

## The role of extensional rheology in polymer processing

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### Abstract

The shear behavior of polymers obtained by means of devices such as capillary and cone-and-plate rheometers is commonly used to assess their processing performance and as a characterization tool. However, the number of instances when two polymers have the same shear properties but perform differently during certain types of processing operations (e.g. film blowing and sheet extrusion) indicate that shear properties alone may not be sufficient to characterize polymeric fluids. We begin by defining the kinematics of shear-free or extensional flow and the associated material functions. The extensional and shear behavior of three different types of polyethylene (PE) are then compared to illustrate the points that one cannot ascertain the extensional properties of polymer melts from their shear properties and, furthermore, there may not be a simple relation between properties obtained from one type of extensional flow and those of another type. The kinematics of most processing flows are extensional rather than shear in nature, and, hence, the performance of polymers during processes such as fiber spinning, film casting, film blowing, thermoforming, blow molding, and even extrusion is more readily accounted for through extensional viscosity measurements. Methods for carrying out extensional flow measurements are then reviewed including approximate methods. To illustrate the sensitivity of extensional viscosity measurements to subtle changes in the molecular architecture of PEs, results are presented for samples with a narrow molecular weight distribution but with varying numbers of long chain branches. Finally, constitutive equations which allow one to separate shear and extensional flow behavior are discussed as any attempts to simulate the subtle processing differences between two polymers will require constitutive equations of this nature.

### 1. Introduction

The shear flow properties of polymers are frequently used to characterize polymer melts and to distinguish their processing performance. For polyolefins especially the melt flow index, which is in essence a single point viscosity, is used to guide the selection of a resin for certain applications. The melt flow index (MFI) for a given resin family is used as a measure of molecular weight. When more information about the processing performance is needed, then a full flow curve (i.e. viscosity versus shear rate) is measured. Small strain dynamic oscillatory properties are sometimes determined which allow one to obtain information about both the elastic and viscous response of a polymer.

There are, however, a number of situations when two polymers have identical shear flow properties, but process differently. For example, Meissner (1979) reported the film blowing performance of three LDPE resins in which two of the resins performed identically while the third could not

be drawn down as much. The traditionally measured melt flow characteristics of the three resins exhibited no consistent differences. In particular the melt flow indices and zero shear viscosities of the resins were very similar which was in contrast to their processing performance. The flow curves of the three resins were identical within experimental error. The extensional stress growth behavior of the three resins, on the other hand, was distinctly different with the resin exhibiting the highest extensional stress also being the resin which could not be drawn down as much. The differences in the resins were attributed to differences in the degree of long chain branching. It is apparent that subtle changes in molecular architecture due to factors such as branching and the presence of a high molecular weight tail in the distribution are readily detected in the processing performance of a polymer but are not readily detected in the shear flow properties. Furthermore, these subtle differences seem to be more readily visible in extensional deformations.

This paper is concerned with the role of extensional rheology in the processing of polymer melts. Because extensional properties of melts are rarely measured, we begin by defining the kinematics of extensional deformation

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and the associated material functions. Methods for measuring extensional rheological properties of polymer melts, including approximate methods, are discussed next. From this point we discuss the role played by extensional viscosity in the flow of polymer melts in processing equipment. In particular, we investigate the flow behavior of melts in a range of processing operations including extrusion (melt fracture), film casting, film blowing, fiber spinning, thermoforming, and porous media flow. From this investigation we realize that many of the processing difficulties of polymer melts are associated with their extensional flow properties. As an example of the sensitivity of extensional viscosity to molecular features of polymers we consider the behavior of slightly branched (less than one long chain branch per 10,000 carbon atoms) metallocene catalyzed polyethylenes relative to a similar system with no long chain branching. Finally, we realize that it is possible for polymers to have identical shear flow properties but different extensional properties. This leads to the discussion of constitutive equations which have the capability to handle fluids with rheological properties of this kind.

## 2. Kinematics and Materials Functions for Shear-free Flow

The kinematics of shear-free flows are summarized below:

$$v_x = -\frac{1}{2}\dot{\epsilon}(1+b)x \quad v_y = -\frac{1}{2}\dot{\epsilon}(1-b)y \quad v_z = \dot{\epsilon}z$$

Uniaxial extensional flow is given by  $b=0$  and  $\dot{\epsilon} > 0$  while biaxial extensional flow is given by  $b=0$  and  $\dot{\epsilon} < 0$ . Planar extensional flow is given by  $b=1$  and  $\dot{\epsilon} > 0$ . The material functions for the various types of shear-free flows are given in Table I.

