Role of Processing Aids in the Extrusion of Molten Polymers

E. C. ACHILLEOS', G. GEORGIOU', and S. G. HATZIKIRIAKOS

1Department of Mathematics and Statistics
P.O. Box 20537
University of Cyprus
1678 Nicosia, Cyprus

2Department of Chemical Engineering
The University of British Columbia
2216 Main Mall
Vancouver, BC V6T 1Z4, Canada

Product quality and, in general, processing windows and rates of production in the extrusion of molten polymers are limited by various flow instabilities (mainly melt fracture) that are observed at high production rates. While there still are unresolved issues in comprehending these phenomena, industry demands for process optimization dictate the employment of processing aids (PAS) for product quality improvement and energy requirement reduction. In this review paper, most commercially used processing aids (PAS) are discussed, namely, fluoroelastomers, stearates, small amounts of polymers blended with the process polymer, and the newly discovered boron nitride as pure and in combination with other fluoroelastomers. This paper focuses on the appropriate and optimum usage of the various PAS as well as on the mechanism that underlies their action for flow enhancement and instability elimination. Finally, numerous experimental observations are discussed, and several examples are illustrated.

1. INTRODUCTION

It is well known that commercial polymer processing operations, such as fiber spinning, film blowing, profile extrusion, and various coating flows, exhibit flow instabilities, which manifest themselves as distortions on the product surface. Consequently, these distortions pose a limitation in the rate production that threatens the economic feasibility of the processes (1-8). These phenomena of surface irregularities are collectively known as sharkskin/melt fracture phenomena. Other types of instabilities that may occur in polymer processing at high rates of production, such as draw resonance and elastic instabilities, will not be examined in the present review.

In extrusion processes, the extrudate distortions are first observed when the volumetric flow rate, and, consequently, the shear stress, exceed a critical value. The severity of the distortions (amplitude and irregularity) increases with increasing flow rate (3, 9-12). Thus, the production rates of commercially acceptable products are limited to the ones below these critical values. In order to overcome these difficulties and to render the processes economically feasible, processing aids (PAS) are frequently used. PAS eliminate flow instabilities or postpone them to higher flow rates. The end result is an increase of the productivity as well as an energy cost reduction, while high product quality is maintained.

The purpose of this review is to examine traditional and new processing aids that have been investigated over the past two decades and to discuss their performance in melt fracture elimination, so as to elucidate the role of these materials in instability elimination and polymer processability improvement. The effect of PAS on the rheological properties and the instability (melt fracture) elimination is also discussed. The factors that determine the additive performance, such as concentration, dispersion quality, and interactions between additives, additive and polymer, and additive and die surface, are also examined. The various mechanisms by which different types of processing aids help eliminate the instabilities are reviewed as well. Section 2 discusses the various melt fracture phenomena in

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*Author responsible for correspondence, email: hatzik@interchange.ubc.ca

* Dedicated to the memory of Dr. Charles W. Stewart, an investigator who made several exceptional contributions to the area of processing aids.
general and their origin. Wall slip, which is normally present, is also briefly discussed and its relation to melt fracture is addressed. Section 3 reviews the traditional processing aids such as stearates, fluoropolymers, lubricants and coatings of die materials. Polymer blending in general with concentrations of the minor component of the order of 0.1% and higher, as a means of processing aid is also presented. Section 4 discusses new processing aids, such as boron nitride powders, as well as combinations of boron nitride with fluoroelastomers. These new PAs eliminate melt fracture and enable polymer processing at shear rates that are significantly higher than those permitted by conventional ones. In fact, they postpone the critical shear rates for the onset of instability at rates within the gross melt fracture regime, rates not accessible with conventional PAs. The conclusions and general directions for future investigations are summarized in Section 5.

2. THE NATURE AND ORIGINS OF POLYMER EXTRUSION INSTABILITIES

2.1. The Flow Curve

The flow instabilities that occur in extrusion processes can be better explained by looking at the different flow regimes of the apparent flow curve (3, 4, 11, 12). This is a logarithmic plot of the wall shear stress versus the apparent wall shear rate when a capillary rheometer is used, or the plot of the pressure drop versus throughput rate when a processing equipment is used. In the latter case, it is more strenuous to extract the fundamental quantities of shear stress due to the large pressure associated with the entrance. Figure 1 depicts a typical apparent flow curve of a linear polyethylene melt, obtained using a capillary rheometer. The apparent shear rate, \( \dot{\gamma}_A \), is defined as (13):

\[
\dot{\gamma}_A = \frac{32Q}{\pi D^3}
\]

where \( Q \) is the volumetric flow rate, and \( D \) is the diameter of the capillary. The wall shear stress, \( \sigma_w \), is defined as (13):

\[
\sigma_w = \frac{\Delta P - \Delta P_{end}}{4L/D}
\]

where \( L \) is the length of the capillary, \( \Delta P \) is the total pressure drop driving the flow, and \( \Delta P_{end} \) is the end correction for the pressure drop. Figure 1 also represents typical behavior of a linear polymer in general. Polymers such as LDPE and PP do not exhibit the stick-slip flow regime as explained below. Four distinct flow regimes can be identified in Fig. 1. Initially, the flow is stable, and the shear stress increases "linearly" (log-log plot) with apparent shear rate (power-law behavior), while the extrudate has a smooth and glossy appearance. When the shear stress reaches a first critical value (\( \sigma_{c1} \)), small amplitude, periodic distortions

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**Fig. 1.** Typical flow curve for linear polyethylene extruded in a piston driven capillary illustrating the various regions of instability.
appear on the extrudate surface. This instability is accompanied by a change in the slope of the flow curve, as reported by many investigators [3, 4, 14-16]. This instability is observed up to the end point of the left branch of the flow curve (often referred to as the low flow rate branch) and is generally referred to as sharkskin or surface melt fracture. A second instability occurs when the shear stress exceeds a second critical value (\( \tau_{c2} \)) and only within a certain range of apparent flow rate values. It corresponds to the region separating the two branches of the flow curve, and is usually referred to as stick-slip instability or spurt phenomenon or oscillating melt fracture. In this regime, the flow ceases to be stable when a controlled rate capillary rheometer is used. Instead, pressure, and thus shear stress, oscillates between two extreme values and alternate distorted and smooth zones appear on the extrudate surface [3, 4, 9, 11, 12, 17-19]. Finally, at even higher apparent shear rate values, the flow becomes again stable, whereas the extrudate exhibits gross, irregular and chaotic distortions. This type of instability is referred to as gross melt fracture, and corresponds to the right branch of the flow curve (1, 3, 4, 11, 12, 20, 21, 22).

