Rheological behaviors of concentrated suspensions in pressure-driven tube flow

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2008

Wang, Z. (2008). Rheological behaviors of concentrated suspensions in pressure-driven tube flow. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/13457>

<https://doi.org/10.32657/10356/13457>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**RHEOLOGICAL BEHAVIORS OF CONCENTRATED
SUSPENSIONS IN PRESSURE-DRIVEN TUBE FLOW**

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**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

2008

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2008

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Professor Lam Yee Cheong, for his invaluable guidance, constant support and encouragement throughout the research work. Without his help, the project would be impossible to accomplish and the attainment would be much compromised.

My sincere thanks would be extended to research fellow, Dr. Chen Xing, for his contribution in the numerical modeling and valuable discussion in the research. I am grateful to Dr. Jiang Long for his guidance in the experimental work.

Thirdly, I wish to show my special thanks to the technicians in Materials Lab A and Biomaterial Lab for their technical assistance and operation.

Next, I would like to express my deepest gratitude to my husband, Dr. Che Faxing, for all of his valuable encouragement and dedication, and to my lovely son, Che Luyang, for his healthy growth bringing the happiness in the hard time.

Last but not least, I would like to thank my friends and many others who have in one way or another contributed to the completion of the work.

ABSTRACT

The flows of concentrated suspensions occur in many practical applications. Thus the characterization and understanding of their rheological behaviors are important.

Ethylene vinyl acetate (EVA) 460 and glass microspheres were used as the model suspension system. Rheological measurements were conducted on the binder system of pure polymer EVA460 and the concentrated suspension with glass microspheres dispersed in EVA460 polymer melt.

In the characterization of the rheological behavior of pure EVA and concentrated suspension in capillary flow, entrance and exit losses and slip velocity should be obtained. Entrance and exit losses were measured using an orifice die and were calculated by Bagley correction. Due to the difficulty in ensuring the extruded suspension to be clear from the die wall in the expansion region of the orifice die, the entrance and exit losses measured by the orifice die were higher than those by Bagley correction. It was also observed that Bagley plot exhibited good linearity for EVA but not for concentrated suspension. In addition, for concentrated suspension, the nonlinearity increased with increasing particle concentration.

The true viscosities of EVA460, which exhibit shear-thinning effect and decrease with temperature increasing, were obtained at different temperatures. The material constants in the viscosity models were determined. Due to the non-Newtonian behavior of EVA, the conventional Mooney method, which was proposed for Newtonian fluid where the slip velocity is linear to wall shear stress, cannot be used to calculate the slip velocity of a non-Newtonian fluid. Thus a modified Mooney method was proposed. In the investigated

range of flow rate, pure EVA exhibited only slight slip at higher flow rate and the slip was negligible at low flow rate.

Experiments on concentrated suspension were performed to determine the yield stress, entrance and exit losses, and slip velocity. The various key parameters and their interactions on the behaviors of the concentrated suspension were investigated. There was shear-induced particle migration for a concentrated suspension in a nonhomogeneous shear flow, which was a function of the shear rate gradient, particle concentration and viscosity. The slip at the interface between the suspension and the die wall was significant and could not be ignored. With high viscosity and low thermal conductivities, in combination with high shear rate, considerable heat could be generated as a result of viscous dissipation, especially near the capillary wall. These phenomena, which interacted with one another, were reflected in the measurements of pressure in a capillary flow.

For a better understanding of the various mechanisms and their interactions, numerical model describing the various behaviors was proposed. Modeling and analyses of the rheological behaviors of the concentrated suspension were achieved by employing numerical methods. The model developed accounted for the followings: (i) shear induced particle migration (ii) wall slip (iii) heat generation due to viscous dissipation and (iv) interactions of these phenomena.

The diffusive coefficients were determined iteratively by minimizing the square of the difference between the experimental measurement of pressures and those calculated using a numerical algorithm, which takes into consideration of particle migration, wall slip and viscous heating. The model could predict the velocity distribution and particle

concentration profile of concentrated suspension in a capillary flow under different conditions. It can be observed that particle migration and wall slip blunt the velocity distribution in the flow section and cause the nonuniform distribution of particle concentration. In addition, the slip velocity is not uniform along the flow length, and decreases with increasing hydraulic pressure in a capillary. The predicted slip velocities by the numerical model agree well with the calculated results using the modified Mooney method based on the experimental data obtained by a capillary rheometer.

The predicted pressures under different conditions employing the assumptions of particle migration (with and without) and wall slip (with and without) were compared with experimental data. If there is only particle migration, the predicted pressure curves in a Bagley plot become convex. The larger ratio of die length to radius (L/R), the more significant would be the effect of particle migration. With wall slip but without particle migration, the curves in a Bagley plot become concave. As the range of shear rate investigated was limited to relatively low values, the effect of viscous heating was negligible. Good agreements were obtained between the measured and predicted pressures at isothermal condition employing both the assumptions of wall slip and particle migration.

Through Bagley correction and slip velocity correction, the true viscosities of concentrated suspensions with different particle concentrations and different particle sizes were determined, which can be described by Krieger model. The material constants in the Krieger model and the slip model were obtained by data fitting. The finding indicates that particle size has an effect on the viscosities of the suspensions.

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ABBREVIATIONS AND SYMBOLS

ATR	Attenuated Total Reflection
EIT	Electrical Impedance Tomography
EVA	Ethylene Vinyl Acetate
FTIR	Fourier-transform Infrared
LDA	Laser-Doppler Anemometry
MI	Melt Index
MPIV	Microscopic Particle Imaging Velocimetry
MRI	Magnetic Resonance Imaging
NFLV	Near-field Laser Velocimetry
NMR	Nuclear Magnetic Resonance
PE	Polyethylene
TGA	Thermogravimetric Analysis
a	Particle radius (mm)
b	Flow length (mm)
C	Molar concentration of the macromolecules (mol/m ³)
D	Diffusion coefficient (m ² /s)
e	End correction value in Bagley plot
E	Activation energy (J/mol)
f	Recovery coefficient
h	Heat transfer coefficient (W/m ² K)
L	Die length (mm)
m	Power-law index in Krieger model

m_0	Constant in power-law viscosity model of pure polymer (Pa.s ⁿ)
M	Flow consistency (Pa.s ⁿ)
n	Power-law index
N_c	Flux of particles due to a gradient in interaction frequency
N_η	Flux of particles due to the effective viscosity variation
N_b	Flux of particles due to Brownian diffusion
K	Thermal conductivity (J/kg.K)
k_B	Boltzmann coefficient (J/mol.K)
k_c	Phenomenological parameter
k_η	Phenomenological parameter
P_e	Pelcet number
P	Pressure (MPa)
Q	Flow rate (cm ³ /s)
R	Die radius (mm)
R_g	Universal gas constant (J/mol.K)
u	Fluid velocity (mm/s)
u_s	Slip velocity (mm/s)
T	Temperature (K)
$\dot{\gamma}$	Shear rate (1/s)
$\dot{\gamma}_a$	Apparent wall shear rate (1/s)
$\dot{\gamma}_w$	Slip-corrected wall shear rate (1/s)

β_s	Slip coefficient (Pa ^{-k} .mm/s)
η	Viscosity (Pa.s)
η_0	Newtonian viscosity at zero shear-rate (Pa.s)
η_b	Viscosity of pure polymer (Pa.s)
η_∞	Constant viscosity approached at the infinite shear limit (Pa.s)
ϕ	Particle concentration
ϕ_c	Maximum particle concentration
δ	Slip layer thickness (μm)
W_{adh}	Work of adhesion (N/m)
τ_w	Wall shear stress (Pa)
σ_n	Normal stress (Pa)
τ_y	Yield stress (Pa)
ΔP	Pressure drop (Pa)
η_a	Apparent viscosity (Pa.s)
ΔP_e	Entrance and exit losses (MPa)
ρ	Density (kg/m ³)
C_p	Specific heat (J/K)
Λ_z	Pressure gradient (Pa/mm)
β_η	Temperature sensitivity of viscosity (1/K)
N_a	Nahme-Griffith number
N_B	Buoyancy number

Bi Biot number

Nu_z Nusselt number

Re Reynolds number

T_a Constant in power-law viscosity model of pure polymer (K)

CHAPTER 1 INTRODUCTION

1.1 BACKGROUND

Suspensions of solid particles in polymers are encountered in a variety of natural and industrial processes, such as paints, inks, paper coating, and many industrial dispersion processes. Textile inkjet printing can involve two- phase fluids, consisting of pigment molecules encapsulated into hydrophilic carrier particles. These particles can jam print heads causing nonuniform distribution on the surface. Therefore, their complex rheology behaviour has attracted a great deal of attention. The flow and deformation of suspension has been a subject of interest for many years and there has recently been a considerable increase in research activities, including particle migration, wall slip, viscous heating and flow instabilities. From a practical viewpoint, the importance of this subject comes from the various industrial applications where the processing and transport of suspensions are important operations. Of equal importance is a need for the fundamental understanding of the physical phenomena occurring in the suspension.

Reliable characterization of the rheological behaviour of materials is important for many reasons: developing new materials with specific flow properties, design of processes using rheological data for existing materials or for quality control of materials in production processes. The occurrences or onset of slip and particle migration in flow complicate both the measurement of properties and the modelling of flow behaviour.

The rheological characterization of suspension requires the careful specimen preparation, which includes the preparation of particles, well-mixed suspension, and the elimination of entrapped air into the suspension. After obtaining the raw

data with viscometers, to obtain true viscosity, apparent viscosity, shear rate, pressure drop, wall slip, viscous heating etc., are to be analyzed and corrected.

This work focuses on the investigation of particle migration, wall slip and viscous heating in a non-homogeneous shear fields under pressure driven flow in a channel by numerical simulation and experiments, where the inertial effect is considered negligible.

1.2 RESEARCH MOTIVATION

Wall slip at the interface between the suspension and the solid die wall was confirmed by flow visualization experiments [Lukner and Bonnecaze, 1999] and was documented by Yilmazer and Kalyon (1989) and Kalyon (2005). Independently, particle migration in suspension has been observed experimentally [Altobelli et al., 1991; Sinton and Chow, 1991; Phillips et al., 1992; Chow et al., 1994; Altobelli and Fukushima, 1997; Han et al., 1999]. Particle migration can alter the concentration distribution of a suspension, and thus has a significant effect on the effective viscosity of concentrated suspension as well as the slip coefficient in a significant way [Jana et al. 1995]. The effect of wall slip is to reduce the driving force for shear-induced particle migration and the decrease of wall concentration from the initial concentration [Allende and Kalyon, 2000]. Therefore, particle migration and wall slip are closely related and affect the rheological behaviour of concentrated suspension.

The effect of particle migration or wall slip can be shown in the pressure necessary to drive the flow at a constant flow rate, but there is no detailed research on how they interact. Therefore, it is necessary to explore their interactions and their effects in the flow behaviour of suspension.

The Mooney method is commonly used by many researchers to calculate the slip velocity of polymer melts and concentrated suspensions in a capillary flow. However, this method was established based on the assumption of a Newtonian fluid, where the slip velocity is proportional to the wall shear stress. Upon this basis, the gradient in the plot of the apparent shear rate versus the reciprocal of die radius is four times the slip velocity. For a non-Newtonian fluid, the slip velocity was proposed to be nonlinear to the wall shear stress [Chauffoureaux et al., 1979; Lau and Schowalter, 1986; Ramamurthy, 1986; Hatzikiriakos and Dealy, 1991; Cohen and Metzner, 1985; Yeow et al., 2003]. Thus the gradient in a Mooney plot is no longer four times the slip velocity. Therefore, the proper determination of the slip velocity of a non-Newtonian fluid is to be resolved.

In addition, the effect of viscous heating should be considered in the characterization of the flow behaviour of a concentrated suspension. With high shear rate and high deformation, there will be significant viscous dissipation in the flow. Considerable heat might generate resulting in lower feedstock viscosity.

In summary, particle migration, wall slip and viscous heating influence the flow of a concentrated suspension. To characterize their effects is the major focus of this investigation.

1.3 OBJECTIVES

The research focuses on:

- Determining the effects of die diameter, particle concentration, shear rate and temperature on the entrance and exit losses in a capillary flow, and proposing a formula to describe their relationship;

- Modifying the conventional Mooney method to calculate the slip velocity for a generalized-Newtonian fluid;
- Establishing the slip model including the key factors for a non-Newtonian fluid;
- Measuring the yield stress of a concentrated suspension;
- Establishing a numerical model to investigate the effects of shear-induced particle migration, wall slip and viscous heating for powder-binder mixture;
- Predicting the non-Newtonian flow patterns of mono-modal suspensions in a pressure-driven tube flow, especially the slip velocity distribution along the flow length under an applied pressure;
- Calculating the true viscosities of pure EVA and glass particles filled EVA system by Bagley correction and slip correction;
- Determining the constants in the Krieger model by data fitting.

1.4 SCOPE OF WORK

In this study, glass microspheres with diameter in three ranges (1-15 μm , 53-63 μm , 106-125 μm) and ethylene vinyl acetate (EVA) 460 are chosen as model materials. The selection of different particle sizes is to determine if there is any colloidal effect on the rheological measurements. The range of particle volume fraction investigated is 10-45%. Uniform feedstock was prepared by mixing powder with EVA in a Haake Rheomix 600 torque mixer. A torque analysis was performed to determine the homogeneity of the mixture. Due to the fact that mixing in the mixer and extruding from the capillary rheometer were performed at high temperature, a Thermogravimetric Analysis was carried out to determine the degradation temperature of the polymer.

Experiments were conducted on pure EVA 460 and concentrated suspensions by a capillary rheometer under different shear rates. The pressure losses due to entrance and exit effects were determined by Bagley plot with dies having the same radius but with different ratios of die length to radius. In addition to Bagley plot, entrance and exit losses were also measured by an orifice die. The slip velocities of pure EVA and concentrated suspensions were calculated from capillary rheometer experiments using dies with the same ratio of die length to die radius ($L/R=40$) but with different radii ($R=0.25$ mm, 0.375 mm, 0.5 mm and 0.625 mm). For pure polymer, Bagley and Rabinowitsch corrections were employed to obtain its true viscosity. The constants in the viscosity model were determined by data fitting.

In the diffusive flux model for particle migration of concentrated suspension, the phenomenological parameter, k_c , is proposed to be a linear function of particle concentration, $k_c = k'_c \phi$, while k_η remains constant for a generic material. The values of k'_c and k_η were obtained by minimizing the errors between predicted and experimental data under the same flow rate but with different die lengths.

By simulation, the distributions of velocity and particle concentration were predicted under different conditions with or without particle migration and/or wall slip. The relationship between the slip velocity and pressure was also predicted. The predicted pressures combining the effects of particle migration, wall slip and viscous heating were compared with the experimental data.

Finally, with corrections of entrance and exit losses, and slip velocity, the true viscosities of concentrated suspensions with different particle concentrations and different particle sizes were calculated, thus the constants in the Krieger model can be determined.

CHAPTER 2 LITERATURE REVIEW

2.1 INTRODUCTION

Particle migration and wall slip are two important issues in the study of suspension rheology.

The occurrence of wall slip in concentrated suspensions will alter the velocity and the shear rate distributions in comparison to flows without slip. On the other hand, particle migration can alter the concentration distribution and thus complicates the rheological characterization. Particle migration and wall slip are closely correlated. The non-uniform particle concentration due to shear-induced particle migration can affect the effective viscosity of concentrated suspension as well as the slip coefficient in a significant way [Jana et al., 1995]. The effect of wall slip is to reduce the driving force for shear-induced particle migration and the decrease of wall concentration from the initial concentration [Allende and Kalyon, 2000].

Hitherto, no detailed research was conducted in how they affect each other. The development of concentration gradient in the flow direction is detectable from the generally time-dependent nature of the pressure necessary to drive the flow at a constant flow rate [Yilmazer and Kalyon, 1989]. Wall slip can also affect pressure, but in a different way. Therefore, it is necessary to explore their interactions and their effects in the flow behaviour of suspensions.

In addition to particle migration and wall slip, yield stress and viscous heating are two important issues in the study of rheological behaviour of suspension. This chapter presents the current status on the above issues.

2.2 PARTICLE MIGRATION

2.2.1 Mechanism and Modeling of Particle Migration

A suspension consists of solid particles dispersed in a polymer solution. The addition of rigid particles affects the flow field and rheological properties of a fluid. It is generally observed that particles migrate from the regions of higher shear rate to the regions of lower shear rate when the particle Reynolds number is sufficiently small ($\sim 10^{-4}$) such that inertia is not significant and particle size lies beyond the colloidal range to preclude colloidal effects. Colloidal particles are about $1\text{ }\mu\text{m}$ in diameter [Jeffrey and Acrivos, 1976].

For a suspension flow in a capillary, at the inlet of the capillary, the suspending flow is considered as laminar and the particle concentration is uniform. As the suspension travels down the channel, the concentration profile will become non-uniform because of the shear-induced migration of particles from the region of high shear, i.e. near the wall, to the centre, where the shear deformation vanishes because of symmetry. However, this particle flux will be opposed by a reverse flux from the regions of high concentration to low concentration, i.e. from the centre to the wall, until a fully-developed concentration profile is formed at a distance from the entrance, i.e. the entrance length.

For suspension fluids containing neutrally buoyant particles, some mechanisms were proposed for particle migration.

Eckstein et al. (1977) were the first to identify shear-induced diffusion as an important mechanism for the migration of particle across streamlines in creeping flow. They determined experimentally the coefficient of lateral self-diffusion in the direction normal to the fluid velocity and the vorticity by monitoring the random

motion of a tagged spherical particle in a suspension being sheared in a Couette device.

Tirrell and Malone (1977) presented a framework for the analysis of stress-induced migration in inhomogeneous flow fields. The inhomogeneous stress field produces a force F_m , which drives the molecules to a domain of lower stress, given by the gradient of a potential field $U(r)$:

$$F_m = -\nabla U \quad (2.1)$$

where

$$U = k_B T \left\{ \frac{1}{3} (\varpi \dot{\gamma})^2 - \frac{1}{2} \ln \left[1 + \frac{2}{3} (\varpi \dot{\gamma})^2 \right] \right\} \quad (2.2)$$

The corresponding flux of the affected molecules is:

$$j_m = \beta_T C F_m \quad (2.3)$$

where $\beta_T = D/k_B T$ is the mobility and C is the molar concentration of the macromolecules. The concentration gradient so set up is countered by the Brownian diffusion flux, and the net flux is given as:

$$j = -D \left[\frac{\partial}{\partial r} C + \frac{C}{k_B T} \frac{\partial}{\partial r} U \right] \quad (2.4)$$

where D is a diffusion coefficient, k_B is Boltzmann constant, T is temperature.

The equation of continuity is obtained as:

$$\frac{\partial C}{\partial t} + \bar{u} \cdot \frac{\partial C}{\partial r} = -\nabla \cdot j \quad (2.5)$$

where $\bar{u}$ is the average fluid velocity.

Leighton and Acrivos (1987a, 1987b) suggested that particle surface roughness could give rise to irreversible particle interactions, thus resulting in distinct migration rates for particles with different surface characteristics.

Graham and Abbott (1992) established a diffusion equation that described the evolution of particle concentration profiles over time. This equation is the second order and nonlinear in the particle volume fraction ϕ , and could be solved in conjunction with the equations of motion for a Newtonian fluid with concentration-dependent viscosity to yield both the time dependent and steady state concentration and velocity profiles.

The conservative equation for solid particles can be written in a Lagrangian frame:

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot (N_c + N_\eta + N_b) \quad (2.6)$$

The left side of Eq. (2.6) is the rate of accumulation of particles. N_c is the flux of particles due to a gradient in interaction frequency, N_η is the flux of particles due to the effective viscosity variation, N_b is the flux of particles due to Brownian

diffusion. However, N_b can be neglected as the Pelcet number $\left(P_e = \frac{6\eta\dot{\gamma}a^3}{k_B T} \right)$ is

generally very large (where a is the radius of the particle, $\dot{\gamma}$ is the shear rate, η is the viscosity).

There are many types of potential interactions in the concentrated suspension of particles. Among these interactions, two-body interactions play a large role in the migration. Ordinarily, two smooth, spherical particles suspended in a shear flow undergo reversible interactions. However, if the migration from regions of high to low shear rate occurs, then the particles cannot return to their original position. Significantly, two-body interactions are not always reversible if the particles do not have perfectly smooth surfaces. These effects of surface roughness are important in concentrated suspensions. In addition, as noted by Leighton and Acrivos (1987a, 1987b), even smooth particles could be permanently displaced

from their original streamlines by three-body interactions. However, measurements of the diffusive flux induced by three-body collisions are approximately an order-of-magnitude lower than those induced by two-body interactions. Thus, the diffusion flux is dominated by the effect of two-body irreversible interactions.

Since two-body collisions can cause a particle to be moved from its original streamline, a particle which experiences a higher frequency of collisions from one direction than from the opposing direction will migrate normal to its shear surface and in the direction of the lower collision frequency. If the particles in a concentrated suspension are assumed to undergo a shearing motion, then the number of collisions experienced by a test particle will scale as $\phi\dot{\gamma}$. So the flux N_c can be summarized as:

$$N_c = -k_c a^2 \left(\phi^2 \nabla \dot{\gamma} + \phi \dot{\gamma} \nabla \phi \right) \quad (2.7)$$

where k_c is a proportionality parameter of order unity.

The first term on the right side of Eq. (2.7) implies that, even without gradient in the particle volume fraction, migration will result from higher $\nabla \dot{\gamma}$. The second term states that a gradient in particle concentration will cause a spatial variation in the frequency of interactions.

In addition to collision frequency, an interaction between two particles will be affected by spatially varying viscosity caused by the existence of gradients in particle concentration. The flux for this effect can be quantitatively expressed as:

$$N_\eta = -k_\eta a^2 \dot{\gamma} \phi^2 \frac{1}{\eta} \frac{\partial \eta}{\partial \phi} \nabla(\phi) \quad (2.8)$$

where η is the effective viscosity dependant on the local particle concentration, k_η is a constant of order unity. Eq. (2.8) implied that N_η is independent of the magnitude of viscosity, η .

The third mechanism of particle migration was suggested by Krishnan et al. (1996). He proposed that particles migrate in a shear field with curved streamlines with non-uniform curvature toward regions with lower streamline curvature, and the curvature-induced flux has the form:

$$N_\rho = +k_r a^2 \dot{\gamma} \phi^2 / \rho \quad (2.9)$$

The plus sign indicates that the flux is in the opposite direction of the previous ones in Equations (2.7) and (2.8). In a tube flow, the radius of curvature of the mean particle path is very large, so that N_ρ can be negligible.

In concentrated suspensions, it is quite difficult to determine the microstructure from exact theories since particle interactions in these suspensions intrinsically involve the interaction of many particles. Considerable progress in understanding the microstructure of a concentrated suspension has been made through numerical techniques [Bossis and Brady, 1984; Durlofsky et al., 1987; Brady and Bossis, 1988]. This approach, termed as Stokesian dynamics, simulates the behaviour of a suspension by following the trajectories of a discrete number of spheres in a cell, which is periodically replicated to approximate an unbounded suspension. The hydrodynamic interaction between the spheres is modelled using the exact two-sphere mobility and resistance functions. This technique had also been used to simulate the behaviour of bounded suspensions by taking into account the presence of plane walls [Durlofsky and Brady, 1989], and by considering the suspensions in which Brownian motion, van der Waals, and electroviscous forces are present [Bossis and Brady, 1984; Bossis et al., 1988].

While this simulation procedure does an excellent job of capturing the purely hydrodynamic interaction between ideal particles, it is unclear how the simulation results correspond to the behaviour of physical suspensions of particles. Real particles will come into contact in a sheared suspension, and it is as yet unresolved how to model contact forces in these numerical simulations.

Pakdel and Kim (1991) developed a numerical technique to directly simulate the behaviour of N particles interacting in a sheared suspension where the particles are not necessarily spherical. This simulation method can directly account for the presence of large-scale surface roughness on spheres, as well as highly non-spherical particles such as flakes and rods. However, this technique requires a large amount of computer time.

