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Theory for the plastic deformation of glassy polymers

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We present a theory to account for how a stress field can induce plastic flow in glassy polymers. We consider a molecular model in which chains are constituted from isotropic oriented elementary links embedded in a deforming continuum. The shear-stress field causes a redistribution of such links governed by a balance equation in orientation space. After detail calculations of the number of oriented units in certain directions, the net jump rate of the molecular links is given by an exponential form, according to the transition state theories of Adam and Gibbs [6]. These considerations are compared with the study of Boyce *et al.* [5] that included the effects of deformation rate, pressure and strain softening. The calculation of the plastic properties for polymethyl methacrylate and polycarbonate for various types of deformation has been made, and the corresponding results fitted the experimental data reasonably well.

1. Introduction

The plastic properties of many glassy polymers have been shown experimentally to exhibit three distinct regions. At small strains, after an elastic deformation appears at the beginning, a yield behaviour is revealed and the material starts to plastically deform. As the deformation proceeds further, most glassy polymers possess a response characterized by a true strain softening. Finally at strains over about 30% the material usually exhibits orientation hardening. Mechanical tests executed on representative glassy polymers such as polycarbonate (PC) and polymethyl-methacrylate (PMMA) show these distinct characteristics on a strain curve. Such tests also show that the plastic behaviour is proceeded by the nucleation and growth of shear bands inclined on the tensile or compression axis. The shear bands, generated on a small-scale at the beginning, are the result of a molecular realignment when the material begins to be stressed.

A number of different approaches are used to describe how a shear stress can induce structural changes in a glassy polymer thereby breaking the rigidity of the glass and allowing it to flow. The earliest quantitative model used to describe the plastic flow of polymers is that due to Eyring [1]. This model assumes that molecular segments are vibrating in a potential well with an energy barrier. The applied stress induces an energy bias on the height of the barrier, for a jump in the forward direction. The stress dependence of the rate of the transition appears through an hyperbolic sine term, but the simple Eyring equation cannot give detailed fits of experimental data. Another notable attempt to model the plastic flow of glassy polymers has been made by Robertson [2]. He assumes that at any time the molecular segments of the polymer chains are distributed between a population of *cis* and *trans* conformations. The effect of the applied stress is to cause certain segments to change over from the *trans* to the *cis* conformation, thereby sufficiently increasing the *cis* population to allow yielding to occur. Although this transition is a matter of intermolecular forces, Robertson assumes that the polymer can generally be changed from the glassy to the liquid state by whatever means that reduce the intermolecular or the intramolecular forces.

This analysis has been extended by Duckett *et al.* [3] to incorporate the effect of the hydrostatic component of the stress tensor on the yield stress. Considering the simplifications inherent in the model, it predicts the general features, such as the variation of the yield stress with temperature and strain rate, remarkably well. Following an analogous trend another approach has been considered by Argon [4]. This model considers that plastic flow occurs when the intermolecular resistance of the material to segment rotation has been overcome. Argon has derived the necessary free energy change, to produce segment rotation against the surrounding chains that are modelled as an equivalent elastic medium. Once the material begins to flow, molecular alignment occurs, which decreases the configurational entropy of the material. This is the second source of deformation resistance. This entropic resistance is modelled by using a Langevin approximation for the rubber elasticity in order to obtain a hardening response as larger strains are approached.

The Argon approximation has been extended by Boyce *et al.* (BPA model) [5] to include the effects of deformation rate, pressure, true strain softening, and temperature on the plastic resistance. A three-dimensional constitutive model has been developed and the physical mechanism associated with each of these phenomena has been described.

In the theory that follows we consider that each molecular chain is constituted from a number of isotropic oriented elementary links, which act as a small rigid stick embedded in a deforming continuum. When a shear-stress is developed in localized regions, the isotropic orientation of the rigid links is altered, and a new direction of the material lines occupied by each link is determined. The polymer flow starts as a sequence of molecular jumps governed by some kind of activated process. The main source of this activation process is the intermolecular forces developed among the segments of polymer chains. Following the idea of Adam and Gibbs [6] that the transition in glasses has a co-operative nature, we assume that the macroscopic strain rate of the sample is proportional to the net jump rate of the molecular links towards a certain direction. This jump rate is given by an exponential form of the energy barrier multiplied by the number of links oriented along the revealed shear bands. To complete the present study the three-dimensional constitutive model introduced by Boyce *et al.* [5] will be applied. Detailed discussion of the predictions of this analysis will be made on the experimental results used by previous authors.

