Computational Mechanics

Deformation Behaviour of Glassy Polymers
Consequences of thermorheological complex behaviour

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Summary

To improve the mechanical performance of a polymer material, a thorough understanding of the relation between the deformation behaviour and the underlying molecular processes can be of great importance. Generally, polymer physics only provides a link between molecular mechanisms and the deformation behaviour for a specific range of deformation, for example, linear viscoelasticity. Therefore, a constitutive model correctly describing the entire range of deformation behaviour (linear viscoelastic, nonlinear viscoelastic and plastic deformation) could be used to identify the contribution of a specific molecular process to the remaining deformation ranges. The knowledge which process contributes to a particular loading situation can be of help, either in optimizing the molecular structure to suit the loading situation, or in the decision on the relevance of a contribution, allowing for a well-founded simplification of the constitutive relation.

To gain this understanding, a material, polycarbonate, with only a single (active) molecular mechanism is selected as a model material. Using this thermorheological simple material, a constitutive model based on time-stress superposition is derived. This principle states that all relaxation times are influenced in the same way by the total applied stress, comparable to the time-temperature superposition principle where all relaxation times are the same function of temperature. The influence of stress is quantitatively described by the Eyring theory of nonlinear flow. The applicability of time-stress superposition is demonstrated for the model material, showing an excellent agreement between the stress nonlinearity obtained from time-stress superposition and the nonlinearity obtained from yield experiments. Furthermore, it is demonstrated that the complete deformation behaviour up to yield is determined by the linear relaxation/retardation time spectrum combined with a single nonlinearity parameter, which is governed by the activation volume $V^\star$.

Since the majority of polymers exhibits at least two molecular processes, the approach is extended to account for an additional process. Based on linear viscoelastic theory, this extension could be achieved, either by adding a process in parallel, or in series. Experiments in the range of plastic deformation suggested, however, an approach based on stress additivity, that is, two molecular processes in parallel. The resulting model consisted of two linear relaxation time spectra in parallel, each having its own characteristic stress and temperature dependence.
Whereas in the case of a single process the influence of stress and temperature was comparable, this is no longer true for two processes since the molecular processes only depend on a part of the total stress rather than on the total stress itself. Numerical predictions using the extended representation showed that the model correctly describes the yield behaviour observed in practice. Simulations of creep experiments at various stress levels and temperatures showed a good qualitative agreement with experimental observations in literature.

In material characterization, it is commonly assumed that material parameters are constant. Polymer glasses are, however, nonequilibrium thermodynamic systems, which, in the course of time, attempt to reach equilibrium. This process is termed physical aging, and manifests itself in a decrease of volume and an increase of relaxation times with time. The effects of physical aging can be erased by applying a thermal or mechanical load. The latter is usually referred to as mechanical rejuvenation, and causes a decrease of the relaxation times. Since, neither physical aging, nor mechanical rejuvenation were taken into account in the modeling, deviations can be expected with respect to aging and non-monotone loadings. In the final part of this report, both physical aging and mechanical rejuvenation are addressed. It is hypothesized that the effects of these phenomena are not equally distributed over the total relaxation time spectrum, whereas in the classical approach it is assumed that all relaxation times are affected in a similar manner.
Notation

Tensorial Quantities

\( \alpha, a, A \) scalar
\( a, A \) vector
\( \alpha, A \) second order tensor
\( \alpha, A \) fourth order tensor

Operations and functions

\( ab, AB \) dyadic product
\( a \cdot b, A \cdot B \) inner product
\( A : B \) double inner product
\( A^T \) transposition
\( A^{-1} \) inversion
\( \text{tr}(A) \) trace
\( \det(A) \) determinant
\( I_A \equiv \text{tr}(A) \) first invariant of \( A \)
\( II_A \equiv \frac{1}{2}(I_A^2 - \text{tr}(A \cdot A)) \) second invariant of \( A \)
\( III_A \equiv \det(A) \) third invariant of \( A \)
\( A^d = A - \frac{1}{3} \text{tr}(A)I \) deviatoric part of \( A \)
\( \dot{A} \) material time derivative of \( A \)
\( A \) Jaumann (co-rotational) derivative of \( A \)
\( \nabla \) Truesdell (upper-convected) derivative of \( A \)
\( \text{div}(a) \) divergence of \( a \)
Chapter 1

Introduction

1.1 General Introduction

Over the last decade, considerable attention has been directed towards the development of constitutive relations for polymeric materials. The background for these activities is generally the wish to predict the material behaviour during processing as well as the mechanical performance of the final product. The development of such numerical tools gives the possibility to detect difficulties in production and design in advance, thus offering the opportunity to correct these and optimize processing parameters and design. The choice of the constitutive equation that is best applicable should follow after a thorough consideration of the properties that have to be predicted.

In materials technology, constitutive relations also come to hand as an aid in improving material properties. A good example is the work of van der Sanden (1993), who blended brittle polymers with non-adhering core-shell rubbers, thus creating a microstructure consisting of a matrix with small holes. He showed that with an increasing volumefraction of holes a change in failure mode from crazing to shearing could be obtained, thus tremendously improving the impact performance of the material. To avoid a trial-and-error-like process, it is of importance to gain better understanding of what actually happens on a microscale. Numerical calculations combined with a suitable constitutive equation could provide this understanding. Moreover, it could also offer a tool to determine the optimum number and dimensions of the holes: microstructural optimization.

Another point of view is given by polymer physics as it provides numerous links between, for example, temperature dependence or linear viscoelastic deformation, and the molecular processes present in polymer materials. Since constitutive equations relate different loading situations, it is also possible to assign aspects of, for example, nonlinear deformation to a specific molecular process. This gives the opportunity to adjust the mechanical behaviour by influencing the molecular
processes, for example, by altering the molecular structure of the material. An excellent example of this is Carilon®, a terpolymer of carbon monoxide, ethylene, and propylene (Wakker et al., 1995), which can be given different types of mechanical behaviour by changing the catalyst system, and thus the molecular configuration: molecular optimization.

Understanding which molecular process is responsible for a specific mode of deformation also aids in the process of choosing the best applicable constitutive relation, since based on a thorough fundamental understanding it can simply be established whether, in a given situation, the contribution caused by a specific process is relevant or not.

### 1.2 Deformation Behaviour

In describing the deformation behaviour of solid polymers, a distinction is usually made between three stages (Figure 1.1): firstly, the linear viscoelastic regime at low stress, secondly, at intermediate stresses the nonlinear viscoelastic response, and finally the yield behaviour at high stress (Ward, 1983). In the following subsections, a short review will be given of constitutive models used in each of these stages.

**Figure 1.1:** The three different stages in the deformation behaviour up to yield.

#### 1.2.1 Linear Viscoelastic Deformation

*Constitutive models*

Linear viscoelastic deformation is usually described using linear response theory, which results in the well-known Boltzmann single integral representation (Ferry, 1980; Tschoegl, 1989). Depending on the quantity that has to be described, the
1.2 Deformation Behaviour

Boltzmann integral can assume two different forms, (i) a relaxation form, and (ii) a retardation form:

(i) \( \sigma(t) = \int_{-\infty}^{t} E(t - t')\dot{\varepsilon}(t')dt' \) \( \text{and (ii)} \) \( \varepsilon(t) = \int_{-\infty}^{t} D(t - t')\dot{\sigma}(t')dt' \)

Each of these two forms supplies a stress-strain relation that is capable of predicting the deformation behaviour in any, stress and/or strain prescribed situation, thus in theory, either representation can be used. For practical situations however, the relaxation form is preferred in deformation prescribed situations, whereas the retardation form is used in stress prescribed situations.

**Viscoelastic Functions**

The characteristics of the deformation behaviour, described by the linear stress-strain relations shown previously, are governed by the viscoelastic functions, stress relaxation modulus \( E(t) \), and creep compliance \( D(t) \). These functions contain the information on the time-dependent behaviour of the material, and are related by

\[
\int_{-\infty}^{t} E(t - \tau)D(\tau)d\tau = t
\]

This relation implies that both the relaxation modulus \( E(t) \), and compliance \( D(t) \), hold the same information and it is therefore arbitrary which function is used.

Linear viscoelastic behaviour is often represented by a mechanical analogy in terms of springs and dashpots. To a first approximation, the relaxation modulus is represented by a single Maxwell element, while the compliance is represented by a single Kelvin-Voigt element. Considering that these models exhibit only a single relaxation time, and are therefore not capable of describing the time-dependent behaviour correctly, their value is educational rather than practical. However, the description can be improved by increasing the number of elements, leading to a generalized Maxwell or Kelvin-Voigt model. Increasing the number of elements to infinity, changes the discrete representation to a continuous, employing a relaxation spectrum \( H(\tau) \) or retardation spectrum \( L(\tau) \) (Ferry, 1980; Tschoegl, 1989).

**1.2.2 Nonlinear Viscoelastic Deformation**

At intermediate stress levels, the material behaviour starts to deviate from the linear theory, showing a response that depends on the applied stress or strain but which is still time-dependent. If only integral representations are considered,
constitutive models describing this so-called nonlinear viscoelastic behaviour can be divided into multiple and single integral representations.

Multiple integral representations are essentially extensions of the Boltzmann single integral representation using higher order stress or strain terms to account for the nonlinear behaviour (Findley et al., 1976). The major drawback of this approach is the large number of variables, which has led to the proposition of many simplified kernel functions (Findley et al., 1976), however, with limited success.

Single integral representations are usually nonlinear variants of the Boltzmann single integral representation and can be divided in:

- Representations based on factorizability; these representations use a nonlinear stress or strain measure through which the stress-strain relation can be treated according to the linear viscoelastic theory (Leaderman, 1943):

\[
\sigma(t) = \int_{-\infty}^{t} E(t - t') \frac{df(\varepsilon)}{dt'} \, dt'
\]

or

\[
\varepsilon(t) = \int_{-\infty}^{t} D(t - t') \frac{dg(\sigma)}{dt'} \, dt'
\]

In practice this type of nonlinear behaviour can be recognized from the fact that, in a double logarithmic plot, measurements at different stresses or strains can be superimposed by purely vertical shifting.

- Representations based on reduced time; contrary to the previous, these representations do not linearize stress or strain, but use stress and strain to nonlinearize the time-scale by means of a strain or stress-reduced time. However, similar to the preceding representation this introduces the possibility to treat the nonlinear stress-strain relation according to linear viscoelasticity:

\[
\sigma(t) = \int_{-\infty}^{t} E(\rho - \rho') \varepsilon(t') \, dt'
\]

where \( \rho = \int_{-\infty}^{t'} \frac{dt''}{a_\varepsilon[\varepsilon(t'')]} \) and \( \rho' = \int_{-\infty}^{t'} \frac{dt''}{a_\varepsilon[\varepsilon(t'')]} \)

or

\[
\varepsilon(t) = \int_{-\infty}^{t} D(\psi - \psi') \dot{\sigma}(t') \, dt'
\]

where \( \psi = \int_{-\infty}^{t'} \frac{dt''}{a_\sigma[\sigma(t'')]} \) and \( \psi' = \int_{-\infty}^{t'} \frac{dt''}{a_\sigma[\sigma(t'')]} \)
1.2 Deformation Behaviour

Whereas the representation based on factorizability could be recognized by purely vertical shifting, the current representation can be recognized by a possible superposition of measurements at various stresses and strains, using a purely horizontal shift along the time-axis.

- A special class are the models derived by Schapery (1969), which combine the features of both previous representations:

\[
\varepsilon(t) = g_0(\sigma) D_0 \sigma + g_1(\sigma) \int_{-\infty}^{t} \Delta D(\psi - \psi') \frac{dg_2(\sigma)}{dt'} dt'
\]

where \( \psi = \int_{-\infty}^{t} \frac{dt''}{a_\sigma[\sigma(t'')]}, \) \( \psi' = \int_{-\infty}^{t} \frac{dt''}{a_\sigma[\sigma(t'')]}, \)

or

\[
\sigma(t) = h_0(\varepsilon) E_0 \varepsilon + h_1(\varepsilon) \int_{-\infty}^{t} \Delta E(\rho - \rho') \frac{dh_2(\varepsilon)}{dt'} dt'
\]

where \( \rho = \int_{-\infty}^{t} \frac{dt''}{a_\varepsilon[\varepsilon(t'')]}, \) \( \rho' = \int_{-\infty}^{t} \frac{dt''}{a_\varepsilon[\varepsilon(t'')]}. \)

Since this is a combination of the two previous types of representation, it displays both vertical as well as horizontal shifts, which is also the explanation for the widespread use of this type of stress-strain relation.

In spite of the fact that all three types of representation can be treated according to linear viscoelasticity, the choice of the nonlinearity (either stress or strain) is crucial, since the relaxation and retardation form are, unlike in linear viscoelasticity, no longer interchangeable.

1.2.3 Plastic Deformation

In the classical approach, solid polymers are considered to be ideally-plastic materials, similar to metals. This implies a description of the yield behaviour by means of a yield criterion, that is, a critical stress below which the material behaves elastically and above which it behaves plastically. The yield behaviour of polymers, however, strongly depends on strain rate and temperature. This has led to a change in description from solid-like to a fluid-like approach. In this latter approach, solid polymers are regarded as strongly nonlinear viscoelastic fluids with very high relaxation times. This resulted in a new class of constitutive models, describing the large strain plasticity of solid polymers, such as the “BPA-model” (Boyce et al., 1988), the “full chain model” (Wu and van der Giessen, 1993), and more recently the “modified Leonov model” (Tervoort, 1996). In all these models, no explicit use is made of a yield criterion. Instead, the deformation behaviour is determined by a single, temperature and stress-activated,
relaxation time. This results in a sharp transition from solid-like to fluid-like behaviour, almost identical to an elastic-perfectly plastic response employing a rate-dependent yield criterion. Since this sort of behaviour is never observed in practice, Tervoort et al. (1996) used a spectrum of Leonov-elements to account for the time-dependent behaviour normally observed. This leads to a spectrum of relaxation times, where all relaxation times are the same function of stress, resulting in a much more gradual transition to yield. In terms of the nonlinear viscoelastic models discussed previously, this approach results in a model of the stress-accelerated type, and gives a good description of the nonlinear viscoelastic behaviour.

1.3 Thermorheological Behaviour

The deformation behaviour of polymer materials strongly depends on the experimental time-scale and temperature. This can be visualized by a double logarithmic plot of one of the viscoelastic functions against time (or frequency), alternatively for different temperatures (Figure 1.2).

