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Strain Hardening in Glassy Polymers: Influence of Network Density on Elastic and Viscous Contributions

Coen C. W. J. Clarijś, Leon E. Govaert
Polymer Technology, Eindhoven University of Technology, P.O. Box 513, 5600MB, Eindhoven, The Netherlands
Correspondence to: L. E. Govaert (E-mail: I.e.govaert@tue.nl)

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ABSTRACT: In this study, the rate- and temperature-dependent strain hardening and the Bauschinger effect is studied for three glassy polymers. It appeared that for all materials, an equal distribution of elastic and viscous hardening was necessary to accurately predict the Bauschinger effect, as well as the rate- and temperature-dependent strain hardening response. As for the elastic contribution, the viscous contribution appears to increase with an increase in entanglement network density. Investigating the effect of temperature on the Bauschinger effect revealed that at elevated temperatures the model predictions are not accurately enough. It is shown that this is caused by the magnitude of the elastic hardening contribution; to improve the predictions, a temperature-dependent elastic contribution is necessary. © 2019 The Authors.

INTRODUCTION
The use of computational methods has become a standard tool in predicting polymer material behavior. These methods are getting more and more advanced, attempting to connect the different length scales involved, like, for example, multilevel finite element methods or molecular simulations. Furthermore, advances are made on the level of constitutive macroscopic models that aim at describing polymer material behavior on a macroscopic scale. An important feature of polymer deformation and failure is the relation between (plastic) strain localization and the intrinsic material response, which should therefore be captured accurately. Several research groups have been working on the development of such constitutive models; examples are the Boyce-Parks-Argon (BPA) model, the Oxford Glass Rubber (OGR) model and the Eindhoven Glassy Polymer (EGP) model.

In recent years, the progress in constitutive modeling has mainly focused on the strain hardening response, that is, the typical upswing in stress at large strain. Following the suggestion of Haward and Thackray, the strain hardening response was initially modeled with rubber elastic models. They hypothesized strain hardening as an entropy-elastic contribution of the entanglement network, motivated by the observation that the plastic deformation of a polymer glass can be fully recovered by heating above the glass transition. Several research groups built on this idea; examples of entropic hardening descriptions used are the three-chain and eight-chain models used in the BPA model, the full chain model used by Wu and van der Giessen, the Edwards-Vilgis model in the OGR model, and the neo-Hookean description employed in the EGP model. Other approaches are based on a two-subsystem (also called two-temperature) framework and have resulted in accurate descriptions of the strain hardening response. Although all these models are capable of quantitatively capturing strain localization and failure, there are many arguments against a pure entropic description of strain hardening: first, the strain hardening modulus is orders of magnitude larger than the one calculated from the network density. Second, strain hardening decreases with increasing temperature, whereas an entropic description predicts an increase. Furthermore, the strain hardening response is affected by strain rate and pressure, which are both not accounted for in rubber elastic models. Finally, the rubber elastic models fail to capture the Bauschinger effect, which is the asymmetry in tensile and compressive stress in oriented materials. Therefore, recent improvements of the strain hardening models were sought in a more appropriate, combination of elastic and viscous processes. The underlying physics of a viscous contribution are sought in a deformation-induced orientation of polymer chains and modifications in chain packing.

A promising route to add a viscous hardening contribution to a macroscopic constitutive model appeared to be the introduction of a deformation-dependent flow stress, as first proposed by Wendlandt et al. Experimental data were successfully
captured by introducing a deformation dependence of the activation volume in the Eyring flow term. Senden et al.\textsuperscript{17} also demonstrated that the rate- and temperature-dependent strain hardening of polycarbonate (PC) could be described by adding a deformation dependence to their Eyring flow term, however, doing so for the initial viscosity and activation energy, and using a constant activation volume. Additionally, this enabled an accurate description of the Bauschinger effect. It should be noted that an elastic component in the strain hardening description is still necessary to correctly describe the experimentally observed Bauschinger effect.\textsuperscript{30} This was already pointed out by Botto et al.\textsuperscript{46} who showed, based on shrinkage stress and yield stress measurements on oriented poly(methyl methacrylate) (PMMA), that the Bauschinger effect is related to a frozen-in network stress. Furthermore, the full recovery of plastic deformation by heating above the glass transition\textsuperscript{19–22} is a strong argument for the existence of an elastic contribution.

