

Mechanism of Plastic Deformation for Polycarbonate Under Compression by a Laser Extensometer Technique

G. SPATHIS, E. KONTOU

Department of Engineering Science, Section of Mechanics, National Technical University of Athens, 5 Heroes of Polytechnion, GR-15773, Athens, Greece

Received 31 July 1998; accepted 11 June 2000

ABSTRACT: The large strain behavior of a glassy polymer was studied in terms of compression tests at various rates, while the local deformation was evaluated with a noncontact laser extensometer. The main features of yield and postyielding were described with a constitutive model from nonlinear viscoelasticity, combined with a kinematic formulation for the separation of total deformation into a viscoelastic and a plastic part, respectively. The concept of plastic shear transformations introduced elsewhere was used to develop a mathematical model for the rate of plastic deformation. The entire experimental true stress–strain curves (including strain hardening and strain softening) could, through this model, be identified in a self-consistent manner. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2534–2542, 2001

INTRODUCTION

The plastic deformation behavior of glassy polymers has been the subject of a variety of research works, dealing mainly with the elastoviscoplastic response at small strains and a strain-hardening effect after yield.^{1–8} Oleinik et al.^{9–11} proposed an interesting plastic deformation mechanism for polymeric glasses. The whole process consists of two main stages: nucleation and growth of special shear defects, called plastic shear transformations (PSTs) and their disappearance. The main feature of plastic deformation of glasses is the storage of large amounts of internal energy during the deformation procedure.

This approach is based on various experimental data obtained by deformation calorimetric studies, thermally stimulated creep, differential scanning calorimetry, and residual strain recovery tests. It has been found that the large amount of energy stored in the material is related to es-

sential structural rearrangements of the polymeric glassy state.⁹

In a recent work,¹² the yield behavior of an amorphous glassy polymer was studied with true tensile stress–strain curves, obtained at various crosshead speeds using a new experimental method. A constitutive equation from nonlinear viscoelasticity was used, with the further assumption that the material, during deformation, follows subsequently two distinct paths: a nonlinear viscoelastic and a plastic one. The maximum strain, where this distinction is manifested, was treated as a control parameter, while the strain rate was experimentally evaluated. The decomposition of deformation was made with a suitable kinematic formulation, proposed in the literature.¹³ The theoretical results describe in detail the experimental curves.

In this work, the constitutive model that was developed in ref. 12 was applied. This theory combined with the concept of PSTs that are evolved in a deformed glassy polymer has led to a physical model that presents the mechanisms of plastic deformation in glassy polymers qualitatively and to a mathematical model for the evaluation of the

Correspondence to: G. Spathis.

Journal of Applied Polymer Science, Vol. 79, 2534–2542 (2001)
© 2001 John Wiley & Sons, Inc.

rate of plastic deformation. This model was proved to be flexible enough to predict the exhibited stress yield and stress drop, using only the value of the macroscopic yield strain. Although strain softening is apparent in most cases of plastic deformation of glassy polymers, there has not been established yet a correct model for yielding, accounting for this effect in a self-consistent manner.¹⁴ Strain softening is accompanied by a series of effects such as small volume decreases,¹⁵ extended-chain conformations,¹⁶ and internal energy increment up to a constant value.⁹

The extracted expression of the rate of plastic deformation and the associated parameters are of determinant importance for the detailed description of yield and postyield behavior of the glassy state. The glassy polymer selected for this treatment was polycarbonate (Lexan) that exhibits all the main features of yielding, that is, yield stress rate dependence and strain softening. Combining this model with the kinematic formulation introduced by Rubin,¹³ all these features were accurately described. The material was tested in terms of compression experiments at three different crosshead speeds. The experimental device used for the deformation measurements is described elsewhere¹⁷ and permits the evaluation of the strain and strain rate of a localized region of the entire gauge length.

EXPERIMENTAL

The material tested was polycarbonate, with the commercial name Lexan, provided in plate form. Cylindrical specimens with an average diameter of 10 mm and height of 20 mm were constructed for the compressive experiments. To eliminate any prehistory effects, the samples were annealed at a temperature above the T_g for 1 h. The compression experiments were carried out with an Instron 1121 tester at room temperature. Three different crosshead speeds were used, namely, 0.1, 1, and 10 mm/min, which coincide with a total effective strain rate equal to 8.3×10^{-3} , 8.3×10^{-4} , and $8.3 \times 10^{-5} \text{ s}^{-1}$, correspondingly. The longitudinal strain could be measured, with the laser extensometer, which permits a noncontact measurement of the longitudinal deformation distribution of samples. This experimental method was presented in detail in ref. 17.

