FLOW INDUCED COATING OF POLYMER PROCESSING ADDITIVES: DEVELOPMENT OF FRUSTRATED TOTAL INTERNAL REFLECTION IMAGING

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Abstract

In the extrusion of polyethylene (PE), fluoropolymer-processing additives (PPA) are used to eliminate the surface defect known as "sharkskin" by coating the die wall and inducing slip at the PPA/PE interface. We describe a method to carry out *in situ* measurements of the coating kinetics by exploiting the optical phenomenon of frustrated total internal reflection (F-TIR). The estimated coating thickness was found to be significantly lower (60 to 350) nm than reported previously (5 to 15) μm [1]. The proposed coating mechanism may have origins at the die entrance.

Introduction

Flow instabilities in important polymer processing operations such as extrusion, injection molding, and wire coating have a significant impact on the product appearance and performance. In the present work we focus on polymer extrusion, and specifically on the broadly explored instability known as "sharkskin". While the origin of this defect is widely debated, recent visualization studies indicate that it is likely to arise when the material reaches a critical stress at the die exit [2]. One of the methods to eliminate sharkskin is to introduce a small quantity of a fluoropolymer PPA into the PE. The PPA is known to migrate to the die wall [2, 3]. Due to the weak interaction between the two polymers, there is slippage at the polyolefin/PPA interface that reduces the wall shear stress. However, some argue that it is the improvement of the adhesion of polyolefin/PPA interface, which prevents the sharkskin [4, 5]. In either case, there is general agreement [6, 7] that the origin of sharkskin lies at the die exit, whereas more severe distortions such as gross melt fracture occur at higher shear rates and originate at the die entrance. Previous *in situ* optical microscopy measurements allowed visualization of PPA streaks at the die wall and showed that in case when the PPA was a fluoroelastomer, slippage would occur at its interface with polyethylene [2]. However, microscopy does not permit measurement of the kinetics of the polymer coating process in real time, nor does it give information on the thickness; thus the development of a new measurement technique is vital.

Measurements of the thickness and the refractive indices of thin films were carried out decades ago [8, 9]. The techniques were based on the phenomenon of total internal reflection (TIR), arising from the difference in refractive indices of materials. Utilizing TIR, the dynamic behavior of a weakly interacting fluid at molecular distances from a wall was characterized at high shear, revealing the existence of strong slip [10]. The refractive indices of PE and the PPA used in our work are also distinct, allowing application of the TIR to study such optically mismatched interfaces. By utilizing this technique in the extrusion of PPA/PE blends it should be feasible to describe the PPA coating kinetics at the die wall (provided the wall is transparent, and that it has the largest refractive index), and to visualize the surface coverage by the PPA along the finite segment of the die perimeter.

Experimental Procedure

The *in situ* coating kinetics is studied in a modified capillary rheometer (Goettfert Rheotester-2000), (Figure 1a) [11]. To facilitate TIR measurements, we extrude through a custom made cylindrical sapphire die (l/D = 38.2 mm/1.6 mm), which replaces a conventional metal one, and is attached via a metal fitting and a Conax die holder. The sapphire die has an estimated refractive index (n) of 1.766 ± 0.002 (unless otherwise noted, the ± represents standard uncertainties of the measured values and refers to one standard deviation of the observed value) with its c-axis oriented in the flow direction what circumvents the materials' inherent birefringence (Figure 1b, inset). All experiments were performed using linear low-density polyethylene (LLDPE 1001.09) or ("PE") produced by ExxonMobil Company with an estimated n of 1.471 ± 0.002. This polymer has melt flow index of 1.0, and readily shows the sharkskin melt fracture at a temperature of 180 °C and shear rates above 35 s^{-1}. The PE and the PPA ("Viton") were received from Dupont-Dow Elastomers (DDE). The latter is a copolymer of vinylidene flouride and hexafluoropropylene (in 3/2 mass ratio) with an estimated n of 1.371 ± 0.002. It is nearly twice as dense as PE and has a zero shear rate viscosity which exceeds that of PE by about a factor of 10. However, in the range of shear rates studied in our work both PE and PPA possess comparable viscosity numbers. Starting with mass fraction of 5 % (master batch obtained from DDE), 0.1 % and 0.5

% PPA/PE blends were prepared at the NIST polymer processing facility, using a HAAKE twin-screw extruder [2], operating at 1.36 rad/s and barrel section temperatures of 160 °C, 180 °C and 190 °C.