For uniaxial extensional flow  $\eta_1 = \eta_e$  and  $\eta_2 = 0$  while

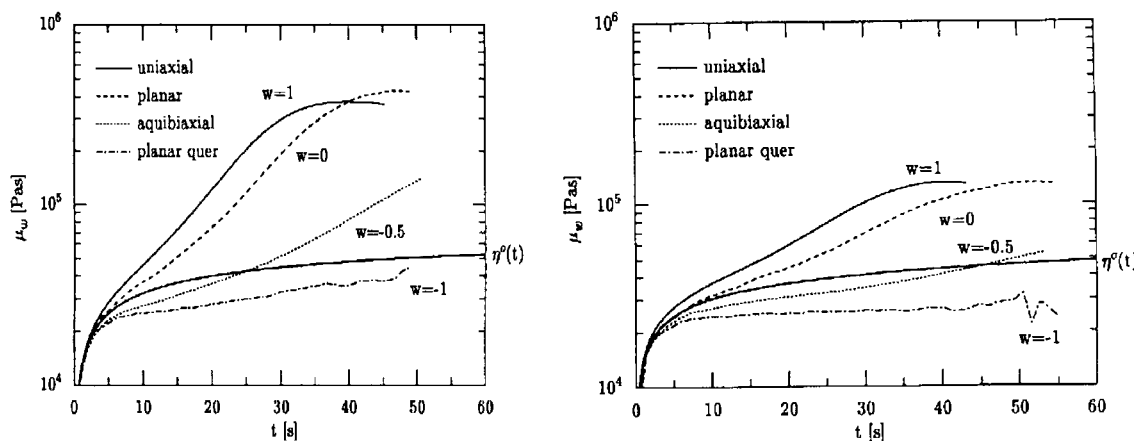
**Table I.** Definition of Material Functions for Shear-free Flows

Flow	Material Function	Defining Equation
Steady Flow : $\epsilon = \text{Const.}$	$\eta_1(\epsilon), \eta_2(\epsilon)$	$\tau_{zz} - \tau_{xx} = -\eta_1 \dot{\epsilon}$ $\tau_{yy} - \tau_{xx} = -\eta_2 \dot{\epsilon}$
Stress Growth on Inception of Steady Flow	$\eta_1^+(t, \epsilon), \eta_2^+(t, \epsilon)$	$\tau_{zz} - \tau_{xx} = -\eta_1^+ \dot{\epsilon}$ $\tau_{yy} - \tau_{xx} = -\eta_2^+ \dot{\epsilon}$
Elongational Creep ( $b=0$ ) $\tau_{zz} - \tau_{xx} = 0$ for $t < 0$ $\tau_{zz} - \tau_{xx} = \sigma_0$ for $t \geq 0$	$D(t, \Phi_0)$	$\epsilon(0,t) = -D\Phi_0$
Free Recovery after Steady Flow ( $b=0$ ) $\tau_{zz} - \tau_{xx} = \sigma_0$ for $t < 0$ $\tau_{zz} - \tau_{xx} = 0$ for $t \geq 0$	$\epsilon_r(0,t, \sigma_0)$ $\epsilon_\infty(\sigma_0)$	$\epsilon_r = \int \epsilon(t) dt'$ $\epsilon_\infty = \lim_{t \rightarrow \infty} \epsilon_r$

for equi-biaxial extensional flow  $\eta_1 = \eta_b$ . For planar extensional flow,  $\eta_1 = \eta_p$  and  $\eta_2 \neq 0$ . Material functions for various types of transient deformation history are presented in Table I also. Representative extensional stress growth data for the three types of extensional deformation for HDPE and LDPE are shown in Fig. 1 along with the zero shear viscosity. For LDPE, which is highly branched, we see that both the uniaxial and planar extensional viscosities exhibit similar strain hardening behavior while the equi-biaxial extensional viscosity strain hardens mildly at higher strains.

