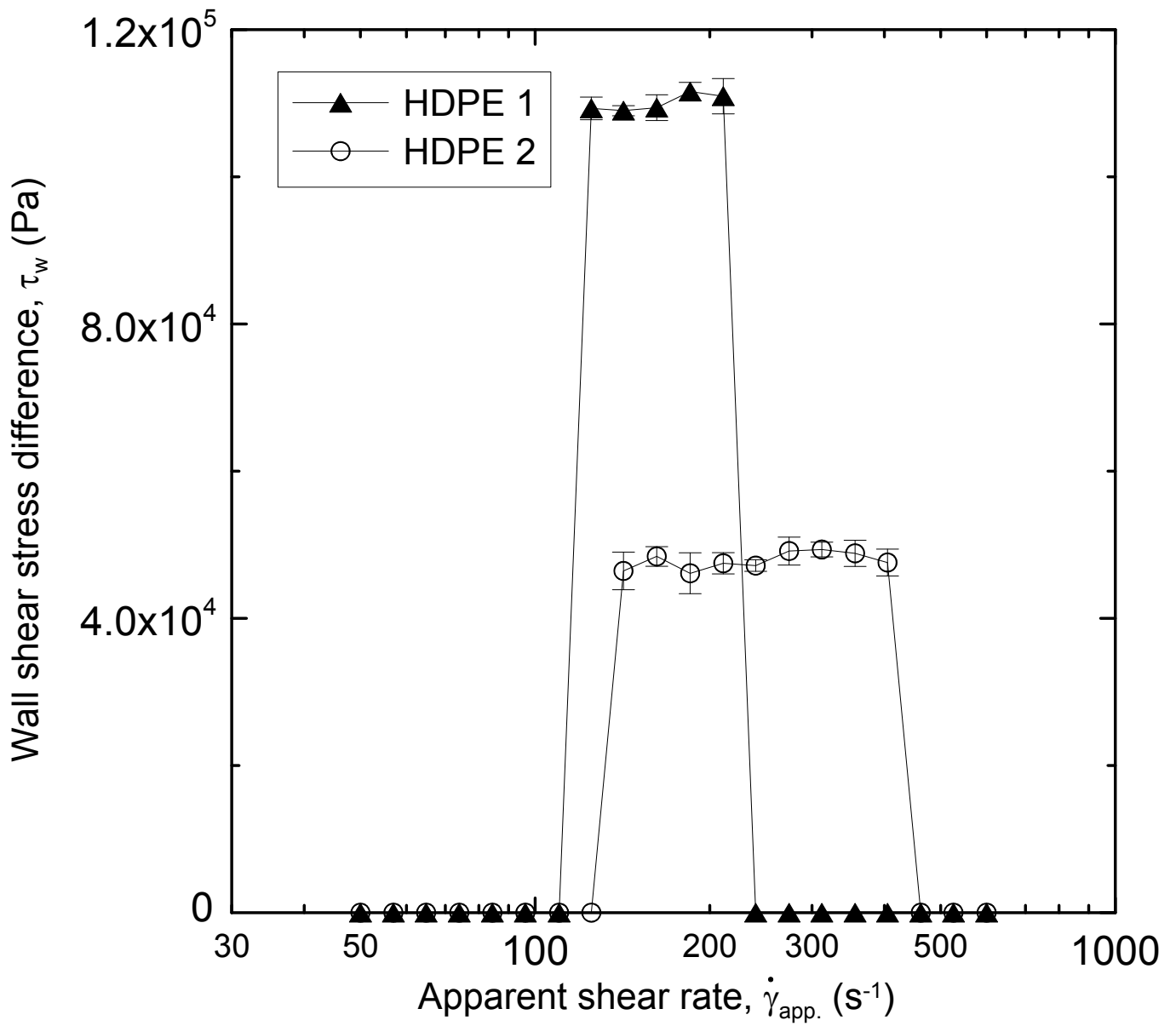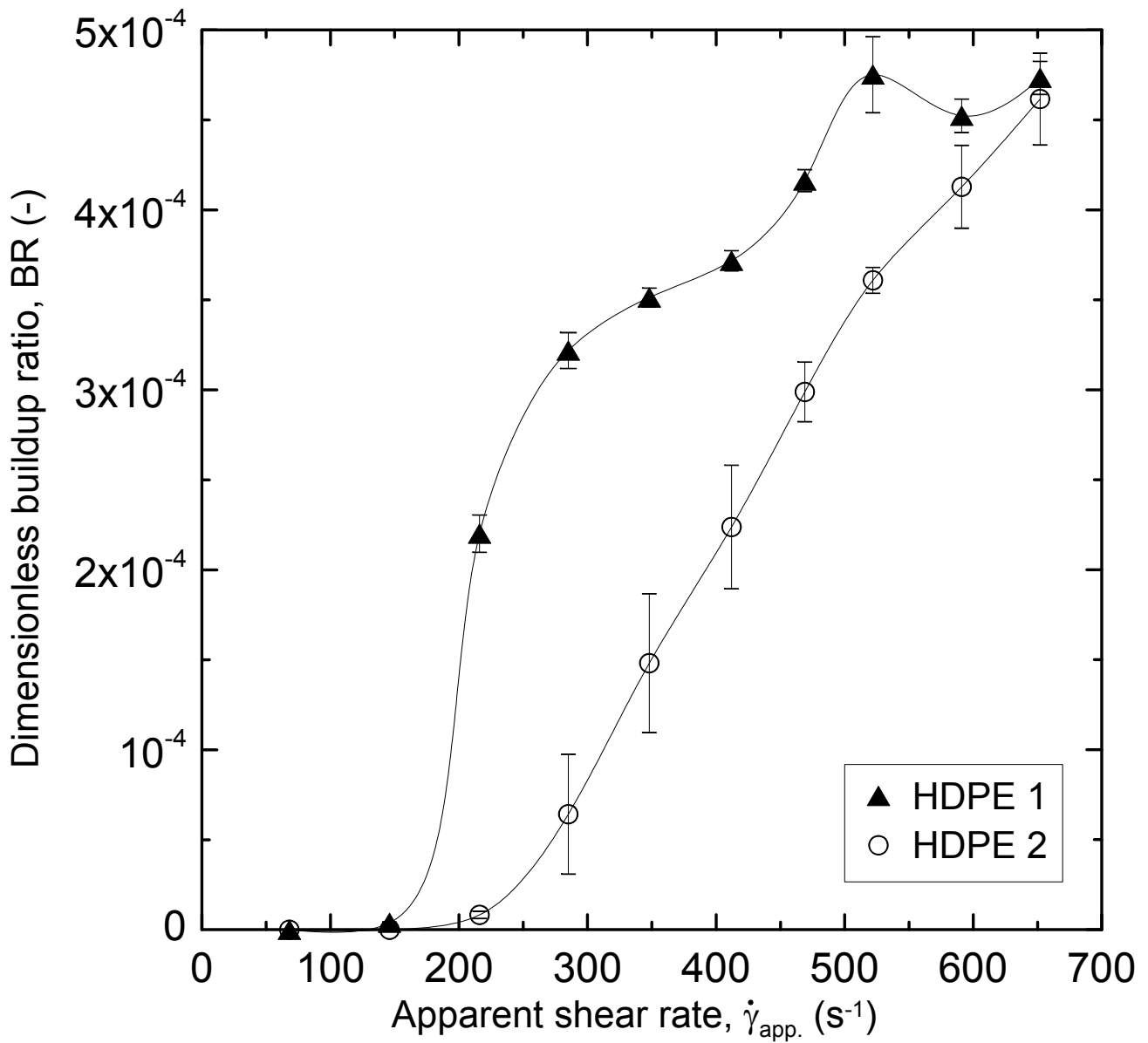
Figure 12 Wall shear stress difference as a function of apparent shear rate for both investigated HDPE polymer melts determined at 160°C.
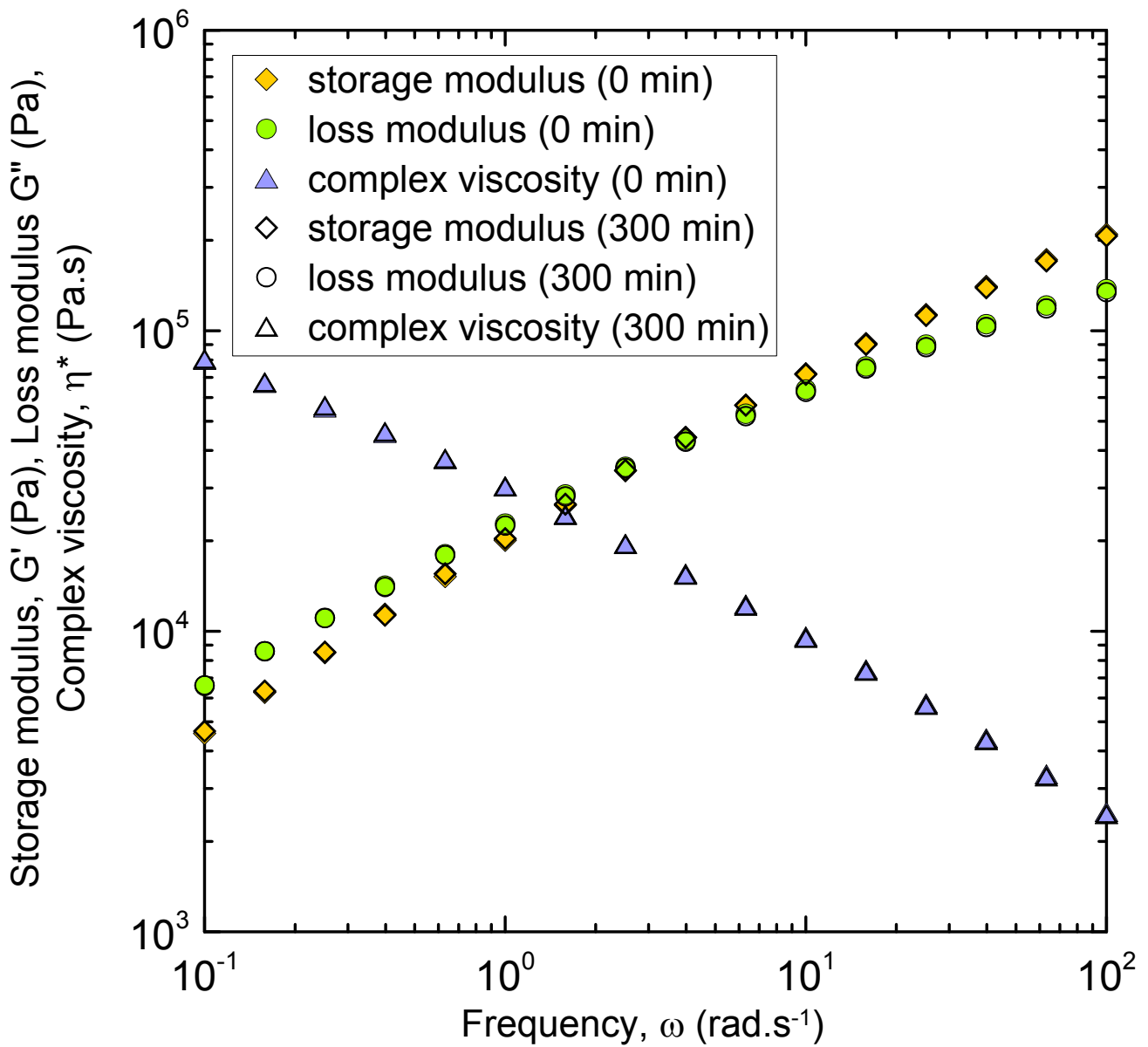
Figure 13 Complex viscosities, η^*, storage, G', and loss, G'', moduli for HDPE 1 at zero time (close symbols) and after 300 min test (open symbols).
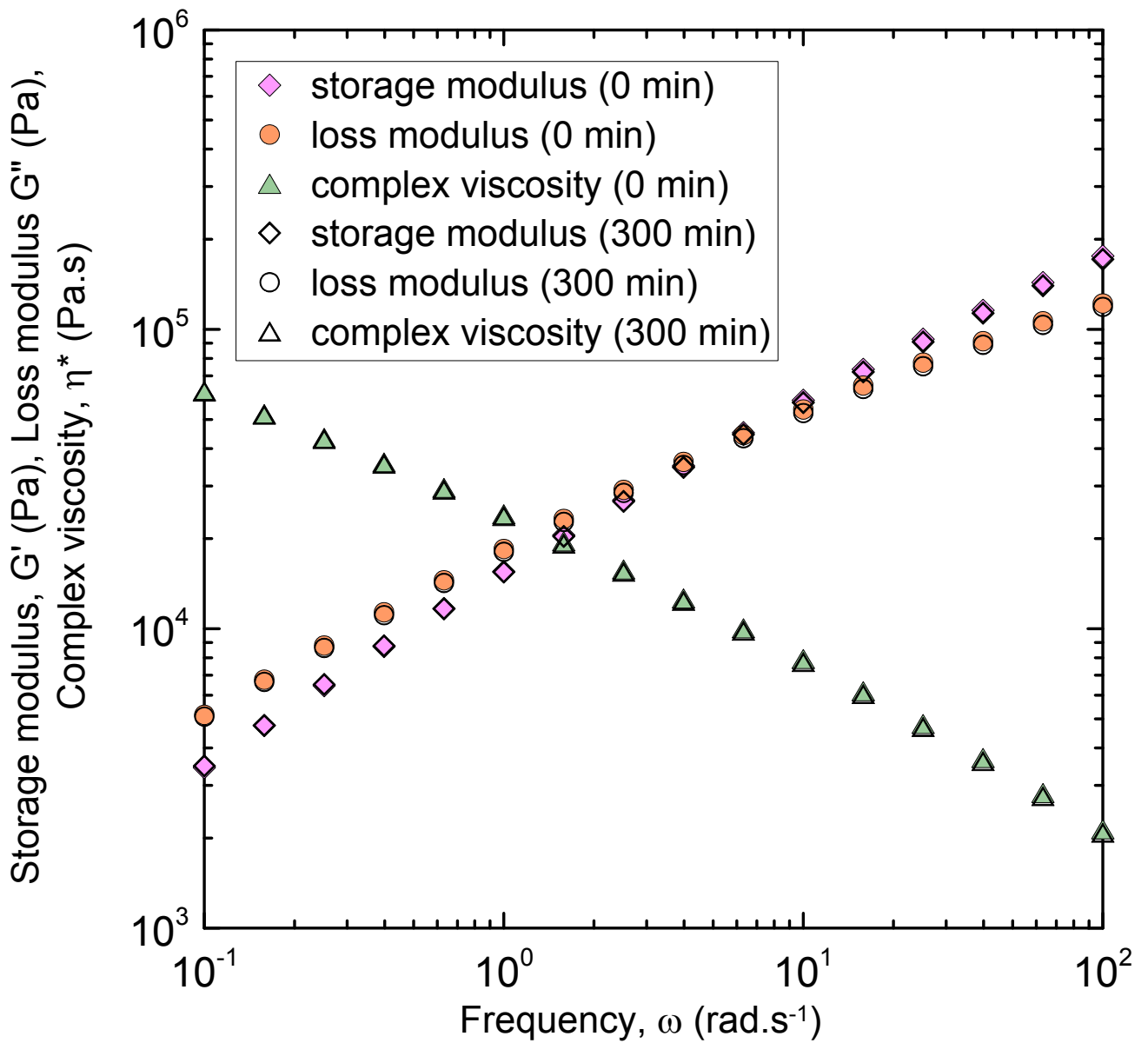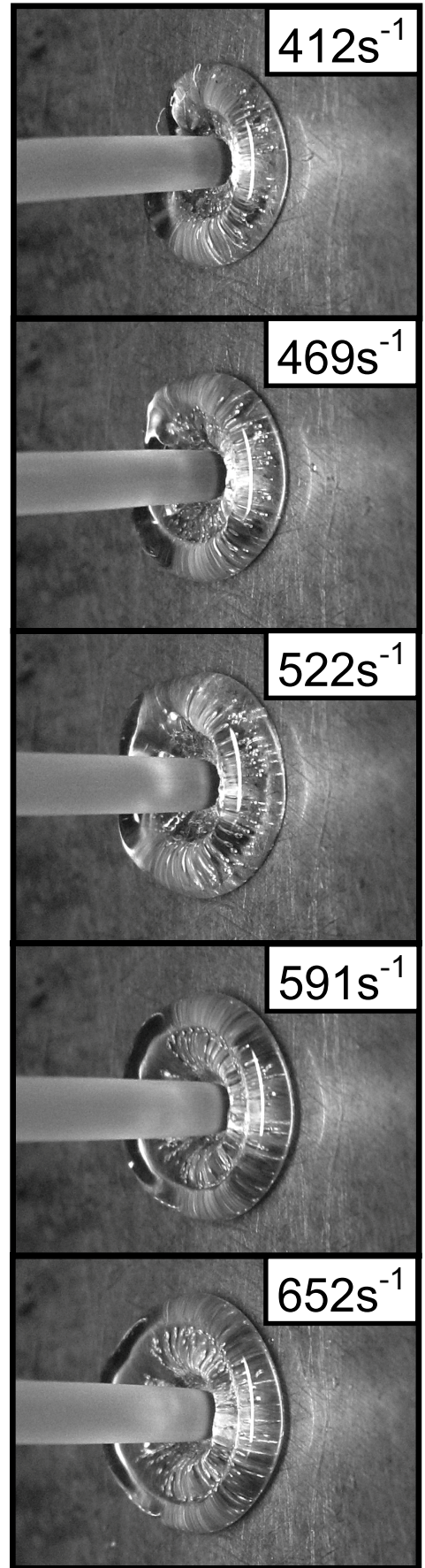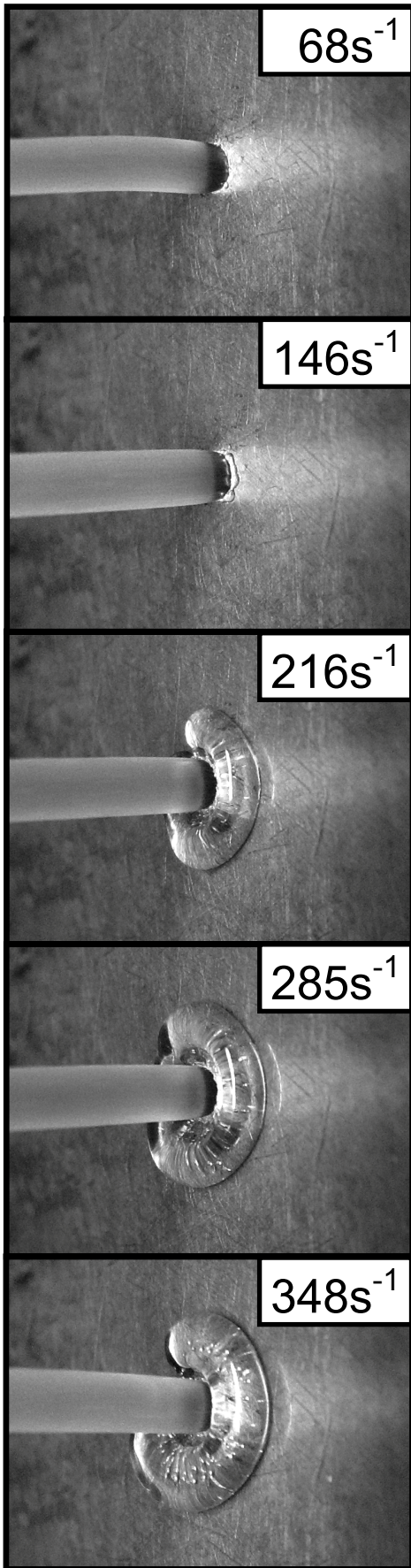
Figure 14 Complex viscosities, η^*, storage, G', and loss, G'', moduli for HDPE 2 at zero time (close symbols) and after 300 min test (open symbols).
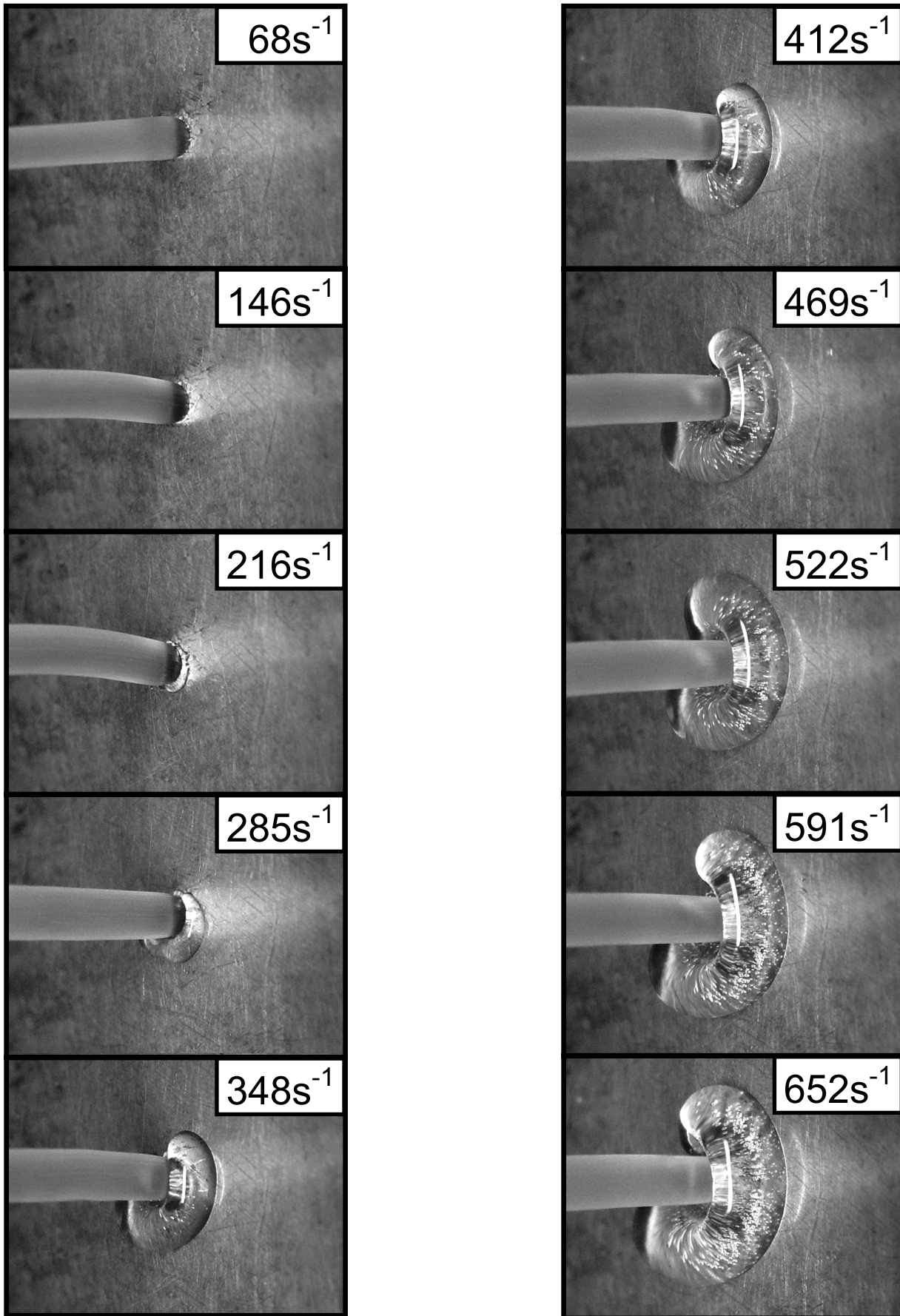
Figure 15 Dimensionless buildup ratio (10 minutes of extrusion) as a function of apparent shear rate for both investigated HDPE polymer melts determined at 160°C.
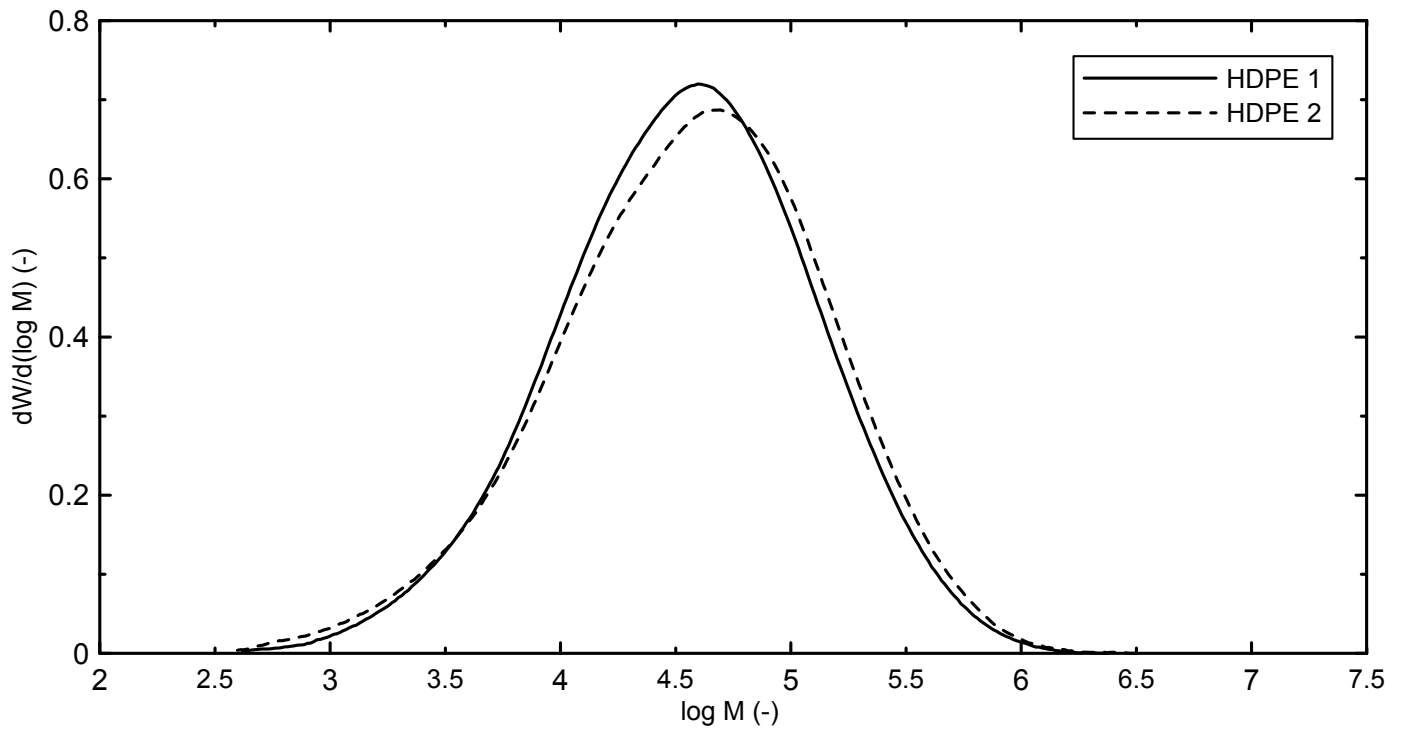
Figure 16 Die exit face visualization after 10 minutes of extrusion of HDPE 1 at different apparent shear rates, $T = 160°C$.
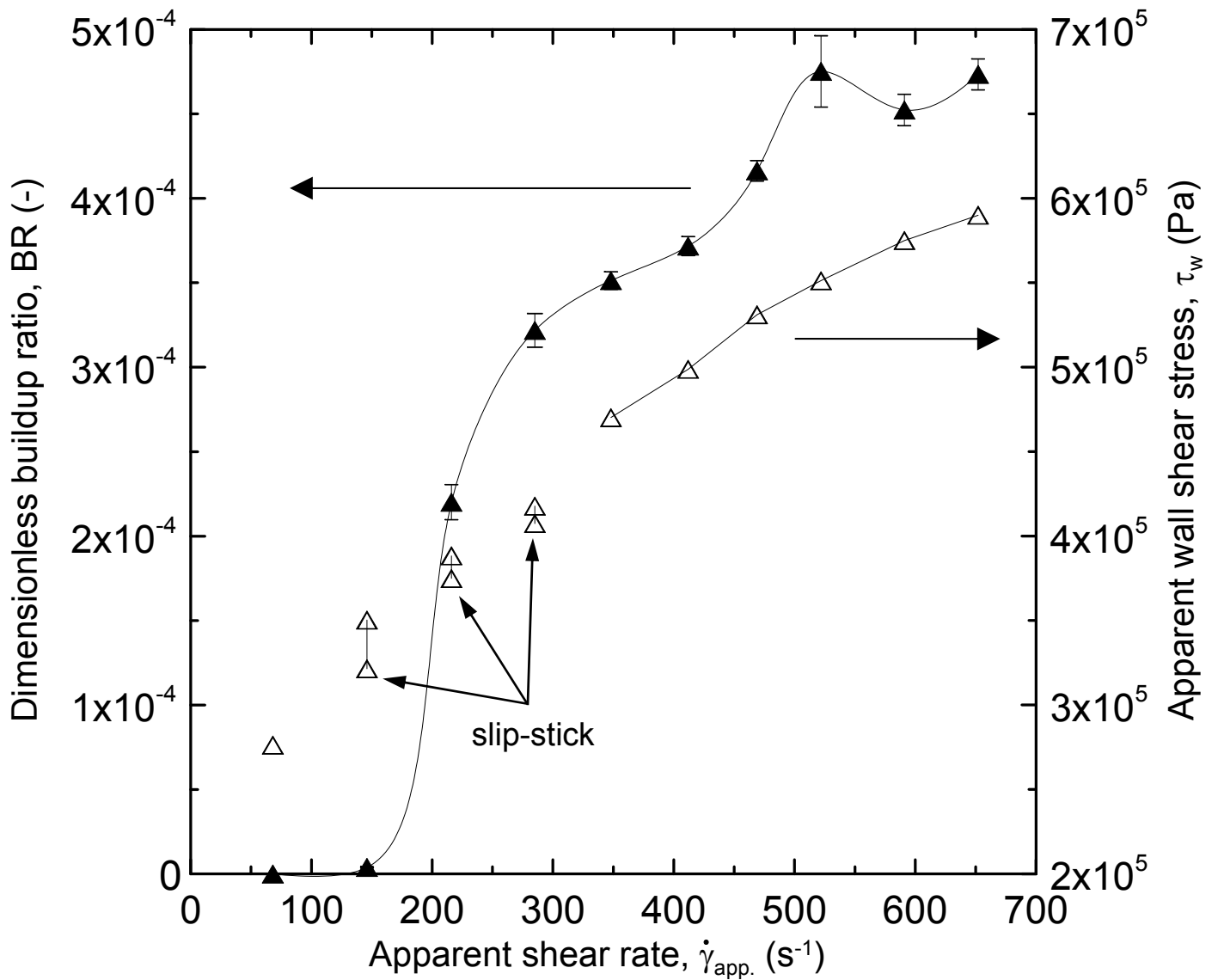
Figure 17 Die exit face visualization after 10 minutes of extrusion of HDPE 2 at different apparent shear rates, $T = 160°C$.