We utilize a He-Ne laser (λ = 633 nm), with the fast polarizer axis parallel to the plane of incidence (p-polarized wave). For this polarization, the losses due to reflections at the interfaces along the optical path are the lowest. The optical signal is monitored (2 ± 0.1) mm upstream of the die exit using a photodetector on a rotary platform. The critical angle for TIR is found using Snell's Law [12]:

$$\frac{\sin(\alpha_1)}{\sin(\alpha_2)} = \frac{n_2}{n_1} \qquad (1)$$

where n_1 and n_2 are the refractive indices of the materials at the interface (sapphire/PE or sapphire/PPA), α_1 is the incident angle and α_2 = 90° (TIR). To characterize the transmitted and reflected waves as a function of light polarization, amplitude and phase, the Fresnel relations [12] are employed:

$$R_p = \frac{\tan^2(\alpha_2 - \alpha_1)}{\tan^2(\alpha_2 + \alpha_1)} \qquad R_s = \frac{\sin^2(\alpha_2 - \alpha_1)}{\sin^2(\alpha_2 + \alpha_1)} \qquad (2)$$

where R_p and R_s are the reflectivities measured with the polarization parallel (p) and perpendicular (s) to the plane of incidence. Figure 1b shows both experimental and fitted curves for R_p component of PE and PPA. The window of operational angles is identified by the critical angles for TIR of PE and PPA (50.94° and 56.42°, respectively), which can be easily translated into the circumferential length. Intuitively, as the PPA/PE blend is extruded, a transition from a reflection curve associated with PE to that of PPA will be observed (Figure 1b).

As the TIR occurs, the light partially penetrates into the second medium without transferring any energy into it. Such penetration is known as the evanescent field, and for a system of three dielectric media (sapphire/PPA/PE), when one of them is a thin film of thickness *d* between the other two, it lowers the net reflectance at the boundary, thereby 'frustrating' the TIR (hence, "F-TIR"). The thickness of the film *d* can be found according to [13]:

$$d = d_p \arcsin h\left[\frac{1}{\xi}\left(\frac{1}{1 - R_p} - \beta\right)\right]^{0.5} \qquad (3)$$

here, ξ and β are coefficients which account for a phase change upon the reflections at each interface and depend on the polarization state of light. They are expressed in terms of the incident angle and refractive indices of the sapphire, PE, and PPA; d_p is the penetration depth of the evanescent field and R_p is experimentally measured reflectivity. More detailed information on the theoretical aspects of (3) is given elsewhere [13]. Calculation of the film thickness at a given incident angle (α_1 = 52.77° was arbitrarily chosen), may be limiting in terms of the visualization of a coating process, as the probability of PPA streak to appear at the locus is very low. To enrich the information about the circumferential coating profile, angular sweeps (from 51.18° to 55.73°) are performed at the end of each extrusion run (note that the narrower range mentioned above was chosen to minimize the error in calculation of *d* in proximity to the critical angles of PPA and PE). Using (3), film thickness (*d*) may be estimated and consequently plotted against the circumferential length (L) of the die wall.

