The reactive extrusion of thermoplastic polyurethane
Verhoeven, Vincent Wilhelmus Andreas

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 24-05-2019
3 Rheo-kinetic measurements in a measurement kneader

3.1 Introduction

To establish reliable kinetics of thermoplastic polyurethane polymerization is not a straightforward task. The monomers from which thermoplastic polyurethane is produced in general are poorly miscible. Therefore, a combination of diffusion and reaction determines the reaction rate observed for each measurement of the kinetics. Diffusion limitation may be noticeable during the initial part of the reaction and at high conversions. In the early phase of the reaction, mixing will enhance the observed reaction velocity, through improvement of the micro-stoichiometry and through enlargement of the contact surface of the immiscible monomers. At the end of the reaction, the mobility of the end-groups and of the catalyst is much lower due to the large polymer molecules that have formed. This limited diffusion at high conversions may also have an impact on the observed reaction velocity. As a consequence of the competition between diffusion and reaction, the measurement of the kinetics for TPU polymerization are best performed at the same temperature and the mixing conditions as occur in the application for which the kinetic investigation is intended. For instance, for reactive injection molding the reaction takes place at temperatures between 30°C and 120°C, the reaction mass initially experiences a high shear and after the injection the reaction mass remains stagnant. Adiabatic temperature rise experiments (ATR), which are performed under the same stagnant conditions, are for that reason best suited to establish the kinetics in reactive injection molding.

Applying this requirement to reactive extrusion would mean that measurement of the kinetics should be performed under shear conditions and at high temperatures (150°C-225°C). These conditions are available in a rheometer and in a measurement kneader. However, both instruments are not specifically designed for measurement of the kinetics. Measurement kneaders, for instance, are mostly used for (reactive) blending of polymers as was done by Cassagnau et al. (1) or for rubber research (2). Both instruments have a drawback if they are used for measurement of the kinetics: in both instruments the extent of the reaction can only be followed indirectly through the increase in torque. In order to correlate the torque to the reaction conversion, a calibration procedure is necessary for which samples must be taken. Simultaneous measurement of conversion in the rheometer or kneader would make
this sampling procedure superfluous. Unfortunately, no obvious method is available. An adiabatic method as applied by Lee et al. (3) or Blake et al. (4) is not apt, due to the lack of heat production at higher conversions. A combination of rheology with a spectroscopic method, for example with fiber optic IR or Raman spectroscopy, has not been reported yet for polyurethanes. The accuracy at high conversion is not sufficient, and a stagnant polymer layer may form on the measurement cell.

If we return to the comparison between a rheometer and a kneader, a rheometer seems more suitable for measurement of the rheo-kinetics, since, in a rheometer, the viscosity can be measured directly. Nevertheless, a measurement kneader is preferred in this research. The reasons for this are:

- The mixing behavior in a kneader resembles the mixing behavior in an extruder more closely, with both dispersive and distributive mixing action and both simple shear and elongational flow.
- Highly viscous material can be processed more accurately in a kneader, because in a rheometer, constant shear experiments at shear rates that are comparable to those occurring in an extruder are sensitive to edge failure and demand a high torque.
- Sampling of a small amount of material does not disturb the measurements in a kneader, whereas rheology measurements are gravely affected by taking (several) samples.
- Temperature control in a kneader is straightforward. In a rheometer, temperature control becomes complicated at temperatures above 150°C since both cone and plate must be heated in that case.

There are several studies known in which the kinetics of TPU polymerization is measured under mixing conditions (3 - 8). All of these measurements were performed at relatively low temperatures (<90°C) and mostly on cross-linking systems. Therefore, no high conversions could be reached, since the gelation temperature was reached reasonably early in the reaction (around 70% conversion). Methods for measuring the kinetics that do reach high conversions are largely ‘zero-shear’ methods. As is the case for radical polymerization (9), little attention has been paid to the interaction between mixing and reaction in step polymerization. Often it is expected for step polymerization that shear does not have a major impact on the reaction velocity due to the relatively high mobility of the reactive end groups of a polymer chain. Malkin et al. (10), for instance, state
that any observed acceleration of the reaction speed for poly-condensation reactions can usually be ascribed to viscous heating of the reaction mass. Schollenberger et al. (11) performed the only study known to us in a measurement kneader. Unfortunately, no quantitative data were obtained in this study. So no reliable data on the kinetics exist on TPU polymerization in an extruder, although this is a large industrial process. Therefore, this chapter focuses on the acquisition of relevant data on the kinetics for extruder modeling. A new method is presented, which is based on performing experiments in a measurement kneader. In a kneader, the measurement conditions are more similar to those in an extruder in comparison to existing methods for measuring the kinetics. Quantitative kinetics and rheological data can be obtained through this method; moreover, the effect of mixing on the polymerization reaction can be investigated.