From a theoretical point of view, there have been three general approaches to study the “hydrodynamic diffusion” process. Firstly, in the computational equivalent of an experiment, Brady (1993) carried out dynamic simulations of pressure-driven flow of a suspension of non-Brownian particles in a two-dimensional channel. For a monolayer of identical spherical particles, these simulations demonstrate the gradual migration of particles toward the center of the channel, leading to a concentration maximum near the centerline, and a blunting of the particle velocity profiles. Secondly, following the lead of earlier studies by Jenkins and McTigue (1990), Nott and Brady (1994) proposed a model for concentrated suspensions, in which the concept of a hydrodynamic temperature was used as a measure of the intensity of the velocity fluctuations of the particles. The hydrodynamic temperature is defined as [Nott and Brady, 1994]:

$$T = \langle u' \cdot u' \rangle_p \quad (2.10)$$

where u' is the velocity fluctuation of a particle about its local mean velocity and the angle brackets denoting an ensemble average over all particles. The “hydrodynamic temperature” is of interest because it is closely related to the diffusivity and because spatial variations in temperature can be used to develop a non-local theory of suspension transport, which is necessary to explain the experimental observations. This model produced results for channel flow that agreed with the authors’ numerical simulations results.

Thirdly, Phillips et al. (1992) adapted the scaling arguments of Leighton and Acrivos (1987a, 1987b), together with an empirical relationship between the suspension viscosity and the particle concentration, to obtain predictions using the generalized diffusion equation [Christopher et al., 1994].

Chen and Lam (2003) used a continuum diffusive-flux model to investigate the shear-induced particle migration for a creep flow of nickel-powder-filled polymers. The model, together with flow equations, was employed for solving the generalized-Newtonian flow patterns and non-uniform particle concentration distribution of mono-modal suspensions in a pressure-driven tube flow. Chen et al. (2004) employed a phenomenological diffusive flux model coupled with flow equations to describe the shear-induced particle migration in a concentrated suspension. The two phenomenological parameters in the diffusive flux model k_c and k_η were determined inversely by employing a least square analysis on the experimental results with different capillary die ratios of length to diameter.

Jana (2003) developed a shear-induced particle migration model of monodispersed non-colloidal spherical conductive filler particles in the suspension of a power-law type polymeric liquid. A direct evidence of migration of conductive carbon particles was obtained in the form of loss of surface and volume electrical

conductivity of carbon black-filled polypropylene compounds. Table 2.1 summarized the major propositions on particle migration.

Table 2.1: Research findings for the mechanism of particle migration

Year	Authors	Propositions	Importance
1977	Eckstein et al.	Identified shear-induced diffusion as the mechanism for particle migration	Provided the experimental basis for the determination of self-diffusion coefficient for lateral dispersion of particles.
1987	Leighton and Acrivos	Proposed mechanism for particle migration based on the spatial variation in the viscosity and interparticle interactions	Significant development in the mechanisms for particle migration based on hydrodynamic interactions. However, migration was attributed to irreversible interactions as particle surface roughness, which could not explain migration of smooth spherical particles.
1992	Phillips	Predicted particle migration using a generalized diffusion equation.	This model computes particle concentration and velocity fields in concentrated monomodal suspensions with Newtonian binder. However, it failed to explain the phenomena of outward migration in cone and plate geometry [Chow et al., 1994].
1996	Krishnan, Beimfohr and Leighton	They proposed the third flux called the curvature flux for curved geometries where the streamline curvature has an effect on particle motion.	The curvature flux is to account for the effect of normal stress. In curvilinear shear flows, normal stresses play a role in particle migration.
2002	Chen and Lam	Proposed a hybrid FEM/FDM algorithm for particle migration for a non-Newtonian fluid	The non-Newtonian viscosity of binder is considered.
2003	Chen and Lam	Predicted particle migration using a continuum diffusive flux model under non-isothermal conditions for a non-Newtonian fluid	Their model is extended to high shear rate with viscous heating effect.

2.2.2 Existing Experimental Techniques of Particle Migration

Experiments performed showed that particles in initially well-mixed suspensions migrate to the low-shear-rate region in non-homogeneous shear flows [Goldsmith and Mason, 1962; Gadala-Maria and Acrivos, 1980; Hookham, 1986; Sinton and Chow, 1991; Graham et al., 1991; Abbott et al., 1991; and Koh et al., 1994]. Four main techniques employed are Laser-Doppler Anemometry, optical technique with tracer particle, Electrical Impedance Tomography (EIT) and Nuclear Magnetic Resonance (NMR) Imaging. In addition, Fourier-transform infrared spectroscopy was developed to measure the concentration within micrometer distances from the wall [Hartman Koh et al., 2002].

Kowalewski (1980) used Ultrasound-Doppler Anemometry to measure the velocity profile for concentrated suspensions of solid and liquid particles in tube flows. However, this method could not distinguish between the particle velocities and the fluid velocities. The measured velocity profile is presumably a mass or a volume averaged value. Hookham (1986) modified the Laser-Doppler technique to measure the velocity and concentration profiles for the flow of concentrated suspensions in a rectangular channel. He measured the Doppler signals from a trace fraction of the particles that were fluorescent-dyed. Microstructural changes accompanying the shear flow of colloidal suspensions composed of both spheres and fibers have been inferred via light-scattering techniques [Salem and Fuller, 1985; Ackerson and Pusey, 1988]. Koh et al. (1994) developed a modified Laser-Doppler anemometry technique to measure the velocity and concentration distributions in a rectangular channel flow of concentrated suspensions. As the particle size increases relative to the channel width, the velocity distributions become increasingly blunted and the maximum velocity thus decreases. More

recent Laser-Doppler Anemometry experiments on shear-induced migration were carried out by Lyon and Leal (1998). The measurements were for higher concentrations and were taken at further distances from the inlet of the channel.

The second method to keep track of particle motion is tracer observation, in which optical techniques were employed together with the use of refractive index matched suspensions. Karnis et al. (1966) reported the blunting of velocity profiles for suspensions flow through a tube. The velocities were determined by visually measuring the velocity of tracer particles from photographs taken through a microscope. One disadvantage of this technique is that it is generally only possible to obtain averaged information about the suspension such as the local concentration or the local particle velocity.

This shortcoming was partially overcome by Graham and Bird (1984) through the use of information theory. Each particle was labeled with numbers so that they could be uniquely identified. Tracer particles were then added to the suspension. In operation, the suspension was observed using two synchronized video cameras oriented at right angles to each other, and the third video camera to track the motion of the belts driving the flow. From these images it was possible to directly calculate the absolute position of each of the tracers within the field of view. These observations can be used to calculate concentration velocity distributions. Breedveld et al. (1998) measured the shear-induced particle self-diffusivity in a concentrated suspension by applying the spatial correlation procedures to successive images of tracer particles in a fixed imaging volume. Merhi et al. (2005) used a technique based on the detection of tracers by means of light absorption to measure the time evolution of particles concentration profiles.

Electrical Impedance Tomography (EIT) was employed by Butler and Bonnecaze (1999) to investigate particle migration in a suspension undergoing pressure-driven flow through a tube. EIT is a non-intrusive imaging technique, which constructs an approximation to the conductivity distribution of an object from electrical signal applied and measured at the boundaries. This technique suffers from the transmission effects in electrically non-conducting samples.

Kose et al. (1985) used a two-dimensional Nuclear Magnetic Resonance (NMR) flow imaging technique to measure both the velocity profiles and concentration distributions. It showed that the velocity distribution of water in a circular pipe was parabolic and agreed well with that of Poiseuille flow. Caprihan et al. (1986) developed a frequency-encoded one-dimensional (1D) NMR technique, which can be expanded to 2D and 3D velocity distributions. NMR imaging experiment was conducted by Majors et al. (1989) on dilute suspensions. Altobelli et al. (1991) extended this method to concentrated suspensions. Graham et al. (1991) studied the shear-induced particle migration of concentrated suspension in the flow between rotating concentric cylinders by NMR imaging. They found that particles migrate from the higher shear rate regions near the rotating inner cylinder to the lower shear rate regions near the stationary outer wall, with a large concentration gradient. The migrations of concentrated suspension by cone-and-plate rheometer, Couette and parallel-plate rheometer were conducted by Sinton and Chow (1991) and Chow et al. (1994). Han et al. (1999) used a magnetic resonance imaging (MRI) technique to investigate the particle migration in a tube flow for a wide range of particle loading and particle Reynolds number using a magnetic resonance imaging technique. Both the velocity and particle concentration distributions were

measured. It was found that particle migration was dependent on the Reynolds number.

The Laser-Doppler technique and MRI technique are proven techniques for measuring concentration and velocity distributions in the suspension flows. However, due to the resolution accuracy, they are limited in determining the concentration very near to the wall. For example, the typical resolution achieved with MRI is approximately 25-100 μm . In 1995, an ATR (Attenuated Total Reflection) technique based on light scattering, was used by Polverari and van de Ven (1995) to measure the particle concentration near the wall for an impinging jet. This technique is good for concentrated suspension but not for dilute suspension. Later, a Fourier-transform infrared (ATR/FTIR) spectroscopy was developed to measure the particle concentration within micron distances from the wall [Hartman Koh et al., 2001].

Generally, direct measurement techniques can provide a visual evidence of particle migration and nonuniform particle distribution along the flow. However, some techniques involve complex procedures and are time consuming. For example, nuclear magnetic resonance (NMR) is a complicated experimental method. The experiments for measuring one kind of properties are quite different from others, including the instrumentation and software required. Even the signal intensity depends not only on the spin density but also on a host of parameters depending on how the experiment is conducted [Fukushima, 1999].

2.2.3 Factors Influencing Particle Migration

The effect of particle size distribution on migration was studied by many researchers. Graham et al. (1991) and Husband et al. (1994) found that separation

of particle sizes occurs and larger particles accumulate at the lower shear zone near the outer stationary cylinder when a well mixed bidisperse suspension is sheared in a wide gap Couette cell. Krishnan et al. (1996) also studied the system with various size particles sheared in a parallel-plate device. They modified the experiments of Chapman (1990) and Chow et al. (1994), in which a monodisperse suspension was sheared in a parallel plate device, by adding the second fraction of tracers of different size in minute quantities. Contrary to the finding of Graham et al. (1991) and Husband et al. (1994), experiment demonstrated that tracer particles migrated outwards, i.e., to the high shear region when they were bigger than the particles in the bulk of the monodisperse suspension. The migration was observed inward when the tracers were smaller than those in the suspension. It indicated that the particle migration and particle concentration distribution is dependent on the particle size. Thus, to have a good representation of the particle behaviours in a suspension, similar size of tracer particles should be used to measure the particle migration.

In addition, material properties of polymer and particle and particle concentration in the suspension affect the degree of particle migration. Han et al. (1999) measured the migration of particles in tube flow using a magnetic resonance imaging (MRI) technique; the suspension consisted of monodisperse particles. They reported that particle migration is dependent on Reynolds number, R_e , and particle concentration. With smaller R_e , the blunting of particle distribution in the tube was larger. It also suggested that when the Reynolds number is larger than 0.1, the inertial effect cannot be neglected.

2.2.4 Summary

For concentrated but far from saturated suspension with neutrally buoyant particles, the hydrodynamic interactions are responsible for the migration of particles.

Shear-induced diffusion of particles in the steady state shear flow was observed by experiments [Eckstein et al., 1977]. Shear-induced diffusion was proposed by Leighton and Acrivos (1987b) to explain the particle migration of concentrated suspension subject to inhomogeneous shear flow. They applied scaling arguments and identified three causes of particle migration and diffusion, i.e. shear-rate gradients, relative viscosity gradients and concentration gradients. Phillips et al. (1992) proposed a constitutive equation to calculate particle concentration and velocity fields in concentrated monomodal suspensions with Newtonian binder. Particle volume fraction and velocity field can be predicted.

However, the work of Phillips failed to explain the phenomenon of outward migration in cone and plate geometry [Chow et al., 1994]. Krishnan et al. (1996) proposed the third flux called the curvature flux for curved geometries where the streamline curvature has an effect on particle motion to account for the effect of normal stress.

Furthermore, Chen and Lam (2002, 2003) extended the diffusive flux model to non-Newtonian fluid and non-isothermal condition where the viscous heating effect can be accounted for.

2.3 WALL SLIP

2.3.1 Introduction of Slip Behavior

The idea of wall slip was proposed by Mooney as far back as 1931 [Mooney, 1931]. Slip phenomenon is the occurrence of a relative velocity between the fluid at the wall and the wall itself.

The existence of wall slip has been experimentally observed by Muller-Mohnssen et al. (1987, 1990). Using a Laser Differential Micro-Anemometer, they measured velocity profiles down to a minimum distance of 0.15 μm from the wall. Extrapolation of the profiles resulted in finite “effective slip velocity”, u_s , at the wall. Another manifestation of slip is that one obtains different results in different sized geometries when calculating viscosities from formula that assume no slip in the flowing fluid. In particular, the apparent viscosity calculated in this way always decreases with a decrease in geometry size, such as the diameter of a capillary die. With the inclusion of particles in a polymer melt, its rheological properties change significantly compared to that of a pure polymer. Therefore, the slip behaviour would be discussed separately for polymer solutions and concentrated suspensions.

2.3.2 Wall Slip Phenomena in Polymer Solutions

The slip mechanism of polymer solutions in shear flow is still not fully elucidated. There is debate if slip occurs due to the failure at the polymer-wall interface (adhesive failure) or the failure within the polymer but very close to the wall (cohesive failure). In the former case, surface energetics and the work of adhesion of the interface should be the key parameters; while in the latter case, rheological

and molecular properties of the polymer should be the controlling factors [Anastasiadis, 1998].

Hitherto, most researchers considered that the wall slip is caused by adhesive failure. Based on Eyring's theory for the viscosity of liquids, Hatzikiriakos and Dealy (1993) developed a theory for slip, hypothesizing that polymer chains at equilibrium are adsorbed at the interface. Under a shear force, the polymeric chains are extended. Once the available stored elastic energy can overcome a fraction of the work of adhesion, fW_{adh} , the polymer chain jumps to a certain length, that is comparable to the radius of gyration of the chain. An expression to describe the adhesion effect on the onset of wall slip was offered by Hill et al. (1990):

$$\tau_c = \frac{2fW_{adh}}{\delta} \quad (2.11)$$

where δ is an elastic pseudolayer thickness of the polymer measured from the interface, and f is a fractional recovery coefficient indicating the layer of the fluid under slip is constrained by the bulk fluid. A similar view is developed by Anastasiadis (1998). He found that the critical shear stress for the onset of slip scales linearly with the work of adhesion, suggesting that slip is a result of adhesive failure of the interface, and the thickness of fluid layer, where all the elastic energy is used to drive the slippage of the polymer, is on the order of 1 μm .

Hill (1998) developed a chemical-type theory for wall slip in polymer melts by modelling the exchange of bridging sites between two opposing polymeric and solid surfaces. He suggested that the slip velocity depends on both shear and normal stresses with a function of the work of adhesion (polymer-solid). His work also agreed with the findings of Anastasiakis and Hatzikiriakos (1998) in that a linear correlation is found between the critical shear stress for the onset of slip and

the work of adhesion of the corresponding polymer/wall interface. Pérez-González (2001) measured the slip of linear low-density polyethylene melt using capillary dies made of stainless and brass, and flow enhancement (slip) in the brass die was observed.

Léger et al. (1997) used a “near-field laser velocimetry” (NFLV) technique to measure the local velocity of the fluid in the immediate vicinity of a solid wall of high molecular weight polymer melts. They observed a succession of three different friction regimes. At low shear rates, weak slip at the wall has a friction coefficient independent of the slip velocity due to the entanglements between the surface-anchored chains and the bulk polymer. On increasing the shear rate, a critical slip velocity is attained with a non-linear friction coefficient between the fluid and the surface. The friction coefficient decreases with increasing shear rates. Finally, at high shear rates, the surface chains are totally disentangled from the melt with a small friction coefficient.

The presence of regions of more aligned molecules within low viscosity regions and a more viscous bulk fluid with less aligned molecules for a given shear stress in capillary flow reflects the existence of a flow curve with a stress plateau. This leads to different rates of entanglement and disentanglement of chains in the bulk in comparison with those at the wall. If a slip layer develops, differences of the shear rates between the slip layer and the bulk region cause a difference of viscosity in the fluid near the wall and in the centre. The presence of slip layers will obviously influence the macroscopic flow behaviour of polymeric solutions, such as flow rate increase and apparent viscosity reduction in capillary flows.

2.3.3 Wall Slip in Concentrated Suspensions

Although numerous studies have been made on the rheological behaviour of polymer solutions, relatively little work has been done on concentrated suspensions. Such concentrated suspensions are usually non-Newtonian and exhibit various degrees of plasticity, dilatancy and/or thixotropy. Due to their complex rheological behaviour, considerable difficulties are often encountered in the experiments. The occurrence of wall slip in concentrated suspensions will alter the velocity and the shear rate distributions in comparison to flow without slip. With wall slip, velocity gradient is reduced at the wall and blunted at the centre of the tube, i.e. the profile of velocity in the cross section becomes more homogeneous.

The flow behaviour of concentrated suspension is affected by various phenomena, including particle migration and the property of the binder, both are in turn affected by wall slip. Allende and Kalyon (2000) demonstrated the effect of wall slip on the migration of particles in the transverse flow direction in a Poiseuille flow. With the inclusion of wall slip, the driving force for particle migration decreases, and hence, the deviation of the concentration at the wall from initial concentration reduces.

Many researchers proposed that wall slip of suspensions is due to the formation of a slip layer between the bulk flow and the wall. Green (1920) detected a thin slip layer with a pure polymeric fluid as early as 1920 in the flow of paint suspensions under a microscope. Bingham (1922) suggested that slip comes from a lack of adhesion between the material and the shearing surface. The result is that there is a layer of liquid between the shearing surface and the main body of the suspension. The importance of this thin layer increases with a decrease of the diameter of a

capillary die. Thus, the slip mechanism of concentrated suspension is believed to be caused by the formation of an apparent slip layer near the wall, consisting mainly of pure suspending fluid. Within this layer, large velocity gradients exist resulting in apparent slippage of the bulk fluid [Vand, 1948]. Hartman Koh et al. (2002) measured the concentration of particles in a layer within 0.3-1.4 μm from the wall using ATR-IR method and detected a considerable decrease of particles, and the degree of wall depletion increases with increasing particle concentration. Their experimental data verified that particle concentration deviated from that in the bulk region.

Yilmazer and Kalyon (1989) determined the ratio of the slip layer thickness over the particle diameter to be 0.06 for a suspension filled with 60% by volume of ammonium sulfate particles. Jana et al. (1995) determined the slip layer thickness over the particle diameter ratio to be 0.063 for suspensions filled with poly (methyl methacrylate) particles in the range of 46% to 52% by volume. Soltani and Yilmazer (1998) characterized the slip layer thickness over the particle diameter ratios for glass beads and Al particles suspended in a polybutadiene binder as 0.04 and 0.07, respectively. Kalyon (2005) measured a layer thickness in the range of 2-30 μm with the suspension of KCl particles (61.9% by volume and with a harmonic mean diameter of 121 μm) in the capillary flow. The ratio 0.09 of the mean slip layer thickness over the harmonic mean particle diameter was obtained. For shear thickening solutions, a slip layer thickness about 100 μm at low shear rates, and 50-60 μm at high shear rates, was determined using Microscopic Particle Imaging Velocimetry (MPIV) [Hu and Larson, 2002].

2.3.4 Methods to Determine Slip Velocity

Many methods have been suggested for the measurement of the slip velocity of polymer melts and concentrated suspension, which can be categorised into direct measurement techniques and indirect methods. Direct measurement involves the velocity measurement of particles in the melts. Indirect methods include Mooney method and Jastrzebski method.

(a) Direct measurement techniques

The slip velocity at the wall can be measured directly by microscopic imaging and high-speed camera, as well as fluorescent technique. Magnetic Resonance Imaging and Laser Doppler Anemometry can be used to measure velocity profile in the bulk region, however, both of them suffer from spatial resolution limitations in measuring slip velocity. For example, the spatial resolution of the Laser Doppler Anemometry technique employed by Jana et al. (1995) was 48 μm .

Migler et al. (1993) used an evanescent wave fluorescence technique to measure the slip velocity during shear flow in a plane-Couette flow device. A sharp transition between weak and strong slip within 100 nm from the solid-liquid interface was observed in the case of weak polymer-surface interactions. With this technique, the velocity could be measured in a zone within about 0.1 μm of the solid surface.

Archer et al. (1995) used an optical microscope to observe the motion of micrometer-sized spherical silica particles suspended in the flowing polymer solutions to determine slip velocity in a glass plate-Couette flow device. Jana et al. (1995) determined the apparent wall slip velocity coefficients in a narrow gap Couette flow by measuring the particle velocities across the gap using a laser

Doppler anemometer system and by extrapolating the results to the walls. Léger et al. (1997) used a technique called “near-field laser velocimetry” (NFLV) to measure the local velocity of the fluid in the immediate vicinity of the solid wall of high molecular weight polymer melts.

(b) Mooney method

The direct consequence of wall slip is the increased flow rate through the tube compared to that without slip. Mooney (1931) suggested a formula, which is an explicit function of experimental quantities:

$$\dot{\gamma}_a = \frac{4u_s}{R} + \frac{4}{\tau_w^3} \int_0^{\tau_w} \dot{\gamma}(\tau') \tau'^2 d\tau' \quad (2.12)$$

According to this method, experiments are performed on capillary dies with different radii but with the same ratio of die length to radius at same wall shear stress. The gradient in the plot of the apparent shear rate $\dot{\gamma}_a = 4Q/\pi R^3$ against $1/R$ is four times the wall slip velocity.

This method is commonly used by many researchers in polymer solutions and concentrated suspensions. However, this equation was established based on the assumption of a Newtonian fluid, where slip velocity is proportional to wall shear stress. For a non-Newtonian fluid, the gradient is no longer four times the slip velocity as the slip velocity was commonly proposed to be a power law function of the wall shear stress [Yeow et al., 2003]: $u_s = \beta_s \tau_w^k$, where β_s is slip coefficient. The slip index of k is unknown and thus the slip velocity cannot be determined directly by the Mooney plot. A detailed discussion is presented in Chapter 3.

Therefore, Mooney method should be modified to account for the non-Newtonian property of a fluid.

(c) Jastrzebski method

Jastrzebski (1967) proposed a slip method on his experimental results of concentrated suspensions with the slip velocity not only related to slip coefficient and the shear stress but also the reciprocal of die radius. That is to say, $u_s = \beta_s \tau_w / R$. Therefore, the flow rate is calculated as:

$$\frac{Q}{\pi R^3} = \frac{\beta_s \tau_w}{R^2} + \frac{1}{\tau_w^3} \int_0^{\tau_w} \tau^2 f(\tau) d\tau \quad (2.13)$$

This method had been used by some researchers in studying the slip in suspensions [Zhou and Li, 2005]. However, it is not derived from fundamental principles and cannot be explained physically. Martin and Wilson (2005) commented that Jastrzebski analysis is only an empirical expression without coherent physical justification. The slip velocity cannot be related to the capillary radius.

2.3.5 Slip Formula

Many researchers believed that slip velocity is dependent on wall shear stress and a friction coefficient. Different formulae were developed to describe the relationship of slip with shear stress. The earliest slip model, a linear relationship between slip velocity with wall shear stress, was proposed by Navier (1827) as:

$$u_s = \beta_s \tau_w \quad (2.14)$$

A number of researchers [Chauffoureaux et al., 1979; Lau and Schowalter, 1986; Ramamurthy, 1986; Hatzikiriakos and Dealy, 1991; Cohen and Metzner, 1985] have fitted a power law equation to relate the slip velocity to the shear stress at the wall with the form:

$$u_s = A' f(\tau_w)^k \quad (2.15)$$

where A' and k are constants.

Georgiou and Crochet (1994) used a form showing the relationship of slip velocity with wall shear stress as:

$$\tau_w = \alpha_1 \left(1 + \frac{\alpha_2}{1 + \alpha_3 u_s^2} \right) u_s \quad (2.16)$$

where α_1 , α_2 and α_3 are constants.

