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THEORETICAL ANALYSIS OF POLYMER MELT FLOW THROUGH A CAPILLARY RHEOMETER

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ABSTRACT

Polymers are considered to be the basic raw material for all the plastic industry. In their fluid state as "polymer melts", they exhibit a variety of characteristics that if well captured can add huge contributions to the development and advancement of such an industry. One of the most primarily and widely used device in the experimental analysis of polymer melt characteristics is the capillary rheometer. Through the capillary rheometer nearly all the material functions associated with the flow of such a fluid can be found, calculated and plotted for further data investigation. Due to the huge importance of such a device, in experimental rheology, came the need to better comprehend what happens to polymer melts as they flow through the rheometer focusing on the complications exhibited by such fluids while they are being tested. The purpose off this work is to analyze theoretically in details the flow of fluids, mainly polymer melts, as they pass through a capillary rheometer. This is done by implementing and solving simplified constitutive equations such as the simplified K-BKZ model (the Wagner model) and the Lodge model for such a flow.

KEYWORDS:

Polymer melts, Capillary rheometer, Material functions, K-BKZ model keywords here.

INTRODUCTION

Flow through a capillary rheometer, which is considered as the most simple and popular melt rheometer, is simply a pressure driven flow through a vertical pipe as shown in figure 1. But several complications might arise on the entrance and exit of the melt to and from the pipe which generally yields misleading results. In the following few pages, we will derive theoretically the governing equations for the flow of LLDPE/LDPE blends which can better allow us to interpret the rheological data for such a blend[1]. Moreover we have to understand that the most important part and the key issue to correctly analyze a flow is the correct choice of the constitutive equation that would best model and resemble the flow under investigation.

For our derivation the Kaye-Bernstein-Kearsely-Zapas model, or most widely known as the K-BKZ constitutive equation was considered to be the best suiting model and could be expected to give the most accurate results. The K-BKZ model was originally introduced in 1963. It is a constitutive model that is though to be inspired by the theory of rubber like elasticity. The complexity of this model arises from the difficulty in choosing its potential function U. That is because the potential U is a function of various quantities and this can be shown as;

$$U = U(I_c, I_{c^{-1}} \ , t - t') \quad 1$$

Here C^{-1} is the inverse of the strain tensor C, where I_c and $I_{c^{-1}}$ are the first and second invariants of these tensors respectively. The term $(t - t')$ relates the potential function to the history of deformation of the tested fluid upon which the constitutive equation is applied. Through several previous research work made by a wide variety of researchers, the K-BKZ model proved to give very good results for most kinds of flows. Moreover the K-BKZ model eliminates any chances of violating the second law of thermodynamics that can be encountered by many other simpler forms of constitutive equations. However, in the non-linear regime, it was found that the K-BKZ model predicted too much of an elastic response especially in the case of LDPE and most of its blends. In order to overcome such a defect, Wagner introduced an irreversible model in 1979. Such a model is referred to as an approximation of the K-BKZ model[1]. More precisely the K-BKZ theory is considered to be exact with respect to the single step response while the Wagner model further improves the double step response. If we would consider the response of a fluid to be in the form;

$$\underline{\underline{\tau}} = \int_{-\infty}^{t} \mu(t-t')H(I_{c^{-1}}, I_c)C^{-1}(t')dt'$$

where H is regarded as a function of $\gamma(t,t')$, then when H=1 we then have the Lodge model equation. Therefore the Lodge equation can be considered as a simplified special case of the Wagner model equation. However, in spite of the huge advantage of being easy to use and solve, the Lodge model equation carries the drawback of not showing any non-linear effect even when used for the analysis of fluids where such behavior is expected to appear[1].

LITERATURE REVIEW

Sombatsompop et al [2] proposed a detailed discussion on the swell ratios of extrudate and velocity profiles of polystyrene PS melt flow through a constant rate capillary rheometer and a single screw extruder. The difference in the two devices forced the swell ratios to vary among them. In general they discovered that PS melt swell ratio was much higher in the extruder than in the rheometer. They managed to illustrate, using velocity profiles for each flow, the inconsistency in radial extrudate swell profiles from the rheometer and the extruder. The work emphasized on the flow of linear density polyethylene (LDPE) and linear low density polyethylene (LLDPE) patterns through a slit contraction. Using the power law they managed to fit the velocity profiles in the pure shear regions, and this showed the resulting shear thinning behavior that occurred for the LDPE and LLDPE. Considering the entrance effects, LLDPE revealed a smooth, steady flow but for LDPE an elevated secondary flow which appears in a two dimensional view as vortices circulating in the corners of the die entrance was confirmed. As for the die length it was proven that choice of such a parameter is done according to the tested material and then pressure gauges must be positioned accordingly.

