

# Elongational rheology of fiber forming polymers

J. COLLIER<sup>\*‡</sup>, S. PETROVAN<sup>\*</sup>, P. PATIL<sup>\*</sup>, B. COLLIER<sup>§</sup>

<sup>\*</sup>Chemical Engineering and <sup>§</sup>Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA

The elongational rheology of some fiber forming polymers, such as polypropylene (PP), polyethylene (PE), nylon 66, and lyocell (cellulose dissolved in N-Methylmorpholine/water) solutions, has been characterized using hyperbolic convergent dies in a capillary rheometer, at different Hencky strains, processing temperatures, and as a function of elongational strain rates up to 600 s<sup>-1</sup>. The influence of melt flow rate (MFR) and molecular parameters is studied and it is shown that the elongational viscosity curves can be shifted with respect to both temperature and Hencky strain. © 2005 Springer Science + Business Media, Inc.

## 1. Introduction

Fiber spinning is essentially elongational flow and the elongational viscosity is one of the most important parameters in this process. In the course of the fiber forming process, orientation of the macromolecular chains occurs due to the elongational flow. The degree of orientation is directly proportional with the elongational strain rate and Hencky strain [1, 2]. Fiber spinning simulation and experimental data show that elongational strain rates up to 100 s<sup>-1</sup> are recorded, depending on the spinning speed [3]. Simulation of the fiber spinning line as an elongational flow process [4] and experimental data collected on an industrial melt blowing line [5] demonstrate even higher elongational strain rates.

The purpose of this paper is to present elongational viscosity of some fiber forming polymer melts and solutions in the range of elongational deformation parameters commonly experienced in the commercial fiber manufacturing processes.

Measurement of the elongational viscosity of a polymer melt or solution at such high elongational strain rates is difficult to perform. The rheometers currently accepted and widely used by the researchers are so called Meissner-type extensional rheometers [6–11]; the commercial versions are referred to as the Rheometrics Extensional Rheometer (RER) and Rheometric Scientific Extensional Melt Rheometer (RME). These Meissner-type devices feature suspension of a sheet of polymer melt on either an oil bath or an air bath and 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 one to ten reciprocal seconds, Hencky strains up to six, and at temperatures for which the polymer melt is very viscous or viscoelastic, usually near the melting point.

Previous research done by the authors [12–21] has shown that an essentially pure elongational flow of polymer melts is apparently generated using hyperbolic (previously referred to as semi-hyperbolic) convergent dies (for which the elongational strain rate along the axis is a constant) [12, 16] in a capillary rheometer. This experimental technique—hyperbolic convergent 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 industrial processes. The current hyperbolic die devices enable Hencky strains of 4 to 7, and strain rates to nearly 740 reciprocal seconds. The high temperature range for the hyperbolic dies is limited by polymer degradation or for lower molecular weight materials by viscosity related gravitational effects. The lower temperature is limited by the pressure required to drive the elongational flow throughout hyperbolic die. Details on the hyperbolic convergent die technique can be found in [13, 21].

The elongational viscosity can be calculated with the equation

$$\eta_e = -\frac{\Delta P}{\dot{\epsilon} \epsilon_H} \quad (1)$$

where  $\Delta P$  is the pressure difference along the die,  $\dot{\epsilon}$  is the elongational strain rate, calculated with the equation

$$\dot{\epsilon} = \frac{v_o}{L} (e^{\epsilon_H} - 1) \quad (2)$$

where  $v_o$  is the velocity of the melt at the die entrance,  $L$  is the die length and  $\epsilon_H$  is the Hencky strain, defined by the Equation 3 as the natural logarithm of the area reduction or increase in length.

$$\epsilon_H = 2 \ln \frac{D_o}{D_e} \quad (3)$$

<sup>‡</sup> Author to whom all correspondence should be addressed.

where  $D_o$  and  $D_e$  are inlet and outlet diameters of the die, respectively.

## 2. Experimental methods

Elongational viscosity of different melts was measured by using an ACER 2000 (Rheometric Scientific) capillary rheometer and hyperbolic dies of Hencky strains 4, 5, 6, and 7. Complex viscosity was measured on an ARES (Rheometric Scientific) instrument using parallel plate geometry. The experimental technique for the measurement of the effective elongational viscosity has been described elsewhere [13].

