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ABSTRACT: Fluoropolymer process aids (PPAs) are commonly used to eliminate melt fracture during the extrusion of polyolefins, and their performance may be quantified directly by measuring the fluoropolymer deposition rate on internal die surfaces, or indirectly by measuring the time needed for the PPA to eliminate melt fracture under a particular set of conditions. Historically, the performance of PPA has been considered optimal when the fluoropolymer enters the die in the form of small discrete particles, less than about 1 µm in diameter. Using both direct and indirect measurements, the present study shows that the reverse is true – performance improves when the PPA is more coarsely dispersed, so that fluoropolymer particles larger than about 2 µm in diameter enter the extrusion die. Based on these observations, a quantitative model of the fluoropolymer coating process is developed. The model fits the experimental data on fluoropolymer coating thickness as a function of fluoropolymer particle size and extrusion shear rate, and also provides insight on other aspects of the PPA coating process. These findings culminated in the development of the Z Technology™ PPAs, which use interfacial agents and a fluoroelastomer having a distinctly different rheology from the traditional fluoroelastomers in PPAs to deliver the large fluoropolymer particles needed to provide reliable, quick elimination of polyolefin melt fracture at low PPA usage levels.

KEY WORDS: polymer process aid, fluoropolymer, blend, melt fracture, polyolefin, polycaprolactone, polyethylene glycol, LLDPE, vinylidene fluoride–hexafluoropropylene copolymer, frustrated total internal reflectance (Frus-TIR), particle size distribution, interfacial agents.

INTRODUCTION

FLUOROPOLYMER PROCESS AIDS (PPAs) are often thought of as additives useful in the extrusion of polyolefins for eliminating melt fracture and reducing die build-up. These, however, differ substantially from the likes of antioxidant, slip, anti-block, acid neutralizer, and other typical additives found in polyolefins, and thus applying the term 'additive' to PPA may be misleading. The typical additive consists either of low molecular weight compounds having a low viscosity relative to the host resin at the temperature used for the processing of polyolefins, or inorganic minerals with a primary particle that neither melts, flows, nor breaks up to any significant degree. In such cases, the goal of incorporating conventional additives into the host resin is to maximize dispersion, and in most situations this is easily accomplished. Process aids, however, comprise high viscosity fluoropolymers (among other ingredients), and are therefore more properly thought of as producing a polymer blend when dispersed in the host resin, rather than as a simple additive to the host resin. The degree of dispersion of the PPA–polyethylene blend depends on the many factors associated with morphology development in all polymer blends – mixing history, rheology of the blend components, dispersed phase concentration, and interfacial tension between the components. Considering PPAs as a polymer blend component rather than an additive involves an important paradigm shift, and has resulted in the development of new, highly efficient PPAs.

Fluropolymer process aids increase the critical shear rate for the onset of surface melt fracture in polyolefins by depositing on internal die surfaces and generating a slip velocity at the polyolefin–fluoropolymer interface, which in turn reduces both the total strain and the strain rate of the extrudate skin layer while exiting the die [1]. In practical use, the concentration of PPA needed in the extrudate depends on the rate of fluoropolymer accumulation at the die surface, because once the die becomes coated, the slip velocity is generally sufficient to raise the critical shear rate well above the shear rate typically encountered in industrial polyolefin extrusion. In the decades since the introduction of PPAs, many researchers have assumed, without experimental evidence, that the ability of a PPA to coat the die surface becomes optimal when the fluoropolymer droplets or particles in the polyolefin host resin are small, e.g., no larger than 0.2–2 μm in diameter [2–6]. The assumption has at times been justified by noting that a highly dispersed PPA generates more fluoropolymer particles, and that small particles migrate more easily towards the die surface. Both these arguments are

intuitively appealing, but turn hollow upon further inspection. Increasing PPA dispersion may well increase the number of particle–die surface interactions, but each interaction brings less fluoropolymer to the die than would a larger particle, so the relationship between PPA dispersion and rate of fluoropolymer accumulation at the die surface is not obvious. Furthermore, both solid and deformable particles in pressure-driven flows are found to move away from, rather than towards, solid surfaces [7,8], so fluoropolymer particle migration appears unlikely to provide an important coating mechanism. This article examines the role of dispersion on the performance of fluoropolymer PPAs, using direct measurements of particle size distributions in fluoropolymer–LLDPE blends delivered to a die.

EXPERIMENTAL

As the details of the materials and experimental procedures have been previously published [9–11], only a brief description follows. All extrusion tests used a gas-phase ethylene–butene linear low density polyethylene (LLDPE) resin having a melt index (MI) of 1.0 g/10 min (190°C, 2.16 kg) and a density of 0.918 g/cm^3, manufactured by ExxonMobil Corporation. The fluoroelastomer components of the extruded blends were vinylidene fluoride–hexafluoropropylene copolymers (60/40 weight ratio). Two types were used in the extrusion tests, denoted FE-X and FE-Z, both of which are used in commercially available process aids from DuPont Performance Elastomers. FE-XT denotes a slightly modified version of FE-X, comprising FE-X blended with 4% of a PTFE fluoroplastic. In addition to FE-X and FE-Z, rheological data are presented for two additional fluoropolymers commercially used in the process aids. FE-A is a fluoroelastomer with the same monomer composition as FE-X and FE-Z, while FP is a semicrystalline fluoroplastic terpolymer. Some extrusion tests incorporate a third ingredient known as an interfacial agent (IA). These materials include polycaprolactone diols PCL-1, PCL-2, PCL-3 and PCL-4, having number average molecular weights of 1000, 2000, 4000, and 32,000, respectively. Another IA is polyethylene glycol (PEG) with a number average molecular weight of 8000.

