M.Sc. Peter Kunzelmann, B.Sc. Stefan Danzer, Prof. Dr. rer. nat. habil. Dirk W. Schubert
Institute of Polymer Materials, University of Erlangen-Nuremberg

Semi-empirical equations for the description of Rheotens measurements

As a lab-scaled spinning device the Rheotens test is a well-established method to evaluate the extensional properties of polymer melts. The study presented proposes novel semi-empirical expressions for the description of the force versus draw ratio curve of Rheotens measurements. As a fact of its relevance for spinning processes, a commercial polypropylene grade was used. For the first time a fitting routine is revealed considering not only the steady-state curve of the experiment but also the force oscillations commonly known as draw resonance. Applying the fit function one has access to the melt strength and the critical draw ratio which are characteristic material parameters. This tool enables one to investigate or benchmark polymers whether they are suitable for fibre spinning.

Semi-empirische Gleichungen zur Beschreibung von Rheotens Messungen

Semi-empirical equations for the description of Rheotens measurements

P. Kunzelmann, S. Danzer, D.W. Schubert

In polymer processing it is often not sufficient to deal with the shear rheological properties in particular when elongational flow dominates the process like in film blowing, film casting or fibre spinning. The so called Rheotens test can be regarded as a process related experiment for the evaluation of the extensional properties of different polymer melts. First developed by Meissner [1], the Rheotens tester is a commercially available device manufactured by Göttfert. In general, during the Rheotens test the force along an extruded melt strand is measured as a function of the draw down velocity. Usually, the experiment is performed under a certain constant acceleration rate. The maximum take-up speed reached during the experiment is defined as the extensibility. The force at this remarkable point is called the melt strength.

1 INTRODUCTION

The most discussed quantity revealed from the Rheotens test is the melt strength. La Mantia and Acierno [2] discussed the influence of the molecular structure of various polyethylenes on the melt strength and showed that with increasing molar mass also the melt strength increases whereas the extensibility of the melt decreases. This fundamental finding was confirmed by Ghijsels and coworkers [3] for polyethylene and by Muke et al. [4] for polypropylene. Not only the molar mass but also the polydispersity influences the draw down behavior. For different polypropylenes having constant weight average molar masses and increasing polydispersity an increase in melt strength was found by Ghijsels and DeClippeleir [5] and Muke et al. [4].

Besides the molecular parameters also the various processing parameters of the Rheotens test influence the measuring result significantly. Muke et al. [4] and Lau et al. [6] investigated the influence of temperature on the melt strength and showed that it is possible to calculate activation energies which are in a good agreement to values determined from the shear viscosity. The same groups found an increase in melt strength with increasing throughput as a consequence of the increasing pre-shearing within the extrusion die and the higher force which is needed to elongate the strand. Increasing the spinning length leads to a decrease of the melt strength which is traced back to a stress relaxation of the molecules passing the spin line [4]. Wagner and coworkers showed that it is possible, at least for thermo-rheological simple materials, to
create a “mastercurve” [7] from Rheotens measurements which is invariant to temperature and molar mass at constant extrusion pressure and fixed die geometry and spinning length. Furthermore, a “supermastercurve” [8] is revealed invariant to either throughput or pressure at constant die geometry and spinning length. In general, the reciprocal correlation between the melt strength and the extensibility holds by varying molecular and processing parameters as well.

However, less attention has been paid to the force oscillations emerging during the Rheotens experiment when a critical take-up velocity is reached. Instead of the velocity usually the draw ratio is taken which is defined as the ratio between the take-up velocity and the die exit velocity. The fluctuation in the measured force values, emerging at a critical draw ratio, corresponds to a fluctuation in the strand diameter. This phenomenon is known as the draw resonance instability which was first observed experimentally by Christensen [9].

Especially in the field of fibre spinning the draw resonance effect has been under investigation since the 1970s. Experimental work showed the influence of processing parameters [10, 11] and molecular parameters [12, 13] on the critical draw ratio, the amplitude and the frequency of the draw resonance. Mathematical framework was established by Kase and Matsuo [14], Pearson and Matovich [15], and Gelder [16] who showed theoretically amongst others that draw resonance is not a polymer specific phenomenon but occurs in the case of purely Newtonian fluids as well. As the Rheotens test can be regarded as a lab-scaled fibre spinning experiment results from the former contributions are of great interest.

