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Biaxial hot-drawing of poly(ethylene terephthalate): dependence of yield stress on strain-rate ratio

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During a study of biaxial hot-drawing of amorphous poly(ethylene terephthalate), the yield stress was determined in the temperature window between the glass transition and the rubber-like plateau, for various values of the strain-rate ratio, with one nominal strain-rate kept constant at 1 s^{-1}. Results were used to test predictions of the constitutive model proposed earlier (Buckley, C. P. and Jones, D. C., *Polymer* 1995, **36**, 3301), which expresses flow in terms of a three-dimensional generalisation of the Eyring rate process. Excellent agreement was obtained for the variation of yield stress with strain-rate ratio. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

There is intense interest in the development of constitutive models for representing polymers in simulations of products and forming processes. A particular target of great practical importance is the modelling of hot-drawing of poly(ethylene terephthalate) (PET), which is subjected to biaxial stretching above the glass transition in production of biaxially oriented films and injection-stretch blow-moulded bottles.

It is well-known that if drawing conditions are chosen appropriately PET in this temperature range will behave as a rubber-like network polymer: see for example the recent study of biaxial drawing by Gordon *et al*.[1]. In general, however, the behaviour is more complex, as illustrated by Buckley *et al*.[2]. In particular, at the lower end of the temperature range of practical interest (*ca*. 80°C), there remains a substantial contribution to the deviatoric stress associated with perturbation of inter- and intra-molecular potentials (i.e. bond-stretching). This relaxes by the self-diffusion flow process enabled by segmental motion at the glass transition; but for a strain-rate of 1 s^{-1} relaxation is not complete until a temperature of *ca*. 95°C. At this point there is close correspondence with behaviour of a rubber-elastic network, until the further processes of relaxation by entanglement slippage and/or crystallisation intervene at high strains and higher temperatures.

There is an urgent practical need to be able to model the behaviour of PET across the range of interest, and this is motivating the development of a constitutive model that encompasses within one set of equations the full three-dimensional response of the polymer. Buckley and Jones[3] formulated a model to describe the hot-drawing of amorphous polymers near the glass transition, and this was applied to PET by Buckley *et al*.[2]. According to the model there are two contributions to the Cauchy stress tensor $\mathbf{\Sigma}$: a 'bond-stretching' component $\mathbf{\Sigma}^b$ (dominating deviatoric response at short times and low temperatures and the hydrostatic response at all times), and a 'conformational' component $\mathbf{\Sigma}^c$ (dominating deviatoric response at long times and high temperatures). The purpose of the present note is to verify one vital feature of the model: representation of the non-Newtonian viscous flow process by which the deviatoric part of $\mathbf{\Sigma}^b$ relaxes. This determines the apparent yield of the model, and it is essential that predictions show correct dependence on the state of biaxial strain. Here we test this, by exploiting results obtained with the Oxford Flexible Biaxial Film Tester (FBFT).

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EXPERIMENTS

Biaxial drawing experiments were carried out using the FBFT[2] on isotropic, amorphous PET homopolymer, with thickness 250 μm and number-average molecular weight $M_n = 19\,000$. This machine allows fast biaxial testing of films up to large extensions, with a high degree of flexibility in choice of strain and temperature sequence. The experiments described here were part of a more comprehensive study of biaxial drawing in PET to be reported elsewhere. The square samples of film, with 60 mm square gauge section, were drawn simultaneously in two orthogonal directions, at constant rates of grip displacement, with one axis (axis 1) having a nominal rate of extension $\lambda_1 = 1\ s^{-1}$, and the other (axis 2) having a nominal rate of extension λ_2. In the following we shall use the term 'strain-rate ratio' θ to mean the ratio of true strain rates thus:

$$\frac{\dot{\lambda}_2}{\lambda_2} = \theta \frac{\dot{\lambda}_1}{\lambda_1} \qquad (1)$$

A series of tests was carried out in which the initial θ was varied between 0 and 1: multiple experiments at each value. We also include a result for uniaxial drawing ($\theta = -0.5$), obtained with the same material and testing machine but using a narrow specimen (width = 10 mm), gripped only at its ends. In all the experiments, strains were deduced from deformation of an ink grid marked on the specimen, measured after quenching to room temperature while constrained at the end of the test. The present experiments were carried out at a specimen temperature of 86.9 ± 1°C. Because of the proximity of this temperature to the glass transition of amorphous PET (65°C according to dilatometry), care was taken to subject each specimen to the same prior thermal history. Specimens were therefore mounted in the FBFT and equilibrated in air at the test temperature for 5 min prior to each test.

From the measured loads acting on centre grips, and the width of specimen held by the centre grips, the nominal 'yield' stress on each axis was determined at the start of the plateau on the respective plot of load versus elongation, as described and illustrated previously[2]. From these and the corresponding extension (approximately 0.3), true yield stresses were computed, assuming the volume to remain constant. Since our aim here is to test the prediction of yield in σ_1^b and σ_2^b, the small contributions from conformational stresses σ_1^c and σ_2^c were computed from the Edwards–Vilgis conformational entropy function[4] for the corresponding stretch at yield using parameters determined previously[2] (maximum value *ca.* 1.3 MPa), and were subtracted from the total true yield stress on each axis.

