Identification of a Visco-Elastic Model for PET Near Tg Based on Uni and Biaxial Results

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Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77545 Marne-la-Vallée, France

Abstract. The mechanical response of Polyethylene Terephthalate (PET) in elongation is strongly dependent on temperature, strain and strain rate. Near the glass transition temperature Tg, the stress-strain curve presents a strain softening effect vs strain rate but a strain hardening effect vs strain under conditions of large deformations. The main goal of this work is to propose a viscoelastic model to predict the PET behaviour when subjected to large deformations and to determine the material properties from the experimental data. The viscoelastic model is written in a Leonov like way and the variational formulation is carried out for the numerical simulation using this model. To represent the non–linear effects, an elastic part depending on the elastic equivalent strain and a non-Newtonian viscous part depending on both viscous equivalent strain rate and cumulated viscous strain are tested. The model parameters can then be accurately obtained through the comparison with the experimental uniaxial and biaxial tests.

Keywords: Identification, viscoelastic, nonlinear behaviour, experimental uniaxial and biaxial tests, numerical simulation.

INTRODUCTION

Polyethylene terephthalate (PET) under conditions of large deformations, during high strain rate elongation at temperature near the glass transition Tg, exhibits a pronounced nonlinear behaviour where non linear viscous and elastic effects appear. Both hyperelastic [1] and viscoplastic [2] approaches fail to show this response. In addition, classical viscoelastic models such as the Upper Convected Maxwell model [3] or the Giesekus model do not adequately demonstrate this reaction. Inspired by Figiel and Buckley [4], the assumption of an additive decomposition of elastic and viscous velocity gradient ($\underline{\underline{D}} = \underline{\underline{D_e}} + \underline{\underline{D_v}}$) is adopted to describe the kinematic structure of the constitutive models. This choice, together with the assumption of zero viscous spin, leads to the Leonov equation [5]. The numerical implementation is presented and compared with analytical solution of uniaxial and biaxial elongation in the linear case (i.e. constant values of shear modulus G and viscosity η). In order to represent the experimental uniaxial and biaxial tests [6] performed on PET, nonlinear forms of elastic and viscous characteristics $G(\varepsilon_e)$ and $\eta(\dot{\varepsilon}_v, \varepsilon_v)$ are proposed. This model may be implemented to simulate the stretch blow moulding process for example.

AN INCOMPRESSIBLE LARGE STRAIN VISCOELASTIC MODEL

Figiel and Buckley [3] suggest to build a viscoelastic model adapted to highly elastic polymers as an extension of the hyper elastic approach used for rubber like materials coupled with a viscous part. In their proposition the viscous part is supposed to be incompressible, the volume variation under pressure is assumed to be purely elastic. In the following, considering the difficulty to provide data to identify the volume variation, we differ slightly considering both parts as incompressible. In the linear case, both relations can be written:

$$\begin{aligned} \underline{\underline{\sigma}} &= 2G\underline{\underline{\varepsilon_e}} - p_e\underline{\underline{I}} \\ \underline{\underline{\sigma}} &= 2\eta\underline{\underline{D_v}} - p_v\underline{\underline{I}} \end{aligned} \tag{1}$$

$\underline{\underline{\sigma}}$ is the Cauchy stress tensor, $\underline{\underline{D_v}}$ is the symmetric part of the viscous velocity gradient and the double underscore means it's a second order tensor. $\underline{\underline{\varepsilon_e}}$ is the elastic part of the Eulerian strain measure defined by:

$$\underline{\underline{\varepsilon_e}} = \frac{1}{2}\left(\underline{\underline{B_e}} - \underline{\underline{I}}\right) \tag{2}$$

where $\underline{\underline{B_e}}$ is the elastic part of the left Cauchy-Green tensor. p_e and p_v are pressures associated with the incompressible conditions of both parts:

$$\det \underline{\underline{B_e}} = 1, \qquad div\vec{V}_v = trace\underline{\underline{D_v}} = 0 \tag{3}$$

where $\vec{V}_v$ is the viscous velocity.

Combining Eqs.1 and the elastic and viscous strain rates in the Oldroyd derivation of the elastic left Cauchy-Green tensor, one can obtain the Leonov like Eq.4:

$$\frac{\delta \underline{\underline{B_e}}}{\delta t} + \frac{1}{\theta}\underline{\underline{B_e}}.\underline{\underline{\hat{B}_e}} = 0 \tag{4}$$

where θ is the relaxation time, ratio of the viscosity η and elastic shear modulus G. The subscript "^" denotes the deviatoric part of the tensor.

