PII: S0032-3861(96)00797-5

A non-linear viscoelastic model for predicting the yield stress of amorphous polymers

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(Received 18 March 1996; revised 3 June 1996)

A non-linear viscoelastic model is introduced by employing a new formulation where the relaxation time of rate processes is directly dependent on the induced deformation state applied to the material. The plastic flow of amorphous polymers is considered as a continuous structural change, and the yield phenomenon is modelled through the corresponding viscoelastic constitutive equations. All material constants necessary to predict the yield stress, the rate and temperature dependence are non-adjustable parameters depending on the particular deformation mode. To verify the results of the proposed model, two independent series of experiments have been performed on specific polymeric materials, and have been proved to satisfy adequately the proposed analysis. © 1997 Elsevier Science Ltd.

(Keywords: yield-stress; amorphous polymer; non-linear viscoelasticity)

INTRODUCTION

Although many polymeric materials behave as elastic solids for small deformations, there is a strain limit beyond which most polymers either fracture or undergo a continuing plastic deformation, called the yield process. This latter phenomenon, which commonly occurs in soft metals, lacks an accurate theoretical description in the case of amorphous polymers. According to McClintock and Argon[1], the yield phenomenon of solids is only possible if imperfections exist in the material. In polycrystalline solids, yield is initiated when the existing dislocations start to migrate, once a stress field is applied to the solid structure. In amorphous polymers, however, the absence of a specific structure also implies the absence of any kind of disturbance inside the material. This difficulty in envisaging any abrupt change in the molecular conformation at the yield point of polymeric materials influences the theoretical approach to modelling the plastic flow of such substances as a continuous smooth structural change during the yield process[2]. This approach considers the yield phenomenon as a non-linear viscoelastic process where a homogeneous change in the polymeric structure takes place. On the other hand, experimental observations have firmly established that yield behaviour in polymers initiates at localized points by the appearance of a neck, or is accompanied by shear bands, which can occur most easily in the plane of the maximum shear stress. These facts suggest the generation of inhomogeneities on a molecular basis during the material deformation[3]. The induced structural changes at the yield point indicate a theoretical approach to treat the plastic behaviour of polymers in the context of classical plasticity models,

where a rigid material before yield deforms as an inviscid fluid according to some specific flow rules after yield[4-8].

In this article, the viscoelastic constitutive equations will be used where yield and postyield behaviour are predicted as a natural consequence of viscoelastic relaxation processes. The non-linear features of these equations will be established on a micromechanical molecular model. By this treatment, which seems to be analogous to that of Eyring[4], the relaxation time is not expressed as a function of stress imposed on the material but depends on the state of deformation. This dependence predicts a maximum yield stress at a specific strain usually common in polymeric materials, in the range of 5–10%. All material constants necessary to predict the yield stress, the rate and temperature dependence, and the strain softening are not adjustable parameters relying on the definite deformation mode. To verify the results of the model presented in this paper, two independent series of experiments will be performed on a specific polymeric material. The first type of experiment is based on a pure mechanical self-vibrating method for determining the viscoelastic parameters of the tested material. The second series of tests constitutes a development of uniaxial compression experiments with various rates of deformation. The yield behaviour of the material is then fully predicted using the viscoelastic parameters as physical constants for describing this phenomenon.

THEORETICAL DEVELOPMENT

The plastic flow in polymer solids appears to be fundamentally different from that of metals, because the experimental yield stress strongly depends on the rate of strain. The dependence of this stress on the hydrostatic pressure and on the temperature environment also

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highlight some differences which can give the impression that the yield phenomenon in polymers is a special case of nonlinear viscoelastic effect. This nonlinearity may be the result of lowering the characteristic time of relaxation process as the induced strain increases during a deformation programme. This phenomenon has been extensively described in previous works by considering the shift in relaxation time either by the free volume theories, where the strain induces material dilation, or in the context of conformational entropy models, where entropy increase is linked also with the volume change[2,9,10].

In the present study we will try to employ a new formulation where the relaxation time is directly dependent on the induced strain under isovolume conditions. Such an analysis can apply without any revision even for shear deformation, because yielding is not considered to be a consequence of volume dilation. More particularly, our formulation takes into account that in the glassy state the reference configuration of polymers is an isotropic state consisting of randomly oriented molecular chains. Each single chain with its end-to-end vector r_0 in the initial state contains a number of rigid links of constant length aligned along a random direction b. Supposing that each link is embedded in an elastic medium, which is constituted from the rest of the molecules of the system, we can assume that under a stress field a 'pseudo-affine' deformation occurs, resulting in a new direction of vector b. We make use of the 'pseudo-affine' model to express the state of orientation in the material after the stress is suppressed. This new direction that is the result of intermolecular interactions with the neighbouring chains leads to a new distribution of the material lines occupied by each link.

