Microfluidics of In-Mold Coating Resins and Dilute DNA Suspensions

THESIS

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By

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Abstract

In-mold coating (IMC) is carried out by injecting a low viscosity thermosetting liquid on to the surface of a substrate at the end of the molding process after it has solidified and while it is still in the mold. The coating then cures and adheres to the substrate. Due to its successful application to exterior body panels made from compression molded Sheet Molding Compound (SMC); IMC is being developed as an environmentally friendly technology that would ultimately replace painting of injection molded thermoplastics. Research has been done to simulate the coating flow during the IMC process assuming the coating to be a power law fluid and using the traditional no-slip boundary conditions. This model adequately predicted the fill pattern but did not predict pressures correctly. This deviation has been attributed to slip (or apparent slip) at the wall, as often found in flow through microchannels, due to microscopic length scale of the flow; and the existence of a high shear rate non-Newtonian plateau for the coating viscosity.

Further research has been done on modeling the rheological behavior of IMC resin at high shear rates. This work points towards the behavior not being true slip but apparent slip due to the carbon black concentration in the resin increasing farther away from the wall. Since IMC resin behaves as a non-Newtonian fluid, we use a dilute salmon DNA solution as a model suspension to make further insights into the apparent slip phenomena encountered during the coating process.
Researchers have been using DNA for flow visualization studies due to its ability to be tagged by a fluorescent dye. Using a confocal micro-particle tracking velocimetry we have measured the velocity profile of stained DNA flowing in micro channels as well as the concentration of DNA as a function of position in the channel. We have found that the DNA concentration increase as we move to the center of the channel. Using this information, we have developed a model that includes a viscosity that is a function of the concentration of DNA, to predict the pressure data without the need to calculate apparent slip.
Dedication

Dedicated to my family, especially my mother who has always pushed me to do my best and my father whose spirit will always be with me.
Acknowledgments

I would like to express my utmost appreciation to my advisor, Dr. Jose Castro, for his support and guidance throughout my graduate studies. I am thankful to him for his dedication to my research and giving me the opportunity to work in his group.

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Finally, I would like to thank my friends and family for always supporting me in all my ventures. I would not have been able to make it this far without their love and support.
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Chapter 1: Introduction

Chapter 1 begins by providing an introduction to in-mold coating as an industrial process, the chemical makeup of in-mold coating resins and their rheology. Then, previous work on microfluidics is presented to explain the motivation for this work.

1.1 In-Mold Coating

1.1.1 Introduction to In-Mold Coating

In-mold coating (IMC) is carried out by injecting a low viscosity thermosetting liquid on to the surface of a substrate at the end of the molding process after it has solidified and while it is still in the mold. The resin is injected and covers the surface of the substrate once it is rigid enough to withstand the injection pressure. The coating then cures by chemical reaction and adheres to the substrate. IMC has many applications and can lower the overall cost of producing high quality polymer parts. The gaps encountered during coating flow vary all the way from the nano scale up to 75 μm, with most of the flow occurring around the 25 μm gap size (Aramphongphun 2006).

IMC has many benefits. IMC of sheet molding compounds (SMC) can achieve extremely high surface quality standards for exterior automotive body parts, transportation and other marine applications. High appearance coating standards have driven the need to fill porosity, reduce sinks, and improve paint adhesion (Omnova Solutions Inc. n.d.). The success of IMC of SMC has led researchers to investigate the
use of IMC for thermoplastics (TP) manufactured by injection molding (IM). Resin can replace external primer for TP. Reducing this external processes can save money and also reduce the amount of volatile chemicals released into the environment (Castro and Griffith 1993).

1.1.2 In-Mold Coating of Sheet Molding Compounds

SMC is a process in which chopped fibers (between 0.5 and 1 inches in length) are combined with a carrier sheet, to produce endless-fiber mats impregnated with a filled resin system, under pressure and sometimes heat in the compactor, shown schematically in Figure 1. The composite sheets typically are compression molded for automotive Class A body panels, high-strength electrical parts, personal watercraft, and various structural components for their high mechanical properties and excellent surface appearance (Castro and Griffith 1993).

IMC can make many improvements to the surface properties of SMC parts, in particular automotive body panels. The main drive for IMC of SMC parts is that the coating process is an environmentally friendly approach of improving the surface quality. IMC can fill porosity, reduce sinks, and improve the overall surface appearance. Coating the substrate while still in the mold with IMC releases no volatile chemicals. IMC can also act as a primer for paint adhesion. The coating is made electrostatically conductive by the addition of carbon black to the base resin which improves the painting process (Aramphongphun 2006).
1.1.3 In-Mold Coating of Thermoplastics

Because of the successful application of IMC to SMC, similar coating techniques are being developed for thermoplastics made by injection molding. Thermoplastics are manufactured by injection molding in a three stage process: filling, packing, and cooling. During the filling stage, polymer pellets go through a screw and heating elements which melt the polymer. The screw acts as a piston to drive the molten polymer into a closed mold. Once the mold is filled, extra polymer melt is packed into to mold to compensate for material shrinkage. Once the polymer cools, the mold is opened and the part is ejected. With this process, reproducible products can be mass produced with relatively short cycle times. IMC would add another step in the process. IMC is injected during the cooling stage, once the part is rigid enough to withstand the injection pressure.

