2003 Best Paper - Fundamentals of Melt Fracture Elimination Using Fluoropolymer Process Aids

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Fundamentals of Melt Fracture Elimination Using Fluoropolymer Process Aids

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Abstract

Fluoropolymer process aids are widely used in polyolefin blown films to eliminate melt fracture. These process aids function by depositing a thin fluoropolymer layer on internal die surfaces, and promoting slip at the fluoropolymer – polyethylene interface. The present work describes how the morphology of fluoropolymer – polyethylene blends can be controlled to increase fluoropolymer deposition rate by using a new, rheologymodified fluoropolymer in combination with an interfacial agent.

Introduction

The performance of fluoropolymer process aids in eliminating polyolefin melt fracture is frequently claimed to vary as a function of the dispersion of the fluoropolymer/polyolefin blend (1-4). These references teach that the functioning of polymer process aids (PPA) improves with increasing dispersion of the fluoropolymer, i.e., reduced fluoropolymer domain size. Although the dogma surrounding fluoropolymer dispersion is intuitively satisfying, upon closer examination the influence of fluoropolymer dispersion on PPA performance becomes non-obvious. Recently, PPAs have conclusively been shown to function by accumulation of fluoropolymer on internal die surfaces (5). Therefore, while a highly dispersed PPA may generate large numbers of particle – die interactions, each interaction brings little fluoropolymer to the die. 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 an extruder die.

These results are then used to develop improved process aids incorporating two features: a new rheologymodified fluoroelastomer, and a low molecular weight interfacial agent that preferentially locates at fluoropolymer – polyethylene interface to reduce shear stresses on the fluoropolymer.

Experimental (additional details in ref. 6)

LLDPE –1 is a gas-phase ethylene-butene resin having a melt index of 1.0 and a density of 0.918, in reactor powder form. LLDPE-2 is a fully stabilized and pelletized version of LLDPE-1. The fluoroelastomers (FE-X and FE-Z) used in the melt fracture tests are copolymers of vinylidene fluoride and hexafluoropropylene in a 60/40 weight ratio, commercially used in process aids manufactured by DuPont Dow Elastomers. In the present work, FE-XT denotes a powdered fluoropolymer mixture consisting of FE-X and PTFE. Rheological data are presented for three additional fluoropolymers used commercially in process aids. FE-Y and FE-A are fluoroelastomers with the same monomer composition as FE-X and Z, while FP is a semi-crystalline fluoroplastic terpolymer. PCL-1, PCL-2, PCL-3, and PCL-4 are polycaprolactone diols having number average molecular weights of 1000, 2000, 4000, and 32000, respectively. PEG is polyethylene glycol with a number average molecular weight of 8000.

PPA masterbatches were produced on a 28 mm corotating, fully intermeshing, 3-lobe twin-screw extruder operating at 300 rpm, with barrel temperature setpoints (feed zone forward) of 140°C, 160°C, 180°C, and 200°C. 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 inch) slot die having a 0.51 mm (0.020 inch) die gap and a land length of 1.016 cm (0.4 inches), to produce a continuous polyethylene tape. Two single-flighted screw types were used: a "metering" screw with no mixing elements, and a Maddock screw, which incorporates a Maddock mixer 5D in length on the screw tip.

In other cases, PPAs were tested on a blown film line using a 63.5 mm, 24:1 L/D extruder delivering approximately 45 Kg/hr of LLDPE-2 at a typical melt temperature of 225°C to a 101.6 mm die with a 0.76 mm gap (nominal shear rate 540 1/s in the die gap).

Fluoroelastomer particle size distributions were measured using a Nikon Microphot-SE compound microscope operated with standard reflective light and a 40x objective configured for digital acquisition. Overall magnification was 400x. A Nikon Transformer model UN set to position 4 provided illumination. Images were captured and digitized using a Sony video camera model DXC-760 MD.

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 being fed to the extruder. To accomplish this, we take advantage of two parameters affecting the development of morphology in multi-phase blends: dispersed phase concentration, and the rheology of the polymer phases (7). Applying these concepts to fluoro-polymer masterbatch compounding suggests that a simple method for altering the fluoropolymer particle size in a masterbatch is to vary the fluoropolymer concentration in the masterbatch.

