

# **Study on the Polymer Solution Strength through the Modulus Behaviour**

By

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Dissertation submitted in partial fulfillment of  
the requirements for the  
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CERTIFICATION OF APPROVAL

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Approved by,

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TRONOH, PERAK

August 2013

## 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.

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(MUHAMMAD HANIF BIN KHALIL)

## **ABSTRACT**

For many years, rheology has been used as semi-quantitative tools in polymer science and engineering. Rheology is the study of deformation and flow of matter under stress. The aspect involves in rheological study are yield stress, viscoelastic effects, memory effects, and shear thickening and thinning. The rheology for simple fluid involves the measurement of viscosity whereby it depends primarily upon the temperature and hydrostatic pressure. Polymer is much complex because polymeric fluids show non-ideal and complex shear viscosity behaviour. The previous work is concerned with experimental result of rheological properties of partially hydrolyzed polyacrylamide(HPAM) in aqueous with different experimental condition such as polymer concentration, temperature and shear rate applied. For further improvement, the rheological properties of partially hydrolyzed polyacrylamide is studied with different concentration varied from lower to an extreme concentration under normal room temperature focused on the storage and loss modulus of the polymer solution.

Chapter 1 give an introduction on the background of the project where the problem statement addressing the main purpose and significance of this research, as well as its objective and scope of study will be presented. A brief literature review illustrating some previous researches regarding rheology of polymer solutions, as well as the concept and underlying principles of the project will be explained in chapter 2. Finally in the last chapter, the research methodology showing the experimental approach as well as the key milestones will be presented to give an overview of the entire research project.

## **ACKNOWLEDGEMENT**

In the name of ALLAH S.W.T, the most merciful and compassionate, praise to Allah, He is The Almighty, eternal blessing and peace upon the glory of the universe, Prophet Muhammad S.A.W, and his family and companions.

The author wish to express his appreciation and gratitude towards his project supervisor, Mr. Mohd Zamri Bin Abdullah for all his assistance, guidance and encouragement throughout the course of this project work. His support and supervision have helped the author in completing the project smoothly.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Background study

Global market on polymer product is increasing nowadays. Polymer is very useful and have many applications. In order to compete with the demand, the need to produce a very good polymer product is very severe. A polymer is a chemical compound or mixture of compounds consisting of repeating structural units created through a process of polymerization. The structure of a polymer is composed of multiple repeating units, from which originates a characteristic of high and low relative molecular mass. In the solid state, polymer molecules pack the space with little voids either in a regular array or at random which form the crystalline and the amorphous structure. In solutions, in contrast each polymer molecules is surrounded by solvent molecules. For polymer solutions, the monomer and the polymer are all soluble in the solvent. The solvent molecules surround all parts of the chains as the polymer chain form. A polymer solution exhibit different behaviour from that of a typical polymer. In the industry, different properties are required for certain processes. The knowledge on rheology is extremely important for polymers, since the flow behaviour is important for the design, selection, and operation involved handling, mixing, pumping, storage, and transportation process.

For example, partially hydrolyzed polyacrylamide are widely used in many applications such as municipal and industrial waste water treatment, mineral floatation, paper making, oil and coal refineries, enhanced oil recoveries and emulsion polymerization reaction which require certain properties of the polymer solution in each application[3].

Relative to the uses of polymer solutions, its behaviour is being investigated or studied further. Researches have been widely done on the behaviour of polymer strength and how it is affected.

## **1.2 Problem statement**

Due to the vast range of polymers available, specific researches have to be done to address to certain polymer. The study on the polymer solution strength through the modulus behaviour implies on how the strength of the polymer solution is affected through the implication of the shear and elastic moduli. Shear modulus is one of the quantities for measuring the stiffness of materials by its response to shear strain and the elastic modulus is a measure of a substance's tendency to be deformed elastically. The flow behaviour of polymer solution is dependent on the strength of the polymer solution and the strength is thus implied by the shear and elastic moduli. Previous studies has investigate on the viscosity of polymer solutions and a correlation has been proposed to predict the viscosity of a polymer solution as a function of temperature, shear rate, and concentration [8]. However, how the strength of polymer solutions is reflected by the modulus behaviour has not yet been thoroughly investigated and thus this project is to study on how does the modulus behaviour affects on the polymer strength. Clarification on this matter is important as polymer have wide application in industries and the needs of different behaviour of polymer solution for different type of processes is crucial. By understanding the modulus behaviour and how it affect the strength of polymer solution, one can predict the behaviour or properties of polymer solutions as it is important for the design, selection, and operation involved in handling, mixing, pumping, storage, and transportation processes.

## **1.3 Objective**

The objective of this project is to investigate the properties or the behaviour of the polymer solutions of water-soluble partially hydrolyzed polyacrylamide (HPAM). The property to be studied in particular is its viscoelasticity i.e. mainly on the elastic and the shear moduli which relates to the strength of the polymer. Various polymer solution concentrations will be varied and the modulus profile will be analyzed accordingly.

#### **1.4 Scope of study**

The project involves experimental work, by which the viscoelastic properties of the water-soluble partially hydrolyzed polyacrylamide will be investigated in particular. The elastic and the shear modulus of the water-soluble polymer solution which relates to the strength of the polymer will be analyzed thoroughly. The behaviour of the water-soluble partially hydrolyzed polyacrylamide is also investigated under different concentration at normal room temperature.

## **CHAPTER 2**

### **LITERATURE REVIEW**

The properties or rheology of a polymer solution is very important as it reflect on the behaviour of the polymer solution itself. Rheology is the study of the flow of matter, primarily in the liquid state, but also as ‘soft solid’ under condition in which they respond with plastic flow rather than deforming elastically in response to the applied force. For many years, rheology has been used as semi-quantitative tools in polymer science and engineering. The relationship between the structure and rheology of a polymer is of practical for two reasons: (1) rheological properties are very sensitive to certain aspect of structure and they are simpler to use than analytical methods, (2) it is the rheological properties that govern the flow behaviour of polymer when they are processed in the molten state. Rheology study mainly focuses on several aspects, which is yield stresses, viscoelastic effects, memory effects, shear thickening and shear thinning. In industry, these aspects give effect on the process design, end use product and product quality.

For polymer solutions, the monomer and the polymer are all soluble in the solvent. As the polymer chain form, the solvent molecules surround all parts of the chains. Polymer solution exhibits different behaviour from that of a typical polymer. The rheology is extremely important for polymer solutions, since the flow behaviour is important in processing and fabricating such polymers. For example, polymer additives are extensively used to modify the rheological properties of solution in a wide variety of industrial applications. An increasingly important application is also found in the field of Enhanced Oil Recovery (EOR), principally as a means of increasing the viscosity of drive

fluids in petroleum reservoirs. Oil still remaining in the earth after water flood can be recovered from the reservoir by improving sweep efficiency and/or reducing the interfacial tension between flood and oil. One effective technique to discharge oil at this stage is polymer flooding. In EOR processes, the polymer solution flows through a complex network of fine pores. The in-situ viscosity, is therefore a very important factor governing both the rate of flows and distribution of polymer solution and associated immiscible liquids in the porous media. Concentration of only a few hundred ppm of polymer in water can provide greatly increased viscosities [8].

The viscoelastic behaviour is mainly attributed by the elastic modulus and the shear modulus which represented by the storage modulus,  $G'$  and the loss modulus,  $G''$ . The storage modulus,  $G'$ , represent the elastic part of PAM while the loss modulus,  $G''$ , represent the viscous part. the oscillatory shearing motion is one of the common forms of motion used to characterized visco-elastic fluids. It is useful to consider here the response of a Newtonian fluid and of a Hookean solid to a shear strain which varies sinusoidally with time as:

$$\gamma = \gamma_m \sin \omega t \quad (1)$$

Where  $\gamma_m$  is the amplitude and  $\omega$  is the frequency of applied strain. For an elastic Hookean solid, the stress is related linearly to strain, i.e

$$\sigma = G\gamma = G\gamma_m \sin \omega t \quad (2)$$

For the linear visco-elastic region, one can define the complex viscosity  $\eta^*$  as follows:

$$\eta^* = \eta' + i\eta'' \quad (3)$$

Where the real and imaginary parts,  $\eta'$  and  $\eta''$ , in turn, are related to the storage ( $G'$ ) and loss ( $G''$ ) moduli as:

$$G' = \frac{\sigma_m}{\gamma_m} \cos \delta \quad (4)$$

$$G'' = \frac{\sigma_m}{\gamma_m} \sin \delta \quad (5)$$

The viscoelastic can be measured through the Oscillatory Rheology. The basic principle of an oscillatory rheometer is to induce a sinusoidal shear deformation in the sample and measure the resultant stress response. The time scale probed is determined by the frequency of oscillation,  $\omega$ , of the shear deformation. In a typical experiment, the sample is placed between two plates, as shown in figure 1(a). A motor rotates the bottom plate, while the top plate remains stationary, which is then imposing a time dependent strain,  $\gamma(t) = \gamma \sin(\omega t)$  on the sample. Simultaneously, by measuring the torque that the sample imposes on the top plate, the time dependent stress  $\sigma(t)$  is quantified. Soft Measuring this time dependent stress response at a single frequency immediately reveals key differences between materials, as shown schematically in figure 1(b). The sample stress is proportional to the strain deformation if the material is an ideal elastic solid, and the proportionality constant is the shear modulus of the material. The stress is always exactly in phase with the applied sinusoidal strain deformation. Vice versa, if the material is a purely viscous fluid, the stress in the sample is proportional to the rate of strain deformation, where the proportionality constant is the viscosity of the fluid. The applied strain and the measured stress are out of phase, with a phase angle  $\delta = \pi/2$ , as shown in the center graph in figure 1(b). Viscoelastic materials show a response that contains both in-phase and out-of-phase contributions, as shown in the bottom graph of figure 1(b). These contributions reveal the extents of solid-like (red line) and liquid-like (blue dotted line) behavior. As a consequence, the total stress response (purple line) shows a phase shift  $\delta$  with respect to the applied strain deformation that lies between that of solids and liquids,  $0 < \delta < \pi/2$ . The viscoelastic behaviour of the system at  $\omega$  is characterised by the storage modulus,  $G'(\omega)$ , and the loss modulus,  $G''(\omega)$ , which respectively characterise the solid-like and fluid-like contributions to the measured stress response.

