# Historical review of die drool phenomenon during plastics extrusion

Jan Musil and Martin Zatloukal

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# Historical Review of Die Drool Phenomenon during Plastics Extrusion

Jan Musil[a] and Martin Zatloukal[a,b]

[a]Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin,
Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic
[b]Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin,
nam. T. G. Masaryka 275, 762 72 Zlin, Czech Republic

**Abstract.** Die drool phenomenon is defined as unwanted spontaneous accumulation of extruded polymer melt on open faces of extrusion die during extrusion process. Such accumulated material builds up on the die exit and frequently or continually sticks onto the extruded product and thus damages it. Since die drool appears, extrusion process must be shut down and die exit must be manually cleaned which is time and money consuming. Although die drool is complex phenomenon and its formation mechanism is not fully understood yet, variety of proposed explanations of its formation mechanism and also many ways to its elimination can be found in open literature. Our review presents in historical order breakthrough works in the field of die drool research, shows many ways to suppress it, introduces methods for its quantitative evaluation and composition analysis and summarizes theories of die drool formation mechanism which can be helpful for extrusion experts.

## STATE OF THE ART

The nature of polymer melts flow is more complex than their Newtonian counterparts by the reason of their viscoelastic behaviour which causes significant natural and structural changes during the flow resulting into unwanted flow phenomena like neck-in, draw resonance, die swell, shark skin, slip-stick, melt fracture, etc. [1-5], which significantly complicate or totally destroy the production process.

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, builds up into a large (toroidal shape in the case of annular extrusion die) usually degraded mass which frequently breaks away from the die, completely (or partly) encloses the extruded product, adheres perseveringly onto extruded product surface and thus damages it. This effect is in extrusion art defined as undesirable spontaneous accumulation of polymer melt at the die exit face and it is termed like "die drool", "drooling", "die lip build-up", "die bleed", "die plate-out", "die deposit", "die drip", "die moustache" or "gummy crust" 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, fiber spinning, film/melt blowing or wire/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 consisting in periodic stops the extrusion line, disassembling of all extrusion die parts and manually cleaning them remains. Clearly, this procedure is time and also money consuming.

On the following pages, large detailed literature overview focused on die drool phenomenon in historical order is provided.

## Breakthrough Works Focused on Die Drool Phenomenon

From the beginning of polymer extrusion, die drool has represented real extrusion problem as can be seen from wide range of patented solutions and ideas to suppression it broadly introduced below. The breakthrough works 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 [6]. 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 [7]. 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 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" [8], "...the sudden release of pressure on the polymer material as it emerges from the die into the atmosphere" [9] 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" [10].

Klein [11] in 1982 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 is related to a die. Second, on the other hand, if the die remains clean for a period of time and the polymer deposit rises suddenly, the problem is in the screw.

In 1997, Gander and Giacomin [12] published the first work summarizing the die drool problem. They conclude 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 dimensionless analysis which provides a unified approach for solving die drool problems.

Chaloupková and Zatloukal [13] in 2009 mathematically modelled polymer melt flow in die outlet zone and they disclosed area of negative pressure near the die exit edge contributing to material separation from the matrix. Further, they concluded that negative pressure is crucial important variable for die drool phenomenon. At last, as a matter of interest, they also discussed the possibility of Newtonian liquid 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.

In 2009 Hogan et al. [14] experimentally investigated possible relationship between die swell and die drool (as Klein [11] earlier speculated) and they concluded that "...die swell is not a root cause of die buildup". However, more interesting finding in their work is gel permeable chromatography (GPC) analysis of die drool sample collected from the die lip. They found that drool 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."

In our recently published series of research papers [15-18] we have been focused on systematic experimental investigation of die drool during HDPE polymer melt extrusion. We found that first, the die drool phenomenon occurring during extrusion of HDPE polymers can be considered as the result of the flow induced molecular weight fractionation which is initiated under the slip-stick flow instability regime, second, an increase in HDPE chain branching, and a decrease in its elasticity reduces die drool phenomenon and finally, only those die exit modifications which promotes continuous release of low molecular weight species from the die exit region by the moving extrudate suppressing die drool phenomenon for HDPE.

Finally, in the latest published work of Schmalzer and Giacomin in 2013 [19] authors present novel idea that cohesive failure (disentanglement of chains in the polymer bulk from chains adsorbed at the die wall very close to die wall) can be the die drool formation mechanism. In their imagination, cohesive failure causes phase separation of polymer layer near die wall from polymer bulk and then this layer can easily build up on die exit face as die drool.

Beside these breakthrough works, a lot of other interesting works focused on die drool have been published. Many of them are reviewed on following pages.