Typical plots of true stress for three different strain-rate ratios are shown in *Figures 1* and *2*, where the yield, flow and strain-stiffening characteristic of hot-drawing of PET can be seen clearly. Moreover, significant variations are visible in the yield stress on axis 2, and in the pattern of strain-stiffening, as θ is varied. From data such as these the mean true yield stresses were computed for each nominal value of θ*. They were corrected by subtraction of the conformational component as described above, and plotted versus initial θ as shown in *Figure 3*. Error bars indicate the uncertainty arising from small variations in temperature between different experiments (standard deviation = 0.5 K): yield of PET is extremely sensitive to temperature in this region. It can be seen that the yield stress as measured on axis 1 (with constant strain-rate) is almost independent of strain-rate ratio, while that measured on axis 2 (with varying strain-rate) rises rapidly but nonlinearly with increasing θ.

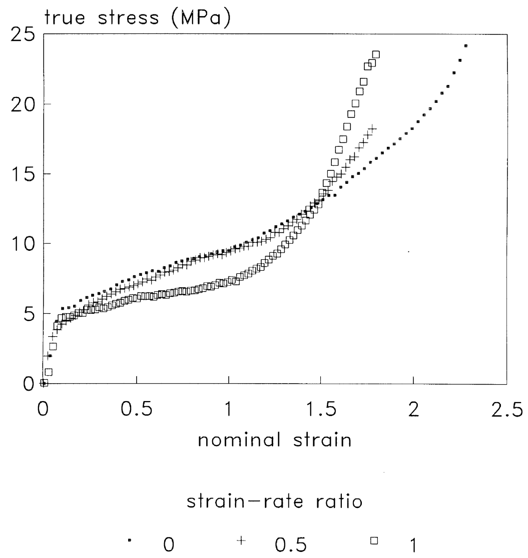

Figure 1 Stress–strain curves on axis 1, obtained during biaxial drawing of PET with various values of initial strain-rate ratio (θ) shown, for a nominal strain-rate of 1 s^{-1} on axis 1

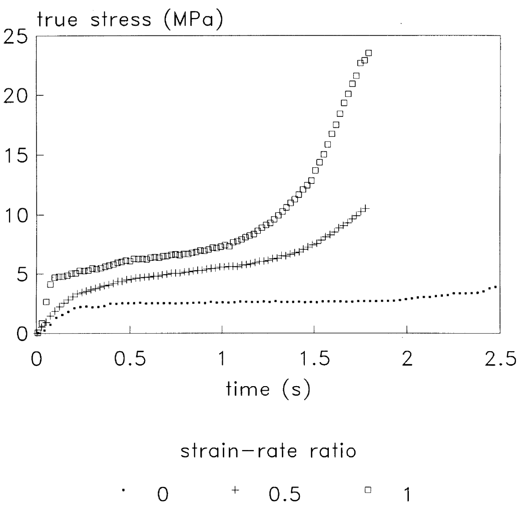

Figure 2 Stress–time curves on axis 2, for the same experiments as *Figure 1*

TEST OF THE CONSTITUTIVE MODEL

The salient feature of the constitutive model is that relaxation of $\mathbf{\Sigma}^b$ takes place by a non-Newtonian flow process at constant volume. Thus during plastic deformation beyond yield (when it is assumed there is no further elastic bond-stretching), the rate of deformation tensor obeys a flow rule of the form:

$$\mathbf{D} = \frac{1}{\mu}\left(\mathbf{\Sigma^b} - \mathbf{I}\, tr\mathbf{\Sigma^b}/3\right) \qquad (2)$$

where μ is a generalised viscosity, dependent on the invariants of $\mathbf{\Sigma}^b$. An unusual feature of the model is that even in its unstrained state $\mathbf{\Sigma}^b$ has a non-zero hydrostatic component σ_{m0}^b balancing a non-zero hydrostatic conformational stress σ_{m0}^c, as explained by Buckley and Jones[3]. If we define the

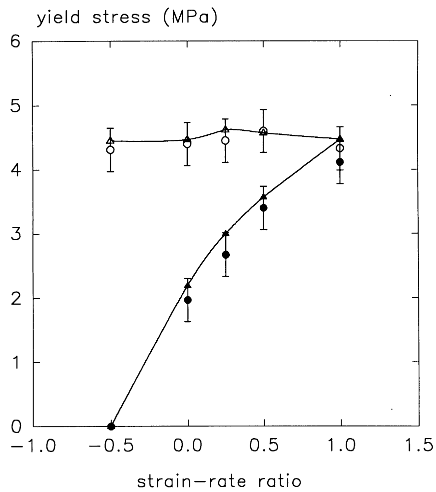

Figure 3 True yield stresses on axes 1 and 2, as measured during biaxial drawing of PET at 87°C, with conformational stress subtracted (see text; open and filled circles for axes 1 and 2, respectively); together with predictions of the constitutive model (equation (5); triangles and full lines)

* Note that tests were carried out with constant rate of grip displacement, therefore true strain-rates varied during each test.

