Rheological characterization of low density polyethylene in planar extension using rheo-optics

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ABSTRACT

Optical techniques such as birefringence and Laser Doppler velocimetry can be used to characterize the flow behaviour of polymeric liquids in complex flow geometries. This use of optical techniques is called rheo-optics.

In the study reported here, rheo-optical measurements were carried out on a low density polyethylene (LDPE) melt in a converging rectangular slit die. Using Laser Doppler velocity measurements as input data, extensional stresses along the centre line of the converging slit were calculated using two different constitutive equations, the Wagner equation and the Phan-Thien and Tanner (PTT) equation. The calculated curves were compared with experimental stress data as obtained from birefringence experiments. It was found that calculations based on the PTT model give a better agreement with the experimental data than Wagner's equation.

The application of rheo-optical measurements has the great advantage that local information is obtained on both the stress field and the velocity field in non-homogeneous flows. However, a number of possible causes of errors are introduced that should carefully be considered. Some of the problems involved in rheo-optical experiments are discussed.

1. INTRODUCTION

Polymeric liquids often exhibit characteristic flow behaviour in which both viscous (Newtonian) and elastic components can be distinguished. Rheological characterization of such behaviour yields valuable information on the molecular chain structure of the polymeric material. Furthermore, a so-called constitutive relation can be defined which relates stresses in the liquid to deformation rates (including their history) in a given flow geometry. This means that when the velocity field in the flow geometry is measured, the stresses can be calculated, and vice versa.

The constitutive equation of a polymeric melt is one of the most important input functions for numerical simulations of polymer processing. These simulations have become increasingly important over the last few decades in predicting properties of moulded or blown polymer products (see e.g. Ref.1). Many forms have been found in the literature for the constitutive equation[2]. In the explicit expressions various parameters have to be determined, which can be obtained by performing rheometric experiments in which stresses are mechanically measured in well-defined homogeneous flow fields. The most important of these is simple shear flow. Most studies are carried out in cone-and-plate rheometers and involve performing dynamic experiments with harmonic deformations over a range of frequencies, supplemented by stress build-up experiments at a given constant shear rate and stress relaxation experiments in which a step deformation is applied and the stress decay followed[3,4]. Furthermore, stress build-up experiments in uniaxial extension can be performed[5].

With most polymeric materials, however, the flow is not homogeneous under processing conditions (e.g. film blowing, injection moulding) and it has been found that the parameters of the constitutive equation determined in one type of homogeneous flow experiment are not valid in more general flows[6]. Additional information has to be found to validate the constitutive equation under processing conditions. An elegant way of finding both stress fields and velocity fields in inhomogeneous flows is the use of optical techniques. It is now possible to obtain local information on both the stress and the velocity in an arbitrary flow geometry. In many polymeric liquids the so-called stress-optical law is valid[7], which states that the principal refractive indices in a homogeneous volume element are proportional to the principal stresses. Here the stress tensor is diagonal with respect to the frame through the optical axes. Birefringence measurements therefore yield local stresses. A prerequisite here is that the material be transparent and the flow homogeneous along the light path (two-dimensional flow). In the same flow Laser Doppler velocity measurements yield the spatial distribution of local velocities. When both stresses and velocities are obtained along a stream line, it is possible to fill in the unknown parameters of the explicit constitutive equation and thus characterize the material in the given flow.

Since the pioneering work by Han and Drexler[8,9], quite recently a large number of publications have appeared that apply optical methods to the flow of polymeric liquids, in order to characterize the material in terms of constitutive equations. These publications concern either birefringence measurements[10-12] or Laser-Doppler measurements[13-15], or a combination of both[16,17].

2. MATERIALS AND METHODS

The material used was an experimental grade low density polyethylene of DSM with a melt flow index of 0.8 g/min and a density of 0.922 g/cm^3. The granules were heated to 190°C under N_2 and compressed for 30 minutes in a ∅50mm cylinder. Then the molten polymer was driven through a flow channel with a plunger pump at constant speed. Two flow channels were used: a rectangular slit die with a cross-sectional area of 10x1mm^2 and a converging slit die with a cross-sectional area that reduced from 10x10mm^2 to 10x1.2mm^2 with a full converging angle of 60°, see Figure 1a. Optical experiments were performed with the light beam on the x-axis incident on the small side of the die. The distance between the exit of the storage cylinder and the position of the windows was 200mm for the straight slit and 60mm for the converging slit. Optical measurements were performed at different positions in the flow channels: perpendicular to the flow direction (y-direction) and along the centre line (z-direction, y=0) in the converging slit.

