

## Oscillating Flow Behavior of High-Density Polyethylene Melts

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### Synopsis

The oscillating flow behavior of a variety of high-density polyethylene and copolymer samples was studied in a constant displacement rate rheometer. At any plunger velocity, the period of the oscillations decreases linearly with melt depth, suggesting a resonance phenomenon. As plunger velocity is increased, the load waveform changes in a regular manner that indicates a progressive increase in the proportion of each cycle spent on the right-hand branch of the flow curve. Little difference was found in the shear stress at which oscillating flow began for samples differing in molecular weight, molecular weight distribution, and manufacturing process. However, the shear rate at which oscillating flow begins depends strongly on both molecular weight and distribution. Oscillating flow is shifted to higher shear rates by broadening distribution, reducing molecular weight, increasing temperature, or decreasing the  $L/D$  ratio of the capillary.

### INTRODUCTION

Oscillating flow occurs during the capillary extrusion of melts of certain high-density polyethylene samples in equipment operating at constant displacement rate.<sup>1-5</sup> There are low and high shear rate regions where the extrusion force remains constant during extrusion at a given shear rate. However, in an intermediate shear rate region, the extrusion force and actual output rate oscillate between two values, even though a piston is displacing the melt from the reservoir at a constant rate. Because this phenomenon has also been observed during the operation of extruders,<sup>4</sup> it clearly is one of practical importance in processing operations.

Such behavior has been attributed to the fact that these materials exhibit a doubly branched flow curve, as shown in Figure 1, rather than a single line.<sup>4,6,7</sup> The oscillations in extrusion force and output rate have been explained in terms of a cycling between upper and lower critical shear stresses on the two branches of the flow curve. The disentanglement or yielding of molecules as well as slip at the capillary wall have been considered as the mechanism responsible for the initiation of oscillating flow. However, few specific details on the nature of the oscillations have been reported. Furthermore, published data on the shear rate at which oscillating flow begins have generally been approximate and limited to a few samples.

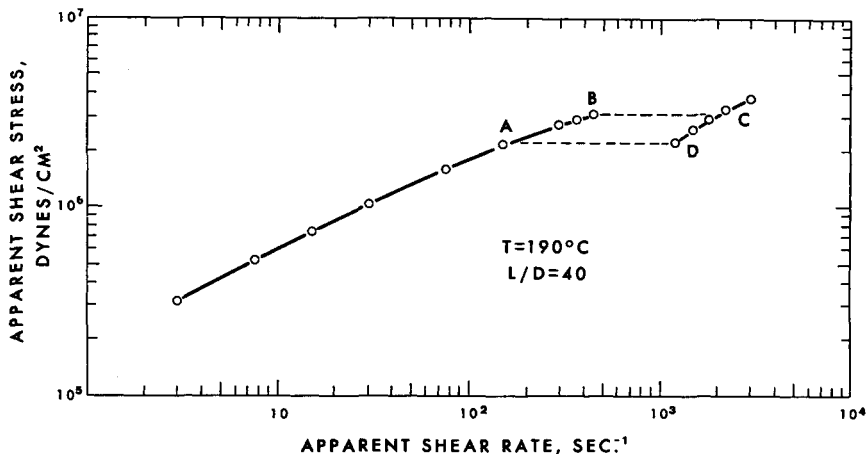


Fig. 1. Flow curve for a high-density polyethylene,  $\bar{M}_w = 265,000$ .

This paper describes studies undertaken to obtain further details on the nature of the oscillations and their relation to the flow curve. In addition, a procedure for determining the shear rate at which oscillating flow begins was developed and applied to over 50 samples of high-density homopolymers and copolymers of ethylene. The effects of molecular weight, molecular weight distribution, and experimental factors on the shear rate for oscillating flow have been investigated.

### EXPERIMENTAL

With one exception, all samples studied represented normal commercial products from the Standard Oil Company (Indiana), Phillips, and Ziegler processes. In addition to polyethylenes from each process, the samples included ethylene-propylene copolymers manufactured by the Standard Oil Company (Indiana) process and ethylene-butylene copolymers from the Phillips process. Unannealed densities ranged from about 0.945 to 0.965 g./cm.<sup>3</sup> and melt index varied from 0.15 to about 3.5 g./10 min.