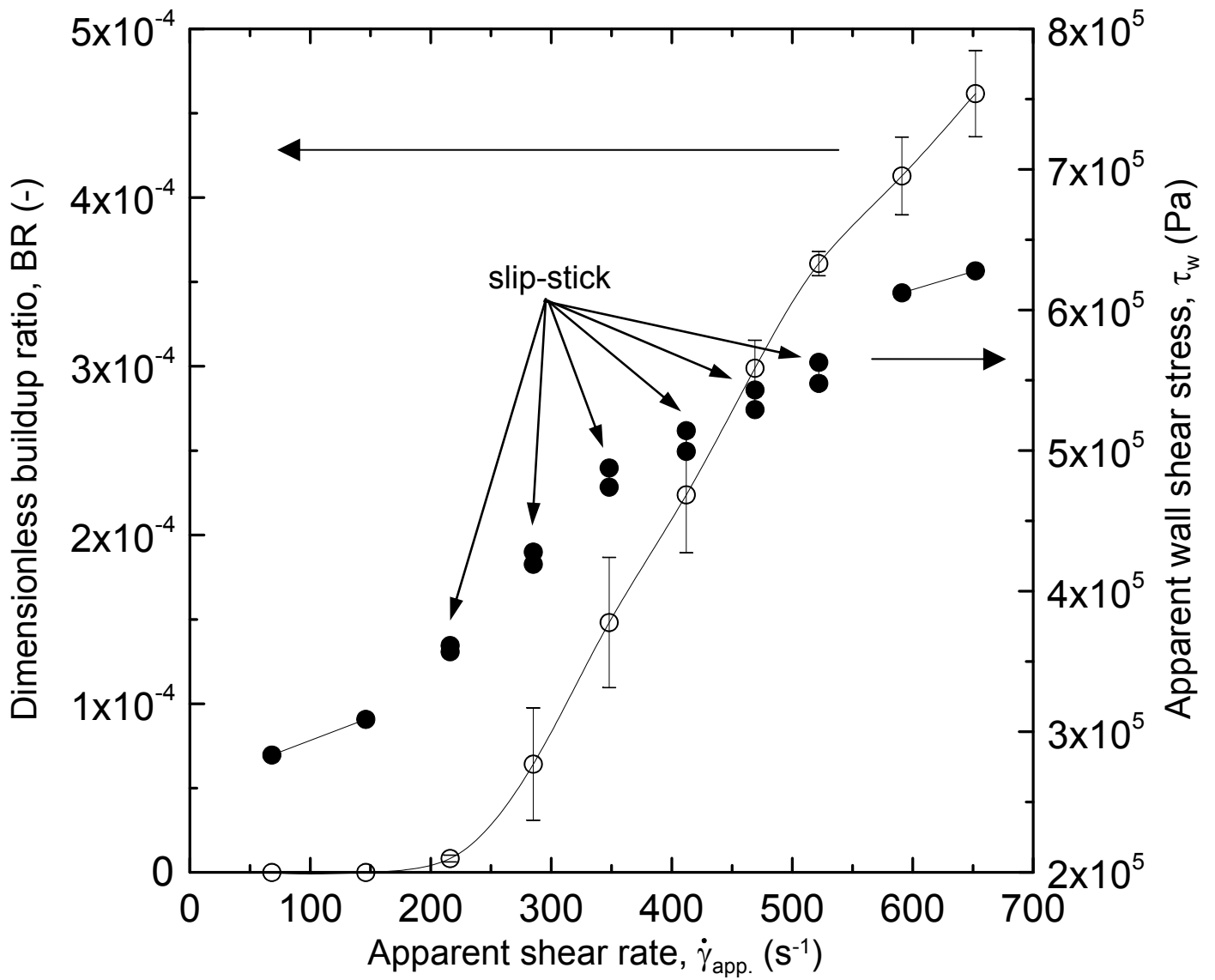**Figure 18** MWD curves for *die drool* samples of both investigated polymers collected under N_2 inert gas atmosphere at apparent shear rate of $348s^{-1}$.

