Study on The Rheological Properties of Partially Hydrolysed Polyacrylamide Solution at Elevated Temperature

by

Mohd Amir Bin Maliki

Dissertation submitted in partial fulfilment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

(MR. MOHD ZAMRI ABDULLAH)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that, the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHD AMIR BIN MALIKI

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ABSTRACT

The main purpose of using polymer in enhanced oil recovery is to increase the viscosity of water. In this aspect, maintaining the viscosity of aqueous polymer solution in harsh environment conditions like high temperature and high pressure is a challenge. Thus, it is important to investigate the rheological behaviour of the polymer under such condition. In this study, partially hydrolysed polyacrylamide (PHPAM) solution was chose as the case study. PHPAM solution was experimented under elevated temperature range from 80°C to 100 °C at atmospheric pressure. PHPAM solution in the range of 500 ppm for master solution and 10 ppm 50 ppm for diluted solution were covered. Brookfield cap 2000+ viscometer is employed for operating, measuring and analysing this experimental investigation. The results obtained are expected to provide better understanding on the flow behaviour of HPAM at elevated temperature.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

The flow of oil-water-gas mixtures in pipelines is a common occurrence in the petroleum industry. Although wells initially contain only oil and natural gas, mature and aging reservoirs produce increasing amounts of water and reservoir pressure may deplete.

Enhanced oil recovery methods may involve pumping natural gas into the well tubing to reduce static pressure losses. It is often not practical and very expensive to separate this oil-water-gas mixture at the well site so the multiphase mixture is pumped through a single pipeline to a central gathering station, where it can be separated. The distances the multiphase mixture must be transported are often many miles and the pressure drop in these pipelines can be very significant.

Drag reduction agents in multiphase flow pipeline is of great interest in petroleum and pipeline industries since production can be increased by decreasing the pressure drop. The oil and gas producing industries have traditionally used Drag Reducing Agents (DRA) to help lower pressure gradients for the transport of single-phase liquids over long distances. Nijs (1995) stated that DRA are type of flow improvers with high molecular weight (10^6~10^8 g/mol) polymers which prevent bursts that create turbulence in the core and interfere with the turbulence being formed, or reduce the degree of turbulence. An example of DRA use in a mature production system, where the liquid and gas are separated at the source, is the transport of oil in the 800 mile Trans-Alaska Pipeline System (TAPS).

DRA have been very beneficial in reducing frictional losses, allowing a greater production flow rate at an economical cost. DRA have not been specifically designed for use in multiphase systems where oil-water-gas mixtures are transported. Modern production facility design requires the transportation of raw wellhead fluids to processing facilities, at ever increasing distances, to remain economically viable. The use of DRA in this application is novel, although it has been tried in existing systems without conclusive results.

1.2 Problem Statement

The idea of the drag reduction is to improve the fluid-mechanical efficiency using passive agents, known as drag reducing agents (DRA). Drag reduction phenomena in multiphase flow system are still far from being well understood in spite of the numerous investigations. Partially hydrolysed polyacrylamide (PHPAM) solution, a drag-reducing long chain polymer is chosen as a case study for DRA. The study of the viscosity change is crucial to explain the effect of drag reduction agents since the polymer injected into the multiphase pipeline is varying with the difference of concentration. It is also important to analyse the effect of hydration periods of PHPAM as this will enhance the drag reduction process thus affect oil recovery. Therefore, the effect of elevated temperature to diluted and high concentration of polymer injected into the multiphase pipeline system is to be investigated.

1.3 Objective

To determine the effect of elevated temperature to rheological properties of high and diluted concentration of partially hydrolysed polyacrylamide (PHPAM) solution.

1.4 Scope of Study

The project involves experimental and modelling work. The rheological properties of the polymer solution are to be investigated through the use of a viscometer, by which the parameters such as shear stresses, shear rates and viscosities will be tabulated graphically. Through this data, various viscosity models will be analysed in order to determine the class of non-Newtonian behaviour that PHPAM fall into. Hence, the consistency index, *k* and the power law index, *n* will allow the interpretation of either the solution behave as a shear-thinning solution or vice versa as the concentrations and hydration periods changes.

1.5 Relevancy of the Project

Water-soluble polymers of high molecular weight have given rise to much interest due to their practical applications and more recently in the preparation of highly viscous solutions in the secondary oil recovery process. One of the most used is PHPAM. The understanding of the rheological behaviour of the polymers in the oil fields requires a complete characterization. However, there is a lack of reliable data in the literature concerning the effect high temperature to the rheological behaviour of the PHPAM. It is the purpose of this work to such data.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Solution and Rheology

Polymer is a chemical compound consists of a number of structural units linked together by covalent bonds and it has high molecular weight (Painter et al., 1997). A monomer is the substance that the polymer is made from. A single polymer molecule may consist of hundreds to a million monomers and may have a linear, branched, or network structure. A structural unit is a group having two or more bonding sites. A bonding site may be created by the loss of an atom or group, such as H or OH, or by the breaking up of a double or triple bond, as when ethylene, $H_2C\text{-}CH_2$, is converted into a structural unit for polyethylene, $\text{-}H_2C\text{-}CH_2\text{-}$.

Polymer properties are broadly divided into several classes based on the scale at which the property is defined as well as upon its physical basis. The most basic property of a polymer is the identity of its constituent monomers. A second set of properties, known as microstructure, essentially describe the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major role in determining bulk physical properties of the polymer, which describe how the polymer behaves as a continuous macroscopic material (Buckley et al., 1997). Chemical properties, at the nano-scale, describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents.

Polyacrylamide (PAM) is a polymer ($\text{-}CH_2CHCONH_2\text{-}$) formed from acrylamide subunits. It can be synthesized as a simple linear-chain structure or cross-linked, typically using *N,N'*-methylenebisacrylamide. PAM is non-toxic. However, un-polymerized acrylamide, which is a neurotoxin, can be present in very small amounts in the polymerized acrylamide (Daughlon et al. 1998), therefore it is recommended to handle it with caution. In the cross-linked form, the possibility of the monomer being present is reduced even further. PAM is a synthetic, water soluble polymer that is highly water-absorbent, forming a soft gel when hydrated. It is used in various applications such as polyacrylamide gel electrophoresis and in manufacturing soft contact lenses. In the straight-chain form, it is also used as a thickener and suspending agent (Lewandowska 2006).

One of the largest uses for PAM is to flocculate or coagulate solids in a liquid. This process applies to wastewater treatment, and processes like paper making. Most polyacrylamide is supplied in a liquid form. The liquid is subcategorized as a solution and emulsion polymer. Even though these products are often called 'polyacrylamide', many are actually copolymers of acrylamide and one or more other chemical species, such as an acrylic acid or a salt thereof. The main consequence of this is to give the 'modified' polymer a particular ionic character.

Another common use of PAM *and its derivatives is in subsurface applications such as* Enhanced Oil Recovery (EOR). High viscosity aqueous solutions can be generated with low concentrations of PAM, and these can be injected to improve the economics of conventional waterflooding. (Geehan et al. 1990)

In a dilute aqueous solution, such as is commonly used for EOR applications, PAM are susceptible to chemical, thermal, and mechanical degradation. According to Geehan and Mckee (1989), chemical degradation occurs when the labile amine moiety hydrolyzes at elevated temperature or pH, resulting in the evolution of ammonia and a remaining carboxyl group. Thus, the degree of anionicity of the molecule increases. Thermal degradation of the vinyl backbone can occur through several possible radical mechanisms, including the auto-oxidation of small amounts of iron and reactions between oxygen and residual impurities from polymerization at elevated temperature. Mechanical degradation can also be an issue at the high shear rates experienced in the near-wellbore region. However, cross-linked variants of PAM have shown greater resistance to all of these methods of degradation, and have proved much more stable.