All rheological measurements were carried out with the Merz-Colwell capillary extrusion rheometer manufactured by Instron Engineering Corporation.<sup>8,9</sup> This is a constant extrusion rate apparatus with the shear rate determined by the rate of plunger travel and capillary dimensions. The apparatus was equipped with a variable crosshead speed control to permit measurements at any selected shear rate within the limitations of the drive assembly and capillary dimensions. Except where noted, all measurements were made at 190°C. with the use of tungsten carbide capillaries 2.00 in. long, 0.05 in. in diameter, and with an entrance angle of 90°.

The apparent shear stress ( $\tau_w$ ) and shear rate ( $\dot{\gamma}_w$ ) at the wall were calculated from relationships published elsewhere.<sup>2,9</sup> Except where

noted, corrections were not made for capillary end effects, reservoir pressure drop, or piston friction. The corrections involved are generally small.

For the frequency and waveform studies, load oscillations were recorded on a Sanborn oscillograph connected to the load cell through a carrier preamplifier-demodulator. This was done to avoid limitations imposed by the response time of the recorder normally used with the rheometer. Zero suppression circuitry permitted the oscillations to be expanded to virtually the full width of the oscillograph chart.

Melt depths during extrusion were established through use of the Instron gage-length dials, which indicated plunger position. During sample extrusion, an event marker on the oscillograph was energized when the plunger passed a reference gage length near the top of the reservoir. The time elapsed since passing the reference position was obtained from the oscillogram. This value, together with the known rate of plunger travel and the gage length determined with the plunger nose seated in the capillary entrance, permitted determination of the melt depth at any moment during the experiment.

Preliminary measurements at a series of fixed plunger velocities provided by a pushbutton speed selector indicated the general shear rate range for oscillating flow. The variable-speed drive unit was then used to gradually and continuously increase plunger velocity until load oscillation began, and this velocity was used to calculate the shear rate for oscillating flow. Repeat measurements on a number of samples have shown that the shear rate for oscillating flow is reproducible within 3-4%.

Weight-average molecular weights ( $\bar{M}_w$ ) were calculated from inherent viscosities through the relationship

$$\{\eta\} = 4.0 \times 10^{-4} \bar{M}_w^{0.70}$$

established by light-scattering measurements on a series of unfractionated high-density polyethylenes. Inherent viscosities were measured in decalin at 135°C. at a concentration of 0.1 g./100 ml. Number-average molecular weights ( $\bar{M}_n$ ) were estimated from infrared measurements of unsaturation, assuming one double bond per molecule.<sup>10</sup> The ratio  $\bar{M}_w/\bar{M}_n$  was used as a measure of the breadth of molecular weight distribution, with a higher value indicating a broader distribution. Selected samples were also fractionated by a column elution procedure to confirm the differences in distribution indicated by solution viscosity and infrared measurements.

## NATURE OF THE OSCILLATIONS

### Frequency

The data presented were obtained on a 0.96 cc./g. density polyethylene of  $\bar{M}_w = 265,000$ . This sample exhibited oscillating flow from 430 to 1,100 sec.<sup>-1</sup>. With the capillary specified, this corresponds to plunger velocities of 2.9-7.6 in./min. A separate run was made at each of a series of velocities within this range, starting with a full reservoir and continuing

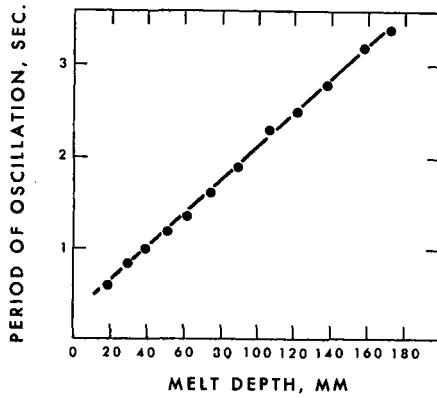


Fig. 2. Dependence of period of load oscillations on melt depth.