To ensure accurate dosage during the extrusion tests, PPAs were first diluted into masterbatches of varying concentration on a 28 mm corotating, fully intermeshing, three-lobe twin-screw extruder operating at 300 rpm, with barrel temperature set points (feed zone forward) of 140, 160, 180, and 200°C. The masterbatches were then comingled with

polyethylene (PE) pellets in the extruder hopper to achieve a particular PPA concentration in the extruder.

Certain PPA performance evaluations were carried out on a Brabender® 19.1 mm diameter extruder with a 25/1 L/D, fitted with a 2.54 cm (1 in.) wide slot die having a 0.51 mm (0.020 in.) die gap and a land length of 1.016 cm (0.4 in.), to produce a continuous PE tape at an apparent shear rate of $400 \, s^{-1}$. Two single-flighted screw types were used: a 'metering' screw with no mixing elements and a Maddock screw, which incorporates a Maddock mixer 5 D in length on the screw tip. In other cases, PPAs were tested on a blown film line using a 63.5 mm diameter, 24 : 1 L/D extruder delivering ≈45 kg/h of LLDPE at a typical melt temperature of 225°C to a 101.6 mm diameter die with a 0.76 mm gap (apparent shear rate of $540 \, s^{-1}$ in the die gap). In the blown film tests, the screw was a barrier type with a Maddock mixing tip.

Fluoroelastomer particle size distributions were measured in extrudate samples using light microscopy combined with manual and computer-aided image analysis, and also using laser confocal microscopy followed by image analysis. Direct measurements of the fluoropolymer layer thickness used a technique known as frustrated total internal reflectance (Frus-TIR); complete details of the Frus-TIR technique are provided elsewhere [10]. Briefly, the Frus-TIR technique takes advantage of the large difference in the refractive index between PE and fluoropolymer. A transparent sapphire capillary die is mounted on a capillary rheometer and, by measuring the intensity of the laser reflection at the die–polymer interface, the thickness of the fluoropolymer layer at that point can be determined. In practice, the laser examines the die coating at a position 2 mm upstream of the die exit, across an area having dimensions 76 μm circumferentially by 1 mm in the flow direction.

RESULTS AND DISCUSSION

One way to alter the size of the fluoropolymer particles delivered to the extruder die is to alter the size of the particles in the masterbatch (MB) being fed to the extruder. To accomplish this, we took advantage of two parameters affecting the development of morphology in multiphase blends: dispersed phase concentration and the rheology of the polymer phases [12]. Applying these concepts to fluoropolymer MB compounding suggests that varying the MB concentration provides a simple method for altering the fluoropolymer particle size within the MB.

Figure 1 shows the results of the melt fracture tests conducted using masterbatches of FE-X ranging in concentration from 0.1 to 75% by weight on the Brabender® extruder. In each case, the MB was let down to a final level of 200 ppm FE-X in LLDPE by dry blending. After 1 h of extrusion, the three lowest concentration masterbatches (0.1, 1, and 5%) failed to clear the melt fracture, whereas the three highest concentration masterbatches (12, 25, and 75%) eliminated melt fracture in about 20 min. The performance differential is quite dramatic, and the sharp break in performance between the 5 and 12% masterbatches suggests a critical threshold exists in this region.

Figure 2 shows that masterbatches with FE-X concentration of 12% or more are not required for good process aid performance. By increasing the melt index (MI) of the MB carrier from 1.0 (as used for the tests in Figure 1) to 25 so that dispersion during the twin-screw compounding is lessened, 1 and 5% masterbatches can be made to perform as well as the higher concentration masterbatches shown in Figure 1. To maintain a constant overall PE viscosity for the tests shown in Figure 2, the appropriate amount of 25 MI PE was added while using the 1.0 MI masterbatches. Compared to the results in Figure 1, this net viscosity reduction modestly improved the performance of the 1 and 5% 1.0 MI masterbaches based on the 1.0 MI PE, though the change is small compared to the enhancement caused by increasing the MI of the MB carrier.
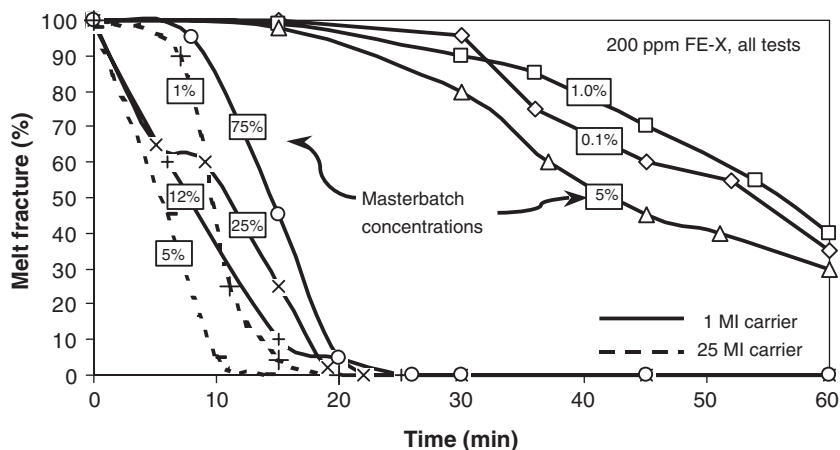