There are more problems that arise with IMC of TP since the molds normally used are land molds, the total force generated by the hydraulic pressure during coating, cannot exceed the clamping force of the mold. If it does, the mold would leak. Timing of the injection is also a critical variable. If the coating is injected too early the substrate would not be rigid enough to withstand the pressure. If the coating is injected too late the mold temperatures would not be high enough to cure the resin and would require exterior heating and a longer cycle time (Straus, McBrian and Thompson 2001).

1.1.4 Chemical Makeup of In-Mold Coating

The typical IMC resin contains unsaturated oligomers and monomers, peroxides, benzonquinone, polyvinylacetate, carbon black and other components, such as filler (talc) and additives (lubricant) (Castro and Griffith 1993). The components are meant to improve the coating process or add value to the surface treatment of the substrate. The
carbon black in the resin is meant to give conductivity to the part for subsequent electrostatic painting.

Carbon black (CB) is a black powdered form of nearly pure elemental Carbon. Initially produced primary particles, known as “nodules”, consist of graphite-like stacks of large polycyclic aromatic ring systems with the diameter of 0.015 to .03 µm. These nodules rapidly coalesce into larger clusters known as aggregates, which have diameters in the range of 0.085 to 0.500 µm. These chemically bonded aggregates come together to form agglomerates, typically 100 to 1,000 µm in diameter. The agglomerates are held together by van der Waals forces. (Boyd 2008). A schematic representation of the carbon black structure can be seen in Figure 2. Carbon black is used to simplify and improve the external painting process. During painting of thermoplastics, an electrostatic charge is applied to the part to improve the bonding between the paint and the outer surface. Carbon black, when used as filler, improves adhesion of the paint to a surface and also provides UV protection (Aramphongphun 2006).

1.1.5 Motivation for Using DNA as Model Material for Flow Visualization

IMC resin is a non-Newtonian fluid. The macroscopic non-Newtonian (shear thinning) effect between the resin with and without carbon black is similar to the addition of DNA to the buffer solution (Cortright 2009). Previous research has shown that IMC flow can be modeled; using continuous mechanics with a true slip boundary condition and a calculated slip length of 3.2 µm (Aramphongphun 2006). The length of stable carbon black aggregates range from 0.085 to 0.500 µm. As a model material we selected: salmon DNA (Sigma-Aldrich, St. Louis, Missouri). The weight-average molecular weight of the salmon DNA was 1.3 x 10^6 g/mol, or approximately 2,000 bp (Sigma-
Aldrich, as received). This results in an approximate length of 0.66 μm. This length was similar to the aggregates of carbon black particles. This similarity led to the assumption that DNA would also slip while flowing in micro-channels. Research has shown that the behavior of CB in suspension is governed by the aggregate diffusion and can therefore be modeled as a suspension with particles on the order of 0.085 to 0.500 μm (Aoki, Hatano and Watanabe 2003). DNA is a flexible polymer that entangles and stretches in solution so it cannot fully model the behavior of rigid CB. The intent here is to make some preliminary insights into the slip phenomena encountered in IMC flow. In Section 6.3 we discuss how researchers are currently using origami DNA folding to create rigid like structures of virtually any shape, which could more accurately model the aggregate and agglomerate structure of CB in suspension.

1.2 Previous Work

1.2.1 Microfluidics

Microfluidics is the study of transport phenomena on the microscale, typically 1 to 100 μm, that do not have the same effects on the macroscale. To accurately model fluid mechanics using a direct analytical model, the correct assumptions need to be made about the type of flow. Assumptions of no slip and constant viscosity often do not apply on the microscale (Gravesen, Branebjerg and Jensen 1993).

Pressure-driven flow is one way to distinguish wall slip phenomenon often associated with polymer melts and dilute colloidal dispersions. True slip and apparent slip are two phenomena that can cause lower pressure drops and overall lower viscosity than predicted with macroscopic models. They are shown schematically in
Figure 3, together with the no-slip case. No slip is the general macroscopic assumption made when the velocity at the wall, \( v_x \), is zero \( (z = h, v_x = 0) \). True slip occurs when a large enough shear stress overcomes the static friction between the wall and the flowing material. True slip occurs when the velocity at the wall is finite and equal to a slip velocity, \( v_s (z = h, v_x = v_s) \) which is associated with a slip length, \( \beta \). In apparent slip, a lower viscosity fluid maintains the no-slip boundary condition at the wall \( (z = h, v_x = 0) \). The lower viscosity suspension next to the wall is associated with the depletion of polymeric or dispersed species. This can be explained by inhomogeneous stress fields or repulsion of particles from the wall (Aramphongphun 2006).

The following sections briefly review previous work on our group toward developing a mathematical model to represent the flow of IMC.

