Constitutive Modelling of Amorphous Polymers at High Strain Rates

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This work presents advances to a physically based constitutive model based on the Oxford Glass-Rubber model for the simulation of the mechanical response of amorphous polymers at high rates of strain. Considerations of adiabatic heating, structural evolution and the presence of the β-transition are applied to experimental data on polycarbonate.

Introduction

Polymers and their composites are frequently used in components that may be exposed to high strain rate loading, such as impact events, in a wide variety of fields from automotive to aerospace to medicine. Examples of such products include car bumpers, aircraft fuselages and bone repair supports. However, their behaviour can vary significantly between quasi-static conditions and impact events, as well as at low and high temperatures. A lack of a sufficient understanding of these differences and their underlying physical origins can inhibit optimisation of the material properties with respect to the structural design of the polymer and composite components. A constitutive model that can simulate a very broad range of rates and temperatures is a major challenge, but is essential to describe the full spectrum of the mechanical behaviour of polymers. The objective of this work is to contribute to the development of such a physically based model, focusing here on the particular challenges present in amorphous polymers at high rates of strain.

Materials and Methods

Although the constitutive model described herein is more generally applicable to glassy polymers, the process of parameterisation is focused on polycarbonate and based on data obtained at the University of Oxford on LEXAN PC 103R (MFR ~6, DBT = -30°C) kindly provided by Sabic. Quasi-static experiments were conducted using screw-driven test machines primarily in compression at a range of temperatures and constant true strain rates to provide input data for the constitutive model. Medium strain rate experiments made use of servo-hydraulic testing, and high strain rate experiments employed the split Hopkinson bar technique. The linear viscoelastic response was measured using dynamic mechanical analysis to obtain isothermal frequency sweeps that were shifted in the frequency domain to produce both viscoelastic mastercurves and shift factors. This was supplemented by linear shear rheology for temperatures above the glass transition.

Our constitutive model is fundamentally based on the Oxford glass-rubber constitutive model [1], inspired by the one-dimensional model first proposed by Haward and Thackray [2], and later developed into a fully 3-dimensional implementation [3,4]. Two contributions are ascribed to the free energy and hence the stress, arising from perturbation of interatomic potentials, relaxed by isotropic segmental flow, and from perturbation of conformational entropy of the entangled molecular network, represented in the glassy state as a crosslinked network. The crosslinked network is modelled here by an Edwards-Vilgis function [5], although other functions have been successfully used in the literature.

The constitutive model describes the material response to a deformation gradient tensor $\boldsymbol{F}$ in terms of the Cauchy stress tensor $\boldsymbol{\sigma}$. The volumetric parts of $\boldsymbol{F}$ and $\boldsymbol{\sigma}$ are separately dealt with assuming linear elasticity such that the mean stress can be defined by $\sigma_{\mathrm{m}} = \frac{1}{3}\mathrm{tr}\boldsymbol{\sigma} = K \ln J = K \ln(\det \boldsymbol{F})$ and $\boldsymbol{S} = \boldsymbol{\sigma} - \sigma_m \boldsymbol{I}$ where K is the bulk modulus. The deviatoric part of the deformation gradient, $\bar{\boldsymbol{F}} = J^{-\frac{1}{3}}\boldsymbol{F}$, is used to determine the deviatoric stress $\boldsymbol{S} = \boldsymbol{S}^{\mathrm{b}} + \boldsymbol{S}^{\mathrm{c}}$ from the separate contributions of bond-stretching and conformational stresses, and mirrors previous approaches [1,3]. The deviatoric rate of deformation tensor $\bar{\boldsymbol{D}}$, obtained in the classical way, is the sum of a linear elastic bond stretching part, and a viscous flow part, and, using an N-mode spectrum [4],

