ANALYSIS OF THE FREE SURFACE INSTABILITIES IN EXTRUSION AND COEXTRUSION FLOWS FOR METALLOCENE BASED POLYOLEFINS

Martin Zatloukal, Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin, TGM 275, Zlin 762 72, Czech Republic
Katerina Chaloupkova, Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin, TGM 275, Zlin 762 72, Czech Republic
Johan De Witte, 3M Belgium N.V. (Dyneon), Canadastraat 11, 2070 Zwijndrecht, Belgium
Jiri Vlcek, Compuplast International, Nerudova 158, 760 01 Zlin, Czech Republic

ABSTRACT

The effect of die design and wall slip on the die drool phenomenon was investigated for metallocene based LLDPE. It has been found that die exit opening and wall slip can significantly reduce the die drool phenomenon. Moreover, theoretical research has revealed that die drool onset can be explained by the negative/non-monotonic pressure profile generated inside the die and/or at the die exit region due to melt elasticity.

In the second part of the paper, recently proposed new slip model based on ‘effective continuum methods’ was developed and used for investigation of process aids interactions with polymer melts in single as well as multi-layer flows. Specific attention has been paid to understanding the role of process aids on stabilization of the zig-zag type of interfacial instabilities in film blowing coextrusion.

PART A:

EFFECT OF DIE DESIGN AND WALL SLIP ON DIE DROOL PHENOMENON FOR METALLOCENE BASED LLDPE: THEORETICAL AND EXPERIMENTAL INVESTIGATION

INTRODUCTION

Die drool is a phenomenon occurring in melt extrusion of polyolefins, PVC, and filled polymers, which manifest itself as an undesirable build-up of material, normally on the lip or open face of extrusion dies (see Figure 1).

![Die drool accumulation](image1.png)

In commercial extrusion processes, die deposit can have a significant influence on the productivity, as it requires shutting down the processing line periodically to clean the die. Furthermore, die deposit can also affect the quality of the extruded product. This phenomenon has been extensively studied both theoretically as well as experimentally [1-8]. Recently, this phenomenon has been investigated experimentally for mLLDPE at different processing conditions (mass flow rate and die exit temperature were varied) [7-8]. Consequently, these experimental data were followed by viscoelastic FE calculations with the aim to find out simple to use criterion for detection of the die drool phenomenon. It has been suggested that possible explanation for the die drool phenomenon onset is the high value of negative pressure occurrence at the die exit region [7-8]. It has been found that for mLLDPE the critical value of
such pressure is -1.6 MPa. This idea is explored here in more detail. Firstly, the effect of the die exit design on the
die drool phenomenon will be investigated. Secondly, the effect of the wall slip on the die drool phenomenon from
the negative pressure criterion point of view will be discussed and finally, deeper discussion about the negative
pressure significance will be provided.

EXPERIMENTAL

The laboratory measurements were performed on 19 mm conventional Brabender single-screw extruder with a
length \( L = 25D \) equipped by a specially developed annular extrusion die (Figure 2) developed at Polymer Centre,
Tomas Bata University in Zlin. The extrusion sections (from the hopper to the die) were heated to the following
temperatures: \( T_1 = 135^\circ C \), \( T_2 = 180^\circ C \), \( T_3 = 190^\circ C \), \( T_4 = 190^\circ C \), whereas the annular tube between extruder and
annular die was heated to the temperature \( T_5 = 125^\circ C \) only. During the experiments, the digital camera has been used
to quantify the level of the die drool phenomenon at the die lip area. For such purpose Die Drool Amount (DDA)
variable has been proposed.

\[
DDA = \frac{A_D}{A_{Die}} \frac{t_D}{t_{Die}}
\]

where \( A_D \) is area occupied by the die drooled material during the accumulation cycle, \( A_{Die} \) represents capillary die
area, \( t_D \) stands for die drool accumulation time and \( t_{Die} \) is time between die drool accumulation cycles. In this work,
the mLLDPE Exact 0201 (octane-1 plastomer, metallocene type) has been used.

Figure 2: Annular extrusion die with internal cooling system for the die lip.