2. Theory

While the yield phenomenon of metals can be described by changes in the local atomic conformation through the dislocation motion, in amorphous polymers there are as yet no suitable models for such a description, because of the absence of a specific structure and also the extinction of any kind of disturbance inside the material. On the other hand experimental observations have firmly established that yield behaviour in polymers is initiated in localized regions inside the bulk. This fact implies the generation of an amount of inhomogeneity during the material formation. It is known that the free volume in polymers is unequaly distributed amongst the molecules and this results in a different packing density at various points in the material.

In the present study we will attempt to employ this fact in a quantitative formulation of the yield initiation in amorphous polymers. More particularly we will investigate the possible existence of a hidden structure inside the amorphous materials, and the concept that a disturbance of such a structure is responsible for the yield initiation. At temperatures below the glass transition temperature, T_g, of a glassy polymer, the reference configuration is the isotropic state of the material 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 links of constant length, b. If the material is completely isotropic and totally homogeneous, we can assume that it consists of an ensemble of elementary units that reflect the isotropy and homogeneity of the bulk material. This assumption implies that at any point of the polymeric material there always exists an elementary space, that contains a constant number of molecular links uniformly distributed in various directions.

An illustrative way to make this consideration more clear is to use what we call "orientation space" for a one-to-one correspondence of the area with the molecular conformation (topology) in real space. Fig. 1 illustrates this correspondence for a complete isotropic and homogeneous polymeric material. According to this representation we can assume that a hidden structure exists inside the amorphous substance, which is clearly visible in the "orientation space". By analogy with crystalline materials we can say that the repeat unit of this structure is the elementary volume with a constant number of uniformly distributed links. However, it is known that the free volume shared amongst the elementary molecular units is not distributed uniformly. This requires that the repeat units of the orientation space have a varying number of molecular links.

There is a distribution function which expresses the number of links, N_i of the ith element that should be extracted from the way in which the free volume is distributed around the molecular links. This problem has been rigorously treated by Cohen and Turnbull [7], and has also been solved in a simple manner by Bueche [8]. For the present it will be assumed that, if the number of links for the case of equivalent elements is N, then the probability for the ith element to contain N_i links ($N_i = N/q$, where q is an integer) will be equal to the probability for a particular link to share q packets of the total free volume.

According to the approximation used by Bueche this probability can be expressed as:

$$p(q) = (1/2\pi q)^{1/2} \exp[-q(\ln q - 1) - 1] \qquad (1)$$

It is plausible to assume that the mechanical properties of each separate element are related to the number of links N_i, in particular the elastic constants should be proportional to this number. If this assumption is valid then there will be some regions inside the material with a different strength to the overall mean value. The above mentioned distribution function even permits the existence of some areas with deviations of one order of magnitude in the mechanical strength. These deviations are responsible for the preferential formation of yield bands during mechanical deformation. In

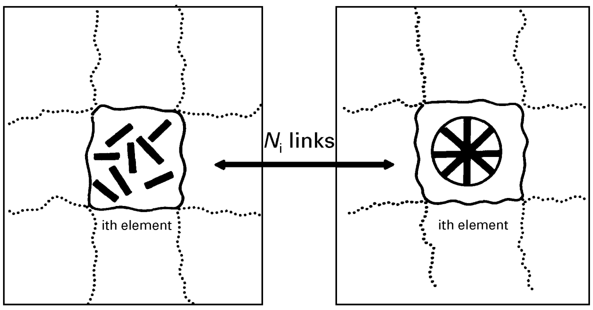

Figure 1 Schematic representation of the one-to-one correspondence between the isotropic regions of an amorphous polymer and the equivalent elements of the "orientation space".

the following sections we will describe how this event evolves when a stress field is developed inside the glassy polymer. It should be noted at this point that the isotropy of the material is still conserved because the initial distribution of the free orienting links in each element is considered to be uniform.

In the theory that follows, we consider the effect of the stress field on the direction of the vector b. Supposing that each link is embedded in an elastic medium, which is constructed 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 for the vector b. We make use of the "pseudo affine" model to express the state of orientation still existing in the material after the stress is removed. 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 [9] have developed the idea of an orientation distribution function to describe the evolution of a rubber network consisting of a large number of molecular chains that is initially randomly oriented in space. In our consideration we will follow 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 Fig. 2(a–c), 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 $1/4\pi$. After the imposition of a deformation, F, a new density distribution, n, will be conformed. In the proximity of a material point a sphere of radius $\mathrm{d}X$ will deform in an ellipsoid as is shown in Fig. 2c, with a corresponding radius $\mathrm{d}\chi = F\,\mathrm{d}X$. Supposing that the total number of links, N, directed around a material point is conserved after the deformation, we may write [10],

$$Nn_0\,\mathrm{d}\Omega_0 = Nn\mathrm{d}\Omega \quad \text{or} \quad \frac{n}{n_0} = \frac{\mathrm{d}\Omega_0}{\mathrm{d}\Omega} \tag{2}$$