For the deformation measurements a high-contrast tape pattern code was applied to the gauge length of the sample, namely, four white stripes

(three zones) on a dark background. The space between the stripes was 2 mm.

During the compression tests, the load was recorded simultaneously with the percentage strain, and the data acquisition was made with a software developed by the Gabo-Qualimeter Co. It was possible to measure the deformation at every zone separately, and the one with the maximum strain (reference zone) could be detected. In Figure 1, the deformation in respect to real time is plotted for the three zones, in the case of a crosshead speed of 1 mm/min. The zone with the maximum deformation was the intermediate one (2–3), far apart from the plates of the Instron tester. Therefore, the friction effects were minimized, and the response of the material in pure compression testing could be studied. As shown, the distribution of macroscopic strain along the gauge length is not so inhomogeneous in respect to the tensile tests, where necking instability occurs.¹² The construction of engineering and true stress-strain curves (making an isovolume assumption) was then made in respect to that reference zone, and these plots are presented in Figures 2 and 3, correspondingly. Stress drop is obvious from these figures, even though the cross section is increased during deformation.

Moreover, the experimental strain rate could be recorded for every zone in respect to the stretch ratio. The true experimental strain rate is plotted for the three crosshead speeds in Figure 4, in respect to the localized zone. As is observed, the true strain rate of a small reference gauge length becomes much higher (one order of magnitude) than is the total effective imposed strain rate (which are mentioned above) and is related to the intrinsic response of the material. This effect will be discussed later.

CONSTITUTIVE EQUATIONS FOR UNIAXIAL STRESS

In a recent work,¹² the large deformation behavior of glassy polymers was described with a set of constitutive equations that are obtained with an analysis, based on the idea that there are two distinct paths, followed by the material during the deformation procedure. In the first stage, at small strains, the viscoelastic path is dominant, and the corresponding constitutive relations, according to the nonlinear viscoelastic description by Matsuoka,¹⁸ are expressed as the product of a strain-dependent term with a time-dependent

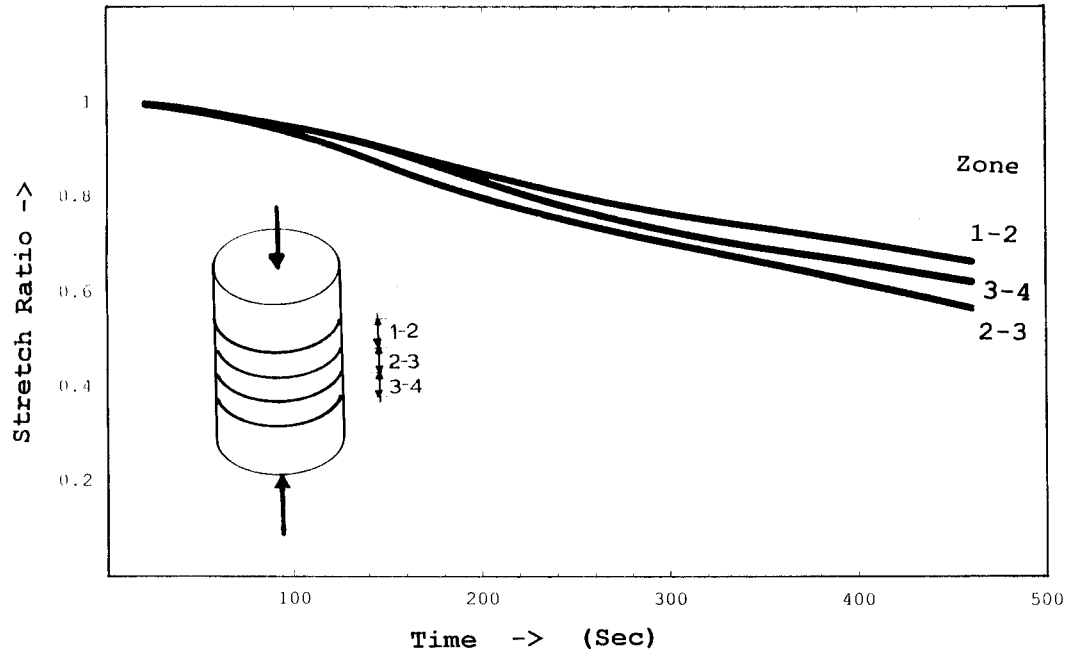


Figure 1 Local stretch ratio varying with time, for a crosshead speed of -1 mm/min.

