

Modeling of Postyield Behavior of Glassy Polymers

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SYNOPSIS

The yield stress of amorphous glassy polymers depends strongly on the strain rate, temperature, and hydrostatic pressure. On the other hand, the yield criteria, valid for metals, do not describe this behavior. Therefore, the yield phenomenon of the polymeric glassy state must be mainly a nonlinear viscoelastic effect. In this work, an analysis based on the concept of activation volume tensor, described elsewhere, and using fundamental equations of nonlinear viscoelasticity, is presented. It has been confirmed that this consideration leads to a satisfactory description of the postyield behavior, including strain softening and strain hardening. The strain rate and temperature effect have also been modeled for various rates and temperatures. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Amorphous glassy polymers under constant rate straining exhibit nonlinear viscoelastic behavior such as yielding and cold flow. The yield and postyield behavior appears to have some distinct characteristics, namely, an initial stress peak (depending on pressure, thermal prehistory, strain rate, and temperature), followed by a stress softening due to inhomogeneous deformation. As the strain becomes higher, the configurational entropy of the system changes because of the molecular alignment and the material exhibits strain hardening. As has been reported,¹ the time and temperature dependence of the yield point in polymers has been explained mainly by two distinct classes of theory. The mechanisms related to these two classes have been termed "nucleation"-controlled² and "velocity"-controlled.^{3,4}

The yield point of glassy polymers has been considered as the point where plastic flow begins. For the description of this mechanism, the Eyring⁵ equation has been applied to describe the viscosity of a fluid. However, in Roetling analysis,⁶ it has been suggested that the Eyring equation was not applicable to the yielding of glassy polymers, while a two-stage process is proposed using the Ree-Eyring equation.⁷ Moreover, Bauwens et al.⁸ concluded that

in the T_g region, where yielding behavior is more complicated than in the glassy state, the Eyring-type mechanism must be of little use.

On the other hand, the question whether a structural change occurs at the yield point has been the subject of many works. Robertson⁹ proposed that the glassy structure changes to liquidlike at the yield point.

In a work of Ngai et al.,¹⁰ constitutive equations based on the nonlinear viscoelasticity were developed with the use of a coupling model. Contrary to these considerations, where a homogeneous change of the polymeric structure is assumed, Lefebvre and Escaig^{11,12} studied the contribution of nucleation of molecular defects to the plastic strain and proposed the inhomogeneous structural change during yielding. Physical explanations for changes in the deformation regime have also been provided by Perez et al.¹³

For the complete description of the strain-softening and strain-hardening effects, in a uniaxial state of deformation, Haward and Thackray¹⁴ used an Eyring dashpot for the intermolecular resistance connected with a Langevin spring to express the strain hardening.

The mechanisms of inelastic deformation of glassy materials under monotonically rising stress were discussed by Argon¹⁵ and linked to the structure of the materials studied. Argon¹⁶ also introduced a micromechanical model to describe the intermolecular resistance to segment rotation and attributed

the strain hardening to the subsequent molecular alignment.

Later, this work was extended by Parks et al.¹⁷ and by Boyce et al.¹⁸ for three-dimensional states of deformation, where also the effects of deformation rate, pressure, and temperature were included for a realistic simulation of the entire process.

The effect of pressure on the shear yield stress of a polymer can be very well represented by the equation

$$\tau = \tau_0 + \alpha p \quad (1)$$

where τ is the shear yield stress at pressure p ; τ_0 , the shear yield stress at atmospheric pressure; and α , the coefficient of increase of shear yield stress with hydrostatic pressure, equivalent to the friction coefficient μ .

The correlation between shear yielding and secondary relaxations were also examined.¹⁹ It was found that the activation of cooperative secondary relaxation at the temperature and time scale of the experiment is necessary for yield to occur.

In a series of recent works by Chow,^{20,21} the prediction of the yield behavior was based on the concept of the local configurational rearrangements of the molecular segments, which result in different domain sizes due to the application of different stress fields. By combining this fact with the effect of an external stress on the viscoelastic relaxation, Chow²¹ calculated the external work done by σ_{ij} acting on the hole cell during yielding, using the concept of the activation volume tensor. This quantity strongly affects the relaxation time, having an important role in nonlinear viscoelasticity. However, by this treatment only, the strain softening after the stress peak at yielding can be described.

In this work, following the analysis developed by Chow,²¹ an attempt was made to predict the post-yield behavior of glassy polymers, i.e., strain softening and strain hardening. A stress back tensor was introduced analogous to that proposed elsewhere.¹⁸ In all cases, comparison with experimental data of the literature was made.