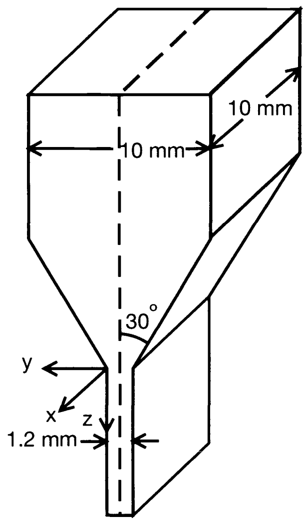

Figure 1a. Dimensions of the converging slit die.

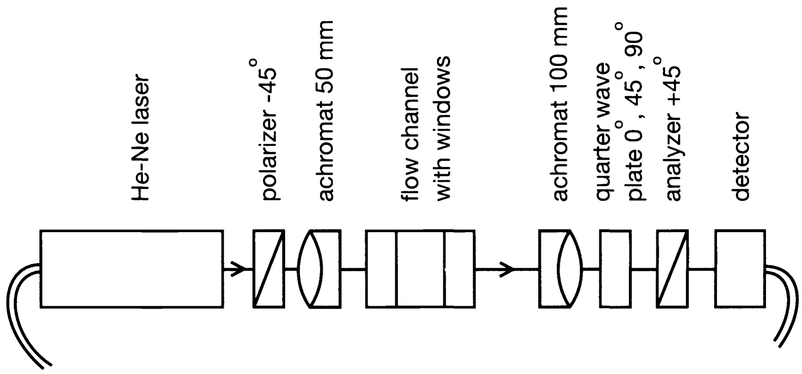

Figure 1b. Schematic drawing of the optical arrangement.

Birefringence measurements were carried out using a 2mW HeNe laser and two crossed (Glan-Thomson) polarisation prisms at an angle of 45° with respect to the flow direction. Between the flow channel and the second polarizer (analyzer) a 633nm quarter wave plate was positioned with the long axis at either 0°, 45° or 90° with respect to the flow direction. Windows in the flow cell were 6mm thick and made of synthetic fused silica (Oriel). Detection was performed with a PIN-10DP diode detector (UDT) and a 101C amplifier (UDT), and data collection was done with a DAS-8GPA ADC-card (Keithley MetraByte) in the computer and using the acquisition software program EASYEST (Keithley Asyst). To ensure a good spatial resolution the laser beam was focused in the flow cell with a 50mm achromat, yielding a waist of 60μm and a beam diameter of 90μm at the windows. The three settings of the quarter wave plate yielded three intensities: $I(0) = \frac{1}{2}I_0(1-\sin\delta\cos 2\chi)$, $I(45) = I_0\cos^2 2\chi\sin^2(\delta/2)$ and $I(90) = \frac{1}{2}I_0(1+\sin\delta\cos 2\chi)$, from which the retardance $\delta = 2\pi\Delta n d/\lambda$ and the extinction angle χ could be calculated. The extinction angle is the angle between the local optical axis and the z-direction, Δn is the birefringence (the difference between the principal refractive indices along the optical axis and perpendicular to it, but in the zy-plane), d=0.01m is the depth of the flow channel and λ=633nm the wavelength of the HeNe-laser. The shear stress σ_{12} and the first normal stress difference N_1 can now be calculated from[7]: $\sigma_{12} = (\Delta n/2C)\sin 2\chi$ and $N_1 = (\Delta n/C)\cos 2\chi$, where C is the stress-optical coefficient.

