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Temperature Dependence of the Back-Stress in Shear for Glassy Polycarbonate

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Summary: Back-stress is the equilibrium stress and represents conditions under which relaxation events in the material stop and the material can carry an applied load indefinitely without a change in strain. In most models for glassy polymers, back-stress plays a central role since relaxation in materials is closely related to the distance of the current conditions from equilibrium. A number of these models that are commonly used for modeling glassy polymers use a modeling structure similar to large deformation plasticity. The flow rule for the plastic strain in these models are directly connected to the "over-stress," a properly invariant difference between the stress and the back-stress. The importance of correctly evaluating the back-stress to use in these models is clear. For this class of models, the authors have recently developed a method for directly calculating the back-stress under shear deformations. This method is based on evaluating the slope of the stress-strain response under conditions of similar elastic and plastic strain, but different strain rates. Since plastic flow goes to zero at equilibrium, the back-stress can be found by locating points of zero plastic strain rate. Using the proposed method, the back-stress in glassy polycarbonate has been evaluated under shear in isothermal tests going from room temperature to 120 °C, just below the glass transition temperature for polycarbonate. The proposed method provided a full map of the back-stress for polycarbonate over a large range of shear strain and temperature.

Keywords: equilibrium stress; mechanical properties; polycarbonate; shear; yielding

Introduction

For glassy polymers there exist equilibrium loading conditions under which the relaxation processes stop so the loads may be held at constant strain indefinitely. Under quasistatic conditions the material response tends towards these equilibrium conditions. The stress associated with such conditions is called the "back-stress"or "equilibrium stress." Due to the fast relaxation times above the glass transition temperature, the back-stress can be readily observed and evaluated in this temperature range, but this is not the case below the glass transition temperature. For example, the location of the back-stress in PMMA at 140°C is clearly seen in Figure 1 where PMMA is approximately 40 °C above its glass transition temperature. As can be seen, at constant strain the stress either drop or increases, moving toward the equilibrium response, and then indefinitely stays there.

Below the glass-transition temperature the relaxation processes slow down substantially, and identifying true equilibrium becomes more and more difficult, frequently resulting in the identification of a range of stresses which seem to exhibit the equilibrium conditions. An alternate experi-

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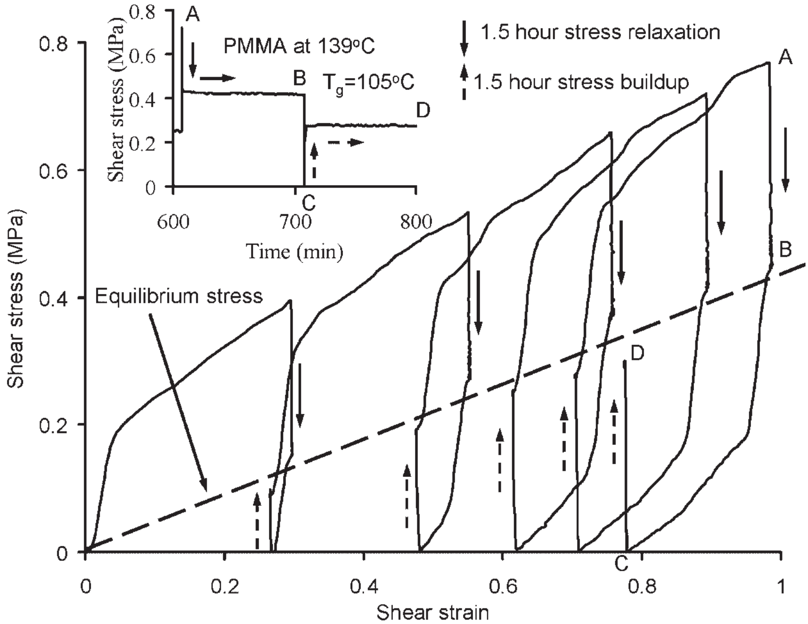

Figure 1.
Stress buildup and stress relaxation seen in PMMA above its glass-transition temperature (From Negahban[19]).

mental method that does not require directly following the long relaxation processes is, therefore, very desirable. The authors have proposed exactly such a method.[1] where they have also provided preliminary results of implementing the procedure.