Figure 19 Dimensionless buildup ratio and apparent wall shear stress as the functions of apparent shear rate (material HDPE 1, die exit temperature 160°C), $\dfrac{\partial BR}{\partial \dot{\gamma}_{app}} = 2.2896\text{x}10^{-6}$ s.
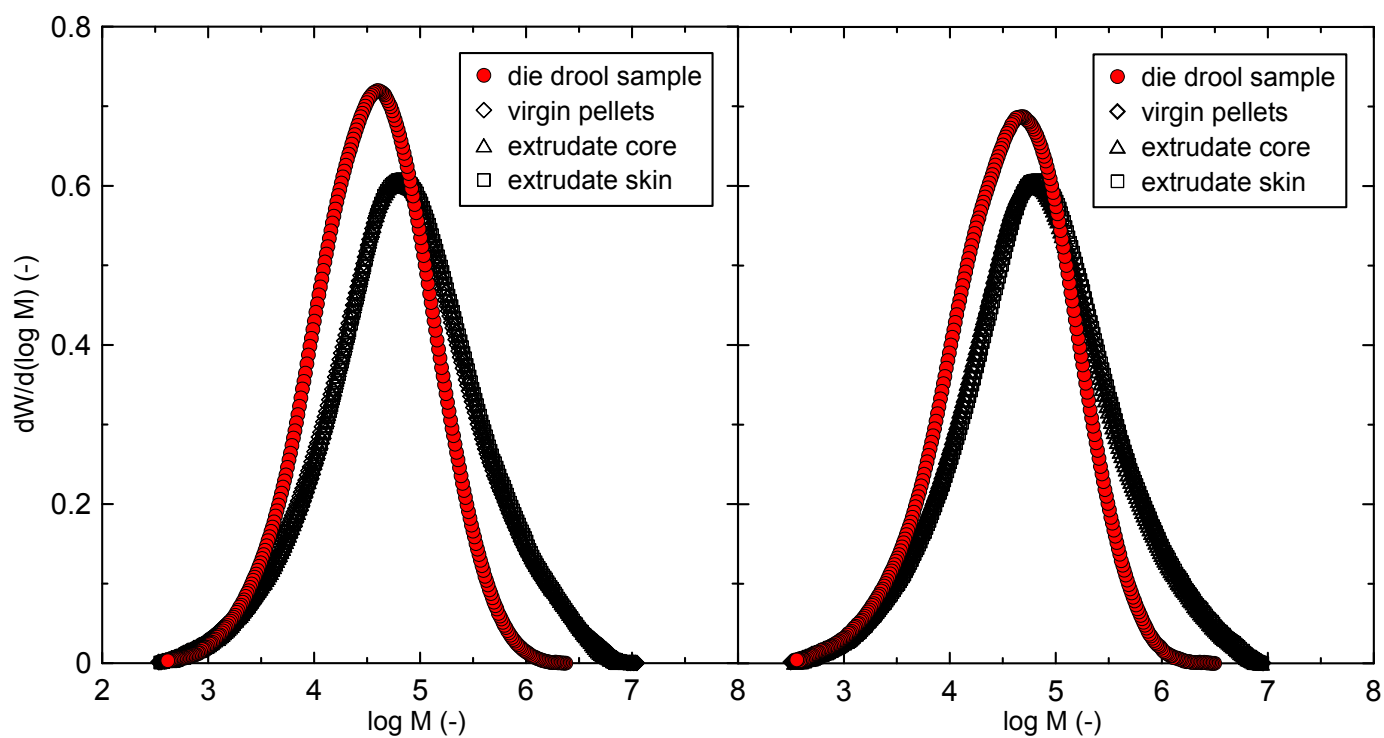
Figure 20 Dimensionless buildup ratio and apparent wall shear stress as the functions of apparent shear rate (material HDPE 2, die exit temperature 160°C), $\dfrac{\partial BR}{\partial \dot{\gamma}_{app}} = 1.1827 \times 10^{-6}$ s.