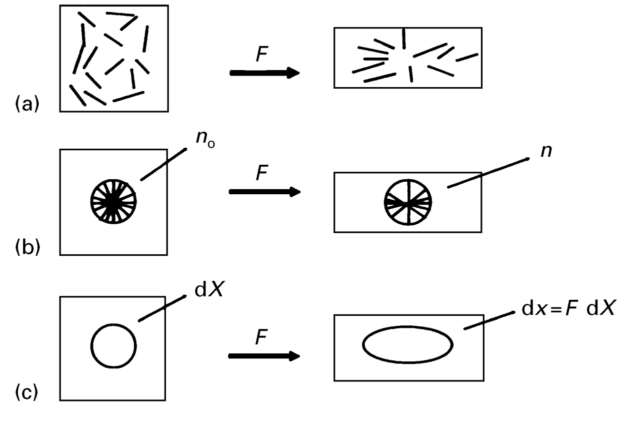

Figure 2 A single element in an unstrained and a strained state: (a) isotropic conformation of molecular links in amorphous polymer, (b) uniformly distributed links in "orientation space", (c) deformation of a sphere of radius $\mathrm{d}X$ in the proximity of a material point.

Where $\mathrm{d}\Omega_0$ and $\mathrm{d}\Omega$ are the solid angles in the undeformed and deformed state correspondingly. Expressing $\mathrm{d}\Omega_0$ and $\mathrm{d}\Omega$ with respect to $|\mathrm{d}\chi|$ and $|\mathrm{d}X|$ we obtain:

$$\frac{n}{n_0} = \frac{\mathrm{d}\Omega_0}{\mathrm{d}\Omega} = \left(\frac{|\mathrm{d}\chi|}{|\mathrm{d}X|}\right)^3 \frac{1}{J} = \frac{\lambda^3}{J} \tag{3}$$

Where $\lambda = |\mathrm{d}\chi|/|\mathrm{d}X|$, 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 in every state of the deformation mode. The stretch ratio λ, is then calculated for each direction as a function of the polar co-ordinate angles and the components of the deformation gradient tensor F.

Applying these results in the case of uniaxial elongation then the deformation gradient tensor is given by:

$$F = \begin{vmatrix} \lambda_1 & 0 & 0 \\ 0 & (\lambda_1)^{-1/2} & 0 \\ 0 & 0 & (\lambda_1)^{-1/2} \end{vmatrix}, \quad J = \det F = 1 \tag{4}$$

The ratio of density distributions will now be given by the following expression

$$\frac{n}{n_0} = \lambda^3 = \frac{\lambda_1^3}{(\lambda_1^3 + (1 - \lambda_1^3)\sin^2\vartheta\cos^2\varphi)^{3/2}} \tag{5}$$

This equation has its minimum values for each direction determined by the angle $\varphi = \pi/2$

$$\frac{n_{\min}}{n_0} = \lambda^3 = \frac{1}{\lambda_1^{3/2}} \tag{6}$$

Applying the above results in the case of simple shear where the deformation gradient tensor F is given by:

$$F = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad J = \det F = 1 \tag{7}$$

The ratio of density distributions will be expressed as follows:

$$\frac{n}{n_0} = \lambda^3 = \frac{1}{[1 + \gamma\sin^2\vartheta\,\sin\varphi(\gamma\sin\varphi - 2\cos\varphi)]^{3/2}} \tag{8}$$

The minimum value of this formula is obtained in the directions determined by the angles $\varphi = \pi/2 + \frac{1}{2}\tan^{-1}(2/8)$, $\theta = n/2$.

$$n_{\min} = \frac{1}{4\pi}\left(\frac{2}{2 + y^2 + \gamma\sqrt{\gamma^2 + 4}}\right)^{3/2} \tag{9}$$

In the following sections we will make use of this density distribution function to explain the mechanism by which plastic flow occurs. When a glassy polymer is subjected to a stress field, yield initiates in localized regions with decreasing strength. What is assumed is that the macroscopic strain rate or the rate of the volumetric plastic deformation, $\dot{e}^{\mathrm{p}}_{\mathrm{eq}}$, of the sample, is proportional to the net jump rate of the links towards a certain direction. Based on the idea that this jump constitutes a transition effect, for that part of the material which supports plastic flow, the theory of Adam and Gibbs [6] that such transitions in glasses have a co-operative nature can be applied. This means that the rate of plastic deformation can be given by the following exponential form:

$$\dot{e}^{\mathrm{p}}_{\mathrm{eq}} = \dot{e}_0 \exp\left(-\frac{n^* \Delta H}{KT} \right) \tag{10}$$