Back to the Rheotens test hardly data can be found describing the oscillation during the experiment and hence the complete Rheotens curve. A few authors derived equations to describe the steady-state case of the Rheotens curve neglecting the oscillation but with the aim to get access to elongational viscosity data. Rauschenberger and Laun [17] developed an iterative model which takes into account the pre-history of the melt. Wagner et al. [8] presented an analytical model using a power-law approach and Doufas [18] used a modified Giesekus constitutive equation to model the force versus velocity curve. Without discussing the method how the critical draw ratio was taken from Rheotens data, Muke et al. [4] show a reciprocal relationship between the melt strength and the critical draw ratio. Recently, Zavinska et al. [19] used in particular the constant velocity mode of the Rheotens test to get access to the onset of the draw resonance instability. The frequency of the oscillation was assumed to be a characteristic “fingerprint” of the material.

From an industrial point of view the critical draw ratio is the crucial limiting parameter for processes where the polymer melt is elongated. For example in fibre spinning inhomogeneous fibre diameters are revealed for draw ratios beyond the critical draw ratio which make the final product useless for any applications. Therefore, it would be desirable to find a reliable and manageable algorithm in order to get access to the critical draw ratio from Rheotens data.
In this study a semi-empirical approach is proposed to evaluate the melt strength and the critical draw ratio as well. Finally, a complete description of the Rheotens curve is given revealing parameters which allows one to evaluate the draw down behavior of different polymer melts.

2 EXPERIMENTAL

In figure 1 the experimental set-up of the Rheotens test is shown in detail. A melt strand is extruded via a standard capillary rheometer (Rheograph 2003, Göttfert) driven with a constant piston speed $v_p$ and a fixed piston diameter ($A_p$ is the area of the piston). $v_p$ is set to 0.5 mm/s and the piston diameter is 12 mm. The die has a diameter of 2 mm and a length of 20 mm ($A_0$ is the area of the die, $v_0$ the mean velocity of the melt within the die). The extrusion pressure is measured to ensure that a constant pressure value is reached during the Rheotens measurements. The spinning length $L$ is chosen short enough so that quasi-isothermal conditions can be assumed ($L = 100$ mm). Passing the spinning way the melt strand is pulled down with the counter-rotating wheels of the Rheotens tester, figure 1.

The 16 teeth of the self-constructed rolls are designed as parallel bars which are mounted on a cylinder in equal distance. The diameter of each bar is 4 mm. The wheels are installed at the Rheotens tester in that way that the bars of the wheels are placed face to face to their counterparts. The gap $\Delta$ between the rolls is fixed at (350 ± 50) $\mu$m. The velocity $v$ of the rolls and the force $F$ which is needed to elongate the melt strand are measured. At the beginning of the experiment the velocity $v$ of the wheels is adjusted to the velocity $v_s$ of the strand so that the force is zero. As a consequence of the extrudate swell the start velocity $v_s$ is smaller than the mean velocity $v_0$ within the die. As a measure of the extrudate swell a swell ratio $S$ can be defined ($S = v_0 / v_s$).

The velocity of the wheels is increased linearly with a constant acceleration $a$. Thus, a draw ratio $D_R$ can be defined as the ratio between the current velocity $v$ of the wheels and the start velocity $v_s$. Experiments are performed at various acceleration rates (1.2, 2.4, 6, 12 and 24 mm/s$^2$) and at three different temperatures (180 °C, 200 °C and 220 °C). (Note that the acceleration rate cannot be altered continuously, certain steps are given from the measuring software.) At least 5 measurements were made in order to proof the reproducibility. In section 3 the average mean values are shown. The error bars correspond to the standard deviation.
A typical measuring result of the Rheotens test is depicted on the right hand side of figure 1 for linear polypropylene at fixed processing conditions. The force $F$ versus the draw ratio $D_R$ shows first a steep increase because the elastic properties of the material control the elongation behavior at low draw ratios. At a certain draw ratio the curve reaches a plateau like region where viscous flow dominates. In section I, under stable experimental conditions, the strand diameter and the measured force are homogeneously increasing with increasing draw ratio. When a critical draw ratio is reached (section II) the force curve starts to fluctuate which correlates with a fluctuation in the strand diameter. This phenomenon is called draw resonance. With increasing velocity (or draw ratio) the amplitude of the oscillation increases which leads finally to a failure of the strand (section III). For this study an isotactic polypropylene with a linear chain architecture was used (PP505P, Sabic). No strain hardening behavior was observed in elongational rheological measurements performed with an oil bath rheometer at 180 °C and at various strain rates from 0.01 – 0.5 s$^{-1}$. Important material properties are shown in Table 1.