VARIATIONAL FORMULATION FOR NUMERICAL SIMULATION

Using the Eq.1, the weak form of the problem leads to an ill-conditioned problem, so we use a Zener like model by adding a Newtonian branch. We choose a small value of the viscosity η_N in the Newtonian branch so the behaviour law can be written:

$$\begin{cases} \underline{\underline{\hat{\sigma}}} = 2G\underline{\underline{\hat{\varepsilon}_e}} = G\underline{\underline{\hat{B}_e}} \\ \underline{\underline{\hat{\sigma}}} = 2\eta \underline{\underline{D_v}} \end{cases} \quad and \quad \underline{\underline{\sigma}} = 2\eta_N \underline{\underline{D}} + \underline{\underline{\hat{\sigma}}} - p\underline{\underline{I}} \tag{5}$$

We assume that the body and gravitational forces can be neglected. In the plane stress cases of uni and equibiaxial elongations, considering the incompressibility, the pressure p is given by Eq.6:

$$\sigma_{33} = 0 \Rightarrow p = -2\eta_N\left(D_{11} + D_{22}\right) + \frac{G}{3}\left(\frac{2}{B_{11}B_{22} - B_{12}^2} - B_{11} - B_{22}\right) \tag{6}$$

Therefore, the searched solution is a mixed velocity $\underline{V}$ and $\underline{\underline{B_e}}$ formulation. Considering the Eqs.4 to 6, the weak form over the entire volume Ω is given by:

$$\begin{aligned} &2\eta_N \int_\Omega \underline{\underline{D}}^* : \underline{\underline{D}} d\Omega + G\int_\Omega \underline{\underline{D}}^* : \underline{\underline{\hat{B}_e}} d\Omega + 2\eta_N \int_\Omega tr\left(\underline{\underline{D}}^*\right)\left(D_{11} + D_{22}\right) d\Omega \\ &- \frac{G}{3}\int_\Omega tr\left(\underline{\underline{D}}^*\right)\left(\frac{2}{B_{11}B_{22} - B_{12}^2} - B_{11} - B_{22}\right) d\Omega = 0; \end{aligned}$$

$$\int_\Omega \underline{\underline{B}}^* : \left(\frac{\delta \underline{\underline{B_e}}}{\delta t} + \frac{1}{\theta}\underline{\underline{B_e}}\underline{\underline{\hat{B}_e}}\right) d\Omega = 0 \tag{7}$$

RESULTS

In the cases of homogeneous and plane stress uniaxial and equibiaxial elongations, the Cauchy stress tensor $\underline{\underline{\sigma}}$ and the strain rate tensor $\underline{\underline{D}}$, writes:

$$\underline{\underline{\sigma}} = \begin{pmatrix} \sigma_U & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \text{ and } \underline{\underline{D}} = \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon}/2 & 0 \\ 0 & 0 & -\dot{\varepsilon}/2 \end{pmatrix} ; \underline{\underline{\sigma}} = \begin{pmatrix} \sigma_B & 0 & 0 \\ 0 & \sigma_B & 0 \\ 0 & 0 & 0 \end{pmatrix} \text{ and } \underline{\underline{D}} = \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & \dot{\varepsilon} & 0 \\ 0 & 0 & -2\dot{\varepsilon} \end{pmatrix} \quad (8)$$

One can solve Eq.4 and then, substituting in Eq.5, can obtain the elongation uniaxial and biaxial stresses, respectively σ_U and σ_B versus time or global elongation. For uniaxial and biaxial elongations, the related elastic elongations λ_e are given from the differential relations:

$$\dot{\lambda}_e/\lambda_e + \left(\lambda_e^2 - 1/\lambda_e\right)/3\theta = \dot{\varepsilon} \; ; \; \dot{\lambda}_e/\lambda_e + \left(\lambda_e^2 - 1/\lambda_e^4\right)/6\theta = \dot{\varepsilon} \quad (9)$$