Results and Discussions

To describe the coating kinetics, we correlate three signals: the pressure drop, the reflectivity and the extrudate surface appearance. Figure 2 demonstrates this for the 0.5 % PPA/PE blend. Figure 2a shows a plot of the pressure drop versus time along with optical microscopy images demonstrating that sharkskin disappears gradually i.e., via formation of smooth streaks. Simultaneous reflectivity measurements are displayed in Figure 2b. The reflectivity signal *during* the extrusion is fluctuating (Figure 2b, inset), which is thought to be caused by a number of factors, such as the motion of PPA droplets of different sizes and speeds near the die walls. The flow induced molecular orientation of the blend and the pressure dependent refractive index of the sapphire die may also contribute to the magnitude of these fluctuations. Therefore, the coating thickness was measured at the *end* of each run, allowing the sample to relax. In such instances, the reflectivity remains static, and is subsequently converted to *d* (Figure 3). The standard uncertainty in our coating thickness measurements was estimated from extrusion of several loads of pure PE, collecting the reflectivity signals. Based on that, the sensitivity of the measurement appears to be ± 10 nm. After the first run of the blend (t = 9 min) we estimate the average film thickness *d* = (25 ± 10) nm. At this time the sharkskin was still present, though its amplitude and wavelength decreased compared to the fracture of the pure PE (Figure 2a). As the coating thickness is only marginally greater than the sensitivity of our measurement, the standard uncertainty after the first run is high. However, the relative uncertainty is reduced as the coating builds up i.e., at the end of the second run *d* is estimated to be (286 ± 10) nm at α_1 = 51.18° and *d* = (115 ± 10) nm at α_1 = 55.73°. At this time, (85 ± 2) % of the sharkskin was eliminated. In an attempt to correlate the appearance of the *first* sharkskin-free streak with the reflectivity and pressure, we find that the initial sign of the cohesive interfacial failure is seen via reduced pressure (t = 2.0 min). After that, there is an increase in reflectivity (t = 3.5 min), and only then there appears the *first* smooth streak (after 2.3 min in the second run). A qualitatively similar chronological observation was also made for the 0.1 % PPA/PE blend extruded at 112.5 s^{-1}. It is important to

acknowledge that our measurement covers only 1.26 % of the total die circumference, which limits the optical determination of the appearance of initial streaks. After about 40 min in the blend extrusion, both the pressure and the coating thickness reached a steady state (17.5 MPa ± 0.2 MPa and 324 nm ± 110 nm, respectively) (Figures 2-4). Here, the ± represents the fluctuating nature of the values in steady state. At this time the sapphire die was examined using optical microscopy, and a characteristic width of (5 ± 2) μm of PPA streaks was found (Figure 3, inset), agreeing well with the earlier measurements [14]. By studying the coating profile obtained by F-TIR approach (Figure 3), we conclude that the streaks are (7 ± 2) μm wide, which is in reasonable agreement with optical microscopy images. Figure 4 summarizes the effect of PPA content on the coating kinetics, showing that longer times to reach the steady state (experiment was terminated before it was reached) are needed for the blend containing the lower mass fraction of PPA. For such a blend, the pressure drops more slowly, and the coating quality is reduced.

Interestingly, when pure PE had been extruded right after the steady state in pressure and PPA thickness was reached in the extrusion of the 0.5 % PPA/PE blend (past 120 min in Figure 2 and past 70 min in Figures 3, 4), the coating thickness decreased rapidly, while the reduced pressure was still maintained. After 53 min the coating 'thinned' down to (60 ± 15) nm (Figure 3). Here ± represents the variation in coating thickness. We also found that the surface was still free of any fracture. This suggested that even though the PPA thickness was greatly diminished from its steady state value, the coating was *uniform* and still sufficient to induce slippage at the PPA/PE interface.

To elucidate the mechanism by which the PPA droplets coat the die wall, a test was conducted in which a die (180° - entrance steel-made slit or round-hole) was 'reversed' (turned upside down) at the time when (17 ± 2) % of sharkskin was eliminated (at t = 3.2 min, Figure 5a). Upon continuation of the blend extrusion, the sharkskin disappeared *instantaneously* and *completely*. When running the experiment in the 'normal' mode (Figure 5b), sharkskin disappears slowly (even though the pressure drops significantly), then the process accelerates, after which it slows down again, with (19 ± 2) % of sharkskin still remaining after 6 min of extrusion. Based on these two experiments, we suggest that during the blend extrusion, the PPA droplets first adsorb at the die entrance (which may explain the reduced pressure), the process of which may be greatly influenced by die entrance geometry [15] and blend viscoelasticity. After that, the droplets migrate toward the die exit under the influence of the shear field.