Thorough reviews on extrusion instabilities have been published, and the mechanisms responsible for these instabilities have been the subject of ongoing debate (1, 5, 6, 7, 23, 24). Various polymer rheological properties, such as wall slip, melt compressibility, melt viscoelasticity, non-monotonic shear stress-shear rate law, viscous heating, viscoelastic rupture, and local stick-slip, which may be simultaneously involved, can be held accountable (5, 6, 7, 24, 25, 26). One has to distinguish between the mechanisms responsible for each type of instability. For the case of sharkskin melt fracture, there is general agreement about its location of occurrence. It takes place at the exit of the die, either because of rupture, as the boundary condition changes from no-slip or partial slip to a shear-free one, which results in a highly extensional flow (14, 27, 28, 29), or because of local stick-slip at the exit as a result of polymer molecule disentanglement (30). On the other hand, gross melt fracture occurs at the entrance of the die because of the abrupt contraction (20, 31). Since this review focuses on the elimination and not on the mechanisms that cause these instabilities, the latter will not be discussed further.

2.2. Wall Slip

Wall slip usually accompanies the instability phenomena under discussion. It is, indeed, the phenomenon most thoroughly studied in the literature, both experimentally and computationally.

Sharkskin instability has been attributed by many researchers to small departures from the no-slip boundary condition, which can be accompanied by a sharp change in the flow curve slope [3, 4, 11, 32, 33]. Some experiments have indicated that sharkskin or surface melt fracture is suppressed by increasing the adhesion between the fluid and the wall (3, 34), whereas others have shown that slip promotion suppresses the instability (28, 35, 36). Slip velocity increases when certain additives are used and as a result shear stress is reduced, shifting the flow curve to higher shear rates (37, 38). This is because both the slip velocity and the critical shear stress for slip are strong functions of the work of adhesion between polymer and interface (37-40). It is the shear stress reduction, rather than the slip velocity increase, that suppresses the instability at a particular flow rate, when additives are used. Moreover, it is also the type of slip that causes sharkskin to occur. Over clean surfaces, polymer slips locally by a stick-slip mechanism that creates the well-known Schallamach waves similar to those in the sliding of elastomers over metallic surfaces (41). Polymeric fluids are not much different from elastomers at high enough shear rates, since their elastic properties prevail in short time scales.

At low shear rates, slip was speculated to be caused by an adhesive failure, that is, stress-induced strain detachment of polymer molecules form the wall [3, 4, 11, 42, 43]. Experiments have shown that there is a strong correlation between the work of adhesion of the polymer/wall interface and the onset of slip (39, 40) and this finding implies adhesive failure. As discussed above, experiments have indicated that the sharkskin originates at the die exit region because of polymer rupture, as a result of the high stresses that develop around the die exit (14, 27, 44, 45). This mechanism is certainly consistent with the violation of the no-slip boundary condition. Gross melt fracture originates near the die entry region, where unstable vortices appear and symmetry is lost (35, 44, 46, 47). Cohesive failure, that is sudden chain disentanglement and rupture of chains near the wall, can account for slip in the gross melt fracture regime, and thus for the unstable and virtually plug-flow behavior (20, 48). Overall, the experiments in the literature indicate the presence of weak slip (small deviations from the no-slip conditions) in the sharkskin regime, which is attributed to adhesive failure and of strong slip in the gross melt fracture regimes, which can be explained by cohesive failure.

Other experiments have shown that slip is not at all present in the sharkskin regime, indicating that other phenomena also contribute to this instability (30, 35, 49, 50). The stick-slip and the gross melt fracture instabilities have been modeled by many researchers using a combination of a slip law with the small but finite compressibility of polymers (51-56) or with a viscoelastic model (57-60). Both compressibility and viscoelasticity can account for the storage of elastic energy that sustains the pressure and flow rate oscillations in the stick-slip regime. Melt compressibility in the reservoir was shown to be a necessary (9) but not sufficient condition (61) for the variations in the pressure and flow rates in the stick-slip regime. Cohesive failure at high shear rates was attributed to hardening of the polymer, which undergoes a relaxation transition from a fluid to a highly elastic solid-like state (47,
62–66). Elucidation of the phenomena that cause flow instabilities is important in understanding the different mechanisms by which the processing aids lead to their elimination.

Processing aids used for instability elimination include additives and surface coatings. Most of these additives or modifications target at slip promotion that leads to lower stresses and pressures. Additives used as dispersions at low concentrations in the base polymers act as lubricants. They increase slip through reduction of the apparent viscosity, and as a result the pressure required for the extrusion process is reduced, thus shifting the instabilities to higher flow rates (67–69). Surface coatings also act as lubricants and modify the melt-wall interfacial interactions, decreasing the pressure, and consequently the shear stress required for a specific flow rate (30, 70). They thus prevent the rupture of the polymer as it exits the die. Many industrial patents have been issued for the incorporation of various processing aids in extrusion processes (71–73), which justifies the ongoing intense academic and industrial research contacted in this area.

3. TRADITIONAL PROCESSING AIDS

3.1 Fluoropolymers

Fluoropolymers have been traditionally used as processing aids in the extrusion of commercially important polymers, including linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), polypropylene (PP), copolymers of ethylene, propylene and hexadiene (EDPM), and others. Low concentrations of fluoroelastomers (down to 500 ppm) in dispersion with the processing polymer can significantly enhance product quality and processability, not only by eliminating surface defects, but also by reducing torque and power requirements as well as die plate pressure (67, 68). Fluoroelastomers used as PAs include DuPont’s DYNAMAR® coating, DuPont’s VITON® (a copolymer of vinylidene fluoride, hexafluoropropylene, and/or tetrafluoroethylene), DuPont’s TEFLOM®, and DFL (dry film type).

An important effect that fluoropolymers have, when used in dispersion with the processing polymers, is the increase of slip velocity, which is accompanied with a reduction of pressure. Thus, the apparent shear stress needed to extrude the polymer at a particular flow rate is much lower, or alternatively, an increase in the throughput rate is obtained at a given pressure drop (67, 68, 70, 74). This is accompanied by a delay of the sharkskin instability to higher shear stresses. Athey et al. (68) found that when a version of VITON® (vinylidene fluoride, hexafluoropropylene 60:40) was used in dispersion with HDPE, LLDPE, and PP, the shear stress was reduced and the flow curve was shifted so that the sharkskin instability was postponed to higher shear rates. The reduction of shear stress took place up to shear rates of 1000 s⁻¹, therefore eliminating only the sharkskin and the stick-slip instability but not the gross melt fracture. Similar results were found when using a DYNAMAR® brand additive (PPA-2231) in extrusion of HDPE and LLDPE (67). Comparing DYNAMAR® and TEFLOM®, Wang (30) concluded that while both induce slip and reduce stresses in the extrusion of HDPE and eliminate the sharkskin instability, TEFLOM® is more effective in coating the die surface, and, in addition, in eliminating the stick-slip instability. Similar conclusions were reached by Hatzikiriakos et al. (70). The shift of the flow curve and instability onset to higher flow rates is depicted in Fig. 2, typically for an HDPE. The wall shear stress is plotted as a function of the apparent shear rate at a temperature of 180°C. The data obtained by using an instron capillary rheometer and several dies of various lengths and diameters to apply all required corrections (17).

