Nonlinear Viscoelastic Behaviour of Thermorheologically Complex Materials

A Modelling Approach

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Abstract. In previous work, a phenomenologically constitutive model was presented describing the finite, nonlinear, viscoelastic behaviour of polymer glasses up to yield. This model was, however, restricted to thermorheologically simple materials. In this paper this restriction is removed, thus extending the model to materials behaving thermorheologically complex. Based on linear viscoelasticity, this extension can be achieved by either adding a process in parallel, or in series. Experiments in the plastic range suggested an approach based on stress additivity, i.e. two processes in parallel. The resulting model consists 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 Whereas in the case of a single process the influence of stress and temperature is comparable, this is no longer valid for two processes since the molecular processes depend on a part of the applied stress rather than on the total applied stress itself.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.

Key words: mathematical models, polymers, temperature dependence, viscoelasticity, yield

1. Introduction

In previous work (Tervoort et al., 1996) we presented a phenomenologically constitutive model describing the finite, nonlinear, viscoelastic behaviour of polymer glasses up to yield; the so-called multi-mode (compressible) Leonov-model. The basic building block of this model is the single Leonov mode (Tervoort et al., 1998), a Maxwell element employing a relaxation time that depends on an equivalent stress proportional to the Von Mises stress. Although a single element suffices to correctly describe the yield behaviour, it cannot describe the typical time-dependent deformation behaviour observed in the linear viscoelastic regime (Ferry, 1980; Tschoegl, 1989). Under the assumption that the material behaves thermorheologically simple, i.e. the deformation behaviour is governed by a single molecular process, the model was therefore enhanced to a spectrum of Leonov modes, each mode having the same (nonlinear) stress dependence. At small deformations this representation shows purely linear viscoelastic behaviour, whereas for high stresses the model reduces to a nonlinear fluid with a highly nonlinear stress dependence.
(Tervoort et al., 1998), comparable to the ‘BPA model’ (Boyce et al., 1988). At intermediate stresses the model displays time-stress superposition, the relaxation times being shifted horizontally by stress. For a linear geometrical case this is equivalent to the Schapery model (Schapery, 1969) with merely a stress-dependent shift \( a_\sigma \).

For the model material polycarbonate it proved possible to obtain a single set of parameters, giving a good description of both tensile tests at different strain rates, as well as nonlinear stress-relaxation experiments up to \( 10^4 \) s. Due to the additional assumption that the physical state of the material is not altered by the deformation history (i.e. no physical aging or rejuvenation), it is however, expected that for increasing loading times and cyclic loading deviations can and will be observed. These effects are known to introduce additional shifts (Struik, 1978), not only horizontally along the time axis but also vertically.

Unfortunately, these are not the only assumptions which will no longer hold in practice, since most materials will display thermorheologically complex rather than thermorheologically simple deformation behaviour. This means that the deformation behaviour is governed by at least two molecular processes. In linear viscoelasticity the contributions of different molecular processes are usually separated (Nakayasu et al., 1961; Read, 1981), either in a parallel or a serial representation. Remarkably, a similar approach is applied when regarding the yield behaviour of thermorheologically complex materials (Roetling, 1965; Bauwens-Crowet et al., 1972), this time however, only in parallel. In this light it seems straightforward to extend the previously described representation to account for additional molecular processes. This way a correct description of both the linear viscoelastic regime, as well as the plastic range, can be obtained. Thus the question remains, how will this improved model behave at intermediate stresses in the nonlinear viscoelastic range. In this paper an attempt is made to further elaborate on this question by primarily enhancing the model, and subsequently investigating the consequences numerically. For simplicity it is again assumed that there will be neither physical aging nor mechanical rejuvenation.

2. Experimental

All experiments 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. 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, and for PMMA and PP from 30 to 70°C. 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. Deformation Behaviour

3.1. THERMORHEOLOGICALLY COMPLEX VERSUS SIMPLE

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).

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 α-transition), which is associated with main-chain segmental motion. Below the glass-
Figure 2. Influence of temperature on the spectra of a thermorheologically simple material (a), and a thermorheologically complex material (b).

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 **thermorheologically 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 2a).