2.2 Polymer Viscosity

Viscosity is an internal property of a fluid that offers resistance to flow. The flow properties of liquids can be divided into three main groups (i) Newtonian; (ii) Non-Newtonian, time dependent (iii) Non-Newtonian, time independent. The viscosity of a Newtonian liquid is constant and independent of the applied shear rate (shear stress). The relation between the applied shear rate and the obtained shear stress is constant over the whole shear rate range. Liquids which show Newtonian flow behaviour are often simple, single-phase liquids and solutions of liquids with low molecular weights (Annika 1998).

Polymers have a unique ability to dramatically increase the viscosity of a liquid they are dissolved in, even at very low concentrations. Viscosity of a polymer solution depends on concentration and size (i.e., molecular weight) of the dissolved polymer. By measuring the solution viscosity, it enables us to estimate the molecular weight. The viscosity techniques are very popular because they are experimentally simple. They are, however less accurate and the determined molecular weight, the viscosity average molecular weight, is less precise. Despite these drawbacks, viscosity techniques are very valuable.

2.3 Properties of Viscosity

The viscosity of the liquid is the ratio of the applied shear stress to the resulting strain rate (or equivalently, the ratio of the shear stress required to move the solution at a fixed strain rate to that strain rate). The shear strain in Figure 2.1 is

$$\gamma \frac{du}{dy}$$

where u is displacement in the x direction. The strain rate is therefore

$$\dot{\gamma} = \frac{d\,du}{dt\,dy} = \frac{d\,du}{dy\,dt} = \frac{dv_x}{dy}$$

Where v_x is velocity in the x direction. The relations between viscosity (η), shear stress (τ) and shear rate ($\dot{\gamma}$) are

$$\tau = \eta\dot{\gamma}$$

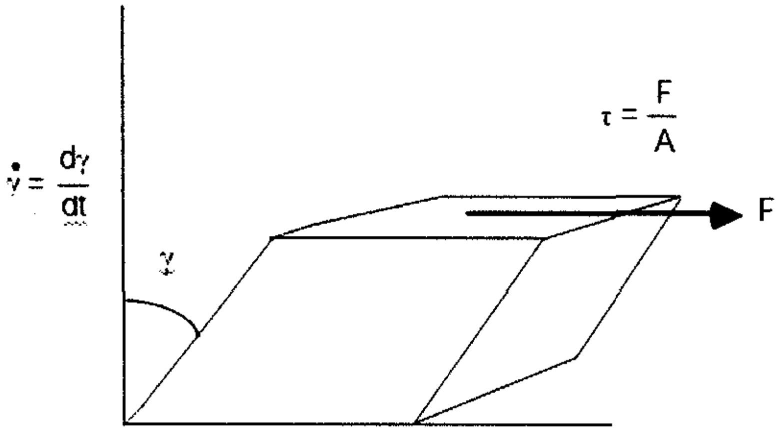


Figure 2.1: A piece of a liquid moving at shear rate $\dot{\gamma}$ under an applied shear stress of τ

A Newtonian fluid is one in which the viscosity is independent of the shear rate. In other words a plot of shear stress versus shear strain rate is linear with a slope η. In Newtonian fluids all the energy goes into sliding molecules by each other. In non-Newtonian fluids, the shear stress/strain rate relation is not linear. Typically the viscosity drops at high shear rates, described by a phenomenon known as shear thinning. Although the following development will not discuss shear rate effects in detail, the possibility of experimental results being affected by the shear rate of the measurement should be kept in mind. Plots of shear force vs. shear rate for Newtonian and non-Newtonian fluids are given in Figure 2.2.

Let η_0 be the viscosity of the pure solvent and η is the viscosity of a solution using that solvent. Several methods exist for characterizing the solution viscosity, or more specifically, the capacity of the solute to increase the viscosity of the solution. That capacity is quantified by using one of several different measures of solution viscosity. The most common solution viscosity terms are:

Table 2.1: Relation of viscosity terms

Name	Definition
Relative viscosity, η_r	$\frac{\eta}{\eta_o}$
Specific viscosity, η_{sp}	$\frac{\eta}{\eta_o}-1$ or $\frac{\eta-\eta_o}{\eta_o}$
Inherent viscosity, η_i	$\ln\frac{\eta_{rel}}{c}$ or $\ln\left(\frac{\eta}{\eta_o c}\right)$
Intrinsic viscosity, $[\eta]$	$\lim\left(\frac{\eta_{sp}}{c}\right)_{c\to 0}$

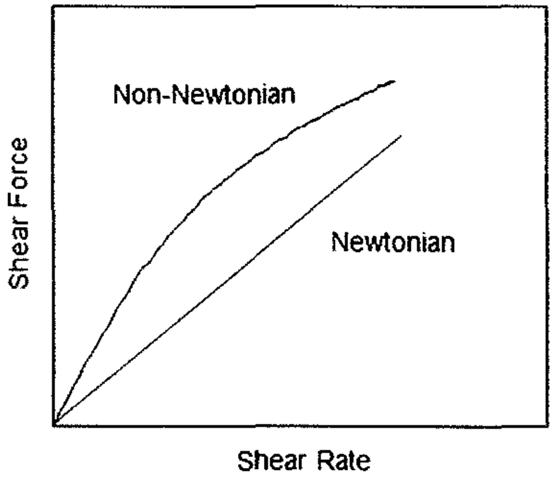


Figure 2.2: Schematic plots of shear force vs. shear rate for Newtonian and non-Newtonian fluids

In these equations, η is solution viscosity, η_0 is viscosity of the pure solvent, and c is concentration.

Relative viscosity is simply the ratio of the polymer solution viscosity to the viscosity of pure solvent. Specific viscosity expresses the incremental viscosity due to the presence of the polymer in the solution. Normalizing η_{sp} to concentration gives η_{sp}/c which expresses the capacity of a polymer to cause the solution viscosity to increase; i.e. the incremental viscosity per unit concentration of polymer. As with other polymer solution properties, the solutions used for viscosity measurements will be non-ideal and therefore η_{sp}/c will depend on c. As with osmotic pressure, it will probably be useful to extrapolate to zero concentration. The extrapolated value of η_{sp}/c at zero concentration is known as the intrinsic viscosity, $[\eta]$. In general, the intrinsic viscosity of linear macromolecular substances is related to the molecular weight or degree of polymerization. With linear macromolecules, viscosity number measurements can provide a method for the rapid determination of molecular weight when the relationship between viscosity and molecular weight has been established.

The remaining form for the viscosity is the inherent viscosity. Like η_{sp}, ln η_r is zero for pure solvent and increases with increasing concentration, thus ln η_r also expresses the *incremental viscosity due to the presence of the polymer in the solution.* Normalizing ln η_r to concentration or ln η_r/c gives the inherent viscosity In the limit of zero concentration, η_i extrapolates the same as η_{sp}/c and becomes equal to the intrinsic viscosity. This can be proved by:

$$\lim_{c\to 0}\frac{\ln n_r}{c} = \lim_{c\to 0}\frac{\ln(1+\eta_{sp})}{c} = \lim_{c\to 0}\frac{\eta_{sp}}{c} = [\eta]$$

We can thus find $[\eta]$ be extrapolating either η_{sp}/c or η_i to zero concentration. When c is not equal to zero the specific viscosity and inherent viscosities will be different, even for an ideal solution. In ideal solutions η_{sp}/c will be independent of concentration, but n_i will depend on concentration.

2.4 Measurement of Viscosity

The *instruments for viscosity measurements* are designed to determine "a fluid's resistance to flow," a fluid property defined above as viscosity. The fluid flow in a given instrument geometry defines the strain rates, and the corresponding stresses are the measure of resistance to flow. If strain rate or stress is set and controlled, then the *other one will, everything else being the same, depend on the fluid viscosity. If the flow* is simple (one dimensional, if possible) such that the strain rate and stress can be determined accurately from the measured quantities, the absolute dynamic viscosity can be determined; otherwise, the relative viscosity will be established. For example, the *fluid flow can be set by dragging fluid with a sliding or rotating surface, falling body* through the fluid, or by forcing the fluid (by external pressure or gravity) to flow through a fixed geometry, such as a capillary tube, annulus, a slit (between two parallel plates), or orifice. The corresponding resistance to flow is measured as the boundary force or torque, or pressure drop. The flow rate or efflux time represents the fluid flow for a set flow resistance, like pressure drop or gravity force. The viscometers are classified, depending on how the flow is initiated or maintained (Whorlow 1992).