Laser Doppler velocity measurements were carried out with the 488nm line of a Lexel 85 Argon-ion laser operating at 1W. The optical train was built up by Dantec modular optics, consisting of two quarter wave plates, a beam waist adjuster, a polarizing beam splitter prism, a Bragg cell in one of the two beams introducing a 40 MHz optical frequency shift, a beam expander and a 310mm focal lens. The half angle between the two beams (in air) was 5.5° and the probe volume was approximately $\phi 80\mu m$ x 0.8mm. The fringe spacing was 2.5 μm. The system operated in the back-scattering geometry and detection was performed with a RCA 4526 photomultiplier tube. The signal was electronically shifted down to 10 kHz and fed into a Dantec 57N10 Burst Spectrum Analyser. Data were collected in a PC and the average velocity was calculated from the frequency distribution. Only velocities in the z-direction were measured.

Titanium oxide tracer particles of $10\mu m$ diameter were introduced into the polymeric melt at 0.1% by weight through cryogenic milling of the polyethylene granules and vigorous shaking of both components before heating up. Point-by-point measurements of both birefringence and velocity were performed by using translational stages in the y- and z-directions.

Rheological characterization in simple shear was performed with a Rheometrics 800 mechanical spectrometer in the plate-plate geometry. Dynamic measurements were carried out in the frequency range between 0.05 and 500 s^{-1} at 190°C. Furthermore, stress build-up experiments were carried out at various shear rates. Uniaxial extensional stress build-up experiments were performed for various strain rates on a Göttfert Rheostrain. For experimental details see[3].

3. THEORY

Constitutive equations of both the integral and differential type were used. The equation of the integral type was Wagner's modification of the equation proposed by Kaye and by Bernstein, Kearsley and Zapas[2,18], defined as:

$$\sigma(t)=\int_{-\infty}^{t} m(t-t')h(t,t')C^{-1}_{t}(t')dt' \tag{1}$$

where σ(t) is the time-dependent local stress tensor and m(t-t') the memory function, defined as:

$$m(t-t')=\sum_{i=1}^{N}\frac{G_i(\tau_i)}{\tau_i}\exp\left(\frac{-(t-t')}{\tau_i}\right) \tag{2}$$

where G_i and τ_i define the discrete relaxation spectrum, C^{-1}_t is the Finger tensor and h(t,t') the non-linearity function. Here we follow the form proposed by Wagner et al.[19]:

$$h(t,t')=a\exp(-n_1\sqrt{J-3})+(1-a)\exp(-n_2\sqrt{J-3}) \tag{3}$$

where J= αI+(1-α)II, I being the first and II the second invariant of the Finger tensor and a, n_1, n_2 and α are fit parameters. The relaxation spectrum was determined from the dynamic mechanical measurements, while the parameters in the non-linearity function were found by performing stress build-up experiments both in shear and in extension.

Along the centre line of the converging slit pure planar extension takes place. When the velocity field along the centre line is known, Eq.(1) can be rewritten as:

$$\sigma_e(z)=\sigma_{11}-\sigma_{22}=\int_{-\infty}^{z} m(z-z')h(z,z')\left[\frac{v(z)^2}{v(z')^2}-\frac{v(z')^2}{v(z)^2}\right]\frac{dz'}{v(z')} \tag{4}$$

where z is the positional coordinate along the centre line at which the stress has to be calculated, z' the upstream coordinate with respect to which the integration is performed and v the velocity. We note here that for planar extension the first and second invariants of the Finger tensor are equivalent, I=II, so that the parameter α does not enter Eq.(4).

As a constitutive equation in differential form we used the one proposed by Phan-Thien and Tanner[2,20]:

$$\tau_i\left(\frac{D\sigma_i}{Dt}-\nabla v.\sigma_i-\sigma_i.\nabla v^T+\xi(D.\sigma+\sigma.D)\right)+\exp\left(\frac{\epsilon}{G_i}tr(\sigma_i)\right)\sigma_i=2G_i\tau_i D \tag{5}$$

where σ_i is the stress belonging to the i-th relaxation time, $\mathbf{D}$ is the deformation rate tensor, $tr(\sigma_i)$ is the trace of the stress tensor, ξ a slip parameter and ϵ the non-linearity parameter. The total stress tensor σ is the sum over all individual σ_i's. The relaxation spectrum (G_i and τ_i) was determined from the dynamic mechanical measurements; the slip parameter and the non-linearity parameter were determined using the stress build-up experiments in shear and extension.