## Die Drool Causes and Elimination Methods

Although the fundamental drooling formation mechanism is still not fully understood yet, wide range of causes and elimination methods of this unwanted extrusion phenomenon can be found in open literature. Generally, they can be divided into three groups. First, design changes inside or outside of extrusion die second, 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.

## Die Design Modifications

From historical point of view, elimination of die drool was originally solved by die design changes. In above-mentioned US patent from 1946 [6] is proposed polytetrafluoroethylene (PTFE) coating of the die exit surfaces or creating whole die from this well-slipping polymer. Nevertheless, main disadvantage of this idea consists in extremely rapid wear-out of such polymer. In Figure 1 is shown further solution presented by Foster [7]. 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 end. Toroidal drool shape is thereby broken into small harmless drips.
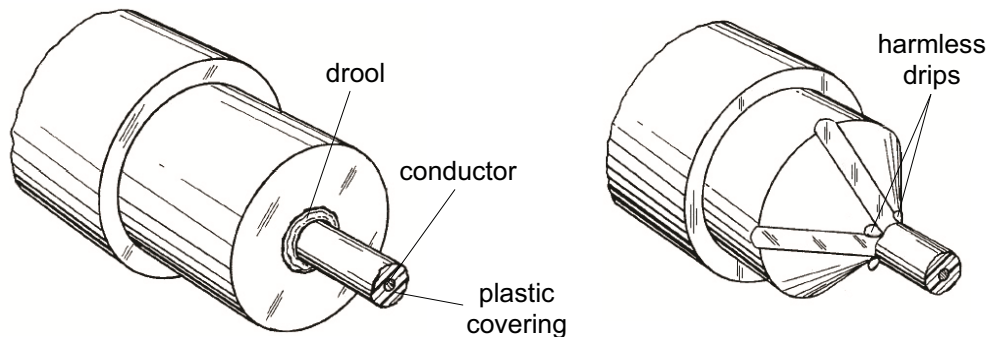


**FIGURE 1.** Original (left) and modified (right) die exit surface according to Foster (adapted from [7]).

Another idea [20] is focused on modification of channel shape between die and wire guiding tip inside a cable coextrusion die and the authors found that "...a low-pressure polyethylene extrusion die (i.e., one which offers little resistance to compound flow) tends to drool more than dies which have more resistance to compound flow." Figure 2 depicts Budenbender's [9] modification which suppresses 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.

Interesting way to die drool suppression is using surface-modified dies as presented by Kurtz and Szaniszlo [21]. 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 invention can be found in another US Patent from 1995 [22] where authors extruded EVOH material through die coated by fluoroelastomer (0.5% of Dynamar FX-2231 from 3M in acetone) and time to die drool occurring was extended from 10 minutes to 30 minutes. Moreover, different die surface materials (stainless steel, PTFE-coated die and fluoroethylene propylene-coated die) were investigated in [23] with conclusion that formation rate of die drool decreases as the surface energy of the die-wall material decreases. This reduction author attributes to a decrease in the work of adhesion which is related to the surface energies of the die-wall material and the polymer melt.
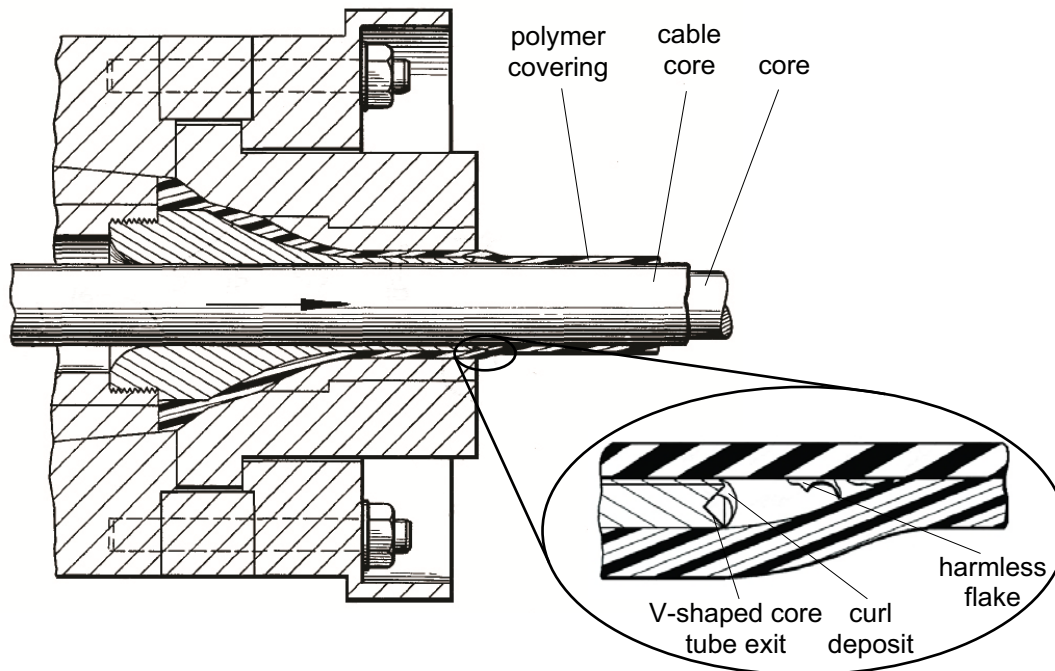
19

