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Some theoretical and experimental relations between simple shearing and simple extension

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A new kind of shear-elongational rheometer capable of measuring the shear properties of polymeric solutions in a viscometric flow situation through a concentric cylindrical device and relating the results to simultaneous measurements on elongational flow has been described earlier by Gama and coworkers [1992]. The viscometric flow between concentric cylinders provides torque and first normal stress difference measurements, and imposes a viscometric pre-shearing history on the fluid. A suction device applied through an orifice at the bottom of the gap between the concentric cylinders provides a uniaxial extensional flow. The average tensile stress is measured through flush mounted pressure transducers in the Couette device, and the change in the filament diameter in the extensional flow region between the orifices provides a measurement of the instantaneous rate of elongation. The influence of the pre-shearing history upon the elongational properties is measured directly by transducers and computed using the average value of the tensile stress growth coefficient. Measurements are presented for a constant shear viscosity, elastic fluid of the Boger type. Next, by considering a simple, single integral model, it is shown that the tensile stress growth coefficient is affected by pre-shearing, and is higher than without any pre-shearing. This theoretical result, obtained also for a KBKZ model [1], demonstrates that the increase depends on the extensional flow rate, the shear rate, the relaxation time and the first normal stress difference.

Keywords: Elogational viscosity; shear viscosity; rheometry

Un nuevo tipo de reómetro elongacional y de corte, capaz de medir propiedades simultáneas en esfuerzo cortante simple y en flujo extensional uniaxial, ha sido reportado por Gama et al (1992). Un flujo viscométrico entre cilindros concentricos proporciona mediciones de torque y primera diferencia de esfuerzos normales al mismo tiempo que impone una historia de deformaciones conocida sobre el material en estudio. A continuación, un flujo uniaxial extensional se forma mediante succión através de un orificio colocado en la parte inferior del intersticio entre los cilindros concéntricos. El esfuerzo de tensión sobre el filamento se mide mediante transductores de presión montados al ras en lugares estratégicos del aparato y la rapidez de elongación es medida ópticamente al observar el cambio de diámetro del filamento con una cámara de alta resolución. La influencia de la historia de deformaciones sobre las propiedades elongacionales se refleja como un cambio en la viscosidad elongacional o coeficiente de crecimiento de esfuerzo de tensión. Se presentan mediciones para un fluido elástico de viscosidad al corte constante del tipo Boger. A continuación se demuestra que para un modelo integral simple y para un modelo del tipo KBKZ [1], los resultados teóricos predicen un aumento en la viscosidad elongacional cuando el fluido ha sido sometido a una historia previa de deformaciones. Dicho aumento depende del flujo extensional, de la rapidez de deformación, del tiempo de relajamiento y de la primera diferencia de esfuerzos normales del material.

Descriptores: Viscosidad elongacional; viscosidad al corte; reometría.

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1. Introduction

Elongational properties of polymeric materials may depend strongly on the way they have been deformed prior to elongation [Walters, 1992]. In particular, viscosity measurements are quite sensitive to the deformation history, which almost always includes some shearing. However, commercially available viscometers which provide elongational viscosity measurements [Barnes, Hutton & Walters, 1989] do not take this into account, leaving the data open to uncertain interpretation.

A new elongational viscometer, which aims at correcting this situation by applying a well known, controllable pre-shearing motion, has been described by Gama and coworkers [1992]. In this system, the fluid is subjected to a Couette simple shearing regime as it enters the gap between two concentric cylinders and flows in a descending spiral. This provides the controlled pre-shearing motion, after which the liquid exits through a small hole at the bottom of a cone and plate arrangement. It is worth noting that, even though the flow is indeed helicoidal, the vertical component of the motion is so much weaker than that along the principal direction that, for all practical purposes, all the fluid feels is simple shearing between parallel plates. Moreover, the time of residence within the gap between the two cylinders is long enough for the fluid to behave as if such a state of deformation is all it has ever been through. Care has been taken not to exceed shear rates so high that inertia would be likely to play a role. As it is, it plays none whatsoever in this experimental setup.

