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DIE DROOL AND POLYMER DEGRADATION

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ABSTRACT

Die drool is an operational problem associated with polymer extrusion. Extrudate collects outside of the die, necessitating periodic disruptions for cleaning. There exists some debate as to the mechanism that produces die drool: stress induced fractionation or thermal degradation. This paper examines the latter. In cohesive failure, a slip discontinuity develops in the velocity profile, where heat is generated by friction. This slip heating can contribute to resin degradation, resulting in lower molecular weight fragments in the die drool. This paper examines the kinetics of this degradation, its influence on die drool rates, and on the resulting polymer concentration profiles in the drool layer and in the bulk.

Keywords: Die drool, slip heating, cohesive slip, polymer degradation, scission

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I. INTRODUCTION

This paper extends a model for die drool and the resulting slip heating [1] by exploring the role of degradation within the drool layer. We incorporate current theory of die drool mechanics, rheology, tribology and polymer scission kinetics.

(i) Die Drool

Die drool is the accumulation of molten plastic on the open face of an extruder die [1]. Die drool affects the quality of the extruded product; for example, die drool can scratch the extrudate, creating *die lines* [2]. The appearance of die drool also lowers productivity, as production must be shut down to remove the drool from the die face [3].

Die drool has been attributed to external mechanical forces and internal rheology. External die drool generates small flakes or powder in a very short time frame (seconds-minutes), whereas the internal die drool accumulates in compact shapes over a longer time frame (tens of minutes to hours) [4]. Mechanically, external die drool has been attributed to negative (suction) pressure that occurs in the die exit edges (see Figure 1) [4]. External die drool formation can be mitigated through proper extruder and die design, specifically through die geometry [5,6], die coatings or die material selection [7]. This external die drool formation has been proven to be independent of die swell, even though both swell and drool are dependent on similar properties [8]. The formation of internal die drool has been hypothesized to be the result of:

Molar polymer weight fractionation

Shear induced fractionation could cause low molecular weight material to migrate to the die wall [9]. As a result, the high stresses near the exit may cause this lower molecular weight material to separate from the extrudate and accumulate on the die surface [10]. This theory has been supported experimentally; gel permeation chromatography [11] and static laser light scattering [12] have demonstrated that die drool has a markedly different composition than the bulk extrudate. Theoretically, models have supported these experimental findings [13]. The die drool exhibits a larger fraction of lower molecular weight polymer. The actual source of this lower molecular weight material is widely contested; when this fractionation is induced artificially in experimental apparatuses, the time frame for fractionation is orders of magnitude longer than the on-stream time of an extruder (say, 100 to 1000 hours) [14].

Stress-induced cohesive chain disentanglement (slip) theory

The fluid slips on itself creating a drool layer and a bulk fluid layer, separated by a theoretical boundary defined by a step discontinuity in the fluid velocity profile (Figure 1) [15]. In other words, the polymer chains are not entangled across this layer, and the bulk and drool flow can be considered separately. This cohesive slip layer (drool layer) will emerge from the die and collect on the exterior of the die, forming the die drool. This theory, similar to the fractionation theory, is not exclusive of the adhesive failure mechanism (wall slip) [4]. The fractionation of the resulting die drool has been proposed to the result of thermal degradation, caused by slip heating at the cohesive slip layer.

Schmalzer and Giacomini derived the drool rate relative to the overall bulk fluid flow rate. This relationship is called the buildup ratio [1,15].

$$BR \equiv \frac{Q_d}{Q_b} \quad (1)$$

which we will use throughout this work.

(ii) Slip Heating

According to cohesive slip theory, the step discontinuity in the velocity profile will give rise to frictional heating, also called *slip heating*. The slip velocity is the difference between the velocity of the bulk and drool at the cohesive slip interface [16, 17, 18, 19].

$$v_s = v_b - v_d \quad (2)$$

The drool layer thickness is a function of pressure drop in the extruder and of cohesive fracture strength:

$$d = \frac{h}{2} + \frac{\tau_c L}{\Delta P} \quad (3)$$

The dimensionless form of the cohesive fracture strength is always unity regardless of the values of τ_c , ΔP , and L . This is a result of the dependence of the bulk height, b , on ΔP , L , and τ_c [16]:

$$\sigma_c = \frac{\tau_c L}{b \Delta P} \quad (4)$$

The magnitude of the frictional heat flux is the product of the shear stress and slip speed [16]:

$$q_x = v_s \tau_{xy} \Big|_{x=0} \quad (5)$$

This theory supposes that the shear stress at this slip boundary is material specific, and is referred to as the cohesive fracture strength, τ_c . The slip heating of a fluid in an extruder is a function of this heat flux and the distance between the wall and the slip interface. The steady state temperature profiles (see Figure 1) of a Newtonian fluid (drool and bulk, respectively) in a slit extruder has been derived from the equation of energy (Eq. B.8-1 of [20]), assuming negligible convective heat transfer [16].

$$\Theta_{d,\infty}(\zeta) = F(\zeta + a) + \Theta_w; -a \leq \zeta \leq 0 \quad (6)$$

$$\Theta_{b,\infty}(\zeta) = Fa + \Theta_w; 0 \leq \zeta \leq 1 \quad (7)$$

which we will use below.

(iii) Polymer Scission

The drool contains significantly more low molecular weight material than the virgin resin [21]. Additionally, spiking polyethylene film with low molecular weight polyethylene wax accelerates drool [10, 22, 23]. In these spiking

experiments, we observe a power-law relationship of buildup ratio with polydispersity (Eq. (25) of [10]):

$$BR \cong \alpha_0 \left(\frac{M_w}{M_n} \right)^\beta \quad (8)$$

This suggests that, if low molecular weight material is produced upstream of an extrusion die, and specifically, through chain scission, then accelerated drool is likely to result. Assuming fractionation is negligible, this abundance of low molecular weight material implies that the polymer undergoes scission during the drool formation process. Polymer chains under high temperatures undergo this degradation reaction, splitting to form smaller sub-unit chains. The simplest model that describes scission assumes that a polymer, A, will degrade into two chains, B, which are exactly half of original molecular weight.

In practice, the molecular weight of a polymer extrusion will vary. This range of molecular weights is described by the molecular weight distribution (MWD) or, more concisely, with the polydispersity index [3].

(iv) Rate Kinetics

Rate kinetics dictate the reaction rate. Evolving concentration profiles can be constructed from rate kinetics data, where the extent of reaction varies as the reaction progresses. In an extruder, the time dependence (or *time on-stream*) of the reaction progression can be expressed in terms of position within the flow field and velocity. For slit flow:

$$t_s(y) = \frac{y}{v_y(x)} \quad (10)$$

where Figure 1 and Figure 2 illustrate the slit flow, and Table 1 and Table 2 define the variables.

The dimensionless steady state velocity profiles for the bulk and drool flows have been developed for cohesive slip in a slit die [18]:

$$\varphi_d(\xi) = \frac{a}{\ln^2 \eta_{i,\infty}} \left[\eta_{i,\infty}^{-\left(1+\frac{\xi}{a}\right)} a + \eta_{i,\infty}^{-\left(1+\frac{\xi}{a}\right)} \ln \eta_{i,\infty} (\xi - \sigma_c) - a + \ln \eta_{i,\infty} (\sigma_c + a) \right]; -a \leq \xi \leq 0 \quad (11)$$

$$\varphi_b(\xi) = -\frac{1}{2\eta_b} \xi^2 + \frac{1}{\eta_b} \xi + \frac{a}{\ln^2 \eta_{i,\infty}} \left[\frac{a - \sigma_c \ln \eta_{i,\infty}}{\eta_{i,\infty}} - a + \ln \eta_{i,\infty} (\sigma_c + a) \right] + \varphi_s; 0 \leq \xi \leq 1 \quad (12)$$

Reaction rates depend on the component concentrations and on rate constants. The simplest kinetics expression for the decomposition of a polymer, A, is the irreversible first order reaction [24].

$$\frac{dc_B}{dt} = -2 \frac{dc_A}{dt} = kc_A \quad (13)$$

whose first order rate constant, k , depends on temperature, and this dependence is normally given by the Arrhenius equation [24]:

$$k = Ae^{\frac{-E_a}{RT}} \quad (14)$$

which we will use below.