1.2.2 Xu Chen

Xu Chen developed a two-dimensional mathematical model for IMC flow on a compressible thermoplastic substrate. In this work, Chen used the standard no slip at the wall boundary condition and a power law viscosity model to predict the rheological behavior of the coating. This model predicted the fill patterns accurately but could not predict the filling pressures. Comparison of experimental and predicted pressure rises demonstrated that theoretical predictions initially over predicted the experiments, but under predicted them at the end of filling (Chen 2003).

The discrepancy in predicting the pressure can be attributed to two factors, slip flow phenomena at the wall and the use of power law. At the beginning of the coating process when the gaps are relatively smaller the IMC resin slips at the wall, causing an apparent decrease in viscosity. The power law, shown schematically in Figure 4,
accurately models the linear region of a non-Newtonian fluid but fails to model the low and high shear rates. Higher shear rates are seen at higher flow rates as well as smaller channel gaps.

1.2.3 Chuckaphun Aramphongphun

Aramphongphun developed a microslit rheometer test to verify the viscosities measured by a parallel plate rotational rheometer at high shear rates. Aramphongphun tested IMC resin to analyze rheological models and determine slip parameters. The microslit rheometer used a high-precision syringe pump to control the flow rate through a microslit die and measure the pressure at high shear rates. The results yielded an average slip length (β) for IMC resin. The slip length was then used to model the slip flow and predict pressure needed to drive IMC through a given channel (Aramphongphun 2006).

1.2.4 Narayan Bhagavatula

Bhagavatula developed and experimentally verified a mathematical model for IMC flow using the Carreau constitutive equation and allowed for true slip at the wall. The computer code iteratively solved for the viscosity and ultimately the pressure difference of pressure-driven flow through parallel plates. Bhagavatula used a combination of true slip and the Carreau viscosity model to accurately predict the rheological behavior of a carbon black suspension. Figure 5 shows how the Carreau model accurately models the low and high shear rates as well as the linear portion of the non-Newtonian fluid (Bhagavatula 2006).
1.2.5 Emily Cortright

Emily Cortright evaluated the use of DNA, to visualize the slip flow phenomena assumed by Aramphongphun and Bhagavatula. Cortright used calf and salmon DNA in her studies. Cortright used the same method to test the DNA in a microslit rheometer as Aramphongphun to validate the assumptions made about true slip and Carreau viscosity. Cortright also used a confocal micro-particle tracking velocimetry (CM-PTV) (VisiTech International, Sunderland, United Kingdom) system to record stained DNA flowing through micro-channels. The intensity of the fluorescent dye was measured at different locations and these values were converted to percentages, as shown in Figure 6. The term intensity was a measured value of the quantity of light given off by the stained DNA particles, in an absolute scale and measure by confocal camera system. In the absolute scale, complete black would produce zero and white would produce the maximum reading. It was assumed that the light from the fluorescently stained particles was the only light being collected by the camera system.

The results indicate there is a distinct increase in intensity at the center of the channel compared to the sections closer to the wall. The intensity profiles also indicate a gradual reduction in intensity at the wall, which is associated with a decreasing number of DNA particles closer to the wall. From these results, it was concluded that the decrease in overall viscosity was due to apparent slip and a region of lower viscosity fluid at the wall. The video files were also used to measure the velocity field and compare it to the calculated true slip model assumed. Single DNA particles were tracked over a measured distance and timed to measure their velocity. The true slip velocity field model
does generally represent the macroscopic effects of DNA flow, in a manner similar to IMC flow.
Figure 1: Schematic Representation of Sheet Molding Compound Process (Castro and Griffith 1993)
Figure 2: Schematic Representation of Carbon Black Structure (Boyd 2008)
Figure 3: Schematic representation of the boundary conditions at the fluid-wall interface for (a) no-slip, (b) true slip, and (c) apparent slip (Aramphongphun 2006)
Figure 4: Power Law Viscosity Model
Figure 5: Carreau Viscosity Model
Figure 6: Snapshot Showing Intensity Profile and Average Intensity Values at Three Different Regions across the Channel (Cortright 2009)
Chapter 2: In-Mold Coating Rheology

The viscosity of the IMC base resins, a 50/50 blend Urethane/Epoxy and a commercial IMC formulation GENGLAZE® EC-2500 (Omnova, as received) with and without 2.8\% carbon black, were measured using a TA ARES rotational rheometer (TA Instruments, New Castle, Delaware) with 25 mm diameter parallel plates at room temperature (25°C). The parallel plates were rotated from 1 to $10^3$ s$^{-1}$ to measure the shear viscosity, a macro-scale bulk material property. Results are shown in Figure 7. GENGLAZE® is a liquid, heat activated conductive coating designed to improve the surface of reinforced plastics, automotive, truck FRP body panels, or any molded part. Inhibitor is added to prevent reaction during flow (OMNOVA Solutions Inc. n.d.).

The IMC resin follows the same trend as the addition of DNA into buffer solution. With the addition of CB the solution becomes non-Newtonian. This is analogous to the addition of DNA in buffer solution. DNA solutions can be thought of as suspensions with long chain molecules, leading to entanglements and shear thinning, carbon black is suspension of rigid particles; however the macroscopic shear thinning effect on both solutions is similar. They both also experience similar slip behavior. (Cortright 2009).

