THE EFFECT OF NON-NEWTONIAN RHEOLOGY ON GAS-ASSISTED INJECTION MOLDING PROCESS

DISSERTATION

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by

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* * * * *

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ABSTRACT

The process of less viscous fluid penetrating through viscous fluid in simple geometry has practical application in gas-assisted injection molding technology (GIM or GAIM). A Hele-Shaw cell geometry was employed to study the process of gas penetration through Newtonian, pure viscoelastic and shear thinning fluids. Hele-Shaw cells with different width to height ratio were employed in the experiment and the data of fractional coverage as function of capillary number was collapsed by considering the geometrical effect in the modified capillary number. Also the dependence of bubble stability on fluid rheology, bubble velocity and geometry was studied. The viscoelasticity tends to destabilize the finger while shear thinning has stabilizing effect. The effect of temperature gradient on the process was studied by injecting gas bubble through Newtonian fluid in capillary tube under non-isothermal condition. The final resin thickness on the tube’s inner wall is a complex function of melt rheology, mold design and processing conditions. Two specific Newtonian fluids with flow activation energies of 7324.7 K and 1090.4 K were chosen and their rheological characteristics are analyzed. Isothermal and non-isothermal experiments are performed in simple tube geometry. A coating is formed by filling the tube with a polymer and then injecting the gas through the tube. Results show that the fractional coverage passes through a maximum and then
gradually approaches the isothermal value at very long delay times. The results were explained on the basis of radial temperature and velocity profiles. The fractional coverage is found to be a strong function of fourier number and capillary number. A Frozen Layer model was set up to predict the fractional coverage as function of delay time and the calculated values agreed well with the experimental data. Three characterized highly shear thinning Carbopol water solutions were tested in gas/oil assisted injection process. The dependence of coating layer thickness on the degree of shear thinning, bubble viscosity, geometry was studied experimentally. Simulation was done based on measured bubble profiles by fixing bubble position and shape in the mesh setup and assuming full slip along the interface. The simulation method was tested based on previous experimental result.
Dedicated to my parents
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CHAPTER 1

INTRODUCTION

1.1 Motivation

The displacement of less viscous fluid in inviscid viscous fluid has practical applications in several commercial processes like flow through porous media in enhanced oil recovery, production of hollow fiber membranes, blood flow and cavitation phenomena. One importance application in polymer processing field is gas-assisted injection molding technology (GIM or GAIM).

Gas-assisted injection molding was divided into three stages: polymer injection, gas injection and mold filling complete (packing) stage (Fig 1.1). As a newly developed technology, Gas-assisted injection molding makes the production of parts with complex geometry, precise dimension, high surface quality and high strength to weight ratio possible. Additional advantages include reduction of weight and cycle times, smaller holding pressure and less clamp forces, which results in substantial material and process savings. Also the process provides higher flexibility in part design, especially for complex parts with thick and thin sections.
With the gas penetration through viscous fluid, the displacement causes instability of the interface between the two fluids, resulting in a single long bubble penetrating into the viscous fluids. The coating layer thickness of the viscous fluid left on the inner wall depends on the bubble velocity, flow geometry and the flow field property, for which temperature and fluid rheological property are the critical factors. Our study will concentrate on how these factors will affect the coating thickness and bubble shape.

With the development of computer technology, simulation was employed in the process analysis and mold design. This spares the trial and error process and saves money in making the mold, which is usually the most expensive part in GAIM. While in the current softwares which are capable of simulation on GAIM, they can not predict the wall thickness or location of the bubble accurately. It was usually assumed plug flow far in front of the bubble because free surface flow problem can be too expensive in calculation time. Commercial moldfilling software like MOLDFLOW can predict the temperature gradient under non-isothermal condition but can not evaluate its effect on the wall thickness. The model which will be discussed in Chapter IV was based on physical conditions like temperature gradient and rheological behavior of the polymer material. Thus it can be incorporated into moldfilling software, combined with the temperature gradient calculated with the software, it can give a much more accurate prediction of the wall thickness. This model can also be modified to calculate the process of gas-penetrating through non-Newtonian fluid under non-isothermal condition.
1.2 Background of bubble penetration process

1.2.1 Rheology of polymer

Newtonian fluid is an ideal viscous fluid, which is defined according to the Newtonian law of viscosity law: The shear stress developed in a steady shear flow of the material is proportional to the shear rate. The constant of proportionality is the intrinsic rheological property of the material:

\[ \eta = \frac{\dot{T}_{xy}}{\gamma}, \quad \dot{\gamma} = \frac{dv_x}{dy} \]  \hspace{1cm} (1.1)

where \( \eta \) is the shear viscosity.

While in reality the polymers often do not behave like a Newtonian fluid. Polymer material may exhibit different Non-Newtonian property between different materials or even for the same material under different processing condition. Usually polymer may have viscoelasticity, shear thinning or shear thickening effect, and be temperature sensitive. The deviation from Newtonian behavior is mainly due to the existence of large molecules in the polymer material, which, stay coiled and entangled under steady state, will stretch and be oriented under shear and extensional flows existing in any injection molding process. Temperature also has effect on the flexibility of the molecular strings, which was represented by a change in the viscosity with temperature variation. Thus for injection molding process having temperature gradient throughout the mold, the variation in temperature will also result in a Non-Newtonian effect on the coating layer thickness.
1.2.2 Bubble penetration process and key parameters

The schematic of bubble penetration process for gas-assisted injection molding was displayed in Fig 1.2 with the definition of the residual hydrodynamic coating layer thickness. Two types of geometry are employed in the study: Hele-Shaw cell (Fig 1.2) and capillary tube (Fig 1.3). Bubble width fraction $\lambda$, which is the parameter used to characterized the thickness of the coating layer, is defined as below for Hele-Shaw geometry:

$$
\lambda = \frac{W_{\text{BUBBLE}}}{W_{\text{CELL}}}
$$

where $W_{\text{BUBBLE}}$ is the width of bubble and $W_{\text{CELL}}$ is the width of the Hele-Shaw cell. Fractional coverage $m$, the parameter presenting the thickness of coating layer for capillary tube geometry, is defined as below:

$$
m = \frac{R_o^2 - R_b^2}{R_o^2}
$$

where $R_o$ is the radius of capillary tube and $R_b$ is the radius of penetrating bubble.

Another important dimensionless group is the capillary number $Ca$ which is defined as the ratio of viscous force to the interfacial surface tension force:

$$
Ca = \frac{U_b \eta}{\sigma}
$$

where $U_b$ is the bubble velocity, $\eta$ is the viscosity of the displaced fluid and $\sigma$ is the interfacial surface tension between the fluid of low and high viscosity, gas-liquid, etc.
Capillary number, shown in equation (1.4), is defined as function of viscosity. For Newtonian fluid, the viscosity will remain constant at various shear rates, which makes the calculation of capillary number very simple under different bubble penetration rates. But for Non-Newtonian fluid, of which the viscosity depends on shear rate, the viscosity will change across the flow field resulting in variation of the capillary number. Usually the shear rate was used at the wall away from the bubble to calculate capillary number and that simply corresponds to the maximum shear rate in the steady Pouiselle flow of a shear-thinning fluid. The flow field near the bubble front is too complicated to be described as a Pouiselle flow.

1.3 Research Outline

The main tasks of this object are listed below:

1) Examine the effect of elasticity and shear thinning separately on bubble width fraction and bubble finger pattern in Hele-Shaw cell under isothermal condition. Determine the influence of geometry on width fraction as well.

2) Study non-isothermal influences on bubble fractional coverage in capillary tube for a Newtonian fluid with high activation energy. Certain temperature gradients were maintained for bubble penetration process. A semi-empirical model was built to predict the change of fractional coverage with capillary number.

3) Investigate the effect of yield stress and high shear thinning on fractional coverage and bubble front shape under isothermal condition.
The proposal was divided into six Chapters. Chapter I was the introduction. Chapter II provided an overview of the works done on the penetration of a low viscosity fluid, gas, etc. through inviscid viscous fluid in different geometry and some research on the interfacial phenomena, which could be correlated to the gas penetration process.

Chapter III talked about the gas-assisted injection process in Hele-Shaw cell. The non-Newtonian fluids were characterized using different GNF models. The results of experiments were compared with theoretical prediction by Amar and Poire (1999). Selection of geometrically modified Capillary number collapsed data for each Newtonian fluid in different geometries onto single master curves. The asymptotic value of the width fraction at high modified Capillary number was different for each non-Newtonian fluid from the Newtonian results.

In Chapter IV the effect of radial temperature gradient on fractional coverage was studied. Two water baths were maintained at constant temperature. Six temperature gradients were considered in the experiments. Stainless steel tube was the flow geometry. A Newtonian fluid with high flow activation energy was tested under non-isothermal condition in gas-assisted injection process. Tube full of polymer was first immersed in on water bath, after polymer achieved a constant temperature throughout the tube, the tube was taken out and put into the other water bath. After a certain delay time, gas was injected through the tube. The experiments were carried out at very high Capillary number such that the fractional coverage should be the asymptotic value of 0.6 and any deviation from the value would be due to the temperature gradient. The fractional coverage was recorded as function of delay time. A one dimensional heat transfer model was set up and finite difference method was employed to solve the temperature profiles.
Viscosity profiles were calculated based on the temperature profiles. Frozen layer model was suggested and designed to predict the change of fractional coverage as function of delay time.

Chapter V was devoted to the study of strong shear thinning effect, tube geometry and properties of displacing fluid on the fractional coverage. Fluid other than gas was tested in the experiments. Effect of fluid properties and tube diameter on the bubble shapes were also studied using a CCD camera to record the bubble shapes under different penetration velocity in various tubes. Simulation was carried out based on the measured bubble profiles.

Chapter VI demonstrated the simulation carried out using Powerflow and Fluent regarding the gas bubble penetrating through pure viscoelastic and highly shear thinning fluid, which were the Non-Newtonian fluid used in Chapter V. The simulation technique was easy to use and the result was compared with experimentally measured flow field and good agreement was achieved.

Chapter VII was employed to describ the future work plan.
Figure 1.1: The three stages in the gas-assisted injection molding process
Figure 1.2: Schematic of gas-assisted injection molding process in Hele-Shaw cell
Figure 1.3: Schematic of gas-assisted injection molding process in capillary tube
2.1 Gas-assisted displacement of Newtonian and Non-Newtonian fluid in Hele-Shaw cell

The penetration of a single gas bubble, or 'finger', through a non-Newtonian fluid contained in a Hele-Shaw cell is a problem with practical applications in both of gas-assisted injection molding and in the polymer flooding method for enhanced oil recovery. Polymer-augmented flooding water uses an aqueous polymer solution as a driving fluid, to push viscous oil out of wells after the initial recovery has been completed. The potential for recovery using this method is often reduced by an interfacial 'viscous fingering' instability, which reduces sweep efficiencies and recoveries, Boger (1988). Gas-assisted injection molding is an innovative polymer processing operation, in which a mold is partially filled with a polymer melt, followed by injection of high-pressure nitrogen gas to fill out the mold. This two-step process results in hollow parts with reduced weight, higher strength-weight ratio, reduced frozen-in stresses, and higher surface finish quality. One drawback to this process, however, is the unwanted
protrusion, or fingering, of the nitrogen gas bubble into thin-walled sections of the part, which can cause a subsequent decrease in part strength and deduction in product quality.

This current work is directed at understanding some of the complex phenomena that occur at the gas-polymer interface, which cause this fingering. The two-step process is studied by using an inviscid gas to displace viscous and viscoelastic fluids contained in a Hele-Shaw flow cell.

Some of the first studies of the instability of a liquid surface were performed by Taylor (1950), who looked at the instabilities that can develop when an initial disturbed interface between two fluids is accelerated in a direction perpendicular to the interface. Lewis (1950) designed an apparatus to accelerate various fluids at rates on the order of 50 times the acceleration of gravity and discovered that as the interface disturbance progresses, it begins to take the form of large round-ended columns of penetrating fluid.

Saffman and Taylor (1958) made use of the Hele-Shaw analog developed in 1898. This analog states that the penetration of a fluid into a porous media is mathematically equivalent to the motion of a viscous fluid between two parallel plates separated by a very small gap, which corresponds to the experimental setup in our study. Experimental studies led to the discovery of the dependence of finger shape and fractional coverage of finger on the capillary number Ca, which represents the ratio of viscous to surface tension forces in the flow. For Newtonian fluids, the finger width fraction as a function of capillary number resulted in a single master curve. Pitts (1980) offered a theoretical account of the previous work and developed a theory to improve the agreement between
the experimental results and theory presented by Saffman and Taylor. McLean and Saffman (1981), in a similar work, attempted to resolve the indeterminacy of the growth of the Saffman-Taylor finger by introducing surface tension effects into the boundary conditions of the two-phase interface. Park and Homsy (1985) performed experiments on a single finger to investigate this proposed capillary number scaling, which was termed $Ca'$, the modified capillary number. The researchers performed their own experiments as well as replotted the original work of Saffman and Taylor (1950) based on the modified capillary number. The data from both research groups collapsed onto a single curve, which became the basis for concluding that the proposed scaling of McLean and Saffman was indeed correct. In addition, Park and Homsy (1985) discovered that when the modified capillary numbers exceeds 100 for a Newtonian fluid, the predominant finger undergoes a periodic tip splitting phenomena. The tip splitting pattern becomes more complex and loses its periodicity as the modified capillary number increases. Some more detailed theoretical and experimental studies of this hydrodynamic finger instability included works done by Saffman and Taylor (1959), Park et. al.(1984), and Saffman (1986).

Later the two-phase Hele-Shaw flow was studied theoretically and experimentally in both longitude and thickness directions by Homsy's group. Using a double asymptotic expansion technique in the theoretical study by Park and Homsy (1984), and by taking pictures of the air bubble pushing its way through the displaced fluid (i.e., viscous oil) in the experimental study by Park et. al. (1984), the theory and experiments agreed well with each other within the measurements accuracy. Spaid and Homsy (1994), (1996) and
(1997) also studied rivulet instabilities in centrifugal spin coating of viscous Newtonian and non-Newtonian fluids. The spreading dynamics of a viscous thin liquid film on a solid plate involves three types of interfaces between a solid, the air and a liquid. The effects of elasticity on a spinning drop were studied theoretically and experimentally.

Other works utilizing non-Newtonian fluids were performed in radial Hele-Shaw cells to eliminate the complicating effect of wall boundaries. Daccord et. al. (1986) found that the fingering pattern only grows through consecutive splitting of the leading tips, with no growth in the interior of the pattern. Allen and Boger (1988) used combinations of Newtonian and non-Newtonian fluids as both the pusher and displaced fluids in their investigation of the viscous fingering that occurs in a radial flow cell. Shear thinning and ideal elastic Boger fluids were studied, with the shear thinning fluid producing a more highly branched fingering pattern. The effect of shear-thinning on the fingering pattern was also studied theoretically and experimentally. Kondic et. al. (1996) and (1998) generalized Darcy's Law by using the shear-thinning fluid model, with the result being a nonlinear boundary value problem. Simulations were performed and the shear-thinning effect was found to have a stabilizing effect on the tip splitting in radial Hele-Shaw flow. Amar and Poire(1999) solved the Saffman-Taylor instability problem theoretically for weak shear-thinning fluid and predicted that the finger width would decrease towards zero as the bubble velocity increased. Their results were used as a theoretical background for comparing over the experimental results.

By using various dilutions of a shear thinning polymer solution, Lindner et. al. (2000) studied the shear thinning effect on the Hele-Shaw flow. The degree of shear
thinning was changed by changing the concentration of the solution. Good agreement between experimental results and theoretical prediction was found for weak shear thinning fluids. In the work of Greffier et. al. (1998) on needle formation, the needle widths were observed to decrease towards zero under a rapidly increasing tip velocity. Vlad et. al. (1999) studied the finger dynamics and determined that a jump in finger velocity, which characterizes the flow discontinuity, was correlated with the non-Newtonian property of a displaced fluid.

The effect of geometry on viscous fingering patterns was considered. Zhang et. al. (1998) carried out the stability analysis for the Hele-Shaw cell geometry with lifting plates. The dependence of viscous fingering on anisotropy in a linear Hele-Shaw cell was studied by Kawaguchi (1999). Grillet et. al. (1999) studied the flow instabilities of recirculation flows in eccentric cylinder geometry and compared the results for Newtonian and Boger fluids.

Some of the work examining non-Newtonian fluids involves the use of a pusher fluid that is miscible with a high viscosity fluid. Nittmann et. al. (1985) used water to displace high viscosity polysaccharide solutions of differing concentrations while van Damme et. al. (1987) and (1988) injected water into a colloidal suspension of clay particles. The use of miscible fluids creates a system with a surface tension close to zero and a capillary number approaching infinity. This results in a highly branched fractal fingering pattern. In Wit and Homsy's work (1999), diffusion and chemical reaction were considered as part of the process. New mechanisms of finger propagation were identified and studied in details. Zimmerman and Homsy (1992) carried out simulations in 2-D by Tan and Homsy (1992) and 3-D.
The goal of our work is to determine the effects of polymer rheology on a single finger of gas penetrating through a Hele-Shaw cell filled with non-Newtonian fluids. Three fluids were specifically designed to allow isolation of the specific rheology of Newtonian, elastic, or shear thinning behavior, so as to determine their individual effects on the gas bubble dynamics. The measured parameters were the width fraction of the bubble and the degree of tip splitting, as functions of the fluid rheology, modified capillary number, surface tension parameter, Deborah Number, and cell geometry.

2.2 Gas-assisted displacement of Newtonian and Non-Newtonian fluid in capillary tube

The problem of gas bubble penetrating through viscous fluid in capillary tube is a type of problem that is important in understanding the process of gas-assisted injection molding. It was first studied experimentally by Fairbrother and Stubbs (1935). The purpose of their study was to determine the relation between the bubble penetration velocity and the liquid flow rate. They arrived at an empirical relation between the capillary number and fractional coverage for Newtonian fluid, \( m = 1.0 \ (Ca)^{1/2} \), which predicted that the fractional coverage will go to infinity with increase of capillary number. It is obvious that there is discrepancy between this empirical prediction and real experimental result at high capillary number.

In Taylor's work (1961), he studied the problem in more detail by carrying out experiments in which four viscous Newtonian fluids were penetrated through by gas bubble in three capillary tubes of different diameters. The coating thickness of Newtonian fluid vs. capillary number is plotted and found to collapse onto a single curve regardless
tube diameter and fluid viscosity. The result is compared with that of Fairbrother and Stubbs. They fits well with each other up to Ca = 0.09, while from Taylor's results, the fractional coverage m increased to an upper limit of 0.56 at high Ca value instead of infinity superposed by Fairbrother and Stubbs. Taylor also suggested two types of streamlines patterns in the flow field near the bubble front tip. When fractional coverage is smaller than 0.5, a reverse flow may occur in front of the bubble tip, while for fractional coverage greater than 0.5, a complete by-pass flow may be developed.