Wu and Van Der Giessen[11] have developed the idea of the orientation distribution function to describe the evolution of a rubber network consisting of a large number of molecular chains that are initially randomly oriented in space. We will take a similar approach, where instead of the affine deformation for each chain we will examine only the orientation change of each link. This approach is schematically shown in *Figure 1a*, where the initial uniformly distributed links are forced to orient along a mean direction parallel to the major principal axis of macroscopic local strain. The isotropic distribution in

the undeformed state can be represented by a radial arrangement of chain links corresponding to a density distribution, n_0, equal to $1/4\pi$ (*Figure 1b*). After the imposition of deformation F a new density distribution, n, will be established. In the proximity of a material point a sphere of radius dX will deform in an ellipsoid as shown in *Figure 1c*, with a corresponding radius $d\chi = F\,dX$. Supposing that the total number of links N directed around a material point is conserved after the deformation. We may then write[12]

$$Nn_0\,d\Omega_0 = Nn\,d\Omega \quad \text{or} \quad \frac{n}{n_0} = \frac{d\Omega_0}{d\Omega} \quad (1)$$

Where $d\Omega_0$ and $d\Omega$ are the solid angles in the undeformed and deformed states correspondingly. Expressing $d\Omega_0$ and $d\Omega$ with respect to $|d\chi|$ and $|dX|$ we obtain

$$\frac{n}{n_0} = \frac{d\Omega_0}{d\Omega} = \left(\frac{|d\chi|}{|dX|}\right)^3 \frac{1}{J} = \frac{\lambda^3}{J} \quad (2)$$

where $\lambda = |d\chi|/|dX|$ is the stretch ratio, and J is the volume change. In the case of isovolume deformation, J is equal to unity and $n = \lambda^3/4\pi$. The above relation can be applied to every state of the deformation mode. The stretch ratio λ is then calculated for each direction as a function of the polar coordinate angles and the components of the deformation gradient tensor F.

Taking into account that the yield phenomenon is accompanied by slipping or twinning, which can occur most easily in the plane of the maximum shear stress, even when a sample is subjected to uniaxial tension or compression, we apply the above results considering that the shear strain on this plane is γ, and the deformation gradient tensor F is given by

$$F = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad J = \det F = 1 \quad (3)$$

The ratio of the density distribution can be expressed as follows:

$$\frac{n}{n_0} = \lambda^3 = \frac{1}{[1 + \gamma \cdot \sin^2 \vartheta \sin \phi(\gamma \sin \phi - 2\cos \varphi)]^{3/2}} \quad (4)$$
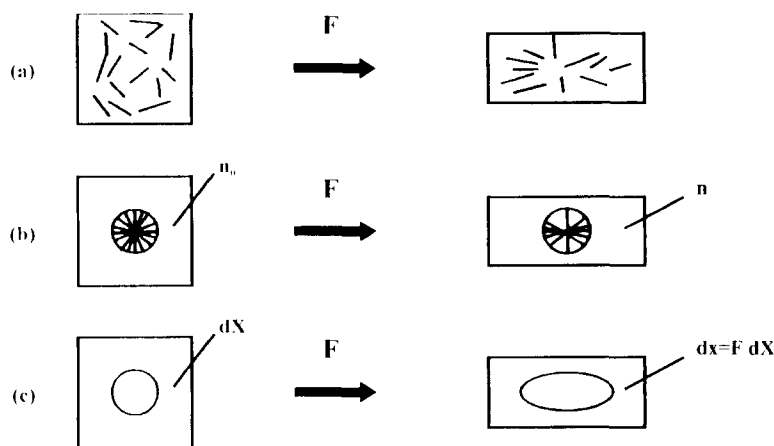

Figure 1 A single element of an amorphous polymer constituted from rigid links in the unstrained and strained states: (a) isotropic conformation of molecular links, (b) schematic representation of uniformly distributed links, (c) deformation of a sphere of radius dX in the proximity of a material point

The minimum value of this formula is obtained in the directions determined by the angles ($\vartheta = \pi/2$, $\varphi = \pi/2 + \frac{1}{2}\tan^{-1}(2/\gamma)$):

$$n_{\min} = \frac{1}{4\pi} f(\gamma) = \frac{1}{4\pi} \left(\frac{2\sqrt{4 + \gamma^2}}{(2 + \gamma^2)(\sqrt{4 + \gamma^2}) + \gamma^3 + 4\gamma} \right)^{3/2} \tag{5}$$