II. LITERATURE

The die drool phenomenon has been widely studied, but the theories vary widely for its cause. This paper addresses the internal causes of die drool and is independent of previous papers addressing extruder and die design, as per Ding *et al.* [2], Musil *et al.* [6] and Zatloukal *et al.* [25]. Section I summarizes current literature on internal die drool theory and slip heating, and Table 3 classifies and compares these papers.

III. LIMITATIONS

This paper will build on a previously constructed solution [18, 37]. The fluid examined in this paper is Newtonian, and convective heat transfer has been neglected. Moreover, our solution neglects diffusion of the low molecular weight species generated by the polymer scission, and the solution for slip heating was developed for a monodisperse polymer. As soon as the polymer degrades, a concentration gradient develops. The diffusion of the species B through A would add another layer of complexity to the proposed solution. We address this diffusion with the equation of continuity for a binary system (Eq. B.11-2 of [20]):

$$\rho \left(\frac{\partial \omega_B}{\partial t} + v_x \frac{\partial \omega_B}{\partial x} + v_y \frac{\partial \omega_B}{\partial y} + v_z \frac{\partial \omega_B}{\partial z} \right) = \rho \mathcal{D}_{BA} \left[\frac{\partial^2 \omega_B}{\partial x^2} + \frac{\partial^2 \omega_B}{\partial y^2} + \frac{\partial^2 \omega_B}{\partial z^2} \right] + r_B \quad (15)$$

See Section VII below for an order of magnitude analysis of [diffusion](#).

We neglect the variations in the scission reactions that could arise from the slip heating, and we attempt to address this factor at the most elementary level. However, in practice, the following five factors could complicate scission:

Polydispersity

The heterogeneity of chain lengths will affect the rheological and reaction analysis. Further, polydispersity has itself been linked to the die lip buildup ratio [see Eq. (8)].

Uneven Split

Though it is unlikely that the resulting polymers would be exactly half of the initial length [26], scission near the chain ends (less than one full entanglement length from the end is far less likely than anywhere else. We do expect, however, that on average, the single-step scission simplification in a molar average sense will be accurate, so long as, scission stops with the initial step [see Eq. (19)]. There is the potential for other reactions, such as crosslinking between the degraded polymer chains, which has been observed experimentally [32]. Of course, in

many polymer chemistries, the production of radicals is a necessary condition for crosslinking.

Heat of Degradation

The thermal scission of polymers can generate or consume heat. The endo/exothermicity of scission is material chemistry dependent [27]. Since scission is generally a low-concentration event, we do not expect this to matter. However, we have yet to carry out a proper transport phenomena analysis of this.

Effect of Degradation on Cohesive Slip Strength

Theory predicts that slip velocity will vary with the miscibility of the polymers present in the mixture [28]. With the generation of new polymer products, the slip heating term derived to approximate the thermal degradation will also change. This effect on the slip heating has been considered negligible so long as the concentration of the smaller chain polymer, B , is insignificant when compared to the polymer, A .

Low Molecular Weight

Shear thinning behavior complicates die drool, but our analysis is restricted to polymeric systems whose molecular weights fall below the entanglement molecular weight (such as commercial grades of condensation polymers such as nylon, polyester and polycarbonate).

IV. TEMPERATURE INDEPENDENT CHAIN SCISSION KINETICS

We approximate polymer scission stoichiometry as:

so that:

$$\frac{dc_B}{dt} = -2 \frac{dc_A}{dt} \quad (17)$$

where each polymer molecule splits in half, and if there is no low molecular weight polymer in the feed (special case):

$$C \equiv c_A + \frac{1}{2}c_B; c_{B0} = 0 \quad (18)$$

Polymer scission into two equal chains only happens in a number averaging sense. Stoichiometry given by Eq. (16) also neglects further scission:

If there is low molecular weight polymer (B) in the feed (general solution):

$$C \equiv c_{A0} + c_{B0} = c_A + \frac{1}{2}c_B + c_{B0}, c_{B0} \neq 0 \quad (20)$$

We have defined a system with a first-order reaction, whose *degrade* production rate can be described in terms of the high molecular weight material, A :

$$\frac{dc_B}{dt} = kc_A \quad (21)$$

By *degradata*, we mean the degradation product, B , in Eq. (16). In a flowing degrading system, such as plastics extrusion, the relevant time t is *time on-stream* of the high molecular weight reactant (not to be confused with its residence time or of the extruder run time). Time on-stream differs from streamline to streamline, and in extrusion dies, time on-stream increases near no-slip boundaries. Absent wall slip, the time on-stream at the wall is infinite. In this paper, we consider only the steady state solution, and thus, we express time on-stream as:

$$t = \frac{y}{v_y(x)} \quad (22)$$

Replacing the differential time in Eq. (21) with the expression from Eq. (22) and rearranging yields a degradate concentration gradient as a function of velocity, and position rather than time:

$$\frac{dc_B}{dy} = \frac{kc_A}{v_y(x)} \quad (23)$$

which holds when diffusion can be neglected. See Section VII below for an order of magnitude analysis of diffusion. Were diffusion important, the concentration gradients diminish, and thus:

$$\frac{dc_B}{dy} < \frac{kc_A}{v_y(x)} \quad (24)$$

The concentration of c_A can be expressed as a function of the virgin resin concentration, c_{A0} , and the localized degraded resin concentration, c_B :

$$c_{A0} = c_A + \frac{1}{2}c_B \quad (25)$$

Rearranging Eq. (23), and replacing c_A in Eq. (25) yields:

$$\frac{dc_B}{dy} = \frac{k\left(c_{A0} - \frac{1}{2}c_B\right)}{v_y(x)} \quad (26)$$

which can be rearranged to:

$$\frac{dc_B}{dy} = \frac{k}{v_y(x)}c_{A0} - \frac{k}{2v_y(x)}c_B \quad (27)$$

which has general form:

$$\frac{dy}{dx} = C_1 - C_2y \quad (28)$$

which has general solution:

$$y = \frac{C_1}{C_2} + C_3e^{-C_2x} \quad (29)$$

and thus, for our problem:

$$C_1 = \frac{kc_{A0}}{v_y(x)} \quad (30)$$

and:

$$C_2 = \frac{k}{2v_y(x)} \quad (31)$$

and hence:

$$C_B = 2c_{A0} + C_3 e^{-\frac{k}{2v_y(x)}y} \quad (32)$$

which we will use below.

(i) Partially Degraded Feed

Using Eq. (32), an alternative constant can be defined for the new boundary conditions. To find C_3 , we can use the entry condition, $y = 0$, where the concentration of C_B is now C_{B0} , by definition. This condition can be substituted into Eq. (30) to yield:

$$c_{B0} = 2c_{A0} + C_3 e^{-\frac{k}{2v_y(x)}(0)} \quad (33)$$

which simplifies to:

$$C_3 = c_{B0} - 2c_{A0} \quad (34)$$

which, when combined with Eq. (32), gives:

$$c_B = 2c_{A0} + (c_{B0} - 2c_{A0}) e^{-\frac{k}{2v_y(x)}y} \quad (35)$$

which we will use below.

(ii) Special Case: Virgin Feed

For the special case of undegraded feed, the entry ($y = 0$) condition is $c_B = 0$. Substituting this condition into Eq. (35) gives:

$$c_B = 2c_{A0} - 2c_{A0} e^{-\frac{k}{2v_y(x)}y} \quad (36)$$

(iii) Nondimensionalizing Degradate Concentration

Eq. (36) can be nondimensionalized using Table 2 of Gilbert and Giacomini [37] and by defining the dimensionless concentration:

$$Y \equiv \frac{c_B}{c_{A0}} \quad (37)$$

and the dimensionless inlet resin purity index:

$$g \equiv \frac{c_{B0}}{c_{A0}} \quad (38)$$

Inserting Eq. (37) and (38) into (36) yields:

$$Y(\xi, \varsigma) = 2 + (g - 2) e^{-\frac{\epsilon}{2} \frac{\xi}{\varphi_\varsigma(\xi)}} \quad (39)$$

which we will use below.