MATHEMATICAL MODELING

Non-isothermal viscoelastic steady two-dimensional finite element simulations were performed by solving the well-
known mass, momentum and energy equations using the commercially available Compuplast software VEL 6.1. In
this study, the modified White-Metzner (mWM) constitutive equation according to Barnes and Roberts [9] is
employed. The non-isothermal mWM model is given by Eqs. (2) - (5).
\[ \tau + \lambda(I_d)\tau = 2\eta(I_d)d \]  
\[ \eta(I_d) = \frac{\eta_0 f}{[1 + (K_1 f I_d)]^{\eta_0 n}} \]  
\[ \lambda(I_d) = \frac{\lambda_0 f}{1 + K_2 f I_d} \]  
\[ f = e^{\frac{E_a}{RT}} \]  

where \( E_a \) is the activation energy, \( R \) is the gas constant, \( T_r \) is the reference temperature, \( T \) stands for the temperature, \( d \) represents the rate of deformation tensor, \( I_d \) means the second invariant of the rate of deformation tensor, \( \tau \) is the stress tensor, \( \tau^v \) is the upper convected time derivative of stress tensor. \( \lambda(I_d) \) means the deformation rate-dependent relaxation time and \( \eta(I_d) \) stands for the deformation rate-dependent viscosity, where \( \eta_0 \) represents Newtonian viscosity, \( \lambda_0, K_1, K_2, n \) and \( a \) are constants. The model parameters for the used mLLDPE material are provided in our previous work [7-8].

The FEM grid used to describe the flow in capillary die is shown in Figure 3. The typical pressure profile at the die exit region is depicted in Figure 4 for reference die having sharp die exit corner (Figure 5a). It is nicely visible that negative pressure occurs at that region which has been suggested in our previous work as the one factor causing the die drool phenomenon [7-8]. In the next section, the negative pressure will be discussed in more detail with respect to experimental data and melt elasticity.

**Figure 3:** FEM grid used for the die exit modeling.  
**Figure 4:** The predicted pressure field for the extrusion of mLLDPE Exact 0201 (1 kg/h, 90°C).
RESULTS AND DISCUSSION

The effect of the die design
The effect of the die exit wall angle \( \alpha \) on the Die Drool Amount is visualized in Figure 6. It is nicely visible that the die exit geometry can suppress the die drool phenomenon significantly. In more detail, the modification of the reference die (depicted on Figure 5a), by chamfering of the die exit wall under angle \( \alpha = 15^\circ \) (Figure 5b) has been found to decrease the die drool from 100\% (predicted negative die exit pressure =-1.76 MPa) down to 3.3\%. Full die drool suppression has been found to be for the die exit wall chamfering under angle \( \alpha = 45^\circ \) (Figure 5b). Note that the predicted negative die exit pressure has been found to be -1.27 MPa in this case. In both cases, the processing conditions were kept the same i.e. mass flow rate=0.4kg/h, die exit wall temperature 85\°.

The effect of the wall slip introduced by PPA
It has been found theoretically that introducing the wall slip at the end of the die leads to significant reduction of the negative pressure. In more detail, it has been revealed that during extrusion of mLLDPE Exact 0201 (1 kg/h, 90\°C), the introduction of the wall slip (melt velocity at the die exit wall was equal to 0.016667 m/s) causes reduction of the negative pressure from 100\% down to 60\%. It means that the use of proper type of PPA in extrusion of mLLDPEs leads to significant reduction of the die drool phenomenon which is in good correspondence with the experimental reality.

Figure 5: Sketch of the die exit regions for the capillaries used during the experimental work; 5a) Reference capillary die having sharp die exit corner; 5b) Modified capillary dies (\( \alpha = 15^\circ \) and 45\°).

Figure 6: Effect of the Die Drool Amount on the die exit angle \( \alpha \). The points represent the measurements (0.4 kg/h, 85\°C).

The effect of the external cooling of the die exit by the air flow
The table ventilator has been used to cool down the end of the die lip by the air flow with the aim to investigate its effect on the die drool appearance. We have chosen the flow conditions which were stable without external cooling (mass flow rate 0.3kg/h, die exit temperature 95\°C). It has been observed that the application of the external cooling
leads to the significant die drool phenomenon development as documented in Figure 7. It supports an idea that the die drool phenomenon is predominantly related to the die exit region in the mLLDPE extrusion.

