Orientation Number in elongational flow of polymer melts and solutions

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Introduction

Extensional deformation plays a dominant role in many processing operations that involve rapid shape change [1], including intentional orientation development processes such as fiber spinning, film blowing, blow molding, and melt blowing. Consequential orientation development processes, including injection molding and profile extrusion, are also affected. There are different types of elongational rheometers for directly measuring the elongational viscosity of polymer melts and solutions, each having its advantages and limitations. The primary type of direct measurement devices that are widely used are the Meissner-type extensional rheometers [2,3]. The commercial versions of this type of devices are referred to as the Rheometrics Extensional Rheometer (RER) and Rheometric Scientific Extensional Melt Rheometer (RME). These Meissner-type devices feature the suspension of a sheet of polymer melt on either an oil bath or an air bath, and then deformation essentially without shear at the surface with an effectively unconstrained surface. To achieve a constant elongational strain rate, the sheet is deformed at an exponentially increasing deformation rate. These devices are particularly effective at low elongational strain rates up to about one reciprocal seconds, Hencky strains at an upper limit of six (but usually lower, such as three or four due to sample failure), and at temperatures for which the polymer melt is very viscous or viscoelastic, usually near the melting point. Fiber drawing on an Instron or similar device is also accomplished in a shear free environment, and like the Meissner-type devices, is dependent upon a very viscous or viscoelastic melt. The Meissner-type and Instron devices are sensitive to melt imperfections and flow instabilities, particularly at higher Hencky strains corresponding to longer times and more extensive deformation. All of the devices are excellent within their temperature, strain, and strain rate ranges, and generally give comparable results in areas of common testing conditions.

Previous research done by the authors [1, 4, 5] has shown that an essentially purely elongational flow of polymer melts or solutions is apparently generated using hyperbolic (previously referred to as semi-hyperbolic) convergent dies in a capillary rheometer under certain testing conditions. This experimental technique enables measurement of the elongational viscosity of polymer melts and solutions at the processing strain rates and temperatures of many intentional orientation development processes. The current hyperbolic die devices enable Hencky strains of 4 to 7, and strain rates to nearly 1,000 reciprocal seconds. The upper temperature limit for the hyperbolic dies is determined by degradation or, for lower molecular weight polymers, by viscosity related gravitational effects. The lower temperature limit is determined by the pressure required to force the melt to flow through the die. Intentional orientation development processes for polymer melts and concentrated solutions would typically have the initial melt temperature 30 to 50°C above the melting point or solidification temperature. Hencky strains would range from about four to five and elongational strain rates in the hundreds of reciprocal seconds for solution spinning and some melt drawing of fibers and films, to Hencky strains of nine to ten and elongational strain rates in the lower thousands for melt blowing nonwovens. These processing ranges are generally within the limits of the hyperbolic die technique.

The authors of this report have noticed that for some polymer melts the elongational viscosity data from hyperbolic die technique are in an almost perfect agreement with the data obtained by using the Meissner-type device or Instron techniques. They also noticed some differences, for other polymer melt samples.

In this report, a modified Weissenberg type number, Orientation number, is suggested to explain the agreement and disagreement between the elongational viscosity data measured by different techniques. According to the value of this number, the whole flow regime can be devided in two domains. At low orientation numbers, the flow is in a relaxation dominant regime, as compared with the orientation dominant flow, generally at orientation numbers higher than one.

Flow through a hyperbolic convergent die

The theoretical foundation for the hyperbolic die technique to characterize the elongational rheology of polymer melts and solutions was established previously [1,4]. Hyperbolic convergent dies were designed to generate a constant elongational strain rate throughout the channel under appropriate processing conditions. This is accomplished by machining the flow channel surface area to conform to the equation

$$r^2 = \frac{A}{z + B} \qquad (1)$$

where z is the axial flow direction, r is the radius of the flow channel and A and B are geometry-defined constants. A is controlled by the convergence of the channel and B is very small. The four hyperbolic convergent dies used in this research had Hencky strain, ε_H , of 4, 5, 6, and 7. The Hencky strain is defined as:

$$\varepsilon_H = \ln\left(\frac{r_0^2}{r_e^2}\right) \qquad (2)$$

where r_o is the entrance radius and r_e is the exit radius. For a constant volume process this is equivalent to the natural logarithm of the ratio of the die entrance area to exit area. Convergent dies of Hencky strain 4, 5, 6, and 7 correspond, respectively, to area reductions of 55/1, 150/1, 400/1 and 1,100/1.