**FIGURE 2.** Budenbender's modification of core tube exit design (adapted from [9]).

Another contribution contains chamfer of the die exit edge [13]. Surprisingly, if the chamfered die exit edge angle is 45° accumulated drool mass is then dramatically reduced. However, it should be noticed that this reduction is possible only for certain polymers drooling externally (e.g. metallocene based LLDPE [13,24] or polypropylene [25] polymer melts). "External die drool" is related only to die exit region not to whole flow channel in the extrusion die. This other type is then termed as "internal die drool" (typical for HDPE polymer melts [15-18]) and in this case dependence of die drool vs. die exit angle can be strongly non-monotonic as shown in [18]. Moreover, rounded die exit edges reducing die drool can be also found in [26].

Next very successful invention proposing flared die exit was independently patented by Ohhata et al. [27] and Rakestraw et al. [28] (see Figure 3). Moreover, in both patents suitable range of particular dimensions of flared end section are proposed.
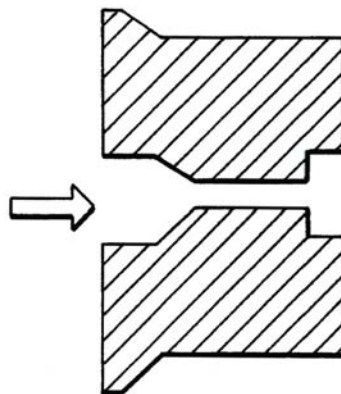


**FIGURE 3.** Flared die exit (adapted from [27]).

20

The explanation why flared dies are so effective was searched by Ding et al. [29]. 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 values at the die lip to governs die drool reduction.

Further, flared and also chamfered dies during HDPE melt extrusion were recently investigated [18]. It has been found 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 capilary length ratio of 2/15. Moreover, authors suggest 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.

Idea how to remove accumulated die drool from die lips without interruption of extrusion process is described in [30]. It is based on replaceable inserts on both sides of flat extrusion die opening section as shown in Figure 4. When the accumulated drool becomes sufficient to contaminate the extruded product, or before that time, the die inserts are simply removed and replaced without disrupting the production line.
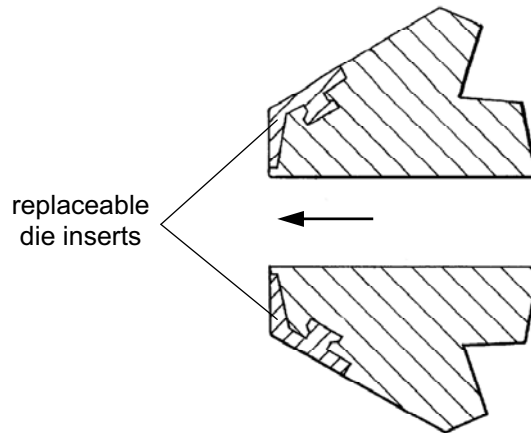


**FIGURE 4.** Replaceable die inserts for removing die drool without interrupting of extrusion process (adapted from [30]).

Another way uses thin rigid wire or wire-like part moving across the die face from one side to another to remove built-up polymer [31]. In this case, polymer material simply flows around the wire while the wire crosses through the extrudate. Authors claim that "...the great advantage of the method is that the interval between the sweeps of the wire should be relatively short, no production time is lost and there is no or virtually no wastage of the extrudate. This is because the sweep of the wire does not cause the breakage of the continuous liquid extrudate."

Other very interesting solution for suppression not only die drool but also other polymer melt flow instabilities is suggested in [32]. It is based on silicon rubber coating of the inside die exit wall. The authors also investigated other die wall

21

materials (e.g. glass, stainless steel, brass, PTFE or boron nitride) with conclusion that none of these materials markedly shifts critical shear rate over it well known slip-stick, shark-skin and also melt fracture instabilities appear. On the other hand, in the case of rubber-coated dies this critical shear rate is at least 10 times higher in comparison with previously mentioned inside die wall materials. Further, in this work is also shown, in our knowledge for the first time in open literature, that die drool arises only if slip-stick or shark-skin regions are overrun. Further, hard chrome die was found to be drool eliminating in the case of HDPE melt extrusion [33].