**Figure 7: Extrusion of mLLDPE Exact 0201 (0.3 kg/h, 95°C) with external cooling.**

- a) Die exit region
- b) Surface of the extrudate

**Significance of the negative pressure**

Discussion about the reasons for the negative pressure occurrence in the studied flow domain and its impact on the die drool phenomenon is explored here in more details. Firstly, the question is what the reasons for the negative pressure are. It has to be pointed out that the melt elasticity and streamline curvature may lead to the normal stress generation which consequently causes the non-monotonical local pressure decrease in the pressure profile during the polymer melt flow. An example of such flow situation is provided in [10-12] where the so called ‘pressure hole’ effect is described in more detail. At the die exit region where the melt elasticity and level of the streamline curvature (due to velocity rearrangement) is very high the non-monotonic pressure profile can also be observed i.e. pressure becomes non-monotonic having a local extreme (minimum) there. Here, the absolute value of the pressure may become negative because this situation happens very close to the area where the pressure is 0 (i.e in the post die area where the velocity profile is constant in the extrudate). It seems that the negative pressure (local pressure minimum) seems to ‘help’ to the melt with the velocity rearrangement at the die exit region. The importance of the local pressure minima in the melt (or negative pressures at the die exit regions) with respect to the die drool phenomenon is that the negative pressure is also felt by possibly present surrounding low molecular weight components or fillers. The occurrence of the negative pressure can promote their separation, migration and accumulation at the die exit region.

Secondly, the question is whether a more realistic constitutive equation than mWM model will also predict non-monotonic pressure profile at the die exit region. Due to the fact that level of non-monotonicity in the pressure profile depends on the streamline curvature and corresponding normal stress generation, as discussed above, the use of the more advanced constitutive equation will leads to the more precise determination of the normal stresses/non-monotonic pressure profile at the die exit region than in case of the mWM model which artificially predict Weissenberger number to be constant at very high flow rates [9]. On the other hand we can say that any constitutive equations capable to represent melt elasticity at least quantitatively should be able to predict non-monotonic pressure profiles at the die exit region.

Finally, we have investigated theoretically the effect of melt elasticity on the pressure profile inside the virtual die having the diverging die exit region (with no free surface region) having both, smooth transition at the top wall and sharp transition at the bottom wall (see Figure 8a). The Figure 9a shows the pressure profiles for highly elastic
polymer melts along the top and bottom wall. It is clearly visible that firstly, negative pressure may occurs inside the die and secondly, the higher value of the negative pressure corresponds to the sharp transition.

Figure 8: Flow of the viscoelastic melt inside the virtual extrusion die having diverging exit region with smooth (upper wall) and sharp (bottom wall) transition; 8a) Predicted pressure gradient magnitude field; 8b) Predicted principle stress difference field.

Figure 9: Calculated pressure profile (for two chosen pathlines) during the melt flow in the virtual extrusion die depicted in the Figure 8; 9a) Melt with high level of elasticity; 9b) Melt with very low level of elasticity.

This suggests that possible low molecular weight components/fillers separation from the viscoelastic polymer melt matrix may occur also inside the dies which can contribute to the higher accumulation level at the die exit wall. Figure 9b shows practically the same results as in the Figure 9a but for very low elastic fluid. It is clearly visible from comparison between Figures 9a and 9b that decrease in the melt elasticity significantly reduces negative pressure occurrence inside the die. With the aim to quantify the internal/external die drool phenomenon as much as possible from the theoretical point of view, the magnitude of the pressure gradient, defined by Eq. 6, might also be considered because this variable is very sensitive to the abrupt change in the pressure profile which usually occurs usually at the pressure profile minimum or maximum.

\[
\overline{\nabla p} = \sqrt{\left(\frac{\partial \overline{p}}{\partial t}\right)^2 + \left(\frac{\partial \overline{p}}{\partial n}\right)^2}
\]  

(6)

If we compare the pressure gradient magnitude field (Figures 8a, 10 and 11) with the Principle Stress Difference (PSD) field for studied virtual die (Figures 8b) we can see that sensitivity of the \(\overline{\nabla p}\) to the transition smoothness into the diverging channel is much higher than in the case of the PSD. Finally, the normal component of the pressure
gradient $\frac{\partial p}{\partial n}$ can also be useful from the die drool point of view, because it quantifies the possible separation force, occurring due melt elasticity or die bad design, in the normal direction (toward the die wall) with respect to the flow direction. Therefore the use of the pressure, $\nabla p$ and $\frac{\partial p}{\partial n}$ with respect to the internal/external die drool phenomena can be recommended.

