FLOW VISUALIZATION OF POLYMER PROCESSING ADDITIVES EFFECTS

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Abstract

Flow visualization was used to understand how polymer-processing additives (PPA) eliminate sharkskin in linear low-density polyethylene (LLDPE). A sapphire capillary die was used to image the coating of the PPA onto the die wall. Depth resolved optical microscopy was used to measure the velocity profiles. When added, the PPA migrates to and coats the die wall, induces slippage, and eliminates sharkskin. The interface between the PPA and LLDPE is characterized by long stripes in the flow direction.

Introduction

The throughput of several classes of polymers is limited by a processing surface defect known as "sharkskin". The surface of the polymer becomes rough, resulting in a change in certain surface properties and gloss. Sharkskin occurs beyond a critical throughput and affects operations such as film blowing, film casting, extrusion blown molding, tube extrusion, and wire coating.

The situation has become more critical in recent years with the increasing use of linear low density polyethylenes (LLDPE) and metallocene linear low density polyethylene (mLLDPE). These materials are desirable for their good mechanical properties, but are limited by flow instabilities such as sharkskin [1]. A substantial effort to understand and overcome sharkskin has been underway since it was first reported over 40 years ago [2].

In the 1960s, the accidental discovery that sharkskin could be reduced or eliminated by the incorporation of a fluoropolymer polymer processing additive (PPA) allowed processors to increase throughput, reduce energy consumption, and enhance processing quality [3]. Since then, the use of fluoropolymer PPAs has become widespread in polyolefins; in fact, resin manufacturers often add it to their polymer resins as part of an additive package. Fluoropolymer additives migrate to the die surface during extrusion where they lower the surface energy, allowing the main polyolefin to slip at the wall [3].

However, the study of polymer process additives is made difficult for two reasons. First, there are no available in-situ measurement tools. Thus, it is difficult to know whether a given additive migrates to the surface, and if so, does it induce slippage? Second, at a fundamental level the cause of sharkskin and the precise reason that fluoropolymer additives reduce it are still under debate. This lack of understanding of the mechanism makes it conceptually difficult to rationally design new materials.

In this work, we used a capillary rheo-optics instrument that uses stroboscopic optical microscopy to complement the rheological studies [4,5]. The optical microscope is used for both velocimetry measurements and to directly image the coating of the PPA onto the die wall.

The use of a fluoropolymer as a processing aid is particularly interesting in that it represents one of the most important examples of polymer-polymer slippage. Experimentally polymer-polymer slip has been indirectly observed by rheology in multi-layers of polymer films [6]. In a fluoropolymer/PE system the data of Dealy and Hatzikiriakos can be interpreted as polymer-polymer slippage [7]. In all these experiments, one observes reduced viscosities in the systems with interfaces.

Laser Doppler velocimetry was successful in measuring slippage of a HDPE during extrusion through a steel capillary slit, and mapped out interesting flow behavior during cyclic melt fracture [8]. The relationship between slippage and the surface conditions has been shown by various optical techniques [9-. Stroboscopic optical microscopy was utilized to monitor the flow profiles, as discussed below [13,14] and preliminary evidence for slippage was found upon addition of a fluoropolymer additive to polyethylene [Error! Bookmark not defined.].

Experimental

In this study, we utilize stroboscopic optical microscopy to visualize the mLLDPE / fluoropolymer system as they are extruded through a transparent capillary die. It was used to make velocimetry measurements, and to directly image the polymer-polymer interface. The equipment is described elsewhere [4,5]. This technique has been described in more detail in the case of a slit die [Error! Bookmark not defined.]. For velocimetry measurements, we record video data from a standard CCD camera onto a standard S-VHS video recorder. The stroboscopic light source is synchronized to flash twice per video frame (typically between 1ms and 5 ms) giving two images on one video frame.

The velocity was measured from either the distance between the two particle images and the time between flashes or the time for a particle to travel a distance over several video frames.

The depth of field, *D* is a crucial parameter in this experiment as well as particle size. Large particles are in focus over a greater depth than are small ones. For smaller particles, the depth of field is approximately $D = 50\mu$ m. In performing velocimetry measurements, care must be taken to measure small particles ($\approx 2 \mu$ m) or the error in the depth of that particle will be too large. In this experiment, the "particles" are the naturally occurring gels, dust particles and miscellaneous foreign objects that have found their way into the extruder. These need only be present in very small quantities to make measurements feasible.

The curvature of the outer diameter of the sapphire tube causes spherical aberrations in the optical image; the solution is to slide a polished (on two side) sapphire cube with a polished hole drilled through its center, over the sapphire tube. PDMS is placed in the narrow gap between the tube and the cube's sleeve to minimize the index of refraction difference. Distortions due to the rounded sapphire / polymer interface are not serious.