(iv) Drool and Bulk Concentration Profiles

The profile given by Eq. (39) is function of the velocity in the y – direction. There are four boundaries in this cohesive slip model: two for no wall slip, and two for the cohesive slip boundaries. Gilbert and Giacomini [37] have derived two dimensionless expressions from this model, one for the drool layer:

$$\varphi_d(\xi) = \frac{a}{\ln^2 \eta_{i,\infty}} \left[\eta_{i,\infty}^{\left(-1+\frac{\xi}{a}\right)} a + \eta_{i,\infty}^{\left(-1+\frac{\xi}{a}\right)} \ln \eta_{i,\infty} (\xi - \sigma_c) - a + \ln \eta_{i,\infty} (\sigma_c + a) \right]; -a \leq \xi \leq 0 \quad (40)$$

and another for the bulk:

$$\varphi_b(\xi) = -\frac{1}{2\eta_b} \xi^2 + \frac{1}{\eta_b} \xi + \frac{a}{\ln^2 \eta_{i,\infty}} \left[\frac{a - \sigma_c \ln \eta_{i,\infty}}{\eta_{i,\infty}} - a + \ln \eta_{i,\infty} (\sigma_c + a) \right] + \varphi_s; 0 \leq \xi \leq 1 \quad (41)$$

Our model will also require four boundary conditions: two for the walls, where the mole fraction of B will approach unity, and two at the cohesive slip boundaries, defined by the step discontinuity in the velocity profile φ_s :

$$Y_s(0, \varsigma) = 2 + (g - 2) \exp\left(-\frac{\epsilon}{2\varphi_s} \varsigma\right) \quad (42)$$

The concentration in the drool layer is thus given by:

$$Y_d(\xi, \varsigma) = 2 + (g - 2) \exp\left(-\frac{\epsilon}{2} \frac{\varsigma}{\varphi_d(\xi)}\right) \quad (43)$$

Inserting Eq. (40) into Eq. (43), we find:

$$Y_d(\xi, \varsigma) = 2 + (g - 2) \exp\left(\frac{-\frac{1}{2}\epsilon\varsigma}{\frac{a}{\ln^2 \eta_{i,\infty}} \left[\eta_{i,\infty}^{\left(-1+\frac{\xi}{a}\right)} a + \eta_{i,\infty}^{\left(-1+\frac{\xi}{a}\right)} \ln \eta_{i,\infty} (\xi - \sigma_c) - a + \ln \eta_{i,\infty} (\sigma_c + a) \right]}\right) \quad (44)$$

The concentration in the bulk is given by:

$$Y_b(\xi, \varsigma) = 2 + (g - 2) \exp\left(-\frac{\epsilon}{2} \frac{\varsigma}{\varphi_b(\xi)}\right) \quad (45)$$

Inserting Eq. (41) in Eq. (46), we obtain:

$$Y_b(\xi, \varsigma) = 2 + (g - 2) \exp\left(\frac{-\frac{1}{2}\epsilon\varsigma}{-\frac{1}{2\eta_b} \xi^2 + \frac{1}{\eta_b} \xi + \frac{a}{\ln^2 \eta_{i,\infty}} \left[\frac{a - \sigma_c \ln \eta_{i,\infty}}{\eta_{i,\infty}} - a + \ln \eta_{i,\infty} (\sigma_c + a) \right] + \varphi_s}\right) \quad (46)$$

which we will use to determine viscosity.

V. TEMPERATURE-DEPENDENT KINETICS

The concentration profile will depend on temperature, as the degradation rate will follow Eq. (14). The dimensionless steady state temperature is a function of the distance from the slip interface and the heat flux that arises from this step discontinuity:

$$\Theta_{d,\infty}(\xi) = F(\xi + a) + \Theta_w; -a \leq \xi \leq 0 \quad (47)$$

$$\Theta_{b,\infty}(\xi) = Fa + \Theta_w; 0 \leq \xi \leq 1 \quad (48)$$

From these equations, we can see that the temperature does not vary as a function of distance travelled through the channel, only the distance from the wall. Thus:

$$k = k(x) \quad (49)$$

Reexamining Eq. (27) using the insight from Eq. (49):

$$\frac{dc_B}{dy} = \frac{k(x)}{v_y(x)} c_{A0} - \frac{k(x)}{2v_y(x)} c_B \quad (50)$$

and following the method used to develop Eq. (35) yields:

$$c_B(x, y) = 2c_{A0} + (c_{B0} - 2c_{A0}) e^{-\frac{k(x)}{2v_y(x)} y} \quad (51)$$

The concentration becomes dependent on position in the gap, when temperature dependence is incorporated. Nondimensionalizing Eq. (51) with the dimensionless groups in the Table 2 yields a general solution for concentration in both the bulk:

$$Y(\xi, \varsigma) = 2 + (g - 2) \exp \left[-\frac{r}{2} \exp \left(-\frac{s}{1 + \Theta} \right) \frac{\varsigma}{\varphi(\xi)} \right] \quad (52)$$

and the drool:

$$Y_d(\xi, \varsigma) = 2 + (g - 2) \exp \left[-\frac{r}{2} \exp \left(-\frac{s}{1 + \Theta_d} \right) \frac{\varsigma}{\varphi_d(\xi)} \right] \quad (53)$$

Inserting Eqs. (47) and (40) into Eq. (53), we find:

$$Y_d(\xi, \varsigma) = 2 + (g - 2) \exp \left\{ -\frac{r}{2} \exp \left(-\frac{s}{1 + F(\xi + a) + \Theta_w} \right) \frac{\varsigma}{\frac{a}{\ln^2 \eta_{i,\infty}} \left[\eta_{i,\infty}^{-\left(1+\frac{\xi}{a}\right)} a + \eta_{i,\infty}^{-\left(1+\frac{\xi}{a}\right)} \ln \eta_{i,\infty} (\xi - \sigma_c) - a + \ln \eta_{i,\infty} (\sigma_c + a) \right]} \right\} \quad (54)$$

Eq. (54) yields a drool degrade concentration profile that quickly decreases with distance from the wall, ξ (see Figure 3). Near the wall, the dimensionless concentration of the degraded polymer is 2, which indicates that only degradate is present. This observation matches theory since the melt near the wall does not move, and thus spends infinite time degrading. As expected, the concentration of the degraded polymer in the bulk increases as the melt progresses through the extruder (see Figure 3).

The concentration in the bulk layer is given by:

$$Y_b(\xi, \varsigma) = 2 + (g - 2) \exp \left[-\frac{r}{2} \exp \left(-\frac{s}{1 + \Theta_b} \right) \frac{\varsigma}{\varphi_b(\xi)} \right] \quad (55)$$

Inserting Eqs. (41) and (48) into Eq. (55), we get:

$$Y_b(\xi, \varsigma) = 2 + (g - 2) \exp \left(-\frac{r}{2} \exp \left(-\frac{s}{1 + Fa + \Theta_w} \right) \frac{\varsigma}{-\frac{1}{2\eta_b} \xi^2 + \frac{1}{\eta_b} \xi + \frac{a}{\ln^2 \eta_{i,\infty}} \left[\frac{a - \sigma_c \ln \eta_{i,\infty}}{\eta_{i,\infty}} - a + \ln \eta_{i,\infty} (\sigma_c + a) \right] + \varphi_s} \right) \quad (56)$$

Eq. (56) describes a nearly constant bulk degrade concentration profile across the die cross-section (see Figure 4). The narrow range of c_B is unsurprising as the range of velocities is much smaller across the bulk flow. As expected, the concentration of the degraded polymer in the bulk increases as the melt

progresses through the extruder (see Figure 4). Interestingly, the temperature dependent and independent concentration profiles nearly match.