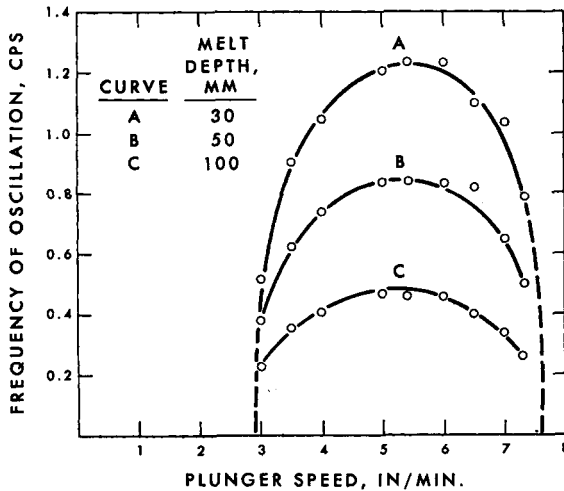


Fig. 3. Dependence of frequency of load oscillations on plunger speed.

until the plunger was 0.5 in. short of the capillary entrance. Oscillation occurred over the full range of travel.

The results of a typical run are given in Figure 2, which shows the period of oscillation at a given plunger velocity is a linear function of melt depth. Similar relationships were obtained at all velocities. The linear relationship between the period and melt depth suggests the system is behaving as a cavity resonator with the plunger acting as the reflection plane.

Figure 3 shows that the frequency of oscillation at a given melt depth for this sample passes through a maximum as plunger velocity increases. When the velocities for the onset and cessation of oscillating flow are included (dotted lines), the curve is essentially symmetrical in this particular case. Thus, the same frequency can be encountered at two widely separated plunger velocities.

### Waveform

The load oscillations were similar in shape to those obtained from a relaxation oscillator. The manner in which the waveform varied with plunger velocity is shown in Figure 4. The waveforms at 3.5 and 7.0 in./min. are especially pertinent, since both velocities gave approximately the same frequency at a given melt depth. The waveform at 3.5 in./min. is essentially the inverse of that at 7.0 in./min., in terms of the increasing and decreasing load portions of the cycle.

During oscillating flow, the oscillation between two shear rate ranges produces an extrudate with alternating segments of small and large diameter, because swelling ratio increases with shear rate. This permitted

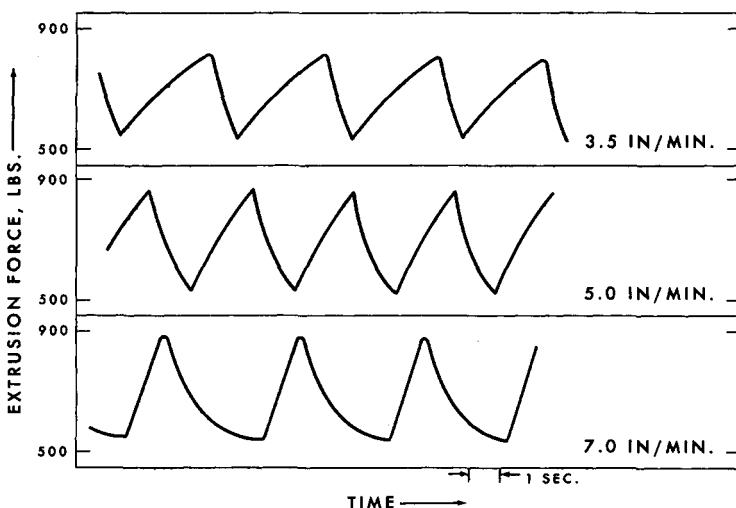


Fig. 4. Change in waveform with increasing plunger speed.

determination of the portion of each cycle spent on each branch of the flow curve. The capillary exit was observed, and an event marker on the oscillograph was activated during the emergence of successive large diameter segments, while recording the load oscillations. Emergence of the large diameter segments (representing the right-hand branch of the flow curve) coincided quite accurately with the decreasing load portion of the cycle.

