A new modelling approach to rate dependent softening in glassy polymers

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Abstract

At the Eindhoven University of Technology an effort is made to understand and predict mechanical behaviour of polymers. This is done by mechanical experiments and by numerical simulations and calculations. One of the targets in this research is the behaviour of glassy polymers in compression. In this report the compressive behaviour of two glassy polymers, Polymethylmethacrylate (PMMA) and Polystyrene (PS) is measured. The reason these materials are used is that they exhibit thermorheological complex behaviour. This means that they show another molecular transition next to the glass transition. The compression tests are performed at several strain rates and temperatures to observe the influence of these parameters. The results of the compression tests are used to compare them to numerical calculations. These calculations make use of a constitutive model that describes the intrinsic behaviour of the material. The constitutive model that is used in this report is the compressible Leonov model, which is extended to materials that exhibit two transitions. Several parameters are determined to fit the numerical analysis over the experimental results. This way the compression behaviour can be predicted over a wider range of temperatures and strain rates. The results can be used to give more information about materials in active service. The numerical calculations agree well with the experimental results for PMMA, but show some difficulties for PS. An explanation can be found in the fact that PS exhibits a third transition, which is not integrated in the present constitutive model.
**Chapter 1**

**Introduction**

In recent years, modelling of polymer materials has been a main target in polymer research. Considerable efforts have been made to describe and understand deformation behaviour of glassy polymers. The main reason for these research activities is the need to predict the material behaviour during assimilation and while in active service. Besides this, accurate modelling can also lead to improvement of the material properties.

When describing the deformation behaviour of glassy polymers in a stress strain curve, three stages can be distinguished. At low strains a viscoelastic response can be observed, followed by yielding behaviour and finally plastic behaviour at high strains. The viscoelastic response can be divided in a linear viscoelastic part at low stress and a non-linear viscoelastic section at higher stresses. A general stress strain curve for glassy polymers is given in figure 1.1 [1].

![Stress strain curve](image)

*Figure 1.1: Stress strain curve*

In the viscoelastic part of the stress strain curve (A-B), the stress rises with increasing strain to a maximum, the yield stress (B). The elasticity modulus $E$ can be determined from the slope of the graph in the linear viscoelastic part (A). After reaching the yield point, the stress remains constant for a little while before decreasing with increasing strain (B-C). This phenomenon is called strain softening or yield drop. When the strain softening has reached a minimum, strain hardening will commence, causing the stress to increase again (C-D).

In this report the strain rate and temperature dependence of polymethylmethacrylate (PMMA) and polystyrene (PS) in compression will be investigated. Both PMMA and PS are thermorheological complex materials, which means that they exhibit more than one molecular process. An attempt will be made to describe the deformation behaviour by means of constitutive modelling. First the used materials and performed experiments will be dealt with. In chapter 3 the constitutive modelling will be discussed in some more detail, including the Leonov model and the extension to thermorheological complex materials. Chapter 4 will go through the results from the compression tests and numerical calculations of PMMA. The same strategy will be used in chapter 5 for PS. Finally, conclusions will be drawn and recommendations for future work are given.
Chapter 2

Experimental set-up

The preparations of the test specimens and the experiment itself, as well as the conditions of the experiments have a profound influence on the results of the experiments. This chapter will give an overview of these conditions in some detail, starting with the properties of the test samples, followed by the test conditions.

2.1 Materials and test specimen preparation

The tested materials are Polymethylmetacrylate (PMMA) and Polystyrene 660 (PS). PMMA is received as a rod with a diameter of approximately 6 mm, whereas PS is first compressed in plates and then cut into rods with a 6 mm diameter [2]. These rods have to undergo a heat treatment to ensure a homogeneous structure with no internal localised stresses. An inhomogeneous structure could lead to errors during and after the experiments. Therefore the rods are placed in an oven and heated to a temperature above T_g. PMMA was heated to 120°C and PS to 125°C, both for a period of 1 hour. After heating the rods were quenched in ice water, thus maintaining the homogeneous structure the material obtained during heating. The heat-treated rods were cut into pieces with a length of approximately 6 mm. Both diameter and length were measured more accurately before testing, using a micrometer. The exact dimensions of the samples are essential when calculating the (true) stresses and strains. Lubrication of the test specimens is very important in order to prevent friction and thus ensuring the samples deformed without barrelling. Too little lubrication will lead to a higher strain hardening at larger deformations and will accordingly influence the modelling parameters. To enhance lubrication, a layer of PTFE tape (3M5480, PTFE skived film) is put on each end of the sample. Then a soap solution, consisting of 1 part soap and 1 part water, is added between the tape and the compression plates of the test system, in order to lubricate the plates (figure 2.1). This method of lubricating works fine at lower temperatures but can cause problems at temperatures above 40°C, because the soap dries up before the experiment has finished. Since PS is also tested at 60°C and 80°C, another lubrication method needs to be found to accomplish these experiments. The choice was made to use the PTFE tape with Silicon Spray HR 280 instead of a soap solution. It must be noted that the experiments were not reproducible when the true strain exceeds 0.7, indicating that friction does play a role at higher strains. However, this does not affect further calculation, because the effects at higher strains are relatively irrelevant.