Some others believed that normal stress is also a factor influencing slip behavior [Hatzikiriakos and Dealy, 1992; Rao and Rajagopal, 1999; Vinogradov and Ivanova, 1968]. An equation to account for the effects of both shear stress and normal stress was proposed by Hatzikiriakos and Dealy (1992) as:

$$u_s = \xi f_1(T) \left[1 - c_2 \tanh \left(\frac{E + c_3 \frac{\sigma_n}{\tau_w}}{R_g T} \right) \right] \tau_w^m \quad (2.17)$$

where ξ , c_2 , c_3 and E are constants, R_g is the universal gas constant, and f_1 is a function of temperature, σ_n is the normal stress.

Person and Denn (1997) proposed an equation for the slip velocity in the form:

$$u_s = \alpha \tau_w^k \exp(-\beta_p P) \quad (2.18)$$

where α , k and β_p are constants and P is the pressure.

2.4 YIELD STRESS

The structure in a concentrated suspension can be sufficiently rigid that it permits the material to withstand a certain level of deforming stress without flowing. Most suspensions consist of continuous, three-dimensional networks and exhibit yield-stress behavior. The suspension flows only when the stress is large enough to break down the structure.

2.4.1 Measurement Methods

A strong interest in yield stress in the last two decades has led to developments of a variety of experimental methods and techniques for measuring the yield stress property [Nguyen and Boger, 1992].

The most common technique is the indirect measurement of the yield stress, which involves extrapolation of shear stress-shear rate data obtained by conventional rheometers to zero shear rate. The extrapolated yield stress relies on accurate experimental data in the low shear rate range. However, this is often difficult to obtain owing to the inherent nature of the yield stress material.

Direct measurement of the yield stress relies on an independent assessment of the stress at which the material starts to flow, which includes the vane, slotted plate, penetrometer and inclined plane techniques.

An alternative approach for the determination of the yield stress is dynamic oscillatory measurements, in which the material is subject to a sinusoidal strain and the resulting stress is measured as a function of time and frequency. Dynamic measurements in the linear viscoelastic region have revealed a low-frequency plateau where the linear viscoelastic functions are independent of frequency. This plateau has been explained by the existence of a network structure, and attempts have been made to correlate the plateau storage modulus with yield stress [Ghandi and Salovey, 1988].

The determination of yield stress in any system is difficult as the result obtained is usually dependent on the measurement technique and apparatus, and/or the model used to evaluate rheological data [Nguyen and Boger, 1992; Nguyen et al., 2006]. Even in controlled rheology experiments the same problem is well documented: depending on the measurement geometry and the detailed experimental protocol,

very different values of the yield stress can be found [James et al., 1987; Barnes and Nguyen, 2001]. Therefore, there is no accepted standard procedure for determining the yield stress, and there are many different views on the concept of the yield stress.

Moller et al. (2006) suggested that yield stress of a fluid is difficult to determine experimentally due to the lack of consideration of the thixotropy of yield stress fluids. The idea was proposed on the basis of two phenomena. The first one is the fact that the yield stress of a fluid has turned out to be very difficult to measure; the second reason is shear localization. The fluid is assumed to be homogenous at the measured shear rates. However, shear localization in a small region with high local shear rate could occur while the remaining part of the fluid behaves like a solid. This could occur even in a cone-plate geometry where the stress is essentially constant [Britton and Callaghan, 1997; Coussot et al., 2002]. This could be caused by shear banding (localization) or slip between the sample and the measuring geometry used in a rheometer. Recently very precise experiments strongly suggested that shear localization is the rule below a critical shear rate [Huang et al., 2005].

Moller et al. (2006) also pointed out yield stress of a fluid is not a material property since it depends on the shear history of the material. The relationship of yield stress with thixotropy was also described by Liddell and Boger (1996) where the yield stress increases with increasing recovery time. The recovery time is defined as the time after cessation of preliminary shearing. The data showed that to ensure reproducibility of yield stress measurements, it is necessary to measure the yield stress of the suspension after a given recovery time, corresponding to a constant level of structure.

2.4.2 Yield Stress Models

The most popular formulae that have been used to describe liquids with yield stresses are Bingham (1922), Casson (1959) and Herschel-Bulkly (1926), expressed as:

$$\tau = \tau_y + \eta_p \dot{\gamma} \quad (\text{Bingham}) \quad (2.19)$$

$$\sqrt{\tau} = \sqrt{\tau_y} + \sqrt{\eta_\infty \dot{\gamma}} \quad (\text{Casson}) \quad (2.20)$$

$$\tau = \tau_y + k' \dot{\gamma}^{n'} \quad (\text{Herschel-Bulkley}) \quad (2.21)$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, τ_y is the yield stress, η_p is a characteristic viscosity, η_∞ is the constant viscosity approached at the infinite shear limit, k' and n' are constants.

2.5 CAPILLARY MEASUREMENTS AND CORRECTIONS

In the measuring of shear flow behaviour, there are various types of rheometers, such as capillary rheometer, sliding plates, concentric cylinders, cone and plate rheometer, and parallel plate rheometer. Capillary rheometer is most widely used and its principle and characteristics will be explained in the following sections.

2.5.1 Capillary Rheometer

Capillary rheometer is the most common method to measure the flow properties of polymer melts. It is simple to operate, and its long capillaries can give accurate viscosity data. In addition, the closed channel flow has no free surface in the test region, which eliminates solvent evaporation and other problems that plague rotational devices with free surface. Capillary flow process also resembles many of the industrial process such as extrusion and injection moulding.

Figure 2.1: Schematic diagram of capillary rheometer [Macosko, 1994]

Figure 2.1 is a schematic diagram of a capillary rheometer. A capillary tube of radius R and length L is connected to the bottom of the reservoir. Pressure drop and flow rate through this tube are used to determine viscosity. The equations governing the capillary rheometer are as follows [Macosko, 1994]:

Apparent wall shear rate at the capillary wall:

$$\dot{\gamma}_{aw} = \frac{4Q}{\pi R^3} \quad (2.22)$$

Apparent shear stress at the capillary wall:

$$\tau_{aw} = \frac{\Delta P \cdot R}{2L} \quad (2.23)$$

Apparent viscosity:

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_{aw}} \quad (2.24)$$

where Q : Mass flow rate

ΔP : Pressure drop in the capillary

R : Radius of capillary

L : Length of capillary

Capillary rheometers measure pressure above the reservoir. In order to determine the true shear stress, a number of corrections must be adopted.

2.5.2 Rabinowitsch Correction

For a non-Newtonian fluid, its viscosity changes with shear rate. To account for this property for a capillary viscometer, Rabinowitsch correction is to be employed. Without this correction the viscosity is generally referred as apparent viscosity.

For the power-law viscosity model, $\eta_a = \eta \dot{\gamma}^{n-1}$, its true viscosity, η , can be obtained with Rabinowitsch correction:

$$\eta = \eta_a \left(\frac{4n}{3n + 1} \right)^n \quad (2.25)$$

where η_a is the apparent viscosity of fluid and n is the power-law index.

The true shear rate at the wall for a non-Newtonian fluid (pure solvent) could be obtained [Macosko, 1994]:

$$\dot{\gamma}_w = \dot{\gamma}_{aw} \left[\frac{3}{4} + \frac{1}{4} \frac{d \log(\dot{\gamma}_{aw})}{d \log(\tau_w)} \right] \quad (2.26)$$

2.5.3 Bagley Corrections

The pressure measured in a typical piston-driven capillary rheometer is made up of a number of contributions [Macosko, 1994]:

$$\Delta P = \Delta P_f + \Delta P_r + \Delta P_{en} + \Delta P_c + \Delta P_{ex} \quad (2.27)$$

where ΔP_f is the pressure loss due to friction between the piston and the reservoir wall, ΔP_r is the pressure drop in the reservoir, ΔP_{en} is the pressure consumed in the converging flow from the large reservoir to the smaller capillary, ΔP_c is the pressure along the tube with $\Delta P_c = 2\tau_w L / R$, ΔP_{ex} is the loss at capillary exit due to flow elasticity. For $R/R_r < 0.2$ (where R_r is the radius of the reservoir) and higher pressures, both friction and the reservoir loss can be neglected. The entrance and exit losses can be lumped together with $\Delta P_e = \Delta P_{en} + \Delta P_{ex}$.

Figure 2.2: Schematic diagram of Bagley correction in a capillary flow

There are some available ways to determine ΔP_e . The most common method is to make a Bagley plot with pressure vs. L/R . At least two dies of different length but of the same diameter are to be employed, see Figure 2.2. In Bagley correction, the end correction value e (the intercept value at x-axis) is obtained by extrapolation to zero pressure. It corresponds to the true shear stress equation [Bagley, 1957]:

$$\tau_w = \frac{\Delta P - \Delta P_e}{2L/R} = \frac{\Delta P}{2\left(e + \frac{L}{R}\right)} \quad (2.28)$$

where: ΔP : Pressure drop

L/R : Aspect ratio

ΔP_e : Sum of entrance and exit losses

Although Bagley correction predicts a linear relationship for pressure drop versus L/R at a certain flow rate, there are three main contributing factors, which may cause the departure of this linear relationship. If a polymer viscosity is a strong function of pressure, Bagley plot exhibits a curvature upwards. If viscous heating effects prevail, the Bagley plot exhibits a concave curvature. In addition, wall slip can cause Bagley plot to deviate from linearity. As wall slip reduces shear rate and slip velocity changes with pressure, the shear rate will depend on the axial position in the channel. This will result in a nonlinear Bagley plot [Hatzikiriakos and Dealy, 1992]. If there exists particle migration in a concentrated suspension, Bagley plot exhibits a convex curvature as particle migration reduces the required pressure to extrude the melt and the effect of particle migration on pressure increases with flow length.

At the case of upward curvature in Bagley plot, the entrance and exit losses can be determined in terms of a quadratic fit [Macosko, 1994]:

$$\Delta P = \Delta P_e + 2\tau_w \left(\frac{L}{R}\right) + x \left(\frac{L}{R}\right)^2 \quad (2.29)$$

where x is a term for the correction of the nonlinearity in a Bagley plot.

Another approach is to measure ΔP_e directly with an orifice die ($L/R \cong 0$) and use it to correct the data from a long die. One advantage of this method is the elimination of the errors due to the pressure dependence of viscosity, viscous

heating and wall slip. The parameters of an orifice die related to the measurement of ΔP_e are: the L/R of the orifice, the entrance angle, and the contraction ratio (barrel diameter over orifice diameter). This method usually requires using two different transducers because of the great difference in pressure [Mocosko, 1994].

However, this method has its limitations. Firstly, the total pressure measured is small and subject to large experimental errors. Secondly, the contribution of entrance flow to the end correction is calculated at low pressure levels, and it may be different for longer capillary dies. In addition, in the measuring of the entrance and exit losses using an orifice die, it is difficult to ensure the extruded suspension not to stick to the die wall in the expansion region. Kim and Dealy (2001) thought that the diameter in the orifice exit section is also an important factor as it influenced the flow of the extruded melt. If the melt were stuck in the expansion region, the measured data would be higher than those with a smooth flow. As such, it is expected that the measured entrance and exit losses with orifice die will be larger than the actual losses.

Entrance and exit losses ΔP_e are highly related to flow rate. Jastrzebski (1967) found that ΔP_e could be correlated with the volumetric flow rate Q by an exponential relationship similar to the power law equation:

$$\Delta P_e = A_r Q^t \quad (2.30)$$

where t is a material constant, A_r is a constant dependent on the concentration of a suspension and on the radius of the tube. The constant A_r can be expressed as:

$$A_r = B \exp(cR) \quad (2.31)$$

where B is a characteristic constant for a particular concentration of a suspension, c is the slope of the curve on the plot of A_r vs. R .

The relationship of the entrance and exit losses with the influencing factors was firstly summarized into an expression.

2.5.4 Viscous Heating

Temperature is one of the most important parameters in controlling and modelling polymer processing because of the coupling between the energy and momentum equations. It plays a fundamental role in determining the flow characteristics, degradation phenomenon, phase transitions, and morphology of the final products. It is not realistic to assume isothermal condition in the study of polymeric fluids, especially at high shear rates. With high viscosity and low thermal conductivities, in combination with high shear rates, considerable heat may be generated as a result of viscous dissipation, especially near the capillary wall. The heat generated produces a local temperature rise with a consequent decrease of the viscosity which may significantly change the temperature and velocity profiles. Moreover, it has been shown that a temperature-dependent thermal diffusivity can cause even greater shear localization because a lower diffusivity with an increase in temperature can trap the heat locally [Iwai et al., 1996].

The effect of viscous heating is mainly controlled by the Peclet number, the Nahme number, the flow rate and the thermal boundary conditions. In addition, it is more pronounced for capillary dies having a large diameter since heat is conducted less efficiently radially in large dies. The non-isothermal study of die flows is also relevant to rheological properties such as shear viscosity, particle migration and wall slip in capillary measurements.

Brinkman (1951) may be the first investigating viscous dissipation theoretically. He examined the temperature distribution in the entrance region of a cylindrical

tube using the Graetz type of series expansion. Bird (1955) extended Brinkman's work to power-law fluids but the solutions are readily obtainable only in cases where the reciprocal of the power-law index is an integer value greater than unity. Power-law fluid is defined as a type of generalized Newtonian fluid for which shear stress is a power-law function of shear rate.

Winter (1975, 1977) examined the heat transfer problem with viscous dissipation for a power-law fluid whose shear viscosity decreases exponentially with temperature, using an iterative finite-difference scheme. Cox and Macosko (1974) solved numerically the equations of conservation of mass, momentum and heat transfer for the flow of non-Newtonian fluids with temperature-dependent shear viscosity in a cylindrical tube, and annular and slit dies. Ybarra and Eckert (1980) obtained analytical solutions for a fully developed flow with viscous heat generation for power-law fluids in a slit die, while Dinh and Armstrong (1982) considered both cylindrical tube and slit dies.

Basically, when considering the non-isothermal flow of viscoplastic fluids, the inertia effect is usually negligible because of the highly viscous nature of the viscoplastic materials used in die flow and the low Reynolds number of the resulting flow. In addition, viscoplastic fluids generally have low thermal conductivity and moderately high value of heat capacity; hence they exhibit high Prandtl numbers. Based on the above conditions, the fundamental equation of a thermal problem can be described by the equation [Lawal and Kalyon, 1996]:

$$\rho C_p u_z \frac{\partial T}{\partial z} = \frac{K}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \eta |\dot{\gamma}|^2 \quad (2.32)$$

where K , ρ and C_p are the thermal conductivity, density and specific heat, respectively. η is the shear viscosity, $|\dot{\gamma}|$ is the magnitude of the rate-of-shear tensor.

For adiabatic wall condition, since viscous dissipation increases as the velocity gradient increases, the maximum temperature rise occurs at the wall where the velocity gradient is at a maximum. However, if the wall temperature is fixed, i.e. constant wall condition, then the maximum temperature rise occurs at some distance from the wall.

2.6 VISCOSITY MODELS FOR CONCENTRATED SUSPENSION

A variety of models had been proposed to depict the viscosity-concentration behaviour of suspension. Frankel and Acrivos (1967) suggested a theoretical equation, which can predict the viscosity trend in the region of high concentration levels:

$$\frac{\eta}{\eta_b} = \frac{9}{8} \left[\frac{(\phi / \phi_c)^{1/3}}{1 - (\phi / \phi_c)^{1/3}} \right] \quad (2.33)$$

where ϕ_c is the maximum particle concentration, η_b is the viscosity of a suspending fluid.

Thomas (1965) recommended the empirical equation:

$$\eta / \eta_b = 1 + 2.5\phi + 10.05\phi^2 + A' \exp(B'\phi) \quad (2.34)$$

where A' and B' are constants related to material properties.

Besides these models, two other models commonly employed are the Batchelor model and Krieger model. They are suitable for concentrated suspension with mono-disperse rigid spheres, where the potential interaction forces can be ignored,

but Brownian forces dominate. The effect of Brownian motion of particles can be represented by the action of coupled or interactive steady ‘thermodynamic’ forces on the particles, which have both direct and indirect effects relevant to the bulk stress in the suspension. These two effects to the bulk stress due to Brownian motion are of the order ϕ^2 . The effective viscosity representing the stress system can be written as [Batchelor, 1977]:

$$\frac{\eta}{\eta_b} = 1 + 2.5\phi + 6.2\phi^2 \quad (2.35)$$

The effect of Brownian motion is to diffuse particles away from each other, thus affecting the rheological properties of the suspension, and hence contributing to the bulk stress.

Krieger model was proposed to account for the variation in viscosity with particle concentration [Krieger, 1972]:

$$\frac{\eta}{\eta_b} = \left(1 - \frac{\phi}{\phi_c}\right)^{-m} \quad (2.36)$$

where m is a material constant.

Another empirical formula that obeys both the high and low concentration limits was given by Eilers [Ferrini et al., 1979]:

$$\frac{\eta}{\eta_b} = \left(1 + \frac{\frac{1}{2}[\eta]\phi}{1 - \phi/\phi_m}\right)^2 \quad (2.37)$$

2.7 SUMMARY

In this chapter, the rheology of polymer melts and concentrated suspension was reviewed. In capillary flows, three main phenomena (particle migration, wall slip and yield stress) are addressed in detail from their mechanisms to measurement

methods. Wall slip changes the shear rate and velocity profile in the flow, particle migration alters the concentration distribution in the axial direction of the flow, thus affecting slip behaviour. At the same time, wall slip reduces the driving force for shear-induced particle migration, causing less decrease of the concentration at the wall from the initial concentration. Therefore, the interaction between particle migration and wall slip is an interesting issue necessary to be explored.

In the characterization of the slip behaviour of concentrated suspension, Mooney method and Jastrzebski method are commonly used. However, Mooney method was proposed on the basis of a Newtonian fluid where the slip velocity is regarded to be linear with wall shear stress. Therefore, the slip velocity of a Newtonian fluid can be calculated from the gradient in Mooney plot with apparent shear rate against the reciprocal of the radius, which is four times the slip velocity. For a non-Newtonian fluid, the slip velocity was proposed by many researchers to be a power-law of the wall shear stress. In this case, Mooney method should be modified in the determination of the slip velocity of a non-Newtonian suspension. Jastrzebski method was employed by some researchers for concentrated suspension, but this method was criticized for lack of a physical basis.

In addition, entrance and exit losses are important in capillary rheometry for the calculation of viscosity and wall shear stress. Jastrzebski had provided a formula summarizing the influence of some factors, which include flow rate, particle concentration, and capillary radius.

As such, the focus of this research is to study the rheological behaviour of concentrated suspension by experimental investigations and numerical simulation. As no other researchers presented these factors systematically, this work contributes a better understanding in these aspects.

CHAPTER 3 THEORETICAL BASIS AND NUMERICAL MODELING

3.1 INTRODUCTION

A pressure-driven flow in a capillary rheometer has nonuniform velocity with velocity gradient reaching a maximum at the wall and zero in the center of the flow. A sketch of capillary rheometer is shown in Figure 2.1. Cylindrical coordinates can be employed such that the coordinate z is along the axis of the tube and r is in the radial direction. The velocity is assumed to be only in the z direction [Bird et al., 1987] as u_z . The pressure drop for a given flow rate through this tube is used to determine the viscosity of a fluid.

Due to a nonuniform velocity gradient, and thus shear rate, there exists particle migration in the flow of a concentrated suspension of a powder filled polymer system. In addition, wall slip and viscous heating can be important under certain conditions. This chapter introduces the governing equations for particle migration, wall slip and viscous heating of a generalized Newtonian fluid in a capillary flow. These equations are proposed on the basis of the following assumptions:

1. Steady and incompressible flow;
2. Viscoelasticity is not included. In addition, normal stresses are neglected in comparison with shear stress;
3. The powder particles are mono-sized and spherical in shape;
4. The viscosity of the suspension is a function of shear rate, particle concentration, pressure and temperature;
5. Brownian motion is not considered;

6. Buoyant, inertial and colloidal effects are neglected;
7. The flow is symmetric about the tube axis;
8. $\partial/\partial z \ll \partial/\partial r$, $u_r \ll u_z$;
9. Pressure is independent of radial direction;
10. Heat conduction in the direction of flow is negligible in comparison with conduction in the radial direction;
11. Thermal convection in the radial direction is neglected.

3.2 FLOW EQUATIONS

For a concentrated suspension, creeping flow can be applied with spherical particle of size far beyond the colloidal range ($\gg 1 \mu\text{m}$), and with Reynolds number (R_e) sufficiently small (10^{-2} - 10^{-4}) such that the bulk inertia has little influence, i.e. $R_e = [\rho]UL/\eta \ll 1$ where $[\rho]$ is the mixture density, U and L are the velocity and length scales of the bulk flow, η is the bulk fluid viscosity. The conservation and equilibrium equations for a steady state, incompressible flow are [Phillips et al., 1992]:

$$\nabla \cdot \vec{u} = 0 \quad (3.1)$$

$$-\nabla P + \nabla \cdot \bar{\bar{\tau}} = 0 \quad (3.2)$$

where P : the hydrostatic pressure

$\bar{\bar{\tau}}$: the extra stress tensor

$\vec{u}$: the velocity field

For a generalized Newtonian fluid, the extra stress tensor $\bar{\bar{\tau}}$ is given by:

$$\bar{\bar{\tau}} = \eta(|\dot{\gamma}|, T, \phi) \dot{\gamma} \quad (3.3)$$

For an axisymmetric flow in the cylindrical coordinates (r, z, θ) , the magnitude of $|\dot{\gamma}|$ for the shear rate tensor $\dot{\gamma}$ is obtained as [Chen et al., 2003]:

$$|\dot{\gamma}| = \left[\frac{1}{2} \left\{ \dot{\gamma} : \dot{\gamma} \right\} \right]^{1/2} = \left[\frac{1}{2} \left\{ \dot{\gamma}_{rr}^2 + \dot{\gamma}_{\theta\theta}^2 + \dot{\gamma}_{zz}^2 + 2\dot{\gamma}_{rz}^2 \right\} \right]^{1/2} \quad (3.4)$$

The components in Equation (3.4) are given by:

$$\dot{\gamma}_{rr} = 2 \frac{\partial u_r}{\partial r}, \quad \dot{\gamma}_{\theta\theta} = 2 \frac{u_r}{r}, \quad \dot{\gamma}_{zz} = 2 \frac{\partial u_z}{\partial z}, \quad \dot{\gamma}_{rz} = \frac{\partial u_z}{\partial r} + \frac{\partial u_r}{\partial z} \quad (3.5)$$

Therefore, equations (3.1) and (3.2) can be written as:

$$\frac{\partial u_r}{\partial r} + \frac{u_r}{r} + \frac{\partial u_z}{\partial z} = 0 \quad (3.6)$$

$$-\frac{\partial p}{\partial r} + \frac{\partial \tau_{rr}}{\partial r} + \frac{\tau_{rr}}{r} + \frac{\partial \tau_{rz}}{\partial z} - \frac{\tau_{\theta\theta}}{r} = 0 \quad (3.7)$$

$$-\frac{\partial p}{\partial z} + \frac{\partial \tau_{rz}}{\partial r} + \frac{\tau_{rz}}{r} + \frac{\partial \tau_{zz}}{\partial z} = 0 \quad (3.8)$$

Due to axisymmetry, $\tau_{rz} = \tau_{zr}$. For a pressure-driven tube flow, $\partial/\partial z \ll \partial/\partial r$, $u_r \ll u_z$, $u_z = u_z(r, z)$ and $p = p(z)$. Based on these assumptions, known as the lubrication approximation theory [Wang and Lee, 1989], equations (3.7) and (3.8) can be simplified as [Bird et al., 1960]:

$$\frac{\partial p}{\partial z} - \frac{1}{r} \frac{\partial}{\partial r} (r \eta \frac{\partial u_z}{\partial r}) = 0 \quad (3.9)$$

The global continuity equation associated with the above equations is given by:

$$Q = 2\pi \int_0^R r u_z(r) dr \quad (3.10)$$

where Q is the volumetric flow rate, R is the radius of the capillary tube. Consistent with above flow equations, appropriate boundary condition in the radial direction are given by:

$$\frac{\partial u_z}{\partial r} = 0 \quad \text{at } r = 0 \quad (3.11)$$

$$u_z = u_s \quad \text{at } r = R \quad (3.12)$$

where u_s is the slip velocity at the wall.

