Viscosity of Radial Hydrogenated Styrene-Isoprene and Block Ethylene-Propylene Copolymer Solutions Under Conditions of High Shear Rate and Small Channel Size

by

David Erickson

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science.
Graduate Department of Mechanical & Industrial Engineering
University of Toronto

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Abstract

In many lubrication applications, polymer containing lubricating oils are subject to conditions of high shear rates through small clearance channels. The objectives of this study are to design and construct two viscometers, each capable of independently examining one of these conditions, and then to use them to characterize the high shear rate and channel size dependent viscosity of two polymer additives, a radial hydrogenated styrene-isoprene copolymer and an A-B-A type block ethylene-propylene copolymer.

During the capillary viscometer high shear rate tests the styrene-isoprene additive exhibited significant shear thinning, while the more highly concentrated ethylene-propylene solutions showed a region of shear thickening. Using the specially designed microchannel viscometer a viscosity dependence on channel size was observed for all solutions. In the upper shear rate range (>500 1/s) the smaller channels exhibited a lower
viscosity while in the lower shear rate range all solutions exhibited a significant increase in viscosity.
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Chapter 1 – Introduction

1.1 Motivation

The viscosity of an oil is the key parameter which affects its performance as a lubricant. As a method of improving high temperature performance, all modern lubricants contain long chain polymer additives as rheology modifiers. In many industrial situations, these lubricating oils are subject to conditions of extremely high rates of shear through very small clearance channels. It is critical then to the evaluation of new VI (Viscosity Index) improving polymer additives that their performance under both these conditions is well understood. While the importance of characterizing the shear thinning or thickening behaviour associated with conditions of high shear rate is well developed, much less attention is paid to the channel size effects during the polymer design phase.

The purpose of this research was to design and construct two viscometers capable of independently characterizing the effects of high shear rate and channel size on the viscosity of a polymer containing lubricant. The viscometers were then used to study the behaviour of two VI additives, namely a radial hydrogenated styrene-isoprene copolymer (Imperial oil product, trade name Shellvis 200c) and a ethylene-propylene block copolymer (Imperial oil product, trade name Paratone 8941) in a light hydrocarbon base oil (Imperial oil product, trade name EHC 45).
1.2 Overview of High Shear Rate Characterization

High shear rate measurements require that the test fluid and the measurement surface move at high relative velocities to one another. To accomplish this while avoiding difficulties associated with traditional rotational viscometers, a specially designed capillary viscometer was built. The device consists of a high pressure (5000 PSI, 35 MPA) precision pump that delivers the test fluid at a constant flow rate to a capillary tube 115 microns in diameter. The measured pressure drop and flow rate can then be combined with the capillary dimensions to deduce the viscosity from fundamental flow relationships. Using the specially designed capillary viscometer, the viscosity of the additives has been measured over a range of wall shear rates from $10^4$ 1/s to $10^6$ 1/s at mass concentrations ranging from 0 to 2.0% for the styrene-isoprene additive and 0 to 1.5% for the ethylene-propylene polymer.

A consequence of the high shear rates and shear stresses in the fluid during these measurements is that a significant amount of viscous heating may occur. By coupling the equations for continuity, momentum and energy, a viscous heating model was developed which showed that significant temperature and viscosity gradients exist within the capillary. Using this model these effects were subtracted from the results thereby reducing the experimental data to viscosity values at a common pressure and temperature for comparison. As part of the data correction procedure further experiments were conducted to characterize the viscosity dependence on temperature of the polymer solutions.
As is detailed in chapter 3, over the range of shear rates examined the styrene-isoprene solutions exhibited typical shear thinning behaviour. In addition to shear thinning at the higher shear rates, a shear thickening region was observed in the more concentrated ethylene-propylene solutions. As the polymer concentration increased, the degree of shear thickening was shown to be more severe and the critical region was observed at lower shear rates. Several potential mechanisms for the apparent shear thickening behaviour are discussed and evaluated.

1.3 Overview of Channel Size Effect Characterization

The spatial clearances in traditional viscometers are much greater than the characteristic size of the long chain polymers. As a result, the bulk viscosity is measured and the effects of channel size cannot be determined. To investigate this effect here a specialized microchannel viscometer has been designed and built. The main component of the viscometer is the parallel plate microchannel array, which consists of a series of slit channels each with the same geometric features (length, width, and most importantly height). As in the previous case, knowledge of the channel geometry is combined with pressure drop/flow rate measurements to deduce the effective viscosity of the test fluid.

Using this microchannel viscometer, the dimension sensitive flow properties of the same two polymer additives were investigated by examining the effective viscosity over a range of shear rates in a series of slit microchannels varying in height from 4.5 to 11.5 µm. As in the previous case, concentrations ranging from 0 to 1.5% by mass were examined, over a much lower shear rate however, from 50 l/s to 2000 l/s.
As is discussed in Chapter 4, all solutions exhibited a significant viscosity dependence on channel size. In the range of higher shear rates it was observed that generally the smaller channels exhibited a lower apparent viscosity, which was attributed to the presence shear induced concentration gradients near the channel wall. As shear rate decreased however, all solutions exhibited a significant increase in viscosity. Generally, this observed increase in viscosity is more dramatic in the smaller channels and often led to a cross over point, below which the smaller channels exhibited a higher viscosity. Possible causes of these behaviours are investigated.
Chapter 2 - Polymer Additives

2.1 Some Previous Investigations

As mentioned above two VI (Viscosity Index) improving polymer additives are of interest to this study; a radial hydrogenated styrene-isoprene copolymer and an A-B-A block type ethylene-propylene copolymer (both supplied by Imperial Oil). The rheology of block styrene-isoprene copolymers has been investigated in various forms by a number of authors [1-3], however a literature review shows that little work has been done on the radial form. The ethylene-propylene copolymer used here is comprised of approximately 60% ethylene units concentrated in the middle of the chain with the propylene units forming the outer edges (the polymer is manufactured in a tubular reactor which allows the position of the ethylene units along the chain to be controlled). At low temperatures the ethylene segments tend to associate, reducing the overall hydrodynamic volume of the polymer and thus the low temperature viscosity of the solution. This gives it a cold cranking viscosity advantage over more amorphous (non-associating) polymers. The rheology of similar ethylene-propylene block copolymers has been studied by a number of investigators [4-6]. For example Han and Rao [6] measured the high shear rate behaviour of such a polymer at 240°C, while Kucks and Ou-Yang [5] studied its aggregation in different hydrocarbon solvents. Note that all these studies have concentrated on either high temperature or low shear rate bulk viscosity measurements.
2.2 Polymer and Solution Characterization

2.2.1 Molecular Weight Analysis

The molecular weight distribution of the two polymers was determined using a gel permeation chromatography technique which yielded \( M_w = 497,000 \) and \( M_n = 472,000 \) for the styrene-isoprene copolymer and \( M_w = 235,000 \) and \( M_n = 205,000 \) for the ethylene-propylene copolymer. The analyses were carried out in Professor Manners' laboratory in the department of Chemistry, University of Toronto by using a Waters 2690 separation unit and a Viscotek T90A dual light scattering and viscometry detector.

2.2.2 Solution Characterization

An important parameter in the characterization of polymer solutions is the critical concentration, \( c^* \), marking the boundary between a dilute and semi-dilute (where significant coil overlap occurs) solution. Eq. (2.1) represents the criterion for determining this critical concentration [7],

\[
c^* \eta = 1,
\]

where \( \eta \) is the intrinsic viscosity. Using this criterion and the intrinsic viscosities of similar polymer solutions from Filiatrault and Delmas [8], a critical concentration of approximately 0.5% was estimated for the ethylene-propylene polymer, which is of the order quoted in Kucks et. al. [5]. Therefore the higher concentrations of this polymer examined in this study are likely to enter the semi-dilute range and thus be under conditions of significant coil overlap. The intrinsic viscosity of the styrene-isoprene
copolymers in similar solutions was not known, however the order of magnitude estimates from ref. [9] suggest that the solutions examined here lie within the dilute range.

2.2.3 Solution Preparation

For all experiments, solution preparation was done by dissolving the polymers in the base oil by heating the solution to over 100°C and intermittently stirring over the course of 48 hrs. At this temperature evaporative losses of the base oil were found to be very small, less than 0.1%, and did not affect the final solution concentration. Solution preparation was carried out in a fume hood.
Chapter 3 – High Shear Rate Characterization

As mentioned above, most base oils exhibit Newtonian behaviour, i.e., the viscosity of the fluid is independent of the rate at which it is being sheared. When long-chain polymers are added as rheology modifiers to improve high temperature performance, the polymer solutions tend to exhibit non-Newtonian behaviour, i.e., the viscosity of the fluid is not dependent on the rate at which it is being sheared. At high shear rates, which can be of the order of $10^6$ 1/s in many industrial lubrication applications [10,11], a temporary decrease in the viscosity is observed due to the alignment of these polymer molecules with the shear rate gradient [12]. While this high shear rate performance is important in determining, for example, cranking resistance at startup, other applications such as pumpability of crankcase oil have been found to be more closely related to low shear rate performance [13]. Thus, an understanding of the viscosity performance of the polymer solution over a range of shear rates is critical in determining the true effectiveness of a particular additive.

Typically, fluid viscosity is measured using either a rotational or capillary viscometer. Rotational viscometers have the advantage of being geometrically similar to many of the high shear rate regions of typical engines and are able to study the time dependent phenomena by applying a constant shear rate over very long periods of time. However they are generally more complex in design and construction than their capillary counterparts [14]. Additionally they have difficulty attaining the high shear rate levels required for this study.
To overcome the difficulties, capillary systems have been used in a number of recent papers to study the non-Newtonian behaviour of different fluids. For example, Rein and Alexander [13], and Hewson and Carey [14] have both used similar systems to study high shear rate behaviour of engine oils, while Davies et. al. [15] studied the viscous behaviour of a New Zealand coal at temperatures above 680K. Such systems have the advantage of being much simpler in design, construction and operation than rotational devices. Additionally the flow regime is generally confined to very low Reynolds number, well below those associated with a transition to turbulence. Generally the geometric differences between capillary and rotational systems are considered unimportant when the results are to be used for characterizing oils.