The basic principle of all viscometers is to provide as simple flow kinematics as possible, preferably one-dimensional (isometric) flow, in order to determine the shear strain rate accurately, easily, and independent of fluid type. The resistance to such flow is measured, and thereby the shearing stress is determined. The shear viscosity is then easily found as the ratio between the shearing stress and the corresponding shear strain rate.

2.5 Types of Rheological Behaviour in Simple Shear

In order to analyse the results obtained from the experiment, it is often necessary to make assumptions about general nature of the rheological properties of the material being tested. As a matter of fact, some mathematical fluid model will be presented in restricted form, as relationships between shear stress, τ , and shear rate, $\dot{\gamma}$, in simple shear flow (Whorlow, 1992).

Newtonian Fluid Model

A Newtonian fluid is a fluid whose stress versus strain rate curve is linear and passes through the origin. The constant of proportionality is known as the viscosity. A simple equation to describe Newtonian fluid behaviour is,

$$\tau = \mu \frac{du}{dy}$$

where τ is the shear stress, μ is the fluid viscosity and $\frac{du}{dy}$ is velocity gradient perpendicular to the direction of shear. Types of Newtonian fluids include all gases, all liquids having simple chemical bonds such as water, alcohols and organic solvents, and most dilute solution of simple molecules like aqueous solution of metal ions and sugar in water.

Bingham Model

A Bingham plastic is a viscoplastic material that behaves as a rigid body at low stresses but flows as a viscous fluid at high stresses. It is used as a common mathematical model of mud flow in offshore engineering, and in the handling of slurries. A common example is toothpaste which will not be extruded until a certain pressure is applied to the tube. It then is pushed out as a solid plug.

The stress that a particular fluid needs to overcome in order to flow is called yield stress, σ_0. The Bingham fluid model is defined as:

$$\sigma = \sigma_0 + k\dot{\gamma}$$

Where k is called the plastic viscosity and equal to the slope of the flow curve, $\dot{\gamma}$ is shear rate andσ_0 can be determined through the y-intercept.

Power Law Fluid Model (or Ostwald-de Waele Model)

A Power-law fluid, or the Ostwald–de Waele relationship, is a type of generalized Newtonian fluid for which the shear stress, τ, is given by

$$\tau = k\left(\frac{\delta u}{\delta y}\right)^n$$

Where k is the flow consistency index ($Pa\cdot s^n$), $\partial u/\partial y$ is the shear rate or the velocity gradient perpendicular to the plane of shear (s^{-1}), and n is the flow behaviour index (dimensionless).

Also known as the Ostwald–de Waele Power Law this mathematical relationship is useful because of its simplicity, but only approximately describes the behaviour of a real non-Newtonian fluid. For example, if n were less than one, the power law predicts that the effective viscosity would decrease with increasing shear rate indefinitely, requiring a fluid with infinite viscosity at rest and zero viscosity as the shear rate approaches infinity, but a real fluid has both a minimum and a maximum effective viscosity that depend on the physical chemistry at the molecular level. Therefore, the power law is only a good description of fluid behaviour across the range of shear rates to which the coefficients were fitted.

There are a number of other models that better describe the entire flow behaviour of shear-dependent fluids, but they do so at the expense of simplicity, so the power law is still used to describe fluid behaviour, permit mathematical predictions, and correlate experimental data.

Figure 3 shows a typical behaviour of fluids based on the model used.

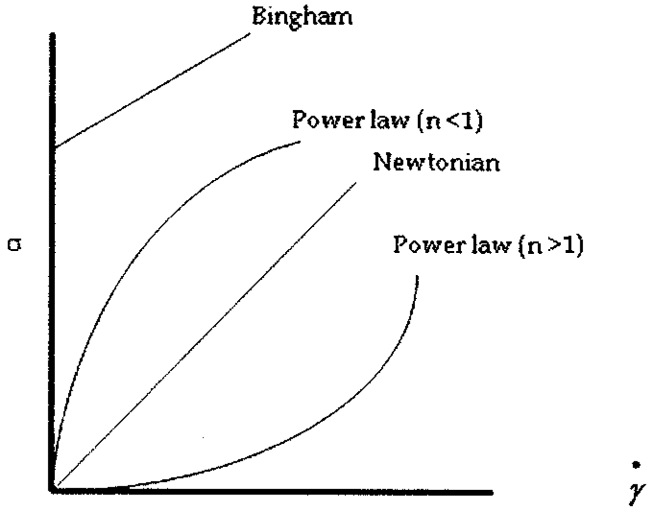


Figure 2.3: Typical curve for the fluid model used.

2.6 Effect of Drag Reducing Agents

One of the more intriguing advances in single-phase turbulence is the finding that the introduction of small amounts of long-chain polymers into a liquid flow can cause large decreases in the frictional resistance at the wall (Toms, 1948). Recent studies with laser Doppler velocimetry (Harder; Wei and Warholic) have revealed how the turbulence properties differ from those of the solvent. Warholic and Hanratty (1999) used a solution of a co-polymer of PAM and sodium-acrylate in water. The authors realized significant drag-reduction with a concentration as low as 0.25 ppm.

Studies of the effect of the drag-reducing polymer on frictional losses have been made by Rosehart et al. (1972) and by Otten and Fayed (1976) for bubbly and plug flows. Kang et al. (1997) studied the influence of an additive (which is not identified) on three-phase flow (oil, water and carbon dioxide). They found a drag-reduction of 35% at the two highest superficial gas velocities that were studied, U_{sg}=13, 14 m/s.

2.7 Previous Study of Polyacrylamide

A number of rheological studies on PAM have been carried out under different conditions. In the pulp and paper industry, PAM has been used to maintain the efficiency of operation and quality of products. It is effective in increasing fibre bonding and in improving dry strength, filler retention, rosin sizing, and drainage rate. It has been used in many additional applications including water treatment, mineral processing, dust control, and sugar manufacturing. PAM is one of the best polymers used as a DRA and a vortex inhibitor due to its flexibility and long chain. The drag reduction is defined by the reduction in pressure drop in the polymer solution relative to the pure solvent alone at the same flow rate. Drust et al. (1982) and Bewer (1982) who reported that PAM could be used as a drag reduction polymer have confirmed this point.

Kadi et al. (1987) have carried out an experimental study to investigate the rheological properties of partially hydrolyzed polyacrylamide (PHPAM) solutions and reported that the salt had a stabilizing effect on the viscosity levels and less viscosity. This shear thinning effect is behaviour characterized by lower as salt concentration is increased. Lakatos et al. (1995) have studied the effect of carbon dioxide ($C0_2$) on the rheological properties and structure of PAM solutions with the aim of using them in enhanced oil recovery. They concluded that high molecular weight non-hydrolysed or slightly (5-10%) hydrolysed PAM must be used in order for the polymer to contact with $C0_2$.

Hisham and Kevin (1993) have studied the interfacial behaviour of crude oil and alkali systems in the presence of PHPAM and reported that, at sodium carbonate concentrations less than 0.2 mass %, the dynamic interfacial tension (IFT) of crude oil/alkali systems did not change with respect to time. Increasing polymer concentration in this alkali concentration range caused a slight drop in IFT. At sodium carbonate concentrations equal to 0.2 mass %, addition of polymer up to 2000 ppm had no significant effect on the minimum IFT. However, the time required to reach a minimum IFT substantially increased with polymer concentration. At sodium carbonate concentrations greater than 0.2 mass %, addition of polymer resulted in lowering of the minimum IFT and long term (2 h) IFT values. Again, the time to reach the minimum IFT significantly increased with polymer concentration.