Equation (3.9) can be transformed into:

$$\int r \frac{\partial P}{\partial z} dr = r\eta \frac{\partial u_z}{\partial r} + C' \quad (3.13)$$

Since P is independent of r , integration of equation (3.13) with respect to r , using boundary condition of equation (3.11), then $C' = 0$, results in:

$$\frac{\partial u_z}{\partial r} = \frac{r\Lambda_z}{2\eta} \quad (3.14)$$

where $\Lambda_z = -\partial P / \partial z$ is the pressure gradient along the flow direction.

After a second integration of equation (3.14) together with boundary condition of (3.12), obtains:

$$u(r) = u_s + \Lambda_z \int_0^R \frac{r}{2\eta} dr \quad (3.15)$$

From equation (3.14) and the definition of shear rate $\dot{\gamma}$, it follows that the absolute value of the shear rate is:

$$\dot{\gamma} = \left| \frac{r\Lambda_z}{2\eta} \right| \quad (3.16)$$

In addition, by substituting (3.15) into (3.10) and integrating by parts, the flow rate can be represented by:

$$Q = \Lambda_z \pi S + Q_s \quad (3.17)$$

where $Q_s = \pi R^2 u_s$ is the flow rate contributed by slippage at the wall. S is the flow conductivity, given as:

$$S = \int_0^R \frac{r^3}{2\eta} dr \quad (3.18)$$

3.3 CONSERVATION OF ENERGY

When a highly viscous concentrated suspension is driven through a capillary at high deformation rates, considerable heat may be generated as a result of viscous dissipation, in particular at the region next to the capillary wall where the shear rate is the highest. The increase in temperature due to viscous heating will lower the viscosity of the suspension, which will be most pronounced at the region next to the wall. Viscous energy dissipation could lead to significant increase in local temperature [Lawal and Kalyon, 1996].

The energy equation taking into account the concentration-dependent density, thermal conductivity and specific capacity of the suspension in cylinder coordinates can be expressed as [Bird et al., 1987]:

$$\begin{aligned} \rho C_p \left(\frac{\partial T}{\partial t} + u_z \frac{\partial T}{\partial z} + u_r \frac{\partial T}{\partial r} + u_\theta \frac{\partial T}{\partial \theta} \right) = \\ \frac{1}{r} \frac{\partial}{\partial r} \left(rK \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(K \frac{\partial T}{\partial z} \right) + \frac{\partial}{\partial \theta} \left(K \frac{\partial T}{\partial \theta} \right) + \Phi \end{aligned} \quad (3.19)$$

In equation (3.19), Φ is the heat generated due to viscous dissipation and is given generally as:

$$\Phi = 2\eta(|\dot{\gamma}|, T, \phi) \left[\left(\frac{\partial u_r}{\partial r} \right)^2 + \left(\frac{u_r}{r} \right)^2 + \left(\frac{\partial u_z}{\partial z} \right)^2 \right] + \eta(|\dot{\gamma}|, T, \phi) \left(\frac{\partial u_z}{\partial r} + \frac{\partial u_r}{\partial z} \right)^2 \quad (3.20)$$

With assumptions (10) and (11) in section 3.1, the energy equation (3.19) can be simplified to:

$$\rho C_p \left(\frac{\partial T}{\partial t} + u_z \frac{\partial T}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left(rK \frac{\partial T}{\partial r} \right) + \Phi \quad (3.21)$$

The expression for the heat generation due to viscous dissipation and a vanishing velocity gradient in the axial direction can be written as:

$$\Phi = \eta(|\dot{\gamma}|, T, \phi) \left(\frac{\partial u_z}{\partial r} \right)^2 \quad (3.22)$$

The effective density ρ and specific heat C_p for a concentrated suspension can be estimated using a simple linear rule of mixture [Rhee, 1992]:

$$\rho = (1 + \varepsilon\phi)\rho_b \quad \text{where } \varepsilon = \frac{\rho_p - \rho_b}{\rho_b} \quad (3.23)$$

$$C_p = (1 + \mathcal{G}\phi)C_{pb} \quad \text{where } \mathcal{G} = \frac{C_{pp} - C_{pb}}{C_{pb}} \quad (3.24)$$

where the subscript b and p denote quantities associated with polymer binder and powder respectively. Concentrated suspensions have been found to have an anomalously higher thermal conductivity than that predicted by the macroscopic linear rule theory [Hunt and Tien, 1988]. Although some efforts have been made to address this effect [Shin and Lee, 2000], no generic relationship has been obtained. Here, the Jeffery model based on the effective medium theory, one of the most frequently used models for concentrated suspensions and composites, is adopted for the calculation of the thermal conductivity K of the suspension [Hamilton and Crosser, 1962; Rhee, 1992]:

$$K = \left[1 + 3\zeta\phi + \phi^2 \left(3\zeta^2 + \frac{3}{4}\zeta^3 + \frac{9\zeta^3}{16} \frac{\chi+2}{2\chi+3} + \frac{3\zeta^4}{64} \right) \right] K_b \quad (3.25)$$

where $\chi = K_p / K_b$, $\zeta = (\chi - 1)/(\chi + 2)$.

The energy equation (3.21) is subjected to the boundary condition for temperature at the centerline:

$$\frac{\partial T}{\partial r} = 0 \text{ at } r = 0 \quad (3.26)$$

The temperature profile at the inlet is prescribed as:

$$T = T_0 \text{ at } z = 0 \quad (3.27)$$

In practice, the condition for temperature at the wall of the tube is likely to involve both the melt temperature and its first derivative with respect to radius, which is unknown. Since the heat generated by shear heating during the suspension flow is mainly dissipated through the capillary wall to the surrounding environment, a conjugate heat transfer problem is solved to account for heat conduction in both the suspension and the capillary wall [Winter, 1970]. The governing equations for heat transfer at the interface in the capillary inner wall and heat conduction in the capillary wall are given as:

$$K \left. \frac{\partial T}{\partial r} \right|_{r=R^-} = K_s \left. \frac{\partial T}{\partial r} \right|_{r=R^+} \quad (3.28)$$

$$\frac{1}{r} \frac{\partial}{\partial r} \left(K_s r \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(K_s \frac{\partial T}{\partial z} \right) = 0 \quad (3.29)$$

where K_s is the thermal conductivity of steel.

In general, the heat flux at the capillary die wall depends on the temperature difference between the wall interface and the surroundings. Therefore in this investigation, the temperature gradient in the fluid layer next to the wall is taken to be proportional to the outer temperature difference:

$$-K_s \left. \frac{\partial T}{\partial r} \right|_{r=R+\delta} = Bi \left(\frac{T_s - T_w}{R} \right) \quad (3.30)$$

where T_s is the surroundings temperature, T_w is the wall temperature, Bi is the Biot number and is given as [Winter, 1970]:

$$Bi = \frac{K_s}{K \cdot \ln(1 + d/R)} \quad (3.31)$$

where d is the outer diameter of the steel tube .

The limiting cases of the thermal boundary conditions are represented by $Bi = \infty$ for a constant wall temperature and $Bi = 0$ for an adiabatic wall condition. For heat transfer between a flowing concentrated suspension and the channel wall, a heat balance in a layer close to the wall gives:

$$h = \frac{\left(K \frac{\partial T}{\partial r} \right) \Big|_{r=R}}{T_{avg} - T_w} \quad (3.32)$$

where h is the heat transfer coefficient. The average fluid temperature T_{avg} is given as:

$$T_{avg} = \frac{\int_0^R T \rho u r dr}{\int_0^R \rho u r dr} \quad (3.33)$$

Once the temperature field is obtained, equations (3.32) and (3.33) are used to calculate the convective heat transfer coefficient. The results are expressed in terms of the Nusselt number, defined as [Wen and Ding, 2005]:

$$Nu_z = \frac{2hR}{K \Big|_{r=R}} \quad (3.34)$$

The importance of shear heating in rheometry is estimated by the Nahme-Griffith number, N_a , which determines the level of temperature influences on viscosity.

For capillary flow, Nahme-Griffith number can be calculated as [Macosko, 1994]:

$$N_a = \frac{\beta_\eta \tau \dot{\gamma} R^2}{4K} \quad (3.35)$$

where β_η is the temperature sensitivity of viscosity, which can be given as [Bird et al., 1987]:

$$\beta_\eta = \frac{E}{k_B T^2} \quad (3.36)$$

where E is the activation energy (J/mol), k_B is Boltzmann's constant (J/mol.K).

Viscous heating could be important in the study of polymer solutions and melts because the thermal sensitivity of the fluid tends to increase monotonically as the molecular weight and the viscosity of the fluid increase [Winter, 1977]. Significant error can occur in capillary measurement if the effect of viscous heating is not considered when $Na \geq 1$.

3.4 CONSTITUTIVE EQUATIONS

In general, the bulk suspension stress consists of two parts: one is the contribution from the bulk fluid binder system, the other is from the particle system i.e. $\tau = \tau_b + \tau_p$. The fluid phase stress is assumed to be [Bird et al., 1960]:

$$\tau_b = -P\mathbf{I} + 2\eta_b \mathbf{E} \quad (3.37)$$

where P is the fluid phase averaged pressure, $\mathbf{I}$ is the identity tensor, η_b is the viscosity of a suspending fluid. $\mathbf{E}$ is the local rate of strain defined as [Bird et al., 1960]:

$$\mathbf{E} = \frac{1}{2} [\nabla \mathbf{u} + \nabla \mathbf{u}^T] \quad (3.38)$$

The constitutive law for the particle stress in the absence of a normal stress portion is given as [Miller and Morris, 2006]:

$$\tau_p = 2\eta_b \eta(\phi) \mathbf{E} \quad (3.39)$$

Thus, the bulk suspension stress can be expressed as [Batchelor and Green, 1972]:

$$\tau = \tau_b + \tau_p = -P\mathbf{I} + 2\eta_b[1 + \eta(\phi)]\mathbf{E} = -P\mathbf{I} + 2\eta\mathbf{E} \quad (3.40)$$

where $\eta = \eta_b[1 + \eta(\phi)]$ is a particle concentration-dependent shear viscosity. The theoretical calculation of the viscosity of suspensions of solid particles can be approached in several ways. First, the viscosity may be determined either from the velocity gradient [Bird et al., 1987]:

$$\tau_{ik} = -\eta \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) \quad (3.41)$$

or from the energy dissipation in the bulk of the fluid [Bird et al., 1987]:

$$E_v = -\eta \int_V \frac{\partial u_i}{\partial x_k} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) dV \quad (3.42)$$

The principal difference between the last two approaches is that the first assumes no long-range interaction between particles whereas the latter one does. In general, there is good agreement among the different theoretical studies in that the viscosity of extremely dilute suspensions is a simple function of the volume fraction solids [Thomas, 1965]:

$$\frac{\eta}{\eta_b} = 1 + k_1\phi \quad (3.43)$$

The value of k_1 is commonly accepted to be 2.5 for no-slip laminar flow when solid sphere diameter is large in comparison to the molecular dimensions but small in comparison to the characteristic length of the measuring instrument. Equation (3.43) is only valid for concentration of volume fraction on the order of 0.01 [Einstein, 1906].

In a concentrated suspension, there are many potentially important types of inter-particle interactions even after neglecting the electrical forces between particles,

inertial effect, van-der Waals force and other non-hydrodynamic forces. It is necessary to account for the hydrodynamic interaction of particles, particle rotation, collision between particles, mutual exclusion of particles, doublet and higher order agglomeration of particles, and ultimately mechanical interference between particles. Perhaps the greatest difficulty in arriving at a theory for concentrated suspensions is the fact that the random structure of the suspension cannot in general be represented by a simple model. The true rheological property of a concentrated suspension has been hidden in many viscosity experiments due to the confounding effects of wall slip, variation in particle distribution, and shape of the particles. In treating the particle suspension as a single continuum, one must account for variation in viscosity with particle concentration and wall slip etc. This variation in viscosity of concentrated suspension can be obtained as a simple correction to the solvent viscosity. The functional relationship of η can take several forms that adequately model viscosity data for concentrated suspension fluids [Jeffrey and Acrivos, 1976]. The viscosity formulation of a concentrated suspension described by the Krieger model, which is shear deformation and concentration dependent viscosity, is adopted here [Lam et al., 2004]:

$$\eta = \eta_b \left(1 - \frac{\phi}{\phi_c} \right)^{-m} \quad (3.44)$$

where m is a fitting constant with experimental flow data, and ϕ_c is the critical loading of concentrated suspension in pressure-driven tube flow. This rheological model describes the effect of the volume fraction of the powder on the flow behavior of powder/binder mixture, which can be applied to a concentrated suspension. The most commonly used viscosity for polymeric binder system is the

power-law fluid model with Arrhenius-type temperature dependence [Hieber and Shen, 1980] which can be expressed as:

$$\eta_b = m_0 \exp\left(\frac{T_a}{T}\right) \dot{\gamma}^{n-1} \quad (3.45)$$

where m_0 is a material constant with unit of Pa.s^n , T_a is a material constant related to temperature (K).

From equations (3.16) and (3.45), it follows that:

$$\dot{\gamma} = \left| \frac{r \Lambda_z \left(1 - \frac{\phi}{\phi_c}\right)^m}{2m_0 \exp\left(\frac{T_a}{T}\right)} \right|^{1/n} \quad (3.46)$$

Hence, from equations (3.44)-(3.46), it can be obtained:

$$\eta = m_0 \exp\left(\frac{T_a}{T}\right) \left(1 - \frac{\phi}{\phi_c}\right)^{-m} \left| \frac{r \Lambda_z \left(1 - \frac{\phi}{\phi_c}\right)^m}{2m_0 \exp\left(\frac{T_a}{T}\right)} \right|^{1-1/n} \quad (3.47)$$

Substituting equation (3.47) into equation (3.18), results in:

$$S = \left(\frac{\Lambda_z^{1/n-1}}{2m_0}\right)^{1/n} \int_0^R \left(\frac{\left(1 - \frac{\phi}{\phi_c}\right)^m}{\exp\left(\frac{T_a}{T}\right)} \right)^{1/n} r^{3+1/n} dr \equiv \left(\frac{\Lambda_z^{1/n-1}}{2m_0}\right)^{1/n} f(\phi, T) \quad (3.48)$$

That is, the temperature and particle concentration dependence of S can be factored out and explicitly evaluated. In particular, by exploiting this fact, the computing time in simulation can be reduced significantly.

It should be noted that the power-law model is adequate only for those materials whose Newtonian viscosity is limited to very small shear rate. More generally, the modified Cross model can be employed to describe the viscosity of the binder,

which describes a shear-thinning behavior at moderate shear rate and constant Newtonian behavior at very low shear rate [Macosko, 1994]:

$$\eta_b = \frac{\eta_0}{1 + (\eta_0 \dot{\gamma} / \tau^*)^{1-n}} \quad (3.49)$$

where η_0 is the Newtonian viscosity at zero shear-rate or for sufficient small shear rate $\dot{\gamma}$, n is flow index, $\eta_0 = B \exp(T_b / T)$, where B (Pa.s) and T_b (K) are material constants. At high shear rate, equation (3.49) can be simplified to a power-law model:

$$\eta_b = (\eta_0 \dot{\gamma}_0^{1-n}) \dot{\gamma}^{n-1} \quad (3.50)$$

where $\dot{\gamma}_0 = \tau^* / \eta_0$ with unit of 1/s, τ^* is a stress parameter (Pa).

3.5 PARTICLE MIGRATION

3.5.1 Modified Diffusive Flux Model

In a capillary flow, a nonhomogeneous distribution of shear rate and shear force exist. Under these circumstances, three diffusive phenomena may occur; (1) particles migrate from regions of high shear to regions of low shear (shear induced particle migration) [Acrivos, 1995]. (2) diffusion from regions of high concentration or viscosity to that of low concentrations or viscosity, which have competing effect with (1); (3) self-diffusion of particles in a suspension of uniform concentration, which is usually one order in magnitude less than that caused by (1) and (2) and thus is neglected in this investigation [Phillips et al., 1992]. As a consequence of (1) and (2), a homogeneous suspension with particles flowing in a capillary tube will generate a profile of increasing concentration from the wall to

the center, which can cause nonhomogenous distribution of particles, and thus significant nonuniform viscosity distribution for a given cross-section.

Particle migration is related to particle concentration. The rheological behavior is different for dilute suspension, medium concentrated suspension and saturated suspension due to the difference of frequency of particle interactions. As the concentration level corresponding to a critical packing of the solid particles is approached, there is no free space for movement of spherical solid particles and no particle migration is possible. Therefore, this research focused on the concentrated suspension but far from the saturated suspension.

In addition to the diffusive effect of particles, buoyancy forces could also affect particle migration when the particle density differs significantly from that of the suspending fluid. The effect of buoyant forces can be evaluated by the buoyant number as following [Norman et al., 2005]:

$$N_B = \frac{2(\rho_p - \rho_b)gR^2}{9\eta U} \quad (3.51)$$

where ρ_p is the density of the particles, ρ_b is the density of the fluid, e.g. a polymer melt, g is the acceleration due to gravity, R is the radius of the pipe, η is the viscosity and U is the average axial velocity.

Carpen and Brady (2002) found that as the density difference between the particles and the suspending fluid increases, the instability becomes more pronounced.

However, the effect of buoyancy of particles on particle flux can be neglected in this study due to the high viscosity of EVA employed in the investigation, where the buoyant number N_B is less than 0.01.

On the basis of these mechanisms, a diffusive flux model to predict the concentration profiles based on a Newtonian binder system was developed [Phillips et al., 1992, Morris and Brady, 1998]:

$$\frac{D\phi}{Dt} = -\nabla \cdot J \quad (3.52)$$

$$J = N_c + N_\eta + N_b \quad (3.52a)$$

$$N_c = -k_c a^2 \phi \nabla (\phi \dot{\gamma}) \quad (3.52b)$$

$$N_\eta = -k_\eta \phi^2 \dot{\gamma} \left(\frac{a^2}{\eta} \right) \nabla \eta \quad (3.52c)$$

$$N_b = -D \nabla \phi \quad (3.52d)$$

where k_c and k_η are two phenomenological parameters. N_c accounts for the effect of spatially varying interaction frequency, N_η describes the effect of a spatially varying viscosity, N_b accounts for Brownian diffusion of the particles.

Substituting equations 3.52(b), (c) and (d) to equation (3.52a), obtains:

$$J = - \left\{ k_c a^2 \phi^2 \frac{\partial \dot{\gamma}}{\partial r} + k_\eta \phi^2 \dot{\gamma} \left(\frac{a^2}{\eta} \right) \frac{\partial \eta}{\partial r} + a^2 \dot{\gamma} \left(k_c \phi + \frac{D}{a^2 \dot{\gamma}} \right) \frac{\partial \phi}{\partial r} \right\} \quad (3.53)$$

If the particle Peclet number $P_e = a^2 \dot{\gamma} / D$, defined in terms of the local shear rate $\dot{\gamma}$, particle radius a and the diffusivity D , is large for concentrated suspension flow in a capillary rheometer, i.e. $a^2 \dot{\gamma} \gg D$, the term $D / a^2 \dot{\gamma}$ (associated with Brownian motion) in equation (3.53) is very small ($\frac{D}{a^2 \dot{\gamma}} \ll k_c \phi$) and can be neglected. This implies that Brownian motion has negligible contribution.

The boundary condition of no particle flux through the wall of the cylindrical tube has to be enforced:

$$\{k_c \phi \nabla (\phi \dot{\gamma}) + k_\eta \phi^2 \dot{\gamma} \nabla \eta\} \cdot n = 0 \quad (3.54)$$

The constants k_c and k_η must be determined by data fitting of the predictions of the model to the experimental measurements [Phillips et al., 1992; Lam et al., 2004]. Both k_c and k_η in the original Phillips model were determined from Couette flow and Poiseuille shear flow experiments to be 0.43 and 0.65 respectively for a Newtonian binder system [Phillips et al., 1992]. Lam et al. (2004) extensively investigated further on particle migration in Poiseuille flow for a non-Newtonian binder system, i.e. EVA460 and nickel powder, and obtained $k_c = 0.20$ and $k_\eta = 0.58$ for particle concentrations of 30% and 40%.

Other experimental evidence [Tetlow et al., 1998] suggested that particle migration is not only due to particle roughness but also size and shape. An alternative source of irreversibility is the occurrence of multi-body interactions [Nott and Brady, 1994]. The number of interactions experienced by a test particle would be a function of particle concentration ϕ [Graham et al., 1998], which may result in the change of phenomenological parameters. Thus, k_c , which accounts for particle concentration effect, is proposed to be a linear function of concentration ϕ and given as:

$$k_c = k'_c \phi \quad (3.55)$$

where k'_c is a constant for a certain particle filled polymeric system. The parameter, k_η , which accounts for the viscosity effect, is assumed to be a constant in this investigation.

3.5.2 Extension of Diffusive Flux Model

As noted by Phillips et al. (1992), particle migration is caused by the effects of spatially varying in interaction frequency and viscosity. Its main implication is that

an inhomogeneous fluid flow field drives the particle flux. For a generalized-Newtonian suspension system, the effect of the spatially varying viscosity is not only caused by a non-uniform particle distribution but also by shear thinning and viscous heating etc. in a capillary fluid flow. Thus, these effects should be taken into account during the characterization of the rheological behavior of a concentrated suspension in a capillary flow.

(a) Shear-thinning effect

For a flow through a cylindrical tube, $\phi = \phi(r, t)$, where r is the radial coordinate in a cylindrical coordinate system. Following Phillips et al. (1992), with consideration of particles immersed in a generalized-Newtonian binder system, the particle flux due to the spatial variation in viscosity in equation (3.52c) can be written as:

$$N_\eta = -k_\eta \phi^2 \dot{\gamma} \left(\frac{a^2}{\eta} \right) \nabla \eta = -k_\eta \phi^2 \dot{\gamma} \left(\frac{a^2}{\eta} \right) \left(\frac{\partial \eta}{\partial \phi} \nabla \phi + \frac{\partial \eta}{\partial \dot{\gamma}} \nabla \dot{\gamma} \right) \quad (3.56)$$

Thus, the modified expression of equation (3.52) is:

$$\frac{\partial(u_z \phi)}{\partial z} = \frac{a^2}{r} \frac{\partial}{\partial r} \left[k'_c \phi^2 \nabla(\phi \dot{\gamma}) + k_\eta \phi^2 \dot{\gamma} \left(\frac{1}{\eta} \frac{\partial \eta}{\partial \phi} \nabla \phi + \frac{\partial \eta}{\partial \dot{\gamma}} \nabla \dot{\gamma} \right) \right] \quad (3.57)$$

As the migration effect of particles is dependent on the viscosity, the viscosity effect can be assumed to be a lumped concentration effect [Chen et al., 2003]. Thus, the particle conservation equation for pressure driven tube flow can be simplified to:

$$\frac{\partial(u_z \phi)}{\partial z} = \frac{a^2}{r} \frac{\partial}{\partial r} \left[k'_c \phi^2 \nabla(\phi \dot{\gamma}) + k_\eta \phi^2 \dot{\gamma} \left(\frac{\partial \ln \eta}{\partial \phi} \nabla \phi \right) \right] \quad (3.58)$$

Accordingly, the boundary condition of no particle flux through the wall of the cylindrical tube has to be modified:

$$\left\{ k'_c \phi^2 \nabla \left(\phi \frac{\partial u_z}{\partial r} \right) + k_\eta \phi^2 \frac{\partial u_z}{\partial r} \frac{\partial \ln \eta}{\partial \phi} \frac{\partial \phi}{\partial r} \right\} \cdot n = 0 \quad (3.59)$$

(b) Nonisothermal effect

When considering the temperature change due to viscous heating, the particle flux of the spatial variation in viscosity (equation 3.52c) in the diffusive flux equation could be further modified by the chain rule:

$$N_\eta = -k_\eta \phi^2 \dot{\gamma} \left(\frac{a^2}{\eta} \right) \nabla \eta = -k_\eta \phi^2 \dot{\gamma} \left(\frac{a^2}{\eta} \right) \left(\frac{\partial \eta}{\partial \phi} \nabla \phi + \frac{\partial \eta}{\partial T} \nabla T \right) \quad (3.60)$$

Thus, the diffusive equation (3.52) with consideration of viscous heating effect can be written as:

$$\frac{\partial(u_z \phi)}{\partial z} = \frac{a^2}{r} \frac{\partial}{\partial r} \left[k'_c \phi^2 \nabla(\phi \dot{\gamma}) + k_\eta \phi^2 \dot{\gamma} \left(\frac{1}{\eta} \frac{\partial \eta}{\partial \phi} \nabla \phi + \frac{1}{\eta} \frac{\partial \eta}{\partial T} \nabla T \right) \right] \quad (3.61)$$

Accordingly, the boundary condition of no particle flux through the wall of the cylindrical tube has to be modified:

$$\left\{ k'_c \phi^2 \nabla \left(\phi \frac{\partial u_z}{\partial r} \right) + k_\eta \phi^2 \frac{\partial u_z}{\partial r} \left(\frac{1}{\eta} \frac{\partial \eta}{\partial \phi} \nabla \phi + \frac{1}{\eta} \frac{\partial \eta}{\partial T} \nabla T \right) \right\} \cdot n = 0 \quad (3.62)$$

3.6 WALL SLIP

Wall slip is particularly important for concentrated suspensions because it influences the macroscopic rheological behavior and results in the reduction of apparent viscosity.