Clearly, a combination of elastic and viscous hardening strongly improves the description of the large-strain material behavior. However, it is not easy to measure and quantify both contributions separately and independently. Since, in general, an increase in entanglement density leads to an increase in the total hardening response,\textsuperscript{30} an intuitive decision would be to link the hardening modulus of the elastic contribution to the entanglement density using Gaussian network theory: \( G_r = N_c k_B T \), with \( N_c \) the entanglement network density, \( k_B \) Boltzmann’s constant, and \( T \) the absolute temperature, and the remainder can be accounted for by a viscous contribution. However, Senden et al.\textsuperscript{40} found for PC that a quantitative description of the Bauschinger effect required an equal distribution of elastic and viscous hardening, yielding an elastic hardening modulus \( G_r \approx 7 \text{ MPa} \) for PC.\textsuperscript{17} In contrast, the plateau modulus of PC \( G_0 \approx 2.7 \text{ MPa} \),\textsuperscript{47} which yields a value of \( \approx 4.5 \times 10^{26} \text{ m}^{-3} \) for \( N_c \), and consequently a hardening modulus \( G_r \approx 1.8 \text{ MPa} \) at room temperature. Similar observations were already made by van Melick et al.\textsuperscript{30} Wendlandt et al.\textsuperscript{35} Kramer,\textsuperscript{31} Tervoort and Govaert,\textsuperscript{29} and Engels et al.\textsuperscript{32}; calculating the network density from the hardening modulus measured below the glass-transition temperature \( T_g \) yields much higher network densities than observed above \( T_g \) in the melt.

Summarizing, there are clearly two contributions to the strain hardening response of glassy polymers: a viscous contribution and an elastic one. The latter is generally modeled using entropic models such as the neo-Hookean or Edwards-Vilgis model, and it has been shown that increases in network density in general lead to an increase of strain hardening, see, for example.\textsuperscript{30} However, the viscous component has not yet been investigated systematically. Goal of this article is to thoroughly investigate how elastic and viscous hardening contributions depend on molecular structure. A series of three amorphous polymers is being used, having a similar molecular backbone structure: polyphenylsulfone (PPSU), polysulfone (PSU), and polyethersulfone (PESU). These are complemented with previously obtained results on PC.\textsuperscript{17,40} The EGP model, as presented in ref. 17, is applied to the three glasses, focusing on the strain hardening response. The Bauschinger effect is employed to separate the elastic and viscous components. Furthermore, the influence of temperature on the Bauschinger effect is studied in detail. The obtained results are discussed with respect to the (recent) literature.

THE EGP MODEL

The EGP model used in this study is taken from previous work performed in our group. For clarity, below the governing equations of the EGP model of interest for the present study are summarized, and as mentioned in the Introduction section, focus will be on the strain hardening response. Therefore, the model is used in its single-mode form.\textsuperscript{15} Additionally, a multiprocess approach is used\textsuperscript{46} to take two molecular relaxation processes into account, as well as an extension to incorporate a viscous contribution to strain hardening.\textsuperscript{17} In the model, the total Cauchy stress is split in a hydrostatic component and a deviatoric component:

\[
\sigma = \sigma^h + \sigma^d
\]

The hydrostatic part is described by a constant bulk modulus \( K \) and the volume change ratio \( J \):

\[
\sigma^h = K (J - 1) I
\]

The deviatoric part consists of elasto-viscoplastic driving stress and an elastic hardening stress:

\[
\sigma^d = \sigma_s + \sigma_r
\]

Regarding the elasto-viscoplastic driving stress, two processes are assumed to work in parallel: an \( x \)-process (related to the primary glass transition, i.e., main-chain segmental motion) and a \( \beta \)-process (related to the secondary glass transition, i.e., partial main-chain or side-chain motion). These primary and secondary transitions are often observed in PSUs.\textsuperscript{49} The expression for the driving stress is:

\[
\sigma_s = \sigma_{s\alpha} + \sigma_{s\beta} = G_n \bar{B}_r^\alpha + G_p \bar{B}_r^\beta
\]

with \( G_r \) the shear modulus and \( \bar{B}_r^\alpha \) the deviatoric part of the isochoric, elastic left Cauchy–Green strain tensor. The subscript \( x \) refers to the specific process (\( \alpha \) or \( \beta \)). The elastic hardening stress is modeled using the Edwards–Vilgis model for rubber elasticity,\textsuperscript{17,25} with a strain hardening modulus \( G_r \), total isochoric left Cauchy–Green strain tensor \( \bar{B}^d \) and a tensor \( \bar{Z} \):

\[
\sigma_r = \frac{G_r}{J} (\bar{B} \cdot \bar{Z})^d
\]
where $Z$ is given by:

$$Z = \frac{\alpha^2 (1 + \beta^2)(1 - \alpha^2)}{1 - \alpha^2 \text{tr}(\dot{B})} \left( B \cdot (I + \xi B)^{-1} \right) I$$

$$+ \frac{\beta^2 (1 - \alpha^2)}{1 - \alpha^2 \text{tr}(\dot{B})} \left( (I + \xi B)^{-1} - \beta(I + \xi B)^{-1} \cdot (I + \xi B)^{-1} \dot{B} \right)$$

$$+ \frac{\alpha^2}{1 - \alpha^2 \text{tr}(\dot{B})} I$$

(7)

where $\alpha_e$ is a parameter capturing the limited extensibility of the network, and $\xi_e$ captures the mobility of entanglements. Since the entanglement network of a glassy polymer remains intact during plastic deformation, the mobility of entanglements $x_e$ is taken to be zero in this study. The tensor $B$ is the isochoric left Cauchy–Green strain tensor, and $I$ is the identity tensor. Note that in case of $\alpha_e = \xi_e = 0$, $Z$ equals the identity tensor, and the expression reduces to the neo-Hookean one.

