

# Elongational Rheology by Different Methods and Orientation Number

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**ABSTRACT:** The elongational rheology of polymer melts was measured by the authors using the hyperbolic convergent die technique and the results were compared with the same samples measured using a Meissner type device or an Instron tensile tester. Polyethylene and polystyrene samples were tested at Eidgenössische Technische Hochschule-Zürich or Virginia Polytechnic Institute, and the polyisobutylene was part of a world wide "Round Robin" comparison. A modified Weissenberg number, i.e., an Orientation number, is suggested to explain the agreement between techniques for some samples and lack of agreement for others. The Orientation number is the product of Hencky strain, elongational strain rate, and average relaxation time. When it is less than one a relaxation dominant regime results, when greater than one an orientation dominant regime results, and near one a transition occurs. For the hyperbolic convergent die technique, in which the polymers are transversely con-

strained by the walls, the extrudates in the transition regime have slight surface defects and the pressure fluctuates more than in the other regimes. If the transition occurs after significant time, i.e., lower elongational strain rates, in the free boundary Meissner and Instron devices, the samples apparently experience more relaxation since unconstrained transversely (and perhaps differential thinning) leading to disagreement with the hyperbolic die measurements. The orientation related body forces are magnitudes larger than the shearing forces and cause slip at the wall in the hyperbolic dies in the orientation dominant regime. Even in the relaxation dominant regime, shear near the wall is a minor contributor to the necessary pressure force. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3551–3561, 2007

**Key words:** elongational rheology; orientation number; hyperbolic convergent die

## INTRODUCTION

Extensional deformation plays a dominant role in many processing operations that involve rapid shape change,<sup>1</sup> 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 focus of this article is on comparisons of direct measurement devices; indirect techniques and techniques for lower concentration solutions, although valuable are outside the scope of this article. The primary type of direct measurement devices that are widely used are the Meissner-

type extensional rheometers.<sup>2,3</sup> The commercial versions of this type of devices are referred to as the Rheometrics Extensional Rheometer (RER) and Rheometric Scientific Extensional Melt Rheometer (RME). The 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 second, 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

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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. Although not part of this study, there is a new, promising technique for measuring elongational viscosities, e.g., the SER universal testing platform (Xpansion Instruments LLC) that features a vertical sample and rotating drums capable of Hencky strains to 4.5.<sup>4</sup> Deforming samples in the SER unit exhibit a hyperbolic shape, and as discussed later in this article that shape is characteristic of many elongational deformation processes.

Previous research done by the authors<sup>1,5-7</sup> has shown that an essentially pure elongational flow of polymer melts or solutions is apparently generated using hyperbolic (previously referred to as semihyperbolic) convergent dies in a capillary rheometer under certain testing conditions. Earlier work by Everage and Ballman<sup>8-10</sup> demonstrated that similar converging flow measurements in a sheath/core geometry yielded results comparable to the Meissner-type devices. Our research has extended the research to demonstrate that under proper conditions that a sheath layer is not necessary and as these conditions are approached, the shear contribution is small, yet agreement exists. The Meissner and the convergent flow techniques (including hyperbolic) are steady in an Eulerian sense, but not in a Lagrangian sense. In these techniques the Hencky strain is increasing with time during flow. Therefore, the elongational viscosity measured in the convergent flow techniques is a Hencky strain averaged value, analogous to many fabrication processes. The hyperbolic die 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 hyperbolic die technique has been used to characterize polymer melts and nondilute solutions at elongational strain rates between  $10^{-1}$  and nearly  $10^3 \text{ s}^{-1}$ , and Hencky strains of four to seven. The upper temperature limit for the hyperbolic dies is determined by degradation or, for lower molecular weight polymers, by gravitational effects. The lower temperature limit is determined by the pressure required to force the melt or solution to flow through the die or by room temperature if die and reservoir cooling is not available. Intentional orientation development processes for polymer melts and concentrated solutions would typically have the initial melt processing temperature 30–50°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 9–10 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 and, as discussed in this article, within the orientation dominant flow regime. The orientation number introduced in this article indicates the dominant flow regime. Furthermore, since flow through the convergent dies is transversely constrained by the die walls, this measurement system does not allow as much relaxation and is not as sensitive to flow instabilities and sample defects as the free boundary, transversely unconstrained Meissner-type and Instron devices.

Part of the focus of this article is to suggest the relationships between measurements and the flow regime in which the polymer melt or concentrated solution responds to the imposed conditions. Polyethylene (PE) samples with different molecular characteristics, a polystyrene (PS) and a polyisobutylene (PIB) are studied in this article, all of which had been characterized in elongational deformation in other laboratories using other techniques. Corollary results in convergent dies are also included for a polypropylene (PP), and a PE that is crystallized after convergent flow and prior to exiting from the confined region demonstrating imposed orientation.

The authors of this article have noticed that for some polymer melts and testing conditions the elongational viscosity data from hyperbolic die technique are in excellent agreement with the data obtained by using Meissner-type devices or Instron techniques. They also noticed significant disagreement, for other polymer melt samples.

In this article, 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 divided in three 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, and an intermediate transition regime. The transition regime may be somewhat dependent upon molecular architecture.