The fraction of the load cycle corresponding to a decreasing load was determined from the oscillograms for each of the plunger speeds used in Figure 3. As shown in Figure 5, the fraction of the load cycle corresponding to the right-hand branch of the flow curve increases regularly with increasing plunger velocity. The ratio of the length of large to small diameter extrudates increased in a similar manner. The plunger rate at which equal portions of the cycle were spent on each branch of the flow curve corresponds with that for the maximum frequency in Figure 3. Thus, the oscillating flow region represents a gradual transition from one flow regime

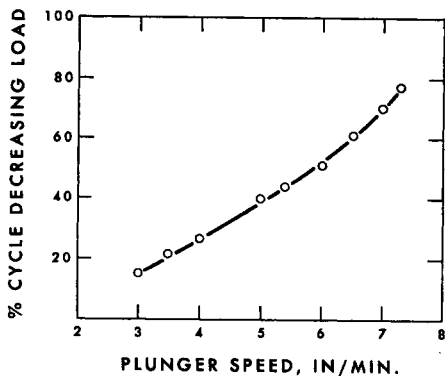


Fig. 5. Portion of load cycle corresponding to right-hand branch of flow curve as a function of plunger speed.

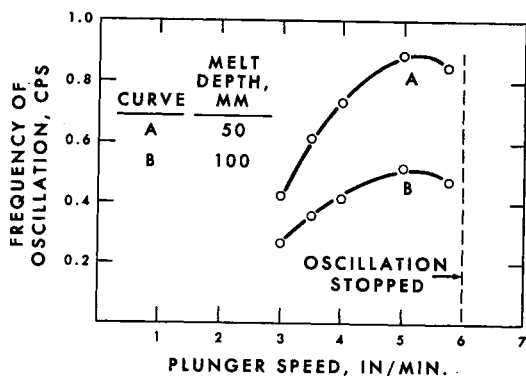


Fig. 6. Frequency vs. plunger speed;  $\bar{M}_w = 180,000$ .

to another with an increasing amount of time spent on the right-hand branch as plunger velocity increases.

The relationship between frequency and plunger velocity does not always take the exact form of Figure 3. Figure 6 shows the results of a similar study on a sample of  $\bar{M}_w = 180,000$  which gave oscillating flow between 3.0 and 6.0 in./min. Although there is evidence of a frequency maximum, a symmetrical curve was not obtained. The proportion of the cycle representing decreasing load increased to only 60% at 5.75 in./min. The shape of the hysteresis envelope in the flow curve clearly affects the results obtained.

### Relation to Flow Curve

The results obtained are consistent with the interpretation of oscillating flow as a series of recurring shifts between the two branches of the flow curve<sup>4</sup> and initiation through a mechanism involving yielding or a disentanglement of molecules.<sup>1,3</sup> At a plunger velocity within the oscillating flow range, the cycle begins as shear stress increases along the segment

A-B of Figure 1. When the upper critical shear stress is reached, yielding or chain disentanglement occurs. Flow then shifts to the right-hand branch, and stress decreases along C-D as the melt flows through the capillary at a rate greater than the plunger velocity. Re-entanglement of molecules occurs as stress decreases to the lower critical value and flow reverts to the left-hand branch to complete the cycle.

For the data at low plunger velocities in Figure 3, re-entanglement apparently occurs rapidly. Therefore, in this region, frequency at a given melt depth increases with increasing plunger velocity. However, as the plunger velocity more closely approaches the rate of flow of polymer on the descending branch of the flow curve, the molecules remain disentangled a proportionately longer time, and frequency decreases with plunger velocity until the two rates are matched and oscillation ceases.

For many samples studied, "melt fracture," characterized by severe extrudate distortion, has been noted when the shear stress again reached the upper critical value at shear rates above those where oscillating flow stopped. This could not be established accurately because of the difficulty of deciding what degree of distortion constituted melt fracture. However, the observation suggests the two phenomena may be related but the manifestation is different because of the different time scales involved.

### FACTORS AFFECTING OSCILLATING FLOW REGION

The critical shear stress and shear rate were determined for over 50 samples of commercial high-density polyethylenes and copolymers. While the majority of the samples were produced by the Standard Oil Company (Indiana) process, the group included 15 samples produced by the Phillips process and several produced by the Ziegler process. Shear rates for the onset of oscillating flow ranged from 400 to nearly 4,800  $\text{sec.}^{-1}$  among the various samples. However, the uncorrected shear stress for oscillating flow varied only between  $2.9 \times 10^6$  and  $3.3 \times 10^6$   $\text{dyne/cm.}^2$ . The average value for all samples was  $3.1 \times 10^6$   $\text{dyne/cm.}^2$ . The shear stress variations were random and could not be correlated with melt index, polymerization process, or whether the sample was a homopolymer or copolymer.

