DEVELOPMENT OF CONSTITUTIVE EQUATIONS FOR SOLID PHASE DEFORMATION OF POLYMERS WITH TIME-VARYING TEMPERATURE

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Abstract

The large deformation, nonlinear viscoelastic behaviour of polymers has been explored at elevated temperatures. Experiments consist of uniaxial tensile stress relaxation experiments. For isothermal experiments, the results can be represented using models consisting of Eyring processes and elastic networks. Experiments have also been carried out on specimens subject to controlled cooling, to simulate the development of the room-temperature mechanical properties of processed products. Progress in extending the Eyring-based theories to these conditions is reported.

1. Introduction

The great majority of polymer processing takes place at elevated temperatures. In solid phase processing, suitable constitutive equations have been developed (1, 2, 3) that enable the shapes of polymer products, subject to large isothermal deformations, to be predicted. Such products are often highly oriented, and so their final room-temperature mechanical properties, such as stiffness, are enhanced relative to an isotropic body such as would be formed by melt processing. The prediction of the properties of the final cooled product is therefore of considerable interest. The ideal way of achieving this is to use a constitutive equation which functions over the whole forming and cooling process. The degree of locked-in orientation in the final product, and therefore the associated stiffness, would be predicted using such a constitutive model.

Polymers are nonlinear viscoelastic, and in this context are subject to large deformations. The constitutive equation must take account of this while remaining valid for non-isothermal conditions. The experiments, which include stress relaxation tests, are designed to probe the viscoelastic properties of the material.

2. Isothermal Deformation

The polycarbonate material used is Bayer Macrolon, supplied in 3 mm sheets. Initial investigations were aimed at understanding the isothermal, large strain behaviour at elevated temperatures. Step stress relaxation experiments have been carried out and analysed in terms of models involving Eyring activated processes combined with molecular network models. A simplified approach has been adopted in which the model consists of the minimum number of elements consistent with the observed behaviour.

3. Experimental Procedure For Isothermal Deformation

An Instron testing machine together with an environmental chamber was used for the experiments. Dumbbell specimens have been stretched rapidly (strain rates between 0.05 and 0.2 s^{-1}) in tension at 130 and 110 °C to uniform extension ratios of 2.2, and then allowed to stress relax at constant extension. During the stretching process, shear bands form, but they propagate through the specimen gauge length so that it is essentially uniform when the full extension is attained, Figure 1. Typical stress time data for the three temperatures is shown in Figure 2.

4. Analysis of Isothermal Deformation

We have made use of Eyring processes to model the mechanical behaviour. For an Eyring element, a simplified equation gives the strain rate $\dot{e}$ in terms of the stress σ as

$$\dot{e} = A\sinh(sV) \qquad (1)$$

where A and V are constants, the latter being simply related to the activation volume. When such an element is in series with an elastic element, the resulting model has been shown by Guiu and Pratt (4) to exhibit stress relaxation approximately in the form

$$\sigma(t) = \sigma(0) - \frac{1}{V}\ln(1 + t/c) \qquad (2)$$

where t denotes time and c is a constant. This equation can be fitted to our stress relaxation curves to good accuracy; for example, stress relaxation at 130°C up to 800s can be represented with V = 0.84 MPa^{-1} and c = 0.036s with an average error of 0.7%. Overall prediction errors for all three temperatures are shown in Figure 3.

5. Experimental Procedures for Non-Isothermal Deformation

We have used an environmental chamber that is capable of cooling at controlled rates to perform tensile stress relaxation experiments as the specimen cools. By compensating for thermal contraction of the specimen and load train, the specimen is held at a constant natural length. The same specimens have been used as for the isothermal work. A stress relaxation result is shown in Figure 4, for the case of loading at 130°C and then cooling at 1.5°C/min to 110°C.

6. Analysis of Non-Isothermal Deformation

To model non-isothermal behaviour, some basic issues need to be addressed, such as whether the stress depends on current temperature only, or on the temperature history.

