

Investigation of the Oscillating Flow Phenomenon in High Density Polyethylene

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Synopsis

The nature and causes of the oscillating flow phenomenon in high density polyethylene are examined in this report. Empirical equations are developed describing the onset (both stress, SSOF, and rate, SROF) of oscillating flow in terms of molecular structure. The SSOF is not constant, but is found to vary slightly with the molecular weight distribution. The SROF is shown to be predictable in terms of molecular weight distribution. The physics of the oscillations is critically examined, and the simple model of Okubo and Hori describing these oscillations has been successfully tested. The model involves alternating compression of the polymer in the capillary rheometer barrel and decompression after a material breakdown in the die, in which flow from the capillary exceeds that expected from the rheometer output for an incompressible material. The point for initiation for oscillating flow is positively identified to be in the die, not, as some have suggested, in the die entrance region. Examination of the critical shear stress for random ethylene-propylene rubbers suggests that the reason why linear polyethylene appears unique is that the critical stress may be unattainable in other polymers and that the magnitude of the effect tends toward being vanishingly small. A critical shear strain criterion seems to describe the variations in critical stress with ethylene-propylene copolymer composition, but the critical strain criterion appears to be an oversimplification in general.

INTRODUCTION

The phenomenon of oscillating flow in high density polyethylene (HDPE) is a most striking rheological instability. Unlike melt fracture, commonly referred to as inlet fracture, oscillating flow occurs at a very well-defined stress and rate for a given sample, and unlike melt fracture, it leads to a definite discontinuity in the flow curve (see Fig. 1). Additionally, and unlike melt fracture, one can often get out of the unstable flow region by going to higher apparent shear rates. In addition to HDPE, only Teflon has been conclusively shown to exhibit oscillating flow. Just why HDPE appears to be almost unique in this respect is not understood at this time.

The phenomenon of oscillating flow was first reported by Bagley, Cabot, and West¹ in 1958. Later, Tordella² coined the term "land fracture," since the origin appeared to be in the die land, as opposed to melt fracture, where the origin of the melt instability was thought to be in the die entry region. An in-depth study of the nature of the oscillations, the effects of molecular weight and molecular weight distribution, and the experimental factors for oscillating flow have been reported by Myerholtz.³

The birefringence experiments of Tordella⁴ suggested that the initiation sites for linear and branched polyethylenes were different, although a recent paper by Rudin et al.^{5,6} appears to contradict this conclusion.

The objective of this present study is to further elucidate the molecular factors

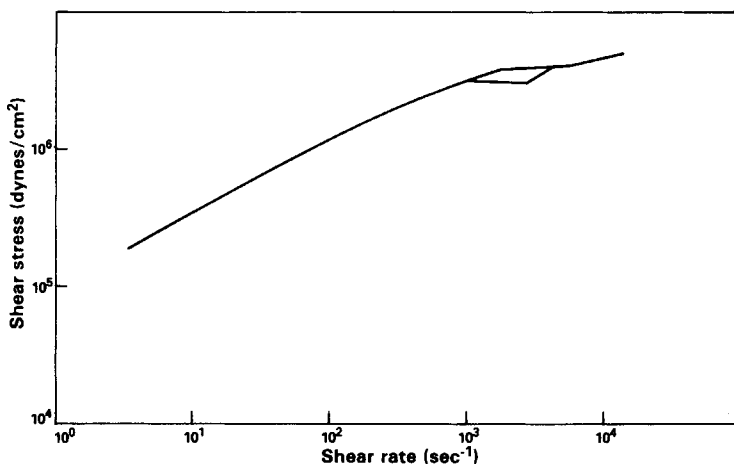


Fig. 1. Typical flow curve for linear polyethylene showing flow curve discontinuity.

controlling oscillating flow and to test the physical model of Okubo and Hori⁷ for describing and oscillations. Also included are the results of an experiment to demonstrate that the origin of the instability is in the die, and not the die entrance as has been recently suggested by Rudin and Chang.⁵

EXPERIMENTAL

The high density polyethylene samples involved in this study were various commercial and experimental samples. Pertinent data on resins studied in detail here are given in Table I. The ethylene-propylene rubber (EPR) samples were commercial materials, whose compositions were determined from nuclear magnetic resonance measurements. The compositions of these resins are given in Table I.

Rheological measurements were made using an Instron capillary rheometer at 190°C. The load and extrudate diameter oscillations were monitored using a Hewlett-Packard Model 7402A Oscillographic Recorder. The extrudate di-

TABLE I
Molecular Characterization of Samples Used in this Study

Sample	Polymer	Melt index (g/10 min)	$\times 10^{-3}$			Mol % propylene	SSOF (dyn/cm ²)
			\bar{M}_n	\bar{M}_w	\bar{M}_z		
A	PE	0.68	16.3	124	835		
B	PE	0.34	11.4	216	1341		
C	PE	4.4	14.3	111	915		
D	PE	<0.01	29.6	315	1410		
E	PE	0.70	12.1	158	732		
F	PE	0.69	28.2	148	559		
G	EPR	0.28		broad MWD		45	7.60×10^6
H	EPR	1.4		broad MWD		25	6.35×10^6
I	EPR	1.6		narrow MWD		47	7.94×10^6
J	EPR	0.20		narrow MWD		15	5.2×10^6
K	EPR	1.7		broad MWD		17	5.18×10^6

ameter was measured with a Zygo Model 120 laser measuring device, where the beam was approximately $1/16$ in. from the die exit.

