Capturing the mechanical aging kinetics by thermal analysis

D.J.A. Senden
MT06.35

Coaches:

Dr.Ir. L.E. Govaert
Ir. T.A.P. Engels

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Chapter 1

Introduction

Polymers are a class of materials that are becoming increasingly popular for use in a wide range of products. At this moment the mechanical properties that the end-product has to possess, are reached by a trial and error method. This is not ideal, firstly because it costs a lot of time and money to optimize the production this way. Secondly, the actual mechanical testing of products with complex geometries in order to find local yield strengths is often not possible.

One of the most common techniques to process polymers is injection molding. In this process the polymer is cooled rapidly from it’s molten state to it’s solid state. In it’s molten state (at temperatures higher than the glass transition temperature $T_g$), the material is in thermodynamical equilibrium. In it’s solid state (at temperatures below $T_g$), however, the material is not in thermodynamical equilibrium, unless it is cooled from it’s molten state with an extremely low cooling rate. In practical situations, the cooling rate will always be higher which results in a product that is not in thermodynamical equilibrium. The material will strive for equilibrium and because of low scale mobility in the material, material properties will change over time. This process, aging, results for example in a decrease of the volume and an increase in yield strength of the material. Manufacturers want to be able to predict the properties of their product for the entire lifetime of the product, for obvious reasons (warranty, ...). A method is therefore needed, which predicts the material properties of a product as a function of the initial state of the product as a result of processing conditions, conditions during the utilization of the product and time.

From a mechanical point of view, aging results in an increase in yield strength. Thermally however, aging results in an increase of the enthalpy overshoot that is observed in the glass transition zone. The yield point in a mechanical test can be seen as the equivalent of the glass transition temperature in a thermal test. The yielding process and the glass transition process are both assumed to be dominated by the same kinetics, segmental chain mobility.

The correlation between the mechanical- and thermal analysis of aging has been studied before and Bauwens-Crowet and Bauwens have shown that the enthalpy overshoot and the increase in yield strength both depend linearly on the logarithm of the annealing time [1]. Similar observations were made by Adam, Cross and Haward, who showed that a linear relation exists between the enthalpy overshoot and the increase in yield strength, both a result of annealing [2].
There is a lot of experience with mechanical analysis in our group. Thermal analysis however, has some interesting advantages. It is less time consuming and much less material is needed. It is therefore much less expensive, which is an important issue if it is going to be used in industry.

The goal of this project is to quantify the correlation between mechanical analysis and thermal analysis. Because a quick characterization method is sought, annealing times up to 30 hours are used, whereas Bauwens-Crowet and Bauwens use annealing times up to 1000 hours. This is quite optimistic and this might result in more scatter in the experimental data. A subgoal in this project is to get experience with DSC (Differential Scanning Calorimetry) measurements, because in our group this is a new research field.

This report will start with a brief description of mechanical analysis. Thermal analysis, or more specifically DSC, is more elaborately discussed as this is a major focus in this project. After describing the experimental procedure the results are shown and compared with data that is obtained from literature. Finally, the results and observations are discussed and conclusions drawn.

Another aspect of this project is the use of a new technique in TMDSC (Temperature Modulated Differential Scanning Calorimetry) measurements: TOPEM®. This technique is based on a stochastic temperature modulation superimposed to a conventional DSC temperature program. This technique claims to offer some advantages compared to other TMDSC techniques. For the purpose of this project, the most important advantages are that a better division of the heat flow into quasi static reversing and non-reversing heat flows can be made and that all system related effects (e.g. inertia, asymmetry, thermocouple contact, etc) are filtered from the measurement. This technique will be used and two different approaches will be used for processing the data in order to evaluate this new technique.
Chapter 2

**Mechanical Analysis (theory)**

In a mechanical test the effect of aging on yield strength is measured for a number of annealing times and -temperatures. The effect is qualitatively shown on the left side in Figure 2.1. The physical property that determines the yield strength of a material is the viscosity. On the right side of Figure 2.1 the actual aging process is illustrated. At temperatures higher than the glass transition temperature $T_g$, a polymer material is in a state of thermodynamical equilibrium. When an amorphous polymer is cooled from it’s rubbery state, it maintains it’s state of thermodynamical equilibrium until it reaches $T_g$. The mobility in the material becomes too small to be able to remain the equilibrium state and what follows is that the material is in a non-equilibrium glassy state. When the material is now held at a certain annealing temperature $T_a$, the material will strive for equilibrium, resulting in an increase of the viscosity. It is important to note that the fictive temperature $T_f$ decreases as a result of aging. The fictive temperature at a certain point is basically the temperature that corresponds with the equilibrium state of the material. A more formal definition of $T_f$ can be found in reference [3]. Since yield strength and viscosity are directly related, mechanical analysis has the advantage that the desired property is measured directly.