Rubio, P. et al [3] studied the “pom-pom” model and used it for melt viscosity predictions in start-up of extensional flows and simple shear flow. The model is shown to calculate a strain hardening behavior for the second normal stress difference in planar extension, which was considered as a qualitative disagreement with experimental data. This same disagreement was also found for the full multi-mode pom-pom model in start-up of shear flow as it observed an amount of stress overshoot and shear thinning of LDPE melt. The differential approximation agreement with the experimental data of LDPE melt is seen to be due to the approximation for the Doi–Edwards DE configuration tensor introduced. The stress relaxation phenomenon, after sudden deformation, was also investigated. For shear flow, the model was found to provide a description for relaxation modulus measured for monodisperse polybutadine after step-strain. It was concluded that the differential approximation is a basic simple approximation of the DE model for high Debrah number De flows and for planar extension. However the model didn’t verify the classical time-strain separability law, which is valid for LDPE melts over several decades of relaxation time

Tsenoglou, J.C. et al [4] investigated using the simplest form of damping effect of large deformations on the viscoelastic memory, in order to obtain a closed form expressions for time dependent, stored energy, and a variety of rheological properties. The nonlinear viscoelastic behavior of the material was seen to be an inverse measure of the network connectivity strength of the underlying microstructure. Moreover, the tested constitutive equation leads to analytical expressions for the viscoelastic stream in extensional flows. The stress damping function of the used equation was based upon the power-law, a dependence that was later supported by the strain thinning behavior of polymers tested under several elongation modes. However, phenomena such as stress over shoot of uniaxial elongation and rate of shear thickening at the intermediate strain rate cannot be accounted for.

Mitsoulis, E. et al[5] used the K-BKZ constitutive equation to model melt flow after altering the integral equation to account for strain hardening in planar extensional flow. The values of the constants were obtained numerically by fitting dynamic data as well as the viscosities and normal stresses data measured in shear. Applying experimental tests and numerical simulations to two branched low-density polyethylene melts in the entry region of a 14:1 planar contraction revealed a small vortex with increasing flow rate for one and vortex growth in the same range of flow rates for the other. Results showed good agreement between experimental tests and numerical solutions. Rheological data have been measured over a wide range of shear and elongational rates and demonstrated a difference in the rheological behavior of the two polymer melts with LDPE 2 being more elastic and strain hardening than LDPE 1. The LDPE 2 also showed substantial strain hardening in the planar extensional viscosity for all strain rates which is mainly responsible for the huge vortices in the entry flow. Furthermore, in order to account for the obtained high value for the first normal stress (N1), a new damping function has been utilized. The differences in flow behavior of the two branched melts are found to be attributed to huge differences in the average relaxation times, giving rise to difference De numbers or dimensionless stress ratio SR, for the same flow rates and another rise to high Trouton ratios TR was made due to the extensional strain-hardening behavior of the vortex producing polymer. It was concluded that it is possible for two similar branched LDPEs to behave in a different manner while processing through dies in the same range of flow rates as evidenced by their flow patterns in planar contractions and this was proven by the results obtained for LDPE 1 and LDPE 2.

Olley, P. [7] presented the KBKZ equation specialized in its ‘separable’ form, which proved to result in shear thinning, allowing strain hardening response in both planar and uniaxial elongation. Through model demonstration, this was done using the altered form of the damping function, h(S), where S=f (I1, I2) permitted modeling of strain hardening while simultaneously giving shear softening in planar flow. This is vital because such a characteristic can be revealed by many industrial materials such as LDPE. The new damping model showed vortex growth for LDPE at both planar and axisymmetric contraction flows, which are considered as advancement to previous models that failed to comprehend vortex growth in planar contraction flows. Obtained results using the new damping model are compared with the well established results using an existing damping model for 4:1 axisymmetric contraction flow. Moreover, the new model damping function adaptation was in agreement with the time-strain separability assumption of the Wagner's form of damping function h (I1,I2). A close fit to steady-state experimental data for uniaxial elongation and shear stress was done using chosen forms of S and h(S). A good resulting fit was obtained, although it was considered to be over predicting for the transient shear stress. Finally the proposed modified damping function of the model was proven to have the ability to be used to simulate LDPE polymer melt flow in both planar and axisymmetric flows.