Because of kinematic choices, the rate of deformation tensor has to be specified. This is achieved with a non-Newtonian flow rule relating the driving stress to rate of deformation tensor:

$$D_{\tau} = \frac{\sigma_{\tau_e}}{2\eta_0(T, \tau_e, p, S_{\text{iso}}, I_r(B))}$$

(8)

with $\eta_0(T, \tau_e, p, S_{\text{iso}}, I_r(B))$ the viscosity. The expression for the viscosity is:

$$\eta = \eta_0(I_r(B)) = \frac{\xi_e/\tau_0}{\sinh(\tau_e/\tau_0)} \exp\left( \frac{\Delta H_0(I_r(B))}{R T} \right) \exp\left( \frac{\mu_p}{\tau_0} \right) \exp(S_e)$$

(9)

with initial viscosity $\eta_0$, characteristic shear stress $\tau_0$, activation enthalpy $\Delta H_0$, universal gas constant $R$, absolute temperature $T$, pressure dependence parameter $\mu_p$, and state parameter $S_e$ which initial value uniquely defines the thermomechanical state of the material. In this work, since the focus is on the strain hardening response, all simulations are performed with $S_e = 0$, effectively neglecting intrinsic strain softening. The characteristic shear stress $\tau_0$, the pressure $p$, and the equivalent shear stress $\tau_e$ are given by:

$$\tau_0 = \frac{k_B T}{V_e}; \quad p = -\frac{1}{2} \text{tr}(\sigma); \quad \tau_e = \sqrt{\frac{1}{2} \sigma_e \cdot \sigma_e}$$

(10)

in which $k_B$ is Boltzmann constant and $V_e$ is the shear equivalent activation volume. The viscous contribution to the strain hardening response is obtained by means of a deformation dependent viscosity. In the expression for the viscosity, the activation enthalpy and initial viscosity are made deformation dependent using an invariant function $I_r(B)$ of the isochoric left Cauchy–Green strain tensor $B$. For more details and discussion regarding the specific choices made that lead to these expressions, see refs. 17,40,50. The deformation dependence of the initial viscosity and the activation enthalpy are described by $^{17}$:

$$\eta_0(I_r(B)) = \eta_0 \exp\left( -C_{1,a}(I_r(B)) \right)$$

(11)

$$\eta_0(I_r(B)) = \eta_0 \exp\left( -C_{1,b}(I_r(B)) \right)$$

(12)

$$\Delta H_0(I_r(B)) = \Delta H_0 + C_{2,a}(I_r(B))$$

(13)

$$\Delta H_0(I_r(B)) = \Delta H_0 + C_{2,b}(I_r(B))$$

(14)

where $C_{1,a}, C_{1,b}, C_{2,a}$, and $C_{2,b}$ are constants, effectively determining the magnitude of the viscous strain hardening component. The invariant function $I_r(B)$, also referred to as equivalent strain, $^{17}$ is given by:

$$I_r(B) = \sqrt{\frac{1}{2} \dot{B}^d \cdot \dot{B}^d} = \sqrt{\frac{1}{2} (I_1(B))^2 - I_2(B)}$$

(15)

with

$$I_1(B) = \text{tr}(\dot{B}) ; I_2(B) = \frac{1}{2} (\text{tr}^2(\dot{B}) - \text{tr}(\dot{B} \cdot \dot{B}))$$

(16)

**EXPERIMENTAL AND NUMERICAL METHODS**

**Materials and Sample Preparation**

Materials used are commercially available PSU, PESU, and PPSU kindly supplied by Solvay Specialty Polymers (Alpharetta, GA, USA), see Table 1. Materials are used as-received. Extruded rod of PSU and PPSU was obtained via Solvay Specialty Polymers.

Three different sample geometries are used in this study to quantify EGP parameters: rejuvenated (by large strain torsion), axisymmetric tensile bars for both tensile and compression tests to assess the Bauschinger effect; cylinders (with an aspect ratio of 1) for uniaxial compression tests; and finally, compression and tensile samples with similar thermal history, to determine the pressure dependency parameter $\mu$. More details are given below.

