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# Strain-hardening behavior of polycarbonate in the glassy state

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## Synopsis

This paper presents an experimental characterization of the three-dimensional strain-hardening response of polycarbonate in the glassy state. Using a special mechanical conditioning technique, large homogeneous deformations were obtained in tension, compression, and shear. The experimental results are compared to a number of existing network models. It was found that the state-of deformation dependence of the strain-hardening response was adequately described by neo-Hookean behavior with a shear modulus  $G = 26$  MPa. Up to the deformations applied in this study, no sign of a finite extensibility of the entanglement network was observed. © 2000 The Society of Rheology. [S0148-6055(00)01006-3]

## I. INTRODUCTION

A characteristic feature of polymer systems is their composite structure on a molecular level, consisting out of covalent bonded chains, held together by secondary forces. At the yield point, the applied stress is high enough to overcome intermolecular forces, and large scale segmental motion is initiated. The primary bonds survive this segmental jump process, and give rise to steric hindrance (“chains cannot mutually cross”), which results in strain-hardening behavior, the topic of this paper. The reinforcing effect of the covalent chains, prevents segmental motion from leading to fracture like in low molecular weight glasses. Instead, the deformation is spread throughout the material, and leads to crazing or shear bands. For this reason, polymers are intrinsically very tough materials, with a critical energy release rate which is orders of magnitude larger than the (Van der Waals) surface energy.

The steric hindrance between the polymer chains is also of prime importance for the flow behavior of polymer melts, where the thermal energy is sufficient to facilitate the rapid interchange of macromolecular conformations. It is well known that, above a certain molecular weight and on a restricted time scale, a polymer melt behaves like a rubbery solid [Larson (1988), Chap. 4]. Comparing this behavior to that of a real (chemically cross-linked) rubber, leads to the definition of *entanglements*. Entanglements are

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envisaged as physical knots, which can not unravel on the time scale of the experiment. The molecular weight between these entanglements is calculated from the “stiffness” (plateau modulus) of the melt, using the classical theory of rubber elasticity. In this way, the molecular weight between entanglements  $M_e$  provides a scalar measure of the diffuse steric hindrance between the covalent chains.

It is, therefore, not surprising that the concept of entanglements play an important role in the large-strain deformation behavior of polymer solids as well. For example, it is now widely accepted, that strain hardening in glassy polymers originates from the rubber-elastic response of the entanglement network. Moreover, it is often assumed, that the entanglement network, like a chemically cross-linked network, has a limited extensibility. This leads to the concept of a *maximum draw ratio*  $\lambda_{\max}$  [Allison and Ward (1967)], which can be estimated from the maximum extensibility of a single strand in the entanglement network. It was shown by Donald and Kramer [(1982a, 1982b)] that this maximum draw ratio of the entanglement network correlates remarkably well with the extension ratio of craze fibrils and within shear bands.

Haward and Thackray (1968) were the first to incorporate these two features of strain-hardening behavior, a rubber-elastic response, and finite extensibility, into a constitutive equation. This one-dimensional equation was extended to the three-dimensional “BPA model” by Boyce *et al.* (1988), who used the “three-chain model” [James and Guth (1943)] to describe the strain-hardening response. The BPA model was later refined with respect to strain hardening by introducing better representations of the spatial distribution of molecular chains, leading to the “eight-chain model” [Arruda and Boyce (1993b)], and the “full-chain model” [Wu and van der Giessen (1993)].

Although finite extensibility is relevant for a *chemically* cross-linked rubber, it seems less obvious that it also applies to a (thermoplastic) glassy polymer, which can ultimately flow. In fact, for most semicrystalline polymers, the strain-hardening response is accurately described by neo-Hookean behavior and finite extensibility was not observed [G’Sell *et al.* (1992)]. In the case of glassy polymers, however, the postyield behavior is largely dominated by strain softening, which hampers a straight forward analysis of the strain-hardening response in tensile deformation [Haward (1993)]. For this reason, large deformation studies on glassy polymers were predominantly conducted in compressive loading geometries [Boyce and Arruda (1990)].

The purpose of this study is to analyze experimentally and theoretically the large strain behavior of an amorphous polymer, polycarbonate, in compression, shear and, most notably, in tension, using a mechanical preconditioning technique to ensure homogeneous deformation.

## II. THEORY

First some of the rubber elastic network models, which are used to describe strain hardening, will be reviewed. In what follows, it will be assumed that the Helmholtz free energy  $A$  only depends on the left Cauchy–Green strain tensor  $\mathbf{B}$  at constant volume  $\tilde{\mathbf{B}}, \tilde{\mathbf{B}} = J^{-2/3}\mathbf{B}$ , with the relative volume deformation  $J$  (determinant of the deformation gradient) [Tervoort *et al.* (1998)]. The evolution equation of  $\tilde{\mathbf{B}}$  follows from kinematics

$$\dot{\tilde{\mathbf{B}}} = \mathbf{L}^d \cdot \tilde{\mathbf{B}} + \tilde{\mathbf{B}} \cdot (\mathbf{L}^d)^T = \tilde{\mathbf{A}} : \mathbf{L}, \quad (1)$$

where the dot denotes the material time derivative,  $\mathbf{L}^d$  is the deviatoric part of the velocity gradient, and the fourth order tensor  $\tilde{\mathbf{A}}$  is defined through Eq. (1). The reversible (elastic) part of the deviatoric Cauchy-stress tensor  $\mathbf{T}^d$  is then determined by the thermo-