We have made the assumption that the stress does not depend on the temperature history. In stress relaxation during temperature change, we assume that the rate of stress decay at any temperature is the same as would apply at the same temperature under isothermal conditions (see Figure 5). This can be expressed as

$$\sigma_R(t,T) = \sigma_R(0,T(0)) + \int_0^t \frac{\partial \sigma_R(\tau,T(\tau))}{\partial \tau} d\tau . \qquad (3)$$

When the stress σ_R in isothermal relaxation is given by the Guiu-Pratt expression, this becomes

$$\sigma_R(t) = \sigma(0,T(0)) - \int_0^t \frac{d\tau}{V(T(\tau))\big(c(T(\tau)) + \tau\big)} \qquad (4)$$

where V and c are interpolated from the isothermal information. Numerical integration then gives the predictions for which the errors are shown in Figure 6.

7. Conclusions

Both isothermal and non-isothermal experiments have been carried out, the latter with the aid of new developments in experimentation. Stress relaxation at extension ratio of 2.2 at constant elevated temperatures has been modelled accurately using the Guiu-Pratt equation, which is based on the Eyring Process. These isothermal results have been used to predict stress relaxation under conditions of cooling. To do this, it is necessary to make an assumption about the link between isothermal and non-isothermal stress relaxation. The assumption takes the form that, when temperature is varying, the *rate* of relaxation of stress is the same as would occur at the same strain and the same time after straining as in the isothermal case. This simple approach, whereby temperature history effects are neglected, has proved highly successful. Thus, accurate predictions of stress relaxation of the extended cooling specimens have been produced.

Acknowledgements

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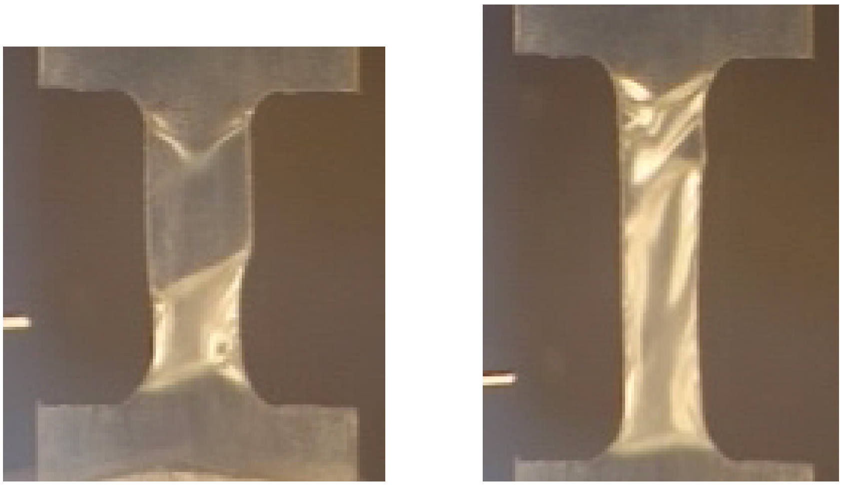