Axisymmetric tensile bars were machined from the extruded rod. These samples were subjected to a mechanical pre-treatment, consisting of large-strain reversed torsion. This treatment is known as mechanical rejuvenation, and effectively eliminates strain softening in glassy polymers, leading to homogeneous deformation in a uniaxial tensile test. $^{1,2}$ The bars were clamped in a lathe and manually twisted over at least $720^\circ$, and subsequently twisted back over the same angle. To obtain samples with a different preorientation, the rejuvenated bars were strained up to a true strain of 0.6 (see Fig. 1). After reaching the prestrain, the sample was unloaded to zero force. From the

---

**TABLE 1** List of Materials Used. Data Provided by Solvay Specialty Polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade Name</th>
<th>$M_w$</th>
<th>$T_\theta$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU</td>
<td>Udel®</td>
<td>35,900</td>
<td>180</td>
</tr>
<tr>
<td>PESU</td>
<td>Veradel®</td>
<td>26,000</td>
<td>220</td>
</tr>
<tr>
<td>PPSU</td>
<td>Radel®</td>
<td>29,900</td>
<td>220</td>
</tr>
</tbody>
</table>
center of the tensile bar, a compression sample was machined measuring $5 \times 5$ mm$^2$ (diameter × height). For PESU, this treatment was not possible to perform; all samples fractured during the mechanical pretreatment.

For compression tests on as-molded material, plates of 1 cm thick were compression molded at a temperature of 350 °C (PSU) to 370 °C (PPSU and PESU). Granules were allowed to melt under atmospheric pressure in a mold covered with aluminum foil. Subsequently, the material was compressed up to 100 kN for 2 min. The mold is placed in a cold press at 20 °C, applying little pressure, and allowed to cool down. The skin layers of the plates were removed by a milling operation. Cylindrical samples measuring $6 \times 6$ mm$^2$ (diameter × height) were machined from the plates on a turning lathe. To determine the pressure dependency parameter $\mu$, compression samples of $4 \times 4$ mm$^2$, as well as small tensile bars, were milled from the center of another plate to assure both sample geometries have the exact same thermal history.

**Experimental Methods**

All compression tests, at different true strain rates and test temperatures, were performed on a Zwick 1475 tensile tester equipped with a temperature chamber. Friction between sample and steel plates was reduced by applying PTFE-tape (3M 5480) to the sample and PTFE spray (Griffon TF089) to the plates. True strain rate control was used, under the assumption of incompressibility and true stress and true strain signals were recorded. Tensile tests on torsion rejuvenated samples were performed on a MTS hydraulic tensile tester equipped with a temperature chamber at a strain rate of $10^{-3}$ s$^{-1}$, at several temperatures. True stress and true strains were calculated assuming incompressibility. Tensile tests on the samples used to determine the pressure dependency parameter $\mu$ were performed on a Zwick Z010.
tensile tester, at different strain rates, at room temperature. Stress and strain signals were recorded.

**Numerical Methods**

Finite element simulations are performed using the commercial software package MSC Marc/Mentat. The EGP model is implemented in the HYPELA2 user subroutine. Uniaxial compression and tensile simulations are performed using a single linear, quadrilateral axisymmetric element with uniaxial boundary conditions.

**RESULTS AND DISCUSSION**

All material parameters of the EGP model can be uniquely determined. To obtain them, several steps have to be performed, of which the results will be discussed here. For a full review of the procedures, the reader is referred to Klompen et al.,15 van Breemen et al.,16,48 and Senden et al.17

First, the pressure dependency parameter $\mu$ is determined from a series of compression and tensile tests on samples with similar thermal histories. The difference between the tensile and compressive yield stresses is in this case fully accountable to the difference in hydrostatic pressure. Using a pressure-modified Eyring expression,$^{51,52}$ the pressure dependency can be captured accurately. The results of these experiments and the subsequent fit with the pressure-modified Eyring equation can be found in the Appendix. The obtained values for $\mu$ are 0.055, 0.061, and 0.060 for PPSU, PSU, and PESU, respectively. These values are comparable in magnitude to values obtained for other polymers (for an overview, see ref. 53, table III). Next, the bulk $\kappa$ and shear modulus $G$ are