Processing conditions that cause the flow to be in an orientation dominant regime result in slip at the wall being induced, and the flow is then in an essentially purely elongational flow. Under these conditions, when the melt flows through the hyperbolic channel, the interface between the polymer melt or solution and the die wall may be viewed as a set of streamlines experiencing the same conditions. Furthermore, the hyperbolic shape is one that provides a constant elongational strain rate, and the flow is a linearly accelerating plug flow.

The elongational viscosity can be calculated with the following equation

$$\eta_e \equiv \frac{\Delta P}{\dot{\varepsilon}\varepsilon_H} \tag{3}$$

where ΔP is the pressure drop between the entrance and die exit and $\dot{\varepsilon}$ is the elongational strain rate defined by equation (4)

$$\dot{\varepsilon} = (v_0/L)(\exp \varepsilon_H - 1) \tag{4}$$

where L is the length of the die and v_0 is the entrance velocity. Detailed development of the above equations is given in [1]. The residence time in a hyperbolic die has been shown to be $t = \varepsilon_H / \dot{\varepsilon}$ [5].

Agreement between hyperbolic die technique and Meissner-type and Instron devices data

Elongational viscosity curves for a LDPE and PS, obtained by using a Meissner-type rheometer at ETH (Eidgenössische Technische Hochschule-Zürich) [6] and hyperbolic die technique at UTK, are presented in Figures 1 and 2. The elongational viscosities curves were obtained in UTK laboratory using the hyperbolic converging dies at Hencky strains of 4, 5, 6, and 7 and at ETH at Hencky strains of 1, 2, and 3. Very good agreement occurred for broad molecular weight distribution LDPE (Figure 1). For the PS sample there is a pretty good agreement at elongational strain rate arround 1 reciprocal seconds, as indicated by Figure 2.

Since there is only a small effect of temperature on the elongational viscosity of PIB, comparisons of tests made at different temperatures showed reasonable agreement with the results from a Meissner-type rheometer (Figure 3) and Instron fiber data (Figure 4) [7-9].

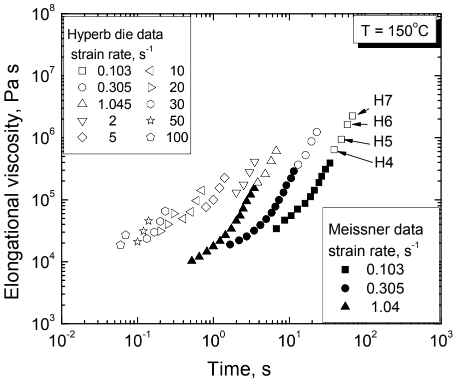

Figure 1. Meissner and hyperbolic LDPE.

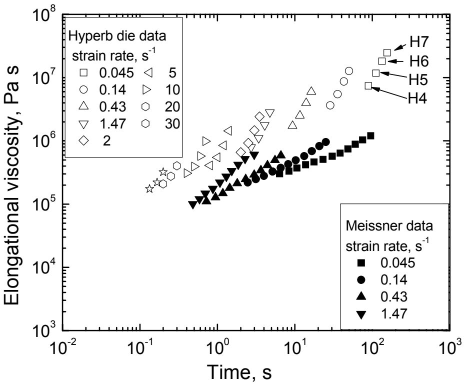

Figure 2. Meissner and hyperbolic PS.

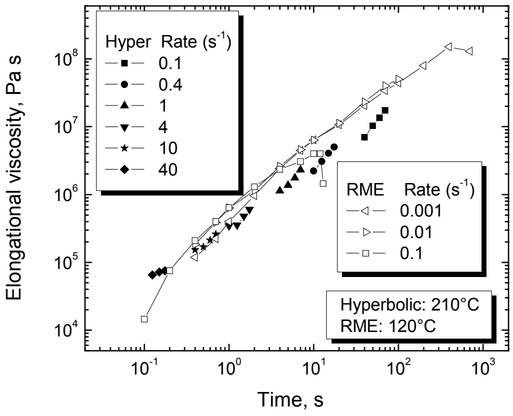

Figure 3. Meissner and hyperbolic PIB.

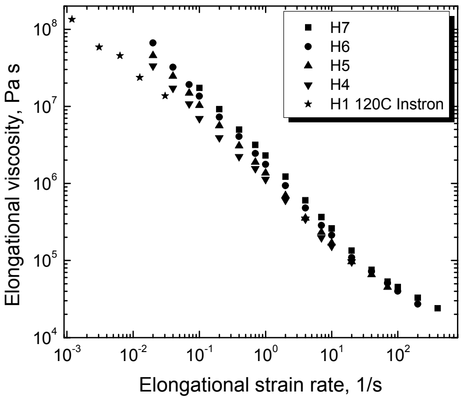

Figure 4. Instron and hyperbolic PIB.