A theoretical solution was first provided by Bretherton (1961) to predict the process of bubble penetration through Newtonian fluid within the range of Ca < 10⁻³. Experiments using Newtonian viscous fluid were also conducted at capillary ranging from 10⁻⁷ to 10⁻². The cases of bubble moving in horizontal and vertical capillary tube were considered. A method of matched asymptotic expansion was employed to carry out the theoretical analysis. The theoretical analysis employed a perturbation model and the result fit comparatively well at higher end of capillary number region while the agreement at the low end is poor. Without an accurate explanation of the discrepancy, Bretherton suggested the possible reason to be the hardening of the free surface of the penetrating gas bubble caused by dissolved impurities or surface charges. The final conclusion is that the fractional coverage is uniquely determined by the conditions at the bubble front. Bretherton provided the first theoretical analysis of fractional coverage at low capillary number.

The problem of bubble penetrating through Newtonian fluid under gravitational effect was studied by Goldsmith and Mason (1962), visual studies of the bubble shape
and flow field of bubble front were first carried out in their work. By directly observing
the bubble penetration through a microscope traveling along with the bubble and
measuring the coating layer thickness via use of a calibrated micrometer eyepiece, flow
patterns in gas and liquid phases and the shape of bubble tip were determined. The
velocity profile was obtained through introduction of aluminium tracer particle in the
appropriate phase and by taking cine films through the microscope during the bubble
penetration. The capillary number region is between $10^{-4}$ and $10^{-2}$. A theory was
suggested and tested with the experimental observation, and quantitative agreement was
achieved in the velocity profile in film and bubble shape. The bubble end was found to be
semi-spherical and the deformation of the bubble was independent of the bubble rate and
viscosity of the displaced fluid under a fixed interfacial surface tension. The film
thickness was constant from the leading to the trailing edge of bubble. Internal circulation
was observed with the transmission of shear stress throughout the interface indicated by
the measured velocity profile.

Cox (1962), extended Taylor's work by employing carbon tetrachloride bubble as
the displacing fluid instead of gas. The asymptotic value of $m$ at high $Ca$ is found to be
around 0.6, larger than that of Taylor's results. One important aspect pointed out by Cox
is that the bubble will achieve stable after it travels just the distance of one half of tube
diameter. A simplified theoretical analysis was shown to test his experimental results by
neglecting inertia and gravity. Excellent agreement was achieved, justifying Cox's
conclusion that the dynamic surface tension effects can be neglected, which indicates
static interfacial surface tension can be employed to calculated capillary number In his
later work. Cox (1964) extended his earlier experiments with the addition of photographic equipment and aluminum tracer particles to record the flow field patterns. He observed that the flow at about one and half diameters away from the bubble tip obeyed Hagen-Poiseuille’s law and the effect of the bubble penetration was very local. Because showed in the images that the streamlines are well undisturbed except those in the core of the fluid defined by the bubble radius and are located very near the bubble tip. Instead of two cases suggested by Taylor (1961), Cox found three stages of streamlines evolution. When the fractional coverage is smaller than 0.5, a distinct reverse flow occurred in the tube center. For fractional coverage above 0.5, the only possible streamline pattern was found to be complete by pass flow with no circulation near the bubble, which justified Taylor's suggestion. As fractional coverage is near 0.5, the streamlines are similar to the case of fractional coverage greater than 0.5 except there is a stagnation line in the tube center in front of bubble.

Schwartz et al. (1986) pointed out that Bretherton's result is more suitable for bubble having length less than 20 tube radius and extend the analysis to the case of long bubble penetrating through viscous fluid experimentally and theoretically. Schwartz's approach to experimental study was similar to Bretherton's method except the variation in displacing fluid, bubble formation and the variable used to describe the bubble. Other factors like finite viscosity ratio between the two inviscid fluids were also considered in his work. The capillary number ranging from $10^{-6}$ to $10^{-3}$ in the experiments. Bubbles of different lengths were tested and the results obtained with sufficient short bubbles agree well with the prediction of lubrication model, while the results for long bubbles are different from those of short bubbles. As the bubbles lengths are large enough, the
fractional coverage was found to be totally independent of bubble length, which is very important because the bubbles in our experiments are of half indefinite length.

Relnelt (1987) calculated the problem of bubble penetrating through Newtonian fluid in vertical tube numerically. The capillary number range of the solution is $10^{-4} < Ca < 10^{-1}$. The effect of gravity was studied via Bond number, which is defined as the ratio of gravitational force to the interfacial surface tension. An iterative method was used to calculate the fractional coverage at certain capillary number. His results were compared with the perturbation results of Bretherton (1961) and they agree with other well at small values of Ca except for the region where capillary number approaches zero.

Ratulowski (1989) studied bubbles in circular and square capillary tubes and extended Bertherton's result to higher Ca value by introducing an 'arclength-angle formulation of a composite lubrication equation'. This makes possible the matching of numerical solution using lubrication theory at transition flow region to the static region away from the inner wall of tube. Bubbles of both infinite and finite length, which exceed the tube diameter, were calculated numerically.

Shen and Udell (1985) did simulation of the process of stable bubble penetrating through inviscid fluid. A cylindrical tube was used as the geometry. By neglecting the bubble viscosity, inertial force and gravitational force, finite element was employed to describe the flow field and the shape of the bubble. The method works well in predicting the flow field, bubble shape etc., also both of them were found strongly dependent on Capillary number. The effective Ca range is $5 \times 10^{-3}$ to $2 \times 10^{-1}$. Martinez and Udell
(1989) used boundary integral analysis to determine the dependence of bubble shape, flow field pattern etc. on capillary number. The well predicted range of Ca is for Ca < 0.1.

Camp et al. (1990) measured velocity profiles for Newtonian fluid flowing in a tube with square cross section. A microcomputer-based image analysis system was used to record and analyze the tracer particles' velocity profile in the flow field. The velocity profiles were obtained by using a particle image velocimetry (PTV) technology in frame analysis of the taken images. The theoretically predicted velocity profiles in a square channel agree with the experimental results pretty good.

Kolb and Cerro (1991) carried out three dimensional flow visualization experiments for Newtonian fluid flowing in square cross section tube using PTV technology. The capillary number ranges from $10^{-2}$ to 10. With non-axis-symmetric tube cross section, the bubble radius was observed to approach circular gradually. The streamlines predicted by Taylor (1962) and Cox (1962) was found in the experiment. The fractional coverage is greater than results using capillary tube with circular cross section and approach an asymptotic value of 0.64 with the increase of capillary number.

Fong and De Kee (1994) studied the effect of interfacial tension gradient on bubble shape penetrating through viscoelastic fluid. The surface tension gradient was achieved by applying temperature gradient across the tube. The bubble shape was found independent of surface tension gradient. But for viscoelastic fluid, distortion of the bubble occurred due to the surface tension gradient. While neglecting the change of viscosity, density et al. with temperature, theoretical analysis was compared with
experimental result and due to the absence of variation of certain factors, no quantitative agreement was achieved. The surface gradient may have effect on the bubble penetration velocity for small bubbles.

Poslinski (1995) carried out experiments of gas bubble penetrating through Non-Newtonian fluid in capillary tube. Viscoelastic liquids like silicon pastes were used as displaced liquid, which has both of yield stress and shear thinning effects. The experiments were conducted in Newtonian regime of the material rheology property. The tube was first partially filled at first, which allowed the gas bubble to accelerate downstream. At high capillary number, the asymptotic limit of coating thickness is the same as that of Newtonian fluid. While in low capillary number regime, the coating thickness is much thinner than that of the Newtonian fluid. An isothermal model was proposed and combined with a one-dimensional heat-transfer analysis to simulate the process of gas-assisted injection molding. It was found that due to the lack of considering the effect of molten plastic deposited on the mold surface, which is the cold part, the simulation always tends to underestimate the coating thickness.

Huzyak and Koelling (1997) are the first to isolate the effect of elasticity on the fractional coverage of viscous fluid left on the tube inner surface after penetrated through by a long gas bubble. Four types of fluids, two Newtonian and two highly viscoelastic fluids of constant shear viscosity, were used in the experiments. Tubes of different diameters were used to check the effect of geometry on the results. Fractional coverage \( m \) was plotted vs. capillary number for each fluid. Deborah number \( De \) was used to characterized the extent of elasticity. For Newtonian fluid, the plots of fractional
coverage m vs. capillary number Ca were found to collapsed onto a master curve regardless of the tube diameters used. But for viscoelastic fluid, the plots were found to be dependent on the tube diameters and capillary number can no longer collapse the data onto a single curve. As De increases, the fractional coverage for viscoelastic fluid becomes bigger than that of Newtonian fluid at the same capillary number. Finally, The fractional coverage data obtained at different tube diameters can be collapsed onto a single curve by plotting them versus De.

More detailed study of long bubbles penetrating through viscoelastic material in capillary tubes was carried out by Gauri and Koelling (1999). Three tailored ideal elastic fluids, designed to present different viscoelastic functions while holding similar steady shear rheology characters, were used in the experiments. This achieved the object of isolating elasticity and extensional property and checks their effects on the flow field and fractional coverage respectively. Tubes with different diameters were used to check the effect of De on the flow. PTV was used to analyze the flow field near the bubble front. The results show that at the same capillary number, the fractional coverage increases with the increase of elasticity, and as the tube diameter increases, the fractional coverage decreases. De can be used to approximately collapse the data for the same fluid in different tubes or for the three kinds of fluids in the same tube. Giesekus constitutive formula was used to calculate De. From the results of flow visualization experiments, it was found that near the interface, high extensional rates exist. At similar strain rates, fluids with different extensional properties display different fractional coverage values. So he concluded that the extensional rheology is the primary reason for the increment of fractional coverage for different Boger fluids.
Using FEM method, Poslinski and Coyle (1994) carried out numerical simulations of the bubble penetrating through pure shear thinning fluid. A Cross-type generalized Newtonian fluid model including an upper Newtonian region was used. The asymptotic value of fractional coverage at high Ca is found be smaller than that of Newtonian fluid. An overshooting of the fractional coverage was found, followed by a decreasing till under the value of Newtonian results. Numerically simulated shapes of the bubbles were presented too.

Poslinski and Coyle (1997) extended the problem to gas penetration through pseudoplastic and viscoplastic liquids. Axisymmetric and planar geometries were used for the analysis. The process was assumed isothermal. Coyle (1984) developed the finite element procedure employed in this procedure for roll coating process. In conclusion, the factional coverage result of Newtonian fluid is the upper limit for all the Non-Newtonian fluids. The fractional coverage for the Non-Newtonian fluids may go to maximum and minimum values when the parameters characterizing the rheology are in certain range. Flow fields show more complexity than previously assumed. Their predictions of the fractional coverage and bubble shape for Non-Newtonian fluids were used as the theoretical background in our work.

Thermal force was used to drive the bubble through the viscous fluid in cylindrical capillary tubes by Homsy (2000). By imposing constant temperature gradient on the wall of the tube, the bubble moved from cold to hot side. The bubble is of finite length and constant film thickness was formed in the regime bounded by the two end caps of constant curvature.
Our work on flow in capillary tubes is divided into two parts. First three well-characterized pure shear thinning fluids were used to study the effect of rheology on the coating thickness and the bubble shapes experimentally. Tubes of three diameters were employed to study the effect of geometry on the process, especially when combined with Non-Newtonian rheology properties. Two types of displacing fluids were tested to study the difference may exist due to variation of rheological properties of penetration bubble. The simulation result of Poslinski (1997) was used for comparison in this paper. For the second part, temperature gradient was imposed on the tube in cross section direction. Newtonian fluid with high activation energy, which means the fluid is highly temperature sensitive, was used as displaced fluid with gas bubble penetrating through it. Experiments were carried out at high capillary number region and fractional coverage was measured with the record of bubble penetration velocity. A frozen model was proposed and fractional coverage was calculated using this model. Qualitative agreement was achieved.
CHAPTER 3

INFLUENCES OF ELASTICITY AND SHEAR THINNING EFFECTS ON GAS PENETRATION THROUGH VISCOUS FLUID IN HELE-SHAW CELL

J. D. Ackerman, who used to be a graduate student in my group, did the fluid design and all the experiments. My work in this chapter will focus on the analysis of the experimental data.

3.1 Experimental Apparatus and Technique

Fig 3.1 was the schematic of the Hele-Shaw cell used for this work. The base plate was a 27.94 cm x 109.22 cm aluminum plate with a thickness of 1.905 cm. The Hele-Shaw cell was formed by sandwiching together the base plate and a glass top plate of dimensions 20.32 cm x 101.6 cm x 1.27 cm, with an aluminum bar bracing system bolted at 12.7 cm intervals. An inlet tube, approximately 1 cm in diameter, was placed at the end of the plate and connected into a 1.27 cm deep, 15.24 cm (0.5x6 in) long channel machined into the top surface of the base plate. A neoprene rubber gasket of either 0.08 or 0.16 cm in thickness between the glass plate and the aluminum base was used to
control the thickness of the Hele-Shaw cell. The gasket lined three sides of the glass plate, while the fourth side was left open to the atmosphere. The width of the cell was also varied at 2.54, 5.08, and 15.24 cm by using different widths of the rubber gasket lining. Fig 3.2 showed the cross section of the four Hele-Shaw flow cells used in this study.

A Harvard Apparatus syringe pump (model 55-2083) was connected to the Hele-Shaw cell via stainless steel tubing. The syringe pump was used to fill the cell with the test fluid prior to each experiment. Since bubbles trapped in the fluid affect the developing flow pattern, care was taken to remove all of the trapped air bubbles resulting from the filling process before performing any experiments. Tilting the cell during and after filling allowed the buoyant force to carry the bubbles out the open end of the cell. Tilting also allowed a flat interface to be established between the test fluid and the driving fluid (air) present in the cell.

After filling the cell with a test fluid, the syringe pump was used to draw the fluid out of the cell at a specific volumetric flow rate between 0.4 and 4 cm³/sec. Since one end of the cell was open to the atmosphere, pulling fluid out of the closed end of the cell with the syringe pump was analogous to using air to push fluid out of the cell. Using the pump for fluid removal allowed for a constant volumetric flow rate of fluid out of the cell, to maintain a nearly constant average bubble velocity.

For convenient analysis of the results, a photographic technique was employed. A 35mm camera loaded with either Kodak technical pan or Kodak TMAX100 film was mounted approximately six feet above the apparatus. The camera was used to capture images of the predominant finger as it developed. The photographs were used to calculate
both width fraction of the bubble and the velocity of the advancing tip. The photographs were taken at known times so the velocity could be determined by calculating the distance the bubble tip progressed between subsequent pictures, then dividing by the time interval between pictures. The slides made from the pictures of the bubble growth were used in two ways to determine the width fraction of the bubbles. For stable bubbles, a direct measure of the bubble width with respect to the cell width was sufficient for the calculation. For complex, unstable bubbles, the fractional coverage was calculated by measuring the ratio of the bubble area to the total cell area.

3.2 Fluid characterization

The test fluids, shear and dynamic viscosities were measured using a Rheometrics Fluids Spectrometer, RFS II. Viscosities were measured with a 34mm-diameter Couette tool with a bob length of 32mm in a 34mm diameter cup, as well as a 50mm-diameter parallel plate system. Shear rate sweeps were performed to determine the dependence of viscosity on the shear rate for each fluid, at temperatures ranging from 10 to 30 °C. Dynamic frequency sweeps were performed within the same temperature range to determine the storage and loss moduli for each fluid, the dynamic viscosities, and the elastic material function. The resulting data was shifted to a reference temperature of 25 °C using time-temperature superposition as outlined in Quinzanni et. al. (1990). The shift was based on Equation 16 and discussed later. The interfacial surface tensions were measured using a CAHN dynamic contact analyzer, DCA 322, by the Wilhemy plate technique. Table 3.1 includes the surface tension data for all the testing fluids.

The first fluid tested was an 80-weight percent glycerin/water solution, which exhibits Newtonian rheology. The fluid was used both to validate the experimental
technique and the apparatus by comparing our results to those obtained by previous researchers. It was also used to create a basis of comparison for future tests using non-Newtonian fluids.

The second test fluid used was an ideal elastic Boger fluid. This type of fluid exhibits elastic properties while maintaining a Newtonian shear dependence, which allows the elastic properties to be isolated. This particular Boger fluid was created by adding 0.244 wt% high molecular weight polyisobutylene or PIB (Aldrich $M_w=4.7\times10^6$ g/mol), to a 7 wt% hydrocarbon solvent (K-1 kerosene)-93 wt% polybutene (Amoco Indopol L-65 Polybutene, $M_w=435$ g/mol) solution. The Giesekus model was introduced to characterize the elastic fluid.

The third test fluid was designed to exhibit both shear thinning and elasticity. The fluid consisted of 1 wt% PIB (Fisher $M_w=4.7\times10^6$ g/mol) and 99 wt% Decalin (Fluka). By using this type of fluid, shear-thinning effects could be isolated, as compared to results from other fluids. For convenience, this type of fluid was defined as a shear-thinning fluid. The shear viscosity behavior for this fluid was fit to four rheological models: Giesekus, the power law, the modified Ellis and the Carreau models, for ease in analyzing results. The fit of the Giesekus model for the shear thinning fluid was compared to the result for the elastic fluid.

To show the difference of elasticity of the two fluids, the four models were described as following equations in section 3.2.1 to 3.2.2.
3.2.1 Giesekus model

The basic equations for Giesekus Model in multi-mode form are:

\[ \tau = \tau_s + \sum_{i=1}^{n} \tau_i \]  
(3.1)

\[ \tau_s = -\eta_s \dot{\gamma} \]  
(3.2)

\[ \tau_i + \lambda_i \tau_i - \alpha_i \frac{\lambda_i}{\eta_i} \{ \tau_i \cdot \tau_i \} = -\eta_i \dot{\gamma} \]  
(3.3)

(a) For small amplitude oscillatory shear flow, the Giesekus model reduces to linear viscoelastic behavior, the dynamic viscosity \( \eta' \), and the elastic part of the complex viscosity \( \eta'' \), can be determined as follows:

\[ \eta' = \eta_s + \sum_{i=1}^{N} \frac{\eta_i}{1 + (\lambda_i \omega)^2} \]  
(3.4)

\[ \eta'' = \sum_{i=1}^{N} \frac{\eta_i \lambda_i \omega}{1 + (\lambda_i \omega)^2} \]  
(3.5)

Thus by fitting the experimental data to equations above, relaxation times can be determined for both of the fluids. The fitting results of 1 mode and 4 mode models for the Boger fluid were shown in Fig 3.3, and for the shear thinning fluid were shown in Fig 3.4. The difference in elasticity between the Boger and shear thinning fluids were shown in Fig 3.5.

(b) For shear flow, the analytical solutions in steady state are (Bird, Armstrong, Hassager, 1987):

\[ \tau_{yx,i} = \eta_i \dot{\gamma}_{yx} \left( \frac{(1-f_i)^2}{1 + (1-2\alpha_i)f_i^2} \right) \]  
(3.6)
\[
\tau_{xx,j} = \frac{\eta_i f_i}{\lambda_i} \left(1 - 2 \frac{1 - \alpha_i f_i}{\alpha_i (1 - f_i)}\right)
\]

(3.7)

\[
\tau_{yy,j} = \frac{\eta_i f_i}{\lambda_i} ; \quad \tau_{zz,j} = 0
\]

(3.8)

Where:

\[
f_i = \frac{1 - \chi_i}{1 + (1 - 2\alpha_i)\chi_i}
\]

(3.9)

\[
\chi_i = \sqrt{\frac{1 + 16\alpha_i (1 - \alpha_i)(\dot{\gamma}_{yx}\lambda_i)^2}{8\alpha_i (1 - \alpha_i)(\dot{\gamma}_{yx}\lambda_i)^2}} - 1
\]

(3.10)

So below are the expressions for viscosity and normal stress coefficient:

\[
\eta = \eta_k + \eta_i \left(\frac{(1 - f_i)^2}{1 + (1 - 2\alpha_i)f_i}\right)
\]

(3.11)

\[
\Psi_1 = \sum_k \frac{2\eta_i f_i (1 - \alpha_i f_i)}{\lambda_i \dot{\gamma}^2 \alpha_i (1 - f_i)}
\]

(3.12)

The fitting results of the normal stress coefficient \(\Psi_1\) and the shear viscosity \(\eta\) using the 1-mode and 4-modes Giesekus model for Boger fluid were shown in Fig 3.6. The fitting results of the shear viscosity \(\eta\) using 1-mode and 4-modes Giesekus model for shear thinning fluid were shown in Fig 3.7. The parameters for 1 and 4-mode models were shown in Table 3.2-1, 3.2-2.