The proposed method is based on the modeling structure of many of the models used to characterize the thermo-mechanical response of glassy polymers.[2–18] Within these proposed modeling structures, one can develop a method that evaluates the back-stress indirectly using results of cyclic loading profiles in shear.[1] A short description of the method is presented in the following and is then used to evaluate the back-stress of glassy polycarbonate in shear under isothermal conditions from room temperature to 120 °C.

Thermodynamic Model

The experimental method used is based on a one-dimensional thermodynamic model for shear. The independent variables in the model are shear strain γ and temperature θ. In addition, plastic shear strain γ^p is included as an internal parameter in the model. It is assumed that the relation between the elastic shear strain γ^e and the other kinematic variables are given by

$$\gamma = \gamma^e + \gamma^p. \tag{1}$$

This assumption is justified under large strains if the following hold: (a) in the plane of the shear one gets only small normal strain parallel and perpendicular to the direction of shear, which was measured to be true in the deformed samples, and (b) the plastic deformation gradient is not too different from the total deformation gradient (see [1]). The assumption of additive elastic and plastic shear strain then follows from the expressions obtained for superposition of two large plane-stress simple shears.

In this development, the dependent variables are the specific free-energy ψ, shear stress τ, and specific entropy η, all three assumed to be functions of our two independent variables and plastic strain. This is denoted by

$$\psi = \psi^+(\gamma^e, \gamma^p, \theta), \quad \tau = \tau^+(\gamma^e, \gamma^p, \theta), \quad \textit{and} \quad \eta = \eta^+(\gamma^e, \gamma^p, \theta), \tag{2}$$

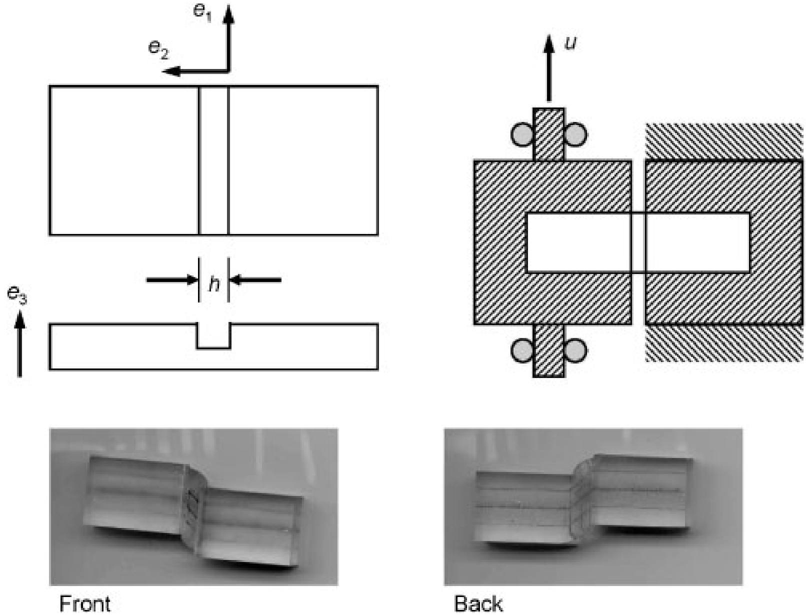

Figure 2.
Schematic of sample geometry and loading method, and pictures of the deformed sample.

where a superscript "+" will denote the function for evaluating the dependent variable. Assuming the process to be homogeneous, the heat flux is eliminated from consideration.

The evolution equation for the internal parameter γ^p is assumed to be given by the following relation

$$\dot{\gamma}^p = \dot{\gamma}^{p+}(\gamma^e, \gamma^p, \theta). \tag{3}$$

This assumed that the flow rule depends on the state of the material, but not the rate of change it, is common, and actually results in a rate dependence in the final response.