In the following we will make use of this density distribution function to express the rate of viscoelastic relaxation processes. When a material is subjected to a constant strain rate e, a shear stress is developed in a certain direction. The isotropic orientation of the rigid links is altered, and a new direction of the material lines occupied by each link is then determined. The yield point is attained as a sequence of molecular jumps governed by some kind of activated process. Following the idea of Adam and Gibbs[13] that configurational change in glasses has a cooperative nature, the relaxation time is given by an exponential form of the energy barrier multiplied by the minimum number of cooperative links oriented along the revealed shear bands:

$$\tau = \tau_0 \exp\left(\frac{n^* \Delta H}{kT} \right) \tag{6}$$

where ΔH is the activation energy of the relaxation process, n^* is the number of links acting cooperatively as a unit to make a configurational rearrangement, T is the absolute temperature and k is Boltzmann's constant. Combining equations (6) and (5) we obtain the relation

$$\tau = \tau_0 \exp\left(\frac{N \Delta H}{4\pi kT} f(\gamma) \right) \tag{7}$$

where $n^* = n_{\min} N$, with N the total number of links contained in the region where cooperation takes place. To obtain the exact temperature dependence of the above expression we use the concept of configurational entropy S to calculate the number of co-operative links N:

$$N = \frac{N_A s_n}{S} \tag{8}$$

where N_A is Avogadro's number and s_n is the entropy of a link. In the present study, adopting a procedure developed by Hodge[14] for the calculation of configurational entropy, we have the following expression for the temperature dependence of relaxation time τ:

$$\tau = \tau_0 \exp\left(\frac{A}{T(1 - T_2/T_f)} f(\gamma) \right) \tag{9}$$

where T_2 is the temperature of zero configurational entropy, and T_f is the fictive temperature, which is equal to the current temperature in the equilibrium state, while in the glassy state it is constant with a value below but close to the glass transition temperature T_g.

The constitutive equation for an isotropic viscoelastic solid in the limit of infinitesimal uniaxial deformations is given by

$$\sigma(t) = [E_r e] + \int_{-\infty}^{t} E(t^* - \xi^*) \frac{\partial e(\xi)}{\partial \xi} d\xi \tag{10}$$

where $E(t)$ is the viscoelastic tensile stress relaxation modulus for a specific axial strain history $e(t)$, and E_r is the equilibrium or relaxed modulus.

The variables t^* and ξ^* are reduced times given by two integral formulas expressing the non-uniform expansion of the viscoelastic timescale induced by the deformation processes:

$$t^* = \tau(0) \int_0^t \frac{dX}{\tau(X)} \qquad \xi^* = \tau(0) \int_0^\xi \frac{dX}{\tau(X)} \tag{11}$$

Since real polymers comprise various regions where molecules perform many modes of motions, a spectrum of relaxation times should be used to describe in detail every relaxation process. On the other hand, the Kohlraus–William–Watts (KWW) equation[15] is also one of the best equations to fit relaxation phenomena, especially from the solid-like stage up to the transition region of glassy polymers. Taking into account this fact, we choose the following relation for the relaxation modulus $E(t)$:

$$E(t) = E_0 \exp\left[-\left(\frac{t}{\tau} \right)^\beta \right] \tag{12}$$

where the parameter β is often found to be approximately 0.5 for polymers.

For spatially homogeneous uniaxial deformation, the maximum shear strain γ of equation (7) is developed along the direction of 45° from the extensional axes, and is directly related to the displacement strain $e(t)$.

Equations (11) along with equation (9) can be integrated for a given strain rate deformation. These results are substituted in equation (10) and, via numerical calculation stress, $\sigma(t)$ are determined.

DETERMINATION OF VISCOELASTIC PARAMETERS

The set of equations (9)–(12) presented above could predict the yield stress behaviour of amorphous polymers, if the physical parameters of these relations have been previously determined. To verify these constants, independent experiments have been performed based on dynamic mechanical spectroscopy. We use a compound pendulum (dynamic mechanical analyser (DMA) from Du Pont Instruments) to measure the sample modulus E', and the energy dissipation E''. This instrument operates on the compound resonance principle in which the sample is vibrated in a unique stress-producing geometry. This geometry consists of two sample arms, each attached to a rigid base through flexure pivots. The pivots function as highly accurate torsional springs with near-zero hysteresis in the horizontal direction and high rigidity in the vertical direction. When a solid sample is mounted between the ends of the sample arms and the arms are deflected from the equilibrium position, a compound resonance system is formed. The resonant frequency is mathematically related to the sample modulus, and the decay of the amplitude envelope (expressed as 'damping') is a measure of the energy dissipation E''. The instrument electronically displays the sample frequency and damping. The whole system is placed in an oven in which the rate of temperature rise is controlled.

