Liquid crystalline solutions of cellulose in phosphoric acid for preparing cellulose yarns
Boerstoel, H.

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5. Elongational viscosity of solutions of cellulose in phosphoric acid
H. Boerstoel, J.B. Westerink, G. Dubbeldam, H. Maatman

Abstract
Velocity profiles were recorded during drawing in the air gap in dry jet wet spinning isotropic and liquid crystalline solutions of cellulose in superphosphoric acid. It was found that the velocity varies exponentially with the distance from the spinneret, indicating a constant elongational viscosity. This was confirmed by the force after the coagulation bath being inversely proportional to the air gap length. The elongational viscosity was found to be very high, viz. 20 kPa.s for a solution containing 17 % w/w cellulose, the Trouton ratio far exceeding the value 3. The elongational viscosity, which was determined from force as a function of reciprocal air gap length, was proportional to the third power of the concentration, as expected from the Doi theory. No difference was found between solutions that were either isotropic or anisotropic in the quiescent state, which showed that in the flow field of the spinneret and the air gap these phases no longer differed.

5.1 Introduction
5.1.1 Air gap spinning
Liquid crystalline solutions are good precursors for high modulus, high tenacity yarns. Examples of such lyotropic systems are poly(p-phenylene terephthalamide) (PpPTA) in sulfuric acid, and rigid rod polymers such as polybenzoxazole (PBO) in polyphosphoric acid. Recently a new rigid rod fiber spun from an anisotropic solution in polyphosphoric acid was developed by Akzo Nobel: Poly[2,6-diimidazo[4,5-b:4',5'-e]pyridinylene-1,4-(2,5-dihydroxy)phenylene] (PIPD or "M5"). The one mentioned first is known under the trade names Twaron® (Akzo Nobel) and Kevlar® (Du Pont). In the spinning processes use is made of the local orientation which is already exhibited by the liquid crystalline solutions. Local orientation is transformed into global orientation by applying an elongational flow field, which is very effective in bringing about a good alignment of the rigid macromolecules. This elongational flow field is in the entrance zone of the capillaries of the spinneret and in the air gap, where a draw ratio in the order of 10 is imposed. Apart from the orientation, that is achieved here, the drawing is necessary to obtain the low filament linear density desired in wet spinning processes. The speeds at which the filaments are coagulated and washed in order respectively to freeze the structure and remove the solvent are limited by diffusion and thermal conduction. A low filament linear density will speed up the coagulation and washing processes allowing a higher, and hence economically more favorable process speed.

It was found that cellulose dissolves rapidly in superphosphoric acid with formation of liquid crystalline solutions. These solutions were used for the preparation of high tenacity cellulose yarns. The transport of the solution through the various machine components can be divided
into shear flow and elongational flow fields. The rheological behavior of solutions of cellulose in superphosphoric acid in shear flow is described in Chapter 4. In Chapters 5 and 6 the response of the solution towards elongation is shown, both with respect to the tensions related to the deformations and the orientation induced by the flow field. To that end a combined online measurement of the velocity and the birefringence was used, the latter being treated in Chapter 6. Here, however a description is given of the velocity profiles and a method for the online determination of the elongational viscosity. Since the elongational viscosity determines the tension in the fiber forming step, knowledge of the value of this elongational viscosity is important in air gap spinning. A high tension may not only prohibit possible relaxation effects during coagulation, it may also cause damage to the fragile filament in the initial stage of the coagulation process. Moreover, the pressure drop across the spinneret is to be attributed in part to the elongational flow field. Although in the capillaries the shear rate is much higher than the elongational rate, the elongational flow will contribute significantly to the spinning pressure in the case of a high elongational viscosity.

5.1.2 Devices for the determination of the elongational viscosity
Over the years much research has been done with a view to arriving at a technique for the determination of the elongational viscosity. Quite a few devices were developed. For example: one kind of extensional rheometer is based on a tensile tester with a variable clamp speed in order to obtain a constant elongational rate. Smook determined the elongational viscosity of high molecular weight polyethylene by using a constant clamp speed. Another technique makes use of the so-called spinning balance, with a filament being drawn. The force applied to the filament in order to draw it is transmitted to the spinning machine, where it is measured. Additionally a local diameter or velocity measurement of the filament may be carried out for the determination of the elongational rate. The interpretation of the force measurement is extremely difficult. The polymer flowing through the tubes also brings about forces; moreover, the drawing force is small in relation to the mass of the machine. Use is also made of a four-roller device equipped with a birefringence measurement, and an open syphon technique.

5.1.3 Doi's theory
As discussed in Chapter 4 Doi and Edwards describe the dynamics of solutions of rodlike macromolecules. The classification of the concentration regimes is specified in Chapter 4. In the nematic phase the shear viscosity depends on the number density $n$, the molecular weight of the rods $M$, and the order parameter $S$:

$$\eta \propto n^3 M^6 f(S)$$

(5.1)
In practice the molecules are longer than the persistence length, which probably reduces the power to the molecular weight. The order parameter $S$ is defined by:

$$ S = \left( \frac{3}{2} \cos^{2} \theta - \frac{1}{2} \right) $$

(5.2)

where $\theta$ is the angle of the rods at the director, with the brackets referring to the averaging process.

