TECHNICAL BULLETIN

MELT FRACTURE, SYMPTOMS AND SOLUTIONS

1 Introduction

Melt fracture is a surface instability produced during the polymer transformation process (more pronounced in polyethylenes) which limits the production rate in many processes such as profile extrusion, tubular and flat film extrusion, blow molding and coatings. In these processes, the melt mass of the polymer exiting the die often shows surface distortions at shear rates (processing speeds) that are above a critical value. As a result of these instabilities, final products become unattractive and commercially unacceptable. Some parameters that affect the distortion degree of the extrudate are: process temperature, flow velocity, concentration and type of additive, geometric dimensions of the die (nozzle and head), the chemical nature of the polymer, etc. (1)

Frequently, occurrence of melt fracture is evaluated by visual inspection of an extrudate surface from a capillary die. In general, distortions seen during extrusion process get worse through time. As the shear rate or shear stress increases, the extruded surface undergoes a transition from stable extrudate to loss of gloss on the product surface (there is also a haze increase), then small periodic amplitude distortions (known as shark skin), and finally, large irregular distortions at high extrusion rates (thick fracture). Figure 1, illustrates this transition process (2).

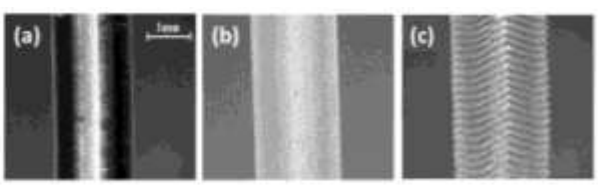

Figure 1 Transition process from stable extruded to shark skin (a) Glossy surface, (b) less glossy surface or fracture beginning, (c) Melt fracture. LLDPE extrudate at 140°C.

2 Mechanisms of fracture (3)

The cause of shark skin surface instability has explanations from different studies of specialists. The interfacial molecular instability mechanism (IMI) (4), proposed by Barone in 1998, establishes an interaction between the molecules of the molten polymer and the wall of the head or nozzle. In this case, entangled molecules of the polymer within the melt are subjected to increasing stresses by increasing shear rate in the area near die exit, causing a stretching and shrinking transition in nozzle wall area, with repetitive cycles of molecules stretching and shrinking that unravel and return to their initial state, after releasing applied stress (Figure 2).

Another physical model, proposed by Ramamurthy in 1986, attributes shark skin phenomenon to a failure of adhesion at the polymer/head interphase (5), characterized by periodic slides at the die exit followed by almost complete slides produced in gross melt fracture regime. Further studies (6) confirmed that this adhesion failure is actually attributed to fluid cracking due to thinning of polymer melted layer which is in contact with the die wall, induced by high shear stress in that zone overcoming melt strength.

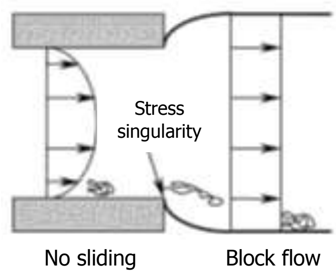

Figura 2 Capillary die exit geometry **- s**chematic diagram, showing block flow condition[(i)] and no sliding extrudate, with inherent stress singularity[(ii)]. High stresses located at the head outlet plane create strong deformations of polymer chains and great tensile stresses (3).

[(i)] In block flow (or plug flow), flow velocities are the same in any position of the capillary, without vertical mixing of flowing particles.

[(ii)] In Fracture Mechanics, a stress singularity is the geometrical locus at a crack tip whose radius is nearly zero, so the stress becomes theoretically infinite. In practice, stress singularities are always associated with discontinuities in the geometry or the change in type of boundary conditions.

According to Schut, melt fracture is caused by two distinct phenomena: pulsations in melt pressure and melt skin breakage (7). The pulsations are caused by the melt slip-stick phenomenon in the die. The pressure rises and falls when the polymer adheres to the die metal and then is released from its surface. These pulsations are transmitted through the melt as it leaves the die. The melt skin layer rupture occurs when the layer surface is stretched too fast at the die outlet. The new emerging layer swells and stretches at the same time that it is impacted by cold air currents. The skin layer rupture generally occurs only on the outer surface as stretching and cooling occur simultaneously and rapidly, causing micro cracks.

3 Melt fracture characterization

Miller and Rothstein used a technique to measure the melt fracture based on photomicrograph of a capillary extrudate (Figure 3).