The molecular weight distributions of the polyethylene samples were determined on the Waters Model 200 Gel Permeation Chromatograph at 135°C using trichlorobenzene as solvent. Calibration was effected using the universal calibration procedure.

The dynamic modulus was determined at 190°C using the Rheometrics mechanical spectrometer with 25-mm parallel plates.

RESULTS AND DISCUSSION

On the Nature of Oscillations. At first glance the apparent oscillating flow behavior depicted in Figure 1 appears rather anomalous. Recently, a couple of models have been reported.^{6,7} The second of these models suggested that the oscillations are due to a slip-stick conditions within the die and a compression and decompression of a compressible fluid within the reservoir. In what follows I shall attempt to verify, test, and extend these ideas.

We shall regard the molten polyethylene as a compressible fluid with a bulk modulus,⁸ $E_v = 1.098 \times 10^5$ psi. Further, we shall visualize a stress buildup to a critical stress, during which the plunger moves faster than the flow out of the die (compression). This compression phenomenon has been confirmed by the work of Rudin.⁵ At the critical stress in the die the polymer "yields" at or near the die wall (point of maximum stress). During this stress-relaxation phase, the flow rate from the die exceeds that predicted from the plunger movement.⁵ As the compressed melt in the reservoir compresses and the stress decreases, the yielding stops (perhaps because of a structural rebuilding of the entanglement network) and the compression phase starts.

From simple bulk property relationships we can relate the following mathematically as

$$f_c = \frac{E_v}{\langle h \rangle \Delta L} (S - \langle \dot{l} \rangle_{ss}) \quad (1)$$

and

$$f_R = \frac{E_v}{\langle h \rangle \Delta L} (\langle \dot{l} \rangle_{OF} - S) \quad (2)$$

where f_c and f_R refer to the reciprocal of the times during the compression and relaxation part of the cycles, $\langle h \rangle$ the barrel height in the Instron capillary rheometer, ΔL the load fluctuation during oscillation, S the velocity in the absence of the compression of the melt (i.e., the volumes of polymer exiting the die being equal to that predicted from the plunger travel), and $\langle \dot{l} \rangle_{OF}$ the average plunger velocity if the plunger were moving fast enough to keep up with flow during the relaxation phase. $\pi R^2(S - \langle \dot{l} \rangle_{ss})$ is the net change in volume during the compression phase and $\pi R^2(\langle \dot{l} \rangle_{OF} - S)$ the net volume change during the decompression (stress-relaxation) phase.

$\pi R^2 \langle \dot{l} \rangle_{ss}$ and $\pi R \langle \dot{l} \rangle_{OF}$ are not definitely known, since they represent averages of continuously changing outputs during the compression and decompression phase of flow. However, a number of checks of the model can, nevertheless, be made. Equations (1) and (2) predict that the total period for one cycle should

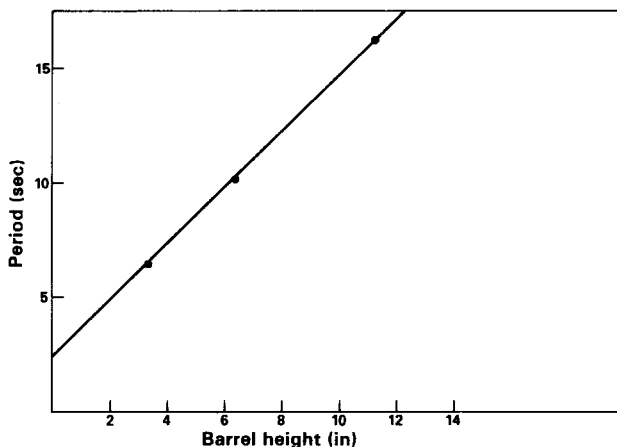


Fig. 2. Effect of oscillation period on Instron barrel height.

be proportional to the barrel height. This has previously been demonstrated by Myerholtz³ and is shown in Figure 2. The slope of f_c and f_R as a function of crosshead speed can also be predicted, involving the bulk modulus.⁸ The predictions are shown in Figures 3 and 4 to predict the effect of S on f_R and f_c ; the predicted lines have been arbitrarily shifted for best register with the experimental data. This agreement is taken as strong evidence for the essential correctness of the model of Okubo and Hori, since the predicted slope contains no adjustable parameters.