one. This behavior is extended up to a critical value of deformation, which acts as a control parameter of the whole behavior of the material. At this point, a localized domain breakage takes place inside the structure of the material, accord-

ing to Matsuoka's treatment, revealing this way a totally new behavior. Hereafter, the plastic path prevails. Hence, Matsuoka used a constitutive equation from linear viscoelasticity (derived from a single Maxwell model) of the form

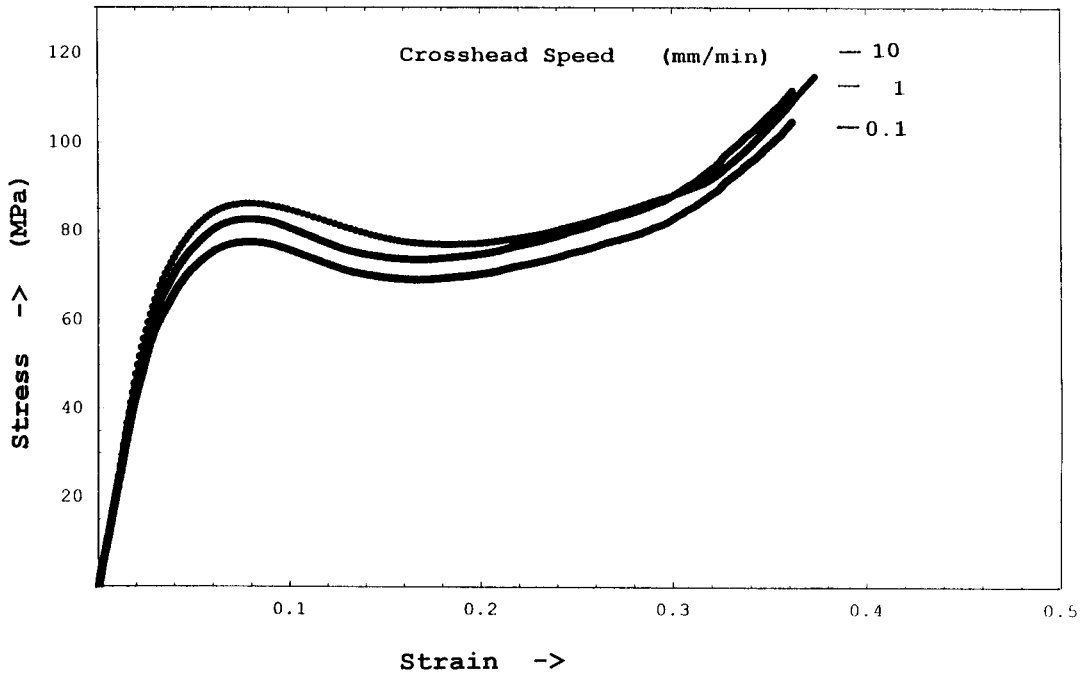


Figure 2 Engineering compression stress strain curves of polycarbonate at three different crosshead speeds.

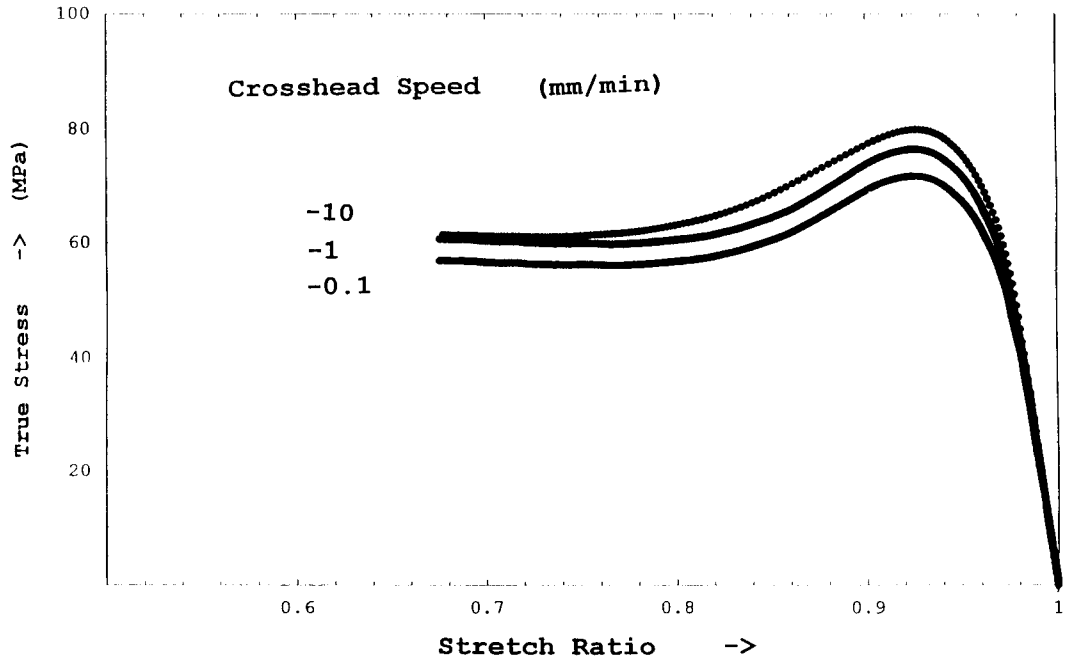


Figure 3 Compressive true stress strain curves of polycarbonate at three different crosshead speeds.

