The use of a new viscous process in constitutive models of polymers

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In constitutive models of polymers, there has been a long history of the use of strain-rate dependent viscous processes, such as the Eyring and Argon models. These are combined with elastic elements to generate viscoplastic models that exhibit typical phenomena such as rate dependent yield, creep and stress relaxation. The Eyring process is one of the most frequently used such mechanisms. It has two significant drawbacks: it implies a temperature dependence of mechanical behaviour that is in an opposite sense to that observed; and it predicts a strain rate dependence of yield stress that is less complex than that observed, leading to the requirement for two or more Eyring processes. In recent years, new ideas for amorphous polymers have been developed that lead to an alternative plastic mechanism that addresses these concerns. In this paper a constitutive model that incorporates this mechanism is developed, and its effectiveness in modelling macroscopic mechanical behaviour of polymers is explored with respect to published data.

Introduction

There are many examples of constitutive models of polymers that consist of a combination of elastic and viscous elements. Since polymers become nonlinear even at modest levels of strain, it is desirable that the viscous mechanism be nonlinear to reflect this phenomenon. The Eyring process [1] is frequently used. When combined with a single elastic element, the resulting Maxwell-like model exhibits nonlinear creep, nonlinear stress relaxation and strain-rate dependent yield. The Eyring process provides an elegant way of producing quite simple models that show usefully complex behaviour [2,3,4].

While the Eyring process has a number of attractive features, there are some drawbacks. The most important of these concerns temperature dependence. Temperature is included in the process such that it directly affects the predicted plastic strain rate. If the Eyring parameters are kept constant and temperature is changed, the result is that plastic strain rate becomes smaller as temperature increases. Since this is the opposite of what is observed, a separate set of parameters needs to be fitted for each temperature. The usual consequence is that activation volumes must be set to increase with temperature, which cannot be readily justified. Another problematic feature is the form of the dependence of yield stress on rate of strain. The Eyring process predicts an Arrhenius type relation, in which yield stress varies linearly with the logarithm of rate. This is a useful relation as long as the range of strain rate is limited, but for a wide range some nonlinearity is usually seen. A number of workers have addressed this problem by creating a model that includes two Eyring processes, as pioneered in [5].

In a series of papers (such as Chen and Schweizer [6], Chen and Schweizer [7], Riggleman et al. [8]) a theory of deformation for polymer glasses that is significantly different from that of Eyring has been set out and applied. In this paper we shall present a constitutive model based around it, and explore its predictions for yield and stress relaxation.

Theory and constitutive model

For the purposes of macroscopic modelling, the core of the theory is a plastic mechanism, where shear stress τ and plastic shear strain rate $\dot{\gamma}$ are related by [6]:

$$\tau(T) = \tau_{abs}(T)\left[1-\left(\frac{-kT\ln(\dot{\gamma}\tau_0)-\varepsilon}{a_c F_B(T)}\right)^h\right] \qquad (1)$$

where τ_{abs} represents an absolute upper limit to the stress, T is the absolute temperature, k Boltzmann's constant and F_B is an energy barrier. τ_0, a_c and ε are physically significant constants, whereas h is a fitting exponent arising from a power-law representation of the energy barrier as a function of stress. h was given the value 0.4 by Chen and Schweizer [6], based on calculations for PMMA. In this paper we shall study uniaxial deformations only. Then, shear stress and shear strain are simply related to tensile stress and strain respectively and the theory can be written in the same form for tensile stretching. For stress σ and plastic extension ratio λ_p we can write

$$\sigma = \sigma_{abs}\left[1-\left(A\ln(C\dot{\lambda}_p/\lambda_p)-D\right)^h\right] \qquad (2).$$

The constants A, C and D have been introduced for simplicity and expressions for them can be deduced by comparing Eq. 1 and Eq. 2.