## 3. Elongational viscosity

Fig. 1 shows the elongational viscosity of a melt blowing grade PP. The influence of temperature decreases as the elongational strain rate increases. Also, mainly at low strain rates and high temperatures, a trend towards leveling off of the elongational viscosity occurs, a pattern similar with that for shear viscosity dependence on temperature and shear rate.

Presented in Fig. 2 is the elongational viscosity for the same polymer but at different Hencky strains at 220°C. Increasing the Hencky strain results in an in-

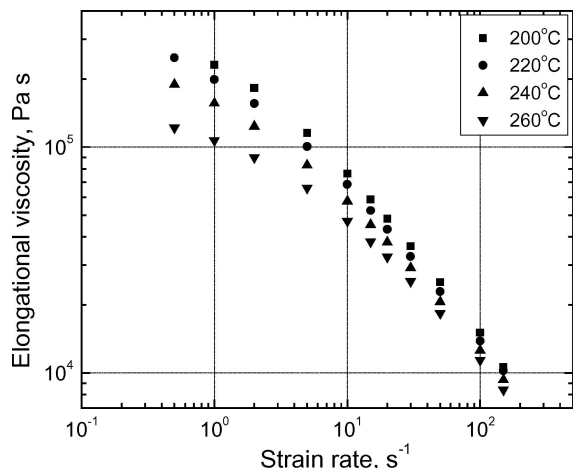


Figure 1 Elongational viscosity of 35 MFR PP at Hencky strain 6.

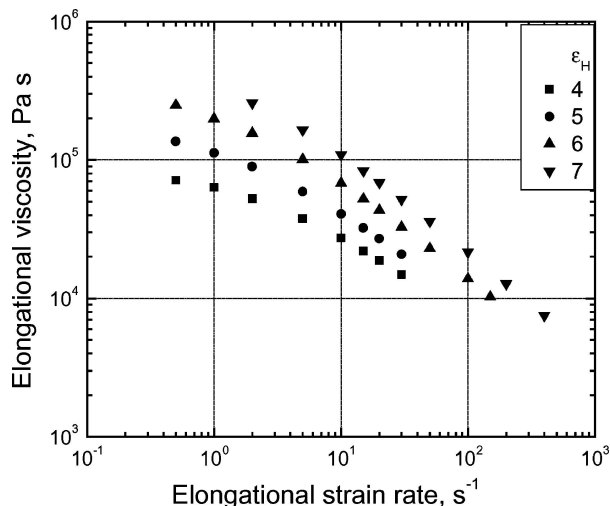


Figure 2 Elongational viscosity of 35 MFR PP at different Hencky strains and 220°C.

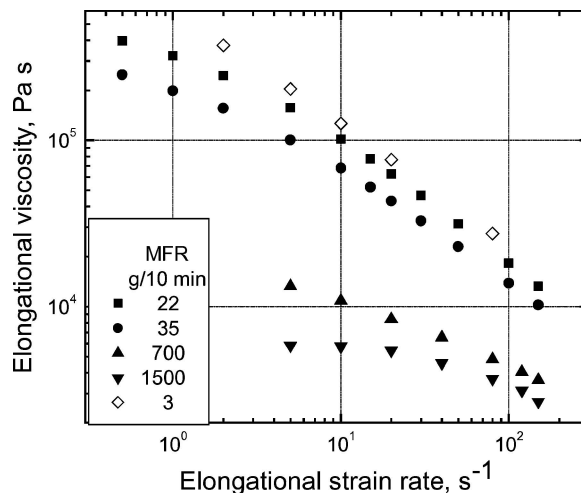


Figure 3 Elongational viscosity of PPs of different melt flow rates at 220°C and Hencky strain 6.

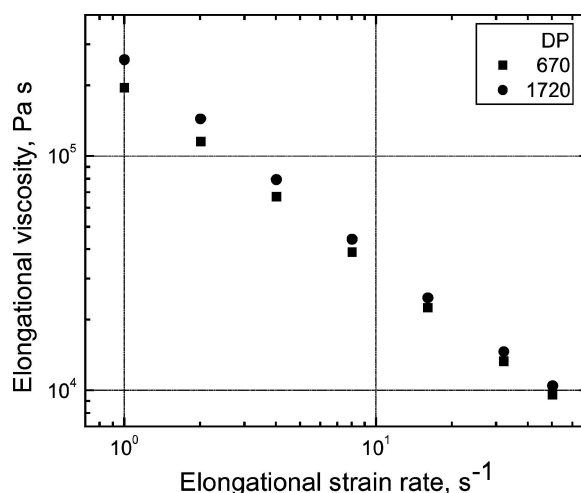


Figure 4 Elongational viscosity of lyocell solutions at 90°C.

crease in elongational viscosity, and this effect decreases slightly as the elongational strain rate increases.