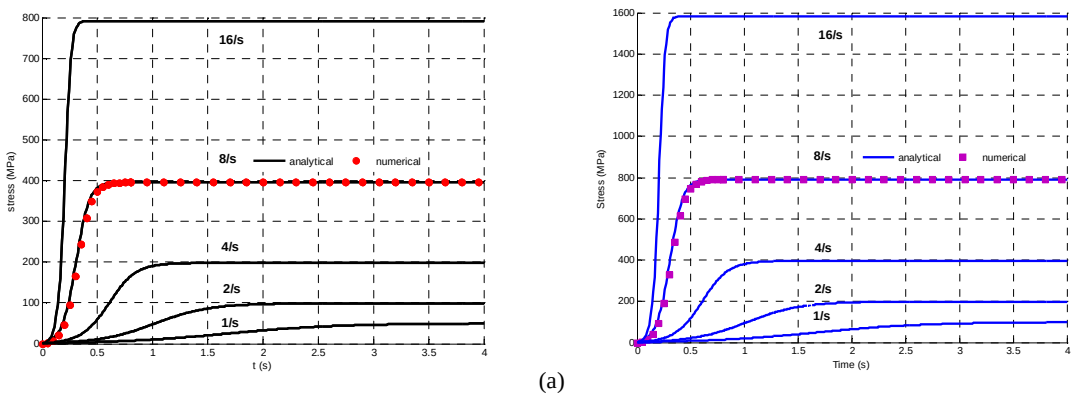
where $\dot{\varepsilon}$ is the global strain rate. The related stresses are then:

$$\sigma_U = 3\eta_N \dot{\varepsilon} + G\left(\lambda_e^2 - 1/\lambda_e\right) \qquad \sigma_B = 6\eta_N \dot{\varepsilon} + G\left(\lambda_e^2 - 1/\lambda_e^4\right) \quad (10)$$

TABLE (1). Material parameters used

Property	**Value**
Viscosity η	16.5 MPa.s
Viscosity η_N	200 Pa.s
Shear modulus G	3.29 MPa

From Table 1, the relaxation time θ is 5 s. Uni and biaxial elongations at constant extension rate $\dot{\varepsilon}$ are considered. Figure 1 shows the results of the analytical and numerical solutions are equal, for both elongation cases (uniaxial and biaxial) at a strain rate 8 s^{-1}. Furthermore, it shows that the stress-strain curves for PET are strongly dependent on the strain rate. As the strain rate increases, the whole stress level is found to increase. Even if the modelling for uniaxial and biaxial elongations does not highlight any singularity, the comparison with experimental results of similar tests managed on PET at a temperature slightly over T_g, is not satisfactory. First, the experimental data presents a strain hardening effect (stress increases); second, double the strain rate does not double the asymptotic stress (viscosity presents a softening effect with strain rate); last, at the same value of the elongation λ, biaxial stress is not twice the uniaxial stress. For all these reasons, a non linear version of this model is necessary and discussed in the following.



(a) (b)

FIGURE 1. *Uniaxial (a) and biaxial (b) responses of the linear form of the viscoelastic model; Analytical results VS numerical results at a strain rate 8 s^{-1}.*

TOWARD A NON-LINEAR VISCOELASTIC MODELLING

Beyond the linear case, the structure of the viscoelastic model allows to test all non linear behaviour of the form:

$$\begin{aligned} \underline{\underline{\sigma}} &= 2G_0 f\left(\overline{\varepsilon_e}\right)\underline{\underline{\varepsilon_e}} - p_e \underline{\underline{I}} \\ \underline{\underline{\sigma}} &= 2\eta_0 g\left(\overline{\dot{\varepsilon}_v}, \overline{\varepsilon_v}\right)\underline{\underline{D_v}} - p_v \underline{\underline{I}} \end{aligned} \tag{11}$$

where $\overline{\varepsilon_e}$ is respectively the equivalent elastic strain, $\overline{\dot{\varepsilon}_v}$ is the equivalent viscous strain rate and the equivalent viscous strain $\overline{\varepsilon}_v$. In order to model the strain hardening effect, first, an hyperelastic model is chosen for the elastic part. The Yeoh model, for example, can be used but the results of simulations show that using the non-linear elastic part do not lead to a strain hardening effect. This is quite natural since the global strain rate is constant, when the viscous part reaches a constant value, the stress stop increasing and elastic strain rate becomes null: even if the hyperelastic shows an increasing evolution, that does not impact the viscoelastic model.