As a result of the slipping, the shear stress at a given apparent shear rate is reduced. Consequently, the power/torque requirements for a given production rate are reduced, and the production efficiencies are increased (67, 68). This can be seen from Fig. 2, where distortions in the presence of PA are only obtained at the point indicated as the onset of gross melt fracture. That is the point where the two flow curves merge. Therefore, the benefit from using a PA is that for a given power requirement the production rate is increased, while the product maintains its high quality, since the additives suppress the instabilities. As discussed below, it was concluded from experiments, that the additives migrate to the surface of the die, creating a thin surface of coating and acting as lubricants. Recently, Migler et al. (75, 76) used optical microscopy to prove this mechanism of migration and die coating convincingly.

The phenomenon of PA particle migration to the wall is also supported by the fact that fluoropolymer coatings of the die wall also lead to slip enhancement and shear stress reduction. Hatzikiriakos et al. (37) used VITON® and TEFLOM® PA to coat the surface of the plates in a sliding plate rheometer. They found that the coatings resulted in a significant decrease of the critical shear stress for the onset of wall slip and in an increase of the slip velocity. The critical shear stress for the onset of slip, which is 0.1 MPa for the clean plate, could be as low as 0.027 MPa with a TEFLOM® and 0.043 MPa with VITON® coating. The shear stress reduction ranged from 20 to 50%, depending on the extrusion rate. TEFLOM® also increased the slip velocity and reduced the required shear stress for the flow of PP in sliding-plate and capillary experiments (77). TEFLOM® was found to suppress the extrude distortions of various LLDPEs up to about 1500 s⁻¹ (70). The effect of the TEFLOM® coating on the flow curve was similar to the one depicted on Fig. 2. Two other additives, DYNAMAR® and DFL coated on capillary rheometer dies for the extrusion of HDPE, also resulted in instability suppression for shear rates up to 1000 s⁻¹ (34). However, it was found that while DYNAMAR® promoted slip and reduced shear stress, DFL promoted adhesion, and had no effect on the flow curve (34). Experiments by Xing and Schreiber (78) also indicate
that when dies are coated with either DYNAMAR® or VITON®, via extrusion of the fluoropolymers prior to the processing polymer, slippage is enhanced and shear stress is reduced.

When an additive is present either dispersed in the polymer or as a coating, proper die conditioning is needed prior to any equilibrium measurements. Kazatchkov et al. (77) found that when PP was extruded through TFELO®-coated capillary dies, the shear stress was reduced more with each subsequent run (Fig. 3), indicating that the fluoropolymer coating was initially imperfect and after a long induction time it was smoothed out, providing better lubrication and larger reduction in the extrusion pressure. This phenomenon is even more pronounced when the additives are used in dispersion. As the polymer is extruded, the fluoropolymer molecules accumulate on the die wall causing a pressure/shear stress reduction. As the extrusion proceeds with time, the pressure is reduced until equilibrium is reached, and complete elimination of the sharkskin takes place (68, 74). As the additive level increases, the pressure reduction is higher, and the time needed to equilibrium is shorter (74).

Increasing the additive level typically results in greater pressure reduction, higher shear rates, and thus higher production efficiencies (67, 74). While the extrusion pressure and shear stresses are reduced as a result of lubrication, an excessive amount of lubricant should be avoided, because it might lead to lubrication of the extruder barrel, which can have undesired effects (67).

In addition to the additive level, other factors that critically affect the additive performance and need to be optimized, include the dispersion quality, the particle size, and the interactions with other additives present in the processing polymer. Generally, the dispersion quality improves when the additive has a small particle size (i.e. 5 μm) and a homogeneous dispersion is prepared with intensive mixing. A two-step procedure in which a master batch is first prepared and pelletized, and then mixed with the process polymer is an effective route for preparing homogeneous dispersions (67, 74). In the case of VITON®, diluting the fluoroelastomer in acetone prior to mixing was found to be beneficial (79). The interactions with other additives that might be present need to be minimized if not eliminated completely (74, 80, 81, 82). Priester et al. (74) found that the presence of anti-block agents slow the conditioning curve (time needed for steady state) and that higher additive concentration is required in order to have the same conditioning curve as in the case of no additive.

It is generally agreed that fluoropolymers when used in dispersion migrate to the wall of the die and create thin coatings (68, 74, 75, 76, 79). Generally, fluoropolymers are more polar than the process polymers so they migrate more easily to the wall. They are deformable at the extrusion temperatures so they can easily form a coating on the die wall (68). The creation of secondary flows as a result of sharp entrance effects, which create eddies, can assist particle migration to the wall (79). As in the case of coated dies, the interfacial conditions determine the molecular mechanisms that can either promote or suppress slip, with subsequent results on the shear rate reduction and/or instability suppression. Experiments show that with the exception of DFL (34) fluoropolymers act as lubricants, promoting...
slip. Slip promotion is attributed to the incompatibility of the host polymer with the fluoropolymer layer (38, 68, 78). The experiments of Hatzikiriakos and co-workers have shown that when fluoropolymers are employed as PAs, the slip velocity increase is accompanied with a decrease of the critical stress for the onset of slip (34, 37, 38, 70, 77).

In addition, Anastasiades and Hatzikiriakos (40) used a sessile drop method to measure the work of adhesion between HDPE/LLDPE and clean as well as FE-coated stainless steel. They found that VITON® and, more profoundly, TEFLON® reduce the work of adhesion between polyethylene and the surface. These findings support the hypothesis that slip is a result of adhesive failure, and that slip velocity and critical shear stress for the onset of slip depend on the work of adhesion. Slip models taking these phenomena into account have been developed by Hatzikiriakos (38), Hill et al. (39) and Stewart (43). The fact that instability enhancement is associated with the onset of slip for virgin resins is somewhat inconsistent with the instability suppression effect that fluoropolymers have when they act as lubricants. Hatzikiriakos and Dealy (34), however, point out that the presence of either an adhesion or slip promoter can alter the variation of slip along the die, and reduce the extensional strain upstream the die exit, which according to Kurtz (14) is a determining factor for the stresses that develop at the die exit and thus for the occurrence of the instability.