Figure 1. Melt fracture vs time, as a function of FE-X masterbatch concentration (Brabender® extruder with metering screw).
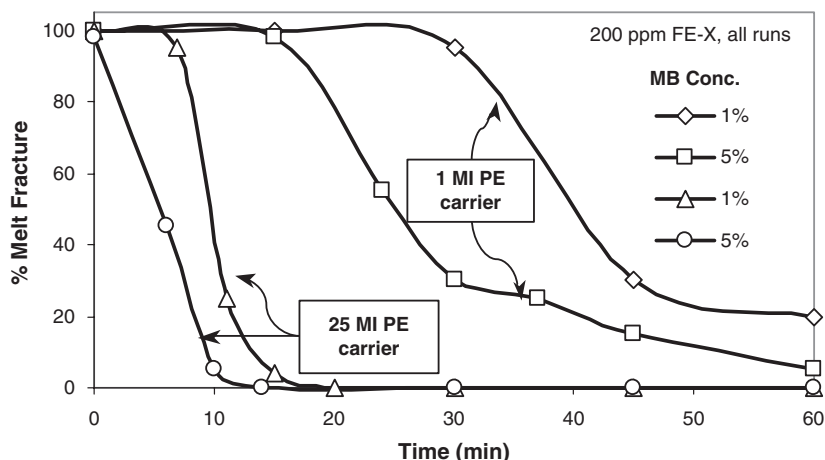
Figure 2. Melt fracture vs time, as a function of the melt index of the masterbatch carrier resin (Brabender® extruder with metering screw).
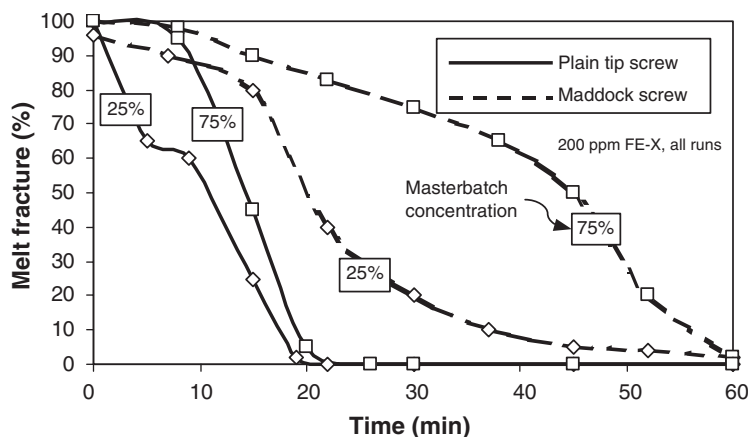

Figure 3. Effect of screw mixing element on high concentration FE-X masterbatch performance (Brabender® extruder).

Figure 3, however, shows how increasing the dispersive capability of the Brabender® extruder using a Maddock-tipped screw causes a striking decrease in the performance of the high concentration masterbatches. Overall, these results indicate that the extrusion conditions expected to result in increased fluoroelastomer dispersion

actually tend to degrade the performance of PPA, thereby suggesting that fluoroelastomer accumulates on die surfaces more quickly when large, rather than small, FE-X particles are fed to the extruder.

To explicitly examine the role of fluoroelastomer dispersion on the rate of melt fracture elimination, FE-X particle sizes in the masterbatches and the extrudable compositions discussed earlier were measured. The results are given in Table 1, in terms of weight average particle diameter (WPD). A WPD, rather than a number average diameter, is an appropriate descriptor for fluoroelastomer dispersion due to the process under investigation, i.e., the rate of accumulation of fluoroelastomer on the die surface. As such, the total number of particle–die wall collisions is of less interest than the total mass of fluoroelastomer colliding with the die surface. Therefore, an indication of the size distribution where most of the fluoroelastomer mass resides is more useful than a measure of which size range holds the greatest number of particles.

The WPD characterization of FE-X particles delivered to the die confirms the surprisingly strong influence of particle size on fluoroelastomer deposition rate. Consistently, extrusion runs in which the FE-X particles delivered to the die having a WPD $\leq 2\,\mu m$ have poor ability to eliminate melt fracture, whereas coarser dispersions function far more effectively. The low concentration masterbatches (0.1–5%) using the 1.0 MI carrier contain particles in the 1.7–2 μm WPD range, which enter the die essentially unchanged in size and leave melt fracture streaks on the LLDPE tape even after 1 h of extrusion. Table 1 shows that as either the MB concentration or the carrier MI increases, the FE-X dispersion in the MB coarsens. When the metering screw is used, these coarse masterbatches result in large FE-X particles (4.5–6.6 μm) entering the die, and melt fracture disappears quickly. Replacing the metering screw with the Maddock screw, however, disperses these large FE-X particles present in the MB before they enter the die, and melt fracture remains after 60 min of extrusion.

While the forgoing experiments use the elimination of melt fracture as an indication of the rate that fluoropolymer accumulates at the die surface, direct measurements of the development of the fluoropolymer layer have been carried out using a technique known as Frus-TIR [10,11]. Figure 4 shows the results of Frus-TIR experiments in which blends of 1000 ppm FE-X in LLDPE flow at an apparent shear rate of $215\,s^{-1}$ through an initially clean sapphire die, while simultaneously observing the melt fracture on the extruded strand. The chart shows the growth of the fluoropolymer layer inside the die for FE-X blends having a WPD of 2.3, 3.1, and 5.6 μm, as well as the total blend volume extruded

Table 1. Fluoroelastomer weight average particle size distributions.