![Figure 1.2: Creep compliance of PS (M_w = 3.85 · 10^5), as measured at the indicated temperatures. Reproduced from Schwarzl (1990).](image)

Such graphs show a pattern of certain zones on the time (or frequency) scale
where these functions have characteristic shapes; molecular transitions. The most important of these molecular transitions is the glass-transition (primary- or \( \alpha \)-transition), which is associated with main-chain segmental motion. Below the glass-transition temperature, the mobility of the main-chain segments decreases but does not disappear completely, thus causing a spectrum of relaxation times. Besides the primary transition, the majority of polymers exhibit one, or even more, secondary transitions (\( \beta \), \( \gamma \)-transition) originating from the motions of side groups, end groups or restricted motions of the main chain. Similar to the primary transition, the secondary transitions give rise to a spectrum of relaxation times, through which they contribute to the overall time-dependent behaviour.

As was mentioned previously, in addition to time-dependent behaviour the viscoelastic functions also show a pronounced temperature dependence. This is due to the molecular transitions, each of which displays a characteristic temperature dependence. Consequently, relaxation times caused by a specific transition all depend in the same way on temperature, leading to an equal acceleration for each relaxation time attributed to that particular transition. Assuming that the material exhibits only one, or only one active, molecular transition, the material behaves thermorheological simple, meaning that all relaxation times have the same temperature dependence. Therefore, the spectrum of relaxation times will only shift along the time-axis, whereas the shape of the spectrum, and the deformation behaviour related to this spectrum are unaffected (Figure 1.3).

![Figure 1.3: Thermorheological simple behaviour.](image)

![Figure 1.4: Thermorheological complex behaviour.](image)

This is the basis of the well-known time-temperature superposition principle, which states that viscoelastic data obtained at different temperatures can be superimposed onto a master curve, only using horizontal shifting along the logarithmic time, or frequency, axis. The observation of a purely horizontal shift is sometimes used to identify thermorheological simple material behaviour (Schwarz and Staverman, 1952). The principle of time-temperature superposition was first observed by Leaderman (1943), to describe this behaviour he introduced a reduced
time $\phi$:

$$\phi = \int_{-\infty}^{t} \frac{dt''}{a_T(T(t))}$$

where $a_T$ is the ratio of the relaxation times at temperatures $T$ and $T_0$. The analogy with the stress and strain reduced time mentioned previously should be noted.

However, usually a material exhibits two (or more) molecular transitions in which case there are two (or more) spectra, each shifting according to their characteristic temperature dependence. Because of differences in the temperature dependences, this will lead to a change in the shape of the total spectrum (Figure 1.4), which in its turn affects the deformation behaviour of the material. This type of behaviour is termed thermorheological complex, and the magnitude of the effect is mainly determined by the relative position of the transitions on the time-scale. Due to the changing shape, the data of a viscoelastic function at different temperatures are no longer superimposable by purely horizontal shifting and therefore the principle of time-temperature superposition is no longer applicable. In practice, however, for some polymers it has been noted that smooth master curves can still be obtained by application of both horizontal and vertical shifts (McCrum and Morris, 1964).

1.4 Scope of the Report

In the previous two sections a short overview of the deformation behaviour of glassy polymers was given together with some of the constitutive equations used to describe it, and the underlying molecular mechanisms. The main objective of this report is to develop a model that can be employed to identify the separate contributions of the various transitions to the macroscopic deformation behaviour of polymers in general. To achieve this goal it is assumed that the contribution of each molecular mechanism can be modeled as a separate spectrum of relaxation times possessing its own characteristic temperature and stress dependence.

In Chapter 2, a model is derived based on the assumption that the material behaves thermorheological simple, model parameters are obtained experimentally, and the model is verified numerically. The assumption of thermorheological simple behaviour is dropped in Chapter 3, and the previously derived model is extended to account for the contribution of an additional molecular process. Consequences of the resulting modification are investigated numerically. Since in both Chapter 2 and Chapter 3 the influence of physical aging and mechanical rejuvenation is neglected, this will be addressed in Chapter 4. In Chapter 5, the obtained insights are used to generalize the approach to finite strains. Finally, some overall conclusions will be drawn in Chapter 6.
Chapter 2

Deformation Behaviour of Thermorheological Simple Materials

2.1 Introduction

In the introductory chapter, an one-dimensional outline of the deformation behaviour of glassy polymers up to yield was given. Furthermore, the molecular origin of the deformation behaviour, as well as the influence of temperature, was discussed, hereby distinguishing between two types of material behaviour, thermorheological simple and thermorheological complex. Since the objective of this report is to attribute characteristics of the deformation behaviour to underlying molecular processes, the most logical first step is to take a material that behaves thermorheological simple, and to investigate the accompanying deformation behaviour.

To verify some aspects of the deformation behaviour, a suitable model material is required. For this purpose polycarbonate was selected, since from this material it is known that the secondary transition is only relevant at low temperatures or high strain-rates. The suitability of the material was verified by performing a Dynamic Mechanical Thermal Analysis, the result of which is shown in Figure 2.1.

From the figure it can be seen that, at approximately 155 °C, the loss angle shows a peak, denoted by α, corresponding to a state of increased molecular mobility, in this case the onset of main-chain segmental motion (glass transition). As no other peaks are observed above 0 °C, it can be assumed that polycarbonate behaves thermorheological simple at temperatures equal or above room temperature and moderate deformation rates.

In this chapter, the deformation behaviour of polycarbonate is studied. Firstly,

\(^1\)Reproduced in part from Tervoort et al. (1996)
the material behaviour in both the linear viscoelastic and the plastic range is modeled using mechanical model analogies. By considering the similarities between the results for the two different regions, a model based on time-stress superposition is proposed, that correctly describes the material behaviour in monotone loading paths up to yield. Introduction of a stress-reduced time leads to a single integral stress-strain relation, with separated stress and time dependences. After experimental verification of the time-stress superposition and determination of the required material parameters, the stress-strain relation is validated numerically.

Although it is well-known that physical aging has a pronounced influence on the viscoelastic behaviour, it will not be taken into account in this chapter. The effects of aging as well as the influence of non-monotone loading paths will be dealt with in Chapter 4.

2.2 Experimental

All experiments, unless stated otherwise, were performed on injection moulded tensile bars, produced according to ISO R527, from General Electric polycarbonate Lexan® 161R. As pointed out previously, polycarbonate was selected as a model polymer since, at room temperature, it exhibits only a single relaxation mechanism; the glass transition.

Both tensile experiments and creep experiments were performed on a Zwick Rel servo-hydraulic tensile tester, equipped with an extensometer and a thermostatically controlled oven. In the latter case the extension was measured using an Instron (2620-602) strain gauge extensometer with a measure length of 50 mm and a range of ± 2.5 mm. The relative accuracy in the force and strain measurements was 1%.
2.3 Deformation Behaviour

2.3.1 Linear Viscoelastic Deformation

Linear viscoelastic deformation is commonly described using the Boltzmann single integral representation, either in its relaxation, or retardation form. The information concerning the time-dependent material behaviour is contained in the viscoelastic functions, the relaxation modulus $E(t)$ and the compliance $D(t)$. A characteristic example of the time dependent material behaviour is shown schematically in Figure 2.2, representing the logarithm of the creep compliance against the logarithm of time.

![Figure 2.2: Schematic representation of the compliance versus time for a polymer glass.](image)

After an initial elastic response, the material shows time dependent creep until, at a certain point, a constant rate of deformation is established, that is, the material is flowing. Due to the large molecular weight, this flow can be stabilized by the presence of a physical entanglement network, resulting in the rubber plateau. The “apparent” flow occurring in the glass-rubber transition region can only be observed if the difference in modulus between the glassy and rubbery region is sufficiently high. Because of the presence of entanglements this flow deformation...
will result in an ongoing molecular orientation within the material. It should therefore not be confused with the flow behaviour occurring beyond the rubber plateau, where deformation and orientation are no longer coupled.

The form of the time dependence of relaxation modulus and compliance can be imitated by the behaviour of a mechanical model with a sufficient number of elastic and viscous elements (Ferry, 1980). Here the influence of the rubber contribution will be neglected, since this contribution is only relevant at large deformations. As a consequence, the constitution of the mechanical analogies, which are shown in Figure 2.3 \((E(t))\), and Figure 2.4 \((D(t))\), is that of a linear viscoelastic liquid.

\[
E(t) = \sum_{i=1}^{n_1} E_i \exp \left( -\frac{t}{\tau_i} \right)
\]

\[
D(t) = D_g + \sum_{i=1}^{n_2} D_i \left[ 1 - \exp \left( -\frac{t}{\tau_i} \right) \right] + \frac{t}{\eta_0}
\]

where \(E_i, \tau_i (= \eta_i / E_i)\) refer to the \(i\)th Maxwell element and \(n_1\) is the number of elements, while for the generalized linear Kelvin-Voigt model results

Instead of a graphical representation, the mechanical model analogies can also be expressed in an analytical form. For the generalized linear Maxwell model this results in

\[
E(t) = \sum_{i=1}^{n_1} E_i \exp \left( -\frac{t}{\tau_i} \right)
\]

where \(E_i, \tau_i (= \eta_i / E_i)\) refer to the \(i\)th Maxwell element and \(n_1\) is the number of elements, while for the generalized linear Kelvin-Voigt model results

\[
D(t) = D_g + \sum_{i=1}^{n_2} D_i \left[ 1 - \exp \left( -\frac{t}{\tau_i} \right) \right] + \frac{t}{\eta_0}
\]

where \(D_g\) is the elastic response, \(D_i, \tau_i (= \eta_i D_i)\) refer to the \(i\)th Kelvin-Voigt element, \(n_2\) is the number of elements, and \(\eta_0\) represents the flow viscosity.

From both the figures and equations it should be clear that the generalized Maxwell and Kelvin-Voigt model represent exactly the same behaviour as described previously; initially elastic, followed by time dependent deformation, and for times beyond the longest relaxation time Newtonian flow. The latter condition is, however, seldom observed in a real linear experiment at room temperature, since the longest relaxation/retardation time normally by far exceeds the time of the experiment.
2.3 Deformation Behaviour

2.3.2 Plastic Deformation

The yield behaviour of a polymer glass is usually described using a fluid-like approach, thereby regarding the material as a strongly nonlinear fluid with a very high relaxation time. In this approach the deformation behaviour is described using a nonlinear Maxwell model with a single, temperature and stress-activated, relaxation time. This principle dates back to Tobolsky and Eyring (1943), and was used later by Haward and Thackray (1968), who added a spring to account for the strain hardening response observed at large deformations. The Haward-Thackray model is schematically represented in Figure 2.5. The initial elastic response is described by the compliance $D_g$, the yield point is determined by the stress dependent viscosity $\eta(\sigma)$, and the strain hardening response follows from $D_r$.

![Figure 2.5: Haward-Thackray model.](image)

![Figure 2.6: Schematic representation of the compliance versus time for the Haward-Thackray model at different stress levels.](image)

The effect of the stress dependence of the single relaxation time is most clearly demonstrated in creep tests at different stress levels. At low stress levels, the relaxation time is constant, and the behaviour is linear (independent of stress). At higher stresses, the relaxation time decreases with stress, resulting in a horizontal shift of the compliance curve along the logarithmic time axis towards shorter times (Figure 2.6).

Haward and Thackray assumed, that the stress dependence of the relaxation time originated solely from the plastic flow process. For the viscosity they used the Eyring expression (Eyring, 1936), a semi-empirical relation, which describes stress-activated flow of structural units in a material, such as segments in the case of polymers. The Eyring equation, which relates the plastic strain-rate to
the applied stress $\sigma$, and temperature $T$, reads

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp \left( -\frac{\Delta U}{RT} \right) \sinh \left( \frac{\sigma V^*}{RT} \right)$$  \hfill (2.3)

where $V^*$ is the activation volume, determining the stress dependence, $\Delta U$ the activation energy, determining the temperature dependence, $\dot{\varepsilon}_0$ is a rate constant, and $R$ is the universal gas constant. That this relation indeed gives a correct description of the yield behaviour can be demonstrated by yield experiments using the selected model material. First of all, however, the Eyring relation, Eq. (2.3), is rewritten as stress in terms of strain rate

$$\frac{\sigma}{T} = \frac{R}{V^*} \sinh^{-1} \left( \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0^*} \right)$$  \hfill (2.4)

where

$$\dot{\varepsilon}_0^* = \dot{\varepsilon}_0 \exp \left( -\frac{\Delta U}{RT} \right)$$  \hfill (2.5)

For high stresses, $\sinh(x) \approx \frac{1}{2} \exp(x)$ and a plot of $\sigma_y/T$ against $\log(\dot{\varepsilon})$ produces a series of straight lines, the slope of which is determined by the activation volume $V^*$. Figure 2.7 shows the results of the yield experiments on polycarbonate for various strain rates and two different temperatures.

![Figure 2.7: Measured ratio of yield stress to temperature as a function of the strain rate for polycarbonate. The markers represent measured data and the lines are calculated from Eq. (2.4).](image)

From the figure it is clear that Eq. (2.4) gives a good description of the rate dependence of the yield behaviour for both temperatures. The parameters that result from fitting the data, using Eq. (2.4), are tabulated in Table 2.1.

The value found for the activation volume is in reasonable agreement with the values obtained by Robertson (1963), 3.22 nm$^3$, and Bauwens-Crowet et al. (1969),
2.3 Deformation Behaviour

\[
V^* \hspace{1em} \Delta U \hspace{1em} \dot{\varepsilon}_0 \\
[\text{nm}^3] \hspace{1em} [\text{kJ mol}^{-1}] \hspace{1em} [\text{s}^{-1}]
\]

\begin{array}{c|c|c}
2.96 & 274.094 & 1.118 \cdot 10^{27} \\
\end{array}

Table 2.1: Eyring parameters for polycarbonate obtained from fitting the yield data in Figure 2.7 with Eq. (2.4).

3.28 nm\(^3\) (both values were recalculated according to Eq. (2.4)).