3.2.2 The Power Law, Ellis and Carreau Models

The power law model equation expresses the dependence of viscosity on the shear rate. The general equation is of the form:

\[
\eta = m \dot{\gamma}^{n-1}
\]

(3.13)
The Ellis model equation expresses the viscosity of the fluid in terms of the magnitude of the shear stress in the flow. The general equation is of the form:

\[
\frac{\eta_0}{\eta(\tau)} = 1 + \left( \frac{\tau}{\tau_{1/2}} \right)^{\alpha-1}
\]

Where \( \eta(\tau) \) is the shear stress dependent viscosity, \( \eta_0 \) is the zero shear viscosity, \( \tau_{1/2} \) is the shear stress value at which the viscosity is half of its zero shear value, and \( \alpha - 1 \) is the slope of the curve \( \log(\eta_0/\eta) \) versus \( \log(\tau/\tau_{1/2}) \) (Tadmor and Gogos, (1979)).

The Carreau model predicts the viscosity in terms of the shear rate in the flow field such that:

\[
\frac{\eta(\dot{\gamma}) - \eta_\infty}{\eta_0 - \eta_\infty} = \left[ 1 + \left( \frac{\dot{\gamma}}{\lambda} \right)^2 \right]^{\frac{n-1}{2}}
\]

Where \( \eta_0 \) is again the zero shear viscosity, \( n \) is the shear thinning exponent, \( \lambda \) is the inverse of shear rate at which the viscosity begins to deviate from Newtonian behavior, and \( \eta_\infty \) is the infinite-shear-rate viscosity. The fitting results were shown in Table 3.3.

Fig 3.8 showed the shear viscosity as a function of shear rate for the three fluids. At a very low shear rate approaching zero, the two non-Newtonian fluids exhibited very similar shear viscosities, and their values were about one order of magnitude higher than the Newtonian fluid. The graph showed that both the Newtonian and Boger fluids maintained a constant viscosity, regardless of the shear rate. In contrast, the shear
thinning fluid began to shear thin at a shear rate of approximately 1 s\(^{-1}\). Model fitting of the four-mode Giesekus model to the Boger and Shear thinning fluids were also shown in Fig 3.8.

From Fig 3.5, it was observed that a significant deviation for \(2\eta''/\omega\) at low frequency but at dynamic frequencies larger than 1 s\(^{-1}\), the two materials exhibited a very similar behavior. It is possible to surmise, in light of these two figures, that at deformation rates higher than 1 s\(^{-1}\), the major difference between the two fluids was the shear rate dependence of viscosity.

### 3.3 Width Fraction Experiments

The goal of these experiments was to determine the effects of Newtonian, elastic, and shear thinning behavior on the gas bubble distribution. Fig 3.9 showed the schematic of a typical experiment highlighting the relevant dimensions needed in the analysis of the results.

The measured parameter in these experiments was the bubble width fraction, \(\lambda\), which was defined as:

\[
\lambda = \frac{W_{\text{BUBBLE}}}{W_{\text{CELL}}} \quad (3.16)
\]

where \(\lambda\) is the fraction of the cell width swept out by the penetrating bubble. The bubble width was measured as a function of the capillary number \(\text{Ca}\), which represented the ratio of viscous forces to surface tension forces in the flow field:

\[
\text{Ca} = \frac{U_b \eta(\dot{\gamma}_w)}{\sigma} \quad (3.17)
\]
Where $UB$ is the penetrating bubble velocity, $\eta(\gamma_w)$ is the shear rate dependent viscosity of the fluid, $\gamma_w$ is the shear rate at the wall of the Hele-Shaw cell, and $\sigma$ is the interfacial surface tension. The shear dependent viscosity was used in order to quantify the shear thinning effect of the fluids used in the experiments. The shear rate at the wall was chosen as a representative shear rate. The modified capillary number, $Ca'$, is the capillary number multiplied by a cell geometry factor such that:

$$Ca' = \left( \frac{UB \eta(\gamma_w)}{\sigma} \right) \left( \frac{a}{b} \right)^2$$  \hspace{1cm} (3.18)

Where $a = W_{CELL}/2$ and $b$ is the thickness of the Hele-Shaw cell (Park & Homsy, 1985).

Fig 3.1b showed the cross sectional flow area for each cell geometry, including the corresponding $a/b$ values, used in this study.

To compare the experimental result of shear thinning fluid with theoretical prediction, another parameter $k$ was introduced, which is the ratio of surface tension force to the viscous force

$$k = \frac{\sigma b^2 \pi^2}{12\mu_0 U_B^n (1-\lambda)^2 \Omega_0/\lambda}$$  \hspace{1cm} (3.19)

Where $\Omega_0 = (U\lambda)^{1-n/2}$. The relation between $k$, $Ca'$ and bubble velocity $UB$ is shown in Fig 3.16.

In cases where the shear viscosity of the fluid remained constant, the modified capillary number depended only on the bubble velocity and was relatively simple to calculate using Equation 6, since all the terms were constant except for the bubble velocity. For a shear thinning fluid, the viscosity was dependent on the shear rate in the flow field, which made the modified capillary number dependent on both shear rate and
the bubble velocity. Tadmor and Gogos (1979), by integrating the equations of motion for pressure flow of an Ellis fluid through a slit, obtained expressions for volumetric flow and shear rate at the wall such that:

\[
Q = \frac{W_{\text{CELL}} b^3 \Delta P}{12 \eta_0 L} \left[ 1 + \left( \frac{3}{2 + \alpha} \right) \left( \frac{b \Delta \Delta}{2 L \tau_{1/2}} \right)^{a-1} \right]
\]  

(3.20)

\[
\gamma_w = \frac{b \Delta P}{2 \eta_0 L} \left[ 1 + \left( \frac{b \Delta \Delta}{2 \tau_{1/2} L} \right)^{a-1} \right]
\]  

(3.21)

Where \(Q\) is the volumetric flow rate, \(W_{\text{CELL}}\) is the width of the cell, \(\Delta P\) is the pressure drop along the length of the cell, and \(\eta_0, \alpha, \) and \(\tau_{1/2}\) are Ellis model constants. Equations 3.23 and 3.24 were combined to yield an equation for calculating the wall shear rate based only on the fluid model parameters, cell geometry, and volumetric flow-rate of the fluid. This shear rate was then used in the calculations of \(C_a'\) and \(D_e\).

3.4 Results and Discussion

3.4.1 Width Fraction Results of Newtonian, Boger and Shear thinning fluids

Fig 3.10 showed the results of experiments using air to displace a Newtonian fluid in which fractional coverage was plotted vs. modified capillary number. The tests were performed in several different geometries ranging in size from \(a/b = 16\) to \(a/b = 96\). In Fig 3.11 width fraction was plotted as function of \(k\) to test Amar and Poire's prediction of Newtonian fluid (Power Law index \(n = 0\)). The two graphs both have different stages of bubble marked as function of \(C_a'\) and \(k\). In Fig 3.10 the results of width fraction of the finger as function of modified capillary number will collapse into a single curve. The data were compared with those from two previous research groups, Saffman and Taylor (1958) and Park and Homsy (1985) to test the correctness of the experimental setup and
they agreed very well with each other. In Fig 3.11, similar to Fig 3.10, the data approximately collapsed onto a master curve. But because the plot was in the range of low bubble velocity, for which gravity and surface tension play important roles in the process, the data from different geometry shifted a small amount from each other. The theoretical prediction made by Amar and Poire agreed with the experimental data pretty well when the geometry (a/b = 96) approximated the assumption of 2-D phenomena of Hele-Shaw flow best.

The fractional coverage as function of modified capillary number for Boger and shear-thinning fluids were plotted and were found to collapse onto single curves for each fluid.

Fig 3.12 included plots of width fraction as function of modified capillary number for air penetrating through the Newtonian, Boger and shear thinning fluids for the same geometry of a/b = 48. For Boger fluid the fractional coverage plateau at $\lambda \approx 0.35$, while for shear thinning fluid, the asymptotic value was $\lambda \approx 0.2$.

To compare the theoretical prediction of bubble width by Amar and Poire[19] with the experimental results for the shear thinning fluid, first the new parameter $k$ was introduced into the analysis, which was plotted in Fig 3.13 with $Ca'$ as functions of bubble penetration. In Fig 3.13, k changed in the inverse trend with variation of $Ca'$. The width fraction $\lambda$ vs. $k$ was plotted in Fig 3.14. From experimental result it was known that the finger will became unstable and finger splitting will occur with increase of bubble velocity. In Fig 3.15, the stages of bubble finger from stable through unstable to splitting was shown as function of $k$ values measured in the experiments. This gave us a better idea of the finger's situation at different $k$ value. In the theoretical prediction, Amar and
Poire assumed power law fluid behavior. The experimental results followed the same trend as the theoretical prediction, but there were some differences. The points representing the experiment did not fall between the lines $n = 0.3$ and $n = 0.4$, although they were expected to do so since $n = 0.35$ for the experimental fluid. At a high $k$ value (corresponding to a low bubble velocity), the asymptotic value of the fractional width was around 0.46 for the experimental results, but around 0.58 as predicted by the theory. The discrepancy at high $k$ value (where the shear rate was low) may be due to the test fluid not behaving like a power law fluid since the viscosity of the test fluid approached a constant value of $\eta_0$. At low $k$ value, (indicating a very high modified capillary number), the theory predicts the fractional coverage will approach zero as the finger became needle like. But our experimental data showed that instability occurred and the average fractional coverage achieved an asymptotic value of 0.2. The difference may be due to the elasticity existing in the test fluid, although the fluid was dominated by shear thinning effect.

3.4.2 Bubble Shape Comparison

As shown in Fig 3.16, the degrees of complexity of the tip splitting were different for the three testing fluids. Fig 3.16 was a visual comparison of the bubble-fingering pattern obtained in each fluid at a similar modified capillary number of 250 in geometry of $a/b = 48$.

Based on the rheology of the test fluids, it is possible to conclude that the elastic behavior of the Boger fluid causes an increased tendency for a bubble to split at higher
modified capillary numbers. In contrast, the shear-thinning behavior tends to have a stabilizing effect on the degree of tip splitting as witnessed by a decrease in the overall finger density obtained in the shear thinning fluid.

### 3.5 Conclusion

The displacement of a high viscosity fluid by a low viscosity fluid was a complex process that occurred in gas-assisted injection molding and enhanced oil recovery, as well as in many other applications. Unfortunately, it is not completely understood especially when the high viscosity fluid is non-Newtonian in nature. To gain insight into this problem, this two-phase displacement of non-Newtonian fluids was investigated using the very simple geometry of the Hele-Shaw cell. Using specifically tailored polymer solutions, the individual effects of two rheological characteristics was isolated: elasticity and shear thinning. In addition, the width and thickness of the Hele-Shaw cell was adjusted to determine the role of geometry in this problem.

A series of experiments were carried out by J. D. Ackerman in which three fluids, a Newtonian, an ideal elastic (Boger), and a shear thinning fluid, contained in a Hele-Shaw cell, were displaced by a gas bubble of increasing velocity. The bubble size (width fraction) and shape (smooth or complex outline) were measured as a function of modified capillary number and geometry aspect ratio. At high-modified capillary numbers, the elastic component of a fluid was found to decrease the asymptotic bubble width fraction to 35% of the cell width, compared to the Newtonian result of 50%. At modified capillary numbers higher than the critical value elasticity also increased the frequency and complexity of the fingering pattern. For shear thinning fluids, theoretical predictions and experimental results were compared. The reasons for the discrepancy between theory and
experimental results may be (1). Finger instability occurred at high Ca’ while the theory assumes there was no finger splitting occurs. (2). There was elasticity existed in the shear thinning fluid while the theory assumed that the fluid was pure shear thinning. (3). The power law model used to simulate the fluid was too simplified and the flow field near the bubble tip was not very accurately described by the theory. But as seen in Fig 3.16, as the velocity approached infinity, the asymptotic value approached 20%. This was smaller than for an elastic fluid, for which the asymptotic value of width fraction may approach 40%, regardless of the gravity force effect. The shear-thinning behavior also had a significant effect on the tip splitting seen in both Newtonian and Boger fluids. In cases where tip spitting did occur in the shear thinning fluid, the fingering pattern was less complex than in either of the other fluids for the same geometry aspect ratio.

The tip splitting pattern in the shear thinning was much less complex than in the elastic fluid, and still less complex than that in the Newtonian fluid. The overall complexity of tip splitting for the three fluids in ascending order is: Shear-thinning fluid, Newtonian fluid and viscoelastic fluid. Fluid elasticity tends to destabilize the bubble finger, while the shear-thinning behavior has a stabilizing effect.
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<thead>
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<th>Parameter</th>
<th>Fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Newtonian</td>
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<tr>
<td>$\eta_0$ (P)</td>
<td>0.45</td>
</tr>
<tr>
<td>$\sigma$ (dynes/cm)</td>
<td>44</td>
</tr>
<tr>
<td>$\Delta H/R$ (K)</td>
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Table 3.1: Physical and model parameters for the test fluids used
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<thead>
<tr>
<th>Fluid</th>
<th>η₀ (Pa·s)</th>
<th>λ₁ (s)</th>
<th>λ₂ (s)</th>
<th>α</th>
</tr>
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<tbody>
<tr>
<td>Boger</td>
<td>3.05</td>
<td>0.123</td>
<td>0.075</td>
<td>0.044</td>
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<td>Shear thinning</td>
<td>3.17</td>
<td>0.152</td>
<td>0.0317</td>
<td>0.291</td>
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<th>2</th>
<th>3</th>
<th>4</th>
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<tr>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Boger solvent</td>
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<tr>
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<td>0.0008</td>
<td>0.0499</td>
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<tr>
<td>Shear thinning solvent</td>
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<td>η (Pa·s)</td>
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<tr>
<td>λ (s)</td>
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<td>0.0499</td>
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Table 3.2: Parameters of 1 mode and 4 modes Giesekus model fitting
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<td>3</td>
</tr>
<tr>
<td></td>
<td>$\eta_\infty$</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$\lambda$</td>
<td>0.154</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>0.61</td>
</tr>
</tbody>
</table>

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CHAPTER 4

INFLUENCE OF TEMPERATURE GRADIENT ON GAS PENETRATION THROUGH NEWTONIAN FLUID IN CAPILLARY TUBE AND MODEL SETUP

The experiments and basic model setup were done by Minesh R. Tendulkar. My task is to complete the model setup and make the model capable of predicting the experimental data more accurately.

4.1 Experimental Apparatus and Technique

Gas-assisted injection molding, as a newly developed polymer processing technique, was usually conducted under non-isothermal condition. To simplify the process for the sake of convenience in study, a capillary tube was used and the flow geometry. Fig 4.1 showed the bubble penetration process under non-isothermal condition, which will be studied in this Chapter. During the bubble penetration, if the outer temperature was low enough, there will be a frozen layer formed on the inner wall during the penetration. A coating layer will form between the frozen layer and gas bubble. This was not exactly what happened in our experiment, but it provided a basic idea for the
setup of a model to calculate the fractional coverage in the experiment of bubble penetrating through non-isothermal viscous fluid which behaved as Newtonian fluid isothermally.

Fig 4.2 showed the schematic of the apparatus used to study the penetration of gas bubble through Newtonian fluid under non-isothermal condition. As an extension of the apparatus used by Hyzyak and Koelling (1995), the experiments were carried out using precision bore stainless steel tubes, each with a length of 30.5 cm. Three tubes with outer diameters of 1/2", 3/8" and 1/4" were used in the experiments. The corresponding internal diameters were 1.0922 cm, 0.7747 cm, and 0.4928 cm respectively. The inlet of each tube was connected through three-way valve and flexible stainless steel hoses to a gas reservoir and a pressure vessel filled with the polymer. There was a small stainless steel flow restriction tube connected to the tube via swagelok fittings to control the volume flow rate of polymer during the gas penetration at an approximate constant. The diameter and length of the restriction tube was selected that the ratio of the final volume flow to the original volume flow rate was less than 1.1.

Two water baths were maintained at different constant temperatures. The tube filled with polymer was first immersed into a water bath, after the polymer inside the tube achieved uniform temperature distribution; the tube was taken out and put into the other water bath. It was assumed that when the Fourier number (Fo) becomes equal to 1, the temperature distribution will be homogenous. Fourier number was defined as

\[
Fo = \frac{\alpha \theta}{R_0^2}
\]  

(4.1)

Where \( \alpha \) is the thermal diffusivity, \( \theta \) is the time and \( R_0 \) is the inner radius of the tube.
After the tube stayed in that water bath for a certain delay time, the three-way valve was switched to the gas reservoir and gas bubble penetrate through the Newtonian fluid, pushing part of the fluid out of the tube. The weight of the fluid that has been pushed out was measured to calculate the fractional coverage. The experiments were done at delay time ranging from 0 to 500 sec, which corresponded to the fourier number 0<\(F_o<1\). The experiments were carried out at very high bubble penetration rate, which can make the change of temperature gradient during the penetration negligible so it was assumed that the temperature only varied in radial direction and thus make the heat transfer model in one dimension. The capillary number range was from 20 to 1000. There were six temperature gradients formed between the two water baths, from the one in which the tube was first immersed to the one the gas-assisted injection experiments were carried out. They were 25-0, 50-0, 50-25, 65-25, 35-25 and 25-50, which was the reversed temperature gradient. Below are the definition of fractional coverage in different terms

\[
m = 1 - \frac{R_b^2}{R_0^2} \tag{4.2}
\]

\[
m = 1 - \frac{w}{\rho_f \pi R_0^2 L} \tag{4.3}
\]

where \(R_b\) is radius of bubble, \(R_0\) is the inner radius of the tube, \(w\) is the weight of fluid that has been pushed out, \(\rho_f\) is fluid density and \(L\) is the tube length.

### 4.2 Fluid Characterization

Test fluids were a high molecular weight polybutene (Amoco Polybutene Indopol H-300, \(M_w = 1340 \text{ g/mol}\)) and silicone oil (Dow Corning, DC 200). Shear viscosities
were measured using the Rheometrics Fluid Spectrometer, RFSII. Viscosities were measured using a 25 mm couette tool with a temperature controlled bath in the steady shear sweep test. The tests were carried out under temperature ranging from 10°C to 60°C and data were plotted in Fig 4.3 and 4.4 respectively. The data showed the fluids were of Newtonian type and temperature sensitive. The flow activation energy of a polymer was measured by fitting the viscosity data to the Arrhenius model, as shown below

\[ \eta(T) = A \exp \left( \frac{\Delta H}{RT} \right) \]  

(4.4)

where \( \eta \) is the shear viscosity, \( A \) is the frequency and \( \Delta H / R \) is the flow activation energy. The parameters were shown in Table 4.1. The larger the activation energy, the more the material was sensitive to temperature change. From Table 4.1 it can be told that PBH-300 was more temperature sensitive than DC 200. The surface tensions were obtained from literature. The surface tension for PBH-300 was 27.2 dynes/cm at 25°C, while DC-200 has a surface tension of 21.5 dynes/cm at 25°C.