The combination of high shear stresses and shear rates results in significant viscous heating and thus a temperature rise in the test fluid. Capillary viscometers are inherently less sensitive to this effect than rotational viscometers, where the same sample is sheared continuously throughout the entire measurement, since the sample is only heated for the length of time it takes to pass through the capillary tube [16]. Since the magnitude of this effect becomes more significant at higher shear rates and an increase in temperature generally results in a decrease in viscosity, it is easy to see how viscous heating can be misinterpreted as non-Newtonian shear thinning behaviour. In addition to a temperature-viscosity relation some fluids are known to exhibit a pressure dependent viscosity. Thus a change in viscosity would be expected as the pressure drops along the length of the capillary. In addition to the above, other effects such as kinetic energy of the exiting stream, entrance and exit zones, and viscoelastic effects are inherent in any capillary
viscometer measurements. Further details on these limitations are given by Appeldoorn and Devore [17].

As outlined in section 1.2, the purpose of this half of the study is to investigate the high shear rate behaviour of solutions of the two polymer additives of interest. At mass concentrations ranging from 0 to 2.0% for the styrene-isoprene additive and 0 to 1.5% for the ethylene-propylene polymer, the viscosity has been measured at wall shear rates ranging from $10^4$ 1/s to $10^6$ 1/s, using a capillary viscometer. Details regarding the design and construction of the capillary viscometer and the experimental procedure are presented in section 3.1 and the results of the high shear rate tests are discussed in section 3.4. To correct for the effects of viscous heating and pressure dependent viscosity, a data correction procedure has been developed which required a detailed numerical analysis of capillary flow as well as further experiments to characterize the viscosity dependence on temperature for the solutions of interest. Details of the correction procedure and the results of the temperature-viscosity experiments are given in section 3.2. The overall effectiveness of the procedure is evaluated in section 3.3. A copy of the MATLAB code used to perform the data analysis is given in Appendix A.

3.1 Experimental

3.1.1 Apparatus

Figure 3.1 is a diagram of the constant flow rate capillary viscometer designed for and used in this study. As can be seen the principal elements in the apparatus are the
precision pump, pressure and temperature instrumentation, heat exchanger and water bath, and the stainless steel capillary.

Generally capillary viscometers can be divided into two classifications; constant flow rate, and constant pressure. Since shear rate is uniquely determined by the geometric properties of the capillary and the volumetric flow rate, constant flow rate designs have the advantage of being able to repeat tests for different solutions at exactly the same shear rate, facilitating the accurate comparison of different polymer solutions at a given shear rate. Because of these favourable qualities, a constant flow rate this device was built for this study using a Ruska Instruments high-pressure precision piston pump, which had a flow range of between 2.5 to 560 ml/hr to an accuracy of ± 0.02 ml/hr at pressures as high as 70 MPA. The use of a piston type is preferred over a gear type positive displacement pump, which may preshear the fluid prior to reaching the capillary, resulting in immeasurable amount of permanent viscosity loss [14].

A significant advantage of a constant pressure based system however, is in its ability to control the system pressure. Plugging of the capillary in a constant flow rate system can result in a rapid pressure rise leading to instrumentation damage and operator safety concerns. To limit this problem, pressure triggered circuit breakers, which cut power to the pump if the pressure rose above a pre-set safety limit, were used.

The pressures observed in this study ranged from 0.5 MPA to 40 MPA. Thus to ensure suitable accuracy over the range of test conditions three pressure transducers, of varying
range and accuracy, were used. The low pressure transducer was used exclusively for the low shear rate, temperature-viscosity experiments and had a range of 0 to 1.8 MPA. The majority of the shear rate-viscosity measurements were made using the medium pressure transducer that had a range of 0 to 20 MPA, which had a much higher resolution and accuracy than the 0 to 70 MPA high pressure transducer used to make measurements above 20 MPA. All instruments were calibrated with a dead weight tester, which had a maximum error of ± 0.5%.

The capillary tubes used to make the shear viscosity measurements were all 115 µm in diameter and varied from 10.8 mm to 12.9 mm in length, while the temperature viscosity measurements were made using a 235 µm capillary, 51.2 mm long. The diameter of the capillary was determined by experimental calibration with the Newtonian test oil of known viscosity and verified by direct measurement under a microscope. Though both measurements were in general agreement, the direct measurement revealed that the capillary end had a slightly elliptical shape. The elliptical deformity was attributed to the cutting process and was assumed to be confined to the region very near the end of the capillary. Therefore to simplify the data analysis a perfectly circular cross section was assumed.

In general shorter capillaries are preferred to longer ones to reduce the required pressure drop at a given flow rate. The low Reynolds number regime observed in this study, Re<45, allowed for such short tubes to be used while keeping the entrance region to less than 2% of the total length. The tubes were constructed by successively fitting larger ID
tubing around the smaller capillary and bonding them using an epoxy, until the final 1/16" nominal OD tube could be attached to the apparatus using swagelok type fittings. Such a mounting allowed for quick and easy removal of the capillary for cleaning or replacement.

3.1.2 Experimental Procedure

The viscometer is filled with the test solution by drawing in the fluid through the bleed valve on the precision pump. Care was taken to ensure that the pump head was clean prior to filling in order to minimize contamination. Once filled, the tubing system was flushed with the test solution and the air purged through the bleed valve. The heat exchanger was not required for the shear-viscosity measurements and thus was removed from the apparatus shown in Figure 3.1 for those tests.

The shear-viscosity tests were conducted at 9 different shear rates ranging from $10^4$ 1/s to $10^6$ 1/s. Typically measurements were made by fixing the flow rate of the pump to the desired setting and allowing the system to come to a steady state, which was assumed to have been achieved once the pressure stopped fluctuating. At this point a flow rate measurement was made through mass collection at the capillary exit, and the capillary wall temperature was recorded using a type k thermocouple. All measurements were repeated a minimum of three times for each of the test solutions.

Temperature-viscosity measurements were made using a similar technique with only a few small changes. All measurements were made at the same relatively low wall shear
rate, $1.2 \times 10^4$ l/s, to eliminate the possibility that the non-Newtonian behaviour of the solution may affect the results and to ensure that viscous heating is minimized. Temperature of the fluid was varied by adjusting the temperature of the water bath in which the heat exchanger was placed and measured with the type k thermocouple immersed in the exit stream. Again flow rate was measured through mass collection at the capillary exit and all measurements were repeated three times.

3.2 Data Analysis

While it is relatively easy to design and build a capillary viscometer where measurements of the pressure drop and volume flow rate can be made with high accuracy, secondary flow effects can make it difficult to extract meaningful results. Ideally one would like to account for these effects in such a way that the experimental data can be reduced to viscosity results at a common temperature and pressure for comparison. Previous studies have accomplished this by either experimental calibration [13,17] or a mathematical solution to the Navier-Stokes equations [15-16, 18-20]. The former generally requires that extensive experimental measurements be made for several different Newtonian fluids over a range of conditions and the results compared with previously known viscosity values to produce a series of calibration curves [17]. Mathematical techniques however do not require such extensive background data and can be applied directly to experimental results.

In all cases the mathematical treatment involves a simultaneous solution of the equations for continuity, momentum and energy. Some analytical solutions have been proposed,
for example that by Kearsley [18], however the assumptions required to reduce the equations to a solvable form limit their widespread applicability. More popular in modern studies are numerical solutions to a more exact form of the equations. Gerrard et. al. [16, 19] developed a two dimensional solution using a finite difference scheme, which considered both temperature and pressure effects on the viscosity of a Newtonian fluid, for the cases of an adiabatic and isothermal capillary wall. Their results showed that significant temperature gradients exist within the channel resulting in large changes in the fluid viscosity. Duda et. al. [20] further extended the model to cases of higher Reynolds number and used it to predict the shear behaviour of non-Newtonian fluid solutions.

3.2.1 Governing Equations

By applying common scaling/symmetry arguments related to the large L/D ratio of the capillary [16, 20], the governing equations (in dimensional form) reduce to Eq. (3.1a) (continuity), Eq. (3.1b) (momentum) and Eq. (3.1c) (energy),

\[
\begin{align*}
\frac{1}{r} \frac{\partial}{\partial r} (rv_r) + \frac{\partial v_z}{\partial z} &= 0, \quad (3.1a) \\
\frac{\partial P}{\partial z} - \frac{1}{r} \frac{\partial}{\partial r} (\tau_{rz}) &= 0, \quad (3.1b) \\
\rho c_p \left( v_z \frac{\partial T}{\partial z} + v_r \frac{\partial T}{\partial r} \right) - k \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) &= \tau_{rz} \left( \frac{\partial v_z}{\partial r} \right). \quad (3.1c)
\end{align*}
\]

where \(v_r\) and \(v_z\) are the components of velocity in the radial and axial directions, \(\tau_{rz}\) is the shear stress, \(\rho\) is the density, \(k\) is the thermal conductivity and \(c_p\) is the specific heat. Specifically these scaling/symmetry arguments are;
1. Flow symmetry exists about the capillary axis and that the angular component of velocity is negligible.