Wagner, M.H. [8] analyzed, in terms of an integral constitutive equation, the uniaxial elongational flow data of well characterized LDPE melt. The memory function was altered to be separated into a product of two functions for uniaxial flow, one describing the time dependence and the other the strain dependence of memory function. The used constitutive equation was derived from the Lodge's rubberlike- liquid equation, which is a valid description of material behavior in the linear viscoelastic range, after modifying it. Modification such as assuming that the memory function is a function of the relative strain applied as well as a function of the time difference between observation and network junctions' creation was made. Comparing such model results with the limited available experimental data showed general satisfactory agreement for Hencky strain € up to €=4, while higher strains lie above experimental results.

THEORETICAL ANALYSIS AND DERIVATIONS

Like any classical rheology flow problems, our solving steps can be summarized in two main phases. Phase one is to find the best appropriate tensorial expression for stress as a function of the deformation, using the best chosen constitutive equation to match our behavior. The second phase would be to use such an expression or relation with the equations of motion and the continuity equation that describes our flow in the capillary rheometer in order to find the appropriate velocity and pressure profiles that best describes such a flow. And in a future work phase, this can be further verified experimentally through experimental tests done using the capillary rheometer for the flow of LLDPE/ LDPE blend in its melt state. The flow of the LLDPE/LDPE blends through a capillary rheometer is assumed to be steady, incompressible and unidirectional, flowing in the Z axis direction as shown in figure 1. Moreover, the flow is considered to be axisymetrical. The material function under investigation in our flow, is the non linear shear stress growth coefficient, $\eta^+(t,\dot{\gamma})$. An expression for $\eta^+(t,\dot{\gamma})$ can be found using equation (1);

$$\eta^+(t,\dot{\gamma}) = \frac{-\tau_{12}}{\dot{\gamma}} \qquad 1$$

where $-\tau_{12}$ is the stress component that affects our material function and $\dot{\gamma}$ is the rate of strain. As mentioned earlier the field dependent characteristic or the shear stress can be found using our proposed constitutive equation. Due to the vital importance of such a step we will first try using a relatively simple constitutive equation as explained earlier, which is the Lodge equation, to check for the feasibility of the analysis.

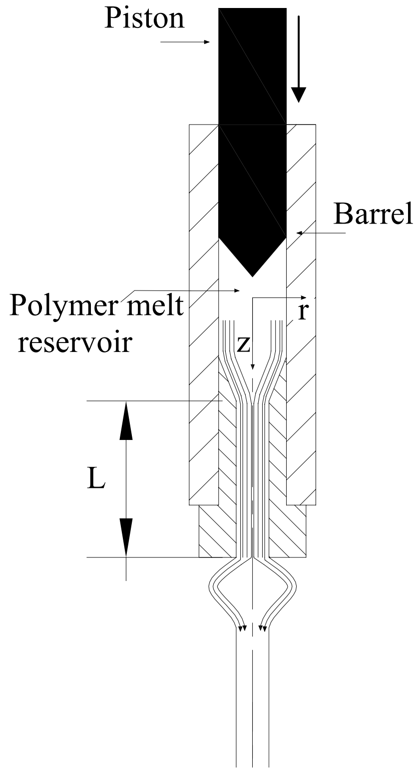

Figure (1) Capillary Rheometer with chosen coordinate system [6]

The Lodge equation takes the general form;

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{-(t-t')/\lambda} \underline{\underline{c}}^{-1}(t',t)\,dt' \qquad 2$$

where $\underline{\underline{\tau}}(t)$ is the shear stress tensor at time t, which we aim to find through such a model.

The material standard flow that can represent such a flow in the capillary rheometer is the start up of steady shear with the following kinematics which are presented in figures (2a) and (2b) as follows;

$$v = \begin{pmatrix} \dot{\gamma}_{12}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123}, \qquad \begin{matrix} \dot{\gamma}_{21} = 0 & & t \le 0 \\ & \text{for} & \\ \dot{\gamma}_{21} = \dot{\gamma}_o & & t \succ 0 \end{matrix}$$