Sodium carbonate further hydrolysed partially hydrolysed polyacrylamide. This hydrolysis caused the apparent viscosity to increase with time, especially at 60°C. Such a change in viscosity should be considered when evaluating the effect of the aqueous phase viscosity on dynamic IFT.

Temperature has a significant effect towards viscosity since the molecular structure of the polymer will behave differently as temperature increases or reduces. At low shear rates, Sehyun et. al. (1993) found out that the aqueous PHPAM solution was very sensitive to the temperature, whereas at higher shear rates, the viscosity dependence on temperature is almost negligible. On the contrary, Esmail et. al (1997) discovered that higher shear rates causes a much pronounced effect as viscosity decreases with temperature.

Dupuis et al (1994) demonstrated the rheological properties of solutions of high molecular weight PHPAM in mixtures of glycerol and water. The author concluded that its viscosity depends on time and displays a transient regime with strong instabilities followed by a steady state. The non-Newtonian viscosity of these solutions was affected by *time and showed slight shear thickening.*

Yang (1999) studied the rheology behaviour of PHPAM as a function of temperature and concentration over a range of the temperature range 20 to 50°C and concentration range 20 to 50 ppm, using a coaxial cylinder viscometer. The author founded that the shear stress increased with an increase shear rate. The shear stress also increased with an increase concentration and the shear stress decreased with an increase temperature. The shear stress was found to be a highly nonlinear function of the shear rate in the temperature range 20~50°C and concentration range 20~50 ppm.

Garvin et. al. (1970) used a pipe rheometer to determine fluid properties from lower laminar flow to fully turbulent flow with temperatures up to 180°C. Water-based drilling fluids were used as the testing fluid and concluded that the Bingham Plastic model gave a reasonable fit with the model in laminar flow, but data started to diverge under transition flow. They also concluded that plastic viscosity decreases with increasing temperature, yield point may increase or decrease with increasing temperature depending upon the solid content of the fluid, power law index (n) decreases with increasing temperature and consistency index (K) increases with increasing temperature.

Mordie et.al., (1975) used a BHC viscometer to determine the viscosity of the oil based muds at temperature up to 350°C and pressure up to 140 MPa and temperature interval of 20°C - 200°C under laboratory conditions. They concluded that the change in density of the drilling fluids is independent of its initial density; and oil based drilling fluids become denser at high pressure and temperature due to greater compressibility compared to water-base drilling fluids.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Research Methodology

The project involves experimental and modelling work. The rheological properties of the partially hydrolysed polyacrylamide (PHPAM) solution are to be investigated through the use of a Brookfield cap 2000+ viscometer. Through the variations of temperature and shear rate, as well as the solution diluted concentrations, the parameters such as shear stresses, shear rates and viscosities will be tabulated graphically. From this raw data, various viscosity models will be investigated accordingly in order to determine the appropriate type of model PHPAM falls under. Hence, the consistency index, *k* and the power law index, *n* will allow the interpretation the Newtonian or non-Newtonian behaviour of the solution at the elevated temperature.

The rheological study for the polymer solution is performed using the Brookfield cap 2000+ viscometer. It is semi-automated system which can accurately determines the rheological properties of fluids and drilling fluids in terms of shear stress, and shear rate, at temperature up to 235°C.

Figure 3.1 shows the Brookfield cap 2000+ viscometer.

Figure 3.1: Brookfield cap 2000+ viscometer

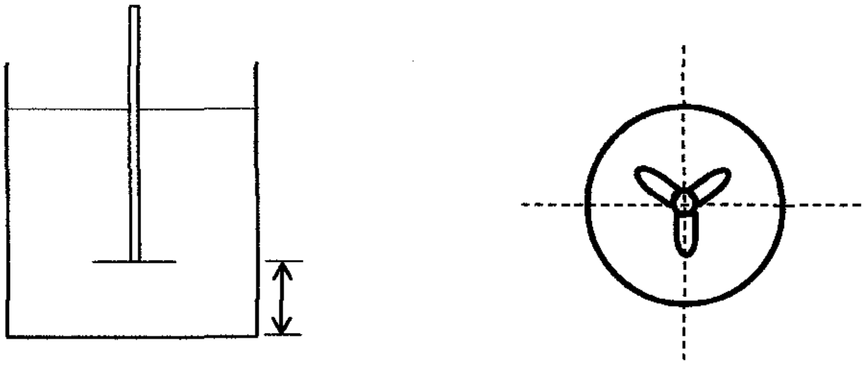
Minimums of three repetitions are performed at all measurements to increase reproducibility of the data.

3.2 Polymer solution preparation method.

In this study, the type of polymer used is a poly(acrylamide-co-sodium acrylate) with a trade name of ZETAG 4120, bought from BASF Chemical Company. It is also commonly called partially hydrolysed polyacrylamide (HPAM). The molecular weight of this polymer is unknown but it is assumed to be in the range of 10 – 15 x 10^6 g/mol.

The polymer solutions are prepared extensively in this experiment. In the preparation phase, polymers in powder form are used. In order to prepare the master solution (500ppm), a ratio between the volume of water (in litres) to the mass of the polymer powder (in grams) is used based on the concentration. As of 500ppm solution, 5.00g of polymer will be dissolved in 10.0L of deionized water. Deionized water is utilised as the solvent to avoid any impurities and dissolved metal ions that could react and retard the solutions and the process.

The polymer powder is sprinkled to the bottom of an empty tank. Then deionized water is poured into the tank, allowing the polymer to be dispersed naturally. The solutions are mixed in an un-baffled, flat bottom tank and stirred using 3 blade propeller (marine propeller) for approximately 2 hours at 50 RPM. The slow speed stirring is applied to reduce the effect of high shear rate that would degrade the polymer solutions. The impeller was positioned at the center, height of 1/3 from the bottom of the tank based on the total height of water, as shown in figure 3.2 below.



(a) Side view

(b) Top view

Figure 3.2: Position of the impeller

After 2 hours of stirring, the solution is rested at room temperature for 24hours period for hydration to occur. For this experiment, 10.0L of 500ppm polymer solutions are prepared repeatedly.

The solution is further diluted into different concentrations ranging from 10ppm to 50ppm by drawing out equivalent amount from the master solution. On this matter, the master solution is scooped using a beaker while the volume is measured using a graduated cylinder, instead of being pipetted out. This is to avoid the master solution from being pre-sheared prior to viscosity study which otherwise would affect the overall results. The solution is then dissolved with deionized water in a volumetric flask.

In order to perform the reading, the diluted solution is further kept for 24hours for hydration to occur. The schematic diagram of the preparation method is shown in Figure 3.3.