Figure 1 shows the results of 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 masterbatch was let down to a final level of 200ppm FE-X in LLDPE-1 by dry blending. After one hour 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 minutes. 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 very high concentration masterbatches are not required for good process aid performance. By increasing the MI of the masterbatch carrier from 1.0 (as used for the tests in Figure 1) to 25 so that dispersion during 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. On the other hand, Figure 3 shows that increasing the dispersive capability of the Brabender® extruder by using a Maddock-tipped screw causes a striking decrease in the performance of the high concentration masterbatches. Overall, these results indicate that extrusion conditions expected to result in increased fluoroelastomer dispersion tend to degrade PPA performance, 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 above were measured. Results are given in Table I, in terms of weight average particle diameter. A weight average particle diameter (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 where in the size distribution 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 have a WPD less than or equal to 2 microns 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 to 2 micron WPD range, which enter the die essentially unchanged in size and leave melt fracture streaks on the LLDPE tape even after one hour of extrusion. Table I shows that as either the masterbatch concentration or the carrier MI increases, the FE-X dispersion in the masterbatch coarsens. When the metering screw is used, these coarse masterbatches result in large FE-X particles (4.5 – 6.6 u) entering the die, and melt fracture quickly disappears. Replacing the metering screw with the Maddock screw, however, disperses these large FEX particles present in the masterbatch before they enter the die, and melt fracture remains after 60 minutes.

The results in Table I show conclusively that the rate of melt fracture elimination, and by extension the rate of FE-X deposition on the die surface, is intimately linked to the FEX particle size distribution, but in a manner opposite to traditional assumptions. A possible explanation for the role of particle size in process aid performance is illustrated in Figure 4. Consider two PE/fluoropolymer blends with different morphologies delivered to an extruder die. Assume Blend A contains uniformly distributed, mono-disperse spherical particles, while Blend B has the same uniform fluoropolymer distribution and concentration, but the particles are larger. Next, assume that particle migration perpendicular to the flow direction (i.e., normal to the die surface) is negligible. In this scenario, there are two simple reasons why Blend B, containing large particles, brings more fluoroelastomer into contact with the die surface. First, Blend B has a larger mass of fluoropolymer that actually is in contact with the die surface, or is so close to the die surface that tumbling of non-spherical particles or nonlaminar flow disturbances can allow wall contact. The dotted line in Figure 4 illustrates this by proposing a "process aid boundary layer", which is an imaginary line beyond which fluoroelastomer particles have zero probability of contacting the wall. Fluoropolymer particles having a large dimension perpendicular to the flow direction move the boundary layer farther from the die surface, and because both blends A and B contain the same bulk concentration of fluoropolymer, Blend B has a larger mass of fluoropolymer inside the critical boundary layer. A second, and possibly more important feature is the proposition that the fluoropolymer particles in Blend B within the process aid boundary layer are moving faster. As shown in Figure 4, steep velocity gradients exist at the wall. As a result, within the process aid boundary layer the average polymer velocity surrounding a large particle is greater than the polymer velocity in the vicinity of a small particle. Thus, large fast-moving fluoropolymer particles increase the mass flowrate of fluoropolymer available to deposit on the die surfaces, thereby improving process aid performance.

The foregoing establishes the rationale for FE-Z, a new rheology-modified fluoropolymer for process aids. Figures 5 and 6 illustrate the key features of FE-Z, comparing complex viscosity and tan delta for FE-Z and 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 FP. 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. Also, the high elasticity of FE-Z (corresponding to a low tan delta) help FE-Z increase the thickness of the process aid boundary layer, as the FE-Z particles tend to retain a spherical shape rather than become flattened by shear in the die.