Through a second, smaller hole, vertically aligned with this one a few centimeters below, the liquid is pulled by means of a vacuum pump. Pressure transducers located on the outer (fixed) cylinder, along with a vacuum meter at the suction orifice, provide a measurement of the tensile stress which drives the elongation of the fluid filament. This is monitored with a video camera and the image is digitalised through a computer, allowing for the determination of the rate of elongation and the axial variation of the filament diameter. From these measurements we are able to establish the extent of the test zection, in which the rate of elongational is essentially constant (Figure 5).

Here, we present experimental results for both Newtonian and non-Newtonian fluids, and a theoretical analysis which shows how the tensile stress growth coefficient is affected by the shearing motion which precedes the elongation.

2. Experimental results

The apparatus was first calibrated with a well characterised Newtonian oil (Mobil SAE-30) with a shear viscosity of 3.6 poise [Gama *et.al*, 1992]. Even for such a low value, this elongational viscometer succeeds in reproducing the predicted value of Trouton's ratio. Measurements of this kind are scarcely found in the literature [Gupta & Sridhar, 1988].

Next, we tested a commercial transmission oil (Roshfran's 30) which behaves like a Boger fluid (Figures 1 and 2). Although not extremely elastic, its shear viscosity remains almost constant while its elongational properties vary notoriously. Fig. 3 shows how the tensile stress, as a function of axial distance, increases on the pre-sheared flows. A momentum balance along the filament has been used to determine, through an iterative numerical procedure [Gama, 1992], the tensile stress.

In Fig. 4, the elongational modulus is seen to be greater for those flows which have been subjected to shearing prior to elongational. In other words, a greater tensile stress is required to elongate a fluid fiber which has been pre-sheared. The rate of elongation in the test section remained virtually constant; this may be inferred from Fig. 5, where the axial velocity varies linearly with axial distance.

The experiments lead to the following conclusions:

1.- The flow field in the test section approximates quite well that of uniaxial extension at a constant rate of elongation, except for the immediate vicinity of the orifices.

2.- Shearing the fluid previous to elongation brings about the following changes:

a) velocity increases along the filament;

b) so does the tensile stress;

c) as the rotational speed of the Couette viscometer increases, so does the tensile stress growth coefficient, $\eta_E^+(t,\dot{\varepsilon})$;

d) the tensile stress growth coefficient, $\eta_E^+(t,\dot{\varepsilon})$, increases along the axis of elongation.

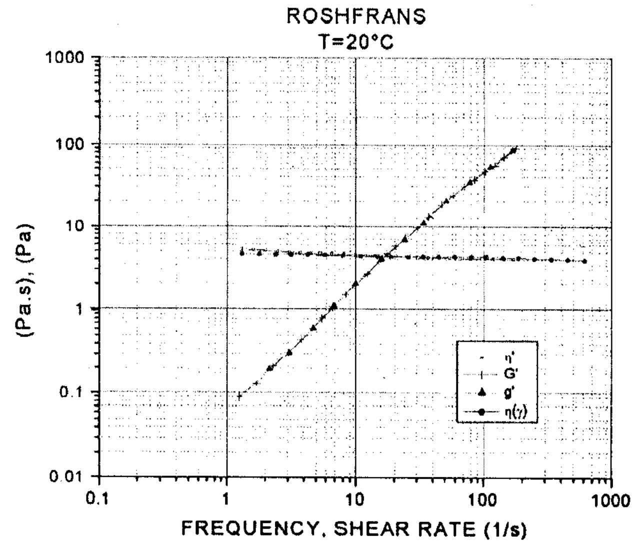

FIGURE 1 Rheometric data for a constant viscosity elastic commercial oil.

3.- Accurate shear and elongational viscosity measurements can be obtained with this apparatus for Newtonian fluids, even for low viscosity solutions. For dilute and semidilute polymer solutions, average values of the elongational modulus are provided within a larger range of elongation rates than other viscometers can, and with no less accuracy.

3. Theoretical analysis

Consideration of the kinematics of simple shear followed by steady elongation will show, at least qualitatively, that the tensile stress growth coefficient $\eta_E^+(t,\dot{\varepsilon})$ should indeed be an increasing function of the rotational speed of the Couette viscometer, and grow with axial distance along the fiber.