2. Radial pressure gradients are negligible when compared with axial the axial gradient.

3. Axial heat conduction is small compared to radial conduction.

In addition to the dimensional scaling assumptions, this form of the equations assumes that the Reynolds number is sufficiently low such that the flow remains laminar and the entrance region is small, and that density, thermal conductivity and specific heat are all constant. In eliminating the momentum convection terms in Eq. (3.1b) it has been assumed that the flow is sufficiently unidirectional such that momentum diffusion dominates. Though this assumption is likely valid for this geometry it is important still to note that in-channel viscosity gradients will result in a small radial velocity component, which has been incorporated into Eq. (3.1c) for completeness.

Under the same dimensional scaling arguments, the shear stress distribution can be described by, \( \tau_{rz} = \mu \frac{\partial v_z}{\partial r} \), where in general \( \mu \) is a function of temperature, pressure and shear rate for non-Newtonian fluids such as those considered here. In most previous studies [15, 16] it has been assumed that for the purposes of predicting the magnitude of viscous heating, a solution based on a theoretical Newtonian fluid can be made. Duda et. al. [20] discussed this assumption and showed that it is generally valid, however tends to yield slightly higher viscosity results at very high shear rates. To compensate for this they suggested a procedure that involved an additional iterative step for determining the best-fit value of the exponent for a fluid exhibiting a power law type viscosity shear
dependence, given that the low shear rate viscosity and the range of the initial Newtonian plateau are known. However they acknowledge that this technique is largely empirical since the index is adjusted to obtain agreement between theory and experiment. While this technique may be applicable to a single fitted parameter, for more complex fluids, where multiple fitted parameters would be required, implementation of such an iterative technique may not be successful and could lead to even larger errors. Therefore, in this study the theoretical Newtonian fluid assumption is used for determining the magnitude of the shear heating, realizing that while the majority of the effect will be captured, the procedure may lead to a slight over-correction at higher shear rates.

In most studies it is assumed that viscosity depends in some fashion exponentially on both pressure and temperature [14-16, 18-22]. By superimposing the two influences the simplest viscosity transport relation is given by Eq. (3.2),

$$\mu(T, P) = \mu_0 e^{(k_p P - a AT)} ,$$

(3.2)

where, $\Delta T$ is the temperature rise above $T_o$, $\alpha$ is the temperature viscosity coefficient, $k_p$ is the pressure coefficient of viscosity, $P$ is the gauge pressure and $\mu_0$ is the viscosity at atmospheric pressure and temperature. Note that in this expression the effects of temperature and pressure have been considered as additive, which is a common assumption made by a number of authors; again see ref. [21].

With the viscosity transport relation defined, the problem becomes well defined by subjecting the above equations to the appropriate velocity and temperature boundary conditions. By assuming a uniform temperature profile at the capillary entrance and thus
uniform viscosity, it can be shown from Eq. (3.1b) that the entrance velocity profile must be parabolic in nature. As a result the entrance conditions on temperature and velocity are given by,

\[ v_z(r, z = 0) = \frac{(R^2 - r^2) \partial P}{4 \mu(T_o, P) \partial z}, \]  \hspace{1cm} (3.3a)

\[ T(r, z = 0) = T_o. \]  \hspace{1cm} (3.3b)

The no-slip condition at the wall and the assumption of flow symmetry provides the following boundary conditions on the velocity components,

\[ v_z(r = R, z) = 0, \]  \hspace{1cm} (3.3c)

\[ v_r(r = R, z) = 0, \]  \hspace{1cm} (3.3d)

\[ \frac{\partial v_z}{\partial r}(r = 0, z) = 0, \]  \hspace{1cm} (3.3e)

\[ v_r(r = 0, z) = 0. \]  \hspace{1cm} (3.3f)

Similarly the symmetry condition is applied to the temperature profile at the centre axis of the capillary,

\[ \frac{\partial T}{\partial r}(r = 0, z) = 0. \]  \hspace{1cm} (3.3g)

Thus all that remains is a temperature boundary condition on the exterior wall to fully define the model. The two simplest possible conditions on the surface would be either an adiabatic surface (\( \partial T/\partial r = 0 \)) or an isothermal surface (\( T = T_o \)). While both Gerrard et. al. [16,19] and Duda et. al. [20] have compared both of these conditions to experimental results and concluded that generally the isothermal condition is more accurate, it is generally accepted that the true boundary condition would lie somewhere between these two extremes. In section 3.3 both these conditions along with a prescribed temperature
boundary condition corresponding to the measured capillary wall temperature will be investigated, to determine which shows the more promising results.

3.2.2 Data Reduction Procedure

The most logical approach to the problem of separating the effects of viscous heating and pressure dependence from true non-Newtonian behaviour is to consider the flow of a Newtonian liquid through a capillary and see if the observed change in viscosity can be attributed to these effects [18]. Thus the goal of the above analysis is to determine the value of $\mu_0$ in Eq. (3.2) that provides a common reference point for comparison. To do this the following iterative procedure has been used,

1. Begin by assuming an initial temperature and pressure field within the capillary, $T = T_0$ and $\partial P/\partial z = \Delta P/L$, and an initial guess for $\mu_0$ given by $\mu_i$.

2. Combining the viscosity transport relation with Eq. (3.1b) it can be shown that the $v_z$ profile at each location along the $z$ axis is then given by,

$$v_z = \frac{1}{2\mu_0} \frac{\partial P}{\partial z} \int_0^R r \frac{e^{(-\alpha \delta T + \delta T)}}{\int_0^r e^{(-\alpha \delta T + \delta T + \omega \delta z \mu_0)}} \, dr$$

(3.4)

3. The measured value of $Q$ is introduced by applying the global continuity relation to the above velocity profile,

$$Q = 2\pi \int_0^R rv_z \, dr = \frac{\pi}{\mu_0} \frac{\partial P}{\partial z} \int_0^R r \frac{r \left( \int_0^r e^{(-\alpha \delta T + \delta T + \omega \delta z \mu_0)}} \, dr \right)} \, dr$$

(3.5)

which can be rearranged to isolate $\mu_0$ and $\partial P/\partial z$ as below,
\[
\frac{1}{\mu_0} \frac{\partial P}{\partial z} = q = \frac{Q}{\pi \int_0^R \left( \int_r^R e^{-(\alpha/4) z \rho r} dr \right) r dr}
\]  \hspace{1cm} (3.6)

4. By recognizing that the integral of \( \partial P/\partial z \) along the length of the channel must be the measured value of \( \Delta P \), the updated value of \( \mu_0 \) can be extracted from the value of \( q \) as is shown in Eq. (3.7),

\[
\mu_0 = \frac{\Delta P}{\int_0^L q dz}
\]  \hspace{1cm} (3.7)

With \( \mu_0 \) determined the updated pressure field can also be found from Eq. (3.8),

\[
\frac{\partial P}{\partial z} = \mu_0 q
\]  \hspace{1cm} (3.8)

5. With \( \partial P/\partial z \) and \( \mu_0 \) defined, \( v_z \) can be solved for at each node using Eq. (3.4), and the continuity relation, Eq. (3.1a), can be used to solve for \( v_r \). The energy relation is then used to solve for the updated temperature field.

6. With the updated temperature and pressure fields steps 3-6 are repeated until a convergence tolerance on \( \mu_0 \) is obtained. The final value of \( \mu_0 \) represents the viscosity at a reference temperature and pressure, equivalent to the ambient temperature \( T_0 \) and the atmospheric pressure \( P_0 \).

Based on the above procedure a MATLAB program was developed for analysing the experimental data. The program is based on a finite-difference solution to the differential equations and employs Simpson's rule to perform the necessary integrations numerically. Copies of the script m-files have been included in Appendix A.
3.2.3 Further Corrections

When applied to non-Newtonian fluids, the apparent viscosity and apparent shear rate, \( \gamma_{aw} \), obtained from the numerical procedure outlined above, were then corrected using the Weissenberg-Rabinowitsch [7] equation as below,

\[
\dot{\gamma}_w = \frac{1}{4} \dot{\gamma}_{aw} \left[ 3 + \frac{d(\ln Q)}{d(\ln \Delta P)} \right],
\]

(3.9a)

\[
\mu_w = 4 \mu_o \left[ 3 + \frac{d(\ln Q)}{d(\ln \Delta P)} \right]^{-1},
\]

(3.9b)

where \( \gamma_w \) and \( \mu_w \) are the true shear rate and viscosity at the capillary wall.

In addition to the above, a kinetic energy correction is required as a result of the fact that the entrance pressure was measured in the fluid static state while the exit pressure is only known for the dynamic case. As a result the dynamic pressure head of the fluid exiting the capillary must be subtracted from the measured pressure drop as shown below [23],

\[
\Delta P = P_{obs} - \frac{\rho}{2} \left( \frac{Q}{A} \right)^2
\]

(3.10)

where \( Q/A \) is the volume flow rate divided by the cross sectional area of the capillary, equivalent to the average velocity of the exiting stream, and \( P_{obs} \) is the observed static pressure at the entrance to the channel. While in studies conducted for lower viscosity fluids this correction has been shown to be significant [14], the higher pressures observed in this study limit the effect of this correction to less than 2% of \( P_{obs} \).

In the analysis presented in section 3.2.1 it has been assumed that the flow is fully developed over the entire region of the capillary. It is well known that for all flows there
is a transition region in which the fluid is accelerated from its original static state. The size of this entrance region is proportional to the Reynolds number and diameter of the capillary as shown below in Eq. (3.11) [23].

\[ L_e = 0.06 R_e D \]  \hspace{1cm} (3.11)

According to White [23] the above relation should be valid for all Reynolds numbers within the laminar range (i.e. below \( Re = 2300 \)). In this study the maximum observed Reynolds number was 42 at a capillary diameter of 115\( \mu \)m, resulting in an entrance length of less than 250\( \mu \)m or under 2\% of the total length. In other studies an L/R ratio of 60 has been considered a limit above which the flow rate is nearly completely dominated by shear within the capillary. For this study the minimum L/R ratio was 189 which is well above this limit.