2.1 Slip Coefficient for Carbon Black

The viscosity of IMC resin at high shear rates ($> 10^3$ s$^{-1}$) was studied using a microslit rheometer, previously designed by Chuckaphun Aramphongphun. The setup
consists of a high-precision syringe pump, stainless steel tubing, and a microslit die. The high-precision syringe pump (model 100DX from Teledyne ISCO, Lincoln, Nebraska) pumped the sample through the stainless steel tubing (OD = 0.125 in or 3.175mm) into the microslit die at a specified flow rate. The flow rates were limited by the maximum capability of the syringe pump. This pump had a maximum capacity of 103 mL and was capable of achieving flow rates between 0.00001 and 50 mL/min and pressures up to 10,000 psi. The on-pump pressure transducers related the total pressure drop ($\Delta p_{\text{tot}}$) to the display screen on the pump. A shim stock was used between the two halves of the die to allow for easier cleaning and placing shims of different heights. In order to account for and remove the pressure drop in the entrance region of the die ($\Delta p_{\text{end}}$), separate dies and shims were built to exclusively represent the entrance region. The pressure drop recorded across this region ($\Delta p_{\text{end}}$) was subtracted from the total pressure drop ($\Delta p_{\text{tot}}$) to find the pressure drop across the straight region of the channel ($\Delta p$). The pressure drop versus flow rate data were converted to viscosity versus shear rate values, and then compared to the data gathered from the rotational rheometer (Aramphongphun 2006).

The developed rheological equations were used to analyze the viscosity data and determine the values of slip length ($\beta$), summarized below.
No Slip Boundary

\[ \tau_w = \frac{H}{2L} \Delta P \]

\[ \dot{\gamma}_w = \frac{2}{wH^2} \left( 2Q + \Delta P \frac{dQ}{d\Delta P} \right) \]

\[ \eta = \frac{\tau_w}{\dot{\gamma}_w} \]

Slip Boundary Condition

\[ \tau_w = \frac{H}{2L} \Delta P \]

\[ \dot{\gamma}_w = \frac{2}{wH^2 \left( 1 + \frac{4\beta}{H} \right)} \left( 2Q + \Delta P \frac{dQ}{d\Delta P} \right) \]

\[ \eta = \frac{\tau_w}{\dot{\gamma}_w} \]

Table 1: No-Slip and True Slip Shear Stress and Viscosity Equations

In each case the shear stress (\(\tau_w\)) calculated using the channel dimensions, \(H\) is the channel height and \(L\) is the channel length, as well as the \(\Delta P\) measured in the syringe pump. The shear rate (\(\dot{\gamma}_w\)) was then calculated using the same channel dimensions; with \(w\) as the channel width, \(Q\) as the flow rate in m/sec and \(\frac{dQ}{d\Delta P}\) calculated from the results for the microslit rheometer. The ratio of the reduced viscosity due to the wall slip (\(\eta_{SL}\)) to the no-slip viscosity (\(\eta_{NS}\)) was then used to determine the slip length (Aramphongphun 2006). Please note that the original equations derived by Aramphongphun have a slight misprint as corrected by Cortright. In the denominator for true slip shear rate, the equation showed \(1 - \frac{4\beta}{H}\) instead of \(1 + \frac{4\beta}{H}\) (Cortright 2009).

The value of the slip length was then used to correct the wall slip in the channel and to obtain the true viscosity of the suspension, which is independent of the channel geometry. With this setup the slip length was determined to be 3.2 \(\mu m\).
Figure 7: Viscosity versus Shear Rate for the Base Resin and Typical IMC with and without 2.8% Carbon Black (CB)
Chapter 3: DNA Rheology

A TA ARES rotational rheometer (TA Instruments, New Castle, Delaware) was used to determine the best fit parameters for the power law and Carreau models. Similar to the IMC test, 25 mm diameter parallel plates were rotated from $10^2$ to $10^3 \text{ s}^{-1}$, in a steady rate sweep test. The results indicate as the percentage of DNA increases, the viscosity increases. All the DNA samples demonstrated non-Newtonian shear-thinning behavior, although the buffer solution alone was measured to be Newtonian, with a viscosity 0.00107 Pa-s. This confirms that the addition of DNA makes the solution non-Newtonian, much like the trend found with IMC resins when adding carbon black as mentioned earlier.

3.1 DNA as Model Suspension for Flow Visualization

Researchers have shown that DNA can be used to understand the interplay of polymer microstructures in flow. DNA is simply a biopolymer made up of repeating units of sugars, amino acids and nucleotides (Cortright 2009). One of the unique characteristics of DNA flow visualization is the fact that DNA can be tagged by florescent dye and can be used to validate fluid dynamics models. In ultra dilute solutions the effect of flow on the polymer microstructure can be separated from the effect of the polymer microstructure on the flow. The DNA molecules experience the same stretch and relaxation caused by the velocity gradient and intramolecular forces in flow as larger polymer molecules would experience (Aoki, Hatano and Watanabe 2003).
DNA in this study is being used to evaluate the slip phenomena, experienced by polymeric and CB solutions. DNA can be tagged and each strand can be tracked in a flow field. Although DNA does not behave as CB, the slip phenomena mechanism encountered in IMC can be assumed to have similar origins. One way of more accurately modeling CB would be using origami DNA as discussed in Section 6.3. Origami DNA uses a top-down, self-assembly method of folding DNA molecules to create structures of virtually any shape or pattern. Origami DNA could model both the aggregate and agglomerate particles that make up CB in suspension.