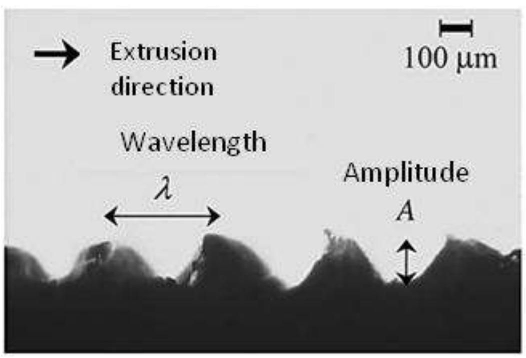

Figure 3 Extrudate microphotography with shark skin, showing amplitude and wavelength parameters.

In their study, qualitative visual inspection of the extruded surfaces indicated that amplitude and wavelength of the shark skin effect increased with production rate. Based on this, they decided to quantify melt fracture as a function of these two parameters. (3)

On the other hand, the American Patent 4,282,177A uses a method based on illuminating the capillary nozzle extrudate from one side and examining it under a 40X magnification microscope. The obtained image is analyzed qualitatively and is located in one of four stages of melt fracture (glossy surface, matt surface or shark skin beginning, shark skin and gross melt fracture) (8). In a similar way, Mavridis and Shroff analyze the fracture by qualifying it according to the level of intensity in: very light, moderate, full, severe or extreme; however, this observation is made on tubular film surfaces (9). An example of extreme fracture and a non-fractured surface is shown in Figure 4.

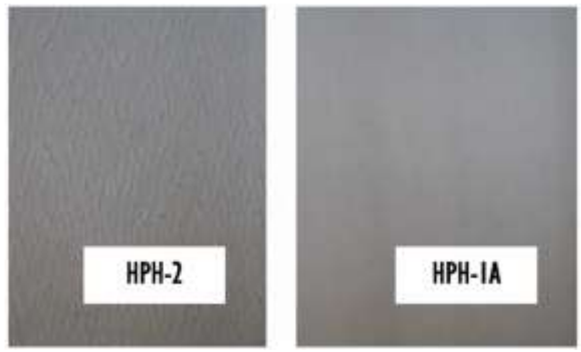

Figure 4 Examples of films with extreme melt fracture (HPH-2) and no melt fracture (HPH-1A)

Finally, Mavridis and Fronek used a technique to measure fracture amount of material formed in a film sample by placing a layflat tubular film in a transparency projector to project the image onto a larger surface (Figure 5). This method reports melt fracture at the surface as a percentage of the layflat. (10).

Figure 5 Photograph of melt fracture of a LLDPE extruded film.

4 Control of surface instability

Limitations in extrusion speed and loss of acceptance of the quality of melted polymers for commercial applications have been the result of elastic surface instabilities that arise when high yields of transformation processes are pursued. The need to prevent onset of melt fracture has motivated many investigators to conduct studies on the characterization of instability and to present solutions to problems according to speed ranges used. (11)

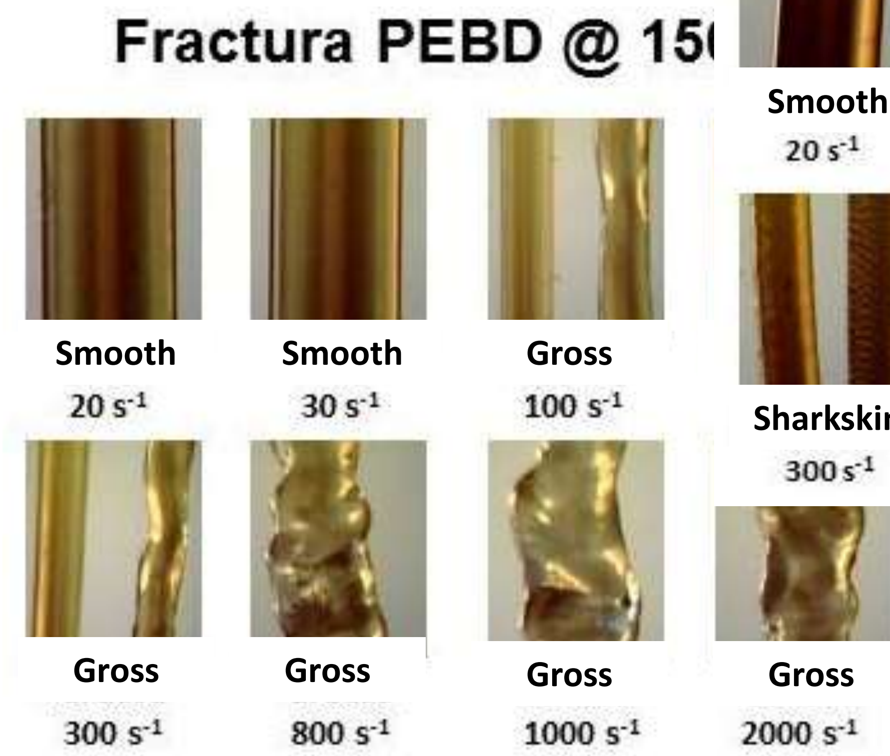

Figure 6 LDPE melt fracture at different shear speeds in a capillary rheometer (11).