3.3 Evaluation of the Analysis Procedure

To validate the capillary flow model the EHC 45 base oil, which is known to exhibit Newtonian behaviour, will be used. The fluid had a density of 850 kg/m\(^3\), a specific heat of 1.9\( \times 10^3 \) J-K/kg and a thermal conductivity of 142\( \times 10^{-3} \) W-K/m. A pressure viscosity coefficient of 0.25\( \times 10^{-8} \) 1/Pa was used which is of the same order as that quoted for paraffinic base-stocks in [14].

3.3.1 Temperature Viscosity Coefficient

As part of the data correction procedure the temperature viscosity coefficient, \( \alpha \), was determined experimentally using the technique described in section 3.1.2. The tests were
conducted over a 20°C range above the ambient temperature, which was the limit of the expected viscous heating. As is mentioned above, all tests were conducted at a constant shear rate near the lower end of those examined here (1.2x10^4 1/s) in order to ensure that internal heat generation was negligible and that any shear related non-Newtonian influences did not affect the result.

Figure 3.2 is typical of the results obtained during these tests and represents the temperature-viscosity relationship for the 1.0% solutions of the styrene-isoprene polymer solution. Tests were conducted up to a temperature rise of 20°C which coincided with the maximum temperature rise observed in the shear rate measurements. As can be seen in when the natural logarithm of viscosity vs. temperature rise is plotted, a linear relation with a high R^2 value is obtained; suggesting that viscosity of the solution does depend exponentially on temperature.

The data from these experiments were fitted to an exponential curve using a least squares regression algorithm to determine the best-fit value of the coefficient α in Eq. (3.2), the results of which are listed in Table 3.1. Based on these results it is apparent that the value of the viscosity temperature coefficient, α, does not change appreciably due to the addition of the polymer over the range of temperatures of interest, staying within ±4% of its median value of α=0.053 1/K. The high R^2 values suggest that the assumption of an exponential viscosity temperature relationship is valid for all the examined polymer concentrations.
3.3.2 Analysis of Capillary Flow Model and Boundary Conditions

In section 3.2 the capillary flow model was developed, with the purpose of predicting and correcting for viscosity gradients due to changes in pressure and temperature along the capillary axis. As was alluded to at that time the effectiveness of such a model is largely dependent on the proper assignment of the temperature boundary condition at the capillary wall. In this study the effectiveness of the isothermal and adiabatic boundary conditions used in previous studies will be compared with a prescribed temperature boundary condition, corresponding to the measured capillary wall temperature. The three will be compared and the capillary flow model validated by performing the calculations for the aforementioned base oil.

Figure 3.3 compares the results of the three boundary conditions of interest with the uncorrected viscosity results for the EHC 45 base oil (note that all results are shown and no data averaging was used). As can be seen the raw, uncorrected data mistakenly predicts a decreasing trend in viscosity as the wall shear rate increases. When the numerical procedure is used to correct these results, Figure 3.2 shows that the different capillary wall temperature boundary conditions yield dramatically different results. As is apparent the prescribed temperature boundary condition (i.e. a fixed temperature boundary condition corresponding to the measured capillary wall temperature) yields a nearly perfect Newtonian result while the isothermal condition doesn’t provide sufficient correction and the adiabatic condition overcorrects. Based on these results the prescribed temperature boundary condition was used in the final analysis to correct for pressure and temperature effects on viscosity.
Figure 3.4a shows the viscosity profile in the capillary for the base oil at a wall shear rate of $10^6$ 1/s as predicted using the capillary flow model with the prescribed temperature boundary condition. As can be seen significant viscosity gradients exist within the capillary, with the overall value ranging from over 0.05 kg/ms at the entrance to just above 0.02 kg/ms at the minimum near the channel wall at the exit. Due to the high shear rate and thus high degree of viscous heating in this region, the most significant viscosity deviations are observed nearest the channel wall. Nearer the centre of the channel heat generation is much less significant, however a lower viscosity is still predicted due to the pressure drop along the capillary axis and heat conduction from the regions nearest the wall. Using the correction procedure described in section 3.2, $\mu_0$, the viscosity at the reference temperature and pressure can be calculated at each node yielding the result shown in Figure 3.4b. As expected, after the effects of temperature and pressure changes are removed, the corrected viscosity is constant at each point within the capillary.

3.4 Results and Discussion

As mentioned earlier the main purpose of this portion of the study was to investigate the high shear rate viscosity of the radial hydrogenated styrene-isoprene and the ethylene-propylene viscosity improving polymer additives in the EHC 45 base oil. Figures 3.4a and 3.4b show the relationship between the corrected viscosity and the wall shear rate for solutions of the two polymer additives. Since only relatively small amounts of the additives were used in each case, the thermal properties listed above for the base oil were
assumed constant, independent of the polymer concentration for use in the data analysis procedure. All results are shown and no data averaging was used.

In the case of the styrene-isoprene additive, Figure 3.5a, it is apparent that for all concentrations the viscosity drops nearly linearly with logarithmic shear rate, over the examined range of shear rates. This effect is very pronounced in the higher concentration solutions and decreases gradually until nearly Newtonian behaviour was observed in the lower concentration solutions. This shear thinning behaviour is typical of such oil based polymer additives and results from the shear gradient aligning the polymer molecules in the flow direction. As the rate of shear increases this alignment becomes stronger until a point is reached where little or no more alignment can occur, at which point increasing the shear rate further has no significant effect on the viscosity. Since all polymer concentrations show a continuously decreasing viscosity up to and including the highest attainable shear rate, it can be assumed that this point of transition to Newtonian behaviour lies somewhere beyond the $10^6$ 1/s shear rate.

As can be seen in Figure 3.5b the ethylene-propylene polymer solutions exhibited a much more complicated and atypical viscosity behaviour. While shear thinning was observed at the highest shear rates for all concentrations, the two most highly concentrated solutions appear to exhibit a shear thickening stage, where the viscosity was observed to increase to as much as 150% of its prethickening value before shear thinning was again exhibited. The range over which the apparent shear thickening was observed varied from
3\times 10^4\text{ }1/s\text{ to }3\times 10^5\text{ }1/s, depending on the concentration, with the critical region appearing at a lower shear rate for higher concentrations.

Before examination of the possible shear thickening mechanism present here a more thorough discussion of the different phenomena associated with the measurement technique, such as slip flow, surface adsorption and viscoelastic influences, which may contribute to such behaviour is warranted. Slip flow is a well-observed phenomenon in polymer rheology, the analysis of which dates back to Mooney's original derivations [24]. Since that time authors have explained the apparent slip originally in terms a depleted layer near the capillary wall [25] or more recently through cross-streamline polymer migration [26-27]. In either case the presence of a slip layer would result in a decrease in the apparent viscosity and thus could not account for the anomalous behaviour observed here. Others, for example Cohen [28], have examined the role of surface adsorption on the flow of polymer solutions through capillaries. Their studies revealed that in all cases the thickness of the adsorbed layer decreased with increasing shear stress, and thus could not account for this behaviour.

When forced into the capillary, work is done on a viscoelastic fluid to set up elastic stresses as it converges through the narrow opening. This work is recovered after the fluid leaves the capillary however the pressure work done to induce the stresses is lost. Moan et. al. [29] have examined this effect and have shown that above a certain critical shear rate this increased pressure drop becomes significant and could yield results suggesting an apparent increase in viscosity. This effect was shown to be strongly
dependent on the Reynolds number and the L/R ratio of the capillary. To test for this here the high concentration experiments were repeated with a different capillary and a much smaller L/R (89 compared with 224) where this influence should be significantly more dramatic. Both capillaries exhibited the exact same behaviour suggesting that this effect is not the dominant cause of the viscosity increase.

In their theoretical and experimental works Peterlin and coworkers [30,31] investigated the effects of intramolecular hydrodynamic interactions on the intrinsic viscosity of polymer solutions. By using a hydrodynamic resistance coefficient to account for the nonuniform changes in the intermolecular distances, they showed that the intrinsic viscosity should initially decrease to a minimum and then increase in what they called the upturn effect. The behaviour was then observed experimentally in a highly viscous solvent ($\mu = 0.5$ kg/ms) with a very high molecular weight polymer ($M_w = 7 \times 10^6$). Though this effect cannot be completely disregarded the high solvent viscosity and polymer molecular weights that are generally required suggest that this effect is again not dominant here.

The experimental evidence available to date is insufficient to provide detailed information regarding the shear thickening mechanism present here; however a brief examination of some of the possible causes is warranted. A number of authors [32-37] have investigated the role of flow induced phase separations and concentration fluctuations on the rheological properties of polymer solutions. Studies, such as those by Yanase et. al. [34] and Moldenaers et. al. [33], have observed drastic shear thickening
and have attributed it to a transition in the direction of the alignment of concentration fluctuations from the vorticity axis to the flow axis. McHugh and coworkers have examined the influences of phase transformations leading to flow induced crystallization [38,39] and the results of this behaviour on the rheological properties of several crystallizable polymer solutions [40]. Their results were very similar to the behaviour shown in Figure 3.5b.