The capillary rheo-optics apparatus is situated at the exit of a Haake torque rheometer with a co-rotating twinscrew extruder attachment. In this experiment the length of the capillary is L = 25.4 mm and the radius is R = 0.80mm.

Materials

The tests were carried using a well-stabilized commercially available polyolefin POP (AFFINITY^{*} EG 8100 Polyolefin Plastomer). It is characterized by a melt index of 1.0 and a density of 0.870 g/cm³. This material was selected for its clarity, its overall low level of additives, and the absence of PPA in its formulation. It is however, a mLLDPE type resin.

The processing additive used in this study was a commercially available copolymer of hexafluoropropylene and vinylidene fluoride (DynamarTM PPA - FX-9613). It was added at a 1000 ppm level to the base resin through tumble blending of a commercially available 3% concentrate in a 2.0MI LLDPE (Ampacet). Before the test, the equipment was purged using a commercially available purge compound (HM-10, Heritage Plastics) comprising 70% mass ratio of CaCO3 in a 10MI LDPE.

Procedure

The goal of the experiment is to visualize the PPA on the die surface and its effects. For this purpose, velocity measurements across the flow channel were done at five throughputs, with and without PPA.

We used the twin screw extruder in starve feed mode. The feed rate/RPM ratio was kept constant, to maintain the same approximate fill ratio. The three heating zones of the extruder and the die were set to (from feed to die) 130° C, 150° C, 210° C and 210° C. The flow rate, RPM, pressure at the die entrance, and screw torque were monitored.

Before the experiment, the extruder was cleaned with an abrasive purge compound and then flushed with the base resin until clear before installing the sapphire die. Before the velocity measurement, the system was allowed to reach equilibrium. With the PPA present, this included a coating time. The coating process was also recorded.

Results

Figure 1 shows a plot of the wall shear stress vs. the apparent shear rate. The (uncorrected) wall shear stress is:

$$\boldsymbol{s}_{w} = RP_{c}/2L \tag{1}$$

where P_c is the pressure upstream of the capillary die. This is typical of a capillary experiment, where the PPA additive reduces the pressure across the capillary.

Without PPA sharkskin is observed for all throughputs and its intensity is increasing with throughput. Velocimetry results in the absence of PPA are shown in Figure 2. The velocity profiles are taken from the center (r = 0) to the wall (r = 0.8 mm) where r is the radial distance from the center and R is the radius of the capillary. The curves are fits obtained by using a power law model for the viscosity:

$$V(r) = V_s + V_o[1 - (r/R)^{1+1/n}]$$
(2)

where V_s is the velocity at the surface, V_o is the velocity at the center, and *n* is the power law index. On a linear scale, it appears that all curves converge to the noslip condition $V_s = 0$. Because the particle used to monitor the flow have a finite size, and because of the depth of field (50 µm) does not allow to differentiate between the particles at the wall and a few microns from it, the measured velocity at the wall is slightly greater than zero.

For the plot of Figure 2, the data point near the wall at r = 0.80 mm corresponds to the smallest velocity that was measured. However, we do observe a continuous range of velocities at this point. This will contrast with the velocity with PPA. The fit parameters from Eq. (2) are shown in Table I.

After the extruder was purged and then flushed with pure POP, the resin with the PPA was added to the extruder. The throughput was set to 7.0g/min for which sharkskin is easily observable by the unaided eye. Initially, we extruded POP without the PPA

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The importance of the cleanliness of the extruder in such an experiment is critical. It is almost impossible to clean the equipment to a degree that would be ideal for microscopic examination. Consequently, some side effects of the PPA can be observed in this study. The importance of the purge procedure and its effect on the PPA performance was already published [15]. It is often observed commercially that the PPA will clean a dirty extruder, releasing the accumulated degraded materials or purge material from the metal surfaces of the extruder [3]. It is also known that the PPA will prevent the formation of oxidized gels by presumably coating the die metal and preventing stagnation of the PE against the metal [16]. y the same mechanism, it will prevent die build-up. In summary, the PPA can prevent adhesion of decomposition products and release the materials that have adhered to the metal.

An example of this type of behavior was observed here. At approximately 15 min., we observed gel-like particles at the wall. Once the coating is established, these gel-like particles are not visible or do not adhere to the die.

The shear stress decreases by 15% to reach its equilibrium value between t = 30 min and t = 70 min. We start to see a reduction in sharkskin at t = 30 min and by t = 45 min, it is eliminated-the surface is smooth. Concurrently, at t = 45 min, we begin to see, the formation of streaks at the surface. In Figure 3 we show a micrograph taken after 2 hours, showing the streak phenomenon. The streaks are approximately 5 μ m in width. The streaks are not static; clearly, they are the due to the structure of the fluoropolymer at the surface.

