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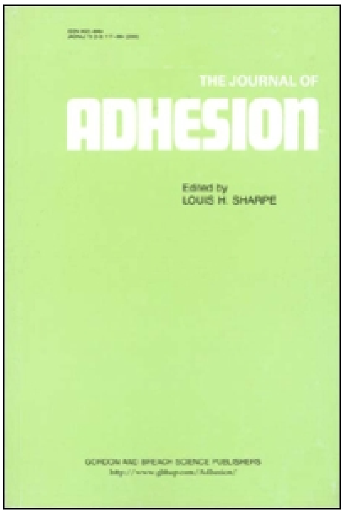

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Flow Instability in LLDPE Processing and Its Control by Fluoropolymer Additives*

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Flow instabilities during the capillary extrusion of an octene-LLDPE have been measured by signals from an elongational rheometer used to wind up the extruding polymer filaments. The presence of fluoropolymers at concentrations above 400 ppm suppressed or eliminated the instability signal, but only after several minutes of extrusion. The time required to suppress instability was used as an indicator of additive effectiveness. Fluoropolymers were found to increase in effectiveness with increasing degree of polarity, as measured by acid/base interaction indexes and by non-dispersion surface energies. The relative apparent melt viscosities of host and additive polymer also were involved in effectiveness ratings. It is suggested that fluoropolymer additives suppress sporadic adhesive failure of the matrix polymer by forming an interphase between the extruder (die) wall and the flowing bulk polymer.

KEY WORDS polymer flow instability; fluoropolymer interphase; specific interactions; acid/base parameters; apparent melt viscosity.

INTRODUCTION

Flow instabilities, known as shark-skin and slip-stick, or cyclic melt fracture, have preoccupied processors of thermoplastic melts for many years. These limitations to effective processing are particularly serious in the extrusion of linear low density polyethylenes (LLDPE), where their occurrence restricts substantially the economy of processing. The effective use of this polymer group, therefore, often hinges on understanding the causes of flow limitations and on their elimination. The addition to LLDPE of small quantities of certain fluoropolymers has proven to be successful in palliating the flow instability problem. The basic causes of flow instability in LLDPE processing nevertheless remain subjects for active investigation, as do inquiries into the mechanisms whereby the processing problems are controlled by fluoropolymer flow additives. In an earlier publication[1] we contributed to the debate by introducing an instrumental method for objective determinations of the onset of

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flow instabilities, and by showing that these are related to the molecular weight distribution and the structure of LLDPE polymers. In this paper we begin reporting on an inquiry into the mechanisms whereby fluoropolymers control flow instabilities, focussing on the role played by the additive's polarity. As in the earlier paper,[1] we refer to flow instabilities generically, rather than focussing on the somewhat vague individual manifestations of shark-skin or slip-stick fracture.

REVIEW OF RECENT LITERATURE

Peculiarities in the extrusion of polyolefin melts, such as inlet melt fracture[2] and the existence of double-valued viscosity/shear relationships, have long been recognized.[3] Renewed attention to limiting events in the extrusion of LLDPE arose from the report by Ramamurthy,[4] who suggested that above a characteristic flow rate, sporadic adhesive failure at the interface between the flowing polymer melt and the extrusion die wall was responsible for the distortions and flaws which mark LLDPE extrudates. Calculations of slip velocities at the polymer/die interface, using Mooney's method,[5] showed that an abrupt change from zero to finite slip velocities took place at shear rates similar to those leading to flow instability. Supporting the suggestion of adhesive failure was an apparent dependence of shear rates for the onset of flow limitations on the material used for the construction of extrusion dies. However, the surface energies of all materials used for die construction greatly exceeded the surface energy of molten polyethylenes. The polymers should therefore have wetted and, presumably, adhered to the walls of all of these dies, leaving the suggested cause/effect relationship open to question.