<table>
<thead>
<tr>
<th>MFI (230 °C / 2.16 kg) *</th>
<th>$\eta_0$ (180 °C) **</th>
<th>$T_m$ ***</th>
<th>$M_w$ §</th>
<th>$M_w / M_n$ §</th>
</tr>
</thead>
<tbody>
<tr>
<td>g / 10 min</td>
<td>kPas</td>
<td>°C</td>
<td>kg / mol</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>29.4 ± 0.1</td>
<td>162.4 ± 0.3</td>
<td>426 ± 9</td>
<td>5.5 ± 0.6</td>
</tr>
</tbody>
</table>

*supplied by the manufacturer, **evaluated from creep measurements with a shear rheometer (AR-G2, TA Instruments), ***from differential scanning calorimetry (Q2000, TA Instruments): peak temperature from second run, §from size exclusion chromatography (PL-GPC-220, Varian) coupled with a multi-angle light scattering device (Dawn Eos, Wyatt) in TCB at 140 °C.
3 RESULTS AND DISCUSSION

3.1 Description of the steady-state Rheotens curve

In figure 2 Rheotens measurements are shown for the linear polypropylene at a temperature of \( T = 200 \, ^\circ\text{C} \) and different acceleration rates \( a \). The curves for 6 mm/s\(^2\) and 12 mm/s\(^2\) are shifted to get a better insight as indicated by numbers.

![Figure 2: Typical Rheotens curves using the above described linear polypropylene – Measured force \( F \) as a function of the draw ratio \( D_R \) for three acceleration rates \( a \). The curves for \( a = 6 \text{ mm/s}^2 \) and \( a = 12 \text{ mm/s}^2 \) are shifted. The grey lines correspond to a fit utilizing equation 1.](image)

For the description of the steady-state Rheotens curve an empirical fit function according to equation 1 was used which neglects the oscillation.

\[
F(D_R) = \frac{A \cdot (D_R - 1)^n}{1 + B \cdot (D_R - 1)^m}
\]

(Eq. 1)

\( A, n, B, m \) are adjustable parameters. The dimension of \( A \) is cN, whereas all other parameters are dimensionless.

We propose equation 1 because it turns out that fitting is quite easy and numerical stable (The fit function was implemented using the data analyzing software Origin 8.5. A Levenberg-Marquardt algorithm is used to adjust the fit function to the measuring data). Additionally, up to now we have never had Rheotens measurements not adjustable utilizing equation 1 which holds for
various acceleration rates. In particular, equation 1 is also applicable to Rheotens measurements of polymers beyond linear polypropylene, like long-chain branched polypropylene and blends of both types. The fit parameters A, n, B, and m are not further discussed because they are not correlated to physical phenomena. It just should be mentioned that in the case when n equals m the function reaches a plateau for draw ratios tending to infinity. This value is expressed by the quotient of A and B (= A / B). However, for all fits examined in this study n > m was found.

With the help of equation 1 a mean force value can be calculated considering the draw ratio where the strand fails. This draw ratio is called extensibility $D_{R,a}$, the force at the extensibility $F(D_{R,a})$ is called melt strength $F_m$. In the following, the melt strength will be discussed as a function of the acceleration and the temperature to proof the proposed fitting routine.

In figure 3 the melt strength is shown as a function of the acceleration rate at three different temperatures from 180 °C to 220 °C.

![Figure 3: Melt strength $F_m$ as a function of the acceleration $a$ for three different temperatures (180 °C, 200 °C and 220 °C).](image)

It is obvious from figure 3 that the melt strength decreases with increasing temperature which is a consequence of the decreasing viscosity of the polymer melt. At 200 °C and 220 °C the melt strength is independent of acceleration. It seems that at 180 °C the melt strength decreases slightly with decreasing acceleration. However, this behavior is roughly indicated by the measuring points at the lowest accelerations. In order to proof the acceleration dependence it would be necessary to extend the investigations to lower acceleration rates.

Similar to these results Muke et al. [4] found also for a linear polypropylene an acceleration independent behavior of the melt strength within a range of...
accelerations from 6 – 60 mm/s². They varied the throughput and the spinning length instead of the temperature. In contrast, Steffl [20] showed for a LLDPE that no constant values are reached for accelerations from 2.4 – 120 mm/s². Although only linear polymers are considered in the mentioned references the acceleration dependence seems to be material specific. One can assume that in the case of long-chain branched polymers showing distinct strain hardening a more complex relation could be revealed. The acceleration dependence has to be taken into account if the melt strength will be used to compare different materials.

As mentioned above the melt strength decreases with increasing temperature. The relation was further studied using an Arrhenius type equation which is known to describe the temperature dependence of the viscosity of semi-crystalline polymers. In figure 4 the melt strength is plotted semi-logarithmically as a function of the inverse temperature.