VI. Flow Rate Estimation

The volumetric flow rate can be defined by the equation of motion (written in terms of velocity) in Cartesian coordinates (see B.6-2 of [20]):

$$1 = \frac{d}{d\zeta} \left(-\eta(M_w, \Theta) \frac{d\varphi}{d\zeta} \right) \quad (57)$$

where the viscosity depends on temperature and molecular weight, both of which depend on position within the flow field. For simplicity, we neglect this temperature dependence. Assuming that the flow is Newtonian, and thus without entanglements, the viscosity can be described using:

$$\mu = KM_w \quad (58)$$

The weight-average molecular weight is defined by [29]:

$$M_w \equiv \frac{\sum_{i=1}^n x_i M_i^2}{\sum_{i=1}^n x_i M_i} \quad (59)$$

where x_i is the mole fraction of species i . Hence, for the binary degradation described by Eq. (9):

$$M_w = \frac{x_A M_A^2 + x_B M_B^2}{x_A M_A + x_B M_B} \quad (60)$$

Using the simplifying assumption that molecular weight of B is exactly half of A yields:

$$M_w = \frac{x_A M_A^2 + \frac{1}{4} x_B M_A^2}{x_A M_A + \frac{1}{2} x_B M_A} \quad (61)$$

Eq. (61) can be rearranged to get:

$$M_w = \frac{M_A (x_A + \frac{1}{4} x_B)}{x_A + \frac{1}{2} x_B} \quad (62)$$

or, in terms of B:

$$\frac{M_w}{M_A} = \frac{1 - \frac{3}{4} x_B}{1 - \frac{1}{2} x_B} \quad (63)$$

The dimensionless viscosity, $\tilde{\eta}$, can be written as:

$$\tilde{\eta} \equiv \frac{\mu}{\mu_A} \quad (64)$$

Replacing both viscosities in Eq. (64) with Eq. (58) and assuming K to be the same for both, because the miscibility of a polymer in a longer chain polymer of itself is high, we find:

$$\tilde{\eta} = \frac{M_w}{M_A} \quad (65)$$

Replacing the molecular weight ratio in Eq. (65) with Eq. (63) yields:

$$\tilde{\eta} = \frac{1 - \frac{3}{4}x_B}{1 - \frac{1}{2}x_B} \quad (66)$$

The mole fraction of B , written in terms of the concentrations, is:

$$x_B = \frac{c_B}{c_A + c_B} \quad (67)$$

Substituting the stoichiometric definition of c_A from Eq. (20) into Eq. (67), we get:

$$x_B = \frac{c_B}{(c_{A0} - \frac{1}{2}c_B) + c_B} \quad (68)$$

Simplifying Eq. (68):

$$x_B = \frac{c_B}{c_{A0} + \frac{1}{2}c_B} \quad (69)$$

Nondimensionalizing Eq. (69):

$$x_B = \frac{Y_B}{1 + \frac{1}{2}Y_B} \quad (70)$$

Substituting Eq. (70) into Eq. (66):

$$\tilde{\eta} = \frac{1 - \frac{3}{4}\left(\frac{Y_B}{1 + \frac{1}{2}Y_B}\right)}{1 - \frac{1}{2}\left(\frac{Y_B}{1 + \frac{1}{2}Y_B}\right)} \quad (71)$$

which simplifies to:

$$\tilde{\eta} = 1 - \frac{1}{4}Y_B \quad (72)$$

(i) Simplification: Constant Average Concentration Through Taylor Series

Substituting Eq. (72) into Eq. (57), for any velocity profile $\varphi^*(\xi, \zeta)$:

$$1 = \frac{d}{d\zeta} \left(-\tilde{\eta}(M_w) \frac{d\varphi^*}{d\zeta} \right) \quad (73)$$

The first integration yields:

$$\frac{d\varphi^*}{d\zeta} = \frac{C_1 - \zeta}{[1 - \frac{1}{4}Y(\xi, \zeta)]} \quad (74)$$

To simplify Eq. (74), the drool concentration can be approximated with a Taylor series expansion with respect to ζ , and then integrated along the ζ -axis, and finally divided by the dimensionless length, l . This method reduces the concentration expression in Eq. (74) to a constant value, Y_d^* , which does not depend on position. The average drool and bulk concentrations will thus take the form:

$$Y_d^* = \int_0^1 \left[\frac{T_d(-a) + T_d(0)}{2} \right] d\zeta \quad (75)$$

$$Y_b^* = \int_0^1 \left[\frac{T_b(0) + T_b(1)}{2} \right] d\zeta \quad (76)$$

Where T_d and T_b represent, for the bulk and drool layers, the lowest order Taylor series about the boundary conditions: the wall ($y = -a$), the slip interface ($y = 0$), the midplane of the bulk flow ($y = 1$). Evaluating the truncated Taylor series in Eq. (75) and reinserting them yields:

$$Y_d^* = \frac{1}{2} \int_0^1 4 + (g-2) \exp \left[\frac{-\zeta r \exp \left(\frac{s}{\Theta_w + Fa + 1} \right)}{-a + (\ln \eta_{i,\infty})(a + \sigma_c) + \frac{a}{\eta_{i,\infty}} - \frac{\sigma_c (\ln \eta_{i,\infty})}{\eta_{i,\infty}}} \right] d\zeta \quad (77)$$

Integrating Eq. (77) with respect to ζ then yields:

$$Y_d^* = \left\{ 2\zeta - \frac{(g-2) \left(-a + (\ln \eta_{i,\infty})(a + \sigma_c) + \frac{a}{\eta_{i,\infty}} - \frac{\sigma_c (\ln \eta_{i,\infty})}{\eta_{i,\infty}} \right)}{-2r \exp \left(\frac{s}{\Theta_w + Fa + 1} \right)} \right\} \bigg|_{\zeta=0}^{\zeta=1} \times \exp \left[\frac{-\zeta r \exp \left(\frac{s}{\Theta_w + Fa + 1} \right)}{-a + (\ln \eta_{i,\infty})(a + \sigma_c) + \frac{a}{\eta_{i,\infty}} - \frac{\sigma_c (\ln \eta_{i,\infty})}{\eta_{i,\infty}}} \right] \bigg|_{\zeta=0}^{\zeta=1} \quad (78)$$

or:

$$Y_d^* = 2 + \frac{(g-2) \left(-a + (\ln \eta_{i,\infty})(a + \sigma_c) + \frac{a}{\eta_{i,\infty}} - \frac{\sigma_c (\ln \eta_{i,\infty})}{\eta_{i,\infty}} \right)}{2r \exp \left(\frac{s}{\Theta_w + Fa + 1} \right)} \times \left\{ \exp \left[\frac{-r \exp \left(\frac{s}{\Theta_w + Fa + 1} \right)}{-a + (\ln \eta_{i,\infty})(a + \sigma_c) + \frac{a}{\eta_{i,\infty}} - \frac{\sigma_c (\ln \eta_{i,\infty})}{\eta_{i,\infty}}} \right] + 1 \right\} \quad (79)$$

Similarly, for the bulk fluid, the truncated Taylor series can be evaluated around 0 and 1 to approximate the average:

$$Y_b^* = \int_0^1 2 + \frac{(g-2)}{2} \exp \left(\frac{-r\zeta}{C} \exp \left(\frac{-s}{\Theta_w + Fa + 1} \right) \right) + \frac{(g-2)}{2} \exp \left(\frac{-r\zeta}{C + \frac{1}{2\eta_b}} \exp \left(\frac{-s}{\Theta_w + Fa + 1} \right) \right) d\zeta \quad (80)$$

The integration of Eq. (80) yields:

$$\Upsilon_b^* = 2 + \frac{C(g-2)}{2r \exp\left(\frac{s}{\Theta_w + Fa + 1}\right)} \left(1 - \exp\left\{-\frac{r}{C} \left[\exp\left(\frac{s}{\Theta_w + Fa + 1}\right) \right] \right\} + \frac{2\eta_b + \frac{1}{C}}{2\eta_b} \left(1 - \exp\left\{-\frac{r}{C + \frac{1}{2\eta_b}} \exp\left(\frac{s}{\Theta_w + Fa + 1}\right) \right\} \right) \right) \quad (81)$$

In most circumstances, the average concentration in the bulk fluid is vanishingly low. The average dimensionless concentration of A of the drool fluid calculated in this manner is usually one, as the concentration near the wall is two and the concentration near the slip interface is also vanishingly low.