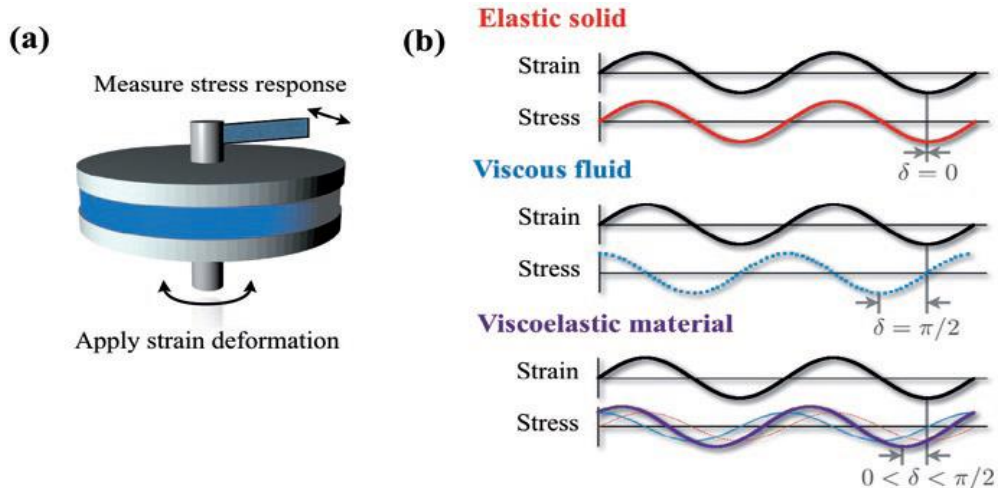


FIGURE 1 : (a) Schematic representation of a typical rheometry setup, with the sample placed between two plates. (b) Schematic stress response to oscillatory strain deformation for an elastic solid, a viscous fluid and a viscoelastic material.[31]

This project will focused on partially hydrolyzed polyacrylamide(HPAM). Polyacrylamide is a brittle, white, odorless polymer, which can be manufactured by free radical polymerization of acrylamide monomer. Polyacrylamide is water soluble at all concentration, temperatures and pH values. Polyacrylamide molecules are both very flexible and long with a relatively small diameter thereby making them susceptible to shear degradation or mechanical breakage. The average molecular weight of commercial polyacrylamide ranges approximately from  $2 \times 10^3$  to  $15 \times 10^6$ .

TABLE 1 : Properties of Polyacrylamide

Solid Properties	Freeze dried: White, amorphous, cotton-wool like Great affinity to humidity Precipitated in methanol and dried: Glass hard, partly transparent
Density	$1302 \text{ g cm}^{-3}$ at $23^\circ\text{C}$
Glass transition temperature	$153^\circ\text{C}^{65}$ $165^\circ\text{C}^{66}$ $165^\circ\text{C}^{67}$

Solvents	Water Formamide Ethylene glycol
Formula	$\left[ \text{CH}_2 - \underset{\begin{array}{c}   \\ \text{C}=\text{O} \\   \\ \text{NH}_2 \end{array}}{\text{CH}} \right]_x$

Numbers of forms and particles size distribution of solid polyacrylamide is available depending on the type of polymerization, drying, and grinding process employed. . Polyacrylamide can be converted from a dry sheet to a powder by grinding, but only a small fraction of very small particle is desirable. These small particles can go into the solution and generate viscosity much too fast to get a good dispersion of the remaining polymer. Since the project focus on polyacrylamide in aqueous, the properties of its aqueous solutions are important. The viscosity of polyacrylamide in water increases dramatically with molecular weight while it decreases with increasing temperature. Higher molecular weight polymer exhibits a greater apparent viscosity than their low molecular weight polymers under similar conditions. At relative low shear rates, aqueous solutions of polyacrylamide are pseudoplastic. However, at high shear rates rupturing the polymer chains can degrade the molecular weight.



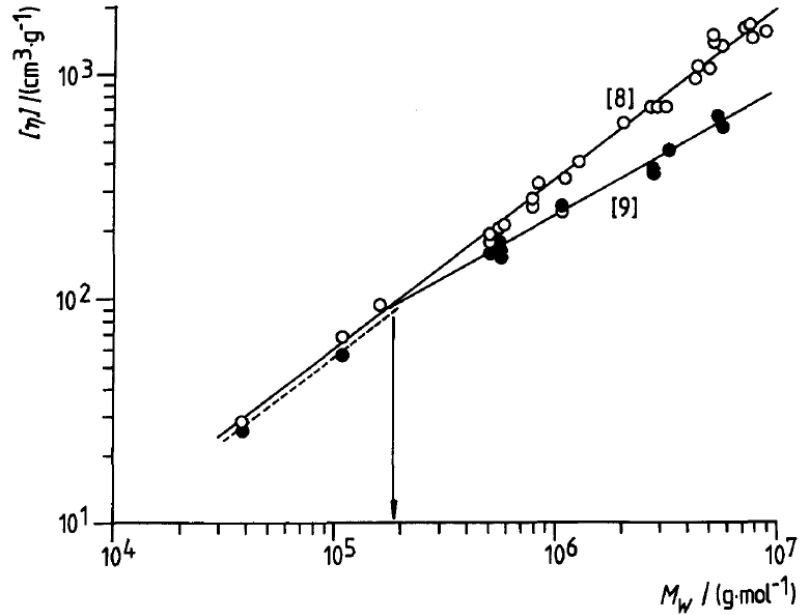


FIGURE 2: Intrinsic viscosity as a function of molecular weight in water [8], ethylene glycol [9] at 25°C.[1]

Acrylamide based on homo- and copolymers have been used in the industrial application, as flocculents, dispersants, retention aids, steric stabilizers, and associate thickeners in areas as diverse as municipal and industrial waste water treatment, mineral flotation, paper making, oil and coal refineries, and emulsion polymerization reactions[6].

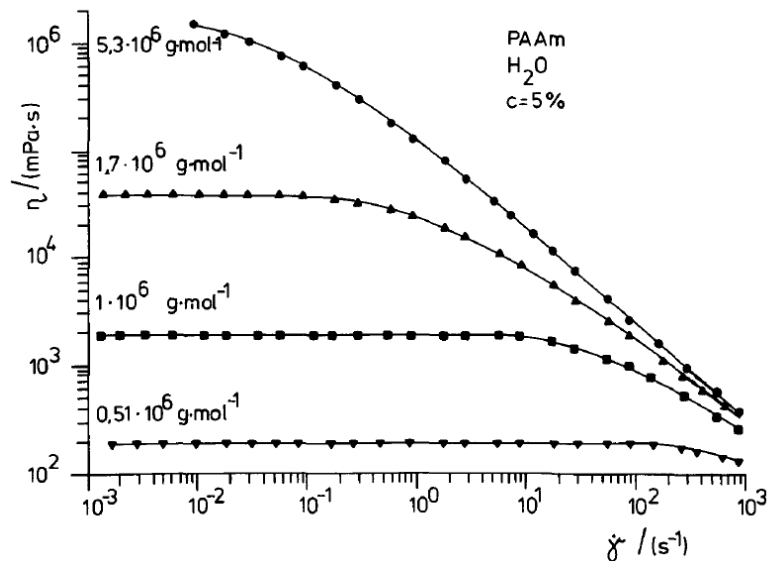


FIGURE 3: Viscosity as a function of shear rate for aqueous solutions of PAM of different molecular weights at a given concentration.  $M_w/M_n \cong 2.5$ ,  $T = 25^\circ\text{C}$ . [1]

At a given polymer concentration, as the molecular weight increases, the solution viscosity increases. The extent of polyacrylamide hydrolysis affects solution viscosity, polymer adsorption on rock, and flow resistance properties. Acrylamide polymers and copolymers are used to reduce friction losses during fracturing operations. Generally anionic polymers (usually those containing carboxylate groups) have been found to produce the greatest friction reduction in aqueous fluids. The use of acrylamide-containing polymers to thicken injection water to provide mobility control in enhanced oil recovery operations is well known. Important considerations for choosing a flood polymer are shear sensitivity, tendency to adsorb on the formation, compatibility with the formation fluids, heat stability, and, of course, the effectiveness of the polymer in question as a viscosifier[7].