![Figure 4: Melt strength Fm as a function of the inverse temperature for acceleration rates of 2.4 mm/s² and 6 mm/s² – The fit function corresponds to an Arrhenius type equation. The activation energy EA is calculated from the slope of the linear curve fitting. The deviation of the activation energy relates to the error of the fit.](image)

As can be seen from figure 4 the data points for the acceleration rates of 2.4 mm/s² and 6 mm/s² superimpose. The linear curve fitting according to an Arrhenius type equation takes both data sets into account. From the melt strength an activation energy of E_A = 33 ± 3 kJ/mol can be calculated which is in good agreement with values determined from the shear viscosity. For example Stange [21] and Auhl [22] determined values from shear rheological measurements around 36 kJ/mol for different linear polypropylenes. One can conclude that the temperature dependence of the melt strength is controlled by
viscous flow of the material. Muke et al. [4] and Lau et al. [6] could also show that an Arrhenius behavior holds.

Moreover, the activation energy does not depend on acceleration at least in the range investigated, figure 4. This result accompanies with the acceleration independent behavior of the melt strength shown in figure 3.

Although the melt strength is not a well-defined rheological quantity because of the non-uniform temperature distribution around the die exit and the spin line, the non-constant strain rate along the spinning length and the pre-shearing occurring within the die [23], it follows rheological principles like flow activation. One has to mention that in the case of thermo-rheological complex materials this finding could fail.

From a mathematical point of view equation 1 is a monotonically increasing function providing an inflexion point, further called $D_{R,x}$. As can be seen from figure 2 this behavior is also observed from the measuring data. For example the curve for an acceleration of 6 mm/s$^2$ shows a slight S-shaped start-up. From the fit according to equation 1 the inflection point $D_{R,x}$ can be calculated using the second derivative:

$$\frac{d^2 F(D_R)}{d D_R^2} = 0 \implies D_{R,x}$$

(Eq. 2)

From the first derivative the slope $m_x$ at the inflection point $D_{R,x}$ can be revealed:

$$\left. \frac{d F(D_R)}{d D_R} \right|_{D_{R,x}} = m_x$$

(Eq. 3)

We propose $D_{R,x}$ and $m_x$ as characteristic features of the material which will be shown in the following. In figure 5 the inflection point $D_{R,x}$ is shown as a function of the acceleration $a$. The small insert depicts the temperature dependence of $D_{R,x}$.
Figure 5: Inflection point $D_{R,x}$ as a function of the acceleration $a$ – The insert shows the dependence of the inflection point on the temperature for a constant acceleration of 2.4 mm/s$^2$.

As could be seen from figure 5 the inflection point shifts slightly to higher draw ratios for higher acceleration rates. A dependence from temperature cannot be found which holds for all accelerations investigated.

Greater interest has to be spent on the slope $m_x$ at the inflection point. As pointed out by Muke et al. [4] the “initial slope” of the Rheotens curve can provide important links to the processability of the material. At the beginning of the Rheotens test the strains as well as the strain rates are rather small. For the measurements presented one can deduce that for draw ratios smaller than 5 the apparent strain rates are smaller than 0.5 s$^{-1}$. In this region the elastic properties of the material dominate which lead first to a steep increase of the Rheotens curve, figure 2. One can assume that the slope provides qualitatively information about effects observed in extensional flow only, e.g. strain hardening.

In this study a linear polypropylene was used which does not show strain hardening. As shown in figure 4 the melt strength reacts sensitively on the processing temperature. Thus, it is obvious that different processing conditions show also an impact on the slope $m_x$.

In figure 6 the slope $m_x$ is shown in an Arrhenius type plot for different acceleration rates.
Figure 6: Slope $m_x$ at the inflection point as a function of the inverse temperature at various acceleration rates $a$ – The fit function corresponds to an Arrhenius type equation. The activation energy $E_A$ is calculated from the slope of the linear curve fitting. The deviation of the activation energy relates to the error of the fit. The insert shows the swell ratio $S$ (calculated from the die exit velocity $v_0$ and the start velocity $v_s$ of the Rheotens experiment) as a function of the temperature.

As the swell ratio $S$ is a measure for the elastic properties, the melt elasticity is independent of temperature and the change in the slope $m_x$ as a function of temperature is caused mainly by viscous flow.