The dependence of oscillation frequency on crosshead speed is given in Figures 5 and 6. A similar plot showing a maximum was reported by Myerholtz.³ The maximum is easily understood in terms of the model discussed earlier and from Figures 3 and 4. At low crosshead rates, but in the oscillating flow regions, the total frequency will increase with S . However, at high crosshead speeds the

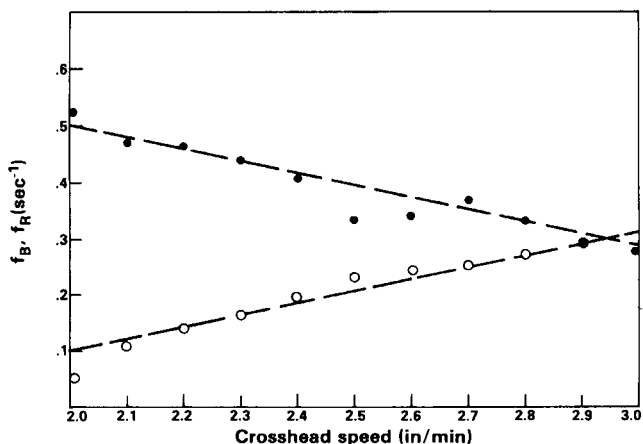


Fig. 3. Dependence of the reciprocal of the buildup f_B and the relaxation f_R times for the oscillation as a function of crosshead speed for Sample A. Dashed lines are predictions of slopes based on eqs. (1) and (2), which have been vertically shifted to obtain a best fit to the data.

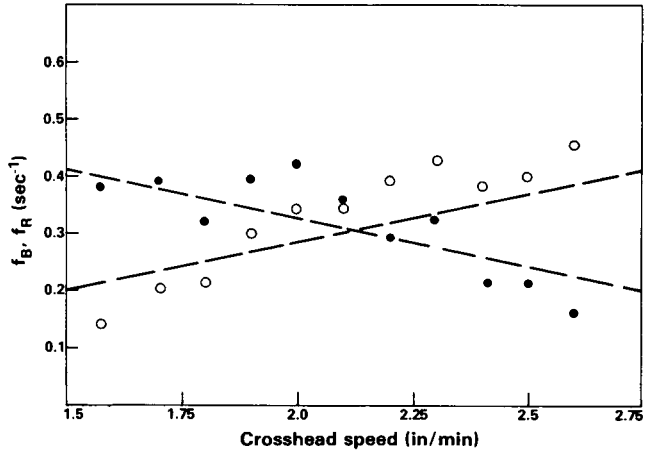


Fig. 4. Dependence of the reciprocal of the buildup and relaxation times for the oscillation as a function of crosshead speed for Sample B. Dashed lines are predictions based on eqs. 1 and 2.

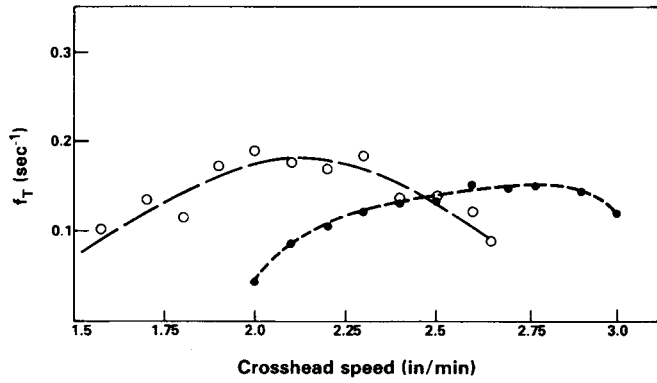


Fig. 5. Variation of oscillation frequency f_T with crosshead speed for Samples A (---) and B (---).

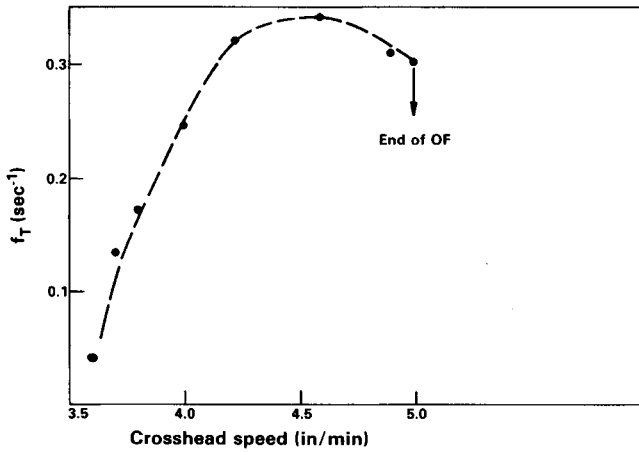


Fig. 6. Variation of oscillation frequency with crosshead speed for Sample C.