3.2 Experimental section

3.2.1 The kneader

The kneader used in this research was a Brabender W30-E measurement mixer. A picture of the non-intermeshing torque mixer is shown in figure 3.1. Two triangular paddles counter-rotate in a heated barrel. The barrel can be closed with a (heavy) plug. The volume of the kneader is 30 cm³.

![Figure 3.1 The Brabender measurement kneader.](image)

The kneader is driven by a Brabender 650-E Plasticorder. Two heating elements in combination with two control thermocouples (one in the back-plate and one in the kneader section) keep the kneader on the set temperature \( T_{\text{set}} \). A thermocouple
sticking in the non-intermeshing zone of the kneading chamber is used for the measurement of the temperature of the melt ($T_{\text{meas}}$). The torque and temperature development in the kneader can be followed by means of a data acquisition system.

3.2.2 Experimental method

Preparations before an experiment

The TPU system for the experiments discussed in this chapter consisted of:

- A polyester polyol of mono-ethylene glycol, di-ethylene glycol and adipic acid (MW = 2200 g/mol, f = 2).
- Methyl-propane-diol (Mw = 90.1 g/mol, f = 2).
- A eutectic mixture (50/50) of 2,4 diphenylmethane diisocyanate (2,4-MDI) and 4,4 diphenylmethane diisocyanate (4,4-MDI). (Mw = 250.3 g/mol, f = 2).

The percentage of hard segments was 24%. The reaction was catalyzed using bismuth octoate. Both the polyester polyol as the methyl-propane-diol were dried under vacuum at 60°C and stored with molecular sieves (0.4 nm) prior to use. The isocyanate was used at 50°C. Just before an experiment the polyol, diol, isocyanate, and catalyst were weighed in a paper cup and mixed, using a turbine stirrer at 2000 rpm for 15 seconds. Experience showed that this premixing was necessary to obtain reproducible results. About 30 grams of the premixed reaction mixture was transferred to the kneader with a syringe. The exact amount of reaction mixture was determined by weighing the syringe before and after filling the kneader. The kneader measurement was started upon filling.

Sampling

In order to relate torque to molecular weight, samples were taken and analyzed (see theoretical section). The sampling method consisted of removing the stamp of the kneader, collecting the sample with tweezers, followed by quenching the material in liquid nitrogen. After taking a sample the stamp was put back on the kneader; the whole sampling routine had a negligible influence on the torque during a very short period. In order to inactivate the still reactive isocyanate end-groups the samples were dissolved in THF with 5% di-butylamine. The samples were subsequently dried and used for size exclusion chromatography analysis.

3.2.3 Size Exclusion Chromatography (SEC)

Samples were analyzed for their molecular weight distribution by size exclusion chromatography (Polystyrene calibrated). The chromatography system consisted of
two 10 µm Mixed-B columns (Polymer Laboratories) coupled to a refractive index meter (GBC RC 1240). The columns were kept at 30°C. Tetrahydrofuran (THF) was used as mobile phase and the flow rate was set to 1ml/min. The molecular weight distribution was analyzed using Polymer Laboratories SEC-software version 5.1. About 25 mg of polymer was dissolved in 10ml of THF; the dissolved samples were filtered on 0.45-µm nylon filters.

3.3 Theory of measurement of the kinetics

The objective of this study is to determine the reaction rate constant for the formation of the thermoplastic polyurethane under investigation. Therefore, the torque and temperature curves measured in the kneader must be translated into a time-dependent conversion curve. For condensation polymerization conversion, molecular weight (M) and viscosity (η) are related in a straightforward way. However, it is impossible to derive the conversion (p) directly from the viscosity. This is called the ‘direct rheo-kinetic problem’ by Malkin (10). The relationship between viscosity and molecular weight has to be established first, before conclusions can be drawn on the reaction pattern (figure 3.2). In addition, there is a complicating factor in a measurement kneader. Due to the complicated flow profile in a kneader it is not immediately clear how the measured torque can be related to the viscosity. Nevertheless, a (simplified) flow analysis can tackle this problem. Subsequently, the relationship between the torque and the molecular weight can be established.