The "adhesive failure" view contrasted with those[6,7] which hold that instability during shear flow is a fundamental rheological manifestation in polymers which display double-valued viscosity/shear rate (or stress) functions in a defined range of the shear variable. The work of Denn and coworkers,[8,9] however, advanced the cause of adhesive failure mechanisms by showing that peel test determinations of bond strengths at the polymer/metal interface were consistent with observations of slip velocities in specific extrusion processes. The current, painstaking work of Hatzikiriakos and Dealy,[10,11] aimed at modelling polymer flows in the two regimes of double-valued viscosity/shear functions, indicates that there is slip along a failure line near the die wall when the polymer is in the high-flow branch of its flow curve, that is, when there is surface distortion. The polymer adheres to the die wall, however, when in the low-flow branch of the flow curve. In an earlier communication[12] these authors also commented on the effects of fluoropolymer chemicals; they reported that some fluorocarbons (*e.g.* "Dry-film Lube," Percy Harms Corp.) when coated onto viscometer plates actually promoted adhesion between the wall and the flowing polymer, thereby delaying the onset of instability, while others (*e.g.* Dynamar 9613, 3M Corp.) acted as die lubricants, promoting polymer slip. The latter view agrees with that expressed in a paper by Duchesne and coworkers.[13]

The bulk of experimental evidence gathered by ourselves tends to support sporadic adhesive failure at the polymer/die wall interface as a leading cause of flow instabilities in LLDPE processing. Thus, evidence accumulates to support this point of view. Contrasting opinions, however, are not to be neglected. For example, Piau and coworkers[14] have observed distortion in polymer extrudates obtained in orifice extrusion, *i.e.* without the use of a restraining die. The identity between these distortions and ones associated with instabilities in normal LLDPE extrusion is uncertain, however. The contemporary work of DeGennes *et al.* also is pertinent.[15,16] This proposes a model wherein macromolecules adhering (in the model, grafted) to a restraining wall at low flow velocities disentangle from the flowing polymer bulk at shear rates above some critical value, creating a slip boundary some distance away from the die/polymer interface. The model clearly requires an abrupt change in the adhesion/slip situation as shear forces are increased, and seems to introduce the concept of an **interphase,** consisting of the disentangled polymer layer bounded by the die wall and the flowing bulk polymer. In this regard a similarity exists to the present work. An important conclusion advanced here is the postulate of a lubricating interphase consisting of the fluoropolymer additive, which is able to eliminate the characteristic limitations in the extrusion of LLDPE.

EXPERIMENTAL

Materials and their Characterization

An octene-LLDPE polymer was used throughout this research as the matrix. It was supplied by Dow Chemical Co. Molecular weights, melt flow index and density data are entered in Table Ia. Molecular weights were obtained from size exclusion chromatography, using universal calibration protocols and trichloro benzene (TCB) at 135°C as solvent. For extrusion measurements the host polymer was stabilized against thermal damage by the addition of 0.07 wt% "Santonox" (Monsanto Chemical Co.). The polymer was also compounded with a total of 6 fluoropolymer flow additives, supplied by 3M Canada, Inc. These are labelled FA-1 through FA-6. They are characterized by the data in Table Ib. Included are Mooney viscosities,

TABLE I
Characterization of materials

Ia. Host polyethylene:
Octene-comonomer LLDPE (Dow Chemical Co.)
$M_n = 28{,}000$. $M_w = 103{,}000$. $M_z = 240{,}000$.
MFI = 1.6 d = 0.9226 g/ml.

Ib. Fluoropolymer additives (3M Canada Inc.):

Sample code	Mooney η	K_a	K_d	γ_s^d (mJ/m^2)	γ_s^{nd}
FA-1	55	3.3	1.7	22.0	1.3
FA-2	46	3.8	1.5	22.3	1.7
FA-3	90	4.4	1.3	19.8	2.2
FA-4	48	4.3	1.3	20.0	2.2
FA-5	33	4.4	1.2	20.2	2.0
FA-6	46	4.9	1.1	21.6	2.8

dispersion and non-dispersion surface energies $(\gamma_s)^d$ and $(\gamma_s)^{nd}$, and acid/base interaction parameters K_a and K_d. The additives were compounded with LLDPE in a Brabender mixer set at 190°C and 50 rpm. Additive concentration was from 200–1200 ppm based on the weight of LLDPE. In every instance mixing was continued until a steady-state torque reading was obtained, signalling dispersion of the fluoropolymer. The mixed samples were then removed, manually cut into small pieces, and the material was remixed at 190°C but at a higher rotational speed of 80 rpm, again to the attainment of a torque equilibrium. Total mixing times varied from 18 to 35 min.