Figure 21 MWD curves for materials HDPE 1 (left graph) and HDPE 2 (right graph) in the form of *die drool* sample, virgin pellets, extrudate core and extrudate skin (apparent shear rate 348s^{-1}, *die drool* sample collected under inert N_2 atmosphere).

PAPER IV

Effect of Die Exit Geometry on Internal Die Drool Phenomenon during Linear HDPE Melt Extrusion

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ABSTRACT

In this work, the effect of die exit design on the *internal die drool* phenomenon occuring during extrusion of HDPE has been experimentaly investigated. It has been revealed, that firstly, the effect of flared length and die exit angle on the *internal die drool* intensity during extrusion of HDPE has non-monotonic character and secondly, flared dies are more stabilizing in comparison with chamfered dies. It has been suggested that suppresion mechanism of the *internal die drool* phenomenon through die exit modification can be understood throught the balance between the melt pressure/normal stresses at the die exit, adhesion at metal wall/flowing melt interface and extensional stress induced by the extrudate draw off, which can lead to flow situation at which low molecular weigth species are effectively removed from the die exit region by the moving extrudate and only small portion of them remains at the die exit face.

INTRODUCTION

During extrusion process, there is a tendency for some of the extruded polymer materials to adhere to exit edges or open faces of extrusion die from which the extruded material emerges. The material so deposited on the die exit, can build up into a large compact usually degraded mass or can form drips, flakes or powder which frequently break away from the die, adhere perseveringly onto extruded product surface and thus damage 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 plate-out"*, *"die deposit"*, *"die drip"* or *"die moustache"* and the accumulated material is generally named *"drool"*[1, 2].

Die drool phenomenon can appear in all common extrusion techniques like pipe and profile extrusion, film casting, fibre spinning, film blowing, or cable sheathing. In some of these techniques, *drool* can adhere not only to the outside faces but also to the inside ones which makes simple cleaning procedure based on manually collecting of *drool* mass from the die exit face virtually impossible. Then, only one way consists in periodic stops the extrusion line, disassembling of all extrusion die parts and their mechanical cleaning remains. Clearly, this procedure is time and also money consuming.

Historically, one of the original remarks about "…difficulty in the extrusion of thermoplastic resins because of adhesion of hot thermoplastic resin to the extrusion die and, occasionally, because of die corrosion from small amounts of heat decomposition products from the resins" can be found in US Patent from 1946 [3] and probably firstly used term *"drooling"* in writing form could be found in the patent of Foster in 1958 [4]. During the years, extrusion experts and researches tried many ways to suppress *die drool* widely described in patents and research papers. They tested inside or outside extrusion die edges design changes [4-10], extruded polymer melts modifications [11-16] and also processing conditions changes [2, 17-18]. However, no experimental method has been found to be universal; each of them can be used only for particular polymer material and extrusion process/extrusion die. Furthermore, in some patents authors even speculated that *drooling* can be caused by "...incompatibility of polymer

with certain other substances mixed with it before extrusion" (1960, [12]), "...the sudden release of pressure on the polymer material as it emerges from the die into the atmosphere" (1964, [6]) or "…part of the fillers, such as clay, which…may be forced out of the matrix at the point of highest extrusion pressure which is a point along the extruder die area" (1971, [13]). Later, some papers in which authors searched *die drool* formation mechanism have been published [1, 2, 10, 16, 19-23]. It is generally accepted that there are two types of the *die drool* phenomenon; "*external die drool* phenomenon", which is generated just at the end of the die due to the extrudate free surface creation and negative pressure generation (causing the suction effect) [2, 10] and "*internal die drool* phenomenon", which is initiated inside the processing equipment as the results of degradation [22] or flow induced molecular weight fractionation [16]. In fact, there is number of material, processing and die design based parameters promoting and suppressing the *die drool* phenomenon and some of them have been recently documented such as pressure fluctuations in screw [19], volatiles, low molecular fractions of the polymer, fillers, poor dispersion of pigments [24], *die swell* [19, 22], processing near degradation temperature [23, 25], dissimilar viscosities in blends [26], broadening molecular weight distribution [27], increasing melt elasticity [16, 23], *shark skin* [2, 10], *slip-stick* phenomenon [16, 28], or abrupt corners at the die lips [7, 8, 10] have been found to promote *die drool*. On the other hand, chain branching increase [16], polymer processing aids addition [26], using ceramics dies [29] or dies with PTFE chemically/physically locked in die wall [24], silicon rubber coated surface of extrusion die [28], hard chrome dies [30], flared [7, 8, 10] or chamfered [10] die exits, have been found to reduce this phenomenon. With respect to the stabilizing role of the die design, it was initially believed that flared dies are so effective due to occurrence of stress undershoot inside flared section [1]. However, Ding et al. [9] mathematically modeled stress field inside the flared section and they concluded that stress undershoot is not the main reason for suppressing accumulation of *drool* mass at the die lips. They have suggested that the history of the stresses upstream of the exit, not just their instantaneous values at die lips, governs the *die drool* reduction in flared dies. Recently, Chaloupková and Zatloukal [10] were able to correlate stabilizing efficiency of die exit chamfering, die opening and die exit flaring

with negative pressure, pressure gradient and normal component of the pressure gradient during extrusion of the metallocene based LLDPE at which the *external die drool* has occurred.

In this work, experimental analysis has been performed for extrusion dies at which chamfer angle and flared length were systematically varied in order to understand the role of die design for the internal type of *die drool* phenomenon as well as to explore the knowledge about parameters which could allow more efficient die design optimization.

EXPERIMENTAL

In this work, well stabilized unfilled virtually linear HDPE polymer melt (*HDPE Liten FB 29 E2009 3220 4479*, extrusion grade, Unipetrol RPA, Czech Republic, material characterization is summarized in our previous work [27]) has been used.

The *internal die drool* measurements were performed on specially designed extrusion line equipped by replaceable capillary (see Figure 1), which has already been used in our previous studies [16, 23, 27]. The line was consisted of 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 $L_3 = 12D$*), transition annular part, specially designed annular extrusion die, photo camera *Canon 600D* model (Canon, Inc., Japan) with resolution of 18 Mpx equipped with Canon macro lens EF 100 mm placed near the die exit for *die drool* visualization and finally draw-off mechanism.

The *die drool* experiments were performed as follows. Extruder 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, $T_5 = T_6 = 160$°C. The low exiting temperature 160°C for the HDPE melt was chosen to achieve highly pronounced fractionation effect due to high efficiency of melt to store elastic energy as well as to suppress any thermal/oxidative degradation. Further, mass flow rate (MFR) was chosen 750g.hr^{-1} (apparent shear rate 673 s^{-1}) to ensure that the flow condition lies above the *slip-stick* phenomenon, i.e in the "*superflow*" regime at which the *die drool* intensity is the highest as shown in [27]. In order to measure fractionated (*drooled*) polymer mass accumulated at the die exit, the following methodology was used. The extruder was stopped after 10 minutes of extrusion and the accumulated material was carefully manually removed from the die lip by a tweezer, weighted on a sensitive analytical balance and the procedure was repeated three times for each capillary to calculate standard deviation. Before each set of three independent 10 minutes tests (for given capillary), barrel, screw and all parts of the die have been disassembled and perfectly manually cleaned. Finally, *die drool*

intensity has been expressed in dimensionless form through buildup ratio *BR* (introduced by Gander and Giacomin in [1]):

$$BR = \frac{\dot{B}}{\dot{m}} \tag{1}$$

where $\dot{m}$ is total mass flow rate of extruded polymer melt and $\dot{B}$ means buildup rate:

$$\dot{B} = \frac{B}{t_e} \tag{2}$$

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

To evaluate die exit design effect on accumulated *drool* mass following stainless steel capillaries were used.

The <u>straight capillary</u> with abrupt die exit edge angle of 0° having diameter D_1 = 1.6 mm and *L/D* ratio of 9.375 (see Figure 1 and Figure 2a) and its two modifications: <u>chamfered die</u> (see Figure 2b) with three different die exit angles (α = 15°, 30° and 45°) and <u>flared die</u> (see Figure 2c) with four different flared lengths (L_{C1} = 1 mm, 2 mm, 5 mm, 8 mm). For both modified dies, the outer diameter D_{C1} and die exit angle α were kept to be 2 mm and 45°, respectively.

RESULTS AND DISCUSSION

In this section, experimental results for different die exit angles and different flared lengths are shown and discussed in more detail.

Effect of die exit angle on die drool intensity

Die exit visualization and corresponding dimensionless buildup ratio for different die exit angle values are provided in Figure 3 and Figure 4, respectively. As can be seen, this dependence has interestingly strongly non-monotonic character with one minimum for 15° die exit angle representing reduction of accumulated *drool* mass intensity by 56% in comparison with the straight die. Importantly, for greater die exit angles, *drool* mass again increases even up to the value measured on the straight die (i.e. when the die exit angle reached 45°).