## BACKGROUND

### 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 in this group.<sup>1,5,7</sup> Hyperbolic convergent dies were designed for the melt or solution to generate a constant elongational strain rate throughout the core under appropriate processing conditions. This is

accomplished by machining the flow channel surface area to conform to the equation:

$$R^2 = \frac{A}{z + B}, \quad (1)$$

in which  $z$  is the axial flow direction and  $R$  is the radius of the flow channel, which is a function of  $z$ .  $A$  and  $B$  are geometry-defined constants,  $A$  is controlled by the convergence of the channel and  $B$  is very small and therefore neglected in most of the analysis. The streamlines follow the same geometry and when full slip at the wall occurs and essentially pure elongational flow develops the pressure profile is a function of the potential function. The stream and potential functions in terms of  $z$ , the radial position,  $r$ , and the elongational strain rate,  $\dot{\epsilon}$ , are respectively:

$$\psi = -\frac{\dot{\epsilon}}{2} r^2 z \quad (2)$$

$$\Phi = \dot{\epsilon} \left( \frac{r^2}{4} - \frac{z^2}{2} \right). \quad (3)$$

The four hyperbolic convergent dies used in this research had Hencky strain,  $\epsilon_H$ , values of four, five, six, and seven. Hencky strain is defined as the natural logarithm of the ratio of the length to the original length, which for a constant volume process is also the natural logarithm of the area reduction. Therefore:

$$\epsilon_H = \ln \left( \frac{R_0^2}{R_e^2} \right), \quad (4)$$

where  $R_0$  is the entrance radius and  $R_e$  is the exit radius. The Hencky strains in the convergent dies of four, five, six, and seven correspond respectively, to area reductions of 55/1, 150/1, 400/1, and 1100/1.

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 pure elongational flow. Apparently, the body forces related to orientation development at these processing conditions are sufficient to overcome the wall related shearing forces and slip at the wall occurs. Momentum balance calculations indicate that the orientation related body forces are orders of magnitude larger than shearing forces and result in the high measured driving pressures. 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, under these conditions the hyperbolic shape is one that provides a constant elongational

strain rate, and the flow is a linearly accelerating plug flow.<sup>1</sup> The elongational viscosity is:

$$\eta_e \equiv \frac{\Delta P}{\dot{\epsilon} \epsilon_H}, \quad (5)$$

where  $\Delta P$  is the imposed pressure drop and the elongational strain rate is:

$$\dot{\epsilon} = \frac{v_0}{L} (\exp \epsilon_H - 1), \quad (6)$$

in which  $L$  is the centerline length of the die, and  $v_0$  is the inlet velocity.<sup>1</sup> The residence time in a hyperbolic die with slip at the wall has been shown to be<sup>6</sup>:

$$t_r = \epsilon_H / \dot{\epsilon} \quad (7)$$

This equation is also applicable to the Meissner-type devices. As discussed later in this article, under the conditions used in this study, when slip at the wall does not occur in the hyperbolic dies, the effect of shear is small and eq. (7) is an approximation of the average residence time and could lead to some disagreement in the data.

## 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 specific to that sample and die, and that the extrudate surface is slightly disrupted in this region but not at either lower or higher elongational strain rates. This observation and the agreement between results on the Meissner-type elongational rheometers and the hyperbolic die results for some samples and disagreement on other, suggest that there may be different flow regimes. 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. To test the hypothesis of different flow regimes and the dependence on these variables, a modified Weissenberg number was defined that is referred to herein as an Orientation number:

$$N_{OR} = \lambda \dot{\epsilon} \epsilon_H, \quad (8)$$

where  $\lambda$  is a characteristic relaxation time, and in this article an average value was used as determined from the reciprocal of the crossover point angular velocity 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 archi-

texture chains. As noted earlier,  $\varepsilon_H$  is the Hencky strain and  $\dot{\varepsilon}$  is the elongational strain rate. Furthermore, it is expected that imposed orientation should increase as any one of the terms in the product increases when the others are held constant. Furthermore, Ferguson et al.<sup>11,12</sup> and Odriozola<sup>13</sup> predicted that the elongational rheology was dependent upon both the elongational strain rate and time (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  $\lambda\dot{\varepsilon}\varepsilon_H$  is probably more general than just for hyperbolic dies, particularly, since the hyperbolic shape is implied by an assumption of a constant elongational strain rate in a shear free mode. Furthermore, the hyperbolic shape represents a minimum in the viscous dissipation term,  $\tau:\nabla v$  and many systems would tend toward this minimum.

When the defined orientation number has a value of one, this probably indicates a near balance of the effects controlling the flow regime. The orientation development should be proportional to  $\dot{\varepsilon}\varepsilon_H$ , the relaxation is proportional to  $1/\lambda$ , and therefore the ratio of the orientation development to the relaxation should be the orientation number as noted to be  $\lambda\dot{\varepsilon}\varepsilon_H$ . This suggests that there is a relaxation dominated flow for values less than one, and an orientation dominated flow with 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. Conversely, at orientation numbers less than one in a relaxation dominant flow, slip probably does not occur and relaxation is inhibited by the transverse constraints of the die walls. At orientation numbers less than but approaching one, the orientation development related body forces should cause the velocity profiles to approach the profiles for slip at the wall.