Ballard, Buscall and Waite [41] as well as others [42] have proposed detailed molecular models describing the role of intermolecular associations to the formation of shear induced gel-type network structures (such a formation differs from a true gel in that it does have a finite viscosity due to the transient nature of the crosslinks). As is detailed in their paper [41], intramolecular associations present in the quiescent medium are broken at low shear rates as the polymer molecule is extended and begins to align itself with the shear gradient. Above a critical shear rate, when a sufficient number of the intramolecular associations have been broken, it is thought that the molecules will become entangled and associations will reform in an intermolecular fashion since the molecule is now in an elongated state, resulting in an increase in the solution viscosity. As the shear rate is further increased, the shear gradient is sufficiently strong to disentangle the molecules and break the intermolecular associations leading to a final shear-thinning region. As mentioned earlier the ethylene-propylene polymer examined here is known to exhibit intermolecular associations at the temperatures examined here and the concentrations where the shear thickening behaviour was observed are above the critical concentration where significant coil overlap exists, thereby making such
intemolecular associations plausible. However with the limited data available here it is impossible to provide an exact interpretation of the shear thickening mechanism.

To emphasize the concentration dependence on viscosity the two polymer solutions are compared at a relatively low shear rate of $2 \times 10^4$ 1/s, Figure 3.6a, and a high shear rate of $10^6$ 1/s, Figure 3.6b. The results presented in these figures represent the average result of measurements taken at equivalent shear rates. As a result of the shear thinning, it is apparent that at the lower shear rate (Figure 3.6a) the 2% styrene-isoprene solution shows a viscosity increase of nearly 300% over the base oil, while at the higher shear rate (Figure 3.6b) the improvement is reduced to 200% of the base oil viscosity. In all cases, the ethylene-propylene polymer exhibited a higher viscosity at a given concentration (than the styrene-isoprene polymer), especially at the higher shear rates where the results are influenced by the shear thickening stage.
FIGURE 3.1: HIGH SHEAR RATE CAPILLARY VISCOMETER. WATER BATH AND HEAT EXCHANGER USED ONLY IN TEMPERATURE—VISCOITY MEASUREMENTS
FIGURE 3.2: RELATIONSHIP BETWEEN TEMPERATURE AND THE NATURAL LOG OF VISCOSITY FOR 1.0% STYRENE-ISOPRENE COPOLYMER IN EHC 45 BASE OIL ($T_0 = 21.5^\circ$C)
FIGURE 3.3: EFFECTIVENESS OF CAPILLARY FLOW MODEL AT CORRECTING FOR THE EFFECTS OF PRESSURE AND TEMPERATURE DEPENDENCE ON VISCOSITY USING VARIOUS CAPILLARY WALL TEMPERATURE BOUNDARY CONDITIONS
FIGURE 3.4A: VISCOITY PROFILE OF EHC 45 BASE OIL FLOWING THOUGH A CAPILLARY AT A WALL SHEAR RATE OF 10^6 1/S
FIGURE 3.4B: EFFECTIVENESS OF THE CAPILLARY FLOW MODEL AT REMOVING THE EFFECTS OF TEMPERATURE AND PRESSURE AND CALCULATING THE VISCOSITY $\mu_0$ AT A REFERENCE TEMPERATURE AND PRESSURE
FIGURE 3.5A: RELATIONSHIP BETWEEN VISCOSITY AND SHEAR RATE OF RADIAL HYDROGENATED STYRENE-ISOPRENE COPOLYMER SOLUTIONS AT VARIOUS BY MASS CONCENTRATIONS (RESULTS REDUCED TO 21.5°C AND 100 KPA FOR COMPARISON)
Figure 3.5b, Relationship between viscosity and shear rate of (A-B-A) block type ethylene-propylene copolymer solutions at various by mass concentrations (results reduced to 21.5°C and 100 kPa for comparison)
Figure 3.6a: Viscosity increase with polymer concentration at low shear rates, $2 \times 10^4$ 1/s
Figure 3.6b: Viscosity increase with polymer concentration at high shear rates, $10^6$ 1/s
<table>
<thead>
<tr>
<th>Solution</th>
<th>$\alpha$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Oil</td>
<td>.053</td>
<td>.99</td>
</tr>
<tr>
<td>0.5% SI</td>
<td>.053</td>
<td>.99</td>
</tr>
<tr>
<td>1.0% SI</td>
<td>.053</td>
<td>.99</td>
</tr>
<tr>
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<td>.053</td>
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</tr>
<tr>
<td>2.0% SI</td>
<td>.051</td>
<td>.99</td>
</tr>
<tr>
<td>0.5% EP</td>
<td>.56</td>
<td>.99</td>
</tr>
<tr>
<td>1.0% EP</td>
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</tr>
<tr>
<td>1.5% EP</td>
<td>.51</td>
<td>.98</td>
</tr>
</tbody>
</table>

**Table 1:** Best fit values of viscosity temperature coefficient, $\alpha$, for styrene-isoprene (SI) and ethylene-propylene (EP) copolymer solutions
Chapter 4 – Channel Size Effect Characterization

Likely the earliest interest in the dimension sensitive viscosity of polymer solutions was in the mid 1960’s while oil companies were studying the flow of polymer containing injection water through fine pores (on the order of 1 to 20 µm in size) as a method of enhancing oil recovery. Chauveteau and colleagues [25,43] studied this effect for a number of different polymers and compared the results to bulk rheological data. In general it was found that the effective viscosity decreased with decreasing pore size, however more complex behaviour was noted when the pore diameter approaches the size of the polymer chain. Chauveteau et. al. proposed that this effect was the result of a depleted layer near the channel wall of constant thickness, independent of the pore size, creating an effective wall slip. Along these lines Aubert and Tirrell [44,45] developed a flow model based on a linear elastic dumbbell polymer model and showed that the presence of the wall tends to align the polymer molecules in the flow direction, reducing their overall contribution to the fluid stress. The results of their model were shown to be consistent with Chauveteau’s observations, however it suggested that cross streamline polymer migration (i.e. a net flux of polymers molecules across a streamline) could only occur in the presence of a curvilinear flow field. Later measurements by Metzner et. al. [46] revealed that the presence of shear gradients in slit flow was sufficient to promote polymer migration across streamlines resulting in significant concentration gradients in the channel cross section (consistent with the depleted layer hypothesis). These cross streamline polymer migration effects were later modelled by a number of authors, for example see Ianniruberto et. al. [27] using the two-fluid theory.
In addition to polymer migration there are a number of other effects, for example surface adsorption [28,47-51], which may have significant influences on the effective microscale viscosity but be nearly unobservable in bulk measurements. While all these aforementioned studies have revealed that solutions with macromolecular components do exhibit dimension dependent flow properties, very little work has been done in quantifying this influence on the performance of modern viscosity improving polymer additives. Therefore, as mentioned in section 1.3, the objective of this half of the study is to experimentally investigate the dimension sensitive flow properties of the base lubricating oil with the two polymer additives by examining the effective viscosity over a range of shear rate in a series of slit microchannels varying in height from 4.5 to 11.5 μm. Similar to the high shear rate tests, solutions of the two polymers at mass concentrations ranging from 0.5% to 1.5% will be investigated. Details regarding the development of the microchannel viscometer and the experimental procedure are outlined in section 4.1. Section 4.2 outlines the data analysis that was performed and section 4.3 presents and discusses the experimental results.

4.1 Experimental

4.1.1 Apparatus

The microchannel viscometer consists of a microchannel test cell, a Validyne DP22-70 differential pressure transducer, a Barnant Model 75225-00 constant pressure precision pump and a liquid reservoir. The pressure transducer was calibrated using a dead weight tester and had an accuracy of better than ±0.5% over the expected pressures range (0 to
700 kPa. After attaining a steady state, the pump pressure was stable within ±2% over the course of a typical viscosity measurement.

Figure 4.1a shows a schematic of the head of the microchannel viscometer developed for this study. Not shown in this diagram are the upstream components including the fluid reservoir, constant pressure precision pump and pressure transducer that are used to store the fluid, control its delivery and measure the input conditions to the viscometer. As is implied by Figure 4.1a, the precision pump delivers the fluid to the head, increasing the pressure in the viscometer and forcing the test fluid through the microchannel blocks at the lower end. The removable cap at the top of the device facilitates cleaning and allows test fluids to be changed relatively rapidly without fear of contamination. To contain the pressures required to force highly viscous fluids through micron size channels at relatively high shear rates, a series of pressure containment devices and O-ring seals was also implemented.

As can be seen in Figure 4.1b, the microchannel array is formed by a series of five parallel plates separated by constant height spacers, to create four channels of equal height. This method of multiple channels was developed to increase the sample volume flow rate through the small microchannels, thereby reducing the amount of time required to make a measurement. For relatively large channels, on the order of 15 μm and greater, a well developed technique using a thin film spacer to create the channel side walls has been used successfully in previous microchannel studies [52]. However for creating even smaller microchannels required for this study, a new technique was developed to form the
spacers by directly coating two strips of thin polymer film on the surface. Using this film coating technique, the side walls of a parallel plate slit channel are built up by successively depositing thin layers of a coating substance on the edges of one plate. A specially designed high-precision dip-coating apparatus was developed for this purpose. The coating substance used to create the channel walls was the Fluorad surface modifier FC-732 (3M Product) which is a fluorochemical acrylate polymer dissolved in an fluorinated inert solvent that evaporates in air leaving an extremely thin transparent film. The uniformity of the coated film thickness is better than 25 nm as examined by using a Tencor surface profilemeter (TSP). By repeating this coating process, the coated film thickness can be controlled from 2 to over 12 microns. A slit microchannel is formed by putting another plate on top of this plate, holding these two plates in a specially designed clamp, and applying epoxy glue to seal the outside gap between the plates. The channel heights formed in this way were calibrated in the microchannel viscometer by using the Newtonian base oil at the known viscosity.