Figure 7 shows how FE-Z performs in melt fracture tests, added as a low concentration (2%) masterbatch to the Brabender extruder at 200ppm, using both the metering and Maddock screws. In both cases, FE-Z clears melt fracture in less than 50 minutes, with little change in performance due to the Maddock screw. As shown in Table I, the WPD of FE-Z delivered to the die was 2.3 microns, or slightly greater than the critical 2 micron limit. These results show that FE-Z outperforms FE-X when masterbatch compounding or extrusion conditions cause excessive dispersion.

Another approach to improve PPA performance is through the use of an interfacial agent (IA), which coats FE particles with a slippery layer to suppress particle break-up. Although an IA alone has little or no effect on melt fracture, an IA-FE combination can be much more effective than FE alone. The experimental results shown in Figure 8 demonstrate the use of polycaprolactone (PCL) as an IA by incorporating a range of PCL-3 levels (0 to 3%) into masterbatches containing 1% FE-XT. The masterbatches are then let down to 200ppm FE-XT for melt fracture tests on the Brabender extruder and tape die. At the conclusion of each run, the weight average particle diameter (WPD) of FE-XT delivered to the extruder die is measured. These extrusion results, shown in Figure 8, indicate that the introduction of PCL-3 dramatically reduces the time needed to clear melt fracture in the presence of FE-XT. On the other hand, using PCL-3 in the absence of FE-XT, melt fracture remains present over the entire surface of the extrudate during the 60 minute test.

The relationships between weight average particle diameter (WPD) of fluoroelastomer delivered to the die, the PCL-3 level, and the time to clear melt fracture for the tests described above are illustrated in Figure 9. These results show that the presence of PCL-3 increases the size of fluoroelastomer particles entering the extruder die, which accounts for the improvement in melt fracture elimination rate. Again, a critical lower limit of about 2 microns (WPD) for the FE domain size is found.

To function effectively, an IA 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. Extremely low molecular weight IA, however, may become soluble in the FE phase, and prevent formation of a stable layer. Figure 9 also illustrates these effects using FE-XT and PCL, the latter ranging in molecular weight from 1000 to 32000. While 2000 or 4000 molecular weight PCL enables fast melt fracture elimination and delivers large (5 to 6 micron) FE-XT particles to the die, both 1000 and 32000 molecular weight PCL allow FE-XT to become dispersed below the 2 micron limit, resulting in poor PPA performance.

Having separately demonstrated improvements in PPA performance through optimizing fluoroelastomer rheology or use of an interfacial agent, the following section examines the performance of FE-Z when combined with IA. Using a commercial-scale blown film line extruding LLDPE-2, Figure 10 shows the response of conventional (FE-X) and rheology-modified (FE-Z) fluoroleastomers to the addition of IA at a constant FE level of 200ppm. In these tests, the conventional PPA formulation (FE-X + PEG) leaves residual melt fracture at low levels of PEG (200ppm or less), and begins to deliver acceptable melt fracture elimination performance only at high PEG levels (600ppm). Drawbacks of such a high PEG formula include extruder output loss and emissions from PEG thermal degradation (8). In contrast, FE-Z clears melt fracture rapidly as IA is introduced. As a result, effective PPA formulations containing low IA levels become possible, thereby minimizing the impact on film properties caused by thermal degradation of a conventional IA such as PEG. Figure 10 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. Because 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 extreme 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 (6).

Conclusions

Process aids are a twig on the tree of polymer blend technology. Like all polymer blends, the final properties depend on 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 polyethylene producers and users searching for a reliable and economical solution to melt fracture, the alternative is worse: unpredictable performance, unexplained failures, overdosing 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 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.