3.2 Decreasing Concentration Rheology

Using the viscosity data from the TA ARES rotational rheometer (TA Instruments, New Castle, Delaware), parameters for the power law and Carreau models were fit for each sample. Salmon DNA (Sigma-Aldrich, St. Louis, Missouri) was dissolved in buffer solution into 2%, 1%, .5% and .25% concentrations. Each sample was tested three times with 25 mm diameter parallel plates, rotated from $10^{-2}$ to $10^{3}$ s$^{-1}$, in a steady rate sweep test at room temperature.

The average data was then compiled and the viscosity model parameters were calculated using least squares regression. The fitted power law and Carreau model lines for samples can be seen in Figure 8 and Figure 9 respectively.

Table 2 shows the power law parameters from Figure 8 and

Table 3 shows the Carreau model parameters from Figure 9. The decreasing viscosity is consistent with the pattern of the dilute suspension behaving more as a Newtonian fluid as the concentration of polymer decreases.
3.3 Slip Coefficient for Salmon DNA

The 1% salmon DNA solution was tested in the same setup as the IMC resin in Chapter 2: In-Mold Coating Rheology. The developed rheological equations in Table 1 were used to analyze the viscosity data and determine the values of slip length ($\beta$). The value of the slip length was then used to correct the wall slip in the channel and to obtain the true viscosity of the suspension, which is independent of the channel geometry. Experimental data points were plotted with the viscosities from the conventional rheometer and are shown before (a) and after slip correction (b), shown in Figure 10. The plots also show the fitted power law and Carreau lines for reference.

3.4 Apparent Slip versus Concentration Profile

With the confocal microscope studies by Emily Cortright, it was shown that a concentration distribution develops in the pressure-driven polymer flow of microchannels (Cortright 2009). The macroscopic effect of having a concentration profile across the flow channel is similar to the effect produced by the true slip. Inhomogeneous stress fields in the flow field and Brownian forces can be attributed to the causes of the decreased concentration at the walls (Aramphongphun 2006).
Table 2: Fitted Parameters for the Power Law Model

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</tbody>
</table>

Table 3: Fitted Parameters for the Carreau Model
Figure 8: Power Law Fitting for Salmon DNA Concentrations

- $y = 32.898x^{-0.934}$
- $y = 7.878x^{-0.866}$
- $y = 1.8293x^{-0.764}$
- $y = 0.2988x^{-0.611}$
Figure 9: Carreau Fitting for Salmon DNA Concentrations
Figure 10: (a) Salmon 1% Viscosity before Slip Correction. (b) Salmon 1% Viscosity after Slip Correction
Chapter 4: Modeling Flow through Thin Channels with Variable Concentration Profile

The following sections explain the calculations done assuming a concentration profile for the DNA flow. The concentration profile model and previous true slip model are compared for the flow through the microslit rheometer.

4.1 Assumptions

Several assumptions were made when deriving the concentration profile flow model. The main assumption made was that the concentration profile was independent of channel width and flow rate. The following equation was used to fit the experimentally measured concentration profile across the microchannel:

\[
C = \frac{\text{concentration} \times (m+1)}{m} \left[ 1 - \left( \frac{z}{h} \right)^m \right]
\]  

Equation 4.1 was developed empirically to make the average of the function equal to the nominal concentration of the DNA solution in the microchannel. The maximum of the function is slightly higher than the nominal concentration so the overall average of the function would be equal to nominal concentration. Figure 11 shows the Equation 4.1 concentration profile as a function of \( z \), channel height. The variables are defined as follows: \( m \) is a fitting parameter that controls the shape, \( z \) is the position in the channel and \( h \) is half the height of the channel (\( h = \frac{H}{2} \)).
The Carreau parameters were then obtained as a function of DNA concentration. The distribution of decreasing viscosity with decreasing concentration, shown in Figure 9, indicated a pattern in parameters used in the Carreau viscosity. Each of the Carreau parameters were plotted as function of concentration. Figure 12, Figure 13, Figure 14, and Figure 15 show the continuous functions for $n$, $\lambda$, $n_o$ and $n_\infty$ all as a function of concentration, respectively. The equations were then used in the Carreau model with diminishing concentration to show that the viscosity converges to that of the buffer solution, 0.00107 Pa-s, as shown in Figure 16. Equation 4.1 was used to convert the parameter equations from concentration to position. The Carreau parameters were also plotted as a function of channel height, shown in Figure 17, to verify all equations converged to realistic values.