The specific free-energy will be assumed to be a sum of two parts. One part which is readily available and another which drives the long term delayed response. This is written as

$$\psi^+(\gamma^e, \gamma^p, \theta) = \psi^{e+}(\gamma^e, \theta) + \psi^{b+}(\gamma^p, \theta), \tag{4}$$

where ψ^e is the more readily available part and is associated with the "elastic response," and ψ^b is associated with the delayed response (a back-stress). This selection is consistent with models such as Arruda, Boyce, and coworkers[2–14] that assume the back-stress is fully determined by the plastic strain and temperature (even though these models are not thermodynamically based they should follow the results presented). Defining the back-stress τ^b as follows

$$\tau^b = \rho \frac{\partial \psi^b}{\partial \gamma^p}, \tag{5}$$

from the entropy production inequality one gets a relation for stress τ and a restriction on the plastic flow as

$$\tau = \rho \frac{\partial \psi^e}{\partial \gamma^e}, \tag{6}$$

$$-[\tau - \tau^b]\dot{\gamma}^p \leq 0. \tag{7}$$

As can be seen from this equation, when the stress is above the back-stress, the plastic strain will increase and when the stress is below the back-stress, the plastic strain will decrease. As a result, the back-stress identifies the locus of points (stresses and plastic strains) on which the plastic strain rate is zero. If in an experiment one arrives at such a point and makes the strain and temperature become constant, then the stress will become constant. Therefore, in this sense the back-stress represents a stress at which equilibrium can be maintained at constant strain and temperature without any relaxation events.

Experimental Methodology

Based on the proposed model an experimental procedure can be developed for evaluating the back-stress. The procedure is based on consecutive loading and unloading cycles. The loading cycles are setup as shown in Figure 3 so that on each cycle the sample is sheared more on the loading than on the unloading. As a result, the shear strain increases after each cycle. A typical response to the cyclic shearing is shown in Figure 4.

To analyze these results focus was put on the behavior of the slope of the stress-strain plot. Based on the modeling assumptions, the slope M of the response in such a plot can be calculated as

$$M = \frac{\dot{\tau}}{\dot{\gamma}} = \rho \frac{\partial^2 \psi}{\partial \gamma^{e2}} \frac{\dot{\gamma}^e}{\dot{\gamma}} + \left[\rho \frac{\partial^2 \psi}{\partial \theta \partial \gamma^e} + \frac{d\rho}{d\theta} \frac{\partial \psi}{\partial \gamma^e} \right] \frac{\dot{\theta}}{\dot{\gamma}}. \tag{8}$$

As the temperature changes in these experiments were not more than $\pm 0.3\,^\circ$C, as measured directly on the sample, the temperature rate can be set to zero and the slope for such isothermal processes can be written as

$$M = \rho \frac{\partial^2 \psi}{\partial \gamma^{e2}} \left(1 - \frac{\dot{\gamma}^p}{\dot{\gamma}} \right). \tag{9}$$

If one can setup conditions of similar elastic and plastic strain but different strain rate, Equation (9) can be used to evaluate the plastic flow rate $\dot{\gamma}^p$. Denoting by M_- and $M_+$the slope at strain rates $\dot{\gamma}_-$ and $\dot{\gamma}_+$, respectively, for points of identical elastic and plastic strains, then it is shown by Negahban, et. al.[1] that

$$\dot{\gamma}^p = \frac{M_+ - M_-}{\frac{M_+}{\dot{\gamma}_-} - \frac{M_-}{\dot{\gamma}_+}}, \tag{10}$$

$$\rho \frac{\partial^2 \psi}{\partial \gamma^{e2}} = \frac{\frac{M_+}{\dot{\gamma}_-} - \frac{M_-}{\dot{\gamma}_+}}{\frac{1}{\dot{\gamma}_-} - \frac{1}{\dot{\gamma}_+}}. \tag{11}$$

As shown in Figure 5, these relations are used to analyze adjacent points of loading taken from unloading in one cycle and loading in the next cycle of the proposed experiments of Figure 3 and 4. For the analysis to be correct, the two adjacent points A and B shown in the Figure need to represent points with identical values of elastic strain and plastic strain, this will