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Figure 1 % Melt Fracture vs. Time, as a function of FE masterbatch concentration (metering screw)

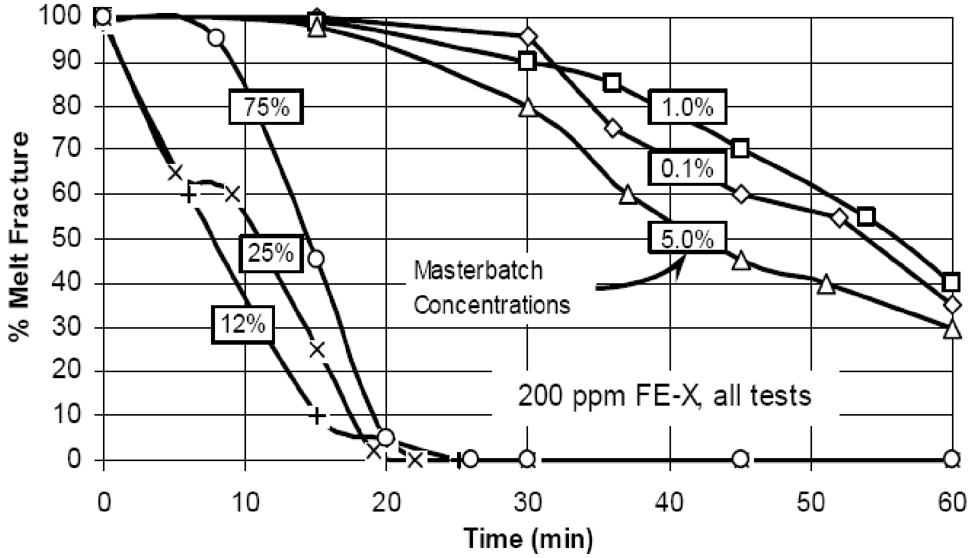


Figure 1

Figure 2 % Melt Fracture vs. Time, as a function of the masterbatch carrier MI (metering screw)

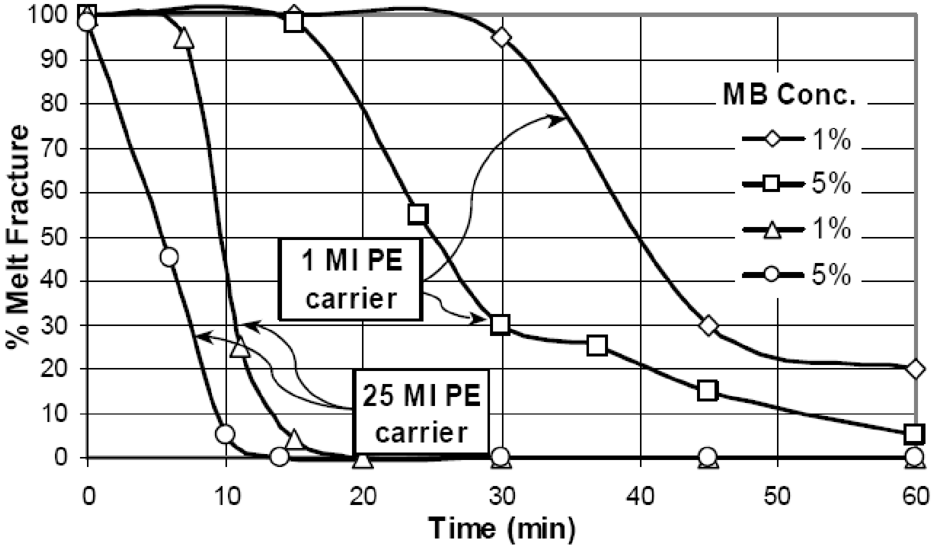


Figure 2

Figure 3 Melt Fracture vs. Time, high concentration FE-X masterbatches, metering and Maddock screws