Conclusion

Using newly developed technique based on F-TIR and the die 'reversal' experiment, we conclude that during the extrusion of PPA/PE blends the PPA droplets adsorb at the die entrance, and then migrate toward the die exit, apparently forming streaks. At the PPA/PE interface of these streaks, the wall shear rate is lowered. Monitoring the streak kinetics suggests that they are circumferentially non-uniform, which may be explained by the wide distribution of PPA particle sizes and their dispersion characteristics in PE matrix. Despite the steady state coating thickness reached ≈ 350 nm, the *necessary* coating thickness of the PPA layer is found to be much smaller (≈ 60 nm). This is lower than the (5 to 15) μm reported earlier [1]. A thickness comparable to the radius of gyration of the fluoroelastomer appeared to be sufficient to induce the interfacial slippage, as long as the die exit was coated *uniformly*.

References

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Key Words

Reflectivity, coating, sharkskin, polyethylene.

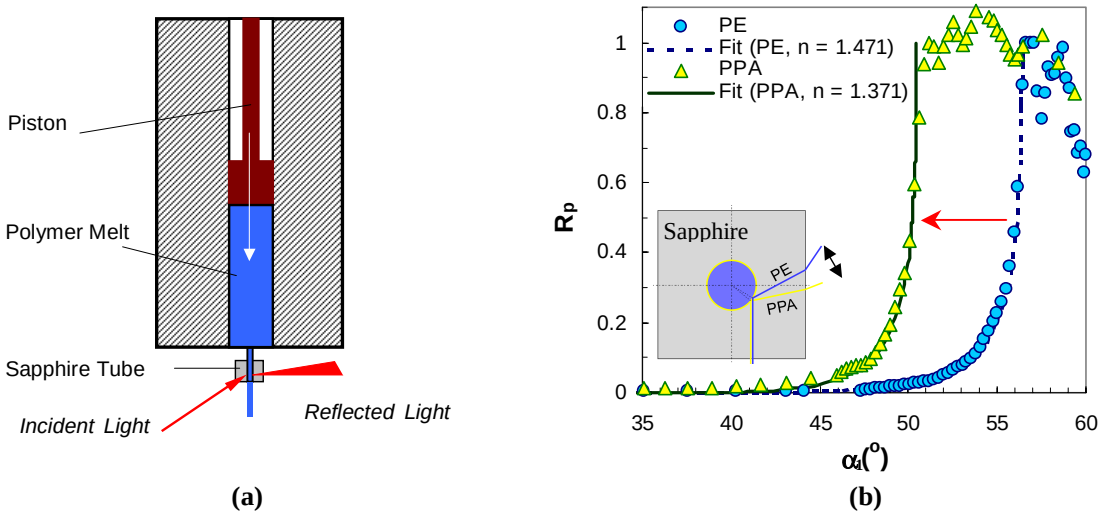


Figure 1. Development of a new measurement technique: a) Rheo-optical apparatus for the F-TIR; b) Anticipated transition (shown by the arrow) from PE to PPA reflectivity during the extrusion of PPA/PE blend. Inset shows the TIR for the sapphire die wall with the *curved* interface. The double arrow shows the range of incident angles of interest.