$$\bar{\boldsymbol{D}} = \frac{\hat{\boldsymbol{S}}_j^{\mathrm{b}}}{2G_{\mathrm{b}}} + \frac{\boldsymbol{S}_j^{\mathrm{b}}}{2G_{\mathrm{b}}\tau_j} \quad \text{and} \quad \boldsymbol{S}^{\mathrm{b}} = \sum_{j=1}^{N} \upsilon_j \boldsymbol{S}_j^{\mathrm{b}}, \quad \sum_{j=1}^{N} \upsilon_j = 1$$

where G_b is the shear modulus, and τ_j and υ_j are the *j*-th relaxation time and modal fractions respectively. Here as previously $\hat{\boldsymbol{S}}_j^\mathrm{b}$ is the material rate of stress and implemented as the Jaumann rate. The linear viscoelastic shear relaxation spectrum is used to obtain the modes as shown in Figure 1a.

Each relaxation time is referred back to an unstressed relaxation time $\tau^*_{j,0}$ at a reference temperature T^* and structural state T_f^* such that $\tau_j = a_\mathrm{T} a_\mathrm{s} a_{\sigma,j} \tau^*_{j,0}$ through shift factors for temperature, structure and stress respectively, which are defined as

$$a_\mathrm{T} = \exp\left[\frac{\Delta H}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right],\quad a_\mathrm{s} = \exp\left[\frac{C}{T_\mathrm{f}-T_\infty}-\frac{C}{T_\mathrm{f}^*-T_\infty}\right] \quad \text{and} \quad a_\sigma = \frac{V_\mathrm{s}\tau^\mathrm{b}_{\mathrm{oct},j}}{2RT}\exp\left(-\frac{V_\mathrm{p}\sigma_\mathrm{m}}{RT}\right)\left[\sinh\left(\frac{V_\mathrm{s}\tau^\mathrm{b}_{\mathrm{oct},j}}{2RT}\right)\right]^{-1}$$

Results and Discussion

Model parameterisation

Parameters ΔH, C and T_∞ can be obtained by optimisation on the experimental data, but care needs to be taken to, at this stage, ignore data past the β–transition and in the proximity of the α-transition (where T_f is known to be ill-defined). A comparison of the combined effect of the temperature and structure shift factors, otherwise known as the classical Macedo-Litovitz (ML) equation in viscosity terms, is shown in Figure 1b vs experimental data.

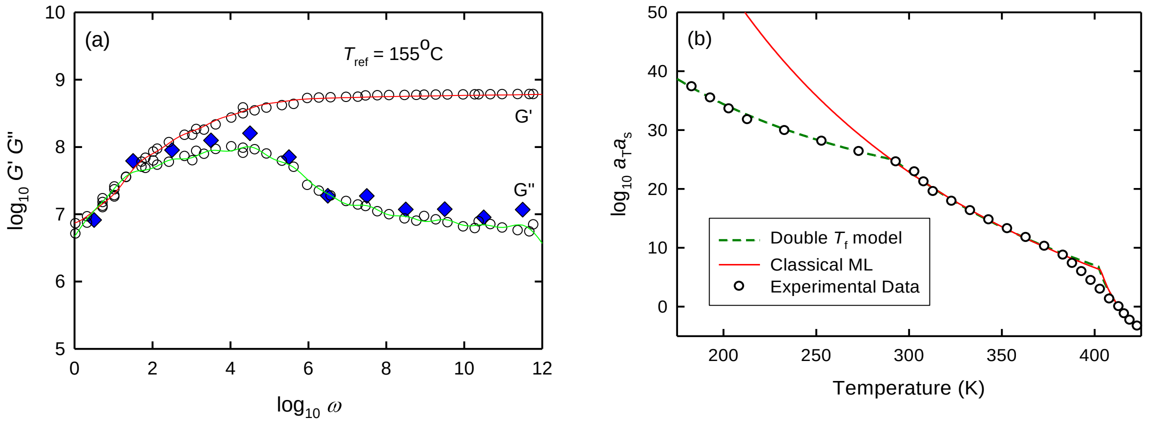

Figure 1 (a) The experimental linear shear viscoelastic relaxation spectrum (circles), the Maxwell modes (diamonds) and the constitutive model response (lines); (b) the shift factors obtained experimentally (circles), the classical ML model (solid line), and the double T_f model (dashed line).