In both the Meissner-type devices and the hyperbolic dies the Hencky strain experienced by the fluid elements increases with time. The data from both techniques agree when the transition from relaxation dominant to orientation dominant flow occurs at a low Hencky strain in the Meissner-type devices. However, when the transition occurs at a higher Hencky strains for the samples in the free boundary Meissner-type devices, i.e., after extensive deformation and longer times, the samples may have relaxed significantly since they are transversely unconstrained. They have also thinned considerably perhaps even 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 six represents a 400/1 decrease in thickness 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 system the overall Hencky strain in a given die is set by the degree of convergence and the value of the Hencky strain increases through the die. In hyperbolic dies the samples are transversely constrained by the die wall inhibiting relaxation, causing any instabilities and flaws to be compressed, and preventing failure of the samples as they pass through the transition region. The conical shape in the hyperbolic dies also lends more stability to this system since the Hencky strain is related to the square of the transverse direction (diameter), whereas for the sheet structures with an essentially constant width of the Meissner-type devices the Hencky strain is related to the thickness to the first power. Therefore the thinning of the samples in the Meissner-type devices is a stronger function of Hencky strain than the samples in the hyperbolic dies.

## PROCESSING IMPLICATIONS

During processing, significant 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 crystallization or vitrification by cooling, concentration change or reaction. Orientation induced crystallization should lock in orientation in the crystalline phase if the crystallinity is not lost after deformation; however the noncrystalline phase and noncrystallizable materials should begin to relax as deformation ceases, unless they have vitrified.

As shown previously<sup>1</sup> the elongational strain rate thinning behavior of the elongational viscosity causes the orientation development to asymptotically approach a limiting value as would be anticipated by molecular arguments. Besides being strain rate thinning the materials are also strain hardening.

It should be noted that the relaxation behavior is governed by a spectrum of relaxation times related to the molecular weight distribution of the material and the molecular architecture of the molecules, and only the average values for the relaxation time are reported herein. The relaxation time distribution can also be approximated from the dynamic moduli measurements using a spectral decomposition approach and this approach has been used to determine the molecular weight average and distribution for some of the polymers in this article.



TABLE I  
Characteristics of the Samples Provided by ETH

Polymer lot no., $T$ °C	Density at 20°C (kg/m <sup>3</sup> )	Density at $T$ °C (kg/m <sup>3</sup> )	Zero shear viscosity at $T$ , Pa s	MFI (g/10 min)	$M_n$ (g/mol)	$M_w$ (g/mol)	PI
LDPE 1810, S4918, 150°C	917	778	65,000	1.2	16,600	188,000	11.3
HDPE 870, S5011, 150°C	951	778	160,000	0.84	18,900	104,000	5.5
PS 158K, 939534574, 170°C	1050	979	195,000		125,000	336,000	2.85

## EXPERIMENTAL

The hyperbolic dies described in the background were substituted for the standard capillary dies in a Rheometric Scientific Advanced Capillary Extrusion Rheometer (ACER) (Rheometric Scientific, Inc., Piscataway, NJ). Four hyperbolic dies, each 20 mm in entry and external diameter and 25-mm long were used, manufactured separately by electro discharge machining to overall Hencky strains of four, five, six, and seven. A Rheometric Scientific (currently TA Instruments, New Castle, DE) Advanced Rheological Expansion System (ARES) rheometer was used to determine the dynamic shear rheology of the samples. Dynamic strain sweep tests were conducted to ascertain that the dynamic shear data was in the linear viscoelastic range and it was determined that the results were well within this range for the shear strain of one percent used in this study. As a result the crossover point angular velocity determined in dynamic frequency scans of the storage and dissipated moduli ( $G'$  and  $G''$ ) versus angular velocity was the reciprocal of the average relaxation time of each sample tested.

Details of the experimental techniques for the Meissner-type devices used at the other laboratories are given elsewhere.<sup>2,3,11,14</sup> The PE and PS samples and their molecular characteristics were supplied by the Meissner group at Eidgenössische Technische Hochschule-Zürich (ETH), and the Baird research group of Virginia Polytechnic Institute and State University (VPI). The PIB sample was provided by Dr. Hudson of the University of Strathclyde and has been characterized by other rheologists.<sup>10-12</sup> The PIB sample was tested in our laboratory at temperatures of 210, 220, 230, and 240°C.

The molecular characteristics of the ETH PE and PS samples are shown in Table I,<sup>14</sup> and the VPI PE samples in Table II.<sup>3</sup> Dynamic moduli, complex viscosity, and relaxation time (measured as the reciprocal of the crossover point angular velocity) measured at University of Tennessee (Knoxville, TN) for the two ETH PE samples are shown Figures 1 and 2. The relaxation times for the ETH and VPI samples measured at UTK and Orientation numbers calculated at UTK are given in Table III. The orientation numbers are calculated for an elongational strain rate of 1 s<sup>-1</sup> and Hencky strains of three and seven.