dynamic force  $\mathbf{M} = \partial A / \partial \tilde{\mathbf{B}}$  and the evolution equation of  $\tilde{\mathbf{B}}$  through  $\tilde{\mathbf{\Lambda}}$  [Jongschaap *et al.* (1994); Tervoort *et al.* (1998)],

$$\mathbf{T}^d = \mathbf{M} : \tilde{\mathbf{\Lambda}}. \quad (2)$$

### III. RUBBER ELASTIC NETWORK MODELS

In the classical theory of rubber elasticity it is assumed that the internal energy remains constant upon isochoric deformations. Therefore, at isothermal conditions, the thermodynamic force is only dependent on changes in entropy

$$\mathbf{M} = \left( \frac{dA}{d\tilde{\mathbf{B}}} \right)_T = \left( \frac{dU}{d\tilde{\mathbf{B}}} \right)_T - T \left( \frac{dS}{d\tilde{\mathbf{B}}} \right)_T = -T \left( \frac{dS}{d\tilde{\mathbf{B}}} \right)_T. \quad (3)$$

The change in entropy is a consequence of the distortion of the molecular network and can be calculated from statistical mechanical arguments [Treloar (1975)]. The most simple expression follows from the so-called ‘‘Gaussian network approximation,’’ where it is assumed that the end-to-end distance vectors of a chain between two crosslinks, are described by a Gaussian distribution function [James and Guth (1943)]. In this case, the entropy will depend on deformation as

$$S = -\frac{1}{2}nk(I_{\tilde{\mathbf{B}}}-3), \quad (4)$$

where  $n$  is the number of (randomly oriented) chains per unit volume in the network,  $k$  is Boltzmann’s constant, and  $I_{\tilde{\mathbf{B}}}$  is the first invariant of  $\tilde{\mathbf{B}}$ . Using the evolution equation for the isochoric elastic strain [Eq. (1)], and the expression for the Cauchy-stress tensor [Eq. (2)], the Gaussian network approximation leads to neo-Hookean behavior

$$\mathbf{T}^d = G\tilde{\mathbf{B}}^d \quad (5)$$

with the shear modulus  $G = nkT$ .

A more accurate expression for the configurational entropy of a stretched molecular chain, taking into account the effect of finite extensibility, was first derived by Kuhn and Gr $\ddot{u}$ n (1942). Considering a single ideal chain, containing  $N$  links of length  $l$ , having a root-mean-square distance  $\sqrt{\langle r_0^2 \rangle} = \sqrt{N}l$  and a maximum draw ratio  $\lambda_{\max} = \sqrt{N}$ , they derived an expression for the Helmholtz-free energy as a function of draw ratio  $\lambda$

$$A = nkT \left( \frac{\lambda}{\sqrt{N}} \beta + \ln \left[ \frac{\beta}{\sinh \beta} \right] \right) - A_0, \quad (6)$$

$$\beta = \mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{N}} \right), \quad (7)$$

where  $A_0$  is an arbitrary constant and  $\mathcal{L}(\beta)$  is the Langevin function defined by

$$\mathcal{L}(\beta) = \coth \beta - \frac{1}{\beta}. \quad (8)$$

A useful expression is the first Pad $\acute{e}$  approximant of the inverse Langevin function [Cohen (1991)]

$$\mathcal{L}^{-1}(x) \approx x \frac{3-x^2}{1-x^2}. \quad (9)$$

For elastic behavior, at isothermal conditions, the total power input  $\sigma \dot{\epsilon}$ , with  $\dot{\epsilon} = \dot{\lambda}/\lambda$ , is equal to the rate-of-elastic energy storage  $\dot{A} = (\partial A/\partial \lambda)\dot{\lambda}$ . Hence, the (one-dimensional) stress-strain relation becomes

$$\sigma = \lambda \left( \frac{\partial A}{\partial \lambda} \right)_T = kT \sqrt{N} \lambda \mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{N}} \right). \quad (10)$$

In this equation, the stress becomes infinitely large, as the draw ratio  $\lambda$  approaches its limiting value  $\lambda_{\max} = \sqrt{N}$ . Invoking the affine deformation scheme, Wu and van der Giessen (1993) extended this one-dimensional equation to describe three-dimensional behavior, by calculating the exact spatial distribution of the molecular chains. This so called ‘‘full chain’’ model, though mathematically exact, has the disadvantage that it cannot be solved analytically. Three-dimensional extensions of Eq. (10) that lead to analytical expressions, were obtained by sampling the orientational distribution function only in a discrete number of directions, like the ‘‘three-chain’’ model of James and Guth (1943), and the ‘‘eight-chain’’ model of Arruda and Boyce (1993b). The ‘‘four chain’’ model of Flory and Rehner, Jr. (1943) also approximates the real distribution of orientations, but does not lead to an analytical equation.

The three-chain model was obtained by assuming that Eq. (10) can be used to calculate the principle stresses  $\sigma_i$  from the principle stretches  $\lambda_i$

$$\sigma_i = \frac{1}{3} nkT \sqrt{N} \lambda_i \mathcal{L}^{-1} \left( \frac{\lambda_i}{\sqrt{N}} \right), \quad (11)$$

with  $n/3$  chains per unit volume in each of the principle stretch directions.