VISCOELASTIC MODEL FOR YIELD BEHAVIOR

According to the Chow analysis, the work done by σ_{ij} on a hole cell during yielding is

$$\Delta W = -\sigma_{ij}\omega_{ij}/f \quad (2)$$

where σ_{ij} and ω_{ij} are the stress and activation volume components respectively, while the ratio (ω_{ij}/f) expresses the volume of the polymer segment needed to move as a whole for plastic yield to occur. The relaxation time is then equal to

$$\tau = \tau_0 \exp \left[-\frac{\sigma_{ij}\omega_{ij}}{2fbRT} \right] \quad (3)$$

where τ_0 is the preexponential factor and is analogous to the quantity

$$\tau_0 = A^{-1} \exp \left[-\frac{\bar{e}}{bf_r RT} \right] \quad (4)$$

with A being a constant, analogous to $\tau_r^{-1} \times \exp[\bar{e}/bf_r RT]$, where \bar{e} is the thermal activation energy for the hole transition equal to 2.51 kcal/mol; f_r , equal to 0.0336; τ_r , a reference relaxation time; R , the gas constant; and T , the temperature, and b expresses the shape of the relaxation spectrum.

Following the ideas of Eyring,⁵ yielding occurs when the product of relaxation time and the applied strain rate is constant:

$$\dot{\epsilon}\tau = \text{constant} \quad (5)$$

On the other hand, the relaxation modulus of glassy polymers may be given by the well-known Kohlrausch-Williams-Watts (KWW) equation:

$$E_{ijkl}(t) = E_{ijkl}^0 \exp \left[-\left[\frac{t}{\tau} \right]^b \right] < b < 1 \quad (6)$$

where E_{ijkl}^0 is the unrelaxed modulus, τ is the relaxation time, and b expresses the broadening of the distribution of relaxation times.

By taking into account that stress and strain are related by

$$\sigma_{ij}(t) = \int_0^t E_{ijkl}(t-s) \dot{\epsilon}_{kl} ds \quad (7)$$

we obtain

$$\sigma_{ij}(e_{kl}) = E_{ijkl}^{e_{kl}} \times \int_0^{e_{kl}} \exp \left[-\frac{e'_{kl} \exp \left(\frac{2.303\sigma_{kl}(e'_{kl})}{K_{kl}} \right)}{\dot{\epsilon}_{kl}\tau_0} \right] de'_{kl} \quad (8)$$

where $\dot{\epsilon}_{kl}$ is the rate of deformation, and K_{kl} , the slope of the plot of the yield stress vs. logarithmic strain rate.

Considering eqs. (3) and (5), this plot is a straight line for a wide range of strain rates, in a similar way as in the Eyring analysis. By this approach, however, only the strain softening can be predicted, as was described by Chow.²¹

In an attempt to describe the strain hardening that follows strain softening for many types of amorphous glassy polymers, it was taken into account that after stress overshooting a molecular alignment occurs. This effect leads to the change of the configurational entropy of the system. For the material to overcome this type of resistance, an internal variable is introduced, namely, the back stress tensor B_{ij} , similar to that proposed by Haward and Thackray,¹⁴ and which was extended by Parks et al.¹⁷ for 3-D problems.

By assuming that the free-energy change due to intra- and intermolecular changes is negligible compared to the change of the configurational entropy, which is large due to the orienting of chains,¹⁸ the back stress tensor was related to the entropy change. Following this assumption, the entropic resistance defined in the stretched material above T_g represents an internal resistance "locked" in the material below T_g .

This variable, B_{ij} , for the description of the orientation hardening is defined by a non-Gaussian statistical mechanics theory of rubber elasticity as reported by Treloar.²² In eq. (8), the stress σ of the second part of eq. (8) is replaced with the difference $\sigma_{ij} - B_{ij}$, where σ_{ij} is the Cauchy stress and the back stress B_{ij} is expressed by the following relation:

$$B_{ij} = C_R \frac{N^{1/2}}{3} \left[\lambda_i L^{-1} \frac{\lambda_i}{N^{1/2}} - \left(\frac{1}{3} \right) \sum_{j=1}^3 \lambda_j L^{-1} \frac{\lambda_j}{N^{1/2}} \right] \quad (9)$$

where λ_i is the stretch ratio; λ_j , the stretch ratio in the other principal direction, calculated with the assumption of the isovolume deformation during yielding, and T , the temperature. C_R is the rubbery modulus, equal to $n k T$, n being the number of chains per unit volume, k , the Boltzmann constant, and L^{-1} is the inverse Langevin approximation. N is the number of rigid chain links between entanglements.

