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D.S.A. De Focatiis, J. Embery and C.P. Buckley (2010), *Large deformations in oriented polymer glasses: experimental study and a new glass-melt constitutive model.* Journal of Polymer Science Part B: Polymer Physics, 48 (13), pp 1449-1463. doi: 10.1002/polb.22028

Other related journal articles:

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D.S.A. De Focatiis and C.P. Buckley (2011), *Prediction of frozen-in birefringence in oriented glassy polymers using a molecularly-aware constitutive model allowing for finite molecular extensibility*, Macromolecules, 44 (8), pp 3085–3095. doi: 10.1021/ma102906z

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Constitutive modelling of large deformations in oriented polymer glasses: bridging the gap between molecularly aware melt rheology and solid-state deformation

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This paper presents experimental evidence of the effect of molecular orientation on large tensile deformation of polystyrene in the glassy state, and a new molecularly aware constitutive model being developed for this task. Comparisons between experiments and simulations illustrate that the model requires additional physics to cope with deformation involving sub-entanglement orientation.

Introduction

The ability to predict the large deformations of processed entangled glassy polymers such as atactic polystyrene (PS) presents a number of challenges. In the melt, molecules are oriented by the flow and stretched within their entanglement constraint tubes. The development of orientation and stretch is particularly sensitive to details of the nanoscale structure of the polymer, such as molecular length. When subsequently deformed in the glassy state, both orientation and stretch continue to evolve in conjunction with viscous flow and structural evolution. This combination of experimental and modeling techniques constitutes an attempt to shed more light on this challenging aspect of polymer science, and puts forward a modeling methodology that incorporates elements from both the rheological literature and the traditional solid-state modeling approaches. It has been made possible largely due to the support of the Microscale Polymer Processing Consortium enabling collaboration between a wide range of academic and industrial establishments.

Experimental method

The materials studied in this work were atactic linear PS: two monodisperse grades 262kg/mol (AF) and 518kg/mol (AG), and one commercial grade $M_w = 216$ kg/mol PDI=2.54 (R). The linear viscoelastic spectrum was obtained from linear oscillatory shear experiments and from experimental DMA data (torsion of a rectangular bar). The obtained curves were shifted using time-temperature superposition to provide a single master curve at a reference temperature of 120°C, shown in Figure 1 for material AG.

Oriented specimens were obtained by hot-drawing in an Instron tensile testing machine fitted with environmental chamber using two procedures: (1) immediately quenching after drawing; (2) allowing a controlled dwell time (stress-relaxation at constant strain) prior to quenching. For procedure (1) the drawing conditions were temperatures ranging from 105°C to 135°C at a nominal strain rate of $0.02s^{-1}$ to a stretch of $\lambda=3$ for all materials. For procedure (2) the conditions for material AF were temperature of 120°C and nominal strain rate of $0.02s^{-1}$ to a stretch of $\lambda=3$, with dwell times from 1s to 100000s, and for material R temperature of 105°C and nominal strain rate of $0.02s^{-1}$ to a stretch of $\lambda=3$, with dwell times from 1s to 100000s.

Birefringence was measured on all oriented specimens at room temperature using an Olympus transmission optical microscope fitted with a Berek rotary compensator. The constitutive response of oriented specimens in the glassy state was investigated by tensile testing in an Instron testing machine at $96\pm1^{\circ}$ C (below T_g) at a nominal strain rate of 0.001 s^{-1} .

In PS this lies in the very narrow window of temperature and rate in which the material is in the glassy state and yet is not too brittle to test in tension. Strain was monitored using an Instron, non-contact, video extensioneter following thin transverse lines marked on each specimen.



Figure 1 – The linear viscoelastic spectrum of a 518kg/mol PS (AG). Also shown is the discrete spectrum used in the constitutive model, computed from a spectrum of Maxwell modes.

Constitutive model

The modelling methodology used here consists of the combination of two existing constitutive models in a coherent framework. The conformational behaviour is modelled using the well-known Rolie-Poly (RP) equations, intended for use in monodisperse polymer melts. The glassy non-linear viscoelasticity is modelled using the Oxford glass-rubber constitutive model, intended for use in polymers across the glass transition.

The combined glass-RP constitutive model is assembled from a spectrum of Maxwell modes obtained by fitting to the full linear viscoelastic spectrum of the material, shown in Figure 1. Using multiple monodisperse grades of PS fitted to the full linear theory of Likhtman and McLeish [1], the entanglement modulus (a material parameter for PS) was determined as $G_e=286.2$ kPa, and used as the sum of the conformational modes. The remaining modes were assumed to be glassy. The constitutive equations for the RP modes can be found in ref [2], although in the present implementation a finitely extensible version of the RP model is used with a finite extensibility of $\lambda=3.99$ (as computed from a Kuhn chain analogy). The first Maxwell mode is fixed at the longest reptation time; the values of Rouse and reptation times for all other RP modes are then calculated using the material property τ_e at 120°C and the relationship between τ_R and τ_d in ref [3].