![Figure 3.2](image)

*Figure 3.2* The rheokinetic scheme (10).
3.3.1 Rheology basics

A simplified model of the kneader forms the basis of the flow analysis. The true geometry of the kneader is simplified as shown in figure 3.3.

![Figure 3.3](image)

Figure 3.3  A simplification of the flow geometry in the measurement kneader.

The shear stress can then be calculated using a flat-plate approach for which the paddle is considered stationary and the barrel moves with a velocity \( V_b \). The shear stress \( (\tau) \) at the wall is then equal to:

\[
\tau = -\eta_{app} \gamma = -\eta_{app} \cdot \left( M \frac{N \pi D}{H} \right)
\]  

(3.1)

The factor \( M \) can be calculated through a flow analysis, for which the height \( H \) is a function of the angular coordinate. The viscosity is written as the apparent viscosity \( (\eta_{app}) \), since for our polymeric material a Newtonian approach is inaccurate. The value of the torque acting on a paddle is opposite to the torque value experienced by the barrel wall, and is equal to the force acting on the wall times the lever arm.

\[
\text{Torque} = (\text{Area} \cdot \text{Shear Stress}) \cdot \text{Lever Arm} = (\pi DW \cdot \tau) \cdot (D/2)
\]

(3.2)

For two paddles, this equals:

\[
\text{Torque} = \frac{M \pi^2 D^3 W}{H} \cdot N \cdot \eta_{app} = C \cdot N \cdot \eta_{app}
\]

(3.3)
Rheo-kinetic measurements in a measurement kneader

C can be considered as a geometry factor. The manufacturer of the kneader gives a similar equation to correlate torque to viscosity, with the constant \( C \) equal to 50. Equation 3.3 shows that for a Newtonian fluid the torque is directly proportional to the viscosity of the material in the kneader. If we consider the polyurethane as a power-law liquid, equation 3.3 can be rewritten to:

\[
\text{Torque} = C' \cdot N^n \cdot \eta_0 \quad (3.3a)
\]

The next step, necessary for tackling the direct rheo-kinetic problem is to correlate the viscosity of the polymer to its weight average molecular weight. It is well established experimentally as well as theoretically that for an ‘entangled’ linear polymer:

\[
\eta = A(T) \cdot M_w^{3.4} \quad (3.4)
\]

\( A(T) \) is a proportionality-factor that is temperature dependent. For linear amorphous polymers \( A(T) \) can be described with a Williams-Landel-Ferry-equation (WLF-equation) or with an Arrhenius-type of expression. In general, for a temperature less than 100°C above the glass transition temperature \( (T_g) \) of the polymer, a WLF-equation is preferable. For higher temperatures, an Arrhenius-type expression is best-suited (12). For polyurethanes, the value of \( T_g \) is dependent on the specific chemicals used but for most polyurethanes \( T_g \) does not exceed 320K (13). An Arrhenius-type of expression should therefore be suitable to describe the temperature dependence of viscosity for the temperature range under consideration (400 - 475K).

If equation 3.3a and 3.4 are combined, the following equation results:

\[
M_w = \left( \frac{\text{Torque}}{A'(T)} \right)^{\frac{1}{3.4}} \quad \text{with} \quad A'(T) = A(T) \cdot C' \cdot N^n \quad (3.5)
\]

The torque is now related to the molecular weight. If the function \( A'(T) \) is known, the weight average molecular weight versus time for the TPU-reaction can be calculated from the logged torque and temperature values. By analogy with the temperature dependence of the viscosity the temperature dependence of \( A'(T) \) can be described using an Arrhenius-type equation:
In order to relate torque to the molecular weight, the flow activation energy \( (U_A) \) and pre-exponential factor \( (A_0) \) in equation 3.6 must be known. These constants can be found through a ‘calibration procedure’. For this procedure, samples are taken from the kneader and analyzed for their molecular weight with size exclusion chromatography (SEC). Samples of different molecular weights and samples taken at different reaction temperatures are necessary for the procedure. The molecular weight can be calculated from torque and temperature \( (T_{\text{measure}}) \) values using equation 3.5 and 3.6. The calculated and measured molecular weight can be compared, and the optimal value for \( A_0 \) and \( U_A \) can be found through a least-square fitting routine.