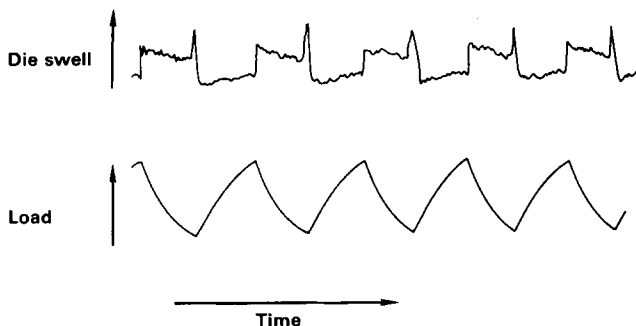


Fig. 7. Dual traces of die swell and load during oscillating flow.

period tends to be dominated by the relaxation process and the frequency decreases. Additionally, as the molecular weight decreases and the crosshead speed for the onset of oscillating flow increases, the curve can be seen to become asymmetric, and for very high flow rates the maximum may disappear. This is because the buildup phase dominates over the entire oscillating flow range; material tends to flow from the capillary more rapidly at the shear stress for oscillation flow (SSOF), and therefore it takes correspondingly longer to compress the polymer in the reservoir.

It is concluded that the model relating the oscillations to a compression of the molten polymer in the barrel, a yielding at a given shear stress, stress-relaxation with flow from the die exceeding that predicted from the plunger velocity, and finally structural reformation with subsequent stress buildup, is essentially the correct model describing the oscillations. This description is not too dissimilar from the suggestion by Myerholtz³ that the system behaves similar to a cavity resonator.

Effect of Oscillating Flow on Die Swell. From Figure 7 it is seen that the swell during the stress decay (fast flow portion of the flow curve in Fig. 1) is generally larger than during the stress buildup portion of the curve. This alternating die swell behavior is illustrated in Figure 8. Similar behavior has been noted by others.^{2,3,5} Figure 7 shows an oscillographic trace of the laser die swell and the rheometer load trace. As can be seen from this figure, the onset of this increase in swell corresponds very closely with the onset of fast flow. The puzzling part of the discontinuous change in swell is that the higher swell occurs at lower stresses than the slow flow phase of the oscillation; if one decreases the stress on an elastic body, one generally expects less stored strain, which in our case is manifested by die swelling. One explanation of this may involve the decreased residence time in the die during the fast flow phase. In other words, the swell could rise due to an effectively smaller capillary L/D (shorter residence time) during the fast flow phase; Bagley et al.⁹ have shown that the swell contribution from entrance memory effects decreases with L/D or equivalently volumetric flow rate. Superimposed on the jump in swell appears to be a steady decrease in swell during the fast flow (high swell) phase. This component seems to be due to the decrease in stress. The origin of the peak in swell at the end of the fast flow is not known, but it would seem instrumental (the laser) in origin, since the extrudates do not show this maximum.

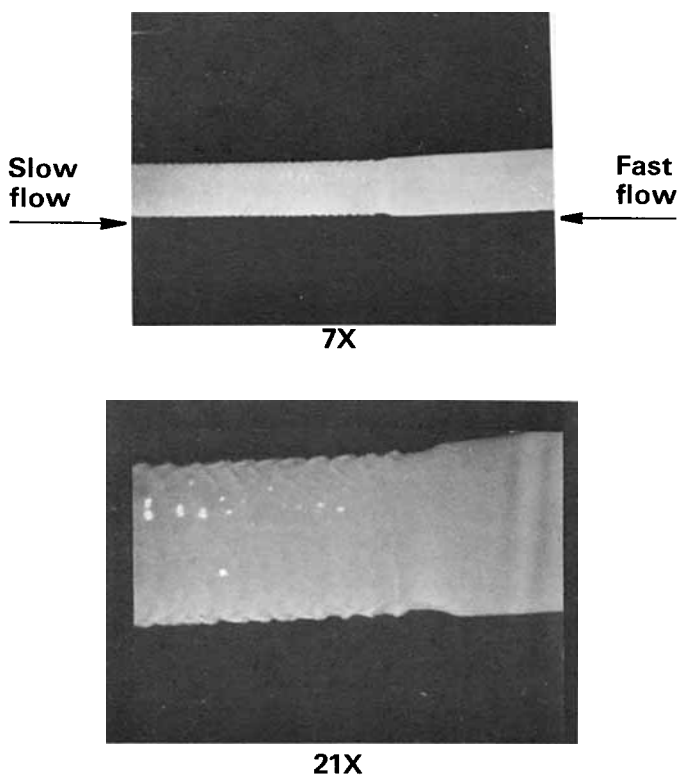


Fig. 8. Micrographs of extrudate during the fast (stress-relaxation) and slow (stress buildup) phases of the oscillation.