The influence of molecular weight is seen in Fig. 3, for PPs of different melt flow rates. The increase of melt flow rate brings about a decrease in the elongational viscosity.

Very low viscosity resins, that is melt blowing grades, show a very large domain of strain rates of an almost constant elongational viscosity, as is the case of 1500 MFR PP. The extrusion grade PP of 3 g/10 min MFR shows the highest elongational viscosity.

The elongational viscosity of a lyocell solution is presented in Fig. 4. As expected, the elongational viscosity is higher for a higher degree of polymerization of the dissolving pulp used to prepare the lyocell solution. The influence of the degree of polymerization is diminished as the elongational strain rate increases. The elongational viscosity of lyocell solutions is comparable with that of 22 and 35 MFR melt blowing grades of PP.

Elongational viscosity of different nylon 66 resins is presented in Figs 5 and 6, for different relative viscosities (RV) of neat samples and for resins obtained by solid state polymerization to a different final relative viscosity.

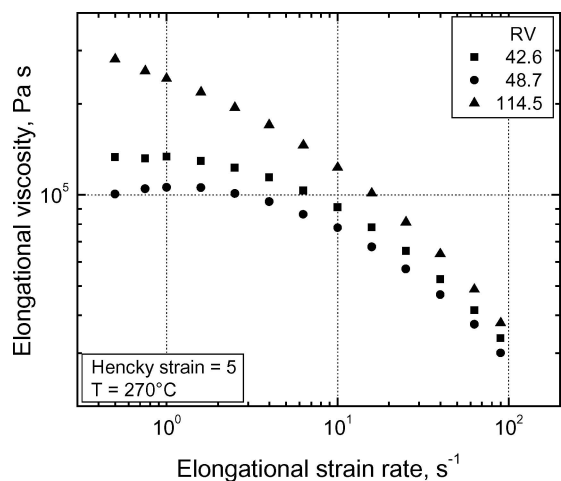


Figure 5 Elongational viscosity of neat nylon 66 resins of different relative viscosities.

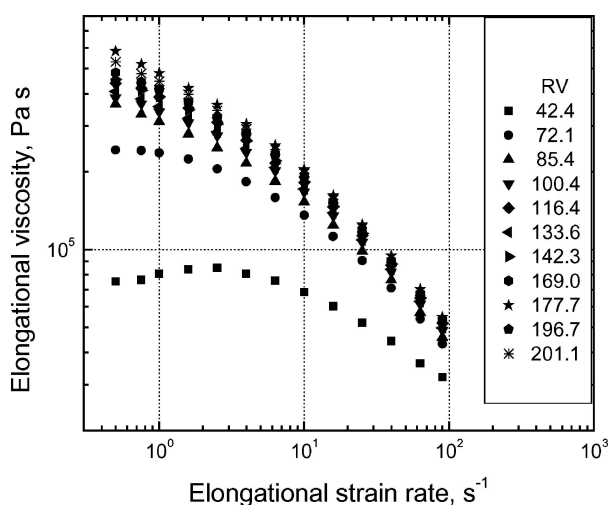


Figure 6 Elongational viscosity of solid state polymerized nylon 66 resins at different relative viscosities.

There is a general trend of increasing the elongational viscosity as the relative viscosity of the resin increases. In other words, this shows the influence of the molecular weight, which is more prominent at low strain rates.

The elongational viscosity is not only influenced by the molecular weight of the polymer but also by the molecular weight distribution, as is displayed in Fig. 7 for 5 samples of low density PEs. Metallocene PEs show a higher elongational viscosity, as compared with Ziegler-Natta ones, and this may be due to the narrower molecular weight distribution of the metallocene grades or the lubricating effect of the lower molecular weight fraction from the broader molecular weight distribution of the Ziegler-Natta catalyzed polyethylenes.