![Figure 2.1: Lubrication](image)

Figure 2.1: Lubrication
2.2 Experiments

The compression experiments were performed on an MTS 831.10 Elastomer Test System. In this system, the samples were clamped between two compression plates. The top plate is in a fixed position, while the bottom plate is hydraulically operated. The motion of the bottom plate is displacement controlled, which in turn depends on the chosen strain rate. This way, the true logarithmic strain rate is kept constant by the Multi Purpose Test ware programme during an experiment, using the following equation.

\[ h(t) = h_0 \cdot \exp(\dot{\varepsilon} \cdot t) \]  

(2.1)

where \( h_0 \) is the initial height of the sample, set at 6 mm, \( \dot{\varepsilon} \) is the logarithmic strain rate \( [s^{-1}] \) and \( t \) is the time \([s]\). If the measured height of the specimen is not exactly 6 mm, it has to be corrected in the MPT programme. Without the correction, the true logarithmic strain rate will not have the desired value and this will lead to irregularities in the true stress. The tests on both PMMA and PS are carried out at logarithmic strain rates of \( 10^{-4} \text{ s}^{-1} \), \( 3 \cdot 10^{-4} \text{ s}^{-1} \), \( 10^{-3} \text{ s}^{-1} \), \( 3 \cdot 10^{-3} \text{ s}^{-1} \) and \( 10^{-2} \text{ s}^{-1} \). PMMA is also tested at strain rates of \( 3 \cdot 10^{-2} \text{ s}^{-1} \) and \( 10^{-1} \text{ s}^{-1} \).

To accurately control and measure the displacement of the compression plate, an extensometer (MTS 634.25F-25 SIN 1153324) is placed on the plates. This is shown in figure 2.2. The extensometer gives a more accurate output displacement signal, because the stiffness of the machine is no longer relevant. The accuracy of the system is enhanced from \( \pm 0.02 \text{ mm} \) of the compression tester alone, to \( \pm 0.001 \text{ mm} \) with the addition of the extensometer. The measured displacement of the extensometer is also used to regulate the imposed strain rate dependent displacement. The maximum displacement is set at –5 mm. The force signal of the compression is measured by a force cell, which is calibrated up to 15 kN. For safety reasons, the test is stopped when the measured force exceeds 14.5 kN, regardless of whether or not the maximum displacement is reached.

Not only are the experiments performed at different strain rates, but the temperature was varied as well. Compression tests on PMMA are carried out at 10°C, 23°C and 35°C, whereas PS is tested at 0°C, 20°C, 40°C, 60°C and 80°C. To keep the temperature constant at the...
desired value during an experiment, an environmental chamber (MTS 651 Environmental Chamber) is placed around the compression plates, see figure 2.3. The test specimens are put in the chamber for about 15 minutes prior to the test, to adapt to the temperature. The data-acquisition occurs at a certain frequency. The frequency is adjusted for each strain rate in order to obtain approximately 3000 points for each experiment. The output file contains columns of time, displacement and force. These latter two quantities are used to calculate the true stress and strain, which will be used as a reference for the numerical analysis.
Chapter 3

Theoretical background

The mechanical behaviour of glassy polymers strongly depends on time and temperature. This is caused by the molecular transitions. The most important of these transitions is the glass-transition or $\alpha$-transition, which is associated with the main-chain segmental motion. Polymers that exhibit only one transition (within a certain range on the time-temperature scale) are called thermorheological simple materials. Most polymers however exhibit one or more secondary transitions ($\beta$, $\gamma$-transitions) besides the glass transition. These are attributed to motion of side groups and/or end groups or to restricted motion of the main chain. This effect on the deformation behaviour is called thermorheological complex behaviour. The extent of the effect depends primarily on the relative positions of the transitions on the time and temperature scales. This chapter will deal with the constitutive model that is used to describe the deformation behaviour.

3.1 The compressible Leonov model

Numerical calculations are a useful tool to predict the response of the material under different loading conditions. This also requires an accurate constitutive model that describes the intrinsic behaviour of the material. There are several constitutive equations available at present. The choice of the best suitable model depends on the properties that need to be predicted. Haward and Thackray [3] developed a one-dimensional model that accounted for strain rate dependency of the yield point and for the strain hardening. They used a linear spring to describe the initial elastic response and a so-called “Langevin-spring” to account for the strain hardening. The yield point was determined by a non-linear dashpot with a stress dependent Eyring viscosity [4]. Boyce et al [5] modified this model to three dimensions using the Argon theory and the three-chain model. This lead to the BPA model. The model was then modified with regards to the strain hardening response [6, 7] and rejuvenation is added [8]. More recently Tervoort [9] formulated a three dimensional model for non-linear viscoelastic behaviour. This model is commonly referred to as the compressible Leonov model. The big advantage of this model is that it can easily be extended to a spectrum of relaxation times, using a multi-mode model. This model thus also covers the non-linear viscoelastic response before yield.

It has been shown that a single Leonov mode can well be used to describe thermorheological simple behaviour [9, 10], but it will become clear that adaptations are needed to predict thermorheological complex behaviour. This will be discussed in the next sections. In this section the object is to gain more insight in the basic compressible Leonov model. A schematic 1-D representation of this model is given in figure 3.1. In this model $G$ describes the initial elastic response, while the yield point is determined by the stress dependent viscosity $\eta$, and the strain hardening response follows from $G_r$.

![Figure 3.1: 1-D representation of the compressible Leonov model](image)

A distinction is made between the contribution of secondary interactions between polymer chains that determine the viscoelastic properties at small deformations and yield behaviour, and the entanglement network that governs the large strain behaviour. The total Cauchy stress
tensor is therefore composed of a driving stress tensor \( s \) and a hardening stress tensor \( r \), according to

\[
\sigma = s + r \tag{3.1}
\]

The hardening stress is related to the total deformation of the polymer. The equation that defines the hardening tensor \( r \) is based on a Gaussian approach that leads to the following neo-Hookean relation

\[
r = G_f \tilde{B}^d \; \text{; with} \quad \tilde{B} = J_e^{-\frac{3}{2}}F \cdot F^c \tag{3.2}
\]

in which \( G_f \) is the hardening modulus, \( F \) is the deformation gradient tensor and \( \tilde{B} \) is the isochoric left Cauchy Green deformation tensor, with the superscript \( d \) indicating the deviatoric part of the tensor. The driving stress tensor \( s \) is divided in a hydrostatic part \( s_h \) and a deviatoric part \( s_d \). The driving stress is subsequently formulated according to

\[
s = s_h + s_d = K(J_e - 1)I + G\tilde{B}_e^d \tag{3.3}
\]