We have now seen that for both constitutive equations velocities along the z-axis are necessary input parameters, apart from the unknown fit parameters in the memory function and in the non-linearity function, Eqs.(2) and (3). In Eq.(4) the velocities v(z) are explicitly listed, while in Eq.(5) they are found in the deformation rate tensor **D** and as a gradient ∇v. The extensional stresses σ_e can now be calculated. On the other hand, one can imagine that the unknown parameters in m(t-t') and h(t,t') can be found when both σ_e(z) and v(z) are measured.

The velocities that were used in the calculations were fits of experimental data along the centre line according to v(z) = 1/(a+bz), where a and b are fit parameters. In the straight part of the slit the velocities were assumed to be constant. Stresses were calculated using both models. Furthermore, calculations were performed using the Wagner model and assuming linear visco-elastic behaviour, i.e. h(t,t')=1. It is important to realise here that at the centre line planar extension occurs, which differs from shear or uniaxial extension. The influence of the various deformation symmetries on the non-linearity function are discussed in detail by Wagner and Demarmels[21].

4. RESULTS AND DISCUSSION

The frequency dependence of the dynamic modulus as obtained from dynamic mechanical measurements is shown in Figure 2, together with stationary shear stresses from steady-state shear and capillary measurements as a function of shear rate. The validity of the Cox-Merz relation[22] $G_d(\omega)=\sigma_{12}(\dot\gamma)$ for $\omega=\dot\gamma$ is nicely illustrated here. A very commonly used fit through the dynamic measurements is given by the so-called Carreau-Yasuda equation[23]:

$$\eta=\eta_0[1+(\lambda\omega)^a]^{(n-1)/a} \tag{6}$$

where η_0 is the Newtonian viscosity and λ, a and n are fit parameters. This simple equation is introduced here for some convenient calculations further on.
From the dynamic measurements, together with stress build-up and stress relaxation experiments at 190°C, the unknown parameters in the two constitutive equation are extracted. The various values are listed in Table 1.

In order to be able to calculate stresses from birefringence measurements, the stress-optical coefficient (SOC) C should be known. Values for low density polyethylene reported in the literature vary roughly between 1.1 and 2.1 x 10^{-9}/Pa[24-26], depending on the material used and the temperature. Since we were not able to measure the SOC ourselves, we used the following method to obtain a reasonable value:
Birefringence measurements were carried out in the straight slit at throughputs of 6.5 and 15 mm^3/s. Assuming fully developed flow and no slip at the wall we calculated the velocity profile and the shear stress using the Carreau-Yasuda equation, Eq.(6), and adapted the SOC to fit the calculated shear stress to the measured value. The shear stress as a function of position y for a throughput of 6.5 mm^3/s is given in figure 3. The calculated SOCs for throughputs of 6.5 and 15 mm^3/s were 1.66 and 1.50 x 10^{-9}/Pa respectively. In the following we use the average value of 1.58 x 10^{-9}/Pa.

The measured velocities as a function of the lateral position y in the straight part of the converging slit (at z=8mm below the centre where the converging part ends), for a throughput of 15 mm^3/s, show the usual parabolic profile, see Figure 4. From the statistical frequency distribution an average error in the velocity measurements of about 15% was found. This error is also reflected in the scatter of the data. The continuous curve was calculated with the help of Eq.(6), using the same parameters as found above (Table 1). Good agreement between experiment and calculation was observed. Here we see that the velocity profile is already that of a fully developed shear flow, while the stresses due to the contraction are not yet fully relaxed (as will be seen below). We conclude that the velocity profile is less sensitive to the visco-elastic properties of the polymeric liquid than the stress field.