A number of rheological studies on polyacrylamide have been carried out under different conditions. These studies have shown, along with earlier studies, that polyacrylamide solutions possess complex behavior that can restrain industrial uses. In a different studies, an experiment have been carried out to investigate the rheological property of partially hydrolyzed polyacrylamide solutions by analyzing the effect of salt on the viscoelastic properties of HPAM. The viscosity and primary normal stress differences was measured using Weissenberg rheogonimeter and a Contraves low-shear viscometer. It is reported that the salt had a stabilizing effect on the solution viscosity [12]. This effect is characterized by lower viscosity levels and less shear thinning behaviour as salt concentration is increased.

A creep-recovery test has been done to investigate the viscoelastic response of partially hydrolyzed polyacrylamide for several concentrations. Viscoelasticity is a combination of viscous and elastic properties and the term refers to a material that exhibits viscous and elastic properties. It is found that the partially hydrolyzed polyacrylamide behave like viscoelastic material in all concentrations [3]. However, the viscous part was always higher than the elastic part. The viscoelastic properties are investigated through the elastic and shear modulus. Elastic modulus measure the stiffness of an elastic material and define as the ratio of stress to strain while shear stress is a measure of a stiffness of a material and defined as the ratio of shear stress to shear strain.

A rheological measurement in terms of steady, transient, creep and oscillatory have been carried out for aqueous PAM solutions with a concentration range up to 1% and also the temperature effect on the behaviour of the PAM solutions is discussed over the range of 10-50°C. It is reported that The PAM solution showed shear-thinning behaviour for all concentration of 0.25-1.0% up to a critical shear rate value, which depended on the concentration [10]. The PAM solutions showed a thixotropy behaviour which increased with concentration from 0.25-1.0%. A time-dependent response was found for the creep and recovery phases at a lower applied shear stress. However, at higher shear stress, the creep and recovery phases are time-dependent. PAM solution showed elastic behaviour at low range of frequency and viscous response at a higher range of frequency, thus the viscoelastic behaviour of PAM solutions depends strongly on the concentration in the range of 0.25-1.0%. [10]

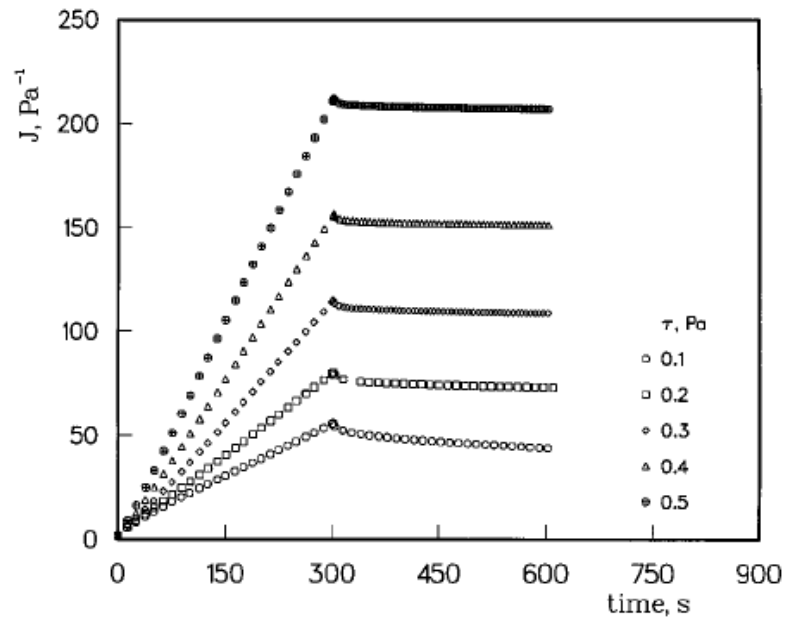


FIGURE 4: Viscoelastic response of 0.25% PAM.[10]

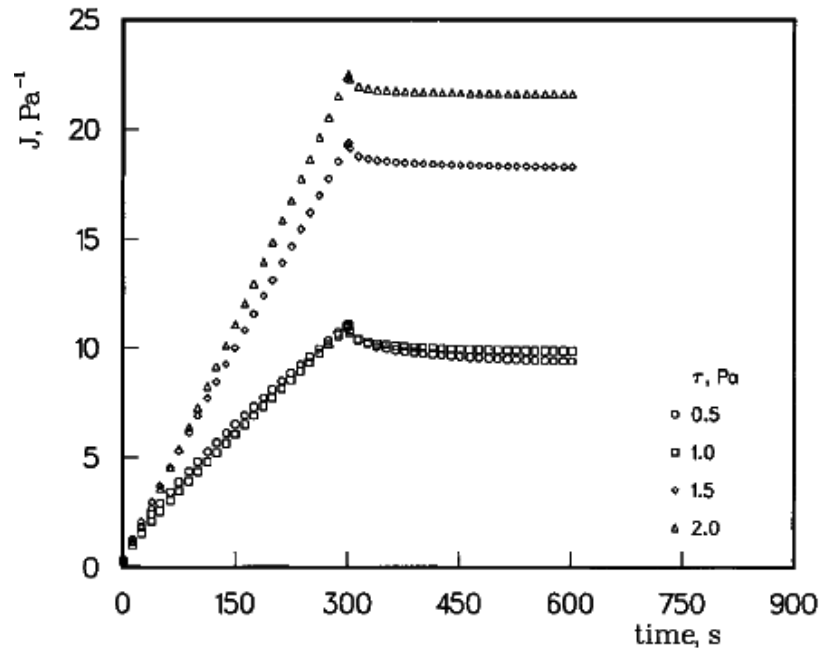


FIGURE 5: Viscoelastic response of 1.0% PAM.[10]

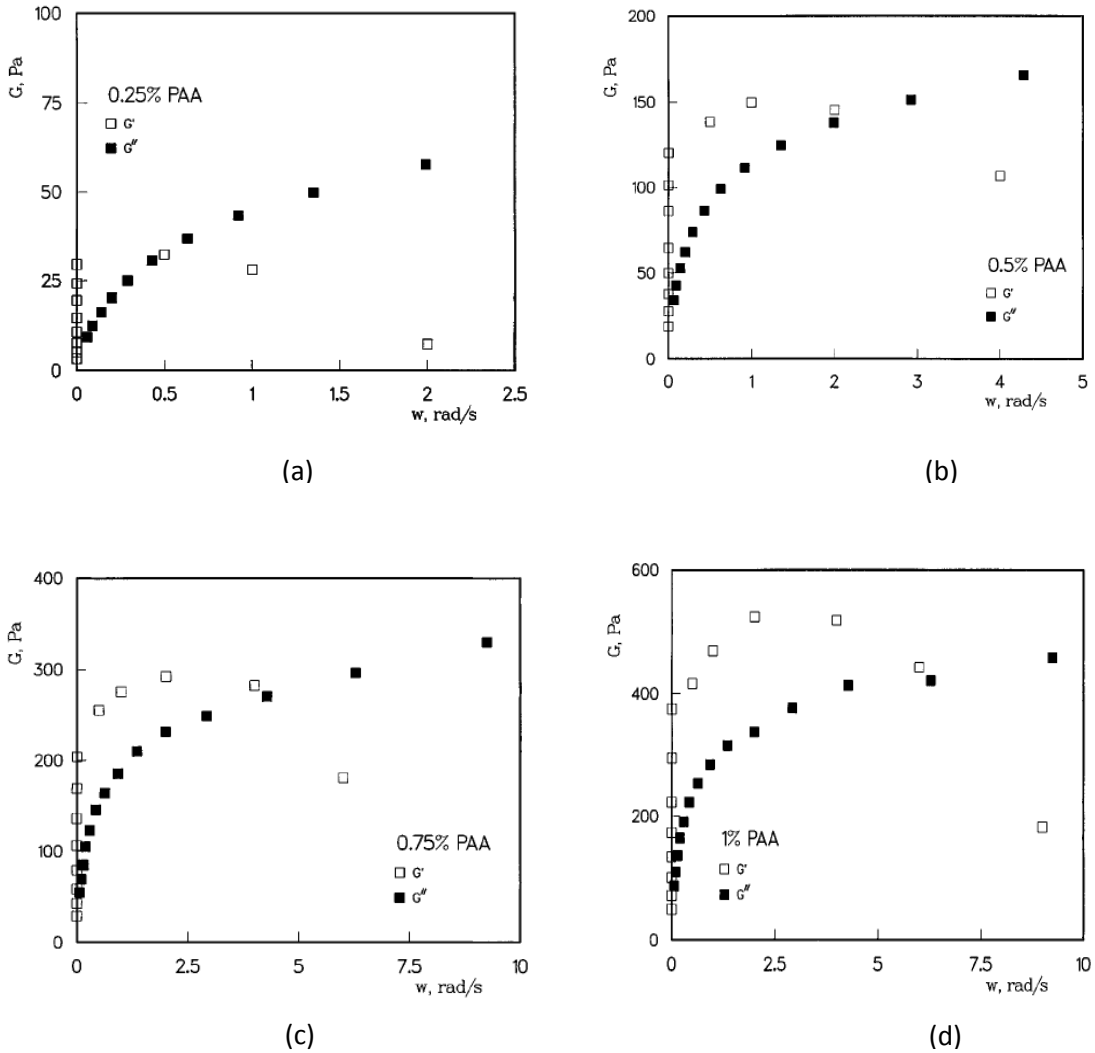


FIGURE 6: Storage modulus,  $G'$  and loss modulus,  $G''$  for PAM solution. (a)  $G'$  and  $G''$  for 0.25% PAA, (b)  $G'$  and  $G''$  for 0.5% PAA, (c)  $G'$  and  $G''$  for 0.75 PAA, (d)  $G'$  and  $G''$  for 1% PAA.[10].