Figure 1: Shear band formation and destruction

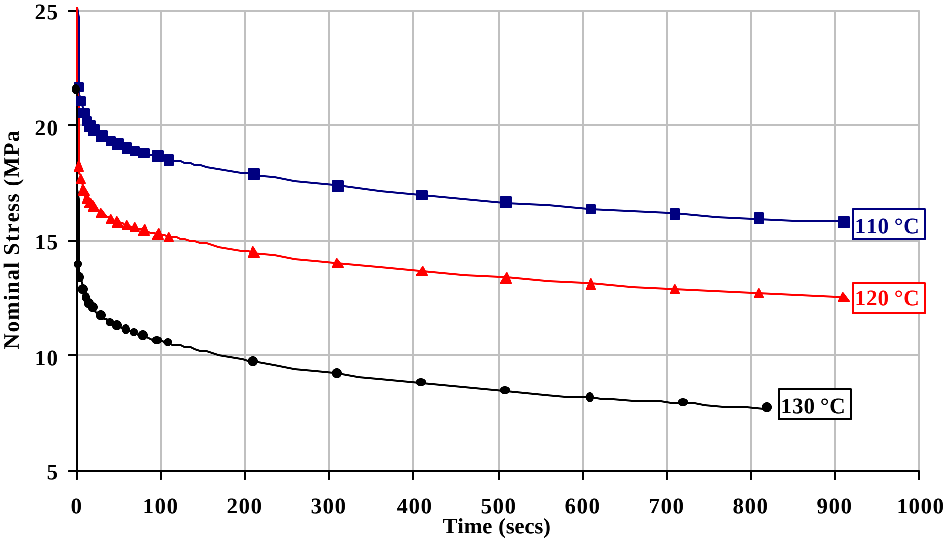

Figure 2: Isothermal stress relaxation at three temperatures

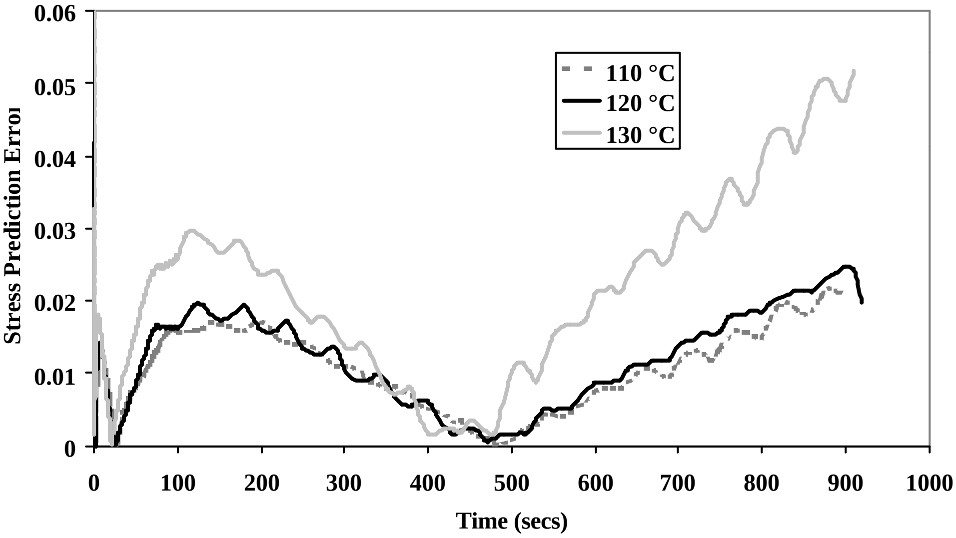

Figure 3: Error in Isothermal Stress Predictions

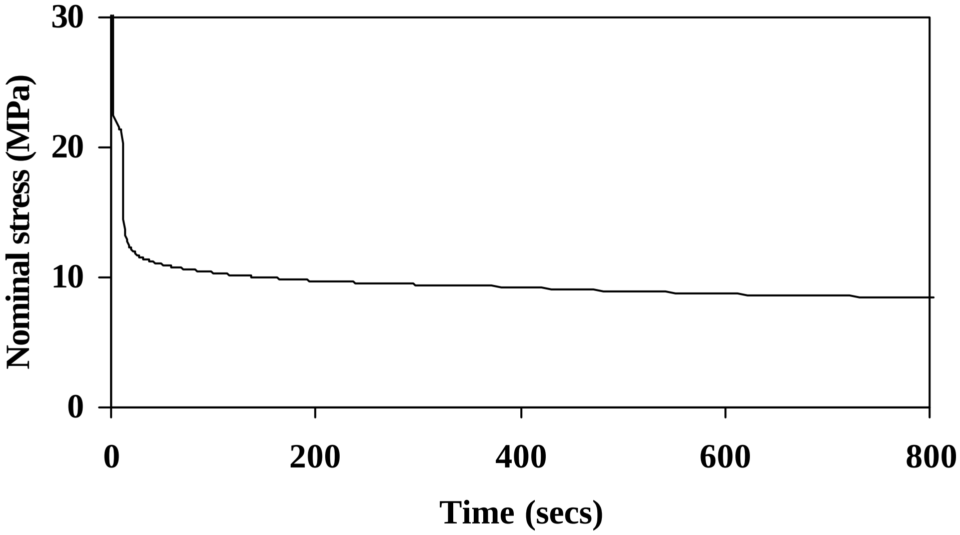