$$\sigma = E_0 \varepsilon_y \left[1 - \exp\left(-\frac{\varepsilon}{\varepsilon_y}\right) \right] \quad (1)$$

where E_0 is the apparent elastic modulus; ε , the strain; and ε_y , a characteristic feature of the ma-

terial, associated with the maximum yield stress. As has been mentioned elsewhere,¹⁸ this value represents the maximum elastic strain, is material-dependent, and has a value for glassy polymers lower than 10%. This quantity controls the

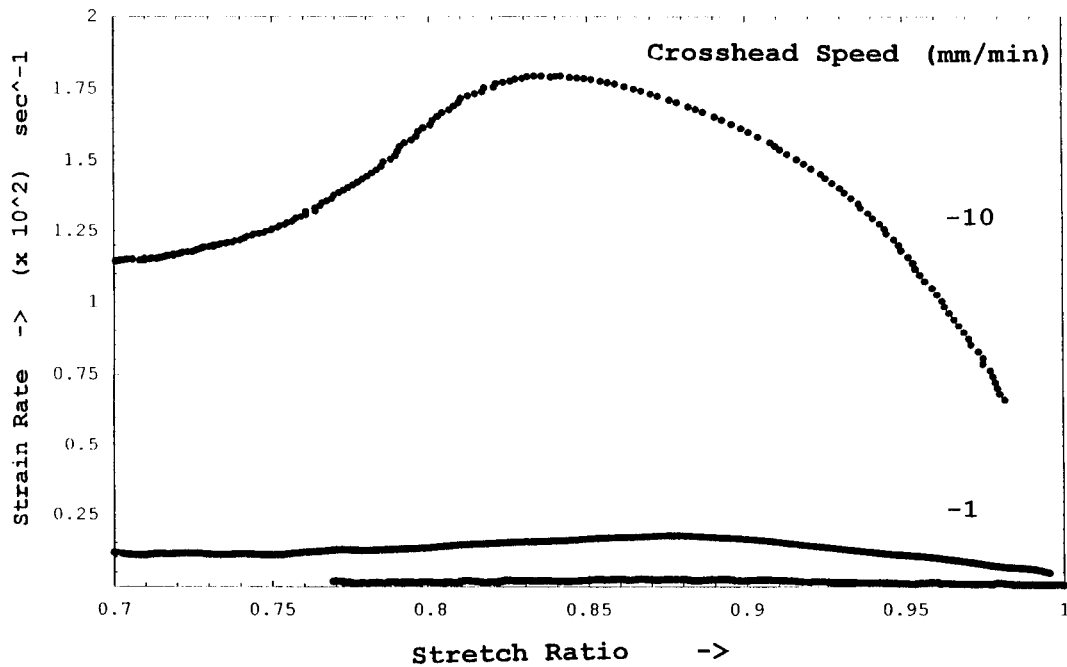


Figure 4 Strain rate in respect to stretch ratio of the reference zone 2-3 for all crosshead speeds tested.

initiation of plastic behavior or, equivalently, the transition from viscoelastic to plastic behavior.

Afterward, for establishing a nonlinear dependence of the viscoelastic stress from the strain rate, Matsuoka introduced the following scaling rule: A stress–strain curve at $\dot{\epsilon}_2$ can be predicted from an experimental stress–strain curve obtained at $\dot{\epsilon}_1$ by multiplying the stress and strain in the experimental curve by the scaling factors $(\dot{\epsilon}_2/\dot{\epsilon}_1)^n$ and $(\dot{\epsilon}_2/\dot{\epsilon}_1)^m$ for the stress and strain, respectively. The power coefficient m is typically two-thirds of n .