To summarize this section, fluoroelastomers such as DYNAMAR®, TEFLON®, VITON®, can be effective processing aids in extrusion processes, eliminating sharkskin and stick-slip instabilities, and providing a wider range of production at lower cost. Optimization of the additive performance requires knowledge of the effect of the different process parameters on the extrusion process as well as understanding of the instability suppressing mechanism involved. Fluoropolymers can be used as additives to the resins (dispersed at sizes less than 5 μm, by means of preparing a master batch) or as coating agents to the die walls. They work properly at clean surfaces and optimum concentrations (500–1000 ppm), and exhibit induction times before a full effect is observed.

3.2 Stearates

Stearates, such as calcium and zinc stearates, are present in several commercial resins of both linear and long-chain branched polyethylenes (83). While there is no experimental indication that stearates act as processing aids for linear low-density polyethylenes, there is strong evidence that they promote slip and aid in the reduction of instabilities in the case of metallocene low-density polyethylene copolymers with long chain branching (83). In typical transient capillary extrusion experiments of linear low-density polyethylenes, the load rises initially with time until it reaches a steady state. However, in the case of metallocene polyolefins

Fig. 3. The effect of a Teflon® coating on the shear stress in the continuous extrusion of polypropylene (transient capillary experiments).
that contain stearates, the die-conditioning phenomenon is observed, similar to the one depicted in Fig. 3. In several experimental runs, Hatzikiriakos et al. (83) showed that in capillary experiments with metallocene long chain branched LDPEs that contain stearates, the pressure initially rises and then starts dropping. After several consecutive capillary extrusions, i.e., by reloading the reservoir of the rheometer, pressure attained its steady state value, indicating that complete conditioning of the die surface has been achieved. Comparison of different resins has shown that the conditioning is longer as the amount of long chain branching is increased. The critical shear stress for the onset of slip for these resins was 0.05 MPa, significantly lower than the one corresponding to linear low-density PE resins (0.1 MPa). Furthermore, sharkskin and stick-slip instabilities were observed only in the transient experiments, whereas in steady state, only gross melt fracture is observed. Gross melt fracture, accompanied with a change in the slope of the flow curve, was observed at 0.33 MPa, which is similar to the shear stress values observed for polymer having conventional PAs.

Overall, the processing behavior of metallocene polyolefins was similar to that of polyethylene when fluoropolymers are used. Since no other additive was detected in the metallocene resins, it was concluded that calcium stearate, which are present in concentrations of about 1000 ppm, act as processing aid with a mechanism similar to that discussed for fluoropolymers. The fact that stearates do not, to our knowledge, enhance the processability of linear low-density polyethylenes could possibly be explained by investigating possible interactions between stearates and LDPE as well as with metallocene polyolefins having a small degree of long chain branching. More experimental evidence and systematic studies for resins with various concentrations of stearates are needed for more conclusions to be drawn.

3.3 Other Polymer Blends

Hydrocarbons blended with the process polymer can also act as PAs. This technique might involve not only dispersing a small quantity of PA into a process polymer, but also polymer blending to ratios of the same order of magnitude. Although the notion of a processing aid has a meaning at small concentrations (typically less than 1%), blending at higher concentrations might also improve processing. Examples from the literature are included here.

Blending of polypropylene (PP) with polyethyl vinyl acetate (EVA) for flow instability reduction of PP was examined by Montoya et al. (84) with capillary rheometer experiments. They tested blends of concentrations ranging from 0% to 100% and found that the critical shear rate for the onset of fracture increased with EVA concentration. Mechanical property measurements have shown that while pure EVA has completely elastomeric behavior, blends of 50% PP and higher exhibit thermoplastic behavior with yield stress that increases with PP content. It was thus concluded that 15%-20% EVA-PP blends provided good balance between the mechanical properties and melt fracture behavior.

Fujiyama and Kawasak (85) studied the capillary flow properties of blends composed with various ratios of PP and HDPE with low (L), medium (M) and high (H) melt flow index (MFI). They found that the flow curves of the different blends (PP/PEH, PP/PEM, PP/PF, PPH/PEM, PFP/PEM) were located between the flow curves of the two virgin components. In the blends in which PP had a lower or equal MFI with the PE, the slope of the curves increased with decreasing PP content. The critical shear rate and the critical shear stresses for the onset of melt fracture of the blends were close to the ones determined by logarithmic additivity of the values that correspond to individual component.

Blending of two incompatible polymers, a fluoropolymer (VITON®) and EDPM, in various proportions, in order to improve the performance of one or the other polymer, was experimentally examined by Shih (86, 87). Addition of a small amount of VITON® (down to 0.4%) in EDPM, significantly reduced the shear stress and improved the appearance of the extrudate. EDPM improved the processing of VITON® in a similar fashion. This effect was more pronounced as the VITON® concentration increased up to concentrations of 5%; no improvement was observed with further increase of VITON® concentration. It was experimentally determined that, during the extrusion of blends, the polymer used in small concentration created a build-up layer on the die wall, indicating that a phase separation had occurred, in which the polymer used as additive accumulated on the wall.

The geometry of the die can also affect the additive performance. Kanu and Shaw (79) found that dies with 180° entrance angles promote the migration of VITON® particles to the wall during EDPM extrusion. Reduction of the capillary diameter in extrusion of EDPM, with VITON® as a PA, resulted in a shift of the flow curve to higher flow rates (86, 87). This indicates that longer dies also promote particle migration. Detailed studies of the sharkskin instability in various diameter dies showed that when no additive is used, the critical stress for the onset of instability for LDPE extrusion is the same, but the amplitude of sharkskin increases with increasing diameter (29).