The possible explanation of non-monotonic buildup ratio vs. die exit angle dependence could be understood through *"detachment point"* and *"effective length"*, $L_{\text{eff.}}$, location as depicted in Figure 5 for all die exit angles. Here the *detachment point* represents location at which extrudate detaches metal die (due to the melt pressure/normal stresses at the die exit, adhesion at metal wall/flowing melt interface and extensional stress induced by the extrudate draw off) whereas the *effective length*, $L_{\text{eff.}}$, is the distance in which fractionated low molecular weight species are in touch with the extrudate free surface as well as with the die wall. Clearly, if the $L_{\text{eff.}}$ is high, there is high probability that the low molecular weight fractioned polymer is effectively removed from the die exit region by the moving extrudate and only small portion of it remains at the die exit face. This could happen for the most stabilizing case (i.e. die exit angle equal to 15° as visualized in Figure 5b). On the other hand, a decrease in the die exit angle down to 0° or increase it up to 30° or 45° could continuously decrease the $L_{\text{eff.}}$ down to zero resulting to the extreme situation at which the low molecular weight fractionated polymer is not removed from the die exit region and only its intensive accumulation takes place at the die exit face resulting in intensive *die drool* phenomenon.

Effect of die exit flared length on die drool intensity

Die exit visualization and corresponding dimensionless buildup ratio for different die exit flared lengths (expressed here in the dimensionless form as the flared length, L_{C1}, divided by the capillary length, $L = 15$ mm, i.e. by L_{C1}/L ratio) values are provided in Figure 6 and Figure 7, respectively. As can be seen, this dependence has also strong non-monotonic character having one minimum at 2/15 dimensionless flared length for which *drool* mass reduction is the highest (equal to 97% in comparison with the straight die having abrupt die exit edge angle of 0°) and then, *drool* mass again increases for 8/15 dimensionless flared length. It seems that in this case, the non-monotonic dimensionless buildup ratio vs. dimensionless flared length could also be explained through the *detachment point* location and *effective length*, which are visualized in Figure 8 for all studied flared dies. Here the flow situation inside flared section can also be viewed as the special case of two-layer coextrusion (the low molecular weight species as the skin and the main polymer as the core). Due to abrupt channel opening at the die exit, low enough pressure, normal stresses, adhesion and high extensional stress from draw off *"interface expansion"* could take place during which the low molecular weight layer decelerates, expands in thickness and core layer starts to be separated from the skin layer (*detachment point*) far away from the die exit (*effective length* is high) at which low molecular skin layer becomes intensively dragged with the core extrudate layer out of the die, thus suppressing its builds up at the die exit face. Thus, as long *effective length*, $L_{eff.}$, as effective given flared die in *drool* suppression can be. It seems that for the given HDPE polymer melt and chosen processing conditions $L_{eff.}$ has maximum at 2/15 dimensionless flared length due to low pressure and low normal stresses, which increase the effect of the extensional stress from the drawn off on the flow field in the upstream direction, i.e. the *detachment point* is moved in the upstream direction too, which is stabilizing. On the other hand, for the longer dimensionless flared sections (5/15, 8/15), *detachment point* presumably starts to move closer to the die exit (i.e. $L_{eff.}$ decreases) due to increasing pressure and the normal stresses in flared section resulting in smaller efficiency of the extensional stress from the drawn off to influence the flow field in the upstream direction i.e. the position of the *detachment point* is moved more closer to the die exit, which is destabilizing.

CONCLUSION

It has been revealed experimentally, that the effect of die exit angle and flared length on the *internal die drool* intensity during extrusion of HDPE has non-monotonic character. It has been found that the optimum value for the die exit angle and dimensionless flared length is 15° and 2/15, respectively. It has been proved that flared dies are more stabilizing in comparison with chamfered dies. In more detail, 56% and 97% reduction in accumulated *drool* mass has been achieved with respect to straight die having abrupt die exit edge angle of 0° for the optimum value of die exit angle and dimensionless flared length, respectively, for the HDPE material and given processing conditions. It has been suggested that suppresion mechanism of the *internal die drool* phenomenon through die exit modification can be understood throught the balance between the melt pressure/normal stresses at the die exit, adhesion at metal wall/flowing melt interface and extensional stress induced by the extrudate draw off, which can lead to flow situation at which low molecular weight species are effectively removed from the die exit region by the moving extrudate and only small portion of them remains at the die exit face. This work suggests that for the simulation based die design optimization with respect to *internal die drool* phenomenon, fully viscoelastic constitutive equation together with proper boundary conditions (including adhesion forces between die wall and polymer melt and considering the extensional stresses due to extrudate draw off) should be utilized in order to precisely determine the location inside the die at which free surface of the extrudate starts to occur.

ACKNOWLEDGEMENT

REFERENCES

1. Gander, J. D., Giacomin, A. J. *Review of Die Lip Buildup in Plastics Extrusion.* Polym. Eng. and Sci. **37(7)**, 1113-1126 (1997).

2. Chaloupkova, K., Zatloukal, M. *Theoretical and Experimental Analysis of the Die Drool Phenomenon for Metallocene LLDPE.* Polym. Eng. Sci. **47(6)**, 871-881 (2007).

3. Berry, K., Downing, J. R. *Extrusion Apparatus.* US Patent 2,403,476 (1946).

4. Foster, A. G. *Extruding Dies.* US Patent 2,863,169 (1958).

5. Henning, G. E., Richter, M. W. *Apparatus for Extruding Plastic Compounds.* US Patent 3,121,255 (1964).

6. Budenbender, H. *Extruder Core Tubes.* US Patent 3,151,357 (1964).

7. Rakestraw, J. A., Waggoner, M. G. *Polymer Extrusion Die and Use of Thereof.* US Patent 5,458,836 (1995).

8. Ohhata, T. at al. *Die Plate for Plastics Extruder.* US Patent 5,417,907 (1995).

9. Ding, F., Zhao, L., Giacomin, A. J., Gander, J. D. *Flaring Dies for Suppress Die Drool.* Polym. Eng. Sci. **40(10)**, 2113-2123 (2000).

10. Chaloupkova, K., Zatloukal, M. *Effect of Die Design on Die Drool Phenomenon for Metallocene Based mLLDPE: Theoretical and Experimental Investigation.* J. App. Polym. Sci. **111(4)**, 1728-1737 (2009).

11. Havens, C. B., Mason, A. J., Widiger, A. T. *Composition Comprising a Vinilidene Chloride Polymer and an Organic Phosphate.* US Patent 2,935,490 (1960).

12. Henning, G. E. *Method of Making Plastics Articles.* US Patent 2,960,482 (1960).

13. Loser, T. N., Jones, T. *Solid Lubricant for Reducing Die-Plating and Die-Drag during the Extrusion of Viscous Rubber and Elastomeric Plastic Compositions.* US Patent 3,600,309 (1971).

14. Yanagisawa, K., Kobayashi, H., Tayama, Y. *Method for Extrusion Coating Electric Wires with a Foamed Polyolefin Resin Involving Reduced Die-Plateout.* US Patent 3,882,209 (1975).

15. Lee, C. D. *White Polyolefin Compositions Having Reduced Die Drool.* US Patent 2007/0037905 (2007).

16. Musil, J., Zatloukal, M. *Experimental Investigation of Flow Induced Molecular Weight Fractionation During Extrusion of HDPE Polymer Melts.* Chem. Eng. Sci. **66(20)**, 4814-4823 (2011).

17. Bild, F. *Extrusion Process and Apparatus Thereof.* US Patent 3,244,786 (1966).

18. Spencer, A. W. *Method of Controlling Contaminant Buildup on Extrusion Dies Used in Casting Thermoplastic Sheeting.* US Patent 3,502,757 (1970).

19. Klein, I. *Die drool: What Causes It, How to Avoid It.* Plastics World **39(5)**, 112-113 (1981).

20. Shelby, M. D., Caflisch, G. B. *Shear Field Induced Diffusion and Molecular Weight Fractionation During Polymer Processing.* Polym. Eng. and Sci. **44(7)**, 1283-1294 (2004).

21. Brachet, P., et al. *The Problem of Die Drool in the Extrusion of Recycled Polyethylene.* Progress in Rubber, Plastics and Recycling Technology **25(4)**, 199-211 (2009).

22. Hogan, T. A., Walia, P., Dems, B. C. *Investigation of the Relationships Between Die Build up and Die Swell.* Polym. Eng. and Sci. **49(2)**, 333-343 (2009).

23. Musil, J., Zatloukal, M. *Investigation of Die Drool Phenomenon for HDPE Polymer Melt.* Chem. Eng. Sci. **65(23)**, 6128-6133 (2010).

24. Kurtz, S. J., Szaniszlo, S. R. *Reduction in Die Drool in Filled Resins and Product Improvement.* US Patent 5,008,056 (1991).

25. Holtzen, D. A., Musiano, J. A. *Die Lip Plate-Out: A Proposed Mechanism*, Technical Papers, Regional Technical Conference – Society of Plastics Engineers (1996).

26. Priester, D. E. *Effect of Die Surface Characteristics on Processing Additive Performance.* Annual Technical Conference – ANTEC, Conference Proceedings **2**, 2059-2061 (1994).

27.   Musil, J., Zatloukal, M. *Experimental Investigation of Flow Induced Molecular Weight Fractionation Phenomenon for Two Linear HDPE Polymer Melts Having Identical M_n and M_w but Different M_z and M_{z+1} Average Molecular Weights*. Chem. Eng. Sci. (submitted for publication in 2012).

28.   Kulikov, O., Hornung, K. *A Simple Way to Suppress Surface Defects in the Processing of Polyethylene*. J. Non Newtonian Fluid Mech. **124(1-3)**, 103-114 (2004).

29.   Moore, S. Modern Plastics, **8**, 37 (1994).

30.   Musil, J., Zatloukal, M. *Effect of Processing Conditions and Die Design on Die Drool Phenomenon for HDPE Polymer Melt*. Annual Technical Conference – ANTEC, Conference Proceedings **2**, 1181-1185 (2011).
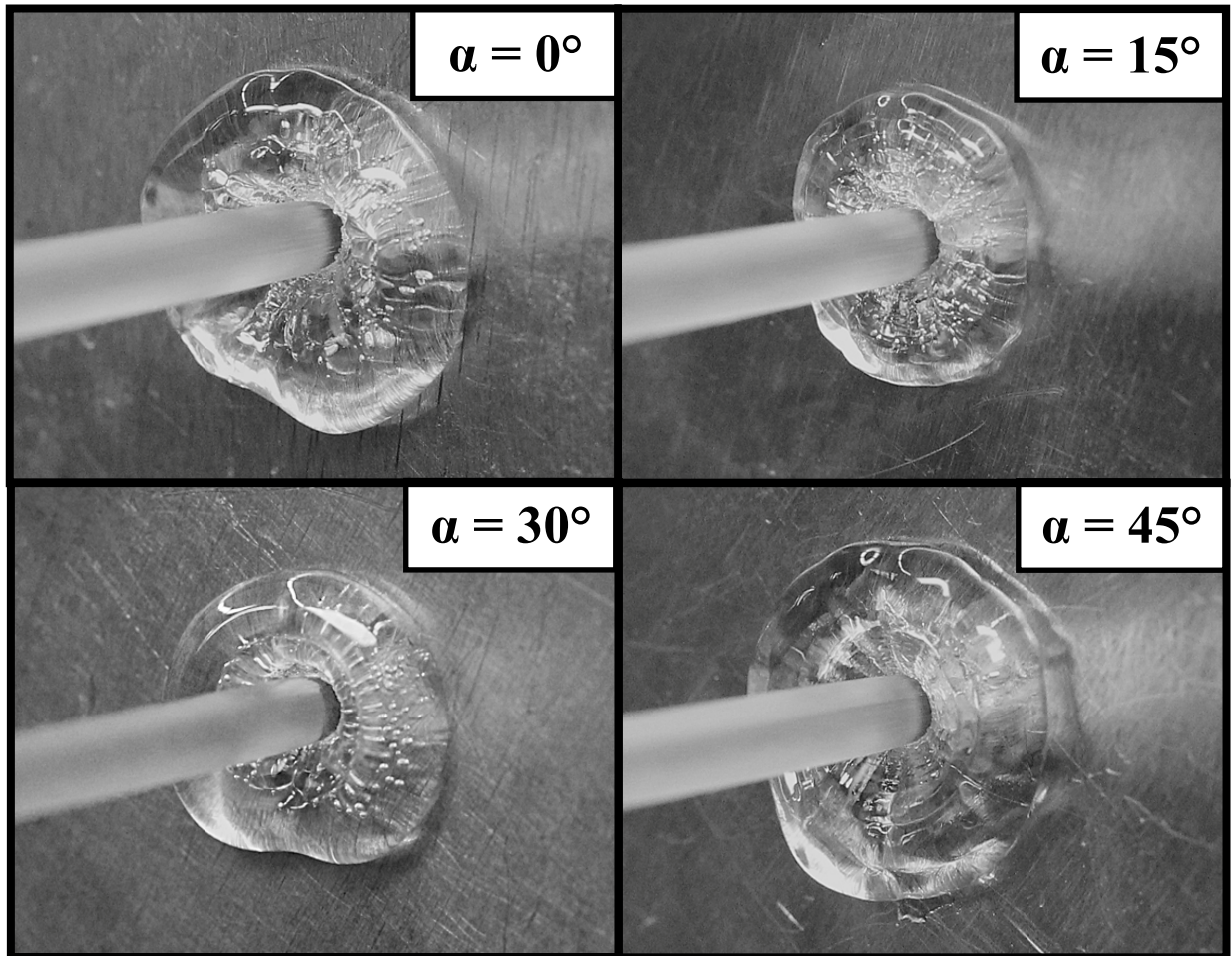
A-A