In the eight-chain model, Eq. (6) is assumed to hold, multiplied by the number of chains per unit volume  $n$  and using an average chain-stretch parameter  $\lambda_{\text{chain}}$

$$\lambda_{\text{chain}} = \frac{1}{\sqrt{3}} \sqrt{\lambda_1^2 + \lambda_2^2 + \lambda_3^2} = \frac{1}{\sqrt{3}} \sqrt{I_{\tilde{B}}}. \quad (12)$$

Here, it should be noted that  $\sqrt{I_{\tilde{B}}/3}$  equals the average change in length of a line element at a point  $P$ , averaged over all possible orientations [Macosko (1994), Chap. 1]. The thermodynamic force for the eight-chain model becomes

$$\mathbf{M} = \frac{\partial A}{\partial \tilde{\mathbf{B}}} = \left( \frac{\partial A}{\partial \lambda_{\text{chain}}} \right) \left( \frac{\partial \lambda_{\text{chain}}}{\partial I_{\tilde{B}}} \right) \left( \frac{\partial I_{\tilde{B}}}{\partial \tilde{\mathbf{B}}} \right), \quad (13)$$

where

$$\left( \frac{\partial A}{\partial \lambda_{\text{chain}}} \right) = nkT \sqrt{N} \mathcal{L}^{-1} \left( \frac{\lambda_{\text{chain}}}{\sqrt{N}} \right), \quad (14)$$

$$\left( \frac{\partial \lambda_{\text{chain}}}{\partial I_{\tilde{B}}} \right) = \frac{1}{6} \sqrt{3} I_{\tilde{B}}^{-1/2} = \frac{1}{6 \lambda_{\text{chain}}}, \quad (15)$$

$$\left( \frac{\partial I_{\tilde{\mathbf{B}}}}{\partial \tilde{\mathbf{B}}} \right) = \mathbf{I}. \quad (16)$$

The constitutive relation for the eight-chain model then follows from the evolution equation for  $\tilde{\mathbf{B}}$ , Eq. (1), and substitution of Eqs. (13)–(16) in the general expression for the stress tensor, Eq. (2):

$$\mathbf{T}^d = \frac{1}{3} nkT \sqrt{N} \mathcal{L}^{-1} \left( \frac{\lambda_{\text{chain}}}{\sqrt{N}} \right) \frac{1}{\lambda_{\text{chain}}} \tilde{\mathbf{B}}^d = G(I_{\tilde{\mathbf{B}}}) \tilde{\mathbf{B}}^d. \quad (17)$$

In the original derivation [Arruda and Boyce (1993b)], the total—instead of the isochoric strain—was used, under the assumption of incompressible behavior. This leads to a relation between the extra stress tensor and the Green–Lagrange strain tensor and is, therefore, slightly different from Eq. (17). This applies also to the other rubber-elastic models in this paper. Note that the eight-chain model can be envisaged as a neo-Hookean relation, employing a shear modulus which is dependent on the first invariant of  $\tilde{\mathbf{B}}$ .

The three-chain model samples only the principle strain directions, while the eight-chain model samples none of the principle strain directions. Therefore, the three-chain model will overestimate the network stiffness, whereas the eight-chain model underestimates the network response. Since the response of the full-chain model is always between the upper and lower bound provided by the three- and eight-chain model, Wu and van der Giessen (1992) proposed a simple analytical mixing rule to approximate the full-chain model response

$$\sigma_i^{\text{ful-ch}} = (1 - \rho) \sigma_i^{\text{3-ch}} + \rho \sigma_i^{\text{8-ch}}, \quad (18)$$

$$\rho = 0.85 \frac{\lambda_{\text{max}}}{\sqrt{N}}, \quad (19)$$

where  $\sigma_i^{\text{full-ch}}$ ,  $\sigma_i^{\text{3-ch}}$ , and  $\sigma_i^{\text{8-ch}}$  are the principle stresses for the full-, eight- and three-chain model, respectively, and  $\lambda_{\text{max}}$  is the maximum principle stretch.

When considering the state-of-deformation dependence, it should be realized that, in a geometrical sense, all possible isochoric deformations are bounded by uniaxial extension and uniaxial compression (which is equivalent to biaxial extension). This is quantified by the difference between the first and the second invariant of the isochoric elastic strain,  $I_{\tilde{\mathbf{B}}} - \text{II}_{\tilde{\mathbf{B}}}$ , which is called the *alignment strength* [Larson (1988), Chap. 7]. A deformation for which  $I_{\tilde{\mathbf{B}}}$  is larger than  $\text{II}_{\tilde{\mathbf{B}}}$  is called strongly aligning, when  $I_{\tilde{\mathbf{B}}} = \text{II}_{\tilde{\mathbf{B}}}$ , the deformation is neutrally aligning, and for  $I_{\tilde{\mathbf{B}}} < \text{II}_{\tilde{\mathbf{B}}}$ , the deformation is weakly aligning. In this study, uniaxial compression, uniaxial tension, and shear experiments were performed in order to determine the state-of-deformation dependence of the strain-hardening response.