## RESULTS

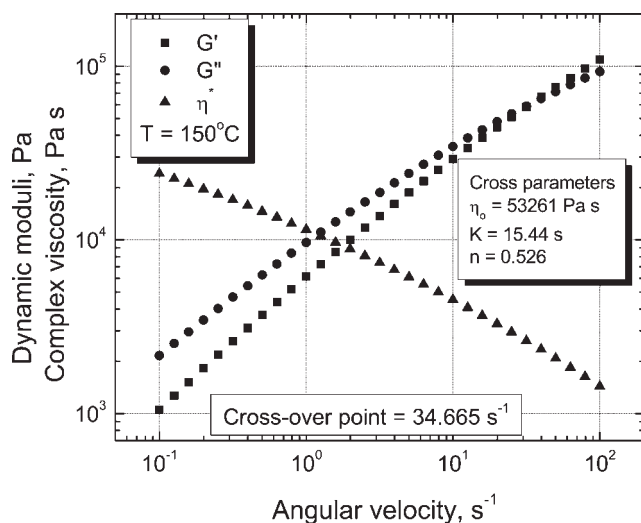
### Comparison of hyperbolic die, Meissner-type, and Instron devices data

Elongational viscosity curves for a LDPE and HDPE, obtained by using a Meissner-type rheometer at ETH<sup>14-16</sup> and hyperbolic die technique at UTK, are presented in Figures 3 and 4. The UTK laboratory elongational viscosities curves were obtained using the hyperbolic converging dies at Hencky strains of four, five, six, and seven, and generally lower Hencky strains are reported using the Meissner device at ETH. To use the same basis for the data, the hyperbolic converging die data were shifted by dividing by three, to be consistent with the Trouton factor used in the definition of the linear viscoelastic elongational viscosity<sup>14</sup> for the Meissner-type data. Very good agreement occurred for broad molecular weight distribution LDPE (Fig. 3). For the HDPE sample agreement indicated by Figure 4 of the data from the Meissner-type devices and the hyperbolic dies is not as good as it is for the ETH LDPE. How-

TABLE II  
Characteristics of the LDPE Samples Provided by VPI

Sample ID	Source	Density at $T$ °C (kg/m <sup>3</sup> )	MFI (g/10 min)	$M_w$ (g/mol)	PI	$M_z$ (g/mol)	LCB <sup>a</sup> (1/10 <sup>4</sup> °C)
PE-1	Dow affinity PL 1840	909	1.0	87,400	2.43	160,200	0.57
PE-2	Exxon exact 0201	902	1.1	88,700	2.14	158,900	0.79
PE-3	Exxon exact 3132	900	1.2	111,000	2.04	180,400	
PE-4	Dow affinity PL 1880	902	1.0	115,800	2.12	183,700	0.18
PE-5	Equistar NA 952	919	2.0	116,000	9.1		
PE-6	Mobil NTX 101	917	0.9	122,700	3.44	319,700	

<sup>a</sup> Long chain branches.



**Figure 1** Dynamic moduli and complex viscosity, ETH HDPE 870H at 150°C.

ever, it should be noted that the elongational strain rate increases from right to left in these figures and that the disagreement lessens at higher elongational strain rates. Good agreement of the VPI LDPE-5 (Figs. 5 and 6) similar to that for the ETH LDPE; however, the other VPI LDPE samples (see for example LDPE-2 in Fig. 6) do not show good agreement. Both the ETH LDPE and the VPI LDPE-5 have orientation numbers of one and larger at Hencky strains of three and higher as shown in Table III, whereas the ETH HDPE and the other VPI LDPE's<sup>4</sup> have at least an order of magnitude lower orientation numbers. The good agreement occurs in samples that pass through the transition region at an order of magnitude lower Hencky strain than the samples that show poor agreement. The PS data shown in Figure 7 also indicates increasing agreement at higher elongational strain rates.

There are at least three possible reasons for the poorer agreement of the samples with lower relaxation times and lower orientation numbers in the relaxation dominant regime. Since the transverse surfaces of the samples are unrestrained in the free boundary Meissner-type devices more relaxation of developing orientation could occur than could in the hyperbolic dies where the transverse surfaces are restrained by the die walls. As shown in Figure 4, the agreement is poorer at lower strain rates for this polymer with a relaxation time an order of magnitude lower than the polymer in Figure 3. However as the strain rate increases in Figure 3 the agreement improves. The second possible reason for the poor agreement in some samples may result from differential thinning of samples at increasing Hencky strains in Meissner-type devices. A hypothesis on the comparison of the agreement for the VPI PE-5

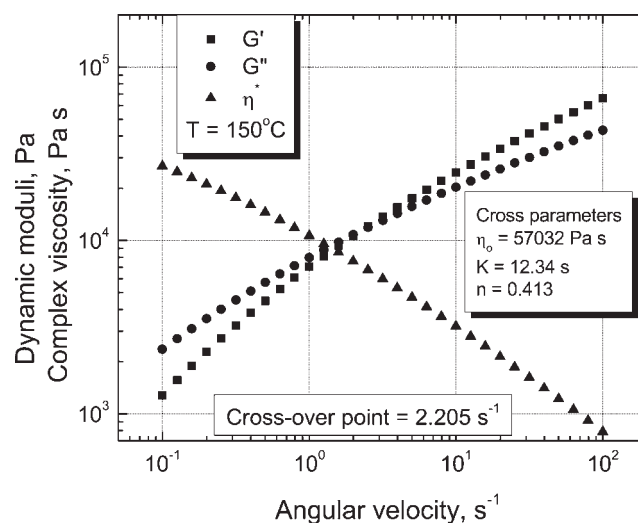
and lack of agreement for VPI PE-2 could be due to differential thinning of the VPI PE-2. The third reason for disagreement could be that the residence time calculated by eq. (7) is an average value when slip at the wall does not occur.