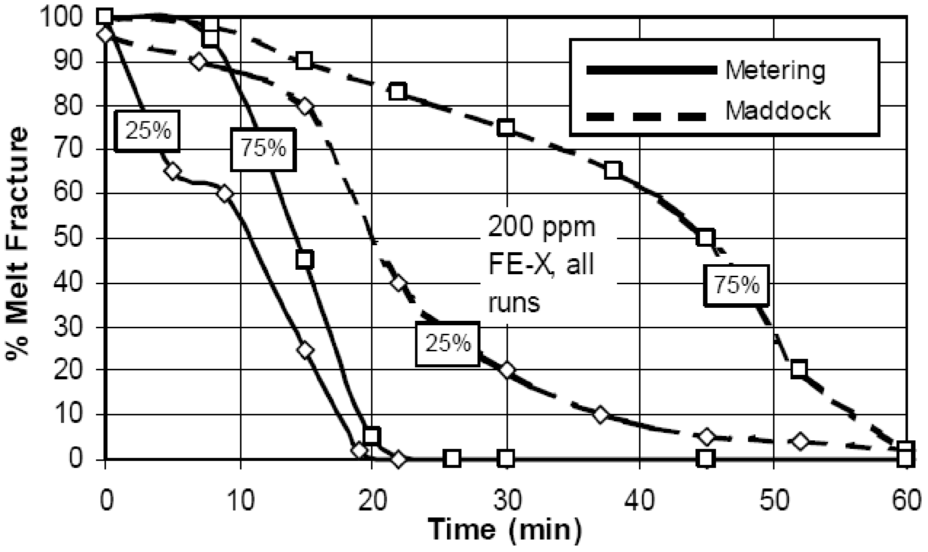
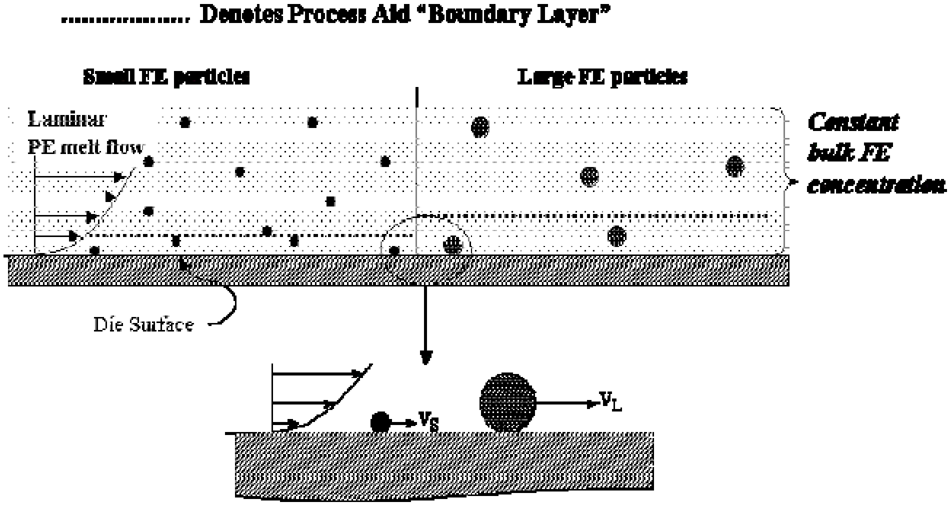


Figure 3

Figure 4 Diagram of fluoropolymer particles in PE, flowing past die surface



Both the particle velocity and the total fluoroelastomer contained within the boundary layer increase with larger particle size