Figure 2 shows representative diagrams from the electronic device indicating the dependence of the resonance frequency and damping on temperature T. The storage and loss moduli of the three tested specimens are then calculated, following the relative expressions furnished in the instruction manual of the dynamic analyser, and plotted against temperature in *Figure 3*. To
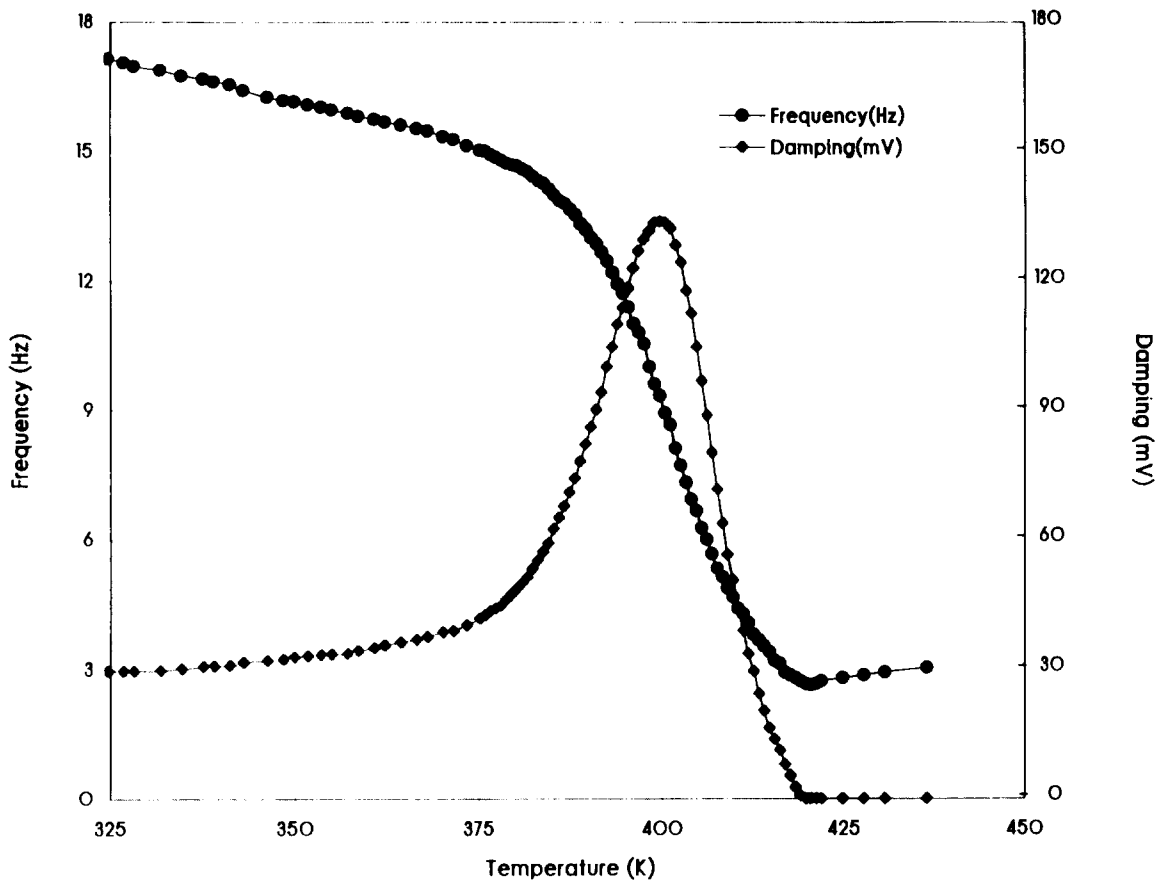
Figure 2 Representative diagrams from the electronic device for the resonance frequency and damping of the tested specimens with respect to temperature
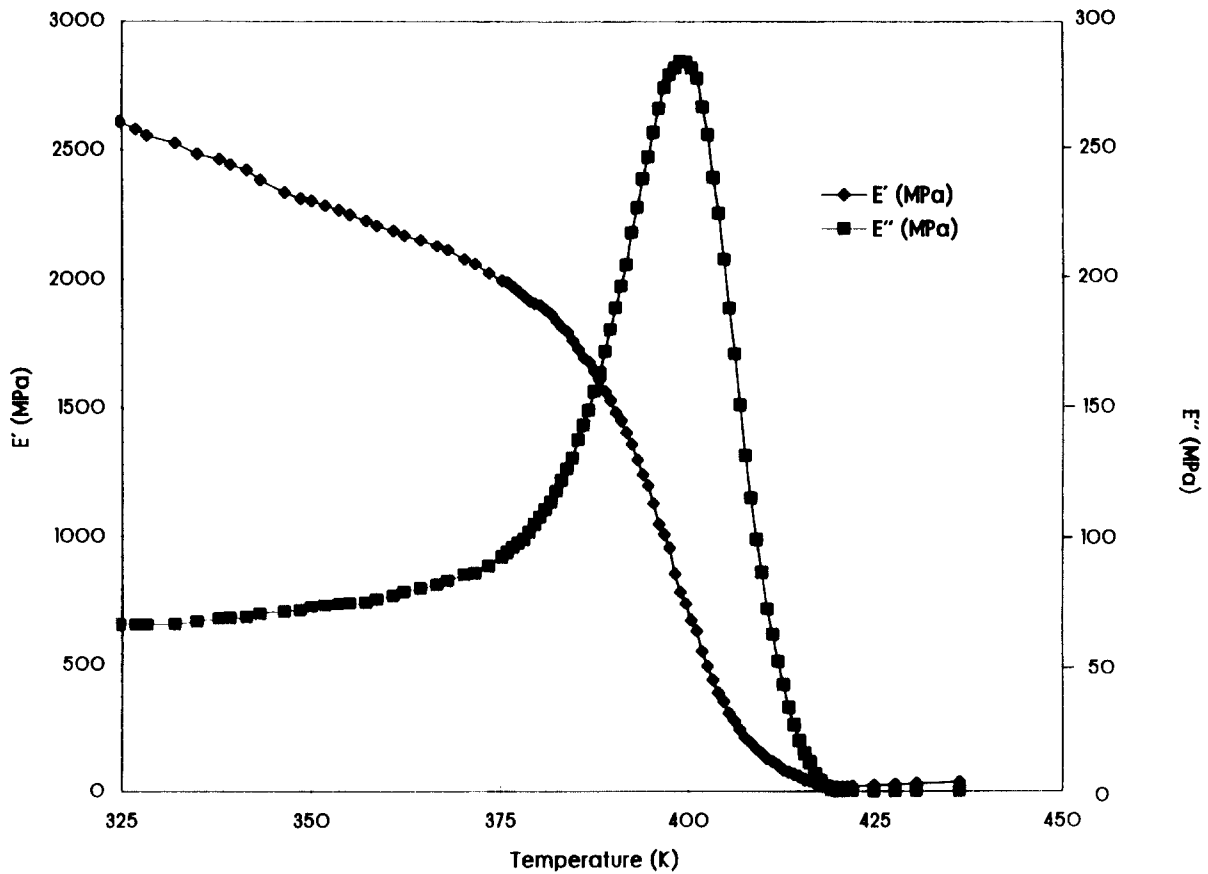