All network models introduced in this section converge to simple neo-Hookean behavior at small chain stretch [see for example Eq. (17) in case of the eight-chain model]. Since the bulk modulus of a rubber is several orders of magnitude larger than its shear modulus, in general, deformation of a rubber proceeds at nearly constant volume (except for pure volume deformations). Therefore, to a good approximation, the isochoric-elastic strain tensor  $\tilde{\mathbf{B}}$  is equal to the left Cauchy–Green strain tensor  $\mathbf{B}$ . According to neo-Hookean behavior [Eq. (5)], in the case of uniaxial extension in the  $x$  direction, the tensile stress  $\sigma = \mathbf{T}_{xx}^d - \mathbf{T}_{yy}^d$  then equals

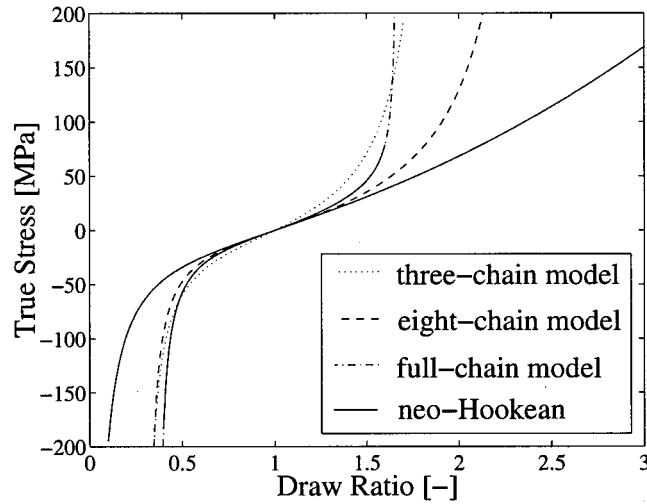


FIG. 1. Comparison of the different network models in their description of the strain-hardening response of polycarbonate in uniaxial deformation. Network parameters according to Table I.

$$\sigma = G \left( \lambda^2 - \frac{1}{\lambda} \right). \quad (20)$$

From this last equation it is clear that even neo-Hookean behavior, which has no finite extensibility, results in a (quadratic) upswing of the stress in a  $\sigma$ - $\lambda$  plot. The effect of finite extensibility is revealed more clearly in a graph of the stress versus  $\lambda^2 - 1/\lambda$ . In this case, neo-Hookean behavior will yield a straight line and the effect of finite extensibility will manifest itself as a deviation from this straight line.

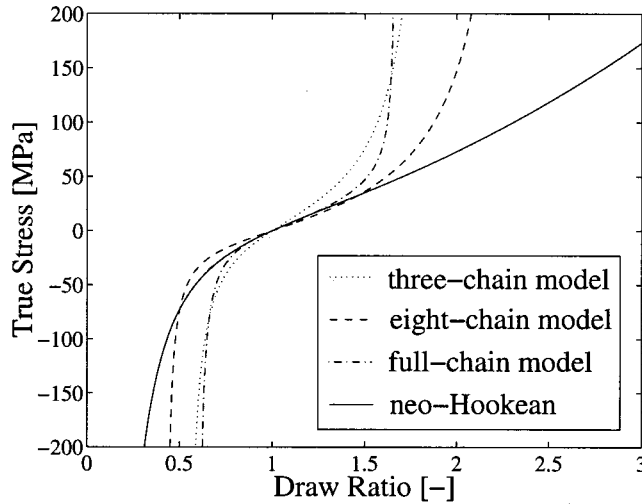
All network models with finite extensibility discussed so far have two adjustable parameters: the number of segments  $N$ , which determines the maximum chain stretch and the number of chains per unit volume  $n$  which, given  $N$ , determines the initial modulus (at constant temperature). The Gaussian-network approximation leads to neo-Hookean behavior with only one parameter: the initial modulus. The response of these various network models in uniaxial and planar extension, is depicted in Fig. 1 and 2, using the three-chain, eight-chain, and full-chain parameters reported by Arruda (1992) and Wu and van der Giessen (1993) for the strain-hardening behavior of polycarbonate in uniaxial compression (see Table I).

The value of the shear modulus of the Gaussian-chain model in Table I was chosen to coincide with the initial shear modulus of the eight-chain model  $G_8$

$$G_8 = \frac{1}{3} nkT \frac{1 - \frac{1}{N}}{3 - \frac{1}{N}} \quad (21)$$

using the Padé approximation of the inverse Langevin function [Eq. (9)].

It follows from Table I that all network models predict an extremely low number of monomers per subchain. For example, using the Gaussian approximation, a strain-hardening modulus of 19.5 MPa leads to  $n = 4.7 \times 10^{27}$  subchains/m<sup>3</sup> ( $G = nkT$ ).



**FIG. 2.** Comparison of the different network models in their description of the strain-hardening response of polycarbonate in planar extension (equivalent to simple shear). Network parameters according to Table I.

Since the density of polycarbonate is  $1200 \text{ kg/m}^3$ , and the monomeric weight is  $250 \text{ g/mol}$ , this leads to  $0.6$  monomers per subchain. This number is far too small to justify the use of the Gaussian approximation. Also the values of  $N$  from Table I for the other chain models are far too low to justify the use of the inverse Langevin function.