## 2. Extensional Rheometry

The techniques primarily available for measuring the extensional properties of polymer melts are limited to uniaxial extensional flow. One method that has been available commercially is that due to M $\ddot{u}$ nstedt (1980) and is shown in Fig. 2. The polymer sample is glued to clips which attach to the load cell and drive mechanism. The sample is melted and suspended in an oil bath with the oil



**Fig. 1.** A comparison of the various types of extensional viscosity for a LDPE ( $M_w = 188,000$ ,  $M_w/M_n = 11.3$ ,  $\eta_0 = 65,000$  Pa s and HDPE: 104,000, 5.5, 160,000, respectively) (Hachmann, 1996)

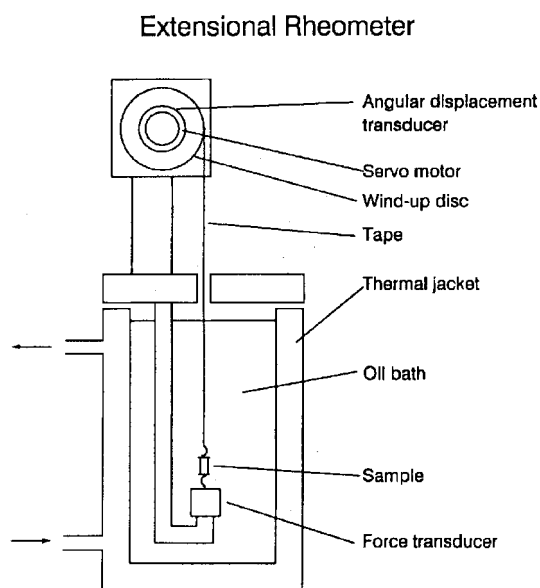


Fig. 2. Schematic drawing of an extensional rheometer for polymer melts based on the method of Muenstedt.

consisting of the same density as the polymer. The sample is then stretched either at constant rate or under constant stress. In order for this technique to function properly the samples must be prepared to minimize sample inhomogeneities and the oil and polymer density must match closely. Meissner (Hachmann, 1996) improved on the method as shown in Fig. 3 by using double rollers and supporting the resin on a bed of talc. This technique was further improved by supporting the polymer on an air cushion as shown in Fig. 3 also (Hachmann, 1996). Higher strains and strain rates can be reached using this approach especially for high molecular weight samples.

Measurements in equi-biaxial and planar extensional flows have been primarily carried out in Meissner's laboratory on specialized equipment. The devices designed by Meissner are shown in Fig. 4. These devices consist of multiple synchronized clamps which lead to the desired strain histories. Laun and Schuch (1989) designed a device for generating planar extensional deformation consisting of a tubular fluid element which could be stretched in the

axial direction while being pressurized with oil to keep the diameter constant.

Fortunately, a knowledge of uniaxial extensional viscosity is most crucial to understanding the processing behavior of polymer melts and planar extensional viscosity seems to mirror uniaxial behavior. Equi-biaxial extensional viscosity exhibits very little strain hardening and more resembles the shear viscosity.

Approximate methods for obtaining the extensional viscosity for polymer melts have been developed (Laun and Schuch, 1989). One method is based on essentially fiber spinning and provides an estimate of  $\eta_e$  as a function of extension rate,  $\dot{\epsilon}$ . The other uses entrance pressure losses to estimate  $\eta_e$ . Remarkable agreement between values of  $\eta_e$  obtained by means of values estimated from the entrance pressure and directly measure values has been reported by Laun (1989). Lubricated squeezing flow has been considered as a method for measuring equi-biaxial extensional viscosity (Sockey and Winter, 1985), but the technique is limited to low strains because of loss of the lubricant.

### 3. Correlation of Extensional Properties to Processing Performance

The three most prevalent polyolefins, LDPE, HDPE, LLDPE, have distinctly different extensional viscosity behavior and processing characteristics. In particular, LDPE which contains a high degree of long chain branching exhibits a significant degree of strain hardening. LLDPE, which contains only short chain branching and a fairly narrow MWD (4 to 5) exhibits only mild strain hardening while HDPE, which is linear but usually of broad MWD (>5), exhibits behavior intermediate to LLDPE and LDPE.