![Figure 2.1](image-url): The effect of aging on mechanical properties (left) and the physical basis of the aging process from a mechanical point of view (right).
For yield strength, Klompen et al. modeled aging kinetics in polycarbonate. The evolution of the yield strength as a function of annealing time was measured for different annealing temperatures, the results of which are shown on the left side of Figure 2.2. Time temperature superposition was then applied to construct a mastercurve, which is shown on the right side of Figure 2.2. This procedure shifts the curves corresponding with a higher annealing temperature than the reference curve to higher values of the annealing time $t_{a}^{shift}$:

$$t_{a}^{shift} = \frac{t_{a}}{a_{t}}$$  \hspace{1cm} (2.1)

The shift factors $a_{t}$ used in this equation were found to be accurately described by the following Arrhenius relation:

$$a_{t} = \exp \left( \frac{U_{a}}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right)$$  \hspace{1cm} (2.2)

Herein is the activation energy $U_{a}$ the characteristic value, corresponding with a certain material. The value found by Klompen et al. is $205 \text{kJ/mol}$.  \[4\]

Figure 2.2: Measurement data (left) and the yield strength mastercurve (right) as found by Klompen et al.  \[4\]
Chapter 3

Thermal Analysis (theory)

In thermal analysis, the effect of aging on heat capacity is measured, in our case by DSC (Differential Scanning Calorimetry) measurements. A qualitative representation of this effect is shown on the left side of Figure 3.1. The underlying physical process, the actual aging, is depicted on the right side of Figure 3.1. The thermal aging process as shown here is very similar to the mechanical aging process explained in Chapter 2. An important difference with mechanical analysis is that the desired parameter is measured indirectly, since the heat capacity corresponds with the temperature derivative of the enthalpy. This is a clear disadvantage.

Figure 3.1: The effect of aging on thermal properties (left) and the physical basis of the aging process from a thermodynamical point of view (right).

3.1 DSC

Differential Scanning Calorimetry is a technique which can be used to determine the change in enthalpy ΔH between two states. This change can be caused by endothermic processes (glass transition, melting or evaporation) and therefore increase the enthalpy, or by exothermic processes (crystallization, progressive curing, decomposition), which decrease the enthalpy. Since enthalpy cannot be measured directly, the heat capacity is measured instead. These quantities are related by Equation (3.1).
\[ \Delta H = \int c_p \cdot dT \]  

(3.1)

The DSC method used in this project, heat-flux DSC, consists of a furnace in which the pan holding the sample and the empty reference pan are heated (or cooled) together, see Figure 3.2. The furnace temperature is controlled and the temperature difference \( \Delta T \) is measured. As long as the sample and the reference pan respond the same, this temperature difference remains constant. When, for instance, endothermic processes start affecting the sample, the temperature of the sample \( T_s \) starts lagging behind the temperature of the reference pan \( T_r \). [5]

![Figure 3.2: Working principle of a heat-flux DSC](image)

The temperature difference \( \Delta T \) is a direct measure of the heat flow into the sample \( \Phi_m \), which is directly proportional to \( c_p \), with a proportionality factor defined by the sample mass \( m \) and the heating rate \( \dot{T} \), Equation 3.2

\[ c_p = \frac{\Phi_m}{m \cdot \dot{T}} \]  

(3.2)

In standard DSC the input consists of a temperature program \( T(t) \) which is basically a ramp with a constant heating rate \( \beta_u \), Equation 3.3. The output information that this technique gives, is the total heat flow into the material sample \( \Phi_{tot} \).

\[ T(t) = T_0 + \beta_u t \]  