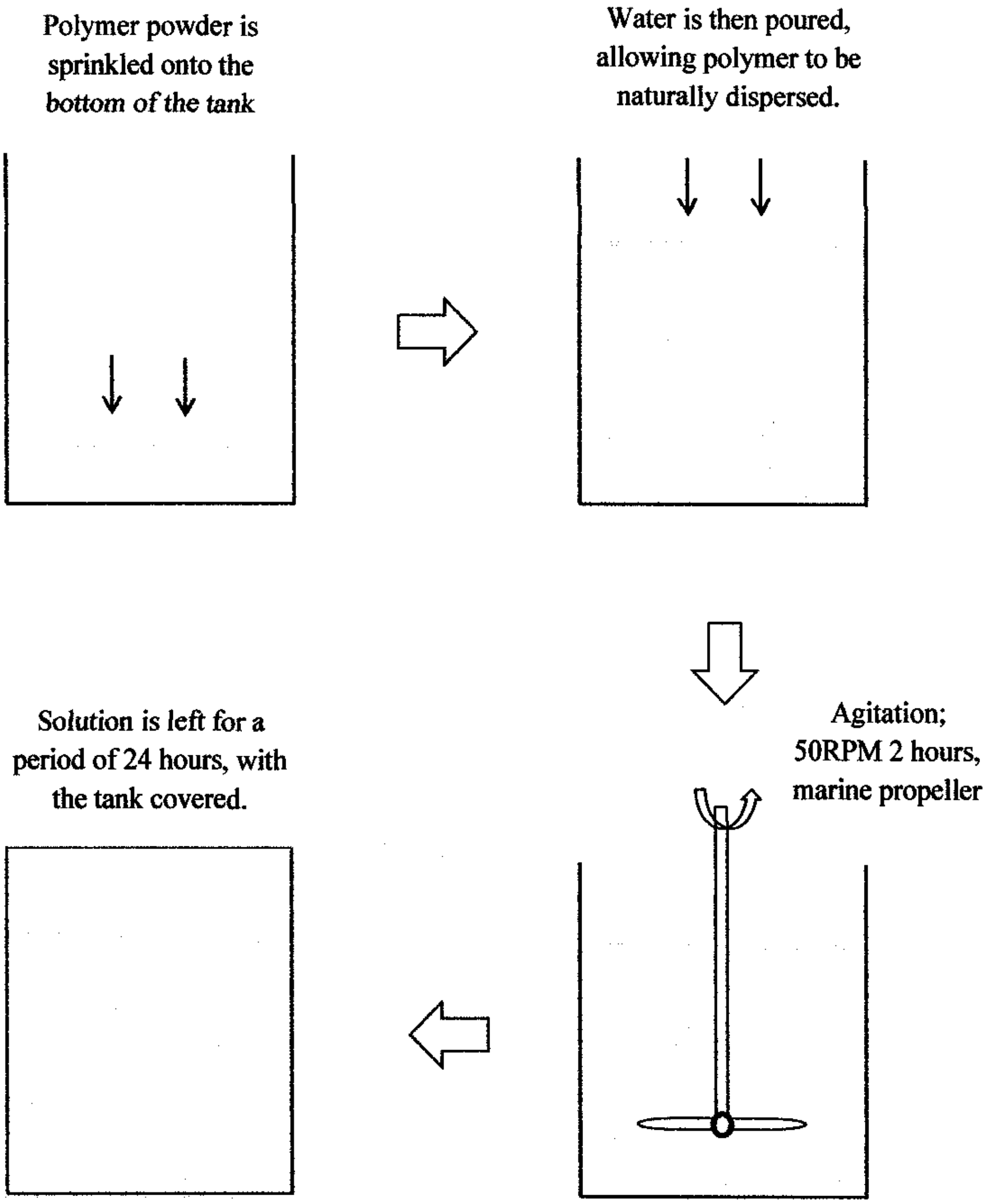


Figure 3.3: Preparation diagram

3.3 Study on the rheology of the polymer solution

After 24hours of hydration period, the master solution is measured by the viscometer. The solution is tested at various shear rates ranging from 100 – 3000 1/sec at two designated temperature (80°C and 100°C). The same procedure is applied to the diluted solution. After 24hours of hydration period, the dilute solution is tested. Reading is collected and the expected graph and calculated data will conclude this experiment.

The polymer solutions are tested in 2 different methods. In all techniques, the same viscometer is used which is Brookfield cap 2000+ viscometer. The methods are outlined as follows:

Method 1

In this method, the HPAM solution has been dropped on the viscometer plate and tested for a particular temperature and shear rate. To test in another shear rate and temperature, different HPAM solution has been dropped on the plate. This is happening continuously until the viscosity at each tested shear rate has been completed. The results will be *discussed on the next section.*

Method 2

In this method, the principle is to use the same polymer solution at all the reading. In the beginning, a first drop of polymer solution is tested at the lowest shear rate. By using the same tested solution, the polymer solution is further tested up to the maximum desired shear rate.

The diagram and analysis of this method is shown in the next page.

3.4 Work Breakdown

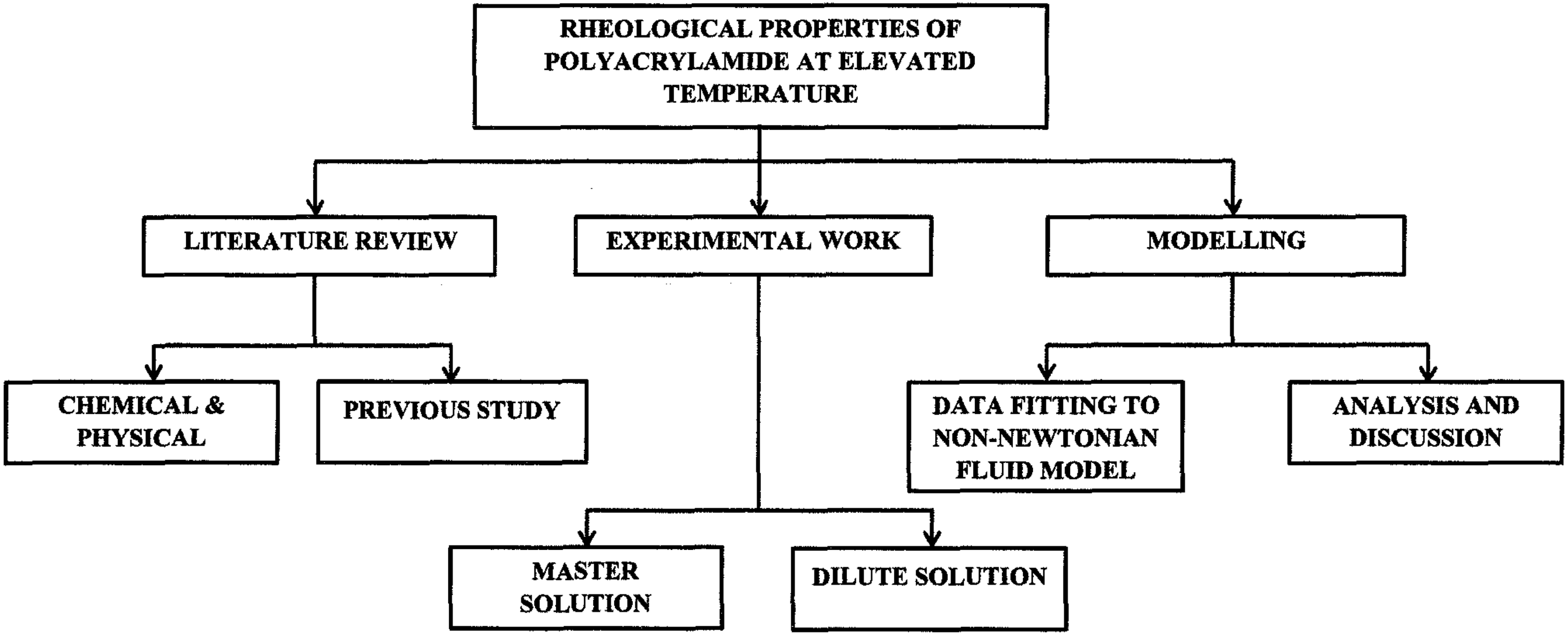


Figure 3.4: Work breakdown structure

3.5 Milestone

Key Milestone and Gantt chart for Final Year Project I

Table 3.1: FYP 1 Milestone

No.	Activities /Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Planning	🟩													
2	Preliminary Research Work		🟩	🟩	🟩	🟩									
3	Extended Proposal Submission						🟪								
4	Study on Rheological Behavior of Fluid						🟩	🟩	🟩						
5	Study on Apparatus to be Used in the experiment							🟩	🟩						
6	Study on Polymer Preparation							🟩	🟩	🟩	🟩				
7	Proposal Defense Presentation									🟪					
8	Studies on the Data Required									🟩	🟩	🟩	🟩	🟩	
9	Submission of the Interim Report														🟪

🟪 Key Milestone

🟩 Process

Key Milestone and Gantt chart for Final Year Project II

Table 3.2: FYP 2 Milestone

No	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project Work Continues	🟩	🟩	🟩	🟩	🟩	🟩	🟩	**Mid-Semester Break**							
2	Progress Report Submission									🟪						
3	Project Work Continues									🟩	🟩	🟩	🟩			
4	Pre- EDX											🟪				
5	Draft Report Submission												🟪			
6	Dissertation Submission (soft copy)													🟪		
7	Submission of Technical Paper													🟪		
8	Oral Presentation														🟪	
9	Project Dissertation Submission (hardbound)															🟪

🟩 Process 🟪 Key Milestone

CHAPTER 4

RESULT AND DISCUSSION

4.1 Result and Discussion

The contact between the polymer and the deionized water can be increased by increasing the surface area. The idea why the polymer powder is sprinkled first at the bottom of the tank and continues with pouring the water into the tank is to increase the associations between the molecules. This process is achieved by creating a momentum effect through the force during the addition of water into the tank. When the water is poured into the tank, potential energy of water will create a force when it strikes the bottom of the tank. This force will lift the powders, and encouraged wetting of individual particles. Layer of polymer is ensured to be as thin as possible to avoid any entanglements occurs and might affect the performance of the result.