### 3.3.2 Basics of the kinetics

From the molecular weight versus time curve, the kinetics of TPU-polymerization can be obtained. Although the exact reaction mechanism is more complex, the TPU polymerization reaction is often described successfully with a second order rate equation (14), as is described in chapter 2.

\[
M_W = M_{\text{rep}} \cdot (1 + 2 \cdot [\text{NCO}]_0 \cdot k(T,\text{[Cat]}) \cdot t) \tag{2.15}
\]

Equation 2.15 shows that the molecular weight increases linearly in time. Since \( M_{\text{rep}} \) and \( [\text{NCO}]_0 \) are constants, the slope of the molecular weight versus time curve is proportional to the reaction rate constant \( k(T,\text{[cat]}): \)

\[
\frac{dM_W}{dt} = 2 \cdot M_{\text{rep}} \cdot [\text{NCO}]_0 \cdot k(T,\text{[Cat]}) \tag{3.7}
\]

If \( A_0 \) and \( U_A \) are known, the torque versus time graph can be translated into a molecular weight versus time graph (equation 3.5). From the slope of this curve and by applying equation 3.7, the value of the reaction rate constant can be calculated. If experiments are performed at different temperatures and at a constant catalyst level, an Arrhenius-expression can be established for the reaction rate constant.
There is just one limitation. According to equation 2.15, the molecular weight will rise to infinity at longer reaction times. In practice, this will not happen. Several phenomena may cause a leveling off the molecular weight and torque values at longer reaction times:

- The initial ratio of alcohol groups to isocyanate groups will never be exactly unity. This stoichiometric imbalance will limit the maximum conversion.
- Chain scission. The long molecules that are present at longer reaction times are prone to scission due to shearing.
- Depolymerization (chapters 2.3.4, 2.3.8)
- Allophanate formation (chapter 2.3.6). The high concentration of urethane bonds together with the continuous presence of a small portion of free isocyanate groups due to depolymerization can give rise to allophanate formation. Allophanate formation causes branched molecules. Polydispersity will therefore increase but since also the stoichiometry of reactants is affected, the net effect on the molecular weight is not clear. Due to branching the A-factor in equation 4 may change.
- A last reason why \( M_w \) will not rise to an infinite value is degradation. This will of course limit the maximum \( M_w \).

All of these factors gain importance at longer reaction times and at higher molecular weights. Therefore, reliable data for the kinetics using the measurement kneader are best obtained during the initial stage of the reaction.

### 3.4 Results

#### 3.4.1 A typical kneader experiment

Figure 3.4 shows a typical graph obtained for a kneader experiment. The torque and the temperature are shown as a function of time. As expected, the torque increases over time due to the polymerization reaction. The torque curve in figure 3.4 reaches a steady value after 15 minutes. After an initial drop due to the filling of the kneader, the temperature also rises steadily to a constant value.
Figure 3.4  The torque and temperature versus the time in the measurement kneader. $T_{\text{set}} = 175^\circ\text{C}, 80 \text{ RPM}$.

Clearly, viscous dissipation plays an important role in the kneader; the dissipated heat cannot be completely removed through the walls. In general, the measured temperature exceeds the set temperature (in figure 3.4 $T_{\text{set}} = 175^\circ\text{C}$). Analysis of the experimental curves shows that the temperature increase due to viscous dissipation ($\Delta T_{\text{viscous}} = T_{\text{measure}} - T_{\text{set}}$) is proportional to the torque value with a proportionality factor of 2 $^\circ\text{C} / \text{Nm}$.