(3.3)
3.2 TMDSC

Temperature Modulated DSC is a technique which has the advantage that superimposed effects (thermally reversible and non-reversible) can be separated. This is of particular interest in this project, because the enthalpy overshoot originating from aging (a non-reversible effect) can easily be separated from the enthalpy changes originating from the glass transition (a reversible effect), which makes the interpretation of the results clearer. The difference with standard DSC is that a modulated temperature program is superimposed to the standard temperature program, Equation (3.3). When a low underlying heating rate $\beta_0$ is used, the resolution of the data will be high, while the steep periodic rise in the modulated program results in high sensitivity, which is another advantage of this technique.

$$T(t) = T_0 + \beta_0 t + A_T \sin(\omega t) \tag{3.4}$$

As mentioned, the output information with this technique consist of the reversing heat flow $\Phi_{rev}$ and the non-reversing heat flow $\Phi_{non}$. With Equation (3.5), the total heat flow can be calculated.

$$\Phi_{tot} = \Phi_{rev} + \Phi_{non} \tag{3.5}$$

Physically, however, the total heat flow into the sample is not divided into a reversing and a non-reversing part, but into a sensible and latent part, Equation (3.6). The sensible heat flow $\Phi_{sens}$ (first term on the righthand side of Equation (3.6)) originates from the instantaneous heating rate $\beta$, while the latent heat flow $\Phi_{lat}$ (second term on the righthand side of Equation (3.6)) originates from physical and/or chemical processes in the sample.

$$\Phi(T, t) = mc_p \beta + m\Delta h_r \frac{d\alpha}{dt} \tag{3.6}$$

In the limiting case $\omega \rightarrow 0$, it holds that:

$$\Phi_{rev} = \Phi_{sens} \tag{3.7}$$

$$\Phi_{non} = \Phi_{lat} \tag{3.8}$$

Since this situation is only hypothetical, in practice a complex heat capacity $c_p^*$ is introduced, consisting of a fast changing mode and a slow changing mode. The latter is complex, where the imaginary part describes the phase lag that is introduced when non-zero frequencies are used, Equation (3.9). For non-zero measuring frequencies, Equations (3.7) and (3.8) are replaced by Equations (3.10) and (3.11).

$$c_p^*(T, \omega) = c_r(T) + c'_s(T, \omega) - j c''_s(T, \omega) \tag{3.9}$$

$$\Phi_{rev} = \Phi_{sens} + m\beta \cdot j c''_s(T, \omega) \tag{3.10}$$

$$\Phi_{non} = \Phi_{lat} - m\beta \cdot j c''_s(T, \omega) \tag{3.11}$$
3.3 TOPEM®

TOPEM® is a new technique in TMDSC in which the modulation consists of step like temperature changes with a constant step height and random interval lengths, Equation 3.12. Because of this stochastic modulation using step functions, the modulated function contains a maximum of frequency information in a single measurement, which is one of the advantages of the TOPEM® technique. The most important advantage is that this technique should be able to make a more accurate division of the total heat flow into a reversing and a non-reversing part.

\[
T(t) = T_0 + \beta_0 t + \delta T(t)
\]  

Equation 3.12

The actual DSC cell temperature naturally differs somewhat from the temperature program, since the inertia of the system makes it impossible to instantaneously change the temperature, this is depicted in Figure 3.3.

\[
\Phi(t) = g(t) \ast \beta(t)
\]

Equation 3.13

\[
\Phi_{rev} = m \cdot \beta_u \cdot c_{p,0}
\]

Equation 3.14

Figure 3.3: Difference between temperature program and actual DSC cell temperature due to inertia of the system. Courtesy of Mettler Toledo.

To extract all the information from a TOPEM® measurement, a mathematical correlation analysis of the input and output signals is done, Equation 3.13. The part of the total heat flow that does not correlate with the instantaneous heat flow, is \( \Phi_{non} \). The part that does correlate corresponds with the quasi static heat capacity \( c_{p,0} \), from which \( \Phi_{rev} \) can be calculated according to Equation 3.14. The quasi static heat capacity is the heat capacity for the limiting case of \( \omega \rightarrow 0 \).

\[
\Phi(t) = g(t) \ast \beta(t)
\]

Equation 3.13

\[
\Phi_{rev} = m \cdot \beta_u \cdot c_{p,0}
\]

Equation 3.14
The claim is that by using this analysis all system related effects (e.g. inertia, asymmetry, thermocouple contact, etc) are filtered from the measurement because $g(t)$ is a transfer function describing the whole system. The entire mathematical procedure is explained in detail in reference [6].
Chapter 4

Experimental procedure

4.1 Experimental setup

All experiments were performed with Lexan141R (polycarbonate) on a Mettler Toledo DSC823e. The samples were disks with a diameter of 5mm punched from a 1mm thick, injection molded plate. The typical mass of the samples was 25mg. The pans used were standard aluminium 40µl pans with a typical mass of 48mg.