To obtain an analytical expression for the nonlinear flow in terms of a stress-dependent viscosity, Eq. (2.3) is substituted in

\[
\eta = \frac{\sigma}{\dot{\varepsilon}}
\]

(2.6)

If it is assumed that the temperature is constant, \(T_0\), this results in

\[
\eta(\sigma) = \eta_0 \frac{(\sigma/\sigma_l)}{\sinh (\sigma/\sigma_l)}
\]

(2.7)

where \(\sigma_l\) is a nonlinearity parameter

\[
\sigma_l = \frac{RT_0}{V^*}
\]

(2.8)

and \(\eta_0\) the zero-viscosity

\[
\eta_0 = \frac{\sigma_l}{\dot{\varepsilon}_0} \exp \left( \frac{\Delta U}{RT_0} \right)
\]

(2.9)

Introduction of a stress dependent shift function \(a_\sigma\), defined as

\[
a_\sigma(\sigma) = \frac{(\sigma/\sigma_l)}{\sinh (\sigma/\sigma_l)}
\]

(2.10)

further reduces Eq. (2.7) to

\[
\eta(\sigma) = \eta_0 a_\sigma(\sigma)
\]

(2.11)

For stresses below \(\sigma_l\), the stress shift function \(a_\sigma\) equals one and the material behaves Newtonian, whereas for stresses above \(\sigma_l\), the stress shift function \(a_\sigma\) decreases exponentially and the material behaves strongly non-Newtonian.

If temperature \(T_0\) is set equal to 22.5 °C, the nonlinearity parameter \(\sigma_l\) and the zero-viscosity \(\eta_0\) can be calculated from the parameters in Table 2.1 using Eqs. (2.8) and (2.9). The results are tabulated in Table 2.2.
2.3.3 Nonlinear Viscoelastic Deformation

In the previous two subsections, the material behaviour in the linear viscoelastic and plastic range was described using mechanical model analogies. The time dependence, characteristic for the linear viscoelastic range, including the ultimate flow behaviour was modeled using a spectrum of linear relaxation times, whereas the stress-dependent yield behaviour, characteristic for the plastic range, could be modeled using a single stress-activated relaxation time. Since the nonlinear viscoelastic range lies in-between the linear viscoelastic and plastic range, a model is proposed that contains the characteristics of both bounding regions. The proposed model consists of a spectrum of nonlinear stress-dependent relaxation times. Moreover, the stress dependence $a_\sigma$, which is governed by the activation volume $V^*$, is the same for each relaxation time. This leads to a situation that is comparable to a thermorheological simple material where all relaxation times are the same function of temperature. The resulting model is shown in terms of mechanical model analogies in Figure 2.8 (relaxation modulus) and Figure 2.9 (compliance).

Instead of graphical, the models can again be represented analytically, yielding
the following expression for the generalized nonlinear Maxwell model

$$E(t) = \sum_{i=1}^{n_1} E_i \exp \left( -\frac{t}{\tau_i(\sigma)} \right)$$

(2.14)

where $E_i, \tau_i(\sigma) = \tau_i a_\sigma(\sigma)$, refer to the $i$th Maxwell element and $n_1$ is the number of elements. Whereas for the generalized nonlinear Kelvin-Voigt model results

$$D(t) = D_g + \sum_{i=1}^{n_2} \left[ 1 - \exp \left( -\frac{t}{\tau_i(\sigma)} \right) \right] + \frac{t}{\eta(\sigma)}$$

(2.15)

where $D_g$ is the elastic response, $D_i, \tau_i(\sigma) = \tau_i a_\sigma(\sigma)$ refer to the $i$th Kelvin-Voigt element, $n_2$ the number of elements, and $\eta(\sigma)$ is the stress-dependent viscosity (Eq. (2.7)).

The models correctly describe the material behaviour in the linear viscoelastic and plastic range, since for stresses below $\sigma_l$, the shift function $a_\sigma$ equals one and all relaxation times become linear, whereas for high stresses all relaxation times decrease exponentially resulting in yield. The typical stress and time-dependence observed in the nonlinear viscoelastic region is obtained at intermediate stresses.

An important feature of the proposed model is that all relaxation times are the same function $a_\sigma$, of the total stress $\sigma$, since according to the Eyring theory the stress activation of a molecular process is governed by the total applied stress. As a consequence, this approach implies that the material behaviour will show time-stress superposition, which is similar to time-temperature superposition where all relaxation times are the same function of temperature. In accordance with this analogy, a stress-reduced time $\psi$ can be defined

$$\psi = \int_{-\infty}^{t} \frac{dt'}{a_\sigma(\sigma(t))}$$

where $a_\sigma$ is the ratio of the relaxation time at a stress $\sigma$ and the linear relaxation time (relaxation time for a stress well below $\sigma_l$).
To verify whether or not the derived model is capable of accounting for the entire range of deformation behaviour, experiments will have to be compared with model predictions. For these predictions a constitutive relation is needed, which can be obtained by using the concept of stress-reduced time in combination with the Boltzmann single integral representation. This even leads to two possible stress-strain relations, since the Boltzmann single integral can be used in both its stress and strain form

\[ \sigma(t) = \int_{-\infty}^{t} E(\psi - \psi') \dot{\varepsilon}(t') dt' \quad \text{and} \quad \varepsilon(t) = \int_{-\infty}^{t} D(\psi - \psi') \dot{\sigma}(t') dt' \quad (2.16) \]

where

\[ \psi = \int_{-\infty}^{t} \frac{dt''}{a_\sigma[\sigma(t)]]} \quad \text{and} \quad \psi' = \int_{-\infty}^{t} \frac{dt''}{a_\sigma[\sigma(t')]]} \]

The major advantage of a stress-strain relation of this form is the separation of the stress and time-dependence through which the relation can be treated according to linear viscoelastic theory.

Before any calculations can be performed, the necessary material parameters need to be determined, in this case the linear relaxation modulus \( E(t) \), or compliance \( D(t) \), and the shift function \( a_\sigma \) by means of the nonlinearity parameter \( \sigma_l \). First of all, however, the applicability of time-stress superposition has to be verified experimentally. This can be done in a way similar to the verification of time-temperature superposition (Ferry, 1980). Data obtained at constant stress levels must shift horizontally along the logarithmic time-axis to a smooth master-curve for a certain reference stress, and the resulting shift factors plotted as a function of stress must obey a “familiar” relationship, in this case the shift function derived from the Eyring theory. This will be dealt with first. Next, the material parameters are determined and finally predictions are compared with actual experiments.

### 2.4 Results

In section 2.3 it was argued that the deformation behaviour of a thermorheological simple behaving polymer is determined by the linear relaxation or retardation spectrum which is shifted to shorter times when stress is applied. In this section, the required model parameters will be determined. First, however, the applicability of the time-stress superposition principle is verified experimentally. Finally, model predictions will be compared to experimental data using a constant strain-rate experiment.
2.4 Results

2.4.1 Applicability of Time-Stress Superposition

To verify the applicability of time-stress superposition experimentally for polycarbonate, it was first attempted to construct a smooth master-curve from a number of creep tests at different stress levels as described in section 2.3. The results of the creep tests are shown in Figure 2.10.

![Figure 2.10: Creep compliance of polycarbonate at 22.5°C and various stress levels.](image)

These curves were shifted horizontally along the logarithmic time axis with respect to the 15 MPa reference curve. The resulting master curve is shown in Figure 2.11.

![Figure 2.11: Master curve of the data in Figure 2.10, for a reference stress of 15 MPa.](image)

From Figure 2.11 it is clear that a smooth compliance master curve can be constructed by horizontal shifting of the creep tests at different stresses. It must be emphasized that the compliance curve at 15 MPa is a “virtual” curve that will strongly deviate from an experimental creep test on the same time scale, due to aging effects. The logarithm of the shift factors \( \log(a_{15}) \), necessary to construct
the master compliance curve at 15 MPa (Figure 2.11), are tabulated in Table 2.3 as a function of the creep load

<table>
<thead>
<tr>
<th>$\sigma$ [MPa]</th>
<th>14.9</th>
<th>19.8</th>
<th>24.7</th>
<th>29.8</th>
<th>34.5</th>
<th>39.8</th>
<th>44.5</th>
<th>49.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log(a_{15})$</td>
<td>0</td>
<td>-1.55</td>
<td>-3.25</td>
<td>-4.80</td>
<td>-6.25</td>
<td>-7.80</td>
<td>-9.30</td>
<td>-10.75</td>
</tr>
</tbody>
</table>

Table 2.3: Values of $a_{15}(\sigma)$ obtained from the construction of the master curve in Figure 2.11.

The second part of the experimental verification of time-stress superposition consists of fitting the shift data from Table 2.3 with the Eyring shift equation, Eq. (2.10). Although the shift function at the reference stress was set equal to one, comparison with the previously obtained value for $\sigma_l$ learns that the reference stress is in the nonlinear range. To correct for this deviation from linearity the shift data are fitted using a modified shift function

$$ a_{15}(\sigma) = c a_{\sigma}(\sigma) $$

where $c (= a_{\sigma}^{-1}(15))$ is a constant that accounts for the shift of the 15 MPa master curve with respect to the linear range. The constant $c$ does not affect the form of the shift function which is completely determined by the parameter $\sigma_l$. A plot of the shift factors with respect to the 15 MPa reference curve is shown in Figure 2.12.

From Figure 2.12 it is clear that the obtained shift data can be described using a single Eyring function. Therefore, the second condition is also met, and it may be assumed that time-stress superposition is allowed. Furthermore, the fit yields $\sigma_l=1.334$ MPa, which is in very good agreement with the value for $\sigma_l$ obtained in the previous yield experiments, and $\log(c) = -\log(a_{\sigma}(15))=3.496$. 
2.4.2 Linear Viscoelastic Behaviour

In the previous subsection it was verified experimentally that time-stress superposition applies to polycarbonate. Since the nonlinearity parameter is already known, only the viscoelastic behaviour has to be determined in terms of the linear relaxation/retardation time spectrum. In section 2.4.1, the 15 MPa compliance master curve was obtained through application of the time-stress superposition principle. However, it was already pointed out that the 15 MPa compliance master curve does not constitute the true linear compliance curve. The value of the nonlinearity parameter $\sigma_l$ indicates that above a stress of 1.336 MPa, polycarbonate already behaves in a nonlinear way. Therefore, the true linear compliance curve could only be obtained indirectly by shifting the 15 MPa master curve horizontally by a factor $a^{-1}_\sigma (\sigma = 15 \text{ MPa})$. The resulting linear compliance curve is shown in Figure 2.13.

![Figure 2.13: Construction of the linear compliance from the 15 MPa master curve, including the fit using a generalized linear Kelvin-Voigt model (solid line).](image)

To obtain an expression that can be used for further calculations, the linear compliance curve is approximated using the generalized linear Kelvin-Voigt model (Eq. (2.2)), which is the solid line in Figure 2.13. From the fit a value of $2.74 \times 10^{21}$ MPa s was found for $\eta_0$, which is in reasonable agreement with the value obtained from the yield experiments. The resulting Kelvin-Voigt parameters are tabulated in Appendix A. Instead of the linear compliance the linear relaxation modulus can also be used. However, to obtain the linear relaxation modulus the linear compliance has to be converted, using the following relation

$$\int_0^t D(t - \tau) E(\tau) d\tau = t$$

The linear relaxation modulus that results from the conversion is shown in Figure 2.14.
Finally, the relaxation modulus is approximated using the generalized Maxwell model represented by Eq. (2.1), the resulting Maxwell parameters are tabulated in Appendix A. It must be emphasized that these linear Maxwell and Kelvin-Voigt parameters bear no physical meaning, only the relaxation modulus $E(t)$ or compliance $D(t)$ themselves are material functions.

### 2.4.3 Model Verification

In section 2.3.3 it was argued that the nonlinear viscoelastic behaviour of a polymer glass is determined by the linear relaxation/retardation time spectrum, which is shifted to shorter times when stress is applied. In the previous subsection 2.4.2, the linear spectra for a model polymer, polycarbonate, were approximated using a discrete Maxwell and Kelvin-Voigt model, the relaxation/retardation times of which are all subdued to the same stress dependence. In this subsection, the stress-strain relations of Eq. (2.16) will be verified by constant strain-rate experiments (uniaxial tensile tests).

The verification experiment considered is a standard uniaxial tensile test at various strain rates (constant cross head speed). Figure 2.15 shows a comparison between the experimental data (open symbols) and the numerical predictions (solid lines).

From this figure it is clear that the model gives a good description of the nonlinear viscoelastic behaviour and provides a quantitative description of the strain-rate-dependent “yield behaviour” of polycarbonate. However, after the yield point the predictions deviate from the experiments due to strain localization and strain softening, which are not incorporated in the model. With regard to strain softening some remarks will be made in Chapter 4.
2.5 Conclusions

The present work was aimed at the development of a model, that can be employed, to identify the separate contributions of the various molecular processes to the macroscopic deformation behaviour. By considering a material with only a single (active) molecular process, that is, a thermorheological simple material, a constitutive model describing all types of deformation behaviour up to yield was obtained. The model is based on the assumption that the material behaviour is determined by a spectrum of linear relaxation times, which shifts to shorter times under the influence of stress. Moreover, the influence of stress is equivalent for each relaxation time, which is comparable with the influence of temperature, since all relaxation are the same function of temperature (thermorheological simple). Therefore, the material should show time-stress superposition in analogy with time-temperature superposition. By means of creep experiments at different stress levels it was shown that time-stress superposition is indeed applicable for the model material. Moreover, the stress nonlinearity which could be obtained from the resulting shift parameters showed good agreement with the stress non-linearity determined from yield experiments. From the constructed master curve the remaining model parameters could be determined. Concluding simulations of a tensile test for various strain rates gave very good agreement with experimental data.

Figure 2.15: Tensile tests at various strain-rates (symbols), compared to model predictions (solid lines).
Chapter 3

Deformation Behaviour of Thermorheological Complex Materials

3.1 Introduction

In Chapter 2, a constitutive model was derived based on the assumption of thermorheological simple material behaviour. The deformation behaviour appeared to be completely determined by the linear relaxation modulus or compliance, and a nonlinear stress-dependent shift function. Unfortunately, most polymers exhibit at least two molecular mechanisms, that is, behave thermorheological complex. In the introductory chapter, it was already pointed out that for different temperatures this leads to difficulties due to differences in the temperature dependence of the transitions. Therefore, in this chapter it is investigated, what the consequences are for the previously derived stress-strain relation, and if it is possible to isolate the contributions to the overall deformation caused by the different mechanisms.

To enable a verification of some aspects of the deformation behaviour, three model materials were selected, each possessing two (active) molecular transitions. The first two materials, polycarbonate (PC) and polymethylmethacrylate (PMMA), are amorphous polymers and were selected to demonstrate the effect of the position of the transitions and their in-between distance. The difference is shown by comparing a Dynamic Mechanical Thermal Analysis of both materials, as can be seen in Figure 3.1.