Now to focus on analysis of the quasi-static experimental constant true strain rate data. Measurements of the compressive yield stress as a function of strain rate are used to determine the shear activation volume V_s. We then consider that, in a constant true strain rate experiment and following saturation of the yield process, the flow stress remains constant. This means that data for compressive strains ε > 36% can be used to obtain the conformational stress. Optimised parameters N, α and σ_flow, corresponding to the network constraint density, the finite extensibility parameter, and the constant flow stress respectively, are determined on the range of data available. As shown for four selected temperature examples in Figure 2a, there is remarkable agreement between this simple model and the broad range of data. The finite extensibility parameter α was found to remain approximately constant at a value of 0.27±0.02, while both N and σ_flow, are dependent on rate and temperature, but in a manner consistent with the shift factors obtained earlier, as shown for the example in Figure 2b. Unfortunately, it is not possible to obtain conformational parameters with confidence in high strain rate experimental data.

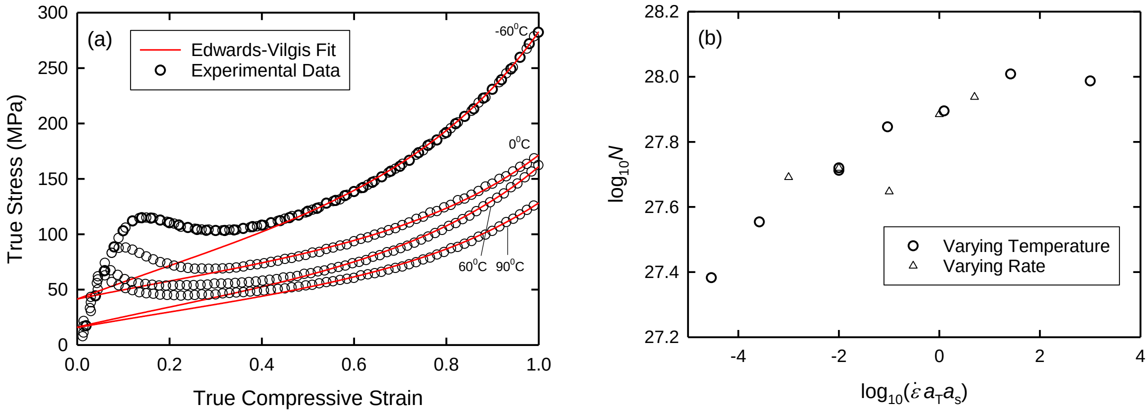

Figure 2 (a) Selected examples of compressive stress-strain data (circles) overlayed with simplified model simulations of an Edwards-Vilgis function with an added constant flow stress (lines); (b) the network density as a function of reduced rate obtained from a range of temperature and rate experiments.

Structural evolution

To account for structural change within the polymer, the glass structure is defined in terms of the fictive temperature T_f. Previous implementations employed an approximate semi-empirical description of the evolution of T_f [4]. In order for the model to be applicable to as broad a set of rates and temperatures as possible, the differential form of the structural evolution equations first proposed in [6] for the modelling of high strain rate deformations in epoxy resins and later implemented for polypropylene by [7,8] is used here,

$$\dot{T}_f = \frac{T_f - T}{\bar{\tau}^* a_s a_T} + \kappa \dot{\bar{\varepsilon}}_v$$

where $\bar{\tau}^*$ is the geometric mean reference relaxation time, $\dot{\bar{\varepsilon}}_v$ is the rate of effective viscous strain and κ is a constant. This model produces a rise in T_f with plastic strain, which leads to a stress drop after yield, and an eventual saturation of the rise in T_f which depends on both rate and temperature.