The processing behavior of these three types of PE's appears to be closely related to their general extensional behavior. For example, the flow stability of these polyolefins in extrusion, film blowing and fiber spinning is distinctly different. LDPE is known to form tapered entry flow patterns with intense vortices in the corners of the die entry region. As the flow rate increases, the fluid can no

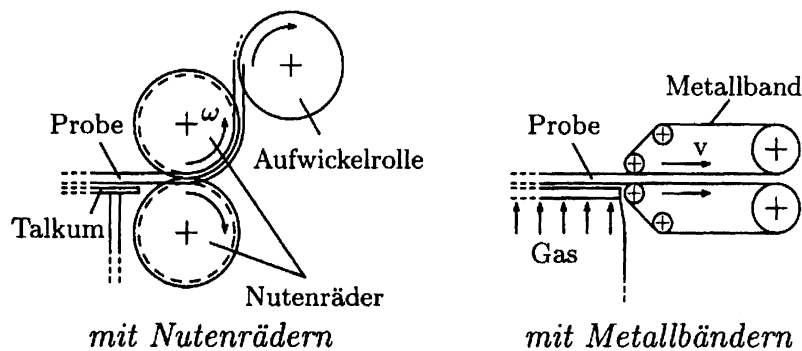


Fig. 3. Improved Rotary Clamp Design Employs Belts (Hachmann, 1996 with permission).

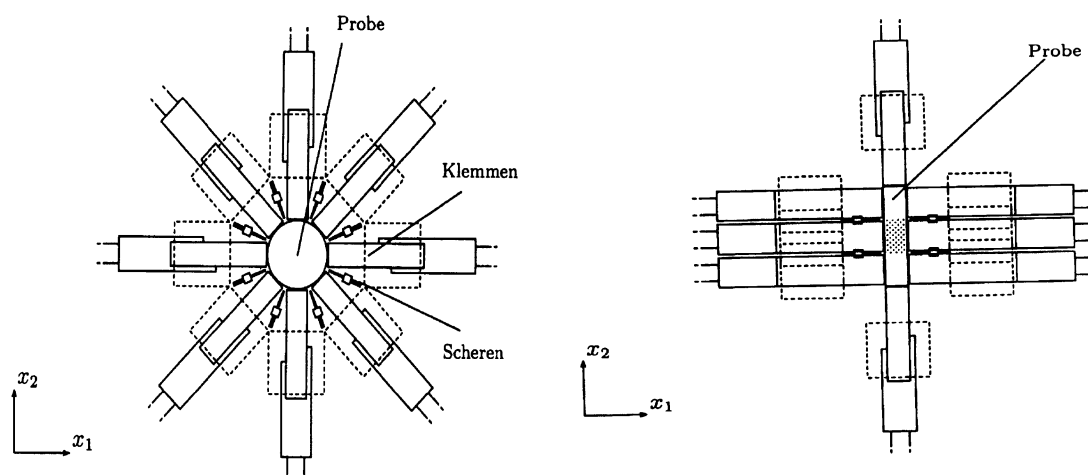


Fig. 4. Schematic drawing of equi-biaxial and planar extensional devices designed and constructed in Meissners laboratory (Hachmann, 1996, with permission) .

longer increase the degree of taper and the vortices begin to swirl and oscillate leading to an extrudate with an irregular appearance which is associated with melt fracture. LLDPE, on the other hand, does not form vortices or a tapered entry region. It first exhibits a surface irregularity referred to as "sharkskin", which is initiated at the die exit, and then "slip-stick" fracture which initiates in the die land. As the flow rate increases LLDPE can completely slip leading to a smooth extrudate. HDPE behaves similarly to LLDPE in terms of slip-stick fracture, but as the flow increases, it can exhibit a gross fracture similar to LDPE. The formation of vortices and a tapered entry region has been shown to be related to extensional strain hardening.

Extensive studies on the stability of the three PE's in fiber spinning, film casting, and blow film, have been carried out by Minoshima and White (1986). In the case of fiber spinning under critical draw conditions the diameter is observed to oscillate periodically along the fiber. This phenomenon is referred to as draw resonance. In the case of film blowing the phenomenon can manifest itself in various forms including fluctuations in the frostline, fluctuations in the bubble shape, and a spiral motion of the bubble. Stability and instability regions are shown in Fig. 5 for the three PE's, and here we see that LDPE is the most stable followed by HDPE and then LLDPE. It is believed that the strain hardening behavior of LDPE offers a stabilizing influence in processes such as film blowing.