4.2 Governing Equations

The equations for the no-slip and true slip conditions for the microslit rheometer, derived by Chuckaphun Aramphongphun by simplifying the balance of linear momentum equations and applying the boundary conditions, are summarized below in Table 4. A computer code was implemented to iteratively solve these equations with the rheological models for power law and Carreau respectively and compare them to experimental predictions.


<table>
<thead>
<tr>
<th>Boundary Condition</th>
<th>Shear Rate Equation</th>
<th>Pressure Governing Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) No Slip: (v_x(z = h) = 0)</td>
<td>(\frac{dv_x}{dz} = \left(-\frac{\Delta p}{L}\right)\frac{z}{\eta(z)})</td>
<td>(\Delta p = \frac{Q}{2whL} \int_0^h \frac{z^2}{\eta(z)} dz)</td>
</tr>
<tr>
<td>(b) True Slip: (v_z = v_x(z = h) = \beta \frac{dv_x}{dz})</td>
<td>(\frac{dv_x}{dz} = \left(-\frac{\Delta p}{L}\right)\frac{z}{\eta(z)})</td>
<td>(\Delta p = \frac{Q}{2wh} - v_z h \int_0^h \frac{z^2}{\eta(z)} dz)</td>
</tr>
</tbody>
</table>

Table 4: Boundary Conditions and Governing Equations for Analytical Viscosity Solutions

The variables are defined as follows: \(Q\) is the flow rate in m/sec; \(\Delta p\) is the pressure drop in Pa; \(w\) is the width of the channel, \(L\) is the length of the channel, \(H\) is the height of the channel, \(h\) is half the height of the channel \((h = \frac{H}{2})\), and \(\beta\) is the slip length, in meters (Aramphongphun 2006).

4.3 Software Calculation Scheme (Block Diagram)

The calculation scheme used in the computer code to solve for the viscosity and ultimately pressure drop of a non-Newtonian fluid in pressure-driven flow was similar to that developed by Emily Cortright. Modifications were made to the iteration process to also make the variables in the Carreau model parameters a function of the concentration which in itself varied as a function of the channel position. The block diagram is shown in Figure 18. The computer code is given in Appendix A and Appendix B.
4.4 Software Verification

The experimental data from Emily Cortright’s microslit rheometer tests with salmon DNA were used to compare the predicted pressure drop of various rheology models; Carreau with true slip, Carreau no slip, and Carreau with variable concentration. Due to the high viscosity of the 2% samples, these were not tested on the microslit rheometer. The remaining two samples (salmon 0.5%, and salmon 1%) were tested with three channel heights: 5 mil (127 μm), 1 mil (25.4 μm), and 0.5 mil (12.7 μm). The experimental results for salmon 1% are plotted with the predicted results in Figure 19 through Figure 21 and results for salmon .5% are plotted in Figure 22 through Figure 24.

The prediction assuming a concentration profile had similar results to the standard Carreau predictions in the 5 mil channel because the length of the concentration profile slope had less of an effect over the viscosity over the larger channel height. The concentration profile more accurately predicted the actual pressure drop in 1 mil and .5 mil channels. This is similar to the case with true slip. The slip effect is negligible for the large channel but makes considerable effect in the thinner channels.

The velocity profiles for the concentration profile and true slip assumptions were calculated and compared to single DNA tracked by Emily Cortright in the confocal microscope study, as shown in Figure 25. Both velocity calculations use the Carreau viscosity model. Both models are close to the experimental results.
Figure 11: Equation Fit to Concentration Profile of .5% Salmon DNA from Confocal Microscope
Figure 12: Continuous Function for n with Equation as a function of Concentration

\[ y = -0.123 \ln(x) + 0.1607 \]

\[ R^2 = 0.9923 \]
Figure 13: Continuous Function for $\lambda$ with Equation as a function of Concentration

$y = 5x^{-1}$

$R^2 = 1$
Figure 14: Continuous Function for $n_o$ with Equation as a function of Concentration

$$y = 34.194x^2 - 7.3742x + 3$$

$R^2 = 1$
Figure 15: Continuous Function for $n_\infty$ with Equation as a function of Concentration

\[ y = -0.0013x^2 + 0.0055x \]

\[ R^2 = 0.9604 \]
Figure 16: Decreasing Salmon DNA Concentration
Figure 17: Carreau Variables and Concentration Profile for 1mil Channel
Figure 18: Carreau Software Iteration Scheme with Variable Concentration Profile
Figure 19: Salmon 1% Experimental and Predicted Pressure Results for 5 mil Channel
Figure 20: Salmon 1% Experimental and Predicted Pressure Results for 1 mil Channel
Figure 21: Salmon 1% Experimental and Predicted Pressure Results for .5 mil Channel
Figure 22: Salmon .5% Experimental and Predicted Pressure Results for 5mil Channel
Figure 23: Salmon .5% Experimental and Predicted Pressure Results for 1mil Channel
Figure 24: Salmon .5% Experimental and Predicted Pressure Results for .5mil Channel
Figure 25: .5% Salmon DNA Velocity Profile for Concentration Profile and True Slip Calculations with Tracked DNA
Chapter 5: Conclusions

