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A NEW SOLID-STATE CONSTITUTIVE MODEL FOR MELT-STATE ORIENTED AMORPHOUS POLYMERS

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This study explores the possibility of combining the well known Rolie-Poly (RP) conformational melt model and the Oxford constitutive model for glassy polymers in an effort to understand and predict the solid-state deformation of melt-state oriented polymers. Tensile experiments are performed on two monodisperse grades of polystyrene, through controlled hot pre-deformation above \( T_g \), and re-testing below \( T_g \). The model is parameterised through the full linear viscoelastic spectrum, appropriately partitioned into RP and glassy modes. Comparison of experimental data with simulations from a numerical implementation of the model illustrates that the model can qualitatively capture a range of features of pre-oriented materials, such as the amount of pre-stretch, the effect of the pre-deformation temperature, and the effect of varying molar mass. However, for a quantitative fit to experimental data, the model needs to be expanded.

Introduction

The ability to predict the solid-state performance of polymer products with process-induced molecular orientation is critically dependent on the existence of constitutive models applicable to both solid and melt states. Additionally, a desirable goal for such models is to incorporate information about the chemical structure of the polymer, such as molecular length or architecture. This would enable the concurrent design of compatible materials and processes to produce optimised products with the desired properties. In an effort to achieve this ambitious goal, we investigate the possibility of combining an existing constitutive model for solid-state glassy polymers with an existing constitutive model for melts.

A basis for solid-state constitutive models of polymeric materials is provided by the ideas of Haward and Thackray [1]. Two contributions are ascribed to the stress, arising from (a) the local glassy interactions and (b) an underlying rubber-like entanglement network [2-4]. Previous attempts to model the effects of melt-state deformation rely on empirical equations describing the relaxation of the entanglement network [5, 6], and there is little hope for the introduction of molecular awareness.

Meanwhile, there has been much recent progress in developing molecularly aware rheological models for polymer melts. Deformation of monodisperse polymer melts, where the interaction between stretching and relaxation of the entanglement network dominates the behaviour, has been successfully modelled using a full linear theory of polymer melts [7]. The Rolie-Poly (RP) equations have been derived as a simplification of the full linear theory more amenable to large-scale computation [8].

In this work we investigate the combination of a set of RP equations with the solid-state constitutive model for deformation of glassy polystyrene (PS) developed in our laboratory [9]. The combined model is parameterised through the full linear viscoelastic spectrum, and its performance is scrutinised in the context of large non-linear deformations. The behaviour of the model is compared with experimental measurements of the solid-state tensile response of two monodisperse grades of amorphous PS oriented at a range of temperatures above \( T_g \). Specimens are pre-deformed at different temperatures above \( T_g \), to different draw ratios, and subsequently frozen. The conditions used in pre-deformation cover a wide range of orientations of the entanglement network, and represent a variety of processing conditions. The specimens are then re-tested below \( T_g \).

Results demonstrate that the combined model can qualitatively capture the effects of a wide range of melt-state deformations and resulting orientations with the desired molecular awareness. Quantitatively the model performs better where the residual orientations in the polymer are concentrated in the longer length-scales. Modelling of short-scale orientation is more challenging, and will require a more complete description of non-linear viscoelasticity originating at the sub-entanglement level.

Experimental

Materials

Two anionically polymerised polystyrenes with narrow molar mass distributions kindly provided by Dr L. Hutchings of Durham University were used in this study. The molar mass distribution of each polymer was characterised using triple detector size exclusion chromatography and weight and number averages are given in Table 1.

<table>
<thead>
<tr>
<th>Code</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w$ (kg/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF</td>
<td>250.9</td>
<td>262.4</td>
<td>1.05</td>
</tr>
<tr>
<td>AG</td>
<td>449.1</td>
<td>517.6</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Isotropic specimens were produced by compression-moulding at 170ºC using a manually operated Moore heated press. The moulds were designed to produce thin rectangular bars ready for tensile testing with no further machining necessary in order to minimise waste. The temperature history of a specimen determines the ageing state of its glass structure, and in order to produce isostructural specimens the same procedure was adhered to in preparing all mouldings [10].

Method

Molecular orientation was introduced by melt-drawing in an Instron 4204 testing machine fitted with environmental chamber at a range of temperatures at a nominal strain rate of 0.02s$^{-1}$. The specimens were stretched to a range of draw ratios λ between 2 and 4, and subsequently frozen to below $T_g$ using a cold spray at the end of the drawing at a cooling rate of approximately 15°C/s.