cooling channel
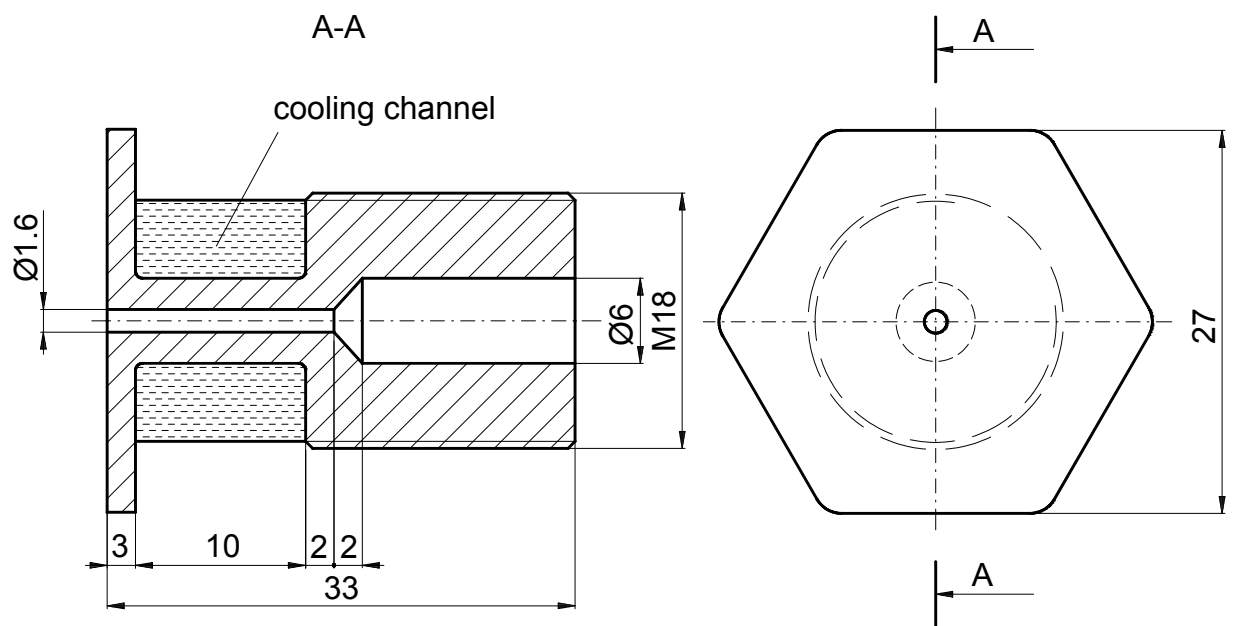
Figure 1 Section view of basic replaceable capillary die with dimensions.
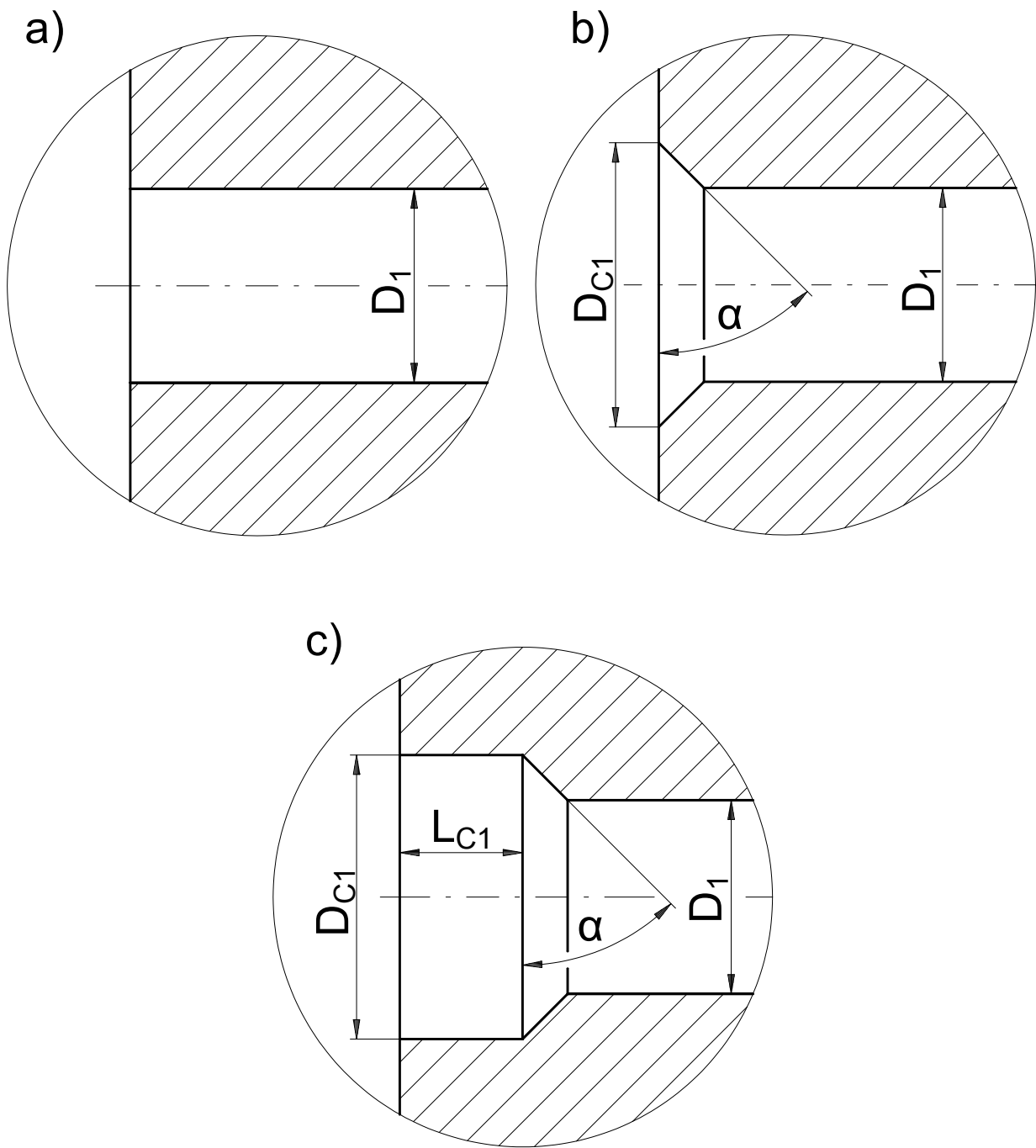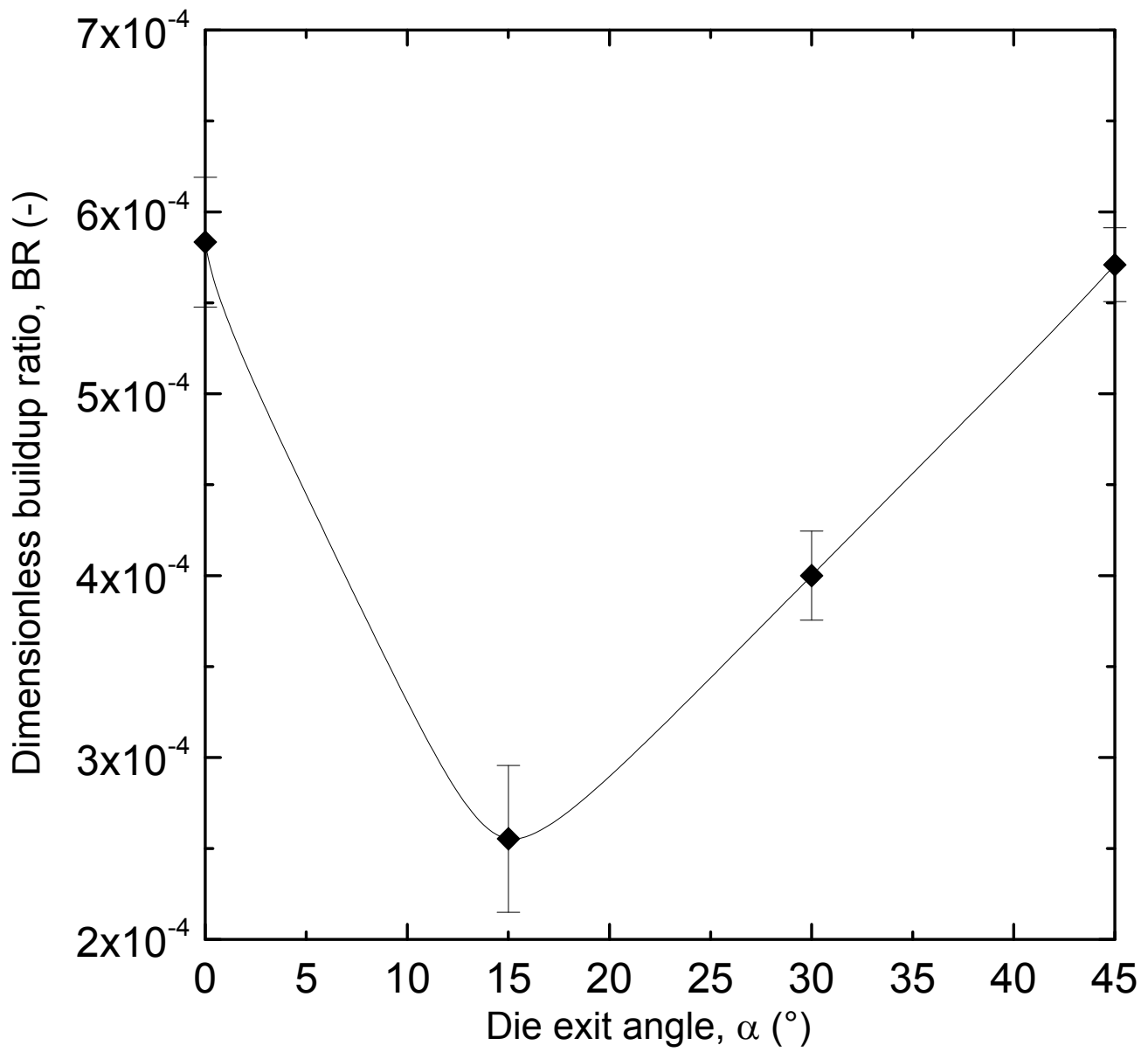
Figure 2 Detailed section views of capillary exit regions: (a) straight capillary, (b) chamfered die, (c) flared die.
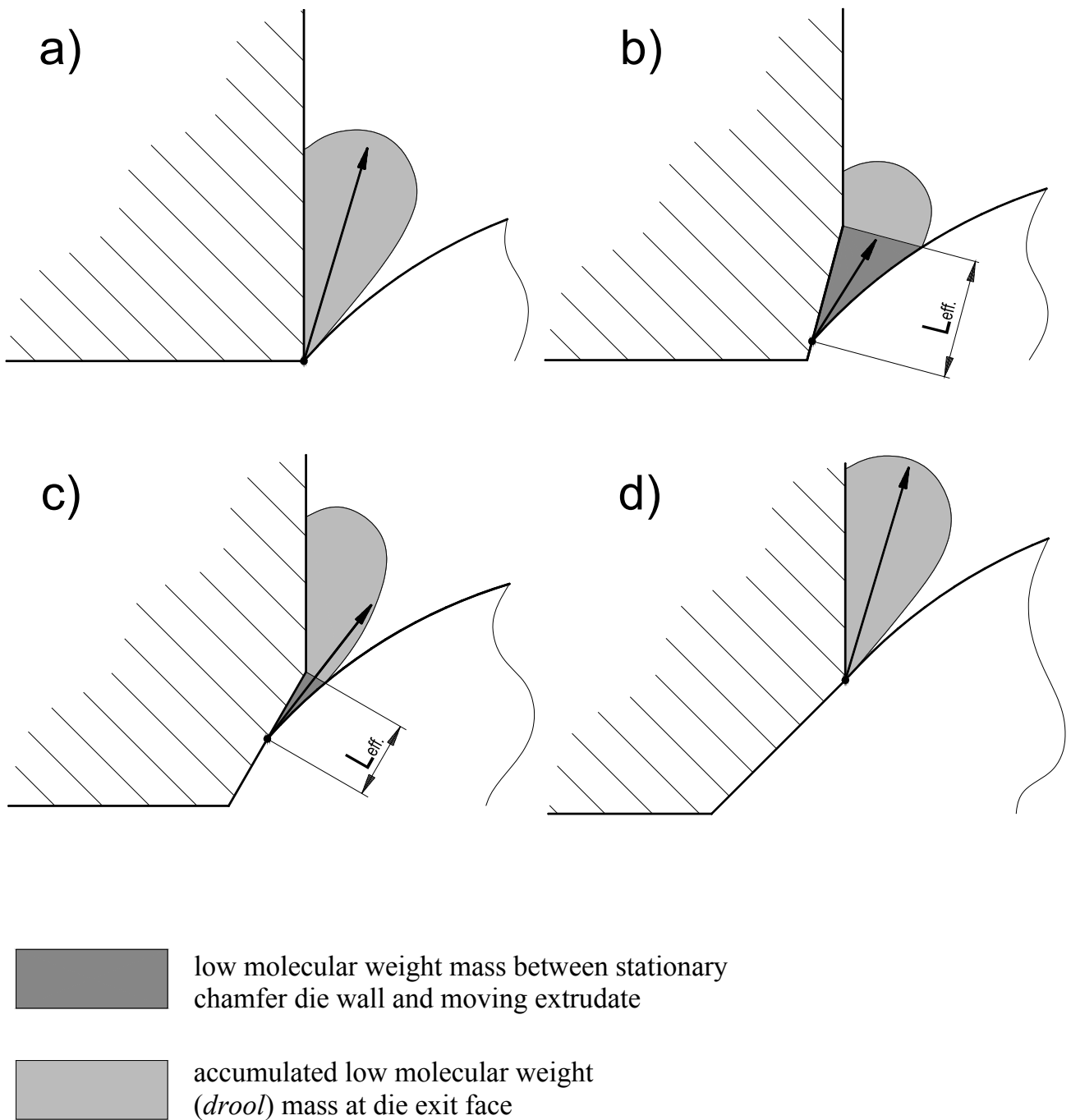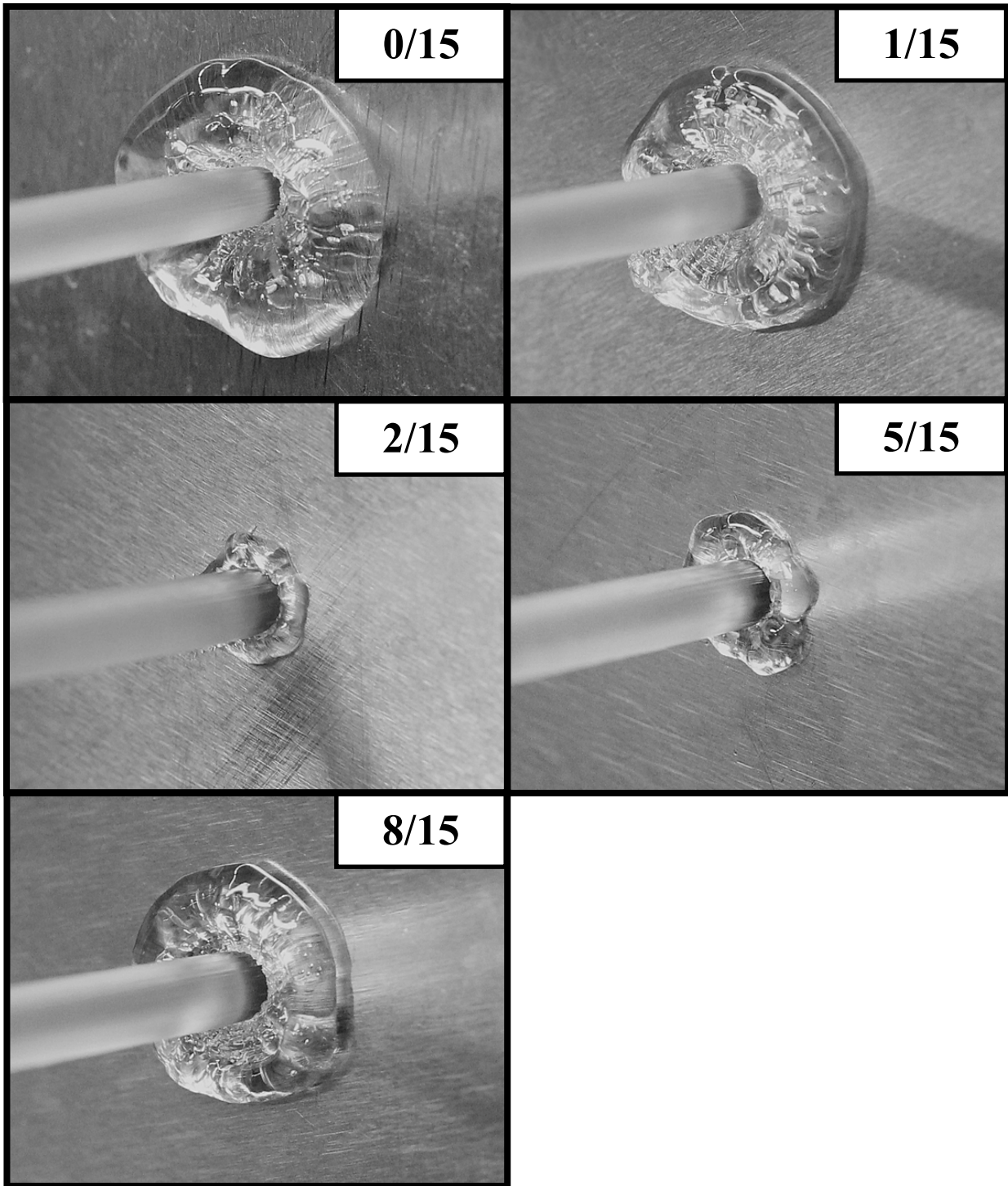
Figure 3 Die exit visualization for different die exit angles (after 10 minutes of extrusion).