(ii) Estimating the Drool Flowrate

Adapting Eq. (74) for the drool layer and assuming a constant average viscosity:

$$\frac{d\varphi_d^*}{d\xi} = \frac{C_1 - \xi}{\left[1 - \frac{1}{4}\Upsilon_b^*\right]} \quad (82)$$

The boundary conditions for the drool layer are the wall, where the drool velocity is zero, and the drool slip boundary, where the shear stress is equal to the cohesive fracture strength. Applying the first boundary condition, the slip shear stress can be expressed as a function of the cohesive fracture strength of the polymer, σ_c , and the viscosity at the interface, $\eta_{i,\infty}$:

$$\left. \frac{d\varphi_d^*}{d\xi} \right|_{\xi=0} = \frac{\sigma_c}{\eta_{i,\infty}} = \frac{C_1 - 0}{\left[1 - \frac{1}{4}\Upsilon_d^*\right]} \quad (83)$$

and thus:

$$C_1 = \frac{\sigma_c \left(1 - \frac{1}{4}\Upsilon_d^*\right)}{\eta_{i,\infty}} \quad (84)$$

Inserting Eq. (84) into (82) and integrating yields:

$$\varphi_d^* = \frac{-1}{2\left(1 - \frac{1}{4}\Upsilon_d^*\right)} \xi^2 + \frac{\sigma_c}{\eta_{i,\infty}} \xi + C_2 \quad (85)$$

Applying the second boundary condition, where the velocity drops to zero at the wall:

$$\varphi_{d,-a}^* = 0 = \frac{-(-a)^2}{2\left(1 - \frac{1}{4}\Upsilon_d^*\right)} + \frac{\sigma_c}{\eta_{i,\infty}}(-a) + C_2 \quad (86)$$

and:

$$C_2 = \frac{a\sigma_c}{\eta_{i,\infty}} + \frac{a^2}{2\left(1 - \frac{1}{4}\Upsilon_d^*\right)} \quad (87)$$

Substituting into Eq. (85) yields:

$$\varphi_d^* = \frac{-1}{2(1-\frac{1}{4}\Upsilon_d^*)} \xi^2 - \frac{\sigma_c}{\eta_{i,\infty}} \xi + a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2(1-\frac{1}{4}\Upsilon_d^*)} \right) \quad (88)$$

Figure 5 shows the drool velocity profile as nearly linear (see similar shape in [16]). The velocity of the bulk is higher than the drool, despite the lower drool viscosity brought about by the degraded polymer. The drool flowrate can be derived from the velocity profile, Eq. (88), by integrating along the cross-sectional area and then multiplying by 2 to account for the symmetry of the die drool flow:

$$Q_d^* = 2 \int_0^W \int_{-a}^0 \varphi_d^* d\xi dW^* \quad (89)$$

Substituting Eq. (88) into Eq. (89):

$$Q_d^* = 2 \int_0^W \int_{-a}^0 \left[\frac{-1}{2(1-\frac{1}{4}\Upsilon_d^*)} \xi^2 + \frac{\sigma_c}{\eta_{i,\infty}} \xi + a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2(1-\frac{1}{4}\Upsilon_d^*)} \right) \right] d\xi dW^* \quad (90)$$

Integrating twice yields:

$$Q_d^* = 2W \int_{-a}^0 \left[\frac{-1}{2(1-\frac{1}{4}\Upsilon_d^*)} \xi^2 + \frac{\sigma_c}{\eta_{i,\infty}} \xi + a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2(1-\frac{1}{4}\Upsilon_d^*)} \right) \right] d\xi \quad (91)$$

and applying the boundary conditions gives:

$$Q_d^* = 2W \left[\frac{-1}{6(1-\frac{1}{4}\Upsilon_d^*)} \xi^3 + \frac{\sigma_c}{2\eta_{i,\infty}} \xi^2 + a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2(1-\frac{1}{4}\Upsilon_d^*)} \right) \xi \right] \Bigg|_{\xi=-a}^{\xi=0} \quad (92)$$

$$Q_d^* = \frac{2Wa^2}{(1-\frac{1}{4}\Upsilon_d^*)} \left[\frac{\sigma_c(1-\frac{1}{4}\Upsilon_d^*)}{2\eta_{i,\infty}} + \frac{a}{3} \right] \quad (93)$$

(iii) Estimating the Bulk Flow Rate

Adapting Eq. (74) for the bulk melt:

$$1 = \frac{d}{d\xi} \left(-\eta^*(M_w) \frac{d\varphi_{b,2}}{d\xi} \right) \quad (94)$$

and integrating gives:

$$\xi = -\eta^*(M_w) \frac{d\varphi_b^*}{d\xi} - C_1 \quad (95)$$

Assuming that the viscosity can be calculated from an average:

$$\xi = -\left[1 - \frac{1}{4}\Upsilon_b^*(\xi, \varsigma) \right] \frac{d\varphi_b^*}{d\xi} - C_1 \quad (96)$$

At $\xi=1$, the dimensionless velocity peaks, thus:

$$C_1 = 1 \quad (97)$$

Inserting Eq. (97) into Eq. (96)

$$\xi = -\left[1 - \frac{1}{4}\Upsilon_b^*(\xi, \varsigma) \right] \frac{d\varphi_b^*}{d\xi} - 1 \quad (98)$$

Solving for the velocity profile:

$$\frac{d\varphi_b^*}{d\xi} = \frac{1-\xi}{1-\frac{1}{4}Y_b(\xi, \zeta)} \quad (99)$$

Following the procedure that we used above for the drool layer, we average the concentration profile over the crossflow direction:

$$\frac{d\varphi_b^*}{d\xi} = \frac{1-\xi}{1-\frac{1}{4}Y_b^*} \quad (100)$$

Integrating Eq. (100) with respect to ξ :

$$\varphi_b^* = \frac{-1}{2(1-\frac{1}{4}Y_b^*)} \xi^2 + \frac{1}{1-\frac{1}{4}Y_b^*} \xi + C_1 \quad (101)$$

At the slip interface, the bulk velocity is defined as the drool velocity at the slip layer added to the slip velocity [the slip velocity can be calculated from Eq.(88)]:

$$\varphi_b^*|_{\xi=0} = \varphi_d^*|_{\xi=0} + \varphi_s \quad (102)$$

Substituting Eq. (102) into Eq. (101) at the boundary reveals:

$$C_1 = \varphi_b^*|_{\xi=0} + \varphi_s \quad (103)$$

and substituting the bulk velocity at the boundary into Eq. (103) gives:

$$C_1 = a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2(1-\frac{1}{4}Y_d^*)} \right) + \varphi_s \quad (104)$$

Substituting Eq. (104) into (101), we get:

$$\varphi_b^* = \frac{-1^2}{2(1-\frac{1}{4}Y_b^*)} \xi^2 + \frac{1}{1-\frac{1}{4}Y_b^*} \xi + a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2(1-\frac{1}{4}Y_d^*)} \right) + \varphi_s \quad (105)$$

As expected, the bulk velocity profile is curved (see Figure 6). The velocity profile expressed by Eq. (105) resembles the profile found in Giacomini and Gilbert [16], but the velocity at the slip interface is greater than that found in [16]. The bulk flowrate can be derived from the velocity profile by integrating along the cross-sectional area (above the midplane) and by then multiplying by 2 (to account for the flow symmetry):

$$Q_b^* = 2 \int_0^1 \int_0^1 \varphi_b^* d\xi dW^* \quad (106)$$

Substituting Eq. (105) into Eq. (106) gives:

$$Q_b^* = 2 \int_0^1 \int_0^1 \left(\frac{-1^2}{2(1-\frac{1}{4}Y_b^*)} \xi^2 + \frac{1}{1-\frac{1}{4}Y_b^*} \xi + a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2(1-\frac{1}{4}Y_d^*)} \right) + \varphi_s \right) d\xi dW^* \quad (107)$$

and then integrating:

$$Q_b^* = 2W \left(\frac{-1^2}{6(1-\frac{1}{4}Y_b^*)} \xi^3 + \frac{1}{2(1-\frac{1}{4}Y_b^*)} \xi^2 + \left[a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2(1-\frac{1}{4}Y_d^*)} \right) + \varphi_s \right] \xi \right) \Bigg|_{\xi=0}^{\xi=1} \quad (108)$$

Applying the boundary conditions to the definite integral:

$$Q_b^* = \frac{2W}{\left(1 - \frac{1}{4}Y_b^*\right)} \left\{ \frac{1}{3} + \left(1 - \frac{1}{4}Y_b^*\right) \left[a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2\left(1 - \frac{1}{4}Y_d^*\right)} \right) + \varphi_s \right] \right\} \quad (109)$$

Following Gander and Giacomini [10], we normalize the drool flow rate with bulk flow rate to obtain the *build up ratio* [15]:

$$BR \equiv \frac{Q_d^*}{Q_b^*} \quad (110)$$

Analytically, this ratio can be obtained from Eqs. (93) and (109):

$$BR \equiv \frac{a^2 \left(1 - \frac{1}{4}Y_b^*\right) \left[\frac{\sigma_c \left(1 - \frac{1}{4}Y_d^*\right)}{2\eta_{i,\infty}} + \frac{a}{3} \right]}{\left(1 - \frac{1}{4}Y_d^*\right) \left\{ \frac{1}{3} + \left(1 - \frac{1}{4}Y_b^*\right) \left[a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2\left(1 - \frac{1}{4}Y_d^*\right)} \right) + \varphi_s \right] \right\}} \quad (111)$$

The buildup ratio described by Eq. (111) reveals a larger buildup ratio (by about 20%) compared to the work done by Giacomini and Gilbert [16]. This is because the lower drool viscosity enhances the drool flow rate.