Special shape of extrusion die nozzles for melt strands eliminating die drool can be found in [34]. The schematic view of it is depicted in Figure 5 and authors discovered that "... surprisingly, it has been found that cylindrical dies with conically convergent inflow channel and conically divergent outflow channel in conjunction with a long melt-outflow region with respect to the melt-inflow region have substantially better suitability for the avoidance of die deposits than dies which have comparable geometry but have a shorter melt-outflow region."
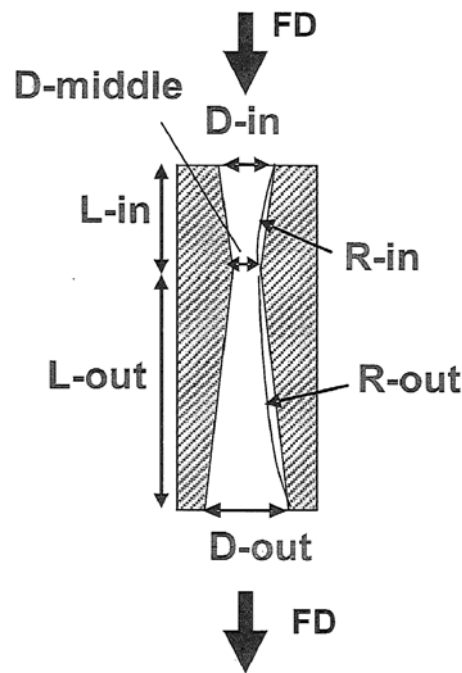


**FIGURE 5.** Schematic view of converging/diverging extrusion die geometry reducing die drool (adapted from [34], FD means flow direction).

Finally, for peroxide cured thermoplastics and thermoplastic elastomer compositions tapered die flow design with angle from 5° to 20° (smaller at die front, larger at die back) was found to be die drool eliminating [35].

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

22

## Polymer Material Modifications

With slight delay in comparison with die design, extrusion experts began to investigate also polymer material modifications. Historically, Havens at el. [36] in 1960 can be considered as the first ones who were interested in finding suitable composition of polyvinylidenechloride (PVDC) showing no drooling capability. They found that several types of stearyl phosphates (disodium, aluminium, calcium or barium) in range of 0.5 wt.% to 2 wt.% significantly inhibiting die drool. In the same year, Henning [8] discovered that diethylene glycol (DEG) as low molecular substance added to the polyethylene prior extrusion in range between 0.5 up to 1 by weight, to approximately 100 parts of polyethylene by weight, has significant die drool reducing effect. In further patent from 1971 [10] very efficient additive in the form of polytetrafluorethylene (PTFE) granular powder having average particle size of at least 0.5 micron 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 additional 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. However, negative interaction between the processing aid and inorganic pigment can lead to more intensive die drool [37]. In searching of suitable anti-drooling agents continued Yanagisawa et al. [38]. They provide large number of such agents based on low molecular substances like ethylene glycol, glycerin propyl alcohol etc. They found that materials with solubility parameter more than 12 are good anti-drooling agent candidates for foamed polyolefin resin. Nevertheless, in order to increase extruding capability of conventional block copolymers (such as hydrogenated block copolymers of styrene and butadiene or isoprene) substantial amounts of polyolefines, extending oils, tactifying resin and waxes and/or other processing aids causing die drool are usually added [39].

Low volatility is an important characteristic of stabilizers used in any applications where high temperatures are encountered. Low volatility will prevent loss of the stabilizer during processing and high temperature end-uses. Besides this, low volatility minimizes die drool [40-42]. This finding is also noted in [43] where authors write that "…the presence of little or no die lip build up may be related to the volatiles content of the conductive composition." In recent patent from 2007 [44] die drool problem is solved for white (or opaque) filled polyolefin composition compares three different antioxidants (zinc 2-mercaptotolylimidazole, 2-mercaptotolylimidazole and Irganox 1010). From the results it is clear that at the same processing conditions the first two antioxidant types generate approximately half drool amount in comparison with the last one.

Moreover, from recently published papers [16,17] focused on the effect of molecular structure on die drool intensity during HDPE melt extrusion results that increase in HDPE chain branching, and a decrease in its elasticity and shear viscosity significantly reduce the die drool phenomenon. Further, alpha-olefin polymers prepared using Ziegler-Natta catalysis with addition of metallic stearates of zinc, magnesium, and/or calcium as acid acceptors can also cause die drool problems [45]. In another patent [46] can be found that isotactic polypropylene polymers formed from

23

supported metallocene catalysts have significant advantages than ones prepared by Ziegler-Natta catalysts. As noted "…the narrow MWD of the metallocene polypropylene polymers gives resultant films...lower concentration of low molecular weight extractables/migratory polymer, and lower concentration of volatiles...and enables more uniform comonomer incorporation (if desired), leading to decreased sticky polymer plating-out on film lines."