Orientation number definition

It has been noted in our research with hyperbolic dies that, for some samples, there is an operating region for which there is more scatter in the data in an elongational strain rate range specific to that sample, and that the extrudate surface is disrupted in this narrow region. This observation, and the agreement between the results on the Meissner-type elongational rheometers and the hyperbolic die results for some samples and disagreement on others, suggest that there may be different flow regimes occuring. If there are different flow regimes present, then the relationships between the sample average relaxation time, elongational strain rate, and Hencky strain should be important. In order to test the hypothesis of different flow regimes, as well as the dependence on these variables, a modified Weissenberg number was defined, which is referred to herein as an **orientation number**:

$$N_{Or} = \lambda \dot{\varepsilon} \varepsilon_H \qquad (5)$$

N_{Or} is the orientation number, λ is a characteristic relaxation time, and, in this document, an average value was used as determined from the reciprocal of the cross-over point for the storage and dissipative moduli in dynamic shear rheology. It is possible that a different relaxation time is more appropriate due to the relative contribution from different molecular architecture chains. It is expected that imposed orientation should increase as any one of the terms in the product increases when the others are held constant. Ferguson and Hudson [7-9] predicted that the elongational rheology was dependent upon both the elongational strain rate and time (and therefore Hencky strain) and that a surface on a three dimensional plot of elongational viscosity versus elongational strain rate and time could be generated to display this effect. In many devices, the Hencky strain increases with process time. The product $\lambda \varepsilon_H \dot{\varepsilon}$ is probably more general than just for hyperbolic dies, particularly since the hyperbolic shape represents a minimum in the viscous dissipation term, $\boldsymbol{\tau} : \nabla \mathbf{v}$, and many systems would tend toward this minimum. Furthermore, the hyperbolic shape is implied by an assumption of a constant elongational strain rate in a shear free mode.

When the defined orientation number has a value of one, this probably indicates a near equality of the “forces,” i.e., a balance of the effects controlling the flow regime. The extent of orientation development should be proportional to $\dot{\varepsilon}\varepsilon_H$ and the relaxation is proportional to 1/λ, and therefore the ratio of the orientation development to the relaxation should be the orientation number, $\lambda \dot{\varepsilon} \varepsilon_H$. This suggests that there is a relaxation dominated flow for values less than one, and an orientation dominated flow for values greater than one, with a transition region near one. It is further suggested that slip at the wall in hyperbolic convergent dies occurs when the orientation number is greater than one in orientation dominant flows. Whereas at orientation numbers less than one, in a relaxation dominant flow, slip probably does not occur. If the transition occurs at a low Hencky strain in the Meissner-type devices, agreement results. However when the transition occurs at a higher Hencky strains, i.e., after extensive deformation and longer times, the Meissner-type devices do not indicate an increasing viscosity with time, perhaps indicating imminent failure of the samples. It should be noted that, in the Meissner-type devices, the Hencky strain increases with time, and a Hencky strain of 6 represents a 400/1 increase in length of the deforming sheet. Furthermore, to accomplish a constant strain rate in the Meissner-type and Instron devices, the deformation of the sample increases at an exponential rate. However, in the hyperbolic convergent die, the

Hencky strain is set by the degree of convergence and the samples are being pushed and compressed against the die wall, causing any instabilities and flaws to be compressed, and the samples do not fail as they pass through the transition region.

Processing implications. During processing, substantial orientation should be imposed if the orientation number is greater than one. The degree of orientation imposed during deformation should be a function of the orientation number. However the resultant orientation will be a function of both that imposed during orientation and the fraction retained as the material solidifies by transition to a crystalline or glassy state, or concentration change. Orientation induced crystallization should lock in orientation in the crystalline phase if the crystallinity is not lost after deformation; however the non-crystalline phase and non-crystallizable materials should begin to relax as deformation ceases, unless they have become glassy.

Theoretical evidence for orientation in hyperbolic dies

Modeling. In a recent paper by Feigl et al. [5], a finite element method was applied to model the flow of Newtonian PE melts flowing through the hyperbolically converging dies. The results showed that if the sample experienced full wall-slip within the die, as opposed to the usual no-slip boundary conditions of fluid mechanics, then the die could be used to measure a time-dependent “true” elongational viscosity. This analysis also showed that, if the usual no-slip boundary and no reduction in shear viscosity were assumed, then the device was not a valid tool for measuring true elongational viscosity.