The pipe flow of aqueous polyacrylamide solutions have been studied by means of nuclear magnetic resonance imaging. They found that, at a low bulk flow rate, steady laminar flow characterizes aqueous polyacrylamide solutions. As the bulk flow rate increases, unsteady motion appears and the mean velocity profile becomes more blunted [14].

The temperature effect on the non-Newtonian viscosity of aqueous polyacrylamide solution has also been studied and It is reported that the viscosity of the solution was very sensitive to temperature at low shear rate[12]. However, it was almost independent of temperature at high shear rates. In a different study, it is reported that the viscosity of polyacrylamide solutions significantly decreases with temperature [11].

Previously, the effect of temperature on the viscosity has been studied. The study measured the Non-viscosity of a 0.1% polyacrylamide solution over a range of temperatures. The steady-shear viscosity of the polyacrylamide solution was measured as a function of shear rate by a falling needle viscometer and a Brookfield viscometer. It is concluded that, particularly at low shear rate, the viscosity was found to be very sensitive to temperature whereas that at a high shear rate it is almost independent of temperature. However, the time constant, the fluid behaviour index, and the fluid consistency index varies with temperature.[4]

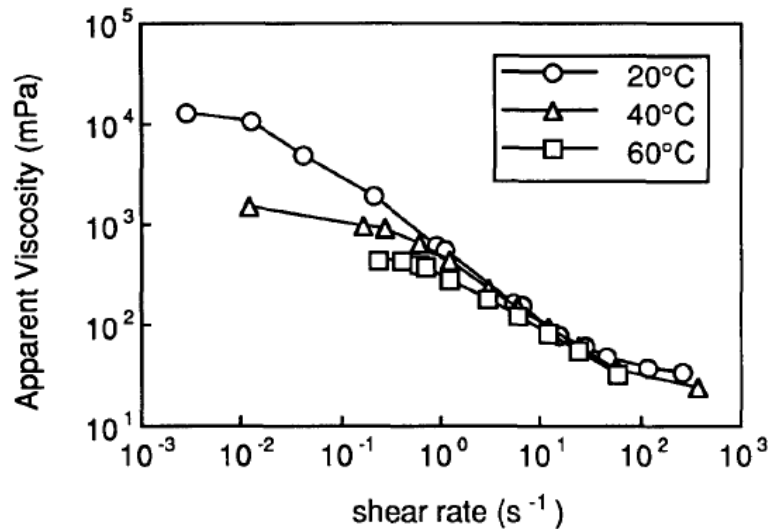


FIGURE 7 : Viscosity versus shear rate curve for aqueous polyacrylamide solution(0.1%) at three different temperatures.[4]

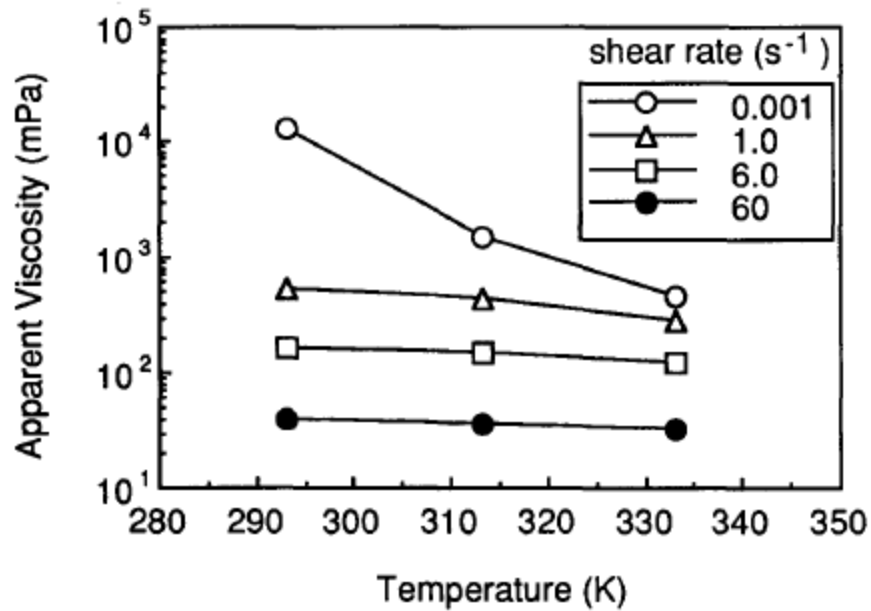


FIGURE 8 : Viscosity versus temperature curve for aqueous polyacrylamide solution(0.1%) at four different shear rates.[4]

However, despite of all the studies being made, there is no serious study that have been done to investigate how does the viscoelasticity of HPAM is affected by the concentration and temperature and to what extend does the viscoelasticity of HPAM is affected by the concentration i.e. the concentration of master solution and diluted solution and also on the different temperature of the solutions. Thus, there is a need to further study and investigate on the viscoelastic properties of HPAM and to comes out with a proper documentation to justify on the stated matter.

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Research approach**

The viscoelasticity of the water-based polymer, partially hydrolyzed polyacrylamide (HPAM, commercial name: ZETAG 4120) will be analyzed using a rotational rheometer. Several parameters will be varied, which includes:

- I. the concentration of polymer master solution
- II. the concentration of diluted solution from the master solutions, and

The studies of the viscoelastic behaviour through the analysis of its shear and elastic moduli at various parametric will determine the strength of the polymer solution under normal room temperature at 25°C. The viscoelastic explains the behaviour of the polymer solution, how does it flow and how strong are the polymer solution.

#### **3.2 Polymer Solution Preparation**

##### **3.2.1 Master Solution**

Four master solution which are of 1000ppm, 2000ppm, 5000ppm and 10000ppm of HPAM (Zetag 4120) are to be prepared for this experiment. The method is described below:

- I. Polymer powder (Zetag 4120) is sprinkled to the bottom of an empty tank.



- II. Water is then poured to the tank, allowing the polymer to be dispersed naturally due to momentum created.
- III. After mixing, the polymer solution is further rested at room temperature overnight for hydration to occur.
- IV. The schematic diagram of the preparation method is shown below.

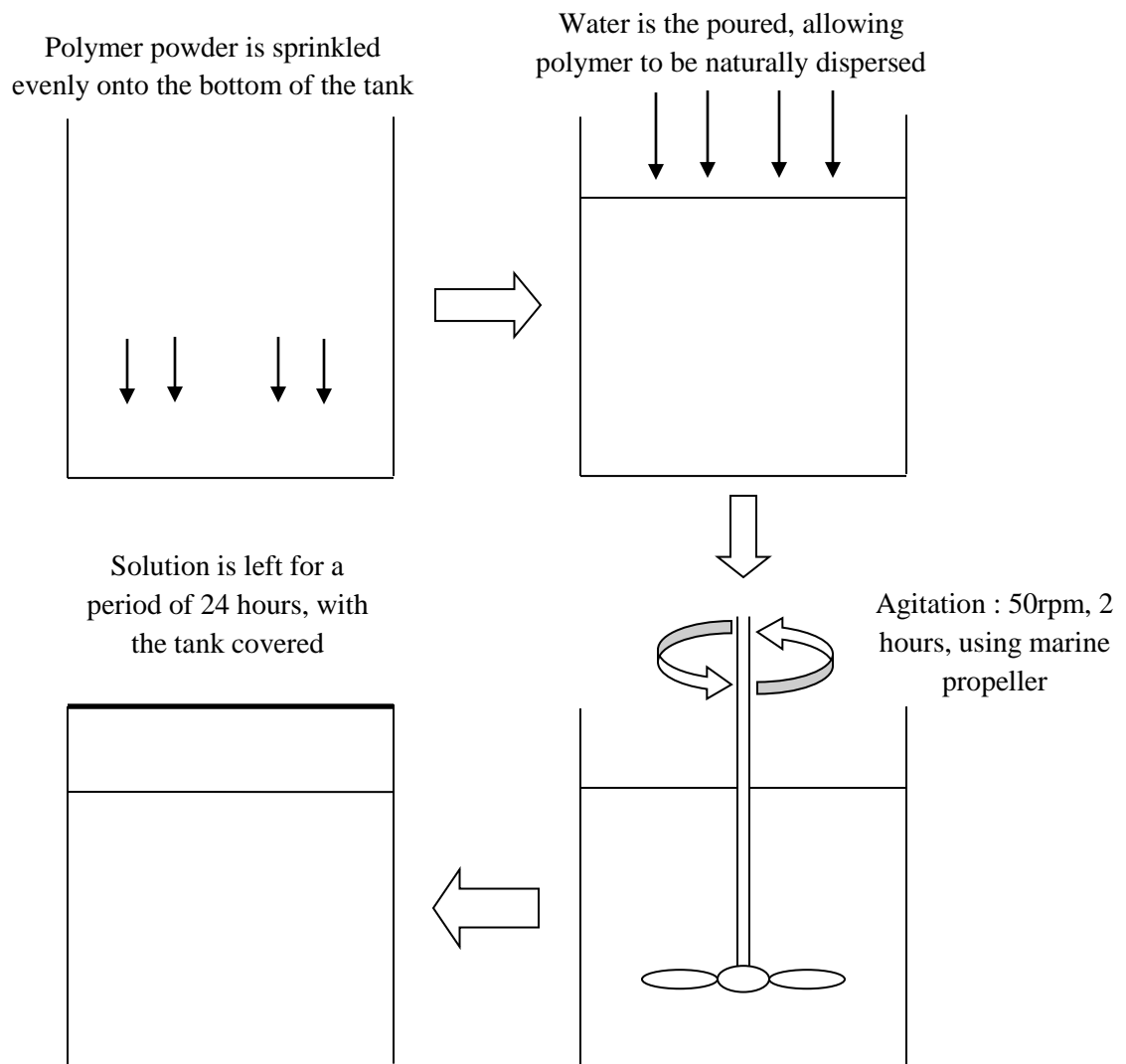


FIGURE 9 : Polymer master solution preparation diagram

After mixing, the solution is stirred for 2 hours at a constant rotation speed of 40 rpm. The reasons for the slow agitation speed in preparing the solution is due to the fact that

high agitation speed will cause the high shear rate, which eventually may degrade the polymer solution through scissoring of polymer-chains.