Following works are focused on die drool in the case of multimodal (means two or more molecular weight peaks) polyethylene extrusion. These materials are easier and faster processable with a reduced energy requirements and increased output and they show less flow disturbances in thermal processing. However, as written in [47] "…multimodal polyethylenes often represents a unique die buildup problem. Unlike high molecular weight mono-modal polyethylene extrusion, die buildup in multimodal polyethylene extrusion often cannot be sufficiently reduced or eliminated by adding an antioxidant. This is partly because multimodal polyethylene inherently contains some low molecular weight polymer that causes die buildup. Antioxidants, although helpful in reducing die buildup by preventing polyethylene from degradation and forming low molecular weight polymers, are not sufficiently effective in reduction of die buildup in multimodal polyethylene extrusion." Moreover, it is believed that "…high hexane extractables in polyethylene contribute to the problem of die build-up during extrusion and a build-up of low molecular weight olefinic material on fabrication equipment" [48]. The reduction of drool in the case of bimodal polyolefines was investigated in [49] where authors prepared broad bimodal molecular weight distribution ethylene resin not by physical blending of low and high molecular weight components during which high level of gels is generated [50] but by tandem process polymerization (one reactor for low and second for high molecular weight component are used) where the level of gels is significantly lower. They also claim that narrower distribution of low molecular weight component significantly reduces die drool ability due to absence of very low molecular weight tail.

Number of patents is focused on elimination of die drool by using homo- or co-polymers of fluorinated olefins (e.g. tetrafluoroethylene, hexafluoropropylene, ethylene-tetrafluoroethylene, tetrafluoroethylene-propylene etc.) [47, 51-58]. During extrusion of fluoroelastomer copolymer (tetrafluoroethylene and propylene) with using low melt viscosity materials (dimethyl methyl phosphonate as plasticizer and trioctyl phosphate as processing aid) "…no die drool is observed and smooth surface is produced" [59]. However, even if extruded product is composed from fluoropolymers, e.g. FEP (tetrafluoroethylene/hexafluoropropylene) copolymer and PFA (tetrafluoroethylene/perfluoro(alkyl vinyl ether)) copolymer die drool can occur [60] due to high melting temperature difference (around 45°C) between these two copolymers, high shearing conditions phase separation and sloughing off copolymer particles.

Die drool in the case of filled thermoplastic compositions used for floor covering is investigated in [61]. Authors found that compositions with higher level of filler produces higher amount of drool and dependence of die drool vs. filler level dramatically increases for more than 30% of filler by weight. Similar experimental result can be found in [62] where authors claim that concentration of anatase or rutile type titanium dioxide (size between 0.1 μm and 0.4 μm) over 20% by weight in

24

polyethylene leads to significant die drool increase. Also production of breathable polymer films where polymer melt is filled by substantial quantity of high density inorganic filler such as calcium carbonate is extruded to a thin film is also susceptible to die drool problem. In order to reduce die drool, some manufactures have sought to reduce the amount of stearic acid (coating agent) on the surface of filler. Unfortunately, this often results in a poorly processable film [63]. In another work [64], stabilization surface treatment of titanium dioxide was found to be very important from die drool minimization point of view. The authors claim that "...if sodium salts instead of potassium salts as metal catalysts for such purpose are used die drool no more occurs." The mechanism why the use of sodium salt can prevent die drool is not clear but authors speculate that reactivity of sodium with the polymer is lower in comparison with potassium and due to this polymer terminal modification which is the cause of die drool is reduced. Also hydrotalcite (inorganic compound containing magnesium, zinc and aluminium increasing thermal insulating property and thermal stability) mixed into polyolefin resin or a copolymer can cause die drool [65]. As authors claim: "…Na (sodium) contained in the surface or in the interior of the hydrotalcite has a large effect on the occurence of die drool to be produced when using the hydrotalcite as a neutralizer of an acid catalyst residue in a polyolefine resin or a copolymer thereof obtained by polymerization using an acid catalyst...therefore, it is possible to decrease the die drool...by reducing the sodium content in the hydrotalcite to a level of 100 ppm or less."

Further, in [66,67] molten thermoplastic composition comprising 0.01 wt.% up to 0.15 wt.% of polyorganosiloxane or a mixture of polyorganosiloxane during film extrusion was found to be effective to reduce die drool. Similar idea is described in [68] where authors used polydialkylsiloxane additive reducing friction between polymer and metal die and drool in this case was significantly reduced. They also claim that "…it is contemplated that the incompatible blend of polymers of the surface layer results in die drool because the lower molecular weight materials migrate to the die surface and form a deposit which builds-up over time." Finally, in another work [69] can be found note that "…die drool occurs very fast when the molten polymer layer contains interference pigments."