Fluoroelastomer type	MB conc. (%)	MI of MB carrier	Weight average particle diameter		Time to 0% MF (min)	Residual MF at 60 min (%)	Screw type
			Delivered to die	Masterbatch			
FE-X	0.1	1.0	2	2	>60	35	Metering
FE-X	1	1.0	1.7	1.7	>60	40	Metering
FE-X	5	1.0	2	2.1	>60	30	Metering
FE-X	12	1.0	4.8*	4.1	25	0	Metering
FE-X	25	1.0	6.6	13.1	22	0	Metering
FE-X	25	1.0	1	13.1	>60	2	Maddock
FE-X	75	1.0	4.5	Co-continuous	26	0	Metering
FE-X	1	25.0	6	4.6	20	0	Metering
FE-X	5	25.0	6.6	7.3	14	0	Metering
FE-Z	2	1.0	2.3	nm	45	0	Metering
FE-Z	2	1.0	2.1	nm	48	0	Maddock

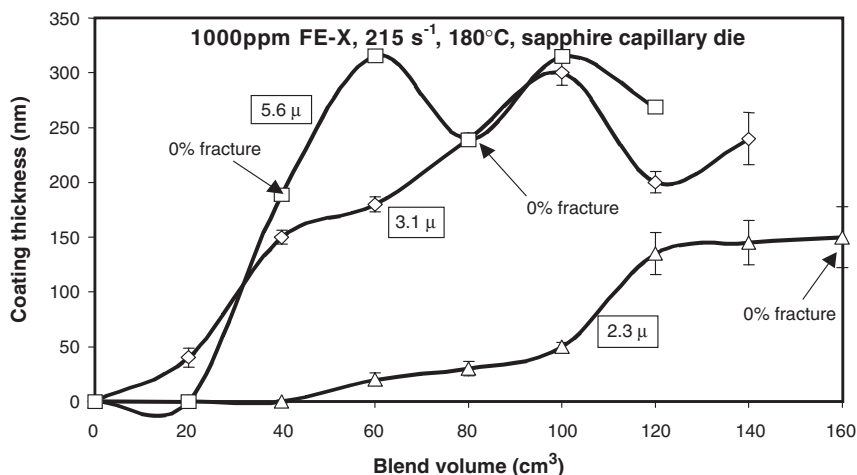*4.56 μm, measured by confocal laser (1100 particles); nm = not measured.

Figure 4. Fluoroelastomer coating thickness vs blend volume extruded, measured by Frus-TIR.

at the time melt fracture completely disappeared. These results corroborate the Brabender® extruder tests, showing that the blend containing the largest FE-X particles eliminates fracture after 34 cm^3 of blend volume passes through the die, whereas the blends with the mid-sized and smallest particles require 65 and 160 cm^3, respectively. Most significantly, however, these results confirm that as the fluoropolymer particle size increases, the die coating accumulates more quickly, and reaches a greater steady-state coating thickness. Although this steady-state coating thickness fluctuates over time, a clear trend is evident: the blend with the largest particles yields an average thickness of 315 ± 120 nm, compared with 200 ± 34 nm for the midsized blend, and 150 ± 33 nm for the highly dispersed blend. At the point when fracture is eliminated, the layer thickness is in the 150–240 nm range, suggesting that the most coarsely dispersed blend deposits more fluoropolymer than needed to maintain a fracture-free extrudate. The ability to reduce the fluoropolymer concentration by controlling the particle size delivered to the die forms the basis for the highly efficient Z Technology™ process aids discussed here.

The observation that the deposition of PPA on die surfaces increases with increasing fluoropolymer particle size is at odds with the traditionally held view that PPAs coat a die surface by migrating across streamlines towards the die surface [2,6,13]. Large particles in

pressure-driven flows are observed to move away from stationary surfaces faster than small particles [7,8], hence if migration plays any role in the die coating process, large particles should be at a disadvantage. Instead, the present observations support a deposition scheme depicted in Figure 5, in which only the fluoropolymer particles traveling on streamlines carrying them very close to the die surface are able to contact and coat the surface. The key feature of this model is the presence of a 'boundary layer' at the surface of the die containing active fluoropolymer particles, i.e., those close enough to contact the surface through Van der Waals attractions, tumbling of the particles, or other small-scale disturbances. Any particle outside the boundary layer simply flows through the die without contributing to coating formation. In the absence of any significant cross-streamline migration of particles, the boundary layer must be very thin, perhaps close to one particle diameter in thickness.
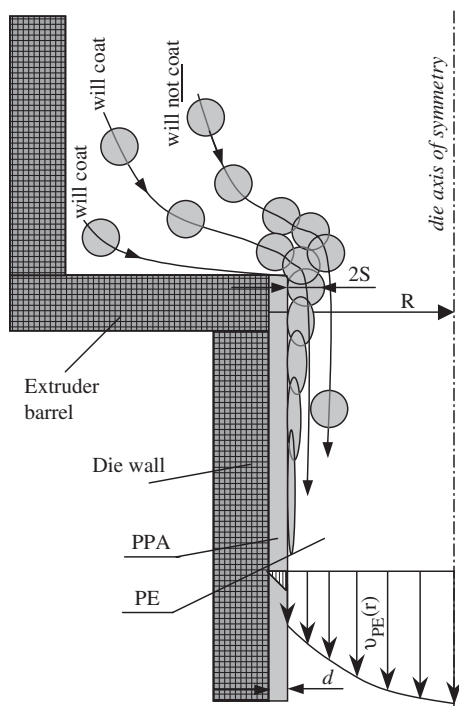

Figure 5. Schematic of boundary layer deposition model (reprinted from *J. Rheol.*, 47(6), 2003).