It would appear unlikely that the increased swell is due to some anomalous process taking place throughout the volume of the die from the following arguments. Oscillating flow seems to be a critical shear stress phenomenon at or near the die wall. Therefore, any change in material flow in this narrow region would no doubt be confined, since material in the interior of the die would be at much lower shear stresses. It seems likely, therefore, that the phenomenon involves a cohesive failure near the die wall for a thin annulus of material, but that the bulk of the material continues to undergo laminar flow similar to below the oscillating flow region, only having a relative slip velocity relative to the die.

The Point of Initiation for Oscillating Flow. While most authors agree that the oscillating flow phenomenon is associated with the die, some authors⁵ have suggested the point of initiation for the instability is due to tensile forces generated in the entrance region. The following experiment was devised in order to test these ideas.

A very low flow rate (<0.01) HDPE resin was chosen because of the low output rate ($\dot{\gamma} \approx 30 \text{ s}^{-1}$) at which oscillating flow took place. A 4 in. \times 0.03 in. capillary was run with the chosen HDPE, but material left in the die undisturbed. The entrance (90°) was cleaned and the die replaced in the Instron at 190°C . The barrel was filled with low density polyethylene, which does not exhibit oscillating flow. Flow at a plunger rate, at which the oscillating flow was known to take place, was initiated (i.e., no HDPE was in the entrance region). Figure 9 gives

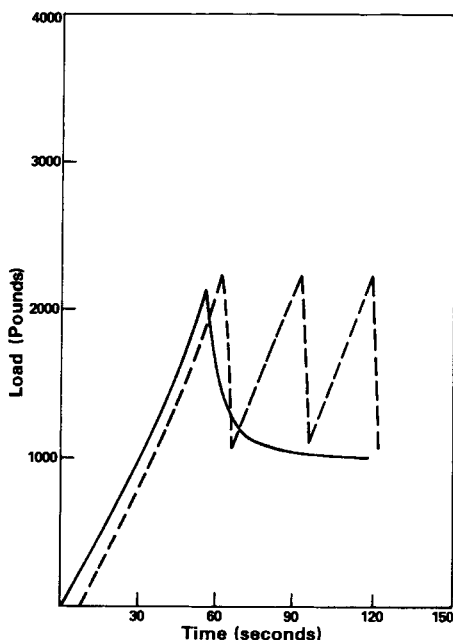


Fig. 9. Load vs. time traces at constant crosshead speed: (---) linear polyethylene (Sample D) in barrel, die, and die entrance; (—) LDPE in die entrance and barrel with linear polyethylene in capillary.

the results of this experiment, as well as results for the HDPE; the figure clearly shows the first cycle of the oscillating flow phenomenon took place where LDPE was in the entrance region; no further oscillations took place since all the HDPE was displaced in the capillary. In any case, *the results definitely show that tensile failure of HDPE in the entrance region is not the initiation site for oscillation flow.*

On the Constancy of the Shear Stress for Oscillating Flow (SSOF). In order to test for constancy of the SSOF, two resins having widely different SSOF

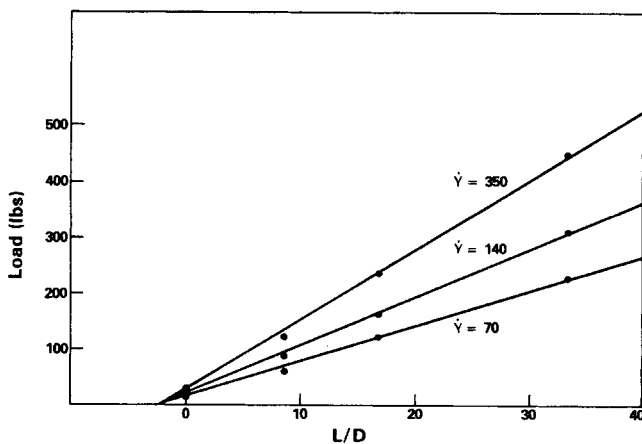


Fig. 10. Bagley plot for Sample A.

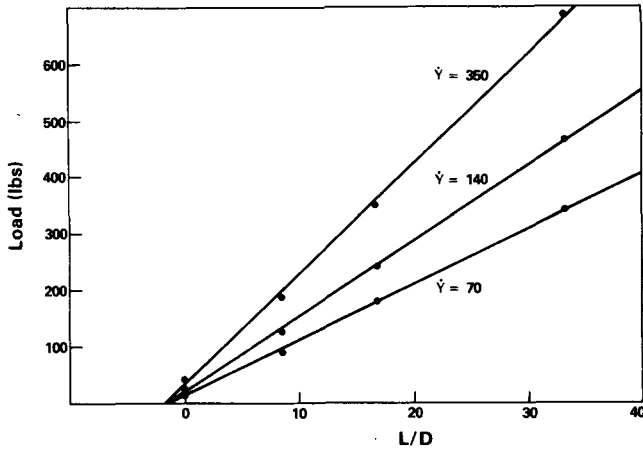


Fig. 11. Bagley plot for Sample E.

values were chosen, both of which were nominal 0.7 MI materials. Bagley end correction plots are given in Figures 10 and 11. The uncorrected SSOF values were found to be 2.98×10^6 dyn/cm² and 3.81×10^6 dyn/cm² for samples E and F, respectively. The respective corrected values were found to be 2.77×10^6 and 3.61×10^6 . It therefore appears that the correction is small and cannot account for the rather sizeable differences in SSOF between these resins. This is contrary to the results reported by Myerholtz.³ It may be that the differences in SSOF reported by Myerholtz were much smaller than reported here. In any case, the present results suggest that the SSOF varies for different HDPE materials and that the capillary end corrections are negligible compared to the range in SSOF values.