Where the pre-exponential factor $\dot{e}_0$ would be equal to the elementary Debye frequency, ΔH is the energy barrier that has to be overcome for the transition to occur, n^* is the number of links acting co-operatively as a unit to make a rearrangement, T is the absolute temperature and K is Boltzman's constant. Most of the current theories for the shear-induced plastic flow of glassy polymers are based on the idea that the stress acts as an energy bias on the height of the barrier ΔH. Argon [4] has calculated the activation free enthalpy for formation of a pair of molecular links based on the work of Li and Gilman [11] for wedge disclination loops. More accurately, they computed the elastic energy stored in regions outside the disclination cores where the assumption of linear elasticity holds. In the present study we assume that what is mainly changed under the applied stress is the number of co-operative units (links) that make suitable rearrangements to initiate the plastic flow. According to the above presented calculations, Equation 3 gives the density distribution of reoriented molecular links after a stress field has been imposed. The maximum value of the plastic strain rate is taken in the direction where the number of co-operative links is a minimum. Taking into account this assumption Equation 10 can be rewritten as:

$$\dot{e}^{\mathrm{p}}_{\mathrm{eq}} = \dot{e}_0 \exp - \frac{\Delta H N_{\mathrm{i}}}{4\pi KT} \lambda^3 \tag{11}$$

for uniaxial elongation where the volumetric rate deformation is equal to the strain rate in the load direction ($\dot{e}^{\mathrm{p}}_{\mathrm{eq}} = \dot{\varepsilon}^{\mathrm{p}}_{11} = \dot{\varepsilon}^{\mathrm{p}}$), the above equation becomes:

$$\dot{\varepsilon}^{\mathrm{p}} = \dot{\varepsilon}_0 \exp - \frac{\Delta H N_{\mathrm{i}}}{4\pi KT} \frac{1}{\lambda_1^{3/2}} = \dot{\varepsilon}_0 \exp - \frac{\Delta H N_{\mathrm{i}}}{4\pi KT} \frac{1}{(1+\varepsilon)^{3/2}} \tag{12}$$

For simple shear deformation the corresponding relation takes the form:

$$\begin{aligned} \dot{\gamma}^{\mathrm{p}} &= \dot{\gamma}_0 \exp - \frac{\Delta H N_{\mathrm{i}}}{4\pi KT} \left(\frac{2}{2 + \gamma^2 + \gamma\sqrt{\gamma^2 + 4}} \right)^{3/2} \\ &= \dot{\gamma}_0 \exp \\ &\quad - \frac{\Delta H \alpha}{4\pi KT} G_{\mathrm{i}} \left[\frac{2}{2 + (2/G_{\mathrm{i}})^2 + 2/G_{\mathrm{i}}\sqrt{(2/G_{\mathrm{i}})^2 + 4}} \right]^{3/2} \end{aligned} \tag{13}$$

where $\dot{e}^{\mathrm{p}}_{\mathrm{eq}} = \dot{\gamma}^{\mathrm{p}}/(3)^{1/2}$, has been taken into account.

To obtain the above relations, the number of co-operative links has been substituted by the density distribution, n_{min}, multiplied by the total number of links, N_{i}, of the microstructure where the plastic flow occurs. The strain ε of Equation 12 can be substituted by the tensile stress divided by the tensile modulus, E_{i}, of the region where yield is initiated ($\varepsilon = \sigma/E_{\mathrm{i}}$). Correspondingly, the shear strain, γ, of Equation 13 has been written as the ratio of the shear stress divided by the shear modulus G_{i}, ($\gamma = \tau/G_{\mathrm{i}}$). The magnitude of the constants E_{i}, and G_{i}, is less than the modulus of the whole material. These values are proportional to the number of links, N_{i}, of the ith element ($N_{\mathrm{i}} = \alpha G_{\mathrm{i}}$: where α is a material specific constant which depends on the molecular strength and the intermolecular potential). At the flow state, the steady state flow dilatation results in a decreased intermolecular interaction that reduces the material strength. This fact can be used to model the yield and post yield behaviour of glassy polymers that exhibit strain softening and pressure dependence. Extending the above expression to include such effects, with internal parameters that will be treated in a similar way as the athermal shear strength introduced in the BPA model [5]. It should be noted at this point that the corresponding expression for the plastic shear strain as developed by Argon and extended by Boyce *et al.*, is given by the following relation:

$$\dot{\gamma}_{\mathrm{p}} = \dot{\gamma}_0 \exp\left\{ -\frac{A s_0}{T} \left[1 - \left(\frac{\tau}{s_0} \right)^{5/6} \right] \right\} \tag{14}$$