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, using horizontal shifting along the logarithmic time, or frequency, axis and only small vertical shifts. The observation of a purely horizontal shift is sometimes used to identify thermorheologically simple material behaviour (Schwarzl and Staverman, 1952). The principle of time-temperature superposition was first observed by Leaderman (1943). To describe this behaviour he introduced a reduced time $\phi$:

$$\phi = \int_{-\infty}^{t} \frac{dt''}{a_T[T(t'')]}, \quad (1)$$
where \( a_T \) is the ratio of the relaxation times at temperatures \( T \) and \( T_0 \).

However, polymer materials usually exhibit 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 leads to a change in the shape of the total spectrum (Figure 2b), which in turn affects the deformation behaviour of the material. This type of behaviour is termed thermorheologically 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 through application of both horizontal and vertical shifts (McCrum and Morris, 1964).

3.2. **Linear Viscoelastic Deformation**

Linear viscoelastic deformation behaviour is commonly described using the Boltzmann single integral representation, whereas the information concerning the time dependence is contained in the relaxation modulus \( E(t) \) and compliance \( D(t) \). The shape of these viscoelastic functions reveals the contribution of the additional molecular transition, examples of which are shown in Figure 3.

The viscoelastic functions can be represented by either a generalized Maxwell or Kelvin–Voigt model, whereby a distinction can be made in the contributions caused by specific molecular transitions to these functions. Neglecting the rubber contribution, this leads to the mechanical model analogies shown in Figure 4. As
can be seen, for both models a distinction is made between relaxation/retardation times due to a particular transition, indicated by $\alpha$ and $\beta$ of which each has its own specific activation energy $\Delta U_\alpha$ and $\Delta U_\beta$.

Instead of a graphical representation, the models can also be expressed analytically, yielding for the generalized Maxwell model:

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

(2)

where $\tau_{p,i} = \eta_{p,i} / E_{p,i}$, $E_{p,i}$ refers to the $i$th Maxwell element of process $p$; and $m_1$, $n_1$ are the number of elements. The generalized linear Kelvin–Voigt model results in:

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

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

(3)

where $D_0$ is the elastic response; $\tau_{p,i} = \eta_{p,i} D_{p,i}$, $D_{p,i}$ refers to the $i$th element of process $p$; and $m_2$, $n_2$ are the number of elements. $\eta_0$ represents the end flow viscosity. Again it should be noted that the relaxation/retardation times $\tau_\alpha$ are influenced differently by temperature compared to $\tau_\beta$. 

Figure 4. Mechanical model analogies of the generalized Maxwell model (left) and generalized Kelvin–Voigt model (right), each with separated contributions from an $\alpha$ and $\beta$ process.
An excellent example of the latter approach is that of Read (1987), who also distinguishes between an $\alpha$- and a $\beta$-contribution to the creep compliance. This is expressed by the following equation:

$$ D(t) = D_U + D_\beta(t) + D_\alpha(t), $$

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 schematic representation shown in Figure 5. A similar approach is also employed by others, including 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 noteworthy differences between these approaches originating from the distinction of two processes. Firstly, the Maxwell model distinguishes between the initial elastic response due to a certain transition, while the Kelvin–Voigt model only shows a single initial deformation independent of any particular transition. Secondly, and probably the more important difference, lies in the description of the flow behaviour. The Maxwell model shows two independent contributions to the flow behaviour, whereas the Kelvin–Voigt model only shows a single flow contribution. If the latter difference is relevant, it can become clear from an investigation of the
yield behaviour, since in previous work (Tervoort et al., 1996) it was recognized that the yield behaviour can be regarded as stress-accelerated flow.

3.3. Plastic Deformation

It was shown by Tervoort et al. (1998) that the plastic deformation behaviour can be described using a single Leonov mode, which is essentially a single, stress-dependent Maxwell element. The stress dependence of the model is accounted for by the Eyring theory of nonlinear flow (Eyring, 1936). Furthermore, it was shown that a single Eyring process gives a good description of the yield behaviour of a material behaving thermorheologically simple. Whether this observation is still valid for thermorheologically complex materials can easily be verified by performing tensile tests at various strain-rates. To increase the scale of the strain-rates covered by the tests, the tests are performed at different temperatures. For three model materials (PC, PMMA, and PP) the results are shown in Figure 6.