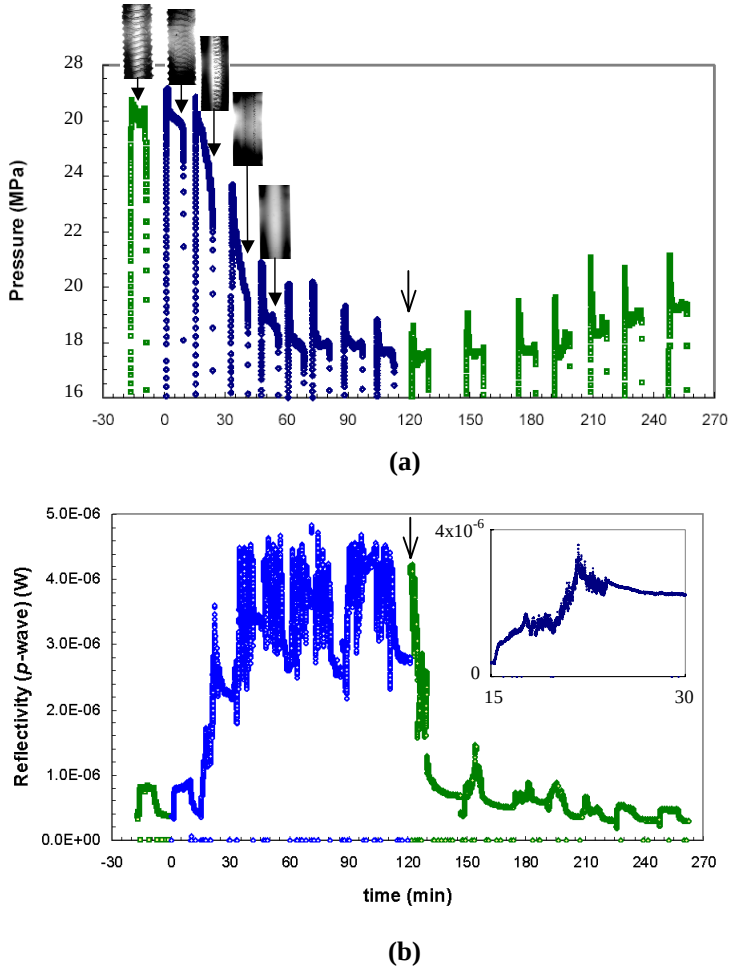


Figure 2. Effect of the development of the PPA coating during the extrusion of 0.5 % PPA/PE blend (t = 0 min) followed by the extrusion of pure PE (shown by the arrow) on the: (a) Pressure; (b) Reflectivity. Measurements conducted at $\dot{\gamma} = 112.5\ s^{-1}$, T = 180 °C and $\alpha_1 = 52.77°$.

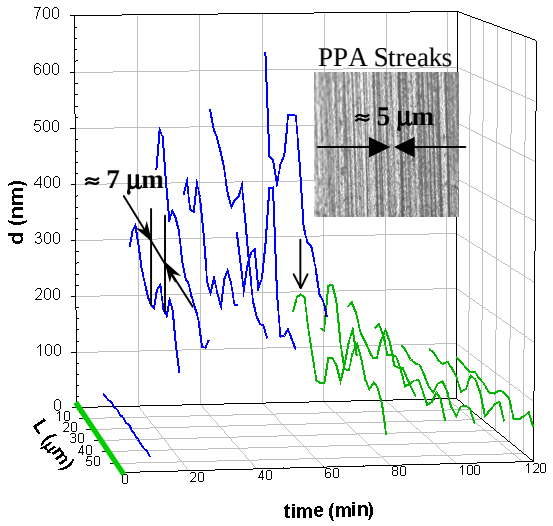


Figure 3. 'Visualization' of the PPA coating kinetics during the extrusion of 0.5 % PPA/PE blend followed by the extrusion of pure PE (shown by the arrow) at $\dot{\gamma}$ = 112.5 s^{-1} and T = 180 °C.