3.4.2 The determination of the flow activation energy and the pre-exponential factor

The torque-temperature graph can be converted into a molecular weight versus time graph using equation 3.5. To do so, the function $A'(T)$ must be known, which means that the flow activation energy ($U_A$) and flow pre-exponential factor ($A_0$) have to be established. To determine these constants, experiments were performed at four different set-temperatures (125, 150, 175, 200°C). Every experiment was repeated three times; 4 to 5 samples were taken per experiment at different reaction times. The molecular weights of these samples were determined and obviously, the value of the torque and the temperature at the moment a sample was taken is also known. $U_A$ and $A_0$ can now be established by fitting the measured molecular weight to equations 3.5 and 3.6, with $U_A$ and $E_A$ as the fit parameters. Figure 3.5 shows the resulting parity plot in which the measured molecular weight is plotted against the calculated one. For the whole range of molecular weights, the agreement is good.
The values obtained for $U_A$ and $A_0$ are respectively 42.7 kJ/mol and $7.2 \times 10^{-22}$ N·m·mol$^{3.4}$/g$^{3.4}$ (see Table 3.1). In general, thermoplastic polyurethanes have a much higher flow activation energy (100 - 200 kJ/mol) than is normally expected for linear polymers. The hard segments that are present in thermoplastic polyurethanes cause this effect. Hard segments are associated in hard domains and are physically cross-linked, which gives rise to a higher resistance to flow. Dissociation of the hard domains takes place at temperatures between 150°C and 200°C, depending on the composition of the polyurethane. Beyond that temperature, the flow behavior will be that of a normal linear polymer. However, for the polymer under investigation, the hard segments will dissociate at a much lower temperature.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_A$ (kJ/mol)</td>
<td>42.7</td>
</tr>
<tr>
<td>$A_0$ (N·m·mol$^{3.4}$/g$^{3.4}$)</td>
<td>$7.2 \times 10^{-22}$</td>
</tr>
<tr>
<td>$E_A$ (kJ/mol)</td>
<td>61.3</td>
</tr>
<tr>
<td>$k_0$ (mol/kg K)</td>
<td>$2.18 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Table 3.1 The flow and kinetic parameters for the TPU under investigation.

This is caused by the relatively low percentage of hard segments (24%) and the composition of the hard segments. The hard segments are built from a bulky chain extender and an isocyanate blend containing 50% 2,4-MDI. Steric hindrance, therefore, complicates association of the hard segments and improves the compatibility of the hard and soft segments. The flow activation energy found (42.7
Chapter 3

kJ/mol) confirms this expectation, as it falls within the expected range for linear polymers (15). This result implies that for the TPU under investigation the hard segments are molten and completely dissolved in the soft segments, already at 125°C.

3.4.2 The determination of the reaction rate constant

The torque and temperature versus time curves of figure 3.4 can be translated into a plot of molecular weight versus time by applying equations 3.6 and 2.15. Figure 3.6 shows this plot for three repeated experiments at 175°C. The lines represent the molecular weights as calculated from the torque and temperature and the dots are the measured molecular weights. The agreement between the three experiments is reasonably good. In general, the reproducibility was somewhat better at higher temperatures. Long reaction times in combination with higher molecular weights seemed to cause the reproducibility to become worse. The initial slopes are straight, which supports the second order assumption of the rate equation.

![Figure 3.6](image)

**Figure 3.6** The weight average molecular weight versus time in a measurement kneader. $T_{set} = 175^\circ C$, 80 RPM.

The reaction rate constant can be derived from the relation between molecular weight and time by determining the initial slope of the curves (e.g. in figure 3.6 the average slope between 0 and 4 minutes). As stated earlier, the initial slope gives the most reliable information on the kinetics. In table 3.2, the different slopes with their confidence intervals are shown as well as the value for the reaction rate
constant $k$. The reaction rate-constant is calculated using equation 3.7. It increases, as expected, with increasing temperature. The temperature in table 3.2 is the measured temperature, $T_{\text{measure}}$. Since the kneader does not operate completely isothermally, there is always a temperature range over which the slope is determined. The mentioned temperature, $T_{\text{measure}}$, is the average temperature over which the slope is measured. This temperature range never exceeded 5°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Slope ($M_w$/min)</th>
<th>Average slope / 1000 ($M_w$/min)</th>
<th>$k$ (kg/mol s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>194.3</td>
<td>42154 47070 44246</td>
<td>44 +/- 6</td>
<td>0.37 +/- 0.06</td>
</tr>
<tr>
<td>173.4</td>
<td>17030 17684 18316</td>
<td>17.6 +/- 1.6</td>
<td>0.147 +/- 0.014</td>
</tr>
<tr>
<td>149.6</td>
<td>7134 6546 7784</td>
<td>7.2 +/- 1.6</td>
<td>0.060 +/- 0.012</td>
</tr>
<tr>
<td>123.3</td>
<td>2172 2416 2332</td>
<td>2.3 +/- 0.4</td>
<td>0.0192 +/- 0.002</td>
</tr>
</tbody>
</table>