From the figure it is obvious that a single process is no longer sufficient to describe the yield data of 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:

$$\frac{\sigma}{T} = \sum_{p=\alpha,\beta} \frac{R}{V_p^*} \sinh^{-1}\left(\frac{\dot{\varepsilon}^*}{\dot{\varepsilon}_{0,p}^*}\right),$$

where

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

Using the modified theory, a very good description of the yield data is obtained once more as shown by the solid lines in Figure 6. Apparently, each molecular process contributes to the yield behaviour, and the proper way of describing this is 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 I.

Bauwens-Crowet et al. (1972) found for polycarbonate the values $V_\alpha^* = 3.13$ nm$^3$ and $V_\beta^* = 1.02$ nm$^3$; and 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 Equation (7)). These values show some deviations when compared to the values tabulated in Table I, 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), for example, uses a visual verification for the goodness of the fit, whereas the values in Table I are obtained from a least-squares fit.
Instead of a single viscosity there is now a viscosity due to the \( \alpha \)-process and a viscosity due to the \( \beta \)-process. These viscosities are defined as:

\[
\eta_p = \frac{\sigma_p}{\dot{\varepsilon}}, \quad p = \alpha, \beta, \quad (9)
\]

where \( \dot{\varepsilon} \) is the applied strain rate; and \( \sigma_p \) 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:

\[
\dot{\varepsilon} = \dot{\varepsilon}_{0,p}^* \sinh \left( \frac{\sigma_p V_p^*}{RT} \right), \quad p = \alpha, \beta. \quad (10)
\]

Substitution in the definition for the viscosities, Equation (9), and assuming a constant temperature \( T_0 \) yields:

\[
\eta_p(\sigma_p) = \eta_{0,p} \frac{(\sigma_p/\sigma_{l,p})}{\sinh(\sigma_p/\sigma_{l,p})}, \quad p = \alpha, \beta, \quad (11)
\]

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

\[
\sigma_{l,p} = \frac{RT_0}{V_p^*} \quad (12)
\]

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

\[
\eta_{0,p} = \frac{\sigma_{l,p}}{\dot{\varepsilon}_{0,p}} \exp \left( \frac{\Delta U_p}{RT} \right). \quad (13)
\]

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

\[
a_{\sigma_p}(\sigma_p) = \frac{(\sigma_p/\sigma_{l,p})}{\sinh(\sigma_p/\sigma_{l,p})}, \quad p = \alpha, \beta \quad (14)
\]

reduces Equation (11) to:

\[
\eta_p(\sigma_p) = \eta_{0,p} a_{\sigma_p}(\sigma_p), \quad p = \alpha, \beta. \quad (15)
\]

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

Using these newly derived viscosity functions the single mode Leonov model can be adapted in order to give a correct representation of the plastic behaviour of a thermorheologically complex material. The modified representation is shown by means of a mechanical analogy in Figure 7, thereby neglecting the strain hardening response. Or analytically:

\[
E(t) = E_\beta \exp \left( -\frac{t}{\tau_\beta(\sigma_\beta)} \right) + E_\alpha \exp \left( -\frac{t}{\tau_\alpha(\sigma_\alpha)} \right), \quad (16)
\]
Figure 7. Two parallel nonlinear Maxwell elements used to describe the plastic deformation behaviour of a thermorheologically complex material.

Table II. Parameters of the nonlinear viscosity function, Equation (15), for polycarbonate, polymethylmethacrylate and polypropylene, at a temperature of 20°C.

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<tr>
<td></td>
<td>( p )</td>
<td>( \sigma_{p}) [MPa]</td>
</tr>
<tr>
<td>PC</td>
<td>( \alpha )</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>( \beta )</td>
<td>1.33</td>
</tr>
<tr>
<td>PMMA</td>
<td>( \alpha )</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td>( \beta )</td>
<td>3.22</td>
</tr>
<tr>
<td>PP</td>
<td>( \alpha )</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>( \beta )</td>
<td>0.87</td>
</tr>
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</table>

where \( \tau_p(\sigma_p) = (\eta_p(\sigma_p))/E_p \), with \( p = \alpha, \beta \). 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 I, the nonlinearity parameters and zero-viscosities of the model materials can be calculated, assuming that \( T_0 = 20°C \) (Table II).