Kharchenko et al. [10] have derived a mass balance on the boundary layer, using the simple assumption that the boundary layer thickness equals the particle diameter. The mass balance provides the following relations:

$$\text{Flux onto the wall:} \quad Q_{\text{in}} = 2RSC\pi\left(\frac{\dot{\gamma}_{\text{PE}}S}{2} + V_{\text{S}}\right) \tag{1}$$

$$\text{Flux leaving the wall:} \quad Q_{\text{out}} = R\rho\dot{\gamma}_{\text{PPA}}d^2\pi \tag{2}$$

$$\text{Steady-state coating thickness:} \quad d = \left(\frac{2CV_{\text{S}}S}{\rho\dot{\gamma}_{\text{PPA}}}\right)^{0.5} \tag{3}$$

where S is the radius of the fluoropolymer particles, d is the steady-state thickness of fluoropolymer on the die wall, R is the die radius, C is the bulk concentration of fluoropolymer in the polyethylene, ρ is the density of the fluoropolymer, $\dot{\gamma}_{\text{PPA}}$ is the shear rate in the fluoropolymer layer on the die surface in which the fluoropolymer is assumed to follow a no-slip boundary condition and possess a linear velocity profile, $\dot{\gamma}_{\text{PE}}$ is the shear rate of the polyethylene, and V_{S} is the polyethylene slip velocity.

The boundary layer model explains both qualitative and quantitative characteristics of the die coating process. For example, the model suggests that fluoropolymer deposition must occur at or very close to the die entrance. In other words, upon entering the die, if a particle is sufficiently large and traveling on a streamline that happens to bring it into contact with the die surface, this collision takes place where the streamlines are compressed due to flow contraction at the die entrance. Once the particles within the boundary have been scavenged at the die entrance, no further deposition can take place downstream, since particles do not migrate towards the die surface. The remainder of the die downstream of the entrance becomes coated as the fluoropolymer layer flows towards the exit, dragged along by the shear stress at the polyethylene–fluoropolymer interface. Die reversal experiments by Kharchenko [10] confirm the entrance-to-exit coating process. Furthermore, in an uncoated die when the slip velocity is zero, Equation (1) predicts the deposition rate to be proportional to the square of the fluoropolymer particle diameter. This result accounts for the strong dependence of the rate of melt fracture elimination on fluoropolymer particle size, as observed in both the Brabender® extrusion and capillary die experiments. Once a section of the die becomes coated and polyethylene slippage occurs, however, the V_{S} term
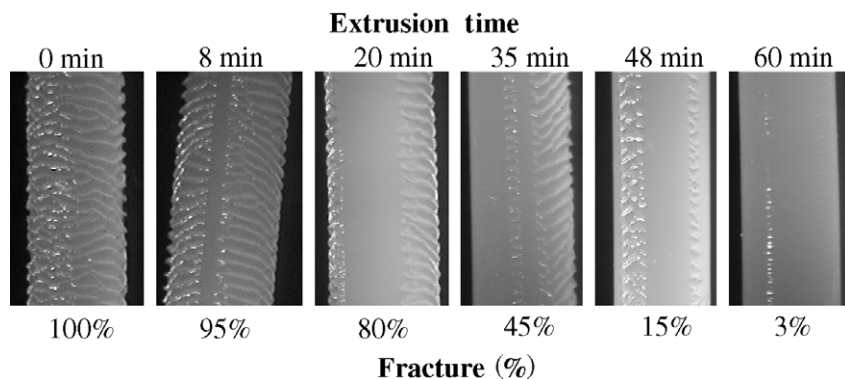
Extrusion time

| 0 min | 8 min | 20 min | 35 min | 48 min | 60 min |

| 100% | 95% | 80% | 45% | 15% | 3% |

Fracture (%)

Figure 6. Example of streaky die conditioning pattern: 400 ppm FE-X from 1% masterbatch in LLDPE, $425\,\text{s}^{-1}$ shear rate, 2 mm capillary die, Brabender® extruder.

in Equation (1) becomes nonzero and the flux of fluoropolymer to the die surface increases.

In this way, the formation of a die coating may be viewed as autocatalytic, i.e., fluoropolymer deposition in a particular location accelerates deposition in the same spot. The self-accelerating process is consistent with the observed pattern of melt fracture elimination when a PPA is introduced to an initially uncoated die. Figure 6 illustrates a typical coating process: a few minutes after polyethylene containing PPA enters a capillary die, thin non-fractured streaks begin to emerge, indicating that narrow portions of the die have become coated. Nearly 1 h later, however, the die is still not completely coated – the extrudate still shows thin fracture streaks. Such a wide range of coating rates should be expected from an autocatalytic process, as random portions of the die entrance become coated, in turn encouraging additional deposition in the same spot, and finally causing a wave of fluoropolymer to flow downstream along a narrow path and coat the die in a streak-like fashion. Equation (3) provides a straightforward means of testing the boundary layer model by providing a relationship between equilibrium fluoropolymer coating thickness and the square root of the fluoropolymer particle diameter. The results of steady-state fluoropolymer coating thickness measured by Frus-TIR experiments conducted by Meillon et al. [11] are shown in Figure 7, using a range of shear rates from 112.5 to $215\,\text{s}^{-1}$ and weight average particle sizes from 2.3 to 5.6 μm. These experiments confirm that the fluoropolymer coating thickness measured is in reasonable agreement with the predictions of Equation (3). More importantly, however, these results show that particle migration
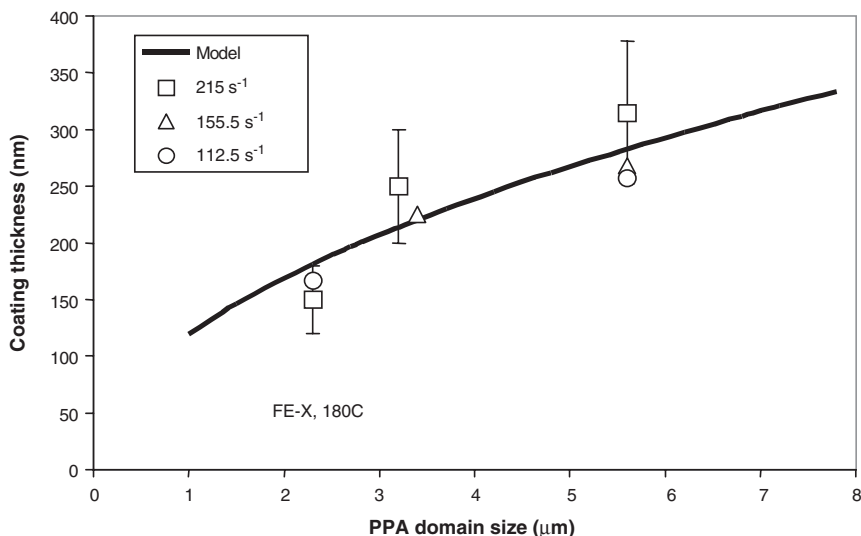
Figure 7. Steady-state fluoroelastomer coating thickness measured by Frus-TIR compared with boundary layer model prediction.