IMC is carried out by injecting a low viscosity thermosetting liquid on to the surface of an injection molded part after it has solidified, while it is still in the mold. The resin is then injected and covers the surface of the substrate once it is rigid enough to withstand the injection pressure. The coating then cures by chemical reaction and adheres to the substrate. IMC has many applications and can lower the overall cost of producing high quality polymer parts. IMC can replace external primer for thermoplastic parts. Eliminating the priming step can save money and also reduce the amount of volatile chemicals released into the environment. One drawback of using IMC is that it can complicate recycling defective parts. High appearance coating standards have driven the need to fill porosity, reduce sinks, and improve paint adhesion (Omnova Solutions Inc. n.d.). The success of IMC of SMC has led researchers to investigate the use of IMC for thermoplastics (TP) manufactured by injection molding (IM). Resin can replace external primer for TP. Reducing this external processes can save money and also reduce the amount of volatile chemicals released into the environment (Castro and Griffith 1993).

Carbon black is used as an additive in IMC resin to give conductivity to the part for subsequent electrostatic painting. As one of the main ingredients, this study has shown that the macroscopic effect on the rheology of adding CB on the base IMC resin is analogous to the addition of DNA to the buffer solution, they both display shear-thinning.
Also in this study, salmon DNA is used to make further insights into the apparent slip phenomena encountered during the coating process. Previous work has shown that a concentration distribution develops in the pressure-driven polymer flow in microchannels (Cortright 2009). The assumption can be made that this distribution is the reason that it seems as if the material slips at the wall.

Overall, it was concluded that DNA concentration profile can accurately model the pressure-driven flow through parallel plates. More research needs to be done on the link between size and shape of DNA with the accuracy of predicting the behavior of CB in suspension for IMC processes.
Chapter 6: Future Work

6.1 Changing Profile

The concentration profile approach is versatile because any profile equation can be assumed and tested. The two main steps are modeling the decreasing rheology and measuring the intensity or concentration of DNA as it flows through microchannels. From these two mathematical models any number of process variables could be assumed and tested. Apparent slip and true slip could even be tested with the same computer code. Various slip lengths and boundary conditions could be entered to solve for the overall pressure rise in the pressure-driven flow system. Further research is needed into the modeling of other DNA strands to measure the effect of chain length on the overall flow behaviors.

Further work also needs to be done on the accuracy of the concentration profile used. Many factors still need to be explored to find a profile that more closely models the distribution of DNA and or other particles in microchannels. In this study only one fitting parameter and shape was used to calculate the viscosity along the channel at different flow rates. More flow visualization studies need to be run to measure the effect of flow rate on the concentration distribution. Other microchannels also need to be tested to also more closely model the other channel heights used in the microslit rheometer tests. Larger aspect ratios would also serve to eliminate the effects of the top and the bottom of the channel.
6.2 DNA Modeling of Nanoparticles

Much advancement has been made in the addition of nanoparticles to polymer melts. Nanoparticles and macroparticles such as fillers, lubricants, pigments and stabilizers have drastic impact on the mechanical properties, processability, as well as the overall cost of the final product. Fillers can decrease the cost of the polymer while in some cases improving the mechanical properties of the final product. Additives such as lubricants and plasticizers can decrease the temperatures and pressures the polymer melt need to be processed at, reducing the cost of the final product. Pigments can also change the final color of the product. Some products that are used outside are susceptible to environmental degradation and require stabilizers to absorb UV and prevent premature degradation. Nanoparticles such as nanoclay and carbon nanotubes have been studied to reinforce the polymer matrix. Activated carbon may be used in nanofoam to aid in achieving smaller cells and increasing the strength of the material per unit mass. The main purpose of using activated carbon is to create smaller cells during foaming. Without using a nucleation site such as activated carbon, cell sizes tend to be on the micro scale. Adding activated carbon creates a nucleation site for the pockets of gas to form around, creating smaller cells. Smaller cells generally results in a more flexible and less brittle polymer product (Zeng, et al. 2003).

With using DNA as a modeling scheme for polymers and additives in polymers, many more insights could come from studying various sized DNA strands. This study only utilized salmon DNA in visualization and rheology experiments but longer, shorter and combinations of DNA in solution to model the addition of additives in polymers to study how they will distribute along the surface. The overall viscosity and phenomenon
of wall slip are important in understanding the interplay of flow and microstructures in microfluidics as a key in designing and controlling production.

6.3 Origami DNA

One innovation in DNA engineering is origami DNA. Origami DNA uses a top-down, self-assembly method of folding DNA molecules to create structures of virtually any shape or pattern. One of the main drives for patterned DNA origami is intricate ‘nanobreadboards’ for molecular biology and device physics. The scaffolded DNA origami could be used in combination with carbon nanotubes or gold particles for complex protein assembly (Rothemund 2006). These DNA structures could also be used to simulate the agglomerate structures of carbon black and other macro and nano particles in non-Newtonian flow. As stated before, DNA is unique in that it can be tagged for flow visualization studies. These studies are important in determining the flow characteristics of complex flows at the micro scale.
References


Omnova Solutions Inc. "In-Mold Coatings: We See Them Through a Molder's Eyes." *OMNOVA IMC Technology and Innovation.*