In this equation \( K \) and \( G \) are the shear modulus and the bulk modulus respectively. These moduli can be derived from the elastic material parameters \( E \) (Young’s modulus) and \( v \) (Poisson ratio) with

\[
K = \frac{E}{3(1-2v)} \quad ; \quad G = \frac{E}{2(1+v)} \tag{3.4}
\]

Furthermore, \( J_e \) is the elastic (indicated by the subscript \( e \)) volume change factor and \( \tilde{B}_e \) is the isochoric elastic left Cauchy Green deformation tensor. These are represented by

\[
J_e = J_e \text{tr}(D - D_p) \tag{3.5}
\]

\[
\tilde{B}_e = (D^d - D_p) \cdot \tilde{B}_e + \tilde{B}_e \cdot (D^d - D_p) \tag{3.6}
\]

where \( \tilde{B}_e \) is the objective Jaumann derivative of \( \tilde{B}_e \). \( D_p \) is the plastic rate of deformation tensor, expressed in the deviatoric part of the driving stress tensor \( s^d \) by using a three-dimensional non-Newtonian flow rule with a stress dependent Eyring viscosity, according to

\[
D_p = -\frac{s^d}{2\eta(\tau_{eq}, D)} \tag{3.7}
\]

The viscosity \( \eta \) can be formulated with the use of a generalised Eyring equation (see appendix A), in which the strong dependence of \( \eta \) on the equivalent stress \( \tau_{eq} \) becomes clear. The model was extended to adopt intrinsic strain softening \( D \) and pressure dependence \( \mu \) [11]. However, the latter does not fall within the scope of this thesis, since we only deal with compression and it is therefore discarded from the viscosity function.

\[
\eta = \eta(\tau_{eq}, D, T) = A(D, T)\tau_0 \frac{\tau_{eq}/\tau_0}{\sinh(\tau_{eq}/\tau_0)} \tag{3.8}
\]
in which the equivalent stress $\tau_{eq}$ is defined as a function of the deviatoric part of the driving stress:

$$\tau_{eq} = \sqrt{\frac{1}{2} \text{tr}(s^d \cdot s^d)},$$  \hspace{1cm} \text{(3.9)}

$A$ and $\tau_0$ are material parameters. The characteristic stress $\tau_0$ is dependent on the activation volume $V^*$ and the temperature (equation 3.10). The time constant $A$ is related to the temperature and to the activation energy $\Delta H$.

$$\tau_0 = \frac{RT}{V^*}$$  \hspace{1cm} \text{(3.10)}

$$A(D, T) = A_0 \exp\left(\frac{\Delta H}{RT}\right) \exp(-D)$$  \hspace{1cm} \text{(3.11)}

where $A_0$ is a constant pre-exponential factor, $R$ is the gas constant and $T$ is the absolute temperature. The evolution of the softening is defined by the softening parameter $D$, which is initially set to zero and then grows to the softening limit $D_\infty$ according to

$$\dot{D} = h \left(1 - \frac{D}{D_\infty}\right) \dot{\gamma}_{eq} \rightarrow D = D_\infty \left[1 - \exp\left(-\frac{h \gamma_{eq}}{D_\infty}\right)\right]$$  \hspace{1cm} \text{(3.12)}

Herein is $h$ a material constant describing the relative softening rate and $\dot{\gamma}_{eq}$ is the equivalent strain rate. In this equation, it is assumed that during and after yielding the equivalent plastic strain rate equals the equivalent strain rate and that the strain rate is constant. The equivalent strain rate $\dot{\gamma}_{eq}$ is described by

$$\dot{\gamma}_{eq} = \sqrt{2 \text{tr}(\mathbf{D}_p \cdot \mathbf{D}_p)}$$  \hspace{1cm} \text{(3.13)}

Equation 3.13 can be combined with equations 3.7 and 3.9 to

$$\dot{\gamma}_{eq} = \frac{\tau_{eq}}{\eta(\tau_{eq}, D)}$$  \hspace{1cm} \text{(3.14)}

Linking this relation up with equation 3.8, the Eyring formula for the equivalent strain rate as a function of the equivalent stress can be deduced:

$$\dot{\gamma}_{eq} = \frac{1}{A} \sinh\left(\frac{\tau_{eq}}{\tau_0}\right)$$  \hspace{1cm} \text{(3.15)}

If the argument of the hyperbolic sine is large, it can be replaced by an exponential function. For the equivalent stress as a function of the equivalent strain rate the following equation can be found

$$\tau_{eq} = \tau_0 \left(\ln 2A \dot{\gamma}_{eq}\right)$$  \hspace{1cm} \text{(3.16)}
This equation can be used to fit the parameters $A_0$ and $\tau_0$ on the experimental data in a $\tau_{eq,yield}$ versus $\dot{\gamma}_{eq}$ graph. The parameters thus obtained can be used in the numerical approach of the stress strain curves. This is done by a program that solves five non-linear differential equations. Boundary conditions used here are homogeneous deformation, uniaxial compression and axisymmetry. With the start values of the requested parameters, the true stress is calculated. The results of the calculations are compared to the experimental results and adaptations of the parameters are made if necessary.

3.2 Validation of the model

Several attempts have been made to validate the compressible Leonov model for different materials. Some previously obtained results will be discussed hereafter.