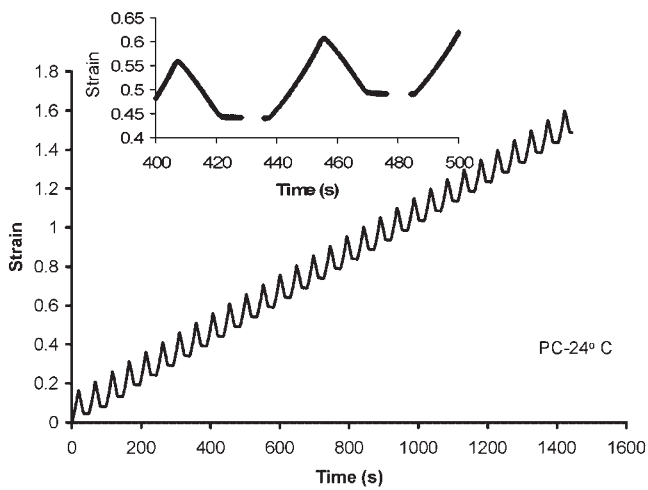

Figure 3.
Shear strain history of the sample during cyclic loading and unloading for the response shown in Figure 4.

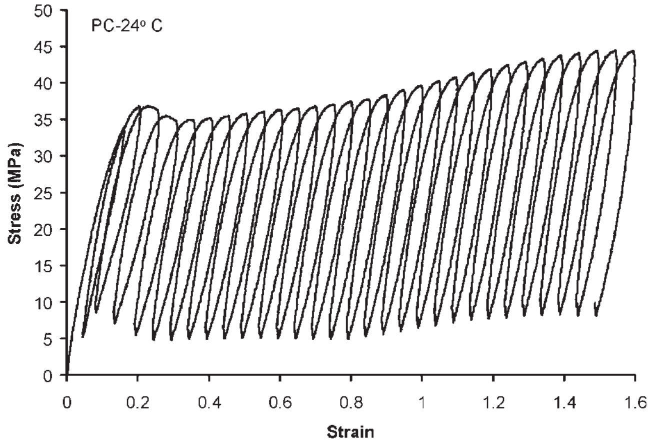

Figure 4.
Cyclic loading and unloading of PC in shear. The loading and unloading are different in value.

assure that the plastic strain rate is the same. Since the two points have identical stresses, and since the stress is a function of the elastic strain, it follows that the two points should have identical elastic strains. The close proximity of the two points in time, and the small magnitude of the plastic strain rates, suggest that there should not be large changes in the plastic strain from B to A, justifying the assumption that the plastic strain is approximately the same.

Using this idea, the following procedure was implemented to evaluate the plastic strain rate, $\rho\frac{\partial^2\psi}{\partial\gamma^{e2}}$, total strain, elastic strain, and plastic strain. A moving regression was used to evaluate $\dot{\gamma}_-$, $\dot{\gamma}_+$, M_-, and M_+ from the data. The strain was taken as the average strain for each value of stress, as shown in Figure 5. The plastic strain rate and $\rho\frac{\partial^2\psi}{\partial\gamma^{e2}}$ were then evaluated using, respectively, Equation (10) and (11). The elastic strain was calculated from Equation (6) using the assumption (4) to get the relation

$$\gamma^e(\tau) = \int_0^\tau \frac{1}{\rho\frac{\partial^2\psi}{\partial\gamma^{e2}}} d\tau, \tag{12}$$

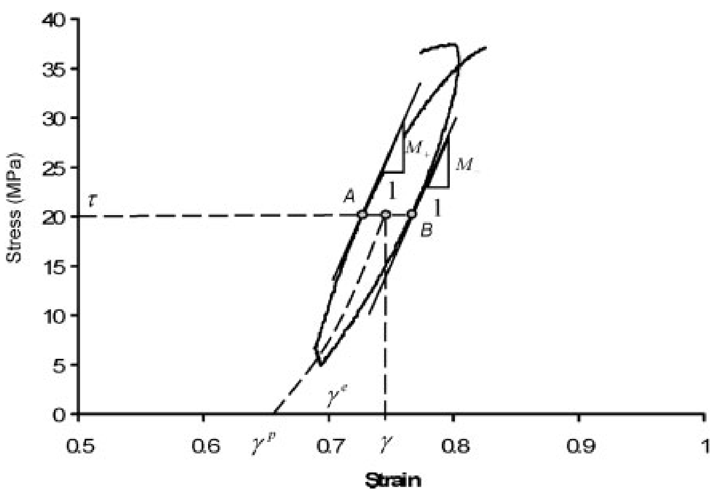

Figure 5.
The two points on adjacent loading cycles used to evaluate $\dot{\gamma}^p$.

where the argument of the integral was fit by a polynomial and then integrated. The plastic strain was evaluated using $\gamma^p = \gamma - \gamma^e$.