The above-stated conclusions are summarized graphically in Figures 5 and 6 for flows through a hyperbolically converging die at six elongational strain rates, under the assumptions of Collier et al. [1, 10]. The simulations were conducted using a finite element method described by Bernstein and co-workers [11-13], applied to a well-characterized LDPE melt [14-18]. The constitutive equation used to model the LDPE melt was a factorized Rivlin-Sawyers expression [19], using a discrete series of eight relaxation modes [5]. In these figures, the hyperbolic die is 25 mm in length, beginning at z=0 and ending at z=25 mm.

In Figure 5, the elongation rates generated by the die along streamlines of various inlet radii for a flow rate of 10 mm^3/s are depicted under typical no-slip boundary conditions. Note that the horizontal dashed line represents the constant value of the elongation rate that is assumed throughout the die under the assumptions of Collier et al. [1, 10]. Note also that the elongation rate decreases as the radial position of the streamline increases; i.e., as the wall is approached, where shear effects begin to dominate the flow field. Near the die walls, a substantial boundary layer of shear flow is present, which extends into the bulk tube flow by up to 35% [5]. Nevertheless, along all streamlines, the elongation rate is approximately constant, with all streamlines averaging out over the value obtained by the analysis of Collier et al. Consequently, if the fluid does indeed experience full no-slip conditions throughout the die, it cannot be used to measure true elongational viscosities, although it can still give good measurements of an “effective” elongational viscosity; however, this should not be construed as a true material property of the test fluid.

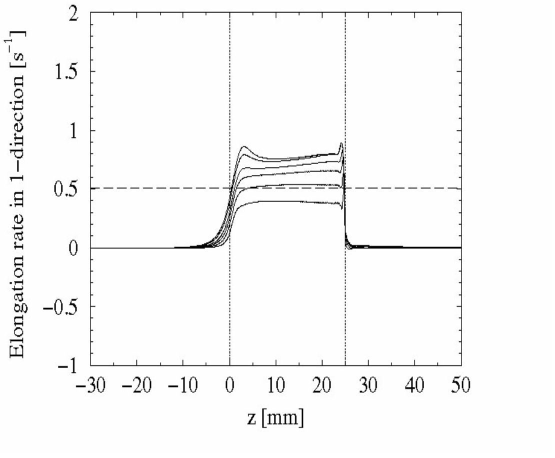

Figure 5. Elongation rates along various streamlines of the LDPE melt with no-slip boundary conditions.

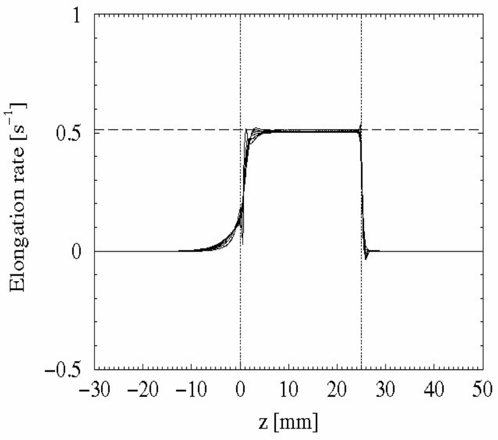

Figure 6. Elongation rates along various streamlines of the LDPE melt with full wall slip boundary conditions.

In Figure 6, the elongation rates generated by the die are presented under the assumption of full-slip conditions at the die walls and under the same conditions of Figure 1. In this plot, it is clearly seen that after an entry region of about 5 mm for this fluid and flow rate, all streamlines attain the same value for the elongation rate, which is constant up to the die exit. Furthermore, this constant value is exactly the same as calculated under the assumptions of Collier et al. As a consequence of this, under full-slip conditions, it should be possible to use this die to measure the true elongational viscosity of viscoelastic fluids.

Wall shear stress in hyperbolic convergent dies effect on pressure. Let us assume that there are shear effects at the wal of the hyperbolic die. Then the pressure difference due to the wall shear stress can be calculated from rheological characteristics of different resins and compared with pressure differences calculated from the elongational viscosity. A Carreau rheological model was used to incorporate material characteristics and the pressure drop due to shear in a convergent die was obtained by integrating the shear stress at the wall over the length of the die. The material parameters of four polymer melts (two PPs, PE, and PIB) with significant difference in rheological behavior were used at low and high elongational strain rates. The range included the relaxation dominant and/or the orientation dominant regimes for the polymers. The maximum contribution of the wall shear stress was 1.16% for the PIB and the lowest was 0.14% for a melt blowing grade PP. Apparently most of the pressure difference recorded in an elongational viscosity measurement using a hyperbolic die seems to be due to orientation effects that requires a corresponding pressure head even in the relaxation dominant regime.