Equation (1) modified with the above scaling rule and combined by a set of expressions obtained by a kinematic formulation that separates the total deformation into plastic and elastic parts, correspondingly, proposed by Rubín,¹³ was used¹⁷ to describe the yield behavior of a glassy polymer at various crosshead speeds in terms of tensile experiments. This kinematic formulation was presented in detail in ref. 17 for three-dimensional problems. According to this treatment, the viscoelastic deformation of each material point was formulated through a triad of vectors \mathbf{m}_i that are related to dilatation, distortion, and orientation of a mean elementary volume, in respect to some reference state. To avoid the decomposition of the deformation gradient tensor into elastic and plastic parts, because these tensors lack an explicit determination in the present configuration of the material elements, Rubín specified an evolution equation for the elastic deformation, including the relaxation effect of plastic deformation, without introducing a plastic deformation tensor explicitly. For uniaxial deformation, the following expression for the time evolution of the stretch ratio $a_m = 1 + \epsilon$ of the viscoelastic deformation was obtained:

$$\frac{\dot{a}_m}{a_m} = \left[\frac{1 + \frac{1 - 2\nu}{2(1 + \nu)} \left(\frac{a_m^3 - 1}{a_m} \right)}{1 + \frac{1 - 2\nu}{6(1 + \nu)} \left(\frac{5a_m^3 - 2}{a_m} \right)} \right] \times \left[\frac{\dot{a}}{a} - \frac{\Gamma_p}{18} \left(\frac{a_m^3 - 1}{a_m^3} \right) (4a_m^3 + 2) \right] \quad (2)$$

where \dot{a} is the imposed strain rate; a , the stretch ratio; and ν , the Poisson ratio and $a_m(0) = 1$. It must be mentioned that the stretch ratio a is equal to $1 - \epsilon$ in a compression test.

The quantity Γ_p expresses the rate of plastic deformation and will be specified in the following.

When yield initiates the stretch ratio, a_{m_y} is equal to $1 - \epsilon_y$ and \dot{a}_m is equal to zero. Then, the second part of eq. (1) is equal to zero, and using the above approximations,^{12,17} we obtain

$$\Gamma_{p_y} \cong \frac{\dot{a}}{a(a_{m_y} - 1)} \quad (3)$$

where \dot{a} is the rate deformation of the reference length.

MECHANISM OF RATE OF PLASTIC DEFORMATION—RESULTS

The treatment, presented below follows a deformation mechanism of glassy polymers introduced by Oleinik et al.⁹ Their approach is based mainly on experimental data in terms of deformation calorimetry, residual strain recovery rate tests, and thermally stimulated creep. It was found that, from the early stages of deformation, a large fraction of the work offered in the material is converted to internal energy, meaning that essential structural rearrangements have occurred. Inelastic strain and consequent steady-state plastic flow proceed via nucleation, growth, and merging of PSTs.

Formation of PSTs starts at the very beginning of deformation, probably at specific localized sites of high free volume or defect regions. A high amount of energy is stored during the deformation procedure, around the PSTs. However, because shear strain associated with every PST is small, high PST concentration is required for the polymeric material to attain an appreciable macroscopic strain. Moreover, contrary to the perfect crystals, glassy polymers exhibit no structural periodicity; therefore, the PSTs remain at its nucleation site. Propagation of PSTs may occur only by merging with the newly emerging neighboring PST.^{9–11}

From this analysis, it is revealed that the kinetics of plastic deformation of glassy polymers is controlled mainly by the PST nucleation rate and its susceptibility to stress. Every PST is associated with a specific value of activation energy ΔE_i for its recovery after unloading. It was proposed⁹ that the distribution of those activation energies is quite broad, and whenever ΔE_i is high enough, the PST transforms into a nonreversible state, related to the plastic deformation. This transition occurs when the imposed stress field is increased.

On the other hand, when a stress field is applied on a material having various types of defects, the strain field induced follows a nonhomogeneous distribution, leading to the development of regions with varying strain. In this case, where nuclei of PSTs already exist, as above-mentioned, it is reasonable to consider that this inhomogeneous strain field is developed around each PST. The PSTs are of varying size and varying activation energy, following a continuous distribution described by a certain probability density in respect to their size as a random variable.

The basic assumption here is that an analogous distribution density will be followed by the strains evolved around the PSTs, through which the appropriate amount of elastic energy is offered for the PSTs transition to a nonrecoverable state. It is reasonable to suppose that the size of PSTs follows a normal distribution and, equivalently, it may be assumed that the strain field ε_i around them follows a normal distribution as well.