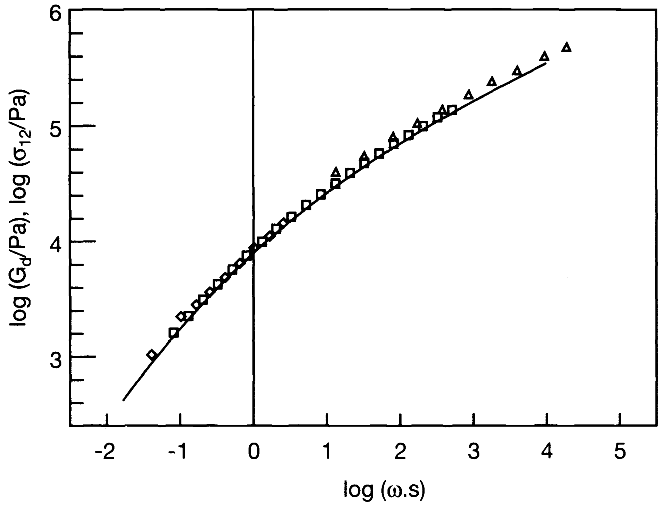

Figure 2. Dynamic modulus G_d as a function of frequency for LDPE at 190°C (□), together with the steady state shear stress from cone-and-plate (◇) and capillary experiments (Δ). The continuous curve is a fit according to Eq.(6).

G_i (Pa)	τ_i (s)
2.72e5	7.7e-5
1.05e5	7.05e-4
6.02e4	5.13e-3
3.16e4	3.59e-2
1.37e4	2.43e-1
4.52e3	1.58
1.01e3	1.02e1
1.46e2	7.13e1

Carreau-Yasuda	η_0=3.9e4Pas,a=0.41,n=0.31,λ=2.58s
Wagner	a=0.96,n_1=0.25,n_2=0.04,α=0.06
PTT	ξ=0.15,ϵ=0.05

Table 1. Experimentally derived fit parameters for the constitutive equations, Eq.(1)-(3), (5) and (6).

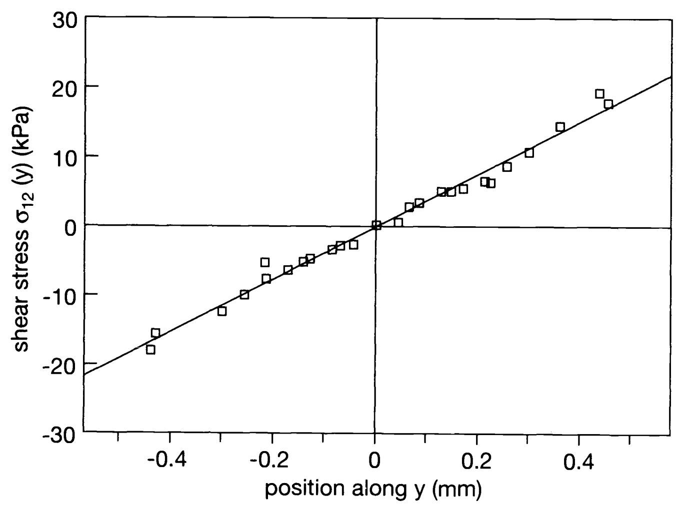

Figure 3. Shear stress as a function of lateral position y in the straight slit at a throughput of 6.5 mm³/s.

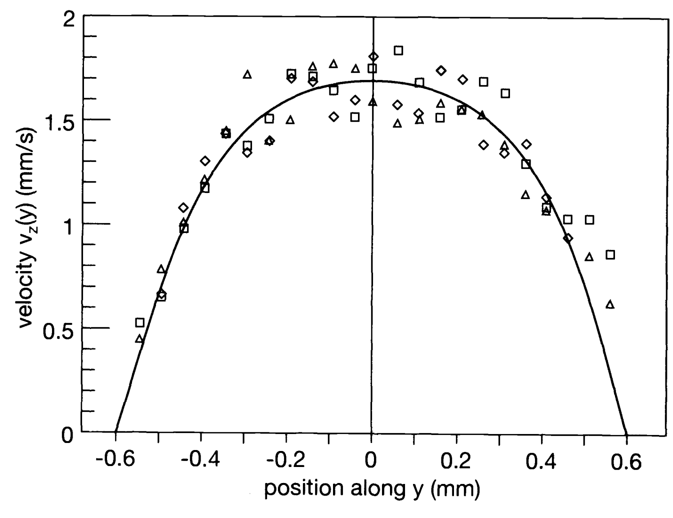

Figure 4. Velocity profile in the straight part of the converging slit at a throughput of 15 mm³/s. Experimental values (Δ, ◇, □) and a fit using the parameters of the Carreau-Yasuda equation, Eq.(6) (see text).