ratio of the strain-dependent parts of the in-plane stresses $\xi = \Delta\sigma_2^b/\Delta\sigma_1^b$, it follows from equation (1) and equation (2) that

$$\xi = \frac{2\theta + 1}{\theta + 2} \tag{3}$$

In the model, the flow process is described by a three-dimensional formulation of Eyring rate-process kinetics. To summarise: flow proceeds by a shear process according to equation (2), but the rate of flow is modulated by the hydrostatic component of stress because the transition state is expected to be a locally dilated state. Under these conditions the strain-rate along axis 1 may be expressed as follows[3]

$$\frac{\dot{\lambda}_1}{\lambda_1} = \frac{2(2-\xi)RT}{3\mu_0 V_s}\left(\frac{\Delta\sigma_1^b}{\tau_{oct}^b}\right)\exp\left(\frac{V_p\Delta\sigma_m^b}{RT}\right)\sinh\left(\frac{V_s\tau_{oct}^b}{2RT}\right) \tag{4}$$

where $\Delta\sigma_m^b$ and τ_{oct}^b are the hydrostatic and octahedral shear components of $\mathbf{\Sigma}^b$, V_s and V_p are shear and pressure activation volumes, respectively, and μ_0 is the viscosity in the low stress (Newtonian) limit.

When the argument of the sinh term in equation (4) is large† compared to unity, the equation may be re-arranged to give an explicit expression for the bond-stretching contribution to the flow stress on axis 1, for a given strain-rate ratio

$$\Delta\sigma_1^b = \frac{6RT}{2(1+\xi)V_p + \sqrt{2}\sqrt{1-\xi+\xi^2}V_s}\left(\ln\left[\frac{1}{\lambda_1}\frac{d\lambda_1}{dt}\right] + \ln\left[\frac{\sqrt{2}\sqrt{1-\xi+\xi^2}\mu_0 V_s}{(2-\xi)RT}\right]\right) \tag{5}$$

The corresponding stress on axis 2 can then be found from ξ calculated via equation (3).

Stress components $\Delta\sigma_1^b$ and $\Delta\sigma_2^b$ were calculated in this way for the actual true strain-rate ratios observed at yield in the experiments described above, making use of the values of parameters V_s, V_p and μ_0 found for PET by Buckley *et al.*[2]. They are plotted as the full lines in *Figure 3*.

It is clear from *Figure 3* that the constitutive model predicts correctly the variation of yield stresses with state of strain, for biaxial drawing of PET in the temperature range considered. Any deviations are smaller than variations in yield stresses due to temperature differences between experiments ($\pm$ 0.5 K in this work). This result confirms an important feature of the model. It shows that three-dimensional application of Eyring kinetics, incorporating the effect of hydrostatic stress, does account successfully for the effects on yield of the biaxiality of strain.

The difficulties of biaxial testing mean there is little data in the literature with which to compare the result reported here. Recently, however, Zaroulis and Boyce[5] have compared results from uniaxial compression and plane strain (constant width) compression tests (i.e. $\theta = -0.5$ and $\theta = 0$) on PET, extending up to the glass transition region. At the highest temperature, 76°C, the measured ratio of yield stresses was approximately 1:3. Such a large difference in yield stresses would not be expected from the present work: the present model predicts a significant difference, but nevertheless a ratio of only 1:1.6. The origin of the discrepancy is unclear. Biaxial hot-drawing experiments on PVC by Sweeney and Ward[6], however, showed behaviour similar but not identical to that reported here for PET. The flow stress was determined under uniaxial, constant width and equibiaxial conditions (i.e. $\theta = -0.5$, 0 and 1), and the flow stress expressed as octahedral shear stress was found to be consistent with Eyring kinetics, apparently without the need for V_p.

† At temperatures above the glass transition, where flow stresses approach zero, this condition may not be satisfied. In the present results, the fractional error from approximating the sin *h* term by an exponential was less than 10^{-4}.

CONCLUSIONS

Biaxial hot-drawing experiments on amorphous PET have enabled a key feature of a constitutive model for this polymer to be tested. Yield stresses observed in the temperature region between the glass transition and rubbery plateau show correct dependence on the in-plane strain-rate ratio. We show elsewhere that the model can also be a good predictor of stresses at higher strains, in the strain-stiffening region[7]. Taken together, these observations provide confidence that the single-stage biaxial drawing of PET is becoming understood at the quantitative level.

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REFERENCES

1. Gordon, D. H., Duckett, R. A. and Ward, I. M., *Polymer*, 1994, **35**, 2554.
2. Buckley, C. P., Jones, D. C. and Jones, D. P., *Polymer*, 1996, **37**, 2403.
3. Buckley, C. P. and Jones, D. C., *Polymer*, 1995, **36**, 3301.
4. Edwards, S. F. and Vilgis, T. H., *Polymer*, 1986, **27**, 483.
5. Zaroulis, J. S. and Boyce, M. C., *Polymer*, 1997, **38**, 1303.
6. Sweeney, J. and Ward, I. M., *Polymer*, 1995, **36**, 299.
7. Adams, A. M., Buckley, C. P. and Jones, D. P., in preparation.