The constitutive response of oriented specimens in the glassy state was investigated by tensile testing the specimens at 96±1ºC (below $T_g$, which for these materials is 105ºC as measured using DSC at 10K/min) at a nominal strain rate of 0.001s$^{-1}$. 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 extensometer following thin transverse lines marked on each specimen.

It was particularly challenging to introduce homogeneous pre-deformation in specimens oriented at lower temperatures, as they were susceptible to necking in the gauge length. Re-testing of specimens pre-deformed at high temperatures was also difficult for the same reason. This problem diminished with increasing orientation. A schematic diagram of the hot-drawing, quenching and subsequent testing below $T_g$ is shown in Figure 1.

Figure 1 - The procedure used to introduce orientation in the PS specimens. The pre-deformation is introduced at a fixed strain rate of 0.02s$^{-1}$ at a range of temperatures and to a range of draw ratios. The restretch was performed below $T_g$ at a temperature of 96ºC and a rate of 0.001s$^{-1}$.

Theory

Basis of the model

The Oxford glass-rubber (GR) constitutive model is a fully 3-D, finite deformation, constitutive model, capable of capturing many features of the elastic, viscoelastic and viscoplastic deformation of amorphous polymers. It has been described in detail previously [4, 9, 11, 12], and only a brief treatment will be given here. It is based on the assumption that a perturbation of the free energy of deformation has two, independent, parts: a ‘bond-stretching’ component and a ‘conformational’ entropy component. The stress is first separated into hydrostatic $\sigma_n$ and deviatoric $S$ components

$$\sigma = S + \sigma_n I$$

where $\sigma_n = \frac{1}{3} \text{tr} \sigma = K \ln J$  \hspace{1cm} (1)

The mean stress is determined from the bulk modulus $K$ and the volumetric part of the deformation gradient $J$. The deviatoric stress is expressed as the sum of bond-stretching and conformational components

$$S = S^b + S^c$$

The bond-stretching component $S^b$ is based on thermally activated diffusion and follows Eyring kinetics. Here we assume that this response is intrinsically isotropic. $S^c$ arises from perturbation of the conformational entropy of the chains. In this work it is computed from the RP equations.
Glassy spectrum

In the absence of finite rotations, the deviatoric rate of deformation $\mathbf{D}$ can be described as the sum of a linear elastic bond stretching part, and a part from the viscous flow of molecular segments. Following Wu and Buckley [9] we use a multi-mode spectrum

$$\mathbf{D} = \frac{\dot{S}_i^b}{2G_b} + \frac{\dot{S}_j^b}{2G_j}, \quad S_j = \sum_{j=1}^{N} u_j S_j^c, \quad \sum_{j=1}^{N} u_j = 1 \quad (3)$$

where $G_b$ is the bond-stretching shear modulus, $u_j$ represents the relative weighting, and $\tau_j$ is the relaxation time associated with the $j$th mode. The glassy relaxation time is referred back to an unstrressed relaxation time $\tau_{j,0}$ at a reference temperature $T'$ and structural state $T'_0$ (defined through the fictive temperature $T_f$) through shift factors for temperature, structure and stress $\tau_j = a_t a_{\text{struct}} a_{\text{stress}} \tau_{j,0}$ where

$$a_t = \exp\left[\frac{\Delta H}{R} \left(1 - \frac{T}{T'}\right)\right]$$
$$a_{\text{struct}} = \exp\left[\frac{C}{T_f - T_{\infty}} - \frac{C}{T_f - T_0}\right]$$
$$a_{\text{stress}} = \frac{V_s \sigma_m}{2RT} \exp\left[\frac{V_s \sigma_m}{2RT}\right] \sinh\left(\frac{V_s \sigma_m}{2RT}\right)$$

The material constants are as in ref [9]: $\Delta H$ is the enthalpy activation free energy, $T_{\infty}$ is the Vogel temperature, $C$ is the Cohen Turnbull constant, $V_s$ and $V_p$ are the shear and pressure activation volumes, and $\tau_{j,0}$ is the octahedral shear stress on the $j$th mode.