We now create a constitutive model by adding an elastic element in series to the mechanism defined by Eqs. 1 and 2. Adopting a large deformation formulation, and using a Neo-Hookean form for the elastic element, then for an elastic extension ratio λ_e, equilibrium requires that

$$\sigma_{abs}\left[1-\left(A\ln(C\dot{\lambda}_p/\lambda_p)-D\right)^h\right]-G\left(\lambda_e^2-1/\lambda_e\right)=0 \qquad (3).$$

where G is the strength of the neo-Hookean mechanism. For a total extension ratio λ on the model, $\lambda_e = \lambda/\lambda_p$ and Eq. 3 becomes

$$\sigma_{abs}\left[1-\left(A\ln(C\dot{\lambda}_p/\lambda_p)-D\right)^h\right]-G\left(\lambda^2/\lambda_p^2-\lambda^p/\lambda\right)=0 \qquad (4).$$

Eq. 4 is solved numerically with time-marching λ to give λ_p and thus the stress σ. The model is capable of predicting yield and stress relaxation.

From an operational point of view, there are some constraints on the values of the parameters in Eq. 2. At zero stress, Eq. 2 gives the result

$$\dot{\lambda}_p/\lambda_p = \exp(1/A+D)/C$$

and at the stress σ_{abs} the same equation gives

$$\dot{\lambda}_p/\lambda_p = \exp(D)/C$$

This shows that the range of rate to which this parameter set can be applied is defined by the ratio of the highest to lowest strain rates and is given by:

$$\exp(-1/A)$$

This gives a constraint on the parameter A that is governed by the range of strain rate covered.

Modelling of yield

We demonstrate the Maxwell-type model for this context using the room temperature results of Kendall and Siviour [9], who have published yield data for PVC over the range of strain rates 10^{-3} to 10^{4} s^{-1}. The parameters used in equation are listed in Table 1. The stiffness G of the neo-Hookean model is included, though it has essentially no effect on yield. The exponent h is fixed at 0.4, as in [6]. The other parameters were fitted.

Table 1 Eq. 4 parameters for yield

σ_{abs}	200 [MPa]
A	-0.026
C	1.4×10^{-4} [s]
D	2.0×10^{-4}
G	1 GPa
h	0.4

The results are shown in Fig. 1. The fit is good, and shows a capability of modelling the nonlinear dependence of yield stress on logarithm of strain rate. It would seem that, if an Eyring-based model were used, several Eyring processes would need to be included, essentially modelling the curve as a sequence of linear slopes.

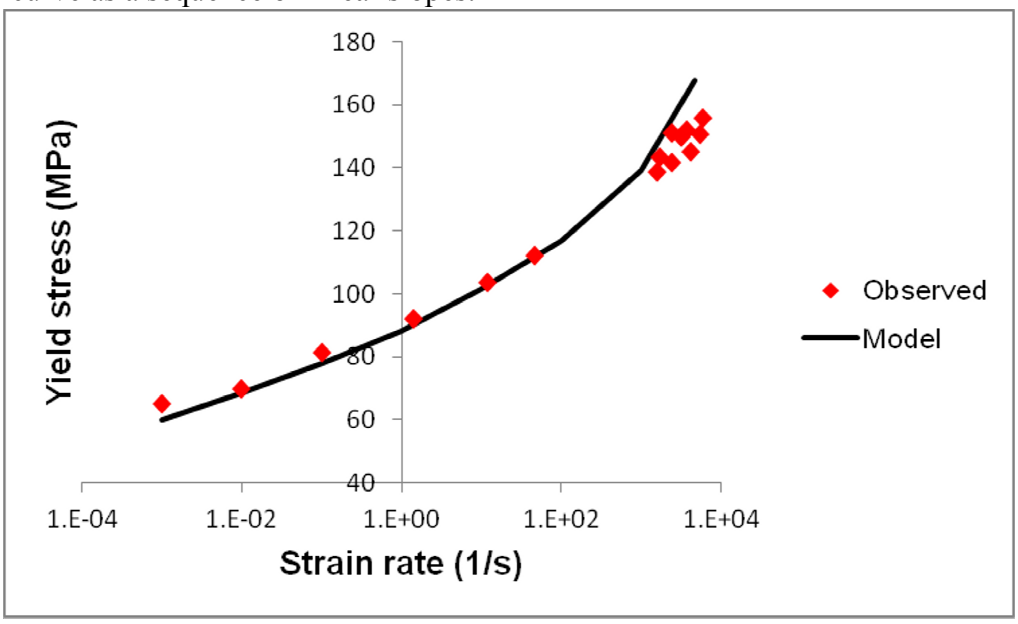

Fig. 1. Comparison of model predictions with yield data in [9].