Trouton ratio for the polypropylene samples, presented in Fig. 8, show values between 100 and 1,000, in general depending on the melt flow rate. Higher melt flow rate PPs show higher Trouton ratios due to the much lower shear viscosity as compared with elongational viscosity. This apparently indicates that these low shear viscosity PPs are still orientable since the elongational viscosity is essentially measuring the resistance to orientation development. All of the PPs shown in this figure indicate a decreasing Trouton ratio with increas-

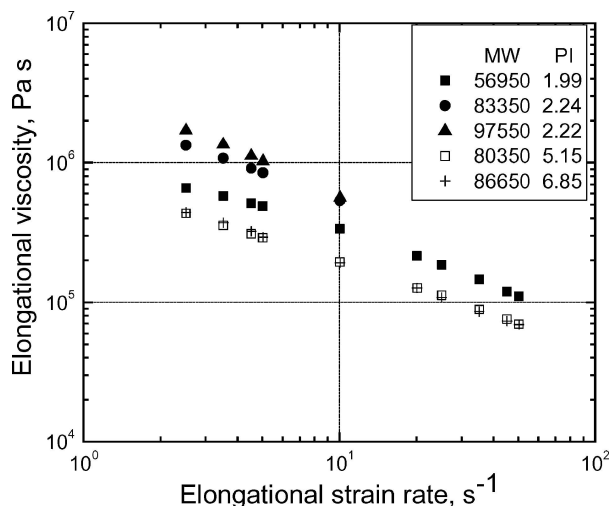


Figure 7 The influence of molecular parameters on elongational viscosity of low density PEs at 220°C and Hencky strain 6 (solid symbols—metallocene grades; open symbol and cross—Ziegler-Natta grades).

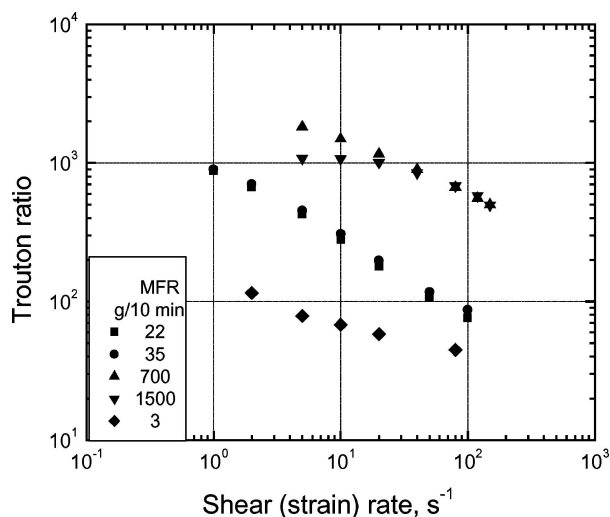


Figure 8 Trouton ratio of PPs at different MFR, 220°C, and Hencky strain 6.

ing strain rate. Since the residence time in the convergent dies is the Hencky strain divided by the strain rate, this decreasing Trouton ratio with strain rate indicates an approach to a Newtonian fluid Trouton ratio of 3 at shorter residence times, consistent with the results of other type measurements of elongational viscosity.

The elongational viscosity curves can be shifted with respect to both temperature and Hencky strain. For shifting with respect to temperature, the shift factors,  $a_T$ , determined from shear viscosity measurements were calculated. Using this procedure, the elongational viscosity curves from Fig. 1 were shifted and the resulted master curve is presented in Fig. 9, showing a very accurate shifting technique.

For shifting with respect to Hencky strain the shift factors were determined using a method based upon the body forces related to orientation development, as shown in Equation 4

$$a_H = \frac{[\eta_e(\dot{\epsilon}_o, \epsilon_H) - 3\eta_s]}{[\eta_e(\dot{\epsilon}_o, \epsilon_{H0}) - 3\eta_s]}, \quad (4)$$