APPENDIX A: Matlab code – solver.m Function
Comments:  solver.m was used to input the desired channel height, concentration and multiple flow rates. This function calls carreau.m for multiple flow rates and outputs the array of pressure drops
*deg fixes the maximum for the different concentration profile equations so the average is always .5%
% Solver for carreau problems
clc
clear
% i=input('value for concentration:
[2 1 .5 .25] \n(1-4) \n');
i=2; %[2 1 .5 .25]
m=input('Mils: \n[5 4 1 .5] \n');
if m==5
    Q=[1 5 10 15 35 40 45 50];
    deg=.51059;
end
if m==4
    Q=[5 10 15 20];
    deg=.5129;
end
if m==1
    Q=[.1 .5 1 3 5 10];
    deg=.5558;
end
if m==.5
    Q=[.05 .1 .5 1 1.5 2];
    deg=.6255;
end
Q
sizeq=length(Q);
n=0;
%% call carreau
for y=1:sizeq
    n=n+1;
    [deltaP_new]=carreau(i,Q(y),m,deg)
    Ans(n,1)=deltaP_new/(10^6);
end
APPENDIX B: Matlab Code – Carreau.m Iteration
Comments: carreau.m function is called to solve for the pressure loss along a channel. Figure 18: Carreau Software Iteration Scheme with Variable Concentration Profile shows the algorithm for this software.

```matlab
function deltap_new = carreau(i,Q,m,deg)
%Carreau Function
% Test conditions
c=[2 1 0.5 0.25];
Q_sec=Q/(60*10^6); %m^3/s
H=m*0.0254/1000; %height of the channel (change mils to mm then micrometer to m)
h=H/2; %half the height of the channel
w=20.32/1000; %channel width (23.02mm to m)
L=63.5/1000; %channel length (63.5mm to m)
% Initial Values
etaO=[125 30 7.5 3.5]; %zero-shear-rate viscosity
etainf=[0.006 0.004 0.003 0.0009]; %infinite-shear-rate viscosity
step=1/10^8; %set divisions of height
etavaverage=(etaO(i)+etainf(i))/2; %estimate initial average viscosity
deltap0=(12*Q_sec*L*etavaverage)/(w*H^3); %initial Newtonian pressure drop
% Gamma Initial (Shear rate array to Eta Initial)
z=0;
convert=(h/step)-(670); %inflection point
d=9; %degree of profile
deg=((c(i)*(d+1))/d);
last=h/step; %last value at wall
M=deg/(convert-last); %slope of line
b=-M*last; %intersect
for j=1:(h+step)/step
    if j<convert
        C(j)=deg; %Fixes concentration until wall~1mil
    end
    if j>=convert
        C(j)=deg*(1-((j-convert+600)/(last/m))^d); %Profile at wall
        if C(j)<0
            C(j)=0; %Negative concentration is turned to zero
        end
    end
    C(j)=deg*(1-(z/h)^d); %Turns off inflection point
% C(j)=c(i); %Turns off the variable concentration
n(j)=-0.123*log(C(j)) + 0.1607;
lambda(j)= 5*C(j)^-1;
etaO(j) =20.59*C(j)^2 - 0.8636*C(j);
etainf(j)= -0.0014*C(j)^2 + 0.0055*C(j);
if n(j)==Inf
    n(j)=.999;
end
if etaO(j)<=.001
    etaO(j)=.001;
end
if etainf(j)<=.001
    etainf(j)=.001;
end
if lambda(j)>1000
    lambda(j)=1000;
end
```

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if lambda(j) == Inf
    lambda(j) = 1000;
end

gamma(j) = (deltaPO * z) / (L * etaaverage);
etainf(j) = eta(j) + eta_0(j) -
etainf(j) * (1 + ((lambda(j) * gamma(j))^2))^(n(j) - 1)/2;
z = z + step;
end

%% New DeltaP
s = length(etaold);
for k = 2:s-1
    sig1(k) = ((k * step)^2) / etaold(k);
end
sig = sum(sig1);
sum1 = (step/2) * ((h^2) / (etaold(s))) + (2 * sig);
deltaP_old = (Q_sec * L) / (2 * w * sum1);
Difference = deltaPO - deltaP_old;

%% Iteration
while abs(Difference) > 1
    z = 0;
    %% (Shear rate array to Eta)
    for j = 1:(h + step)/step
        gamma(j) = (deltaP_old * z) / (L * etaold(j));
etainew(j) = eta(j) + (eta_0(j) -
etainew(j) * (1 + ((lambda(j) * gamma(j))^2))^(n(j) - 1)/2);
z = z + step;
end
    %% DeltaP
    s = length(etaold);
    for k = 2:s-1
        sig1(k) = ((k * step)^2) / etaold(k);
    end
sig = sum(sig1);
sum1 = (step/2) * ((h^2) / (etaold(s))) + (2 * sig);
deltaP_new = (Q_sec * L) / (2 * w * sum1);
Difference = deltaP_new - deltaP_old;
etainew = etanew;
deltaP_old = deltaP_new;
end