No high-density polyethylene or copolymer samples have been encountered in which the shear stress significantly exceeded the given range without exhibiting oscillating flow under the experimental conditions used. Therefore, the critical shear stress for oscillating flow at best varies over a very narrow range and may well be the same for all high-density polyethylene samples. Additional evidence to this effect will be presented later.

If the shear stress for oscillating flow is the same for all samples, then the shear rate at this point could be expected to be a function of the molecular

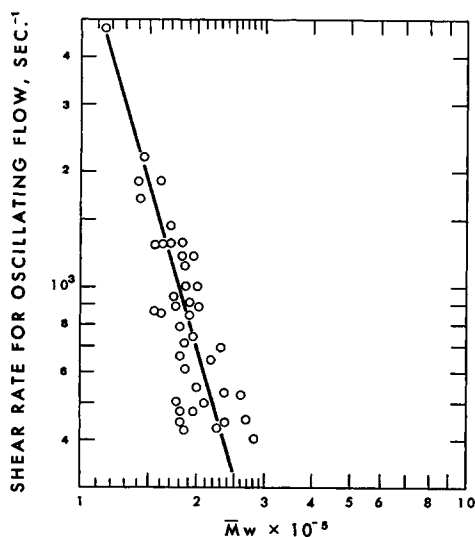


Fig. 7. Dependence of shear rate for onset of oscillating flow on molecular weight;  $L/D = 40$ ,  $T = 190^\circ\text{C}$ .

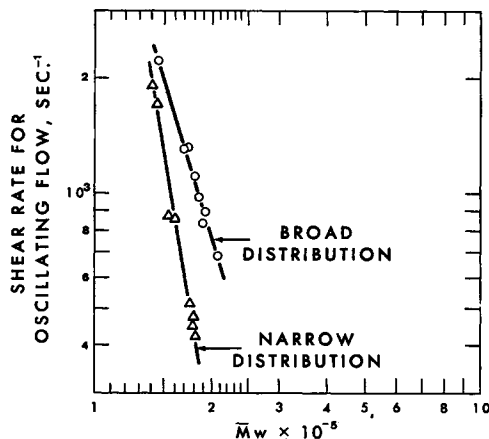


Fig. 8. Effect of molecular weight distribution on shear rate for oscillating flow;  $L/D = 40$ ,  $T = 190^\circ\text{C}$ .

weight and/or molecular weight distribution of various samples. Figure 7 shows that the shear rate for oscillating flow depends strongly on  $\bar{M}_w$ . The data are for the same series of samples mentioned above, with some overlapping data points omitted for clarity.

The scatter in the data is due to the influence of a second factor—molecular weight distribution. Two series of high-density polyethylenes produced by the Standard Oil Company (Indiana) process were used to establish this point. The two series differed significantly in distribution at a given average molecular weight as a result of intentional process



modifications but did not differ significantly in structure. Figure 8 shows that broadening the distribution at a given average molecular weight markedly increases the shear rate for the onset of oscillating flow. This is because the shear stress at a given shear rate is lower for a broad distribution sample than for a narrow one of the same  $\bar{M}_w$ . Consequently, the critical shear stress is shifted to higher shear rates. A reduction in  $\bar{M}_w$  produces a similar trend.

The effect of certain experimental factors on the shear rate for oscillating flow was investigated by using three high-density polyethylenes of  $\bar{M}_w = 180,000$ – $190,000$  but differing appreciably in distribution. Figure 9 shows

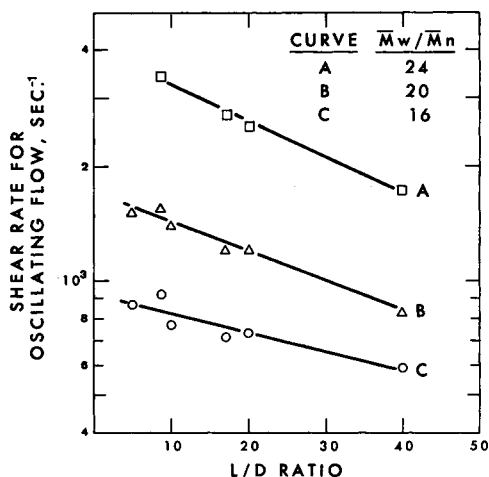


Fig. 9. Effect of  $L/D$  ratio on shear rate for oscillating flow as a function of distribution;  $T = 190^\circ\text{C}$ .