Within the measuring accuracy the data for different accelerations superimposes. Generally the slope $m_x$ increases when the melt temperature decreases. Furthermore, Arrhenius-like behavior is observed. Applying a straight line fit function which takes all data points into account, an activation energy can be calculated which equals to the flow activation evaluated from the melt strength, figure 4. This finding leads to the assumption that the increase in the slope with increasing temperature is dominated by viscous flow and the temperature dependence of the viscosity, respectively. The insert in figure 6 underlines this argument because the swell ratio $S$ ($=v_0/v_s$) which is a qualitative measure for the elastic properties of the material does not depend on temperature. As the throughput and the die geometry are constant for all processing conditions ($v_0 = \text{const.}$) the swell ratio $S$ will increase if $v_s$ decreases. A decrease in $v_s$ corresponds to a stronger extrudate swell. It is generally known that the extrudate swell itself will increase when the elastic properties of the material increase [24]. Fujiyama and Inata [25] showed for various polypropylene-type resins that the extrudate swell is independent of temperature.
The accuracy of determining the slope at the inflection point is mostly influenced by the operator technique which has to be carefully applied in order to get reproducible data. In further investigations on blends of linear and long-chain branched polypropylenes it will be proven whether the slope at the inflection point of the Rheotens curve is accurate enough to be correlated with elastic material effects or strain hardening behavior.

### 3.2 Description of the oscillation behavior

Nevertheless, a weakness of equation 1 is the total disregard of the oscillation. Therefore, equation 1 is augmented by an additional term which takes into account the force oscillations, equation 4.

\[
F(D_R) = \frac{A \cdot (D_R - 1)^n}{1 + B \cdot (D_R - 1)^m} \quad \text{for } D_R < D_{R,c}
\]

\[
= \frac{A \cdot (D_R - 1)^n}{1 + B \cdot (D_R - 1)^m} + C \cdot \exp \left( \frac{(D_R - D_{R,c})}{D} \right) \cdot \sin \left( \omega_f \cdot (D_R - D_{R,c}) \right) \quad \text{for } D_R > D_{R,c}
\]

(Eq. 4)

where

\[C \quad ([C] = cN),\]

\[D_{R,c} = D_R \text{ at the onset of draw resonance } ([D_{R,c}] = 1),\]

\[D = \text{amplitude increase coefficient } ([D] = 1) \text{ and}\]

\[\omega_f = \text{frequency } ([\omega_f] = 1)\]

are adjustable parameters.

The same software and fitting algorithm was used as mentioned in section 3.1. The fit function was implemented using two parts. The first part describes the data for draw ratios smaller than the critical draw ratio \(D_{R,c}\) (\(D_R < D_{R,c}\)). The second part considers also the force oscillations (\(D_R > D_{R,c}\)).

For a first approach an exponentially increasing expression is used to describe the amplitude of the oscillation. The motivation is rather simple. Initiating an instability while passing the critical draw ratio \(D_{R,c}\) can be mathematically treated by a linear stability analysis, where a non-linear set of equations is linearized and corresponding eigenvalues \(\lambda\) are analyzed utilizing typical eigenfunctions of the form \(\exp(\lambda \cdot t)\) [16]. The eigenvalues have a real and an imaginary part at which the imaginary part is related to a corresponding oscillation and the real
part determines the exponential increase or decrease of the corresponding amplitude of physical quantities like the force or the fibre diameter. Therefore, a sinusoidal contribution for the draw ratio dependence of the measured force oscillation is combined with an exponential increase. It can also be found from literature that the draw resonance oscillation follows a sinusoidal behavior [12].

In equation 4 the parameter $\bar{D}$ is an indicator of the strength of the amplitude increase. The frequency of the oscillation $\omega_f$ is a dimensionless quantity. The time-scaled frequency $\omega_t$ depends on the acceleration $a$ and the start velocity $v_s$ as follows:

$$\omega_t = \omega_f \cdot \frac{a}{v_s}$$

(Eq. 5)

In figure 7 Rheotens measurements are shown for the linear polypropylene at a temperature of $T = 200 \, ^\circ C$ and different acceleration rates $a$. The curves for 6 mm/s$^2$ and 12 mm/s$^2$ are shifted to get a better insight.

Figure 7: Typical Rheotens curves using the above described linear polypropylene – Measured force $F$ as a function of the draw ratio $D_R$ for three acceleration rates $a$. The curves for $a = 6 \, \text{mm/s}^2$ and $a = 12 \, \text{mm/s}^2$ are shifted. The grey lines correspond to a fit utilizing equation 4. The red points mark the draw ratio at the onset of the oscillation, called the critical draw ratio $D_{R,c}$.

Pronounced draw resonance behavior appears for the linear polypropylene at all acceleration rates investigated, figure 7. Typically polymers with a linear chain architecture, for example PP [4] or HDPE [3] as well as LLDPE [3], show the draw resonance instability at a certain critical take-up velocity. For branched polymers e.g. LDPE [3] or long-chain branched PP [26] a brittle rupture of the
strand without distinct oscillations is reported. On the other hand Wagner et al. related a LDPE and a HDPE and found resonance behavior for both polymers although the chain architecture is different [7]. Cheng and Phillips investigated irradiated HDPE and LLDPE samples via Rheotens measurements and concluded that the branching degree which depends on the radiation dose determines the resonance behavior as well. Pure LLDPE shows a pronounced draw resonance whereas a brittle break is observed for the modified LLDPE which has a branched molecular structure [27].