Knowing that the finger tensor $\underline{\underline{C}}^{-1}$ equals to:

$$C^{-1} = \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad 6$$

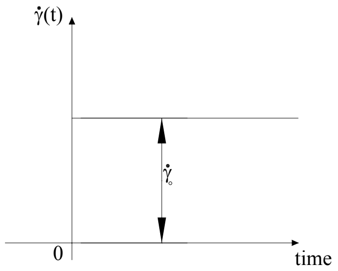

Figure (2 a) showing the flow strain rate vs. time

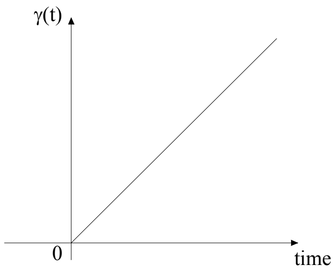

Figure (2 b) showing the flow strain vs. time

Then by substitution in the introduced Lodge equation yields,

$$\tau_{21}(t) = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{-\left(\frac{t-t'}{\lambda}\right)} \gamma dt' \qquad 3$$

$$\frac{-\tau_{21}}{\dot{\gamma}_0 \frac{\eta_0}{\lambda^2}} = \int_{-\infty}^{0} e^{-\left(\frac{t-t'}{\lambda}\right)} t dt' + \int_{0}^{t} (t-t') e^{-\left(\frac{t-t'}{\lambda}\right)} dt' \qquad 4$$

let $s = t - t'$ limits $t' = -\infty$

$t' = 0$ $t' = t$

$ds = -dt'$ $s = \infty$

$s = t$ $s = 0$

$$\frac{-\tau_{21}\lambda^2}{\dot{\gamma}_0 \eta_0} = \int_{t}^{\infty} e^{\frac{-s}{\lambda}} t ds + \int_{0}^{t} s e^{\frac{-s}{\lambda}} ds \qquad 5$$

As shown the equation can be divided into two different regimes.

First for Regime 1:

$$\int_{t}^{\infty} e^{\frac{-s}{\lambda}} t ds = t \int_{t}^{\infty} e^{\frac{-s}{\lambda}} ds = t \left[e^{\frac{-s}{\lambda}} \frac{1}{1/-\lambda} \right]_t^{\infty} = \lambda t e^{\frac{-t}{\lambda}} \qquad 6$$

And for Regime 2 it must be integrated by parts as follows:

Let $u = s$ $dv = e^{-s/\lambda} ds$

$du = ds$ $v = -\lambda e^{-s/\lambda}$

$$\int_{0}^{t} s e^{-s/\lambda} ds = -s\lambda e^{-s/\lambda} \Big|_0^t - \int_{0}^{t} -\lambda e^{-s/\lambda} ds$$

$$\int_{0}^{t} s e^{-s/\lambda} ds = -t\lambda e^{-t/\lambda} + \left(-\lambda^2\right)\left[e^{-t/\lambda} - 1\right] \qquad 7$$

Combining the two regimes in one equation again in order to find an expression for $\eta^+(\text{t}, \dot{\gamma})$ yields,

$$\frac{-\tau_{21}\lambda^2}{\dot{\gamma}_0 \eta_0} = \lambda t e^{-t/\lambda} - t\lambda e^{-t/\lambda} - \lambda^2\left[e^{-t/\lambda} - 1\right] \qquad 8$$

$$\frac{-\tau_{21}\lambda^2}{\dot{\gamma}_0 \eta_0} = -\lambda^2\left[e^{-t/\lambda} - 1\right] \qquad 9$$

$$\frac{\eta^+(\text{t}, \dot{\gamma})}{\eta_0} = -\left[e^{-t/\lambda} - 1\right] \qquad 10$$

$$\eta^+(\text{t}, \dot{\gamma}) = \eta_0\left[1 - e^{-t/\lambda}\right] \qquad 11$$

Where equation (11) represents the expression derived for the non linear shear stress coefficient for the start up of shear for our flow. This can be plotted as shown in figure 3.

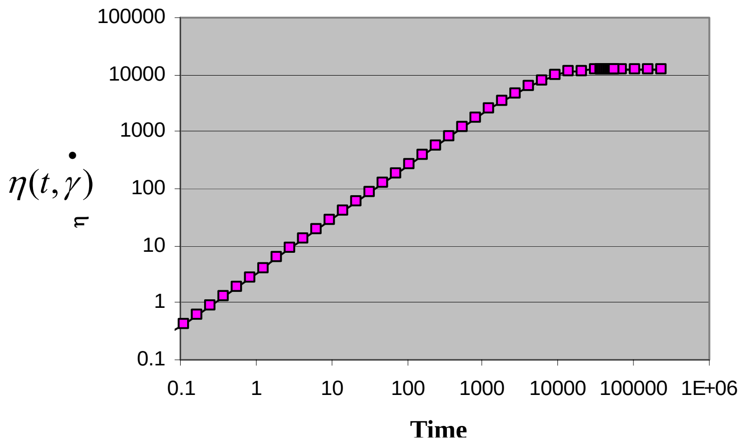

Figure (3) Non linear shear stress growth coefficient vs. time for the proposed Lodge Model