All samples were first heated to 300°C, a temperature well above $T_g$, and held isothermally for 3 minutes to equilibrate and erase any prior temperature history. This procedure also ensures good contact between the sample and the aluminium pan. The samples were then quenched to room temperature, 20°C, by putting them from the furnace onto a metal plate. Next, the samples were annealed at annealing temperatures $T_a = 125, 127.5, 130, 135°C$, for annealing times $t_a = 1, 3, 10, 30h$. At $T_a = 120°C$, annealing was only done for a long period ($t_a = 30h$), because when the annealing temperature is lower, effects will only be visible after longer annealing times.

Subsequent to the annealing, the samples were subjected to a TOPEM® measurement, the temperature ranging from 100°C to 180°C with an underlying heating rate $\beta_u = 1°C/min$, a pulse height $\delta T = \pm 0.5K$ and a pulse length range $15s < \delta t < 30s$.

4.2 TOPEM® evaluation

The evaluation of the TOPEM® data was done with STARe software. This software performs the mathematical correlation analysis as explained in Section 3.3. It uses three main parameters that influence the calculation: width of the calculation window, shift of the calculation window and width of the smoothing window. In all evaluations, the values used are listed in Table 4.1. An evaluation of the influence of these parameters on the results and recommendations for choosing the right values are given in Appendix A.
Table 4.1: Values used for the calculation parameters in the TOPEM evaluation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width of calculation window [s]</td>
<td>120</td>
</tr>
<tr>
<td>Shift of calculation window [s]</td>
<td>5</td>
</tr>
<tr>
<td>Width of smoothing window [s]</td>
<td>90</td>
</tr>
</tbody>
</table>

4.3 Data evaluation

The first step in the evaluation of the data was to normalize $\Phi_{tot}$ and $\Phi_{rev}$ and then calculate the normalized $\Phi_{nom}$ with Equation 3.5. This normalization was found necessary in order to be able to perform calculations on the data. Other methods are possible, but reproducibility of the results could not be ensured. The normalization rule, as described by Hodge [7], is shown in Equation 4.1 and uses the rubber (equilibrium) heat capacity $C_{pe}$ and the glass heat capacity $C_{pg}$.

$$C^N_p(T) = \frac{(C_p - C_{pg})|T}{(C_{pe} - C_{pg})|T} \quad (4.1)$$

Both $C_{pe}$ and $C_{pg}$ are determined in their respective regions and have to be extrapolated into the entire temperature range that is used in the normalization. This was done by fitting a 1st-order polynomial through each region with a least squares fitting method. This procedure and the resulting normalized curve are shown in Figure 4.1 for a total heat flow curve.

![Figure 4.1: Procedure (left) and result (right) of normalizing a total heat flow curve.](image-url)

The quantity of interest in this project is the enthalpy overshoot, which means that the heat flow curves need to be integrated, which is done with a standard midpoint integration rule. The temperature boundaries of this integral were the same for all measurements, on either side of the glass transition zone, 120°C and 160°C, respectively. A reference curve is also needed, to completely define the area corresponding with the enthalpy overshoot. There are two different ways to do this, which will be explained in the following section.
4.4 Reference curve definition

To completely define the integral corresponding with the enthalpy overshoot, a reference curve is required. The first way to do this is very common in literature, for instance Bauwens-Crowet and Bauwens [1]. The enthalpy overshoot $\Delta H$ is then defined as the area enclosed by a curve obtained from an annealed sample and a reference curve obtained from a quenched sample. A very important aspect of this method is that the reference curve is the same for all measurements. The method and the resulting curve, called the relative heat flow $\Phi_{rel}$ are shown in Figure 4.2. The enthalpy overshoot is the integral of the relative heat flow.