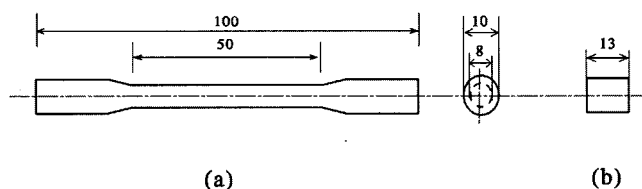
Here, it should be noted that Eq. (10), which is the starting point of all non-Gaussian network theories, was criticized by Flory [Flory (1988), Chap. 8] for a number of reasons. First, from a statistical mechanics point of view, Eq. (10), like the Gaussian approximation, is only correct in the limit of a large number of segments  $N$  and at small chain stretch ( $\lambda/\sqrt{N} \ll 1$ ). It can be shown that, especially at small  $N$ , the Gaussian distribution function is, in fact, a better approximation of the exact distribution function than the Langevin expression over most of the range-of-deformation, except at very high chain stretch. Second, Flory noted that, in a number of cases, the stress upswing in uniaxial extension could also be due to strain-induced crystallization. Therefore, it is probably better to regard Eq. (10) as an empirical relation, which can be used to incorporate finite extensibility.

One should also carefully distinguish between neo-Hookean behavior and “Gaussian” rubber-elastic behavior. Neo-Hookean behavior is a constitutive equation for large strain elastic behavior, characterized by a shear modulus  $G$  and does not depend on the microstructural nature of the material. The theory of rubber elasticity, invoking the Gaussian approximation for the distribution function of the end-to-end vector, relates the shear

**TABLE I.** Network parameters required by the different rubber-elasticity models to describe the strain-hardening behavior of polycarbonate in uniaxial compression [Arruda (1992); Wu and van der Giessen (1993)].

	Three chain	Eight chain	Full chain	Gaussian chain
$nkT$ (MPa)	17.0	12.7	12.7	19.5
$N$ (-)	3.5	2.25	2.8	—





**FIG. 3.** (a) Tensile bar used for mechanical conditioning below the glass transition temperature. (b) Part of the tensile bar (a) used for uniaxial compression testing.

modulus  $G$  to the number of elastic active subchains as  $G = nkT$ , and might not be appropriate for the low number of monomers per subchain found in this and other studies.

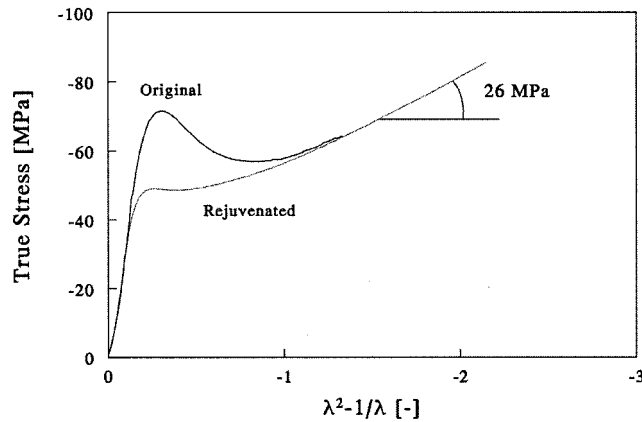
#### IV. EXPERIMENT

The most straightforward way to verify the strain-hardening response of polymer glasses experimentally, is to apply large homogeneous deformations. However, most polymer systems, and especially polymer glasses, are prone to inhomogeneous deformation. G'Sell *et al.* (1992) developed an experimental technique in which locally a constant strain rate could be applied to an axis-symmetric hour-glass shaped sample, by means of video-controlled tensile testing (a digital closed loop system). Arruda and Boyce (1993a) argued that the deformation in uniaxial and planar compression will remain homogeneous, since, contrary to a tensile test, there is no area reduction. This seems to be a rather strong assumption, since the development of shear bands in compression has been observed for a number of polymers [see Bowden (1970)]. On the other hand, finite element calculations of Wu and van der Giessen (1994) have shown that the effect of shear band formation on the global stress-strain behavior is not very large.

In this study, mechanical conditioning will be used to ensure homogeneous deformation. It is generally accepted [Kramer (1983)] that strain localization in polymer glasses is initiated by the nonlinear yield behavior. Strain hardening and intrinsic-strain softening, respectively, stabilize and amplify nonhomogeneous behavior.

A way to promote large homogeneous deformations below the glass transition temperature is, therefore, to reduce the intrinsic strain softening of the material. This can be achieved by mechanical conditioning through plastic deformation. In absence of strain softening, small fluctuations in the stress field are better stabilized by strain hardening, resulting in more homogeneous deformation behavior [Cross and Haward (1978); Bauwens (1978); G'Sell (1986)]. Since intrinsic strain softening increases during physical aging of the polymer, especially during annealing close to the glass transition temperature, the removal of strain softening through plastic deformation is often called "rejuvenation" [Struik (1978); Waldron, Jr. *et al.* (1995)]. Large plastic deformations rejuvenate the material up to a saturation level, which is maintained when the stress is released. As a result, subsequent testing will not lead to strain softening, resulting in more homogeneous deformation behavior. (Elimination of intrinsic strain softening through mechanical conditioning does not necessarily lead to homogeneous deformation behavior. For example, due to their low strain-hardening modulus, polyethylene, and polypropylene, still show necking in a tensile test, despite the fact that they display no intrinsic strain softening.)