Both materials display a primary transition, denoted by \( \alpha \), and a secondary transition, denoted by \( \beta \). For polycarbonate, however, the secondary transition lies well below room temperature and far from the primary transition, while for polymethylmethacrylate the secondary transition lies above room temperature and
just below the primary transition. As a consequence, polycarbonate could be
treated as a thermomechanical simple behaving material in the previous chapter.
This simplification is no longer valid for polymethylmethacrylate, nor for polycarbonate if the limitation to moderate strain-rates and temperatures is removed.

It was already observed by Nakayasu et al. (1961) and Schapery (1969), that semi-
crystalline materials also show signs of thermorheological complex behaviour.
For this reason polypropylene is also included in the investigation. A DMTA-
experiment for polypropylene (PP) is shown in Figure 3.2, displaying two pro-
cesses, a crystalline transition, denoted by $\alpha$, and an amorphous transition, de-
noted by $\beta$.

In the first section, the deformation behaviour is reconsidered, firstly the descrip-
tion of the linear viscoelastic material behaviour is regarded, and the previously
employed mechanical model analogies are extended as to account for an additional contribution. Subsequently, the implications for the yield behaviour are investigated by means of yield experiments, resulting in a suitable modification of the previous approach. This finally leads to a modified model that accounts for the nonlinear viscoelastic deformation. In the remaining part the modified model is numerically investigated to gain insight in the relevant processes underlying the deformation behaviour, including a comparison with literature. Like the previous chapter, this investigation is restricted to monotone loading paths and iso-age tests.

3.2 Experimental

All experiments, unless stated otherwise, were performed on injection moulded tensile bars. Polycarbonate tensile bars were produced according to ISO R527, from General Electric Lexan® 161R, whereas polymethylmethacrylate and polypropylene tensile bars were produced according to ASTM D 638, from Rohm and Haas Oroglas® V052 and DSM Stamylan® P46M10 respectively. Tensile experiments on PC were performed on a Zwick Rel servo-hydraulic tensile tester, equipped with an extensometer and a thermostatically controlled oven. Whereas tensile experiments on both PMMA and PP were performed on a Frank 81565 tensile tester, equipped with an extensometer and a thermostatically controlled oven. The relative accuracy in force and strain measurements was 1%. Tensile tests at various strain-rates were performed for PC from -20 to 40 °C, for PMMA and PP from 30 to 70 °C. Dynamic experiments, using samples cut from 2 mm thick compression moulded sheets, were performed on a Rheometrics Scientific DMTA MK III in uniaxial extension at 1 Hz, and temperatures ranging from -100 to 200 °C for polycarbonate, from -50 to 175 °C for polymethylmethacrylate, and from -25 to 175 °C for polypropylene. Each of the experiments was performed on a new sample. All tests samples had the same age, which exceeded by far the longest time in the experiments.

3.3 Deformation Behaviour

3.3.1 Linear Viscoelastic Deformation

Linear viscoelastic deformation behaviour is invariably described using the Boltzmann single integral representation, whereas the information concerning the time dependence is still contained in the relaxation modulus $E(t)$ and compliance $D(t)$. The form of the viscoelastic functions, however, has changed due to the contribution of the additional molecular transition, examples of which are shown in Figure 3.3.
Despite the changed form, the viscoelastic functions can still be represented by the generalized Maxwell and Kelvin-Voigt model, although the coefficients will change. Since the objective of this study is to analyze the contribution to the deformation behaviour of the separate molecular transitions, a distinction is made between the contributions to the viscoelastic functions caused by specific molecular transitions. In terms of the previously employed mechanical model analogies, where again the rubber contribution is neglected, this leads to the representations shown in Figure 3.4 and Figure 3.5. As can be seen, for both models a distinction is made between relaxation/retardation times due to a particular transition, indicated by $\alpha$ and $\beta$.
3.3 Deformation Behaviour

cally, giving for the generalized Maxwell model

\[ E(t) = \sum_{i=1}^{m_1} E_{\beta,i} \exp \left( -\frac{t}{\tau_{\beta,i}} \right) + \sum_{j=1}^{n_1} E_{\alpha,j} \exp \left( -\frac{t}{\tau_{\alpha,j}} \right) \]  

(3.1)

where \( E_{p,i}, \tau_{p,i} \) refer to the \( i \)th Maxwell element of process \( p \), \( m_1 \) and \( n_1 \) are the number of elements. Whereas for the generalized linear Kelvin-Voigt model results

\[ D(t) = D_0 + \sum_{i=1}^{m_2} D_{\beta,i} \left[ 1 - \exp \left( -\frac{t}{\tau_{\beta,i}} \right) \right] + \sum_{j=1}^{n_2} D_{\alpha,j} \left[ 1 - \exp \left( -\frac{t}{\tau_{\alpha,j}} \right) \right] + \frac{t}{\eta_0} \]  

(3.2)

where \( D_g \) is the elastic response, \( D_{p,i}, \tau_{p,i} \) refer to the \( i \)th element of process \( p \), \( m_2, n_2 \) are the number of elements, and \( \eta_0 \) the flow viscosity.

A very good example of the latter is the approach by Read (1987), who also distinguishes between an \( \alpha \)- and a \( \beta \)-contribution to the creep compliance. This is expressed by the following equation

\[ D(t) = D_U + D_\beta(t) + D_\alpha(t) \]  

(3.3)

where \( D_U \) is the unrelaxed compliance at short times,

\[ D_\beta(t) = (D_{R\beta} - D_U)\psi_\beta(t) \]

and

\[ D_\alpha(t) = (D_{R\alpha} - D_{R\beta})\psi_\alpha(t) \]

In these equations \( D_{R\beta} \) and \( D_{R\alpha} \) are the relaxed compliances for the \( \beta \)- and \( \alpha \)-regions and \( \psi_\beta(t) \) and \( \psi_\alpha(t) \) are normalized creep functions. The various compliances are indicated in the schematical representation shown in Figure 3.6. A similar approach is also employed by for instance Nakayasu et al. (1961) and Chai and McCrum (1984).

Although both the Kelvin-Voigt as well as the Maxwell model give a correct representation of the overall time-dependent material behaviour, there are two differences between the approaches originating from making a distinction between two processes. First of all, the Maxwell model distinguishes between the initial elastic response due to a certain transition, whereas the Kelvin-Voigt model only shows one total initial deformation, independent of any particular transition. The second, and probably more important difference, lies in the description of the flow behaviour. The Maxwell model shows two independent contributions to the flow
behaviour, while the Kelvin-Voigt model shows only one flow contribution. Which of these approaches is correct, or if the encountered differences are irrelevant, might become clear from an investigation of the yield behaviour, since it was recognized in the previous chapter that yield behaviour is in fact stress-accelerated flow.

### 3.3.2 Plastic Deformation

In the preceding chapter, the plastic deformation behaviour was described using the Haward-Thackray model (Haward and Thackray, 1968), which is essentially a single, stress-dependent, Maxwell element. The stress dependence of the model was accounted for by the Eyring theory of nonlinear flow. Furthermore, it was shown that a single Eyring process gave a good description of the yield behaviour of a thermorheological simple behaving material. If this observation is still valid can easily be verified by performing tensile tests at various strain-rates, alternatively at different temperatures. The results of the yield experiments are shown in Figure 3.7 for the three selected model materials. From the figure it is obvious that a single process is no longer sufficient to describe yield data from a material possessing a secondary transition. Instead of a straight line, characteristic for a single transition, a change in slope can be observed. This phenomenon was also observed by Roetling (1965) and Bauwens-Crowet et al. (1969), who then used the Ree-Eyring modification (Ree and Eyring, 1955) of the Eyring theory to describe the yield data. In this modification it is assumed that all species of flow units move at the same average rate, the stresses being additive. Following this procedure, one arrives at an equation of the form

$$\frac{\sigma}{T} = \sum_{p=\alpha,\beta} \frac{R}{V^*} \sinh^{-1} \left( \frac{\dot{\varepsilon}}{\dot{\varepsilon}_{0,p}} \right)$$  \hspace{1cm} (3.4)
3.3 Deformation Behaviour

Figure 3.7: Measured ratio of yield stress to temperature as a function of the strain rate for polycarbonate (top left), polymethylmethacrylate (top right), and polypropylene (bottom). The markers represent measured data and the lines are calculated from Eq. (3.4).

where

\[ \dot{\varepsilon}^*_p = \dot{\varepsilon}_{0,p} \exp \left( \frac{\Delta U_p}{RT} \right) \quad p = \alpha, \beta \]  

(3.5)

Using the modified theory, again a very good description of the yield data is obtained as is shown by the solid lines in Figure 3.7. Apparently, each molecular process contributes to the yield behaviour, and the proper way of describing this is by a parallel configuration of nonlinear flow elements. The resulting parameters from the fit of the yield data for the three model materials are tabulated in Table 3.1.
Table 3.1: Eyring parameters for polycarbonate, polymethylmethacrylate, and polypropylene obtained from the yield data in Figure 3.7.

<table>
<thead>
<tr>
<th></th>
<th>$V^*_p$ [nm$^3$]</th>
<th>$\Delta U_p$ [kJ mol$^{-1}$]</th>
<th>$\dot{\varepsilon}_{0,p}$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>$\alpha$ 3.11</td>
<td>289.785</td>
<td>5.756·10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$\beta$ 2.96</td>
<td>64.677</td>
<td>6.419·10$^{-11}$</td>
</tr>
<tr>
<td>PMMA</td>
<td>$\alpha$ 1.6</td>
<td>281.629</td>
<td>3.99·10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$\beta$ 1.21</td>
<td>87.875</td>
<td>4.304·10$^{-11}$</td>
</tr>
<tr>
<td>PP</td>
<td>$\alpha$ 4.7</td>
<td>273.375</td>
<td>1.332·10$^{-22}$</td>
</tr>
<tr>
<td></td>
<td>$\beta$ 4.49</td>
<td>146.327</td>
<td>4.394·10$^{-20}$</td>
</tr>
</tbody>
</table>

Bauwens-Crowet et al. (1972) found for polycarbonate the following values $V^*_\alpha = 3.13$ nm$^3$ and $V^*_\beta = 1.02$ nm$^3$, Roetling (1965) found for polymethylmethacrylate $V^*_\alpha = 2.00$ nm$^3$ and $V^*_\beta = 0.96$ nm$^3$ and for polypropylene (Roetling, 1966), $V^*_\alpha = 8.28$ nm$^3$ and $V^*_\beta = 2.53$ nm$^3$ (all values were recalculated in accordance with Eq. (3.4)). These values show some deviations when compared to the values tabulated in Table 3.1, in particular the values for the activation volume of the $\beta$-processes. It is difficult to determine the exact nature of the deviations, but it could be caused by differences in the employed materials with regard to additives. A second possibility is the difference in the fit procedure, Roetling (1965) uses a visual verification for the goodness of the fit, whereas the values in Table 3.1 are obtained from a best fit.

Instead of a single viscosity there now is a viscosity due to the $\alpha$-process and a viscosity due to the $\beta$-process. These viscosities are defined as

$$\eta_p = \frac{\sigma_p}{\dot{\varepsilon}} \quad p = \alpha, \beta$$

(3.6)

where $\dot{\varepsilon}$ is the strain rate, $\sigma_p$ the stress response due to process $p$. Since both processes move at the same average rate, the stresses due to both transitions are related to the strain rate $\dot{\varepsilon}$ by

$$\dot{\varepsilon} = \dot{\varepsilon}_{0,p} \sinh \left( \frac{\sigma_p V^*_p}{RT} \right) \quad p = \alpha, \beta$$

(3.7)

if substituted in the definition for the viscosities, Eq. (3.6), and assuming a constant temperature, $T_0$, yields

$$\eta_p(\sigma_p) = \eta_{0,p} \frac{(\sigma_p/\sigma_{l,p})}{\sinh(\sigma_p/\sigma_{l,p})} \quad p = \alpha, \beta$$

(3.8)

where $\sigma_{l,p}$ is the nonlinearity parameter $\sigma_l$ for process $p$

$$\sigma_{l,p} = \frac{RT_0}{V^*_p}$$

(3.9)
and \( \eta_{0,p} \) the zero-viscosity \( \eta_0 \) for process \( p \)

\[
\eta_{0,p} = \frac{\sigma_{I,p}}{\dot{\varepsilon}_{0,p}} \exp \left( \frac{\Delta U_p}{RT} \right)
\]  

(3.10)

Introduction of the stress shift functions \( a_{\sigma_p}, p = \alpha, \beta \), which are defined as

\[
a_{\sigma_p}(\sigma_p) = \frac{(\sigma_p/\sigma_{I,p})}{\sinh(\sigma_p/\sigma_{I,p})} \quad p = \alpha, \beta
\]  

(3.11)

reduces Eq. (3.8) to

\[
\eta_p(\sigma_p) = \eta_{0,p} a_{\sigma_p}(\sigma_p) \quad p = \alpha, \beta
\]  

(3.12)

The major difference with the previous chapter is that the viscosity function of a particular process \( p \) no longer depends on the total stress, but only on that part of the total stress contributed by the specific process.

With use of these newly derived viscosity functions the Haward-Thackray model can be adapted in order to give a correct representation of the plastic behaviour of a thermorheological complex material. The adapted representation is shown by means of a mechanical analogy in Figure 3.8, thereby neglecting the strain hardening response.

![Figure 3.8: Two parallel nonlinear Maxwell elements used to describe the plastic deformation behaviour of a thermorheological complex material.]

Or analytically

\[
E(t) = E_{0,\beta} \exp \left( -\frac{t}{\tau_{\beta}(\sigma_{\beta})} \right) + E_{0,\alpha} \exp \left( -\frac{t}{\tau_{\alpha}(\sigma_{\alpha})} \right)
\]

No expression can be obtained for the compliance, since the retardation form is based on strain instead of stress additivity.