In order to verify that the streaks were not an artifact of the flow visualization technique, a slit die was used. A metal die stack with removable shim was coated using a LLDPE containing 1000 ppm of PPA. After an hour of coating, the pressure reached equilibrium and the die was removed, and disassembled. The stainless steel shim was placed under a reflection microscope equipped with differential interference contrast and the same streak pattern was observed, as shown on Figure 4. The streaks were not visible when no PPA was used.

After the sapphire die is coated with PPA, the velocity of both the LLDPE and the fluoropolymer can be measured independently. There is a significant difference between the two. In Figure 5, we did not include both the fast (LLDPE) and slow (fluoropolymer) values, the slow one being at $V_s \approx 0$ mm/s. This shows however, that the slippage occurs at the POP/PPA interface. In Figure 5, we plot the velocity profiles for the five throughputs. All curves show slip at the wall. Again, the curves are fits to Eq. (2), and the corresponding parameters are given in Table I.

In Figure 6, we plot the velocity of the POP at the surface V_s as a function of wall shear stress. The wall velocities in the presence of PPA range from

approximately $V_s \approx 7$ mm/s at low shear stress to $V_s \approx 60$ mm/s at high shear stress. Note that the wall velocity in the case without PPA is approximately two orders of magnitude smaller.

Table I shows that for both cases (with and without PPA) the power law index, n is a decreasing function of increasing shear rate. We also note that for similar throughputs n is larger in the presence of PPA. This is consistent with the notion that the shear rate is reduced in the presence of the PPA.

Several mechanisms have been proposed to explain sharkskin. Without PPA, our tests did not reveal any slipstick behavior on the die wall and thus does not cause sharkskin. It has been suggested that wall shear rate is the crucial parameter causing sharkskin. However, we show in Figure 7 the shear rate at the wall of the polyolefin as a function of throughput. The PPA greatly reduces the shear rate at the wall. For equivalent shear rate at the wall, sharkskin was observed only in the absence of PPA. Thus, wall shear is not the controlling parameter.

The main difference between the two cases is the shape of the flow profile that could lead to significant differences in the layer rearrangement upon exiting the die. Further work will be required to understand the origin of sharkskin.

Conclusion

In the absence of the PPA, within the experimental uncertainty, no slip in the die is observed and that slip stick in the die is not the cause of sharkskin. Upon addition of PPA, we observe the coating process through direct imaging. We see that the PPA forms elongated structures in the flow direction. The formation of the PPA layer coincides with the disappearance of the sharkskin in the extrudate.

Flow velocimetry in the presence of the PPA then shows that slip occurs for all throughputs. This slip is observed to occur at the interface between the two polymers. The PPA induces slip and decreases the shear rate at the wall.

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Figure 2: Velocity profiles of the pure POP (no PPA)



Figure 1: POP apparent shear stress vs. apparent shear rate with and without PPA.



Figure 3: Micrograph of the polymer-polymer interface. The width of the micrograph is $200 \ \mu m$.

Table I: Parameters obtained by fitting the measured velocity profiles to Equation 2

Output	Shear	No PPA			With PPA		
(Nominal) (g/min)	Rate (1/s)	V _s (mm/s)	<i>V_o</i> (mm/s)	n	V _s (mm/s)	<i>V_o</i> (mm/s)	n
1.2	80	-0.4 ± 0.8	24 ± 1	0.8 ± 0.2	9.2 ± 0.4	10.8 ± 0.5	1.2±0.4
2.2	150	1.0 ± 0.8	43.5 ± 1	0.64±0.1	15.0 ±0.6	19 ± 1	0.8±0.2
3.8	260	0 ± 3	66 ± 3	0.56±0.1	23.7 ±0.6	34.5 ± 1	0.8±0.1
6.8	460	6 ± 3	104 ± 3	0.37±01	41.4 ± 4	63 ± 5	0.75±0.4
13	880	-3 ± 10	201 ± 10	0.36± 01	64 ± 8	117 ± 10	0.35±0.1



Figure 4: Photomicrograph of a PPA coating on stainless steel die (100μ m/div). Left: No coating. Right: Coated with PPA.



Figure 6: Slippage velocity as a function of wall shear stress with and without PPA



Figure 5: Velocity profiles of POP with PPA.

Keywords

Polymer Processing Additive; Sharkskin; Melt Fracture; Wall Slip



Figure 7: Wall shear rate as a function of throughput with and without PPA.