Modelling of stress relaxation

We demonstrate a model for stress relaxation using the room temperature results for polycarbonate of Colucci, O'Connell and McKenna [10], based on the material they denote as "CP PC". We were unable to model their results adequately using the Maxwell type model of the previous section, but the inclusion of a second parallel neo-Hookean model resulted in a satisfactory approach. The model is shown schematically in Fig. 2. The parameter G_2 defines the strength of the second neo-Hookean model, the overall effect of which is to increase the total stress in the model to

$$\sigma = G\left(\lambda^2/\lambda_p^2 - \lambda_p/\lambda\right) + G_2\left(\lambda^2 - 1/\lambda\right) \qquad (5).$$

The loading behaviour of the material is nonlinear, so that at different strain levels the ratio of stress to strain is different. As only the stress relaxation behaviour is of interest, we have generated the correct values for the initial stresses by using appropriate values of G and G_2. For each strain level, we have used the same ratio G/G_2. Strain rates during loading were 5.0×10^{-3} s^{-1} and strain levels in the range 0.01 - 0.045. Parameter values are shown in Table 2., and the strain dependent values for G in Table 3. The parameters in Table 2 were fitted to the stress relaxation at strain 0.02 and used to produce the predictions at all the other strains.

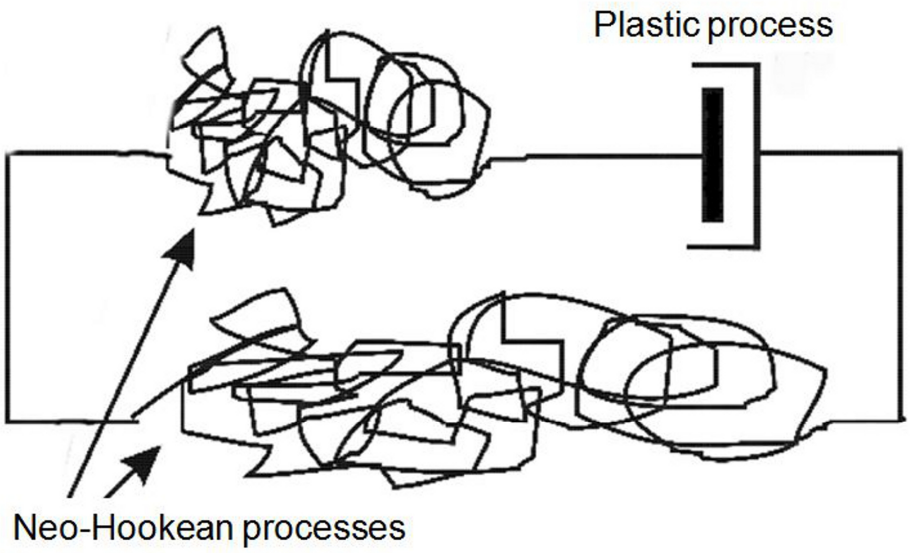

Fig. 2. Constitutive model for stress relaxation.

Table 2 Parameters for stress relaxation

σ_{abs} [MPa]	132
A	-0.0265
C [s]	9.04×10^{-4}
D	2.0×10^{-4}
G/G_2	0.874
h	0.198

Table 3 Strain dependent values of G

Strain	0.01	0.015	0.02	0.025	0.03	0.04	0.045
G [MPa]	343	354	296	277	261	210	192

The model predictions are shown for seven strain levels in Fig. 3, as log-log plots of relaxation modulus. The prediction is worst at the lowest strain (1%), where there is little predicted relaxation. At the other strains the predictions are realistic. The percentage errors are small, especially at higher strain. The increasing rate of stress relaxation as strain is increased is well captured by the model.