Where s_0, is the athermal shear yield strength of the material that becomes equal to the applied shear stress when the absolute temperature T approaches zero, and A, is a material specific constant which is dependent on the mean molecular radius and a net angle of rotation of the molecular segment. Argon [4] has calculated the athermal shear strength s_0 as a function of the material constants using the following relationship:

$$s_0 = \frac{0.077G}{1 - \nu} \tag{15}$$

where G, is the shear modulus, and ν the Poisson's ratio of the tested material. This value has been experimentally verified by measuring the yield shear stress at various temperatures and extrapolating the experimental data to absolute zero [4].

In our consideration we can assume that the shear modulus G_{i} of the ith element with the smallest number of links has almost the same value as the athermal shear strength of the BPA model. This assumption is based on the fact that the shear strain, γ, of the micro-region where a shear band is initiated, is of the order of unity. In what follows however, the exact value of the constant G_{i} will be extracted by fitting Equation 13 for various applied strain rates and measuring the corresponding yield stress.

The above idea, for modelling plastic deformation as a direct result of the orientation of elementary units (links) under a stress field, is also offered as a plausible explanation of stress softening which usually accompanies the yield behaviour of glassy polymers. To qualitatively justify this phenomenon we will recall the mechanical behaviour of oriented polymers. Investigations of the mechanical anisotropy of polymers have for the most part been restricted to the cases where isotropy is considered in a plane perpendicular to the direction of drawing. Choosing the z direction as the axis of symmetry there are five independent elastic constants that appear in the stress–strain relations. Using these constants the tortional or shear modulus G, which is related to the shear deformation in the yz of xz planes, shows a very characteristic variation in respect to the draw ratio of oriented polymers.

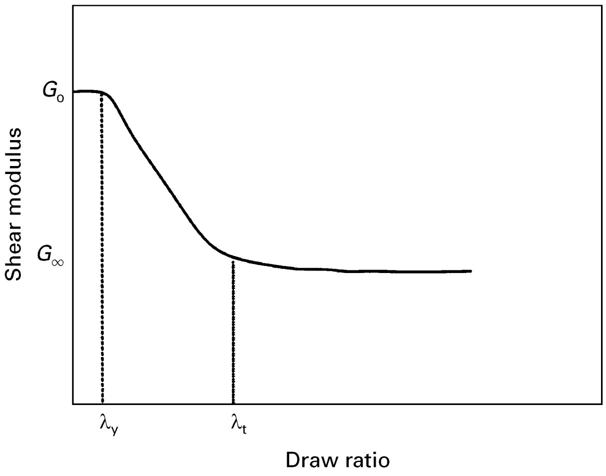

Figure 3 Schematic representation for the variation of shear modulus of the ith element as a function of the draw ratio.

This behaviour that is schematically shown in Fig. 3, has been modelled by many authors by averaging a number of elements with different shear moduli in various directions. The pseudo-affine deformation scheme that is introduced at the beginning of this work, and the corresponding orientation distribution function gives a reasonable first order fit of the experimental results for many oriented polymers [12]. If this result is correct, we can assume that the shear modulus of the activated volume where plastic flow occurs has an analogous behaviour with respect to the induced draw ratio of oriented links, as the strain deformation proceeds. A plausible differential equation describing this variation beyond the yield point can be given as follows:

$$\frac{dG_i}{d\lambda} = h\left(1 - \frac{G_i}{G_\infty}\right) \text{ for } \lambda > \lambda_y \qquad (16)$$

Where h, is the slope of the shear modulus drop with respect to the draw ratio λ in the interval (λ_y, λ_t), G_∞ is the limited value of G, and λ_y is the stretch ratio of the activated region at yield initiation. Dividing the above equation with an elementary time interval dt, and taking the rate of plastic deformation after yield point to be equal to the rate of stretch ratio, we obtain the following time evolution equation for G:

$$\dot{G}_i = h\left(1 - \frac{G_i}{G_\infty}\right)\dot{\gamma}^p \qquad (17)$$

This formula is exactly the same as the one concerning the athermal shear strength introduced from the BPA model to account for the stress softening.

To include the effect of pressure dependence we can substitute G_i by the expression, $G_i + \beta p$, where p is the pressure and β, the pressure dependence coefficient. This expression can be extracted from the experimental results of Rabinowitz *et al.* [13], where the yield shear stress has been measured as a function of hydrostatic pressure. As can be seen from the corresponding diagram, the shear modulus of the tested materials increases linearly with respect of pressure with a proportionality constant equal to β.