The numerical evaluation of eq. (8) was made by replacing time (which is equivalent to the deformation e , due to the constant strain rate) with the reduced time ξ , defined by Hopkins²³:

$$\xi = \tau_r \int_0^t \frac{dt'}{\tau} \quad (10)$$

where t is time; τ , the relaxation time; and τ_r , the relaxation time at some reference state. Generally, ξ is the time required for the material to relax at a reference state of deformation, to the same extent that occurs in time t at a specific deformation state.

To check the validity of the above-mentioned analysis, experimental results found in the bibliography, carried out by Hope et al.,^{24,25} were used. These experimental data concern true stress-strain plots for PMMA at 90°C for various rates of deformation, namely, 10^0 , 10^{-1} , 10^{-2} , 10^{-3} , and 10^{-4} s⁻¹ (see Fig. 1).

From these results, the yield stress vs. logarithmic rate of deformation was obtained in Figure 2. The slope of this straight line corresponds to the magnitude of K_{kl} of eq. (8) and was found to be equal to 3.13 Mpa. Following eqs. (3) and (5), K_{kl} is proportional to the quantity $fbRT/\omega_{kl}$, and in that way, it was possible to have an estimation of the activation volume, which was found to be 50 Å³. This fact implies that the volume of molecular segments needed to move as a whole at yielding is higher than the volume at a single lattice site (equal to 19 Å³). This is evidence of the cooperative nature of yielding in the amorphous glassy state. The concept of cooperation has also been extensively discussed elsewhere.²⁶

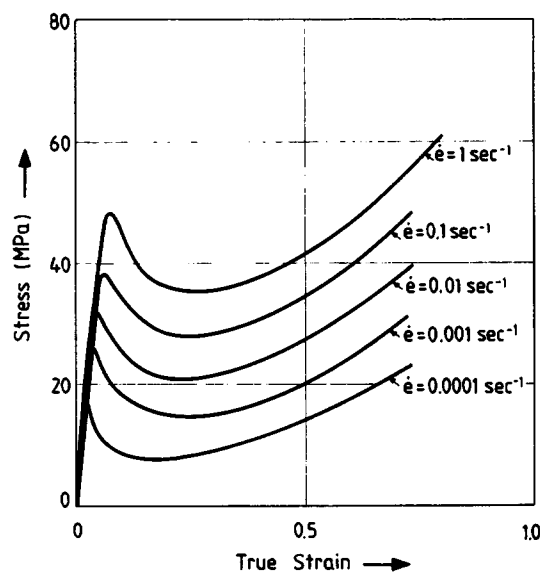


Figure 1 Experimental stress-strain curves of PMMA at 90°C, at three different strain rates, taken from Ref. 25.

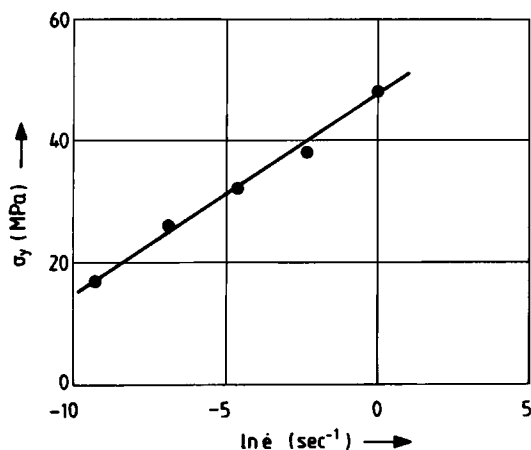


Figure 2 The yield stress plotted vs. logarithmic strain rate for PMMA at 90°C (data from Fig. 1).

Combining eqs. (3), (4), (8), (9), and (10), the yield and postyield behavior of PMMA could be described as shown in Figure 3, where the validity of this approach is tested for three different strain rates from the data of Figure 1. Parameter N is equal to the square of terminal stretch ratio λ , which can be approximately estimated from the experimental data of Figure 1, as mentioned by Boyce et al.¹⁸ The value of N was found to be equal to 9, while the value of the reference relaxation time τ , was of the order of 10^3 s.