![Figure 4.2: Procedure (left) and result (right) of calculating the relative heat flow.](image)

The second way to define the reference curve, is more straightforward for TMDSC, namely the reversing heat flow. In this method the enthalpy overshoot is thus defined as the integral of the non-reversing heat flow. A major difference with the previous method is that in this case the reference curve is different for each measurement, since the reference curve is measured simultaneously with the heat flow curve itself. Figure 4.3 shows the method and the resulting non-reversing heat flow curve.
The discrepancy between these methods is clearly visible in these figures, the enthalpy overshoot calculated from the non-reversing heat flow is significantly larger (25%) than the enthalpy overshoot calculated from the relative heat flow. This phenomenon is caused by the fact that the reversing heat flow ideally has no thermal history (no overshoot is visible in the reversing heat flow in Figure 4.3), while the quenched reference curve will always have some thermal history (small overshoot visible in the reference curve in Figure 4.2). In this project both methods are used and compared in order to check the value of the TOPEM® technique. The discrepancy between the methods will be discussed in more detail in Chapter 6.
Chapter 5

Results

5.1 Literature

For mechanical analysis of aging, it was shown by Klompen et al. that time temperature superposition can be applied to construct a so-called mastercurve, giving the evolution of the yield strength only as a function of annealing time. He also applied this time temperature superposition on the data from Bauwens-Crowet and Bauwens\textsuperscript{1}, Figure 5.1. The activation energy found was $U_a = 220\,kJ/mol$ \textsuperscript{4}, a value that corresponds with our own calculations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure51.png}
\caption{Measurement data (left) and mastercurve (right) for the mechanical measurement literature data. \textsuperscript{1}}\end{figure}

If time temperature superposition is now applied to the thermal measurement literature data, the same activation energy is found, Figure 5.2. This is important, as it shows that - as assumed - the kinetics of both the evolution of the yield strength and the increase in enthalpy overshoot are indeed the same.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure52.png}
\caption{Measurement data (left) and mastercurve (right) for the mechanical measurement literature data. \textsuperscript{1}}\end{figure}

\footnote{For the sake of ease, the dataset obtained from Bauwens-Crowet and Bauwens \textsuperscript{1} will from now on be referred to as the literature data.}
5.2 Experiments

In this section the results will be discussed that are based on a calculation of the enthalpy overshoot using the relative heat flow \( \Phi_{rel} \). A comparison with the results using the non-reversing heat flow \( \Phi_{non} \) will be made in Chapter 6.

On the left side of Figure 5.3 the results are shown for annealing temperatures \( T_a = 125, 130, 135^\circ C \). It might look odd that the enthalpy overshoot is expressed in Kelvin, but that is due to the fact that it was calculated from normalized heat flow curves. The general behavior is as would be expected, a linear dependency of the enthalpy overshoot on the logarithm of the annealing time. A strange outlier can be seen (\( T_a = 125^\circ C \) \( t_a = 3h \)), but still the trend is clearly visible. Unfortunately, no real explanation was found for this particular case. The longer measurements (\( t_a = 10, 30h \)) are left out of the evaluation for \( T_a = 135^\circ C \), because the sample was already approaching the equilibrium state. The linear behavior is no longer observed in that case and it is not within the region of interest of this project. On the right side of Figure 5.3 the same plot is shown, now including the measurement at \( T_a = 127.5^\circ C \). It shows the linear behavior quite well, although the slope is very different from the slopes observed at the other annealing temperatures. The position of the trend line with respect to the other trend lines is very different from what was expected. The reason for this is that, due to problems with the DSC equipment, a new calibration run was necessary, causing the measurements done afterwards (i.e. the ones at \( T_a = 127.5^\circ C \)) to differ substantially from the ones performed earlier. The errors that are observed here clearly show the importance of proper calibration and performing all measurements with the same machine settings. In further analysis of the data, this particular set of measurements was left out of consideration.
When time temperature superposition is applied to this data, an activation energy $U_a \approx 220\text{kJ/mol}$ is found, which corresponds well with the literature data. Furthermore, in order to be able to make a comparison with that data, the results are scaled with a scaling factor representing the difference between the rubber heat capacity and the glass heat capacity $\Delta c_p = 0.2343\text{J/gK}$, obtained from Bauwens-Crowet and Bauwens [1]. This gives the enthalpy overshoot in $\text{J/g}$, Figure 5.4.