Although the lodge equation was derived for the $\eta^{+}(\mathrm{t},\dot{\gamma})$ without any complications in a straight forward derivation it is only a function of the zero shear viscosity η_0 and therefore it couldn't show any non linear behavior for the flow. This is a set back that has to be improved by using more complicated constitutive equation. The next proposed constitutive equation for such a flow analysis is the Wagner equation. The Wagner equation usually takes the form:

$$\underline{\underline{\tau}}(t) = \int_{-\infty}^{t} M(t-t')C^{-1}(t,t')h(I_1,I_2)dt' \quad [7] \qquad 12$$

where $M(t,t')$ is the linear viscoelastic (LVE) memory function that can be approximated by different forms[7], here we will demonstrate two of these forms. Form number one can be described as;

$$M(t-t') = \frac{G}{\lambda}\exp\left(\frac{-(t-t')}{\lambda}\right) \qquad 13$$

And form two which is a series of exponential functions in the form of;

$$M(t-t') = \sum_i \frac{g_i}{\lambda_i} e^{-(t-t')/\lambda_i} \quad [8] \qquad 14$$

where the relaxation modulli and the relaxation time are taken to be g_i and λ_i respectively. Note that these memory function relation constants can be used indirectly to deduce the length L of the capillary rheometer tube that would allow the entrance and exit effects of the flow to be eliminated without affecting our results. The function $h(I_1,I_2)$, is considered as the strain damping function that is responsible for differentiating between the linear and the non linear strain regions. Moreover, I_1 and I_2 are considered as the first and second invariants of the finger tensor $\underline{\underline{C}}^{-1}(t,t')$ respectively. We will show two of the forms used to represent such a function. Form one is given by equation (15) as;

$$h(I_1) = \exp\left[-n\sqrt{I_1 - 3}\right] \qquad 15$$

Moving to the second form for the strain damping function we used the original Wagner exponent to represent it and hence we could write $h(I_1,I_2)$ as;

$$h(I_1,I_2) = e^{-k(\beta I_1 + (1-\beta)I_2)0.5} \quad [8] \qquad 16$$

We can deduce that the first and second invariants of the finger tensor as follow;

$$I_1 = trace\left[\underline{\underline{C}}^{-1}\right] = \gamma^2 + 3 \qquad 17$$

$$I_2 = \underline{\underline{C}}^{-1} : \underline{\underline{C}}^{-1} = \sum_{m=1}^{3}\sum_{p=1}^{3} C^{-1}{}_{mp} : C^{-1}{}_{pm} = \gamma^4 + 4\gamma^2 + 3 \qquad 18$$

Using the simplified form of the Wagner model (i.e. form number one) we can write the shear stress tensor after substitution as;

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \frac{G}{\lambda}\exp\left(\frac{-(t-t')}{\lambda}\right)\exp(-n\gamma)\gamma dt' \qquad 19$$

where using strain rather than strain rate is a little bit more complicated as it must be found as with to a reference time, therefore in our case for start up of shear with the following kinematics

$$\underline{v} = \begin{pmatrix} \dot{\gamma}_0 x_2 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{matrix} t < 0 \\ t \geq 0 \end{matrix}, \quad \begin{matrix} \dot{\gamma}(t) = 0 \\ \dot{\gamma}(t) = \dot{\gamma}_0 \end{matrix},$$

$$\gamma = \dot{\gamma}(t-t') = \dot{\gamma}(t-0) = \dot{\gamma}(t)$$

$$\gamma = \dot{\gamma}(t-t')$$

Then the stress tensor equation is given by;

$$-\underline{\underline{\tau}}(t) = \int_{-\infty}^{0} \frac{G}{\lambda}\exp\left(\frac{-(t-t')}{\lambda}\right)\exp\left(-n\dot{\gamma}t\right)\dot{\gamma}(t)\,dt' + \int_{0}^{t} \frac{G}{\lambda}\exp\left(\frac{-(t-t')}{\lambda}\right)\exp\left(-n\dot{\gamma}t\right)\dot{\gamma}(t-t')\,dt' \qquad 20$$