Hence, the distribution density (normal distribution) of the PSTs in respect to the strain ε_i as a random variable is given by

$$f(\varepsilon_i) = \frac{1}{s\sqrt{2\pi}} e^{[-(1/2)(\varepsilon_i - \mu/s)^2]} \quad (4)$$

where μ is the mean value, and s , the standard deviation of the strain field. The application of the strain field with a rate $\dot{\varepsilon}$ activates the process of nucleation, growth, and merging of the PSTs, leading in some cases to an irreversible state, that is, to plastic deformation. The fraction of the PSTs that have enough activation energy to attain a new nonreversible state is given by the probability

$$P(0 < \varepsilon_i \leq \varepsilon) = F(\varepsilon) - F(0) \quad (5)$$

where $F(\varepsilon)$ expresses the distribution function. Therefore, eq. (5) becomes

$$P(\varepsilon) = F(\varepsilon) - F(0) = \frac{1}{s\sqrt{2\pi}} \int_0^\varepsilon e^{[-(1/2)(\varepsilon_i - \mu/s)^2]} d\varepsilon_i \quad (6)$$

Making the further assumption that the rate of plastic deformation Γ_p is analogous to the fraction of PSTs that have achieved a nonreversible state

and that this transition takes place with an average rate \dot{k} for every PST, we have

$$\Gamma_p = \dot{k}P(0 < \varepsilon_i \leq \varepsilon) \quad (7)$$

The value of \dot{k} can be estimated, assuming that at the yield point, $\Gamma_p = \Gamma_{p_y}$, and at this stage of deformation ($\varepsilon = \varepsilon_y$), because the normal distribution function is symmetric, $P(\varepsilon_y)$ becomes equal to $\frac{1}{2}$; therefore following eqs. (3) and (7), we obtain

$$\frac{1}{2} \dot{k} = \Gamma_{p_y} = \frac{\dot{\alpha}}{a(a_{m_y} - 1)} \quad (8)$$

then

$$\Gamma_p = \frac{\dot{\alpha}}{a(a_{m_y} - 1)} \frac{1}{s\sqrt{\pi}} \int_1^a e^{[-(1/2)(a_i - \mu/s)^2]} da_i \quad (9)$$

where the limits of integration were substituted with the corresponding values of the stretch ratio α instead of strain ε . Parameter μ , which is the mean value of the probability density, is the stretch ratio a_{m_y} , where yield occurs and was taken experimentally equal to 0.935. The standard deviation s , which is the only fitting parameter, was estimated to be equal to 0.033 in the calculation procedure that will be analyzed in the following. From eq. (9), the rate of plastic deformation Γ_p can be evaluated and is presented in Figure 5. The shape of this plot is similar to the shape of the experimental strain rate $\dot{\varepsilon}$ of Figure 4. In the initial stages of deformation, where elastic strain is predominant, Γ_p is lower than is $\dot{\varepsilon}$. After yielding, Γ_p becomes much higher due to the factor $\dot{\alpha}/[a(a_{m_y} - 1)]$. It is important to mention here that this fact is a result of the kinematics applied, according to which yielding occurs when

$$\Gamma_p = \frac{\dot{\varepsilon}}{\text{per unit strain}} \quad (10)$$

Combining eqs. (2) and (9) and incorporating the experimental strain rate $\dot{\alpha}$, the value of the stretch ratio a_m is evaluated at every stage of deformation. This value in terms of deformation ε is used in the constitutive eq. (1) for the stress evaluation. The integration of eq. (2) was made numerically, using small time steps, with the software "Mathematica."¹⁹ By decreasing gradually

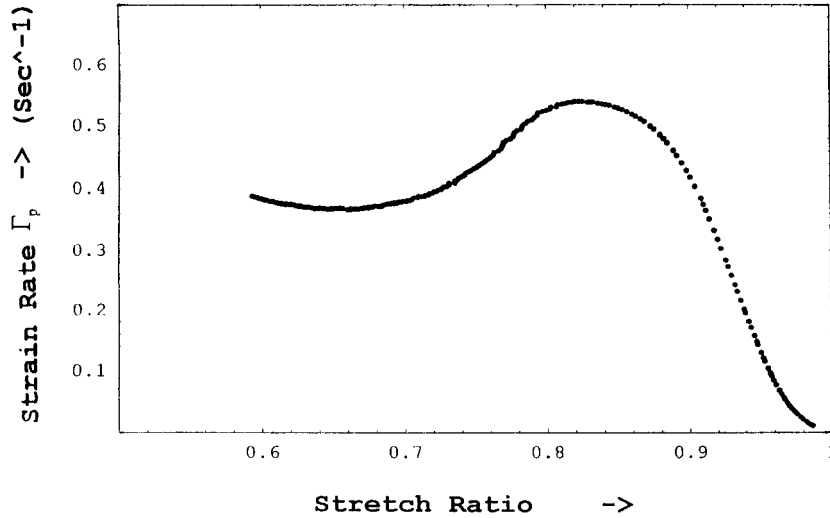


Figure 5 Rate of plastic deformation Γ_p , as derived from eq. (8) for a crosshead speed of -1 mm/min.

the original time step up to one-tenth, a high convergence was obtained.