The slip mechanism of a concentrated suspension is thought to be caused by the formation of a thin slip layer near the wall. The local particle concentration in a

layer near to the wall is lower than that in the bulk region due to the high shear force next to the wall. Thus, a large velocity gradient exists at a small region next to the wall resulting in an apparent slippage of the bulk fluid.

Two slip models are introduced here, namely a slip velocity model and a slip layer model.

3.6.1 Slip Velocity Model

For an incompressible fluid, the flow rate Q through a tube of radius R can be expressed as [Mooney, 1931]:

$$Q = \int_0^R u_z 2\pi r dr = \pi \int_0^{R^2} u_z d(r^2) \quad (3.63)$$

where u_z is the velocity at any point. Integration by parts yields:

$$Q = \pi u_s R^2 - \pi \int_0^R r^2 (du_z / dr) dr \quad (3.64)$$

where u_s is the slip velocity at the wall. Since $f(\tau) = -du_z / dr$ and $\tau / \tau_w = r / R$, flow rate can be obtained if the yield stress of the fluid can be ignored:

$$Q = \pi u_s R^2 + \frac{\pi R^3}{\tau_w^3} \int_0^{\tau_w} \tau^2 f(\tau) d\tau \quad (3.65)$$

where τ is the shear stress at any point and τ_w is the wall shear stress.

Differentiating flow rate against the wall shear stress yields:

$$\frac{\partial Q}{\partial \tau_w} = \pi R^2 \frac{\partial u_s}{\partial \tau_w} + \pi R^3 \frac{\dot{\gamma}_w}{\tau_w} - \frac{3}{\tau_w} (Q - \pi R^2 u_s) \quad (3.66)$$

Multiplied by $4/(\pi R^3)$, Eq. (3.66) can be written as:

$$\frac{\partial \dot{\gamma}_a}{\partial \tau_w} + \frac{3\dot{\gamma}_a}{\tau_w} = \frac{4}{R} \left(\frac{\partial u_s}{\partial \tau_w} + \frac{3u_s}{\tau_w} \right) + \frac{4\dot{\gamma}_w}{\tau_w} \quad (3.67)$$

where $\dot{\gamma}_a$ is the apparent wall shear rate and $\dot{\gamma}_w$ is the slip-corrected wall shear rate. As $\partial \ln x = \partial x / x$, the following expression can be obtained:

$$\frac{\partial \ln \dot{\gamma}_a}{\partial \ln \tau_w} \cdot \dot{\gamma}_a + 3\dot{\gamma}_a = \frac{4u_s}{R} \left(\frac{\partial \ln u_s}{\partial \ln \tau_w} + 3 \right) + 4\dot{\gamma}_w \quad (3.68)$$

For a non-Newtonian fluid with shear-thinning behavior, the modified Cross model, i.e. equation (3.49), is appropriate to describe the flow field in a capillary, which has zero shear rate at the centerline and high shear rate at the wall. However, as will be discussed later, it is impossible to derive a close form solution for equation (3.68) for the apparent shear rate at the wall. Noting that at the wall, the shear rate is high, the behavior of a suspension may be approximated by a power-law equation (3.50) with the Krieger model as equation (3.44). Thus, for negligible yield stress, the relationship between shear stress and apparent shear rate can be written as:

$$\tau_w = (\eta_0 \dot{\gamma}_0^{1-n}) \left(1 - \frac{\phi}{\phi_c} \right)^{-m} \dot{\gamma}_a^n \quad (3.69)$$

Thus, an expression for n can be obtained as:

$$n = \partial \ln \tau_w / \partial \ln \dot{\gamma}_a \quad (3.70)$$

For a non-Newtonian concentrated suspension, the flow property becomes more complicated due to the shear-thinning effect of the pure binder and the slippage at the wall. Therefore, slip is proposed to be described by a power law model [Kwon and Ahn, 1995; Yeow et al., 2003; Gulmus and Yilmazer, 2005]:

$$u_s = \beta_s \tau_w^k \quad (3.71)$$

where β_s and k are slip constants, related to temperature and material properties.

Thus, for a non-Newtonian fluid, by introducing the power-law viscosity model and the slip model (equations (3.69) and (3.71), respectively), the solution of equation (3.68) can be written in a compact form as:

$$\dot{\gamma}_w = \left(\frac{3n+1}{4n} \right) \dot{\gamma}_a - (k+3) \frac{u_s}{R} \quad (3.72)$$

This equation includes the Rabinowitsch correction for a non-Newtonian fluid and the non-linear effect of slip velocity on the wall shear stress. It reduces to the Mooney method for a Newtonian fluid where its viscosity remains constant with $n=1$, and the slip velocity was proposed to be linearly related to the wall shear stress, i.e. $k=1$ [Yilmazer and Kalyon, 1989]. Therefore, equation (3.72) can be reverted to:

$$\dot{\gamma}_a = \frac{4u_s}{R} + \dot{\gamma}_w \quad (3.73)$$

However, for a non-Newtonian fluid, the slip velocity is nonlinearly related to the wall shear stress, so $k \neq 1$. If it is assumed that $k=1/n$ [Kalyon et al., 1993] for describing the non-linearity, equation (3.72) also reduces to Mooney's result directly, but Rabinowitsch correction has to be applied. With this assumption, the corrected apparent shear rate at the wall will be given as [Kwon and Ahn, 1995; Leblanc, 2001]:

$$\dot{\gamma}_a = \left(\frac{4n}{3n+1} \right) \dot{\gamma}_w + \frac{4u_s}{R} \quad (3.74)$$

However, equation (3.74) might not be appropriate or accurate as it might be always appropriate to assume $k=1/n$. Indeed, it is unnecessary to invoke this assumption, as the value of k can be determined directly from experimental results [Lam et al., 2007].

For the slip coefficient β_s , many researchers found it depended on many factors. Hill et al. (1990) and Person and Denn (1997) proposed that it is related to the applied pressure as the slip velocity between a polymeric melt and the die surface should be a function of the normal stress at the wall, similar to the friction between solids. In addition, the slip theories developed by Hatzikiriakos and Dealy (1992), and Stewart (1993) all contain a dependence of the slip velocity on the isotropic pressure. While the physical bases of these theories differ, the slip velocity dependence on pressure is similar. These theories all assume a positive power-law dependence of the slip velocity on shear stress, with power-law exponent ranging from 2 to 6. Therefore, the slip velocity proposed by Hill et al. (1990) was employed:

$$u_s = \alpha' \exp(-\beta_p P) \tau_w^k \quad (3.75)$$

where α' is a parameter dependence on temperature and surface energy, β_p is a coefficient related to pressure, that is typically of the order 10^{-9} Pa^{-1} , P is the absolute pressure.

The effect of pressure on slip velocity can be significant in melt flow experiments in long capillaries [Hill et al., 1990]. This also implies that the slip velocity measured by the dies with different ratio of L/R will be different, decreasing with L/R .

However, the temperature effect on slip is not included in equation (3.75). An expression was proposed for the parameter α' as:

$$\alpha' = \alpha \exp(\lambda T) \quad (3.76)$$

where λ is a temperature-dependent coefficient, indicating the activation energy of the melt. α is a material constant.

Introducing equations (3.75) and (3.76) into equation (3.72), the following expression is obtained:

$$\dot{\gamma}_w = \left(\frac{3n+1}{4n} \right) \dot{\gamma}_a - (k+3) \frac{\alpha \exp(\lambda T - \beta_p P) \tau_w^k}{R} \quad (3.77)$$

As slip velocity for a non-Newtonian fluid is a nonlinear function of wall shear stress and the power law index k is unknown, slip velocity cannot be determined directly from a Mooney plot. Instead, let G to be the gradient in a Mooney plot:

$$G = \left(\frac{4n}{3n+1} \right) (k+3) \alpha \exp(\lambda T - \beta_p P) \tau_w^k = \frac{4n(k+3)}{3n+1} u_s \quad (3.78)$$

The parameters of α , λ , β_p and k can be determined by data fitting. Thus, the slip velocity can be obtained by:

$$u_s = \frac{3n+1}{4n(k+3)} G \quad (3.79)$$

3.6.2 Slip Layer Model

Slip phenomenon may be considered alternatively as the occurrence of a relative velocity between the fluid at the wall and the wall itself. For pure polymer melts, the mechanism of slip is referred as “true slip”. In concentrated suspension, however, true slip might not occur, but rather an “apparent slip” caused by a region of high velocity gradient adjacent to the wall [Soltani and Yilmazer, 1998; Kalyon, 2005]. According to Barnes (1995), slip occurs in the flow of a two-phase fluid because of the displacement of the dispersed phase away from the solid boundary. This results in a very narrow layer, with a typical thickness of 0.1-10 μm , which is enriched with the low viscosity phase. This layer becomes thinner with increasing concentration of the disperse phase. Kalyon (2005) derived a formula to describe the slip velocity at the wall for a concentrated suspension in terms of a slip layer

model. However, his work did not include the effect of particle concentration explicitly. Following his work, the slip layer model was revised and the slip velocity at the wall with consideration of particle concentration was derived.

Due to symmetry, half of the velocity profile is shown in Figure 3.1. The flow in a capillary can be divided into two parts: slip layer ($R - \delta \leq r \leq R$) and bulk flow ($0 \leq r \leq R - \delta$).

Figure 3.1: The sketch of slip layer model

In this model, the velocity at the wall can be assumed to be zero, $u(R) = 0$. A high velocity gradient is formed in the slip layer. The thickness of this layer δ may be determined by assuming a fully developed, two-phase flow in a capillary, with an incompressible slip layer consisting of pure polymer flowing under isothermal, laminar conditions next to the capillary wall.

The velocity in their interface is u_δ at a distance δ from the die wall. In this model, u_s is the velocity calculated by extrapolation u_δ at δ to the wall on the basis of assuming a constant shear rate within the slip layer.

Based on these assumptions of isothermal, incompressible and laminar flow, the relationship between the slip velocity and the wall shear stress can be obtained.

Firstly, in the slip layer ($R - \delta \leq r \leq R$), the momentum equation (3.9) can be simplified as:

$$\frac{1}{r} \frac{\partial}{\partial r}(r\tau) = \frac{\partial P}{\partial z} \quad (3.80)$$

By integration of equation (3.80), the following expression is obtained:

$$r\tau = \frac{1}{2} \frac{\partial P}{\partial z} r^2 + H_1 \quad (3.81)$$

Due to high shear rate occurs near the region of the wall, a power-law model can be employed for the viscosity in the slip layer, which is assumed to consist only of a pure polymeric system, then:

$$\tau = M \left(\frac{\partial u_z}{\partial r} \right)^n = (\eta_0 \dot{\gamma}_0^{1-n}) \left(\frac{\partial u_z}{\partial r} \right)^n \quad (3.82)$$

where $M = \eta_0 \dot{\gamma}_0^{1-n}$ is flow consistency.

Introducing equation (3.82) into equation (3.81), the following expression is obtained:

$$rM \left(\frac{\partial u_z}{\partial r} \right)^n = \frac{1}{2} \Lambda_z r^2 + H_1 \quad (3.83)$$

And shear stress at any point is given by:

$$\tau = \frac{1}{2} \Lambda_z r \quad (3.84)$$

Thus at the position of $R - \delta$, the shear stress is:

$$\tau|_{r=R-\delta} = \frac{\Lambda_z (R - \delta)}{2} \quad (3.85)$$

Substituting equation (3.85) into equation (3.83), the constant H_1 can be determined to be zero. Thus, equation (3.83) is simplified into:

$$\left(\frac{\partial u_z}{\partial r} \right)^n = \frac{\Lambda_z r}{2M} \quad (3.86)$$

The flow velocity can be obtained by integration:

$$u_z(r) = \left(\frac{\Lambda_z}{2M} \right)^{\frac{1}{n}} \int r^{\frac{1}{n}} dr + H_2 = \left(\frac{\Lambda_z}{2M} \right)^{\frac{1}{n}} \frac{n}{n+1} r^{\frac{1}{n}+1} + H_2 \quad (3.87)$$

The value of H_2 can be determined by enforcing the boundary condition $u(R) = 0$.

The flow velocity is thus given as:

$$u_z(r) = \left(\frac{\Lambda_z}{2M} \right)^{\frac{1}{n}} \frac{n}{n+1} \left(r^{\frac{1}{n}+1} - R^{\frac{1}{n}+1} \right) \quad (3.88)$$

Therefore,

$$u_\delta = u_z(R - \delta) = \left(\frac{\Lambda_z}{2M} \right)^{\frac{1}{n}} \frac{n}{n+1} \left((R - \delta)^{\frac{1}{n}+1} - R^{\frac{1}{n}+1} \right) \quad (3.89)$$

For the bulk flow at $(0 \leq r \leq R - \delta)$, equation (3.83) is modified due to the addition of particles as:

$$rM \left(1 - \frac{\phi}{\phi_c} \right)^{-m} \left(\frac{\partial u_z}{\partial r} \right)^n = \frac{1}{2} \frac{\partial P}{\partial z} r^2 + H_3 \quad (3.90)$$

As the flow is symmetrical about the central axis:

$$\frac{\partial u_z}{\partial r} = 0 \quad \text{at } r = 0 \quad (3.91)$$

Enforcing this boundary condition in equation (3.90), H_3 is determined to be zero.

Thus the shear rate in equation (3.90) can be written as:

$$\left(\frac{\partial u_z}{\partial r} \right)^n = \frac{\Lambda_z r}{2M \left(1 - \frac{\phi}{\phi_c} \right)^{-m}} \quad (3.92)$$

The flow velocity is obtained by integration as:

$$u_z(r) = \left(\frac{\Lambda_z}{2M} \right)^{\frac{1}{n}} \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}} \frac{n}{n+1} r^{\frac{1}{n}+1} + H_4 \quad (3.93)$$

At the interface between the two fluid regions, the flow velocity calculated from either of the regions should be the same. Combining equation (3.89) with equation (3.93), H_4 can be determined, thus the flow velocity in the bulk region is expressed as:

$$u_z(r) = \left(\frac{\Lambda_z}{2M} \right)^{\frac{1}{n}} \frac{n}{n+1} \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}} \left\{ r^{\frac{1}{n}+1} - (R-\delta)^{\frac{1}{n}+1} \left[1 - \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}} \right] \right\} \quad (3.94)$$

The velocity difference $u_\Delta (=u_\delta - u_s)$, as shown in Figure 3.1, can be determined by assuming that the shear rate in the slip layer is constant.

$$u_\Delta = \left(\frac{\Lambda_z (R-\delta)}{2M \left(1 - \frac{\phi}{\phi_c} \right)^{-m}} \right)^{\frac{1}{n}} \delta \quad (3.95)$$

The interpolated slip velocity u_s can be calculated as:

$$u_s = u_\delta - u_\Delta \quad (3.96)$$

Introducing equations (3.89) and (3.95), the slip velocity is obtained:

$$u_s = \frac{R \left\{ \frac{n}{n+1} \left(\left(1 - \frac{\delta}{R} \right)^{\frac{1}{n}+1} - 1 \right) - \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}} \left(1 - \frac{\delta}{R} \right)^{\frac{1}{n}} \frac{\delta}{R} \right\}}{M^{\frac{1}{n}}} \tau_w^{\frac{1}{n}} = \beta_s \tau_w^{\frac{1}{n}} \quad (3.97)$$

where the slip coefficient β_s equals to:

$$\beta_s = \frac{R \left\{ \frac{n}{n+1} \left(\left(1 - \frac{\delta}{R} \right)^{\frac{1}{n}+1} - 1 \right) - \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}} \left(1 - \frac{\delta}{R} \right)^{\frac{1}{n}} \frac{\delta}{R} \right\}}{M^{\frac{1}{n}}} \quad (3.98)$$

As the thickness of the slip layer is much smaller than the radius of the capillary

die, $\left(1 - \frac{\delta}{R}\right)^{\frac{1}{n}} \approx 1 - \frac{\delta}{R} \frac{1}{n}$, $1 - \left(\frac{\delta}{R}\right)^2 \frac{1}{n} \approx 1$, then the slip coefficient can be simplified to:

$$\beta_s = \frac{\delta}{M^{\frac{1}{n}}} \left[1 - \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}} \right] \quad (3.99)$$

With an increase of particle concentration, the slip coefficient β_s increases. At the two extrema, i.e. at zero particle concentration β_s vanishes and at particle concentration approaching to critical loading ϕ_c , β_s is at its maximum value:

$$\beta_{s\max} = \delta M^{\frac{1}{n}} \quad (3.100)$$

The above expression is identical to that previously obtained by Kalyon (2005). The thickness of the slip layer with consideration of particle concentration is expressed as:

$$\delta = \frac{\beta_s M^{\frac{1}{n}}}{1 - \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}}} \quad (3.101)$$

It should be noted here that for a non-Newtonian fluid, the thickness of the slip layer has a non-linear relationship with particle concentration. With increasing particle concentration, the thickness of the slip layer decreases.

Referring to the slip layer model in Figure 3.1, the slip length b can be calculated as:

$$b = \frac{u_s}{\dot{\gamma}} \approx \delta \left[1 - \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}} \right] \quad (3.102)$$

The slip length can be further simplified to:

$$b = \beta_s M^{\frac{1}{n}} \quad (3.103)$$

Thus, the slip length shows a linear relationship to the slip coefficient and increases with increasing slip coefficient and vice versa.

In the slip layer model, the flow rate can be calculated by introducing equations (3.88) and (3.94):

$$\begin{aligned} Q &= 2\pi \int_0^R u_z(r) r dr = 2\pi \left[\int_0^{R-\delta} u_z(r) r dr + \int_{R-\delta}^{\delta} u_z(r) r dr \right] \\ &= \pi R^3 \frac{2n}{n+1} \left(\frac{\Lambda_z R}{2M} \right)^{\frac{1}{n}} \left\{ \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}} \left[\frac{n}{1+3n} \left(1 - \frac{\delta}{R} \right)^{\frac{1}{n}+3} - \frac{\left(1 - \frac{\delta}{R} \right)^{\frac{1}{n}+3}}{2} \left[1 - \left(1 - \frac{\phi}{\phi_c} \right)^{\frac{m}{n}} \right] \right] \right. \\ &\quad \left. + \frac{n}{1+3n} \left[1 - \left(1 - \frac{\delta}{R} \right)^{\frac{1}{n}+3} \right] - \frac{1}{2} \left[1 - \left(1 - \frac{\delta}{R} \right)^2 \right] \right\} \quad (3.104) \end{aligned}$$

3.7 NUMERICAL MODELING

Based on Phillips et al. (1992), Lam and Chen [Lam et al., 2002; Chen et al., 2003] extended the particle diffusive model to solve the flow pattern of non-Newtonian concentrated suspensions in capillary flows. This extended model is further improved to take into consideration the interactions between particle migration, wall slip and viscous heating, which were solved by a numerical method. A finite difference numerical scheme in terms of control volume has been implemented, as described in [Lam et al., 2002; Chen et al., 2003]. This approach is adopted since

the resulting formulation lends itself to mass conservation as governed by equation (3.52). More discussions of the formulation will be given in the following sections.

3.7.1 Grid Systems

Due to the high nonlinear characteristic of the flow, energy and mass transfer equations, finite-volume method was employed [Patanker, 1980] to solve these equations.

A grid system is constructed in the radial and flow directions, see Figure 3.2. The subscripts i and j are used to specify the positions of the grid points, with i serving as an index in the axial (i.e. flow) direction and j in the radial direction. The constant axial and radial spacing are Δz and Δr respectively. The grid is divided into N_R divisions in the radial direction and N_Z divisions in the axial direction.

Figure 3.2: Rectangular grid used in the finite difference analysis

3.7.2 Pressure

For a concentrated suspension in a capillary flow with a slip boundary condition, the pressure gradient Λ_z^i at node i is calculated:

$$\Lambda_z^i = \frac{Q_i - Q_s^i}{\pi S_i} \quad (i = 1, \dots, N_z) \quad (3.105)$$

Introducing Krieger model and the modified Cross model for a polymeric system into equation (3.15), the shear rate equation derived from equation (3.14) can be obtained as:

$$\left(\frac{\dot{\gamma}}{\dot{\gamma}_0} \right) - \frac{\Lambda_z^i r}{2\tau^*} \left(1 - \frac{\phi}{\phi_c} \right)^m \left[1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_0} \right)^{1-n} \right] = 0 \quad (3.106)$$

This equation can be discretized as:

$$\left(\frac{\dot{\gamma}_{i,j}}{\dot{\gamma}_0} \right) - \frac{\Lambda_z^i r_{i,j}}{2\tau^*} \left(1 - \frac{\phi}{\phi_c} \right)^m \left\{ \left(\frac{\dot{\gamma}_{i,j}}{\dot{\gamma}_0} \right)^{1-n} + 1 \right\} = 0 \quad (j = 1, \dots, N_R - 1) \quad (3.107)$$

Equation (3.105) is a strong nonlinear system of equations for pressure gradient field and thus requires an under-relaxation iteration procedure to obtain a convergent numerical solution. The pressure gradient Λ_z^i at node i is solved with an iteration procedure. Firstly, the initial value of Λ_z^i is calculated with an initial value of flow conductivity S_i . Subsequently, shear rate $\dot{\gamma}_{i,j}$ at node i can be determined by solving equation (3.106). Then, S_i is updated using equation (3.18). A more accurate Λ_z^i at node i is solved again by equation (3.105). The pressure gradient Λ_z^i is iterated using the above procedures until a converged solution is obtained.

Provided that the pressure gradient and the radial particle concentration at a position along the flow direction are known, the velocity in this position can be obtained:

$$u_{i,j} = u_{i,N_R} + \frac{\Lambda_z^i}{2} \sum_{j=0}^{N_R} \omega_j \frac{r_{i,j}}{\eta_{i,j}} \Delta r \quad (3.108)$$

where $\omega_j = 1/2$ for $j = 1$ or $j = N_R$ and 1 otherwise (i.e. trapezoidal quadrature).