In slow shear flows the increased orientational order determines the decrease in viscosity above the critical concentration for the formation of a nematic phase according to the Doi theory. In shear flow the systems are strongly shear-thinning. At low elongational rates a constant elongational viscosity is predicted, but strain-thinning is predicted at higher deformation rates\textsuperscript{10}. Metzner and Prilutski confirm the prediction based on the Doi theory of a constant elongational viscosity, albeit with a Trouton ratio deviating from the value 3\textsuperscript{12}. The theoretical considerations are supported by experiments on hydroxypropyl cellulose in glacial acetic acid, where a constant elongational viscosity is found. In thermotropic polyesters, however, the elongational viscosity was found to decrease with increasing strain rate\textsuperscript{13}.

Chapter 4 deals with the effect of a flow field on the phase transition from isotropic to nematic. Marrucci and Ciferri, and Mansuripur discuss the effect in this respect of an elongational flow field in this respect\textsuperscript{14,15}. Weyland demonstrates that in spinning poly (para-phenylene terephthalamide) from sulfuric acid no discontinuity in mechanical properties as a function of concentration is observed\textsuperscript{16}.

5.2 Uniaxial drawing

5.2.1 Velocity profile in elongational flow

In the air gap the jets emerging from the capillaries are drawn uniaxially. The boundary conditions suddenly change upon the fluid leaving the capillary. The velocity profile changes from, e.g., parabolic for Newtonian liquids in the capillary to a flat profile downstream. Mostly, a die swell is observed, which depends on the constitution of the material and the geometry of the die. A drawn extrudate is schematically shown in Figure 5.1.

The following simplifications are made:

i) The velocity at the bath surface $v_1$ equals the take up velocity $v$.

ii) The flat velocity profile settles immediately after the fluid leaves the capillary.

iii) The occurrence of a die swell is ignored.

The force balance can be written as\textsuperscript{17}:

$$ F_{ext} + F_{grav} = F_{rheo} + F_{in} + F_{surf} + F_{aero} $$

(5.3)
As we are dealing with a highly viscous material, the gravitational ($F_{grav}$), inertial ($F_{in}$), surficial ($F_{surf}$) and aerodynamical ($F_{aero}$) are considered to be small in relation to the rheological force ($F_{rheo}$). The external force ($F_{ext}$) then balances the rheological force:

$$F_{ext} = F_{rheo}$$  \hspace{1cm} (5.4)

So, under the above mentioned conditions the force is constant throughout the air gap. The tension $\sigma_z$ at a distance $z$ from the spinneret relates to the force via the surface $A_z$:

$$\sigma_z A_z = F_{rheo}$$  \hspace{1cm} (5.5)

From the force balance the velocity profile can be calculated if the constitutive equation is known. The simplest case is the one where the elongational viscosity $\eta_e$ is constant:

$$\sigma_z = \eta_e \varepsilon_z = \eta_e \frac{dv_z}{dz}$$  \hspace{1cm} (5.6)

Combining Equation 5.6 with the force balance of Equation 5.5, while adding the mass balance and considering the boundary condition, gives:

$$\int_0^l \frac{F_{rheo}}{Q \eta_e} dz = \int_{v_0}^{v_z} \frac{1}{\nu_z} dv_z$$  \hspace{1cm} (5.7)

where $Q$ is the volume flow and $v_0$ the velocity at the spinneret surface. Integration gives:

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This means that for a fluid with a constant elongational viscosity while ignoring forces other than the external and rheological forces an exponential velocity profile is found. The velocity at the bath surface is:

\[ v_s = v_0 \exp\left( \frac{F_{\text{rhek}} z}{Q \eta_e} \right) \]  

(5.8)

The velocity can also be written in terms of air gap length \( l \) and velocity \( v_l \) at the bath surface:

\[ \frac{v_z}{v_0} = \left( \frac{v_l}{v_0} \right)^{\frac{z}{l}} \]  

(5.10)

From Equation 5.10 it follows that for fluids with a constant elongational viscosity the velocity as a function of distance \( z \) from the spinneret is completely determined by the extrusion velocity, take up velocity and the air gap length, and that the absolute value of the elongational viscosity is irrelevant.

For a power law fluid with:

\[ \sigma = k \dot{\varepsilon}^m \]  

(5.11)

the velocity as a function of distance is described by:

\[ v_z = \left( v_l^{m-1} - v_0^{m-1} \right) \frac{z}{l} + v_0 \frac{m-1}{m} \]  

(5.12)

which also leads to concave profiles; the more strain thinning the material, the more the deformation will be concentrated in the end part of the air gap.