Using the values for the Eyring parameters tabulated in Table 3.1, the nonlinearity parameters and zero-viscosities of the model materials can be calculated, where it is assumed that \( T_0=20^\circ C \) (Table 3.2).
Table 3.2: Parameters of the nonlinear viscosity function, Eq. (3.12), for polycarbonate, polymethylmethacrylate and polypropylene, for a temperature of 20°C.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{l,p}$ [MPa]</th>
<th>$\eta_{0,p}$ [MPa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>$\alpha$ 1.259</td>
<td>$\beta$ 1.325</td>
</tr>
<tr>
<td></td>
<td>$\eta_{0,p}$ 1.00-10^22</td>
<td>$\eta_{0,p}$ 6.996-10^{-1}</td>
</tr>
<tr>
<td>PMMA</td>
<td>$\alpha$ 2.453</td>
<td>$\beta$ 3.223</td>
</tr>
<tr>
<td></td>
<td>$\eta_{0,p}$ 9.899-10^{-13}</td>
<td>$\eta_{0,p}$ 3.469-10^{-4}</td>
</tr>
<tr>
<td>PP</td>
<td>$\alpha$ 0.833</td>
<td>$\beta$ 0.872</td>
</tr>
<tr>
<td></td>
<td>$\eta_{0,p}$ 3.403-10^{-16}</td>
<td>$\eta_{0,p}$ 2.419-10^{-9}</td>
</tr>
</tbody>
</table>

### 3.3.3 Nonlinear Viscoelastic Deformation

As was the case for thermorheological simple materials, there are a number of similarities between the material behaviour in the linear viscoelastic and plastic range. The time-dependent material behaviour was again described using a spectrum of relaxation times thereby distinguishing between relaxation times caused by a specific transition. The plastic behaviour could be described using two stress-dependent Maxwell elements in parallel, indicating stress additivity. Analogous to the thermorheological simple approach, a new model for the complete range is derived by combining the characteristics from both bounding regions. However, unlike the previous chapter, there only results a single model since the Kelvin-Voigt model is based on strain additivity, and is therefore not capable of describing the typical yield behaviour. The resulting model is shown in terms of a mechanical model analogy in Figure 3.9.

![Figure 3.9: Generalized nonlinear Maxwell model, accounting for two processes.](image-url)
The matching analytical expression reads

\[ E(t) = \sum_{i=1}^{m} E_{\beta,i} \exp \left( -\frac{t}{\tau_{\beta,i}(\sigma)} \right) + \sum_{j=1}^{n} E_{\alpha,j} \exp \left( -\frac{t}{\tau_{\alpha,j}(\sigma)} \right) \]

where \( E_{p,i}, \tau_{p,i}(\sigma_p) (= \tau_{p,i} a_{\sigma_p}(\sigma_p)) \) refer to the \( i \)th Maxwell element of process \( p \), \( m \) and \( n \) are the number of elements.

Again, it can easily be seen that in the above representation the linear viscoelastic and plastic material behaviour are still preserved. For low stress levels, the stress shift functions \( a_{\sigma_p} \) equal one, and the linear form follows, whereas for high stresses both shift functions decrease exponentially resulting in the two yield contributions observed in the experiments.

From this formulation it is clear that each distribution of relaxation times is governed by its own characteristic stress dependence. Therefore, reduced times can be defined for each process separately

\[ \psi_p = \int_{-\infty}^{t} \frac{dt''}{a_{\sigma_p}[\sigma_p(t)]} \quad p = \alpha, \beta \]

where \( a_{\sigma_p} \) is the ratio of the relaxation time at a stress \( \sigma \), and the linear relaxation time (that is, the relaxation time for a stress well below \( \sigma_l \)) for process \( p \).

Using the previously defined reduced time \( \psi_p \), a stress-strain relation can be formulated separating the stress and time-dependences of the present spectra.

\[ \sigma(t) = \int_{-\infty}^{t} \left[ E_{\alpha}(\psi - \psi'_\alpha) + E_{\beta}(\psi - \psi'_\beta) \right] \dot{\epsilon}(t') dt' \quad (3.13) \]

where

\[ \psi_p = \int_{-\infty}^{t} \frac{dt''}{a_{\sigma_p}[\sigma_p(t)]} \quad \text{and} \quad \psi'_p = \int_{-\infty}^{t'} \frac{dt''}{a_{\sigma_p}[\sigma_p(t')]}, \quad p = \alpha, \beta. \]

Before any calculations can be performed, the necessary material parameters need to be determined, in this case the linear relaxation moduli \( E_p \), and the nonlinearity parameters \( \sigma_{l,p} \). However, the time-stress superposition used previously can no longer be used, since due to the different stress dependences the viscoelastic functions will change with applied stress, comparable to the effect of temperature. Unfortunately, both cases are no longer comparable because the stress shift depends only on a part of the total stress rather than on the total stress itself. To gain insight in the possible consequences of this difference for the characterization of a polymer material, a numerical investigation was undertaken, using the previously obtained stress-strain relation.
3.4 Numerical Investigation

In the previous section, it was argued that the deformation behaviour of a thermorheological complex behaving polymer is determined by the linear relaxation time spectra due to the different molecular processes, which are shifted differently to shorter times upon stress application. In this section, the consequences of this representation for the characterization strategy, outlined in the previous chapter, are investigated. For this purpose, firstly, suitable spectra are generated numerically since these are not yet experimentally accessible. Secondly, numerical calculations of creep experiments at various loads are performed, finally leading to conclusions with regard to the characterization strategy employed previously.

3.4.1 Model parameters

As already pointed out, two stress nonlinearities and two linear Maxwell spectra are needed to enable numerical simulations. In subsection 3.3.2, the nonlinearity parameters were determined for the three model materials, of which the values for PMMA are selected for further calculations. As the nonlinearity parameters are known, the two spectra are the last requirement. Since they can not yet be determined experimentally, they will be generated numerically. To ensure that the simulations are as realistic as possible these spectra have to satisfy a number of conditions:

1. the zero-viscosity values for both the $\alpha$- and $\beta$-spectrum should equal the values for polymethylmethacrylate determined from the yield experiments.

2. from DMTA experiments it follows that the initial modulus of the $\alpha$-contribution should be approximately twice as large as the initial modulus due to the $\beta$-process.

3. the spectra should produce yield-like behaviour within 5 to 6% strain.

Using the shape of the spectrum obtained for PC in Chapter 2 as a starting point, the spectra shown schematically in Figure 3.10 were generated. The actual discrete spectra which were used in the calculations are tabulated in Appendix B.

In Appendix B, the first two conditions were verified, whereas to verify the last condition tensile tests were simulated for strain rates ranging from $10^{-10}$ till $10^{-1}$ s$^{-1}$. The results of these numerical calculations are shown in Figure 3.11. From the figure it is clear that for all strain-rates yield was established well within the required 6% strain. Furthermore, it can be observed that at a strain rate of approximately $10^{-5}$ s$^{-1}$ there is an acceleration in the increase of the yield stress with strain rate due to the $\beta$-contribution. This can be visualized more clearly by plotting the resulting yield stresses against the applied strain-rate (Figure 3.12). In this figure, the yield points from the calculations are compared with
3.4 Numerical Investigation

Figure 3.10: Schematical representation of the numerically generated spectrum.

The analytically calculated yield behaviour using Eq. (3.4), showing an excellent agreement.

Figure 3.11: Numerical tensile experiments for log-equidistant strain rates from $10^{-10}$ to $10^{-1}$ s$^{-1}$ (arrow indicates increasing strain rate).

Figure 3.12: Yield stress versus applied strain rate, symbols indicate the values determined from the numerical tensile tests in Figure 3.11, the solid line is the analytical solution (Eq. (3.4)).

The calculations show that the spectra lead to the desired deformation behaviour, and therefore they will be used to calculate creep tests in the following subsection.

3.4.2 Numerical Simulations

As it was verified in the previous section that the obtained spectra were capable of providing the desired behaviour, numerical simulations of creep experiments are performed. Figure 3.13 shows the calculated creep curves at room temperature for stress levels from 5 to 75 MPa. Each load was applied in $10^{-2}$ s, and the
magnitude of the time scale used for the calculations was chosen such that a constant creep-rate was reached.

Based on the observations from section 3.3.1, the lower stress levels show the expected behaviour, initially elastic, followed by time-dependent creep ending with the marked transition where the $\beta$-process starts to flow. A constant plateau creep-rate is, however, not established since the flow behaviour is quickly stabilized because of the relatively small drop in modulus. The subsequent time-dependent creep behaviour is exclusively due to the $\alpha$-process, finally resulting in flow of the $\alpha$-process, which, in this numerical exercise, is not stabilized as the rubber contribution was neglected. For the higher stress levels an increased merging of both processes can be observed, ultimately resulting in the complete disappearance of the marked transition. This type of behaviour was observed in practice by Cessna (1971) for polypropylene creep at various stress levels, and a temperature of 60°C.

A remarkable result of the simulations is the fact that the occurrence of the $\beta$-transition appears to be independent of stress, at least for the lower stress levels. At first sight this may seem odd, since one might expect that it would also shift to shorter times with increasing stress. However, this apparent contradiction can be explained when the stress development for both processes is regarded, as shown in Figure 3.14.

After an initial increase in both stresses, corresponding to load application, the $\beta$-contribution to the total stress starts to decrease due to relaxation, thus automatically increasing the $\alpha$-contribution since the applied stress is constant. For the lower stress levels this process ends as the stress in the $\beta$-contribution reaches zero stress implying that the $\beta$-spectrum has returned to its linear representation ($a_{\beta}=1$). As a consequence, the occurrence of the transition will be independent of stress, and therefore always be observed at the same moment in time. This
Figure 3.14: Development of stress in the $\alpha$-spectrum (left), and the $\beta$-spectrum (right), for creep tests at loads from 5 to 75 MPa.

The process is illustrated in Figure 3.15 for a stress of 15 MPa, by means of the shape of the overall spectrum at different times during the creep experiment.

Figure 3.15: Compliance against time for a stress level of 15 MPa (A). Development of the stress in both the $\alpha$ and $\beta$-process (B). Shape of the spectrum on the times indicated in (B), where the dotted line indicates the initial spectrum before load is applied, and the solid lines the momentary spectra (C and D).

However, as the applied stress is increased, it reaches a level at which the $\beta$-
process cannot completely relax to zero stress, since at that level the time scale of the $\alpha$-process approaches that of the $\beta$. This level is the stress level at which the transition in Figure 3.13 is no longer visible as both processes have merged. This is shown in Figure 3.16, again in terms of the shape of the spectrum at different points during a creep experiment at a stress of 75 MPa.

![Figure 3.16](image)

**Figure 3.16:** Compliance against time for a stress level of 75 MPa (A). Development of the stress in both the $\alpha$ and $\beta$-process (B). Shape of the spectrum on the times indicated in (B), where the dotted line indicates the initial spectrum before load is applied, and the solid lines the momentary spectra (C, D and E).

Considering the fact that the $\beta$-process still contributes to the deformation as
it does not reach zero stress, it should also have a contribution to the final flow behaviour. This can be demonstrated by plotting the applied creep stress against the established plateau creep-rates, which can be determined using Sherby-Dorn plots (Sherby and Dorn, 1958). The results of this procedure is shown in Figure 3.17, where the solid line represents the analytically calculated yield behaviour (Eq. (3.4)).

![Graph showing applied stress against plateau creep rate](image)

**Figure 3.17:** Applied stress against the plateau creep rate determined from Figure 3.13 (symbols), compared to the analytically calculated yield behaviour according to Eq. (3.4) (solid line).

This figure shows that at the higher stress levels there indeed is a contribution to the flow behaviour due to the $\beta$-process, whereas it is absent at lower stress levels. However, the conclusion that the absence of a $\beta$-contribution to the flow behaviour at the lower stress levels implies an absence of the $\beta$-process at these stresses is certainly not true, since both Figure 3.13 and Figure 3.14 clearly show the presence of the $\beta$-process for a certain period of time.

To demonstrate the difference between the behaviour of a thermorheological complex material under constant stresses and constant temperatures, numerical simulations of a creep test at various temperatures are performed, using the temperature dependencies previously determined for polymethylmethacrylate. The results of the calculations are shown in Figure 3.18.
From this plot the difference with the constant stress experiments at a constant temperature should be clear immediately, as it shows that both contributions move to shorter times as temperature increases. Contrary to this, in the case of increasing stress the spectra moved in opposite directions due to relaxation of the $\beta$-process. Furthermore, the simulations show that as temperature increases the so-called relaxed $\beta$-compliance, $D_{R\beta}$, increases, which is in agreement with observations by Tomlins et al. (1994) and Read et al. (1994). However, they attribute this increase to the $\beta$-process, whereas in the previously derived approach it is caused by the $\alpha$-process. Or more precisely, by the fact that the $\alpha$-process has a stronger temperature dependence than the $\beta$-process, and therefore moves faster to shorter times.

### 3.4.3 Consequences for characterization

In subsection 3.3.3, the stress nonlinearities $\sigma_{l,p}$, the temperature dependencies $\Delta U_p$, and the linear relaxation time spectra $E_p(t)$ were identified as the key parameters in the description of the deformation behaviour of thermorheological complex materials. Similar to the previous chapter, both the stress nonlinearities and temperature dependencies could be readily obtained from yield experiments at different temperatures. In the same chapter the linear relaxation time spectrum was determined by means of time-stress superposition. However, in the preceding subsection it was shown that this technique is no longer applicable, since now there are two spectra, each with a different stress dependence. It was also shown that the situation is even more complicated due to the fact that both spectra only depend on a part of the total stress which varies in time. As a consequence, the overlap between the two spectra increases even faster, making it more difficult to separate them. In fact, the calculations show that the initial state is the most favorable for separating the contributions of the different molec-
3.5 Conclusions

Since most polymers exhibit more than one transition, the previously derived approach was extended to account for an additional molecular process. The contribution of this additional process to the linear viscoelastic deformation behaviour could be modeled by either two processes in parallel or in series. The yield behaviour could only be modeled by assuming stress additivity, that is, by means of two parallel processes. This resulted in an extension consisting of two linear relaxation time spectra in parallel, each governed by its own characteristic stress and temperature dependence. Whereas the influence of temperature and stress was comparable in a thermorheological simple material, in a thermorheological complex material it is not. This is due to the fact that the spectra no longer depend on the total stress but rather on a part of the total stress.

Numerical calculations of a tensile test at various strain rates showed that the plastic deformation behaviour predicted by the model showed good agreement with the yield behaviour observed in practice. Moreover, numerical simulations of creep experiments at various stress levels and temperatures showed a good qualitative agreement with experimental results concerning the linear viscoelastic and temperature dependent deformation behaviour observed in literature.
Chapter 4

Physical Aging and Mechanical Rejuvenation

4.1 Introduction

In the two preceding chapters, it was pointed out several times, that two important aspects of the deformation behaviour were not considered, physical aging and mechanical rejuvenation.

When a polymer melt is cooled, the molecular mobility diminishes until, at a certain temperature, the relaxation times start to exceed the experimental time scale, thus preventing the material to reach equilibrium; the melt becomes a glass. The temperature at which this takes place is termed the glass-transition temperature $T_g$, and depends on the cooling rate. Since the material is now in a non-equilibrium state, thermodynamic variables such as volume and enthalpy are greater than in equilibrium (Figure 4.1).