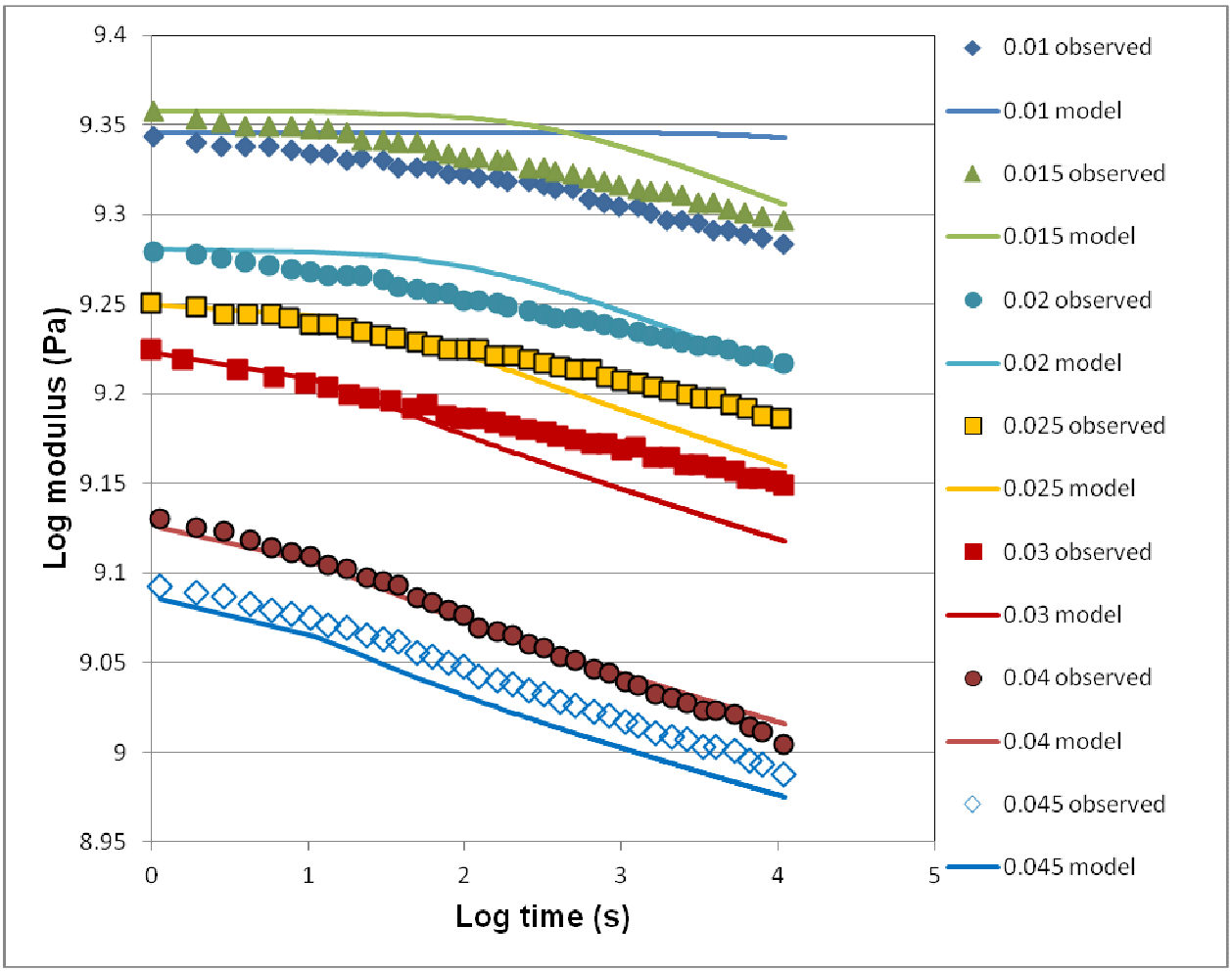

Fig. 3 Comparison of stress relaxation and model predictions for polycarbonate data in [10]. Numbers in the caption refer to strain levels.

Summary

The model of Chen and Schweizer has been incorporated into a constitutive model, by the simple expedient of placing it in series with an elastic process to form a Maxwell type model. The resulting model is then capable of modelling both yield and stress relaxation. Just as with an Eyring model, yield occurs when the strain rate applied to the model is equal to that occurring in the plastic process. The yield stress is shown to be a nonlinear function of the logarithm of strain rate, so that experiments over a large range of strain rate can be modelled by a single process. Stress relaxation in polycarbonate is successfully modelled using a Maxwell model with an elastic element added in parallel to it.

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