To rejuvenate the material through mechanical conditioning, dog-bone shaped, axis-symmetrical tensile bars [see Fig. 3(a)], manufactured from extruded polycarbonate (bisphenol A, Bayer) rod, were subjected to large strain torsion at room temperature. The



**FIG. 4.** Uniaxial compression tests of mechanically conditioned and unconditioned samples, plotted as true stress as a function of  $\lambda^2 - 1/\lambda$ .

torsion was applied manually, by clamping the sample in a universal lathe and turning one side to and fro over  $720^\circ$ . By placing an identifying line mark on the surface of the tensile bar (parallel to the axis), the stable growth of a localized plastic zone along the tensile bar could be monitored in detail. Torsion of the sample back to the original configuration resulted in a complete recovery of the original straight line mark. After predeformation some of the samples were heated to  $180^\circ\text{C}$ , but no motion due to residual stress was observed, and the identifying line mark remained straight. This indicates that, with respect to the strain-hardening response, the samples were returned close to their isotropic state. A disadvantage of the method is that the predeformation is not homogeneously distributed and that the central fiber of the sample will not deform (and, therefore, not rejuvenate) at all.

Immediately after rejuvenation, the samples were tested in uniaxial tension on a ZWICK Rel 1852 servo-hydraulic tensile tester (20 kN). Some of the rejuvenated bars were cut to obtain samples for uniaxial compression testing [see Fig. 3(b)]. In all cases the extension was measured using an extensometer. The relative accuracy in force and strain measurements was 1%. The tensile tests were performed at room temperature, at constant strain rate. The torsion experiments were performed on a custom-made torsion rig, at a rotation speed of 1 rad/s.

## V. RESULTS

### A. Uniaxial testing of samples predeformed in torsion

To verify the effect of plastic predeformation on the strain-hardening behavior, uniaxial compression tests of mechanical conditioned and unconditioned samples were compared. The result, plotted as true stress versus  $(\lambda^2 - 1/\lambda)$ , is depicted in Fig. 4. From this figure, it can be seen that the rejuvenated sample has a much lower yield stress compared to the unconditioned sample. Furthermore, it is clear that the unconditioned sample displays a strong strain softening response, whereas this is virtually absent in the predeformed sample. However, despite these large differences in initial yield behavior, it is also clear from Fig. 4, that the strain-hardening behavior of both samples at larger deformations is very similar. This similarity is a strong indication that the preconditioning has little effect on the strain-hardening response, and can be used to determine the large strain behavior.

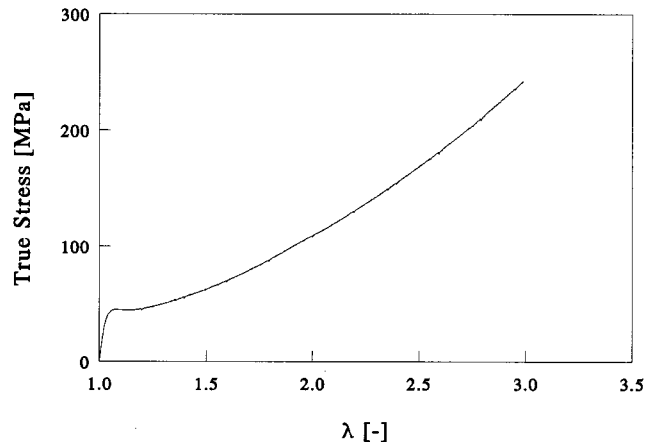


FIG. 5. True stress as a function of draw ratio for a cylindrical tensile bar, conditioned in torsion.

A true stress-strain uniaxial tensile curve of a mechanically conditioned sample is depicted in Fig. 5. In this figure, a small strain-softening response after the yield point can still be observed. This is probably due to the central core of the tensile bar which was not deformed and, therefore, has not been rejuvenated. Visually, however, the deformation of the cylindrical tensile bar remained homogeneous. From Fig. 5 it can also be seen that homogeneous deformations up to  $\lambda = 3$  were reached, in contrast to maximum draw ratios of 2.44 and 2.5 reported by, respectively, Boyce and Arruda (1990) and Donald and Kramer (1982a). The results of the uniaxial tensile and compression tests, plotted as true stress versus  $(\lambda^2 - 1/\lambda)$ , is depicted in Fig. 6 and 7. In these figures, the strain-hardening response appears as a straight line of equal slope in both tension and compression, indicative of neo-Hookean behavior. From the slope the strain-hardening modulus was determined [Eq. (20)] to be:  $G = 26$  MPa. No effect of finite extensibility was observed; there is no deviation from the straight line in a  $\sigma$  vs  $(\lambda^2 - 1/\lambda)$  plot for both uniaxial

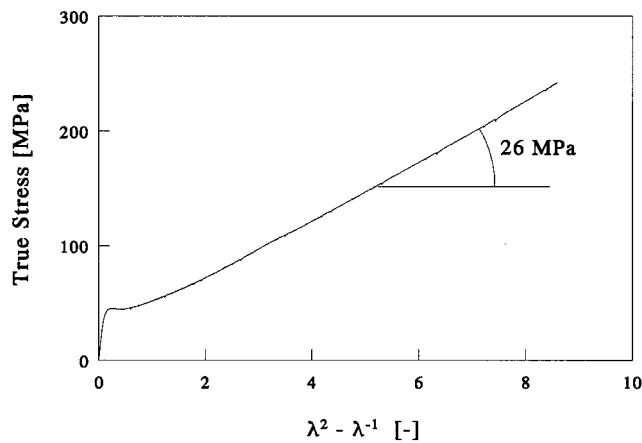


FIG. 6. True stress vs  $(\lambda^2 - 1/\lambda)$  during a tensile test at  $\dot{\epsilon} = 10^{-2} \text{ s}^{-1}$  of a cylindrical tensile bar, conditioned in torsion.