5.2.2 Drawing force

We consider the total force after the bath to be composed of the rheological \( F_{\text{rhek}} \) and the hydrodynamical force \( F_{\text{hyd}} \):
Upon increasing the air gap the angle at which the filaments enter the spinning bath will slightly change. However, upon a first approximation, it does not significantly affect the hydrodynamical force. Therefore, the effect on the hydrodynamical force of changing the air gap is considered negligible as compared with the effect on the rheological force. Combining Equation 5.9 and 5.13 gives the total force as a function of air gap length:

\[ F_{\text{tot}} = F_{\text{rheo}} + F_{\text{hydr}} \]  

(5.13)

Here we can see that, due to the logarithmic term the error made by the assumptions in Section 5.2.1 is not quite as large as we would think at first. Moreover, both \( v_0 \) and \( v_1 \) are overestimated by the assumptions, so that the errors as to either velocity counterbalance each other. From Equation 5.14 we learn that on the present assumptions for a constant elongational viscosity the plot of the total force as a function of reciprocal air gap length should give a straight line, with intercept \( F_{\text{hydr}} \) and slope \( Q\eta \ln(v/v_0) \). This offers the possibility of determining the elongational viscosity.

5.2.3 Temperature effects

Filament cooling in the air gap

Filament cooling when a flat temperature profile is assumed in the filament is characterized by:

\[ \frac{dT}{dz} = \frac{-2\pi h R(T - T_a)}{Q_m c_p} \]  

(5.15)

where \( T \) is the average temperature of the filament at a distance \( z \) from the spinneret, \( R \) the filament radius, \( T_a \) the temperature of the surrounding air, \( Q_m \) the mass flow, and \( c_p \) the heat capacity of the filament.

Integration while introducing the Nusselt number \( \text{Nu} \) gives:

\[ \frac{T - T_a}{T_0 - T_a} = \exp\left(\frac{-\text{Nu} \lambda \pi x}{c_p Q_m}\right) \]  

(5.16)

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The Nusselt number defined by \( \text{Nu} = \frac{2hR}{\lambda} \), \( \lambda \) being the heat conductivity of air, should be a constant for the above Equation to hold. Ziabicki has given the value of Nu for an axially moving filament in stationary air\(^\text{17}\):

\[
\text{Nu} = 0.25 + 0.15 \text{Re}_f^{0.36} \quad 1 < \text{Re}_f < 10
\]

, where the Reynolds number with respect to the filament is defined by \( \text{Re}_f = \frac{\rho v d}{\eta} \); \( \rho \) and \( \eta \) are the density and viscosity of air, respectively, and \( v \) and \( d \) are the velocity and diameter of the moving filament.

Viscous dissipation

Due to viscous dissipation in the drawing process the temperature of the filaments in the air gap will rise. The elastic part of the deformation process will be stored in the internal energy. If we assume the flow to be purely viscous, we can estimate the maximum temperature rise due to viscous dissipation. Knoester and Van der Hout derived that the temperature rise \( \Delta T \) can be approximated by\(^\text{18}\):

\[
\Delta T = \frac{\eta v}{c_p \rho L} (v_i - v_o) \ln \lambda
\]

, where \( c_p \) and \( \rho \) are the heat capacity and density of the solution respectively and \( \lambda \) represents the draw ratio. Moreover, the pressure drop across the capillary and the expansion at the exit will cause changes in temperature.

5.3 Experimental

5.3.1 Preparation of the solution

Solutions were prepared in a Linden Z-kneader equipped with a discharge screw. Orthophosphoric acid (ex La Fonte Electrique SA, Bex Suisse, crystallized 99% w/w \( \text{H}_3\text{PO}_4 \)) and polyphosphoric acid (ex Stokvis 84% w/w \( \text{P}_2\text{O}_5 \)) were mixed at a ratio such that a presolvent was obtained with a \( \text{P}_2\text{O}_5 \) concentration of approximately 74.3% \( \text{P}_2\text{O}_5 \). The terms presolvent and solvent are defined in Chapters 2 and 3. The acid mixture was heated to approximately 50°C to melt the orthophosphoric acid crystals and the mixture was allowed to equilibrate for at least half an hour. The presolvent was brought into the kneader and cooled to 10°C, after which the cellulose (Buckey V60, DP820, approximately 5% equilibrium moisture) was added. Within 10 minutes glossy, fiber forming, birefringent solutions were formed. During mixing the temperature rose, but by cooling the kneader the temperature was
kept below 25 °C. The solutions were kneaded for one hour, the last 30 minutes of which in vacuo (60-100 mbar) for degassing. The 15l containers of the spinning machine were filled by means of the kneader discharge screw. In practically all cases the optical evaluation of the drawing process was conducted on solutions containing 17.1 % w/w dry cellulose, which were prepared in the above-described manner by adding 18 % w/w cellulose, containing 5 % w/w equilibrium moisture to a presolvent of 74.3 % w/w P₂O₅. Deviating cellulose concentrations were only used in experiments, where the influence of cellulose concentration was studied.