In this study all surfaces were constructed from steel and were 15.4 mm wide by 11.0 mm long. A pressure containment clamp was used to keep the surfaces parallel and to limit their deflection when exposed to pressure. It was observed during the channel height calibration tests that the channel did tend deform under high pressure, thus caution was taken to limit the maximum pressure used in this study to 200 kPa. Figure 4.2 shows the results of the viscosity measurements for the Newtonian base oil as made in the three microchannels used in this study.
4.1.2 Experimental Procedure

In the experiment, an oil-polymer additive solution at a desired concentration filled the reservoir container that was connected to the pump. The precision pump was set to a desired pressure and forced the oil to flow through the microchannel test cell. The pressure drop across the channels was monitored and measured by the pressure transducer. When a stable pressure reading was obtained, the system was assumed to have reached a steady state and a measurement could begin. The actual flow rate is then measured by collecting the liquid at the exit of the test cell and weighting it using a Mettler BB240 electronic balance, accurate to within ±1 mg. In order to minimize the error, flow rate measurements were made over a sufficiently long time, on the order of a few hours, so that the collected oil had a total mass greater than 200 mg. The high vapour pressure of the oil minimized the evaporative losses. All measurements were done at 25°C. Precautions were taken to maintain the system temperature to within ±1°C during each measurement.

4.2 Data Analysis

Using the microchannel viscometer, tests were conducted over a series of wall shear rates, ranging from 50 l/s to 3000 l/s, for polymer concentrations of 0.5%, 1.0% and 1.5% at three separate channel heights: 4.5, 7.0 and 11.5 microns, respectively. For comparison the 1.0% solutions were also tested in an additional 105 micron channel. In all cases the true viscosity, \( \mu \), and wall shear rate, \( \gamma_w \), have been calculated by using the Weissenberg-Rabinowitsch equations for slit rheometry, shown below [7],
where the wall shear stress, $\tau_w$, apparent wall shear rate, $\gamma_a$, and apparent viscosity, $\mu_a$, are given by Eqs. (4.2a), (4.2b) and (4.2c),

$$\gamma_a = \frac{6Q}{WH^2}, \quad (4.2b)$$

$$\mu_a = \frac{H^3W \Delta P}{12L \frac{\Delta P}{Q}}, \quad (4.2c)$$

where $H$, $W$ and $L$ are the channel height, width and length. $\Delta P$ and $Q$ are the pressure drop and volume flow rate as defined in the previous chapter. As seen from these equations, the viscosity can be evaluated by measuring the pressure drop, the volume flow rate, and knowing the dimensions of the microchannel. However, as in the capillary viscometer case, proper design and data correction are essential to ensure the results' accuracy. As detailed in section 3.2, effects such as viscous heating, hydrodynamic entrance length and induced viscoelastic stress at the entrance (to name a few) can have significant effects on the measured quantities and can therefore induce significant errors. The latter of these two have been minimized here by design techniques adapted from capillary viscometers, such as the low height to length ratio (on the order of 1:1000 in this case).
The influence of in-channel viscosity gradients, caused by a coupling of viscous heat generation and pressure dependent viscosity, on the results obtained from the capillary viscometry experiments where shown to be very significant. To examine this effect for the slit microchannel viscometer used in this work, the numerical correction procedure outlined in section 3.2 was extended to the slit flow geometry. When applied to the results of this study the correction was shown to be insignificant (due to the relatively low shear rates and applied pressures) and thus these effects were justifiably neglected.

4.3 Results and Discussion

The results of the microchannel viscosity experiments are shown in Figures 4.3 and 4.4 for the styrene-isoprene and the ethylene-propylene copolymers, respectively, at concentrations of 0.5% (a), 1.0% (b) and 1.5% (c). In the higher shear rate range it is apparent in nearly all cases that the effective viscosity of the solution decreases with channel height. It should be noted that due to an equipment limitation (namely a maximum pressure limitation to prevent dilation of the microchannel blocks) sufficiently high shear rates could not be obtained to fully observe this behaviour in the 0.5% ethylene-propylene solution. However, extrapolation from the available results in Figure 4.4a suggests that it would follow this trend. In general this behaviour became more dramatic as polymer concentration increased and appeared to be more significant in the ethylene-propylene polymer solutions. As the wall shear rate decreased, the viscosity did not reach a Newtonian plateau but rather showed an asymptotic increase. Generally, the smaller channels exhibited a more rapid increase in effective viscosity, often leading to a cross over point below which the smaller channels began to exhibit a higher viscosity.
than the larger ones. Note that in Figure 4.3a sufficiently low shear rates could not be obtained so that the cross over point for the smallest channel could not be shown. However, the trend is apparent from the 7 μm channel. In both Figures 4.3b and 4.4b it is apparent that as channel height is increased the results for the 1.0% solutions are converging towards the bulk viscosity (measured with a 105 micron channel) over the entire range of shear rates.

The apparent thinning with channel size observed at the higher shear rates is consistent with the slip flow condition resulting from the cross-streamline migration of the polymers chains. The fact that the thinning or the slip flow appears to be enhanced (i.e., the absolute viscosity loss is greater) with the polymer concentration is in agreement with the results obtained for fine pores by Chauveteau as mentioned earlier [25,43]. As was indicated in section 4.1 the microchannels used in this study were constructed from steel and thus it is possible that the effective thickness of this “depleted zone” was enhanced by the relative roughness of the surface, however further experiments would be required to verify this hypothesis.

In bulk rheological studies, the failure of a polymer solution to reach a Newtonian plateau but rather show an asymptotic viscosity is usually attributed to the presence of a yield stress. Figures 4.5a and 4.5b show typical shear stress vs. shear rate curves for the 1.0% solutions of the two polymers. As can be seen in both figures, the y-intercept (corresponding to the predicted yield stress) changes depending on the channel size with the smaller channels suggesting a larger yield stress. Since the material yield stress
should not be a function of the channel size, this result coupled with the observed presence of a channel size dependent viscosity at the higher shear rates puts into question the applicability and accuracy of these curves. As such a different method of analysis is proposed.

In slit flow, as the wall shear stress is decreased and a significant portion of the cross sectional stress profile falls below the yield stress, a plug-flow type velocity profile is obtained. Under the plug-flow assumption the apparent viscosity in a slit microchannel is described by Eq. (4.3), see ref. [53],

\[ \mu = \mu_a \left( 1 - \frac{3}{2} \frac{\tau_o}{\tau_w} + \frac{1}{2} \left( \frac{\tau_o}{\tau_w} \right)^3 \right) \]  

(4.3)

where \( \mu_a \) is the apparent viscosity as given by Eq. (4.2c). Since the yield stress, \( \tau_o \), is a property of solution and not the channel, it is apparent that the plug-flow correction is a function of the wall shear stress only and should be independent of channel height. If the observed rapid increase in the viscosity values shown in Figures 4.3 and 4.4 were purely the result of a yield stress, one would expect that a plot of the apparent viscosity, Eq. (4.2c), vs. wall shear stress, Eq. (4.2a), would show a consistent increase in apparent viscosity, independent of channel size. Figures 4.6a and 4.6b show such a plot for the 1.5% solutions of the styrene-isoprene and ethylene propylene copolymers. Apparently this is not the case as the smaller channels show a significantly more rapid increase in viscosity than the larger ones. Therefore the presence of a yield stress cannot fully account for the observed behaviour and some other effect must be at least present, if not dominant.
As mentioned above, the formation of adsorption/entanglement layers in flowing high molecular weight polymer solutions has been discussed by a number of authors [28,47-51]. These multi-molecular layers are often thick (up to 100 μm have been reported) and are built up on solid surfaces in contact with the flowing polymer solution, resulting in an effective reduction in the hydrodynamic cross sectional area (the reader is referred to the series of papers by Barham and coworkers [47-50] for complete details of this effect). In general most studies have shown that the effective hydrodynamic thickness (EHT) of the adsorbed/entangled layer is inversely proportional to the wall shear rate. Note that some studies in ultra-fine porous media, where the pore size is near the radius of gyration of the polymer chain, have observed the opposite behaviour [54]. The H/Rₚ ratio for the microchannels examined here is relatively large, therefore, the inverse proportionality is more relevant in this study. For the slit flow geometry considered in this work, the change in the apparent viscosity resulting from the presence of an adsorbed layer can be described by Eq. (4.4),

\[ \mu_a = \frac{\mu}{\left(1 - \frac{2H_{PL}}{H}\right)^{-1}} \]  

(4.4)

which is derived from Eq. (4.2b) by comparing equivalent ΔP/Q ratios for the expected channel height, H, and the true channel height accounting for the thickness of the adsorbed layer, H-2HₚL. From this equation it is apparent that at equivalent HₚL, the effective viscosity in smaller channels will necessarily be higher. Thus as the shear rate is decreased and HₚL increases, the reduced hydrodynamic mobility of the solution due to the adsorbed/entangled layer could begin to dominate over the increased mobility due to
the depleted layer (i.e. effective wall slip), and the smaller channels should begin to show a higher effective viscosity than the larger ones. While such a prediction is consistent with the data shown in Figures 4.3 and 4.4, further experiments, such as a direct measurement of the adsorbed layer thickness, would be required in order to verify the presence of this mechanism.
FIGURE 4.1A: SCHEMATIC OF MICROCHANNEL VISCOMETER HEAD
Figure 4.1B: Block Microchannel Array
FIGURE 4.2: VISCOSITY OF EHC 45 BASE OIL AS MEASURED IN DIFFERENT CHANNEL SIZES
(T = 25°C)
FIGURE 4.3A: VISCOSITY DEPENDENCE ON CHANNEL SIZE FOR RADIAL HYDROGENATED STYRENE-ISOPRENE COPOLYMER SOLUTIONS AT MASS CONCENTRATION OF 0.5% (T = 25°C)
FIGURE 4.3B: VISCOSITY DEPENDENCE ON CHANNEL SIZE FOR RADIAL HYDROGENATED STYRENE-ISOPRENE COPOLYMER SOLUTIONS AT MASS CONCENTRATION OF 1.0% (T = 25°C)
Figure 4.3c: Viscosity dependence on channel size for radial hydrogenated styrene-isoprene copolymer solutions at mass concentration of 1.5% (T = 25°C)
Figure 4.4A: Viscosity dependence on channel size for ethylene-propylene copolymer solutions at mass concentration of 0.5% (T = 25°C)
**Figure 4.4B: Viscosity Dependence on Channel Size for Ethylene-Propylene Copolymer Solutions at Mass Concentration of 1.0% (T = 25°C)**
FIGURE 4.4C: VISCOSITY DEPENDENCE ON CHANNEL SIZE FOR ETHYLENE-PROPYLENE COPOLYMER SOLUTIONS AT MASS CONCENTRATION OF 1.5% (T = 25°C)
Figure 4.5a: Shear Stress vs. Shear Rate for 1.0% Styrene-Isoprene Solution
(T = 25°C)
Figure 4.5b: Shear Stress vs. Shear Rate for 1.0% Ethylene Propylene Solution (T = 25°C)
FIGURE 4.6a: RELATIONSHIP BETWEEN APPARENT VISCOSITY AND WALL SHEAR STRESS FOR 1.5% SOLUTIONS OF STYRENE-ISOPRENE COPOLYMER
Figure 4.6B: Relationship between apparent viscosity and wall shear stress for 1.5% solutions of ethylene-propylene copolymer
Chapter 5 – Summary and Conclusions