3.2.1 Polycarbonate

Polycarbonate (PC) was modelled using the single mode compressible Leonov model, which provided a very good description of the yield and post-yield behaviour [12, 13]. The results are shown in figure 3.2, with the parameters that were used for those results shown in table 3.1. The material parameters consistent with the model were determined for strain rates in the range between $1 \cdot 10^{-4}$ and $1 \cdot 10^{-2}$ s$^{-1}$ at a constant temperature. It was observed that the strain hardening was independent of strain rate. Furthermore a linear relationship between the equivalent yield stress and the equivalent logarithmic strain rate could be determined, consistent with earlier measurements [14]. The rejuvenated stress showed the same linear course. These observations lead to a constant yield drop within the measured range of strain rates (figure 3.3).

![Figure 3.2: Fitting of compression tests of PC](image1)

![Figure 3.3: Yield stress and rejuvenated stress of PC](image2)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ [MPa]</td>
<td>700</td>
</tr>
<tr>
<td>$\nu$ [-]</td>
<td>0.37</td>
</tr>
<tr>
<td>$A_0$ [s]</td>
<td>$9 \cdot 10^{-24}$</td>
</tr>
<tr>
<td>$\tau_0$ [MPa]</td>
<td>0.64</td>
</tr>
<tr>
<td>$h$ [-]</td>
<td>155</td>
</tr>
<tr>
<td>$D_\infty$ [-]</td>
<td>55</td>
</tr>
<tr>
<td>$G_\infty$ [MPa]</td>
<td>44</td>
</tr>
</tbody>
</table>

*Table 3.1: Fit parameters of PC [13]*
3.2.2 Applicability to other polymers

It has been tried to model other polymers as well with the compressible Leonov model, with less promising results. Polymethylmethacrylate (PMMA) for instance does not exhibit a linear relationship between yield stress and logarithmic strain rate (figure 3.4) [15]. At low temperatures and high strain rates, the yield stresses increase more rapidly with increasing strain rate. This change in slope can be explained by the presence of a second ($\beta$) transition. The yield stress as a function of the strain rate is composed of the contribution of two processes. At low strain rates the $\beta$-process is not present yet and when at higher strain rates both processes are to be accounted for, a change in slope is observed. This phenomenon is visualised in figure 3.5 The strain rate independence of the post-yield behaviour, reflected in the softening and the hardening, does not apply [16]. Similar behaviour is observed for PVC, which exhibits a well-known secondary transition in the plastic deformation range [14]. The Ree-Eyring modification of the Eyring theory was used to describe the yield data. From these data a master curve of yield stresses was produced using a shift factor with two components. A shift along the horizontal axis as in the time-temperature-superposition principle is not possible, due to the fact that the yield stress depends on two processes. Polystyrene [16, 17] exhibits similar yield and post yield behaviour as a function of the strain rate. Strikingly, a rise in yield stress is also observed for polystyrene at elevated temperatures. This implies that for higher temperatures the compressible Leonov model is no longer valid. These materials exhibit thermorheological complex behaviour and require adjustments of the compressible Leonov model to be accurately modelled. These adjustments will be discussed in the next section.

![Figure 3.4: Yield stress behaviour of PMMA [15]](image)

![Figure 3.5: Composition of the yield stress](image)

3.3 Extension to thermorheological complex behaviour

Thermorheological complex behaviour is used to describe polymers that exhibit at least two molecular mechanisms, which presents difficulties in modelling the stress strain relation. Instead of just one process, two (or more) processes need to be taken into account to obtain a reliable prediction of the deformation behaviour of the material [19]. In the 1-D representation of the Leonov model, as it was shown in figure 3.1, a modification has to made to account for the extra process(es) [20]. This is shown in figure 3.6 for a material with one secondary transition.
This modification has its main effect on the formula that describes the driving stress (equation (3.3)). The deviatoric part of this tensor now consists of an α and a β part. This means that the total driving stress is altered into:

\[ s = K(J_e - 1)I + G_\alpha \tilde{B}_{e,\alpha}^d + G_\beta \tilde{B}_{e,\beta}^d \]  

(3.17)

The same strategy that was used for just one process can be employed here as well, except for the fact that most calculations have to be done twice: for both the α- and the β-processes. Since there are two isochoric elastic left Gauchy Green tensors in the driving stress equation, they both need to be determined according to

\[ \tilde{B}_{e,k} = (D^d - D_{p,k}) \cdot \tilde{B}_{e,k} + \tilde{B}_{e,k} \cdot (D^d - D_{p,k}), \quad k = \alpha, \beta \]  

(3.18)

Most equations that were discussed in the previous section require similar adaptations and will not be treated here. The most important equations however, those that are directly needed to determine the fitting parameters, will be shortly dealt with. The total viscosity is now formulated according to

\[ \eta = A_\alpha \tau_{0,\alpha} - \frac{\tau_{eq,\alpha}}{\sinh(\tau_{eq,\alpha}/\tau_{0,\alpha})} + A_\beta \tau_{0,\beta} \frac{\tau_{eq,\beta}}{\sinh(\tau_{eq,\beta}/\tau_{0,\beta})} \]  

(3.19)

with

\[ A_k = A_{0,k} \exp\left(\frac{\Delta H}{RT}\right) \exp(-D_k) \]  

(3.20)

and

\[ D_k = D_{\alpha,k} \left[ 1 - \exp\left(\frac{-h_k \gamma_{eq}}{D_{\alpha,k}}\right) \right] \]  

(3.21)

The equivalent strain stress is an addition of α- and β-processes and becomes

\[ \tau_{eq} = \tau_{0,\alpha} \left( \ln 2 A_\alpha \gamma_{eq} \right) + \tau_{0,\beta} \left( \ln 2 A_\beta \gamma_{eq} \right) \]  

(3.22)

These equations are used directly or indirectly to acquire a set of parameters that accurately describes the deformation behaviour of polymethylmethacrylate and polystyrene. This is done by comparing the numerical results to the measured data.
Chapter 4

Validation for Polymethylmethacrylate

4.1 Experimental results

As was mentioned in chapter 2, the compression tests are performed at different strain rates and different temperatures. The effect of strain rate dependence is shown in figure 4.1, where the |true stress| versus |logarithmic strain| graph at constant temperature is depicted. Figure 4.2 emphasises the temperature dependence by showing the |σ<sub>true</sub>| versus |ln(λ)| curves of the compression tests at two strain rates at different temperatures.