**Table 3.2**  *The slopes and the kinetic results obtained from the kneader experiments.*

Now, the kinetic constants can be derived from an Arrhenius plot (figure 3.7). The values obtained for $E_a$ and $k_o$ are respectively 61.3 kJ/mol and 2.18e6 mol/kg K (see also table 3.1). Three conclusions can be drawn from figure 3.7 and table 3.1. First, the straight line in the Arrhenius-plot is an extra confirmation that the second order rate equation holds for the temperature range considered. Secondly, the value of $E_a$ falls within the range reported for TPU-polymerization (30-100 kJ/mol). The scatter in activation energies reported in the literature are caused by the different catalysts and chemicals used. Finally, the plot shows that within the experimental uncertainties that are inevitable for measurement kneader experiments, quantitative kinetic and rheological results can be obtained.
3.4.3 Evaluation of the kinetic model

Model predictions are compared to experimental data in figure 3.8 in order to check the correctness of the obtained kinetic parameters. The slopes of the model prediction and of the experimental results are in good agreement with each other, which is a confirmation of the data on the kinetics. However, both at the start and near the end of the reaction, the model and experiment do not coincide. A closer look at the starting point of the reaction reveals that the initial molecular weight is much higher than anticipated. For this reason, the model equation (equation 2.15) is adapted in figure 3.8, to correct for the initial high molecular weight:

$$M_W = 17000 + M_{rep} \cdot (1 + 2 \cdot [NCO]_0 \cdot k(T, [cat]) \cdot t)$$

The value of 17000 for the molecular weight at t=0 is for all temperatures the same, and is fitted to the experimental curves. This correction is needed, since, at the start of the measurement, the reaction has already started due the premixing procedure. However, the molecular weight at the start of the measurement is unexpectedly high. A calculation learns that, with the kinetic constants obtained in this research, the molecular weight after the premixing procedure should not exceed 1500. The difference corresponds to an observation that other authors (16, 17) have also made for TPU-polymerization. The initial low-viscosity part of the reaction proceeds much faster than the last high-viscosity part of the reaction. This observation has been verified through ATR-experiments for this system (data not...
shown). With an initial temperature of 50°C and the same catalyst level as for the kneader experiments, the reaction reaches a conversion of about 80-90% within 30 seconds.

Figure 3.8  The measured and calculated weight average molecular weight versus time.

The explanation of the tremendous decrease in the observed reaction velocity at higher conversions falls under the term ‘diffusion limitation’. As soon as high molecular weight material is formed the mobility of the catalyst or the end groups decreases, which causes a decrease in the observed reaction velocity. The exact nature of this phenomenon cannot yet be understood due to the limited range of these experiments. This problem will be the subject of further experimental research.

At the end of the reaction, the experimental molecular weight levels off to a steady value. It is improbable that the initial stoichiometric deviation of at most 0.2% is the cause of this. An imbalance of 0.2% in stoichiometry leads to an equilibrium molecular weight of 350,000, which is much higher than the maximum molecular weight reported for this investigation. For the two high temperature runs, it is very probable that depolymerization has a major impact on the last part of the reaction and that, therefore, the reverse reaction is the predominant cause of the leveling of the M_w-curve. For the two low temperature runs, the situation is less distinct. Figure 3.8 shows that for the 200°C and 175°C experiments a higher temperature leads to a lower ‘equilibrium’ molecular weight. This trend is hardly visible for the 150°C run.
and not visible at all for the 125°C run, because these runs are not completed within the time shown. Longer reaction times are here necessary to get to an equilibrium situation. Unfortunately, the results at long reaction times are less reproducible. The color of the polymer coming out of the kneader is light brown/yellow but deepens at longer reaction times. Degradation, therefore, interferes with experiments that last longer. An obvious indication of allophanate formation has not been found.