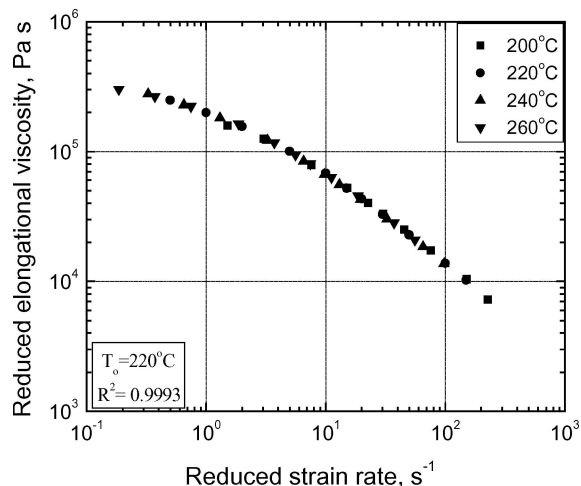


Figure 9 Master curve with respect to temperature of the elongational viscosity curves for 35 MFR PP at Hencky strain 6.

where  $\eta_s$  is shear viscosity and the subscript “o” stays for the reference state. Reduced variables are then calculated with the following relations:

$$(\eta_e)_r = \eta_e \frac{\varepsilon_{Ho}}{a_H \varepsilon_H} \quad (5)$$

$$(\dot{\varepsilon})_r = a_H \dot{\varepsilon}. \quad (6)$$

This method was tested on 10 samples of PEs (5 low density polyethylenes and 5 high density polyethylenes), 3 grades of PPs, and some nylon 66 resins and the values of the coefficient of determination  $R^2$  were in most cases 0.99 or higher. A second method was also developed and tested, where the shift factor with respect to Hencky strain was determined from the ratio of relaxation times. Extensive results on shifting of convergent flow measured elongational viscosity can be found in references [19, 20]. Using Equations 4 to 6 and the elongational viscosity curves from Fig. 2 with Hencky strain 5 as reference the master curve from Fig. 10 was plotted.

Simultaneous shifting, that is shifting with respect to temperature and Hencky strain, respectively, can also

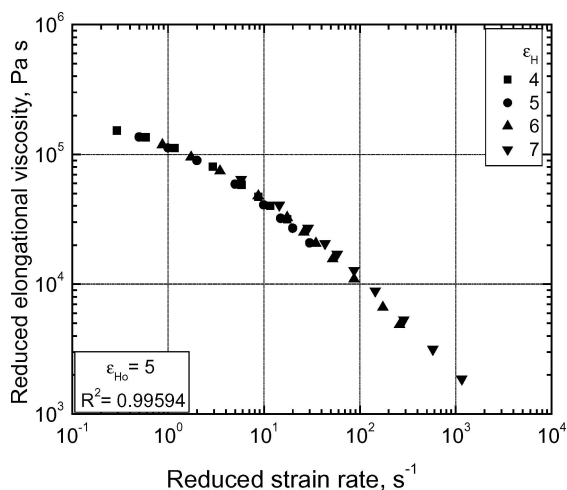


Figure 10 Master curve with respect to Hencky strain of the elongational viscosity curves for 35 MFR PP at 220°C.

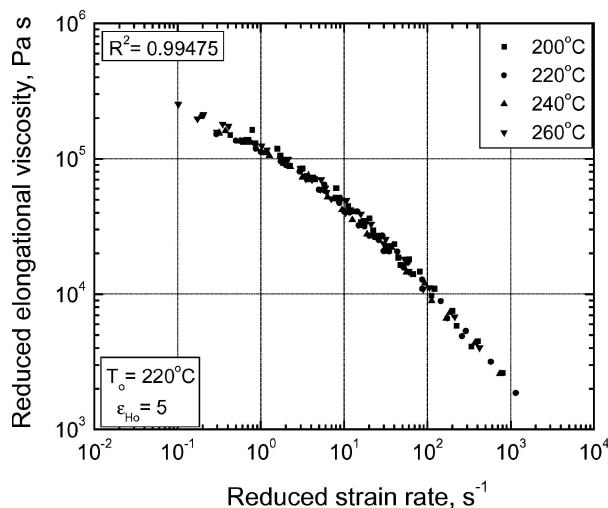


Figure 11 General master curve (for shifting with respect to both temperature and Hencky strain) for 35 MFR PP.