Blending of polymers can also be useful for reducing die drool. For instance, if PPE (polyphenolene ether) is mixed with LLDPE (linear low density polyethylene) in amount greater than or equal to about 1 to greater than or equal to about 10 parts by weight and/or with HIPS (high impact polystyrene) in an amount of about 1 to 40 parts by weight for every 100 parts by weight of the PPE resin in the composition to form a blend die drool is substantially reduced [70]. Further, authors found that increasing amout of LLDPE in the composition increases the time in which die drool occurs. Similar attempt with different amount of LLDPE added into PPE during extrusion of electrically insulating film was made in [71]. It was found that the optimum value of LLDPE from die drool minimization point of view is approximately from 0.6% up to 0.9% by weight. Further, drooling problem during extrusion of resin composition comprising a polyamide, a polyphenylene ether, an elastomer, and an inorganic filler having a mean particle diameter of 0.05 µm to 1 µm was solved by using mixture of high and low viscosity polyamides in specific portions which leads to lower processing temperature [72]. In another invention [73] polyamide was added

25

into polyphenylene ether where causes significant increase the output of extrusion and decrease dissipation energy and level of die drips. Further, die drool in the case of poly(arylene-ether)-polystyrene blends pipe extrusion was significantly reduced by eliminating the content of unhydrogenated poly(conjugated diene) rubber in the extruded composition [74]. Reduction of die drool during thermoplastic vulcanizates (TPV) extrusion can be reached by adding a portion of polyolefin thermoplastic to TPV after the elastomer curing agent has been added to the extrusion chamber (degradation of thermoplastic is reduced) and the elastomer has been successfully cured [75].

Generally, from commercial point of view the most used die drool minimization method is using of polymer processing additive (PPA) based on fluoropolymers in many forms depending on manufacturer because such materials are considered as "universal anti polymer melt flow instabilities agents". However, there are some disadvantages connected with theirs using. For example, high price of such polymer additives, problems with printing such products, sticking of film surface layers (PPA works by migrating to die wall) [37] or problems with conveying of polymer pellets in extruder (slip layer can be activated even in the metering zone which leads to low generated pressure).

## *Effect of Processing Conditions*

As the last methods solving die drool problem effects of inside and outside processing conditions were investigated. For instance, if the drooling collar is cooled before it detached from the die exit face, it may be more easily detached from the profile. This surprising disclosure inspired Bild [76] 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 6.
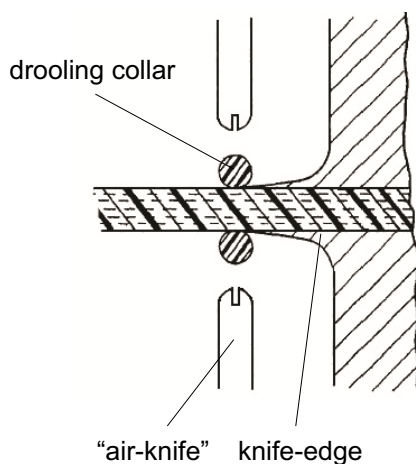


**FIGURE 6.** Bild's imagination of die exit shape and its vicinity suppressing die drool (adapted from [76]).

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 [77] discovered that if a

26

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 completely. His solution with clean hot filtered air distribution plenum is shown in Figure 7. 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). Similar way with inert gas at the die exit edge can be also found in [78-80]. Idea with blowing air at the die exit was also studied in [81] and inventors found that the type of air flow (laminar/turbulent) is also important. As is generally known, when the air stream around an object changes from laminar to turbulent flow, the air resistance received by the object increases. In this case as well, when the jet stream changes to turbulent flow, the air resistance received by die drool increases, and the die drool is readily blown off.
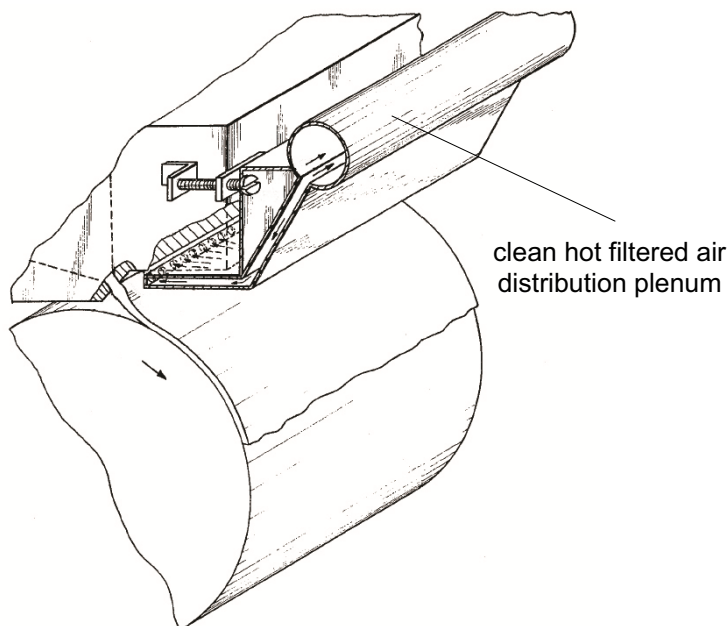