Material and Experimental Setup

All tests were performed on Lexan 9034. Samples were cut from 12.7 mm thick sheets and tested without any thermal conditioning.

All the experiments conducted were shear experiments. The shear sample consisted of a $6.35 \times 12.7 \times 38.1\, mm^3$ rectangular block that was notched at the center (perpendicular to the longer side) of the sample to create a $3.175 \times 3.175 \times 12.7\, mm^3$ shear segment as shown in Figure 2. The sample was mounted on a shear fixture that held the sample from two sides, exposing only the gage section. All tests were conducted in a convection oven. The grips were allowed to come to temperature before the sample was mounted into the grips and the sample was allowed to come to temperature after mounting into the grips. A thermocouple pressing against the gage section of the sample recorded the temperature. There was never more than $\pm 0.3\,^\circ C$ variation in the sample temperature during a test. Two samples were marked with lines drawn on the sample along and perpendicular to the direction of shear and then were subjected to monotonic loading similar to what is shown in Figure 6. One of these samples is shown in Figure 2. As can be seen in Figure 2, the marks on the sample indicated that the gage section underwent predominantly a shear deformation, and the grip sections were left undeformed.

The room temperature response of this material to monotonic loading at four different strain rates from 0.0013 to 0.67 1/s is shown in Figure 6. As can be seen, there is only a slight rate sensitivity for PC in shear at room temperature. For a strain rate of 0.13 1/s, 0.013 1/s, and 0.0013 1/s Figure 7, 8, and 9, respectively, show the response under constant strain rate for different isothermal temperature conditions going from room temperature to 120°C. For PC the glass transition temperature is approximately 148°C.

Results

Figure 10 shows the room temperature plastic strain rate as a function of load for the first three cycles, and Figure 11 shows this for later cycles. The back-stress is the stress at which there is zero plastic strain.

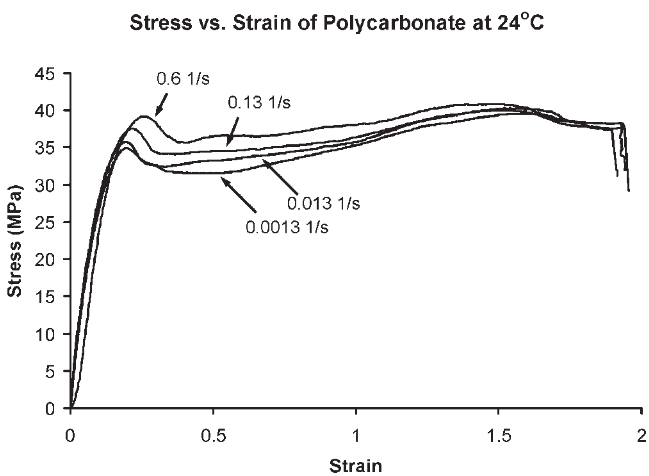

Figure 6.
Stress response of PC under shear at room temperature at four strain rates.

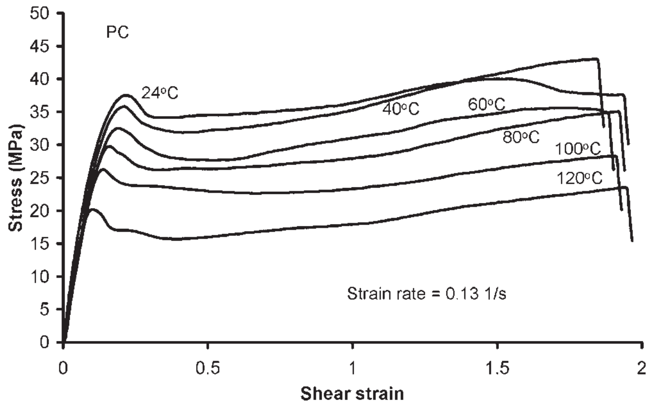

Figure 7.
Stress response of PC under shear at different temperatures for strain rate of 0.13 1/s.