Figure 3 Storage (E') and loss (E'') moduli of a representative specimen with respect to temperature, calculated from the results of *Figure 2*

Table 1 Material parameters fitted from the experimental results of storage moduli and used to predict the stress–strain data of tested specimens

	E_0 (MPa)	E_r (MPa)	τ_0	A (K)	T_f (K)	T_0 (K)	β
ER00	2320	120	$10^{-20.6}$	2880	399	332	0.20
ER20	2300	100	$10^{-19.1}$	2700	359	295	0.26
ER40	2000	90	$10^{-18.0}$	2400	335	275	0.30

fit these experimental results we use the relations known as the 'Alfrey approximation'[16]. According to this approach, the real and imaginary parts of the complex modulus (E', E'') are expressed in terms of the relaxation time spectrum $H(\xi)$:

$$\left[\frac{\mathrm{d}\,E'(\omega)}{\mathrm{d}\,\ln(\omega)}\right]_{1/\omega=\xi} = H(\xi) \qquad [E''(\omega)]_{1/\omega=\xi} = \frac{\pi}{2}H(\xi) \quad (13)$$

This spectrum can be calculated to a similar degree of approximation in terms of the KWW equation given from relation (12):

$$H(\xi) = -\left[\frac{\mathrm{d}\,E(t)}{\mathrm{d}\,\ln(t)}\right]_{t=\xi} = \frac{E_0\beta}{\tau}\exp\left[-\left(\frac{\xi}{\tau}\right)^\beta\right]\left(\frac{\xi}{\tau}\right)^{\beta-1} \quad (14)$$

The relaxation time τ and the equivalent time ξ are related to the corresponding temperature from the Vogel–Fulcher formula as modified by Hodge[14]:

$$\tau = \tau_0\exp\left(\frac{A}{T(1-T_2/T_f)}\right) \qquad \xi = \tau_r\int_0^\xi\frac{\mathrm{d}\,t}{\tau} = \tau_r\int_{T_0}^T\frac{\mathrm{d}\,T}{q\tau} \quad (15)$$

where q is the rate of heating $q = \mathrm{d}T/\mathrm{d}t$, τ_r is the relaxation time at a reference temperature T_0, and T_f is the fictive temperature which is equal to the current temperature in the equilibrium state, while in the glassy state it is constant with a value below but close to the glass transition temperature T_g.

Using a programming package known as 'Statistic Nonlinearfit' from the computer program *Mathematica* as developed by Wolfram in version 2^{17}, the parameters of equations (14) and (15) can be fitted following the experimental results of *Figure 3*.

RESULTS AND DISCUSSION

The predictions of the viscoelastic constitutive equations in uniaxial compression will now be presented. We will consider the isothermal deformation of viscoelastic materials where three constant strain rates are applied for each tested specimen.