Comparison of the elongational viscosity of PIB tests although made at different temperatures showed reasonable agreement with the results from a Meissner-type rheometer (Fig. 8), since the elongational viscosity should be lower at higher temperatures. The Instron fiber data in Figure 9<sup>11-13</sup> is plotted versus strain rate rather than time and it also follows a consistent pattern. The elongational viscosity at a given strain rate increases with increasing Hencky strain, and all the data indicates strain rate thinning behavior, indicating strain hardening and strain rate thinning. Since the temperature and the Hencky strain of the Instron PIB data is much lower than the hyperbolic die data, additional comparisons of this data was not made.

### Theoretical evidence for orientation in hyperbolic dies

#### Modeling

In a recent article by Feigl et al.,<sup>6</sup> a finite element method was applied to model a PE melt flowing through the hyperbolic 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



**Figure 2** Dynamic moduli and complex viscosity, ETH LDPE 1810 at 150°C.

**TABLE III**  
Relaxation Times and Orientation Number

Polymer	PI	Relaxation time, s at 150°C	Orientation number at $\dot{\epsilon} = 1 \text{ s}^{-1}$ , $\epsilon_H = 7$	Orientation number at $\dot{\epsilon} = 1 \text{ s}^{-1}$ , $\epsilon_H = 3$
ETH LDPE1810	11.3	0.4540	3.178	1.362
ETH HDPE 870	5.5	0.0288	0.202	0.086
ETH PS 158K	2.9	1.473 <sup>a</sup>	4.753	2.037
VPI LDPE-1	1.0	0.0260	0.182	0.078
VPI LDPE-2	1.1	0.0280	0.196	0.084
VPI LDPE-3	1.2	0.0244	0.24	0.073
VPI LDPE-4	1.0	0.0253	0.177	0.076
VPI LDPE-5	2.0	0.3360	2.352	1.008
VPI LDPE-6	0.9	0.0292	0.204	0.088

<sup>a</sup> At 170°C.

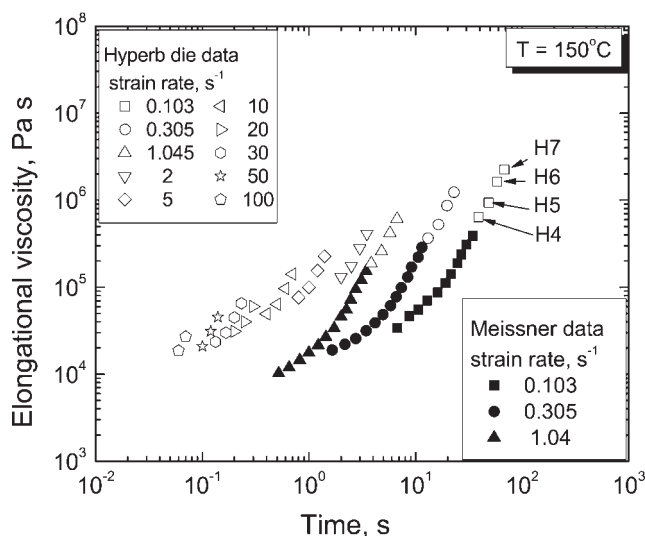
was not a valid tool for measuring “true” elongational viscosity.

The above-stated conclusions are summarized graphically in Figures 10 and 11 for flows through a hyperbolic converging die, under the assumptions of Collier.<sup>1,17</sup> The simulations were conducted using a finite element method described by Bernstein et al.,<sup>18–20</sup> applied to a well-characterized LDPE melt.<sup>21–25</sup> The constitutive equation used to model the LDPE melt was a factorized Rivlin-Sawyers expression,<sup>26</sup> using a discrete series of eight relaxation modes.<sup>6</sup> In these figures, the hyperbolic die is 25 mm in length, beginning at  $z = 0$  and ending at  $z = 25$  mm.

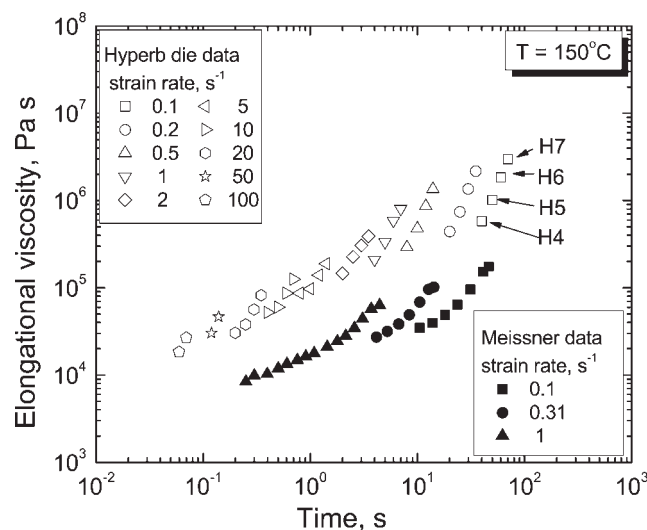
In Figure 10, the elongational strain rates generated by the die along streamlines of various inlet radii for a flow rate of  $10 \text{ mm}^3/\text{s}$  are depicted under typical no-slip boundary conditions. Note that the horizontal dashed line represents the constant value of the elongational strain rate that is assumed throughout the die under the assumptions of Collier, including slip at the wall.<sup>1,16</sup> The elongational strain 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%.<sup>6</sup> Nevertheless, along all streamlines, the elongational strain rate is approximately constant, with all streamlines averaging to near the value obtained by the full slip analysis of Collier et al.<sup>1</sup> 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.