Figure 4 Dimensionless buildup ratio as the function of die exit angle.

Figure 5 Effect of die exit angle on extrudate detachment and accumulation process of low molecular weight mass for (a) 0°, (b) 15°, (c) 30°, (d) 45° dies. (only die geometry dimensions are in scale).

Figure 6 Die exit visualization for different dimensionless flared lengths L_{C1}/L (after 10 minutes of extrusion).
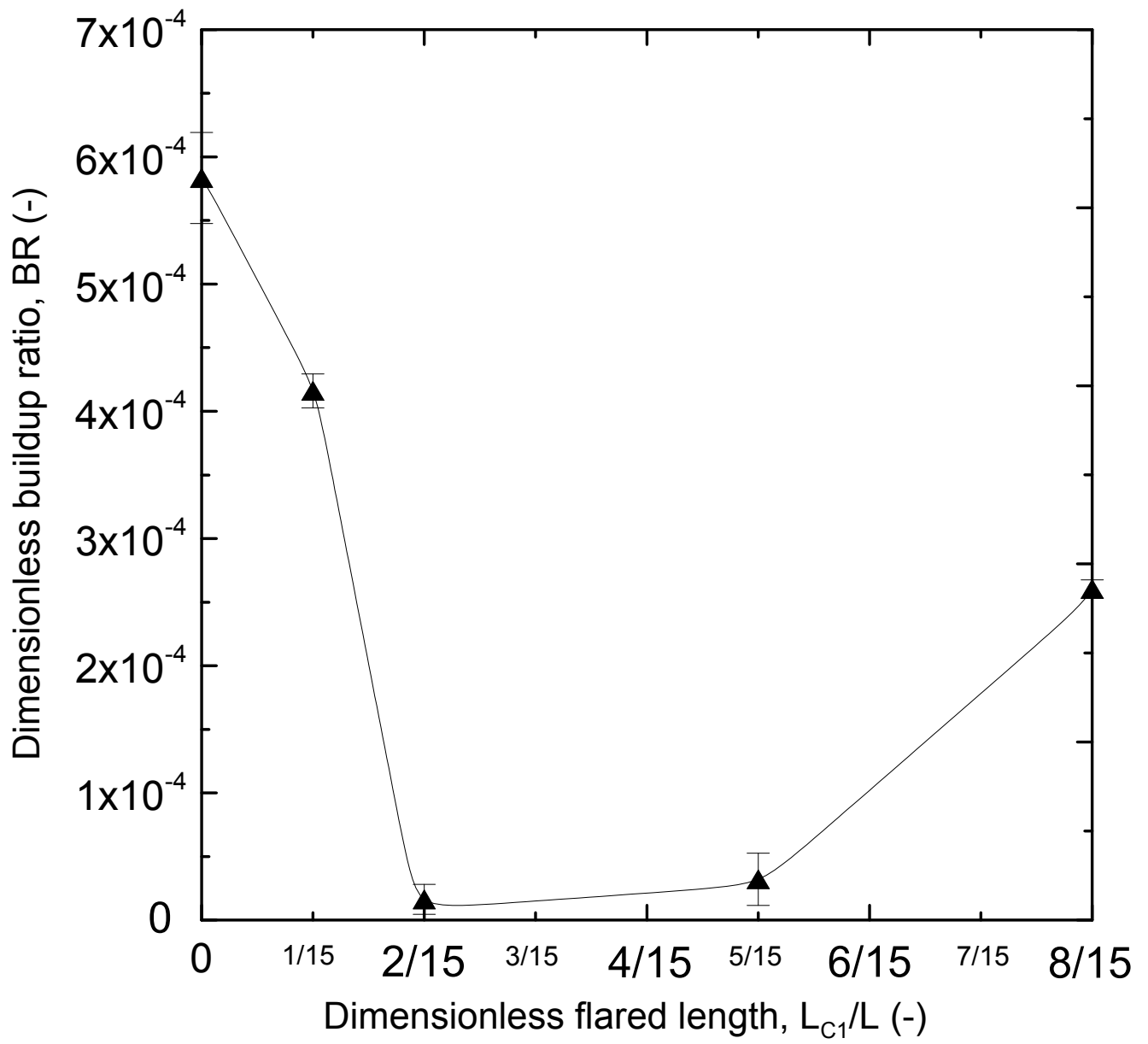
Figure 7 Dimensionless buildup ratio as the function of dimensionless flared length.
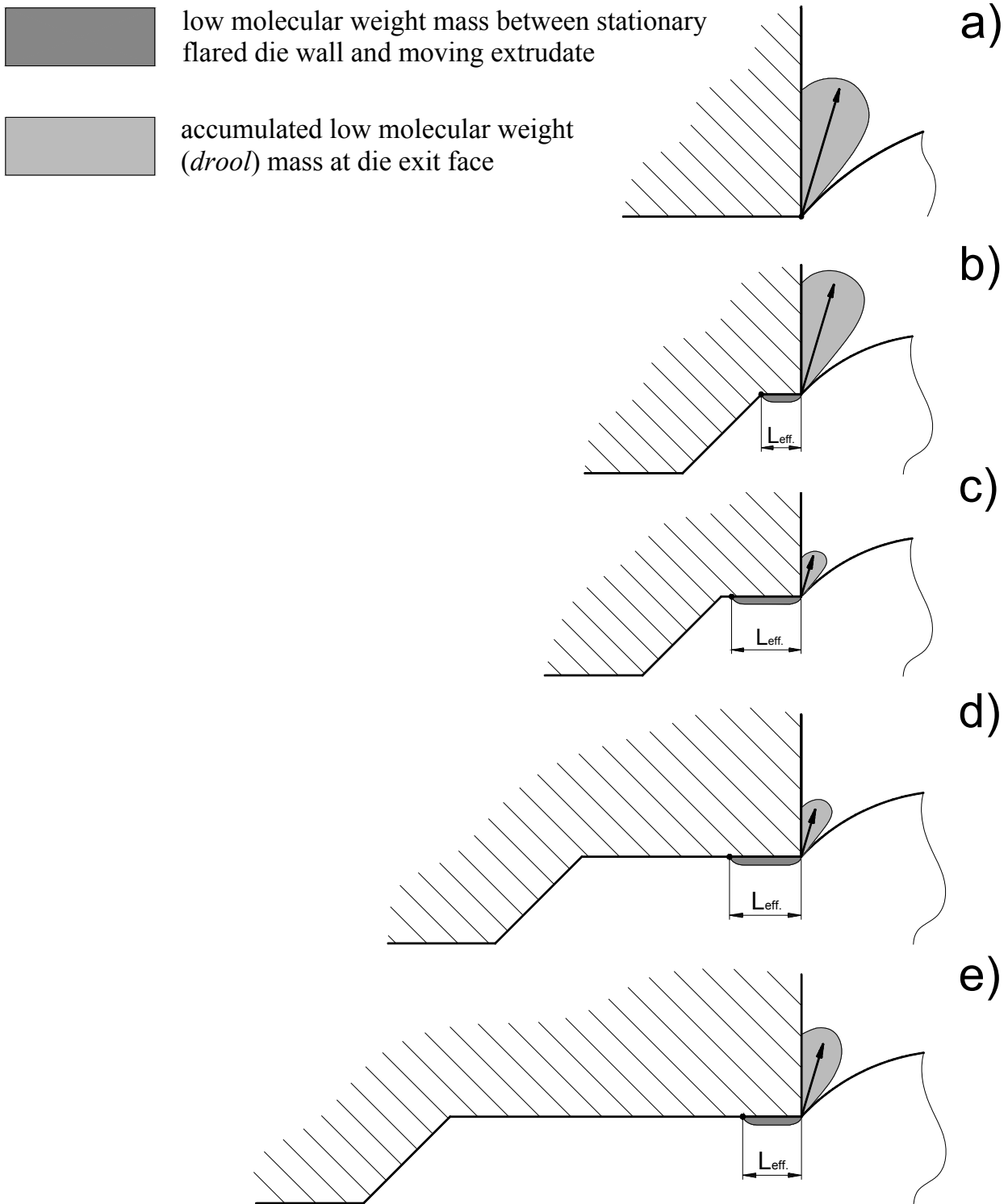
Figure 8 Effect of die exit flared length on accumulation process of low molecular weight mass for (a) 0/15, (b) 1/15, (c) 2/15, (d) 5/15 and (e) 8/15 dimensionless flared lengths (only die geometry dimensions are in scale).