clean hot filtered air distribution plenum

**FIGURE 7.** Sheet casting die exit supplied by clean filtered air (adapted from [77]).

A small notice in [82] suggests that also circulation of hot water around the extrusion die exit reduces drooling. In US Patent from 1995 [83] the problem with die drool during cellulose acetate thin photographic film casting is solved by washing away the agglomerates by stream of solvent directed to the die lip. Furthermore, two different extruders at the same conditions were investigated in [84]. 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. Moreover, in high viscosity compositions, more processing steps lead to extra time under extreme shearing and shear heating conditions, which can lead to material degradation and can contribute to die drool during the final forming processes [42].

From the large above-introduced overview, it is clear that die drool is complex phenomenon that occurs in the majority of polymer extrusion techniques and also wide range of polymer materials (polyolefins, PVC, PET, polycarbonates,

27

polystyrenes, thermoplasic elastomers, rubber, filled compounds etc.) have tendency to form die drool at the die exit faces.

In order to deeper understand die drool phenomenon, quantification and composition analyses, in more detail presented below, have to be performed.

## Quantification of Die Drool Amount

Quantification of drool amount is extremely problematic task. It is caused by several types of drool (toroidal shape, flakes, or drips) and also usually non-uniform 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 [36], 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 [21] utilized graven lines on the die exit surface where each line has represented a 25% drool growth based on the die diameter. The time required to cover various fractions of the die exit surface were then used as a measure of drooling rate. This method was also employed by Lee [85]. Further, Harwood et al. [61] measured head size of die drool after 6 hours of extrusion.

Chan [23] seems to be the first experimentalist who measured drool amount directly. The principle was based on collecting of drooled 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 [25] and further used in [44].

The most precise method for drool amount evaluating, presented by Horwatt and Hattrich [84], is based on shut-off the extruder after chosen 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, the detachment of the deposit must be rigorously collected and also reliable analytical balance is essential. Direct collection of die drool from die exit face followed by its weighting was also used by Chai [86], Yuichi and Uchiyama [75], Fishburn et al. [43], Fortuyn et al. [74] and Musil and Zatloukal [16-18].

Last method [87] 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 [13,15,31 and 47].

As can be seen from above introduced overview, last two methods are the best candidates for drool amount evaluating. 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. It should be further mentioned that in recent work focused on HDPE drooling [15] the DIA method was improved through calibration of high-resolution images and also exponential relationship between relative drool area and absolute drool weight was found.

## Composition Analysis of Drooled Material

In order to deeper understand of die drool phenomenon, it is necessary to know also its chemical and structural composition. However, the number of published research works interested in chemical 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 [10] 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 [85] 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 analyzing drooled material of cable sheath consists of EVA/LLDPE matrix can be found in [88]. In this case, both, TGA and DSC methods, indicate that EVA as a material with higher stickiness and lower melting temperature has higher percentage volume in drool sample than LLDPE.

In recent contribution [89] study of die drool phenomenon for recycled filled LDPE produced by film blowing 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. Die drool sample shows approximately power-law behaviour (in the range of frequecies of 0.1 up to 500 rad.s$^{-1}$) and higher complex viscosity than extruded film sample. This indicates that die drool contains higher level of fillers than extruded film.

In the last research contributions (discussed in detail in other parts of the text) gel permeable chromatography (GPC) analysis of drool deposit has been published by Hogan et al. [14] and Musil and Zatloukal [16,17].

## Outline of Die Drool Sources

During the years, several possible factors, usually in combination, inducing formation of die drool phenomenon have been independently revealed and published. These factors are possible to classify into three main groups including effects of die or screw design, polymer material, and processing conditions.

29

Into the first group we can include abrupt corners at the die lips [13,25], short land length [11], pressure fluctuations in screw [11], and dirty die at start-up [90]. The second group contains low molecular weight fractions, volatiles, fillers, poor dispersion of pigments [16,17,21,40-44,61-65], die swell [11,14], dissimilar viscosities in blends [90], wall slip [32], slip-stick [16,17,32] and shark skin [13,24]. The last group represents high melt temperature [90], processing near degradation temperature [15,91], and draw down [21].