Adiabatic heating

At sufficiently high strain rates, and due to a high thermal diffusivity, polymer deformation occurs under adiabatic conditions. The energy input is transferred into four parts: a recoverable part stored as elastic strain energy in stretched bonds (both in shear and volumetric deformations), a non-recoverable part due to plastic deformation associated with viscous shearing of polymer segments, and two further parts, one associated with structural change and another with conformational change. Although plastic deformation accounts for the majority of the energy post-yield, there is expected to be a reduction in the temperature change due to the rise in fictive temperature, particularly in the proximity of yield. At sufficiently large stresses, where the conformational stress begins to dominate, it is important to consider the entropic nature of the entanglement network. Given sufficient time, the entropy-elasticity will contribute to a further temperature rise, but it is questionable whether this can really be the case at sufficiently high strain rates. Here it may be more reasonable to assume that, at least initially, further energy is stored elastically, and that this may transition to an entropic energy storage (and hence a temperature rise) over a given timescale. At present it is unclear what this timescale may be, but it is reasonable to consider that this may occur at a timescale associated with the Rouse relaxation time of an entanglement length, and thus, for the purpose of impact experiments be elastic rather than entropic [9]. We hope to be able to shed more light on this by careful comparison with experiments.

The β-transition

It is apparent when looking at yield stresses as a function of rate at high strain rates, or by looking at the shift factors obtained at low temperatures in Figure 1b, that the β-transition plays an important role in determining properties at high rates and low temperatures. In polycarbonate, there is still debate in the literature as to the precise molecular origin of the β-transition [10] but there is agreement that it must be associated with segmental motions of parts of the monomer or with relationships between different parts of the monomer. As a means of attempting to capture this somewhat empirically, we propose the introduction of two distinct fictive temperatures, one associated with segmental motions of the entire monomer or Kuhn segment termed $T_{f\alpha}$, and another associated with sub-segmental motions termed $T_{\mathrm{f}\beta}$. We attribute the same meaning to these as the classical fictive temperature defines the structural state out of equilibrium as $T_{\mathrm{f}} > T$. Thus, above the a-transition we have $T_{\mathrm{f}\alpha} = T_{\mathrm{f}\beta} = T$, below the b-transition both $T_{\mathrm{f}\alpha} > T$ and $T_{\mathrm{f}\beta} > T$, but in the intermediate region (at quasistatic rates this corresponds to temperatures between ~20 and ~120 $^{\mathrm{o}}$C), we have $T_{\mathrm{f}\alpha} > T$ but $T_{\mathrm{f}\beta} = T$. Using a similar approach to the Vogel-Tamman-Fulcher equation, we introduce two structural shift factor terms, each with their own constants defined as,

$$a_{\mathrm{s}\alpha} = \exp\left[\frac{C_\alpha}{T_{\mathrm{f}\alpha} - T_{\infty\alpha}} - \frac{C_\alpha}{T_{\mathrm{f}\alpha}^* - T_{\infty\alpha}}\right] \quad \text{and} \quad a_{\mathrm{s}\beta} = \exp\left[\frac{C_\beta}{T_{\mathrm{f}\beta} - T_{\infty\beta}} - \frac{C_\beta}{T_{\mathrm{f}\beta}^* - T_{\infty\beta}}\right]$$

and apply this together with an Arrhenius temperature shift factor to the experimental data. As shown in Figure 1b, this approach can provide a convincing representation to the shift factors below the β-transition whilst maintaining the behaviour above the transition. A full implementation will require some form of evolution equation for $T_{\mathrm{f}\beta}$, and it is clear that this should occur over a much shorter timescale than that associated with $T_{\mathrm{f}\alpha}$, which is currently approximated as the mechanical relaxation time in the absence of stress.

Conclusions

This work has presented developments in a physically based constitutive model for glassy polymers focusing on the requirements of high strain rate simulations. Structural evolution is modelled using a differential equation for the evolution of the fictive temperature, and considerations have been made for the inclusion of adiabatic heating and for the presence of the β-transition. There are still many unanswered questions concerning the behaviour of glassy polymers at high strain rates, but it is hoped that the model will enable progress in this area by careful comparison with forthcoming experimental data at high rates of strain.

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