5.3.2 Spinning equipment
For the optical measurements and the determination of the elongational viscosity use was made of a spinning machine as schematically shown in Figure 5.2.

![Figure 5.2: Dry jet wet spinning of solutions of cellulose in superphosphoric acid.](image-url)
The vessel filled with the solution from the Linden kneader was mounted on the spinning machine. Under Nitrogen pressure the solution was forced to feed a booster pump. The solution passed through a 20µm filter to the spinning pump providing for the spinning pressure. After the spinning pump the solution was heated to the spinning temperature in a static mixer. The spinneret and filters were placed in a heated housing.

For the optical experiments special spinnerets were used, with a central hole and two quadrants, each being provided with 59 capillaries, as displayed in Figure 5.3.

![Figure 5.3: Arrangement of the capillaries in the spinneret for the optical measurements: one central hole (not indicated) and two quadrants with 59 capillaries each](image)

The central capillary was used for optical investigation. The other capillaries provided for a sufficiently high total throughput of spinning solution to be accurately delivered. The capillaries had a diameter of 75 µm (L/d=2) and a conical entrance with an angle of 10°.

The filaments were drawn in an air gap, after which they entered a falling jet coagulation bath containing cold acetone. The velocity of the filaments was set by the first godet. The yarns were washed with water, dried, and wound on a bobbin. They were not used for further analysis. In Chapter 6, however, yarns spun under special conditions will be described.

The flow through the central hole was calibrated with respect to the total throughput in the following manner. For a 17.1 w/w % cellulose solution the central extrudate was wound onto a bobbin for 10 minutes and weighed. The throughput of the entire spinneret was determined by weighing the spinning solution collected in 3 minutes. The ratio of both flows was 119 for the one and 140 for the other spinneret. These values were used for calculating the extrusion speed.

5.3.3 Optical method

In thermoplastic processing, e.g., melt spinning, birefringence is often used as a measure of stresses in the melt. The birefringence and the stress are interrelated via the stress-optical law. In fact both the birefringence and stress are related to the molecular orientation. An on-line method for the determination of birefringence was developed by Harris. Here use is made of
a modified version, which was supplemented with a Laser-Doppler velocity measuring technique. Figure 5.4 gives a schematic presentation of the set-up for simultaneous determination of velocity and birefringence. The latter subject is treated in Chapter 6.

![Diagram of set-up for simultaneously measuring the phase shift and velocity of the filament](image)

**Figure 5.4: Set-up for simultaneously measuring the phase shift and velocity of the filament**

Laser Doppler anemometry

Since the measuring principle is not based on the frequency shift of the laser light, the term Laser Doppler anemometry is rather confusing. For the determination of the velocity the measuring system is equipped with a beam splitting cube. The two coherent monochromatic laser beams formed are brought together in the plane of the filament. In the cross section there occurs an interference pattern with horizontal dark and light lines: the fringe pattern which is also depicted in Figure 5.4. The intensity of the light scattered by defects that pass the fringes will rise and fall at a frequency proportional to the velocity of the particle. The signal is amplified and filtered. A typical pattern (burst) is displayed in Figure 5.5. The spectrum is analyzed by means of a Fast Fourier Transform program. From the frequency $f$ thus determined the velocity $v_z$ can be calculated:

$$v_z = \frac{f\lambda}{2\sin(1/2\alpha)} \tag{5.19}$$
where \( \lambda \) is the wavelength of the laser light (632.8 nm) and \( \alpha \) the angle between the two laser beams.

\[
\tan \alpha = \frac{y}{2x}
\]  

(5.20)

and was found to be 1.27°. This means that the measured frequency \( f \) (kHz) should be multiplied by a factor of 0.86 to arrive at the velocity \( v_c \) (m/min).

The angle \( \alpha \) was determined by projecting the laser beams onto a distant plane and measuring the spacing of the projected beams. At a distance \( x \) of 4.4 m the spacing \( y \) between the spots was 0.195 m. The angle \( \alpha \) was calculated from:

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\]
5.3.4 Force measurement

To check the appearance of a constant elongational viscosity for several cellulose concentrations the force applied to the yarn after the coagulation was determined at various air gap lengths for a number of cellulose concentrations. To that end the same spinning equipment was used as described in Section 5.3.2. The temperature of the solution was measured just before the spinneret and its housing. Instead of the special design used for the optical determinations spinnerets were employed having 100, 250 or 375 capillaries arranged regularly in the spinneret.

As described in our patent application the degree of polymerization (DP) was determined on extruded samples taken at various moments during the experiments. The resulting values are the values interpolated for that experiment.

5.4 Results and Discussion

5.4.1 Velocity profiles

Velocity profiles in the air gap were measured by Laser Doppler Anemometry. The various experiments are listed in Tables 5.1 and 5.2.