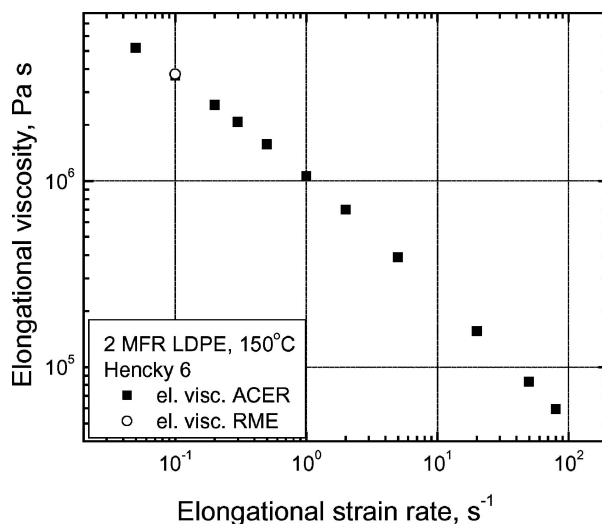


Figure 12 Elongational viscosity of 2 MFR low density PE, measured on ACER and RME rheometers.

be done by using the reduced variables defined by the following equations:

$$(\eta_e)_r = \eta_e \frac{T_o}{a_T T} \frac{\varepsilon_{Ho}}{a_H \varepsilon_H} \quad (7)$$

$$(\dot{\varepsilon})_r = a_T a_H \dot{\varepsilon}. \quad (8)$$

A general master curve is given in Fig. 11, for the same 35 MFR PP. This curve is the result of shifting 15 elongational viscosity curves, for temperatures 180, 200, 220, and 240°C, and for Hencky strains 4, 5, 6, and 7, onto the reference viscosity curve at 220°C and Hencky strain 5.

Independent comparison of the technique presented in this work, by running the ACER and RME extensional rheometers shows a good agreement. Fig. 12 shows the elongational viscosity of a PE [22] perfectly superimposed on the viscosity curve data measured in our rheology laboratory. Fig. 13 shows the excellent agreement between Hachmann and Meissner elongational viscosity data (re-plotted from reference [23])

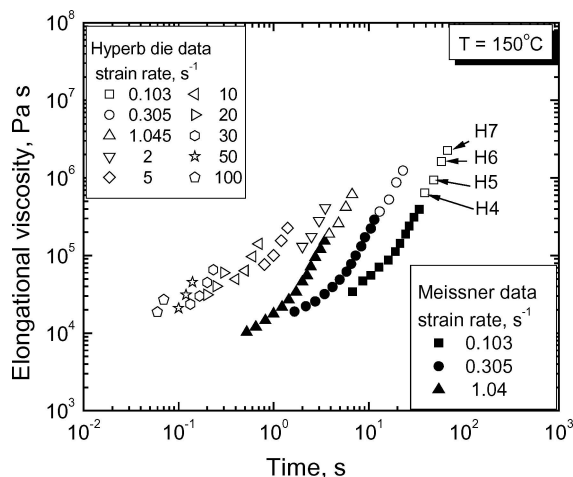


Figure 13 Elongational viscosity of low density PE Lupolen 1810 H at 150°C.

data) and our results on a LDPE Lupolen 1810H. The two domains of low (Hachmann and Meissner data) and high (our data by using hyperbolic die technique) elongational deformation parameters are distinctively depicted in this figure.

#### 4. Conclusions

Elongational viscosity for melt blowing grades of PPs, low density and high density PEs of different molecular parameters, lycell solutions from dissolving pulps of two degree of polymerization, and nylon 66 resins of different relative viscosities has been measured at different elongational strain rates to study the effect of temperature, Hencky strain, and molecular characteristics. It is demonstrated that the elongational viscosity curves can be shifted to generate master curves with respect to temperature or/and Hencky strain and general master curves by simultaneous shifting using general equations for reduced variables of elongational viscosity and elongational strain rate. Experimental data on elongational viscosity at elongational strain rates and Hencky strains in the range of commercial operation are useful for better understanding and operation of polymer melts and solutions processing and also for the design and simulation of industrial processes. The Rheology Laboratory at the Chemical Engineering Department, The University of Tennessee, Knoxville is setting up an Elongational Viscosity Data Bank (EVDB) for polymer melts and solutions of different molecular

parameters, with almost 100 samples data already completed at four temperatures and four Hencky strains and an elongational strain rate between 0.1 to 1 s<sup>-1</sup> and up to as high as 700 s<sup>-1</sup>, for a Hencky 7 hyperbolic die. This would be a range of elongational strain rate commonly met in high speed spinning and melt blowing.

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