**Figure 10:** Predicted magnitude of the pressure gradient at the smooth transition from the parallel into the diverging channel for the virtual extrusion die depicted in Figure 8.

**Figure 11:** Predicted magnitude of the pressure gradient at the sharp transition from the parallel into the diverging channel for the virtual extrusion die depicted in Figure 8.

**CONCLUDING REMARKS**

- It has been found experimentally that chamfering of the die exit wall under angle $\alpha = 15$- $45^\circ$ significantly reduces the die drool phenomenon.
- It has been revealed theoretically that wall slip reduces the negative pressure at the die exit region which is stabilizing effect from the die drool phenomenon point of view.
- It has been speculated that internal die drool can be explained by negative pressure inside the die.
- It has been suggested that pressure, magnitude of the pressure gradient and normal gradient pressure component can be useful variables for theoretical investigation of the die drool phenomenon.

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**REFERENCES**


**Key Word**: Die drool, negative pressure, FEM modeling.

**PART B**

THEORETICAL AND EXPERIMENTAL INVESTIGATION OF ZIG-ZAG INTERFACIAL INSTABILITIES IN COEXTRUSION FLOWS

**INTRODUCTION**

Polymer Processing Additives (PPA) represents specific type of additives which are widely used in single layer extrusion with the objective to suppress different type of extrusion defects. A first group of PPAs usually comprises fluoropolymer-based materials appearing as discrete, micron-sized particles, mostly incompatible with others polymers. Thus, during the single layer extrusion flow, PPA particles migrate to the die wall due to phase separation and a thin fluoropolymer layer is created (dynamic coating). Because the PPA has low surface energy and a high incompatibility with the extruded polymer, slip is induced at the fluoropolymer-polymer interface which reduces the stress at the die wall and increases the melt velocity in that region. This help to suppress external free surface defects (shark skin, die drool phenomenon, degradation) appearing in the film production. Therefore, this type of additives causes external slip (metal wall-PPA-polymer) predominantly. A second group of PPAs includes boron nitride [1] or nanoclay [2] based additives which are flowing along with the polymer melts (no migration to the die wall) and causes internal slip (polymer-PPA-polymer) which may leads to decrease of the extensional viscosity of the melts [1-2]. These types of PPAs have been shown to suppress also gross melt fracture (bulk distortion). Moreover, it has been shown by Hatzikiriakos et al. [1-2] that a combination of nanoclays or boron nitride with traditional PPAs as fluoropolymers produce an enhanced processing additive for single layer extrusion. Even if many useful findings and conclusions have been made in past concerning to the role of PPA in single layer extrusion, there are only a few published papers [3-5] on the effect of PPA on the stabilization of coextrusion flows, where two or more materials are extruded through the single die. In such a case, the free surfaces are not created only at the end of the die, as in the case of single layer extrusion, but also inside the die, which may leads to the onset of interfacial instabilities at critical flow conditions, as documented in literature [6-22]. In specific cases, deformation of the internal interfaces in the converging channels, especially at the end of the coextrusion dies, may lead to highly intensive unbalanced stretching across/along interface which causes the so called zig-zag type of interfacial instabilities [6, 11, 18-22]. The appearance of these interfacial instabilities represents the main limiting factor for coextrusion. Therefore, main purpose of this work is to investigate theoretically and experimentally the interactions between a PPA and the polymer melt in single layer extrusion as well as in coextrusion, flows, with a special focus on the zig-zag interfacial instability.
RESULTS, DISCUSSION AND CONCLUSIONS