Surface energy determinations on FA specimens were by static contact angle measurements using a Rame-Hart goniometer. For the purpose, thin films of the fluoropolymers were molded onto aluminium sheet supports and the freshly-prepared surfaces cleaned by repeated isopropyl alcohol washes. The procedures of Kaelble[17] were applied to compute dispersive and non-dispersive contributions to the surface energy. Acid/base interaction parameters were determined by inverse gas chromatography (IGC), as described in detail in recent communications.[18,19,20] A Perkin-Elmer Sigma-2 instrument with hot wire detection was employed. Polymers were deposited onto "Chromosorb" support from TCB solutions, with the mass of supported fluoropolymer in the range of 8–11 wt% of total solids. IGC determinations were at 30, 45, 60 and 75°C; triplicate injections of vapor probes into helium carrier gas (12 ml/min) resulted in Gaussian retention peaks from which net retention volumes, V_n, were calculated with variations not exceeding 3%. Determination of K_a and K_d followed the procedure of Ref. 20. This calls for establishing a reference line of behavior by measuring V_n for the polymers in contact with extremely dilute concentrations of non-polar alkane vapor probes (normal hexane through decane). The retention volume is then expressed as a function of the normal boiling point of the alkanes, leading to well-defined linear plots, as illustrated in Figure 1 for additive FA-1. Following the Lewis acid/base concepts of Gutmann,[21] and his classification of organic compounds as acids and bases, chloroform and tetrahydrofuran (THF) were selected as reference acid and base probes, respectively. These also were injected into the carrier gas at extremely high dilution, along with other organic vapors included in the Gutmann classification. As shown in Figure 1, the acid chloroform falls close to the alkane line, indicating that this vapor interacts with the polymer primarily through dispersion forces. In other words, FA-1 has few basic (electron donor) sites. The THF datum, however, falls off the reference line showing that FA-1 is able to exert acid/base forces with the basic vapor. Qualitatively, FA-1 ranks as an acid. The quantitative parameters K_a and K_d, expressing the solid's acid and base interaction potential, then are obtained from the expression:

$$(\Delta H_{ads})^{nd} = K_a \cdot DN + K_d \cdot AN \qquad (1)$$

rearranged in the form:

$$(\Delta H_{ads})^{nd}/AN = K_a \ DN/AN + K_d \qquad (2)$$

where $(\Delta H_{ads})^{nd}$ is the adsorption enthalpy determined from plots of R ln V_n *vs.* 1/T, and AN and DN are the acceptor (acid) and donor (base) indexes of the vapors, as given by Gutmann.[21]

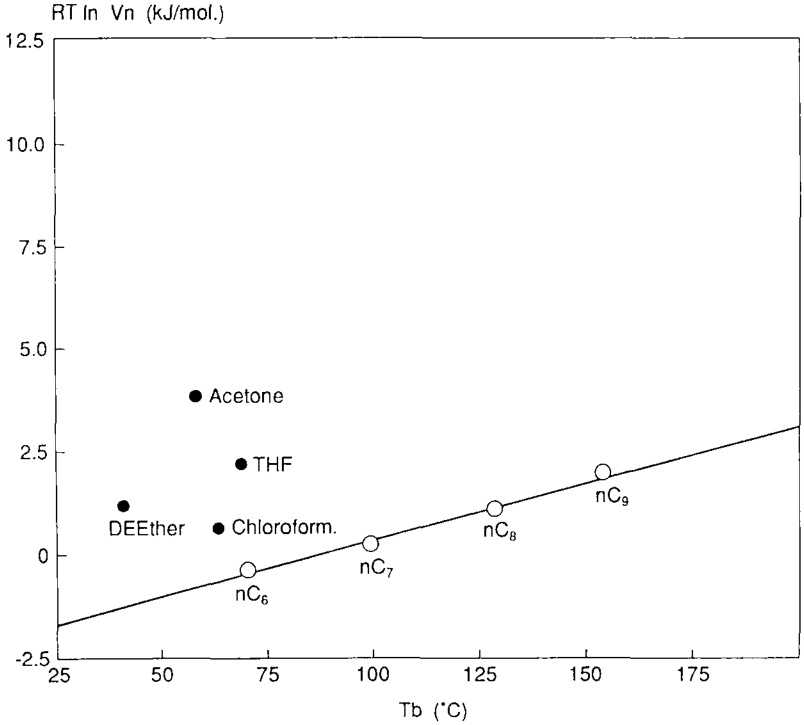

FIGURE 1 Inverse gas chromatographic analysis of fluoropolymer FA-1 at 60°C. Plot of net retention volumes, V_n *vs.* normal boiling temperatures of probes shows polymer to be mildly acidic.