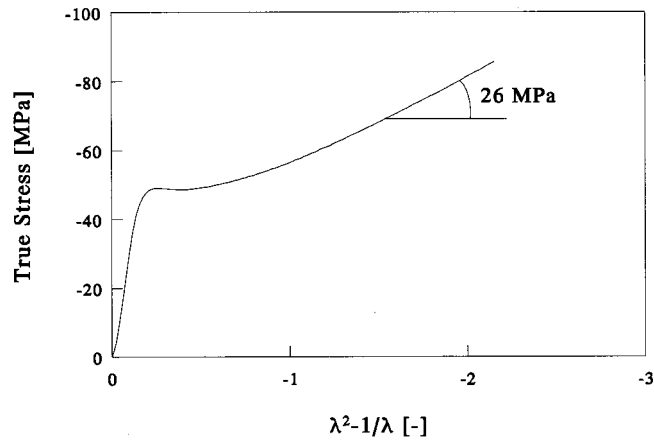


FIG. 7. True stress vs  $(\lambda^2 - 1/\lambda)$  during a compression test at  $\dot{\epsilon} = 10^{-2} \text{ s}^{-1}$  of a cylindrical tensile bar, conditioned in torsion.

tension and compression experiments. This is again in contrast with uniaxial and planar compression data of polycarbonate, published by Arruda and Boyce (1993a).

### B. Shear testing of samples predeformed in torsion

A torsion curve of a mechanically conditioned torsion bar of length  $L$  and with a polar moment of inertia  $I_p$  is depicted in Fig. 8. Assuming *linear* behavior, the relation between torque  $M_w$  and torsion angle per unit length  $\phi/L$ , is given by [Roark and Young (1984)]

$$\frac{\phi}{L} = \frac{M_w}{GI_p} \quad (22)$$

with the shear modulus  $G$ .

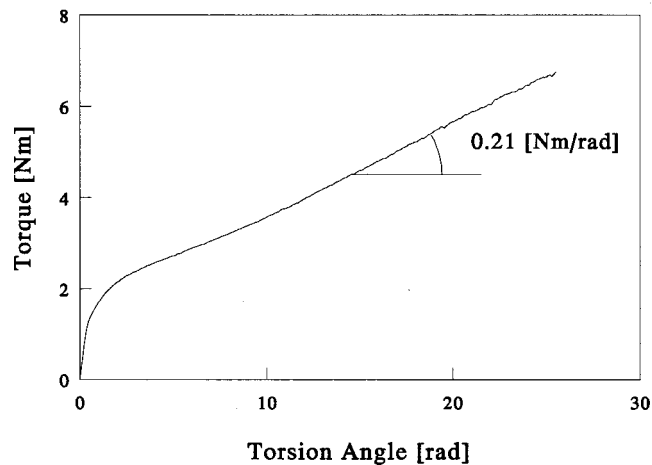


FIG. 8. Strain-hardening of polycarbonate measured in torsion, at a rotation speed of 1 rad/s.

From Fig. 8 it is clear that, also in shear deformation, neo-Hookean behavior is observed. From the slope in the neo-Hookean strain-hardening regime (0.21 N m) in Fig. 8 the shear modulus was obtained as:  $G = 0.21(L/I_p) = 26$  MPa ( $L = 0.05$  m and  $I_p = \pi d^4/32$ , with  $d = 8 \times 10^{-3}$  m), in excellent agreement with the values obtained from the tensile and compression tests. Again, no effect of finite extensibility is observed. The agreement between the values of the shear modulus obtained from tensile, compression, and torsion experiments also indicates that the starting material after the mechanical preconditioning was essentially isotropic.

## VI. DISCUSSIONS AND CONCLUSIONS

Nowadays, it is generally accepted that the strain hardening response of (glassy) polymers originates from a rubber-elastic response of the entanglement network, characterized by the plateau modulus  $G_r$  (which can be measured in the melt, using mechanical spectroscopy). Using the classical theory of rubber elasticity, the plateau modulus can be used to calculate the molecular weight  $M_e$  of a single strand in the entanglement network [Kramer (1983)]

$$M_e = \frac{\rho RT}{G_r}. \quad (23)$$

Assuming that entanglements cannot unravel on the time scale of the experiment, a maximum draw ratio of the network can be estimated as the ratio of the stretched length of a single strand (molecular weight:  $M_e$ ) and its random walk length

$$\lambda_{\max} = \frac{N_e l_b}{\sqrt{C_\infty N_e l_b^2}} = \sqrt{\frac{N_e}{C_\infty}}, \quad (24a)$$

$$N_e = \frac{M_e}{M_0}. \quad (24b)$$

Here,  $N_e$  is the number of monomer units of an entangled strand,  $C_\infty$  is the characteristic ratio (a measure of the chain stiffness), and  $l_b$  and  $M_0$  are, respectively, the length and the molecular weight of a monomer unit.