The structural evolution, visible during mechanical deformation below $T_g$ as a yield peak and subsequent yield drop, is modelled through a semiempirical expression derived in this laboratory connecting the evolution of $T_f$ with viscoplastic strain [12]

$$T_f = T_{f,0} + \Delta T_f \left[1 - \exp\left(-\frac{\tau}{\tau_0}\right)\right] \quad (5)$$

where $T_{f,0}$ and $\Delta T_f$ are the initial fictive temperature and the increase in fictive temperature due to strain, $\epsilon_0'$ is a material parameter, and $\mathbf{F}'$ is the equivalent viscoplastic strain invariant.

Rolie-Poly spectrum

The RP constitutive equation is a simplified form of a full microscopic theory of linear entangled polymer melts, and has been successfully used to model non-linear shear and extensional flows in monodisperse grades of PS [13]. It has also been described in detail previously [8] and only a brief treatment will be given here. In particular, since this study is exploring the applicability to the model in the solid and semi-solid states, we use a version of RP with finite chain extensibility $\lambda_{\text{max}}$. In this preliminary study we do not consider convective constraint release ($\beta = 0$ in ref [8]). Here again we use a multi-mode spectrum to represent the conformational stress

$$\sigma_f^i = G_e \lambda_i \mathcal{L}^{-1}(\lambda_i) (T_f - I)$$
$$S_i^f = \frac{1}{3} \text{tr} (\sigma_f^i), \quad S^f = \sum_{i=1}^{M} u_i S_i^f \quad (6)$$

where $\sigma_f^i$ and $S_i^f$ are the full and deviatoric conformational stresses of the $i$th mode, $G_e$ is the entanglement modulus, $\mathcal{L}^{-1}$ is the inverse Langevin function, $\lambda_i$ is the stretch, $\nu_i$ represents the relative volume fraction of the modes, and $T_f$ is the orientation tensor of the $i$th mode. The stretch and orientation are governed by differential equations as follows

$$\dot{\lambda}_i = \dot{\lambda}_i \left(\frac{L}{3}\right) - \frac{\mathcal{L}^{-1}(\lambda_i) - 1}{\tau_{f,0}}$$
$$\dot{T}_f = L \cdot T + T \cdot \mathbf{E} - 2 \left(\frac{L}{3}\right) T_f - \frac{1}{\tau_{f,0}} (T_f - I) \quad (7)$$

where $\tau_{f,0}$ and $\tau_{x,0}$ are the Rouse and reptation times associated with the $i$th mode and $L$ and $I$ is the isochoric velocity gradient. The relaxation times are referred back to reference times $\tau_{x,0}$ and $\tau_{f,0}$ at temperature $T'$ and structure $T'_0$ through the same shift factors for temperature and structure used in the glassy part of the model, $\tau_{x,0} = a_t a_{\text{struct}} \tau_{x,0}'$ and $\tau_{f,0} = a_t a_{\text{struct}} \tau_{f,0}'$.

Using the optimiser Reptate kindly made available by Ramirez and Likthman [14] and the full linear microscopic theory on linear shear rheological data on both materials, the intrinsic material parameters $G_e$, defined earlier, and $M_a$ and $\tau_x$, the mass and Rouse time of one entanglement length respectively, were established as $G_e = 286.2kPa$, $M_a = 16.6kg/mol$ and $\tau_x = 15.2s$ at $T' = 120^\circ\text{C}$. The first (whole molecule) mode Rouse time and reptation time are found from [13].

A new solid-state constitutive model for melt-state oriented amorphous polymers,

\[ \epsilon^e = Z_1 \dot{\epsilon}^e, \quad \epsilon^e = \left(1 - \frac{2.38}{Z^{3.5}} + \frac{1.15}{Z} \right) Z \dot{\epsilon}^e \] (8)

where \( Z = M_a / M_s \). The finite extensibility of the chains can be derived from the equivalent Kuhn chain between entanglements, and is given by

\[ \lambda_{\max} = \sqrt{\frac{n_b}{C_\infty}} \sin \left( \frac{\theta_b}{2} \right) \] (9)

where \( n_b \) is the number of bonds between entanglements, \( C_\infty = 10 \) is the characteristic ratio for PS, and \( \theta_b \) is the carbon-carbon backbone bond angle, which for PS is 109.28º [15]. \( n_b \) can be deduced from \( G_e \) since

\[ G_e = N k_b T, \quad n_b = \frac{2 N A_1 \rho}{N M_0} \] (10)

where \( N \) is the number density of inter-entanglement strands, \( M_b \) is the molar mass of a monomer unit, and \( \rho \) is the density.