Rosenbaum et al. (88) studied the use of PE as a processing aid in the extrusion of FEP (tetra-fluoroethylene-polypropylene) resins. Capillary extrusion experiments of LLDP (GRSN/7047) dispersed in small quantity (0.1%) in FEP 4100, indicated that PE is an efficient PA for eliminating melt fracture and stick-slip instability in the extrusion of fluoropolymers (Fig. 4). As a result of PE addition, the apparent flow curve is shifted to lower shear stresses allowing for smooth extrudates up to 1000 s⁻¹. It is suggested that PE particles, which have a lower viscosity than FEP, migrate to the wall. Furthermore, the affinity of PE for metal surfaces, which is higher than the affinity of FEP for metal, results in the coating of the surface by PE.
Furthermore, the low friction coefficient at the FEP-PE interface results in the slip of the extruded FEP over the thin PE-layer. Consequently, this results in shear stress reduction and in instability suppression. The wall coating mechanism is illustrated in Fig. 5. This will be discussed in detail in the next section. However, it is sufficient to say here that when a FEP/PE blend is extruded through a clean die, the die-wall coating process starts during extrusion, requiring several runs for reaching steady state. Under constant shear rate, the shear stress goes through a maximum and levels off when the coating is complete (Fig. 6). During this process, particles of FEP are displaced by PE particles. Owing to the higher affinity of PE with the metal wall, the PE particles, upon reaching the wall, cannot be displaced by FEP ones. The time required to obtain steady-state response was found to depend on the process and geometry parameters. The time for achieving steady state decreased with increasing apparent shear rate, and with decreasing diameter or L/D ratio. These findings are consistent with the above mechanism. The latter suggests that the time for achieving steady state is proportional to the time for complete surface coating. A decrease in the diameter or the L/D ratio reduces the area to be coated, and an increase in the apparent shear rate increases the rate of the coating process. In both cases, the time required for complete coating and steady-state operation is reduced.

3.4 Mechanism of Migration and Die Coating

It is perhaps surprising that polyethylene can be used as a processing aid in FEP extrusion for the reduction of the extrusion pressure and the elimination of sharkskin in a similar fashion as fluoropolymers are used in PE extrusion. It is noted that fluoropolymers, such as TEFILON® and FEP, have been used effectively as PAs in the extrusion of PEs (11, 30, 34, 67, 68, 70, 89). As discussed above, it is expected that PE would tend to migrate towards the die wall during extrusion, since its viscosity is lower than that of the FEP. In fact, it is not the viscosity but the work of adhesion that allows this process (migration and wall coating) to take place. It is the energy required to remove the polymer from the metal surface that determines which component eventually coats the die wall. Polyethylene has greater adhesion to metal surfaces than FEP resins, so it is not surprising that during extrusion experiments the metal die surface eventually becomes coated with a very thin layer of polyethylene. Since there is very little adhesion between FEP and polyethylene at sufficiently high shear stress, it appears that FEP slips over the thin polyethylene coating on the die wall.

This, then, raises the question as to why a very small quantity of FEP resin, when finely dispersed in polyethylene, will completely coat the die wall during extrusion. The answer again lies in the relative values of the work of adhesion. Although the work of adhesion of FEP to metal is less than the work of adhesion of polyethylene to metal, the work of adhesion of polyethylene to FEP is much less than either of these. Thus, if a very small FEP particle dispersed in polyethylene comes into contact with the metal die surface during extrusion, there will be very little force at the FEP/polyethylene interface acting to pull the particle off the
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Fig. 5. Wall coating mechanism to illustrate the action of Pas in extrusion processes.

\[ W_{FEP/PE}^{Adh} \ll W_{PE/Wall} \]

\[ W_{FEP/PE}^{Adh} \ll W_{FEP/Wall} \]

Fig. 6. Transient capillary extrusion: the effect of the addition of 0.1% of polyethylene on the transient response in the capillary extrusion of FEP 4100 at 325°C, \( \dot{\gamma}_A = 104.2 \, s^{-1} \), \( L/D = 40 \) and \( D = 0.762 \, mm \).
surface. The polyethylene will slip over this interface and will cause the particle to spread. On the other hand, the force acting to pull the polyethylene off the surface is the result of the wall shear stress during extrusion. The overall result is that the FEP particles accumulate, spread and eventually form a very thin coating on the die over which the polyethylene can slip.

Examination of a broad range of fluorocarbon/hydrocarbon blends has led to the following general observations: To be effective, the minor component must be in a finely divided state of particle diameter less than about 0.2 \( \mu \)m and must be at a very low concentration of less than about 1% by weight. For optimum performance, the viscosities of the two polymers should be approximately equal. The relative work of adhesion between the two polymers and the metal surface and between the polymers themselves determines the final performance. For example, fluoropolymers will displace nonpolar hydrocarbons with low work of adhesion, but will not displace polar polymers such as nylon, polyesters or poly(methyl methacrylate) from metal surfaces because of the very high value for the work of adhesion of these polymers to metals. For such polymers it is difficult to identify a suitable processing aid that would work in the same fashion.

4. BORON NITRIDE: A NEW PROCESSING AID

The influence of a new processing aid, namely boron nitride (BN), used either as an additive in dispersion or in combination with other processing aids, is examined in this section. BN is a solid, inorganic compound, with a structure resembling that of graphite. It is thermally stable and chemically inert, and it is used in combination with a blowing agent as a foaming agent in commercial processing applications of fluoropolymers. Boron nitride was used without a blowing agent in extrusion experiments, in order to examine its ability to improve processing of polyolefins and fluoropolymers. This additive was found to increase, by orders of magnitude, the maximum shear rates at which the extrudate distortions appear, eliminating completely sharkskin and the stick-slip instability, while delaying significantly the gross melt fracture instability. It is noted that no other additive has been reported to be able to delay gross melt fracture.

4.1 Boron Nitride Used as Pure Additive

The use of several BN powders as processing additives in extrusion of metallocene linear low-density polyethylene (m-LLDPE) and TEFLO\textsuperscript{N} FEP/PFA resins was experimentally investigated employing capillary rheometers, with either annular or cross-head dies, and larger-scale extrusion equipment (90–95). The effectiveness of the additive was found to depend on the die geometry, the temperature, the dispersion quality, and the BN concentration and type.

Capillary rheometer experiments have indicated that BN has a strong impact as a processing additive when a cross-head die is used, whereas it has a small effect when a circular die is employed (31, 90, 91, 93). In these experiments, an Instron piston-driven capillary unit, with various annular dies \( D = 0.762 \text{ mm} \) and \( L/D = 0.40, D = 0.254 \text{ mm} \) mm and \( L/D = 40 \), was employed for extrusion of m-LLDPE (Exact 3128 and Exceed 166, Exxon) containing 0.05%–0.1% BN powder (CTF5) at 163°C. For all geometries the virgin m-LLDPE resin exhibited the sharkskin instability around 40 \( \text{s}^{-1} \). Conversely, the sharkskin instability was eliminated when BN was added and the flow became unstable at high shear rates (200–250 \( \text{s}^{-1} \)). The flow curves of the virgin and the BN filled m-LLDPE resins obtained using a capillary rheometer with a die having \( D = 0.762 \text{ mm} \) and \( L/D = 40 \) are depicted in Fig. 7. Even though the addition of BN powder eliminates extrudate distortions in the sharkskin regime, improving the appearance of the extrudate, it has almost no effect on the flow curve. In these experiments, BN completely eliminated the sharkskin instability for the m-LLDPE resin, but suppressed neither the stick-slip nor the gross melt fracture instability.