Let the fluid undergo a simple shearing motion over $-\infty < \tau \leq 0$ after which it flows in simple extension over $0 \leq \tau \leq t$. The relevant quantities for the kinematic analysis are given by the relative strain history tensor, $\mathbf{C}_t(\tau)$, and the deformation gradient tensor, $\mathbf{F}(t)$, both with respect to a reference configuration at time $t = 0$. In terms of the relative deformation gradient,

$$\mathbf{F}_t(\tau) = \mathbf{F}(\tau) \cdot \mathbf{F}(\tau)^{-1}, \qquad (1)$$

one has

$$\begin{aligned} \mathbf{C}_t(\tau) &= \mathbf{F}_t(\tau)^T \cdot \mathbf{F}_t(\tau) \\ &= \left[\mathbf{F}(t)^{-1}\right]^T \cdot \mathbf{F}(\tau)^T \cdot \mathbf{F}(\tau) \cdot \mathbf{F}(\tau)^{-1} \qquad (2) \\ &= \left[\mathbf{F}(t)^{-1}\right]^T \cdot \mathbf{C}(\tau) \cdot \mathbf{F}(\tau)^{-1} \end{aligned}$$

Here, $\mathbf{C}(\tau)$ is calculated with respect to the reference configuration.

Assume the simple shearing motion to be given by the viscometric field

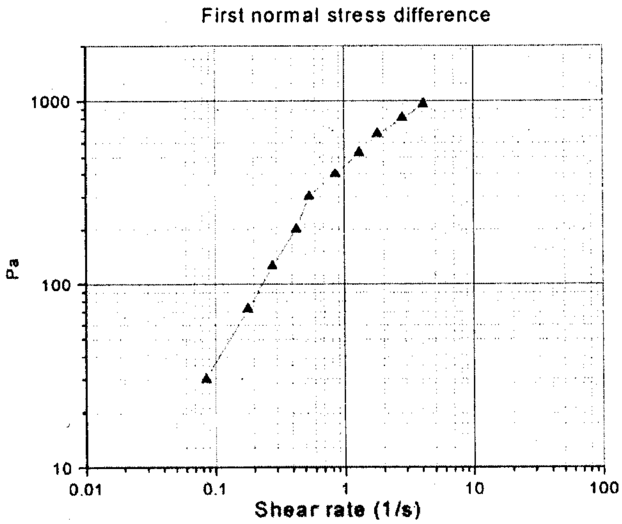

FIGURE 2 First normal stress difference as a function of shear rate for the oil of Figure 1.

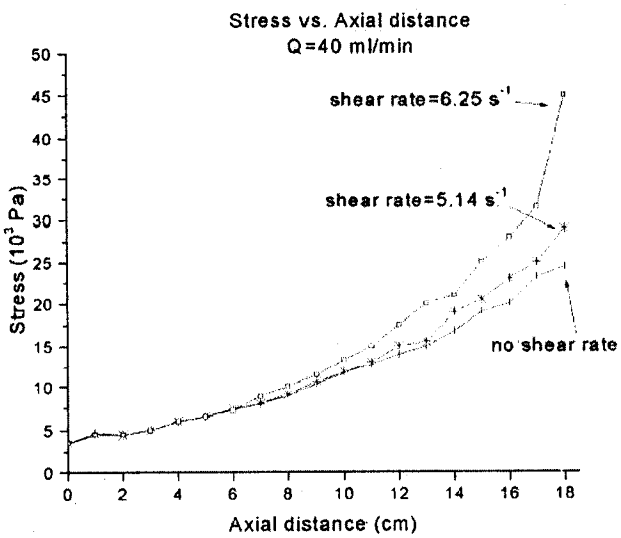

FIGURE 3 Tensile stress as a function of the axial distance at different pre-shearing rates. $Q = 40$ ml/min.