As seen with the analysis for the Lodge model equation, the flow behavior can be divided into two regimes,

For Regime1;

$$\int_{-\infty}^{0}\frac{G}{\lambda}\exp\left(\frac{-(t-t')}{\lambda}\right)\exp\left(-n\dot{\gamma}t\right)\dot{\gamma}(t)\,dt' =$$

$$\frac{G\dot{\gamma}}{\lambda}\int_{-\infty}^{0}\exp\left(\frac{-(t-t')}{\lambda}\right)\exp\left(-n\dot{\gamma}t\right)(t)\,dt' \qquad 21$$

let $s = t - t'$

then $ds = -dt'$

limits $t' = -\infty \quad t' = 0 \quad t' = t$

$s = \infty \quad s = t \quad s = 0$

$$\int_{-\infty}^{0}\frac{G}{\lambda}\exp\left(\frac{-(t-t')}{\lambda}\right)\exp\left(-n\dot{\gamma}t\right)\dot{\gamma}(t)\,dt' = \frac{-G\dot{\gamma}(t)}{\lambda}\exp\left(-n\dot{\gamma}t\right)\int_{t}^{\infty}\exp\left(\frac{-s}{\lambda}\right)ds$$

$$= \frac{-G\dot{\gamma}(t)}{\lambda}\exp\left(-n\dot{\gamma}t\right)\left[\lambda\exp\left(\frac{-s}{\lambda}\right)\right]_{t}^{\infty}$$

$$= -G\dot{\gamma}(t)\exp\left(-n\dot{\gamma}t\right)\exp\left(\frac{-t}{\lambda}\right)$$

For Regime2;

$$\int_{0}^{t}\frac{G}{\lambda}\exp\left(\frac{-(t-t')}{\lambda}\right)\exp\left(-n\dot{\gamma}(t-t')\right)\dot{\gamma}(t-t')\,dt'$$

$$= -\frac{G\dot{\gamma}}{\lambda}\int_{0}^{t}\exp\left(\frac{-s}{\lambda} - n\dot{\gamma}s\right)s\,ds \qquad 22$$

Let $u = s \qquad dv = \exp\frac{-s}{\lambda} - n\dot{\gamma}s$

$du = ds$

$$v = (-\lambda - \frac{1}{n\dot{\gamma}}) * \exp\frac{-s}{\lambda} - n\dot{\gamma}s = (\frac{-\lambda n\dot{\gamma} - 1}{n\dot{\gamma}}) * \exp\frac{-s}{\lambda} - n\dot{\gamma}s$$

$$\int_{0}^{t}\frac{G}{\lambda}\exp\left(\frac{-(t-t')}{\lambda}\right)\exp\left(-n\dot{\gamma}(t-t')\right)\dot{\gamma}(t-t')\,dt'$$

which is equal to

$$-\frac{G\dot{\gamma}}{\lambda}\left[(\frac{-\lambda n\dot{\gamma}-1}{n\dot{\gamma}}) * t * \exp\left(\frac{-t}{\lambda} - n\dot{\gamma}t\right)\right] - \left[(\frac{-\lambda n\dot{\gamma}-1}{n\dot{\gamma}})^2 * \exp\left(\frac{-t}{\lambda} - n\dot{\gamma}t\right) - (\frac{-\lambda n\dot{\gamma}-1}{n\dot{\gamma}})^2\right]$$

Combining the final result for equations 21 and 22 for the two regimes in one equation in order to find an expression for the stress;

$$-\tau_{21} = -G\dot{\gamma}(t)\exp\left(-n\dot{\gamma}t\right)\exp\left(\frac{-t}{\lambda}\right) - \frac{G\dot{\gamma}}{\lambda}\left[(\frac{-\lambda n\dot{\gamma}-1}{n\dot{\gamma}}) * t * \exp\left(\frac{-t}{\lambda} - n\dot{\gamma}t\right)\right]$$

$$-\left[(\frac{-\lambda n\dot{\gamma}-1}{n\dot{\gamma}})^2 * \exp\left(\frac{-t}{\lambda} - n\dot{\gamma}t\right) - (\frac{-\lambda n\dot{\gamma}-1}{n\dot{\gamma}})^2\right]$$