3.4. NONLINEAR VISCOELASTIC DEFORMATION

For materials behaving thermorheologically simple Tervoort et al. (1996) derived a constitutive model by combining the time-dependent behaviour characteristic for the linear viscoelastic range with the typical strain-rate dependence of the plastic range. In the intermediate, nonlinear viscoelastic range this model displays time-stress superposition which reduces for the one-dimensional case to:

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

(17)
where

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

(18)

$\sigma$ being the total applied stress. The model can be classified as a simplified version of the more general Schapery model (Schapery, 1969), with a stress shift $a_\sigma$ equal to:

$$a_\sigma(\sigma) = \frac{(\sigma/\sigma_l)}{\sinh(\sigma/\sigma_l)}.$$

(19)

For materials behaving thermorheologically complex an equivalent approach can be followed based on the observed 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 thermorheologically simple approach a new model for the complete range is derived by combining the characteristics from both bounding regions. However, unlike the thermorheologically simple case, 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 correctly. The resulting model is shown in terms of a mechanical model analogy in Figure 8.

The matching analytical expression reads:

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

(20)

Figure 8. Generalized nonlinear Maxwell model, accounting for two processes.
where \( E_{p,i}, \tau_{p,i}(\sigma_p) (= \tau_{p,i}a_{\sigma_p}(\sigma_p)) \) refers to the \( i \)th Maxwell element of process \( p \); and \( m \) 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

\[
\psi_p = \int_{-\infty}^{t} \frac{dt''}{a_{\sigma_p}[\sigma_p(t'')]} , \quad p = \alpha, \beta, (21)
\]

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 spectra:

\[
\sigma(t) = \int_{-\infty}^{t} \left[ E_\alpha(\psi_\alpha - \psi'_\alpha) + E_\beta(\psi_\beta - \psi'_\beta) \right] \dot{\varepsilon}(t') dt', (22)
\]

where

\[
\psi_p = \int_{-\infty}^{t} \frac{dt''}{a_{\sigma_p}[\sigma_p(t'')]} \quad \text{and} \quad \psi'_p = \int_{-\infty}^{t'} \frac{dt''}{a_{\sigma_p}[\sigma_p(t'')]} (23)
\]

and \( p = \alpha, \beta \).

Before performing any calculations the necessary material parameters have to be determined, in this case the linear relaxation moduli \( E_p(t) \) and the nonlinearity parameters \( \sigma_l,p \). However, the previously used time-stress superposition is no longer applicable, since due to the different stress dependences the viscoelastic functions will change with applied stress, similar to the effect of temperature. Unfortunately, the stress dependence is even further complicated because the stress shifts depend only on a part of the total stress rather than on the total stress itself. To gain insight into 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 equation (22).

4. Numerical Investigation

In the previous section, it was argued that the deformation behaviour of a thermorheologically 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 by Tervoort et al. (1996) are investigated. For this purpose, suitable spectra have to be initially generated numerically since these are not yet experimentally accessible. Secondly, numerical calculations of creep experiments at various loads are performed, before finally leading to conclusions regarding the previously employed characterization strategy.

4.1. Model Parameters

As already pointed out, two stress nonlinearities and two linear Maxwell spectra are required to enable numerical simulations. In Section 3.3, the nonlinearity parameters were determined for three model materials, of which the values for PMMA are selected for further calculations. As the nonlinearity parameters are now known, the two spectra remain to be determined. Since they cannot yet be determined experimentally, they will be generated numerically. To ensure that the simulations are as realistic as possible these spectra have to satisfy the following three 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. DMTA experiments showed 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 behaviour within 5 to 6% strain.

To obtain suitable spectra for the numerical simulations the spectrum for PC determined by Tervoort et al. (1996) at room temperature was used as a starting point. This spectrum was then shifted both horizontally and vertically, until the correct values for the viscosities and moduli were obtained. The resulting spectra for the $\alpha$ and $\beta$-process are shown in Figure 9. It should, however, be kept in mind that these are actually virtual spectra.