Experimental evidence of hyperbolically convergent flow induced orientation

Orientation developed due to elongational flow in PE. Also consistent with the concept of having an orientation dominant regime at orientation numbers greater than one is the high degree of orientation achieved on a low density polyethylene (LDPE) sample (Soltex g60-42) that had a melt index of 0.42. [20]. This LDPE was subjected to a Hencky strain of 5.9 at an elongational strain rate of 800 s^{-1} through a conically convergent die and crystallized prior to exiting from the die. This material was oriented in the convergent section and then crystallized by imposing a sharp temperature gradient in a downstream constant diameter capillary section. Dr. John Southern analyzed the filament formed independently at what was the Pensacola Monsanto Research Center, and he reported that the extrudates had a Hermann's orientation function of 0.996 (1.000 is perfect orientation and 0 is random) [20]. Furthermore, the material had mechanical properties comparable to the solid state extruded material being studied at that time, i.e., a higher degree of crystallinity, and an elevation in melting point of nearly 20^oC. The Orientation number as defined in this proposal would be at least a thousand or more, indicating flow well into the orientation dominant regime.

Birefringence in hyperbolic and cylindrical dies spun fibers. By using the ACER driven spinning line fibers were produced in the Rheology Laboratory at UTK using both cylindrical and hyperbolic dies of the same exit diameter. Retardation was measured with an Olympus Berek Compensator and birefringence calculated with equation

$$\Delta n = \frac{R}{d} \qquad (6)$$

where R is retardation and d diameter of the fiber. It was found that the birefringence of the fibers spun through hyperbolic die was 0.01858, as compared with 0.00723 for the fibers spun through a cylindrical die.

Orientation effect on shear viscosity: Preliminary results at UTK (Figure 7), suggest that the orientation that develops in hyperbolic dies lowers the shear viscosity of the polymer melt by increasing amounts at higher shear rates. These results were obtained

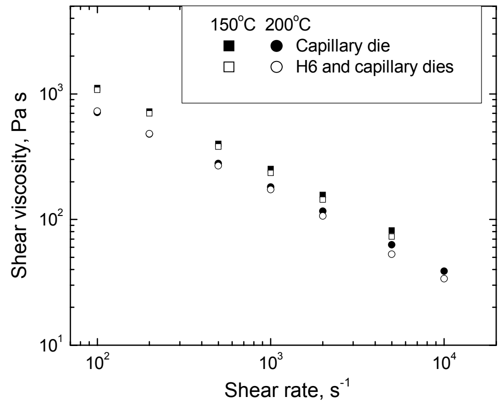

Figure 7. Orientation Effect on Shear Viscosity.

with a special adaptor for the ACER capillary rheometer that enabled two dies to be placed in-line at the discharge of the barrel. For these preliminary experiments, the polyethylene (the same as that in Figure 1) melt first passed through a Hencky 6 die and then through a flat entry straight capillary die. The discharge diameter of the hyperbolic convergent die and the diameter of the capillary die were both 1 mm. The orientation that develops should increase with flow rate through the die, i.e., with elongational strain rate. The driving pressure drop was measured with the Hencky 6 die alone, the flat entry capillary die alone, and with the capillary die entry in-line with the exit from the hyperbolic convergent die. The pressure drop through the hyperbolic die at a given flow rate, i.e., strain rate, was assumed to be the same, whether or not the capillary die was at the exit of the convergent die. Apparently, the increase in orientation decreases the resistance to flow by making it easier for sliding flow to occur, and probably retards the relaxation of the polymer molecules. This should result in an even lower shear flow contribution to pressure drop than that calculated for shear effects only in the hyperbolic dies, the latter being about 5% of the observed pressure drop. This could imply that the calculated elongational viscosity prior to slip at the wall is a reasonable approximation, even in the relaxation dominant regime.

Conclusions

Theoretical and experimental evidence is presented to support the concept of orientation induced in polymeric liquids by the flow in the hyperbolic convergent dies and an orientation number was defined as the product of the average relaxation time, the Hencky strain, and the elongational strain rate, that can be used to assess the character of the elongational flow. This orientation number suggests that the flow is in a relaxation dominant mode below a value of one, an orientation dominant flow at values above one and in a transition at values near one.

In the hyperbolic dies, slip at the wall is apparently induced when the orientation number exceeds one. If the transition occurs at a low Hencky strain in the Meissner-type devices agreement results; however disagreement results when the transition occurs at a higher Hencky strains corresponding in the

Meissner-type devices to longer times and higher extensions perhaps indicating imminent failure of the samples.

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