3.7.3 Temperature

In the present formulation, the temperature has to be first determined such that the flow conductivity, S , in equation (3.48) can be calculated and subsequently for solving the pressure field. Further discretization is made in the radial direction to store the temperature profile, as shown in Figure 3.2. The thermal convection $u_z \partial T / \partial z$ in energy equation (3.21) at node (i, j) is given as:

$$u_z \frac{\partial T}{\partial z} = \frac{T_{i,j} u_{i,j} - T_{i-1,j} u_{i-1,j}}{\Delta z} \quad (3.109)$$

Then the heat conduction in energy equation (3.21) at node (i, j) is calculated as:

$$\frac{1}{r} \frac{\partial}{\partial r} (Kr \frac{\partial T}{\partial r}) = \frac{2}{2j+1} \frac{(j+1)K_{i,j+1}T_{i,j+1} - [(j+1)K_{i,j+1} + jK_{i,j}]T_{i,j} + (j-1)K_{i,j-1}T_{i,j-1}}{\Delta r^2} \quad (3.110)$$

The viscous heating term in the energy equation is obtained by:

$$\eta \dot{\gamma}^2 = \frac{\Lambda_z^2 r_{i,j}^2}{4\eta_{i,j}} \quad (3.111)$$

Based on the above, one can write the energy equation at a node in a matrix form,

$$[K]_i \{T\}_i = \{F\}_i \quad (3.112)$$

The nodal equations can then be assembled to create a stiffness matrix and force vector to be solved for the temperature.

3.7.4 Particle Concentration

The diffusive flux equation (3.52) is a partial differential equation involving the development of particle concentration with respect to both time and the radial coordinate. However, for a typical flow in a capillary rheometer, steady state would have reached in a short time duration. Therefore, the transient term in the

conservation equation can be neglected. The finite difference numerical method with a semi-implicit (Crank-Nicholson) scheme with attractive conservative properties based on control volume is an appropriate and suitable technique for solving the conservation equation. Equation (3.52) based on control volume can be written as:

$$\int_{CV} \frac{\partial(u_z \phi)}{\partial z} dV = a^2 \int_{CV} \frac{1}{r} \psi dV \quad (3.113)$$

where

$$\psi = \frac{\partial}{\partial r} \left[rk'_c \dot{\gamma} \phi^2 \left(\frac{\partial \phi}{\partial r} + \frac{\phi}{\dot{\gamma}} \frac{\partial \dot{\gamma}}{\partial r} \right) \right] + \frac{\partial}{\partial r} \left(\frac{rk_\eta \dot{\gamma} \phi^2 m}{\phi_c - \phi} \frac{\partial \phi}{\partial r} \right) + \frac{\partial}{\partial r} \left(\frac{rk_\eta \phi^2 \dot{\gamma}}{T_0} \frac{\partial T}{\partial r} \right) \quad (3.114)$$

The conservative finite difference approximation of node (i, j) for equation (3.113)

is given as:

$$\begin{aligned} & \left[\mathcal{G}(M_{j+1} + M_j) \right] \phi_{i,j+1}^{t+1} + \left[\mathcal{G}(M_{j+1} + 2M_j + M_{j-1}) + \frac{2\Delta r^2}{\Delta z a^2} j u_{i,j} \right] \phi_{i,j}^{t+1} \\ & + \left[\mathcal{G}(M_{j-1} + M_j) \right] \phi_{i,j-1}^{t+1} \\ & = \frac{2\Delta r^2}{\Delta z a^2} j \phi_{i-1,j}^t u_{i,j} (1 - \mathcal{G}) + \left(\frac{1 - \mathcal{G}}{\Delta z} \right) (M_{j-1} + M_{j+1} - 2M_j) + F_{i,j} \end{aligned} \quad (3.115)$$

Where

$$M_{j+1} = (j+1) \left(k'_c (\phi_{i,j+1}^t)^2 + \frac{mk_\eta (\phi_{i,j+1}^t)^2}{\phi_c - \phi_{i,j+1}^t} \right) \dot{\gamma}_{i,j+1} \quad (3.115a)$$

$$M_j = j \left(k'_c (\phi_{i,j}^t)^2 + \frac{mK_\eta (\phi_{i,j}^t)^2}{\phi_c - \phi_{i,j}^t} \right) \dot{\gamma}_{i,j} \quad (3.115b)$$

$$M_{j-1} = (j-1) \left(k'_c (\phi_{i,j-1}^t)^2 + \frac{mK_\eta (\phi_{i,j-1}^t)^2}{\phi_c - \phi_{i,j-1}^t} \right) \dot{\gamma}_{i,j-1} \quad (3.115c)$$

$$\begin{aligned}
F_{i,j} = & \frac{k'_c \pi}{\Delta r} \left\{ \left[(j+1)(\phi'_{i,j+1})^2 + j(\phi'_{i,j})^2 \right] \dot{\gamma}_{i,j+1} + \left[(j-1)(\phi'_{i,j-1})^2 + j(\phi'_{i,j})^2 \right] \dot{\gamma}_{i,j-1} \right. \\
& - \left. \left[(j+1)(\phi'_{i,j+1})^2 + 2j(\phi'_{i,j})^2 + (j-1)(\phi'_{i,j-1})^2 \right] \dot{\gamma}_{i,j} \right\} \\
& + \frac{K_\eta \pi}{T_0} \left\{ \left[(j+1)(\phi'_{i,j+1})^2 \dot{\gamma}_{i,j+1} + j(\phi'_{i,j})^2 \dot{\gamma}_{i,j} \right] T_{i,j+1} \right. \\
& + \left. \left[(j-1)(\phi'_{i,j-1})^2 \dot{\gamma}_{i,j-1} + j(\phi'_{i,j})^2 \dot{\gamma}_{i,j} \right] T_{i,j-1} \right. \\
& - \left. \left[(j+1)(\phi'_{i,j+1})^2 \dot{\gamma}_{i,j+1} + 2j(\phi'_{i,j})^2 \dot{\gamma}_{i,j} + (j-1)(\phi'_{i,j-1})^2 \dot{\gamma}_{i,j-1} \right] T_{i,j} \right\} \quad (3.115d)
\end{aligned}$$

if $\mathcal{G} = 1/2$, it is the Crank-Nicholson scheme. This means that concentration value at t th iteration and $(t+1)$ th iteration are equally weighted. The system of algebraic equations for equation (3.115) is a tridiagonal-matrix, which was solved by Thomas algorithm [Patanker, 1980].

3.7.5 Boundary Conditions

The boundary conditions for velocity are:

$$u_{i,2} = u_{i,1} \text{ at } r = 0 \quad (i = 1, \dots, N_z) \quad (3.116)$$

$$u_{i,N_R} = u_s \text{ at } r = R \quad (i = 1, \dots, N_z) \quad (3.117)$$

For temperature, the boundary conditions employed are:

$$T_{i,2} = T_{i,1} \text{ at } r = 0 \quad (i = 1, \dots, N_z) \quad (3.118)$$

$$T_{1,j} = T \text{ at } z = 0 \quad (j = 1, \dots, N_R) \quad (3.119)$$

(a) Constant wall temperature:

$$T_{i,N_R} = T_w \text{ at } r = R \quad (i = 1, \dots, N_z) \quad (3.120)$$

(b) Adiabatic wall:

$$T_{i,N_R} = T_{i,N_R-1} \text{ at } r = R \quad (i = 1, \dots, N_z) \quad (3.121)$$

The analysis of particle migration was based on the assumption of no particle flux through the wall:

$$\left\{ k'_c \phi^2 \nabla \left(\phi \frac{\partial v_z}{\partial r} \right) + k_\eta \phi^2 \frac{\partial v_z}{\partial r} \frac{\nabla \eta}{\eta} \right\} \cdot n = 0 \quad (3.122)$$

The resulting first order nonlinear equation derived from equation (3.122) with respect to no particle penetration at the wall is obtained as:

$$\frac{\dot{\gamma} \phi}{\dot{\gamma}_w \phi_w} \frac{1}{\phi_c} = \left(\frac{1 - \frac{\phi}{\phi_c}}{1 - \frac{\phi_w}{\phi_c}} \right)^{mk_\eta / (k'_c \phi)} \quad (3.123)$$

where ϕ_w and $\dot{\gamma}_w$ are the values of ϕ and $\dot{\gamma}$ at the tube wall. The discretized form of equation (3.123) is given as:

$$\frac{\dot{\gamma}_{i,N_R-1} \phi_{i,N_R-1}}{\dot{\gamma}_{i,N_R} \phi_w} \frac{1}{\phi_c} = \left(\frac{\phi_c - \phi_{i,N_R-1}}{\phi_c - \phi_w} \right)^{mk_\eta / (k'_c \phi_{i,N-1})} \quad (i = 1, \dots, N_Z) \quad (3.124)$$

The discretized equation (3.124) for particle concentration at the wall (ϕ_w) is a nonlinear equation, which can be solved by interval halving method [Carnahan et al., 1969]. The control accuracy defined as the final solution accuracy of the interval halving method for the solution is 0.0001. The error in the estimate of the solution must be less than $[2^{-N} \phi_c]$, where N is the number of the iterations performed.

In addition, the particle concentration ϕ is assumed to be uniform initially at the entrance of the tube and can be expressed as: $\phi = \phi_0$, when $0 \leq r \leq R$, at $z = 0$.

3.7.6 Numerical Procedures

The system of equations (3.21), (3.61), (3.105) and (3.106) differs in two aspects from those applied typically in pure fluids. The diffusion coefficients in equation (3.61) depend not only on the scalar ϕ but also on the effective shear rate $\dot{\gamma} = \partial u_z / \partial r$. The term on the right hand side of equation (3.61) involves third-order derivatives of the flow velocity. As seen from equations (3.44) and (3.52a-52c), the viscosity and the diffusion coefficients are all highly non-linear functions of ϕ . To numerically solve this coupled system of non-linear equations, the following steps were employed:

1. Initialize the particle concentration and temperature profile at the entrance.
2. Calculate iteratively flow conductivity and velocity across the tube according to equations (3.48) and (3.15) respectively by assuming a pressure gradient until the specified flow rate at the entrance is reached.
3. The pressure gradient (Λ_z) and wall slip velocity (u_s) is solved in an iterative manner based on the adjustment of the values of particle concentration at the wall. The values of particle concentration at the wall are determined implicitly by imposing the condition that the flow average concentration at any cross section is equal to the initial concentration ϕ_0 , i.e.

$$\phi_0 = \frac{\int_0^R \phi r dr}{\int_0^R r dr} \quad (3.125)$$

To accelerate the convergence of the solution, the initial values of particle concentration at the wall can be determined by the evaluation of the no-flux condition as stated by equation (3.122).

4. Conservative finite difference scheme in space is employed to solve particle concentration and temperature. Subsequently, the viscosity, shear rate, velocity distribution and flow conductivity at every finite difference grid are calculated.

The program was written in Visual C++, run on the computer Intel Pentium 4 with CPU 1.60GHz and 512M RAM. The computational time depends on the grid size, and the ease of convergence. Typically it ranged from several minutes to several hours. The main convergence criteria applied are:

1) the relative ratio of flow rate, $\left| \frac{Q_0 - Q_c}{Q_0} \right| < 1.0e^{-3}$, where Q_0 is the specified flow rate and Q_c is the calculated flow rate;

2) the relative ratio of particle concentration, $\left| \frac{\phi_0 - \bar{\phi}}{\phi_0} \right| < 1.0e^{-3}$, where ϕ_0 is the initial particle concentration and $\bar{\phi}$ is the averaged particle concentration of a cross section.

Simulations were performed to test the convergence of the numerical procedure in terms of the various grid sizes, which are 40×160 , 80×320 , 160×640 , and 320×1280 (in the radial and flow directions respectively). As there was little

difference (less than 2%) in the relative error (defined as $\varepsilon_r = \left| \frac{P_{Pre} - P_{Exp}}{P_{Exp}} \right| \times 100\%$)

beyond a grid of 80×320 , the grid of 80×320 was used for all subsequent calculations.

The reason for a small grid size in the radial direction is to avoid discretization error mathematically at region where there are rapid changes of particle concentration, especially at the region near the wall with high gradient in the particle concentration. With the grid size in the radial direction smaller than the

particle size, the assumption of continuity may not be strictly correct over a single particle. However, the average response of the particles could still satisfy the assumption of continuity, both spatially and temporally due to a distribution of particles. Thus, the predictions of the overall responses of the system, such as pressure, velocity and particle concentration distribution could be described “on the average” (including time averaging) by equations based on the continuity assumption. Indeed, this approach has been employed by other researchers as well [Subia et al., 1998]. Of course, the model will not be able to describe the values of parameters of interest at any specific time over any specific point in the order of a particle diameter.

In the calculations, the values of ϕ at the wall and the pressure gradient Λ_z are solved iteratively until the boundary conditions and imposed volumetric flow rate are satisfied. For the case of pressure dependent slip velocity, the calculations started at the exit of the flow and stepped backwards.

3.8 SUMMARY

The theoretical basis, which includes the flow equations, the energy and mass conservation equations and the constitutive equations, are introduced for describing particle migration, wall slip and viscous heating in capillary flows. These effects are coupled and should be considered simultaneously.

The modified diffusive flux model was used in this study as it can predict accurately particle migration in rectilinear flows where the normal stress differences are not important for a generalized-Newtonian concentrated suspension with and without consideration of viscous heating effect in a capillary flow. The empirical parameter k_c in the modified diffusive flux model (which was constant

in Phillips' original diffusive flux model), is proposed as a linear function of the particle concentration ϕ due to multi-body interactions between particles and the non-Newtonian effect i.e. shear thinning.

For wall slip, the slip velocity model and the slip layer model for concentrated suspension were presented. Based on the assumption of fluid slip on the wall, the slip-corrected wall shear rate and slip velocity were established. The analysis indicated that for a non-Newtonian fluid, it is problematic to calculate the slip velocity directly from the gradient in a Mooney plot as the slip velocity is nonlinear to the wall shear stress. The gradient in a Mooney plot of a non-Newtonian fluid equals to the slip velocity multiplied by an explicit coefficient of $4n(k+3)/(3n+1)$, which takes into account the non-Newtonian effect (parameter n) and the nonlinearity between wall shear stress and slip velocity (parameter k). In the slip layer model, the formulas of the slip layer thickness and slip length were spelt out, which are compatible to the slip velocity model.

Furthermore, the improved numerical model based on the particle diffusive model of Lam and Chen [Lam et al., 2002; Chen et al., 2003] was introduced. The detailed discretized equations for the temperature field, pressure and particle concentration were presented. Due to the high nonlinear characteristic, the finite-volume method was employed to solve the flow equations, energy and mass transfer equations.

CHAPTER 4 EXPERIMENTAL PROCEDURES AND RESULTS

4.1 INTRODUCTION

This chapter describes the materials, the processing procedure and the analytical methods employed in the experiments. Capillary rheometer with different dies was used to characterize the diffusive coefficients in the proposed models for particle migration and wall slip. Experiments were conducted on pure polymer and concentrated suspensions with particles in different size ranges under different volume flow rates and different temperatures.

4.2 MATERIALS

4.2.1 Ethylene Vinyl Acetate

Ethylene vinyl acetate (EVA) is a copolymer of ethylene and vinyl acetate. The two key parameters for EVA copolymers are the percent vinyl acetate (VA) and melt index (MI). As the percent VA increases, the VA disrupts the polyethylene (PE) crystallinity. This is reflected in lower melting and freezing points along with a lower heat of fusion (energy needed to change from solid to liquid). The polymer investigated is EVA 460, manufactured by DUPONT under the trade name ELVAX. EVA 460 contains 18% VA by weight. It has a density of 941 kg/m^3 at 23°C , and is opaque in colour. The structure of EVA is shown in Figure 4.1.

Figure 4.1: Molecular structure of EVA

4.2.2 Glass Microspheres

The model particles employed is glass microspheres, manufactured by MO-SCI Corporation. The sodalime glass contains more than 60% silicon, light green in colour, with a minimum of 90% true spheres in the specified size range. Three different particle sizes, with size in the range of 1-15 μm , 53-63 μm , 106-125 μm respectively, were investigated. Figure 4.2 shows a typical micrograph of glass powder taken by SEM.

Figure 4.2: Glass powder with more than 90% spheres

4.3 EXPERIMENTAL PROCEDURE

The experimental procedure, including equipment and materials, is summarized in the flow chart in Figure 4.3.

Figure 4.3: Flow chart of experimental procedure

From the perspective of materials, the experiments can be divided into two groups: pure EVA460 and concentrated suspensions. For pure EVA460, thermal analysis and capillary experiments were conducted. For concentrated suspension, capillary experiments and yield stress measurements were conducted.

For Göttfert capillary rheometer, its temperature and pressure values should be calibrated. It is essential that the calibration procedure for pressure transducer is carried out when the test channel is empty and the test temperature is reached. The accuracy for both temperature and pressure are within ± 0.01 °C and ± 0.01 bar, respectively.

The concentrated suspension was prepared by mixing glass microspheres with EVA460 with different particle concentrations in a Haake Rheomix600 mixer. The mixing torque-time curve from the mixer can be used to check the level of homogeneity of mixing, see Figure 4.4. The torque increases as binder and powder are added and then decreases gradually. As the mixing progresses, the torque stabilizes gradually. The feedstock is regarded as homogeneous after the torque value remains stable for about 10 minutes. This is a widely accepted technique. The homogeneity of feedstock is imperative in ensuring the validity of subsequent experiments.

To check the effects of particle concentration and particle size, EVA460 was mixed with glass microspheres with different particle sizes in different particle volume fractions.

As pure polymer melt has different experimental conditions from those of concentrated suspensions, polymer EVA460 will be introduced firstly, followed by the results of concentrated suspensions. Both require the determination of entrance and exit losses.

Figure 4.4: Mixing curve of glass particles and EVA460

4.4 EXPERIMENTS ON POLYMER EVA460

4.4.1 Thermal Analysis

The pyrolysis behaviour of the polymer was tested by Thermogravimetric Analysis (TGA) experiments. The objective of TGA is to provide information for setting suitable mixing temperature for the preparation of concentrated suspension to ensure no degradation in the polymer matrix, which could affect the outcome of rheological experiments.

The weight change of the sample was monitored as a function of time or temperature, while it was subjected to a controlled temperature profile (heating, cooling or isothermal holding) in a controlled atmosphere. Degradation could be detected through weight loss during heating. The melting temperature of EVA460 is 88 °C. There are two compositions in the copolymer EVA460: ethylene and vinyl acetate, and their degradation temperatures are different, see Figure 4.5.

Ethylene starts degradation around 340.90 °C, followed by Vinyl Acetate at 453.54 °C. These are much higher than the processing temperature (ranged from 160 °C to 220 °C) and thus no degradation would occur during processing.

Figure 4.5: TGA curve of EVA 460

4.4.2 Viscosity Measurements and Results

Experiments on pure EVA460 were summarized in Figure 4.6. To obtain the true viscosity of polymer EVA, entrance and exit losses are to be determined. In addition, the non-Newtonian nature of EVA460 should be corrected by Rabinowitsch correction. This will allow the true viscosity and true wall shear stress to be calculated. Subsequently, the material constants in the viscosity model for the polymer could then be deduced.

Experiments were conducted at three different temperatures (170 °C, 180 °C and 190 °C) at different flow rates.

Figure 4.6: Experiments of EVA460 on capillary Rheograph6000

(a) Entrance and exit losses

Two methods are commonly employed for the determination of entrance and exit losses (ΔP_e), for flow into a capillary from a larger reservoir in a melt rheometer: direct measurement using an orifice and extrapolation of data by Bagley plot. Both these methods were attempted and compared.

Bagley correction was first conducted on EVA460 with dies of 1mm diameter with five different flow lengths ($L=5, 10, 20, 30, 40$ mm). Figure 4.7 shows the Bagley plot of pure EVA460 at 180 °C. The experiments were repeated three times at same conditions. The error bars indicate that the repeatability of the measurements was good, with less than 4% difference between experiments.

Figure 4.7: Bagley plot of pure EVA460 at 180 °C
(Q: cm³/s)

The curves in Figure 4.7 show good linearity, indicating that viscous heating and pressure-dependent viscosity were negligible. Thus, entrance and exit losses can be determined against different flow rates based on a linear relationship. Bagley correction was employed to calculate the wall shear stress [Bagley, 1957]:

$$\tau_w = \frac{\Delta P - \Delta P_e}{2L/R} \quad (4.1)$$

The entrance and exit losses were also measured by an orifice die with diameter 1mm and die length 0.5 mm. Measured ΔP_e were compared with the results by Bagley correction, see Figure 4.8. It can be observed that the values obtained by the orifice die were around 30% higher than those by Bagley correction. The difference may be due to the flow stuck in the expansion region of the orifice die.

Kelly et al. (1996) found that if the land, L , is not longer than 0.5 mm, it has little effect on the experimental result. In addition, Kim and Dealy (2001) pointed out that the exit shape of an orifice die is an important factor as it influences the flow of the extruded melt. If the melt is stuck in the expansion region, the measured data would be higher than those for smooth flow.

Figure 4.8: Entrance and exit losses measured by orifice die compared with Bagley correction results at 180 °C

Figure 4.9: The sketch of capillary orifice die

The geometry of the employed orifice die was shown in Figure 4.9. With this geometry, the extruded melt can stick to the wall easily as it has not enough time to

cool down. Due to this complication, it was decided that the results obtained by the orifice die were not reliable and were discarded. All entrance and exit losses would be determined by Bagley correction.

(b) Rabinowitsch correction

Rabinowitsch correction can be applied to account for the non-Newtonian nature of the fluid. Wall shear stress values were first plotted against the corresponding values of the apparent shear rate, see Figure 4.10.

Figure 4.10: Wall shear stress against apparent shear rate of polymer EVA460

From the figure, the gradient of $\log(\tau_w)/\log(\dot{\gamma}_{aw})$ can be determined. Subsequently, the true shear rate at the wall for a non-Newtonian fluid could be obtained as [Macosko, 1994]:

$$\dot{\gamma}_w = \dot{\gamma}_{aw} \left[\frac{3}{4} + \frac{1}{4} \frac{d \log(\dot{\gamma}_{aw})}{d \log(\tau_w)} \right] \quad (4.2)$$

After obtaining the wall shear stress, τ_w , and true shear rate, $\dot{\gamma}_w$, the true viscosity of polymer EVA460 can be calculated by:

$$\eta_b = \tau_w / \dot{\gamma}_w \quad (4.3)$$

(c) Viscosity of EVA460 and material constants

To determine the effects of temperature and shear rate on the viscosity of pure polymer, experiments were conducted at three different temperatures (170 °C, 180 °C, 190 °C) with shear rate in the range of 10-5000 s⁻¹. Figure 4.11 shows that the viscosities of EVA460 decrease with increasing temperature with shear-thinning effect.

Figure 4.11: Viscosities of pure EVA460 and fitted modified Cross model at different temperatures

Two viscosity models can be used to fit the experimental data: Power-law model and modified Cross model:

$$\eta_b = m_0 \exp(T_a / T) \dot{\gamma}^{n-1} \quad (\text{Power-law model}) \quad (4.4)$$

$$\eta_b = \frac{\eta_0}{1 + (\eta_0 \dot{\gamma} / \tau^*)^{1-n}} \quad (\text{modified Cross model}) \quad (4.5)$$

The constants in both models were obtained by data fitting on the experimental results and are listed in Table 4.1 and Table 4.2. The fitted modified Cross model is shown in Figure 4.11.

Table 4.1: Material constants of EVA460 in power-law model

m_0 (Pa.s)	24.5
T_a (K)	2780
n	0.38

Table 4.2: Material constants of EVA460 in modified Cross model

B (Pa.s)	1.14×10^{-2}
n	0.38
T_b (K)	5980
τ^* (Pa)	19860

The standard errors of viscosities fitted by power-law model and modified Cross model with experimental results are 0.44 Pa.s and 0.18 Pa.s, respectively. Therefore, modified Cross model can provide higher accuracy than the power-law model.

4.4.3 Slip Velocity Measurement

The slip mechanism of pure polymer is expected to be different from that of concentrated suspension. The slip velocity of pure EVA was measured by a capillary rheometer. The slip contribution by the polymer phase should also be

considered in the investigation of slip of concentrated suspension if the slip of the polymer phase is significant.

(a) Capillary dies

As slip behaviour is related to the die material, the dies used in the measurements should all be the same material with the same surface finish. In addition, although only two different diameters are necessary to determine the slip velocities, to provide added confidence in the data, at least three different diameters should be employed.