For a number of polymers, Donald and Kramer (1982b, 1982a) determined the draw ratio in craze fibrils and shear deformation zones, using transmission electron microscopy. They found that the experimental values correlated reasonably well with the maximum draw ratio of the entanglement network according to Eq. (24a). Their estimate for the maximum draw ratio of polycarbonate was  $\lambda_{\max} \approx 2.5$ . Indications for a finite extensibility of the entanglement network were also found from uniaxial and planar compression tests on polycarbonate and polymethyl methacrylate by Arruda and Boyce (1993a). They estimated, for polycarbonate, from uniaxial compression tests a limiting chain stretch  $\sqrt{N} = 1.5$ , from which a maximum draw ratio in uniaxial extension can be calculated:  $\lambda_{\max} \approx 2.5$ . [According to the eight-chain model, the maximum draw ratio of the network is obtained when the average chain stretch parameter, Eq. (12), equals the limiting chain stretch  $\sqrt{N}$ ].

In this study, a mechanical conditioning technique was used to access the strain-hardening response of glassy polymers, by means of large *homogeneous* deformations. It was shown that the state-of deformation dependence of the strain-hardening response of polycarbonate is adequately described by neo-Hookean behavior, with a shear modulus  $G = 26$  MPa at room temperature. In particular, no effect of a maximum draw ratio was

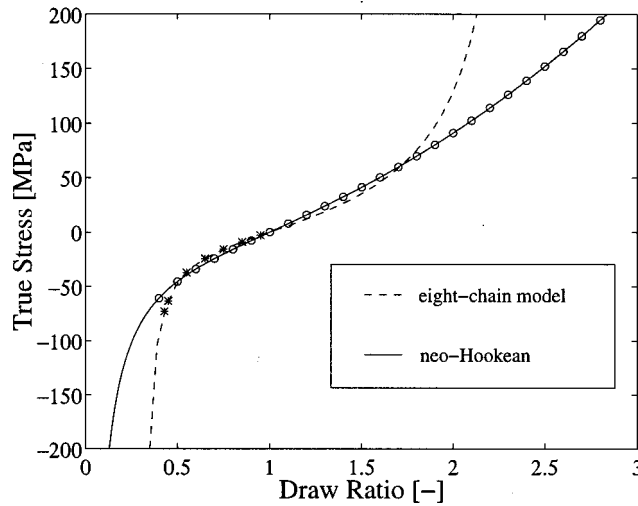


FIG. 9. Comparison between the strain-hardening response of polycarbonate as determined by uniaxial tensile and compression experiments on rejuvenated samples (O), and by uniaxial compression on nonrejuvenated samples (\*) of a different PC grade [Arruda (1992)].

observed, in contrast to the studies mentioned above. The strain-hardening response remained neo-Hookean until fracture occurred at draw ratios  $\lambda \approx 3$  (in uniaxial extension).

It should be noted, that finite extensibility is not a prerequisite to stabilize a local deformation zone. At constant stress, the evolution of the draw ratio in a deformation zone is determined by the stress dependence, and the intrinsic strain-softening response, of the plastic flow process and by the value of the strain-hardening modulus  $G_r$ . Using realistic material parameters, it was estimated [Tervoort (1996), Chap. 4] that the shear strain  $\gamma_{dz}$  at which the neo-Hookean strain-hardening response stabilizes a local plastic deformation zone in polycarbonate, is approximately:  $\gamma_{dz} = 1.4$ . This corresponds to an extension ratio of  $\lambda_{dz} = 1 + \frac{1}{2}\gamma_{dz} = 1.7$ , which is in good agreement with the experimental value as determined by Donald and Kramer (1982a). Thus, in a constant stress situation, stabilization of a deformation zone can be realized by a neo-Hookean strain-hardening response as well [Smit *et al.* (1998)], and does not necessarily result from a finite extensibility of the entanglement network [Haward (1995); Boyce and Haward (1997), Chap. 5].

A comparison between the uniaxial compression data on nonrejuvenated samples by Arruda (1992) of a different PC grade and our compression and tensile data on rejuvenated samples, is depicted in Fig. 9. The lines in this figure are the calculated strain-hardening response of polycarbonate according to neo-Hookean behavior with a modulus of  $G = 26$  MPa, and according to the eight-chain model with the network parameters as determined by Arruda (1992). The initial strain-hardening modulus and the maximum draw ratios in uniaxial tensile and compression, calculated from their network parameters (see Table I), equal:  $G = 19.5$  MPa,  $\lambda_{\max}^{\text{compression}} = 0.3$ , and  $\lambda_{\max}^{\text{tensile}} = 2.44$ . A detailed comparison between the strain-hardening response is not possible since we are dealing with two different PC grades. Nevertheless, from Fig. 9 it is clear that despite possible differences in molar mass, etc., the actual *compression* data do not differ substantially, both rejuvenated and nonrejuvenated samples show an upswing in stress. However, interpreting this stress upswing as resulting from a finite extensibility of the network, using

a non-Gaussian spring model, also leads to a maximum draw ratio in *tensile* deformation, which was not observed experimentally for the deformations applied to the PC grade used in this study. Thus, Fig. 9 illustrates the danger of fitting finitely extensible strain-hardening models in (uniaxial or planar) compression.

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