Consequently, we focus on the non-linear viscous part of the model chosen as in Cosson and Chevalier [2] that identified a non linear incompressible viscoplastic model, which represents macroscopically the strain hardening effect observed during tension for high strain. We choose the same form of the viscous model:

$$\eta = \eta_0 h\left(\overline{\varepsilon_v}\right)\left(\frac{\overline{\dot{\varepsilon}_v}}{\dot{\varepsilon}_{ref}}\right)^{m-1} \tag{12}$$

The hardening effect is related to the *h* function which increase continuously with $\overline{\varepsilon}_v$ that can be obtained by comparison with the experimental tests. Menary *et al*. [6] recently provided experimental tests at different strain rates for TF9 grade PET under equibiaxial deformation at temperature 90°C. In order to identify the *h* function, we propose the following way:

- For each strain rate, the stress-strain curve of the equibiaxial test, the evolution of the related elastic elongations λ_e can be obtain from Eq.10:

$$\begin{aligned} &\sigma_B \approx G\left(\lambda_e^2 - 1/\lambda_e^4\right) \Rightarrow \lambda_e^{\,6} - \lambda_e^{\,4}\left(\frac{\sigma_B}{G}\right) - 1 = 0 \\ &\Rightarrow \lambda_e^{\,2} = \frac{S}{3} + \frac{1}{6}\left(108 + 8S^3 + 12\sqrt{81 + 12S^3}\right)^{1/3} + \frac{2S^2}{3\left(108 + 8S^3 + 12\sqrt{81 + 12S^3}\right)^{1/3}} \end{aligned} \tag{13}$$

where: S = σ_B/G.

- Then, for each strain rate and for different value of the exponent *m*, the *h* function can be computed from the equation following:

$$h\left(\overline{\varepsilon_v}\right) = \frac{G_0}{6\eta_0}\frac{\left(\lambda_e^2 - 1/\lambda_e^4\right)}{\left(\frac{\overline{\dot{\varepsilon}_v}}{\dot{\varepsilon}_{ref}}\right)^{m-1} D_v} \tag{14}$$

where $D_v = \dot{\varepsilon} - \dot{\lambda}_e / \lambda_e$ in the case of equibiaxial test. Eq.14 gives the *h* evolution versus the equivalent viscous strain $\overline{\varepsilon}_v$ for each strain rate condition. The equibiaxial tests have been carried out for five global strain rates (1, 2, 4, 8, 16 s^{-1}).

- Each tension speed gives a different function *h* versus $\overline{\varepsilon}_v$ for each value of exponent *m*. When we fixed the parameter *m*, we can sum the differences between each *h* curve from each strain rate. The minimal dispersion is obtained for *m* equal to 0.25 as shown in figure 2.

The figure 2(a) illustrates the influence of the parameter *m* on the dispersion between the *h* functions. With the optimal value of *m*, we obtain a similar evolution for the 5 curves of *h* for each strain rate as shown in figure 2(b).

- We obtain a master curve for *h* which highlights an asymptotic value for the equivalent viscous strain $\bar{\varepsilon}_v$ at about 2.1. This leads to an important increase of the viscosity and a zero viscous strain rate when strain reaches this asymptotic value.

- The last step of the identification is to propose a model to represent the curve of the function *h* shown in figure 2(b). We can choose the *h* function which varies exponentially with the viscous strain ε_v:

$$h(\varepsilon_v) = \exp\left(a\varepsilon_v^3 + b\varepsilon_v^2 + c\varepsilon_v + d\right) \tag{15}$$