towards the die surface is not required to explain the observed level of fluoropolymer build-up inside an extrusion die, and that the boundary layer model can in fact generate reasonable coating thickness.

The boundary layer model establishes the rationale for FE-Z, a fluoropolymer used in Z Technology™ process aids from DuPont Performance Elastomers, which was selected to deliver large particles to the die so as to increase the boundary layer thickness. Figures 8 and 9 illustrate the key features of FE-Z, comparing complex viscosity and tan δ for FE-Z with other fluoropolymers used commercially in PPAs. At high shear rates, FE-Z has a complex viscosity about the same as the conventional FE-X and FE-A, and is even lower in viscosity than the FP fluoroplastic terpolymer. This enables FE-Z to spread easily on high shear regions of the die surface. At low shear rates, however, FE-Z has a complex viscosity almost an order of magnitude greater than typical fluoroelastomers like FE-X or FE-A, so that continual particle size degradation is suppressed during ordinary low shear processing. In addition, the high elasticity of FE-Z (corresponding to a low tan δ) works to increase the thickness of the process aid boundary layer, because the FE-Z particles tend to retain a spherical shape rather than become flattened by the shear in the die.

Figure 10 shows how FE-Z performs in melt fracture tests, added as a low concentration (2%) MB to the Brabender® extruder at 200 ppm,
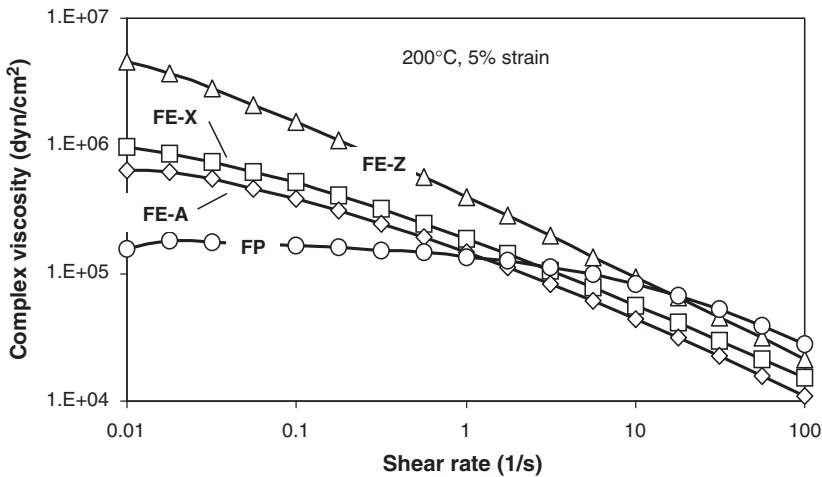
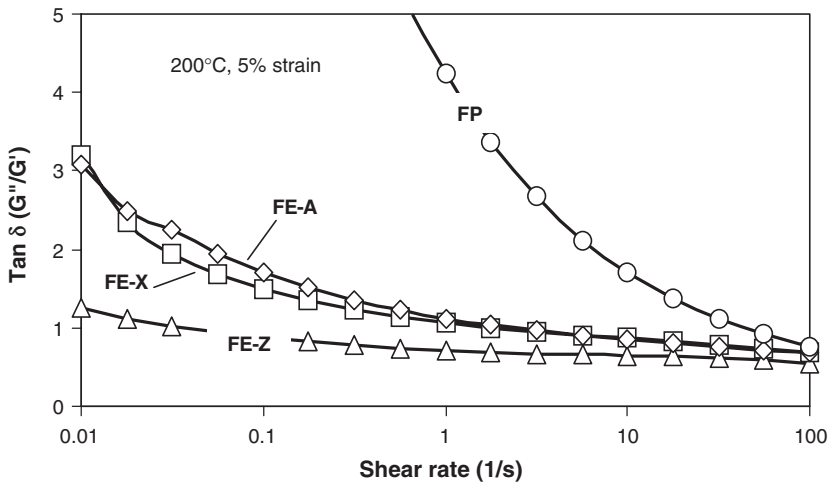**Figure 8.** Viscosity of fluoropolymers used in PPAs.