elt fracture for different shear speeds.

depict melt behavior patterns found resins as they are extruded into a ter. As shear rate increases, surface , from the appearance of shark skin acture, which occurs at high shear rates for LLDPE resin.

To date, different technological advances have been developed to eliminate surface instability problems. Efforts have focused on the following areas:

- *Processing temperatures:* modification of heating system configuration and adjustment of precise temperature controls systems in die or nozzle of processing machines.
- *Changes in materials and / or coatings used for nozzles and dies:* use of elements, parts or pieces of materials different to stainless steel and / or use of fluoropolymer type coatings that promote sliding on die/nozzle wall.

- *Use of processing additives:* incorporation of compounds based on fluoropolymers and / or boron nitride in blends with commercial polymers to promote the surface quality improvement and to eliminate melt fracture.

Developed solutions are described below:

4.1 Influence of head temperature on melt fracture.

Melt fracture has traditionally been identified as a loss of gloss on the extrudate surface. This corresponds to a surface roughness with amplitude of approximately A≈ 10 µm, which can be decreased as die heating is increased. (3)

Figure 8 shows surface roughness modification by an increase of 40 ° C in die temperature, which produces a reduction of the shark skin amplitude.

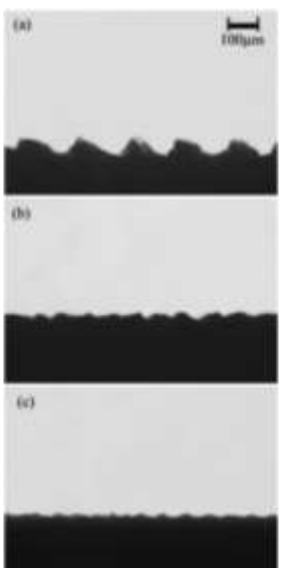

Figure 8 Photographs of melt profiles with constant shear rate of 30 s -1 and constant melt temperature of 140 ° C, with die temperature increases of (a) 130 ° C, (b) 150 ° C, (c) 170 ° C.

These images show a decrease in surface roughness amplitude from A = 90 µm (T = 130 ° C) to A = 25 µm (T = 150 ° C), to A = 9 µm (T = 170 ° C) at constant shear rate of 30 s -1 and a melt temperature of 140 ° C. The variation of melt temperature shows no impact on roughness amplitude changes.

From these observations, it can be inferred that instability related to shark skin is independent of melt viscosimetric properties and it is a function of the rheological properties of the melt in contact with the die wall, and stress levels generated by enormous melt deformations near to exit edge. The localized and precise heating in die zone suppresses shark skin surface instability in LLDPE resins extrusion (3).

4.2 Impact of materials and/or coatings used for extrusion dies and nozzles.

The first conclusions of unstable polymer flow studies indicated that melt slips take place at the die wall, and the material of which it is made affects surface instability onset (2).

Use of bronze dies with low surface roughness, instead of traditional chromed stainless steel dies, demonstrated that surface instability could be eliminated and their disappearance associated with metal type used. Use of fluorinated coatings on metal surface was particularly effective in promoting apparent melt slip throughout extrusion.

Figure 9 shows the extrusion of a transparent material (PDMS) that comes out smooth from the central portion of a slotted die coated with fluoro-polymers, while surface distortions remain in uncoated portions.

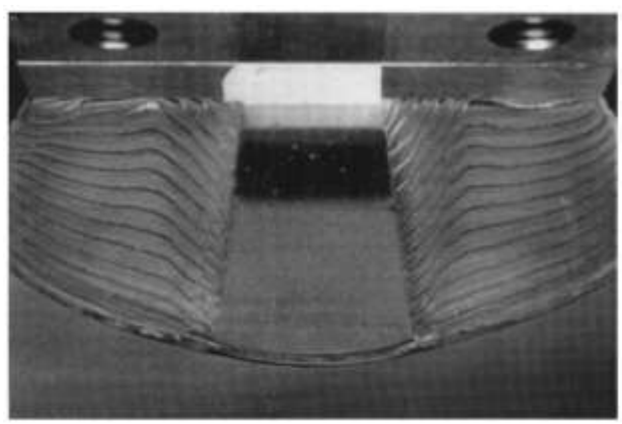

Figure 9. Extrusion of polydimethylsiloxane (PDMS) through a 2 mm thick die with two chambers of its lower and upper faces coated with a fluorinated coating. **(2)**