Results and Discussion

Experimental

Specimens of polymer AG were pre-deformed to a constant \( \lambda = 3 \) at a range of temperatures from 105-135ºC. Redrawing results at a nominal strain rate of 0.001s\(^{-1}\) and a temperature of 96ºC (standard redrawing conditions) are shown in Figure 2 as tensile true stress versus nominal strain. Volume was assumed constant in computing the true stress.

Specimens of polymer AG were also pre-deformed at a temperature of 105ºC to varying draw ratios. Redrawing results at standard redrawing conditions are shown in Figure 3 as tensile true stress versus nominal strain.

Additionally, to probe the effects of molar mass, specimens of polymer AF were pre-deformed to a constant \( \lambda = 3 \) at a range of temperatures from 105-125ºC. Redrawing results at standard redrawing conditions are shown in Figure 4 as tensile true stress versus nominal strain.
Figure 4 - Constitutive response in tension, for drawn specimens of monodisperse polymer AF retested at a rate of 0.001s$^{-1}$ at a temperature of 96ºC. The labels indicate the temperature at which the specimens were pre-deformed at a rate of 0.02s$^{-1}$ to $\lambda = 3$ prior to freezing and testing.

Figure 5 shows the viscoelastic relaxation spectrum for polymer AG, obtained from linear oscillatory shear experiments (cone and plate) for $\omega<10$, and kindly provided by Dr J. Embery of Leeds University. Also on the same diagram is the linear viscoelastic spectrum of a polydisperse commercial grade of PS obtained from experimental DMA data (torsion of a rectangular bar) for $\omega>10$ [9]. The two experimental datasets join almost seamlessly since the spectrum is relatively insensitive to molar mass at higher frequencies.

Material parameters

In order to produce a discrete representation of the linear viscoelastic spectrum, we began with the mode with the longest relaxation time, $\tau_0^*$, and attributed one mode per decade of time to cover the range of data of interest. The relative weights of the 18 modes were calculated using an in-house optimiser written in Matlab, to minimise the error between the experimental and analytical values of $G'$ and $G''$. The weights were attributed to RP modes until the sum of the modes reached $G_s$. In the data shown in Figure 5 this happens at the 6th RP mode. Thus, part of this mode is a RP mode and part of this mode is a glassy mode. The remainder of the modes is glassy. The full unrelaxed shear modulus is $G_s + G_i = 1.28$GPa. The transition from RP to glassy modes occurs very near to $1/\tau_e$. A similar exercise was performed on polymer AF (not shown).

For the glassy part of the model, the material parameters were found using the techniques and data in ref [9], and are listed in Table 2. For the RP part of the model, the material parameters are obtained from the full microscopic linear theory and from the Kuhn chain analogy, as explained earlier in the text. The parameters used are listed in Table 3.

Table 2 – Parameters for the glassy part of the constitutive model for materials AF and AG.

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<td>$V_s$ (m$^3$/mol)</td>
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<td>Ref. [9]</td>
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<tr>
<td>$V_p$ (m$^3$/mol)</td>
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<td>$\Delta H$ (kJ/mol)</td>
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<tr>
<td>$C$ (K)</td>
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<td>$T_\infty$ (ºC)</td>
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<td>$T_g$ (redraw) (ºC)</td>
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<td>$\Delta T_i$ (redraw) (ºC)</td>
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<td>$\epsilon_0^*$ (redraw)</td>
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<td>$G_s$ (GPa)</td>
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<tr>
<td>$K$ (GPa)</td>
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<td>Ref. [9]</td>
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Table 3 – Parameters for the RP part of the constitutive model for polymers AF and AG.

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<td>$M_e$ (kg/mol)</td>
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<td>$\tau_{e\max}$ at 120ºC (s)</td>
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<td>$\lambda_{\max}$</td>
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<td>$\tau_{i\max}^{+}$ at 120ºC (s)</td>
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<td>$\tau_{i\max}^{-}$ at 120ºC (s)</td>
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Polymer AG

<table>
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<td>$\tau_{i\max}^{+}$ at 120ºC (s)</td>
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<td>$\tau_{i\max}^{-}$ at 120ºC (s)</td>
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Simulation results

Simulations replicate the entire time-temperature-deformation history of the specimens during pre-deformation, quenching, unloading, reheating and redrawing. The specimen is hot-drawn at a strain rate of $0.02s^{-1}$ at a given temperature to a given strain; it is then quenched to 0ºC in 12s and unloaded to zero stress. It is then reheated to 96ºC, a process which takes approximately 120s. After a further 600s acclimatisation period in the oven (to ensure thermal stability) the specimen is restretched at a strain rate of 0.001$s^{-1}$. An illustrative example is shown in Figure 6.