(iv) Reworked Example: Sheet Extrusion Drool Rate

A plastic sheet manufacturer aims to estimate the steady drool rate for molten nylon, to be considered for her extrusion operations. For her process, she knows that $T_w = T_0 = 423K$, $\tau_c = 0.18MPa$, $v_s = 30 \text{ mm/s}$, $k = 0.1W/mK$, $C_p = 2.0J/GK$, $\rho = 0.90 \text{ g/mL}$, $\mu_w = 600Pa\cdot s$, $L = 0.50m$, $\Delta P = -31MPa$, $c_{B0} = 0$, $c_{A0} = 1.0M$ and $w = 1.0m$. From Ref. [30], for nylon 6,6 she gleans $A = 20s^{-1}$ and $E_a = 129kJmol^{-1}$. She first calculates the inlet resin purity index from Eq. (38):

$$g = \frac{c_{B0}}{c_{A0}} = 0 \quad (112)$$

and then determines the drool layer thickness using Eq. (18) of [15]:

$$d = \frac{h}{2} + \frac{\tau_c L}{\Delta P} = 0.097mm \quad (113)$$

The bulk fluid thickness is derived from the defining relation for d :

$$b = \frac{h}{2} - d = 2.9mm \quad (114)$$

Applying these values to Eq. (5), and using the cohesive fracture strength, she finds:

$$q_i = v_s \tau_c = 5.4kW/m^2 \quad (115)$$

This heat flux can be nondimensionalized as:

$$F = \frac{q_i b}{kT_0} = 0.348 \quad (116)$$

She then nondimensionalizes the drool thickness:

$$a = \frac{d}{b} = 0.033 \quad (117)$$

and width

$$W = \frac{w}{b} = 344 \quad (118)$$

Using the values above, the temperature profiles can be described with Eqs. (47) and (48). The dimensionless temperature at the wall is zero because, in this example, it matches the initial temperature:

$$\Theta_{d,\infty} = 0.348(\zeta + 0.033); -a \leq \zeta \leq 0 \quad (119)$$

$$\Theta_{b,\infty} = \Theta_{i,\infty} = 1.16 \times 10^{-2}; 0 \leq \zeta \leq 1 \quad (120)$$

Using the method of Gilbert and Giacomini [16], she calculates the interface viscosity:

$$\eta_{i,\infty} = \eta_b = \exp(-\Theta_{i,\infty}) = 0.88 \quad (121)$$

Before estimating the flow rate, she finds the dimensionless fracture strength, dimensionless coefficients and slip velocity:

$$\sigma_c = \frac{-\tau_c L}{b \Delta P} = 1 \quad (122)$$

$$\varphi_s = \frac{v_s \mu_w L}{b^2 \Delta P} = 0.034 \quad (123)$$

$$s = \frac{E_a}{RT_0} = 36.7 \quad (124)$$

$$r = \frac{A \mu_w L^2}{b^2 \Delta P} = 13.6 \quad (125)$$

Substituting Eqs. (121) through (125) into Eq. (54), she finds

$$\Upsilon_d = 2 - 2 \exp \left\{ \frac{3.37 \zeta \exp \left[\frac{-36.7}{0.348 \zeta + 1.01} \right]}{\frac{0.012(\zeta - 1)}{0.88^{30.3 \zeta + 1}} - \frac{0.033}{0.88^{30.3 \zeta + 1}} + 0.17} \right\}; -a \leq \zeta \leq 0 \quad (126)$$

$$= 2 - 2 \exp \left\{ \frac{-1.18 \times 10^{-15} \zeta}{-0.57 \zeta^2 + 1.13 \zeta + 0.238} \right\}; 0 \leq \zeta \leq 1 \quad (127)$$

and then prepares Figure 3 and Figure 4. Using the Taylor series approximations [Eqs. (79) and (81)], she finds the average dimensionless concentration in the bulk and drool layers:

$$Y_d^* = 1; -a \leq \xi \leq 0 \quad (128)$$

$$Y_b^* = 7.2 \times 10^{-16} \approx 0; 0 \leq \xi \leq 1 \quad (129)$$

Using these average degraded polymer concentrations, she describes the velocity profile using Eqs. (88) and (105) and then prepares Figure 5 and Figure 6:

$$\varphi_b^* = -0.5\xi^2 + \xi + 0.383; 0 \leq \xi \leq 1 \quad (130)$$

$$\varphi_d^* = -0.5z^2 - 1.01z + 0.038; -a \leq \xi \leq 0 \quad (131)$$

Using the dimensionless values above, she calculates the expected flow rates from Eqs. (93) and (109):

$$Q_d^* = \frac{2Wa^2}{\left(1 - \frac{1}{4}Y_d^*\right)} \left[\frac{\sigma_c \left(1 - \frac{1}{4}Y_d^*\right)}{2\eta_{i,\infty}} + \frac{a}{3} \right] = 0.437 \quad (132)$$

$$Q_b^* = \frac{2W}{\left(1 - \frac{1}{4}Y_b^*\right)} \left\{ \frac{1}{3} + \left(1 - \frac{1}{4}Y_b^*\right) \left[a \left(\frac{\sigma_c}{\eta_{i,\infty}} + \frac{a}{2\left(1 - \frac{1}{4}Y_d^*\right)} \right) + \varphi_s \right] \right\} = 490 \quad (133)$$

Taking the ratio of Eq. (132) and (133), she finally obtains the buildup ratio:

$$BR = \frac{Q_d^*}{Q_b^*} = 9.0 \times 10^{-4} \quad (134)$$

Mindful of the erratum to our citation [16], she finds that this is about 20% higher than the buildup ratio calculated for the same example (sans polymer degradation) in Question 1 of [16]. Otherwise put, in this worked example, polymer scission significantly accelerates drool.

VII. VALIDATING THE NEGLECT OF DIFFUSION

Whereas Eq. (15) includes [diffusion](#), our equation for time on-stream, Eq. (22), neglects diffusion. In this section, we explore this assumption by first identifying the relevant dimensionless groups and then performing an order of magnitude analysis to compare convection with axial and transverse diffusion.

a. Defining Relevant Dimensionless Groups

We begin with the equation of continuity for species α (Eq. 19.1-10 of [20]):

$$\frac{\partial c_\alpha}{\partial t} = -(\nabla \cdot \mathbf{N}_\alpha) + R_\alpha, \quad \alpha = A, B \quad (135)$$

which is a form of Eq. (15). Substituting Eq. (V) from Table 17.8-1 of [20] into Eq. (135), we find:

$$\frac{\partial c_\alpha}{\partial t} = -(\nabla \cdot c_\alpha \mathbf{v}^*) - (\nabla \cdot \mathbf{J}_\alpha^*) + R_\alpha \quad (136)$$

which describes the accumulation of species α . From left to right, the terms on the right side of the Eq. (136) describe convective mass transfer, diffusive mass

transfer and species generation/consumption through chemical reaction. The left side of (136) vanishes at steady state, and we replace the reaction term with our result for first order kinetics, Eq. (13), to get:

$$0 = -(\nabla \cdot c_B \mathbf{v}^*) - (\nabla \cdot \mathbf{J}_B^*) + kc_A \quad (137)$$

Inserting Fick's law of diffusion:

$$\mathbf{J}_B^* = -cD_{BA} \nabla x_B \quad (138)$$

into Eq. (137) and expanding the divergence for Cartesian coordinates (defined in Figure 2), we find:

$$0 = - \left(\frac{\partial(c_B v_x)}{\partial x} + \frac{\partial(c_B v_y)}{\partial y} + \frac{\partial(c_B v_z)}{\partial z} + \mathcal{D}_{BA} \left(\frac{\partial \left(c \frac{\partial x_B}{\partial x} \right)}{\partial x} + \frac{\partial \left(c \frac{\partial x_B}{\partial y} \right)}{\partial y} + \frac{\partial \left(c \frac{\partial x_B}{\partial z} \right)}{\partial z} \right) \right) + kc_A \quad (139)$$