The velocities along the centre line in the converging slit (y=0), at various throughputs, are shown in Figure 5, together with the fitted curves following 1/v(z) ~ z. In the converging part (-7.6<z<0mm) the velocity increases to a maximum value, while staying more or less constant in the straight part (z>0mm). In spite of the large scatter of the data, it can be seen that the change from the converging to the straight part is more gradual than the fitted curves suggest. Furthermore, in some cases an overshoot is observed, which has also been reported by others[13,14].

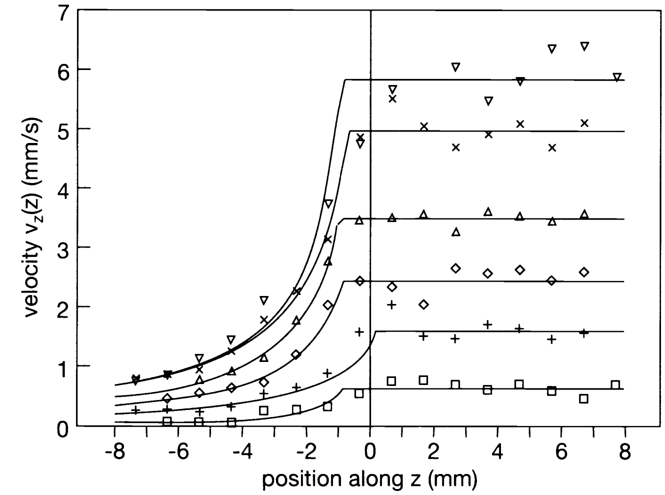

Figure 5. Velocities along the centre line of the converging slit at various throughputs: 6.5 (□), 15 (+), 23 (◇), 31 (Δ), 43 (x) and 56 (∇) mm³/s, together with fits according to 1/v=a+bz in the converging part and v=constant in the straight part.

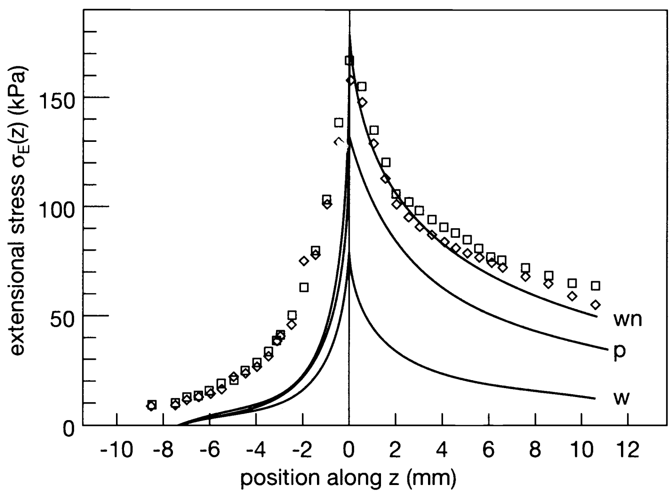

Figure 6. Extensional stresses along the centre line of the converging slit at a throughput of 55 mm³/s. Experimental values (□,Δ) and values calculated using the Phan-Thien and Tanner model (p), the Wagner model (w) and the Wagner model with non-linearity function h=1 (wn).

Using the fitted curves of the velocities we calculated the stresses by means of the two constitutive equations at three different throughputs. Figure 6 gives the measured extensional stresses for a throughput of 55 mm³/s, obtained from birefringence measurements and by applying the SOC as determined according to the procedure given above, together with the calculated stresses from both constitutive models. As a third option the integral equation was applied with h(t,t')=1 in Eq.(4). We observed the remarkable fact that the integral equation based on the assumption of linear behaviour, gives a much better fit than its non-linear counterpart. Comparing the non-linear integral equation, however, with the Phan-Thien-Tanner model, we must conclude that the latter gives a better agreement with the experimental data. We even found that by varying the SOC and subtracting a constant stress it was possible to obtain excellent agreement between the experimental and calculated stresses using the PTT model. Subtraction of a certain value seems to be justified since an additional stress is introduced by both the shear at the windows (σ_{13}) and by residual extensional stresses caused by the contraction from the storage cylinder to the flow cell. This value will, however, not be constant along the centre line z. Furthermore, the assumption of a two-dimensional flow becomes increasingly incorrect further upstream in the converging part. The consequence of a three-dimensional flow in the converging part is that the average birefringence is taken along the light path, which means that the measured value is increased due to the effect of shear at the front and back windows. This effect also causes the stresses to be higher further upstream from z=0 in the converging part. Table 2 gives the maximum values of the (average) measured stresses, together with calculated ones for three different throughputs.

	exp	PTT	Wagner	Wagner (h=1)
6.5mm³/s	26	31	20	37
31mm³/s	105	79	50	95
55mm³/s	163	133	79	178

Table 2. Experimental and calculated values (in kPa) of the maximal planar extensional stress in the converging slit.