The purpose of this research was to investigate and characterize the behaviour of two VI improving polymer additives, a radial hydrogenated styrene-isoprene copolymer and an (A-B-A) type block ethylene-propylene copolymer in an EHC 45 base oil under conditions of high shear rate and ultra small channel size. As is detailed above this was accomplished in this study through the development of two specialized viscometers each of which could examine one of these effects independently. In both cases significant information regarding the rheology of the polymer additives were obtained.

5.1 Conclusions based on High Shear Rate Characterization

As detailed in chapter 3, the purpose of this portion of this section of the research was to investigate the non-Newtonian behaviour of two polymer additives under conditions of high shear rate. Tests were conducted using a specially designed capillary viscometer to characterize the viscosity behaviour of the polymer solutions over a range of shear rates from $10^4$ 1/s to $10^6$ 1/s. A numerical data reduction procedure was developed which used further experimental results, detailing the temperature-viscosity behaviour of the solutions, to account for the effects of pressure and viscous heating and reduce the data to a common reference pressure and temperature for comparison.

The capillary flow model showed that indeed significant viscosity gradients exist within the capillary and failure to account for these can lead to significant errors. In general the model was shown to be most successful when a prescribed temperature boundary
condition, consistent with that measured experimentally, was applied at the channel wall. Adiabatic and isothermal boundary conditions were less successful and either over (adiabatic) or under (isothermal) corrected the experimental results.

The radial hydrogenated styrene-isoprene copolymer additive exhibited typical shear thinning behaviour over the range of shear rates examined. Generally the effect was more dramatic in the higher concentration solutions, however in all cases the viscosity decreased with increasing logarithmic shear rate. The ethylene-propylene polymer additive exhibited more atypical viscosity behaviour in that a region of shear thickening was observed in the more highly concentrated solutions. As the polymer concentration was increased the degree of shear thickening increased and critical region over which it occurs was observed at lower shear rates.

5.2 Conclusions based on Channel Size Effect Characterization

As detailed in chapter 4, the purpose of this portion of the study the channel size effect of “dimension sensitive” viscosity of the polymer additives. Using a specially designed microchannel viscometer, experiments using both polymers at concentrations ranging from 0 to 1.5% were conducted in three slit microchannels with heights of 4.5μm, 7μm and 11.5μm respectively.

This study has shown that both the radial hydrogenated styrene-isoprene and block ethylene-propylene polymer additives in the hydrocarbon base oil do exhibit a significant viscosity dependence on channel height. Generally, at higher shear rates the effective
viscosity decreased with the channel size, which may be attributed to cross-streamline polymer migration resulting in a "depleted zone" near the channel wall and an effective slip velocity. At lower shear rates all solutions exhibited a sharp increase in viscosity, and in most cases a cross over point was reached below which smaller channels began to exhibit a larger viscosity than larger channels. It was discussed that the presence of a yield stress in the solution could not fully account for the observed behaviour. The crossover may result from the reduced cross sectional area of the channel due to the presence of an adsorbed/entangled polymer layer that becomes more significant at lower wall shear rates. While the presence of an adsorbed layer could qualitatively account for the observed behaviour, further experiments are required to confirm this hypothesis.
Chapter 6 – Future Work

As alluded to throughout chapters 4 and 5, both polymer additives exhibited some atypical viscosity behaviour under a variety of conditions. There are a number of cases where some further experimentation could provide some better insight into the mechanisms present to cause such behaviour or further practical information.

The shear thickening behaviour observed at high shear rates in the ethylene-propylene solutions could give it significant advantages over other polymer additives, which typically exhibit a constant shear thinning behaviour, like the styrene-isoprene copolymer. However the ethylene-propylene additive is known to be very unstable under conditions of high shear rate (i.e. a high degree of permanent viscosity loss is observed each time the polymer is exposed to shear), thus it would be critical to determine whether or not this region of shear thickening is still observed after subjecting the solution to a number of shearing cycles, as it would be in practice. To examine this potential degradation of shear thickening region a common experiment could be performed where the polymer solutions are repeatably recycled through the capillary viscometer each time noting the degree of permanent viscosity loss.

As detailed in section 4.3 in the high shear rate range, the solutions in the smaller channels all exhibited a significantly lower effective viscosity than in the larger ones, which was theorized to be the result of a cross-streamline migration of the polymer molecules resulting in a depleted layer near the channel wall. At that time it was mentioned that the relatively high roughness of the steel channels may have enhanced
this effect (possibly due to the localized flow disturbances near the channel wall resulting from the irregular surface). A detailed experimental study using surfaces of similar composition, say steel, but of varying roughness could be conducted with the microchannel viscometer and the same procedure detailed in section 4.1 to verify the hypothesis.

Also in section 4.3 the possible causes of the rapid increase in viscosity at low shear rates were discussed. The cause was proposed to be the result of either a yield stress or adsorbed/entangled polymer layer, though conclusive evidence could not be offered. To examine this in more detail further experiments could be conducted on similar steel surfaces which have been given a surface treatment to repel polymer adsorption, such as was done by Cohen and Metzner [26]. By repeating the experiments detailed in chapter 4 with the treated surfaces a better idea of the magnitude of the adsorption effect could be obtained.
Appendix A: A MATLAB Program for Performing the Capillary Viscometer Data Analysis Procedure

Contained within this appendix are copies of the MATLAB m-files that were developed for carrying out the data correction procedure, outlined in sections 3.2 and 3.3, on the data obtained from the capillary viscometer. Each specific script and function file contains a detailed header explaining its purpose and, if necessary, the proper form of the input data files. Not included in this section are the "non-core" m-files that were used to perform the figure plotting or boundary condition comparison.
This is the main program for subtracting the pressure and viscous heating effects from measurements made with a capillary viscometer.

**Input:**
- The data files are input in the following format
  - Pressure Drop (Pa) | Channel Length (m) | Volume Flow Rate (m³/s)...
  - Capillary Radius (m) | Apparent Wall Shear Rate (1/s) | ...
  - Boundary Temperature (C)
- where | represents a tab space between the data columns.

**Output:**
- For each input file and output file is created in MATLAB .mat format which contains the apparent viscosity and shear rate as well as the corrected true viscosity and shear rate

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```matlab
% start fresh
clear
%
% define numerical variables
nr = 50;
nl = 50;
tol = 1e-6;

% define physical parameter
rho = 850;
cp = 1.91e3;
k = 142e-3;
alpha = .053;
kp= .25e-8;