Flow Measurements

The flow behavior of host polymer and of compounds with FA additives was evaluated with an Instron melt viscometer at 200°C. The viscometer was fitted with a flat-entry die of $L/R = 16.5$. The relationship between shear rate and shear stress for each of the individual materials of this research was determined in duplicate. In order to ensure the cleanliness of extrusion apparatus following fluoropolymer processing, 3–4 loadings of pure polyethylene were passed through the entire apparatus and, in addition, the die was fired at T>600°C in order to restore surfaces to a reproducible state. Similar precautions were followed after extrusion of each of the LLDPE/FA blends. It will become evident that the FA additives act as wall lubricants, detaching the bulk polymer from the extrusion die. Consequently, viscometric data for FA materials and for LLDPE/FA blends are taken to represent the *effective behavior of the polymer system* in contrast to the *true viscosities of the compounds*.

The flow instability in LLDPE and in blends with FA additives was studied using the melt drawdown system described in Ref. 1. Briefly, the extrudates in these experiments were wound up by the rolls of a Rheotens elongational rheometer, fitted with a strain gage. The Rheotens was placed some 70 cm below the exit from the primary extrusion device, and extruded filaments were shock-cooled by an air

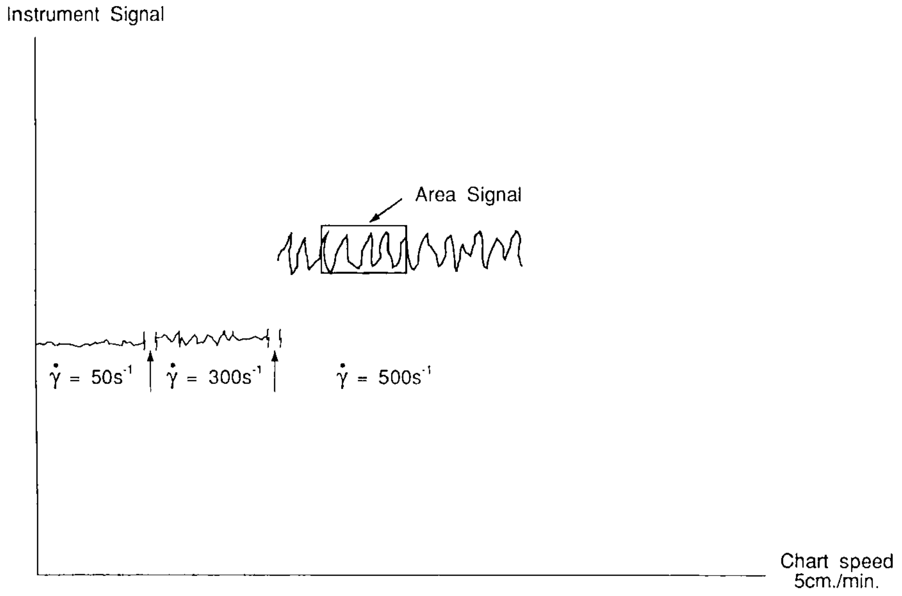

FIGURE 2 Rheotens "noise signal" for LLDPE extrusion at 200°C and shear rates as indicated. Construction defines "area signal."

stream at a point about 10 cm from the wind up rolls. These were operated at speeds ensuring a constant filament draw-down ratio of 6:1, independent of the shear rate in the Instron. The strain signal generated by the Rheotens was near zero during the extrusion of smooth filaments, below the onset of instability. The onset of flow instabilities, however, was marked by systematic, cyclic variations, as illustrated in Figure 2 for the host polymer. The detection method, somewhat similar to that reported by Agassant and coworkers,[22] correlates reasonably well with visual assessments of "shark-skin" and "cyclic melt fracture," but is free from subjective, operator-dependent variables.[1] As shown in Figure 2, an Area Signal, A.S., can be defined to provide a quantitative index of the severity of flow instabilities during polymer extrusion. The A.S. index, given by the area swept out by the Rheotens recorder during 1 min extrusion, will be used throughout this report to characterize the quality of extrusion.