The SSOF varies with temperature as shown in Figure 12. The increase in

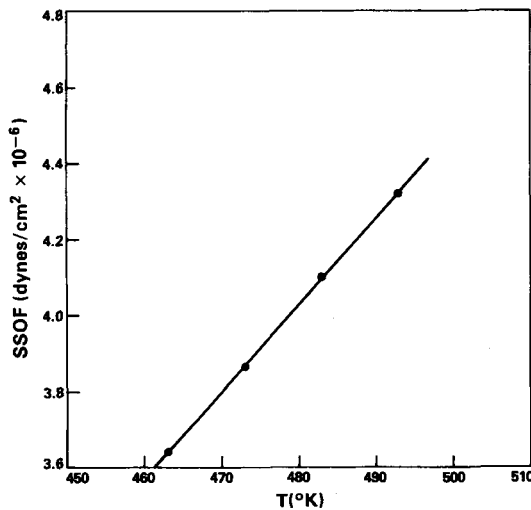


Fig. 12. Variation of the critical shear stress for the onset of oscillating flow (SSOF) with temperature.

SSOF with temperature is not easily explained, since if the process were similar to yielding, then we would expect SSOF to decrease with temperature. Moreover, as will be discussed later, a simple critical shear strain criterion for the onset of oscillating flow is also inconsistent with this dependence.

The Effects of Molecular Weight Distribution. In this section we will explore the effects of molecular weight and its distribution on both the shear stress and rate for oscillating flow (SSOF and SROF, respectively). To a first approximation, since the SSOF varies over a very limited range compared to SROF (decades) variations in SROF between samples merely reflect the variation in viscosity; the relation between SSOF and SROF is

$$\text{SROF} = \frac{\text{SSOF} (\sim \text{constant})}{\text{viscosity at SSOF}} \quad (3)$$

Since, in general, our understanding of the effect of MWD on viscosity is reasonably well understood,^{10,11} we will first concentrate on the SSOF. Multiple regressions were performed with $(\bar{M}_w, \bar{M}_w/\bar{M}_n, \text{ and } \bar{M}_z/\bar{M}_w)$ and $\bar{M}_n, \bar{M}_w, \text{ and } \bar{M}_z$ as independent variables. The first variable set $(\bar{M}_w, \bar{M}_w/\bar{M}_n, \text{ and } \bar{M}_z/\bar{M}_w)$ gave a better fit to the data. The results for SSOF are summarized in Table II.

TABLE II
Summary of SSOF Regression on Molecular Weight Distribution

where	Variable	Coefficient	T Ratio
		4,204,272	29.85
X_1	\bar{M}_w/\bar{M}_n	-76,991	-9.67
X_2	\bar{M}_w	-2452	-3.40
X_3	\bar{M}_z/\bar{M}_w	68,345	3.91

$R^2 = 82\%$

From the T -ratios, \bar{M}_w/\bar{M}_n clearly is seen to be the most significant effect. As shown earlier, this strong distributional effect cannot be attributed to capillary entrance corrections; the SSOF is plotted as a function of \bar{M}_w/\bar{M}_n in Figure 13. A similar regression was performed on SROF, in which the logarithm of SROF was found to produce a better fit with the molecular weight terms than SROF. With SROF as the dependent variable, significant curvature was apparent. A linear regression with the logarithm of SROF as the dependent variable produced a good fit. The following equation resulted from this regression:

$$\text{SROF} = (3.37 \times 10^8) [(\bar{M}_w)^{-3.23}] [(\bar{M}_z/\bar{M}_w)^{1.32}] [(\bar{M}_w/\bar{M}_n)^{0.45}] \quad (4)$$

A summary is given in Table III for the regression of SROF on molecular variables. Equation (4) suggests that SROF increases with a broadening of the molecular weight distribution and strongly decreases with \bar{M}_w . This is not surprising from eq. (3), since the viscosity increases with M_w and a decrease in either \bar{M}_w/\bar{M}_n or \bar{M}_z/\bar{M}_w at constant \bar{M}_w .¹⁰