As can be seen from figure 7 the fit according to equation 4 describes the measuring data quite well. The great advantage of the fit function is the possibility to reveal reliably the critical draw ratio $D_{R,c}$ as a fitting parameter which is an essential material describing parameter relevant for industrial processing. In figure 7 the critical draw ratios are marked as red points. It becomes obvious that the frequency of the oscillation changes with the acceleration at least on the draw ratio scale. The onset of draw resonance seems to vary, too. In the following the influence of the experimental parameters on the onset of draw resonance will be discussed.

In figure 8 the critical draw ratio $D_{R,c}$ is shown as a function of the acceleration rate for different temperatures. The curves for 200 °C and 220 °C are shifted for clarity.

![Figure 8: Critical draw ratio $D_{R,c}$ as a function of the acceleration $a$ for different temperatures $T$. The data points for 200 °C and 220 °C are shifted. The dotted lines are splines. The insert shows the critical draw ratio $D_{R,c}$ for various acceleration rates as a function of the temperature $T$.](image)
It was found that the critical draw ratio changes with the acceleration, figure 8. A maximum is revealed around $6 \text{ mm/s}^2$ which holds for all processing temperatures investigated. Up to now, there is no explanation for this behavior. Further investigations are needed to clarify this result. One can conclude that there is an optimum acceleration for the detection of the critical draw ratio which is probably material specific. As the maximum is temperature independent the melt viscosity seems to play a minor role. The question remains: “What is the true critical draw ratio?” A possible approach to answer this question is to use the constant velocity mode of the Rheotens test. Zavinska et al. [19] used this feature to investigate the critical draw ratio for LLDPE, PP and PS. The velocity was increased stepwise whereat the step time was chosen long enough to equilibrate the system. The velocity step at which the force oscillations become obvious was defined as the onset of draw resonance. Such a procedure has a higher relevance with respect to an industrial spinning process.

In order to depict the influence of temperature on the critical draw ratio the insert in figure 8 shows $D_{R,c}$ as a function of the temperature for different accelerations. For lower accelerations ($1.2 - 6 \text{ mm/s}^2$) the critical draw ratio increases with increasing temperature, the thread stability is enhanced. The influence of temperature is in agreement with literature data for fibre spinning experiments [26]. Additionally, Muke et al. [4] described that with decreasing melt strength the critical draw ratio increases. As can be seen from figure 3 an increasing temperature leads to a decrease in melt strength and so the onset of the oscillation occurs at higher draw ratios. This correlation does not hold for higher accelerations, insert in figure 8. This fact underlines the assumption of the existence of an optimized processing window for the detection of the critical draw ratio in the acceleration mode.

From the fit according to equation 4 one gets also information about the frequency of the oscillation. As described above the frequency from the fit function is a dimensionless quantity which can be transferred into a time-scaled frequency using equation 5. In figure 9 the calculated values of the frequency $\omega_t$ are shown as a function of the acceleration. The data points for $200 \, ^\circ\text{C}$ and $220 \, ^\circ\text{C}$ are shifted.
Figure 9: Time-scaled frequency $\omega_t$ of the force oscillation as a function of the acceleration $a$ for different temperatures $T$ – The data points for 200 °C and 220 °C are shifted.

Figure 9 clearly turns out that the frequency neither depends on the acceleration nor on the temperature. Additionally an influence of the draw ratio on the frequency cannot be found in the acceleration mode. Thus, a single frequency is sufficient in order to describe the oscillation of the Rheotens curve. Moreover, the mean frequency of 1.7 s$^{-1}$ is in good agreement with literature data from Yoo [28] and Zavinska et al. [19]. The latter showed that the constant velocity mode is the more powerful tool to get information about the frequency and denoted the frequency of the oscillation as a characteristic material parameter. Based on the results from spinning experiments an influence of the draw ratio on the oscillation is expectable in the constant velocity mode. For example Han et al. [29] found an increase of the amplitude and the frequency of the oscillation with increasing draw ratio. However, the frequency of the force oscillation during a Rheotens test is a specific feature but with respect to industrial needs the critical draw ratio is the limiting parameter during polymer processing, e.g. fibre spinning.