RESULTS AND DISCUSSION

Flow Behavior of LLDPE Host

The flow instability phenomenon of the host LLDPE is documented in Figure 3. This shows the A.S. parameter as a function of the shear rate imposed in the Instron viscometer. As stated earlier, at low shears, where the extrudate is glossy and undistorted, the A.S. is at a steady value near zero. An abrupt rise occurs at about 360–370 s^{-1}, and the noise signal rises continually, attaining a plateau value near 800

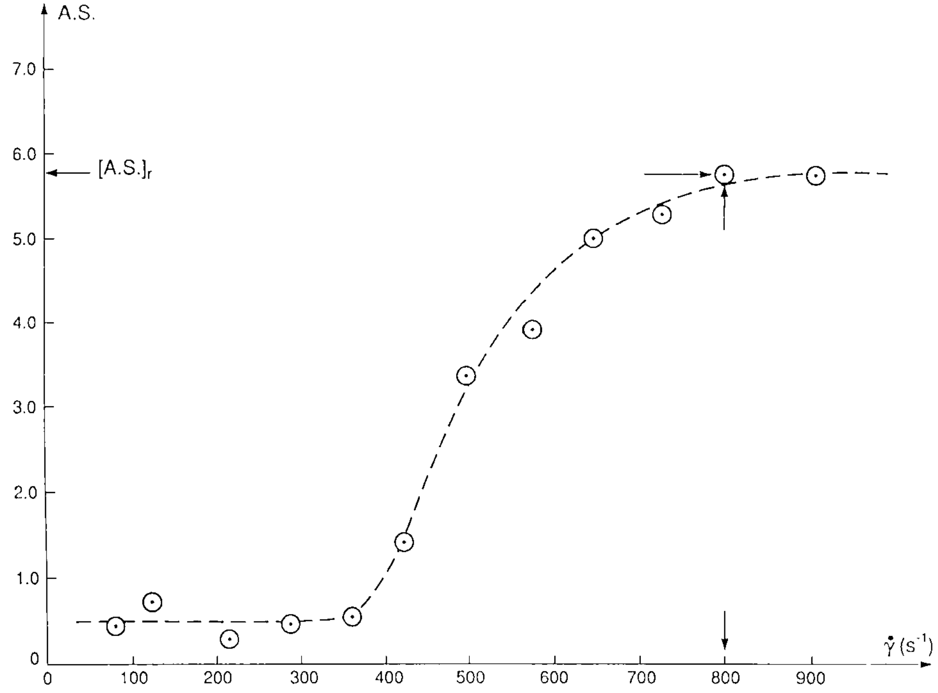

FIGURE 3 Area signal *vs.* shear rate for LLDPE matrix polymer. Extrusion at 200°C.

s^{-1}. Visual evidence of instability, in the form of chevrons or shark-skin patterns, was noted at extrusion above about 350 s^{-1}. The major cause in the increase of the A.S. parameter was observed to be increasing amplitude of excursions such as those shown in Figure 2; their frequency, on the other hand, tended to remain constant. For convenience, the shear rate of 800 s^{-1}, where the amplitude of the A.S. becomes (relatively) independent of shear rate, has been selected as a comparison point and was used throughout this work for evaluations of FA additive effectiveness in suppressing flow instability. The A.S. value for LLDPE at the comparison rate was found to be 5.8 (see Fig. 3).

Performance of Flow Additives

The capability of FA polymers to modify A.S. values, symptomatic of flow instabilities, varied significantly from additive to additive and, for a given fluoropolymer, varied with the additive's concentration. Typical behavior patterns are shown in Figure 4 for the system LLDPE/FA-3. Here the A.S. relative to that for pure LLDPE is plotted *vs.* extrusion time. The result indicates that at concentrations less than 400 ppm the additive is unsuccessful in palliating the instability events. At higher concentrations the A.S. parameter is restored to its base line value, but the effect of the FA additive is felt only some time after extrusion has begun, corrobo-