Figure 4

Figure 5 Viscosity of Fluoropolymers used in PPAs

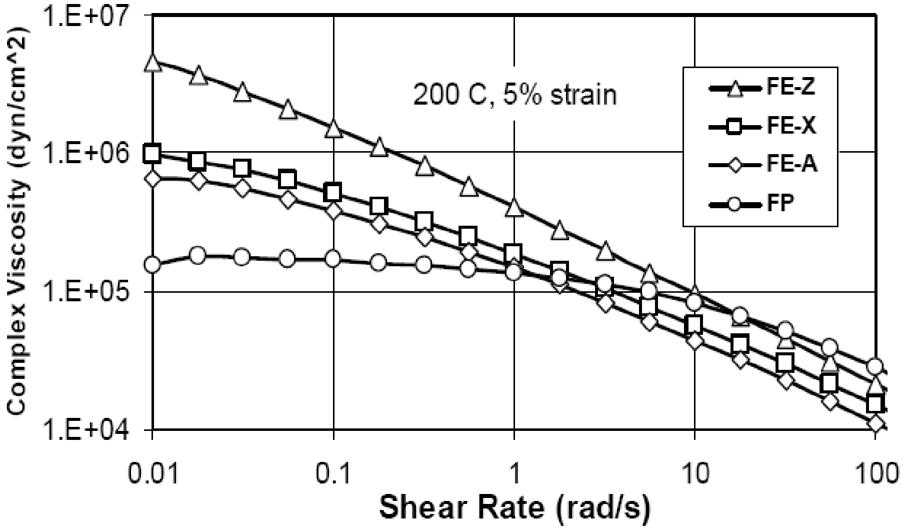


Figure 5

Figure 6 Tan Delta of Fluoropolymers used in PPAs

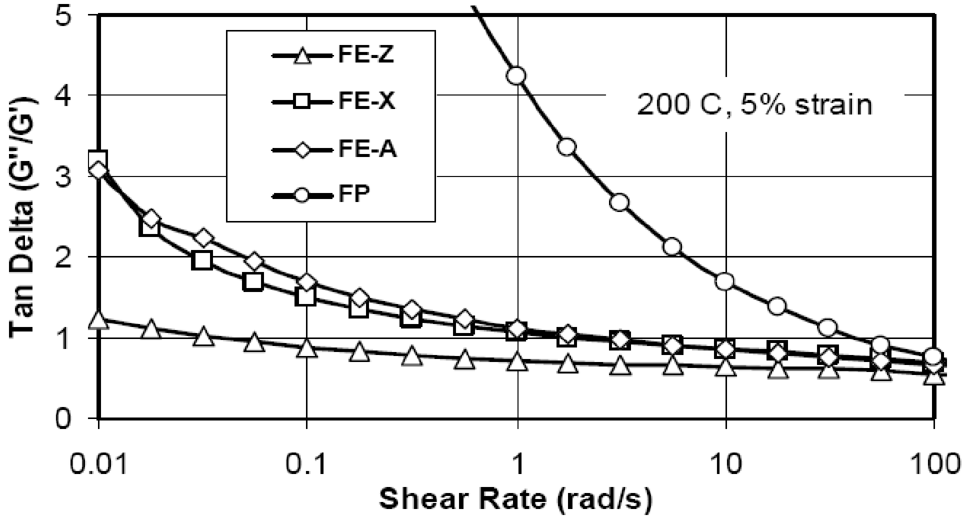


Figure 6

Figure 7 Melt Fracture Tests: 200 ppm FE-Z added via 2% MB, metering and Maddock screws