The density of PBH-300 has been reported (Amoco Chemical Company 1994), the variation of density with temperature was defined in equation 4.5.

\[ \rho = -0.00058T + 0.903 \]  

(4.5)

Where \( \rho \) is the density in g/cm³, \( T \) is temperature in °C. The change of density was included in the handling of the experimental data for a correction.
4.3 Result and model design

4.3.1 Example of experimental result and model setup

Although the gas-assisted injection molding process has many advantages as a polymer processing technique, it is as well a very complicated process. It has not been fully understood. The object was to develop a semi-experimental model to predict how the non-Newtonian rheological behavior of the polymer, which was caused by the temperature gradient existing in the flow filed, delay time in gas injection process, tube diameter and flow activation energy will affect the fractional coverage.

Fig 4.5 showed the plot of fractional coverage as function of capillary number for Newtonian fluid. The data were simulation result by Poslinski (1997) under isothermal condition. From the plot it can be told that after capillary number was greater than 10, the fractional coverage will achieve a constant value of 0.6. This Chapter focused on the effect of different temperature gradient on the fractional coverage, so the experiments were carried out at capillary number greater than 20, for which the fractional coverage should always be 0.6 under isothermal condition. Any deviation from Newtonian results in Fig 4.5 should be due to the temperature gradient. Thus the effect of temperature was isolated and can be studied in more detail.

Fig 4.6 was the result obtained under temperature gradient of 50°C to 25°C. The values of fractional coverage at Fo = 0 and Fo = 1 were both 0.6 (delay time = 0 and 500 sec). The fractional coverage increased from value of 0.6 at the beginning and after it reached a maximum value, it decreased and until it became 0.6 again at Fo = 1 (delay time = 480). The maximum value occurred at Delay time = 40 sec.
To theoretically predict the change of fractional coverage with delay time, a frozen layer model was suggested to do the calculation. Fig 4.7 showed the basic assumption of this model. As can be observed in Fig 4.1, for a non-isothermal gas injection process, regardless of whether there was frozen layer formed on the inner wall, the continuous change of temperature in radial direction caused the velocity profile to deviate from parabolic shape. This was the origin of the difference between the result of isothermal and non-isothermal experiments. In the frozen layer model, it was assumed that there was always a frozen layer formed during the bubble penetrating through non-isothermal polymer melt. The fluid inside the frozen layer has a uniform temperature of $T_i$, which is the inner temperature of the polymer melt obtained during the stay of tube filled with polymer in the first water bath. Thus the fluid inside the frozen layer can be treated as homogenous Newtonian fluid. Because all the experiments were carried out under capillary number high enough to achieve the plateau value of 0.6, so the thickness of the hydrodynamic coating layer can be calculated based on the partial fractional coverage equals 0.6 for fluid inside frozen layer. To find out the total fractional coverage, the only thing needed to be figured out was how to calculate the thickness of frozen layer.

To calculate the frozen layer thickness, different methods were considered. It was assume that the volume flow rate of fluid inside the frozen layer equaled to that of the non-isothermal fluid used in the experiments. Then if the volume flow rate of the non-isothermal fluid can be calculated, by equaling the two flow rates the flow rate of the isothermal polymer melt in the model can be calculated using the parabolic shaped
velocity profile. The thickness of frozen layer can be found. Finite difference method was employed to do the calculation. The process was divided into three stages, which will be discussed as follow.

4.3.2 Calculation of temperature distribution in radial direction

As shown in Fig 4.8, the region from the center of the tube to the outer edge was divided into two parts. One was from center to the inner wall; the other was the steel wall of the tube. For each part, the region was divided into 20 elements.

The calculations below will use PBH-300 as the displaced fluid.

The three steps of heat transfer were illustrated in Fig 4.9, and description of the three steps is as below:

1) Heat transfer inside polymer

The temperature at each node will change with time and the temperature gradients between neighboring nodes were the driving force for the heat transfer inside polymer.

The governing equations are

\[
\frac{\partial T}{\partial \theta} = \alpha_p \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \tag{4.6}
\]

\[
\alpha_p = \frac{k_p}{\rho_p C_{p,p}} \tag{4.7}
\]

When written in finite difference format, the equations are

\[
\frac{\partial T}{\partial \theta} = \frac{T_{\theta_{i+1}} - T_{\theta_{i-1}}}{2dr} \tag{4.8}
\]

\[
\frac{\partial T}{\partial r} = \left( \frac{T_{\theta_{i+1}} T_{\theta_{i+1}}}{\frac{d\theta}{d\theta}} + \frac{T_{\theta_{i}} T_{\theta_{i}}}{\frac{d\theta}{d\theta}} \right) = \frac{T_{\theta_{i+1}} T_{\theta_{i-1}} - 1}{2dr} \tag{4.9}
\]
\[
\frac{\partial^2 T}{\partial r^2} = \left( \frac{T_{\theta_0, i+1}}{dr} \frac{T_{\theta_0, i}}{dr} \frac{T_{\theta_0, i-1}}{dr} \right) \frac{1}{dr} = \frac{T_{\theta_0, i+1}}{dr} + \frac{2T_{\theta_0, i} + T_{\theta_0, i-1}}{dr^2} \quad (4.10)
\]

where a period of time is divided into small time steps in which \( \theta \) is the time of next time step and \( \theta_0 \) is the time of current time step. For the elements divided along radial direction, \( i \) represents the \( i \)th node, the same principle for \( i-1 \) and \( i+1 \). By plugging the Equations 4.8-4.10 into Equation 4.6, the temperature at next time step \( T_0 \) can be solved using values of current temperature at three neighboring nodes \( T_{\theta_0, i-1}, T_{\theta_0, i}, T_{\theta_0, i+1} \). The formula was shown as

\[
T_{\theta_0, i} = T_{\theta_0, i} + \alpha_p d\theta \left( \frac{T_{\theta_0, i+1}}{dr^2} \frac{T_{\theta_0, i}}{dr^2} \frac{T_{\theta_0, i-1}}{dr^2} \right) \quad (4.11)
\]

Boundary condition

\[
T_{\theta_0, i=0} = T_i \quad (4.12)
\]

\[
T_{\theta_0, i=\text{node\_number}} = T_{\theta_0, i=0}^S \quad (4.13)
\]

\[
T_{\theta_0, i=0} = T_{\theta_0, i=1} \quad (4.14)
\]

where \( T_{\theta_0, i=0}^S \) represents the temperature of stainless steel on the inner wall of the tube.

2) Heat transfer inside stainless steel

As shown in Equation 4.15-4.20, similar to formulas of heat transfer process inside polymer, the only difference was the physical properties were those of stainless steel, which were listed in Table 4.1 with those of polymer material.

\[
\frac{\partial T^S}{\partial \theta} = \alpha_s \left( \frac{\partial^2 T^S}{\partial r^2} + \frac{1}{r} \frac{\partial T^S}{\partial r} \right) \quad (4.15)
\]

\[
\alpha_s = \frac{k_s}{\rho_s C_{ps}} \quad (4.16)
\]
\[
\frac{\partial T^S}{\partial \theta} = \frac{T^S_{0,i} - T^S_{0,i-1}}{d\theta} \quad (4.17)
\]
\[
\frac{\partial T^S}{\partial r} = \left( \frac{T^S_{0,i+1} - T^S_{0,i-1}}{d\theta} + \frac{T^S_{0,i} - T^S_{0,i-1}}{d\theta} \right) / 2 = \frac{T^S_{0,i+1} - T^S_{0,i-1}}{2dr} \quad (4.18)
\]
\[
\frac{\partial^2 T^S}{\partial r^2} = \left( \frac{T^S_{0,i+1} - T^S_{0,i-1}}{dr} - \frac{T^S_{0,i} - T^S_{0,i-1}}{dr} \right) / dr = \frac{T^S_{0,i+1} - 2T^S_{0,i} + T^S_{0,i-1}}{dr^2} \quad (4.19)
\]
\[
T^S_{0,0} = T^S_{0,0} + \alpha_r d\theta \left( \frac{T^S_{0,i+1} - 2T^S_{0,i} + T^S_{0,i-1}}{dr^2} + \frac{1}{r_i} \frac{T^S_{0,i+1} - T^S_{0,i-1}}{2dr} \right) \quad (4.20)
\]

Boundary conditions

\[
T^S_{0=0,i} = T_i \quad (4.21)
\]
\[
T^S_{0,i=0} = T^S_{0,0} + \alpha_r d\theta \left( \frac{T^S_{0,i+1} - 2T^S_{0,i} + T^S_{0,i-1}}{dr^2} + \frac{1}{R_{01}} \frac{T^S_{0,1} - T^S_{0,0}}{dr} \right) \quad (4.22)
\]
\[
T^S_{0,i=\text{node number}} = T^\text{Wall} \quad (4.23)
\]

3) Heat transfer outside tube

The heat transfer outside tube was a continuous process across the whole water bath region. This situation can be simplified by assuming the heat transfer just occurred in a region very near the tube outer wall. In other words, it was assumed that there was a thin layer attached to the tube wall and the heat transfer resistance concentrates in it. The physical properties of water were listed in Table 4.2 with those of polymer materials. The heat transfer should obey the formula below

\[
q = -k_w \frac{\partial T}{\partial r} \bigg|_{r=R_{a2}} = h(T_w - T_B) \quad (4.24)
\]
where $k_s$ is the thermal conductivity of stainless steel, $q$ is the heat flux flowing from the tube’s outer wall to the water in which the tube was immersed in. $h$ is the convective heat transfer coefficient of the assumed thin layer “coating” the tube. $T_w$ is the wall temperature while $T_B$ is the temperature of bulk fluid, water. This formula meant the heat transfer rate from tube to the water bath was equal to the heat transfer rate in the heat transfer resistance layer.

When written in finite difference format, Equation 4.24 becomes

$$-k_s \frac{T^S_{0,i=node\_number} - T^S_{0,0,i=node\_number-2}}{2 \Delta r^S} = h \left(T^S_{0,0,i=node\_number} - T_B\right) \quad (4.25)$$

$$T^S_{0,i=node\_number} = T^S_{0,0,i=node\_number-2} - 2 \Delta r^S h \left(T^S_{0,0,i=node\_number} - T_B\right)/k_s \quad (4.26)$$

To solve for temperature at the steel wall at future time $\theta$, $T^S_{0,i=node\_number}$, the value of $h$ needed to be determined.

The heat transfer around the tube was mainly convection. But forced convection and free convection have different way of calculating value of $h$. Thus the first step was to determine the type of convection occurred in our experiments.

Fig 4.10 described the circulation of water in water bath, in which the tube was immersed in. Because the rate of water flowing in and out of the water bath were very small and the size of water bath was comparatively large, so the effect of forced convection heat transfer was neglected and the main heat transfer type was free convection. To calculate the value of heat transfer coefficient $h$, according to “Principles of Heat Transfer” by Frank Kreith (1973), first it’s necessary to specify the values of three dimensionless parameters, average Nusselt number $Nu$, Grashof number and $GrD$, Prandtl number $Pr$, which were defined as below:
\[ \overline{\text{Nu}_D} = \frac{h_c D}{k_f} \] (4.27)
\[ \text{Gr}_D = \frac{\beta g D^3 \Delta T}{\nu^2} \] (4.28)
\[ \text{Pr} = \frac{C_p \mu}{k} \] (4.29)

where \( h_c = h \), which represents the average value of \( h_c \) (local heat transfer coefficient) over surface.

The physical properties of water were listed in Table 4.2. Tube with outer diameter of 1/2” was used to do the calculation as an example. Pr is a constant number which has a result of 1.65 calculated using Equation 4.29.

From Frank Kreith (1973), if \( \text{Pr} > 0.5 \) and \( 10^3 < \text{Gr}_D < 10^9 \), \( h \) can be calculated using the formula below
\[ \text{Gr}_D < 10^3 \), there was a recommended line to relate Nusselt number with \( \text{Gr}_D \text{Pr} \) as shown in Fig 4.11. The line was fitted using polynomial equation to get an analytical result of Nusselt number as function of \( \text{Gr}_D \text{Pr} \) as Equation 4.31
\[ \log(\overline{\text{Nu}}) = 0.0097[\log(\text{Gr}_D \text{Pr})]^3 + 0.131[\log(\text{Gr}_D \text{Pr})] + 0.0454 \] (4.31)

For all the six temperature gradient, the one with \( \Delta T = 50^\circ \text{C} \) corresponds to the highest value of \( \text{Gr}_D \) equals to \( 2.75 \times 10^6 \), which was within the region of \( 10^3 \) to \( 10^9 \). As the heat transfer going on, \( \text{Gr}_D \) will decrease with the decrement of temperature difference between tube and bulk fluid. Thus in our calculation, the value of \( \text{Gr}_D \) for each time step was tested to determine which formula to adopt for the calculation of \( h \). All these works were done in the program written in FORTRAN.
To test the one-dimensional heat transfer model, comparison was made between a set of experiments and the calculation results. The tube outer diameter was 1/2". The experiments were first done by Minesh, and later a similar but more accurate technique was employed to measure the temperature values at different radial position.

Fig 4.12 showed the schematic of my experimental setup of measuring temperature distribution across tube cross section. Two small stainless steel lids were made to seal the tube’s two ends. One of the lids has several small holes at fixed position to let the thermocouple be inserted into the polymer inside the tube. The thermocouple was connected to a data acquisition system (Diana Chart) for measurement. The experimental procedure was first the tube full of polymer with thermocouple fixed at certain radial position was immersed into the water bath with higher temperature and the data acquisition system was on at that time to observe the change of temperature with time. After a certain delay time when Fo equals to 1, the measurement was off and the tube was taken out of the water bath and immersed into another one with lower temperature. The measurement of temperature was on at the same time and the change of temperature was recorded with time.

Totally three temperature gradients were tried in the experiments. Minesh set the gradient to be 51.5°C to 25.3°C, and the two gradients used in my experiments were 65.9°C to 25.3°C and 51.1°C to 25.1°C. The results of experiments and model calculation were shown in Fig 4.13, 4.14 and 4.15.

From Fig 4.13 to 4.15, it was observed that the calculation results were always higher than the experimental results by a small amount. Reason for this difference may be the neglect of forced convection heat transfer occurred in the process. As a summary, the
model works well in predicting the temperature values at different radial position, thus it can be used to calculate the temperature profiles. The calculated temperature profiles were plotted in Fig 4.16 to Fig 4.24. Besides the cases of 1/2” tube filled with PBH-300 immersed in water baths of six temperature gradients, the calculation was also done for other three cases. They were 3/8” tube subjected to gradient of 50°C to 0°C, 1/4” tube subjected to gradients of 25°C to 0°C and 50°C to 25°C. From these added cases, the effect of tube diameter on the relation between the temperature gradients and fractional coverage can be observed.

4.3.3 Calculation of viscosity distribution in radial direction

The viscosity distribution can be calculated according to equation 4.4. The results were plotted in Fig 4.25 to Fig 4.33. As known previously, the viscosity increase with decrement of temperature, and the viscosity at center will be of minimum value for positive temperature gradient. Big viscosity gradient occurred at delay time of 20 to 60 sec, which corresponded to the gradient of temperature at those delay times. The effect of this on radial velocity profiles will be observed later.

4.3.4 Calculation of radial velocity profile

In the calculation of velocity profile, pseudo steady state was assumed. The equation of motion was set up to solve the problem of non-isothermal fluid flowing through a circular tube. Because the flow was non-isothermal, the effect of temperature on viscosity was taken into consideration. The governing equations are

\[
\frac{\partial}{\partial t} \left( \rho \frac{\partial u_r}{\partial r} \right) = \frac{\Delta \text{Pr}}{L}
\]  

(4.32)
where $\eta = A \exp\left(\frac{\Delta H}{RT(r)}\right)$

Boundary conditions

\[ r = r_0, u_z = 0 \]  \hspace{1cm} \text{(4.33)}

\[ r = 0, \frac{du_z}{dr} = 0 \]  \hspace{1cm} \text{(4.34)}

where $\Delta P$ is the pressure gradient, which was maintained at 10 atm in all the experiments. $L$ is the tube length. By combining the governing equation and the first boundary condition, the governing equation was simplified to

\[ \frac{\partial u_z}{\partial r} = \frac{\Delta Pr}{2L\eta} \]  \hspace{1cm} \text{(4.35)}

\[ \eta = A \exp\left(\frac{\Delta H}{RT(r)}\right) \]  \hspace{1cm} \text{(4.36)}

The basic idea behind the calculation was because the effect of penetrating bubble was much localized, the flow field far front of bubble can be assumed as was not affected by the bubble at all. Thus using the equation above, the velocity profile of polymer far in front of bubble can be calculated. To make better comparison of velocity profiles between different cases and get deeper understanding of the process, a normalized velocity $u/\text{umax}$ was considered in the calculation. $u_{\text{max}}$ was the maximum velocity in the velocity profile and was located at the center of tube. A FORTRAN program was written to numerically solve the equation and the calculation was done from outside position at $r = R_{01}$ towards center of tube. The profiles were plotted in Fig 4.34 to 4.42.

As can be observed from the graphs, for profiles in 1/2” tube, for positive temperature gradient, at first the velocity profile decreased in scale from isothermal case,
the maximum deviation from the isothermal velocity profile occurred at delay time around 40 sec, which corresponded to the time when maximum fractional coverage occurred. After occurrence of maximum deviation, the profile began to swift back toward isothermal profile, which was the result of decrement of viscosity gradient as Fourier number increases, after Fo = 1 again at delay time of around 480 sec, the profile collapsed with the profile at the very beginning of Fo = 0. 3/8” tube has 30 sec as the delay time for maximum deviation instead of 40 sec. For 1/4” tube, the critical time for maximum deviation was 20 sec. Summarily, the deviation from isothermal profile represented the change in fractional coverage. The extent of deviation represented the degree of change in fractional coverage. In Fig 4.43 and 4.44, comparison was made for the maximum deviation of different temperature gradients in the same tube and of same temperature gradient in different tubes. Fig 4.43 showed that greater temperature gradient will result in higher magnitude of biggest deviation from isothermal profile. From Fig 4.44 and 4.45 it was obvious that the effect of tube diameter on the extent of deviation was very small.