The constitutive equations for the glassy modes are based on calculation of the deviatoric rate of deformation as the sum of a linear elastic bond stretching part, and a contribution from the viscous flow of molecular segments. The characteristic yield drop seen in Figure 3 is modelled empirically through the evolution of the fictive temperature as a function of viscoplastic strain. In both the RP and the glassy modes, relaxation times shift with temperature and structure (expressed via fictive temperature) using a Macedo-Litovitz equation; additionally, the glassy modes also shift with stress using a 3-dimensional form of the Eyring theory. Full details are in ref. [4].

Results and discussion

Figure 2(a) shows birefringence measurements following procedure (1), and Figure 2(b) following procedure (2). The birefringence model predictions were computed from the constitutive model using a stress-optical coefficient of $C=-4.5\times10^{-9}Pa^{-1}$ [5] multiplied by the orientation tensor contribution from the RP modes of the model. Figure 3(a) shows representative stress-strain curves for pre-oriented material AG redrawn in the glassy state

Constitutive modelling of large deformations in oriented polymer glasses: bridging the gap between molecularly aware melt rheology and solid-state deformation <u>D.S.A. De Focatiis</u>, and C.P. Buckley, 2009.

14th International Conference on Deformation, Yield and Fracture of Polymers Kerkrade, Holland, Apr 6-9 2009.

following procedure (1). Figure 3(b) shows constitutive model simulations for the same conditions. Qualitatively similar behaviour was seen both experimentally and numerically in the other materials, and following procedure (2) (not shown).



Figure 2 - Birefringence measurements of PS specimens after the pre-orientation procedure, with predictions computed from the orientation tensor from the RP part of the model. Preorientation at a range of temperatures followed by immediate freezing (a); pre-orientation at fixed temperature followed by a dwell time (stress-relaxation) prior to freezing (b).



Figure 3 – Glassy tensile stress-strain curves for a 518kg/mol monodisperse PS pre-deformed at temperatures from 105°C to 135°C at a strain rate of 0.02s⁻¹ and immediately frozen, and redrawn in the glassy state at 96°C at a strain rate of 0.001s⁻¹ (a); simulations using the constitutive model (b).

Although not shown here, the combined model accurately captures both the behaviour of isotropic material deep in the glassy state, and the non-linear shear and extensional rheology deep in the melt state. Here in the pre-oriented glassy state, however, it is apparent from Figure 3 that although the model *qualitatively* captures the main features of the pre-oriented specimens, a quantitative fit is yet to be achieved. There are two important pieces of experimental evidence that help to shed light on this. The first comes from considerations of the simulations of birefringence. The model fits are accurate for $Wi_e < 1$, but the birefringence appears to saturate in the model for $Wi_e > 1$. Since birefringence in PS is a measure of orientation of the backbone, this implies that the constitutive model is missing additional modes that provide *orientation*. These are expected to be highly stretched sub-entanglement Rouse modes, although the exact physics for finite deformation of these modes is lacking at present.

The second consideration comes from analysis of the measurements of yield stress, shown in Figure 4 as functions of the τ_e -based (a) and the τ_d -based (b) Weissenberg numbers. Plotting against Wi_d illustrates that the different molecular weights collapse onto one line and appear to drop together towards the isotropic yield stress for decreasing Wi_d . This is a confirmation that the RP model is successful in capturing the effect of molecular weight on *Constitutive modelling of large deformations in oriented polymer glasses:*

bridging the gap between molecularly aware melt rheology and solid-state deformation D.S.A. De Focatiis, and C.P. Buckley, 2009.

14th International Conference on Deformation, Yield and Fracture of Polymers Kerkrade, Holland, Apr 6-9 2009.

reptation. However, plotting against Wi_e shows that for $Wi_e > 1$ there is a secondary increase in yield stress, independent of molecular weight (since Wi_e is the same for both materials), and occurring with orientation on a sub-entanglement length scale ($Wi_e > 1$). This implies that sub-entanglement orientation leads to more anisotropy of yield than is expected just from a conformational contribution. One approach towards the incorporation of this phenomenon is to recognise the intrinsic anisotropy of flow of molecular segments on a sub-entanglement length scale [6].



Figure 4 – Glassy state yield stress (at 96°C at a strain rate of $0.001s^{-1}$) for monodisperse PS materials AF (262kg/mol) and AG (518kg/mol) pre-oriented at temperatures from 105°C to 135°C at a strain rate of $0.02s^{-1}$ and immediately frozen, as a function of the τ_e -based (a) and the τ_d -based (b) Weissenberg numbers.

Conclusions

This study has presented experimental evidence of the effects of molecular orientation on glassy-state deformation, and has proposed a framework for constitutive modelling of processed oriented polymers based on existing melt-state and solid-state models. Although the combined constitutive model is successful in capturing the qualitative behaviour, there are quantitative shortcomings in the regions of deformation where there is sub-entanglement orientation. The experimental evidence suggests that this length-scale, located between an entanglement and a Kuhn length, requires a combination of two approaches: the recognition of the presence of orienting sub-entanglement chains (finitely extensible Rouse modes), and the incorporation of the anisotropy of flow of molecular segments.

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