Figure 7 illustrates the redrawing-only part of simulations of polymer AG hot-drawn to a fixed $\lambda=3$ over a range of temperatures, replicating the experiments of Figure 2.

A stress develops during the re-heating time of the simulation due to the relaxation of the glassy part of the spectrum, currently in compression. This effect is also seen experimentally.

By comparison with Figure 2 it is apparent that the constitutive model captures the behaviour of the specimens hot-drawn at higher temperatures better than those hot-drawn at lower temperatures.

Figure 6 – Temperature, stress and strain as a function of time during the simulation cycle. The specimen is hot-drawn at a strain rate of 0.02$s^{-1}$ at $T=120ºC$ to $\lambda=3$; it is then quenched to 0ºC in 12s and unloaded to zero stress. It is then reheated to 96ºC, and after a further 600s acclimatisation period in the oven (to ensure thermal stability) it is restretched at a strain rate of 0.001$s^{-1}$.

Figure 7 – Simulations of the constitutive response in tension, for specimens of monodisperse polymer AG pre-deformed at a rate of 0.02$s^{-1}$ to $\lambda=3$, retested at a rate of 0.001$s^{-1}$ at a temperature of 96ºC. The equivalent experimental data is shown in Figure 2. The effect of variations in pre-stretch examined experimentally in Figure 3 is shown as simulations in Figure 8. Here again it is apparent that the biggest discrepancy between experimental data and simulations occurs at larger amounts of pre-stretch, where even the orientation of the faster RP modes is large.
This discrepancy indicates that the current modelling approach is too simplistic when dealing with large amounts of chain stretch over length scales shorter than one entanglement length. The problem is more readily seen when looking at yield stress as a function of Deborah number $D_e = \tau_e/t_{exp}$ where $t_{exp}$ is the duration of the pre-stretching process, shown in Figure 9.

There are two increases in yield stress with pre-orientation: a mild increase showing visible molar mass dependence for $D_e < 1$, attributable to the different amounts of residual network stretch after reheating, and a more significant increase for $D_e > 1$, which is currently not accounted for in the model. One approach to address this phenomenon that is being investigated currently in our laboratory is to consider viscosity as an intrinsically anisotropic process [16, 17]. Another effect currently not addressed by the model is the possible change in ageing kinetics resulting from specimens with differing degrees of orientation.

Figure 10 shows simulations of redrawing of polymer AF. These simulations were run after obtaining the full discrete linear viscoelastic spectrum of polymer AF. Only 5 RP modes were necessary to reach the value of $G_e$ (an intrinsic material property for sufficiently entangled polymers).

The effect of chain length on the redrawing behaviour can be discerned by comparison of Figures 7 and 10, on the specimens pre-deformed at higher temperatures. Due to shorter Rouse and reptation times, polymer AF shows less retention of orientation when compared with polymer AG. It appears from both Figure 9 and Figure 10 that the relaxation of the entanglement network is underpredicted by the model in its current form. This may be an intrinsic feature of the lack of convective constraint release in the current implementation of the model, and will be investigated in the future.
Conclusions

This study has investigated the applicability of combining the well known Rolie-Poly conformational melt model with the Oxford constitutive model for glassy polymers in capturing the effects of melt-state pre-deformation on two grades of polystyrene re-tested below $T_g$. The use of the full linear viscoelastic spectrum appropriately partitioned between the glassy and conformational parts ensures that the model is internally consistent.

Comparison of experimental data with simulations from a numerical implementation of the combined model illustrates that the model can qualitatively capture a range of features of pre-oriented materials, such as the amount of pre-stretch, the effect of the pre-deformation temperature, and the effect of varying molar mass.

The model in its current implementation fails to capture the significant increase in yield stress seen in specimens pre-deformed at lower temperatures. Additionally, although the effects of molar mass are visible, they are quantitatively too small to account for the experimental evidence.

Acknowledgements

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