The viscoelastic materials selected to test the model are compounds derived from epoxy resins with various amounts of plasticizer. The epoxy used was Epon 828 with a molecular weight between 370 and 384. The curing agent used was triethylene tetramine (TETA), 8% by weight of epoxy, and postcuring was done at 100°C for 48 h. The polymer was mixed with three different amounts of plasticizer (Thiokol LP3 polysulfide): 0, 20 and 40% by weight of epoxy, corresponding respectively to samples ER00, ER20 and ER40. These materials were selected because they exhibit similar viscoelastic behaviour differing only in the temperature range where the glass transition occurs. In this way we can verify how the
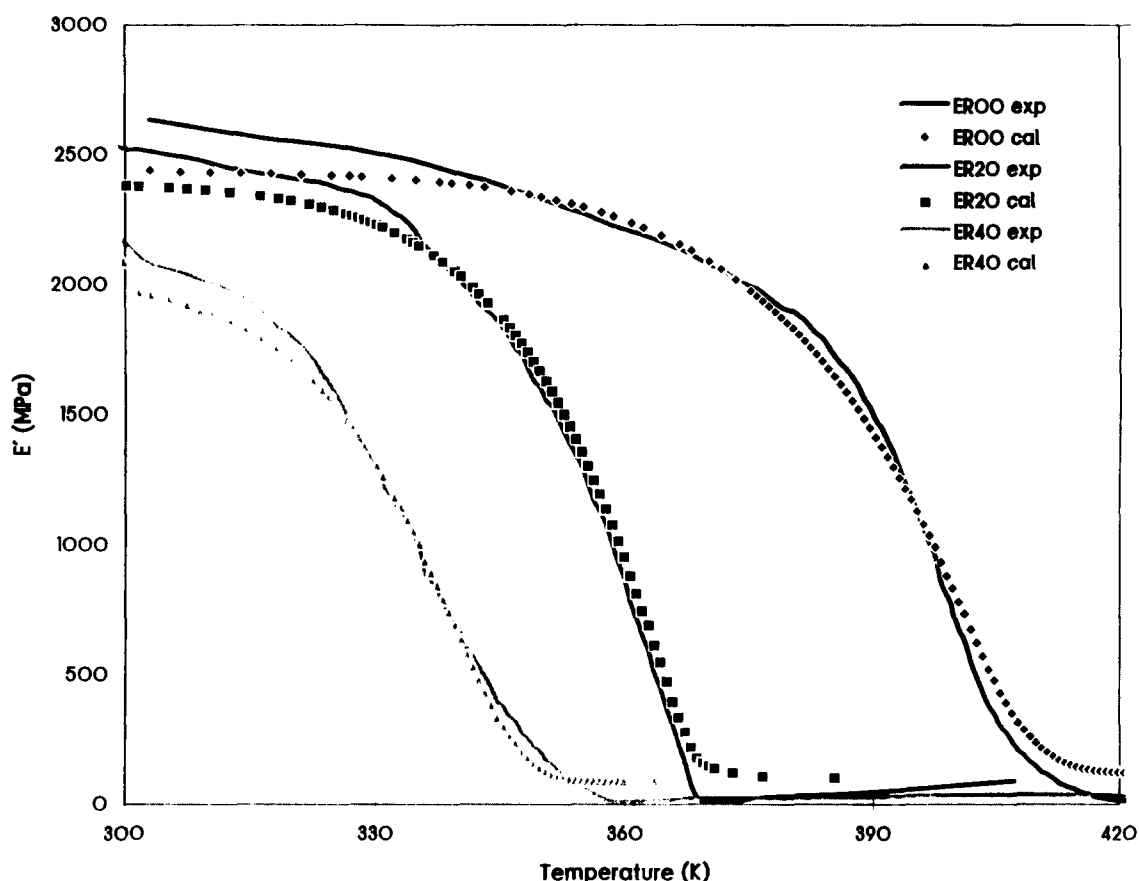
Figure 4 The best fit curves of the experimental storage (E') moduli from equations (13) and (14) for the three tested specimens
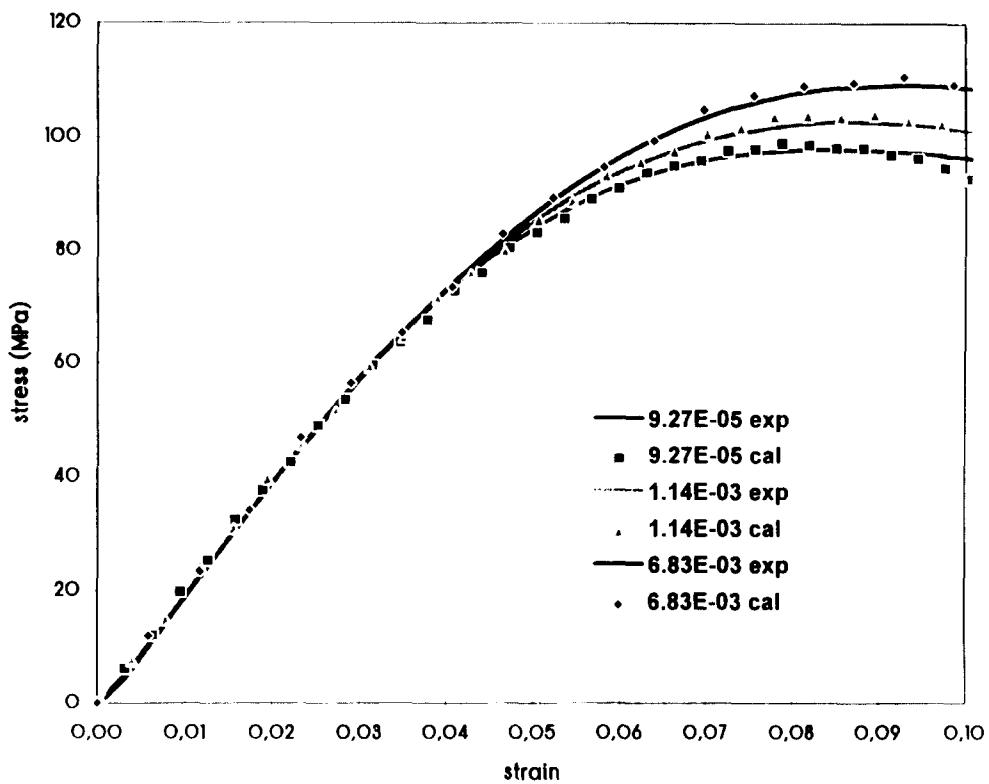
Figure 5 Compressive stress–strain data for three strain rates of deformation for specimen ER00. Calculated *versus* experimental results