To complete the above analysis we will follow, as in the BPA model, the work of Lee [14] on the decomposition of the deformation gradient F into elastic end plastic parts, $F = F^eF^p$ where F^e, is assumed to be symmetric, so that F^p then represents the relaxed configuration obtained by unloading without rotation. Polar decomposition of the plastic deformation gradient results in the expression:

$$F^p = V^pR^p \quad \text{with} \quad R^p = R,\ R^e = 1 \qquad (18)$$

The rate quantity corresponding to this decomposition is the velocity gradient L.

$$L = \dot{F}F^{-1} = D + W = \dot{F}^eL^pF^{e-1} \qquad (19)$$

Where, $L^p = \dot{F}^pF^{p-1} = D^p + W^p$, and D^p, W^p are respectively the symmetric and skew parts of L^p. The tensor L^p is the velocity gradient of the relaxed configuration. The tensor D^p describes the rate of change of shape of the relaxed configuration. The spin of the relaxed state, W^p, is algebraically given as W plus a term dependent on F^e and $D + D^p$. The plastic strain-rate D^p must be constitutively described. In the BPA model, the magnitude of D^p is given by the plastic strain rate $\dot{\gamma}^p$ according to Equation 13, while the tensor direction of D^p is specified by N, so that:

$$D = \dot{\gamma}^pN \qquad (20)$$

The direction N is the deviatoric portion of the driving stress state, T^*, at any material point. This driving stress state is given in the continuum by the tensor:

$$T^* = T - \frac{1}{J}F^eBF^e \qquad (21)$$

Where T is the Cauchy stress tensor, B is the back stress tensor due to strain hardening resulting from molecular alignment, which will be constitutively prescribed below, and J is the volume change given by $\det F^e$. The resulting normalized deviatoric part of the driving stress state, N, is now determined by the relations:

$$N = \frac{1}{(2)^{1/2}t}T^{*\prime}, \quad \tau = \left[\frac{1}{2}\operatorname{tr}(T^{*\prime})^2\right]^{1/2} \qquad (22)$$

Where τ is the effective equivalent shear stress, and $T^{*\prime}$ is the deviatoric portion of the driving stress T^*. The Cauchy stress is assumed to be given by the elastic constitutive law, Anand [15]

$$T = \frac{1}{J}L^e\colon [\ln F^e] \qquad (23)$$

Where L^e, is the usual fourth-order isotropic elastic modulus tensor. With the description of the kinematics and the constitutive connection between stress and elastic deformation, the theory needs to be complemented with a constitutive law for the back stress tensor B due to entropic hardening.

2.1. Orientation hardening

The post-yield behaviour of glassy polymers has been shown to exhibit a true strain softening, which varies in magnitude from one polymer to another. This is observed at strains of 5–50%. However, if deformation continues at larger strains, there almost inevitably follows a rise in the true stress. This observation at large deformations has been regarded as a macromolecular orientation process essentially similar to the extension of a rubber but taking place under conditions of a high internal viscosity, which limits retraction when the stress is removed [16]. The occurrence of this hardening process, which is called "orientation hardening", decreases the configurational entropy of the system, and is responsible for the internal resistance to continuous flow. If orientation hardening is actually a phenomenon related to the straightening out of polymer chains between fixed points then certain analogies with the behaviour of rubber-like materials could be applied. Haward and Thackray [17] have modelled this behaviour for uniaxial extension by means of a back stress determined through a Langevin spring. In the present analysis, we will follow the above approach as has been extended by use of the BPA model, to describe general three-dimensional plastic deformations. According to this work the principal back stress components, B_i, are related to the gradient of the entropy change, ΔS, with respect to the principal plastic stretch, V_i^p, in that tensorial direction.

$$B_i = -TV_i^p \frac{\partial \Delta S}{\partial V_i^p} \tag{24}$$

The network model, which is used to describe the change in entropy, has been incorporated from the work of Wang and Guth [18]. This model, which is applied in a three-chain non-Gaussian network, gives a detailed expression for the back stress in terms of specific molecular characteristics:

$$B_i = C^R \frac{(Q)^{1/2}}{3}\left[V_i^p L^{-1}\left(\frac{V_i^p}{(Q)^{1/2}}\right) - \frac{1}{3}\sum_{i=1}^{3} V_i^p L^{-1}\left(\frac{V_j^p}{(Q)^{1/2}}\right)\right] \tag{25}$$

where Q, is the number of rigid chain links between entanglements, C^R is essentially the rubbery modulus, and L is the Langevin function defined by:

$$L(\beta_i) = \coth(\beta_i) - \frac{1}{\beta_i} = \frac{V_i^p}{(Q)^{1/2}} \tag{26}$$

with the inverse given by

$$L^{-1}\left(\frac{V_i^p}{(Q)^{1/2}}\right) = \beta_i \tag{27}$$

This model has been satisfactorily applied to polymethyl methacrylate (PMMA), but it was not capable of picking up the strain hardening observed experimentally in polycarbonate (PC). This result lead Arruda and Boyce [19] to suggest an eight-chain non-Gaussian network model. The study of the orientation hardening by the eight-chain model reveals a better agreement with experiments than the traditional three-chain model. However, very recently, Wu and Van Der Giessen [9] found that the three-chain and the eighth-chain models are approximate representations of the actual spatial distribution of molecular chains. On the basis of this consideration they have introduced a model accounting for the full network of rubber-like materials, and they have used it to model orientation hardening in glassy polymers. In the present study we will use the three-chain model for the description of orientation hardening, the above analysis will be tested on uniaxial data where every network model fits experimental results with a proper choice of network parameters.

3. Application of the model

The model proposed in this paper for the description of micro mechanism of plastic flow, will be tested against the experimental results of other workers. In the case of uniaxial elongation we will choose the measurements executed on polymethyl methacrylate (PMMA) by Hope *et al.* [20]. In the case of simple shear deformation we will make use of the experimental work presented by G'Sell and Gopez [21], where amorphous polycarbonates (PC) were tested in plane simple shear at various temperatures and shear rates. The application of this model to such experimental data will give the opportunity to compare our analysis with the micro-mechanical model suggested by Argon [4] and extended by Boyce *et al.* [5].

The components of the velocity gradient tensor for uniaxial extension are given with respect to a global Cartesian basis:

$$L = \begin{bmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & \dot{\varepsilon}_T & 0 \\ 0 & 0 & \dot{\varepsilon}_T \end{bmatrix} \tag{28}$$

Three values of strain-rate are applied ($\dot{\varepsilon} = 1, 0.1, 0.01\ \mathrm{s}^{-1}$) and the transverse strain-rate $\dot{\varepsilon}_T$ is determined from the boundary conditions $\sigma_{22} = \sigma_{33} = 0$. The true stresses versus strain results are obtained by numerical integration of Equations 20–23 in combination with the plastic rate expression, Equation 13. The back stress is calculated from the current plastic stretch according to the three-chain network model described by Equation 25. The material parameters used in the model are summarized in Table I. Most of the values of these elastic and

TABLE I Material parameters used in the numerical simulation for the tensile and shear stress–strain data

	γ_o (s^{-1})	$A = \Delta H\ \alpha/4\pi K$ ($\mathrm{K\ MPa}^{-1}$)	G_0 (MPa)	G_i (MPa)	h (MPa)	β	C^R (MPa)	Q	G (MPa)	ν
Tensile test	1×10^{15}	210	78	70	900	0.2	6	9	800	0.3
Shear test	2×10^{12}	180	107	90	500	0.08	10	3	840	0.3

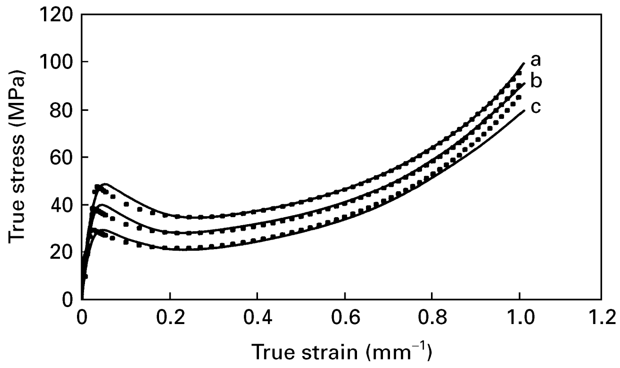

Figure 4 Tensile true stress–strain data on glassy PMMA at 90 °C. The model results are represented by the dashed line whilst the experimental results are represented by the solid line. Data are presented for $\dot{e}$ values of (a) 1.0 s^{-1}, (b) 0.1 s^{-1} and (c) 0.01 s^{-1}.