From these graphs a few things can be noted. The strain hardening of PMMA shows some surprising features. To start with, the strain hardening of PMMA is not constant, but increases with increasing strain rate and decreasing temperature, so \( G_\varepsilon = G_\varepsilon(\dot{\varepsilon}, T) \). Moreover, at high strain rates the yield drop is larger than expected and the softening and hardening collapse, which is even more apparent at lower temperatures (see appendix A). An explanation for this phenomenon is that a thermal softening effect is present, due to internal heat generation [21]. At high strain rates, the generated heat does not have time to dissipate into the environment, causing the internal temperature of the sample to rise above the desired temperature. For this reason, the curves with strain rate \( \dot{\varepsilon} = 10^{-1} \text{ s}^{-1} \) and \( \dot{\varepsilon} = 3 \cdot 10^{-1} \text{ s}^{-1} \) (not shown in figure 4.1) are discarded from the numerical analysis. The values of the equivalent yield stress of these curves are nevertheless used to obtain more accurate values for the yield parameters. This is allowed because the heating has not yet commenced at the yield stress. From the data of each measurement the equivalent stress at the yield points, as well as the equivalent strain rate, are calculated. The equivalent yield stress is divided by the temperature and is plotted as a function of the equivalent strain rate in figure 4.3. The fitting lines, calculated with the use of equation 3.22, are also shown. These fitting lines clearly show a change of slope in accordance with the knowledge that PMMA exhibits two processes. The fit parameters at yield are also determined with the use of the Eyring equations as described in chapter 3 and appendix A. The values of the fit parameters thus found are displayed in table 4.1.
From these values \( A_{0,p} \) and \( \tau_{0,p} \) (with \( p=\alpha, \beta \)) can be easily determined with the following equations

\[
A_{0,p} = \left( \dot{\varepsilon}_{0,p} \exp \left( \frac{-\Delta H_p}{RT} \right) \right)^{-1} \quad \text{and} \quad \tau_{0,p} = \frac{RT}{V^*_p}
\]  

(4.1)

Here is \( A_0=A_0(T) \) and \( R \) is the gas constant, \( V^* \) is the activation volume, \( \Delta H \) the activation energy, \( T \) the absolute temperature and \( \dot{\varepsilon}_0 \) is the characteristic strain rate. It must be noted that in determining the yield parameters the hardening contribution is still present. This means that \( A_{0,\alpha} \) and \( A_{0,\beta} \) will need to be adjusted in the numerical analysis. The values obtained above are indications only and can be used as starting values, but need to be corrected to result in an optimal simulation. This and more concerning the numerical approach will be discussed in paragraph 4.2.

The yield drop is calculated for all measurements and the accompanying results are shown in figure 4.4. The strain softening is constant at first, but increases at higher strain rates. This increase of the yield drop is caused by the fact that the yield stress is not linearly dependent on the strain rate, but it shows the characteristic change of slope that can be seen in figure 4.3. The rejuvenated stress does not exhibit this change in slope, thus causing the rise of yield drop. This phenomenon is depicted in figure 4.5, where only the measurements done at 10°C are represented because of the enhanced clarity.
4.2 Fitting Procedure

4.2.1 One process

The numerical modelling of PMMA starts with determining the $\alpha$-parameters in the lower strain region of the stress strain curve at constant temperature. The $\alpha$ region can be determined more accurately from the Eyring fit (figure 4.3), where the change in slope represents the transition between the two processes. In this region the softening is essentially strain rate independent. In this case the initial determination of the parameters was done for the 35°C stress strain curve. At first softening is neglected, so $h_\alpha=0$. This way the yield point of the simulation can be accurately placed on the measured yield point by altering the modulus $E_\alpha$ and the previously determined pre-exponential factor $A_{0,\alpha}$. After this the strain hardening parameter $G_r$ is determined by calculating the slope at the end of the experimental curve. Adding $G_r$ to the $\alpha$-region causes the computed yield point to shift vertically and this has to be corrected by altering $A_{0,\alpha}$. Both the yield and the hardening parameters are now determined, which leaves the part in between these areas: the softening. Accordingly the $\alpha$ softening parameters $h_\alpha$ and $D_{\infty,\alpha}$ are added, which may again lead to a correction of $A_{0,\alpha}$. Knowing that $h_\alpha$ describes the slope with which the curve descends and $D_{\infty,\alpha}$ describes the size of the yield drop (visualised in figure 4.6), the curve can be completed. The same strategy is followed for the rest of the temperatures as well, but with the restriction that the parameters are temperature dependent. The $\alpha$ parameters therefore have to be chosen with care. They are shown in table 4.2, with the matching curves shown in figure 4.7.
To determine the $\beta$ parameters, a similar strategy is followed. Still concerned with just one temperature, the whole range of strain rates is now looked at, including the higher strain rates, observed after the change of slope in figure 4.3. Once again, the modulus and yield parameters are determined to fit the yield points without softening present ($h_\alpha = h_\beta = 0$). The strain hardening is already computed and needs no more alteration. The $\beta$ modulus $E_\beta$ has to be determined by looking just at the $\beta$ process and shifting the yield point along the strain rate axis. When the $\beta$ yield point is placed on the same value of the strain rate as the $\alpha$ yield point, the $\beta$ modulus can be determined. This way the total yield point is fixed more accurately,
because it is prevented that the $\beta$ softening sets in too early and interferes with the determination of the yield point. This procedure is done for just one strain rate, which may give some problems at higher strain rates, which will be discussed in paragraph 4.2.3. Softening is added, using in a first approximation that $h_{\alpha}=h_{\beta}$ and $D_{\infty,\alpha}=D_{\infty,\beta}$ and then adjusted so that a complete fit is realised. This procedure is then repeated for all temperatures, but with some limitations. Most parameters for instance are temperature dependent, so their values have to be chosen with care and need to fit in a greater perspective. This may mean that the parameters that were found for the initial temperature (35°C) may need to be altered once more. The accordingly found parameters are registered in table 4.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>10°C (283K)</th>
<th>23°C (296K)</th>
<th>35°C (283K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ [MPa]</td>
<td>400</td>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td>$A_0$ [s]</td>
<td>100</td>
<td>58</td>
<td>36</td>
</tr>
<tr>
<td>$\tau_0$ [MPa]</td>
<td>4.84</td>
<td>5.06</td>
<td>5.27</td>
</tr>
<tr>
<td>$h_\beta$ [-]</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$D_{\infty}$ [-]</td>
<td>14</td>
<td>11</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 4.3: $\beta$ fit parameters of PMMA