After the agitation, the tank containing polymer solution will be covered to avoid any impurities to enter and contaminate the solution. It will then be left for a period of 1 day to allow the solution to hydrate. Hydration is a process whereby the molecule of the polymer will take up the molecules of water in order to form the polymer solution. Analysis will be performed the next day after the solution was prepared.

### 3.2.2 Dilution of polymer solution

Each of the master solution prepared is to be diluted into three different concentrations using distilled water. The concentrations for the diluted solution are to be 10ppm, 20ppm and 50ppm, to stimulate the exact concentration injected into the pipeline during the drag reduction process. Dilution of the master solution will be done after 1 day hydration period ends. The dilution process will follow the following relation:

$$M_1V_1 = M_2V_2 \quad (7)$$

$$V_2 = \frac{M_1V_1}{M_2} \quad (8)$$

Where,

M1 = concentration of master solution,ppm

M2 = concentration of dilute solution,ppm

V1 = volume of master solution required for dilution,L

V2 = volume of dilute solution,L

After the dilute solutions are prepared, they will be stored in enclosed containers to prevent any impurities that might contaminate the solution thus affecting the measured results.

### 3.3 Laboratory Testing

After the master solution and the diluted solution are prepared, they will be tested and analyzed using a rotating rheometer (Model: Bohlin Gemini Rheometer) which is available at Block P, Universiti Teknologi PETRONAS.

The normal room temperature of 25°C is chosen for conducting the rheometer test. The behaviour of the master and diluted solutions will be observed accordingly at this temperature. The results obtained will be used to determine the rheological properties of the solutions and more specifically the viscoelastic properties of the solutions.



FIGURE 10: Bohlin Gemini Rheometer

TABLE 2: Rheometer Specification

Item	Specification
Torque Range	0.05 $\mu$ Nm to 200mNm in controlled stress and strain oscillation
Type	Parallel plate Cone & Plate
Torque Resolution	Better than 1nNm
Frequency Range	1 $\mu$ Hz to 150Hz
Step Change in strain	< 10ms
Extended Temperature Cell	Ambient to 550°C

### 3.4 Gantt chart

NO	Detail/week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Detailed research work on polymer solution		■	■	■	■									
2	Detailed study on the previous research of HPAM in flow assurance field			■	■	■	■								
3	Detailed review on the effect of concentration on viscoelasticity of polymer solution				■	■	■	■							
4	Laboratory works to investigate HPAM properties					■	■	■	■	■	■	■	■		
5	Draft report												■		
6	Finalise project report													■	



Suggested milestone



Process

## CHAPTER 4

### RESULT & DISCUSSION

The rheometry measurement conducted using the cone and plate geometry was set as the ‘oscillation test’. The plate used is of ETC cone 5, 4°/40mm with the gap set at 150 micron. The results of the rheological test are being compared in this chapter. First, the master solutions are compared to observe the viscoelastic behavior for several HPAM solutions with hydration period of one day at 25°C.