Although there were some difficulties with the thermal measurements, the scatter $\delta_o \approx 0.5\text{J/g}$ is of the same order of magnitude as the scatter $\delta_b \approx 0.4\text{J/g}$ on the literature data, which looks promising when more experience with DSC is gained in our group. The slope found by Bauwens-Crowet and Bauwens is approximately $0.6\text{ J/g}$ per decade, whereas the slope found
in the measurement data is approximately $0.8 \ J/g$ per decade, thus they are of the same order of magnitude as well, see Figure 5.5. These are considered good results, especially if the fact that Bauwens-Crowet and Bauwens use much longer annealing times - which makes the resolution of the data much better - is taken into account.

**Figure 5.5:** Mastercurve from literature data (left) and mastercurve from measurement data (right).
Chapter 6

Evaluation of TOPEM®

The discrepancy between the enthalpy overshoot calculated from the relative heat flow or from the non-reversing heat flow was already mentioned in Section 4.4. In Figure 6.1 for $T_a = 125, 130 \degree C$, the enthalpy overshoot trend lines are shown, calculated both from the relative heat flow $\Phi_{rel}$ and the non-reversing heat flow $\Phi_{non}$. The discrepancy is significant and increases with increasing annealing time.

![Figure 6.1: The discrepancy between the enthalpy overshoot calculated from $\Phi_{rel}$ and $\Phi_{non}$](image)

This observation has already been made by Hutchinson [8]. Furthermore, he found that for longer annealing times the discrepancy will continuously increase and eventually even increase dramatically. He stated that the non-reversing heat flow is not suitable for calculating the enthalpy overshoot. The conclusion can be drawn that the TOPEM® technique does not put this in a different perspective.

This phenomenon is caused by the fact that the reversing heat flow curve shifts to higher temperatures as a result of aging, which is depicted in Figure 6.2. This means that the
reference curve used to calculate the enthalpy overshoot is affected by the annealing itself and thus can no longer be treated as an independent reference.

Figure 6.2: The effect of aging on the reversing heat flow
Chapter 7

Conclusion

An important first step is made towards quantitatively linking mechanical and thermal analysis of aging. A clear correlation between $\Delta H$ and $\sigma_Y$ is shown, the timescales with which these properties change as a result of aging are the same. In order to make a complete correlation possible, more research is required, concentrating on the absolute values of both the enthalpy overshoot and the yield strength.

With this project, experience with DSC equipment in our group is increasing. Better results (less scatter, better reproducibility, etc) can be expected when more experience is gained. Compared to data found in literature, however, already the results of this project can be considered quite reasonable.

In accordance to the observations made by Hutchinson [8], it can be concluded that the non-reversing heat flow is not suitable for calculating the enthalpy overshoot, especially at longer aging times. The new TOPEM® technique does not cast any new light on this issue. Therefore, the technique offers no advantages for determining the enthalpy overshoot. It might, however, offer advantages in other research fields. TOPEM® looks promising, for instance, for the investigation of the kinetic and dynamic nature of the glass transition and it’s relation to other kinetic events, e.g. rate dependent yielding.
Bibliography


Appendix A

TOPEM® parameters

In this section a closer look is taken on the influence of the different calculation parameters used in a TOPEM® evaluation. This is done by changing one parameter, while keeping the other ones at their default values (see Table A.1). In each case, a qualitative comparison between the different values for the particular parameter is made on the basis of a plot of the non-reversible heat flow as a function of the temperature of the sample. Because in this project the enthalpy overshoot is the actual value of interest, this value is used in a quantitative comparison. The calculation method used is explained in Chapter 3.3. For all calculations in this section a TOPEM® measurement (Underlying heating rate = 1°C/min, excitation = ±0.5°C) of a polycarbonate sample (annealed for 10 hours on 130°C) is used.