The fitting lines that came out of these sets of parameters are plotted on the measured data for all temperatures in figure 4.8. From table 4.3 it becomes clear that most parameters are linearly dependent of the temperature, except for $h_{\beta}$, which is constant. Since figure 4.8 shows a relatively inaccurate fit of the $\beta$ softening, it has been tried to change those parameters to obtain a better fit. With the program presently used this was not possible. It did become clear that there are several sets of parameters that can describe the compression tests to some degree of accuracy. The adopted set showed the most promising results.

![Figure 4.8: Comparing the fitted stress strain curves (black) of PMMA with the measured data (red), strain rates are $10^{-4}$, $3 \cdot 10^{-4}$, $10^{-3}$, $3 \cdot 10^{-3}$ $10^{-2}$ and $3 \cdot 10^{-2}$](image)
Figure 4.8 shows that for all temperatures, the first part of the stress strain curve, up to the yield stress looks fairly well. The magnitude of the yield stress is described very well for all temperatures and strain rates, but in the fitted curves the yield stress is reached at lower strains than in reality. At the yield point the fitting line is also a bit more pointed than the measured curve. Using strain hardening behaviour that only depends on temperature gives very good results, except for the stress strain curves for 10°C at higher strain rates. However, that can partly be explained by the thermal softening effect, as mentioned in paragraph 4.1. The yield drop is the biggest problem when determining the fit parameters. The slope of the strain softening is defined quite nicely for all measurements. The amount of yield drop at lower strain rates, with just one process in play, can be modelled reasonably well, but for higher strain rates, deviation is observed. The yield drop of the computed curves is in this part significantly lower. Thermal effects cause this deviation and adding these effects to the numerical calculations will improve the simulation [22]. As mentioned before, most parameters are temperature dependent, including $A_0$, whose temperature dependence is shown in figure 4.9. It can be seen that $A_0$ is a linear function of the reverse temperature for both the $\alpha$ and the $\beta$ process. This is different for the modulus, where $E_\alpha$ increases for increasing temperature, while $E_\beta$ decreases. This can be explained by the fact that a single mode approach was employed. Using a multi-mode approach will lead to an adjustment of the modulus, thus obtaining a more logical course.

4.2.3 Examples of the predicted behaviour

In figures 4.4 and 4.5 the strain softening behaviour of the experimental results was depicted. It showed that the yield drop was constant for low strain rates, but started to increase for higher strain rates. The numerical model was used to predict what will happen when the strain rate was increased more. The results for 23°C are shown in figure 4.10 where at once it becomes clear that the yield drop becomes constant again for very high strain rates. This can be explained with an analysis of the yield stress and rejuvenated stress, which are visualised in figure 4.11. The experimental results already showed a change of slope of the yield stress and it now becomes clear that the rejuvenated stress shows a similar change, but at a higher strain rate, beyond the reach of the measured strain rates. The graphs can now be divided in three areas: at low strain rates where the yield drop is constant; a second area at medium strain rate where the yield drop increases; and a third section where the yield drop is once again constant, but higher than before.
The third section of figure 4.10 is not entirely constant, but decreases slightly. This is caused by a deflection of the modulus $E_\beta$, which was calculated as explained in paragraph 4.2.2. It was calculated for low strain rates, leading to a deflection of the high strain rates, as can be observed in figure 4.12.

Figure 4.10: Predicted yield drop of PMMA at 23°C

Figure 4.11: Predicted yield stress and rejuvenated stress of PMMA at 23°C

Figure 4.12: Numerical calculations of compression tests of PMMA at strain rates in the range from $3 \cdot 10^3$ to $3 \cdot 10^2$
Chapter 5

Validation for Polystyrene

5.1 Experimental results

The effect of strain rate dependence of PS is shown in figure 5.1, where the |true stress| versus |logarithmic strain| graph at constant temperature (40°C) is shown. Graphs of the compression tests at the rest of the temperatures are shown in appendix A. Figure 5.2 depicts a similar graph, but at constant strain rate.

In contrast with PMMA, the strain hardening of PS is constant. The yield drop is not constant, but increases with increasing strain rate and decreasing temperature. The true stress strain curves of PS at 0°C show strain localisation, indicating that the material is inhomogeneous. These measurements are therefore also not included in the numerical approach. Once again, the equivalent stress at the yield points, as well as the equivalent strain rate, are calculated according to equation 3.6. The equivalent yield stress is divided by the temperature and is plotted as a function of the equivalent strain rate in figure 5.3. The fitting line, calculated with the use of equation 2.22, is also shown.