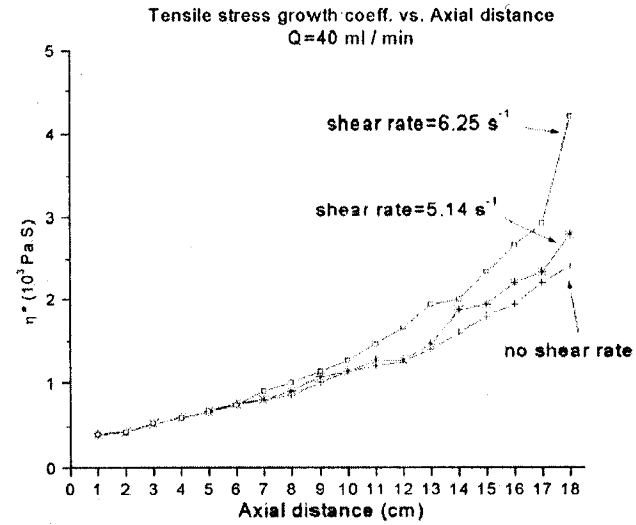

FIGURE 4 Tensile stress growth coefficient versus axial distance at different pre-shearing rates. $Q = 40$ ml/min.

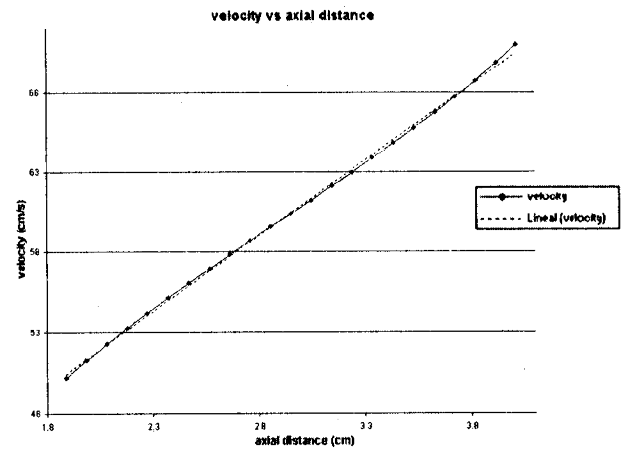

FIGURE 5 Velocity vs. axial distance for the experimental conditions of Figures 3 and 4.

$$\dot{x} = 0, \quad \dot{y} = \dot{\gamma} x, \quad \dot{z} = 0, \tag{3}$$

for all times up to $t = 0$. The strain history corresponding to this part of the motion is

$$\mathbf{C}(\tau) = \begin{bmatrix} 1 + \dot{\gamma}^2\tau^2 & \dot{\gamma}\tau & 0 \\ \dot{\gamma}\tau & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, -\infty < \tau \leq 0. \tag{4}$$

For $t > 0$, a simple extensional regime follows:

$$\dot{x} = -\frac{\dot{\varepsilon}}{2}x, \quad \dot{y} = -\frac{\dot{\varepsilon}}{2}y, \quad \dot{z} = \dot{\varepsilon} z. \tag{5}$$

The deformation gradient is then

$$\mathbf{F}(\tau) = \begin{bmatrix} e^{-\dot{\varepsilon}\tau/2} & 0 & 0 \\ 0 & e^{-\dot{\varepsilon}\tau/2} & 0 \\ 0 & 0 & e^{\dot{\varepsilon}\tau} \end{bmatrix}, \tag{6}$$

and so

$$\mathbf{C}(\tau) = \begin{bmatrix} e^{-\dot{\varepsilon}\tau} & 0 & 0 \\ 0 & e^{-\dot{\varepsilon}\tau} & 0 \\ 0 & 0 & e^{2\dot{\varepsilon}\tau} \end{bmatrix}, \text{ for } 0 \leq \tau \leq t. \tag{7}$$

It is worth noting that

$$\lim_{\tau \to 0^+} \mathbf{C}(\tau) = \lim_{\tau \to 0^-} \mathbf{C}(\tau) = 1,$$

the identity matrix. In this sense, the transition from one regime to the next is a smooth one. Furthermore, flow visualization of the transition region in the actual apparatus [von-Ziegler, 1992] confirmed the absence of vortices or any other disruptive feature. During this transition, the strain history tensor reflects changes occurring after the shearing motion has stopped and during the subsequent build-up of the extensional motion. For the first set of calculations, one uses the expression