The performance of polymers in processes such as thermoforming, extrusion blow molding, and foaming are also related to the degree of extensional strain hardening. For example, in extrusion blow molding the degree of parison sag is partially related to whether the polymer exhibits strain hardening which resists the stretching of the parison under its own weight. Trying to compensate for sag by increasing the zero shear viscosity alone leads to extrusion difficulties. In the thermoforming of semi-crys-

talline polymers, sheet sag and uniformity of wall thickness are related to the degree of strain hardening. Those polymers which tend to strain harden exhibit a more uniform wall thickness in the formed parts. In the foaming of polymer melts it has been reported that polymers such as polypropylene (PP) which ordinarily can't be foamed because the bubbles grow uncontrollably, closed cell structures are possible when PP is branched to provide strain hardening. Increasing the shear viscosity alone through increasing the MW cannot compensate for the processing improvements offered by extensional strain hardening.

#### 4. Extensional Rheology as a Characterization Tool

As an illustration of the sensitivity of extensional viscosity to subtle changes in the molecular architecture of polymer chains we consider three metallocene-catalyzed

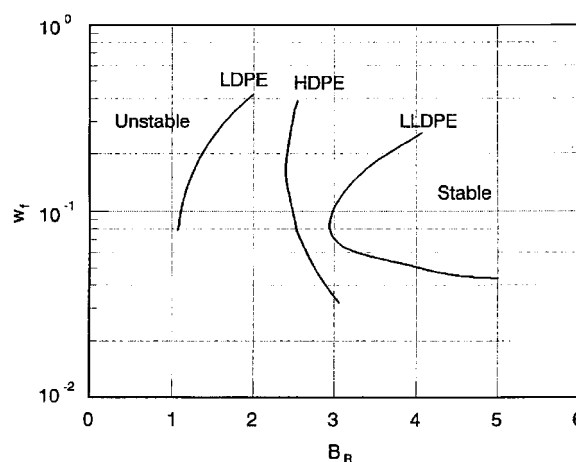


Fig. 5. Instability and stability regions of various types of polyethylenes in film blowing:  $w_f$  is the dimensionless film thickness,  $H_f/R_0$ , and  $B_R$  is the blow-up ratio (Minoshima and White, 1986).

**Table II.** Characteristics of Three Metallocene-Catalyzed LLDPEs

Sample	MFI	$M_n$	$M_w$	$M_z$	$M_w/M_z$	L-C Branches/10,000C	$\eta_0$ 150°C	$\eta_0$ 190°C
Dow Affinity PL 1840	1	36300	87900	160000	2.42	0.5965	47000	15700
Dow Affinity PL 1880	1	55100	116400	183000	2.11	0.1773	46000	17200
Exxon Exact 3022	1	45300	95800	165000	2.11	No LCB	16500	6500

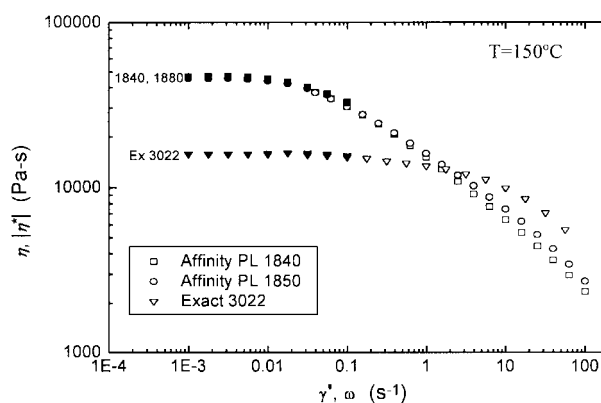
(MC) LLDPEs, whose properties are given in Table II. The molecular characteristics, zero shear viscosities, and branching information of the three MC-LLDPEs are presented in Table II. Here it is observed that both branched samples have similar values of the zero shear viscosity and both values are significantly higher than for the Exxon sample.