The kinetic model obtained in this research appears to have a limited validity. Still, an important part of the reaction is captured with this model. The initial, fast reaction takes only five percent of the total reaction time. Therefore, to predict the necessary residence time in an extruder the kinetic model obtained in this study is indispensable. However, an expansion of the model is desirable. At low conversions, the reaction proceeds much faster than the measured data indicate. On the contrary, at very high conversions the reaction stops, while the model for the kinetics predicts a continuous increase of the molecular weight. For the low conversion part, adiabatic temperature experiments need to be performed to get the kinetic constants for this part of the reaction. Subsequently, these data can be combined with the data obtained from the kneader in order to complete the model of the kinetics. For the very high conversion part of the reaction, depolymerization needs to be taken into account. Future experimental work will be directed towards depolymerization and low conversion experiments, to complement the present results.
3.5 Conclusions

Investigations on the kinetic of TPU polymerization, performed in a measurement kneader, show that quantitative kinetic and rheological data can be obtained using this method. The method has advantages over other measurement methods since the reactants are mixed during the experiment, mimicking real processing conditions. Therefore, for applications where the reaction takes place under mixing conditions, as is the case for reactive extrusion, the parameters obtained for the kinetics will be more accurate. Besides, the effect of mixing on the polymerization reaction can be investigated using this method.

The kinetic data obtained prove that a second order reaction can be used to describe TPU polymerization. The experiments indicated that a fast initial reaction is followed by a slower ‘high conversion’ part of the reaction. At the end of the reaction, the molecular weight levels off due to depolymerization and degradation. More experiments are necessary to elucidate these effects.

Because of the complex geometrical form of the kneader, the viscosity-value obtained with a measurement kneader is not very accurate. Therefore, no attempt has been made to correlate the torque values to viscosity values. Nevertheless, the activation energy of flow could be established. The activation energy of flow falls within the range expected for linear polymers, which indicates that the hard segments are completely dissolved in the soft segments.
### 3.6 List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>Flow pre-exponential constant</td>
<td>N·m·(mol/g)$^{3.4}$</td>
</tr>
<tr>
<td>$A(T)$</td>
<td>Empirical constant which relates viscosity to $M_w$</td>
<td>Pa·s·(mol/g)$^{3.4}$</td>
</tr>
<tr>
<td>$A'(T)$</td>
<td>Empirical constant which relates torque to $M_w$</td>
<td>N·m·(mol/g)$^{3.4}$</td>
</tr>
<tr>
<td>[Cat]</td>
<td>Catalyst concentration</td>
<td>mg/g</td>
</tr>
<tr>
<td>$C, C'$</td>
<td>Geometry factor of the kneader</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$D$</td>
<td>Diameter of barrel</td>
<td>m</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Reaction activation energy</td>
<td>J/mol</td>
</tr>
<tr>
<td>$\overline{H}$</td>
<td>Average distance between barrel and paddle</td>
<td>m</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Reaction pre-exponential constant</td>
<td>mol/kg s</td>
</tr>
<tr>
<td>$M_{rep}$</td>
<td>Average weight of repeating unit</td>
<td>g/mol</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
<td>g/mol</td>
</tr>
<tr>
<td>$n$</td>
<td>Power law index</td>
<td>-</td>
</tr>
<tr>
<td>$N$</td>
<td>Rotation speed</td>
<td>1/s</td>
</tr>
<tr>
<td>[NCO]</td>
<td>Concentration isocyanate groups</td>
<td>mol/kg</td>
</tr>
<tr>
<td>$[NCO]_0$</td>
<td>Initial concentration isocyanate groups</td>
<td>mol/kg</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
<td>J/mol K</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_{\text{measure}}$</td>
<td>Measured temperature of material in kneader</td>
<td>K</td>
</tr>
<tr>
<td>$T_{\text{set}}$</td>
<td>Set temperature of the kneader</td>
<td>K</td>
</tr>
<tr>
<td>Torque</td>
<td>Torque</td>
<td>N·m</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>$U_A$</td>
<td>Flow activation energy</td>
<td>J/mol</td>
</tr>
<tr>
<td>$V_b$</td>
<td>Barrel velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$W$</td>
<td>Width barrel</td>
<td>m</td>
</tr>
</tbody>
</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{\gamma}$</td>
<td>Shear rate</td>
<td>1/s</td>
</tr>
<tr>
<td>$\eta_{\text{app}}$</td>
<td>Apparent viscosity</td>
<td>Pa·s</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>Consistency</td>
<td>Pa·sn</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Shear stress</td>
<td>Pa</td>
</tr>
</tbody>
</table>
3.7 **List of references**