Table 5.1: Experiments for optical measurements, with \( T_e \) representing the clearing temperature (see Chapters 2 and 3), \( T \) the spinning temperature, \( v_0 \) and \( v \) squiring and take up velocity, respectively, and \( l \) the air gap length.

<table>
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<th>( T_e ) °C</th>
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<th>( v ) m/min</th>
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</tr>
<tr>
<td>F</td>
<td>17.1</td>
<td>66</td>
<td>54</td>
<td>29.2</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>G</td>
<td>17.1</td>
<td>66</td>
<td>54</td>
<td>29.2</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>H(^1)</td>
<td>9.5</td>
<td>36</td>
<td>42</td>
<td>22.8</td>
<td>100</td>
<td>49</td>
</tr>
<tr>
<td>I</td>
<td>14.3</td>
<td>56</td>
<td>54</td>
<td>22.8</td>
<td>100</td>
<td>49</td>
</tr>
</tbody>
</table>

\(^1\) DP2300

The velocity profiles are displayed in Figures 5.6 to 5.9. The influence of air gap length is given in Figure 5.6 (exp. A,B, and C), of spinning speed in Figures 5.7 (exp. C,D,E, F, and G), and of concentration in Figure 5.8 (exp. H, I, and C).
Table 5.2: Distance at which squirting speed is reached ($z_0$), and regression parameters for the various experiments. Regression is applied according to $v = v_i \exp(az)$, where $v_i$ represents the extrapolated velocity at the spinneret surface. Also indicated is the estimated velocity at the bath surface $v_e$.

<table>
<thead>
<tr>
<th>experiment</th>
<th>$z_0$ (mm)</th>
<th>$v_i$ (m/min)</th>
<th>$a$ (mm$^{-1}$)</th>
<th>$r^2$</th>
<th>$v_e$ (m/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$^1$</td>
<td>1.2</td>
<td>17.2</td>
<td>0.1421</td>
<td>0.997</td>
<td>109</td>
</tr>
<tr>
<td>B</td>
<td>3.3</td>
<td>20.4</td>
<td>0.0552</td>
<td>0.997</td>
<td>96</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>21.2</td>
<td>0.0309</td>
<td>0.990</td>
<td>96</td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>19.9</td>
<td>0.0342</td>
<td>0.996</td>
<td>106</td>
</tr>
<tr>
<td>E</td>
<td>5.5</td>
<td>19.3</td>
<td>0.0287</td>
<td>0.999</td>
<td>78.8</td>
</tr>
<tr>
<td>F$^1$</td>
<td>5.5</td>
<td>25.1</td>
<td>0.0341</td>
<td>0.996</td>
<td>138</td>
</tr>
<tr>
<td>G$^1$</td>
<td>5.5</td>
<td>24.9</td>
<td>0.0389</td>
<td>0.999</td>
<td>174</td>
</tr>
<tr>
<td>H</td>
<td>5.5</td>
<td>19.4</td>
<td>0.0325</td>
<td>0.998</td>
<td>95</td>
</tr>
<tr>
<td>I</td>
<td>5</td>
<td>19.8</td>
<td>0.0309</td>
<td>0.990</td>
<td>99</td>
</tr>
</tbody>
</table>

Figure 5.6: Velocity as a function of distance from spinneret for air gap lengths of 13 (crosses, exp. A), 28 (squares, exp. B) and 49 mm (circles, exp. C). Spinning speed 100 m/min. Drawn lines are exponential fits as specified in Table 5.2
It should be noted that in all cases a rather smooth concave velocity profile is obtained in a regular drawing process throughout the air gap, unlike polyester melt spinning, where drawing is confined to a small zone. In spinning cellulose from a solution in N-methylmorpholine N-oxide also rather different velocity profiles are found. They are due to the use of a long and conditioned air gap, necessary to suppress draw resonance effects. Due to cooling of the filaments under these conditions convex rather than concave velocity profiles are found.

![Figure 5.7: Velocity as a function of distance from spinneret at a spinning speed of 80 (triangles, exp. E), 160 (open circles, exp. C), 125 (open squares, exp. D), 150 (solid circles, exp. F) and 200 m/min (solid squares, exp. G). Drawn lines are exponential fits as specified in Table 5.2](image)

From the graphs we also learn the occurrence of some die swell: the velocities measured closely below the spinneret are lower than the extrusion velocity. At the first measuring point the velocity was lowest, which is why no exact data on the die swell can be obtained. The minimum velocity, however, seems to be approximately 0.6 -0.7 of the squirting velocity (Figures 5.6-5.8). This corresponds to a die swell ratio of 1.2 to 1.3, defined as the diameter of the jet divided by the diameter of the capillary. For Newtonian liquids the die swell ratio is between 0.87 and 1.13, due to equalization of the velocity profile. Isotropic solutions and melts of flexible polymers exhibit die swell ratios of 2 or more. Die swell is related to normal stresses and particularly to the first normal stress difference. For isotropic flexible polymers this first normal stress difference is usually positive, giving die swell ratios larger than unity. Liquid crystalline polymer solutions sometimes exhibit negative first normal stress differences.
which might lead to die swell ratios smaller than unity\textsuperscript{22,23}. This has experimentally been confirmed: values between 0.7 and 1.2 were found for thermotropic polyesters\textsuperscript{24}.