Employment of a Nylon Mailletier cross-head die, typically used for wire coating applications, having similar configuration with dies used in various processes, resulted in a significant enhancement of the additive performance. Figure 8 illustrates the geometry of such a die. Addition of BN powder (CTF5 type) to m-LLDPE resin increased the maximal shear rate at which extrudates were smooth from 40 \( \text{s}^{-1} \) (corresponding to the virgin resin) to up to 920 \( \text{s}^{-1} \), which is well above the onset of the gross melt fracture instability (500 \( \text{s}^{-1} \)) for the virgin resin (31, 90–95). On the other hand, addition of a small amount of BN (100–1000 ppm) changes very little the flow curve of the polymer. This is illustrated in Fig. 9 for a linear low-density polyethylene (Exact 3128). It can be seen that the flow curve remains the same for all practical purposes, while the melt fracture behavior changes spectacularly. Figure 10 depicts extrudate photos of sharkskin (Fig. 10a) and gross melt fracture (Fig. 10b) obtained with the virgin resin and smooth extrudate (Fig. 10c) obtained in the presence of BN well within the gross melt fracture regime, i.e., conditions similar to those that correspond to Fig. 10b.

At a given temperature, the performance of the additive depends on its concentration at 163°C, the maximal shear rates for smooth extrudate were obtained at low concentrations (0.02% BN), as can be seen in Fig. 11 (31, 90–95). It can be seen that at conditions well within the gross melt fracture regime, the distortions disappear only at low BN concentrations (500 and 1000 ppm), whereas for relatively high concentrations of BN (5000 ppm), these cannot be eliminated.

The effect of the temperature on the critical BN concentration was also studied using an Entwistle extruder (90, 91). At 163°C, the maximum allowable shear rates were slightly higher than those obtained with the rheometer, but their concentration dependence was the same, that is, the low additive concentrations had the
Role of Processing Aids in Extrusion

best effect on instability elimination. However, when the temperature was raised to 204°C, increasing the concentration improved the performance of the additive. The optimum concentration for BN to 204°C was found to be 0.5%. This might be attributed to a temperature dependent critical dispersion concentration, above which the BN particles agglomerate.

When BN was employed with TEFLOW® fluoro-copolymers of tetrafluoroethylene/hexafluoropropylene (FEP 100/3100/4100/5100), the maximum allowable shear rates using the extruder were significantly higher than using the capillary rheometer, possibly because of better mixing of the additive with the polymer in the extrusion barrel (90, 91). Again, the presence of BN increased the maximum allowable shear rates to values well above those corresponding to the onset of gross melt fracture. The performance of the additive was better at higher concentrations. Similar results were obtained for copolymers of tetrafluoroethylene/ perfluoropropyl vinyl ether (TEFLON® PFA340/345/350) (90, 91).

As in the case of fluoropolymers, the method of dispersion preparation has a crucial effect on the dispersion quality and, subsequently, the effectiveness of the
Fig. 9. The effect of BN concentration on the processability of PE Exact 3128. (Extrudable extruder with Nokia Malliefer cross-head die, 3.00 mm die, 1.52 mm tip, 163°C).

Fig. 10. Extrudate samples of metallocene PE Exact 3128 at 163°C: a) sharkskin for pure PE at $\dot{\gamma}_A = 80$ s$^{-1}$; b) gross melt fracture for pure PE at $\dot{\gamma}_A = 800$ s$^{-1}$; c) smooth extrudate for PE with 0.01% BN at $\dot{\gamma}_A = 800$ s$^{-1}$.
The concentration dependence of powder performance depends not be prepared by means of melting a master batch first. The effectiveness in instability elimination than dry mixing of the BN powder with polymer pellets, which resulted in only minor instability suppression \cite{31, 92-95}. This effect is similar to that obtained in the case of traditional fluoroelastomers, where the dispersion should be prepared by means of melting a master batch first.

The effectiveness of BN in eliminating the flow instabilities depends not only on the concentration of the additive but also on the type of powder used. Several BN powders were tested for their efficiency. The basic powder was CTF5, which has an average particle size of 5 \(\mu\)m. CTL40 is an agglomerated version of CTF5, and CTUF contains higher concentration of boron oxide than CTF5. Agglomeration and presence of oxides are two factors significantly affecting the performance of BN as an effective processing aid. Table 2 summarizes the morphological characteristics of the all powders used in literature and the maximum shear rates achieved in capillary extrusion experiments of m-LLDPE at 163°C, using a cross-head die \cite{31, 92-98}. Dispersions of CTF5, CTUF, and CTL40 were prepared using a single-screw extruder, and dispersions of BN427-BN431 were prepared with a twin extruder. The concentration dependence of powder performance and the optimum concentrations for each powder are indicated. The best additives, CTF5 and BN431, were the non-agglomerated powders, in the size range of 5–10 \(\mu\)m, containing minimum amounts of \(\mathrm{B}_\mathrm{2}\mathrm{O}_\mathrm{3} \) \cite{92-97}. Properly dispersed in the polymer, at optimum concentrations, and with the preferable geometry (cross-head die), these two additives can postpone the onset of gross melt fracture to high shear rates (940–1030 s\(^{-1}\)), which are far beyond the value that gross melt fracture appears in the virgin resin (500 s\(^{-1}\)).

![Fig. 11. Extrude samples to illustrate the effect of BN (CTF5) concentration on the extrude appearance of m-LLDPE Exact® 3128 obtained at 617 s\(^{-1}\) and 163°C: 1) pure resin; 2) 0.02% BN; 3) 0.1% BN; 4) 0.5% of BN (CTF5).](image)

The fact that the effectiveness of BN as a processing aid is much more pronounced in cross-head dies than in annular ones indicates that the mechanism by which BN reduces instabilities is geometry-dependent. The cross-head die, illustrated in Fig. 8, has a gradually convergent entrance. The polymer entering the die flows through this converging channel in a smooth fashion. As mentioned in the Introduction, experiments have shown that flow irregularities at the die entrance may be responsible for gross melt fracture. These flow irregularities, which result in symmetry loss, are more prone to occur in annular dies than in the smoothly convergent cross-head die. Yi et al. \cite{93} examined whether gradual reduction of the annular die entrance angle will lead to the results obtained by the cross-head die. They carried out extrusion experiments with m-LLDPE in the presence of BN (CTF50) using capillary dies with angles ranging from 8° to 150°. The reduction of the angle resulted in different flow curves, but it had no effect on the onset of the instability, or the extrudate appearance. Similar results were found by Rosenbaum et al. \cite{90}. Smaller angles, i.e. $< 2°$, might have been more effective in mimicking the cross-head die effect. However, such angles would result in a die length comparable to the one of the reservoir \cite{93}. Reducing the entrance angle of annular dies does not necessarily mimic the flow pattern in the cross-head die, since the flow in the slowly converging channel of the latter resembles more the flow between parallel plates, rather than the flow in a pipe. Even though, for both types of dies, the onset of sharkskin for the pure resin occurs at about the same shear rate, it is possible that BN particles may affect the flow field, reducing the flow irregularities in a complex manner that is geometry-dependent. Further experimental studies, involving detailed flow visualization, are needed in order to resolve this issue.