that the shear rate for oscillating flow increases with a decrease in the length-to-diameter ( $L/D$ ) ratio of the capillary and again emphasizes the profound effect of molecular weight distribution. The uncorrected critical shear stress also increased with decreasing  $L/D$  ratio. However, application of capillary end-effect corrections<sup>11</sup> gave a corrected value of  $2.9 \times 10^6$  dyne/cm.<sup>2</sup> for the critical shear stress for all three samples. This finding, together with those mentioned earlier, supports the concept of a common upper critical shear stress for high-density polyethylenes.

While the upper critical shear stress apparently is independent of molecular weight distribution, the lower one is not. As the lower critical shear rate increases, the lower critical shear stress approaches the upper one. At the same time, the ratio of maximum to minimum shear rates for oscillating flow decreases. Thus, broadening the molecular weight distribution decreases the area of the hysteresis loop between the two branches of the flow curve. A decrease in  $\bar{M}_w$  with a resultant increase in lower critical shear rate appears to have a similar effect.

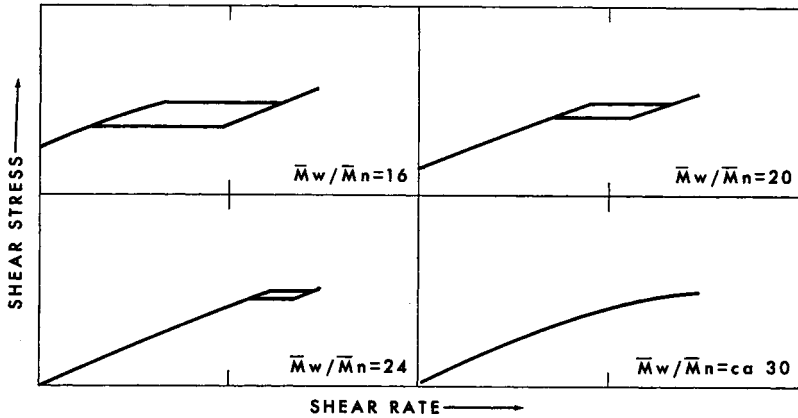


Fig. 10. Effect of molecular weight distribution on hysteresis area;  $L/D = 40$ ,  $T = 190^\circ\text{C}$ .

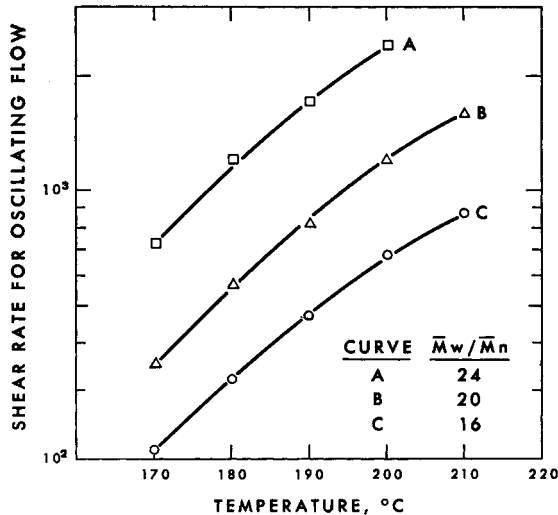


Fig. 11. Effect of temperature on shear rate for oscillating flow as a function of distribution;  $L/D = 40$ .

The effect of distribution on hysteresis area is shown in Figure 10. The curves are for the three samples used for the capillary geometry study, plus a laboratory sample of still broader distribution. The melt index for all samples was  $0.5 \pm 0.05$ . The procedure of continuously increasing the plunger speed was used to establish the shear rates for both the onset and cessation of oscillating flow. For the laboratory sample, the shear stress was still slightly below the critical value at  $3,000 \text{ sec}^{-1}$ , and there was no evidence of oscillating flow up to this point. Thus, by properly altering the distribution at a given melt index, the upper critical shear stress can be displaced to quite high shear rates. Here, again, is an example where melt

index alone is an insufficient basis for comparing the processing behavior of resins.