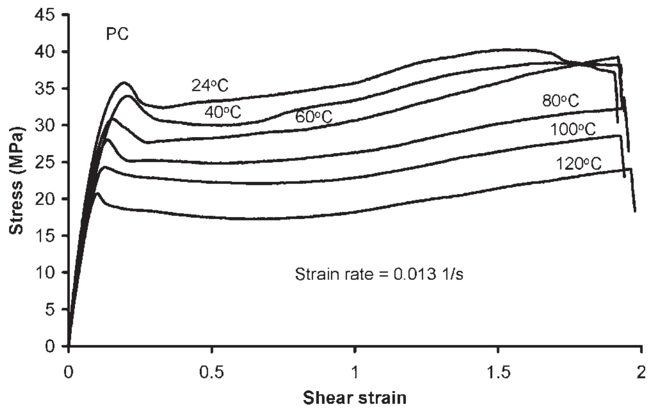

Figure 8.
Stress response of PC under shear at different temperatures for strain rate of 0.013 1/s.

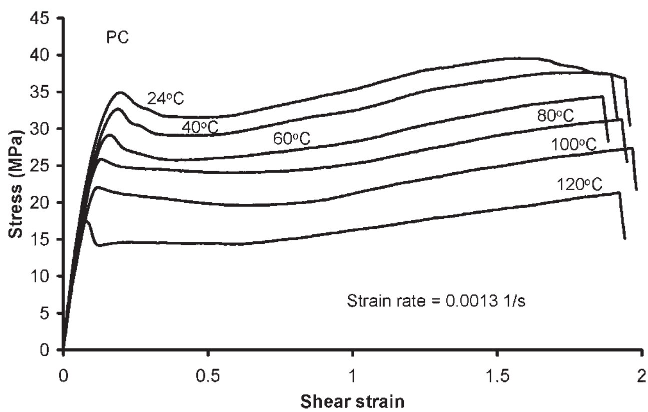

Figure 9.
Stress response of PC under shear at different temperatures for strain rate of 0.0013 1/s.

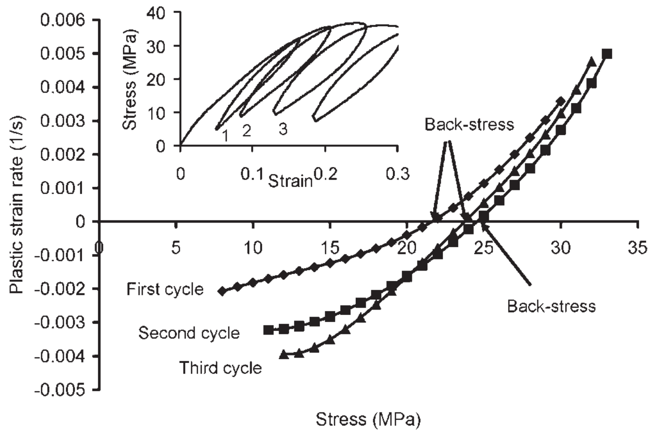

Figure 10.
Plastic shear strain rate evaluated as a function of stress using the mismatch in the loading and unloading slopes (cycles 1, 2, and 3).

As a result, the back-stress can be evaluated from the intercept of these plots with the stress axis. As can be seen, the figure clearly identifies a point of zero plastic strain rate associated with the back-stress for each cycle. Also to be noted is that the plastic strain rate increases nonlinearly above the back-stress, which is responsible for the small rate dependence seen in Figure 6 for monotonic loading [1]. This same method was used in a set of isothermal tests from room temperature to 120 °C to evaluate the back-stress. These results are shown in Figure 12. As expected, the back-stress drops with temperature.