In all the experiments mentioned above, where BN was used as a processing aid, the flow curves did not
show any significant deviation from that of the virgin resin, with the exception of BN431, which had a slight shift to lower shear stresses (31). It was therefore concluded that interfacial slip, which typically results in a shift of the flow curve, cannot account for the instability elimination for the BN powders (which do not shift the flow curve). However, this might occur only locally at the exit of the die, which is the location of the origin of sharkskin. Steady shear experiments were performed with a sliding-plate rheometer in order to determine whether slip is responsible for the effectiveness of BN431 (31, 94). The flow curve of m-LLDPE was gap-dependent, shifting to higher shear rates at higher gap spacing. Reduction of BN concentration diminished this effect, as the flow curve of the virgin resin was gap-independent. It was therefore concluded that slip is indeed the main mechanism by which BN431 aids in instability elimination. While interfacial slip at the exit accounts for the elimination of sharkskin, the mechanism for gross melt fracture elimination is different, and this will be discussed below in a separate section.

In order to investigate the effect of BN surface energy on the elimination of gross melt fracture, the surface energy of different BN powders was measured with a modified high-pressure capillary rise technique (96, 97). The method allowed for uniform compaction of powder, and employed a computerized data acquisition method, which reduced experimental error. The results are summarized in Table 1, along with the overall surface energies and the dispersive and nondispersive components. Powders with small surface energy and relatively high dispersive components were the most effective processing aids. CTUF, which performed poorly as a processing additive, had the higher surface energy, which was justified by its high content in boron oxide. This explanation was also supported by the fact that CTUF performance as processing aid was independent of powder concentration (31). CTF5 and BN427-430 have comparable surface energies. However, only CTF5 eliminated gross melt fracture. This is attributed to the high dispersive energy that CTF5 has in comparison with BN427-430. It was suggested that high surface energy has a negative effect on the lubricating action of the powder because it promotes polymer chain absorption, and that the dispersive component has a positive effect because it promotes particle migration to the wall, which facilitated smoother polymer flow. These findings support the hypothesis of Rosenbaum et al. (90) that even though BN does not promote slip, it can still act as a lubricant by creating apparent slip in the layer adjacent to the wall due to generation of variable viscosity zones.

The effect of BN on the rheological properties of the process polymers and its relation on instability elimination was examined by Hatzikiriakos and co-workers (31, 91, 94). Linear oscillatory shear experiments (frequency sweeps), carried out in a Rheometrics System IV parallel-plate rheometer for virgin and BN (CTF5) filled metallocene PE resins, have shown that for BN-filled resins the slope of the dynamic modulus changes

<table>
<thead>
<tr>
<th>BN type</th>
<th>Approximate Particle size (μm)</th>
<th>Agglomeration</th>
<th>BN₂O₃ content (%)</th>
<th>Dispersion concentration (% of BN)</th>
<th>Maximum shear rate for smooth extrudate (s⁻¹)</th>
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</thead>
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<tr>
<td>Pure resin</td>
<td>10</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>42</td>
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<td>926</td>
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<tr>
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<tr>
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Table 1. Morphological Characteristics of the Various BN Powders Tested, and Additive Performance in Terms of Critical Shear Rate for the Onset of Melt Fracture in Capillary Rheometer Extrusion of m-LDPE Using a Cross-head Die at 163°C.
at small shear rates, which is an indication of longer relaxation times due to the presence of the additive (91). In addition, the complex viscosity of the BN-filled resins was slightly higher than the one of the virgin resins at low shear rates. However, at high shear rates, the storage and dynamic moduli, as well as the complex viscosity curve, coincide for all resins. Similar experiments performed for other types of BN powders (31, 94) showed that, with the exception of BN431, all other powders had a minor effect on these properties, reducing slightly the dynamic and the storage moduli. This effect was more pronounced for BN431, especially as its concentration increased. Based on the sliding plate rheometer results, the effect that BN431 had on the rheological properties was attributed to interfacial slip, rather than to changes of the bulk properties. Cessation of steady-shear and relaxation experiments carried out in an Interlaken sliding plate rheometer have also shown that, at small shear rates, the relaxation times of BN(CF75) filled m-LLDPE resins are longer than the ones of the virgin resin, whereas the relaxation processes are identical at high shear rates (90). It was, thus, concluded that the small effect of BN on the rheological properties of m-LLDPE, which is apparent only at low shear rates, cannot be used as the sole factor for explaining the mechanism by which BN eliminates the flow instabilities.

4.3 Mechanism of Gross Melt Fracture Elimination

Rosenbaum (91) suggested that it is possible that BN alters the tensile deformation properties of the polymer and changes its structure characteristics under stretching, increasing the critical shear rate at which instabilities occur, instead of the critical shear stress. This can explain the elimination of both sharkskin instability, which may result from polymer rupture caused by the high stresses developed at the die exit (14, 27, 29), and gross melt fracture, which may result from polymer rupture at the die entry, again caused by high deformations and stresses. However, if this were the case, the addition of BN should have changed the moduli of the base polymer. It was also suggested that BN might cause small cracks in the bulk of the polymer, and thus release stress, leading to uniform extrudate (90, 91). Another possibility is that when BN migrates to the surface of the die, it suppresses cohesive failure by providing lubrication and, therefore, eliminates gross melt fracture.

Kazatchkov et al. (31) investigated the mechanism of gross melt fracture elimination using a flow visualization technique (laser speckle–high-speed photography) with an experimental setup similar to the ones used by Binnington et al. (99) and Tremblay (100) for polymer flow velocimetry. A quartz capillary rheometer with a sudden contraction from 20 mm to 1.5 mm diameter was interrogated with a focused Neon laser beam and the fluorescent tracer particles from which the flow lines could be induced were visualized with a microscope attached to a photographic camera.