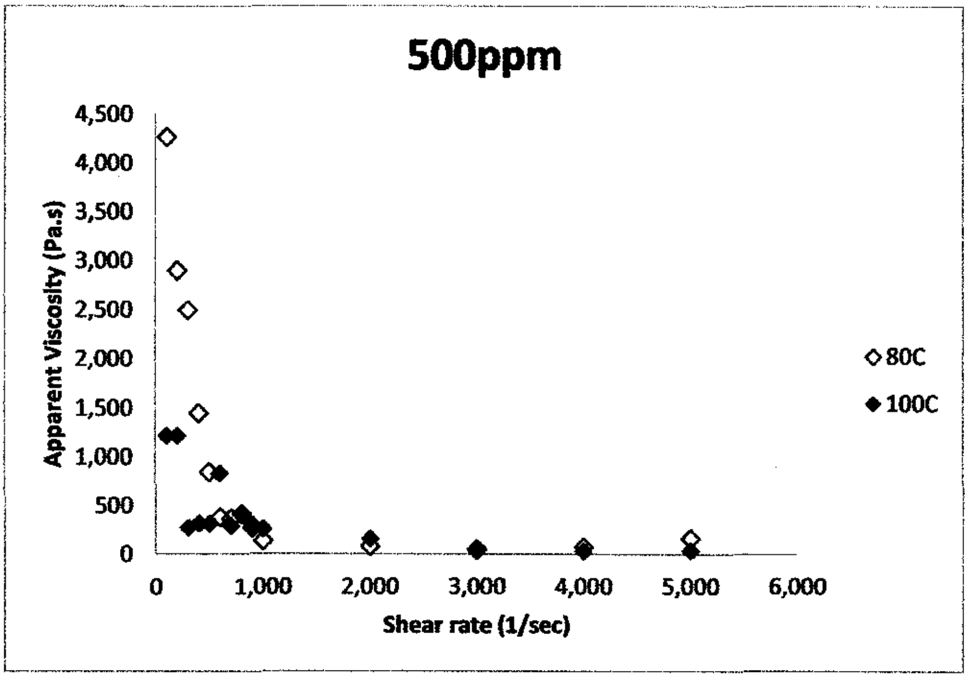


Figure 4.1: Apparent viscosity vs. shear rate for polymer master solution of 500 ppm prepared by method 1.

Figure 4.1 shows the apparent viscosity vs shear rate for polymer master solution (500ppm) prepared by method 1. It can be seen that the graph is not well developed. It is because the polymer solution is sheared with different shear rate for different drop of polymer. The solution will experience the different forces for every test. As a result, the viscosity reading would be inconsistent and the K and n value calculation cannot be calculated accurately.

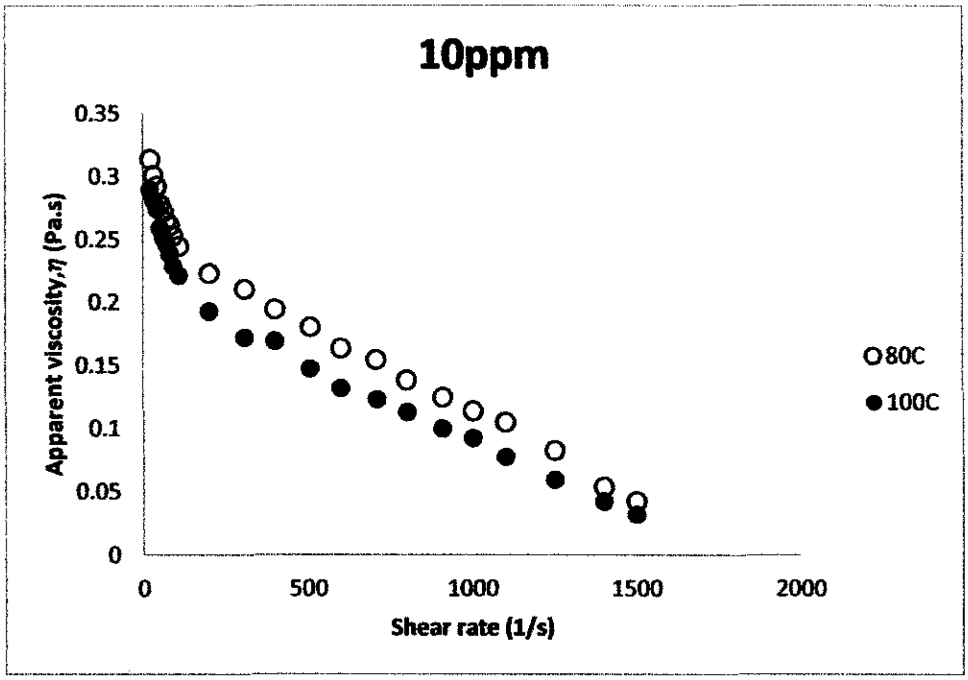


Figure 4.2: Apparent viscosity vs. shear rate for polymer master solution of 10 ppm prepared by method 2.

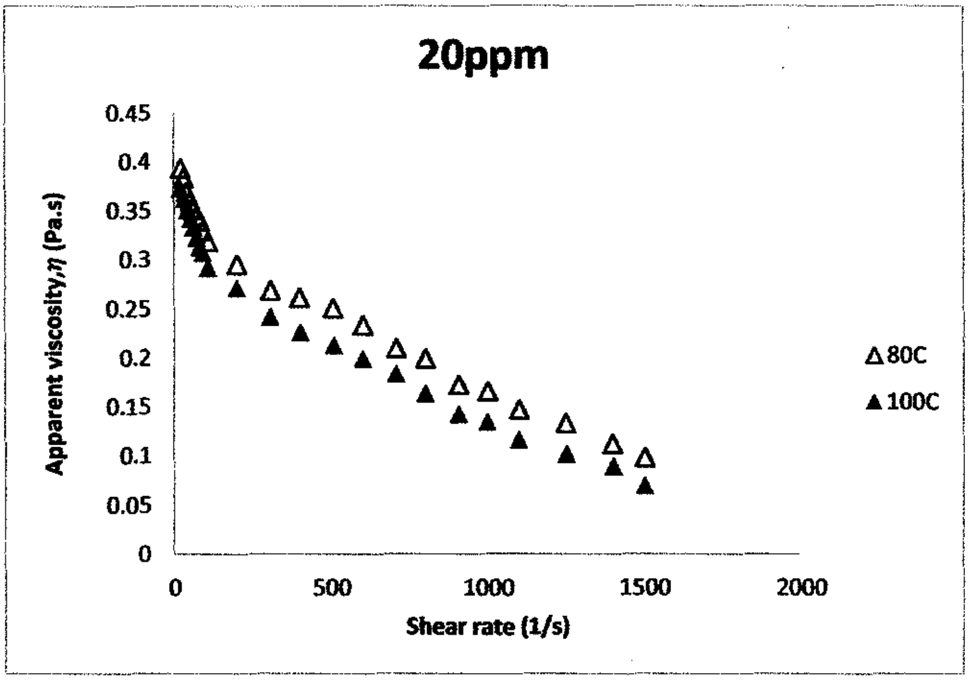


Figure 4.3: Apparent viscosity vs. shear rate for polymer master solution of 20 ppm prepared by method 2.