In the application of the non-linear Wagner equation, only fit parameters from shear experiments were used. The parameter

α in Eq.(3), that is found from uniaxial extensional stress build-up data, vanishes for planar extension. On the other hand, the parameter ϵ in the PTT equation, which is also obtained from extension data, is small and does not influence the results to a large extent.
Our general conclusions that the PTT model gives a better result in planar extension than the Wagner model and, furthermore, that in the latter model omission of the non-linearity function improves the agreement with experiment, are in accordance with findings by others[6,17].

5. SOURCES OF ERROR

The great advantage of the use of rheo-optical measurements in addition to the conventional rheometric experiments is that local information is obtained on both the stress fields and the velocity fields in non-homogeneous flows. However, the above-mentioned experiments show that a number of possible causes of errors are introduced, which should be carefully considered. Here we mention some of them, without going into great detail:

1. The stress-optical coefficient is a critical parameter in the interpretation of the results and should be carefully measured, either directly in a rheometric apparatus equipped with optics[7] or indirectly following the route that we have used. Literature values may easily yield errors higher than 20%.
2. Since a fitted curve through the velocity data is used as input for the calculations of stresses, the accuracy of the fit will determine the success of the results. This means that care should be taken to improve the velocity measurements. One should be aware that the birefringence and velocity measurements are performed in separate experiments and therefore under possibly different circumstances.
3. In the birefringence experiments, the value of the birefringence is averaged over the whole beam volume. Therefore a strictly two-dimensional flow has to be assumed, and shear stresses caused by shear at the windows are neglected. To quantify this effect one should perform velocity measurements in the x-direction or study the influence of the width-depth ratio of the flow channel on the results. However, in the latter case the beam diameter cannot be kept the same. Furthermore, both for birefringence and velocity measurements, due to the finite volume size it is not possible to measure closer to the walls of the flow cell than approximately half the beam diameter.
4. Due to the inhomogeneous stress distribution, small density variations may occur, causing the light beam to deflect. At high stresses this effect may be considerable, making it impossible to interprete the birefringence results.
5. The stiffness of the mechanical part of the set-up is critical in achieving sufficient spatial resolution. Small backlashes in the translation stages or vibrations due to the drive motor may cause errors in obtaining accurate and reproducible positions in the flow cell.
6. Since in polymer melts long relaxation times can occur, the deformation history of the melt prior to the flow cell may not be negligible. In fact, non-zero stresses in the converging slit for $z<7.6$mm may in part be caused by the contraction 60mm upwards from the 50mm diameter storage cylinder to the $10x10mm^2$ slit channel.
7. In highly viscous fluids mixing of tracer particles may be a problem. One should verify the degree of dispersion of tracer particles after the mixing procedure. Furthermore, it should be checked that the tracer particles do not affect the rheological properties of the polymer melt.

A number of these problems are the subject of our current research.

6. CONCLUSIONS

Using rheo-optics it is possible to characterize polymeric fluids in flows of complex geometry. Birefringence measurements yield local shear stresses and first normal stress differences (or extensional stresses), while Laser-Doppler measurements yield the three-dimensional velocity field.

By calculating the planar extensional stress in a converging slit die with the help of velocity measurements, it was found that when the constitutive equation according to Phan-Thien and Tanner is used a better agreement with the experimental data is obtained than with Wagner's integral equation. The best results, however, are obtained by simply omitting the non-linearity function in the integral equation.

Rheo-optical measurements yield valuable information additional to the information provided by traditional rheometric measurements, especially in studying complex flows. A number of sources of experimental error have been identified and refining these is the subject of further work.

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