$$\eta^{+}(t,\dot{\gamma}) = -G(t)\exp\left(-n\dot{\gamma}t\right)\exp\left(\frac{-t}{\lambda}\right) - \frac{G}{\lambda}\left[(\frac{-\lambda n\dot{\gamma}-1}{n\dot{\gamma}}) * t * \exp\left(\frac{-t}{\lambda} - n\dot{\gamma}t\right)\right] \qquad 23$$

$$-\left[(\frac{-\lambda n\dot{\gamma}-1}{n\dot{\gamma}})^2 * \exp\left(\frac{-t}{\lambda} - n\dot{\gamma}t\right) - (\frac{-\lambda n\dot{\gamma}-1}{n\dot{\gamma}})^2\right]$$

The relation presented by equation (23) can be plotted as shown in figure 4.

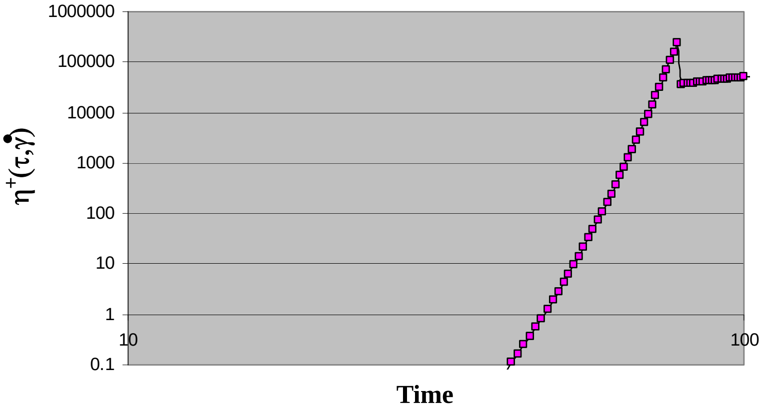

Figure (4) The non-linear shear stress growth coefficient vs. time for the proposed first Wagner Model

The second form of the Wagner equation, which is seen to be the most complicated of all the proposed models, can be derived using the same analyzing steps as illustrated. Once more the integral for the stress tensor presented in equation (12) can be divided into two distinct regimes the first at $t \le 0$ and the second at $t > 0$.

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t}\left(\sum_i \frac{g_i}{\lambda_i}e^{-(t-t')/\lambda_i}\right)\left(e^{-k(\beta I_1 + (1-\beta)I_2)^{0.5}}\right)c^{-1}(t,t)dt'$$

Where I_1 and I_2 are given in equations 17 and 18 respectively and therefore the shear stress coefficient can be written as;

$$-\tau_{12}(t) = \int_{-\infty}^{0}\left(\sum_i \frac{g_i}{\lambda_i}e^{-(t-t')/\lambda_i}\right)\left(e^{-\frac{1}{2}k\left[\gamma^2(-3\beta+4)+\gamma^4(1-\beta)+3\right]}\right)\gamma dt'$$

Dividing the equation into the two distinct regimes;

$$\frac{-\tau_{12}}{\sum_i \frac{g_i}{\lambda_i}} = \int_{-\infty}^{0} \left(e^{-(t-t')/\lambda_i}\right)\left(e^{-\frac{1}{2}k\left[\dot{\gamma}(t)(-3\beta+4)+\dot{\gamma}^4\,(t^4)(1-\beta)+3\right]}\right)\dot{\gamma}(t)\,dt' +$$

$$\int_{0}^{t} \left(e^{-(t-t')/\lambda_i}\right)\left(e^{-\frac{1}{2}k\left[\dot{\gamma}(t-t')(-3\beta+4)+\dot{\gamma}^4\,(t-t')^4(1-\beta+3)\right]}\right)\dot{\gamma}(t-t')\,dt'$$

For Regime1

$$\int_{-\infty}^{0} \left(e^{-(t-t')/\lambda_i}\right)\left(e^{-\frac{1}{2}k\left[\dot{\gamma}(t)(-3\beta+4)+\dot{\gamma}^4\,(t^4)(1-\beta)+3\right]}\right)\dot{\gamma}(t)\,dt'$$

$$= \left(e^{-\frac{1}{2}k\left[\dot{\gamma}(t)(-3\beta+4)+\dot{\gamma}^4\,(t^4)(1-\beta)+3\right]}\right)\dot{\gamma}(t)\left[\lambda_i e^{(-t/\lambda_i)}\right]$$