<table>
<thead>
<tr>
<th>Material</th>
<th>$\mu$ ($-$)</th>
<th>$\kappa$ (MPa)</th>
<th>$G$ (MPa)</th>
<th>$\alpha_r$ ($-$)</th>
<th>$V$ (nm$^{-3}$)</th>
<th>$\eta^*_0$ (MPa $s^{-1}$)</th>
<th>$G$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU</td>
<td>0.061</td>
<td>2050</td>
<td>10.5</td>
<td>0.240</td>
<td>5.00</td>
<td>$8 \times 10^{16}$</td>
<td>570</td>
</tr>
<tr>
<td>PESU</td>
<td>0.060</td>
<td>3300</td>
<td>8.0</td>
<td>0.235</td>
<td>4.30</td>
<td>$1 \times 10^{17}$</td>
<td>400</td>
</tr>
<tr>
<td>PPSU</td>
<td>0.055</td>
<td>4290</td>
<td>16.0</td>
<td>0.258</td>
<td>5.42</td>
<td>$4 \times 10^{17}$</td>
<td>500</td>
</tr>
</tbody>
</table>

**FIGURE 3** (a) Simulated response using a simplified model for an equal distribution of elastic and viscous hardening ($\phi = 0.5$). Reproduced from Senden et al. 40. (b) Mechanical response of PC in cyclic deformation, experimental data taken from Senden et al. 40. Mechanical response of (c) PSU and (d) PPSU in cyclic deformation. The maximum true strain for both materials in tension is 0.6.
derived from the Young’s modulus, using the Poisson’s ratio reported in the manufacturers data sheets.

Characterization of the Strain Hardening Response
To obtain the elastic hardening parameters, a simulation of a tensile test on a mechanically rejuvenated axisymmetric tensile bar (in torsion) or a single compression test is used. Next to the pressure dependency parameter $\mu$ and the bulk and shear modulus, the hardening modulus $G_r$, the limited extensibility parameter $\alpha_r$, the activation volume $V_\alpha$, and the total initial viscosity need to be determined. The activation volume $V_\alpha$ is obtained from the rate dependence of the yield stress at room temperature. The other three parameters are iteratively changed until a good description of the total response is obtained with the simulations. The Edwards–Vilgis hardening modulus $G_r$ is determined at room temperature at a strain rate of $10^{-3}$ s$^{-1}$. The total initial viscosity is fitted to the (rejuvenated) yield stress. In Figure 2(a–c), the result of these simulations for the three materials is shown; EGP model parameters are given in Table 2. With the parameters, an accurate description of the large strain response is obtained. Note that for PESU, a compression test is used, since it was not possible to obtain mechanically pretreated samples.

Characterizing the Viscous Contribution to Strain Hardening
The parameters describing the viscous contribution to strain hardening are determined following Senden et al.$^{17}$ First, the

![FIGURE 4](image) Strain rate (left) and temperature (right)-dependent driving stress as determined from uniaxial compression experiments. Solid lines are fits using eq 18 and markers represent experimental data. (a,b) PSU; (c,d) PESU; and (e,f) PPSU.
ratio of elastic to viscous hardening is determined. Senden et al. proposed to employ the Bauschinger effect to isolate both contributions. A simplified model was used that relies on an additive split of the stress into a viscous flow stress and an elastic hardening stress, where the elastic stress is modeled as a neo-Hookean spring, and the viscous stress with an Eyring relation. A parameter was introduced that represents the magnitude of viscous strain hardening relative to the total strain hardening response. Note that this idea is very similar to the classical approach of describing the Bauschinger effect in metals, using a combination of kinematic and isotropic hardening. The response of the model, for an equal distribution of elastic and viscous hardening, is shown in Figure 3, where the dashed line is the elastic contribution, the dash-dotted line the viscous contribution, and the solid line the total response. As can be seen, the equal distribution of the hardening stress over the elastic (dashed line) and viscous (dash-dotted line) contributions is needed to qualitatively capture experimental results on PC [see Fig. 3(b)]. Experimental results on PSU and PPSU are shown in (c) and (d), respectively, and, interestingly, similar behavior as found for PC is observed. In the tensile part, the stress increases with increasing strain, and upon reversal of the loading direction a Bauschinger effect is observed, with a yield stress approximately equal to the initial yield stress of the material and an absence of strain hardening (in this strain range). For PESU, these experiments could not be performed, as mentioned before, but given the similarity of the molecular backbone structure, the same behavior is assumed for PESU.
From these results, it is clear that a ratio of approximately 50/50 would be required to correctly capture the Bauschinger effect in both PSU and PPSU, and most likely in PESU as well. Therefore, the hardening moduli obtained from the fitting procedure shown in Figure 2 and reported in Table 2, are in further reading halved. Subsequently, the viscous component can be characterized by isolating the driving stress from the total stress using:

$$\sigma_\alpha (\lambda) = \sigma(\lambda) - \frac{\sqrt{3}}{\sqrt{3} - \mu} \sigma_\beta (\lambda)$$

(17)

with $\sigma(\lambda)$ the total stress and $\sigma_\alpha (\lambda)$ the strain hardening stress, now employing half of the value of the hardening modulus reported earlier in Table 2. Next, following the work of Senden et al. and Wendlandt et al., discrete values of the driving stress at certain strain levels in the large strain regime are taken (see Fig. 6 for the experimental stress–strain curves). The obtained driving stresses are shown in Figure 4 (markers) and absolute strain levels are indicated in the figure. With increasing strain rate and decreasing temperature the stress levels increase, as well as with increasing strain level. Similar to PC, it appears that the slopes remain constant, with only a transition from the $\alpha$-process to the $\beta$-process (witnessed by the change in slope), indicating that the deformation kinetics are only shifted horizontally over the strain rate axis. This directly implies that the activation volumes for both processes remains constant, as suggested by Senden et al..