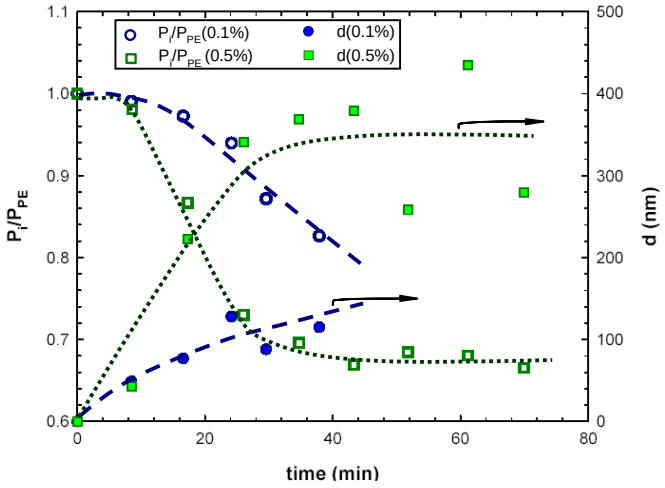
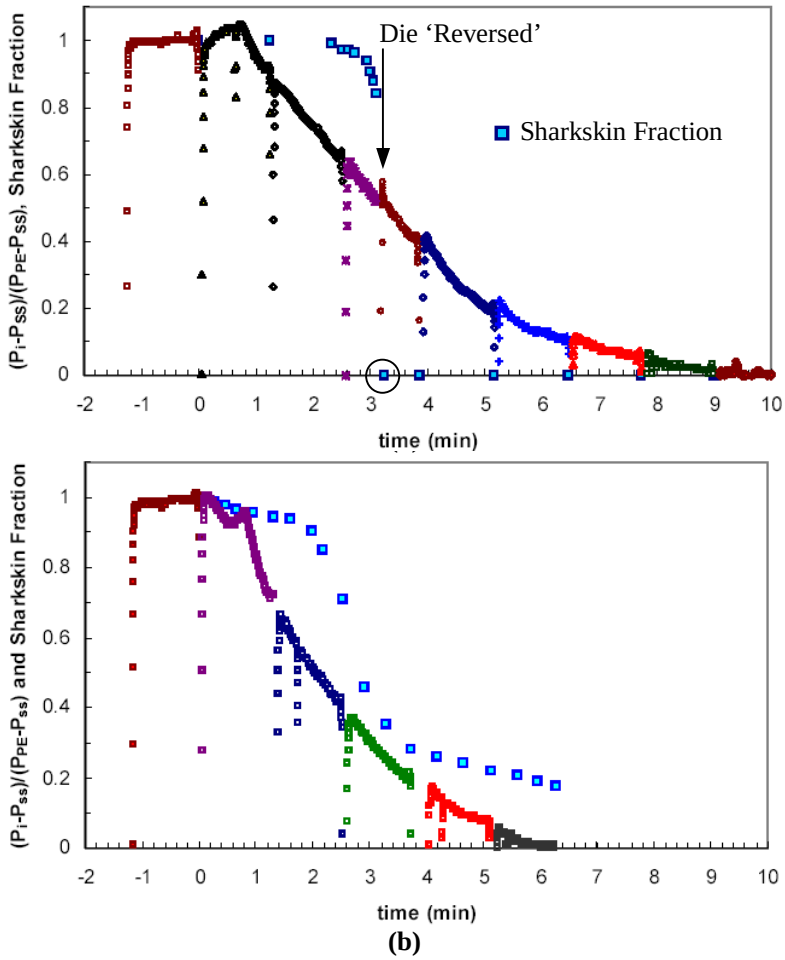


Figure 4. Effect of the content of the PPA in a PPA/PE blend (0.1 % blend - by circles, and 0.5 % blend - by squares) on the coating kinetics. Measurements conducted at $\dot{\gamma}$ = 112.5 s^{-1}, T = 180 °C and α_1 = 52.77°. P_i is the pressure of i^{th} blend run and P_{PE} is the pressure of pure PE. Lines are drawn to aid the reader's eyes.



(b)

Figure 5. Elucidation of the coating mechanism via experiments with: (a) die "reversed" at the time indicated by the arrow; (b) "non-reversed" die. Measurements are conducted with 0.1% PPA/PE blend at $\dot{\gamma}$ = 225 s^{-1} and T = 180 °C, using a slit die. P_i and P_{PE} are defined in Figure 4, and P_{SS} is the pressure in steady state (when the coating is fully developed).