For Regime2

$$\int_{0}^{t} \left(e^{-(t-t')/\lambda_i}\right)\left(e^{-\frac{1}{2}k\left[\dot{\gamma}(t-t')(-3\beta+4)+\dot{\gamma}^4\,(t-t')^4(1-\beta+3)\right]}\right)\dot{\gamma}(t-t')\,dt'$$

$$= \dot{\gamma}\, e^{-\frac{3}{2}k} \int_{0}^{t} s e^{-\frac{s}{\lambda_i} - 1/2k\dot{\gamma}(-3\beta+4)s - 1/2k\dot{\gamma}^4\,(1-\beta)s^4}\, ds$$

and then nonlinear shear growth coefficient can be obtained as;

$$\eta^+(\mathrm{t},\dot{\gamma}) = -\sum_i \frac{g_i}{\lambda_i}\left[\begin{array}{l}\left(e^{-\frac{1}{2}k\left[\dot{\gamma}(t)(-3\beta+4)+\dot{\gamma}^4\,(t^4)(1-\beta)+3\right]}\right)\dot{\gamma}(t)\left[\lambda_i e^{(-t/\lambda_i)}\right]+ \\ \dot{\gamma}\, e^{-\frac{3}{2}k} \int_{0}^{t} s e^{-\frac{s}{\lambda_i} - 1/2k\dot{\gamma}(-3\beta+4)s - 1/2k\dot{\gamma}^4\,(1-\beta)s^4}\, ds\end{array}\right] \quad 24$$

where values for k and β are material constants obtained experimentally. g_i and λ_i , the relaxation modulli and relaxation time respectively, are obtained experimentally at different temperatures for the polymer melt. As it can be seen, equation (24) is the most complicated relation obtained for the non linear shear stress growth coefficient, among all of the chosen constitutive equations for the analysis. The equation complexity and its dependence upon several experimentally measured parameters prevented any plots from being made theoretically, without further experimental work to obtain these parameters. These experiments are intended to be performed later on in our future contribution in such an important field. However, such an obtained theoretical equation allows researchers to relate the relaxation modulli and relaxation time, g_i and λ_i respectively to the fluid flowing through the capillary rheometer fully developed Length 'L' which allows for more accurate measurements to be made using the capillary.

CONCLUSION

Through this work, a theoretical expression for the non linear steady shear growth coefficient $\eta^+(\mathrm{t},\dot{\gamma})$ of the LLDPE/LDPE blend as it flows through a capillary rheometer was obtained using two different constitutive equations, namely the lodge equation and the Wagner equation with two different memory functions. The lodge equation and the Wagner equation with the firstly proposed simplified memory function are seen to be feasible, simple to use and the relation between $\eta^+(\mathrm{t},\dot{\gamma})$ and time was kind of straight forward to obtain and plot as seen in figures 3 and 4 respectively. Moreover, the second memory function proposed for the Wagner model was very complicated as shown prohibiting any plots being made for its verification without further experimental analysis, to obtain several parameters and constants for the equation. However, such an equation had the huge advantage of relating the relaxation modulli and relaxation time and the length L of the capillary rheometer. This relation can help to obtain the correct length of the capillary rheometer L that can allow for the elimination of the entrance and exit effects of capillary rheometer on the melt flow without any loss of accuracy. This can in its turn help to better design experiments using such a rheometer, and to increase the reliability of the obtained data or even design a dedicated rheometer for a specific melt.

NOMENCLATURE

Coordinate system specifications

Z	The Z-axis direction (in the flow direction)
	Radial coordinates (radial distance measured from the center line of the Capillary Rheometer)
L	Length of the developed region of the polymer melts

Mathematical Constants

$\underline{\underline{C}}^{-1}(t,t')$	The finger tensor
$M(t-t')$	The linear viscoelastic (LVE) memory function
$h(I_1, I_2)$	The strain damping function
I_1 and I_2	The first and second invariants of the finger tensor
k and β	Material constants obtained experimentally
g_i	Relaxation modulli of the Polymer Melt

Greek symbols

λ_i	Relaxation Time of the Polymer Melt
$\eta^{+}(\mathrm{t}, \dot{\gamma})$	The non linear shear stress growth coefficient
η_0	The Zero Shear Viscosity
γ	Shear strain
$\dot{\gamma}$	Shear strain rate (1/s)
$\underline{\underline{\tau}}(t)$	Stress tensor (Pa)
$-\tau_{12}$	Shear stress (PaPut nomenclature here.

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