The deformation dependence of the driving stress, at different strain rates and temperatures, is then be described with a modified Eyring expression that can be obtained by rewriting the EGP model to the one-dimensional case (see Klompen et al. for details). The modified Eyring expression is given by:

$$\sigma_\alpha (i, T) = \sum \frac{\sqrt{3}}{\sqrt{3} - \mu} V_x \eta_{\alpha,x} \exp \left( \frac{\Delta H_x}{RT} \right)$$

(18)

where $\eta_{\alpha,x}$ and $\Delta H_x$ depend on the deformation. Equation 18 is fitted to each strain level, as indicated in Figure 4 with the solid lines. For each strain level, the initial viscosity $\eta_{\alpha,x}$ and activation enthalpy $\Delta H_x$ were simultaneously fitted to the experimental stresses, whereas the activation volumes $V_\alpha$ and $V_\beta$ are kept constant, as discussed earlier. For each strain level, a value of the initial viscosity value and activation enthalpy is obtained, and the values are plotted in Figure 5 as a function of the equivalent strain $\epsilon_f$ (see eq 15), to be able to determine the constants $C_{1,\alpha}, C_{1,\beta}, C_{2,\alpha}$ and $C_{2,\beta}$ obtained from uniaxial compression tests. With the addition of a viscous contribution, the rate- and temperature-dependent strain hardening response is accurately captured by the EGP model for all polymers considered, over a fairly large rate and temperature range. The rather sharp transitions at the yield points in the simulations are again caused by the single-mode description of the EGP model, which yields a linear response up to yield. This can be improved by taking a relaxation spectrum into account, which improves the preyield description. Next to that, intrinsic strain softening can be captured in the EGP model with a state parameter, a measure for the thermodynamic state of the material, but this not of interest in the current study.

Next, the performance of the model in describing the Bauschinger effect in PSU and PPSU is checked by simulating the response to cyclic deformation. Results are shown in Figure 7 (solid lines) and as can be seen the chosen equal distribution of elastic and viscous hardening seems to be appropriate and the EGP model successfully captures the observed Bauschinger effect. The small yield peak after reversal of the loading direction is caused by both the single-mode description and the functional shape of the elastic and viscous contributions.

<table>
<thead>
<tr>
<th>TABLE 3 EGP Model Parameters for All Materials</th>
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<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>$\mu$ (−)</td>
</tr>
<tr>
<td>$\kappa$ (MPa)</td>
</tr>
<tr>
<td>$G_\alpha$ (MPa)</td>
</tr>
<tr>
<td>$\alpha_\alpha$ (−)</td>
</tr>
<tr>
<td>$V_\alpha$ (nm$^3$)</td>
</tr>
<tr>
<td>$V_\beta$ (nm$^3$)</td>
</tr>
<tr>
<td>$\Delta H_{0,\alpha}$ (kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>$\Delta H_{0,\beta}$ (kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>$C_{1,\alpha}$ (−)</td>
</tr>
<tr>
<td>$C_{1,\beta}$ (−)</td>
</tr>
<tr>
<td>$C_{2,\alpha}$ (kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>$C_{2,\beta}$ (kJ mol$^{-1}$)</td>
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<tr>
<td>$\eta_{0,\alpha}$ (MPa s$^{-1}$)</td>
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<tr>
<td>$\eta_{0,\beta}$ (MPa s$^{-1}$)</td>
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<td>$G_s$ (MPa s$^{-1}$)</td>
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<td>$G_p$ (MPa s$^{-1}$)</td>
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FIGURE 6 Compressive stress–strain curves of all three materials. Left figures show rate dependence measured at room temperature and right figures show the temperature dependence measured at $10^{-3}$ s$^{-1}$. Solid lines are EGP simulations and markers represent experimental data.