4.3.5 Calculation of values of fractional coverage using calculated velocity profiles

By now the radial velocity profiles for each temperature drops in different tubes has been calculated. It is time to calculate the fractional coverage. As stated before, to find fractional coverage, the thickness of frozen layer needed to be determined. The sections before have introduced how to calculate radial temperature, viscosity and velocity profiles. Three major schemes were employed in the calculation; in each scheme two methods were used. Many methods were tried to find out which one predict the results better and can approach the actual process in a more accurate way.
4.3.5.1 Calculation using temperature profile far in front of bubble

Fig. 4.46 exhibited the idea behind the integrations. By assuming a new parabolic shaped profile, a new radius besides the inner radius of the tube was found. The difference between the two radii was the frozen layer thickness. According to the equivalence of volume flow rate, the governing equations are

\[
2\pi \int_{0}^{R_{01}} ru^{*} dr = 2\pi \int_{0}^{r_{x}} ru^{*}_{x} dr
\]  

(4.37)

\[
\int_{0}^{R_{01}} ru^{*} dr = \int_{0}^{r_{x}} ru^{*}_{x} dr
\]  

(4.38)

where \(u^{*}\) is the normalized velocity at each radial position, \(u^{*}_{x}\) is the normalized velocity of the “equivalent” parabolic shaped profile. \(R_{01}\) is the inner radius of the tube and \(r_{x}\) is the parameter of the parabolic function, which can be expressed as

\[
u^{*}_{x} = \left(1 - \left(\frac{R}{R_{x}}\right)^{2}\right)^{1/2}
\]  

(4.39)

After \(R_{x}\), was found the value of fractional coverage could be calculated according to the equation below

\[
m = 1 - \left(\frac{\sqrt{0.4R_{x}}}{R_{01}}\right)^{2} = 1 - 0.4\left(\frac{R_{x}}{R_{01}}\right)^{2}
\]  

(4.40)

At the beginning of the analysis, the way of obtaining \(R_{x}\) was different from that stated above. Instead of integrating \(ru^{*}\) throughout the flow field, \(u^{*}\) was the object of integration. Because all the difference of fractional coverage from asymptotic value of 0.6 was caused by the deviation of velocity profile from isothermal case, thus integrating \(u^{*}\) will give us a better idea of the effect of the velocity profile’s shape on the fractional
coverage. Fig 4.47 to 4.55 present the results obtained using the two methods of integration were plotted in the same graph for each temperature gradient.

The experimental data were corrected using Equation (4.5) to consider the change of fluid density in radial direction with temperature change. As shown in the plots, in the experiments, the fractional coverage reached a peak value at delay time of 40 sec for 1/2″ tube, 30 sec for 3/8″ tube and 20 sec for 1/4″ tube, which were the same delay time for occurrence of maximum deviation of velocity profile from isothermal profile, then returned to the asymptotic value around 0.6 with increase of delay time. The peak value, when just considering 1/2″ tube, will increase with the increase of temperature gradient.

4.3.5.2 Calculation using temperature profiles far in front of and near the penetrating bubble

Because in the previous calculation, only the temperature profile far in front of penetrating bubble was considered and the local effect of bubble on the result was neglected, to make the model more accurate, the temperature profiles of polymer near the bubble were taken into consideration in this section. As shown in Fig 4.56, it was assumed as the bubble penetrates forward, because the bubble penetration rate was very high, the fluid in front of the bubble was directly squeezed into the region between the bubble and inner wall, the transition region between the bubble tip and static flow field far in front of bubble was neglected for simplicity of calculation by assuming the temperature profile at the tip of bubble was the same as that at far end of the tube. The
region between bubble tip and edge was divided into small elements. It was assumed the shape of bubble penetrating through isothermal Newtonian fluid at very high capillary number could be also used for the calculation under non-isothermal condition. Thus by finding the radial position of the bubble curve at each node, the squeezed temperature profile could be calculated. Then by adding the temperature values of each profile at equivalent radial position together and take the average value, we will get a new but not continuous first derivation temperature profile. Fig 4.57 was an example of the new radial temperature profile. The program was just an extension of the old program calculating temperature profiles.

After all the temperature profiles were calculated, just by following the same steps as in section 4.3.5.1, a new series of fractional coverage vs. delay time data could be calculated. The results were shown in Fig 4.58 to 4.66. The combined temperature profile did not improve the discrepancy in the magnitude of values of fractional coverage between experimental data and model calculation results, but it gave a better delay time fit, especially for the temperature gradient of 65°C to 25°C. Improvement in the model setup will be discussed in Chapter VI.

4.4 Frozen layer prediction for experiments under lower Capillary number

Experiments under same non-isothermal condition were carried out at lower Capillary number. The frozen layer model was tried to predict the fractional coverage as well. Fig 4.67 was an example of this attempt. The agreement was no better than the data for high Capillary number, which may be because that for the model, the change in
temperature profile during the bubble penetration was not considered. At high bubble rate, the change may be neglected, but when bubble rate is low, the assumption will not be valid any more.

The calculation process was similar to the method discussed above. Only the temperature profile far in front of bubble was considered. The major difference was the fractional coverage inside frozen layer was assumed to be the value of experiment using Newtonian fluid under isothermal condition at the same Capillary number.

4.5 Conclusion

The experiments of measuring fractional coverage as function of delay time under non-isothermal condition for Newtonian fluid with high activation energy were carried out by Minesh R. Tendulkar. The basic idea of frozen layer model was first prompted by him as well. In my work, the temperature profile was measured by introducing a data acquisition system, the model was rebuilt using finite difference method. Heat transfer process was analyzed in more detail with the inclusion of heat transfer inside steel shell and bulk fluid layer surrounding the tube where the resistance of heat transfer was assumed to concentrate in. By assuming a frozen layer model, the effect of non-isothermal condition was simplified to be restricted into the frozen layer region. To find the total fractional coverage, the frozen layer thickness was solve by equaling the volume flow rate of fluid in experiments and the calculated result of frozen layer model. The temperature profiles far in front of bubble was used separately and combined with profiles between bubble and tube inner wall to calculate the frozen layer thickness. The profiles between bubble and wall were assumed to be geometrically squeezed into the
region. Qualitatively agreement between experimental data and model calculation results was achieved; also a good prediction of the delay time when the peak value of fraction coverage will occur was achieved.

The frozen layer model was not good for predicting fractional coverage when the experiment was done at low bubble penetration rate. The reason may be that at low bubble rate, during the bubble penetration, the change in temperature profile could no longer be neglected, which make the model prediction not as good as for the high bubble penetration rate experiments.

The frozen layer model may also be used to predict the fractional coverage vs. Capillary number for Non-Newtonian fluid under isothermal condition, which will be discussed in Chapter V.
<table>
<thead>
<tr>
<th>Properties</th>
<th>PBH-300</th>
<th>DC 200</th>
<th>Stainless Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m³) 25°C</td>
<td>889</td>
<td>971</td>
<td>7850</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK) 25°C</td>
<td>0.1125</td>
<td>0.1547</td>
<td>12.22</td>
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<tr>
<td>Specific Heat (J/kg K) 25°C</td>
<td>2100</td>
<td>1456</td>
<td>514.5</td>
</tr>
<tr>
<td>Surface Tension (N/m) 25°C</td>
<td>0.0272</td>
<td>0.0215</td>
<td>–</td>
</tr>
<tr>
<td>Flow Activation Energy (K)</td>
<td>7325</td>
<td>1090</td>
<td>–</td>
</tr>
<tr>
<td>Frequency Factor (Pa -s)</td>
<td>1.538 e-9</td>
<td>0.5276</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4.1: Physical properties of the two test fluids, PBH-300, DC-200 and Stainless Steel
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$</td>
<td>Btu/lbm$\cdot$F</td>
<td>1.0</td>
</tr>
<tr>
<td>$\mu$</td>
<td>lbm/ft$\cdot$sec</td>
<td>$0.1815 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>lbm/ft$^3$</td>
<td>59.45</td>
</tr>
<tr>
<td>$\nu$</td>
<td>ft$^2$/sec</td>
<td>$0.305 \times 10^{-5}$</td>
</tr>
<tr>
<td>$k$</td>
<td>Btu/hr$\cdot$ft$\cdot$F</td>
<td>0.395</td>
</tr>
<tr>
<td>$D$</td>
<td>m</td>
<td>$1.27 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1/F</td>
<td>$4.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>$L$</td>
<td>m</td>
<td>0.305</td>
</tr>
</tbody>
</table>

Table 4.2: Physical parameters of water at temperature of 225 F
Figure 4.1: Bubble penetration through capillary tube filled with polymer melt under non-isothermal condition

\( T_0 \): temperature of the water bath in which the gas penetration experiment was carried out,

\( T_i \): the temperature the polymer melt obtained during the stay of tube in the first water bath.
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Figure 4.7: The frozen layer model assumption

- Frozen layer
- Gas Bubble
- Water bath
- Hydrodynamic coating layer
- Polymer Melt
- Temperature profile
- Velocity profile

Legend:
- T
- Tc
- Velocity profile
- Temperature profile
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CHAPTER 5

INFLUENCE OF SHEAR THINNING AND YIELD STRESS ON GAS-DISPLACEMENT OF FLUID OF LOW VISCOELASTICITY

In this Chapter, the effect of shear thinning and yield stress on the gas-assisted injection process will be discussed. The fluids were Carbopol solutions which had low elasticity and high shear thinning effect. Experiments were done and theoretical calculation were tried to predict fractional coverage as function of Capillary number. The effects of rheology, geometry bubble viscosity and bubble penetration velocity on bubble shape were also studied.

5.1 Experimental Apparatus and Technique

The experiments were divided into two parts. One used silicon oil as the displacing fluid, and the other is gas-assisted injection process. Fig 5.1 and 5.2 were the schematic of the apparatus used in the experiments.

5.1.1 Experimental Apparatus and Technique for water and oil-assisted injection process

Precision bore glass tubes (Wilmad Glass) with radius of 0.15, 0.25 and 0.3 cm (tube1, tube2 and tube3) were used. The inlet to the capillary tube was connected with
both a syringe pump and a water pump through a three-way valve via stainless steel tubing. The syringe pump (Harvard Apparatus, Infusion/withdraw pump, 200 ml) was used to fill the capillary tube with viscous fluid prior to each experimental run. Polybutene H-100 (Newtonian) was used to test the experimental setup and as a comparison base. Distilled water was used as displacing fluid. For the carbopol series, because the carbopol resin was water soluble, so water can no longer be used as immiscible displacing fluid. Instead silicon oil (Polydimethylsiloxane, Dow corning 200 fluid) was used to displace the viscous fluid. Silicon oil of 1, 2 and 5 CS viscosity were used and there was no difference in using the three types of fluids due to the comparatively low viscosity values. In the experiments, the main purpose of using liquid instead of gas was to maintain accurate control of the bubble flow rates. By controlling the bubble penetration rate, uniform coating thickness can be obtained throughout the tube. Also the surface tension and the effect of gravity were minimized by selecting the displacing fluid. A high-pressure syringe pump (ISCO 500-D) and a backpressure regulator setup were used to control flow rate and prevent back flow.

After filling the capillary tube with viscous fluid, the displacing fluid was injected into the tube at a constant volume flow rate. Bubble penetration rate was calculated by measuring the time for each bubble to penetrate through the viscous fluid for a constant distance (20 cm etc.). The hydrodynamic fractional coverage \( m \) was calculated from the above data by using material balance. \( Q \) is the volume flow rate.

\[
m = \frac{R_0^2 - Q}{\pi U_b R_0^2}
\]  

(5.1)
The processes of bubble penetrating through capillary tubes were recorded with CCD camera connected with VCR. The video was first transferred into digital file, and then Adobe software was used to grab the picture best demonstrating the bubble shape out of the digital file. The bubble profiles were figured out based on the bubble picture and used as base for simulation.

5.1.2 Experimental Apparatus and Technique for gas-assisted injection process

Stainless steel tube with radius of 0.16 and 0.25 (tube1 and tube2 were used in this section. The experimental setup for the experiments using gas as displacing fluid was similar to that using water and oil as displacing fluids. The major difference was that a Nitrogen gas cylinder was used to inject gas through polymer filled tube instead of water pump. Stainless tubes with two different diameters were employed in the experiments to study the effect of geometry on the fractional coverage as well. The gas pressure was maintained at constant during the penetration. A restriction part, which was made of a short stainless steel tube with small diameter was connected to the outlet of the tube filled with polymer, was used to control the penetration velocity from increasing to above 1.1 times of the original bubble rate. The weight of fluid that has been pushed out by the penetrating bubble was measured to calculate the fractional coverage as introduced in Chapter 4. The velocity of bubble was determined by measuring the time from the beginning of bubble penetration to the time when bubble pushed its way out of the tube. Velocity was just the ratio of the tube length to the penetration time. PBH-300 was used to test the effectiveness of the experimental setup.
5.2 Fluid characterization

5.2.1 Measurement of rheological properties of Carbopol solutions

Carbopols are synthetic carboxyvinly polymers widely used in the cosmetic and pharmaceutical industries. Its molecular structure consists of polyacrylic acid crosslinked with allyl sucrose. First the Carbopol powder was solved in distilled water with weight concentration of 0.1% and the mixture was magnetically stirred for 3 to 5 hours to achieve complete salvation. Then NaOH solution was added to the solution to neutralize it until pH value 7.0 ± 0.5 was achieved. The polymer particles in the solution will swell dramatically when the carboxyl groups are ionized Ketz et al.(1988), which corresponded to the phenomena that as soon as the pH value achieve around 7.0, the viscosity of the solution will increase dramatically and make the stirring very difficult. The entrapped air bubbles were driven out by centrifugation at 1500 rpm for 20 minutes. The neutralized solution was stored in refrigerator when not needed, avoiding contact with light. Rheology of solution stored in this way was found not to change much after repeatedly being warmed and cooled for use Barry and Meyer (1979), Yoshimura and Prud'homme (1987).

The Carbopols tested were Carbopol 940, 941 910 and 907. The viscosity of Carbopol 907 was found be to too small to neglect the viscosity difference between displacing and displaced fluids, thus finally the fluids used in the experiments were Carbopol 940, 941 and 910. The shear viscosity of the test fluids was measured using a Rheometrics Mechanical Spectrometer, RMS 800 and a Rheometrics Fluids Spectrometer, RFS II. For RMS 800, viscosity were measured with a 50 mm cone and plate system, while for RFS II, a 34mm-diameter Couette tool with a bob length of 32mm in a 34mm
diameter cup was used. At first, Carbopol fluids of different concentration were made to obtain a better understanding of their rheological characters and select a proper concentration for the experiment. When the viscosity became too low, RMS 800 can no longer give the accurate results. So RFS II was used instead. Both steady rate sweep and dynamic frequency sweep tests were carried out for each fluid of a series of concentrations. Besides strong shear thinning effects, they also showed insensitivity to the variation of temperature. Oil cover was used to prevent water from evaporating. Finally 0.1% was selected as the value of concentration used in both oil-assisted and gas-assisted injection experiments. Higher concentrations were selected in addition to 0.1% solution in gas-assisted injection experiments to obtain results in higher capillary number region.

Fig 5.3 contained the plots of shear viscosity of 0.1% solution of Carbopol 940, 941 and 910 as functions of shear rate. Fig 5.4 contained the plots of shear viscosity of 0.2% solution of Carbopol 940, 0.5% solution of Carbopol 941 and 910. Power law model was used to fit the rheological data of these shear thinning fluids.

\[ \eta = m \gamma^{n-1} \]

The solution of Carbopol 941 and 940 also exhibited yield stress at very low shear rate. Stress sweep test was performed on the Carbopol 940 and 941 to measure the yield stress. A Rheometric Scientific SR5 controlled stress rheometer and a 25mm cone and plate geometry were used for these measurements. The results were shown in Fig. 3. Tests were carried out using cone and plate system, and different gap distances were tried to get the best results. From Fig.5.5 it can be told that Carbopol 940 exhibit apparent yield stress, which was about 100 dyn/cm². For Carbopol 941, it is not so clear whether it
has yield stress. But by enlarging the graph the intercept of the plot with y-axis at x=0, it was found to have a yield stress around 5 dyn/cm². So the conclusion was that the two fluids exhibit both shear thinning and yield stress effects.

Also the elasticity of 0.1% water solutions of Carbopol 940, 941 and 910 were measured using RMS 800, results of normal stress as function of shear rate were plotted in Fig 5.6. As observed in the figures, Carbopol solutions exhibited some elasticity, which will be discussed later. Also in Fig 5.7, normal stress coefficient was plotted as function of shear rate for the Carbopol solutions.

The fitting parameters were listed in Table 5.1.

5.2.2 Measurement of interfacial surface tension

In the experiments, there were four types of interfaces in total: water and PBH-100, silicon oil and Carbopol solution, gas and PBH-300, gas and Carbopol solution. The method used to test the interfacial tension between two liquids was the drop-weight technique. A bubble of one of the fluids making up interface was dropped into a small sample of the other fluid using a syringe (radius 0.355-mm), as shown in Fig. 5.8. Since the density of polymer solution was bigger than water or silicon oil, so the high viscosity fluid was injected into the low viscosity fluid to form bubble. The injection speed was very small to achieve a pseudo-steady state. The volume of the bubble at which it dropped from the tip of the syringe needle was used in the following equation to get the surface tension
\[ \sigma = \frac{\Delta \rho g V}{2\pi R} \]  

(5.3)

where \( V \) is the bubble volume, \( \Delta \rho \) is the density difference between the two fluids. \( R \) is the outer radius of the needle.

The method used to measure the interfacial tension between gas and polymer was similar to the one for two liquids, the difference was that a CCD camera was used to capture the shape of a stable polymer drop. Knowing the needle’s outer diameter (2.74 mm), polymer’s density and shape of the drop, a small program written in MATLAB was used to calculate the value of interface tension.

Table 5.2 listed all the interfacial surface tension values with the densities of each fluid. Because for Carbopol solution, which is microgel solution, after the concentration achieved certain value, the interfacial surface tension between gas and the solution will not change apparently with concentration.

5.3 Experimental Results and Discussion

The main purpose of the experiments was to determine the effects of shear thinning combined with tube diameter on the hydrodynamic coating thickness. Because three different displacing fluids were used: water, oil and gas, the effects of displacing fluids’ viscosity were also part of the object.

5.3.1 Experiments using water and silicon oil as displacing fluids

5.3.1.1 Definition of Capillary number

Because in this process tubes with different diameters were used, so it’s necessary to check whether the inertia or gravity places any important role in this process. The definitions of the dimensionless parameters were as follow
\[
\text{Ca} = \frac{U_b \eta}{\sigma}; \quad \text{St} = \frac{(\rho_p - \rho_f)gR_o^2}{U_b \eta}; \quad \text{Re} = \frac{(\rho_p - \rho_f)U_b D}{\eta} \tag{5.4}
\]

where \( \rho_p \) is the density of polymer fluid, and \( \rho_f \) is the density of water or silicon oil. It was found that the experiments using Carbopol solutions were carried out where St and Re were in the range of \( 10^{-6} < \text{Re} < 10^{-3} \) and \( 10^{-8} < \text{St} < 10^{-3} \). Therefore it can be concluded that the inertia and gravity effects on the displacing fluids could be neglected in the experiments. The Deborah number was also calculated for the experiments with non-Newtonian fluids following the procedure of Huzyak and Koelling (1997).

\[
\text{De} = \lambda(\dot{\gamma}_w)\dot{\gamma}_w, \quad \lambda(\dot{\gamma}_w) = \frac{\Psi(\dot{\gamma}_w)}{2\eta(\dot{\gamma}_w)} \tag{5.5}
\]

Based on the measured rheology data of the Carbopol solutions, it was found that De was in the range of \( 10^{-1} < \text{De} < 10^0 \). Therefore the effect of the elasticity of the fluids in the experiments was neglected.