Experiments were performed with virgin and BN-filled PP at various shear rates. The flow lines during flow of the virgin PP were smooth, and large vortices appeared at the corner of the reservoir at low shear rates. With increase of flow rate, vortex suppression was observed initially. At even higher shear rates (around 650 s⁻¹) the flow stopped being continuous at the entrance region. The flow in the entry region appeared to be broken into several layers, and each layer moved with its own velocity. At regular time intervals, different in each layer, the motion stops for a brief period. The closer the layer is to the center of the stream, the larger and more frequent are the jumps and stops inside it. This produced streamlines that looked distorted, and such streamlines were associated with the occurrence of gross melt fracture. Overall, this flow pattern indicated that a cohesive failure in the bulk of the polymer melt results into local stick-slip instability between the multiple polymer surfaces. This cohesive failure of the polymer causes gross melt fracture. Addition of 0.1% BN to the bulk eliminated these discontinuities, and resulted into smooth flow lines. Moreover, smooth extrudate were produced at these high shear rate. It was concluded that BN acts as a lubricant within the bulk material and prevents local stick-slip when the material fails.

4.3 Boron Nitride in Combination With Other Processing Aids

Combinations of BN powders with fluoropolymer additives in order to further improve the processability of the polymers were examined by Hatzikirialros and co-workers (91, 93, 95, 96, 98). Experiments in capillary rheometers with cross-head dies with PE Exact 3128 and PE Exceed 116 demonstrated that the combination of both additives results in greater processability enhancement (91, 93, 96, 98). In the case of PE Exact 3128, addition of 0.05% TEFLO® or BN shifts the critical apparent shear rate for fracture from 50 s⁻¹ to 1300 s⁻¹ or 1800 s⁻¹, respectively, whereas the combination of TEFLO® and BN shifts the critical shear rate to 2400 s⁻¹, as can be seen in Fig. 11 (93, 95, 96, 98). Similar results where obtained for the extrusion of PE Exceed 116 (91, 96, 98). Addition of 0.1% BN shifted the critical apparent shear rate for fracture from 110 s⁻¹ to 900 s⁻¹, whereas combination of 0.1% BN and 0.05% TEFLO® shifted it to 2000 s⁻¹. When used as the sole additive, BN had no or minimal effect on the flow curve whereas combination of BN and TEFLO® resulted in a significant shift of the flow curve. The shear rates at which stable flow was achieved with the combination of the two additives were well above the point that gross melt fracture occurs.

As was previously discussed, TEFLO® acts as a slip promoter, whereas BN does not. The fact that these two additives have a different mechanism for suppressing the instabilities explains why their combination results in further instability elimination, i.e. in steady flows at higher shear rates, whereas increase of the concentration of either one of the additives does not.
CONCLUSIONS

Product quality and, in general, processing windows in extrusion of molten polymers are limited by the various flow instabilities that are observed at high production rates. These instabilities are attributed to the complex rheological and constitutive character of polymers in general, and have been scrutinized by researchers both experimentally and theoretically. While there are still unresolved issues in comprehending these phenomena, the industry demands for process optimization dictate the employment of processing aids for product quality improvement and energy requirement reduction.

Fluoropolymers have been traditionally used by the industry for elimination of the sharkskin and the stick-slip instabilities. Used as coatings, or more effectively in dispersion with the processing polymer, they typically increase the slip velocity of the extrudate, therefore reduce the energy requirements for a particular flow rate. Furthermore, they shift the critical shear rates for the onset of instabilities up to the point of the onset of gross melt fracture, therefore permitting higher production rates. Migration of the fluoroelestoplastic particles to the wall of the die, with consequent die coating and lubrication at the polymer wall interface, was determined to be the dominant mechanism of instability suppression. This was a direct conclusion of die conditioning measurements, and also proven with optical microscopy. Fluoropolymer performance is highly dependent on the dispersion quality; this is achieved using particles in the size range of 1–5 μm, thoroughly mixed with the polymer by means of a master batch. Optimization of the additive level (500–1000 ppm), choice of the appropriate additive with the desired interactions with the polymer and/or the wall and other additives, and use of clean surfaces are also important.

Stearates, which are typically present in several commercial polymer resins, are believed to act as PAs in the case of long-chain branched metaolocene polyolefins. Processing of these metallocene resins, which have no other additives, is very similar to the processing of fluoropolymer-containing resins. Die conditioning associated with a steady-state slip enhancement and instability elimination within a range of shear rates is observed.

Polymer blending is another traditional method for improving processing. Similarly to fluoroelastomers, blending of hydrocarbons, or addition of a hydrocarbon in a fluoropolymer, can lead to significant reduction of the power requirement and elimination of the sharkskin and the stick-slip instability. Hydrocarbon blending results in processing behavior and mechanical properties that are intermediate of the polymers used. The mechanism by which a hydrocarbon enhances the processability of fluoropolymers was shown to be the same as in the case of polymer processing with fluoropolymers as processing aids.

Use of new processing aids, such as BN and combinations of BN with fluoropolymers, results in immense improvement of the extrusion process. BN powders used in dispersion with PE resins result in greater increase of the critical shear rate for the onset of instability, especially when a cross-head die is used. In this case, the instabilities are postponed to shear rates that are well beyond the gross melt fracture regime. Conversely to the behavior of fluoropolymers, BN powders do not promote slip, when they are used as the sole additive. Even though the mechanism by which BN powders suppress the instabilities is not yet completely understood, it has been experimentally shown that these additives help eliminate gross melt fracture by suppressing cohesive failure in the bulk of the polymer. As in the case of traditional polymers, the performance of the additive is best when a high quality dispersion of nonagglomerated particles, in the size range of 5–10 μm, at optimum concentration and processing temperature is used. Additionally, it was determined that BN powders with small surface energy and higher dispersive rather than nondispersive component of free energy are the most effective for suppressing the instabilities.

Finally, the combination of BN with a fluoroelastomer was shown to be the most effective processing aid. Instabilities are eliminated to even higher shear rates, and, in addition, the energy requirements are reduced, as the flow curves are shifted as a result of slip promotion. Since the two additives have different mechanisms for eliminating the instabilities, their combination had a synergistic effect.

Comparison of new and traditional processing aids leads to the conclusion that more than one mechanism is responsible for the onset of instability in each flow regime. Complete comprehension of these phenomena, as well as of the role of the additives in eliminating the instabilities, is important for process optimization. Elaborate techniques employed recently for flow characterization in extrusion processes, such as ATR/FTIR (36), fluorescence label chains for velocity measurements (101), NMR velocimetry (102), Laser Doppler velocimetry (103), and detailed flow visualization through quartz/shaphe/glass capillary (28, 31, 75, 76), can prove valuable in studying the mechanisms of flow instability elimination when processing aids are present.

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