![Figure 4.1: Volume versus temperature for a glass-forming polymer.](image-url)
Although the mobility has decreased it has not reached zero, which gives the material the opportunity to establish equilibrium after all. This gradual approach of equilibrium is termed physical aging (Struik, 1978; McKenna, 1989), as to distinguish it from chemical aging (for example, thermal degradation, photo-oxidation). Besides affecting the thermodynamic properties, physical aging also has a pronounced influence on the mechanical behaviour.

The effect of aging can be neutralized, either by raising the temperature above the glass-transition temperature, or by applying plastic deformation, which is termed mechanical rejuvenation (McKenna and Kovacs, 1984). The most pronounced manifestation of the latter is observed in the form of a significant drop in viscosity after the yield point, and is also known as intrinsic strain softening.

In this chapter, aspects of both physical aging and mechanical rejuvenation are discussed. Firstly, the consequences of physical aging for the deformation behaviour are considered following the classical approach, mainly due to Struik (1978), which assumes that aging equally affects all relaxation times. McCrum (1984) proposed, however, the concept of sequential aging, suggesting that only relaxation times smaller than the aging time are affected. The latter approach is investigated more closely using a combination of experiments, and aspects of the aging behaviour observed in literature. Subsequently, the problem of mechanical rejuvenation is addressed which can be regarded to originate from either nonlinear viscoelasticity or a change in material structure. An approach assuming the latter is further investigated, leading to a concept similar to sequential aging.

### 4.2 Physical Aging in Monotone Loading

#### 4.2.1 Linear Viscoelastic Deformation

When considering the effects of physical aging on linear viscoelastic deformation behaviour, generally, two situations can be distinguished. In the first situation, the experimental time $t$ is smaller than the aging time $t_a$, whereas in the second situation it is larger than the aging time $t_a$.

If the experimental time $t$ is smaller than the aging time $t_a$, this implies that all aging has occurred prior to the experiment, that is, there will be no aging during the experiment. It was observed by Struik (1978) that in this case linear compliance curves shift to longer times with increasing aging time, as is shown schematically in Figure 4.2.

Apparently, physical aging causes an increase in the magnitude of the linear relaxation times. Although the direction differs, the similarity with the effect of a temperature increase is obvious, thus leading to the concept of time-aging time superposition. To describe this kind of behaviour, Struik (1978) defined a
4.2 Physical Aging in Monotone Loading

Figure 4.2: Small strain tensile creep for $t < t_e$, the arrow indicates the direction of increasing aging time $t_e$.

so-called shift rate, $\mu$

$$\mu = -\frac{d\log(a_{t_e})}{d\log(t_e)} \quad (4.1)$$

where $t_e$ is the aging time and $a_{t_e}$ is the ratio of a relaxation time at aging time $t_e$ and the relaxation time at a reference aging time $t'_e$. For polymers the value of $\mu$ is typically about unity, irrespective of the polymer considered, which suggests that all polymers age in the same way.

However, if the experimental time $t$ exceeds the aging time $t_e$, the material will age during the experiment. This was also investigated by Struik (1978), by comparison of the long term creep compliance, of a sample with an initial age $t_e$, and an extrapolation based on short term creep tests. This is shown schematically in Figure 4.3.

The figure shows that at a certain point in time the long term creep compliance starts to deviate from the extrapolated short-term creep compliance. At this point, which is approximately equal to the initial age $t_e$ of the sample, the experimental time has caught up with the aging process. Beyond this point the aging process appears to proceed faster, since the relaxation times are shifted to times longer than expected on the basis of short term experiments. To describe this particular long term aging behaviour, Struik (1978) introduced a so-called effective time $\lambda$, which is defined as

$$\lambda(t) = \int_0^t a(\xi)d\xi \quad (4.2)$$

where $\xi$ is an integration parameter on the $t$-time scale and the acceleration factor
\[ a(t) = \left( \frac{t_e}{t_e + t} \right)^\mu \]  

(4.3)

When Eqs. (4.2) and (4.3) are combined, an analytical expression for the reduced time results

\[ \lambda = t_e \ln \left( 1 + \frac{t}{t_e} \right) \quad \text{if} \quad \mu = 1 \]  

(4.4)

\[ \lambda = \frac{t_e}{\alpha} \left[ \left( 1 + \frac{t}{t_e} \right)^\alpha - 1 \right] \quad \text{if} \quad \mu < 1 \]  

(4.5)

where \( 0 < \alpha = 1 - \mu < 1 \). By only distorting the time scale beyond the point where the experimental time \( t \) approximately equals the aging time \( t_e \), the effective time is capable of describing the long term aging behaviour observed in practice.

### 4.2.2 Nonlinear Deformation

Extrapolating the results obtained for the aging process in linear viscoelasticity, the same shift of the relaxation times might also be expected in the nonlinear viscoelastic range. It was observed by Struik (1978) that nonlinear creep curves are indeed affected by aging, showing a shift to longer relaxation times with increasing aging time \( t_e \). The required shifts \( a_{t_e} \) were, however, less than those expected on the basis of Eq. (4.1). Moreover, the aging shifts \( a_{t_e} \) appeared to decrease as the applied stress was increased. The effect of stress is schematically summarized in Figure 4.4, which shows creep curves at two different aging times \( t_e \) and \( t'_e \) at a linear and a nonlinear stress level. For both stress levels aging
causes a shift to longer times, however, for the higher stress level the shift is smaller.

\[ \log(C) \text{ (Compliance)} \]

**Figure 4.4:** *Schematic illustration of the effects of aging and high stresses on creep according to Struik. \( t_e \) and \( t'_e \) are two different elapsed times (\( t'_e > t_e \)).*

For all stresses, the shift \( \log(a_{t_e}) \) increased almost linearly with \( \log(t_e) \), and therefore, the shifting can still be characterized by a shift rate \( \mu \). Since the shift decreases for increasing stress levels, the shift rate \( \mu \) also decreases as a function of stress (Struik, 1978), which is shown schematically in Figure 4.5.

\[ \text{Shift rate } \mu \]

**Figure 4.5:** *Shift rate \( \mu \) as a function of the applied stress.*

The observation of the aging shift being reduced by a nonlinear stress, also holds for the yield stress (Struik, 1978). This is depicted schematically in Figure 4.6, showing the expected shift in the yield stress, assuming that all relaxation times are equally influenced by aging, and the real shift which is considerably smaller due to the applied high stress. The effect summarized in Figure 4.6, was experimentally verified by Struik (1978) on polyvinylchloride samples of different ages.
4.2.3 Sequential Aging

Whereas Struik assumed that all relaxation times are equally affected by aging, McCrum (1984) proposed a sequential aging hypothesis which states that relaxation times are only influenced if they are equal or less in magnitude than the aging time $t_e$. As a result only the relaxation times smaller than a specific aging time $t_e$ will shift to longer times, as is shown schematically in Figure 4.7.

The sequential approach correctly represents the aging behaviour in the linear viscoelastic range. For experiments with an experimental time shorter than the aging time $t_e$, the normally observed time-aging time superposition is still valid. Moreover, it also explains the deviations in the creep behaviour in the case of long term experiments, where the experimental time overtakes the aging process.
An important implication of the above hypothesis is that aging does not influence the longest relaxation times, since these by far exceed the usually observed aging times. On the other hand, the longest relaxation times can be influenced by aging at elevated temperatures (annealing), as temperature considerably reduces all relaxation times. Whether these assumptions are correct, can be investigated by means of yield experiments using quenched and annealed samples with different ages, since the yield behaviour is determined by the longest relaxation times (Chapter 2). To determine the yield behaviour, uniaxial tensile experiments were performed on a Frank 81565 tensile tester equipped with a thermostatically controlled oven at strain rates ranging from $10^{-4}$ to $10^{-1} \text{s}^{-1}$ and temperatures from 20 to 80 °C. Dumb-bell shaped specimen were cut from compression moulded sheets quenched to room temperature, of General Electric polycarbonate Lexan® 141, 2 mm thick, according to ASTM D 638. One batch was annealed for 15 min at 145 °C, and subsequently quenched to room temperature. The samples were tested after aging at room temperature for 1 day, 10 days, and 266 days respectively. The results are presented by means of master curves for a reference temperature of 20 °C in Figure 4.8, which also shows the temperature shifts required to construct the master curves.

The figure clearly shows that annealing indeed influences the longest relaxation times, which is expressed by an increase in yield stress. Moreover, the figure shows that aging at room temperature or at elevated temperature (annealing), does not affect the activation volume $V^*$ (stress dependence) or the activation energy $\Delta U$ (temperature dependence). These results seem, however, to contradict the previously (subsection 4.2.2) discussed observations by Struik, who observed...
that the yield behaviour is affected by aging. This apparent contradiction can be explained from the fact that Struik used polyvinylchloride (PVC) as model material, whereas in this study polycarbonate (PC) was used. Since the glass-transition temperature of PVC is considerably lower than that of PC, 90 °C versus 155 °C, the longest relaxation time of PVC is much smaller than that of PC, and is therefore more susceptible to aging at room temperature compared to PC.

Additional evidence to support the concept of sequential aging is provided by Bauwens (1987). Bauwens compared tensile stress-strain curves for two polycarbonate samples aged at room temperature for 10 min and 3 years respectively. In a second experiment Bauwens (1987) compares the tensile stress-strain curve of the sample aged for 3 years at room temperature to that of a sample annealed 1 hour at 140 °C. Both cases are represented schematically in Figure 4.9.

![Stress-Strain Curves](image)

**Figure 4.9:** The left figure shows stress-strain curves of samples aged at room temperature for 10 min (a) and 3 years (b). The strain axis of curve b is shifted in order to compare the curves at the yield point. The figure on the right shows the stress-strain curves of a sample aged at room temperature for 3 years (b) and a sample annealed 1 hour at 140 °C (c).

In agreement with the previously performed yield experiments, the figure on the left shows that the yield behaviour is not influenced by aging at room temperature. The slope at the origin differs, however, indicating that the Young’s modulus increases with increasing aging time, which agrees with the observations by Struik (1978). The observed deviations are restricted to the lower relaxation times, thus supporting the concept of sequential aging. In contrast to the previous observation, the right figure shows that annealing affects the yield stress rather than the Young’s modulus. This can be understood considering that annealing at 140 °C is in principle equivalent to aging just below $T_g$, and therefore
only influences the longest relaxation times, which determine the yield behaviour.

More experimental evidence is provided by Venditti and Gillham (1992a,b), who used torsional bread analysis to show that aging at different temperatures only affects the part of the relaxation time spectrum that corresponds with the particular aging temperature.

To describe sequential aging it is assumed that the viscosity of a relaxation time is no longer constant but evolves to an equilibrium value, hereby neglecting the minor increase in modulus due to the densification of the material. The evolution of the viscosity is modeled using the parameter $A = \log(\eta)$, which obeys the following first order equation

$$\dot{A} = -k_a \frac{A - A_\infty}{\tau(A,\sigma)}$$

where $A = \log(\eta)$, $k_a$ is a constant, $A_\infty$ the equilibrium value, and $\tau$ the relaxation time, which depends on stress $\sigma$ and the parameter $A$. If a spectrum of relaxation times is considered, the viscosity in each element evolves according to Eq. (4.6), where $\tau$ is the relaxation time of the specific element.

### 4.3 Rejuvenation at Plastic Deformations

Tensile stress-strain curves of polymer materials frequently exhibit a well defined maximum stress, the yield point. After the yield point often necking occurs, which is accompanied by a drop in the load. Tervoort (1996) argues that this load drop is initiated by the nonlinear flow behaviour, and is enhanced by intrinsic strain softening (rejuvenation). Hasan et al. (1993) demonstrated the existence of rejuvenation by comparison of uniaxial compression experiments on quenched and annealed polymethylmethacrylate samples. Although annealing introduces a considerable difference in the yield stress, the constant stress to which the flow stress evolves is the same for both quenched and annealed samples. Similar effects were observed on the tensile behaviour of quenched and annealed polycarbonate by Tervoort (1996). The level that is reached is usually regarded as a saturation level of rejuvenation. Positron annihilation lifetime spectroscopy by Hasan et al. (1993), showed that both the initially quenched and annealed samples possessed the same post-deformation free-volume distribution, which was larger than the initial distribution. According to Hasan et al. (1993) shear transformations occur in regions of increased free volume, since in these regions the resistance to deformation is lower. To describe the rejuvenation behaviour Hasan et al. (1993) proposed a first order evolution equation for the number density $D$ of such regions.
as a function of plastic strain

$$\frac{dD}{d\gamma_p} = -\frac{D - D_\infty}{\tau_p}$$

(4.7)

where $D_\infty$ is the equilibrium value of $D$, and $\tau_p$ is a relaxation time.

### 4.4 Rejuvenation at Moderate Deformations

In the previous section rejuvenation at large deformations was discussed. It was argued that rejuvenation attains a saturation level independent of the thermal history of the test sample, thus completely erasing the history. Whereas the concept of rejuvenation is generally accepted in the description of this deformation range, in the nonlinear viscoelastic range it is more controversial. Some workers (Struik, 1978; Yee et al., 1988) have stated that rejuvenation also occurs in the nonlinear viscoelastic range, but this is disputed by others (Lee and McKenna, 1990), who argue that the observed effects can also be described using a nonlinear constitutive relation with fading memory.

#### 4.4.1 Observations

In the introduction to this chapter it was already mentioned that the effect of applying plastic deformation is comparable to a temperature quench. As a consequence, any aging prior to the load application will be erased, whereas after unloading, aging will be reinitiated. This effect was demonstrated by Struik (1978), by means of applying the stress history shown in Figure 4.10 to a sample of PVC, which resulted in the linear creep behaviour schematically represented in Figure 4.11.

**Figure 4.10:** Stress history leading to the small-strain creep behaviour shown in Figure 4.11.

**Figure 4.11:** Reactivation of aging in linear viscoelasticity after application of a high stress pulse.
After removal of the applied high stress, aging is reactivated and the creep curves shift towards the curve obtained before application of the high stress pulse.

To demonstrate the characteristic deformation behaviour during and after a stress pulse, creep-recovery experiments were performed on a Zwick Rel hydraulic tensile tester at loads from 10 to 40 MPa for 2000 seconds, whereas the strain was measured using an Instron (2602-602) strain gauge extensometer with a measure length of 50 mm and a range of ± 2.5 mm. The samples used, were injection moulded tensile bars, produced according to ASTM D 638 from General Electric polycarbonate Lexan® 161R, which all had an age of approximately a year. The results of these experiments are shown in Figure 4.12, together with a comparison of the strains upon loading and unloading.