Because besides the Newtonian fluid used in the experiments, all the Carbopol fluids showed great dependence of viscosity on shear rate. The viscosity was calculated using the Power Law model fitted to the fluid rheology properties in Fluid characterization discussed in Section 5.2. So in the definition of the above parameters, the selection of shear rate was the key point in determining the parameters and to collapse the fractional coverage onto a master curve. While for Newtonian fluid, it does not make any difference in the calculation of the parameters. Several ways of selecting the shear rate and defining the capillary number were tried for the non-Newtonian fluids. First the wall shear rate was defined as the one used to calculate the viscosity, which was called case 1.
Wall shear rate for Newtonian fluid

\[ \gamma_{aw} = \frac{4Q}{\pi R^3} \]  

(5.6)

Wall shear rate for shear thinning fluid with Power Law index of \( n \)

\[ \gamma_w = \frac{1}{4} \gamma_{aw} \left[ 3 + \frac{1}{n} \right] \]  

(5.7)

Viscosity of shear thinning fluid

\[ \eta = m \gamma_w^{n-1} \]  

(5.8)

Then in the effort of finding a way to collapse the data and to best represent the shear rate in the flow field, the shear rate at the radius position of the left coating layer of the viscous fluid on the wall was used. The equations used to calculate the shear rate at a specific radius position was shown below, which was called case 2

\[ \gamma_{(r)} = \gamma_w \left( \frac{r}{R_0} \right)^s \quad s = \frac{1}{n} \]  

(5.9)

\[ \eta \left( \gamma_r \right) = m \gamma_r^{n-1} \]  

(5.10)

\[ C_a_r = \frac{U_b \eta \left( \gamma_r \right)}{\sigma} \]  

(5.11)

where \( R_0 \) is the radius of the tube. Here \( r = r_b \), where \( r_b \) is the radius of the penetrating bubble.

In case 3, the definition of normalized shear rate Poslinksi (1997) was used to calculate the shear viscosity, which was defined as below \( (r = r_b) \)

\[ \gamma_e = \frac{U_b}{R_0} \]  

(5.12)
\[ \dot{\Gamma} = \frac{\gamma_{(\ell)}}{\gamma_c} \]  
\[ \text{Ca}_N = \frac{U_b \eta \left( \dot{\Gamma} \right)}{\sigma} \]  

Finally, geometrically modified capillary number was used, which was defined as below, which was called case 4.

\[ \text{Ca}' = \frac{U_b \eta \left( \gamma_w \right)}{\sigma R_0} \]

5.3.1.2 Results of fractional coverage as function of capillary number

The experiments for Newtonian and the three Carbopol fluids were carried out. The result of Newtonian fluid was compared with the prediction from Poslinski's work (1997), which was call the GE prediction for simplicity, to test the experimental setup. The plots were shown in Fig 5.9. It can be told that the experimental result fits well with the GE prediction and the plot for different tubes fall onto a master curve, which showed that the tube diameter has no much effect on the bubble's penetration through Newtonian fluid, especially at high Capillary number. For data obtained in tube 2 and 3 at very low capillary number, there is some deviation from the master curve. In Fig 5.10 St was plotted as function of bubble velocity for experiments carried out using the three tubes. From this figure, in tube3, St was found to be greater than 0.1 at bubble velocity smaller than 0.005, which corresponds to Ca = 0.5. This is the Capillary number where the
deviation became apparent. Similar phenomena happened for data of tube2. Thus the deviation could be due to the increment of inertia effect was so big that it could not be neglected any more.

Then the experiments of bubble penetrating through the three kinds of Carbopol fluids were done and the results for case 1 were shown in Fig 5.11, 5.12 and 5.13 for each fluid respectively. The dot line was GE prediction for Newtonian fluid. From the graphs it can be observed that the data for each fluid did not fall onto a single master curve vs. capillary number defined using shear rate at the wall. This was reasonable because for shear thinning fluid, the viscosity changed with the variation of the shear rate throughout the flow field. Therefore the capillary number defined using the traditional way was not uniform in the flow field. The key was to find a way to best represent the viscosity distribution with a single value such that data obtained from tubes of different diameters could fall onto a single master curve. The viscosity corresponding to the wall shear rate turned out not to be a good choice. But it was found out that for the same capillary number, as the tube diameter increases, the fractional coverage decreased, and the three sets of data were parallel to each other for each fluid. One thing to point out was that for solutions of Carbopol 940 and 941, in the experiments done using tube 1, values of fractional coverage were higher than Newtonian results at certain Carpillary number. This may be due to the elasticity existing in the Carbopol solutions, especially for 940 and 941, which have comparatively high normal stress coefficient at low shear rate, or the way by which the capillary number was calculated was not good enough to represent the flow field of the shear thinning fluids. If the fluids were pure shear thinning with no elasticity effect, the fractional coverage should always be lower than the results of Newtonian fluid.
For case 2, the plots were shown in Fig 5.14, 5.15 and 5.16. From the plots, it’s apparent for results of Carbopol 940 and 941 obtained in tube1, the exceeding in value of m disappeared. But the data were still scattered to some extent.

Fig 5.17, 5.18 and 5.19 showed the plots of fractional coverage as function of CaN, which was calculated according to definition in case 3. The experimental data were compared with GE prediction for fluids having Power Law index of 1.0, 0.3 and 0.1. From the plots it was observed that as CaN became very large, the asymptotic values of Carbopol fluids fell into the range limited by the GE prediction of shear thinning fluids. And the interesting thing was that the collapsing of Carbopol 910 was the best among the three fluids. This was because the simulation used was for pure shear thinning fluid, while Carbopol 940 and 941 both exhibited yield stress and high elasticity compared to Carbopol 910, Carbopol 910 was the one most close to pure shear thinning fluid. So when the normalized shear rate was used defined in Poslinski (1997), the result for Carbopol 910 turned out to fall into a master curve.

Finally, for case 4, the results were plotted in Fig 5.20, 5.21 and 5.22. The data for solutions of Carbopol 940 and 910 collapsed onto a single curve as the modified capillary number was used to account for the geometric effects. Results obtained in tube3 for Carbopol 941 still scattered a little from the other two sets. All the data were well below the results of Newtonian fluid.

The results for different fluids obtained in tube 1 were selected for comparison in Fig 5.23. At very low capillary number, the fractional coverage increased in the order of 940, 941 and 910, where results of 941 and 910 were mixed up a little bit. At higher Ca region, the power law index n decreased, the fractional coverage increased, which meant
the thickness of the coating left on the inner wall increase. This was the same if the data obtained from the other two tubes were plotted in the same way. One thing to notice was that the initial slope of m vs. Ca plot decreased with increment of Power Law index n, which meant the rate, by which m increased with Ca, will decrease with the increment of n.

The change of fractional coverage m with different Power Law index n at the same capillary number in higher Capillary number region was in the reverse trend of that predicted by the simulation from Poslinski (1997), while for data at lower Ca region, it was in accordance with those of Poslinski’s work (1997). This maybe due to the following reasons: 1. the elasticity of the three Carbopol solutions increased with the decrement of n, as plotted in Fig 5.6 and 5.7. This meant the fluid with highest shear thinning effect also has the greatest elasticity. With the increment of elasticity, the fractional coverage will increase at the same Capillary number. At low shear rate (small Ca values), the elasticity of Carbopol solutions was not as announcing as the shear thinning effect, so the results for Carbopol 940, 941 and 910 were in accordance with the prediction of Poslinski (1997). But at high shear rate (larger Ca values), the effect of elasticity overcame the shear thinning effect and result in a reverse order of fractional coverage at higher Capillary number. The difference in the increasing rates of m with Ca for 940, 941 and 910 was a direct result of the reasons stated above. The slopes S of the curve in Fig 5.23 vs. the Power Law index n could be approximately treated as a straight line in logarithm-linear scale, whose equation is \( y = -3.9164x - 0.0406 \). So an expression was obtained to correlate the two variables as:

\[
S = \text{Exp}(3.916n - 0.0406) \tag{5.16}
\]
5.3.1.3 Effects of Power Law index and tube diameter on bubble shapes.

Pictures of bubble shapes were taken for each fluid in the experiment carried out in each tube at different capillary number Ca. An example of the picture showing a bubble penetrating through viscous fluid was shown in Fig 5.24. In Fig 5.25-5.27, the bubble profiles in tube 1 were shown for each fluid at different capillary numbers. It is easy to tell from the graphs that for each fluid, as the capillary number increased, the bubble tip became sharper. For Newtonian fluid (Polybutene H-35), the bubble shape profiles were plotted in Fig 5.28. In contradiction to the shear thinning fluid, the curvature of bubble shape penetrating through the Newtonian fluid did not change with the change of capillary number.

Then bubble shapes were plotted for each fluid at the same capillary number in different tubes to observe the geometrical effect on the bubble shape. The results were shown in Fig 5.29-5.32 for the three Carbopol fluids and the Newtonian fluid. From the figures it can be told that for Newtonian fluid, the bubble shape profiles will not change with the change of tube diameters. But for Carbopol 940 and 941, as the tube diameter becomes larger, the bubble became blunter. For Carbopol 910, there was no apparent trend in the bubble shape change, which may be explained as because the shear thinning effect was comparatively weak for this fluid, so the bubble shape did not change much or at all with the change of tube diameter. This can be concluded as the stronger shear thinning effect, the bigger effect of geometry on the penetrating bubble shape. For Newtonian, there is no such effect on the bubble shape at all, which also justify the method used to scale the bubble shape profiles.
Finally the bubble profiles of different fluids at the same capillary number and in the same tube were plotted in Fig 5.33. Tube 3 was selected because the results for tube 3 are the most apparent showing the variation in bubble shape. From the graph, it can be told as the Power Law index decreases, which meant the stronger shear thinning effects, the blunter the bubble tip.

5.3.2 Experiments using Nitrogen gas as displacing fluids

In this section, by this time, only wall shear rate was used to define the Capillary number.

The experimental results using Newtonian fluid PBH-300 were shown in Fig 5.34. The agreement between experimental data and theoretical prediction was pretty good, which proved the experimental setup worked very well.

0.1% solutions of Carbopol 940, 941 and 910 were tested. The results for data obtained in the two stainless steel tubes for each of the three Carbopol solutions were plotted in Fig 5.35, 5.36 and 5.37. In Fig 5.35, there is apparent difference between data from tube and data from tube2. From Fig 5.35 to 5.37, as the Power Law index n became larger, the collapsing between data obtained from different tubes became better. This may be explained as n increases, the fluid became more like a Newtonian fluid, or the shear thinning effect of fluid became weaker, thus the better the Capillary number based on wall shear rate representing the flow field. For Carbopol 910, the data from two tubes almost fell totally onto a single master curve, which was very near the Newtonian result as well. It looked like even at the small Power Law index n = 0.45, the effect of shear thinning on gas-assisted injection process became very insignificant.
Because by using 0.1% solutions only the data at very low Capillary number could be obtained. To achieve higher Capillary numbers to observe the trend of fractional coverage with increment of Ca, another three Carbopol solutions of higher concentration were employed as stated in 5.2.1. The results using these three fluids were shown in Fig 5.38 to 5.40. From the figures it was obvious that the maximum Capillary number could be as high as 6.0, which occurred in the plot for 0.5% Carbopol 941. The data from different tubes for 0.2% Carbopol 940 were still separate with each other and well below those of Newtonian fluid. For 0.5% Carbopol 941, which has a Power Law index $n = 0.34$, the tube diameter did not make much difference on the results and the data were very close to those of Newtonian fluid, and even a little bit bigger than them. Similar phenomena existed for Carbopol 910. Now the conclusion was that at Power Law index $n > 0.34$, the tube diameter did not have much effect on the curve of $m$ vs. $Ca$. The exceeding in $m$ over Newtonian results may also be attributed to the elasticity in the fluids, which still needed more work to be done.

Results obtained in the same tube for the six shear thinning fluids were shown in Fig 5.41, 5.42, 5.43 and 5.44. The data of Carbopol solutions having higher concentration were separated from those having lower concentrations. This is because the Capillary numbers of the two sets did not have much overlap, thus plotting them together will not make them comparable while making the figure more complicated and difficult to read. From all these figures, it could be concluded that with the increment of Power Law index $n$, at the same Capillary number, the fractional coverage will increase as well, which was in accordance with the prediction by Poslinski (1997), but in the reverse trend with the
results obtained using silicon oil as displacing fluids at higher Capillary number. More work was needed to be done to solve this discrepancy which can be started by studying the viscoelasticity of the Carbopol solutions in more detail.

In Fig 5.45, data obtained using different displacing fluids were plotted for 0.1% Carbopol 941. Tube diameter was 0.5. In the figure, at the same capillary number, silicon oil-assisted injection experiment resulted in smaller fractional coverage than gas-assisted injection experiments, which means that with the increase of displacing fluid’s viscosity, the fractional coverage tended to decrease. Conclusion is that the less shear thinning the fluid, the more injection fluid viscosity will affect the fractional coverage.

5.4 Conclusion

A series of highly shear thinning fluids were tested using silicon oil and gas as the displacing fluid. For the experiments using gas as displacing fluid, results became very close to those of Newtonian fluid under isothermal condition for Carbopol solution having Power Law index higher than 0.34. Three glass tubes and two stainless steel tubes of precision bore were used in the experiments to study how the geometry effect. In the oil displacing experiments, at Power Law index higher than 0.45, change in tube diameter did not have much effect on the fractional coverage. For gas displacing experiments, the critical Power Law index became no smaller than 0.34. Bubble shape of oil as it penetrating through viscous fluid was recorded and analyzed. For shear thinning fluid, the Power Law index and geometry both have effect on the bubble tip; while for Newtonian fluid, none of them affect the shape of the bubble tip. The shear thinning effect tended to make the bubble tip sharper.
Table 5.1: Rheological properties of all the fluids tested in the oil-assisted or gas-assisted injection experiments

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Intercept m (Pa.s)</th>
<th>Power law index n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amoco Polybutene H-100</td>
<td>6.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Amoco Polybutene H-300</td>
<td>58.6</td>
<td>1.0</td>
</tr>
<tr>
<td>0.1% Carbopol 940</td>
<td>11.93</td>
<td>0.127</td>
</tr>
<tr>
<td>0.1% Carbopol 941</td>
<td>8.05</td>
<td>0.25</td>
</tr>
<tr>
<td>0.1% Carbopol 910</td>
<td>1.96</td>
<td>0.448</td>
</tr>
<tr>
<td>0.2% Carbopol 940</td>
<td>177.49</td>
<td>0.069</td>
</tr>
<tr>
<td>0.5% Carbopol 941</td>
<td>21.05</td>
<td>0.34</td>
</tr>
<tr>
<td>0.5% Carbopol 910</td>
<td>3.56</td>
<td>0.48</td>
</tr>
<tr>
<td>Fluid</td>
<td>Density (g/cm$^3$)</td>
<td>Interface tension with water (dynes/cm)</td>
</tr>
<tr>
<td>----------------------</td>
<td>--------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>Amoco Polybutene H-100</td>
<td>0.852</td>
<td>37.6</td>
</tr>
<tr>
<td>Amoco Polybutene H-300</td>
<td>0.89</td>
<td>—</td>
</tr>
<tr>
<td>0.1% Carbopol 940</td>
<td>0.987</td>
<td>—</td>
</tr>
<tr>
<td>0.1% Carbopol 941</td>
<td>0.98</td>
<td>—</td>
</tr>
<tr>
<td>0.1% Carbopol 910</td>
<td>0.98</td>
<td>—</td>
</tr>
<tr>
<td>0.2% Carbopol 940</td>
<td>0.953</td>
<td>—</td>
</tr>
<tr>
<td>0.5% Carbopol 941</td>
<td>0.97</td>
<td>—</td>
</tr>
<tr>
<td>0.5% Carbopol 910</td>
<td>0.976</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 5.2: Densities and interfacial surface tensions of all the fluids tested in the oil-assisted or gas-assisted injection experiments
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Figure 5.39: Experimental results of fractional coverage as function of Capillary number for 0.5% Carbopol 941 solution in stainless tube 1 and 2
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CHAPTER 6

SIMULATION

6.1 Theoretical Background

6.1.1 Governing Equations

The penetration of a long gas bubble in a capillary tube filled with viscous or viscoelastic fluids is governed by the momentum balance and continuity equations. The equation of continuity at steady state, for an incompressible fluid, in cylindrical coordinates can be written as

\[
\frac{\partial u}{\partial z} + \frac{\partial v}{\partial r} + \frac{v}{r} = 0 \quad (6.1)
\]

where \( u \) and \( v \) are the components of fluid velocity in the \( z \) and \( r \) directions respectively (Figure 3.1). The momentum balance equations in the \( z \) and \( r \) directions are respectively

\[
\begin{align*}
-\frac{\partial P}{\partial z} &= \frac{\partial \tau_{rz}}{\partial r} + \frac{\tau_{rz}}{r} + \frac{\partial \tau_{zz}}{\partial z} \quad (6.2) \\
-\frac{\partial P}{\partial r} &= \frac{\partial \tau_{rr}}{\partial r} + \frac{\tau_{rr}}{r} + \frac{\partial \tau_{rz}}{\partial z} - \frac{\tau_{zz}}{r} \quad (6.3)
\end{align*}
\]
where P is the pressure and $\tau_{rz}$, $\tau_{zz}$ and are the components of the extra stress tensor. For the special case of a Newtonian fluid the extra stress tensor can be written in terms of the rate of deformation tensor $D$.

The Newtonian constitutive equation can be written as

$$\tau = 2\eta D$$

(6.4)

or in expanded notation for the current conditions as

$$\tau = \begin{bmatrix} \tau_{zz} & \tau_{zr} & 0 \\ \tau_{zr} & \tau_{rr} & 0 \\ 0 & 0 & \tau_{\theta\theta} \end{bmatrix} = 2\eta D = \begin{bmatrix} 2\frac{\partial u}{\partial z} + \frac{\partial v}{\partial r} & \frac{\partial u}{\partial r} + \frac{\partial v}{\partial z} & 0 \\ \frac{\partial u}{\partial r} + \frac{\partial v}{\partial z} & 2\frac{\partial v}{\partial r} & 0 \\ 0 & 0 & \frac{2v}{r} \end{bmatrix}$$

(6.5)

The $z$ and $r$ components of the equation of motion become

$$\frac{\partial P}{\partial z} = \eta \left[ \frac{1}{r} \frac{\partial u}{\partial r} + \frac{\partial^2 u}{\partial r^2} \right]$$

(6.6)

$$\frac{\partial P}{\partial r} = \eta \left[ \frac{1}{r} \frac{\partial v}{\partial r} + \frac{\partial^2 v}{\partial z^2} - \frac{u}{r^2} \right]$$

(6.7)

6.1.2 Boundary Conditions

(1) No-Slip

At the wall, the no-slip boundary condition holds and we can write in the Lagrangian frame of reference

$$r = b, \ u = -U, \ v = 0$$

(6.8)

The frame of reference is stationary with respect to the bubble, and the wall has a velocity equal to and in the opposite direction of the bubble velocity U.
(2) Bubble Location

The bubble location can be specified as a function of $r$ and we can write

$$z = h(r) \quad (6.9)$$

where $h(r)$ is a unique function in one variable.