![Velocity as a function of distance from spinneret for various cellulose concentrations: 9.5 (crosses, DP 2300, exp. H), 14.3 (squares, DP 800, exp. I), 17.1 % w/w (circles, DP 800, exp. C). Drawn line is exponential fit of experiment I.](image)

The die swell ratio observed here is therefore rather in line with values reported in the literature. Due to the high molecular weight of the cellulose the chain can be considered semiflexible. Therefore effects that are normally observed in flexible polymers, as well as those exhibited by a liquid crystalline phase, contribute to the flow behavior of the solution. The relatively small die swell observed here is attributed to using smooth entrance channels of the capillaries and to the filaments being drawn. In the absence of the elongational flow field in the air gap the die swell might be more considerable. Under normal spinning conditions, however, the draw ratio is still somewhat higher than that used here, viz. 5-10, probably suppressing die swell to an even greater extent.

From the graphs the distance $z_0$ at which the extrusion velocity is exceeded was determined. The values are listed in Table 5.2. The value of $z_0$ is approximately 10 % of the air gap length. The data were fitted by an exponential function, only use being made of the values measured after the die swell, hence of from $z_0$. The results are displayed in Table 5.2. It so happens that excellent agreement with experiments is observed. Using Equation 5.8 we can see that this means that the elongational viscosity is a constant throughout the air gap, despite the varying
deformation rate. This holds for all the spinning velocities of Figure 5.7, covering an even wider range of deformation rates. This means that although the deformation rate is in some other regime, no great difference in flow behavior is observed, which supports the idea of a constant elongational viscosity.

The velocity profile is independent of concentration, as is shown in Figure 5.8. Naturally, these solutions differ in elongational viscosity, although the velocity profile does not depend on the value of the elongational viscosity, but merely on the variation of elongational viscosity with deformation rate. So for the three solutions a deformation rate independent elongational viscosity is found, even though one of them was isotropic at the processing temperature in the quiescent state. Hence between the isotropic and anisotropic solutions no distinction can be made, indicating a flow induced phase transition of the isotropic solution, the clearing temperature of which was only slightly below the processing temperature (see Table 5.1). Evidence will be given in Chapter 6 giving the birefringence profiles.

Due to some uncertainty of the air gap length and to an undefined dip in the surface of the bath, at the point where it is entered by the filaments, the velocity at the bath surface $v_e$ can only be estimated roughly on the basis of the fitted velocity profiles. The values are listed in Table 5.2. In most cases the difference between the velocity at the bath surface and the take up velocity is within 10%, which is also the accuracy with which this value can be determined when using this technique. Only at higher spinning speeds is the estimated velocity at the end of the air gap significantly below the take up velocity. This means that some drawing probably takes places in the coagulation bath, which should be avoided, in that it is a possible source of yarn damage.

5.4.2 Elongational viscosity

In the previous section it was observed that the velocity of the filament in the air gap is exponentially related to the distance from the spinneret, implying a constant elongational viscosity. It was concluded that in that case the rheological force is inversely proportional to the air gap length. It was assumed that the course of the filaments is not altered by the length of the air gap and, hence, that the hydrodynamical force is a constant for all air gap lengths. The force after the bath in the case of a 14.3 % w/w cellulose solution is plotted as a function of the reciprocal air gap length at 54° and 59°C in Figure 5.9. It was indeed found that the force after the bath is inversely proportional to the air gap length, by which it was confirmed that the elongational viscosity of the solution is independent of the rate of deformation. By measuring the velocity profiles it was found that there will be some die swell and that the distance after which the squirting speed was reached was approximately 10% of the entire air gap. This correction could be incorporated into Equation 5.14. But this was not done because it was also observed that the take up velocity was not completely reached at the bath surface, which compensates in part for the error made in the air gap length due to die swell effects.
Therefore, by using Equation 5.14 the error due to the incorrect velocities is less than 10 percent. The intercept is the hydrodynamical force and from the slope the elongational viscosity can be determined.

![Graph](image)

**Figure 5.9:** Force after the coagulation bath as a function of reciprocal air gap length for a 14.3 % w/w solution, at an extrusion speed of 25.2 m/min and a spinning speed of 120 m/min. Spinning temperature 54°C (squares) and 59°C (circles)

The hydrodynamical force appears to be independent of the spinning temperature (approximately 20 cN for the entire bundle), as it should be. From Equation 5.14 the elongational viscosity was calculated to be 14.9 kPas at 54°C and 10.7 at 59°C. The temperatures indicated here are those measured in the machine. Due to viscous dissipation in the spinneret the temperature in the air gap will be higher. The decrease in temperature of the filament in the air gap was neglected. This is discussed below.