To evaluate the dependence of the back-stress on temperature, Figure 13 shows the back-stress as a function of temperature for 50% plastic strain. As expected, the back-stress decreases as the temperature increases, approaching zero as the temperature gets close to the glass-transition temperature for PC of 148°C.

To address the question of reproducibility of the results, some of the tests were repeated both under the same conditions and also under a different strain rate. The results were reproducible, and independent of the strain rate used in the tests. Figure 14 shows the back-stress as a function of strain

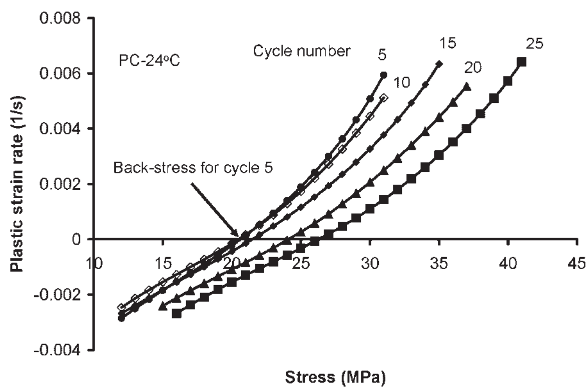

Figure 11.
Plastic shear strain rate evaluated as a function of stress using the mismatch in the loading and unloading slopes.

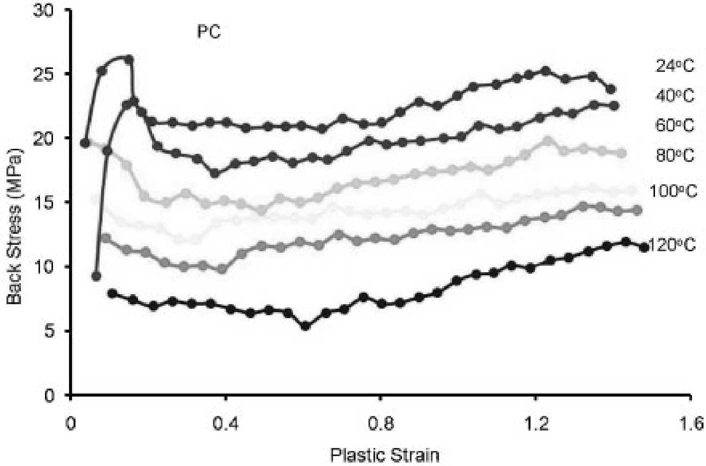

Figure 12.
Back-stress τ^b as a function of plastic strain for different temperatures.

for three different temperatures and evaluated under two different strain rates. In the figure the back-stress for temperatures of 24 °C, 80 °C, and 120 °C and strain rates of 0.13 1/s and 0.013 1/s are plotted against strain. These results show that the back-stress for PC as measured using this method does not depend on the strain rate.

Summary and Conclusions

In the context of shear experiments, a method has been developed by Negahban et. al.[1] that allows evaluation of the plastic strain rate over the entire loading and temperature ranges. This method can be used to evaluated the back-stress from cyclic loading experiments that can be conducted much faster and which provide much more reproducible results than traditional methods.

The experimentally determined back-stresses for PC were evaluated based on the method proposed and for isothermal testing conditions ranging from room temperature up to 120 °C. The method allowed a clear identification of the back-stress, providing

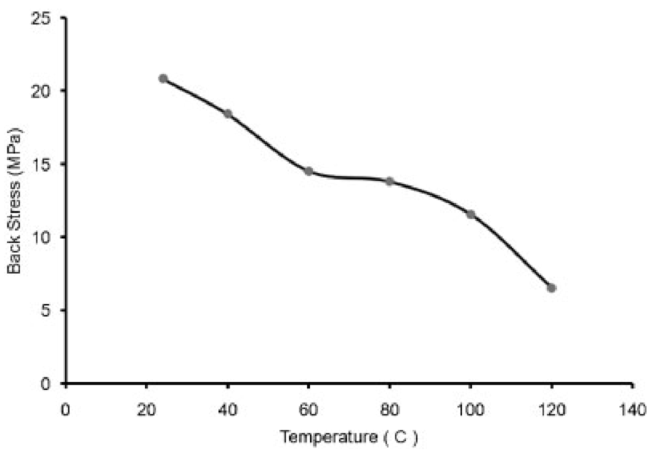

Figure 13.
Back-stress τ^b as a function of temperature for a plastic strain of 50%.