#### 4.1 Comparison of the viscoelastic properties of 1000ppm, 2000ppm, 5000ppm and 10,000ppm HPAM solution

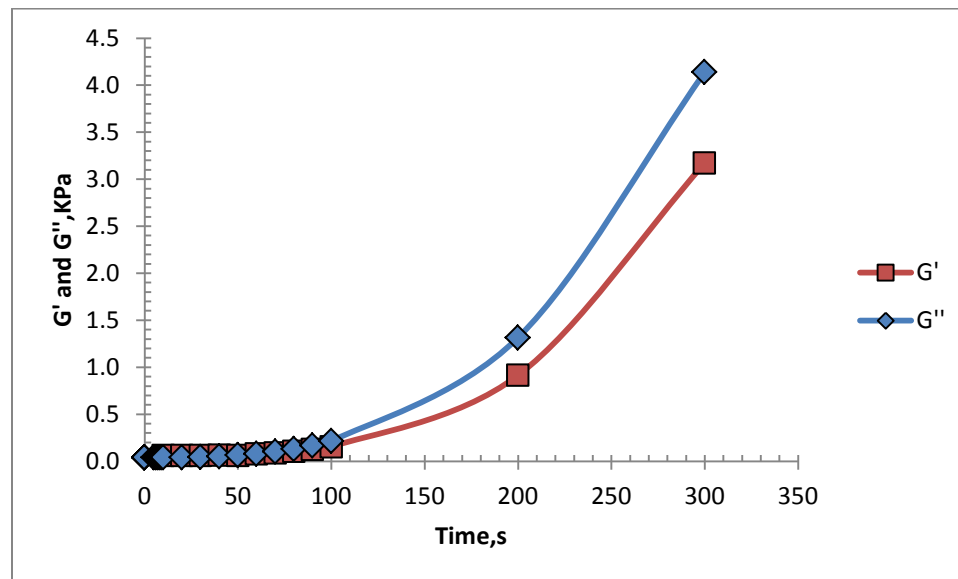


FIGURE 11 : Graph of G' and G'' versus time for HPAM solution of 1000ppm

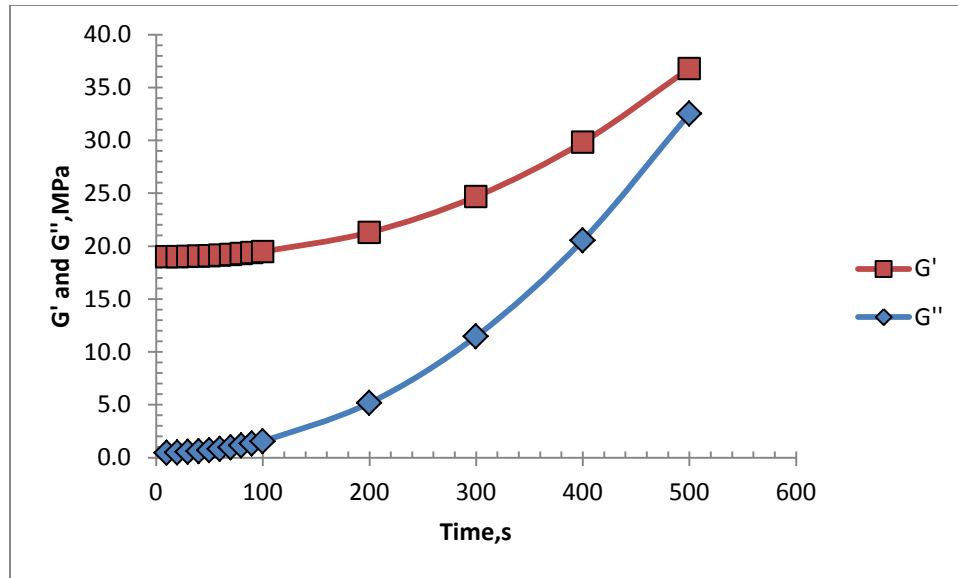


FIGURE 12 : Graph of  $G'$  and  $G''$  versus time for HPAM solution of 2000ppm

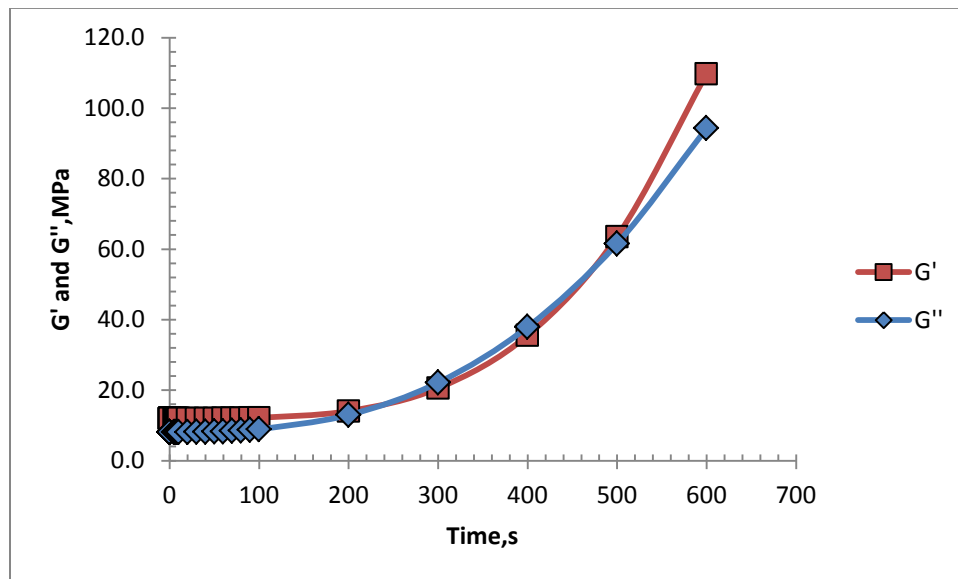


FIGURE 13 : Graph of  $G'$  and  $G''$  versus time for HPAM solution of 5000ppm

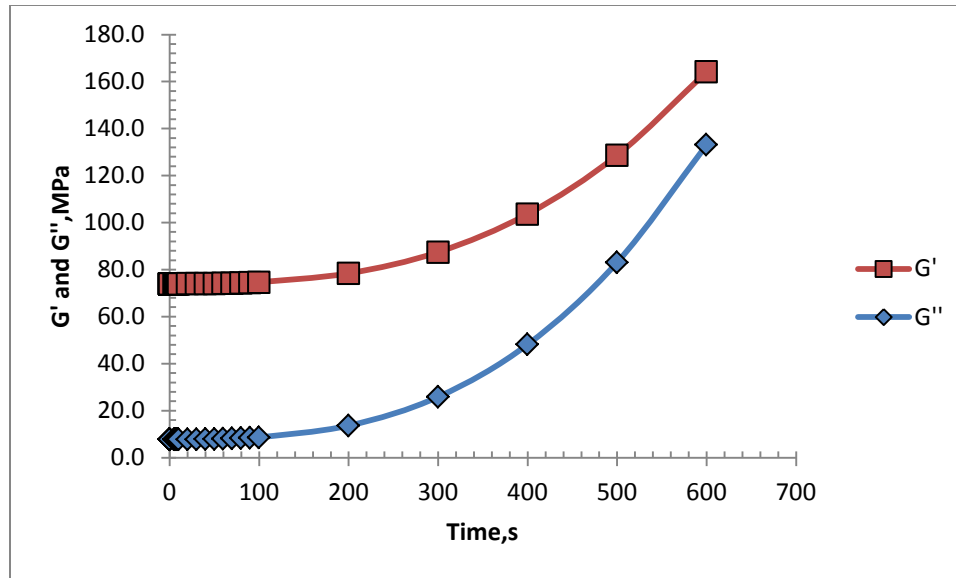


FIGURE 14 : Graph of  $G'$  and  $G''$  versus time for HPAM solution of 10,000ppm

The figure 11, 12, 13 and 14 are the result obtained from the rheological test of the master solution of 1000ppm, 2000ppm, 5000ppm and 10,000ppm at 25°C. All solutions show both elastic and viscous behavior. The value of  $G'$  and  $G''$  is increased when the concentration is increased.

As observed, the HPAM solution of 2000ppm and 10,000ppm shows higher  $G'$  value compared to  $G''$ . This indicates that the polymer solution behave more toward elastic than viscous. They exhibit higher elastic recovery from deformation which occurs during flow. For HPAM solution of 1000ppm, it shows higher value of  $G''$  value compared to  $G'$ . This indicates that the polymer solution behave more towards viscous behavior. When stress is applied, they are more resistant on shear flow and strain linearly with time. The dilute solution of 10,000ppm shows that it behaves in between the viscous and elastic properties.

#### 4.2 Comparison of the Storage Modulus, $G'$ of the master solutions.

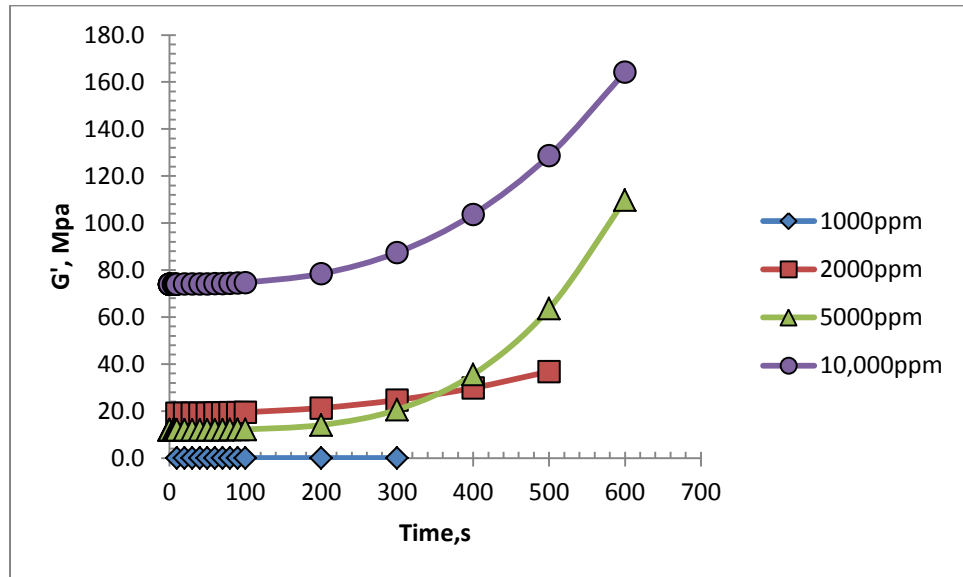


FIGURE 15 : Graph of  $G'$  versus time for HPAM master solutions.

From figure 15, the value of  $G'$  for 2000ppm, 5000ppm and 10,000ppm HPAM solution is increasing throughout time while for 1000ppm, the value of  $G'$  is very small to be compared with other master solutions. For 2000ppm, the value of  $G'$  increased until at some point, the  $G'$  is higher than that of 5000ppm.



### 4.3 Comparison of the Loss Modulus, $G''$ of the master solutions.

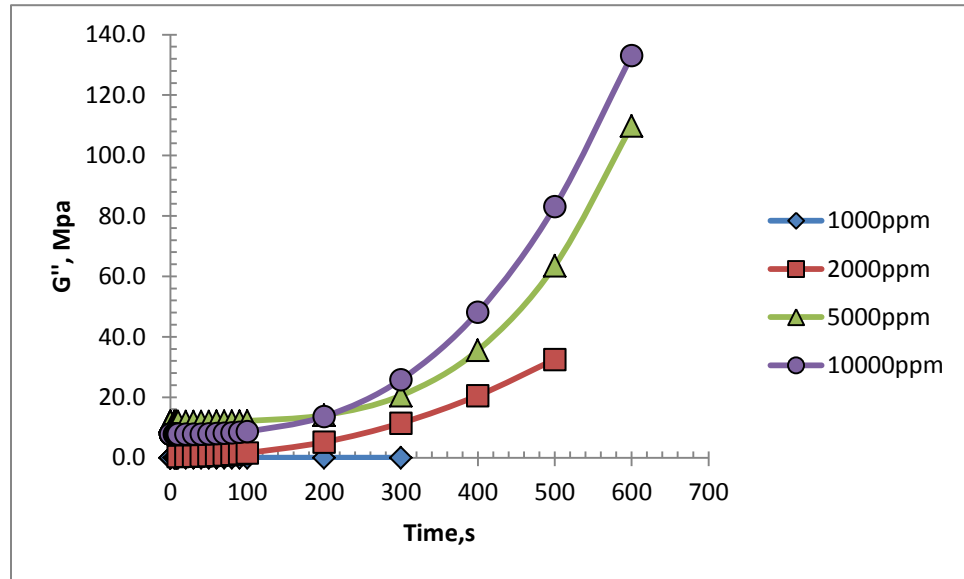


FIGURE 16 : Graph of  $G''$  versus time for HPAM master solutions.

From figure 16, it is shown that the value of  $G''$  is increasing for 2000ppm, 2000ppm and 10,000ppm master solutions. However the value of  $G''$  for 1000ppm is very small to be compared to other master solutions.

### 4.4 Comparing the viscoelastic properties of 10ppm diluted solutions.

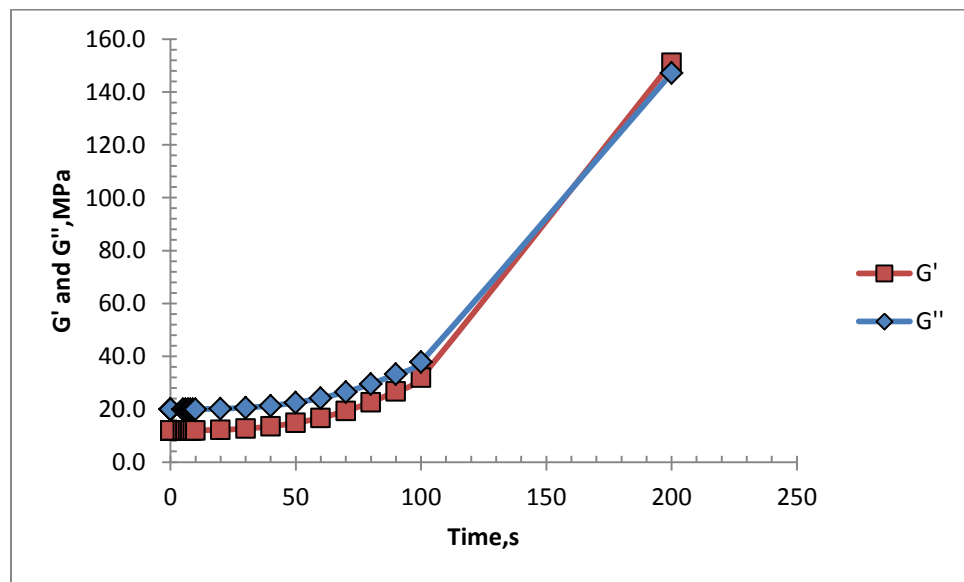


FIGURE 17 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 10ppm of 1000ppm master solution.