![Creep-recovery experiments](image)

**Figure 4.12:** Creep-recovery tests on polycarbonate at various stress levels (left) and the strains upon loading and unloading as a function of creep stress (right).

The figure on the right clearly shows that the difference between the strains upon loading and unloading increases, the strain upon unloading increasing faster, which is in agreement with observations by Mindel and Brown (1973). Since linear viscoelastic, or stress-accelerated models are not capable of describing this typical nonlinear behaviour, Schapery models are commonly used (Schapery, 1969, see also Chapter 1). The strength of these representations lies in the nonlinear functions present in these models which are used to capture the various observed nonlinearities. One of the major disadvantages of the Schapery models is the fact that all creep-recovery data are required to determine these nonlinear functions. Consequently, care should be taken regarding extrapolations outside the experimental window.

In spite of this limitation, this type of models is well-suited to describe the response to a single stress pulse. However, when a material is loaded repeatedly, the Schapery models fail due to the so-called intermittent loading anomaly. This anomaly states that in a given time a high stress will produce more creep when applied intermittently than when applied continuously (Struik, 1978), as is shown schematically in Figure 4.13.
Since according to a Schapery model for high stresses the strain upon unloading exceeds that upon loading, the predicted creep due to repeated loading will be less than that due to a comparable constant load.

Instead of describing the observed behaviour by means of nonlinearities, it could also be hypothesized that it is introduced by a modification of the material structure due to the applied high stress; mechanical rejuvenation. In the previous section it was shown that rejuvenation is generally accepted in plastic deformation where it accounts for the considerable load drop beyond the yield point. Since the plastic deformation behaviour is determined by the longest relaxation times (Chapter 2), it could be argued that the observed viscosity drop also applies to the rest of the spectrum, resulting in a shortening of the relaxation times. To describe this effect a rejuvenation shift $a_r$ is introduced, which equally decreases all relaxation times upon application of a high stress. By implementing the rejuvenation shift $a_r$ in the stress-strain relation Eq. (2.16), it can be evaluated whether this approach can account for the increased strain upon unloading. The unloading strain as function of stress was calculated for various values of $a_r$, and the results of these calculations are shown in Figure 4.14.

Figure 4.14 shows that the increase in the unloading strain can be described by using an $a_r$ that increases with stress. Furthermore, this approach would imply that the strain contribution of each following stress pulse would increase, thus providing a possible explanation for the intermittent loading anomaly.

In the foregoing it was assumed that all relaxation times are equally affected by stress, which was expressed by means of the rejuvenation shift $a_r$. The validity of this assumption can be verified by investigating if a stress below the yield stress can influence the longest relaxation times, that is, the yield stress. To
determine the yield behaviour, uniaxial tensile experiments were performed on a Frank 81565 tensile tester at strain rates from $10^{-4}$ to $10^{-1}$ s$^{-1}$ and room temperature. The samples used, were injection moulded tensile bars, produced according to ASTM D 638 from General Electric polycarbonate Lexan® 161R. A number of samples were mechanically conditioned by applying a load of 40 or 50 MPa for 1000 seconds, and were tested immediately afterwards. The resulting yield stresses are compared to those of untreated samples in Figure 4.15.

Figure 4.14: Unloading strain versus stress calculated for values of $a_r$ ranging from $10^4$ to $10^9$ (solid lines), compared to experimental values (+).

Figure 4.15: Comparison of yield stress versus strain rate for both samples mechanically conditioned at 40 (△) and 50 MPa (○), and untreated samples (+), the solid line represents a fit.

Figure 4.15 shows that the yield stress seems to be unaffected by the mechanical conditioning. Moreover, considering that the slope of the yield stress as function of strain rate also remains the same, this implies that the activation volume $V^*$ is also unaffected. These results suggest that not all relaxation times are involved
in the rejuvenation process, but that the effect is limited to a restricted range of relaxation times. Since this strongly resembles the behaviour observed for aging, a similar concept is proposed, sequential rejuvenation.

4.4.2 Sequential Rejuvenation

In the preceding subsection it was argued that the nonlinearity in the unloading strain of creep-recovery experiments could be described using a rejuvenation shift $\alpha_r$. Furthermore, it was shown that the initial assumption that all relaxation times were equally affected was not correct, leading to the proposition of sequential rejuvenation. This principle states that only those relaxation times that are in equilibrium (that is, are flowing) are rejuvenated, resulting in a reduction of the viscosity and thus of the relaxation time. As a consequence, a comparison of the tensile stress-strain curves of both a treated and an untreated sample, should only show a deviation over a limited range of relaxation times, similar to the observations by Bauwens (1987) for aging. This comparison is shown in Figure 4.16.

![Figure 4.16](image)

*Figure 4.16: In both figures the stress-strain curve for an untreated sample is compared with those of samples treated at 40 and 50 MPa respectively. In the figure on the right the samples were tested immediately after conditioning, whereas for the other figure they were allowed to age for 3 days at room temperature.*

The figure on the left shows that the stress-strain curves indeed show deviations up to a certain stress level which differs for both applied stress levels, corresponding to different relaxation times. Furthermore, it is shown by the figure on the right that if the conditioned samples are allowed to age at room temperature for 3 days the effect has disappeared. This can be understood since the affected relaxation times are not restored to their original value, and as a consequence will be influenced by aging on a much shorter time scale than under normal conditions (that is, no rejuvenation).
It could, however, be argued that the observed effects are due to nonlinear viscoelasticity, rather than due to a change in the material structure. This would imply that rejuvenation in the plastic range should not show this recovery, since this range lacks viscoelastic behaviour. To verify this, tensile experiments were performed on a Frank 81565 tensile tester, at a strain rate of $2.25 \cdot 10^{-3} \text{ s}^{-1}$ and room temperature. For these tests, dog-bone shaped axi-symmetrical tensile bars, manufactured from extruded polycarbonate (bisphenol A, Bayer) rod, were subjected to large strain torsion at room temperature (method by Tervoort (1996)). The samples were tested either immediately after conditioning or after aging at room temperature for several days. The resulting tensile stress-strain curves are shown in Figure 4.17, where they are compared to the tensile stress-strain curve of an untreated sample.

![Tensile stress-strain curves](image)

**Figure 4.17:** Tensile stress-strain curves for an untreated sample (c) and two rejuvenated samples, one tested immediately (a) and one after aging at room temperature for 10 days (b).

After 10 days the conditioned sample has already recovered considerably, it is however to be expected that a complete recovery will take longer since the yield behaviour concerns the longest relaxation times, which are much larger than those responsible for the deviations observed at 40 and 50 MPa.

To describe the sequential rejuvenation process it is assumed that the viscosity of each relaxation time evolves to a saturation level, similar to the strain softening behaviour. Just like sequential aging, this behaviour is modeled by means of the parameter $A = \log(\eta)$, which obeys the following first order evolution law

$$
\dot{A} = k_r \frac{A - A_{sat}}{\tau(\sigma, A)} \sigma
$$

where $A = \log(\eta)$, $k_r$ is a constant, $A_{sat}$ the saturation level, and $\tau$ the relaxation time, which depends on stress $\sigma$ and the parameter $A$. 
If the equation for sequential aging is recalled (Eq. (4.6)), a single equation, describing both the sequential influence of aging and rejuvenation, is obtained

\[ \dot{A} = -k_a \frac{A - A_\infty}{\tau(\sigma, A)} + k_r \frac{A - A_{sat}}{\tau(\sigma, A)} \sigma \]  

(4.9)

For a spectrum of relaxation times this means that the viscosity of each relaxation time evolves according to Eq. (4.9), \( \tau \) denoting the momentary value of a particular relaxation time, which depends on both the stress \( \sigma \) and the parameter \( A \).

### 4.5 Conclusions

In this chapter the influence of physical aging and mechanical rejuvenation was addressed. It was shown that physical aging has an influence on the entire range of deformation behaviour. The classical approach assumes that this influence is equal for all relaxation times. However, by means of experiments and observations in literature it was shown that a sequential approach provides a better explanation for the observed aging phenomena. The influence of rejuvenation is experienced in the nonlinear viscoelastic range, but most pronounced in the plastic range where it causes a considerable drop in the viscosity at yield. Extrapolation of the concept used in the plastic range to all relaxation times, enabled the description of some of the phenomena observed in nonlinear viscoelasticity. The employed strategy assumed that all relaxation times were similarly affected by rejuvenation, yield experiments showed, however, that a sequential approach was more appropriate.
Chapter 5

Generalization to Finite Strains

Tervoort (1996) derived a basic model, the so-called “compressible Leonov mode”, to describe the three-dimensional relaxation behaviour of a polymer glass. Subsequently, assuming a single, active molecular transition, he extended the Leonov model to a “multi-mode” representation to enable a correct description of the stress- and time-dependent deformation behaviour of a polymer glass up to and including yield. After a brief review of this representation the insights obtained in Chapter 3 will be used to extend the single-process approximation to a multiple-process approximation. Finally, the importance of an additional process in the case of impact behaviour is demonstrated, resulting in a simplified set of equations describing the three-dimensional yield behaviour. In all representations the three-dimensional strain hardening response is taken into account, and is described by neo-Hookean behaviour.

5.1 Thermorheological Simple Material

As already pointed out, the basic model is the “compressible Leonov mode”. Such a mode is in essence a single Maxwell element, which splits the total rate-of-strain tensor $\mathbf{D}$ in an elastic part $\mathbf{D}_e$ and a plastic part $\mathbf{D}_p$. The relaxation time, $\lambda = \eta(\tau_{eq})/G$ depends on an equivalent stress $\tau_{eq}$, which is proportional to the Von Mises stress. The nonlinearity in $\eta(\tau_{eq})$ is completely determined by the parameter $\tau_0$ (equivalent with $\sigma_l$ in Chapter 2, and related to the activation volume $V^*$). The Leonov mode is capable of describing finite deformations, and separates the (elastic) hydrostatic stress (constant bulk modulus $K$), and (viscoelastic) deviatoric stress (Tervoort, 1996).

Since a single nonlinear relaxation time can not account for the time-dependent behaviour observed in practice, the representation was extended to a “multi mode” expression. This expression represents a spectrum of Leonov modes which, assuming a single process, are all the same function of the equivalent stress $\tau_{eq,\alpha}$,
and is written as

\begin{align}
T &= K(J - 1)I + \sum_{i=1}^{n} G_{\alpha,i} \tilde{B}_{e,\alpha,i}^d + G_r \tilde{B}_{e,r}^d \\
\dot{J}I &= J \text{tr}(D)I \\
\dot{\tilde{B}}_{e,\alpha,i} &= (D^d - D_{p,\alpha,i}) \cdot \tilde{B}_{e,\alpha,i} + \tilde{\tilde{B}}_{e,\alpha,i} \cdot (D^d - D_{p,\alpha,i}) \\
D_{p,\alpha,i} &= \frac{T_{d,\alpha,i}^d}{2 \eta_{\alpha,i} \left( \frac{\tau_{eq,\alpha}}{\tau_{0,\alpha}} \right)} \\
\eta_{\alpha,i}(\tau_{eq,\alpha}) &= \eta_{0,\alpha,i} a_{\sigma,\alpha} \\
a_{\sigma,\alpha} &= \frac{\left( \frac{\tau_{eq,\alpha}}{\tau_{0,\alpha}} \right)}{\sinh \left( \frac{\tau_{eq,\alpha}}{\tau_{0,\alpha}} \right)} \\
\tau_{eq,\alpha} &= \sqrt{\frac{1}{2} \text{tr}(T_{\alpha,i}^d \cdot T_{\alpha,i}^d)} \\
T_{\alpha,i}^d &= \sum_{i=1}^{n} G_{\alpha,i} \tilde{B}_{e,\alpha,i}^d \\
\tilde{\tilde{B}}_{e,r} &= D^d \cdot \tilde{B}_{e,r} + \tilde{B}_{e,r} \cdot D^d
\end{align}

Here, $T$ is the Cauchy stress tensor, $K$ is the bulk modulus, $G$ the shear modulus, $G_r$ the strain-hardening modulus, $J - 1$ the relative volume increase, and $\tilde{B}_e$ an internal variable, describing the isochoric elastic deformation stored in the Leonov mode.

### 5.2 Thermorheological Complex Material

In Chapter 3 it was demonstrated that a correct extension towards a multiple-process model can be obtained emanating from stress additivity, implying two parallel spectra each depending on its own characteristic stress dependences $\tau_{eq,\alpha}$ and $\tau_{eq,\beta}$. An additional assumption is, however, required regarding the description of the volume response of both processes. Since the volume response is assumed to be elastic, a separate $\alpha$- and $\beta$-contribution to the volume response was not taken into account. Finally, this leads to the following representation

\begin{align}
T &= K(J - 1)I + \sum_{i=1}^{n} G_{\alpha,i} \tilde{B}_{e,\alpha,i}^d + \sum_{j=1}^{m} G_{\beta,j} \tilde{B}_{e,\beta,j}^d + G_r \tilde{B}_{e,r}^d \\
\dot{J}I &= J \text{tr}(D)I \\
\dot{\tilde{B}}_{e,\alpha,i} &= (D^d - D_{p,\alpha,i}) \cdot \tilde{B}_{e,\alpha,i} + \tilde{\tilde{B}}_{e,\alpha,i} \cdot (D^d - D_{p,\alpha,i})
\end{align}
5.3 Simplification for Large Deformations

\[ D_{p,\alpha,i} = \frac{T_{d,\alpha,i}^d}{2\eta_{\alpha,i}(\tau_{eq,\alpha})} \]  

(5.2d)

\[ \eta_{\alpha,i}(\tau_{eq,\alpha}) = \eta_{0,\alpha,i}a_{\sigma,\alpha} \]  

(5.2e)

\[ a_{\sigma,\alpha} = \frac{\left(\frac{\tau_{eq,\alpha}}{\tau_{0,\alpha}}\right)}{\sinh\left(\frac{\tau_{eq,\alpha}}{\tau_{0,\alpha}}\right)} \]  

(5.2f)

\[ \tau_{eq,\alpha} = \sqrt{\frac{1}{2} \text{tr}(T_{d,\alpha}^d \cdot T_{d,\alpha}^d)} \]  

(5.2g)

\[ T_{d,\alpha}^d = \sum_{i=1}^{n} T_{d,\alpha,i}^d = \sum_{i=1}^{n} G_{\alpha,i} \tilde{B}_{e,\alpha,i} \]  

(5.2h)

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

(5.2i)

\[ D_{p,\beta,j} = \frac{T_{d,\beta,j}^d}{2\eta_{\beta,j}(\tau_{eq,\beta})} \]  

(5.2j)

\[ \eta_{\beta,j}(\tau_{eq,\beta}) = \eta_{0,\beta,j}a_{\sigma,\beta} \]  

(5.2k)

\[ a_{\sigma,\beta} = \frac{\left(\frac{\tau_{eq,\beta}}{\tau_{0,\beta}}\right)}{\sinh\left(\frac{\tau_{eq,\beta}}{\tau_{0,\beta}}\right)} \]  

(5.2l)

\[ \tau_{eq,\beta} = \sqrt{\frac{1}{2} \text{tr}(T_{d,\beta}^d \cdot T_{d,\beta}^d)} \]  

(5.2m)

\[ T_{d,\beta}^d = \sum_{j=1}^{m} T_{d,\beta,j}^d = \sum_{j=1}^{m} G_{\beta,j} \tilde{B}_{e,\beta,j} \]  

(5.2n)

\[ \tilde{B}_{e,r} = D^d \cdot \tilde{B}_{e,r} + \tilde{B}_{e,r} \cdot D^d \]  

(5.2o)

Here, \( a_{\sigma,\alpha} \) and \( a_{\sigma,\beta} \) are the shift functions for the relaxation times associated with the \( \alpha \)- and \( \beta \)-process respectively. Since, \( \tau_{0,\alpha} \) and \( \tau_{0,\beta} \) are not the same the response of the shift functions will be differently (see also Chapter 3).