FIGURE 7 Cyclic uniaxial deformation of (a) PSU and (b) PPSU at a strain rate of $10^{-3}$ s$^{-1}$. Solid lines represent EGP simulations and markers represent experimental data.
A viscous contribution to strain hardening clearly improves the model performance; however, some issues are still unresolved. First, the elastic hardening moduli employed are still well above the plateau moduli measured in the melt. This is in contradiction to molecular simulation results that suggest a dominating contribution of the viscous part and only a very minor contribution of the elastic part. In contrast, however, experimental solid-state nuclear magnetic resonance results of Wendlandt et al. and neutron scattering experiments of Casas et al. suggested that an apparent network structure exists in glassy polymers that yield a modulus comparable to the hardening modulus found below the glass transition at room temperature. In Figure 8, the obtained hardening moduli are compared to the corresponding plateau moduli measured in the melt for illustration. With an increase in entanglement density, the hardening modulus increases as well. The plateau moduli are two to three times smaller than the obtained hardening moduli. It should be noted that the magnitude of the hardening modulus greatly depends on the model chosen, that is, it should not be taken to literally. For example, in the absence of viscous hardening, a neo-Hookean description yields a strain hardening modulus of 26 MPa for

![Figure 8](image1)

FIGURE 8 (a) Hardening moduli obtained by the fitting procedure explained in this article as a function of entanglement density. (b) Constants describing the viscous hardening contribution. Values for PC were taken from ref. 17. Entanglement densities are calculated from data reported by Fetters et al., except for PESU where the entanglement density was obtained from a Dynamic Mechanical Thermal Analysis (DMTA) experiment. Dashed lines serve as guide-to-the-eye.

![Figure 9](image2)

FIGURE 9 Cyclic uniaxial deformation of PPSU at different temperatures, at a strain rate of $10^{-3} \text{s}^{-1}$. Markers represent experimental stress–strain curves and solid lines are EGP model simulations.

![Figure 10](image3)

FIGURE 10 (a) Strain hardening modulus $G_\text{r}$ as a function of temperature. Dashed line is a guide-to-the-eye. (b) Cyclic uniaxial deformation of PPSU at room temperature and 80 °C, at a strain rate of $10^{-3} \text{s}^{-1}$. Markers represent experimental stress–strain curves and solid lines are EGP model simulations. The strain hardening characterization was performed at 80 °C.
PC, whereas the Edwards–Vilgis model used here would yield values between 14 and 20 MPa (at room temperature, at a strain rate of $10^{-3}$ s$^{-1}$), depending on the $\alpha_r$ parameter chosen. Since both the total and elastic hardening stress increase with increasing entanglement density, the viscous contribution should too. This is confirmed by the trend shown in Figure 8(b): with an increase in entanglement density, the parameters describing the viscous hardening, that is, $C_{1x}$ and $C_{2x}$, increase as well.

Another unresolved issue, already pointed out by Senden et al., is the deformation dependence of the Eyring parameters in the viscosity function (eq 9). In the current study, a deformation-dependent initial viscosity and activation energy are required to describe the strain hardening response of PPSU, PSU, and PESU, which is also consistent with the physical interpretation of viscous strain hardening and similar to results obtained by Senden et al. on PC. However, this is in contrast to the method proposed by Wendlandt et al., where a deformation-dependent activation volume was employed, also suggested by Pink to successfully describe the large-strain response of linear and crosslinked, PC, polyphenylene oxide, and polystyrene. It should be noted that in their studies, the effect of temperature was not taken in account, which may lead to different conclusions.

The fact that an deformation-dependent initial viscosity and activation energy might not be the appropriate choice for all polymers, was already noted by Senden et al. for isotactic polypropylene (iPP) (using experimental results obtained by van Erp et al.). They showed that a deformation-dependent activation volume captured the yield kinetics of oriented iPP accurately. In a recent study on oriented polyethylene (PE), Sedighiamiri et al. showed that both the initial viscosity and activation volume should depend on deformation. Note that the iPP and PE are semicrystalline materials, and the crystalline regions may have an influence on the mechanisms responsible for a specific deformation dependence of the Eyring parameters. Looking at the results obtained here, the choice for a deformation-dependent initial viscosity and activation energy seems to be an appropriate choice for the three materials considered here.

A final unresolved issue is the fact that little information is known about the temperature dependence of the Bauschinger effect in polymer glasses. Therefore, this is investigated for PPSU, using the same experimental procedure as before; samples are subjected to large strain reversal torsion at room temperature, followed by a tensile test at a specific temperature. From the tensile bar, a compression sample is machined and subsequently a compression test is done at the same specific temperature. Note that because of accelerated physical aging, the temperature range where these experiments can be performed is restricted; the effect of accelerated aging at elevated temperatures causes the yield stress to increase during the initial waiting period to allow the sample to reach the test temperature. With the increase in yield stress also strain softening will return, which results in inhomogeneous deformation.