We next simplify Eq. (139) for uniaxial y direction flow by setting $v_x = v_z = 0$, and after applying the z - coordinate symmetry to neglect concentration differences in the z direction (zero lateral diffusion), we get:

$$0 = - \frac{\partial(c_B v_y)}{\partial y} - \mathcal{D}_{BA} \left(\frac{\partial \left(c \frac{\partial x_B}{\partial x} \right)}{\partial x} + \frac{\partial \left(c \frac{\partial x_B}{\partial y} \right)}{\partial y} \right) + k \left(c_{A0} - \frac{1}{2} c_B \right) \quad (140)$$

where:

$$c_A = c_{A0} - \frac{1}{2} c_B \quad (141)$$

and:

$$c_B = x_B c \quad (142)$$

We make Eq. (140) dimensionless using the expressions in Table 2 to get:

$$0 = -\varphi \frac{b^2 \Delta P}{\mu L} \left(\frac{\partial(Y \cdot c_{A0})}{\partial(\zeta \cdot L)} \right) - \mathcal{D}_{BA} \left(\frac{\partial^2(Y \cdot c_{A0})}{\partial(\zeta \cdot b)^2} + \frac{\partial^2(Y \cdot c_{A0})}{\partial(\zeta \cdot L)^2} \right) + k \left(c_{A0} - \frac{1}{2} Y c_{A0} \right) \quad (143)$$

Simplifying Eq. (143) and using the definition of dimensionless velocity yields:

$$0 = - \frac{\mathbf{v}}{Lk} \frac{\partial Y}{\partial \zeta} - \frac{\mathcal{D}_{BA}}{kb^2} \frac{\partial^2 Y}{\partial \zeta^2} - \frac{\mathcal{D}_{BA}}{kL^2} \frac{\partial^2 Y}{\partial \zeta^2} + \left(1 - \frac{1}{2} Y \right) \quad (144)$$

Transverse and axial species diffusion is described by the second and third terms in Eq. (144). Rearranging Eq. (144) as:

$$0 = - \frac{\mathcal{D}_{BA}}{kL^2} \left[\frac{Lv}{\mathcal{D}_{BA}} \frac{\partial Y}{\partial \zeta} + \left(\left(\frac{L}{b} \right)^2 \frac{\partial^2 Y}{\partial \zeta^2} + \frac{\partial^2 Y}{\partial \zeta^2} \right) \right] + \left(1 - \frac{1}{2} Y \right) \quad (145)$$

we uncover three dimensionless groups: the second Damköhler number (Da_{II}), the mass-transfer Péclet number ($Pé_m$) and the aspect ratio. We therefore determine a necessary condition for neglecting transverse diffusion:

$$\left(\frac{L}{b}\right)^2 \gg 1 \quad (146)$$

which when satisfied, Eq. (145) simplifies to:

$$0 = -\frac{1}{\text{Da}_{\text{II}}} \left[\frac{Lv}{\mathcal{D}_{BA}} \frac{\partial Y}{\partial \zeta} + \left(\frac{L}{b}\right)^2 \frac{\partial^2 Y}{\partial \zeta^2} \right] + \left(1 - \frac{1}{2} Y\right) \quad (147)$$

Similarly, the axial diffusion term can be neglected if:

$$\text{Pé}_m = \frac{Lv}{\mathcal{D}_{BA}} \gg \left(\frac{L}{b}\right)^2 \quad (148)$$

which when satisfied, Eq. (147) simplifies to:

$$0 = -\frac{1}{\text{Da}_{\text{II}}} \left[\text{Pé}_m \frac{\partial Y}{\partial \zeta} \right] + \left(1 - \frac{1}{2} Y\right) \quad (149)$$

For most industrial extrusion operations, the necessary conditions, Eqs. (146) and (148), are satisfied, which justifies the assumptions upon which our solution depend.

b. Order of Magnitude Analysis: Axial Diffusion

We now further support Eqs. (146) and (148) by performing an order of magnitude analysis (see, for instance, **EXAMPLE 1.3-3** of [31]) to compare bulk convection with axial and transverse diffusion.

Eq. (146) can be written as:

$$\left(\frac{L}{b}\right)^2 \frac{\partial^2 Y}{\partial \zeta^2} \gg \frac{\partial^2 Y}{\partial \varsigma^2} \quad (150)$$

which compares the axial and transverse diffusion terms. Expanding the derivatives in Eq. (150), we get:

$$\left(\frac{L}{b}\right)^2 \frac{\partial}{\partial \zeta} \left(\frac{\partial Y}{\partial \zeta} \right) \gg \frac{\partial}{\partial \varsigma} \left(\frac{\partial Y}{\partial \varsigma} \right) \quad (151)$$

To determine the order of magnitude, we replace each partial differential with a total difference between the maximum and minimum limits of each variable:

$$\frac{L^2}{b^2} \frac{1}{\Delta \zeta} \left(\frac{\Delta Y}{\Delta \zeta} \right) \gg \frac{1}{\Delta \varsigma} \left(\frac{\Delta Y}{\Delta \varsigma} \right) \quad (152)$$

where these total differences are:

$$\Delta Y \sim O(Y_L - Y_0) \sim O(2 - 0) \quad (153)$$

$$\Delta \varsigma \sim O(\varsigma_L - \varsigma_0) \sim O(1 - 0) \quad (154)$$

$$\Delta \zeta \sim O(\zeta_b - \zeta_d) \sim O\left[1 - \left(-\frac{d}{b}\right)\right] \quad (155)$$

which, when substituted into Eq. (152), gives:

$$\left(\frac{L}{b}\right)^2 \frac{1}{1 + d/b} \left(\frac{2}{1 + d/b} \right) \gg \frac{1}{1} \left(\frac{2}{1} \right) \quad (156)$$

which simplifies to:

$$\left(\frac{L}{h}\right)^2 \gg 1 \quad (157)$$

As long as this condition is satisfied, as it normally is in plastics extrusion, the axial diffusion can be neglected. We next perform a similar analysis to explore transverse diffusion.

c. Order of Magnitude Analysis: Transverse Diffusion

We begin by comparing axial convection and transverse diffusion:

$$\frac{vL}{D_{BA}} \frac{\partial Y}{\partial \zeta} \gg \left(\frac{L}{b}\right)^2 \frac{\partial^2 Y}{\partial \xi^2} \quad (158)$$

Replacing the derivatives with their total differences, we obtain:

$$\frac{vL}{D_{BA}} \frac{\Delta Y}{\Delta \zeta} \gg \left(\frac{L}{b}\right)^2 \frac{1}{\Delta \xi} \left(\frac{\Delta Y}{\Delta \xi}\right) \quad (159)$$

Substituting Eqs. (153) through (155) into Eq. (159), we find:

$$\frac{vL}{D_{BA}} \frac{2}{1} \gg \left(\frac{L}{b}\right)^2 \frac{1}{1 + \frac{d}{b}} \left(\frac{2}{1 + \frac{d}{b}}\right) \quad (160)$$

which simplifies to:

$$Pe_m \equiv \frac{vL}{D_{BA}} \gg \left(\frac{L}{h}\right)^2 \quad (161)$$

the necessary condition for neglecting transverse diffusion. As long as this condition is satisfied, as it normally is in plastics extrusion, the transverse diffusion can be neglected.

VIII. CONCLUSION

We have chosen the simplest relevant model to explore the influence of polymer degradation on drool rate: polymer scission by an even split with first order kinetics. We combine this with our previously examined model for cohesive slip with both slip heating and viscous dissipation. We find that scission can, indeed, accelerate drool. We include one worked example to show the usefulness of our work. Finally, we perform an order of magnitude analysis to arrive at necessary conditions for neglecting axial and transverse diffusion, foundations upon which our results solidly rest.

IX. ACKNOWLEDGMENT

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Figure 1: Flow profile for proposed cohesive slip creation of die drool [15]

Figure 2: Velocity profiles and concomitant steady state temperature profiles before adjustment for concentration effects on viscosity [15]

Figure 3: Dimensionless drool concentration profile from the slip interface to the wall

Figure 4: Dimensionless bulk concentration profile from the slip interface to the midplane of the bulk flow

Figure 5: Dimensionless drool velocity profiles from the wall to the slip interface.