3.2 Analysis of the amplitude of the draw resonance

Further investigations on the amplitude of the oscillation during Rheotens measurements were performed because it should be proven whether the assumption of an exponential increase of the amplitude expressed by equation 4 is accurate. Therefore, the data of the oscillation regime were taken and the maxima and the minima were connected with line drawings as depicted in figure 10.
Figure 10: Measured force $F$ as a function of the draw ratio $D_R$ in the oscillation regime for a temperature of $200 \, ^\circ C$ and an acceleration of $2.4 \, \text{mm/s}^2$ – The maxima and minima are connected with line drawings (grey lines). At each half period the difference between the upper and lower line were calculated ($\Delta g$).

As a measure for the increase of the amplitude the difference between the upper and the lower line $\Delta g$ were calculated for every half period. As shown in figure 2 the steady-state force curve increases monotonically without reaching a plateau. The $\Delta g$ values consider the slight increase of the steady-state curve in the oscillation regime. Each $\Delta g$ value can be correlated to a certain draw ratio. Figure 11 shows $\Delta g$ as a function of the draw ratio exemplarily for the same data set as used in figure 10.
Figure 11: $\Delta g$ as a function of the draw ratio $D_R$ for a temperature of 200 °C and an acceleration of 2.4 mm/s$^2$ – The continuous grey line corresponds to a fit according to equation 6. The dotted grey line relates to the exponential expression in equation 4.

In a double-logarithmic plot of $\Delta g$ as a function of the draw ratio one can find two regimes with different slopes which correspond to two different power laws, figure 11. It is noteworthy that from a mathematical point of view a similar behavior is observed for the zero shear viscosity $\eta_0$ as a function of the weight average molar mass $M_w$ [30]. Therefore, the expression for $\eta_0(M_w)$ is adapted to the $\Delta g(D_R)$ correlation in equation 6

$$\Delta g = g_0 \cdot D_R^x \cdot \left[1 + \left(\frac{D_R}{D_{R,u}}\right)^y\right]$$

(Eq. 6)

where

- $g_0$ ($[g_0] = cN$)
- $x$ power in regime 1 ($[x] = 1$)
- $y$ power in regime 2 ($[y] = 1$) and
- $D_{R,u}$ transition draw ratio ($[D_{R,u}] = 1$)

are adjustable parameters.

In figure 11 the exponential expression from equation 4 is shown additionally in comparison to equation 6. From a phenomenological point of view the latter seems to be a more suitable description of the amplitude increase than the exponential one. Nevertheless, as can be seen from figure 7 the exponential amplitude increase describes the measured data quite well and is a
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mathematically motivated consequence from non-linear dynamics as mentioned above.

However, from the fit according to equation 6 one gets \( D_{R,u} \) which denotes the transition between the two power laws and can be regarded as a characteristic draw ratio at which the amplitude of the oscillation increases much stronger. The analysis of \( \Delta g \) was then applied to various temperatures and acceleration rates. In the following the \( D_{R,u} \) values are plotted as a function of the temperature for the accelerations of 2.4 mm/s\(^2\) and 6 mm/s\(^2\), figure 12.

![Figure 12: Draw ratio \( D_{R,u} \) as a function of the temperature \( T \) for the accelerations 2.4 mm/s\(^2\) and 6 mm/s\(^2\).](image)

It becomes obvious that \( D_{R,u} \) is independent of temperature whereat a slight increase is observed for a higher acceleration. This finding is quite surprising because the critical draw ratio \( D_{R,c} \) at the onset of draw resonance shows an increase with increasing temperature, figure 8. The temperature independence of \( D_{R,u} \) together with its meaning as a point leading over to a stronger amplitude increase give rise to the assumption that \( D_{R,u} \) is also a border between pure material behavior and a material-device coupling effect. That means that the strand diameter at \( D_{R,u} \) equals the gap distance \( \Delta \) of the wheels.

In order to estimate the thread diameter \( D \) at \( D_{R,u} \) the die exit velocity \( v_0 \) has to be calculated considering the die diameter \( D_0 \) and the throughput \( \dot{V} \), figure 13.
Figure 13: Principle sketch of the take-up of the polymer strand for a steady-state profile of the strand and for a profile in the case of draw resonance – The wheels depict the counter-rotating wheels of the Rheotens tester.