![Figure 11](image-url) Shear equivalent yield stress as a function of strain rate for (a) PESU, (b) PPSU, and (c) PSU, obtained from compression and tensile tests. Markers represent experimental data and solid lines are descriptions with a pressure modified Eyring equation.
In Figure 9, the results of the extra tests on PPSU are shown, for three additional test temperatures. As can be seen, there is an influence of temperature and overall stress levels drop with increasing temperature. Furthermore, in the tensile part, the total hardening response decreases with increasing temperature, as typically observed in many glassy polymers. Upon reversal of the loading direction, the behavior is similar to what was observed before: a yield stress that is approximately equal to the initial yield stress and the absence of strain hardening. The solid lines represent EGP model simulation results, and while the stress–strain response in tension is predicted well, the model appears to fail upon reversal of loading, where the yield point in compression is underestimated for all temperatures except room temperature.

This mismatch appears to increase with increasing temperature. This deviation is most likely caused by the splitting of the total strain hardening stress in an elastic and viscous part in the EGP model. In the characterization step (see eq 17), a constant elastic contribution, determined at room temperature, was assumed. The values of the hardening modulus $G_r$ and $\alpha_r$ (related to the limiting extensibility of the network), are then used in all simulations, irrespective of the strain rate or temperature. While the response at room temperature is then accurately described, at elevated temperatures, the elastic contribution is too large resulting in the underestimation of the yield point upon load reversal. To capture the response properly, the elastic contribution has to decrease with increasing temperature, which can only be achieved by lowering the hardening modulus $G_r$, see Figure 3(a). To test this hypothesis, the characterization is redone, now with the EGP model parameters determined at 80 °C. This results in $G_r = 7$ MPa and $\alpha_r = 0.24$ at 80 °C, compared to $G_r = 8$ MPa and $\alpha_r = 0.258$ at room temperature. The strain hardening modulus does decrease with increasing temperature, as can also be seen in Figure 10(a), where the strain hardening modulus of each experiment shown in Figure 9 is plotted. For comparison, the result of an entropic description, that is, $G_r = N_kBT$, is included. Next, the ratio of elastic to viscous hardening is again found to be 50/50, and the characterization of the viscous part is repeated. This resulted only in a change of $C_{1\rho}$, equal to 23, compared to 27 at room temperature. With these new parameters, the Bauschinger effect is predicted at 80 °C and room temperature. As can be seen from the results presented in Figure 10(b), the effect is now predicted accurately at 80 °C. At room temperature, however, upon load reversal, the yield point is overestimated because of an elastic contribution that is now too small. To improve the model predictions at elevated temperatures, a temperature-dependent elastic contribution is thus necessary.

CONCLUSIONS

To investigate the rate- and temperature-dependent strain hardening and the Bauschinger effect in glassy polymers, a recently proposed extension of the EGP model was successfully applied to three amorphous polymers. An equal distribution of elastic and viscous hardening was found to be necessary, similar to results obtained for PC. The combination of an elastic and viscous contribution greatly improves the description of the Bauschinger effect. Furthermore, the proposed model accurately describes the rate- and temperature-dependent strain hardening response of all polymers over a wide range of strain rates and temperatures. For the three materials investigated, the choice for a deformation-dependent initial viscosity and activation enthalpy in the viscosity function appears to be correct and experimental data could be described accurately. This in contrast to some recent literature, where a deformation-dependent Eyring activation volume was proposed, at present, it is unclear what the cause is for these differences.

From a physics point of view, some aspects of strain hardening remain unclear. First, the magnitude of the obtained elastic hardening moduli for the three materials appeared to be larger than would be expected from the entanglement network. Second, studying the temperature dependence of the Bauschinger effect revealed that at elevated temperatures, the elastic contribution in the model has to decrease to capture the experimental data. Nonetheless, the addition of a viscous contribution to strain hardening in the EGP model, as proposed by Senden et al., could be directly applied to three other polymers, and improves the performance of the model in the description of rate- and temperature-dependent strain hardening, as well as enabling a quantitative description of the Bauschinger effect.

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APPENDIX

To determine the pressure dependency parameters, compression and tensile tests have been performed on samples with similar thermal history, see Figure 11. The markers represent experimental data; the solid lines are descriptions with a pressure modified Eyring equation (see ref. 52 for more details):

$$\tau_{\text{eq}} = \frac{\tau_0}{(1 - \mu \alpha)^{3/2}} \ln \left( \frac{2\gamma_{\text{eq}}}{\gamma_0} \right)$$

where $\tau_{\text{eq}}$ is the shear equivalent yield stress, $\tau_0$ is the characteristic shear stress, $\mu$ is the pressure dependency parameter, $\alpha$ is a geometry factor ($-\sqrt{3}/3$ for uniaxial extension, $+\sqrt{3}/3$ for uniaxial compression), $\gamma_{\text{eq}}$ is the shear equivalent strain rate, and $\gamma_0$ is a rate constant.

REFERENCES AND NOTES

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