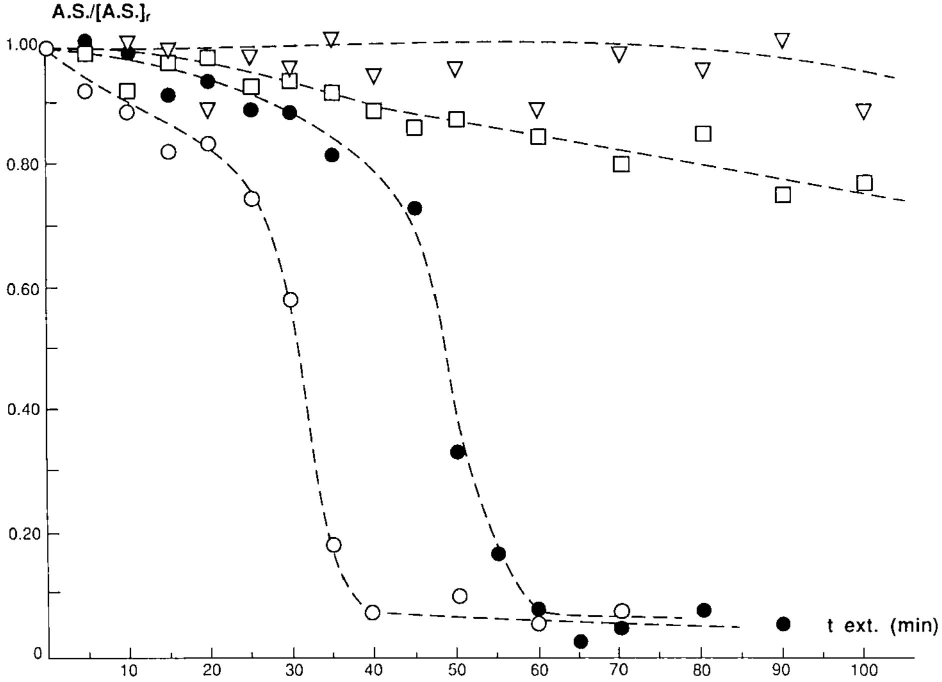

FIGURE 4 Instability suppression effectiveness of FA-3 additive at 200°C and 800 s^{-1} shear rate. Additive concentrations are: ○ 1200 ppm; ● 800 ppm; □ 400 ppm; ▽ 200 ppm.

rating similar earlier accounts.[4,8,9] Thus, at 800 ppm, the instability is suppressed after about 60 min extrusion, while at 1200 ppm the time required is reduced to near 40 min. The time needed to eliminate flow instability, labelled t_c, will be used as a convenient parameter for comparing the performance of various FA agents. The observation of a time-dependent reduction in A.S., valid for each of the FA candidates, supports the notion that the fluoropolymer becomes effective only after it has had sufficient time to accumulate at the die surface, thus forming an interphase between the die wall and the flowing polymer matrix. It is well dispersed in the host polymer at the outset of extrusion and its diffusion to the die wall surface to form an interphase layer would logically vary with its concentration.

The implied mechanism also argues for, at best, limited miscibility between host and additive polymers. The performance of the six FA candidates then may be expected to vary, given the substantial differences in their surface energies and their degrees of polarity, as reported in Table Ib. LLDPE may be considered a neutral substance,[23] capable only of dispersion-force interactions with a wetting fluid. The FA materials are variously polar, however. Each falls into the acid category, the degree of acidity increasing from FA-1 to FA-6, with the group FA-3, -4, -5 at constant acidity. The variation in $(\gamma)_s^{nd}$ is completely analogous, again showing increasing degrees of surface polarity in the sequence FA-1 to FA-6. The dispersion surface energies in the set remain roughly constant. It is reasonable, therefore, that the de-

TABLE II
Critical times for eliminating flow defects by FA addition
(All extrusion at 200°C, die L/R = 16.4)

IIa. At 800 s^{-1} shear rate.			
	t_c (min) ppm concentration:		
Additive:	800	1000	1200
FA-1	85	80	72
FA-2	70	66	60
FA-3	60	52	43
FA-4	50	42	35
FA-5	62	49	45
FA-6	38	30	27
IIb. At 500 s^{-1} shear rate:			
FA-1	90	84	72
FA-2	76	68	63
FA-3	62	55	45
FA-4	50	44	38
FA-5	68	52	45
FA-6	40	33	30

gree of miscibility between host and additive should decrease in the sequence FA-1 to FA-6, with the latter diffusing most rapidly out of the matrix LLDPE. Additives with higher K_a (or K_d) and γ_s^{nd} values would also interact more strongly with the metal die wall, thereby contributing to the formation and the stability of the suggested interphase layer.

The effectiveness parameter, t_c, is given in Table IIa for each of the fluoropolymer additives, with results shown at 800, 1000 and 1200 ppm concentration. Here the comparison is made at an (Instron) extrusion setting of 800 s^{-1}. A second set of results, at 500 s^{-1}, is shown in Table IIb. The anticipated sequence of events is well mirrored in the tabulations. Each of the FA polymers was found able to eliminate flow instabilities at concentrations above 400 ppm, with no apparent variation in that critical quantity. The t_c values, however, decrease significantly from the highest times indicated for FA-1 to the minima for FA-6. There is surprisingly little difference between t_c data in the two sections of the Table. Apparently the kinetics of additive migration are little affected by melt viscosity changes, at least in the somewhat narrow shear rate range covered in the comparison. It is noteworthy, however, that, in spite of the similar K_a and γ_s^{nd} indexes of FA-3, -4, and -5, the t_c values for FA-4 are somewhat lower than for the other two members of this group. The matter is considered again at a later point in the discussion.