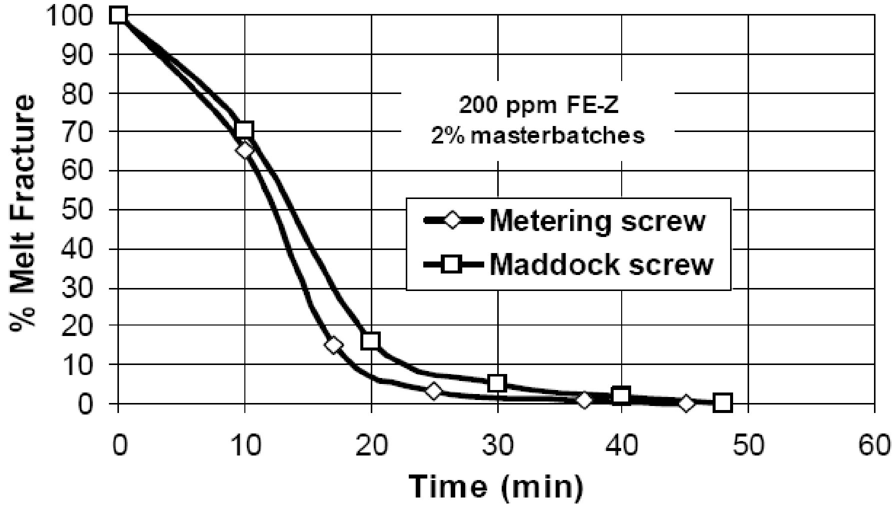


Figure 7

Figure 8 Effect of PCL Level on Melt Fracture Elimination using FE-XT

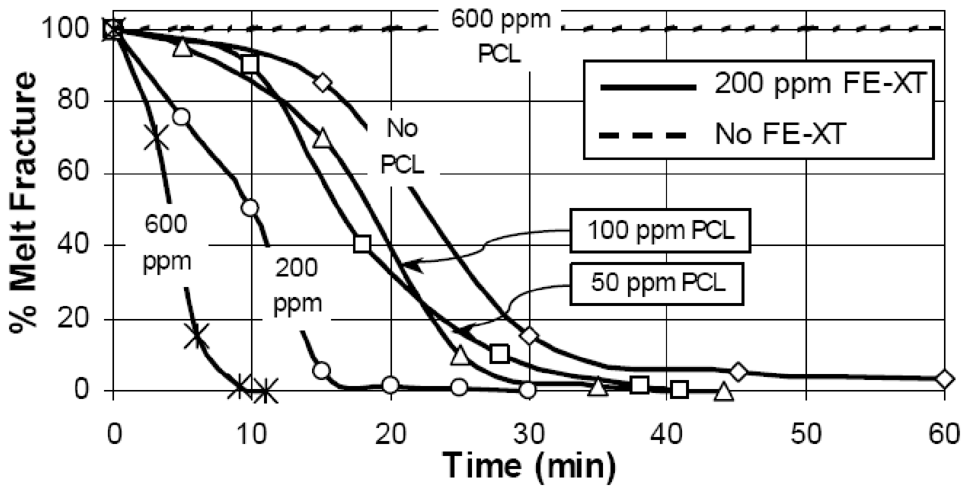


Figure 8

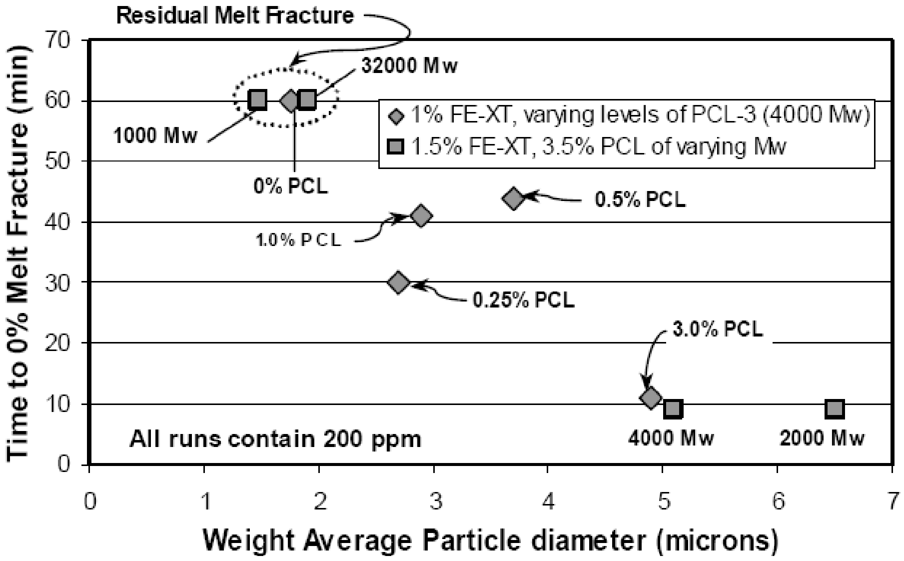


Figure 9 Time to eliminate fracture as a function of WPD of FE-XT particles entering the die