In the selection of die diameters, a broader range of diameters would reduce the uncertainties in the analysis. Unfortunately, too small a diameter will require excessive pressure; too large a diameter will require excessive flow rate. The diameter range is thus limited by these conflicting factors. For the present investigation, diameters in the range of 0.5 mm to 2 mm were selected.

(b) Procedure to determine slip velocity

Entrance and exit losses are function of the contraction ratio [Rides and Allen, 1996]. Therefore, for the dies used for Mooney correction, entrance and exit losses were determined for each die diameter. Thus, the slip velocity is calculated with the following procedure:

1. Measure the apparent wall shear stress, τ_{aw} , against the apparent shear rate, $\dot{\gamma}_{aw}$, at different flow rates using each set of dies with the same diameter but different die lengths to determine the entrance and exit losses;
2. Calculate the true wall shear stress at each apparent shear rate for a die with selected ratio of L/R (die length/die radius), yielding one flow curve for the die;

3. Repeat step 2 for the other dies with different diameters but with the same L/R;
4. Determine the apparent shear rate corresponding to the selected shear stress by interpolation for each die diameter;
5. Plot the (interpolated) apparent shear rate versus the reciprocal of the die radius for each selected shear stress, and determine the gradient of the linear plot;
6. Data fitting the parameters in the slip model and thus determine the slip velocity.

(c) Slip velocity

The shear stress-apparent shear rate for pure EVA is presented in Figure 4.12, the results are obtained by four die diameters (0.5 mm, 0.75 mm, 1 mm and 1.25 mm).

Figure 4.12: Shear stress vs. apparent shear rate for EVA460 measured by four dies at 180°C

The figure indicated that there is only a slight slip at higher shear rate, and the slip is negligible at low shear rate. The slip velocity determined by the modified Mooney method is shown in Figure 4.13, with a maximum value less than 5 mm/s

in the range of parameters investigated. The figure indicates that a power law function can be used to fit the curve of slip velocity against wall shear stress.

Figure 4.13: Slip velocity of pure EVA460 at 180 °C

4.5 YIELD STRESS OF CONCENTRATED SUSPENSION

For fluids with a yield stress, the lower limit of the integral in equation (3.65) should be modified to:

$$\frac{Q - \pi u_s R^2}{\pi R^3} = \frac{1}{\tau_w^3} \int_{\tau_y}^{\tau_w} \tau^2 f(\tau) d\tau \quad \tau_w \geq \tau_y \quad (4.6)$$

where τ_y is the yield stress.

In this study, yield stress was determined indirectly using a parallel-plate rheometer. The value of shear stress at zero shear rate was considered as the shear yield stress, which was obtained by extrapolation of the experimental shear stress-shear rate curve [Nguyen and Boger, 1992]. Figure 4.14 shows the shear stresses of concentrated suspensions with different particle concentrations (35%, 40%, 45%) with particle size in the range of 53-63 μm . The yield stresses can be estimated at the point of very low shear rate. As shown in this figure, the yield stresses so determined are sufficiently small to be neglected.

Particle size affects yield stress, and yield stress increases with a decrease in particle size [Zhou et al., 1999]. Therefore, for another group of concentrated suspension with particle size in the range of 106-125 μm , the yield stress can also negligible. However, it is recognized that for smaller particle size, yield stress could be important.

Figure 4.14: Shear stress vs. shear rate of concentrated suspensions with different particle concentrations at 180 °C

4.6 PRESSURE MEASUREMENTS OF CONCENTRATED SUSPENSIONS

Pressure measurements of concentrated suspensions were conducted at different flow conditions to investigate the effects of key parameters, which include particle concentration, particle size and temperature. A sketch showing the organization of the different experimental conditions is presented in Figure 4.15. The horizontal axis shows that six concentrations (10%, 20%, 30%, 35%, 40%, 45%) by volume and three particle sizes (1-15 μm , 53-63 μm , 106-25 μm) were investigated. The vertical axis indicates that four different temperatures (160 °C, 180 °C, 190 °C,

210 °C) were investigated. The condition at the intersection of the axes was the reference test condition, with test temperature at 180 °C, particle size within 53-63 μm , and particle concentration of 40%. The effect of each parameter was described in the following sections.

Figure 4.15: Sketch of experiment conditions on concentrated suspensions

4.6.1 Effect of Particle Concentration

Particle concentration has a crucial effect on the properties of concentrated suspension. Increasing powder concentration increases the fluid viscosity, resulting in increasing pressure required for a given flow rate.

Figure 4.16 shows that the pressure increases with increasing particle concentration and flow rate. The results were obtained using capillary die with die length of 20 mm and diameter of 1 mm. The error bars indicate that the repeatability of experimental data is good. Results obtained with other dies will be presented in the Bagley plot.

Figure 4.16: Pressures at different concentrations using die length 20 mm and diameter 1 mm at 180 °C

4.6.2 Effect of Flow Length

Assuming that there is no particle migration, wall slip and viscous heating, the pressure drop in a capillary is proportional to the flow length as [Bird et al., 1960]:

$$\Delta P = \frac{8\eta QL}{\pi R^4} \quad (4.7)$$

where η is the viscosity (Pa.s), Q is the flow rate (cm³/s), L is the flow length (cm), and R is the radius of the tube (cm).

However, if there exists particle migration or wall slip, there are complications.

Figures 4.17-19 show the pressures (with error bars) vs. flow rate with different die lengths for concentrated suspensions with $\phi = 35\%$, 40% and 45%, respectively.

The small error bars indicate good repeatability of the experiments.

The figures show that the longer the flow length, L , the larger the pressure drop.

The increase in pressure was not exactly directly proportional to the increase in die length due to entrance and exit losses, particle migration and wall slip.

Figure 4.17: Pressure measured with dies of 1 mm diameter but different die lengths for 35% particle concentration at 180 °C

Figure 4.18: Pressure measured with dies of 1 mm diameter but different die lengths for 40% particle concentration at 180 °C

Figure 4.19: Pressure measured with die of 1 mm diameter but different die lengths for 45% particle concentration at 180 °C

4.6.3 Effect of Particle Size

Figure 4.20 shows the variation of pressure with flow rate for suspension containing 40% glass spheres by volume but in different sizes (1-15 μm , 53-63 μm , 106-125 μm).

Figure 4.20: Pressures for same particle concentration 40% but particle size different at 180 °C with die length 20 mm and diameter 1 mm

Maintaining a constant particle volume in a suspension with different particle sizes of solid phase leads to the difference in the number of particles in the system. A higher number of smaller particles results in more particle-particle interactions and an increased resistance to flow, thus higher pressures are required.

4.6.4 Effect of Temperature

Figure 4.21 compares the pressures obtained with $\phi = 40\%$ at different temperatures (160 °C, 180 °C, 190 °C and 210 °C). The higher temperature reduces the viscosity of the suspension. In addition, the effect of wall slip becomes more important. Therefore, with same flow length and same particle concentration, the pressure decreases with increasing temperature.

Figure 4.21: Pressures of suspension with $\phi = 40\%$ measured at different temperatures (L=20 mm, D=1 mm)

4.7 ENTRANCE AND EXIT LOSSES

As previously discussed in section 4.4.2 for pure EVA460, there were difficulties associated with measurements by an orifice die. As such, the entrance and exit losses of concentrated suspension were obtained only by Bagley correction.

The experiments for Bagley correction were conducted on three groups of dies (die diameter 0.5 mm, 1 mm and 2 mm) to compare the flow behaviours at different diameters. In addition to diameter, die length is another factor affecting the Bagley plot. If the number and range of flow lengths investigated are limited, as with only two flow lengths, the plot of pressure versus L/R for a given flow rate would appear to be linear. However, this would not accurately reflect the characteristics of a concentrated suspension, and would lead to erroneous prediction of entrance and exit losses. As such, it is important to have a sufficient large range of L/R ratio, and at least three ratios, such that any non-linearity of the plot could be identified. In this investigation, the range of L/R employed was from 5 to 80.

4.7.1 Diameter 0.5 mm

Capillary dies of diameter 0.5 mm with length to radius ratios (L/R) of 20, 40 and 80 were studied. This group of experiments were conducted on suspension with $\phi = 40\%$. Experiments were not conducted at higher flow rate as the pressure required would exceed the range of the employed pressure transducer.

The pressure vs. L/R measured at different flow rates is shown in Figure 4.22. The nonlinearity is obvious, especially at higher flow rate. The entrance and exit losses calculated by polynomial Bagley correction are shown in Figure 4.23.

Figure 4.22: Bagley plot for concentrated suspension with $\phi = 40\%$
(Q : cm³/s, $D=0.5$ mm, $T=180$ °C)

Figure 4.23: Entrance and exit losses by polynomial Bagley correction using die diameter 0.5 mm with $\phi = 40\%$ at 180 °C

4.7.2 Diameter 1 mm

Figures 4.24-26 show the Bagley plots of concentrated suspension with 35%, 40%, 45% particle loading, respectively.

Figure 4.24: Bagley plot of suspension with 35% particle concentration
(Q : cm^3/s , $D=1$ mm, $T=180$ °C)

Figure 4.25: Bagley plot of suspension with 40% particle concentration
(Q : cm^3/s , $D=1$ mm, $T=180$ °C)

Figure 4.26: Bagley plot of suspension with 45% particle concentration
(Q : cm^3/s , $D=1$ mm, $T=180$ °C)

Figure 4.27: Entrance and exit losses predicted by polynomial Bagley correction
for concentrated suspensions with different particle concentrations
($D=1$ mm, $T=180$ °C)

The nonlinearity in the Bagley plot became more pronounced with increasing particle concentration from 35% to 45%, and with increasing flow rate from $9.84 \times 10^{-4} \text{ cm}^3/\text{s}$ to $7.36 \times 10^{-2} \text{ cm}^3/\text{s}$. The nonlinearity can be caused by wall slip and particle migration. Therefore, it is better to fit the curve by polynomial Bagley correction than linear correction. The entrance and exit losses determined by the polynomial Bagley correction are shown in Figure 4.27. They increase with flow rate and particle concentration.

4.7.3 Diameter 2 mm

Capillary dies of diameter 2 mm with length to radius ratios (L/R) of 10, 25, 30 and 40 were used. Figure 4.28 shows the Bagley plot. In this group, linear Bagley correction can achieve good accuracy in fitting the experimental data. This means that both particle migration and wall slip were less important than those with diameters 0.5 mm and 1 mm. The entrance and exit losses calculated are shown in Figure 4.29.

Figure 4.28: Bagley plot for concentrated suspension with $\phi = 40\%$
(Q : cm^3/s , $D=2 \text{ mm}$, $T=180 \text{ }^\circ\text{C}$)

Figure 4.29: Entrance and exit losses predicted by linear Bagley correction for concentrated suspension with $\phi = 40\%$ ($D=2$ mm, $T=180$ °C)

4.7.4 Analysis of Entrance and Exit Losses

The entrance and exit losses, ΔP_e , of concentrated suspensions in capillary flow may be characterized by the approach proposed by Jastrzebski (1967), which was correlated with the volumetric flow rate, Q , by an exponential relationship as:

$$\Delta P_e = A_{R,\phi} Q^t = B e^{cR} Q^t \quad (4.8)$$

where $A_{R,\phi}$ is a constant dependent on the concentration of a suspension and on the radius of the die used, t is the power law index. B is a characteristic constant for a particular concentration, c is a constant related to die radius R .

For a capillary flow, the material constants in equation (4.8) can be determined experimentally, following a Bagley plot methodology. However, Jastrzebski did not consider the effect of temperature which may affect the constant t . The higher the temperature, the larger the constant t . Therefore, the entrance and exit losses are proposed as:

$$\Delta P_e = f(\phi) \left(\frac{D}{D_{barrel}} \right)^z Q^{f(T)} \quad (4.9)$$

The equation shows the effects of particle concentration, contraction ratio, flow rate and temperature on the entrance and exit losses.

As discussed in section 4.7.1-4.7.2, the Bagley plot showed obvious nonlinearity for 0.5 mm and 1.0 mm diameter dies. Thus the results obtained by nonlinear Bagley plot (other than 2 mm diameter die) were used for the determination of the constants in equation (4.9). As the entrance and exit losses are related to temperature, particle concentration and die diameter, the constants in equation (4.9) were determined in the following steps:

(1) For a given particle concentration and die diameter, plot $\log(\Delta P_e)$ versus $\log(Q)$ at different temperatures, see Figure 4.30. It shows that $\log(\Delta P_e)$ is linear to $\log(Q)$ at high flow rates, but data points deviated from linearity at very low flow rates. This is because any small experimental error in pressure measurement can result in significant percentage error due to the small pressure registered at low flow rate. Therefore, the deviation from the linearity at very low flow rates can be neglected and from the slopes of the curves, $f(T)$ can be determined.

(2) At a given temperature, the plot of $\text{Log}(\Delta P_e / Q^{f(T)})$ versus $\text{Log}(D / D_{barrel})$ for a given particle concentration is shown in Figure 4.31, showing a linear relationship between them. Therefore, $f(D / D_{barrel})$ can be expressed as:

$$f(D / D_{barrel}) = \left(\frac{D}{D_{barrel}} \right)^z \quad (4.10)$$

where the constant z can be obtained by the slope in Figure 4.31.

(3) For a given die diameter and temperature, plot $f(\phi) = \frac{\Delta P_e}{(D/D_b)^k Q^{f(T)}}$ versus ϕ

for suspensions with different particle concentrations, as shown in Figure 4.32.

$f(\phi)$, which is a linear function of ϕ , can be determined from the fitted line.

Figure 4.30: $\log(\Delta P_e)$ vs. $\log(Q)$ for suspension with 40% particle concentration at different temperatures with die diameter of 1 mm

Figure 4.31: $\log(\Delta P_e / Q^{f(T)})$ vs. $\log(D / D_{barrel})$ for suspension with 40% particle concentrations at 180 °C measured by different dies

Figure 4.32: $f(\phi)$ vs. ϕ for suspensions with different particle concentrations at 180 °C measured by die diameter 1 mm

From these experimental investigations, equation (4.9) can be rewritten as:

$$\Delta P_e = a_1 (\phi + a_2) \left(\frac{D}{D_{barrel}} \right)^z Q^{pT+q} \quad (4.11)$$

The fitted parameters for the system investigated are listed in Table 4.3 with the parameter a_1 has a fitted unit with $MPa \cdot (s / cm^3)^{pT+q}$.

Table 4.3: Fitted parameters in equation (4.11)

$f(\phi)$	a_1	0.1
	a_2	0.7
$f(D / D_{barrel})$	z	-1.84
$f(T)$	P (1/K)	4×10^{-3}
	q	-1.32

However, this investigation was conducted with die diameter in the range of 0.5-2 mm. This equation might not be applicable for cases with die radius outside this range.

4.7.5 Comparisons

The predicted entrance and exit losses using equation (4.11) were compared with those calculated by Bagley correction, see Figures 4.33-36. The figures confirm that the proposed formula can be used to predict the entrance and exit losses.

For pure polymer melts, the entrance and exit losses can be predicted by setting $\phi = 0$. The comparison of the values by Bagley correction and predicted data by equation (4.11) is presented in Figure 4.33.

Figure 4.33: Comparison of entrance and exit losses by Bagley correction and predicted results by Equation (4.11) for pure EVA 460 (T=180 °C, D=1 mm)

Figure 4.34 shows the comparison for the concentrated suspensions with different particle concentrations, showing good agreement between the predictions and experimental observations.

Figure 4.35 compares the entrance and exit losses for suspension with 40% particle concentration by volume measured by different dies. For small diameter, entrance

and exit losses are very sensitive to flow rate. This confirmed the work of Rides and Allen (1996) that entrance and exit losses are function of contraction ratio.

Figure 4.34: Comparison of entrance and exit losses between those by Bagley correction and predictions by equation (4.11) for suspensions with different particle concentrations ($D=1$ mm, $T=180$ °C)

Figure 4.35: Comparison of entrance and exit losses between those by Bagley correction and predictions by equation (4.11) for different die diameters ($\phi = 40\%$, $T=180$ °C)

In the entrance and exit losses, entrance loss plays a major role, and is caused by the contraction of diameters between the barrel and the capillary. It is basically the pressure drop due to the converging flow from the large reservoir to the smaller capillary. Due to the large contraction ratio for smaller diameter die, the entrance and exit losses increase greatly for a small increase in the flow rate. However, this does not mean that small diameter die should not be used as long as the entrance and exit losses are taken into consideration. Indeed, with a set of dies with a range of contraction ratio, entrance and exit losses could be taken into consideration accurately. It further confirmed that in the determination of slip velocity by the Mooney method, all the dies with different diameters should be corrected for ΔP_e . Great error will bring if neglecting the entrance and exit losses, especially for small diameter dies.

Figure 4.36 compares the entrance and exit losses between predictions and experimental results with Bagley correction at different temperatures, respectively.

Figure 4.36: Comparison of entrance and exit losses between those by Bagley correction and predictions by equation (4.11) at different temperatures ($D=1$ mm, $\phi = 40\%$)

4.8 SLIP VELOCITY OF CONCENTRATED SUSPENSION

The procedures to calculate the slip velocity of concentrated suspension are the same as those of pure EVA, see section 4.4.3(b). The effects of particle size, temperature and particle concentration on slip velocity were discussed. Based on the results, a slip model was established.

4.8.1 Slip Velocity Measurement

The plot of wall shear stress vs. apparent shear rate for 35% concentrated suspension for dies with diameters 0.5 mm, 0.75 mm, 1 mm, 1.25 mm is presented in Figure 4.37.

Figure 4.37: Wall shear stress vs. apparent shear rate for four different dies for concentrated suspension with $\phi = 35\%$

The slip is obvious due to the geometry dependence of wall shear stress against apparent shear rate. It is observed that the smaller diameter capillaries yielded lower wall shear stresses. With increasing particle concentration, the geometry dependence is more pronounced, see Figure 4.38 for $\phi = 40\%$ and Figure 4.39 for

$\phi = 45\%$. Based on these figures, the apparent shear rate corresponding to a specified wall shear stress can be interpolated.

Figure 4.38: Wall shear stress vs. apparent shear rate for four different dies for concentrated suspension with $\phi = 40\%$

Figure 4.39: Wall shear stress vs. apparent shear rate for four different dies for concentrated suspension with $\phi = 45\%$

Figure 4.40 gives an example of Mooney plots for a suspension with 40% particle concentration at 180°C. The gradients of these lines are used to determine the slip velocities at the specified wall shear stress values by data fitting. Thus, the slip velocity and the parameters in the slip model can be obtained. The effects of some important parameters on the slip velocity are discussed in the following sections.

Figure 4.40: Mooney plot for suspension with 40% particle concentration at 180°C

4.8.2 Effect of Particle Size

For a suspension containing particles beyond the colloidal range, the larger the particle, the more pronounced the slip behaviour. Figure 4.41 shows slip velocities for a suspension with 40% particle concentration but with particles in different size ranges. The suspension with particle size in the range of 106-125 μm exhibited larger slip velocities compared to those with particle size in the range of 53-63 μm .

Figure 4.41: Slip velocities with 40% particle concentration at 180 °C with particle size in different ranges

However, for a suspension with particle size in the range of 1-15 μm , no dependency of wall shear stress on diameter can be observed, see Figure 4.42. Thus, wall slip of this suspension can be ignored. It is suspected that due to the small particle size, the colloidal effect might play an important role in the flow behaviour of the suspension. It might change the interactions between the suspension and the solid wall. In addition, the apparent slip layer reduced due to decreasing particle migration with a decrease in particle size. As such, suspension with particles in this size range will not be considered in subsequent analysis.

Figure 4.42: Wall shear stress vs. apparent shear rate for the suspension with 40% particle concentration and particle size in range of 1-15 μm

4.8.3 Effect of Temperature

Experiments were conducted on a suspension with particle concentration of 40% but at different temperatures (160 °C, 180 °C, 210 °C). Figure 4.43 shows that increasing temperature results in a steeper slip curve.

Figure 4.43: Slip velocities with 40% particle concentration at different temperatures (160 °C, 180 °C, 210 °C)

4.8.4 Effect of Particle Concentration

The effect of particle concentration was studied with suspensions containing 35%, 40% and 45% particles by volume with particle size in the range of 53-63 μm and 106-125 μm , see Figure 4.44 and Figure 4.45, respectively. They showed that an increase in particle concentration resulted in an increase in wall shear stress, and higher slip velocity.

Figure 4.44: Slip velocities at different particle concentrations with particle size in 53-63 μm at 180 $^{\circ}\text{C}$ (The calculated slip velocities by equation (4.12) are shown)

Figure 4.45: Slip velocities at different particle concentrations with particle size in 106-125 μm at 180 $^{\circ}\text{C}$ (The calculated slip velocities by equation (4.12) are shown)

4.8.5 Slip Model

The slip velocities determined by the modified Mooney method show that slip velocity is a function of wall shear stress, pressure and temperature, and is related to particle size. In addition, as confirmed by Figures 4.43-45, a power law model can be used to fit the slip velocity:

$$u_s = \alpha \exp(\lambda T - \beta_p P) \tau_w^k \quad (4.12)$$

The constants in equation (4.12) can be obtained by data fitting, which are listed in Table 4.4. For the concentrated suspensions with particle size of 53-63 μm and 106-125 μm , the fitted constants λ , β_p and k are the same, but α changes with particle size. Equation (4.12) provides a good fit to the experimental data, see Figures 4.44 and 4.45.

Table 4.4: Constants in the slip model

Constants	53-63 μm	106-125 μm
α (mm/s)	2.14	2.69
λ (1/K)	0.013	0.013
β_p (1/Pa)	1.5×10^{-9}	1.5×10^{-9}
k	3.03	3.03

With these constants, the Mooney plot can be further discussed. The relationship of apparent shear rate with slip velocity as given by equation (3.72) can be transformed to:

$$\dot{\gamma}_a = \frac{4n}{3n+1} \dot{\gamma}_w + \frac{4n}{3n+1} (k+3) \frac{u_s}{R} \quad (4.13)$$

Introducing the values of $n = 0.38$ and $k = 3.03$, the gradient in the plot of $\dot{\gamma}_a$ versus $1/R$ is 4.28 times the slip velocity. This gradient of 4.28 is different from the gradient of 4.0 given by the conventional Mooney method.

4.9 SUMMARY

This chapter presents the experimental results and analyses on the rheological behaviour of a pure polymer system and concentrated suspensions.

For pure polymer, thermal analysis and the procedure to determine its true viscosity were discussed. The results show that polymer EVA460 exhibits a non-Newtonian behaviour. By data fitting, the material constants in the viscosity models were obtained. In addition, the slip velocity of pure EVA was determined by the modified Mooney method. It is observed that the slip velocity of EVA is small at high shear rate and negligible at low shear rate.

For concentrated suspensions, experiments were conducted to obtain the yield stress, entrance and exit losses, and slip velocity. The yield stresses of the concentrated suspensions with different particle concentrations were measured by an indirect method. Results obtained indicate that the yield stresses of the concentrated suspensions are very low and can be neglected. A series of experiments were performed on the concentrated suspensions to study the effects of particle concentration, flow length, particle size and temperature. Entrance and exit losses were determined by Bagley correction. A formula proposed by Jastrzebski (1967) was extended to combine the effects of temperature, flow rate and die radius for the prediction of entrance and exit losses. This modified formula provided predictions that agreed well with the experimental data.

Finally, slip velocities of concentrated suspensions were calculated by the modified Mooney method. The experimental procedure was presented and the key factors (particle concentration, temperature and particle size) were investigated. The proposed slip model was discussed and the constants in the slip model were determined by data fitting.

CHAPTER 5 RESULT DISCUSSIONS

5.1 INTRODUCTION

This chapter discusses pressure, slip velocity, and viscosity of concentrated suspension. Numerical predictions are presented for the profiles of the velocity and the particle concentration. Predicted slip velocities were compared with the results determined by the modified Mooney method. Subsequently, predicted pressures with and without consideration of particle migration, wall slip and viscous heating were compared with experimental data. Finally, the true viscosities of concentrated suspensions were calculated.