From figure 5.3 it becomes clear that the change of slope of the fitting line, characteristic of a multi-process material, is much less pronounced. At 40°C and 60°C a slight change of slope can be observed, but at 20°C and 80°C the fitting line follows a straight course. It can be seen
that the fitting lines at 20°C and 80°C are not parallel. The fitting line at 20°C runs parallel to the part of the 40°C and 60°C fits after the changing slope, at higher strain rates, while the fitting line at 80°C runs parallel to the first part, at lower strain rates. It must be noted that the compression tests of PS were performed over a smaller range in strain rate, which may explain why the change of slope of the 20°C and 80°C fits cannot be observed. The fit parameters at yield that result from this graph can be found in table 5.1.

<table>
<thead>
<tr>
<th>$R/V^*$ [MPa/K]</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.70 $\times$ 10$^{-3}$</td>
<td>3.80 $\times$ 10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$-\ln(\dot{\varepsilon}_0)$ [-]</td>
<td>45.79</td>
<td>34.59</td>
</tr>
<tr>
<td>$\Delta H / R$ [-]</td>
<td>2.11 $\times$ 10$^4$</td>
<td>1.28 $\times$ 10$^4$</td>
</tr>
</tbody>
</table>

Table 5.1: Determination of the yield parameters of PS

The yield drop of PS is also determined and depicted in figure 5.4. For 80°C the accompanying yield stress and rejuvenated stress versus strain rate curve is shown in figure 5.5. The softening of PS is strain rate dependent. The horizontal area at lower strain rates, as was observed for PMMA, is not present. Only the rising part in between the constant levels can be perceived. From figure 5.5 this course of the yield drop is not surprising, since it is obvious that the yield stress increases more steeply than the rejuvenated stress. The characteristic change of slope of the yield stress is not observed, which also became clear of figure 5.3. From the measured data it is not possible to draw a definitive conclusion about the further course of the softening. To be more definite and to examine the presence of the constant levels, additional experiments are required at lower and higher strain rates.

5.2 Fitting procedure

In the compression test graphs of PS it is much less obvious that there are two processes present, which manifested itself in the absence of the characteristic change of slope. This complicates the fitting procedure since there is no pure $\alpha$ region. Therefore the method to determine the fit parameters is a little different compared to PMMA. For PS, $\tau_{0,\alpha}$ as they were calculated from table 5.1 cannot be used directly, because these parameters are determined at the yield point, where in fact $\tau_{o,\alpha}$ hardly plays a role. The total $\tau_{0}$ is correct, but $\tau_{o,\alpha}$ and $\tau_{0,\beta}$ have to be determined anew while fitting the other parameters. The first step is to try to determine the yield parameters for just one process. This is done by fitting lines, without softening present, on the hardening part of the measured data at 20°C as shown in figure 5.6.
τ₀,α is now determined by the distance between the curves in the strain hardening region, which immediately gives τ₀,β since τ₀,β=τ₀,total-τ₀,α. Both moduli E₀ and G₀ are also determined, as well as A₀,α (rejuvenated). The second process is added, still without softening, to determine E₀,β and A₀,β. When the β softening parameters are introduced, A₀,p may again need some adjusting. It was assumed that there was no contribution of the α softening, so h₀,α=0. Adding α softening is possible, but h₀,α would have to be very small and this does not effect the fitting graph in a significant way. Making h₀,α and D₀,a too big will lead to a great deflection of the strain hardening, especially at higher strain rates.

For the rest of the temperatures τ₀,α and τ₀,β are already established from these parameters for 20°C according to equation 4.1. The other parameters are determined equally to the method described above. For 20°C and 40°C the parameters are shown in table 5.2 and the accompanying graphs are shown in figure 5.7.

<table>
<thead>
<tr>
<th></th>
<th>20°C (293K)</th>
<th>40°C (313K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₀ [s]</td>
<td>9.5·10¹²</td>
<td>4.0·10⁶</td>
</tr>
<tr>
<td>τ₀ [MPa]</td>
<td>1.30</td>
<td>2.07</td>
</tr>
<tr>
<td>E [MPa]</td>
<td>1500</td>
<td>800</td>
</tr>
<tr>
<td>D₀ [-]</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>h [-]</td>
<td>0</td>
<td>45</td>
</tr>
<tr>
<td>G₀ [MPa]</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 5.2: Fit parameters for PS

Notable in table 5.2 is that the E-modulus and the softening parameters are independent of the temperature. They appear to be material parameters and the differences measured at different temperatures solely depend on the yield parameters τ₀,p and A₀,p. Furthermore, the strain hardening modulus is low, which was to be expected from the measured data. The results obtained with these parameters are depicted in figure 5.7.
The numerical simulation defines the yield points very well. Both the height and the place on the strain axis are accurate. Likewise the strain hardening is well described. The problems that were noted when simulating PMMA can be observed for PS as well: the strain softening is the most difficult part to describe accurately. For PS, the $\alpha$ softening plays no role and the $\beta$ softening is hard to define properly. Adding $\alpha$ softening is arbitrary and does not lead to any improvement. Adjusting the kinetics may refine the results. For low strain rates the calculated yield drop follows the measurements, but when the strain rate increases the difference in calculated and measured yield drop grows. By adjusting the value of $D_{\alpha,\beta}$ accurate calculations at higher strain rates can be obtained. However, this also leads to deflections at lower strain rates.