4.3 Impact of slip-promoting additives when are mixed with polymers.

Incorporation to polyolefin blends of slip-promoting additives (PPAs) based on fluoropolymers has been widely used to improve this property. Film converters have incorporated these additives to facilitate the polymer extrusion and to avoid (or at least minimize) sharkskin surface instabilities. The mechanism associated with "conditioning the die metal surface" is identified as the surface coating action with the formation of a reduced friction layer at the polymer-metal interface, allowing the melt to slide towards the outlet under reduced stress, and providing a differential reduction of the melt velocity profile to promote a block flow.

This action mitigates the slip-stick phenomenon inside the die and the extrudate surface acceleration rate right at the outlet of the nozzle or die, delaying the onset of melt fracture at high shear stresses and high shear rates (12). These additives show their best performance under conditions of low extrusion temperatures and high shear rates.

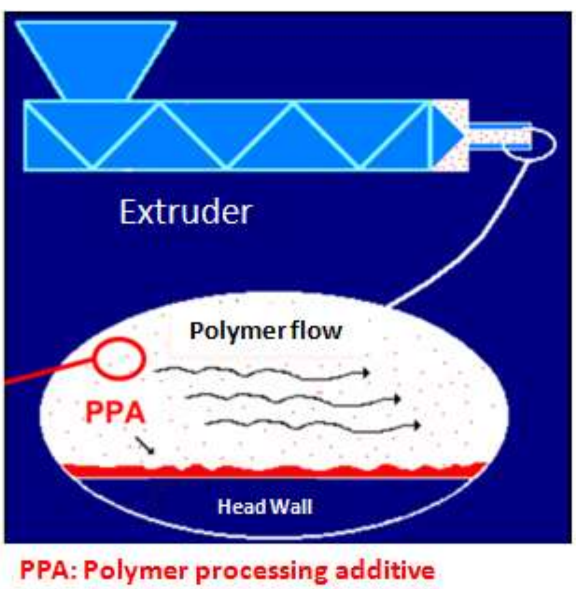

Figure 10 Polymer processing additives (PPA) action mechanism in metal surface coating.

4.3.1 Fluoropolymers used as PPA

Polymer processing additives are based on fluoroelastomers or fluorothermoplastics. They are manufactured by the copolymerization of the following monomers:

VF2, or vinylidene fluoride	$CH_2=CF_2$
HFP, or Hexafluoropropylene	$CF_3CF=CF_2$
TFE, or Tetrafluoroethylene	$CF_2=CF_2$
Ethylene	C_2H_4

Fluoropolymers are characterized by their high inertia towards chemical reactions, high thermal stability, low surface energy and almost complete immiscibility with other polymers.

A key factor in the correct selection of PPAs is based on the specific transformation process (eg blown films) and related process parameters. In addition, the polymer type, its rheology and processing temperatures are important considerations in the appropriate choice of a PPA (14).

5 Conclusions

- Melt fracture is a surface instability produced by the reaction of entangled polymer molecules inside the melt bulk, which are subject to increasing stresses by increasing shear rate in the area close to the die outlet, causing a stretch and shrinkage transition in the nozzle wall region.
- As shear rate increases, surface instability arises, from the appearance of shark skin to gross fracture taking place at high shear rates in semicrystalline polymers.
- Different technological advancements have been developed to eliminate the surface instability problem: processing temperatures, changes in materials and / or coatings used for nozzles and dies, and the use of processing additives.
- Surface instability related to shark skin is independent of viscosimetric properties of the melt and is a function of the rheological properties of the melt closest to die wall

and stress levels generated by large melt deformations near the exit edge.

- The surface coating action developed by the slip promoter additive, forming a layer over the metallic die with reduced friction in the polymer-metal interphase, allows the melted material to slide towards the outlet under a reduced stress, providing a differential reduction of melt velocity profile that promotes block flow.
- Correct selection of a slip promoting additive (PPA) is based on the transformation process, related process parameters, polymer type, rheology and processing temperatures.

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This Bulletin was prepared by the Marketing Management of International Polyolefins, C.A. (POLINTER), with the support of Research and Development, C.A. (INDESCA), in Caracas, Venezuela, in August 2016.

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