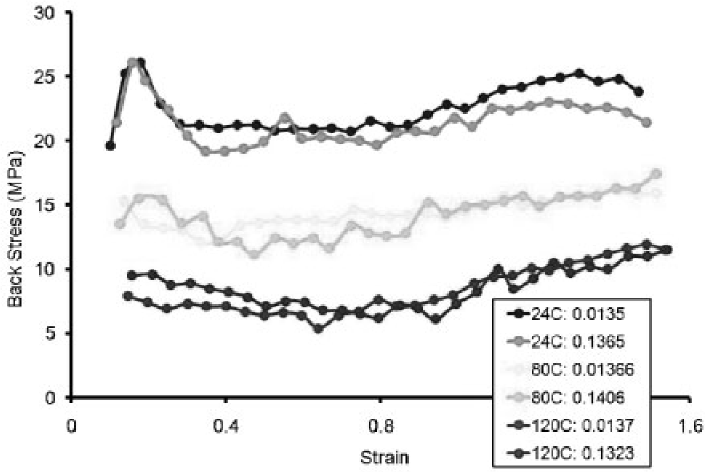

Figure 14.
Back-stress τ^b as a function of strain for different temperatures and strain rates.

more accurate results for use in modeling the response of PC.

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[1] M.Negahban, A.Goel, P.Delabarre, R.Feng, A.Dimick, *ASME Journal of Engineering Materials and Technology* **2006**, *128*, 537.
[2] A. S.Argon, A.S., *Polymer Materials: Relationship Between Structure and Mechanical Behavior, American Society for Materials* **1975**, 411.
[3] A. S.Argon, M. I.Bessonov, *Polymer Engineering and Science* **1977**, *17*, 3.
[4] A. S.Argon, M. I.Bessonov, *Philosophical Magazine* **1977**, *35* 4, 917.
[5] M. C.Boyce, D. M.Parks, A. S.Argon, *Mechanics of Materials* **1988**, *7*, 15.
[6] M. C.Boyce, D. M.Parks, A. S.Argon, *International Journal of Plasticity* **1989**, *5*, 593.
[7] M. C.Boyce, E. M.Arruda, *Polymer Engineering and Science* **1990**, *30* 20, 1288.
[8] E. M.Arruda, M. C.Boyce, *International Journal of Plasticity* **1993**, *9*, 697.
[9] E. M.Arruda, M. C.Boyce, *ASME MD Volume: Use of Plastics and Plastic Composites: Materials and Mechanical Issues* **1993**, *46*, 697.
[10] E. M.Arruda, M. C.Boyce, H.Quintus-Bosz, *International Journal of Plasticity* **1993**, *9*, 783.
[11] M. C.Boyce, E. M.Arruda, R.Jayachandran, *Polymer Engineering and Science* **1994**, *34* 9, 716.
[12] M. C.Boyce, E. M.Arruda, R.Jayachandran, *Mechanics of Materials* **1995**, *19*, 193.
[13] O. A.Hasan, M. C.Boyce, X. S.Li, S.Berko, *Polymer Engineering and Science* **1995**, *35* 4, 331.
[14] E. M.Arruda, M. C.Boyce, R.Jayachandran, *Mechanics of Materials* **1995**, *19*, 193.
[15] E.Krempl, K.Ho, *Polymer Engineering and Science* **1995**, *35*, 310.
[16] E.Krempl, C. M.Bordonaro, *ASTM Special Technical Publication* **2000**, 118.
[17] E.Krempl, F.Khan, *International Journal of Plasticity* **2003**, *19*, 1069.
[18] E.Krempl, F.Khan, *Polymer Engineering and Science* **2004**, *44*, 1783.
[19] M.Negahban, *ASME MD/AMD Volume: Mechanics of Plastics and Plastic Composites* **1995**, MD- 68/AMD-215, 133.