for kk = 1:5
    % load the data file
    % Dp   L   Q   R   1/S
    if kk == 1
        load 'base_oil.txt'
datafile = 'base_oil';
amerun = 'Base Oil';
    elseif kk == 2
        clear dp l q r shear p p_linear dpdz dpdz_linear temp temp_linear
z visc viscosity shear_rate
        load 'five_shell.txt'
datafile = five_shell;
amerun = '0.5 percent shell';
```
elseif kk == 3
    clear dp 1 q r shear p p_linear dpdz dpdz_linear temp temp_linear
    load 'one_shell.txt'
    datafile = one_shell;
    namerun = '1.0 percent shell';
elseif kk == 4
    clear dp 1 q r shear p p_linear dpdz dpdz_linear temp temp_linear
    load 'one_five_shell.txt'
    datafile = one_five_shell;
    namerun = '1.5 percent shell';
elseif kk == 5
    clear dp 1 q r shear p p_linear dpdz dpdz_linear temp temp_linear
    load 'two_shell.txt'
    datafile = two_shell;
    namerun = '2.0 percent shell';
end

% now separate the datafile for each file
pressure = datafile(:,1);
l = datafile(:,2);
q = datafile(:,3);
radius = datafile(:,4)/2*1e-6;
shear = datafile(:,5);
temp_measure = datafile(:,6);

ok = 0;
% now for each point in the columns calculate the viscosity
for kkk = 1:length(pressure)
    ok = ok + 1;
    disp(namerun)
    disp(ok)

    v_scale = 1;
    visc_scale = .046;
    p_scale = visc_scale*v_scale*l(kkk)/radius(kkk)/radius(kkk);
    t_scale = 21.5;
    pr = visc_scale*cp/k;
    re = rho*v_scale*radius(kkk)/visc_scale;
    br = (v_scale)^2*visc_scale/4/t_scale/k;

    r_not = 0:1/(nr-1):1;
    z_not = 0:1/(nl-1):1;

    % correct pressure
    pressure(kkk) = k_cor(pressure(kkk),q(kkk),radius(kkk),rho);

    % define the boundary condition
    boundary_temp = boundary(temp_measure(kkk),nl,t_scale);
    p_not = pressure(kkk)/p_scale;
% Initial conditions - temperature tensor and dpdz vector
dpdz_not(1:nl) = -l*pressure(kkk)/p_scale;

% integrate to determine the pressure vector
p_not = p_vector(dpdz_not,pressure(kkk)/p_scale,nl);
t_not(1:nr,1:nl) = 0;
visc_old = visc_scale;

diff = 1;
it_counter = 0;

while diff > tol

    % now calculate the z - velocity tensor
    [visc_new,vz_not,vz_not,dpdz_not] =
        vz_tensor(r_not,radius(kkk),z_not,l(kkk),t_not,t_scale,p_not,p_scale,alpha,kp,q(kkk),visc_scale,nr,nl,v_scale);
p_not = p_vector(dpdz_not,pressure(kkk)/p_scale,nl);

    % now calculate the r - velocity tensor
    vr_not =
        vr_tensor(v_scale,vz_not,radius(kkk),nr,nl,r_not,z_not,l(kkk));

    % now calculate the new temperature profile
    t_not =
        t_tensor(vz_not,vr_not,visc_not,r_not,z_not,dpdz_not,pr,re,br,radius(kkk),l(kkk),nr,nl,tol,boundary_temp);

    diff = abs((visc_new-visc_old)/visc_new);
    visc_old = visc_new;
it_counter = it_counter + 1;
    visc_save(it_counter) = visc_old;

end

% now save the viscosity result
viscosity(kkk,1) = visc_new;
t_max(kkk) = max(max(t_not*t_scale));

% now calculate the shear result
[shear_rate(kkk,1),shear_change] =
    vz_shear(vz_not*v_scale, shear(kkk),r_not*radius(kkk),nl,nr);

q_calc(kkk) =
    q_calculation(r_not*radius(kkk),vz_not*v_scale,nl,nr);

end

if kk > 1
    % perform the rabinowitch correction
    P = polyfit(log(pressure),log(q),1);
    D = polyder(P);
cor = polyval(D,log(pressure));

    shear_rate_r = 0.25*shear_rate.*(3+cor);
    viscosity_r = 4*viscosity./(3+cor);
end
% save the results for plotting later

if kk == 1
    save base_oil shear_rate viscosity
elseif kk == 2
    save five_shell shear_rate shear_rate_r viscosity viscosity_r
elseif kk == 3
    save one_shell shear_rate shear_rate_r viscosity viscosity_r
elseif kk == 4
    save one_five_shell shear_rate shear_rate_r viscosity viscosity_r
else
    save two_shell shear_rate shear_rate_r viscosity viscosity_r
end
end
function p_actual = k_cor(pressure,q,r,rho)
% ***************************************************************
% k_cor.m
% ***************************************************************
% Purpose:
% this function subtracts the kinematic correction from the actual
% pressure
% ***************************************************************
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% Sept 7, 2000
% ***************************************************************

v = q/pi/r/r;
p_actual = pressure - 0.5*v*v*rho;
function boundary_temp = boundary(temp_measure,nl,t_scale);
% % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % %
% % boundary.m
% % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % %
% Purpose:
% This function applies the temperature boundary condition
% % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % %
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% % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % % %
% % assume constant boundary condition
for i = 1:nl
    temp(i) = temp_measure*i/nl;
end

for i = 1:nl
    boundary_temp(i) = temp(i)/t_scale;
end
function p_not = p_vector(dpdz_not, p_start, nl)
% ************************************************************************
% p_vector.m
% ************************************************************************
% Purpose:
% this is a function which calculates the pressure at each
% point using the values of dpdz
% ************************************************************************
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% Sept 7, 2000
% ************************************************************************

deltal = 1/(nl-1);

% starting pressure
p_not(1) = p_start;

for i=2:nl
    p_not(i) = p_not(i-1) + dpdz_not(i-1)*deltal;
end
function [visc,visc_not,vz_not,dpdz_not] = vz_tensor(r_not,radius,z_not,l,t_not,t_scale,p_not,p_scale,alpha,kp,q,visc_scale,nr,nl,v_scale);

% vz_tensor.m
% ************************************************************************
% Purpose:
% function will determine the velocity profile using a simple
% polygon rule
% ************************************************************************
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% Sept 7, 2000
% ************************************************************************

deltar = l/(nr-1)*radius;
deltaz = l/(nl-1)*l;

% dimensionalise as required
r = r_not*radius;
t = t_not * t_scale;
pressure = p_not*p_scale;

% calculate the viscosity temp relation at each node
for i = 1:nl
    for j = 1:nr
        visc_tp(j,i) = exp(-alpha*t(j,i) + kp*pressure(i));
    end
end

% first compute the areas
for j = 1:nl
    for i = 1:(nr-1)
        area(i,j) = ((r(i)/visc_tp(i,j)) + (r(i+1)/visc_tp(i+1,j)))*deltar/2;
    end
end

% now calculate the f function
for j = 1:nl
    for i = 1:nr
        if i == nr
            f(i) = 0;
        else
            temp = 0;
            for h = i:nr-1
                temp = temp + area(h,j);
            end
            f(i,j) = temp;
        end
    end
end

% now that f is computed calculate the g function
for i = 1:nl
    temp = 0;
    for j = 1:nr-1
temp = temp+(f(i,j)*r(j)+f(j+1,i)*r(j+1))/2*deltar;
end

g(i) = -q/pi/temp;
end

% now to integrate along the channel length

temp = 0;
for i = 1:nl-1
    temp = temp + (g(i)+g(i+1))*deltaz/2;
end

visc = -1*pressure(1)/temp;
dpdz = g*visc;

for j = 1:nl
    for i = 1:nr
        vz(i,j) = f(i,j)/visc/2+-1*dpdz(j);
    end
end

vz_not = vz/v_scale;
dpdz_not = dpdz/p_scale*1;
visc_not = visc_tp*visc/visc_scale;
function vr_not = vr_tensor(v_scale,vz_not,radius,nr,nl,r_not,z_not,1)
% vr_tensor.m
% Purpose:
% calculates the non-dimensional radial velocity
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% dimentionalise as required
vz = vz_not * v_scale;
% calculate deltas
r = radius*r_not;
z = z_not*1;
deltaz = z(2) - z(1);
deltar = r(2) - r(1);
% calculate dvz/dz at each point using appropriate functions
for i = 1:nr
    for j = 1:nl
        if j == 1
            dvzdz(i,j) = 0;
        elseif j == nl
            dvzdz(i,j) = (3*vz(i,j) - 4*vz(i,j-1) + vz(i,j-2))/deltaz;
        else
            dvzdz(i,j) = (vz(i,j+1) - vz(i,j-1))/2/deltaz;
        end
    end
end
% again calulate the area of each point
for i = 1:nl
    for j = 1:nr-1
        if i == 1
            area(j,i) = 0;
        else
            area(j,i) = (r(j)*dvzdz(j,i) + r(j+1)*dvzdz(j+1,i))/2*deltar;
        end
    end
end
% now compute vr
for i = 1:nl
    for j = 1:nr
        if i == 1
            vr(1:nl) = 0;
        else
            if j == nr
                vr(j,i) = 0;
            elseif j == 1
                vr(j,i) = 0;
            else
                vr(j,i) = 0;
            end
        end
    end
end
temp = 0;
for h = 1:j
    temp = temp + area(h,i);
end
vr(j,i) = -1/r(j)*temp;
end
end
end

vr_not = vr/v_scale;
function t_not =
t_tensor(vz_not,vr_not,visc_not,r_not,z_not,dpdz_not,pr,re,br,radius,l,
nl,nr,tol,boundary_temp)
% *******************************************************
% t_tensor.m
% *******************************************************
% Purpose:
% this program solves for the non-dimentional temperature
% distribution in the capilliary each step along the
% capilliary will be solved independently using newtons method
% and the thomas algorithm
% *******************************************************
% David Erickson
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% Sept 7, 2000
% *******************************************************

for i = 1:nl
    diff = 1; % reset the diff counter
    if i == 1
        t_not(1:nr,i) = 0;
    elseif i == 2
        % start with an initial guess and one vector
        t_temp(1:nr) = t_not(1:nr,i-1);
    while diff>tol
        [f,u,d,il] =
        f_firstnode(nr,nl,t_temp,re,pr,br,radius,l,vz_not(:,i),vr_not(:,i),visc
        _not(:,i),r_not,z_not,dpdz_not(i),boundary_temp(i));
        delta = thomas(ll,d,u,-1*f);
        for j = 1:length(delta)
            t_temp(j) = t_temp(j) + delta(j);
        end
        % update delta
        diff = norm(delta);
    end
    else
        % start with an initial guess and one vector
        t_temp(1:nr) = t_not(:,i-1);
        t_temp1(1:nr) = t_not(:,i-1);
        t_temp2(1:nr) = t_not(:,i-2);
    while diff>tol
        [f,u,d,il] =
        f_othenode(nr,nl,t_temp,t_temp1,t_temp2,re,pr,br,radius,l,vz_not(:,i),
        vr_not(:,i),visc_not(:,i),r_not,z_not,dpdz_not(i),boundary_temp(i));
        delta = thomas(ll,d,u,-1*f);
        for j = 1:length(delta)
            t_temp(j) = t_temp(j) + delta(j);
        end
        % update delta
        diff = norm(delta);
    end
end
end

end

if i > 1
    t_not(:,i) = t_temp(:);
end

t_not(nr,i) = boundary_temp(i);

end
References