Furthermore, the Dow sample PL 1840, with apparently more long chain branches per 10,000 carbon atoms, has a higher zero shear viscosity than the Exxon sample even though it is of lower  $M_w$ . The viscosity versus shear rate curves for the three samples presented in Fig. 6 show that the branched samples undergo shear thinning at lower shear rates than the unbranched LLDPE. The two branched samples have nearly identical flow curves. Furthermore, the linear viscoelastic properties are nearly identical for the two branched samples suggesting they have the same relaxation spectrums. There is a distinct difference in the linear viscoelastic spectrums at low frequencies for the branched samples versus the unbranched sample, but at high frequencies the spectrums merge.

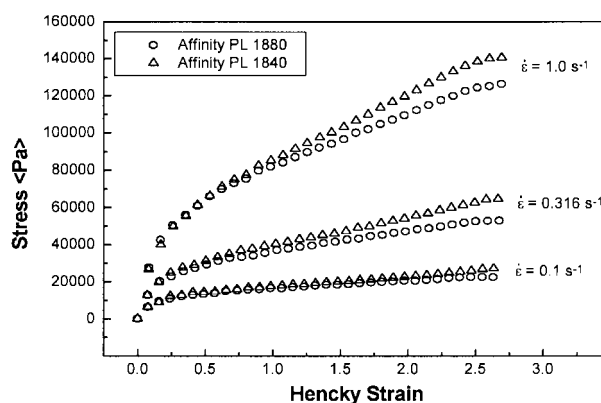
Transient extensional viscosity measurements were carried out on the three samples. Typical of linear polymers with a narrow MWD, the Exxon sample exhibits strain softening. The two Dow samples, however, exhibit strain hardening in extensional deformation with Dow 1840 exhibiting the highest degree of strain hardening as shown in Fig. 7. Even though Dow 1840 has a lower  $M_z$  than that of 1880, it still strain hardens more than 1880. Although it appears that Dow 1840 has a slightly higher MW tail in its MWD, this is not enough to account for the strain hardening difference. It is most likely the LC branching, which affects the strength of the entanglement network, that leads to the strain hardening. There is some theoretical support of this concept based on the theory of Larson and McLeish (1998). It is clear from this example that extensional viscosity measurements are sensitive to factors not readily detectable by means of shear flow measurements. This also means that it is necessary that constitutive equations be available which are able to handle fluids which have no apparent differences in shear flow, but exhibit different extensional behavior.

### 5. Constitutive Equations Suitable for Process Modeling

It is apparent from the discussion above that there are



**Fig. 6.** Viscosity versus shear rate for three LLDPEs. (S. Bin-Wadud, MS Thesis, Extensional Rheology of Slightly Branched Metallocene Catalyzed LLDPEs, Virginia Tech, 1999).



**Fig. 7.** Extensional stress growth response of two lightly branched LLDPEs. (S. BinWadud)

polymer melts which exhibit indistinguishable shear flow properties, yet significantly different extensional properties which can affect their processing performance. Any attempts at the modeling of processes in which melts of this nature are involved will require the use of constitutive equations which allow one to separate the shear flow predictions from the extensional flow predictions. There are at present three constitutive equations which have this capability. The Phan-Thien and Tanner (PTT) model, which is shown below,

$$\exp[\lambda \epsilon \text{tr}(\boldsymbol{\tau}_1)/\eta_1] \boldsymbol{\tau}_1 + \lambda \boldsymbol{\tau}_{1(1)} (\lambda \xi / 2) (\dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\tau}_1 + \boldsymbol{\tau}_1 \cdot \dot{\boldsymbol{\gamma}}) - \eta_1 \dot{\boldsymbol{\gamma}} = 0 \quad (1)$$

is a differential model based on a modification of the Lodge-Yamamoto network theory (Phan-Thien and Tanner, 1977). In Eq. (1) the model is presented for a single relaxation mode. In this form the stress is expressed as the sum of two terms:

$$\boldsymbol{\tau}_1 + \boldsymbol{\tau}_2 = \boldsymbol{\tau} \quad \text{with} \quad \boldsymbol{\tau}_2 = \eta_2 \dot{\boldsymbol{\gamma}} \quad (2)$$

The parameters,  $\xi$ ,  $\lambda$ ,  $\eta_1$  and  $\eta_2$ , are obtained from steady shear data while  $\varepsilon$  is determined from extensional viscosity (extensional stress growth usually) data. If multi-modes are used then this model fits the shear data very well and exhibits all the appropriate extensional viscosity behavior (i.e. depending on the value of the parameter  $\varepsilon$ , extensional strain hardening in both uniaxial and planar extensional flow and very little strain hardening in biaxial extensional flow are predicted).