To describe the material response at various crosshead speeds, the scaling rule by Matsuoka¹⁸ was applied, where $\dot{\epsilon}_2$ represents the imposed strain rate of 10 mm/min and $\dot{\epsilon}_1$ corresponds to the speed of 0.1 mm/min. Both values of these strain rates are taken to be constant, equal to the average value of the imposed crosshead speed

reduced to the total specimen gauge length. Following this scaling law, the data of the intermediate speeds can also be extracted.

The calculation of the exponent n can be made in terms of the slope of the variation of the yield stress plotted logarithmically in respect to the strain rate. Following Figure 6, where the experimental yield stress is presented versus the strain rate, exponent n has been found to be equal to

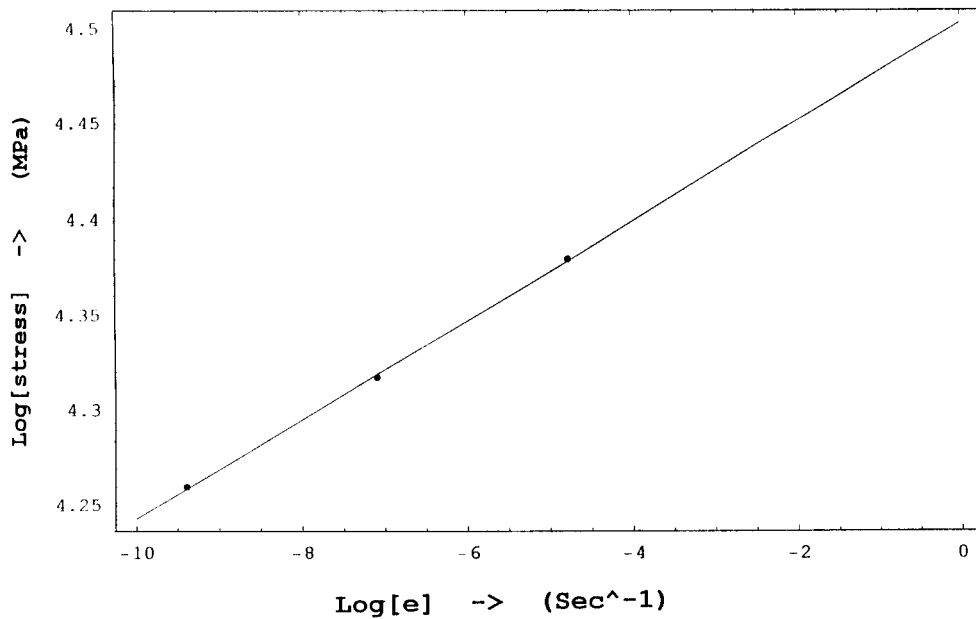


Figure 6 Yield stress versus strain rate plotted logarithmically at three different strain rates examined.