yield stress at a specific temperature T in the glassy state is affected by the difference $T_g - T$. As far as the applied stress is imposed at a temperature close to the glass transition, the relative slippage between the cooperative

units is facilitated, resulting in a lower value of yield stress. All material parameters fitted from the dynamic mechanical analysis are summarized in *Table 1*. The plots of *Figure 4* show the correspondence between the
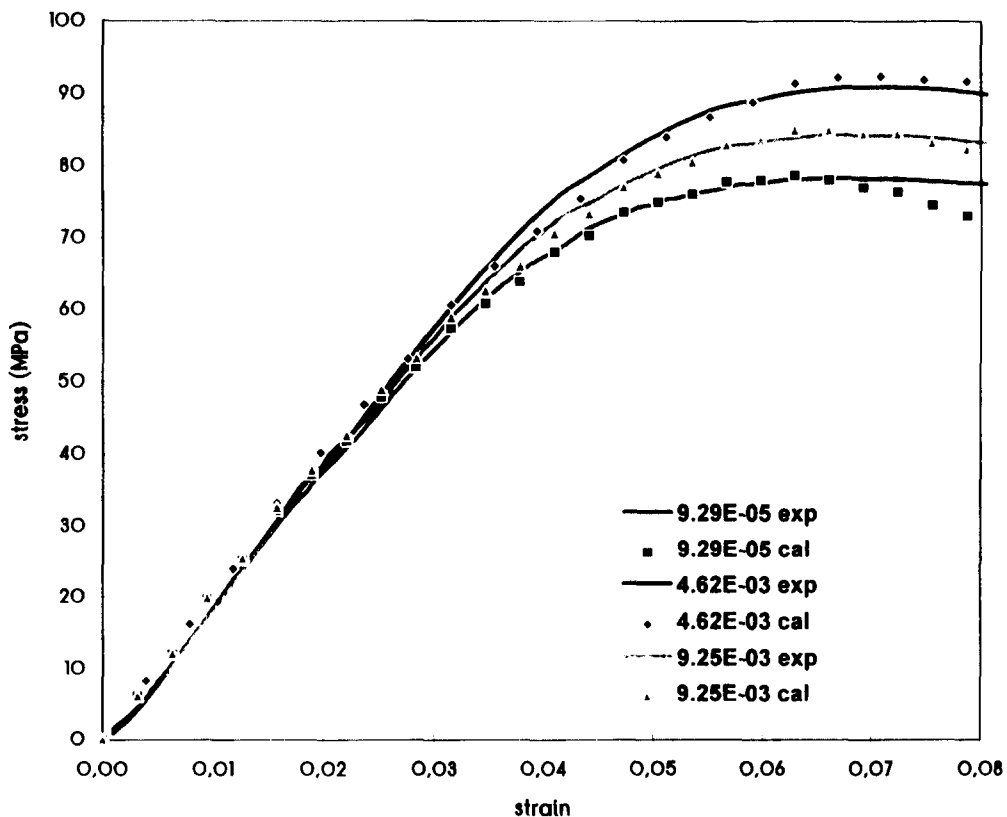