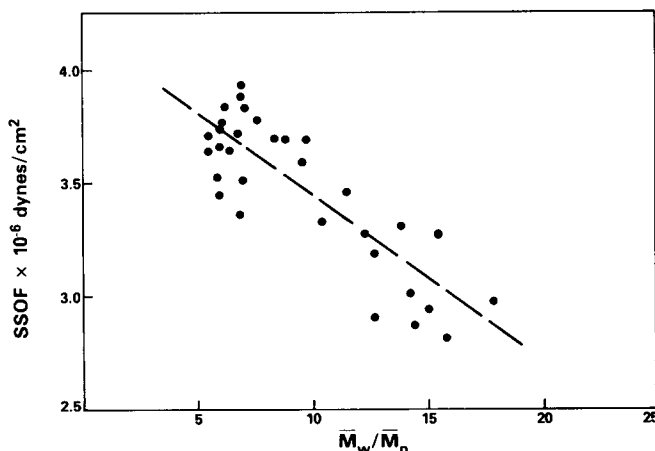


Fig. 13. The variation of the SSOF with polydispersity for various linear polyethylenes.

On the Origin of Oscillating Flow. No completely adequate explanation as to why high density polyethylene appears unique in exhibiting oscillating flow has been put forth. A yielding-like phenomenon, in which absolute reaction theory is applied,¹² would lead us to expect the critical stress to decrease with temperature, which is in sharp contrast to experimental results.

It seems most likely to this author that the onset of fast flow represents a cohesive breakdown in a thin polymer layer near the die wall, which is the place of maximum shear stress. While there may be debate as to whether the "slip" represents adhesive or cohesive failure at or near the die wall, slip has been experimentally verified,^{13,14} and the slip velocity has been shown¹⁵ to be decreased with the addition of low molecular weight material.

While a catastrophic cohesive breakdown in the entanglement network seems plausible, this does not seem to explain the uniqueness of linear polyethylene. Kinetic arguments based on entanglement dynamics seem attractive, but it is also not clear why these kinetic arguments based on entanglement-disentanglement mechanisms should lead to an approximately constant shear stress for oscillating flow. A simple, yet attractive to this author, explanation of the unique behavior of polyethylene would be to assert that the critical shear stress in the die is not reached for materials other than HDPE. Shear stresses equivalent to or exceeding those capable of producing oscillating flow in HDPE have been

TABLE III
Summary of SROF Regression on Molecular Weight Distribution (dependent Variable Log (SROF))

Variable	Coefficient	T Ratio
	8.53	32.01
$\log (\bar{M}_w / \bar{M}_n)$	0.452	4.92
$\log (\bar{M}_z / \bar{M}_w)$	1.32	8.72
$\log (\bar{M}_w)$	3.23	-26.61
$R^2 = 91.2\%$		

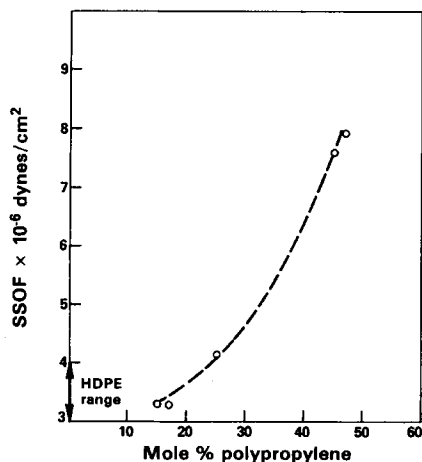


Fig. 14. Variation of SSOF with composition of EPR rubbers, Samples G-K.

found in conventional LDPE, with no discontinuity in the flow curve evident. Consequently, we would have to postulate the shear stress for catastrophic breakdown in the die to be larger for LDPE. One way to test this hypothesis is to examine random copolymers of high density polyethylene with a comonomer, which produces a polymer that does not exhibit the oscillating flow phenomenon, and to examine the trend and extrapolated limit of the critical shear stress for the copolymers of varying composition. Random ethylene-propylene rubbers (EPR) represent ideal materials, since the relative reactivities of the two components are relatively close, such that high comonomer concentrations may be obtained.

An examination of the critical stress for various random EPR rubbers supports this view, as shown in Figure 14; the extrapolated critical shear stress for polypropylene is probably indeed unattainable. The results in Figure 15 show that the magnitude of the effect, namely the extrapolated amplitude of the oscilla-

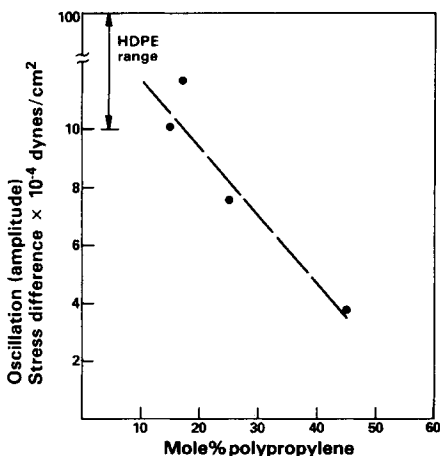


Fig. 15. Oscillation amplitude for Samples G-K as a function of composition.