In this work, a recently proposed slip model [5] is employed. The model is based on the idea that a polymer melt flow with PPA can be viewed as a 5 layer coextrusion where molecular interaction layer between PPA and polymer is described as a moving continuum having specific rheological properties. In the first step of the theoretical investigation, different types of molecular interactions (captured through different interaction layer rheology as visible in Figure 1a) were considered between PPA and polymer melt to reveal their effect on the macroscopic slip capabilities in the capillary die. Figure 1b shows predicted shear stress on the die wall as a function of the apparent shear rate for different level of molecular interactions between PPA and polymer melts. It is not surprising that decreasing of the interaction layer rheology causes higher reduction of the wall shear stress (Figure 1b). The measurements represented in Figures 1c revealed that the reduced wall shear stress, due to small amounts of PPA, takes a ‘S’ shape rather than the shape type (Figure 1b) predicted by the slip model employing the Carreau-Yasuda model for the interaction layer rheology. This suggest that the interaction layer rheology will be more complex than that for only a simple shear thinning or shear thickening fluid.

Coextrusion work: The coextrusion experiments were performed on a Collin laboratory 3-layer coextrusion blown film line equipped by a flat spiral die system. The main results are summarized in Figure 2. In more detail, the Figure 2a shows a film exhibiting the zig-zag type of interfacial instability. Figure 2b shows coextruded film with the presence of the PPA in the outside layers. It is clearly visible that the use of the PPA in this specific way is suppressing the zig-zag interfacial instabilities significantly. With the aim to more deeply understand the stabilization mechanism of the PPAs with respect to the interfacial instabilities, a new slip model has been employed to investigate molecular interactions between PPA and polymer melts in this type of coextrusion flow. The coextrusion experiment described above has been followed numerically by the help of the new slip model. In more detail, the three layer coextrusion (mLLDPE+PPA/HDPE/mLLDPE+PPA) has been modeled as 7 layer coextrusion (PPA/IL/mLLDPE/HDPE/mLLDPE+PPA) where rheology of the PPA, mLLDPE and HDPE was known and the interaction layer rheology was varied. The most important calculated variables are included in Table 1. Three IL rheologies were tested (IL1, IL4, IL7) and they are visualized in Figure 1a. It is not surprising that the presence of PPA decreases both, the wall PSD as well as the interface PSD in comparison to without PPA. However, the interesting point is that presence of the low viscous IL7 causes the highest reduction of the stress at the die wall but not the highest reduction of the stress state on the interface between mLLDPE and HDPE. Better results with respect to the stress state level on the interface are achieved through IL4. The reason for such unexpected results can be
explained by a higher level of shear/extensional rate at the mLLDPE/HDPE interface for IL7 in comparison with IL4. Clarification of this can be achieved through analysis of the velocity profiles at the die wall and in the mLLDPE/HDPE interface area (see Figure 3). It is clearly visible that even if IL7 causes higher slip at the die wall area, the velocity may become more developed in the mLLDPE layer in contrary to a lower wall slip with IL4. This causes increase in the slope of the velocity profile (shear rate) at the mLLDPE/HDPE interface from left side. This finding suggests that specific care has to be paid for the suitable selection of the proper PPA for the maximum interfacial instability suppression.

Figure 2 Clarity test of the coextruded film under different conditions:
2a) mLLDPE/HDPE/mLLDPE structure
2b) mLLDPE+PPA/HDPE/ mLLDPE+PPA structure

Table 1 Calculated variables at the end of the converging section. Note that PSD is principle stress difference.

<table>
<thead>
<tr>
<th>IL no.</th>
<th>Wall PSD</th>
<th>Wall shear rate</th>
<th>IL/mLLDPE PSD</th>
<th>IL/mLLDPE shear rate</th>
<th>mLLDPE/HDPE PSD</th>
<th>mLLDPE/HDPE shear rate</th>
<th>mLLDPE/HDPE extensional rate</th>
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<td>-</td>
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Figure 3 Predicted velocity profiles at the die wall, IL/mLLDPE and mLLDPE/HDPE areas for different level of molecular interaction (IL1, IL4, IL7) between PPA and the polymer melts.

References