Figure 4: Stress relaxation during cooling

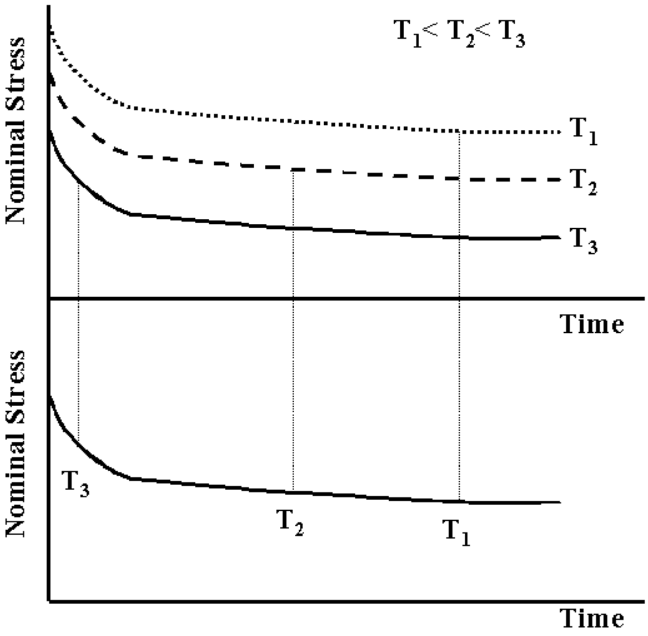

Figure 5: Non-Isothermal stress decay based on isothermal data

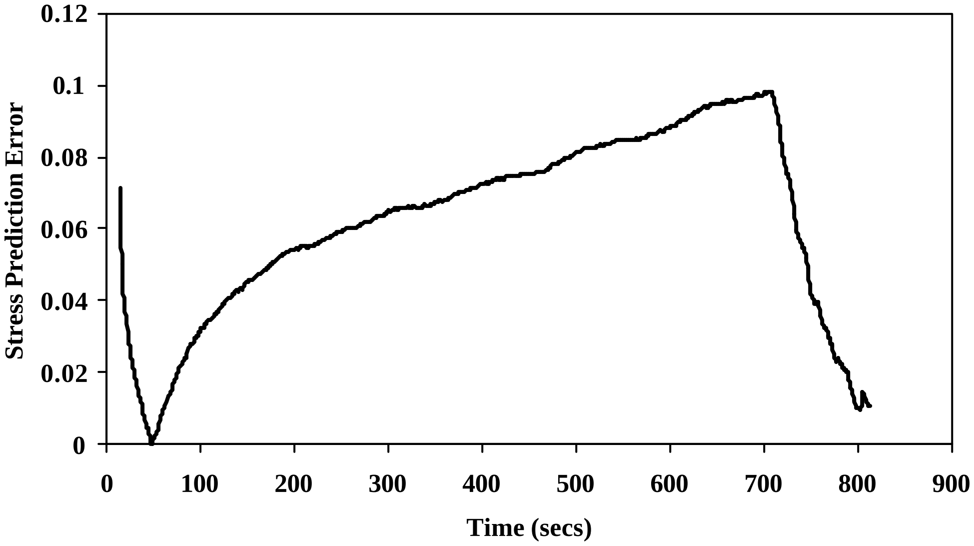

Figure 6: Error in Non-Isothermal Stress Predictions

Keywords: solid phase, constitutive equation, deformation, non-isothermal