Figure 9

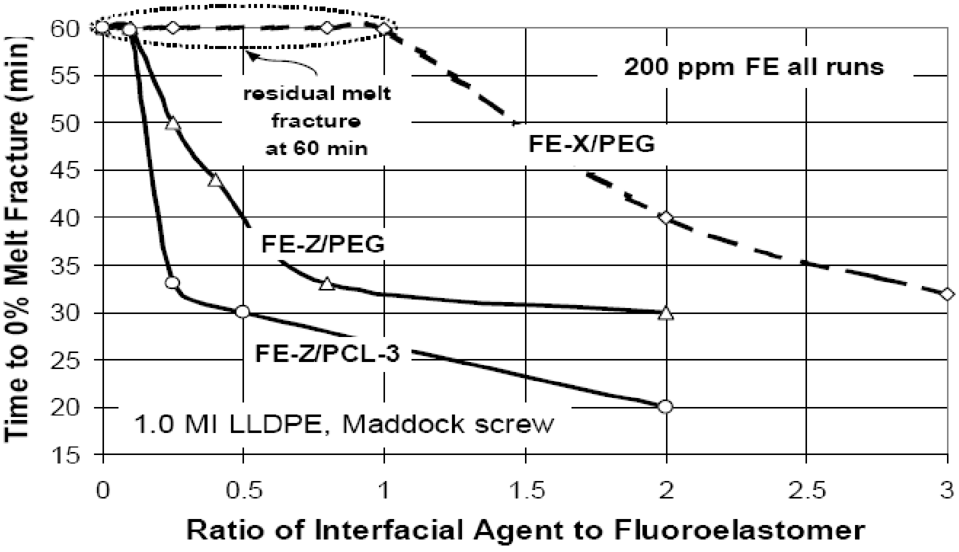


Figure 10 Effect of interfacial agent level on blown film melt fracture elimination

Figure 10

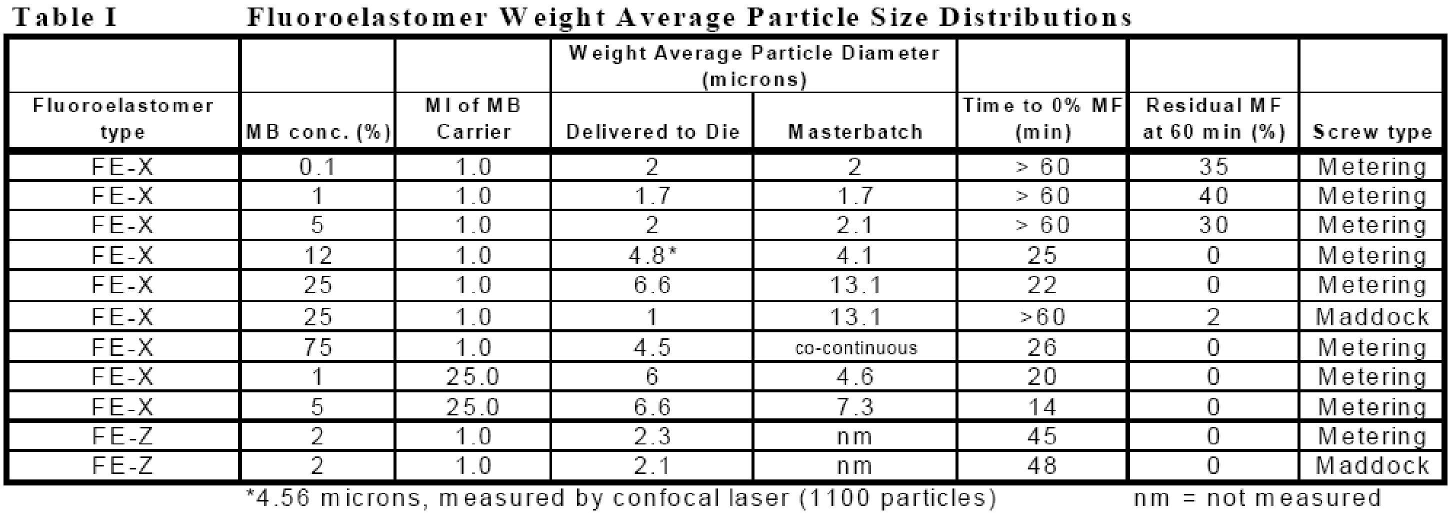


Table I **Fluoroelastomer Weight Average Particle Size Distributions**

Fluoroelastomer type	MB conc. (%)	MI of MB Carrier	Weight Average Particle Diameter (microns) Delivered to Die	Masterbatch	Time to 0% MF (min)	Residual MF at 60 min (%)	Screw type
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 microns, measured by confocal laser (1100 particles) nm = not measured

Table 1