The effect of temperature on the lower critical shear rate is shown in Figure 11. The critical shear rate is approximately doubled by an increase of 20°C. The uncorrected upper critical shear stress increased in a nearly linear manner at a rate of about  $2 \times 10^4$  dyne/cm.<sup>2</sup>/°C.

The capillary entrance angle has only a slight effect on the critical shear rate and shear stress at the onset of oscillating flow. Both critical shear rate and uncorrected critical shear stress tended to decrease somewhat as the entrance angle was increased from 60 through 90 to 180°. At  $L/D = 10$ , the critical shear rate for a 180° entrance was about 20% below that for a 60° entrance. The critical shear stress for a 90° entrance was about 10% less than for a 60° entrance, but there was little further change in going to 180°. At  $L/D = 40$ , the critical shear rate for a 180° entrance was about 10% below that for a 60° entrance and there appeared to be no significant effect upon the critical shear stress.

### CONCLUSIONS

The upper critical shear stress for oscillating flow varies only slightly, if at all, between various high-density polyethylenes and copolymers. However, the lower critical shear stress and the range of shear rate for oscillating flow are well-defined functions of molecular weight and/or molecular weight distribution. Careful delineation of the hysteresis area can be of value in comparing the molecular weight distribution of various samples. The hysteresis area can conveniently be established by continuously increasing the velocity of the rheometer plunger.

From the processing standpoint, the occurrence of oscillating flow can generally be avoided by choice of a resin with the proper balance of molecular weight and molecular weight distribution. For a given sample, selection of operating temperature and die geometry variations provide a further measure of control.

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### Résumé

On a étudié le comportement de l'écoulement oscillant d'une variété d'échantillons de polyéthylène et de copolymères de haute densité dans un rhéomètre à vitesse de déplacement constante. Quelle que soit la vitesse du plongeur, la période des oscillations décroît linéairement avec la profondeur de la phase fondue ce qui suggère un phénomène de résonance. Quand la vitesse du plongeur augmente, la forme de l'onde de charge change d'une manière régulière ce qui indique une augmentation progressive du temps que chaque cycle passe du côté droit de la courbe d'écoulement. Une petite différence a été trouvée dans la tension de cisaillement à laquelle l'écoulement oscillant commence pour des échantillons qui ont des poids moléculaires, des distributions de poids moléculaires et des procédés de fabrication différents. Quoi qu'il en soit, la vitesse de cisaillement à laquelle l'écoulement oscillant commence, dépend fortement à la fois du poids moléculaire et de la distribution. L'écoulement oscillant est déplacé vers des vitesses de cisaillement plus élevées par une distribution plus large, par une réduction du poids moléculaire, par une augmentation de la température ou une diminution du rapport  $L/D$  du capillaire.

### Zusammenfassung

Das Verhalten einer Reihe von Proben von Polyäthylen hoher Dichte und Copolymeren bei oszillierendem Fliessen wurde in einem Rheometer für konstante Verschiebungsgeschwindigkeit untersucht. Bei jeder Kolbengeschwindigkeit nimmt die Oszillationsperiode linear mit der Schmelztiefe ab, was für ein Resonanzphänomen spricht. Mit zunehmender Kolbengeschwindigkeit ändert sich die Belastungswellenform in regelmässiger Weise und lässt eine stetige Zunahme des am rechtsseitigen Zweig der Flusskurve verbrachten Bruchteils eines jeden Zyklus erkennen. Für die Schubspannung beim Einsetzen des Oszillationsfliessens bestehen bei Proben mit verschiedenem Molekulargewicht, verschiedener Molekulargewichtsverteilung und verschiedenen Verarbeitungsbedingungen nur geringe Unterschiede. Dagegen hängt die Schubgeschwindigkeit für Einsetzen des Oszillationsfliessens stark vom Molekulargewicht und seiner Verteilung ab. Das Oszillationsfliessen wird durch Verbreiterung der Verteilung, Herabsetzung des Molekulargewichts, Temperaturerhöhung oder Herabsetzung des  $L/D$ -Verhältnisses der Kapillare zu höheren Schubgeschwindigkeiten verschoben.

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