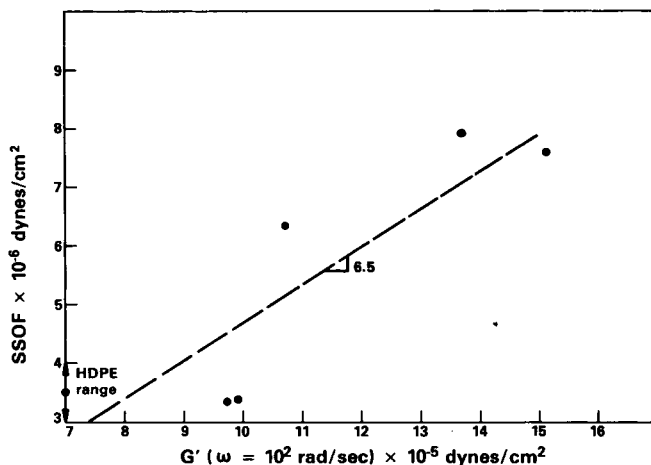


Fig. 16. SSOF as a function of the dynamic modulus for Samples G-K.

tions, also would be markedly reduced for pure polypropylene, such that even if the critical shear stress could be attained, the effect might be too small to measure.

It would appear from the preceding that one part of the question of the uniqueness of linear polyethylene can be restated as to why the critical shear stress for polyethylene is lower than other polymers. The hypothesis of Tordella² and others that both melt fracture ("inlet fracture") and oscillating flow ("land fracture") occur at a critical shear strain level seems attractive. The critical shear stress for oscillating flow is plotted in Figure 16 as a function of the dynamic modulus at the highest angular frequency that could be obtained on our equipment. While considerable scatter is evident, the trend is unmistakable. A least squares line gave a slope of 6.5, which following Tordella² and Bagley,¹⁶ this slope can be interpreted as a critical recoverable strain of approximately 6.5. This is in good agreement for the critical strain levels of 5 and 6.4–6.9 found by Tordella and Bagley,¹⁶ respectively, for the critical shear strain for melt fracture. However, the fact that other polymers, which do not exhibit oscillating flow, are able to reach recoverable shear strains of approximately 6.5 units suggests that a critical shear strain criterion does not differentiate between polymers that do not exhibit oscillating flow and linear polyethylene. Furthermore, the increase in the critical shear stress with temperature is opposed to what would be expected from an Arrhenius decrease in modulus in the terminal zone¹⁷ and from a critical strain criterion. The assumption, that the appropriate modulus is the rubbery modulus¹⁷ instead of that at a lower frequency as used here, is in line with the observed linear increase in SSOF with temperature; however, from the usual relation between the rubbery plateau modulus and the molecular weight between entanglements, M_e , and critical stress criterion, we would be led to expect that polyethylene, which has the lowest M_e of any of the common polymers, would have the highest value of SSOF. This is contrary to the results in Figure 14.

From the preceding, it is concluded that critical strain criterion for the onset of oscillating flow appears to be an oversimplification. The data presented do, however, appear to suggest that the critical shear stress is larger and the mag-

nitude of the oscillation vanishingly smaller for polypropylene relative to linear polyethylene. Whether this can be generalized is not known at this time; I intend to investigate copolymers of ethylene with comonomers other than propylene to ascertain the generality of the work done here.

CONCLUSIONS

The oscillations that occur during oscillating flow for HDPE are quantitatively accounted for by the "slip-stick" model of Okubo and Hori that treats the melt in the Instron barrel as undergoing compression during the stick phase and decompression during the slip (in the capillary die) phase, which occurs at a critical shear stress.

The increased die swell during the "slip" phase of the oscillation appears to be due to the decreased residence time in the capillary during the fast flow region.

The initiation site for the oscillating flow phenomenon is not in the die entrance region as has been suggested by some authors. Rather the breakdown appears to be within the die itself at an approximately constant critical shear stress for linear polyethylene.

The shear stress for oscillating flow (SSOF) is not truly constant, but rather varies somewhat with molecular weight distribution; SSOF increases with $\overline{M}_w/\overline{M}_n$.

The rate at which oscillating flow, SROF, occurs essentially varies with the viscosity at the critical shear stress. A regression equation relating SROF to molecular structure has been developed which appears to adequately account for the large variations in SROF.

The shear stress for the onset of oscillating flow increases regularly with percentage propylene for random ethylene-propylene rubber samples. This suggests that the reason why polyethylene appears unique in exhibiting oscillating flow is that the critical shear stress may not be attainable in other polymers, although the investigation of other copolymers with ethylene is necessary, in order to ascertain the generality of this conclusion. A critical recoverable shear strain of approximately 6 units appears to be a criterion that describes the behavior of the samples studied. However, the response to temperature and molecular structure suggests that a critical shear strain criterion is an oversimplification.

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