A more detailed examination of the postulated relationship between additive effectiveness and its degree of polarity is made in Figure 5. This shows t_c as a function of parameters γ_s^{nd} and K_a at 800 ppm addition and, for comparison, as a function of γ_s^{nd} at 1200 ppm of the FA additives; the extrusion shear rate is 800 s^{-1}. The linear relationships in the Figure are well defined and clearly not fortuitous. Arguably, versions of FA with K_a and $\gamma_s^{nd} = 0$ would not accumulate at the die surface over long periods of extrusion time and would, therefore, be deemed ineffective as

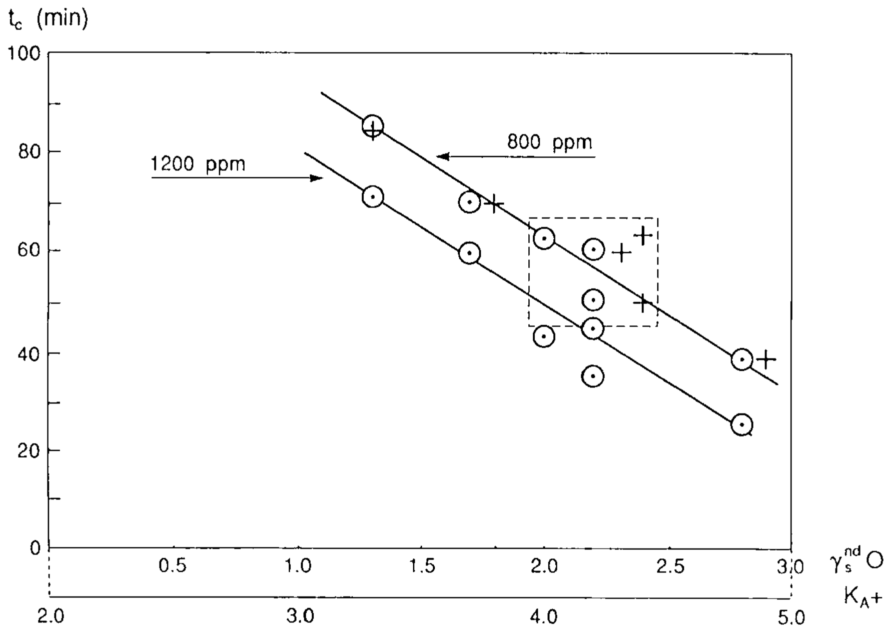

FIGURE 5 Showing instability suppression effectiveness of FA additives (at 800 and 1200 ppm) as a function of their non-dispersion surface energy, and their acidity rating. Extrusion is at 200°C and 800 s^{-1} of shear.

flow instability suppressants. Such homologues of the present FA series would be dispersion-force fluids, like the host polymer, and therefore more likely to be miscible with it. Further with reference to Figure 5, the data for FA-3, -4, and -5 again show an uncommon scatter, in spite of their similarity in degree of polarity. Evidently, factors in addition to the degree of polarity are involved in the performance of the fluoropolymers. It is reasonable to believe that one possible factor may be connected with the postulated need for the additive to migrate toward the viscometer die wall. The requirement to diffuse through the flowing host polymer suggests that the process kinetics may vary with the molecular size (and shape) of the additive polymer. Polymer melt viscosity is a reasonable measure of macromolecular dimensions, therefore it seemed defensible to re-examine the performance data for these polymers from the viewpoint of their rheological properties.

The relationships between apparent viscosities and shear rate for FA-3, FA-4 and FA-5, are given in Figure 6. The decade of shear rates displayed covers the range pertinent to the extrusion protocols discussed above. The data show a substantial change in apparent melt viscosities in the sequence FA-3>FA-4>FA-5, thus paralleling the Mooney viscosities in Table Ib. Inspection of Table II shows that the preferred performer in this group is FA-4. Consequently, the apparent viscosities of the fluoropolymers at 800 s^{-1} do not account for the observed events. A more satisfactory, but empirical, picture is obtained by considering the ratio of additive and matrix viscosities at the extrusion shear rate. The ratios are entered in Table III.