It was mentioned in chapter 2 that measurements on PS were also performed at 60°C and 80°C. Numerical simulations are also carried out on those curves, which lead to some surprising results. The calculated and measured curves at 60°C are depicted in figure 5.8. It is obvious that $\tau_{0,\alpha}$ and $\tau_{0,\beta}$ are too big, which leads to a big deviation at the yield points and at the strain hardening. It implies that the characteristic stresses become smaller for increasing temperature, which is in conflict with equation 4.1. An explanation for this behaviour is that PS exhibits a third ($\gamma$-) transition, which does not become directly clear within the range of the measurements. Therefore a third process should be added to the Leonov model, which amounts to an extra set of $\gamma$ parameters that has to be determined. However, this goes beyond the scope of this thesis, and will not be dealt with here.
Chapter 6

Conclusions

In this report strain rate and temperature dependence of polymers in compression was investigated. The results were compared to a constitutive model and the model parameters were determined.

The compression tests show that the measurements at high strain rates are less accurate due to internal heat generation. For PMMA the characteristic change of slope of the yield stress can be easily determined from the measurements. PS however exhibits a much less obvious second process. The measured yield drop is not strain rate independent as is the case with thermorheological simple behaviour. Instead, a change of slope is observed for PMMA and a linear strain rate dependency for PS.

The numerical results of PMMA are promising. The measured compression behaviour can be very well described, especially the yield stress and strain hardening. The $\alpha$-softening is also accurate, but the $\beta$-softening needs to be improved. Running the program for a wider range of strain rates than was measured lead to an explanation of the strain rate independence of the yield drop. Not only shows the yield stress a characteristic change of slope, but at higher strain rates the rejuvenated stress shows the same behaviour. This leads to two areas of constant yield drop, connected by an area where the yield drop increases linearly. It is mentioned that the strain rate independent strain hardening describes the compression behaviour well. However, since the strain hardening actually is strain rate dependent, further analysis is required to acquire more accurate calculations.

The numerical analysis of PS shows that PS is difficult to describe with the presently used Leonov model, especially at higher temperatures. This can be explained by the presence of a third transition. It is therefore of importance to find a way to execute the compression tests at higher strain rates and to adapt the numerical program to append the third process. As it is now, the model seems roughly adequate for lower temperatures, although the $\beta$-softening shows some deviation. Apart from reviewing and possibly improving the numerical analysis of the $\beta$-softening, adding a third process would improve these graphs as well. The addition of a third process needs to be verified experimentally. It is therefore necessary to improve the homogeneity of the test specimens, which can be done by adjusting the dimensions or by improving the heat treatment.
References


[22] E.T.J. Klompen, personal communication
Appendix A

Eyring equations

From Ward [1] it shows that

\[ \dot{\gamma}_{eq} = \dot{\gamma}_0 \exp\left(-\frac{\Delta H}{RT}\right) \sinh\left(\frac{\tau V}{RT}\right) \]  
(A.1)

\[ \dot{\gamma}_{eq} = \frac{1}{A} \sinh\left(\frac{\tau_{eq}}{\tau_0}\right) \]  
(A.2)

From which follows

\[ A = \frac{1}{\dot{\gamma}} \exp\left(\frac{\Delta H}{RT}\right) = A_0 \exp\left(\frac{\Delta H}{RT}\right) \]  
(A.3)

\[ \tau_0 = \frac{RT}{V} \]  
(A.4)

This leads to the following equivalent stress as a function of the equivalent strain rate:

\[ \tau_{eq} = \tau_0 \sinh^{-1}\left(A \dot{\gamma}_{eq}\right) \]  
(A.5)

For high equivalent strain rates this becomes

\[ \tau_{eq} = \tau_0 \ln(2A \dot{\gamma}_{eq}) = \tau_0 \ln(2A) + \tau_0 \ln(\dot{\gamma}_{eq}) \]  
(A.6)

This shows that for high equivalent strain rates the equivalent stress is linearly dependent of the logarithmic equivalent strain rate.
Appendix B

Compression test results

Figure B.1: Compression tests of PMMA at 10°C

Figure B.2: Compression tests of PMMA at 23°C

Figure B.3: Compression tests of PS at 0°C

Figure B.4: Compression tests of PS at 20°C

Figure B.5: Compression tests of PS at 60°C

Figure B.6: Compression tests of PS at 80°C
Samenvatting

Op de Technische Universiteit Eindhoven wordt onderzoek verricht om het mechanisch gedrag van polymeren beter te begrijpen en te voorspellen. Om dit te bereiken wordt gebruik gemaakt van mechanische experimenten en numerieke simulaties en berekeningen. Een van de doelstellingen in dit onderzoek is het gedrag van amorphe polymeren in compressie proeven. In dit verslag wordt het compressiegedrag van twee amorphe polymeren, te weten Polymethylmethacrylaat (PMMA) en Polystyreen (PS) gemeten. Deze materialen zijn gekozen omdat ze thermorheologisch complex gedrag vertonen. Dit betekent dat deze polymeren naast de glasovergang een tweede moleculaire overgang hebben. De compressie proeven worden verricht bij verschillende reknlheden en temperaturen om de invloed van deze testparameters te bepalen. De resultaten van de compressie testen worden vergeleken met numerieke berekeningen. Deze berekeningen maken gebruik van een constitutief model dat het intrinsieke gedrag van de materialen beschrijft. Het constitutieve model dat in dit verslag is gebruikt is het compressibele Leonov model. Dit model is uitgebreid zodat het geschikt is voor materialen met twee overgangen. Verschillende parameters zijn bepaald om de numerieke analyse over de experimentele resultaten te leggen. Op deze manier kan het compressieve gedrag worden voorspeld over een groter bereik van temperaturen en reknelheden. De resultaten kunnen informatie geven over de materialen als ze in gebruik zijn genomen. De numerieke berekeningen komen goed overeen met de experimentele resultaten van PMMA, maar vertonen afwijkingen bij PS. Een mogelijke verklaring kan zijn dat PS een derde overgang vertoond, hetgeen niet verwerkt is in het gebruikte constitutieve model.