Based on these factors, several theories of die drool formation mechanism have been proposed and experimentally tested. Their summarization is provided below.

## Summary of Die Drool Formation Mechanism Theories

Formation mechanism of die drool cannot be explained by one fundamental theory because this phenomenon occurs during extrusion of simple (unfilled and virgin) polymers as well as very complex (blends, filled and recycled polymers etc.) polymer systems under different processing conditions (low/high processing temperatures, different shear/extensional rates/stresses, various outside cooling conditions etc.) and on various die designs (dies for pipes, wires/cables, profiles, thin films, coextrusion, melt blowing etc.). Moreover, die drool starts to build-up at the die exit edge where three different phases (solid metal die wall, liquid polymer melt and air) are in touch and it is very difficult to experimentally or theoretically study this region.

Generally, polymer melts build-up on the die lips due to presence of negative pressure at the die exit vicinity as presented Chaloupková and Zatloukal [13]. This negative pressure is caused by melt elasticity and streamline curvature which may lead to normal stress generation that consequently causes nonmonotonic (local pressure decrease) pressure profile during polymer melt flow. This negative pressure causes suction effect which is the driving force to build-up polymer on die lips. However, it is crucial to mention that die drool is always connected and influenced by other phenomena (die swell [11,14], shark-skin [13,31], slip-stick [16,17,29], degradation [14,15,91], fractionation of polymer chains [16-18], phase separation of polymer matrix/filler [61,62] or polymer blends [60] inside the die and wall slip [32]) occurring during polymer melt extrusion. Thus, due to this, die drool is very complex problem and it is not possible to solve it only by reduction of negative pressure magnitude at the die exit. It is also important to recognize which type of drool (external or internal) during extrusion occurs. Despite of this complexity, several theories have been proposed and some of them have also been experimentally tested.

Historically, the first reliable theory based on the die swell instability has been formulated by Klein [11]. He claimed that "…drool seems to be closely related to die swell, which is associated more commonly…in wire- or web coating operations, and is considerably less common in fiber, sheet, bar, and similar products. The reason for the difference is the different behaviour of the plastics as the product emerges from the die." Thus, this theory is based on elasticity of the polymer melt and velocity rearrangement influencing also magnitude of negative pressure at the die exit edge. Moreover, Chaloupková and Zatloukal [24] suggested that also high free surface stretching of polymer melt leading to surface rupture (shark-skin instability) can increase die drool through deformation and rupture of free polymer surface.

30

Then, Hogan et al. [14] found that degradation of the extruded polymer melt can cause chain scission leading to creation of low molecular/oligomer species which then build-up on the die lips as die drool. However, also chain cross-linking during degradation of extruded polymer melt can increase die drool intensity due to enhanced elasticity [15]. Thus, also degradation (chemical changes of the polymer structure) was proposed as one of the die drool formation mechanism.

Further, in some research works [20,31,92,93], authors speculate about flow induced molecular weight fractionation (diffusion of short molecules under highly inhomogeneous stress profile towards to die wall) of polymer melt flowing inside the extrusion die as probably one of the basic formation mechanism of die drool phenomenon. This idea was experimentally proved in the recently published works focused on die drool during unfilled, well-stabilized and virtually linear HDPE melts extrusion at very low processing temperatures [16,17]. It has been found 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). Further, 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. Hence, flow induced molecular weight fractionation during which low molecular weight layer causing wall slip near the die wall under highly inhomogeneous stress conditions is created is also acceptable die drool theory. Similarly, also filled/blend polymers can separate fillers/low viscosity material during flow under highly inhomogeneous stress conditions which can be die drool formation mechanism as well. However, there is lack of research works focused on this.

## CONCLUSION

Although, die drool during polymer extrusion is long-time known phenomenon and wide range of patents and research papers focused on its formation mechanisms and methods for its elimination summarized in this paper have been already published it is still not fully understood yet. From this review it is clear that die drool is very complex problem arising during processing of wide range of polymer materials under different conditions. For each polymer material processed under specific conditions the formation mechanism can be different. It can be based on degradation, fractionation, phase separation, wall slip (low molecular weight layer or cohesive failure between polymer chains inside polymer melt very close to die wall) or combination of these mechanisms. Thus, in order to eliminate die drool it is crucial to distinguish what is the main source of drool and then to modify processing conditions, die design, polymer material or theirs combination to reduce this unwanted extrusion phenomenon. Furthermore, there is lack of research papers focused on study of die drool phenomenon in the case of filled polymers or blends. It is believed that this work can provoke this.

31

# ACKNOWLEDGMENTS

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