(3) Kinematic Condition

The velocity of the fluid normal to the bubble is zero at any location along the interface. The normal and tangential vectors to the interface can be easily calculated using the function $h(r)$. The unit vector normal to the interface $\mathbf{n}$ is determined by the gradient of the function $f$ describing the free surface location

$$f = z - h(r) = 0 \quad (6.10)$$

$$\nabla f = i - \frac{dh}{dr} j \quad (6.11)$$

$$\mathbf{n} = \frac{1}{1 + \left(\frac{dh}{dr}\right)^2} \left[ i - \frac{dh}{dr} j \right] \quad (6.12)$$

The velocity component normal to the interface is simply $\mathbf{u} \cdot \mathbf{n}$ where $\mathbf{u} = u\mathbf{i} + v\mathbf{j}$ is the velocity vector. Therefore the boundary condition can be written as

$$\mathbf{u} \cdot \mathbf{n} = \frac{u - \frac{dh}{dr} v}{1 + \left(\frac{dh}{dr}\right)^2} = 0 \quad (6.13)$$

(4) Normal Stress Condition

The component of the viscous stress normal to the interface is balanced by the pressure and the surface tension forces. In mathematical terms it can be written as
\[ P - \tau_{nn} = P_0 - \sigma \left[ \frac{1}{R_1} + \frac{1}{R_2} \right] \]  

(6.14)

where \( \tau_{nn} \) is the viscous stress component normal to the interface, \( P_0 \) is the gas pressure, \( \sigma \) is the interfacial tension between the gas and fluid and \( R_1, R_2 \) are the two radii of curvature at the interface. The traction vector on the plane normal to the interface can be written as

\[ t_n = n \cdot \tau = \frac{1}{\left( 1 + \frac{d^2 h}{dr} \right)^{1/2}} \begin{bmatrix} \tau_{zz} - \frac{d h}{dr} \tau_{zr} \\ \tau_{zr} - \frac{d h}{dr} \tau_{rr} \end{bmatrix} \]  

(6.15)

The normal component of extra stress can be written in terms of the traction vector as

\[ \tau_{nn} = t_n \cdot n = \frac{\tau_{zz} - 2 \frac{d h}{dr} \tau_{rz} + \frac{d h^2}{dr} \tau_{rr}}{1 + \frac{d^2 h}{dr}} \]  

(6.16)

The normal stress boundary condition can then be written as

\[ P - \tau_{zz} - \frac{2}{d h} \tau_{rz} + \frac{d h^2}{dr} \tau_{rr} = P_0 - \sigma \left[ \frac{1}{R_1} + \frac{1}{R_2} \right] \]  

(6.17)

For a Newtonian fluid, the boundary condition can be simplified to

\[ P - 2n \left( \frac{du}{dz} - 2 \frac{d h}{dr} \left( \frac{du}{dr} + \frac{dv}{dz} \right) + \frac{d h^2}{dr} \right) = P_0 - \sigma \left[ \frac{1}{R_1} + \frac{1}{R_2} \right] \]  

(6.18)
From Equation [6.17] the surface tension $\sigma$ could be calculated as

$$
\sigma = \left( P_0 - P + \frac{2\eta}{1 + \frac{dh^2}{dr}} \left( \frac{du}{dz} - 2\frac{dh}{dr} \left( \frac{du}{dr} + \frac{dv}{dz} \right) + \frac{dh^2}{dr} \frac{dv}{dr} \right) \right) \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (6.19)
$$

(5) Shear Stress Condition

The shear stress at the free surface is zero, or the component of the stress tensor tangential to the free surface vanishes at the interface. The tangential component is simply a dot product of the traction vector and the unit tangent vector $s$. The unit tangent vector can be calculated from the derivative of the free surface equation in parametric form intersecting the $\theta = 0$ plane.

$$
s = \frac{1}{\sqrt{1 + \left( \frac{dh}{dr} \right)^2}} \left[ \frac{dh}{dr} i + j \right] \quad (6.20)
$$

The tangential stress condition then becomes

$$
\tau_{ns} = t_n \cdot s = \frac{\frac{dh}{dr} \tau_{zz} + \left( 1 - \frac{dh^2}{dr} \right) \tau_{rz} - \frac{dh}{dr} \tau_{rr}}{1 + \frac{dh^2}{dr}} = 0 \quad (6.21)
$$

For Newtonian fluids the tangential stress condition can be written using [6.5] as

$$
\tau_{ns} = t_n \cdot s = \eta \left( \frac{1 - \frac{dh^2}{dr}}{1 + \frac{dh}{dr} \frac{d^2}{dz^2}} \left( \frac{du}{dr} + \frac{dv}{dz} \right) + \frac{2\eta}{1 + \frac{dh}{dr} \frac{d^2}{dz^2}} \left( \frac{du}{dz} - \frac{dv}{dr} \right) \right) = 0 \quad (6.22)
$$
For Non-Newtonian fluids, different constitutive models were selected to describe the rheological behavior of the materials, which were applied to the equation of motion to calculate the flow field.

Simulation was carried out for the processes of Nitrogen gas penetrating through ideal elastic fluid and of silicon oil penetrating through Carbopol solutions using the finite element program Polyflow. The problem is formulated in the Lagrangian frame of reference with a stationary bubble and the tube wall moving at the desired velocity in the opposite direction to the bubble’s movement. Instead of assuming free surface along the interface between bubble and viscous fluid and calculate for the bubble’s location and profile through remeshing, the bubble’s position and profile were fixed based on the photos of the bubbles taken using the CCD camera and full slip boundary condition was assumed. The geometry and mesh was shown in Fig 6.1. The boundaries were defined as below:

Boundary (1) was specified as axis of symmetry, which resulted in zero shear force and normal velocity. Boundary (2) was defined using the outflow condition provided by Polyflow. It was pointed out that for ideal elastic fluid the outflow boundary condition required a volume flow rate defined as well. At boundary (3) an axial wall velocity was defined equaling to the bubble velocity and in the opposite direction. At boundary (4) shear force and normal velocity were initially imposed. The velocity was defined equal to the wall velocity, which will result in a higher convergence rate. Boundary (5) corresponded to the interface between bubble and viscous fluid, the bubble profile and position were fixed and full slip condition was imposed along the interface.
The applicability of this method was tested based on the comparison between a series of simulation result of bubble penetrating through viscoelastic fluid and corresponding experimentally measured result. Also the error was evaluated by calculating for the values of surface tension at different points along the interface based on the simulation result of the Carbopol experiments.

6.2 Simulation of gas penetrating through ideal elastic fluid

The ideal elastic fluid is Boger fluid consist of 0.25 wt% Polyisobutylene (PIB, \(M_w=1.2\times10^6\), Exxon Vistanex), 95 wt% Polybutene (Amoco H-100) and 4.75 wt% Tetradecane (Fischer). The rheological measurement of this fluid was carried out by Vishal Gauri, a previous graduate student in my group. The rheological data were fitted using 1 mode and 4 modes Giesekus models. Fig 6.2 showed the experimental data and fitting lines. Table 6.1 listed the parameters of the model fitting.

Fig 6.3 showed the experimental set up of gas bubble penetrating through Boger fluid in tube with diameter equals to 6 cm. Aluminum particles were dispersed in the material to illuminate the flow pattern. A Particle Tracking Velocimetry (PTV) technique was employed to obtain accurate velocity field measurements. The local shear and extension rates in the flow field were computed in the region of interest.

The simulation was carried out according to the method described above. The constitutive models employed in the simulation were 1 mode and 4 modes Giesekus models. The bubble shape profiles were from Gauri’s dissertation. Fig 6.4 showed the comparison of shear rate and extensional rate contours using the two models in the
simulation at Ca = 0.4. From the graph it was obvious that the variation in mode did not affect the simulation result apparently. Thus the 4 modes simulation result will be used in the later analysis.

Fig 6.5 showed comparison of local shear rate and extensional rate contour for Boger fluid between PTV and simulation results at capillary number equals to 4.0. It was observed that the distribution and the magnitude of the contour variables agreed with each other very well, which proved the validity of the simulation technique.

Fig 6.6, 6.7 and 6.8 showed the stream line, local shear rate contour and local extensional rate contour for gas bubble penetrating through Boger fluid under capillary number equaled to 0.4, 1.3 and 4.0. From Fig 6.6 it was obvious that at low capillary number originally there was recirculation at the region near bubble front near the center line. With the increase of capillary number, the recirculation will disappear. In Fig 6.7 and 6.8 it could be observed that the high local shear rate and extensional rate concentrated in the region near the bubble front on the center line. With increase of capillary number the high variable region will move backward along the bubble curvature.

In Fig 6.9 the fractional coverage was plotted as function of capillary number for gas bubble penetrating through Newtonian and Boger fluids. For Newtonian fluid, the fractional coverage will increase at the beginning with the increase of capillary number and gradually achieved a constant value of 0.6. For Boger fluid at low capillary number the curve was very close to that of Newtonian fluid. But at high capillary number the fractional coverage will keep increasing instead of plateau to a constant value. The difference between the two curves occurred at capillary number around 4.0 as shown in the graph. Fig 6.10 showed the local shear stress and first normal stress difference
contour for Newtonian and Boger fluids at the critical capillary number. From Fig 6.10 it was apparent although the local shear stress for Boger fluid was slightly lower than Newtonian fluid, its first normal stress was much higher than Newtonian fluid. Higher normal stress difference meant higher contraction force around the bubble, which squeezed the bubble further and resulted in higher fractional coverage.

6.3 Simulation for silicon oil penetrating through shear thinning fluid

In Chapter 5 the silicon bubble profiles were presented and discussed in detail. Based on the measured bubble shapes the geometry and mesh were set up and boundary conditions were set. All the carbopol solutions had concentration of 0.1% (weight percent). Powerlaw model was employed as the constitutive model in the simulation. Because the power law index for the solutions are small, evolution technique was applied to the parameter of power law index n to make the problem converge more quickly. Since Carbopol 940 solution has obvious yield stress which was 10 Pa by measurement, Bingham model was selected to fit the rheological data of Carbopol 940 solution:

\[ \eta = A + \frac{\tau_y}{\gamma} \]  

(6.23)

where \( A = 0.26 \text{ Pa}\cdot\text{s} \) and \( \tau_y = 10 \text{ Pa} \).

Fig 6.11 and 6.12 showed the streamlines of silicon oil penetrating through Carbopol 940 using Power Law model and Bingham model as constitutive models in tube 1 and tube 2 which have diameter equal to 0.3 and 0.5 cm. For the simulation using Power Law model, at low capillary number, there was recirculation near the bubble front. With the increase of bubble velocity the recirculation disappeared. But for the simulation using Bingham model, at low capillary number there is recirculation which will gradually
disappear with increase of capillary number. But in tube 2, as capillary keep increasing, the recirculation will reoccur. To explain the difference between the results using different constitutive model, in Fig 6.13 the streamlines and local shear stress distribution calculated using Power Law and Bingham models were plotted at Ca = 0.23 for Carbopol 940 in tube 2. For Power Law model there is no recirculation while for Bingham model, the recirculation reappeared. In the region at bubble front near the center line there is a concentration of shear stress in negative direction, which is the cause of the recirculation around that location because the shear stress force the fluid flow in the direction along the direction of the stress. In Fig 6.14 the velocity contour for Carbopol 940 in tube 2 at three capillary numbers using Power Law and Bingham models were presented. For the simulation using Bingham model, the flow with recirculation in front of the bubble always had a higher velocity magnitude in that region, especially when compared with results using Power Law model like in the case when capillary number was equal to 0.137.

Fig 6.15 and Fig 6.16 showed the streamlines and velocity contour of simulation of bubble penetration through Carbopol 941 and Carbopol 910 in tube 1. For Carbopol 941, with the increase of capillary number, the recirculation in front of the bubble will disappear. But for Carbopol 910 there was always recirculation, which means with the increase of Power Law index, the capillary number where the recirculation will disappear will also increase. Similar phenomena for flow field in the other two tubes with bigger diameters.

The surface tension at each node along the bubble curvature was calculated according to equation 6.19. Gas pressure P₀ was calculated based on equation 6.18 and
the flow field between the bubble and inner wall far behind the bubble tip.

Experimentally measured interfacial tension was used in equation 6.18. The calculated $P_0$ was plugged in equation 6.19 to calculate interfacial tension along the bubble tip curve and the calculated values were compared with the measured data. In Fig 6.17 the calculated surface tension as a function of radial position was plotted for a bubble penetrating through Carbopol 940 in tube 2 at $Ca = 0.137$. The calculated values fell into the same magnitude as the experimentally measured surface tension. All the other simulation resulted in similar plot. The more accurate the measured bubble profile, the closer the calculated surface tension to the value of the experimental measurement. Also the calculated surface tension could be applied in calculation of the pressure inside the bubble which may provide a start for the free surface simulation.

6.4 Conclusion

Simulation was carried out using full slip assumption along the gas/silicon oil and viscous fluid interface. The bubble profiles were measured and fixed in the geometry set up in the simulation. The process of bubble penetration through a pure elastic fluid and three highly shear thinning fluids were simulated based on the measured bubble shape and the full slip assumption. For the pure elastic fluid case, the simulation result was compared with the experimentally measured flow field using PTV technique. They agreed with each other well, which tested the applicability of this simulation method. The stress distribution from the simulation was employed to explain the difference in the fraction coverage vs. Ca curve between Newtonian and the pure elastic fluid. For the three highly shear thinning fluid, whose rheological data were fitted with Power Law model, the simulation provided a very detailed description of the flow field near the
bubble front. It was observed that with the increase of Power Law index, the critical capillary number where the recirculation will disappear also will increase. Carbopol 940 solution also had large yield stress, which was used as a parameter in the rheology fitting using Bingham model. The simulation result using Power Law model and Bingham model were compared. The simulation using Bingham model will result in reoccurrence of recirculation of fluid in front of bubble which was explained by comparing the local shear stress distribution for the simulation using the two rheological models.
<table>
<thead>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<td>2.61E-03</td>
<td>6.97E-02</td>
<td>2.02E-01</td>
</tr>
</tbody>
</table>

Table 6.1: 4 modes Giesekus model fitting parameters
Fig 6.1 Geometry and mesh for the simulation with the definition of boundary set
Fig 6.2: Rheological data and model fitting for Boger fluid
Fig 6.3: Apparatus for flow visualization experiment
Figure 6.4: Comparison of simulation results using 1 mode (left) and 4 modes (right) Giesekus constitutive models: Shear rate contour (upper row), Extension rate contour (lower row) (Ca = 0.4)
Figure 6.5: Comparison of local shear rate (upper row) and extensional rate (lower row) between PTV (left) and simulation (right) results ($Ca = 4.0$)
Figure 6.6: Stream line contour of gas bubble penetrating through Boger fluid (Ca = 0.4, 1.3 and 4.0)
Figure 6.7: Local shear rate contour for bubble penetrating through Boger fluid (Ca = 0.4, 1.3 and 4.0)
Figure 6.8: Local extensional rate contour for bubble penetrating through Boger fluid (Ca = 0.4, 1.3 and 4.0)
Fig 6.9: Fractional coverage vs. Ca for Newtonian and Boger fluids
Figure 6.10: Comparison of local shear stress (upper row) and first normal stress (lower row) between Newtonian (left) and Boger (right) fluids (Ca = 4.0)
Fig 6.11: Streamlines for Carbopol 940 using Power Law (left) and Bingham (right) models at Ca = 0.088, 0.15 and 0.28 in tube1
Fig 6.12: Streamlines for Carbopol 940 using Power Law (left) and Bingham (right) models at Ca = 0.137, 0.22 and 0.27 in tube 2
Figure 6.13: Stream lines and local shear stress for Carbopol 940 at Ca = 0.27 using Powerlaw (left) and Bingham (right) models
Fig 6.14: Velocity contour of oil bubble penetrating through Carbopol 940 using Power Law (left) and Bingham (right) models at Ca = 0.137, 0.22 and 0.27 in tube 2.
Fig 6.15: The streamlines and velocity contour of Carbopol 941 in tube 1 at Ca = 0.09 and 0.18
Fig 6.16: Streamlines and velocity contour for Carbopol 910 in tube 1 at $Ca = 0.17$ and 2.02
Fig 6.17: Calculated surface tension as function of radial position for bubble penetration through Carbopol 940 in tube 2 at $Ca = 0.137$
CHAPTER 7

FUTURE WORK

7.1 Extension of the experimental study and model calculation of the process using Newtonian fluid under non-isothermal condition.

For the experimental and theoretical studies of gas-assisted injection through Newtonian fluid under non-isothermal condition in capillary tube, the length to diameter ratio of the tube was comparatively small and the bubble penetration velocity was very high. The reasons are: first to reduce the time for bubble penetration such that the radial temperature profile far in front of bubble could be considered as the profile just before the bubble’s penetration; second as we set the bubble velocity very high, we could guarantee the Capillary number would be high enough such that the fractional coverage under isothermal condition for Newtonian fluid should always be 0.6. To understand the effect of temperature gradient on fractional coverage in more detail, bubble velocity could be set at lower value such that the Capillary number region could be enlarged to include the non-plateau region in the Newtonian master curve into our consideration. Again the fractional coverage could be measured at different delay time under different
bubble velocity, or Capillary number. Smaller bubble velocity would result in longer time it takes for bubble to penetration through the tube. During this process, the change of radial temperature profile along axial direction could not be neglected any more. To account for the variation theoretically, we need to expand the frozen layer model to allow non-uniform fractional coverage exist along the tube inner wall. Basic steps could be: The total time for bubble penetrating through the tube could be divided into small time steps. For each time step, a radial temperature profile far in front of bubble should be calculated according to the one dimensional heat transfer model using finite difference method. A fractional coverage could be calculated for this time step, which was the fractional coverage on the inner wall for a certain distance along the tube. The region of the tube where the current fractional coverage is effective corresponds to the distance that the bubble has traveled at the specific penetration velocity during the time step. The velocity could be calculated according to the pressure drop and rheological behavior of the Newtonian fluid far in front of the bubble. This is a more complicated case and a new FORTRAN program based on the program we have should be written to solve this problem. The experimental results could be plotted into two ways, one is to fix the capillary number and plot the fractional coverage as function of delay time, the other is to fix the delay time and plot fractional coverage as function of Capillary number. The plots obtained using the second method could be compared with the results of isothermal Newtonian fluid. Calculated results should be compared with experimental results to test the effectiveness of the model. The definition of Capillary number could be referred to the various definitions we have tried or would try in the work using Carbopol solutions as displaced fluid.
7.2 Application of frozen layer model in experiments using non-Newtonian fluid under isothermal condition, limitation of this model and the method to correct it.

Because in our frozen layer model, the basic idea is all the deviation from Newtonian behavior under isothermal condition is due to the non-constant viscosity throughout the flow field. Whether the varying viscosity is caused by temperature or by non-Newtonian properties of the fluid does not affect the model calculation. The viscosity profile formed under positive temperature gradient is like that formed using a shear-thickening fluid. Similarly, shear thinning fluid could be compared to the negative temperature gradient. Some calculation based on the frozen layer model at different bubble velocity has been done for the experiments using Carbopol solutions. The only difference is the viscosity profile was obtained from the rheological behavior of the materials under isothermal condition. Limitation was found in applying this model to shear thinning fluid.