$$\mathbf{C}_t(\tau) = \begin{bmatrix} e^{-\dot{\varepsilon}\tau/2} & 0 & 0 \\ 0 & e^{-\dot{\varepsilon}\tau/2} & 0 \\ 0 & 0 & e^{\dot{\varepsilon}\tau} \end{bmatrix} \cdot \begin{bmatrix} 1+\dot{\gamma}^2\tau^2 & \dot{\gamma}\tau & 0 \\ \dot{\gamma}\tau & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} e^{\dot{\varepsilon}\tau/2} & 0 & 0 \\ 0 & e^{\dot{\varepsilon}\tau/2} & 0 \\ 0 & 0 & e^{\dot{\varepsilon}\tau} \end{bmatrix}, \tag{8}$$

while for $0 \leq t \leq t$ one uses

$$\mathbf{C}_t(\tau) = \begin{bmatrix} e^{\dot{\varepsilon}(t-\tau)} & 0 & 0 \\ 0 & e^{\dot{\varepsilon}(t-\tau)} & 0 \\ 0 & 0 & e^{2\dot{\varepsilon}(t-\tau)} \end{bmatrix}. \tag{9}$$

A constitutive equation must be specified before any calculation can be made. We propose a single integral model for the extra stress:

$$\mathbf{S}(t) = \mu \int_{-\infty}^{t} e^{(\tau-t)/\lambda} \mathbf{C}_t(\tau)\, d\tau, \tag{10}$$

μ being a constant and λ the relaxation time. The extra stress may be decomposed into contributions from shearing and from elongation, as follows:

$$S(t) = \mu e^{-t/\lambda} \left[\mathbf{F}(\tau)^{-1}\right]^T \left(\int_{-\infty}^{0} e^{\tau/\lambda} \mathbf{C}(\tau)\, d\tau\right) \times \mathbf{F}(t)^{-1} + \mu e^{-t/\lambda} \int_0^t e^{\tau/\lambda} \mathbf{C}_t(\tau)\, d\tau$$
$$= e^{-t/\lambda} \left[\mathbf{F}(t)^{-1}\right]^T \cdot \mathbf{S}^V \cdot \mathbf{F}(t)^{-1} + \mathbf{S}^E \tag{11}$$

The viscometric stress tensor for simple shear, $\mathbf{S}^V$, is given by

$$\mathbf{S}^V = \begin{bmatrix} -N_1 & \eta_0\dot{\gamma} & 0 \\ \eta_0\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \tag{12}$$

with N_1 being the first normal stress difference, η_0 the zero-shear viscosity and $\dot{\gamma}$ the shear rate in (3).

The shearing contribution to the extra stress can then be written as

$$e^{-t/\lambda} \left[\mathbf{F}(t)^{-1}\right]^T \cdot \mathbf{S}^V \cdot \mathbf{F}(t)^{-1} = e^{t(\dot{\varepsilon}-1/\lambda)} \begin{bmatrix} -N_1 & \eta_0\dot{\gamma} & 0 \\ \eta_0\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{13}$$

From this result one can see that the sign of $\dot{\varepsilon} - 1/\lambda$ determines whether the viscometric stresses relax after cessation of the shearing motion –as they would had the subsequent elongation not been there–, or grow, if the argument in the exponential turns out to be positive.

On the other hand, the time dependent extensional stress $\mathbf{S}^E$ in (11), which can easily be shown to be diagonal, is unaffected by the previous history due to the fact that the constitutive equation is linear. In the end, to the contribution from $\mathbf{S}^E$ one must add the corresponding term arising from the modification of the viscometric stresses. Thus, a time t after the extensional flow has started, the total tensile stress is

$$T_{zz}(t) - T_{xx}(t) = S^E_{zz}(t) - S^E_{xx}(t) + e^{t(\dot{\varepsilon}-1/\lambda)} N_1. \tag{14}$$

Dividing by the rate of elongation yields the tensile stress growth coefficient, $\eta_E^+(t, \dot{\varepsilon})$. From our experimental observations [Mena, Huilgol & Phan-Thien] we know that $\lambda \approx 1$s and $\dot{\varepsilon} \approx 10 s^{-1}$, so that $\dot{\varepsilon} - 1/\lambda > 0$, and since the first normal stress difference is also positive and quadratic in $\dot{\gamma}$ at lov shear rates, one concludes that $\eta_E^+(t, \dot{\varepsilon})$ must be an increasin function of the shear rate. Moreover, it can be easily show that $d\left[\eta_E^+(t, \dot{\varepsilon})\right]/dt > 0$, and hence the tensile stress growt coefficient must grow with axial distance along the fiber.