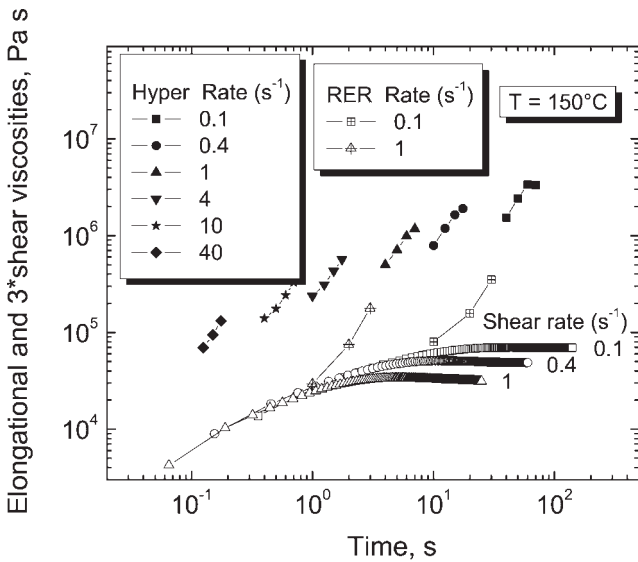
In Figure 11, the elongational strain rates generated by the die are presented under the assumption of full-slip conditions at the die walls and the other conditions the same as those of Figure 10. In this plot, it is shown that after an entry region of about 5 mm for this fluid and flow rate, all streamlines



**Figure 3** Elongational viscosity of ETH LDPE 1810 at 150°C.



**Figure 4** Elongational viscosity of HDPE 870H, at 150°C.

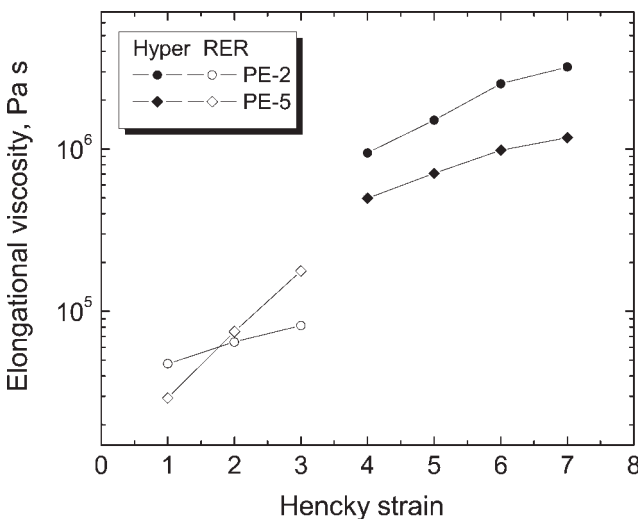


**Figure 5** Elongational viscosity versus time for PE-5 at 150°C.

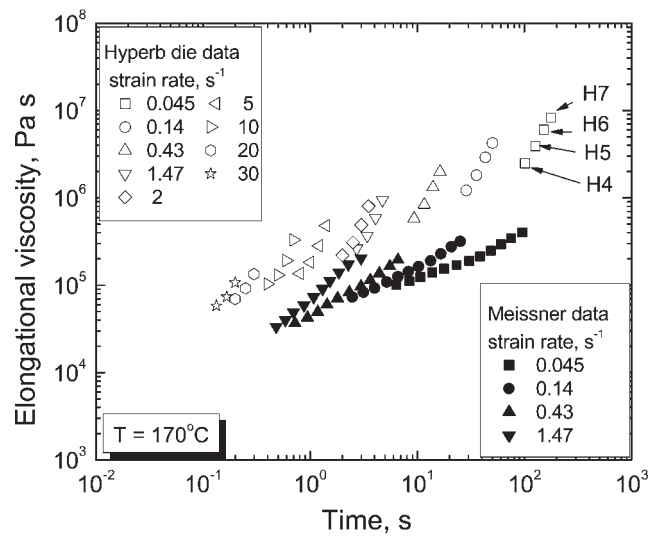
attain the same value for the elongational strain rate, which is constant up to the die exit. Furthermore, this constant value is the same as calculated under the assumptions of Collier et al.<sup>1</sup> As a consequence of this, under full-slip conditions, it should be possible to use this die to measure the true elongational viscosity of viscoelastic fluids.

Wall shear stress in hyperbolic convergent dies effect on pressure

If it is assumed that there are shear effects at the wall of the hyperbolic die, the pressure difference due to the wall shear stress can be calculated and compared with measured pressure differences from which the