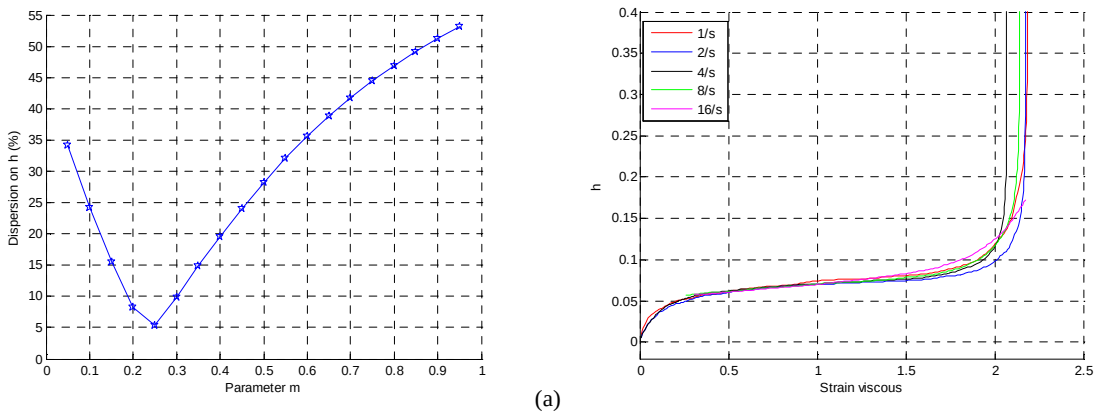


FIGURE 2. *(a) Minimization of differences between h(ε_v) function. An optimal value is obtained for m = 0.25; (b) The h evolution versus the equivalent viscous strain $\bar{\varepsilon}_v$ when m=0.25.*

With the exponential model, even if the steep part of the curve is not perfectly represented, a good representation of the *h* data can be obtained. Therefore, the characteristics of the PET for this model are:

$$m = 0.25,\ a = 7.355,\ b = -10.958,\ c = 5.168,\ d = -3.727.$$

In the following, we implemented this set of parameters into the stress-strain curve. Figure 3 shows that using the viscoelastic model with a non linear viscous part, we can obtain a substantially good representation of the strain hardening effect for different strain rate. The main difference between experimental data and modelled biaxial behaviour is the beginning of the stress-strain curve (when the strain is lower than 0.3): the experimental data initial slope seems to increase when the strain rate rises in contradiction with the results of the viscoelastic model.

This may be corrected by working on the elastic part but since the initial strain is entirely elastic and the stress obtained from this part is not dependent on the strain rate, the goal will not be easy to reach.

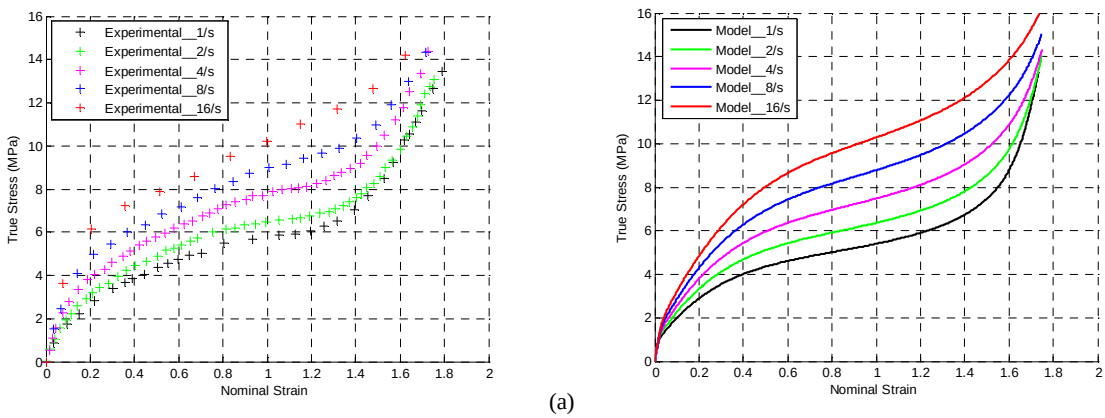


FIGURE 3. *(a) The data experimental [6]; (b) The results of the viscoelastic model.*

The differences between the experimental data and the results of this model are shown in the table 2.

TABLE (2). Errors between the experimental and the results of the model

Strain Rate (/s)	**Absolute Error (%)**
1	8.8
2	9.9
4	8.4
8	7.1
16	12.8

CONCLUSIONS

A basic viscoelastic model is presented in the first part of the paper by introducing both an elastic part and a viscous part that lead to a Leonov like equation. Secondly, the weak form of the problem is proposed for the numerical simulation: simulations fit with analytical solution for uniaxial and biaxial tension tests. This viscoelastic model doesn't highlight singularities in the uniaxial or biaxial elongations for high strain rate and lead to a stale numerical scheme.

Considering the behaviour of PET near T_g exhibits a strain hardening effect, we choose a non-linear viscous model for the viscous part in order to represent this non-linear behaviour. An identification procedure is proposed and leads to a good representation of the experimental data's of biaxial elongation tests.

In further work, we intend to simulate the stretch-blow moulding process together with an improvement of the behaviour law where the viscosity could be related to microscopic variables like crystallization ratio or shape factor of the microstructure. We can also model and identify the temperature effect on PET behaviour. For example, a WLF-like correction is possible to take into account the influence of temperature.

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