The influence of the cellulose concentration was studied at a polymer temperature of approximately 55°C. The various experiments are listed in Table 5.3. Due to pressure limitations of the equipment the number of capillaries and the spinning speed varied, which is why the force had to be rewritten in order to plot the curves in one graph. The hydrodynamical force was determined for the various experiments by applying linear regression. This value obtained was used in the reduced force, which is defined as:

\[
F_{\text{red}} = \frac{F_{\text{tot}} - F_{\text{hyd}}}{Q \ln \lambda}
\]

(5.21)
Now all the experiments can be compared in one graph, the slope of the lines being equal to the elongational viscosity. It should be noted that in Figure 5.10 all plots are linear, which implies that all solutions have a constant elongational viscosity.

Table 5.3: Elongational viscosity $\eta_e$ and hydrodynamical force ($F_{\text{hydro}}$) for the various cellulose concentrations ($c$). $T_{\text{pol}}$ is the polymer temperature measured before the spinneret, and $v_0$ and $v_e$ are the squirting and take up velocity, respectively. On the extruded samples the degree of polymerization (DP) was determined.

<table>
<thead>
<tr>
<th>$c$ % w/w</th>
<th>$T_{\text{pol}}$ ºC</th>
<th>DP</th>
<th>$n$</th>
<th>$v_0$ m/min</th>
<th>$v_e$ m/min</th>
<th>$F_{\text{hydro}}$ N</th>
<th>$\eta_e$ kPas</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.4</td>
<td>55</td>
<td>500</td>
<td>250</td>
<td>31.7</td>
<td>120</td>
<td>0.19</td>
<td>8.2</td>
<td>0.991</td>
</tr>
<tr>
<td>14.3</td>
<td>54</td>
<td>670</td>
<td>250</td>
<td>25.2</td>
<td>120</td>
<td>0.21</td>
<td>14.9</td>
<td>0.984</td>
</tr>
<tr>
<td>14.3</td>
<td>59</td>
<td>650</td>
<td>250</td>
<td>25.2</td>
<td>120</td>
<td>0.20</td>
<td>10.7</td>
<td>0.998</td>
</tr>
<tr>
<td>16.9</td>
<td>56</td>
<td>670</td>
<td>375</td>
<td>15.3</td>
<td>100</td>
<td>0.22</td>
<td>20.6</td>
<td>0.994</td>
</tr>
<tr>
<td>17.1</td>
<td>55</td>
<td>620</td>
<td>250</td>
<td>21.0</td>
<td>120</td>
<td>0.23</td>
<td>19.6</td>
<td>0.985</td>
</tr>
<tr>
<td>19.2</td>
<td>55</td>
<td>630</td>
<td>250</td>
<td>13.5</td>
<td>100</td>
<td>0.18</td>
<td>33.2</td>
<td>0.986</td>
</tr>
<tr>
<td>20.9</td>
<td>53</td>
<td>100</td>
<td>12.7</td>
<td>100</td>
<td>0</td>
<td>44.6</td>
<td>0.983</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.10: Reduced force as a function of reciprocal air gap length at a spinning temperature of 55 ºC, for 11.4, (triangles), 14.3 (squares), 16.9 (crosses), 17.1 (diamonds), 19.2 (open circles) and 20.9 % w/w (solid circles) solutions. The reduced force is defined by Equation 5.21.
From Table 5.3 we learn that for the experiments with 250 filaments the hydrodynamical force is a constant, so that the meaning of this parameter is rather reliable. The elongational viscosity is plotted as a function of concentration in Figure 5.11. Apart from the 11.4 % w/w solution the DP of the various solutions is rather constant.

![Figure 5.11: Elongational viscosity as a function of cellulose concentration at 55°C. The drawn line is the function: \( \eta_e = 4.65 \times 10^6 c^3 \), as defined in Equation 5.21.](image)

The introduction deals with the shear viscosity for solutions of rodlike molecules based on the Doi theory, which uses a reptation model. From Equation 5.1 it follows that the shear viscosity scales with number density \( n \) to the third power at equal orientation. Based on these findings it is assumed here that the same holds for the elongational viscosity. No account being taken of the density difference of solute and solvent, the elongational viscosity depends on the concentration \( c \) as:

\[
\eta_e \propto c^3 f(M, S)
\]  

(5.22)

Therefore, at equal orientation the elongational viscosity is expected to scale with the third power of the concentration. In slow shear flows the increased orientational order determines the viscosity decrease above the critical concentration for the formation of a nematic phase, according to the Doi theory. The question now is whether the order parameter in elongational flow is concentration dependent. This is probably true, but the extent thereof is unknown. In Chapter 6 it will be shown that in elongational flow a uniform orientation profile is found,
irrespective of the polymer concentration. Assume that the influence of concentration on the order parameter in elongational flow is small and that for the elongational viscosity the dependence on the concentration is the same as for the shear viscosity, the former is expected to scale with the third power of the concentration. In Figure 5.11 a line is drawn which satisfies this description, viz.:

\[ \eta_e = 4.65 \times 10^6 \times c^3 \]  \hspace{1cm} (5.23)

where \( c \) is the polymer weight fraction, and the elongational viscosity is expressed in Pas. It should be noted that excellent agreement is found with the experiment.