Figure 9. Tan δ of fluoropolymers used in PPAs.

using both the metering and the Maddock screws. In both the cases, FE-Z clears melt fracture in <50 min, with little change in performance due to the Maddock screw. As shown in Table 1, the WPD of FE-Z delivered to the die – regardless of the screw type – is 2.1–2.3 μm, or slightly greater than the critical 2 μm limit. These results show that FE-Z outperforms a conventional fluoropolymer, such as FE-X when MB compounding or extrusion conditions cause excessive dispersion in this polymer.
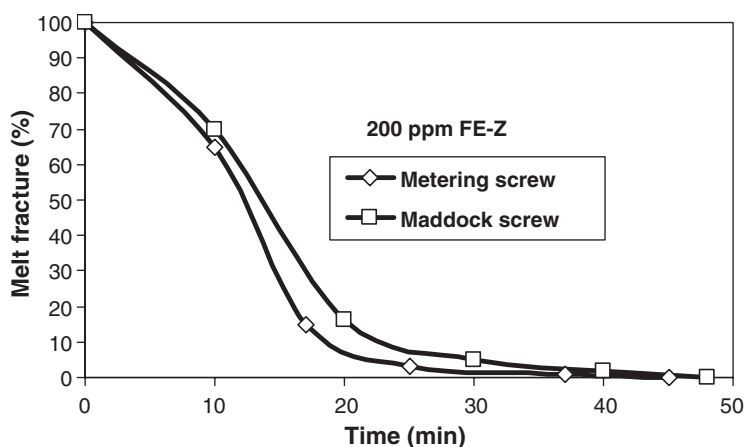
Figure 10. Melt fracture testing on Brabender®: 200 ppm FE-Z added via 2% masterbatch, metering and Maddock tip screws.
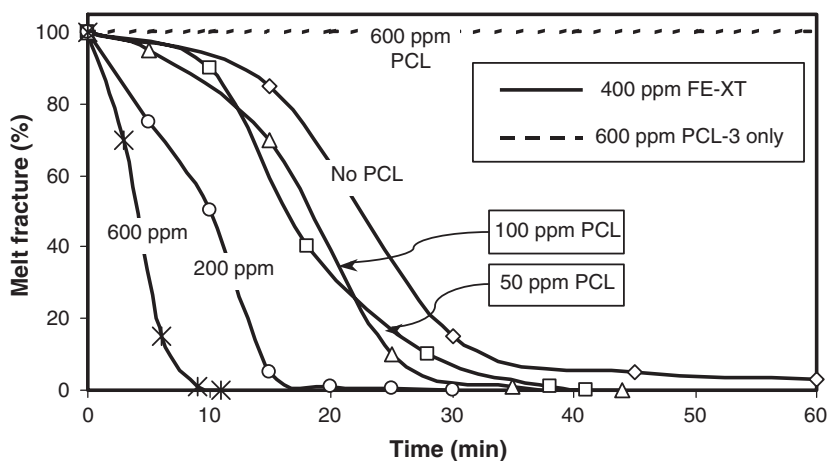

Figure 11. Effect of PCL-3 level on melt fracture elimination using FE-XT.

Another approach to improve the performance of PPA is through the use of an IA, which coats fluoropolymer particles with a slippery layer that suppresses particle breakup. As a result, an IA–FE combination can produce a more effective PPA than FE alone. The data in Figure 11 demonstrate how the performance of a rather easily dispersed fluoropolymer (FE-XT) can be improved using a 4000 molecular

weight polycaprolactone (PCL-3) as an IA during the compounding of 1% masterbatches of FE-XT. PCL-3 levels in these masterbatches range from 0 to 3%. The masterbatches are then let down to 200 ppm FE-XT and 0–600 ppm PCL-3 for melt fracture tests on the Brabender(extruder and tape die. The extrusion results shown in the figure indicate that the introduction of PCL-3 can reduce the time needed to clear melt fracture in the presence of FE-XT by a factor of six or more. On the other hand, using 600 ppm of PCL-3 in the absence of FE-XT provides no ability to eliminate fracture, even after 60 min of extrusion. Thus, the improvement in performance afforded by the presence of the IA is synergistic, i.e., although the PCL-3 does not directly contribute to fracture elimination, it does improve the ability of the fluoroelastomer to fully coat the die surface.

Figure 12 illustrates the mechanism by which an IA improves the performance of PPA, and it also sheds some light on desirable IA characteristics. At the conclusion of each of the extrusion tests shown in Figure 11, samples of the polymer entering the extruder die were collected, and the WPD of FE-XT measured. Without any PCL-3 present, the FE-XT disperses so that the WPD is $<2\,\mu m$, and the fracture remains after 1 h of extrusion. However, as PCL-3 level in the MB rises, the WPD delivered to the die increases up to nearly $5\,\mu m$. These experiments show that the PCL-3 improves the performance of PPA by reducing fluoropolymer dispersion, thus allowing larger
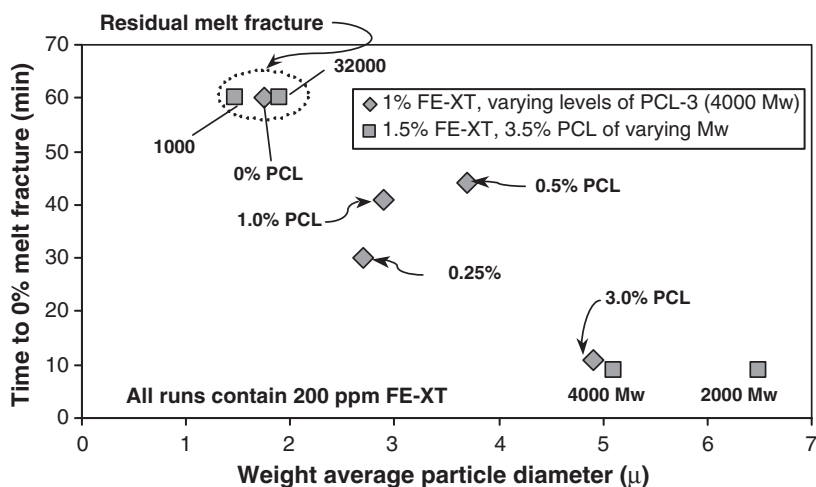

Figure 12. Time to eliminate fracture as a function of the weight average particle diameter of the FE-XT particles entering the die (Brabender[®] extruder, metering screw).