Constant C_R , which is the rubbery modulus of PMMA at 90°C, was fitted from the experimental results equal to 10 MPa. Therefore, n , the number of chains per unit volume, was equal to 19.9×10^{26} (m^{-3}). The best approximation was made for a value of b equal to 1. In this way, it is confirmed that the distribution of relaxation times becomes quite narrow as the temperature is increased, approaching the equilibrium state.

As obvious from the above analysis, temperature affects both the relaxation time as it is defined by eq. (3) and the intermolecular resistance through eq. (9), given that C_R is equal to nkT . To study the flexibility of this viscoelastic analysis to describe also the temperature effect on yielding, the above-mentioned experimental data were used. These tensile true stress-strain curves concern PMMA at three different temperatures, 50, 70, and 90°C, at a constant strain rate of 0.005 s^{-1} .

By taking into account the fact that the rubbery modulus C_R increases with increasing temperature, slightly changing it for the three different temperatures, keeping the set of the other parameters constant, as mentioned above, a satisfactory fitting was made and is presented in Figure 4. For temperatures

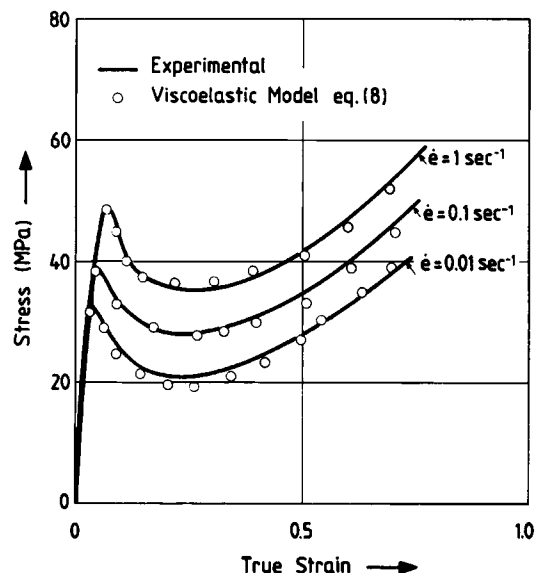


Figure 3 Stress-strain curves of PMMA at 90°C with varying the rate of deformation. Solid line represents the data of Figure 1. Points are obtained using eq. (8).

90 and 70°C, the temperature effect is well modeled. At the lowest temperature of 50°C, an almost slight deviation at the strain softening and strain hardening is observed, exhibiting this way possible limitations of this description at temperatures far from T_g . From the above analysis, it is implied that the scaling of the yield behavior can be successfully made for a wide temperature range, without a further change of parameter values.

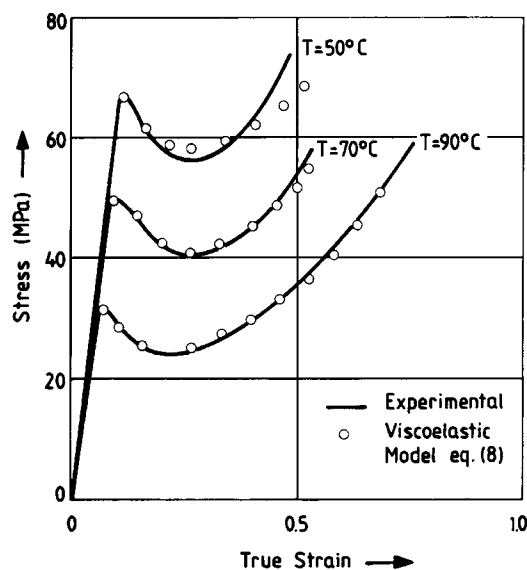


Figure 4 Stress-strain curves of PMMA at three different temperatures, with a constant strain rate of 0.005 s^{-1} (Ref. 24). Points are obtained using eq. (8).

CONCLUSIONS

The prediction of yield and postyield behavior of glassy polymers, based on a microscopic model developed by Chow,²¹ was made as follows: Using this model in respect to the basic expressions of nonlinear viscoelasticity, a constitutive equation is introduced, which can successfully describe the yield behavior of the amorphous glassy state. The strain hardening has been modeled with the use of an internal variable: the back stress tensor.

Effects such as strain softening and strain hardening could be predicted with a good approximation between theory and experiment, as shown in Figure 3. However, it must be noted that using the same set of parameters at even lower strain rates a slight deviation concerning the strain softening is observed. In addition, the temperature effect on yielding was also described with the same analysis. In conclusion, nonlinear viscoelasticity can result to a satisfactory prediction of the entire yield behavior of glassy polymers, describing strain softening and strain hardening, including strain rate and temperature effect.

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