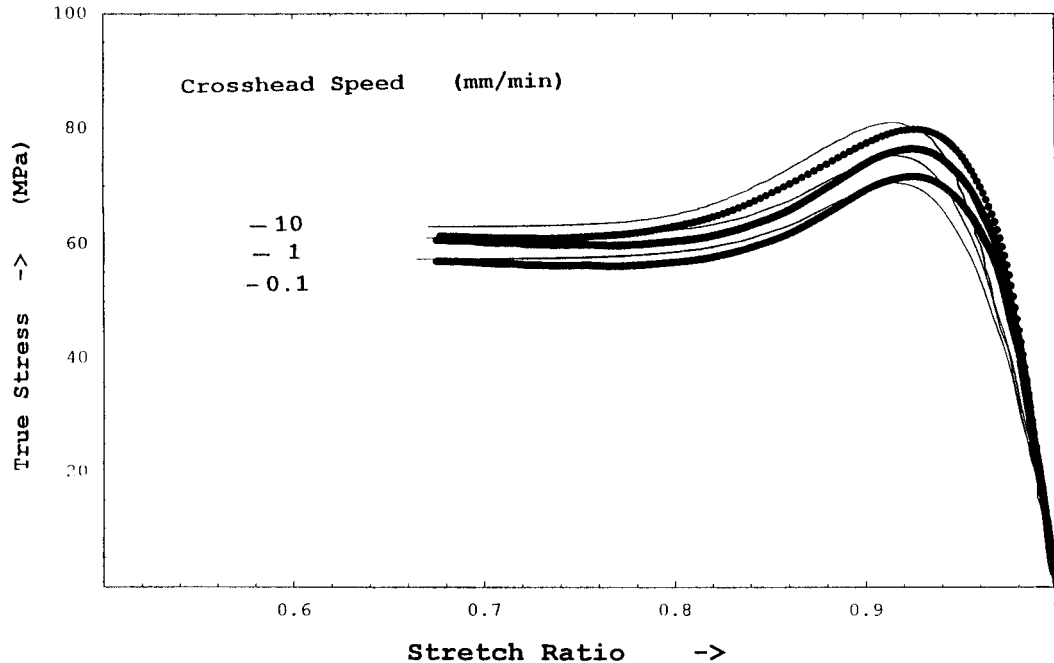


Figure 7 True compressive stress strain curves for polycarbonate. Thick lines: experimental results; thin lines: theoretical results.

0.026 and the exponent m equal to 0.017. The theoretical results obtained are presented in respect to the experimental data in Figure 7, where a good approximation was testified for the entire shape of the true stress–strain curves for all crosshead speeds tested.

CONCLUSIONS

The theoretical model developed in this work leads to the prediction of the entire yield behavior, including yield stress and strain softening exhibited by the material. More specifically, the following summarized points support the introduced analysis:

- (a) The kinematic formulation applied has the advantage, with respect to other plasticity theories, to describe in detail the inhomogeneous deformation through the velocity gradient tensor. This is because, for inhomogeneous deformation, the elastic and plastic parts of the deformation gradient tensor \mathbf{F} are not integrable in the displacement field, while tensor \mathbf{F} is always integrable. This formulation leads to the conclusion that yielding occurs when the rate

of plastic deformation Γ_p becomes equal to the macroscopic strain rate reduced per unit strain.

- (b) The kinetics of plastic deformation of glassy polymers is controlled mainly by the nucleation of PSTs. The strain inhomogeneity developed around each PST, along the reference length, follows a normal distribution with a mean value equal to the measured yield strain and a standard deviation that is selected to identify the experimental evidence.

It was also extracted that, according to this analysis, the strain softening can be predicted in a self-consistent manner, without introducing further internal parameters.

Professor E. F. Oleinik is gratefully acknowledged by the authors for the extended discussion he had with them about his theory for PSTs.

REFERENCES

1. Ward, I. M. *Mechanical Properties of Solid Polymers*, 2nd ed.; Wiley: Chichester, 1990.

2. Tervoort, T. A.; Klompen, E. T.; Govaert, L. E. *J Rheol* 1996, 40, 779–797.
3. Boyce, M. C.; Parks, M.; Argon, A. S. *Mech Mater* 1988, 7, 15–33.
4. Wu, P. D.; van der Giessen, E. *J Mech Phys Solids* 1993, 41, 427–456.
5. Tobolsky, A. V.; Eyring, H. *J Chem Phys* 1943, 11, 125–134.
6. Haward, R. N.; Thackray, G. *Proc Lond Ser Soc A* 1968, 302, 453–472.
7. Bernstein, B.; Shokooh, A. *J Rheol* 1980, 24, 189–211.
8. G'Sell, C.; Hiver, J. M.; Dahoun, A.; Souahi, A. *J Mater Sci* 1992, 27, 5031.
9. Oleinik, E. F.; Salamatina, O. B.; Rudnev, S. N.; Shenogin, S. V. *Polym Sci* 1993, 35, 1532.
10. Oleinik, E. F.; Salamatina, O. B.; Rudnev, S. N.; Shenogin, S. V. *Polym Adv Technol* 1995, 6, 1–9.
11. Oleinik, E. F.; Rudnev, S. N.; Salamatina, O. B.; Topolkaev, V. A. *Macromol Chem Macromol Symp* 1992, 53, 77–80.
12. Spathis, G.; Kontou, E. *J Appl Polym Sci*, in press.
13. Rubin, M. B. *J Solids Struct* 1994, 31, 2653.
14. Haward, R. N.; Young, R. J. *The Physics of Glassy Polymers*, 2nd ed.; Chapman and Hall: London, 1997.
15. Spitzig, W. A.; Richmond, O. *Polym Eng Sci* 1979, 19, 1129–1138.
16. Magonov, S. N.; Vainilovitch, I. S.; Sheiko, S. *Polym Bull* 1991, 25, 491–498.
17. Spathis, G.; Kontou, E. *Polymer* 1998, 39, 135.
18. Matsuoka, S. *Relaxation Phenomena in Polymers*, 2nd ed.; Hanser: New York, 1992; Chapter 3.
19. Wolfram, S. *Mathematica, A System for Doing Mathematics by Computer*, 2nd ed.; Wolfram Research Inc.: New York, 1993.