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Organisation	Tomas Bata University in Zlín, Faculty of Technology, Department of Production Engineering
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Organisation	Secondary Technical School in Zlín

SCIENTIFIC FIELDS OF INTEREST

polymer melt rheology, rotational and capillary rheometry, polymer melt flow instabilities, flow visualization, polymer processing

ORIGINAL PAPERS ABSTRACTED ON WEB OF SCIENCE AND SCOPUS DATABASES

"THE SCIENCES HAVE BITTER ROOTS, BUT THEIR FRUITS ARE SWEET."

PROVERB

1. MUSIL, J., ZATLOUKAL, M. Effect of Die Exit Geometry on Internal Die Drool Phenomenon during Linear HDPE Melt Extrusion. *Chem. Eng. Sci.* (submitted manuscript in 2012).

2. MUSIL, J., ZATLOUKAL, M. Experimental Investigation of Flow Induced Molecular Weight Fractionation for Two Linear HDPE Polymer Melts Having Identical M_n and M_w but Different M_z and M_{z+1} Average Molecular Weights. *Chem. Eng. Sci.* (submitted manuscript in 2012).

3. MUSIL, J., ZATLOUKAL, M. Experimental Investigation of Flow Induced Molecular Weight Fractionation During Extrusion of HDPE Polymer Melts. *Chem. Eng. Sci.* 2011, vol. 66, no. 20, pp. 4814-4823.

4. MUSIL, J., ZATLOUKAL, M. Investigation of Die Drool Phenomenon for HDPE Polymer Melt. *Chem. Eng. Sci.* 2010, vol. 65, no. 23, pp. 6128-6133.

5. ZATLOUKAL, M., MUSIL, J. Analysis of Entrance Pressure Drop Technique for Extensional Viscosity Determination. *Polym. Test.* 2009, vol. 28, no. 8, pp. 843-853.

6. MUSIL, J., ZATLOUKAL, M., GOUGH, T., MARTYN, M. Investigation of Vortex Development during Polymer Melt Flows by Flow Birefringence. *AIP Conference Proceedings* 2011, vol. 1375, pp. 14-25, ISSN 0094-243X.

7. MUSIL, J., ZATLOUKAL, M., GOUGH, T., MARTYN, M. Experimental Investigation of Die Drool and Slip-stick Phenomena during HDPE Polymer Melt Extrusion. *AIP Conference Proceedings* 2011, vol. 1375, pp. 26-42, ISSN 0094-243X.

8. MUSIL, J., ZATLOUKAL, M. Investigation of Internal Die Drool Phenomenon for Different HDPEs. *AIP Conference Proceedings* 2009, vol. 1152, pp. 69-74, ISSN 0094-243X.

9. ZATLOUKAL, M., MUSIL, J. Development of Novel Die Design for Precise Entrance Pressure Drop Measurements. *AIP Conference Proceedings* 2009, vol. 1152, pp. 131-138, ISSN 0094-243X.

CONFERENCE PAPERS ABSTRACTED ON WEB OF SCIENCE OR SCOPUS DATABASES

"THE TEST OF ALL KNOWLEDGE IS EXPERIMENT."

RICHARD FEYMAN (1918 – 1988)

1. ZATLOUKAL, M., MUSIL, J. 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. *Annual Technical Conference – ANTEC, Conference Proceedings* 2012 (accepted).

2. MUSIL, J., ZATLOUKAL, M. On the Formation Mechanism of Die Drool and Slip-stick Phenomena during Linear HDPE Polymer Melt Extrusion. *Recent Advances in Fluid Mechanics, Heat & Mass Transfer nad Biology – Proceedings of the 9th WSEAS Int. Conf. on Fluids 2012*, pp. 156-161, Boston, Harvard, USA, ISBN 978-1-61804-065-7.

3. MUSIL, J., ZATLOUKAL, M. Flow Induced Molecular Weight Fractionation During Capillary Flow of Linear Polymer Melt. *Recent Advances in Fluid Mechanics, Heat & Mass Transfer nad Biology – Proceedings of the 9th WSEAS Int. Conf. on Fluids 2012*, pp. 162-167, Boston, Harvard, USA, ISBN 978-1-61804-065-7.

4. ZATLOUKAL, M., MUSIL, J. Effect of Processing Conditions and Die Design on Die Drool Phenomenon for HDPE Polymer Melt. *Annual Technical Conference – ANTEC, Conference Proceedings* 2011, vol. 2, pp. 1181-1185, ISBN 978-161782960-4.

5. ZATLOUKAL, M., MUSIL, J. Applied Rheology for HDPE Die Drool Phenomenon. *Annual Technical Conference – ANTEC, Conference Proceedings* 2010, vol. 1, pp. 748-751, ISBN 978-161738660-2.

6. ZATLOUKAL, M., MUSIL, J. Development and Testing of Novel Orifice Die Design for Extensional Viscosity Measurements. *Annual Technical Conference – ANTEC, Conference Proceedings* 2009, vol. 2, pp. 1017-1021, ISBN 978-161567327-8.

7. ZATLOUKAL, M., MUSIL, J. Determination of Uniaxial Extensional Viscosity for Polyolefins by Improved Entrance Pressure Drop Measurements. *Annual Technical Conference – ANTEC, Conference Proceedings* 2007, vol. 4, pp. 1943-1947, ISBN 978-160423214-1.

IMPORTANT ENGINEERING ACTIVITIES

"MY METHOD TO OVERCOME A DIFFICULTY IS TO GO ROUND IT."

GEORGE PÓLYA (1887 − 1985)

1. ZATLOUKAL, M., MUSIL, J. Utility Model CZ 19221 U1 entitled as *"Inert Extrusion Orifice Die"* (File number: 2008-20520, submitted 7th November 2008, File number: 19221, accepted 5th January 2009 by the Czech Patent and Trademark Office).

2. ZATLOUKAL, M., MUSIL, J. Submitted Patent PV 2008-714 entitled as *"Inert Extrusion Orifice Die"* (File number: PV 2008-714, submitted 7th November 2008 to the Czech Patent and Trademark Office).

THESES

"ALL GREAT SCIENTISTS HAVE, IN A CERTAIN SENSE, BEEN GREAT ARTISTS; THE MAN WITH NO IMAGINATION MAY COLLECT FACTS, BUT HE CANNOT MAKE GREAT DISCOVERIES."

KARL PEARSON (1857 − 1936)

1.   MUSIL, J. Investigation of Die Drool Phenomenon during HDPE Melt Extrusion, *Doctoral Thesis,* Zlín*, Tomas Bata University in Zlín, Faculty of Technology*, 2012, p. 142.

     supervisor: prof. Ing. Martin Zatloukal, Ph.D.

2.   MUSIL, J. Development of Improved Entrance Pressure Drop Technique for Extensional Viscosity Determination, *Master Thesis,* Zlín*, Tomas Bata University in Zlín, Faculty of Technology*, 2008, p. 156.

     supervisor: prof. Ing. Martin Zatloukal, Ph.D.

3.   MUSIL, J. The Effect of Long Chain Branching on Processibility of Polymer Melts, *Bachelor Thesis,* Zlín*, Tomas Bata University in Zlín, Faculty of Technology*, 2006, p. 101.

     supervisor: doc. Ing. Martin Zatloukal, Ph.D.

WORK ON PROJECTS AND CONFERENCIES

"Research is what I'm doing when I don't know what I'm doing."

Wernher von Braun (1912 – 1977)

2007 – 2011	**Grant GA AV ČR IAA200600703** *Investigation of Flow Behaviour for a Novel Class of Metallocene-Based Polymers* member of research team
2008 – 2010	**Grant MSMT ME08090** *Analysis of Extrusion Post-Die Instabilities for Advanced Viscoelastic Macromolecular Substances* member of research team
2009 – 2013	**Grant GA ČR 103/09/2066** *Analysis and Development of Constitutive Equations for Description of Non-Newtonian Fluids* member of research team
2010 – 2014	**Grant GA ČR P108/10/1325** *Applied Rheology for Advanced Polymer Processing* member of research team
2010	**Grant UTB IGA/3/FT/10/D** *Modeling of the Vortex Development During Polymer Extrusion Process* member of research team
2011	**Grant UTB IGA/2/FT/11/D** *Investigation of Negative Die Drool Phenomenon during Polymer Extrusion* project leader
2011 - 2014	**European Union Project CZ.1.05/2.1.00/03.0111** *Centre of Polymer Systems* part-time employee
2007, 2009, 2011	**Novel Trends in Rheology II, III, IV** *International conferences hosted at Tomas Bata University* member of organization team

SUPPLEMENTARY MATERIAL

Jan Musil

Investigation of Die Drool Phenomenon during HDPE Melt Extrusion

Výzkum jevu die drool během
vytlačování taveniny HDPE

Doctoral Thesis