Figure 6 Compressive stress–strain data for three strain rates of deformation for specimen ER20. Calculated *versus* experimental results
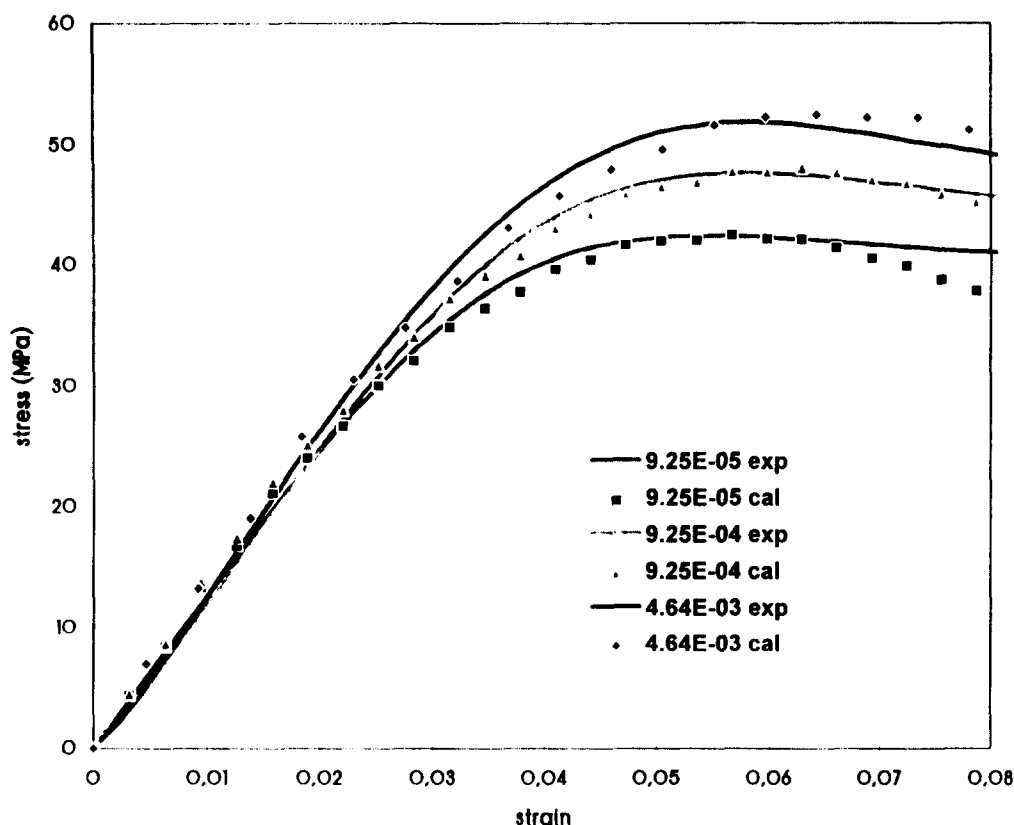
Figure 7 Compressive stress–strain data for three strain rates of deformation for specimen ER40. Calculated *versus* experimental results

experimental results of E' and the calculated functions, in the range of temperature where the parameters have been fitted according to the previous section. Using these parameters, as physical constants for the visco-elastic behaviour of the tested materials, we calculate the imposed compressive stress from the constitutive equation (10). This calculation has been carried out numerically by using as the relaxation function the KWW equation (12), and the non-linear viscoelastic time τ (equation (9)). Based on the concept introduced by this equation, the non-linear viscoelasticity is the result of strain-induced reduction in relaxation time. The lowering of this viscoelastic parameter is accomplished under isovolume conditions. This fact suggests that the same trend will be valid for any kind of deformation, without any revision in the presented formulation. As far as the relaxation function is concerned, the KWW expression is the best known equation to fit the glassy stage of the relaxation process, taking into account that real polymers exhibit many modes of molecular motion. The small value of the stretch exponential β, used to fit the experimental results, is an accepted value for the glassy state of amorphous polymers. The KWW equation, however, is not suitable for describing the response at large strain deformations. The polymeric material at this stage has passed the transition region and responds as a real rubber. The behaviour at this stage of large deformation and the effect of strain hardening will be the subject of a future work. The strain history followed for each tested specimen has been executed for three different strain rates, and these results are represented by the plots of *Figures 5–7*. As shown by these curves, there is a very accurate prediction of the way in which the yield

stress scales as a function of rate deformation. Apart from this success, however, it is worthwhile to mention that all parameters used for the theoretical calculations of the stress–strain response have been fitted from a pure viscoelastic experiment. We believe that the presented model assists previous work, where plasticity and non-linear viscoelasticity are not reated as mutually exclusive effects but are blended in, proving that the same physics is behind these phenomena.

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