particles to enter the die. Figure 12 also depicts a set of experiments examining the effect of molecular weight of PCL on its ability to reduce fluoropolymer dispersion. For an IA to live up to its name and function effectively, it must readily wet the FE surface and have a low viscosity to prevent transmission of shear stresses from the PE to the FE during processing. Facile wetting, however, implies like polarity. An extremely low molecular weight IA, therefore, may dissolve into the FE droplets, preventing the formation of a stable layer. The figure illustrates these trends using FE-XT and PCL of molecular weight (Mn) ranging from 1000 to 32,000. The PCL of 2000 or 4000 molecular weight produces effective PPA formulations that deliver large (5–6 µm) FE-XT particles to the die. Significant decreases or increases in PCL molecular weight, however, prevent the PCL from functioning as an IA. Both a 1000 and 32,000 molecular weight PCL allow FE-XT to become dispersed below the 2 µm limit, resulting in a poor PPA performance.

Having separately demonstrated improvements in the performance of PPA through optimizing fluoroelastomer rheology or incorporating an IA, the following section shows how the Z Technology™ process aids Z100 and Z200 are formed by combining FE-Z with IA. Using a commercial-scale blown film line, Figure 13 shows the response of FE-X- and FE-Z-based process aids to the addition of IA at a constant FE level of 200 ppm. In these tests, the conventional PPA formulation (FE-X + PEG) leaves residual melt fracture at low levels of PEG
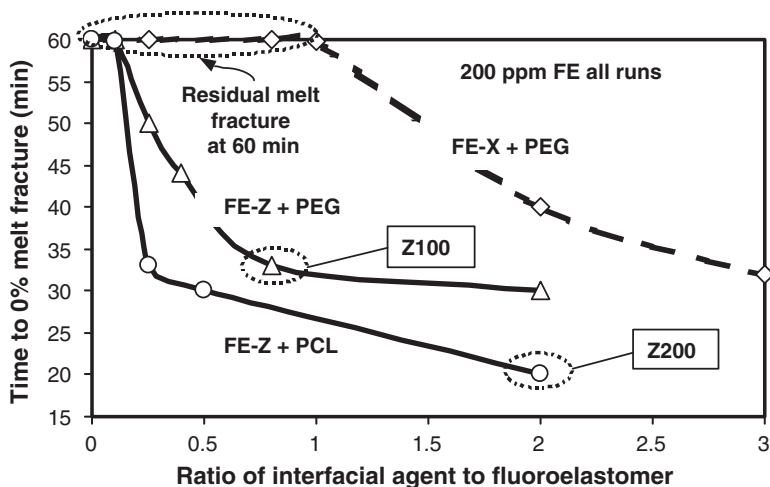

Figure 13. Effect of interfacial agent level and fluoroelastomer type on blown film melt fracture elimination.

(200 ppm or less), and begins to deliver acceptable melt fracture elimination performance only at high PEG levels (600 ppm). Drawbacks of such a high PEG formula include extruder output loss and emissions from PEG thermal degradation [9]. In contrast, the performance of FE-Z improves rapidly as IA is introduced. Consequently, FE-Z produces an effective PPA when combined with a low level of PEG, thereby minimizing the impact on film properties caused by thermal degradation of a conventional IA, such as PEG. FE-Z with a low level of PEG is commercially available as Viton® FreeFlow™ Z100. The figure also shows that for any given IA level, PCL eliminates melt fracture more quickly than PEG, resulting in very fast die conditioning when PCL is combined with FE-Z in a 2 : 1 ratio. As PCL does not cause the extruder output and degradation problems typical of PEG, the advantages of FE-Z and PCL can be fully exploited to deliver very high PPA efficiency, resistance to antagonistic interactions with other additives, mixing tolerance in highly dispersive resins (e.g., metallocene LLDPE), and functionality in high temperature resins and fabrication processes [9]. The FE-Z + PCL process aid is available as Viton® FreeFlow™ Z200.

CONCLUSIONS

Process aids are a twig on the tree of polymer blend technology. Like all polymer blends, the final properties depend on the morphology as well as composition. The study of blend morphology development is a complex and evolving field, and unavoidably this complexity extends to the use and testing of process aids. Unwelcome as the intricacies of polymer blends may be for the polyethylene producers and users searching for a reliable and economical solution to melt fracture, the alternative is worse: unpredictable performance, unexplained failures, overdosage to accommodate severe mixing situations, and no mechanism to scale between laboratory and production processes.

Although process aid technology shares a common foundation with all polymer blends, several unusual features make a critical distinction. Most importantly, the dispersed phase (i.e., the fluoropolymer) has a minimum critical dimension rather than a maximum. Thus, the conventional prescription for improving polymer blend performance by increasing dispersive mixing is turned upside down: increasing the severity of mixing to reduce the fluoropolymer domain size actually degrades the process aid performance. Furthermore, the very low dispersed phase concentration is essentially without peer in polymer

blend technology, causing ordinary extrusion processes to impart a level of dispersive mixing to process aids beyond common expectations. Finally, process aids may be unique in the use of surface-active (interfacial) agents to increase, rather than decrease, dispersed phase domain size.

This dependence of the performance of PPA on particle size suggests that a boundary layer model for fluoropolymer deposition may be a more accurate physical picture than the cross-streamline migration of particles frequently cited in past literature. The boundary layer model provides excellent agreement with the qualitative characteristics of PPA deposition, including the entrance-to-exit coating of extrusion dies, and the streaky nature of the die coating. Measurements of the fluoroelastomer layer thickness as a function of shear rate and fluoroelastomer particle size additionally provide a reasonable quantitative confirmation of the boundary layer model.

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BIOGRAPHY

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