Considering the equation of continuity and with \( v = D_R \cdot v_s \) one gets

\[
D_0^2 \cdot v_0 = D^2 \cdot v \Rightarrow D = D_0 \cdot \frac{v_0}{v} = D_0 \cdot \frac{v_0}{v_s} \cdot D_R^{-1}
\]

(Eq. 7)

Taking into account the statistical spread, the values of \( D_{R,u} \) lie in a range of 19 - 31 for an acceleration of 2.4 mm/s\(^2\), figure 12. The start velocity \( v_s \) was found to be independent of temperature and can be set to 7 mm/s. Assuming a steady-state profile of the fibre as depicted in figure 13, substitution of \( D_R \) by \( D_{R,u} \) in equation 7 leads to the threat diameter \( D \) at \( D_{R,u} \). The calculated values of \( D \) are in the range of 580 – 740 \( \mu \)m which can be regarded as a mean diameter. The gap \( \Delta \) between the wheels was fixed to (350 ± 50) \( \mu \)m which is in the same order of magnitude. As a fact of the draw resonance the real thread diameters at \( D_{R,u} \) can be larger or even smaller than the calculated values from the assumption of a steady-state profile. It is obvious that if the strand diameter is nearly equal to the gap distance the contact area between the strand and the wheels becomes smaller which affects the load transmission, stick-slip effects appear. When the strand becomes too thin, it cannot be taken off by the wheels and the measured force decreases. After a certain extrusion time, enough material is conveyed along the spin line and accumulates in the front of the wheels. The thread diameter becomes thicker and the strand is taken off again whereat the force growth quickly.
4 CONCLUSIONS

This study proposes novel semi-empirical expressions for the description of the force versus draw ratio curve of Rheotens measurements. A fitting routine is revealed considering the steady-state curve of the experiment as well as the force oscillations commonly known as draw resonance. This tool enables one to investigate or benchmark polymers whether they are suitable for fibre spinning. In this study a commercial linear polypropylene was used.

Among the various processing parameters of the Rheotens test only a systematic variation of the extrusion temperature and the acceleration rate were considered. A quantity deduced from the fit function is the melt strength. The temperature dependence of the melt strength follows an Arrhenius like behavior. An activation energy can be calculated which is in good agreement with values determined from the shear viscosity. The melt strength itself and the corresponding activation energy show no acceleration dependence in the range investigated.

Because of its mathematical structure the fit function possesses an inflection point which is considered as a characteristic point of the measured data. We propose the slope of the curve at the inflection point as a further characteristic material parameter. As the elastic properties of the material dominate at low draw ratios, correlations between the slope and for example strain hardening behavior are evident which are subjected to further investigations.

Taking into account the oscillation of the force the critical draw ratio at which the fluctuation starts is revealed as a fit parameter. At a certain acceleration the critical draw ratio reaches a maximum which equals for different temperatures. Currently there is no explanation for this behavior but obviously an optimum parameter set exists for the evaluation of the critical draw ratio which is assumed to be material specific. Moreover, the frequency of the oscillation is neither acceleration nor temperature depended in the acceleration mode of the Rheotens test. Additionally, a constant velocity mode is provided which is rarely discussed in literature. In order to clarify the acceleration dependence of the critical draw ratio this feature has to be taken into account.

Passing the onset of draw resonance an increase of the amplitude of the oscillation with increasing draw ratio becomes obvious. Two different methods are presented to describe the amplitude increase. In a first approach an exponential expression is used which is mathematically motivated and allows stable fitting. An amplitude increase coefficient is revealed which correlates with the strength of the increase. Unfortunately, no further information can be deduced from this fit parameter.

A second approach based on a precise analysis of the amplitude leads to a power law expression describing two regions following different power laws. The border between the two regions is a specific draw ratio, implemented as a fit parameter, at which a dramatically change in the amplitude increase is
observed. Passing this certain draw ratio the amplitude increases much stronger and the strand diameter equals the gap distance between the wheels of the Rheotens tester. Stick-slip effects between the strand and the wheels are the consequence, no longer pure material behavior is measured.
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Autor / author:
M.Sc. Peter Kunzelmann
B.Sc. Stefan Danzer
Prof. Dr. rer. nat. habil. Dirk W. Schubert
Institute of Polymer Materials
University of Erlangen-Nuremberg
Martensstr. 7, 91058 Erlangen

E-Mail-Adresse: dirk.schubert@fau.de
homepage: www.lsp.uni-erlangen.de
Tel.: 09131/85-27752
Fax: 09131/85-28321

Herausgeber / Editor:
Europa/Europe
Prof. Dr.-Ing. Dr. h.c. Gottfried W. Ehrenstein, responsible
Institute of Polymer Technology
University of Erlangen-Nuremberg
Am Weichselgarten 9
D-91058 Erlangen
Deutschland
Phone: +49 (0)9131/85 - 29703
Fax.: +49 (0)9131/85 - 29709
E-Mail-Adresse: ehrenstein@lkt.uni-erlangen.de

Amerika/The Americas
Prof. Prof. hon. Dr. Tim A. Osswald, responsible
Polymer Engineering Center, Director
University of Wisconsin-Madison
1513 University Avenue
Madison, WI 53706
USA
Phone: +1/608 263 9538
Fax.: +1/608 265 2316
E-Mail-Adresse: oswald@engr.wisc.edu

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