5.2 NUMERICAL PREDICTIONS

5.2.1 Parameters

The numerical model requires the knowledge of rheological material constants and phenomenological constants for the prediction of velocity and temperature profiles, and pressure field of a non-Newtonian suspension system.

As discussed in Chapter 3, the interaction frequency of particles is related to particle concentration, and the phenomenological parameter k_c was thus proposed to be a linear function of particle concentration with $k_c = k'_c \phi$, while k_η was regarded as a constant. The phenomenological constants k'_c and k_η were determined inversely by employing least square analysis on the experimental data [Chen et al., 2004] with $k'_c=0.54$, $k_\eta=0.61$.

Table 5.1 lists the material parameters of EVA and glass powder used in the simulation. With these constants, the distributions of velocity, particle concentration, as well as the pressure, were predicted to demonstrate the effects of particle migration, wall slip and viscous heating.

Table 5.1: Material parameters of EVA and glass powder

Material parameters		Value
EVA density, kg/m^3		941
Glass particle density, kg/m^3		2500
Stainless steel density, kg/m^3		7900
Thermal sensitivity of viscosity, K^{-1}		0.033
Activation energy, kJ/mol		56.12
Specific heat capacity, J/(kg.K)	EVA	3173
	Glass particle	770
	Steel	486
Thermal conductivity, W/(m.K)	EVA	0.33
	Glass particle	1.05
	Steel	46

5.2.2 Structure of Numerical Simulations

Predictions were first conducted at isothermal condition. The distributions of radial velocity and particle concentration were predicted as functions of particle migration and wall slip. Particle concentration and flow length were discussed as they influenced the degree of particle migration. Pressures were predicted with the assumptions of with/without particle migration and with/without wall slip. These predictions were compared with experimental data.

The predictions were further extended with the assumptions of the co-existence of both particle migration and wall slip. Predicted slip velocities were compared with

the results determined by the modified Mooney method, and predicted Bagley plots were compared with experimental data.

Figure 5.1: Structure of numerical simulations

Finally, the predictions of pressure were conducted at a constant wall temperature or with an adiabatic die wall to show the effect of viscous heating under the conditions employed. The structure of numerical simulations is summarized in Figure 5.1.

5.2.3 Predictions at Isothermal Condition

At isothermal condition, viscous heating is not considered and the temperature in the flow is assumed to be uniform.

(a) Radial velocity distribution

The development of the velocity profile is gradual and monotonous. If there is particle migration, the velocity profile becomes blunted as the particle travels from wall to center and develops gradually. This leads to the resultant non-uniform effective viscosity in the cross section of the tube, higher at the centre of the tube and lower at the wall. The shear-induced migration is greater for small capillaries [Macosko, 1994; Lam et al., 2002].

With wall slip, velocity gradient is reduced near the wall and blunted at the center of the tube. This is due to the fact that as the velocity increases near the wall, velocity at the center of the tube is therefore blunted to meet the requirement of mass conservation. The larger the slip velocity, the more the velocity blunted at the center of the tube. Figure 5.2 shows the velocity distributions at the exit section under different conditions.

Figure 5.2: Velocity distribution at the exit section
 $(Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}, L/R=40, R=0.5 \text{ mm}, \phi = 45\%, T=180^\circ \text{C})$

Figure 5.3: Velocity distributions for suspension with different particle concentrations at the exit section
 $(Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}, L/R=40, R=0.5 \text{ mm}, T=180^\circ \text{C})$

It was observed that the velocity profile is related to particle concentration and flow length, see Figure 5.3 and Figure 5.4, respectively. Wall slip and particle migration increase with increasing particle concentration, resulting in more blunting of the velocity profile. The larger the flow length, the more pronounced the particle migration. Thus the velocity profile is further blunted with increasing flow length.

Figure 5.4: Velocity distributions at the exit section for different flow lengths ($Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}$, $\phi = 45\%$, $R=0.5 \text{ mm}$, $T=180^\circ \text{C}$)

(b) Particle concentration profile

If no particle migration occurs, the profile of particle concentration will be uniform as the inlet. Therefore, the prediction of particle concentration profile is conducted with the assumption of particle migration, with or without wall slip. Figure 5.5 shows the effect of wall slip on the particle concentration profile. Near plug-like nonuniform concentration profile is formed for non-Newtonian concentrated

suspension during pressure-driven tube flow. Wall slip reduces the degree of particle migration thus particle concentration deviates less from the initial uniform distribution.

Figure 5.5: Particle concentration profile in the exit section with or without wall slip for suspension with $\phi = 45\%$
($Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}$, $L/R=40$, $R=0.5 \text{ mm}$, $T=180 \text{ }^\circ\text{C}$)

Figure 5.6 shows the effect of initial particle concentration on particle migration. With $\phi = 35\%$, there is a concentration gradient at the region near the wall, but the profile of particle concentration can be regarded as uniform at the central region of the tube with little change in particle concentration. With increasing particle concentration, the degree of particle migration increases and thus the distribution of particle concentration becomes more inhomogeneous in the radial direction. With $\phi = 45\%$, there are large concentration gradients at the regions near the wall and at the centerline of the capillary.

Figure 5.6: Particle concentration profile in the exit section with wall slip for suspensions with different particle concentrations ($Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}$, $L/R=40$, $R=0.5 \text{ mm}$, $T=180 \text{ }^\circ\text{C}$)

Figure 5.7: Particle concentration profile in the exit section with wall slip at different flow lengths for suspension with $\phi = 45\%$ ($Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}$, $R=0.5 \text{ mm}$, $T=180 \text{ }^\circ\text{C}$)

In addition to particle concentration, flow length also affects the concentration profile significantly. At longer flow length, more particles accumulate at the centre with particle migration, see Figure 5.7.

(c) Slip velocity

As reported by White et al. (1991), Hatzikiriakos and Dealy (1992), slip velocity is not uniform along the flow length. The predicted results by the proposed model also confirm this finding. It shows that the slip velocity decreases with increasing hydraulic pressure in a capillary, with the smallest slip at the inlet where the hydraulic pressure is the largest, see Figure 5.8.

Figure 5.8: Slip velocity along the flow direction
 $(Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}, L/R=40, R=0.5 \text{ mm}, \phi = 40\%, T=180^\circ \text{C})$

As the slip velocity is not uniform along the flow length, the average value is employed to characterize the slip velocity for a specified capillary. Figure 5.9

shows the average slip velocities for various L/R ratios, which decreases with L/R. The average slip velocity for L/R=80 is only approximately half that of L/R=5. This finding is in agreement with that of Kalika and Denn (1987), i.e. the slip velocity is a function of L/R ratio of a capillary, decreasing with increasing L/R.

Figure 5.9: Average slip velocity versus L/R
 ($Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}$, $R=0.5 \text{ mm}$, $\phi = 40\%$, $T=180 \text{ }^\circ\text{C}$)

Figure 5.10 shows a comparison of the slip velocities between predicted and that obtained experimentally by the modified Mooney method with ratio L/R=40. It was observed that they agree well, which implies that the modified Mooney method can only be used to determine the average slip velocity. To characterize the wall slip along the flow length, the iteratively numerical method has to be employed.

Figure 5.10: Comparison of slip velocity between numerical predictions and by the modified Mooney method
($T=180\text{ }^{\circ}\text{C}$, $L/R=40$, $R=0.5\text{ mm}$)

(d) Bagley plot

The pressures in a Bagley plot (i.e. pressure vs. L/R) with or without particle migration and/or wall slip were predicted for comparison with experimental data.

Figures 5.11-13 show the comparisons for the Bagley plot between predicted and experimental results for concentrated suspensions with particle concentration 35%, 40% and 45% at isothermal condition with flow rate $Q=7.36\times 10^{-2}\text{ cm}^3/\text{s}$.

As expected, the pressures for cases without both particle migration and wall slip are the highest and are linear to the flow length. Due to particle migration, the predicted pressures are lower than those without particle migration. The effect of particle migration increases with the ratio of die length to radius and particle concentration, causing the curves in the Bagley plot to be convex. With $\phi = 35\%$, the pressure with particle migration but without wall slip is reduced about 2.5% at

$L/R = 80$. For $\phi = 40\%$ and $\phi = 45\%$, the pressure is reduced by particle migration by nearly 8% and 15% at $L/R = 80$, respectively.

In comparison, wall slip affects the predicted pressure more significantly and differently, even at low L/R ratio and low particle concentration. As slip velocity decreases with the flow length due to hydraulic pressure effect, the curves in the Bagley plot exhibit become concave.

Figure 5.11: Predicted pressures with or without particle migration and/or wall slip compared with experimental data

($Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}$, $R=0.5 \text{ mm}$, $\phi = 35\%$, $T=180 \text{ }^\circ\text{C}$)

Figure 5.12: Predicted pressures with or without particle migration and/or wall slip compared with experimental data
 $(Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}, R=0.5 \text{ mm}, \phi = 40\%, T=180^\circ \text{C})$

Figure 5.13: Comparison of predicted pressures with or without particle migration and/or wall slip with experimental data
 $(Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}, R=0.5 \text{ mm}, \phi = 45\%, T=180^\circ \text{C})$

From the above figures, it can be observed that predicted curves taking into account of both particle migration and wall slip agree well with experimental data.

Figures 5.14-16 show the Bagley plots of concentrated suspensions with different particle concentrations at different flow rates. The standard error between experimental data and predicted pressures with both particle migration and wall slip is 0.034 MPa. Therefore, Figures 5.14-16 confirm the good agreement between experimental and predicted pressures with particle migration and wall slip.

Figure 5.14: Comparison of predicted pressures with experimental data for suspension with $\phi = 35\%$ at different flow rates (Q : cm³/s, $R=0.5$ mm, $T=180$ °C)

Figure 5.15: Comparison of predicted pressures with experimental data for suspension with $\phi = 40\%$ at different flow rates (Q : cm^3/s , $R = 0.5 \text{ mm}$, $T = 180^\circ\text{C}$)

Figure 5.16: Comparison of predicted pressures with experimental data for suspension with $\phi = 45\%$ at different flow rates (Q : cm^3/s , $R = 0.5 \text{ mm}$, $T = 180^\circ\text{C}$)

5.2.4 Predictions for Different Thermal Conditions

In addition to isothermal condition, viscous heating may occur at higher flow rates and thus affect the behavior of concentrated suspension in a capillary flow. Therefore, simulations were also conducted to include nonisothermal analysis for a constant wall temperature and an adiabatic wall conditions. Figures 5.17-19 show the pressures predicted with particle migration and with wall slip at isothermal condition, a constant wall temperature and an adiabatic wall conditions, and their comparisons with experimental data.

Figure 5.17: Comparison of experimental data with predicted results at different thermal conditions for $\phi = 35\%$ ($Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}$)

Figure 5.18: Comparison of experimental data with predicted results at different thermal conditions for $\phi = 40\%$ ($Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}$)

Figure 5.19: Comparison of experimental data with predicted results at different thermal conditions for $\phi = 45\%$ ($Q=7.36 \times 10^{-2} \text{ cm}^3/\text{s}$)

With $\phi = 35\%$, the predicted pressures at a constant wall temperature and an adiabatic wall conditions were lower than those at isothermal condition. After particle concentration reached 45%, the predictions at isothermal condition were lower than those predicted at other thermal conditions due to the effect of particle concentration. However, in all cases, the predicted results at isothermal condition agree well with experimental data.

The results do not completely conform to conventional theory where the pressures should be always lower under the conditions of adiabatic wall due to higher temperature raised than those under isothermal wall. This is because slip effect may be a dominant factor on pressure drop among the three effects (particle migration, slip and viscous heating) at higher particle concentration i.e. 45%.

5.3 TRUE VISCOSITY OF CONCENTRATED SUSPENSION

After the corrections of slip velocity and entrance and exit losses, the true viscosity of concentrated suspension can be calculated by:

$$\tau_w = \frac{P - \Delta P_e}{2L/R} \quad (5.1)$$

$$\dot{\gamma}_w = \frac{3n+1}{4n} \dot{\gamma}_a - (k+3) \frac{u_s}{R} \quad (5.2)$$

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \quad (5.3)$$

Figures 5.20-22 show the calculated viscosities of concentrated suspensions with different particle concentration (35%, 40% and 45%) and particle size in the range of 53-63 μm by four different dies with $L/R=40$ but with die diameter 0.5 mm, 0.75 mm, 1.0 mm and 1.25 mm, respectively. The corrected viscosities by these different dies falls into one curve, with only a little scatters at low shear rate.

Figure 5.20: True viscosity of suspension with $\phi = 35\%$ measured by four dies with different diameter but same ratio of L/R=40 at 180 °C (53-63 μm)

Figure 5.21: True viscosity of suspension with $\phi = 40\%$ measured by four dies with different diameter but same ratio of L/R=40 at 180 °C (53-63 μm)

Figure 5.22: True viscosity of the suspension with $\phi = 45\%$ measured by four dies with different diameter but same ratio of L/R at 180 °C (53-63 μm)

Figure 5.23 summarizes the viscosities of pure EVA and concentrated suspensions with different particle volumes and particle size in the range of 53-63 μm . It can be observed that the curves are parallel to each other. As discussed in Section (4.4.2c), modified Cross model is a better fit for the viscosity of EVA binder than power-law model. Therefore, the slope of the relationship of viscosity with shear rate at different particle concentrations is not a straight line. On this basis, the constants in the Krieger model can be determined [Krieger, 1972]:

$$\eta = \eta_b \left(1 - \frac{\phi}{\phi_c}\right)^{-m} = \frac{\eta_0}{1 + (\eta_0 \dot{\gamma} / \tau^*)^{1-n}} \left(1 - \frac{\phi}{\phi_c}\right)^{-m} \quad (5.4)$$

The constants m and ϕ_c were determined by data fitting, $m = 1.28$ and $\phi_c = 0.68$.

For another group of concentrated suspensions with particle size in the range of 106-125 μm , their true viscosities were also calculated, see Figure 5.24. For this group, the constants in the Krieger model were determined as $m = 1.08$ and $\phi_c = 0.68$.

Figure 5.23: True viscosities of pure EVA and suspensions with different particle concentrations at 180 °C (53-63 μm)

Figure 5.24: True viscosities of suspensions with different particle concentrations at 180 °C (106-125 μm)

These results indicate that the viscosity of concentrated suspension decrease with increasing particle size. Maintaining a constant volume percentage of particles in a suspension while reducing the particle size of the solid phase will lead to an increase in the number of particles in the system, and this could result in a larger viscosity with smaller particles. A higher number of particles will result in more particle-particle interactions and an increased resistance to flow. This is shown in the Krieger model with the value of m decreasing with increasing particle size.

To show clearly the variation in the value of m , the relative viscosity η_r is adopted:

$$\eta_r = \eta / \eta_b = \left(1 - \frac{\phi}{\phi_c}\right)^{-m} \quad (5.5)$$

The value of m vs. particle size is shown in Figure 5.25 with error bar.

Figure 5.25: Value of m as a function of particle size

The value of ϕ_c depends upon the uniformity of particle size, the effective microstructure of the packed configuration and the type of flow. For uniform diameter particles the value of ϕ_c can vary over a range from 0.52 (simple cubic packing) to 0.74 (face-centred cubic packing) [Krieger, 1972]. Still other values of

ϕ_c are applicable to randomly packed particles and bimodal suspensions. Although the studied particles are in different size ranges, within 53-63 μm and 106-125 μm , respectively, they can be regarded in the same magnitude, and both are of spherical shapes, so the value of ϕ_c could be same for both groups. The critical volume percentage 68% was also employed by Subia (1998) to spherical particles.

5.4 SUMMARY

In this chapter, numerical predictions and comparisons with experimental results were presented. From numerical predictions, it can be observed that for concentrated suspension in capillary flows, particle migration and wall slip blunted the velocity distribution in the radial direction and caused the nonuniform distribution of particle concentration. With particle migration, a near plug-like concentration profile is formed for concentrated suspension in a pressure-driven tube flow. Compared with the case without the wall slip, slip reduces the degree of particle concentration and less deviation of particle concentration from the initial uniform distribution. It implies that wall slip reduces the driving force for particle migration.

In the Bagley plot, pressures are linear to flow length for cases without both particle migration and wall slip. The curves become convex with particle migration. This has an effect on pressure especially at large L/R ratio and high particle concentration. In contrast, the pressure curves become concave with wall slip. The simulation results confirm that the slip velocity is not uniform throughout the capillary length, increasing from the inlet to exit as the hydraulic pressure in the capillary decreases gradually.

In addition, viscous heating effect is examined. As the applied flow rate in the conducted experiments is limited in a small range (0-750 1/s), viscous heating has only a minor effect on the predicted pressures.

The predicted pressures were compared with experimental results. Good agreements for pressures predicted with consideration of particle migration and wall slip at the isothermal condition with experimental data were observed. It was also established that the predicted average slip velocities agreed well with those determined by the modified Mooney method.

Finally, by means of Bagley and slip velocity corrections, the true viscosities of concentrated suspensions were calculated. The viscosities of the suspensions with different particle concentrations can be described by the Krieger model. For the concentrated suspension with particle size in the range of 53-63 μm , the Krieger constants were determined as $m = 1.28$ and $\phi_c = 0.68$. For another group with particle size in the range of 106-125 μm , the constants were determined as $m = 1.08$ and $\phi_c = 0.68$. This indicates that particle size has an effect on the viscosity of the suspensions.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The rheological behaviors of pure polymer (EVA460) and glass powder filled EVA systems were investigated theoretically and experimentally. Experiments on EVA include thermal analysis and capillary rheological experiments. For concentrated suspension, yield stress measurements and capillary rheological experiments were conducted. A numerical model was developed to predict the effects of particle migration, wall slip and viscous heating on concentrated suspension flow in a capillary.

Thermal analysis was conducted to measure the degradation of EVA460. This experiment provided information for setting suitable mixing temperature for the preparation of concentrated suspension to ensure no degradation in the polymer matrix which could affect the outcome of rheological experiments. Capillary experiments were performed on pure polymer at different temperatures to determine its true viscosity. Results obtained indicated that EVA460 exhibits non-Newtonian behavior with shear thinning. Modified Cross model and power-law model were employed in fitting the viscosity of EVA460, with the modified Cross model provided a better fit to the data. By data fitting, the material constants in the viscosity models were obtained.

In the characterization of the rheological behaviors of polymers and concentrated suspensions, entrance and exit losses and wall slip are two important considerations. Entrance and exit losses were measured by an orifice die and

determined by Bagley correction. It was found that the measured values by an orifice were higher than those by Bagley correction, as the extruded melt got stuck easily to the wall in the expansion region of the orifice die. Due to this complication, it was decided that the results obtained by the orifice die were not reliable, and all entrance and exit losses were determined by Bagley correction.

For EVA, the curves in Bagley plots exhibited good linearity. However, for concentrated suspension, the curves in Bagley plots were nonlinear and the nonlinearity increased with particle concentration and flow rate, thus a second-order curve-fitting (instead of linear fitting) of Bagley plot was employed in the determination of entrance and exit losses.

A formula proposed by Jastrzebski (1967) was modified and improved, which considers simultaneously the effects of temperature flow rate and die radius for the prediction of entrance and exit losses. The constants in this formula were determined based on experimental data. This modified formula provided predictions that agreed well with experimental data.

In the determination of slip velocity, a modified Mooney method was proposed, as the conventional Mooney method is only valid strictly for Newtonian fluid where slip velocity is linear to wall shear stress. The modified Mooney method can be used for a generalized-Newtonian fluid where slip velocity may be linear or nonlinear to wall shear stress. The slip-corrected wall shear rate as a function of apparent shear rate and slip velocity was established. For a non-Newtonian fluid, the gradient in a Mooney plot equals to the slip velocity multiplied by an explicit coefficient of $4n(k+3)/(3n+1)$, which takes into account the non-Newtonian effect (parameter n) and the nonlinearity between wall shear stress and slip velocity (parameter k).

The slip velocity of EVA was small and could be neglected. However, for concentrated suspension, the slip velocity increased significantly with wall shear stress. The key parameters on the slip velocity, which include pressure, particle concentration, temperature and particle size, were investigated. A power-law slip model was proposed to describe the effects of temperature, particle size, pressure and wall shear stress. The constants in the slip model were obtained by data fitting. In addition to capillary experiments, yield stresses of concentrated suspension with different particle concentrations were measured by an indirect method. Experimental results concluded that the yield stresses were negligible.

Numerical modeling was conducted to simulate the capillary flow. Based on Phillips et al. (1992), Lam and Chen [Lam et al., 2002; Chen et al., 2003] extended the particle diffusive model to solve the flow pattern of non-Newtonian concentrated suspensions in a capillary flow. This extended model was further improved in the present investigation to take into consideration the interactions between particle migration, wall slip and viscous heating. In addition, the phenomenological parameter k_c (indicating the interaction frequency of particles in the diffusive flux model), which was proposed to be correlated linearly to particle concentration [Graham et al., 1998] due to multi-body interactions between particles, is incorporated in the improved model.

From the simulation results, it can be observed that for concentrated suspension in capillary flows, particle migration and wall slip blunt the cross-sectional velocity distribution. The slip velocity is not uniform, increasing from the inlet to the exit as the hydraulic pressure decreases. For an overall characterization, the average value of slip velocity is employed. Results indicate that the average slip velocity decreases with L/R ratio of a capillary die.

With particle migration, near plug-like non-uniform concentration profile is predicted for concentrated suspension in a pressure-driven tube flow. Compared with the case without wall slip, slip reduces particle migration thus causing less deviation of particle concentration from the initial uniform distribution. It confirms that wall slip reduces the driving force for particle migration.

The effects of particle migration and wall slip on pressure were investigated individually and in combination. These parameters can explain the nonlinearity in a Bagley plot. Without particle migration and wall slip, pressure variation is linear to flow length. The pressure curves in a Bagley plot become convex due to particle migration, which affects the pressure especially at large L/R ratio and high particle concentration. In contrast, with wall slip the pressure curves become concave as the slip velocity decreases with hydraulic pressure.

As the range of shear rate investigated ($0\text{--}750\text{ s}^{-1}$) is limited to a relative low value, viscous heating is negligible and an isothermal condition can be assumed.

Numerical predictions were compared with experimental data. With consideration of both particle migration and wall slip, the predicted pressures by the developed model agree well with experimental data. In addition, the predicted slip velocities by the numerical model agree well with the results obtained by the modified Mooney method derived from capillary experimental data.

Finally, by means of Bagley correction and slip correction, the true viscosities of concentrated suspensions were calculated. The data obtained by different dies with same L/R ratio but different radius collapsed into one master curve. The viscosities of the suspensions with different particle concentrations can be described by the Krieger model. For concentrated suspension with particle size in the range of 53–63 μm , the Krieger constants were determined as $m = 1.28$ and $\phi_c = 0.68$. For

particle size in the range of 106-125 μm , the constants were determined as $m = 1.08$ and $\phi_c = 0.68$. This indicated that particle size has an effect on the viscosity of the suspensions.

6.2 RECOMMENDATIONS

According to this research, the following directions are recommended:

1. The effect of viscous heating is negligible in the present investigation due to the low shear rates employed. For an investigation of the effect of viscous heating, higher shear rate should be considered.
2. Coupling of powder to polymer via surface active agent is an important technology and has attracted much attention recently [Saša et al., 2004; Reinhard and Alexander, 2000]. It can prevent particle interactions (cohesion and reactivity) and improve the flowability of suspensions, and thus affect the rheological behavior.
3. A more rigorous study of the size effect of the powder is to be conducted to determine the upper and lower bound values for the validity of the developed model. It has been demonstrated in the current investigation that the model developed will not be applicable for very small particles, possibly due to colloidal effects. In addition, small particles could have an effect on the yield stress of the suspension. For large particles in the order of the capillary diameter, it is envisaged that the model will not be applicable due to the significant violation of the continuum assumption employed in the model.
4. Anisotropic normal stresses result in differences between the stresses in different directions and are behind some of the unusual behaviors observed for

non-Newtonian fluids. Its effect on particle migration and wall slip should be further explored.

5. Other concentrated suspensions, with different polymers and particles, could be investigated. This is to verify the general applicability of the models developed in this investigation.

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