In summary, the effect of shearing the fluid prior to elor gation, under the circumstances noted above, is to increas the tensile stress needed to perform the extension. These re sults agree qualitatively with our experimental observatior with the Boger type Roshfran's transmission oil. Even thoug Boger fluids like this one are generally modelled as Oldroy B, whereas our theoretical assessment relies on a single i tegral model, the conclusions presented herein are still val because the latter predicts similar values for N_1 and $\eta_E^+(t,$ as the integral part of the Oldroyd-B model.

4. Predictions For A More General Viscoelast Fluid

In order to examine whether the increase in $\eta_E^+(t, \dot{\varepsilon})$ witl is predicted by a non-linear model, we examine a constitut relation of the form

$$\mathbf{S}(t) = \int_{-\infty}^{t} [\mu_{-1}(t-\tau, I_{-1}, I_1)\,\mathbf{C}_t(\tau)^{-1} + \mu_1(t-\tau, I_{-1}, I_1)]\,\mathbf{C}_t(\tau)^{-1}\,d\tau, \quad (15)$$

where μ_{-1} and μ_1 are functions of $t-\tau$, and the invariantes I_{-1} and I_1 are given by:

$$I_{-1} = tr\left[\mathbf{C}_t(\tau)^{-1}\right], \quad \text{and} \quad I_1 = tr\left[\mathbf{C}_t(\tau)^{-1}\right]. \quad (16)$$

Here, tr denotes the trace operator. It is known that in simple shear the normal stress coefficients are given by

$$\begin{aligned} \Psi_1 &= \textstyle\int_{-\infty}^{0} (\mu_{-1} - \mu_1)\,\tau^2 d\tau, \\ \Psi_2 &= \textstyle\int_{-\infty}^{0} \mu_1 \tau^2 d\tau, \end{aligned} \quad (17)$$

when the two invariants satisfy

$$I_{-1} = I_1 = 3 + \dot{\gamma}^2\tau^2.$$

Because $\Psi_1 > 0$ and $\Psi_2 < 0$, it is clear that $\mu_{-1} \geq 0$ and $\mu_1 \leq 0$ for $I_{-1} = I_1 = 3 + \dot{\gamma}^2\tau^2$.

Turning now to the stress at time t due to the initiation of an elongational flow after simple shearing, one finds that the kinematics described in §3 lead to the following two separate integrals:

$$S_{zz}(t) - S_{xx}(t) = \int_{-\infty}^{0} \left(\begin{array}{c} \mu_{-1}\left(e^{2\dot{\varepsilon}t} - e^{-\dot{\varepsilon}t}\right) \\ +\mu_1\left(e^{-2\dot{\varepsilon}t} - e^{\dot{\varepsilon}t}\left(1 + \dot{\gamma}^2\tau^2\right)\right) \end{array} \right) d\tau + \int_{0}^{t} \left(\begin{array}{c} \mu_{-1}\left(e^{2\dot{\varepsilon}(t-\tau)} - e^{-\dot{\varepsilon}(t-\tau)}\right) \\ +\mu_1\left(e^{-2\dot{\varepsilon}(t-\tau)} - e^{\dot{\varepsilon}(t-\tau)}\right) \end{array} \right) d\tau. \quad (18)$$

Here, in the first integral, the invariants are:

$$\begin{aligned} I_{-1} &= e^{2\dot{\varepsilon}t} + e^{-\dot{\varepsilon}t}(2 + \dot{\gamma}^2\tau^2), \\ I_1 &= e^{-2\dot{\varepsilon}t} + e^{\dot{\varepsilon}t}(2 + \dot{\gamma}^2\tau^2). \end{aligned} \quad (19)$$