Due to the way we did the integration, the frozen layer model could be used in experiments of small negative temperature gradient. Large negative gradient may result in negative fractional coverage. For shear thinning fluid under isothermal condition, if the shear thinning effect is too strong (or the Power Law index is too small), the calculated fractional coverage may be negative too. The reason for this error is because in the model calculation, for positive temperature gradient (or shear thickening fluid), we would get a positive frozen layer after the integration, that is, the calculated frozen layer is inside the real tube and the diameter of the region for assumed isothermal Newtonian fluid was smaller than the inner diameter of the tube. This would guarantee a positive fractional coverage bigger than the Newtonian result. But for negative temperature gradient (or
shear thinning fluid), the frozen layer is outside the tube and final fractional coverage would depend on the degree of deviation of viscosity profile from constant viscosity distribution. Thus the possibility for negative result exists. In the calculation talked before we only consider the viscosity profile far in front of the bubble, while the flow field near bubble front and between bubble and inner wall would have effect on the fractional coverage as well. Thus if the deviation of viscosity profile far in front of bubble from constant viscosity distribution is large enough, negative result may occur. To solve this problem, one way is to take into consideration the local effect of bubble by including the viscosity profile near the bubble and the region between bubble and inner wall. In the calculation for Newtonian fluid under non-isothermal condition, the transition flow field between bubble and the region far in front of bubble was neglected due to the lack of information. Simulation need to be done to more accurately describe the localized flow field near the bubble, which would be discussed later. The combination of multiple viscosity profiles were tried by simply adding the overlapped part of the profiles together and taking the average values. More sophisticated method of combination should be tested for better prediction, which may involve average over certain function of viscosity correlated with the calculation of velocity profile, because that may be the most direct way how the viscosity distribution would affect the fractional coverage.

7.3 Study combined effects of non-Newtonian rheological properties and non-isothermal condition experimentally and theoretically

As a newly developed polymer processing technique, the factors controlling the fractional coverage are mainly the temperature and the rheological properties of the polymer melt. We have studied how the temperature gradient and non-Newtonian
rheology may affect the bubble penetration process separately. In real process of gas-assisted injection molding, both of the factors exists at the same time. Next step we consider to design experiments under non-isothermal condition using non-Newtonian fluid. The rheological behavior of the non-Newtonian fluid should be sensitive to temperature variation.

Non-Newtonian fluids should be divided into three categories: pure viscoelastic fluid, pure shear thinning fluid and fluid having both viscoelasticity and shear thinning effects. The third one is the most common polymer material like the Carbopol solutions we have used before. But Carbopol does not show temperature dependence of rheological properties. We still need to find a new fluid which could be temperature sensitive. After determination of the three types of fluids, experiments under non-isothermal condition could be carried out. The basic schematic of the experiment setup could be the same as the non-isothermal setup with temperature gradient maintained by two water baths. Similarly fractional coverage could be measured as function of delay time and Capillary number. After the experimental data were obtained, we could use frozen layer model to do the prediction. The major problem in using frozen layer model under this situation is again how to find the radial viscosity profile far in front of and near the bubble. Finite difference method would be a good choice in doing the calculation. Time region and flow geometry would be divided into small elements, which could make the calculation step forward and consider the effect of temperature and non-Newtonian properties on the viscosity profile at the same time.
7.4 The effect of displacing fluid’s property on gas-assisted injection process or co-injection molding process

In the experimental study of Carbopol solutions, we used two displacing fluids: silicon oil having viscosity similar to water and nitrogen gas. The two sets of results were compared with each other. It was found that at low capillary number region, the plots of fractional coverage as function of Capillary number for the two cases almost overlapped. While at higher Capillary number, the fractional coverage of the experiment using silicon oil as displacing fluid achieve a higher value than that of gas injection process. Also when the gas-assisted process exhibits a plateau tendency, the one using silicon oil does not show the trend yet. In the later work, displacing fluid with different shear viscosity could be tested. The results using displacing fluid with different viscosity could be compared with each other and the deviation of fractional coverage from each other could be studied as a function of the viscosity difference between the two fluids. Immiscible fluid with viscosity close to that of the displaced fluid could also be considered, which may result in some interesting phenomena due to the similarity in rheological behavior of the two materials. As the displacing fluid’s viscosity becomes close to the viscous fluid it will be more like a co-injection molding process and the bubble will pull the coating layer with it. Thus the fractional coverage was also a function of the amount of fluid penetrating through the viscous fluid. As the penetrating fluid approaches infinity, the fractional coverage will become zero. This adds another variable to the study. Bubble shapes using different displacing fluids could be recorded as well.
7.5 Micro scale gas-assisted injection molding process

While the work described in this dissertation was focused on macro scaled process, putting the frozen layer model and simulation technique to the test of micro scaled experiments can be a challenge. It also has application in processes like oil recovery which corresponding to the process of pushing oil out of rocks using less viscous and immiscible fluid. Due to the rocks structure, it is usually a micro scaled flow. Also it has application in micro fluid channel design which is a critical part in micro molding design. The work can be done by using micro channels as flow geometry. Due to the small geometry, high shear rate and break down of polymer may occur. The change of fluid during the flow should also be taken into consideration and therefore more extensive rheological measurement was needed. The process of gas penetrating through Newtonian fluid under non-isothermal condition in micro tube can be a good start.
REFERENCES


Pitts, E., Penetration of Fluid into a Hele-Shaw Cell: the Saffman-Taylor Experiment. (1980), J Fluid Mech., 97, 53-64.


APPENDICES

Appendices A: Programs written in FORTRAN for temperature calculation

use MSIMSL

real(8), dimension(12) :: theta
real(8), dimension(2, 21) :: Temp_f
real(8), dimension(2, 21) :: Temp_s
real(8), dimension(12,21) :: Temp_ff
real(8), dimension(12,21) :: Temp_fs

real(8) ctheta, dtheta, dr1, dr2, R01, R02
real(8) delta_r, alpha_f, alpha_s, k_s, den_s, Cp_s, h, Ti, Tb,r
real(8) ca, cb, Cp_f, u_f, den_f, v_f, k_f, D, bbeta, L, g, GrPr,Nu
integer i, j, k, m, n, count
integer array_d

OPEN(1, FILE = 'DATA.DAT', ACTION = 'WRITE', STATUS = 'old')
onopen(2,file = 'data1.dat', action = 'write', status = 'old')
onopen(3,file = 'data_h.dat', action = 'write', status = 'old')

array_d=21
THETA(1) = 5; THETA(2) = 10; THETA(3) = 20; THETA(4) = 30; THETA(5) = 40;
THETA(6) = 50
THETA(7) = 60; THETA(8) = 90; THETA(9) = 120; THETA(10) = 180; THETA(11) =
240; THETA(12) = 480

dtheta=0.0001; h=100; Ti=51.1; Tb=25.1
R01=5.461*0.001; R02=6.35*0.001; k_s=25; den_s=7850; Cp_s=514.5;
alpha_f=6.0/(10**8)
Cp_f=2325.4; u_f=0.27*0.001; den_f=952.39; v_f=2.834*10*(-7)
k_f=0.3797; D=2*R02; bbeta=4.4/10**4; L=0.305; g=9.81;

delta_r=R02-R01; alpha_s=k_s/(den_s*Cp_s);
dr1=R01/(array_d-1); dr2=delta_r/(array_d-1)
!a=(-h/k_s)*2*dr2 !dr1 is for step change in fluid, dr2 is for change in steel
!b=h/(den_s*Cp_s*delta_r)
do i=1,2
do j=1,array_d
  Temp_f(i,j)=Ti; Temp_s(i,j)=Ti
end do
end do

!Temp_s(1,21) = (Temp_s(1,19)-a*Tb)/(1-a)
!Temp_s(1,21)=Tb; Temp_s(2,21)=Tb
ca=(0.53/D)*k_f*(bbeta*g*D**3*den_f**2*Cp_f/(u_f*k_f))**0.25
h=ca*abs(Temp_s(1,array_d)-Tb)**0.25
write(3,*) "0", h
a=-h*2*dr2/k_s
Temp_s(1,array_d)=(Temp_s(1,array_d-1)-a*Tb)/(1-a)
do k=1,12
  !ca=(0.53/D)*k_f*(bbeta*g*D**3*den_f**2*Cp_f/(u_f*k_f))**0.25
  !h=ca*(Temp_s(1,array_d)-Tb)**0.25
  !a=-h*2*dr2/k_s
  !Temp_s(1,array_d)=(Temp_s(1,array_d-2)-a*Tb)/(1-a)
  write(*,*) "k is ", k
  !cb=ca/(4*den_f*Cp_f*delta_r)
  !write(*,*) ca, cb
  !Temp_s(2,21)=Tb+((Ti-Tb)**(-0.25)+tb*theta(k))**(-4)
  do while(ctheta <= theta(k))
    count = count+1
    ctheta=ctheta+dtheta
    if (((Temp_s(1,array_d)-Tb)*bbeta*g*D**3/(u_f/den_f)**2)>1000) then
      h=ca*abs(Temp_s(1,array_d)-Tb)**0.25
      !!Temp_s(2,21)=Tb+(Ti-Tb)*exp(-b*theta(k))
    else
      GrPr=Cp_f*den_f**2*g*bbeta*D**3*(Temp_s(1,array_d)-Tb)/(u_f*k_f)
      Nu=10**(0.0097*log(GrPr)+0.131*log(GrPr)+0.0454)
      h=Nu*k_f/D
    end if
    Temp_s(2,array_d)=Temp_s(1,array_d-2)-(2*h*dr2/k_s)*(Temp_s(1,array_d)-Tb)
  end do
  !i=21
  !dT_dr=(Temp_s(1,i)-Temp_s(1,i-1))/dr2
  !dT2_dr2=(Temp_s(1,i)-2*Temp_s(1,i-1)+Temp_s(1,i-2))/dr2**2
  !Temp_s(2,i)=Temp_s(1,i)+dtheta*alpha_s*(dT2_dr2+(dT_dr)*1/(R01+dr2*(i-1)))
!cal temper pro inside steel

do i=array_d-1,2,-1
   dT_dr=(Temp_s(1,i+1)-Temp_s(1,i-1))/(2*dr2)
   dT2_dr2=(Temp_s(1,i+1)-2*Temp_s(1,i)+Temp_s(1,i-1))/dr2**2
   r=R01+dr2*(i-1)
   sum=dtheta*alpha_s*(dT2_dr2+(dT_dr)/r)
   Temp_s(2,i)=Temp_s(1,i)+sum
end do

i=1 !cal temper at R01
dT_dr=(Temp_s(1,i+1)-Temp_s(1,i))/dr2
dT2_dr2=(Temp_s(1,i+1)-2*Temp_s(1,i)+Temp_s(1,i))/dr2**2
Temp_s(2,i)=Temp_s(1,i)+dtheta*alpha_s*(dT2_dr2+(dT_dr)/1/(R01+dr2*(i-1)))

!cal temper pro inside steel
Temp_f(2,array_d)=Temp_s(2,1) !continuity
   do i=array_d-1,2,-1 !cal temper pro inside fluid
      dT_dr=(Temp_f(1,i+1)-Temp_f(1,i-1))/(2*dr1)
      dT2_dr2=(Temp_f(1,i+1)-2*Temp_f(1,i)+Temp_f(1,i))/dr1**2
      sum=dtheta*alpha_f*(dT2_dr2+(dT_dr)/1/(dr1*(i-1)))
      Temp_f(2,i)=Temp_f(1,i)+sum
   end do

i=1 !cal temper at R01
dT_dr=(Temp_f(1,i+1)-Temp_f(1,i))/dr1
dT2_dr2=(Temp_f(1,i+1)-2*Temp_f(1,i)+Temp_f(1,i))/dr1**2
!Temp_f(2,i)=Temp_f(1,i)+dtheta*alpha_f*(dT2_dr2+(dT_dr)/1/(dr1*(i-1)))
Temp_f(2,1)=Temp_f(2,2)
!Temp_f(2,1)=Temp_f(1,2)
doi=1, array_d
   Temp_s(1,i)=Temp_s(2,i)
   Temp_f(1,i)=Temp_f(2,i)
end do

end do

do i=1, array_d
   Temp_ff(k,i)=Temp_f(1,i)
   Temp_fs(k,i)=Temp_s(1,i)
end do
write(3,*) ctheta, h
end do

!output the temperature profiles at different delay time
!WRITE(1, 10) "r", "5sec", "10sec", "20sec", "30sec", "40sec", "50sec", "60sec", "90sec", "120sec", "180sec", "240sec", "480sec"
!10 format(13(A16, 1X))
do i=1,array_d

WRITE(1,12) dr1*(i-1) , (Temp_ff(k,i),k=1,12)
12 format(13(E16.10,1X))
end do
do i=2,array_d
write(1,12) R01+dr2*(i-1), (Temp_fs(k,i), k=1,12)
end do
WRITE(1,*) "*********************************************************************
close(1,status='keep')

!output the surface and center temperature at different delay time
write(2,20) "Time", "R/R0=0.9", "R/R0=0"
20 format(3(A8, 1X))
do i=1,12
   write(2,22) theta(i), Temp_ff(i,19), Temp_ff(i,1)
22 format(3(E16.10,1X))
end do
write(2,*) "*********************************************************************
write(2,20) "Time", "R/R0=1.0", "R/R0=0"
do i=1,12
   write(2,22) theta(i), Temp_ff(i,array_d), Temp_ff(i,1)
end do
close (2,status='keep')
close (3,status='keep')
end
Appendices B: Program for temperature calculation using multi-
temperature profiles

real(8), dimension(12) :: THETA
real(8), dimension(12,21) :: vel, Temp_1, Temp_2
real(8), dimension(21) :: radius, r, r_local, mark, position_r
real(8) delta_p, dr1, L, A, delta_H_R, R01, sum, sum1, sum2
real(8) f, Rx, Rx1, Rx2, n_dr1, m_n, dl, position, radial_position, squeeze_ratio, Temp_in
integer i, j, k, n, q, p, position_n

position_n=9
n=21
!R01=1.0922/2*0.01; R02=((1.0/2.0)*2.54*0.01)/2
R01=0.7747/2*0.01; R02=((3.0/8.0)*2.54*0.01)/2
!R01=0.4928/2*0.01; R02=((1.0/4.0)*2.54*0.01)/2
dr1=R01/(n-1); n_dr1=1.0/(n-1)

position_r(1)= 0.77748*R01; position_r(2)=0.775875115*R01;
position_r(3)=0.757790661*R01; position_r(4)=0.721989134*R01
position_r(5)=0.665617809*R01; position_r(6)=0.58273747*R01;
position_r(7)=0.45921235*R01; position_r(8)=0.333237929*R01
position_r(9)=0.238591995*R01

!L=30.5; A=1.538/10**8; delta_H_R=7325
!sum=0; sum1=0; sum2=0

open(1, file='data.dat', action='read', status='old')
open(2, file='data1.dat', action='write', status='old')
! read in temperature data
do i=1, n
   read(1,12) r(i), (Temp_1(k,i),k=1,12)
   do k=1, 12
      Temp_2(k,i)=Temp_1(k,i)
   end do
12 format(13(E16.10,1X))
!x(i)=1-radius(i)
!initialize mark array
mark(i)=1
end do
r(n)=R01
do k=1,12

do i=1,position_n
    position = dl*i
    radial_position = ...
    radial_position = radial_position/R01
    squeeze_ratio = (R01-position_r(i))/R01
    do j=1,21
        r_local(j)=position_r(i)+(j-1)*dr1*squeeze_ratio
    end do

do q=1,21
    do p=1,20
        if (r_local(p)<r(q)) then
            if (r_local(p+1)>r(q)) then
                Temp_in=Temp_1(k,p+1)+(r(q)-r_local(p+1))/(r_local(p)-r_local(p+1))*(Temp_1(k,p)-Temp_1(k,p+1))
            Temp_2(k,q)=Temp_2(k,q)+Temp_in;
        end if
    end if
    mark(q)=mark(q)+1
    end do
end do

do i=1,21
    Temp_2(k,i)=Temp_2(k,i)/mark(i)
    mark(i)=1
end do

end do

!output the new temperature profile

!output the new temperature profile

do i=1,21
    write(2,12) r(i), (Temp_2(k,i),k=1,12)
end do

close(1,status='keep')
close(2,status='keep')
end
Appendices C: Program for fractional coverage calculation using calculated temperature profiles

!calculate vel profile using temperature profile obtained from finite difference method

real(8), dimension(12) :: THETA, m, m1, m2
real(8), dimension(12,21) :: vel, Temp
real(8), dimension(21) :: radius, x
real(8) delta_p, dr1, L, A, delta_H_R, R01, sum, sum1, sum2, f, Rx, Rx1, Rx2, n_dr1, m_n
integer i, j, k, n

n=21
m_n=0.6 !Ca=inf
!m_n=0.38 !Ca=0.2, not exactly
!m_n=0.314 ! Ca=0.1
delta_p=1.013*10**7
R01=1.0922/2.0
!R01=0.7747/2.0
!R01=0.4928/2.0
dr1=R01/(n-1); n_dr1=1.0/(n-1); L=30.5; A=1.538/10**8; delta_H_R=7325
sum=0; sum1=0; sum2=0

open(1, file='data.dat', action='read', status='old')
open(2, file='data2.dat', action='write', status='old')
! read in temperature data
do i=n,1,-1
    read(1,12) x(i), (Temp(k,i),k=1,12)
    x(i)=x(i)*100
    12 format(13(E16.10,1X))
    !x(i)=1-radius(i)
end do
x(1)=R01
do i=1,n
    x(i)=x(i)/R01
end do

do i=1,21
    radius(i)=x(21+1-i)
end do
THETA(1) = 5; THETA(2) = 10; THETA(3) = 20; THETA(4) = 30; THETA(5) = 40; THETA(6) = 50; THETA(7) = 60; THETA(8) = 90; THETA(9) = 120; THETA(10) = 180; THETA(11) = 240; THETA(12) = 480

do k=1,12
    vel(k,1)=0
    do i=2, 21
        f=(n_dr1/2)*delta_p*R01/(2*L*A)*(R01*x(i-1)/exp(delta_H_R/(Temp(k,i-1)+273.13))+R01*x(i)/exp(delta_H_R/(Temp(k,i)+273.13))
        vel(k,i)=vel(k,i-1)+f
    end do
    end do
    do k=1,12
    do i=1,21
        vel(k,i)=vel(k,i)/vel(k,21)
    end do
    end do
    do i=1,21
    write(2,12) radius(i), (vel(k,i), k=1,12)
    end do
    do k=1,12
        sum=0
        sum1=0
        sum2=0
        do i=1,20
            sum=sum+(n_dr1/2)*(vel(k,i)+vel(k,i+1)) !integrate through u*
            sum1=sum1+(n_dr1/2)*((1-radius(i))*vel(k,i)+(1-radius(i+1))*vel(k,i+1)) !integrate through ru*
            sum2=sum2+(n_dr1/2)*(vel(k,i)**2 +vel(k,i+1)**2) !integrate through u*^2
        end do
        Rx=1.5*sum !integrate through u*
        Rx1=2*sum1**0.5 !integrate through ru*
        Rx2=(15.0/8.0)*sum2 !integrate through u*^2
        m(k)=1-(1-m_n)*Rx**2
        m1(k)=1-(1-m_n)*Rx1**2
        m2(k)=1-(1-m_n)*Rx2**2
        write(2,6) THETA(k), m(k), THETA(k), m1(k), THETA(k), m2(k)
    end do
    end do

  6 format(6(E16.10,1X))
end do
end