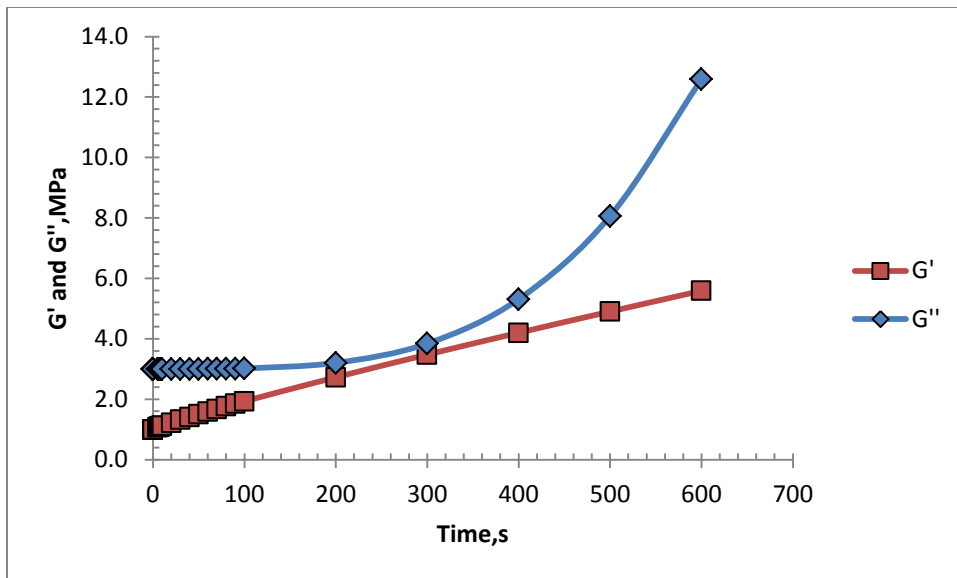


FIGURE 18 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 10 ppm of 2000ppm master solution.

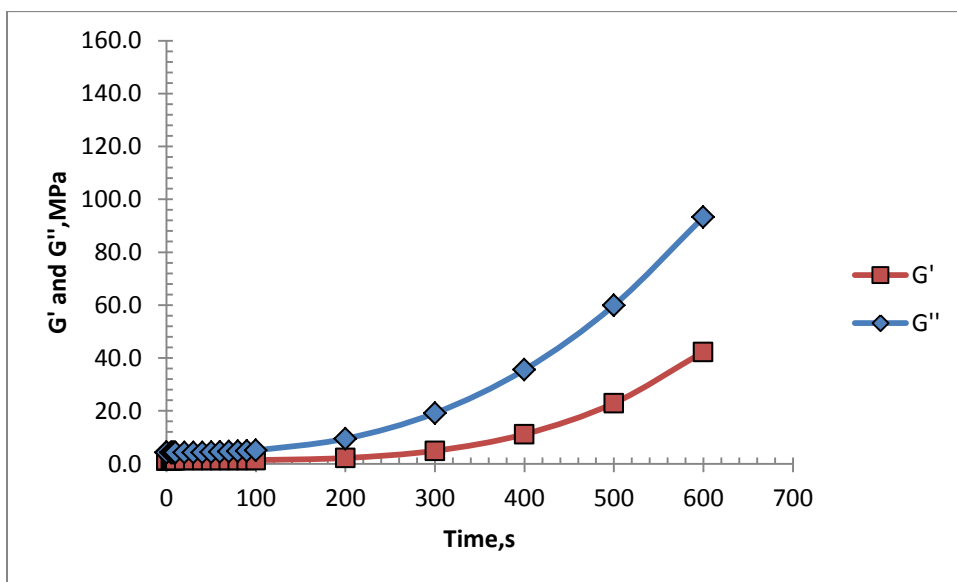


FIGURE 19 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 10 ppm of 5000ppm master solution.

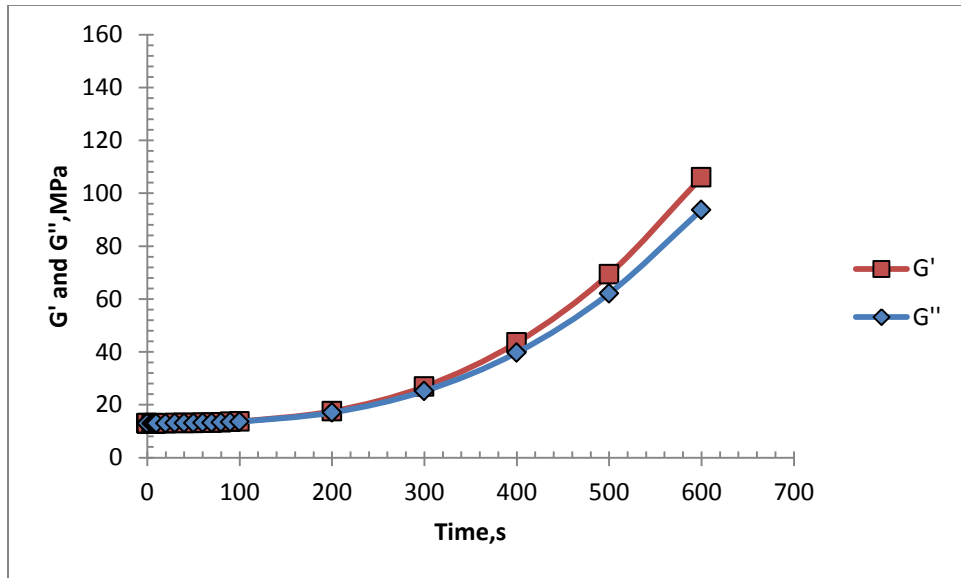


FIGURE 20 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 10 ppm of 10,000ppm master solution.

From the graphs, it is shown that the diluted solution 10 ppm of 2000 ppm and 5000 ppm have higher  $G''$  value than  $G'$ . It means that these solutions behave more towards the viscous behavior. Meanwhile for the diluted 10 ppm solution of 1000 ppm and 10,000 ppm have almost the same value of  $G'$  and  $G''$  which indicates that these solution behave in between the viscous and elastic properties.

#### 4.5 Comparison of the viscoelastic properties of 20ppm diluted solutions.

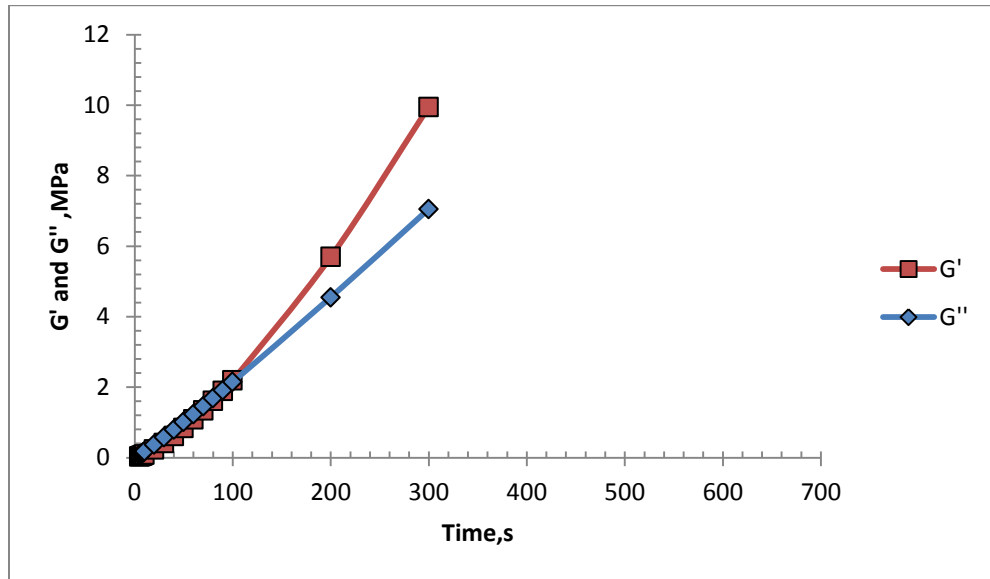


FIGURE 21 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 20 ppm of 1000ppm master solution.