The K-BKZ or Rivlin-Sawyers model, shown in Eq. (3) below, is an integral model in which a non-linear memory function is used.

$$\boldsymbol{\tau}(t) = \int_{-\infty}^t M(t-t') [\phi_1(I_1, I_2) \mathbf{B} + \phi_2(I_1, I_2) \mathbf{B}^{-1}] dt' \quad (3)$$

In Eq. (3)  $\mathbf{B}$  is the Finger Tensor while  $\mathbf{B}^{-1}$  is the Cauchy Tensor and  $I_1$  and  $I_2$  are the first and second invariants of  $\mathbf{B}$ . It is common to use a memory function which factorizes into time and strain dependent parts. The time dependent part is given by the linear viscoelastic memory function,  $M(t-t')$ :

$$M(t-t') = \sum_{i=1}^N (\eta_i / \lambda_i^2) \exp\left(-\frac{t-t'}{\lambda_i}\right) \quad (4)$$

which is obtained from linear viscoelastic measurements while the strain dependent part is obtained from non-linear shear and extensional measurements. Although there are several choices for the strain dependent or damping function, the Papanastasiou, Scriven, and Macosko (PSM) function is most frequently used, Eq. (5):

$$\phi_1 = \frac{\alpha}{(\alpha-3) + \beta I_1 + (1-\beta) I_2} \quad (5)$$

The  $\eta_i$ ,  $\lambda_i$  and  $\alpha$  are obtained from shear flow measurements while  $\beta$  is obtained from uniaxial extensional flow data. In shear and planar extensional deformation these two invariants are identical. Hence, if the parameter  $\alpha$  is determined from shear measurements, then the planar extensional viscosity will be similar to shear viscosity which is strain softening. Hence, the planar extensional behavior may be inappropriately predicted. Otherwise the model above predicts the transient response of polymer melts in shear and uniaxial extension very well.

Recently McLeish and Larson (1998) have proposed a molecular model based on an architecture consisting of a chain segment containing two branch points at the ends

with different numbers of arms. The asymptotic form of the equations consist of a stress tensor:

$$\boldsymbol{\tau} = \frac{15}{4} G_0 \phi_b^2 \lambda^2(t) \mathbf{S}(t) \quad (6)$$

Where  $\mathbf{S}(t)$  is the approximate orientation tensor given by

$$\mathbf{S}(t) = \frac{\mathbf{A}(t)}{\text{tr} \mathbf{A}(t)} \quad (7)$$

and  $\mathbf{A}(t)$  is given by the following evolution equation:

$$\frac{\partial \mathbf{A}(t)}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{A} = \mathbf{K} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{K}^T - \frac{1}{\tau_b} (\mathbf{A} - \mathbf{I}) \quad (8)$$

In Eq. (6)  $G_0$  is the plateau modulus (dynamic data),  $\phi_b$  is the fraction of molecular weight contained in the crossbar, and  $\lambda$  is the backbone extension obtained by equating frictional drag forces on the branch points from the drag of the surroundings to the elastic Brownian force and is given by:

$$\frac{\partial \lambda}{\partial t} = \lambda (\mathbf{K} : \mathbf{S}) - \frac{1}{\tau_s} (\lambda - 1) \quad (9)$$

$\tau_b$  is the relaxation time for the orientation of the crossbar and  $\tau_s$  is the relaxation time for stretch of the crossbar.  $\mathbf{K}$  is the velocity gradient tensor. According to McLeish and coworkers (Inkson and McLeish, 1999) this model when used with multiple modes describes the rheology of LDPE very well and includes the correct prediction of planar extensional flow.

## 6. Conclusions

The successful modelling of processing operations involving polyethylene will require the use of appropriate constitutive equations which will allow one to deal with melts exhibiting similar shear flow properties, but different extensional behavior. There are apparently several choices of constitutive equations with these capabilities. In addition to being able to handle fluids of this nature, it is important that experimental techniques be available which can provide extensional data over a wide range of extensional rates and strains. There is considerable work to be done yet, however, before we can satisfactorily model complex processes such as film blowing and blow molding for melts with subtle changes in their molecular architecture and associated processing characteristics.

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