The first two conditions are satisfied by the spectra shown in Figure 9, whereas the third is verified by simulating tensile tests at strain rates varying from $10^{-10}$ till $10^{-1}$ s$^{-1}$. For this purpose a computer program was written in Fortran which solves Equation (22) using an iterative procedure. The resulting stress-strain curves are shown in Figure 10a. From the figure it is clear that for all strain-rates yield is 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 10b). In this figure, the yield points from the calculations are compared
4.2. NUMERICAL CREEP SIMULATIONS

Since it is verified in the previous section that the obtained spectra are capable of providing the desired deformation behaviour numerical creep simulations are performed. Using the spectra equation (22) was solved iteratively for stress levels from 5 to 75 MPa and room temperature. 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. The resulting calculated compliance curves are shown in Figure 11.
Figure 11. Calculated compliance curves at equidistantly distributed stress levels from 5 to 75 MPa (the arrow indicates the direction of increasing stress).

Based on the observations from Section 3.2, 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 not established however, since the flow behaviour is rapidly stabilized due to 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 is 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.

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 has to remain 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 ($a_{\sigma_\beta} = 1$). As a consequence, the occurrence of the transition will be independent of stress, and therefore will always be observed at the same moment in time. This process is illustrated in Figure 12 for a stress of 15 MPa, by means of the shape of the overall spectrum at different times during the calculated creep experiment.

However, as the applied stress is increased it reaches a level at which the $\beta$-process can no longer completely relax to zero stress, since at that level the time scale of the $\alpha$-process approaches that of the $\beta$-process. This level is the stress level at which the transition in Figure 11 is no longer visible as both processes have
Figure 12. 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)).

merged. This is shown in Figure 13, again in terms of the shape of the spectrum at different points in time during a creep experiment at a stress of 75 MPa.

To demonstrate the difference between the behaviour of a thermorheologically complex material under constant stresses and that under constant temperatures, numerical simulations of creep tests at various temperatures are performed, using the temperature dependences previously determined for polymethylmethacrylate. The results of the calculations are shown in Figure 14.

From this figure the difference with the constant stress experiments at a constant temperature should be immediately clear, 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 also show that as temperature increases the so-called relaxed $\beta$-compliance $D_{\beta R}$ 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. More precisely, it is due to the fact that the $\alpha$-process has a stronger temperature dependence than the $\beta$-process.
Figure 13. Compliance against time for a stress level of 75 MPa (A). Development of the stress in both the θ and β-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)).

4.3. Consequences for Characterization

In Section 3.4, the stress nonlinearities $\sigma_{l,p}$, the temperature dependences $\Delta U_p$, and the linear relaxation time spectra $E_p(t)$ were identified as the key parameters in the description of the deformation behaviour of thermorheologically complex materials. Both the stress nonlinearities and temperature dependences could readily be determined from yield experiments at different temperatures. The linear relaxation spectrum was previously determined using the time-stress superposition principle (Tervoort et al., 1996). 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 favourable for separating the contributions of the different molecular processes, since the in-between distance is then maximum.

Considering this, the characterization is best performed in the linear viscoelastic range as there will be no acceleration of the time scale due to stress. Consequently, it is essential that the experiments cover a time interval that is as large as possible, thereby including the transition zone (Read, 1991). This could be achieved by combining different experimental techniques (Read, 1981; Read and Duncan, 1981), or using temperature to accelerate the time scale. The latter might however, introduce some additional problems, for example, vertical shifts.

If it is not possible to completely eliminate the overlap between contributions of different molecular processes, it will be necessary to make assumptions regarding the shape of at least one of the contributions in the overlapping range, for instance Nakayasu et al. (1961) assume that the $\beta$-contribution is symmetrical. The same assumption is made by Read (1991), whose model also assumes that there is no $\alpha$-contribution in the $\beta$-range, whereas the $\beta$-contribution in the $\alpha$-range is constant.

Since the characterization would also comprise long term measurements, the effects of physical aging can no longer be avoided.
5. Conclusions

Since most polymers exhibit more than one molecular 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 modelled by either two processes in parallel or in series. The yield behaviour could only be modelled 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 thermorheologically simple material, in a thermorheologically 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.

References