Let us rewrite the terms in the first integral in the form

$$\left(e^{2\dot{\varepsilon}t} - e^{-\dot{\varepsilon}t}\right)\int_{-\infty}^{0} \mu_{-1} d\tau + \left(e^{-2\dot{\varepsilon}t} - e^{\dot{\varepsilon}t}\right)\int_{-\infty}^{0} \mu_1 d\tau - e^{\dot{\varepsilon}t}\dot{\gamma}^2 \int_{-\infty}^{0} \mu_1 \tau^2 d\tau. \quad (20)$$

Now, if $0 < t \ll 1$, then the invariants in (19) do not differ too greatly from their viscometric counterparts and thus one may assume that their values are approximately given by

$$I_{-1} = I_1 = 3 + \dot{\gamma}^2\tau^2.$$

Accepting this to be the case and recalling that $\mu_{-1} \geq 0$ and $\mu_1 \leq 0$, we find that each component of the above expression (19) is positive and an increasing function of time t. Moreover, because of the presence of $\dot{\gamma}^2$, the above expression is an increasing function of the shear rate.

Next, it is interesting to note that the contribution from the second integral to the stress difference in (18) does not depend on the viscometric flow. This is because over the time interval $0 \leq \tau \leq t$, the invariants are:

$$\begin{aligned} I_{-1} &= e^{2\dot{\varepsilon}(t-\tau)} + 2e^{-\dot{\varepsilon}(t-\tau)}, \\ I_1 &= e^{-2\dot{\varepsilon}(t-\tau)} + 2e^{\dot{\varepsilon}(t-\tau)}. \end{aligned} \quad (21)$$

Putting it all together, we see that the chosen model predicts that the tensile stress growth coefficient $\eta_E^+(t, \dot{\varepsilon}, \dot{\gamma})$, in an extensional flow after simple shearing, depends on $\dot{\varepsilon}$ and is an increasing function of both $\dot{\gamma}$ and of the axial distance.

It is probably unrealistic to expect an analysis based on Continuum Mechanics, suchs as this, to also offer a physical interpretation of a phenomenon which quite likely stems from the molecular properties of these complex fluids. After all, simple Newtonian fluids, with no elastic response and no dependence on the rate of deformation, do not exhibit any change in elongational properties after being sheared.

Polymeric liquids, on the other hand, do respond to flow deformation at the molecular level. Macromolecules tend to orient themselves along the principal direction of motion, and, if the flow is strong enough locally, they will also find themselves uncoiled and stretched to some degree, despite their internal resistance to such a change in configuration. When they reach the bottom of the cone and plate region, and as they abandon the simple shearing regime without having had a fair chance to relax from their stretched configuration, they are suddenly subjected to an even more demanding deformation regime–uniaxial extension, characterised by an exponential increase in strain with axial distance.

This picture allows one to discriminate between the responses of molecules which have already been stretched during pre-shearing, and those which enter the extensional regime closer to their unperturbed internal configuration. The former, much more streamlined and in configurations corresponding to less restoring energy, would present less resistance than the latter.

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1. Barnes, H.A., Hutton, J.F. and Walters, K. ,*An Introduction to Rheology* (Elsevier, Amsterdam, 1989).
2. Gama, J., *A new kind of shear-elongational rheometer*, B.Sc. Dissertation (Universidad Nacional Autónoma de México, 1992).
3. Gama, J., Nuñez, F., Zenit, R., von-Ziegler, A. and Mena, B., *A New Shear-Elongational Viscometer*, Proc. XIth. Intl. Cong. Rheol., **2** (1992) 917.
4. Gupta,R.K. and Sridhar, T., *Elongational Rheometers*, in A.A. Collyer and D.W. Clegg (Eds.), *Rheological Measurement* (Elsevier Applied Science, London, 1988).
5. Huilgol, R.R. and Phan-Thien, N., *Fluid Mechanics of Viscoelasticity* (Elsevier, 1997).
6. Mena, B., Huilgol, R.R. and Phan-Thien, N. (to be published).
7. Walters, K., *Recent Developments in Rheometry, Proc. XIth. Intl. Cong. Rheol.*, **1** (1992) 16.
8. von-Ziegler, A., private communication, 1994.