Table A.1: Default values of the calculation parameters in the TOPEM® evaluation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width of calculation window [s]</td>
<td>120</td>
</tr>
<tr>
<td>Shift of calculation window [s]</td>
<td>10</td>
</tr>
<tr>
<td>Width of smoothing window [s]</td>
<td>90</td>
</tr>
</tbody>
</table>

A.1 Width of Calculation Window

This parameter defines the time interval covered by the calculation window, in other words, the time interval in which it is assumed that the non-reversing heat flow doesn’t vary too fast. From the qualitative comparison the conclusion that the noise on the results increases with decreasing width of the calculation window is very obvious, see Figure A.1. When the width of the calculation window becomes too small, it will cover just (a part of) a single excitation of the system. The averaging will have less effect and noise is introduced. Because of this undesirable effect a value of at least 120s is recommended. When the width of the calculation window is increased too much, the non-reversible effects are smeared out over an increasing temperature range. In Figure A.1 this results in a lower peak. This is due to the fact that within the calculation window the non-reversing heat flow will vary too fast when the window is too large. This corrupts the results as well, so a middle course has to be adopted. The quantitative analysis shows that the enthalpy overshoot is 2.3% smaller when a value of 240s is used instead of 120s. This is due to the smearing effect. At even higher
values, the enthalpy overshoot becomes larger, while the peak in the non-reversible heat flow is much lower. This is due to the fact that the smearing effect results in much lower, but also much wider curves. On the basis of the peak values in the non-reversible heat flow, these values cannot be trusted. In [9] a recommendation is made that the value of this parameter should be less than one-third of the time span in which a transition occurs. In this case, the temperature span in which the glass transition occurs is approximately 10°C. Since the underlying heating rate is 1°C/min, this corresponds with a time span of 10 minutes. With a width of the calculation window of 120s, this rule of thumb is obeyed.

Table A.2: Quantification of the effect of the width of the calculation window on the enthalpy overshoot.

<table>
<thead>
<tr>
<th>Width of calculation window [s]</th>
<th>120</th>
<th>240</th>
<th>480</th>
<th>960</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deviation from default [%]</td>
<td>0</td>
<td>-2.3</td>
<td>4.5</td>
<td>28.1</td>
</tr>
</tbody>
</table>

Figure A.1: Non-reversing heat flow for various widths of the calculation window.

A.2 Shift of Calculation Window

The shift of the calculation window defines the time increment by which the calculation window shifted during the evaluation. After every shift a new calculation is made. When a large shift factor is used, the calculation time is therefore very small, because not so many calculations have to be made. However, with an increasing shift factor, the noise on the results will also increase. Few calculations result in an average that is more likely to show perturbations. The analysis yields that a value of 10s or less should be used, bearing in mind
that a small shift factor (e.g. 1s) will result in a very large calculation time, but is in theory
the best option. The influence of this parameter on the results is quite small, which can be
seen in Figure A.2 and can also be concluded from the quantitative comparison. The enthalpy
overshoot varies less than 0.6% in the range of shift factors that were included in the analysis.

**Table A.3:** Quantification of the effect of the shift of the calculation window on the enthalpy
overshoot.

<table>
<thead>
<tr>
<th>Shift factor [s]</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deviation from default [%]</td>
<td>0.5</td>
<td>0.6</td>
<td>0.1</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure A.2:** Non-reversing heat flow for various shifts of the calculation window.

### A.3 Width of Smoothing Window

The width of the smoothing window defines the time interval covered by the window used
for the smoothing filter. For this parameter the qualitative conclusion can be drawn that the
noise on the results will increase with decreasing width of the smoothing window, see Figure
A.3. This is due to the fact that with the value 0s the smoothing filter has no influence
on the results. Therefore, a value of at least 45s (even better: 90s) is recommended. In
Figure A.1 can also be seen that when the width of the smoothing window becomes large, the
non-reversible effects are smoothed as well, similar to the effect that occurs with large widths
of the calculation window. When increasing the width of the smoothing window, eventually
nothing remains of the effects. This means that again a middle course has to be adopted.
The quantitative analysis shows that with increasing width of the smoothing window the
calculated enthalpy overshoot decreases quickly, which is, of course, incorrect. The enthalpy overshoot calculated with a value of 45s is only 3.6% larger than with a value of 90s. Since this difference is quite small, a value of 90s is recommended because of the noise reduction this gives.

Table A.4: Quantification of the effect of the width of the smoothing window on the enthalpy overshoot.

<table>
<thead>
<tr>
<th>Width of smoothing window [s]</th>
<th>45</th>
<th>90</th>
<th>180</th>
<th>360</th>
<th>720</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deviation from default [%]</td>
<td>3.6</td>
<td>0</td>
<td>-12.5</td>
<td>-35.8</td>
<td>-59.7</td>
</tr>
</tbody>
</table>

Figure A.3: Non-reversing heat flow for various widths of the smoothing window.