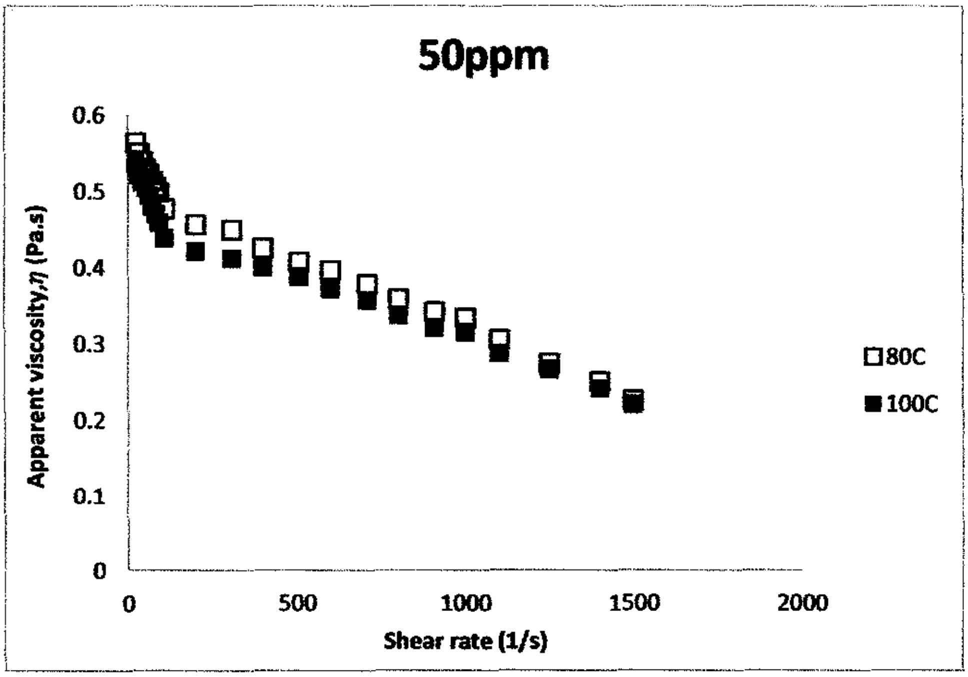


Figure 4.4: Apparent viscosity vs. shear rate for polymer master solution of 50 ppm prepared by method 2.

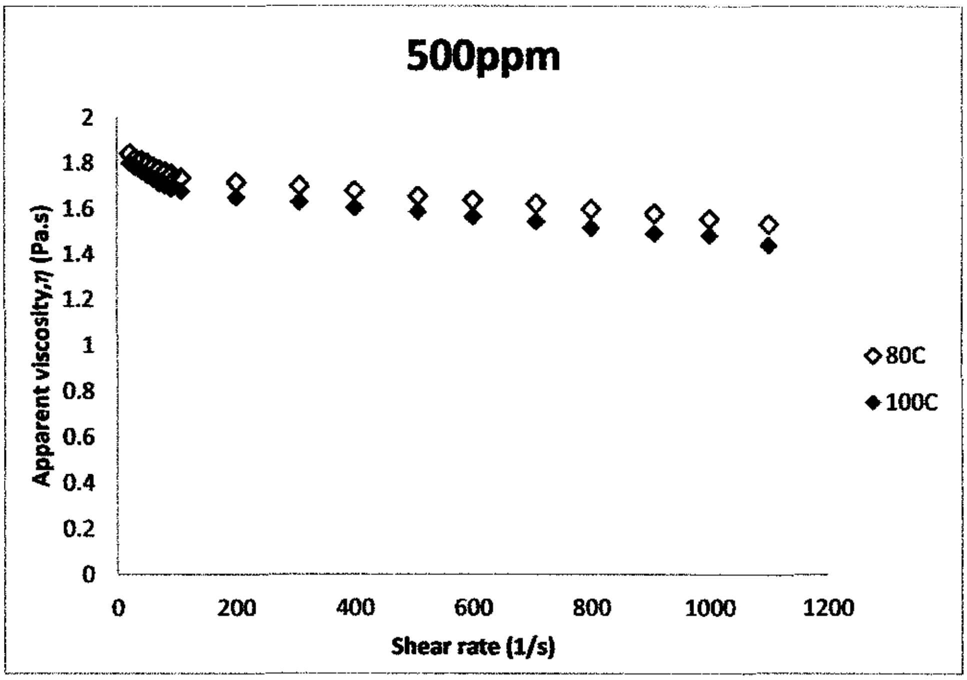


Figure 4.5: Apparent viscosity vs. shear rate for polymer master solution of 500 ppm prepared by method 2.

Figure 4.2 – 4.5 shows the viscosity behavior of polymer solutions at different concentration and temperature. All solutions show shear-thinning behavior with decreasing of apparent viscosity at increasing shear rates. In other word, viscosity increases as the concentration of polymer solution increases.

The trend seems very similar with the founding of Rabiee et. al (2005) who studied the viscosity behaviour of HPAM at various degree of hydrolysis (0-60%). The authors discussed that the polymer solutions show non-Newtonian shear thinning behaviour within the experimental range of shear stress. The elevated temperature seems to be not affecting the viscosity behaviour of the polymer solution that much for this range of polymer concentration and temperature.

The flow curves showed the apparent viscosity decreases with increasing the shear rate of solutions. They claimed that the reduction in viscosity as shear rate increases is an indication of the fact that electrostatic interactions between the particles are surpassed by viscous forces applied to the solutions. As a result, at high shear rate the polymer chains are aligned in the direction of flow that results in viscosity reduction or shear-thinning behaviour.

Lewandowska (2006) who uses PAM and HPAM with degree of hydrolysis varying from 1.5 to 80%, also mentioned that the decrease of the viscosity with shear rate (shear thinning behaviour) is mainly related to the orientation of macromolecules along the streamline of the flow and to the disentanglement of macromolecules with the increasing shear force.

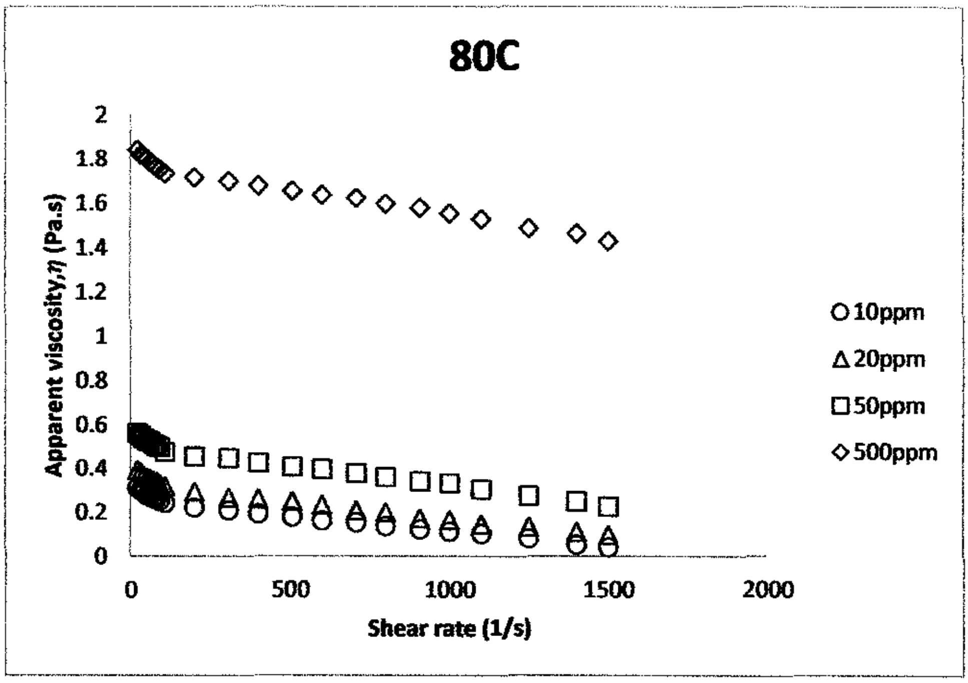


Figure 4.6: Apparent viscosity vs. shear rate for polymer master solution of at 80°C.