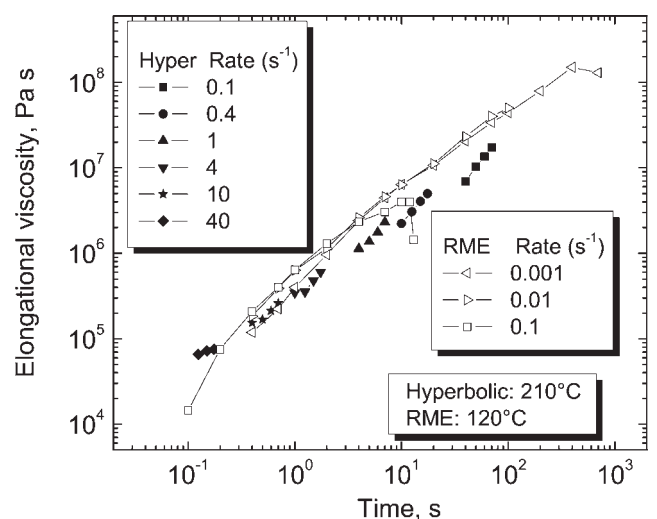


**Figure 6** Elongational viscosity (Meissner-type and Hyperbolic) for VPI PE-2 and PE-5 at 150°C and 1 s<sup>-1</sup>.



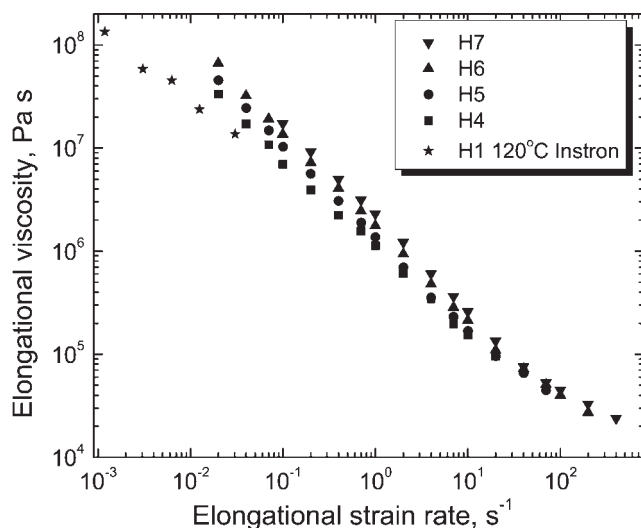
**Figure 7** Elongational viscosity of PS 158K, at 170°C.

elongational viscosities are determined. 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 differences in rheological behavior were used at low and high elongational strain rates. The range included relaxation dominant, transition, and 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



**Figure 8** Elongational viscosity (Meissner-type and hyperbolic) for PIB.

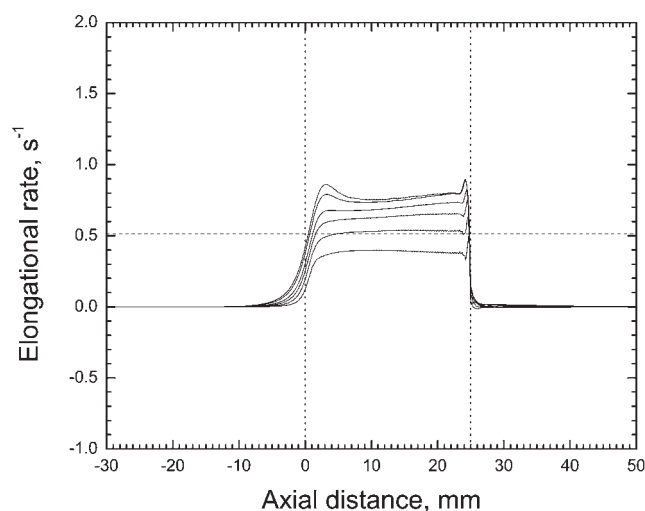




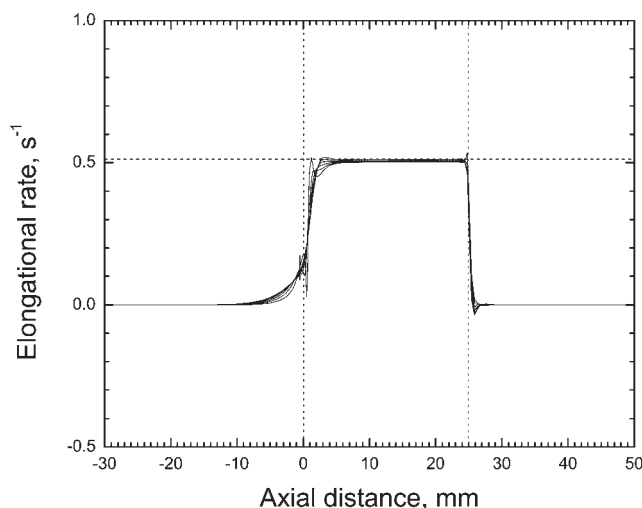
**Figure 9** Elongational viscosity versus elongational strain rate (Instron and hyperbolic) for a Round Robin tested PIB.

die seems to be due to orientation effects that requires a corresponding pressure head even in the relaxation dominant regime. The pressure required for flow in the hyperbolic convergent dies is a continuous smooth function of the flow rate, indicating no discrete changes in response from the relaxation dominant through the transition and orientation dominant regimes. There are only more fluctuations in the transition region but the average values are consistent with the values for the other regimes.

A momentum balance calculation for the ETH LDPE 1810 material at an elongational strain rate of  $10^{-1} \text{ s}^{-1}$  and a Hencky strain of 7, indicated a z-component of the orientational body force times density of 4.4 MPa. This is orders of magnitude higher than the forces and related pressure gradients due to the



**Figure 10** Elongation strain rates on streamlines of a LDPE, no-slip boundary conditions.



**Figure 11** Elongation strain rates on streamlines of a LDPE, full wall slip boundary conditions.

shearing component at the measured shear flow rates and shear viscosities.