5.3 Simplification for Large Deformations

In the previous section the initially single-process multi-mode Leonov model was extended, as to account for an additional process. That such an extension is relevant can be demonstrated by considering the yield behaviour of polycarbonate as was determined in Chapter 3. The yield behaviour is shown in Figure 5.1, together with a fit using two parallel Eyring processes. Furthermore, the \( \alpha \)-contribution is also shown separately.
From this figure it is clear that at high strain-rates, as for instance in impact, a description of the yield behaviour purely based on the $\alpha$-process introduces a considerable deviation from the actual plastic deformation behaviour. To describe the plastic deformation behaviour the previously presented multi-process multimode Leonov model can be simplified considerably, since for high stresses the viscosities of both processes each sum to a single value. This results in the following, simplified representation

\[
\mathbf{T} = K(J - 1)\mathbf{I} + G_\alpha \tilde{\mathbf{B}}_{e,\alpha}^{d} + G_\beta \tilde{\mathbf{B}}_{e,\beta}^{d} + G_r \tilde{\mathbf{B}}_{e,r}^{d} \tag{5.3a}
\]

\[
\dot{J}\mathbf{I} = J \text{tr}(\mathbf{D})\mathbf{I} \tag{5.3b}
\]

\[
\dot{\tilde{\mathbf{B}}}_{e,\alpha} = (\mathbf{D}^d - \mathbf{D}_{p,\alpha}) \cdot \tilde{\mathbf{B}}_{e,\alpha} + \tilde{\mathbf{B}}_{e,\alpha} \cdot (\mathbf{D}^d - \mathbf{D}_{p,\alpha}) \tag{5.3c}
\]

\[
\mathbf{D}_{p,\alpha} = \frac{T_d^\alpha}{2\eta_\alpha(\tau_{eq,\alpha})} \tag{5.3d}
\]

\[
\eta_\alpha(\tau_{eq,\alpha}) = \eta_{0,\alpha} a_{\sigma_\alpha} \tag{5.3e}
\]

\[
a_{\sigma_\alpha} = \frac{\tau_{eq,\alpha}}{\sinh(\tau_{eq,\alpha}/\tau_{0,\alpha})} \tag{5.3f}
\]

\[
\tau_{eq,\alpha} = \sqrt{\frac{1}{2} \text{tr}(\mathbf{T}_{\alpha}^d \cdot \mathbf{T}_{\alpha}^d)} \tag{5.3g}
\]

\[
\mathbf{T}_{\alpha}^d = G_\alpha \tilde{\mathbf{B}}_{e,\alpha}^d \tag{5.3h}
\]

\[
\tilde{\mathbf{B}}_{e,\beta} = (\mathbf{D}^d - \mathbf{D}_{p,\beta}) \cdot \tilde{\mathbf{B}}_{e,\beta} + \tilde{\mathbf{B}}_{e,\beta} \cdot (\mathbf{D}^d - \mathbf{D}_{p,\beta}) \tag{5.3i}
\]
5.3 Simplification for Large Deformations

\[
D_{\gamma,\beta} = \frac{T_d^\beta}{2 \eta_\beta(\tau_{eq,\beta})} \quad (5.3j)
\]

\[
\eta_\beta(\tau_{eq,\beta}) = \eta_{0,\beta} a_{\sigma_\beta} \quad (5.3k)
\]

\[
a_{\sigma_\beta} = \frac{\left(\begin{array}{c} \tau_{eq,\beta} \\ \tau_{0,\beta} \end{array}\right)}{\sinh\left(\begin{array}{c} \tau_{eq,\beta} \\ \tau_{0,\beta} \end{array}\right)} \quad (5.3l)
\]

\[
\tau_{eq,\beta} = \sqrt{\frac{1}{2} \text{tr}(T_d^\beta \cdot T_d^\beta)} \quad (5.3m)
\]

\[
T_d^\beta = G_{\beta} \tilde{B}_d^\beta \quad (5.3n)
\]

\[
\tilde{\tilde{B}}_{e,r} = D^d \cdot \tilde{B}_{e,r} + \tilde{B}_{e,r} \cdot D^d \quad (5.3o)
\]
Chapter 6
Conclusions and Recommendations

6.1 Conclusions

The objective of this report was to find a constitutive relation for the deformation behaviour of polymer materials, and thereby establish a link between the deformation behaviour and underlying molecular processes. For a thermorheological simple material, that is, a material with a single (active) molecular process, it was shown that the entire deformation behaviour was determined by the linear relaxation/retardation time spectrum which is accelerated by stress. The stress dependence is of the Eyring type, and is the same for each relaxation time, implying that time-stress superposition is applicable. This applicability was verified experimentally, using polycarbonate as a model material since it exhibits only a single active relaxation mechanism at room temperature. Moreover, the time-stress superposition principle was used to determine the linear retardation and relaxation time spectrum. Subsequent numerical predictions of a tensile test at various strain rates showed an excellent agreement with experimental data.

Since polymer materials usually exhibit multiple processes, the single process approximation was extended to account for the contribution of an additional process. It was shown that in linear viscoelasticity this extension could be achieved by assuming either stress or strain additivity. Experiments in the plastic range, on the other hand, clearly indicate stress additivity, thus leading to a model consisting of two parallel spectra, each with its own characteristic stress dependence. Contrary to the model based on a single process, these stress dependences are a function of the stress contributed by a specific process, rather than of the total stress. Since the separate spectra were not experimentally accessible, predictions were made using numerically generated spectra. The predictions showed a good qualitative agreement with the deformation behaviour observed in literature.

Physical aging and mechanical rejuvenation are known to have a pronounced influence on the mechanical behaviour of polymer materials. In the classical ap-
Conclusions and Recommendations

proach the influence of aging is presumed to be the same for the entire range of relaxation times. However, yield experiments, and experiments in literature show that aging at a specific temperature only influences a limited part of the relaxation time spectrum. Moreover, it was shown that the aging process has no effect on the activation volume and energy. To describe the aging process, the sequential aging hypothesis therefore appears to be a better choice. The influence of mechanical rejuvenation is most clearly observed after the yield point where it causes a load drop to a saturation stress, since this stress appears to be independent of the thermal history. Experiments in literature and creep-recovery experiments suggest that the same phenomenon also influences the deformation behaviour at intermediate deformations. It was, however, shown by means of yield stress experiments that mechanical rejuvenation below the yield stress does not affect the yield point, indicating that the concept of sequential rejuvenation is more appropriate.

Finally, it was shown that for experiments at high strain-rates, such as impact tests, the contribution due to the $\beta$-process cannot be neglected, and must therefore be accounted for in the constitutive relation used to describe these tests.

6.2 Recommendations

Since the multiple-process model derived in this report could only be validated using numerically generated spectra, it is desirable to investigate the possibilities to an experimental determination of these spectra. This implies determining the relevant viscoelastic properties as well as finding the proper method to correctly separate the contributions due to the different molecular processes.

With regard to physical aging and mechanical rejuvenation much research is aimed at isothermal long-term deformation at constant stress, whereas in practice both the load and temperature will vary. As a consequence, at this moment there is no framework to enable a well-founded estimate for the long term deformation behaviour under practical circumstances. Therefore, it might be worthwhile to further investigate the proposed concepts of sequential aging and rejuvenation, both experimentally and numerically.
References


REFERENCES


Appendix A

Fit parameters of the Kelvin-Voigt and Maxwell model

The linear compliance curve (Figure 2.13) is fitted using a generalized Kelvin-Voigt model (Eq. (2.2)). By means of a nonnegative least squares method (Lawson and Hanson, 1974), the following values were obtained, $D_g = 4.1864835 \cdot 10^{-4} \text{MPa}^{-1}$, $\eta_0 = 2.7399940 \cdot 10^{21} \text{MPa s}$, whereas the values of the remaining parameters are tabulated in Table A.1.

<table>
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<th>$\tau_i$ [s]</th>
<th>$D_i$ [MPa$^{-1}$]</th>
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<td>$8.7840622 \cdot 10^{-6}$</td>
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<td>$5.2435732 \cdot 10^{-6}$</td>
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<tr>
<td>4</td>
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<td>$4.7031689 \cdot 10^{-6}$</td>
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Table A.1: Values for the Kelvin-Voigt parameters.

After conversion of the linear compliance, the resulting linear relaxation modulus (Figure 2.14) was approximated using a generalized Maxwell model (Eq. (2.1)).
By means of a nonnegative least squares method (Lawson and Hanson, 1974) the parameter values tabulated in Table A.2 were obtained.

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<th>(E_i [\text{MPa}])</th>
<th>(\eta_i [\text{MPa.s}])</th>
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<td>(1.0946296 \cdot 10^5)</td>
<td>(1.6668076 \cdot 10^5)</td>
</tr>
<tr>
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<td>(1.2302845 \cdot 10^5)</td>
<td>(1.9463704 \cdot 10^5)</td>
</tr>
<tr>
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<td>(1.6436965 \cdot 10^4)</td>
<td>(1.2840997 \cdot 10^5)</td>
<td>(2.1106701 \cdot 10^5)</td>
</tr>
<tr>
<td>13</td>
<td>(1.7077460 \cdot 10^4)</td>
<td>(1.4149526 \cdot 10^5)</td>
<td>(2.4163797 \cdot 10^5)</td>
</tr>
<tr>
<td>14</td>
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<td>(3.3755816 \cdot 10^5)</td>
<td>(4.1386387 \cdot 10^5)</td>
</tr>
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<td>(1.2468446 \cdot 10^5)</td>
<td>(1.9558338 \cdot 10^5)</td>
</tr>
<tr>
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<td>(1.1726505 \cdot 10^5)</td>
<td>(2.5404006 \cdot 10^5)</td>
</tr>
<tr>
<td>17</td>
<td>(2.7716879 \cdot 10^4)</td>
<td>(7.0982798 \cdot 10^5)</td>
<td>(1.9674217 \cdot 10^6)</td>
</tr>
</tbody>
</table>

**Table A.2:** Values for the Maxwell parameters.
Appendix B

Data for the numerical spectra

For the numerical calculations two discrete spectra have been constructed, using the previously obtained Maxwell spectrum for polycarbonate as a starting point for the shape. This resulted in the values for the parameters of the discrete $\alpha$-Maxwell spectrum tabulated in Table B.1.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\tau_{\alpha,i}$ [s]</th>
<th>$E_{\alpha,i}$ [MPa]</th>
<th>$\eta_{\alpha,i}$ [MPa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5145022 \times 10^{-4}</td>
<td>1.00571 \times 10^{1}</td>
<td>1.52315 \times 10^{-3}</td>
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<tr>
<td>2</td>
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<td>1.25991 \times 10^{1}</td>
<td>1.69965 \times 10^{-2}</td>
</tr>
<tr>
<td>3</td>
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<td>1.56112 \times 10^{1}</td>
<td>1.87587 \times 10^{-1}</td>
</tr>
<tr>
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<td>1.94516 \times 10^{1}</td>
<td>2.08195 \times 10^{0}</td>
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<tr>
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<td>2.41999 \times 10^{1}</td>
<td>2.30716 \times 10^{1}</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>5.80112 \times 10^{1}</td>
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<tr>
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<td>1.76043 \times 10^{2}</td>
<td>1.75840 \times 10^{13}</td>
</tr>
</tbody>
</table>

Table B.1: Parameter values for the discrete $\alpha$-spectrum.

Following a similar approach for the $\beta$-Maxwell spectrum resulted in the parameter values tabulated in Table B.2.
Data for the numerical spectra

To verify if the spectra satisfy the imposed boundary conditions regarding the viscosities of both processes and the ratio of the moduli, these values are calculated for both the $\alpha$- and $\beta$-spectrum:

- $\eta_{0,\alpha} = \sum_{i=1}^{18} \eta_{\alpha,i} = 9.899 \cdot 10^{13}$ MPa\(s\),
- $\eta_{0,\beta} = \sum_{i=1}^{11} \eta_{\beta,i} = 3.4695 \cdot 10^4$ MPa\(s\),

whereas the ratio of the moduli yields

$$\frac{E_{0,\alpha}}{E_{0,\beta}} = \frac{\sum_{i=1}^{18} E_{\alpha,i}}{\sum_{i=1}^{11} E_{\beta,i}} = 2.3$$

It is clear that the viscosity values match the values obtained in Chapter 3 for PMMA (Table 3.2), whereas the ratio of the moduli is approximately 2.

### Table B.2: Parameter values for the discrete $\beta$-spectrum.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\tau_{\beta,i}$ [s]</th>
<th>$E_{\beta,i}$ [MPa]</th>
<th>$\eta_{\beta,i}$ [MPa(s)]</th>
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</thead>
<tbody>
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</tr>
<tr>
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<tr>
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<td>$1.25923 \cdot 10^0$</td>
</tr>
<tr>
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