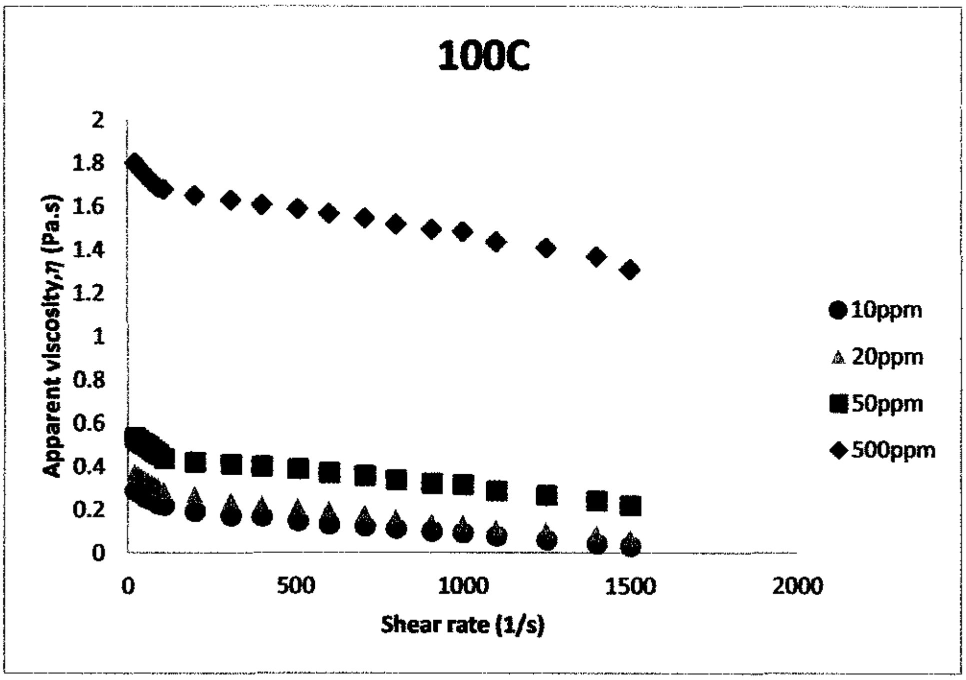


Figure 4.7: Apparent viscosity vs. shear rate for polymer master solution of at 100°C.

Figure 4.6 and 4.7 gives a brief comparison of polymer solution at difference concentration within constant temperature (80°C and 100°C). It can be seen that at very low concentration (10 and 20 ppm), this elevated temperature does not give a huge difference in term of the viscosity behavior of polymer solution. This is mainly because the polymer solution is a very dilute solution and has not much difference with the properties of plain water. At this level, the polymer solutions only can stand up to 100°C and cannot be tested at higher temperature within this range of normal pressure. This is because the diluted solution tends to evaporate and will affect the reading during the experiment. In order to test it at higher temperature, another parameter should be taken into consideration such as increasing the pressure.

Table 4.1: Consistency index, K and power law index, n value for HPAM solution at different concentration and different temperature.

Polymer Concentration	Temperature	Range of shear rate (1/s)	n	k (Pa.s)
HPAM 10ppm	80°C	20 - 107	0.8513	0.4975
		107 - 1000	0.6657	1.317
		1000 - 1500	-1.4933	3799269
	100°C	20 - 107	0.8349	0.4901
		107 - 1000	0.6147	1.4942
		1000 - 1500	-1.5669	4889900
HPAM 20ppm	80°C	20 - 107	0.8754	0.5814
		107 - 1000	0.7156	1.3289
		1000 - 1500	-0.235	850.75
	100°C	20 - 107	0.8561	0.5894
		107 - 1000	0.6604	1.6081
		1000 - 1500	-0.4588	3248.63
HPAM 50ppm	80°C	20 - 107	0.9078	0.7533
		107 - 1000	0.8376	1.0809
		1000 - 1500	0.0814	190.63
	100°C	20 - 107	0.8862	0.771
		107 - 1000	0.8511	1.07374
		1000 - 1500	0.1669	99.54
HPAM 500ppm	80°C	20 - 107	0.9652	2.0531
		107 - 1000	0.9516	2.2151
		1000 - 1500	0.8003	6.183
	100°C	20 - 107	0.9551	2.0759
		107 - 1000	0.9432	2.2289
		1000 - 1500	0.7251	9.9038

The fluid model is used to determine the behavior of the solution. In this case the Ostwald-de Waele model is utilized and based on best point fitting on the flow curve, the parameters, such as the consistency index, *K* and power law index, *n* is calculated. Table 4 summarized the values obtained for the solution.

Consistency index values describe the overall range of viscosities across the part of the flow curve that is being investigated. From the table 4.1, it can be seen that K values increases as concentration of solution increases. This shows that polymer become more viscous as it is more concentrated.

The value of power law index, n shows whether the polymer solution is exhibit either shear-thinning or shear-thickening behavior. For a shear thinning fluid: n<1. The more shear-thinning the product, the closer n is to zero and vice versa. Overall the polymer solution exhibits a shear-thinning behaviour since the values in less than 1.

4.3 Constraint

Upon the completion of the project, there are lots of constraints to be addressed. The major one is the availability and ability of equipment. As this project is expected to yield a huge contribution to the polymer study, the equipment shows a bit upset to the outcome of this project. Using OFITE high temperature high pressure viscometer, the result yields a negative shear stress which is an unacceptable result. From the high temperature and high pressure effect to the polymer solution, the project changes to be focused on the certain elevated temperature only as the equipment gives the unreasonable results.

By utilising Brookfield cap 2000+ viscometer, result for both designated temperature is as expected. However, the viscometer can only read the viscosity with the range of 100 1/sec to 13000 1/sec. To get a better result for *K* and *n* value, it is required to do the experiment at a very low shear rate as low as 0.1 1/sec. this viscometer also perceive inconsistence reading as in order to get a better result, lots of repetition has been applied for each test.

CHAPTER 5

CONCLUSION

5.1 Conclusion

The aim of this study is to investigate the rheological properties of PHPAM at elevated temperature. The solution is studied at 500 ppm master solution and is further diluted into different concentrations ranging from 10 ppm to 50 ppm. The methodology and step to analyse all the data has been finalised.

It is found that through Method 1, viscosity behaviour of the polymer solution shows an inconsistent reading throughout the experiment. This is because the different shear force that has been load toward the different sample. The consistency of the viscosity in the solutions is shown by Method 2. The more concentrated polymer solutions shows greater viscosity compared to the dilute solution within this range of temperature and concentration.

All solutions show shear-thinning behavior with decreasing of apparent viscosity at increasing shear rates. In other word, viscosity increases as the concentration of polymer solution increases. The flow curves showed the apparent viscosity decreases with increasing the shear rate of solutions. The elevated temperature does not show a huge impact toward the diluted concentration because the polymer solutions are tend to exhibit the water viscosity behaviour.

5.2 Recommendation

Due to time constraint, the experimental scope has been reduced. To get a wide range and more meaningful data, the concentration of master solution should be varied. A large range of temperature and pressure should be applied to the experimental procedure in order to understand the flow behaviour of PHPAM in details. As the preparation of solution will affect the result of experiment, the author should focus on the preparation method and apparatus standard.

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