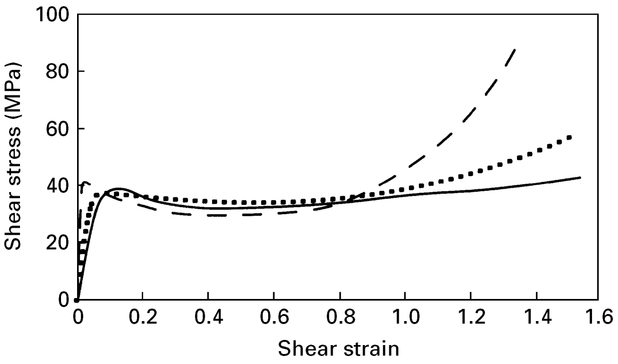

Figure 5 Shear stress response to a large simple shear of 0.003 s^{-1} for PC at room temperature. The experimental data represented as (—) is simulated by the (· · · ·) present model and the (– –) BPA model.

viscoelastic constants are based on the simulation process followed by Boyce *et al.* [5]. The plots in Fig. 4, show the comparison of the present model with the experimental results for uniaxial extension of PMMA [20]. As is shown in these graphs, the uniaxial response is accurately mimiced using the parameter values listed in Table I. The corresponding fitting of the BPA model [5] shows some differences in the strain area where plastic flow initiates. In our case this response takes place at strains over about 4% which is closer to the experimental value.

For further assessment of the adequacy of this model to give a detailed description of the plastic flow of glassy polymers, various types of deformations and materials should be tested. A significantly different deformation process to the uniaxial extension presented above is the simple shear deformation. For that reason we have considered the case of simple shear deformation of polycarbonate (PC) at room temperatures. The components of the velocity gradient tensor for that state of deformation on the x_1–x_2 plane are determined as follows:

$$L = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{29}$$

The principal components, $V^{\mathrm{p}}_{\mathrm{i}}$, are determined via the plastic shear deformation γ^{p}, using the following relations:

$$\lambda^{\mathrm{p}}_{1,2} = \frac{1}{2}(\gamma^{\mathrm{p}} \pm (4 + \gamma^{\mathrm{p}2})^{1/2}), \quad \lambda^{\mathrm{p}}_3 = 1 \tag{30}$$

The axes of V^{p} are then found and the associated B_{i} are calculated from Equation 25. The corresponding principal stretches of $V^{\mathrm{e}}_{\mathrm{i}}$ are given by using the relation, $V = V^{\mathrm{e}}V^{\mathrm{p}}$, and the resulting principal components of the stress tensor can be obtained. The shear component, σ_{12}, in the x_1–x_2 plane is then calculated by rotating the principal axes via an angle θ, given by:

$$\tan\theta = \frac{1}{2}(\gamma + (4 + \gamma^2)^{1/2}) \tag{31}$$

For the numerical integration of the constitutive equations we used the material constants listed in Table I. Some of these values are taken to be the same as in the case of the application of the BPA model by Wu and Van Der Giessen [9]. Fig. 5, shows the shear stress σ_{12} as a function of a shear strain γ with a shear rate $\dot{\gamma} = 3 \times 10^{-3}$ s^{-1}. Also shown is the simulation of the BPA model as obtained by Wu and Van Der Giessen. It is evident from this comparison that the yield initiation is approximated in more detail by the present model. On the other hand the orientation hardening behaviour seems to better fit the experimental results. An improved approximation could however be obtained if we use the full network description instead of the three-chain model for the calculation of the back stresses at a large deformation.

4. Conclusion

In this paper, a new model to describe the plastic flow of glassy polymers has been developed. The present work contributes in a wide sense to the understanding of molecular link orientation during large deformation. Assuming a "pseudo affine" deformation in a continuous sense, the re-orientation of isotropic rigid links embedded in an elastic medium has been described. We have assumed that the main mechanism that operates when plastic flow occurs has a co-operative nature. This allows the derivation of a plausible expression for the plastic shear rate and the yield stress. The kinematics formulation used to produce the model is taken from the original work of Boyce *et al.* [5]. The application of the present analysis to certain materials and modes of deformations, revealed a more flexible description for the determination of the deformation area where plastic flow occurs. In addition to detailed fitting of experimental results the proposed method constitutes an approach for a more profound knowledge of changes in molecular conformation that occur in amorphous polymers at the yield point. Amongst the different aspects of the yield behaviour which are described by this model is the volume dependence during the plastic deformation. The assumption that stress induces a volume increase resulting in a chain segment mobility that underpins most work in the area is not necessary. The assumption made in this theory, that under stress it is a change in the rigid link distribution that produces yield behaviour, does not imply any volume increase. The pressure dependence of the yield stress is also not a direct consequence of the free volume variation, it is a probable redistribution of the free volume packets which results in a change of the shear modulus with respect to hydrostatic pressure. The most important contribution of the present work however is that it explains the yield behaviour by using the concept of co-operative motion, which is the main motive for the most immediate association of plastic flow with the glass transition phenomena of glassy polymers.

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