Hence, the rheological behavior of the cellulose solutions in elongational flow can be described by a constant elongational viscosity. The value of the elongational viscosity is high, especially when compared with that of the shear viscosity, as described in Chapter 4, where shear-thinning behavior was observed. The fact that the elongational viscosity is much higher than the shear viscosity \( \eta \) was also mentioned by Metzner and Prilutksi, who derived from Doi's theory that the ratio of the elongational and shear viscosity as a function of the order parameter \( S \) is\textsuperscript{12}:

\[ \frac{\eta_e}{\eta} = \frac{3(1+S/2)^2}{(1-S)(1+1.5S)} \]  \hspace{1cm} (5.24)

From Equation 5.24 it follows that the viscosity ratio increases with increasing orientation.

A high elongational viscosity causes high rheological tensions in the spinning line, which justifies the omission of all forces other than the rheological and external forces, as presumed in Section 5.2.1. The high tension at the end of the air gap and hence in the first stage of the coagulation bath is an important parameter in the spinning process. For, a high tension may be prohibitive of possible relaxation effects during coagulation, and it may also cause damage to the fragile filament in the initial stage of the coagulation process. Another aspect is the pressure drop across the spinneret. Although in the capillaries the shear rate is much higher than the elongational rate, the elongational flow will contribute significantly to the spinning pressure, due to the high elongational viscosity.

Temperature effects

The effects of both cooling and viscous dissipation can now be estimated, the elongational viscosity being known. The following values were used for the calculations:
\[
\begin{array}{|c|c|c|c|c|}
\hline
\rho & 1.3 \text{ kg/m}^3 & \eta & 20 \text{ kPas} & l & 30 \text{ mm} \\
\hline
\eta_s & 1.8 \times 10^{-3} \text{ Pas} & d & 75 \mu \text{m} & Q_m & 3.5 \text{ mg/ s} \\
\lambda & 0.025 \text{ W/mK} & \nu_0 & 25 \text{ m/min} & T_0 & 55^\circ \text{C} \\
c_p & 1800 \text{ J/kg/K} & \nu_1 & 150 \text{ m/min} & T & 25^\circ \text{C} \\
\hline
\end{array}
\]

with \(d\) representing the diameter of the capillaries, \(l\) the air gap length, and \(Q_m\) the mass flow of solution per capillary.

Due to the stretching \(Re_l\) is not a constant over the air gap. The values at the top and at the bottom are calculated to be 2.3 and 5.4 respectively which leads to values of \(Nu\), by applying Equation 5.17, of 0.45 and 0.53 respectively. The condition that \(Nu\) is a constant over the air gap is thus satisfied. Use being made of an average \(Nu\) of 0.5, and the values listed above, the temperature decrease calculated from Equation 5.16 is approximately 5^\circ C. On the strength of Equation 5.18 the temperature rise due to viscous dissipation is about 1^\circ C. The temperature effects, though not negligible, are not very large, which justifies the assumption of a constant temperature over the air gap.

The thermal effects due to viscous dissipation in and expansion after the spinneret have not been considered.

5.5 Conclusions

Velocity profiles were recorded in the air gap in the process of drawing extrudates of solutions of cellulose in superphosphoric acid. It was found that the velocity varies exponentially with the distance from the spinneret, indicating an elongational viscosity independent of the rate of deformation. The Doi theory only predicts a constant elongational viscosity in the nematic phase at low deformation rates. A method for the on-line determination of the elongational viscosity was developed. This was done by measuring the force as a function of air gap length. As expected for fluids with a constant elongational viscosity, the rheological force was inversely proportional to the air gap length. Due to the high rheological forces it was possible accurately to determine the elongational viscosity. The elongational viscosity could be described by a function of the third power of the cellulose concentration. In the Doi theory this dependence occurs in the equation for the shear viscosity and it is assumed that the same dependence holds for the elongational viscosity. Good agreement was found with the experiments. Data on the elongational viscosity of polymers in general are rare, and even more so for liquid crystalline polymers. Therefore, we feel that these measurements may contribute to the modelling of the dynamics of these systems.
5.6 Acknowledgment

The authors wish to thank Mr Ir. E. Thüss for his preparatory work on the optical measurements, Mr B. Koenders for carrying out some of the force measurements, Mr. G. ten Broeke for the practical support on the optical equipment, and Mr. M. Ypma and Mr. V. van Bomme for their assistance on the measurements.

5.7 References

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