Figure 6: Dimensionless bulk velocity profile from the slip interface to the midplane of the bulk flow

Table 1: Dimensional variables

Name	Symbol	Dimensions	Range
Absolute temperature	T	T	>0
Absolute temperature, bulk	T_b	T	≥ 0
Absolute temperature, drool	T_d	T	≥ 0
Absolute temperature, initial	T_0	T	≥ 0
Absolute temperature, interface (steady state)	$T_{i,\infty}$	T	≥ 0
Absolute temperature, melt degradation	T_D	T	≥ 0
Absolute temperature, wall	T_w	T	≥ 0
Activation energy	E_a	$ML^2t^{-2}\text{mol}^{-1}$	≥ 0
Arrhenius constant	A	t^{-1}	≥ 0
Binary diffusivity coefficient	$\mathcal{D}_{AB}$	L^2t^{-1}	≥ 0
Bulk fluid half-thickness	b	L	≥ 0
Calculated viscosity, material dependent	μ	$ML^{-1}t^{-1}$	≥ 0
Channel depth*	z	L	≥ 0
Cohesive fracture strength	τ_c	$ML^{-1}t^{-2}$	≥ 0
Density	ρ	ML^{-3}	≥ 0
Distance from die entrance	y	L	≥ 0
Distance from slip interface	x	L	$d \leq x \leq b$
Drool layer half-thickness	d	L	≥ 0
Final slit pressure, absolute	p	$ML^{-1}t^{-2}$	≥ 0
First order rate constant	k	t^{-1}	≥ 0
Fluid velocity, bulk flow parallel to die surface	$v_{b,y}(x)$	Lt^{-1}	≥ 0
Fluid velocity, drool flow parallel to die surface	$v_{d,y}(x)$	Lt^{-1}	≥ 0
Gas constant	R	$ML^2t^{-2}\text{mol}^{-1}T$	>0
Initial slit pressure, absolute	p_0	$ML^{-1}t^{-2}$	≥ 0

Inlet degraded polymer concentration	c_{B0}	molL^{-3}	≥ 0
Interfacial slip velocity	v_s	Lt^{-1}	≥ 0
Intrinsic viscosity	$[\eta]$	LM^{-1}	≥ 0
Material dependent constant of proportionality for viscosity [Eq. Error! Reference source not found.]	K	$ML^{-1}t^{-1}$	≥ 0
Molar concentration of degradation product B	c_B	molL^{-3}	≥ 0
Molar concentration of polymer A	c_A	molL^{-3}	> 0
Molecular weight, 2 nd moment	M_w	$M\text{mol}^{-1}$	≥ 0
Pressure differential	ΔP	$ML^{-1}t^{-2}$	≥ 0
Rate of reaction (mass)	r_A	Mt^{-1}	≥ 0
Relational viscosity, unrelated to material	μ_0	$ML^{-1}t^{-1}$	≥ 0
Shear stress	τ_{yx}	Lt^{-1}	≥ 0
Slip heating flux	q_x	Mt^{-3}	≥ 0
Slip velocity	v_s	Lt^{-1}	≥ 0
Slit height	h	L	≥ 0
Slit length	L	L	≥ 0
Time on-stream	$t_x(y)$	t	≥ 0

Table 2: Dimensionless variables.

Name	Symbol	Definition	Range
Absolute temperature, bulk fluid	$\Theta_{d,\infty}$	$\frac{T_b - T_0}{T_0}$	≥ 0
Absolute temperature, drool layer	$\Theta_{b,\infty}$	$\frac{T_d - T_0}{T_0}$	≥ 0
Absolute temperature, wall	Θ_w	$\frac{T_w - T_0}{T_0}$	≥ 0
Activation energy	s	$\frac{E_a}{RT_0}$	≥ 0
Arrhenius coefficient	r	$\frac{\epsilon}{e^{-E_a/RT}} = \frac{A\mu_w L^2}{b^2 \Delta P}$	≥ 0
Buildup ratio	BR	$\frac{Q_d}{Q_b}$	≥ 0
Bulk flow rate*	Q_b	$\frac{\dot{V}_b \mu_w L}{b^4 \Delta P}$	≥ 0
Cohesive fracture strength	σ_c	$\frac{\tau_c L}{b \Delta P}$	≥ 0
Die drool flow rate*	Q_d	$\frac{\dot{V}_d \mu_w L}{b^4 \Delta P}$	≥ 0
Distance down flow field, parallel to the length	ς	$\frac{y}{L}$	$0 \leq \varsigma \leq 1$
Distance from slip interface	ξ	$\frac{x}{b}$	$-a \leq \xi \leq 1$
Drool layer thickness	a	$\frac{d}{b}$	≥ 0
Feed resin purity	g	$\frac{c_{B0}}{c_{A0}}$	$2 \leq g \leq 0$

Interfacial heat flux	F	$\frac{q_i b}{kT_0}$	≥ 0
Kinetic rate constant	ϵ	$\frac{k\mu L^2}{b^2 \Delta P} = \frac{Ae^{\left(-\frac{E_a}{RT}\right)} \mu_w L^2}{b^2 \Delta P}$	≥ 0
Mass fraction of species A	ω_A	$\frac{c_A}{c}$	≥ 0
Material dependent exponential constant for viscosity	α	-	≥ 0
Slip heating flux	F	$\frac{q_i b}{kT_0}$	≥ 0
Slit width	W	$\frac{w}{b}$	≥ 0
Steady state viscosity at interface	$\eta_{i,\infty}$	$\frac{\mu}{\mu_w}$	≥ 0
Velocity, bulk*	$\varphi_b(\xi)$	$\frac{v_b \mu_w L}{b^2 \Delta P}$	≥ 0
Velocity, drool*	$\varphi_d(\xi)$	$\frac{v_d \mu_w L}{b^2 \Delta P}$	≥ 0
Velocity, slip*	φ_s	$\frac{v_s \mu_w L}{b^2 \Delta P}$	≥ 0
Velocity-kinetics normalizer	U	$\frac{k\mu_w L^2}{b^2 \Delta P}$	≥ 0
Viscosity*	$\tilde{\eta}$	$\frac{\mu}{\mu_w}$	≥ 0
Viscosity coefficient	C	$\frac{a}{\ln^2 \eta_{i,\infty}} \left[\frac{a - \sigma_c \ln \eta_{i,\infty}}{\eta_{i,\infty}} - a + \ln \eta_{i,\infty} (\sigma_c + a) \right] + \varphi_s$	≥ 0

Legend: $M \equiv$ mass; $L \equiv$ length; $t \equiv$ time; $T \equiv$ temperature; * identifies the second iteration of dimensionless variables, introduced in this paper in Section X, to help account for concentration profiles associated with scission.

Table 3: Literature relevant to die drool with degradation.

	Material	Method	Investigated Phenomenon	Resulting variables	Geometry	[Ref]
Brachet <i>et al.</i> (2008)	LDPE	EXP	DD _F	-	U	[32]
Yevtushenko and Kuciej (2010)	SP	AN, COM	SH	$T(\xi)$	○	[33]
Musil and Zatloukal (2010, 2012)	HDPE	EXP	DD _F	-	●	[11, 21]
Schmalzer (2013); Schmalzer and Giacomini (2013, 2014)	AM	AN	DD _{CS}	BR	□, ⊙	[1, 15, 34, 35, 36]
Gilbert and Giacomini (2014); Gilbert (2014)	NN	AN	DD _{CS} , SH	$\Theta(\xi), Q_{(d)}, Q_{(b)}$	□	[16]
Gilbert (2014); Gilbert and Giacomini (2014);	NN	AN	DD _{CS} , VD, SH	$\Theta(\xi), Q_{(d)}, Q_{(b)}$	□	[19], [18], [37]
Rorrer and Dorgan (2014)	HDPE, AM	COM	DD _F	$c_B(x, y), \rho, v_y(x)$	□	[13]
This paper	NN	AN	SH, DD _{CS}	$Y_B(\xi, \varsigma)$	□	

Legend: NN = Newtonian, AM = All materials, SP = Solid pad; AN = analytical, COM = computational, EXP = experimental; DD_F = die drool in fractionation paradigm, DD_{CS} = die drool in cohesive slip paradigm, VD = viscous dissipation, SH = slip heating; BR = buildup ratio, Θ = adimensionalized temperature rise, ξ = adimensionalized distance from wall, $Q_{(d)}$ = die drool flow rate, $Q_{(b)}$ = bulk fluid flow rate, T = temperature profile, $c_B(x, y)$ = spatial concentration, Y_B = adimensionalized degradate concentration, ρ = melt density; □ = slit flow, U = blown film, ⊙ = pipe or tube; ● = screw extruder, ○ = parallel-disk.

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