### Experimental evidence of convergent flow induced orientation

Orientation developed due to elongational flow in PE

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.<sup>27</sup> This material would have an even higher relaxation time than the ETH LDPE for which excellent agreement existed between the Meissner-type and hyperbolic die data. This Soltex LDPE was subjected to a Hencky strain of 5.9 at an elongational strain rate of  $800 \text{ s}^{-1}$  through a conically convergent die (not a hyperbolic 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 (one of Everage and Ballman's colleagues) independently analyzed the filament formed at what was the Pensacola Monsanto Research Center, and he reported that the extrudates had a Hermann's orientation function of 0.996 (1 is perfect orientation and 0 is random).<sup>21</sup> Furthermore, the material had mechanical properties comparable to the solid state extruded material being studied at that time, a higher degree of crystallinity, and an elevation in melting point of nearly  $20^\circ\text{C}$ . The Orientation number as defined in this article would be at least a hundred or more, indicating flow well into the orientation dominant regime.

### Birefringence in hyperbolic and cylindrical dies spun fibers

Using an ACER driven spinning line, fibers were produced in the Rheology Laboratory at UTK with both uniform radius and hyperbolic dies of the same exit diameter. Optical retardation was measured with an Olympus Berek Compensator and birefringence calculated with the equation:

$$\Delta n = \frac{\text{RTD}}{d} \quad (9)$$

where  $\Delta n$  is the birefringence, RTD is the retardation, and  $d$  is the 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, indicating higher orientation in the hyperbolic die samples.

### Orientation effect on shear viscosity

Preliminary results at UTK (Fig. 12), suggest that the orientation that develops in hyperbolic dies lowers the shear viscosity of the polymer melt by increasing degrees at higher shear rates. These results were obtained using a special adaptor for the ACER capillary rheometer that enabled two dies to be placed in-line at the discharge of the barrel. For one set of these preliminary experiments, the polyethylene (the ETH LDPE 1810 in Fig. 3) melt first passed through a Hencky 6 die and then through a uniform radius capillary die. The capillary die did not have a tapered entry therefore its entrance was aligned with the exit of the hyperbolic die when the two were used in series. The discharge diameter of the hyperbolic convergent die and the diameter of the capillary die

were both 1 mm. 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. The orientation that develops in the hyperbolic die should increase with flow rate through the die, i.e., with elongational strain rate. Apparently, the increase in orientation in the hyperbolic die 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 no more than 2% 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

The elongational viscosity measured by using two techniques, a Meissner-type device, and the hyperbolic converging die, showed good agreement for a conventional LDPE but not as good for other PE samples and a PS sample. The elongational viscosity of PIB measured by the hyperbolic dies and the Meissner-type and Instron were similar although at different temperatures and showed similar patterns to each other. An orientation number was defined as the product of the average relaxation time, the Hencky strain, and the elongational strain rate. This orientation number suggests the flow is in a relaxation dominant regime below a value of one, an orientation dominant regime at values above one and in a transition regime at values near one. This is consistent with the agreement of two of the PE materials for which the orientation number for Meissner-type devices are in the orientation dominant regime, and the PIB data; whereas for these devices the other samples do not reach the orientation dominant regime. When the orientation number is less than one, the elongational flow is apparently in a relaxation dominant regime with no slip at the wall and when it is greater than one the flow is in an orientation dominant regime with slip at the wall. A transition region apparently exists when the orientation number is close to 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, higher extensions, more relaxation, greater

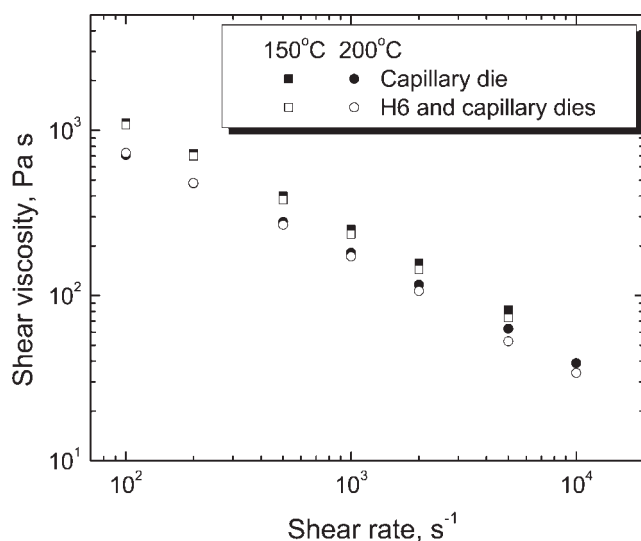


Figure 12 Orientation effect on shear viscosity.

thinning, and perhaps imminent failure of the samples. Higher Hencky strains in Meissner-type devices require longer times at exponentially increasing deformation rates. Since the samples are transversely constrained by the die wall in the hyperbolic convergent die system, relaxation is inhibited and instabilities and flaws are being compressed. The comparison of the measured elongational viscosity by different techniques and theory predictions indicates that the measured elongational viscosity by using the hyperbolic dies is a very good approximation to the material's true elongational viscosity under conditions for which slip at the wall occurs for most of the die and is probably a good approximation under no slip conditions as the Orientation number approaches one. Furthermore, this data suggests the conditions necessary to impose significant orientation on the polymer, whether intentional or consequential to flow conditions. Of course when the elongational flow ceases, the material will begin to relax unless sufficiently constrained by phase transformation. In the hyperbolic dies, slip at the wall is apparently induced when the orientation number exceeds the range of 1–10. Theoretical and experimental evidence is presented to support the concept of orientation induced in polymeric liquids by the flow in the hyperbolic convergent dies.

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