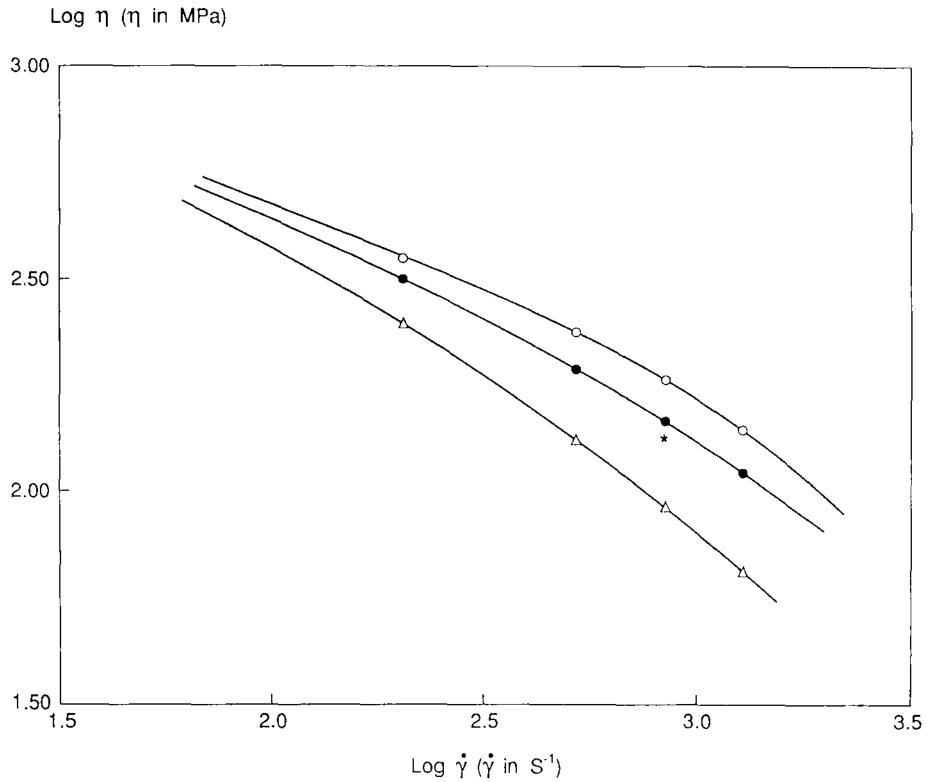

FIGURE 6 Comparing apparent viscosity/shear rate functions of FA additives at 200°C. ○ FA-3; ● FA-4; △ FA-5; *Host LLDPE.

Admittedly, the information in hand does not justify drawing firm conclusions, but there is appreciable inference favoring the performance of FA additives with apparent viscosities falling roughly within 15% of the host polymer. On that basis, FA-4 falls within the favored "rheology window" as does FA-6, with FA-2 on the margin. The performance of lower-viscosity versions of FA-1 and 3, and of a higher-viscosity version of FA-5 should be superior to those documented in this work. Of course, were the hypothesis to be substantiated, then the optimum selection of flow additive may vary with the rheological characteristics of the polymer host. It may also be a function of extrusion rate in those cases where the host and additive polymer are very different power-law fluids.

TABLE III
Melt viscosity ratios of host LLDPE and fluoropolymer additives
η Host LLDPE at 800 s^{-1} = 130 MPa·s

FA-1	FA-2	FA-3	FA-4	FA-5	**FA-6***
1.30	1.15	1.44	1.12	0.70	**1.08***

*Preferred combination of polarity and viscosity match.

CONCLUSIONS

The following may be concluded from information presented in this report:

Flow instability in the extrusion of octene-LLDPE has been eliminated by use of fluoropolymer additives at concentrations exceeding 400 ppm.

The effectiveness of fluoropolymers as suppressants of flow instability increases with the additive's polarity, as evaluated by acid/base interaction parameters and by non-dispersion surface energies. Limited miscibility with the LLDPE host is a factor contributing to the additive's effectiveness.

Suppression of flow instability in blends of LLDPE and fluoropolymers occurs after several minutes of extrusion, indicating that the additive functions as a die lubricant and must diffuse to the die wall in adequate quantity in order to become effective.

Suppression effectiveness also appears to depend on the relative rheological properties of host and additive polymer, with preference given to materials with similar melt viscosities under extrusion conditions. This conclusion, however, is in need of verification by more extensive data.

The fluoropolymer additives are presumed to form an interphase separating the die wall of the extrusion device from the flowing bulk polymer. In so doing, the sporadic adhesive failure between bulk polymer and die wall, thought to be the primary cause of flow instability, is eliminated.

Acknowledgments

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