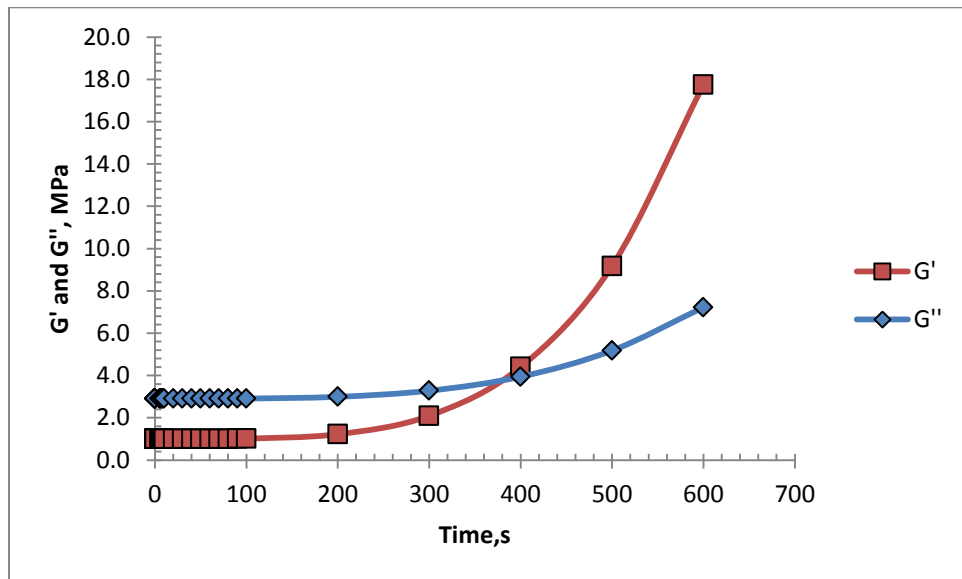


FIGURE 22 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 20 ppm of 2000 ppm master solution.

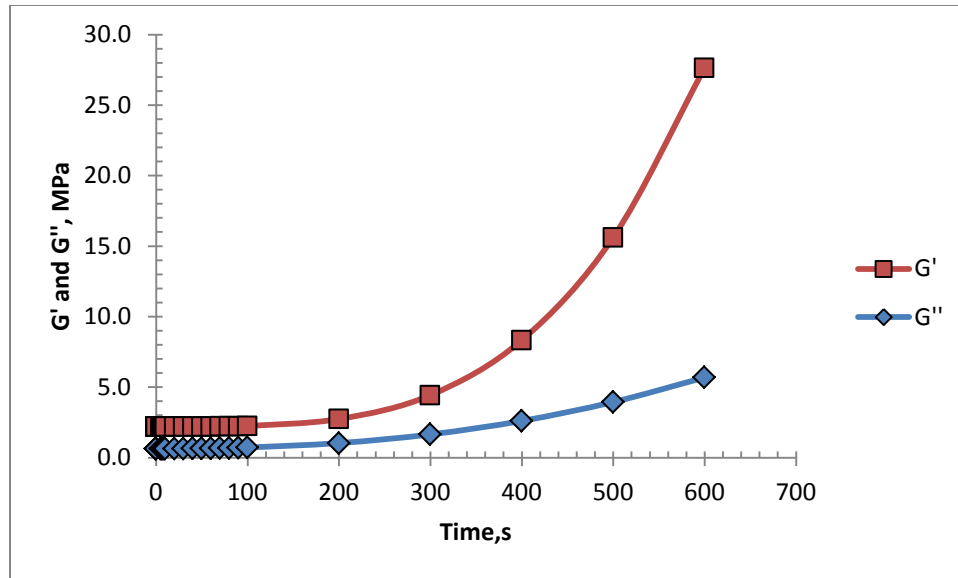


FIGURE 23: Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 20 ppm of 5000 ppm master solution.

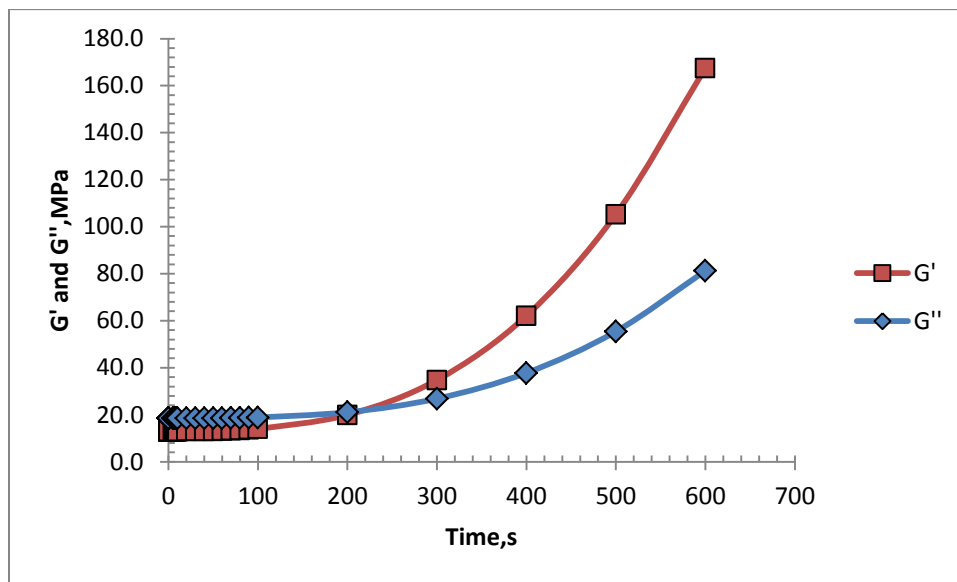


FIGURE 24: Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 20 ppm of 10,000 ppm master solution.

From figure 21 and 24, it is shown that the value of  $G'$  and  $G''$  is almost the same at the beginning of test, however after some time the value of  $G'$  is getting higher than  $G''$ . This indicates that the solution initially behave in between viscous and elastic behavior however after sometime, the solution begin to behave like elastic behavior. From figure

22, it is shown that at first the solution behave like a viscous behavior and after some time the solution then behave like an elastic behavior. From figure 23, it is shown that the value of  $G'$  is higher than  $G''$  which indicates that the solution behave like an elastic behavior.

#### 4.6 Comparison of the viscoelastic properties of 50ppm diluted solutions.

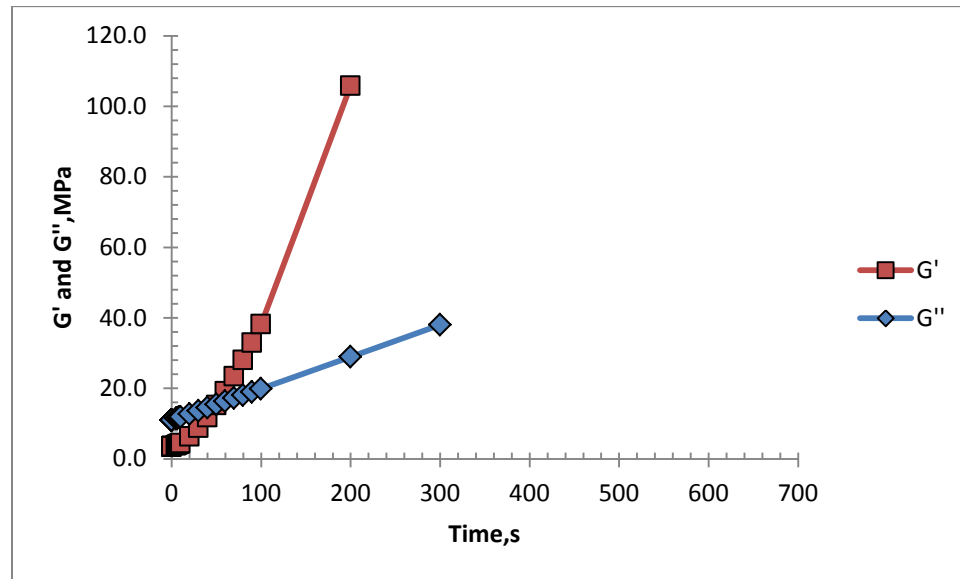


FIGURE 25 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 50 ppm of 1000ppm master solution.

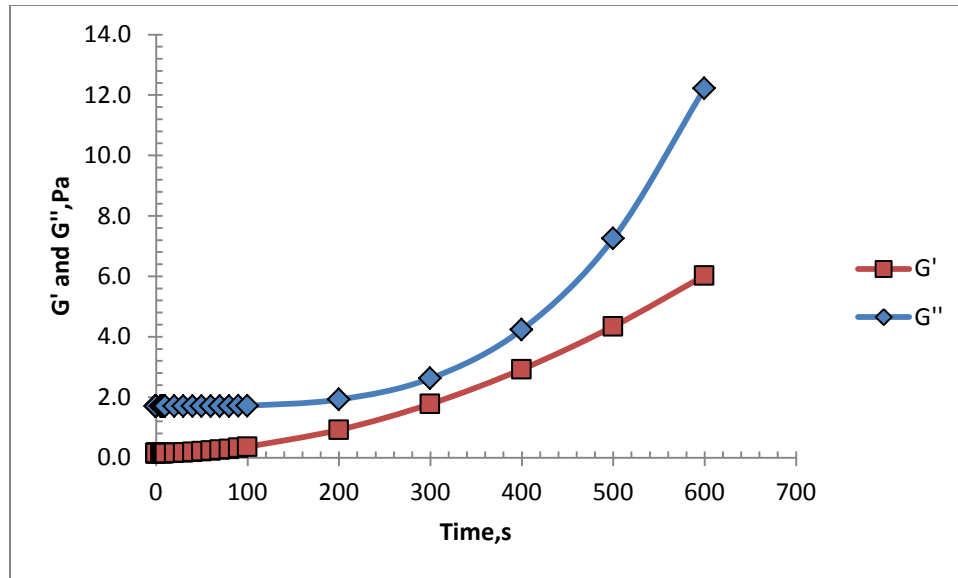


FIGURE 26 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 50 ppm of 2000 ppm master solution.

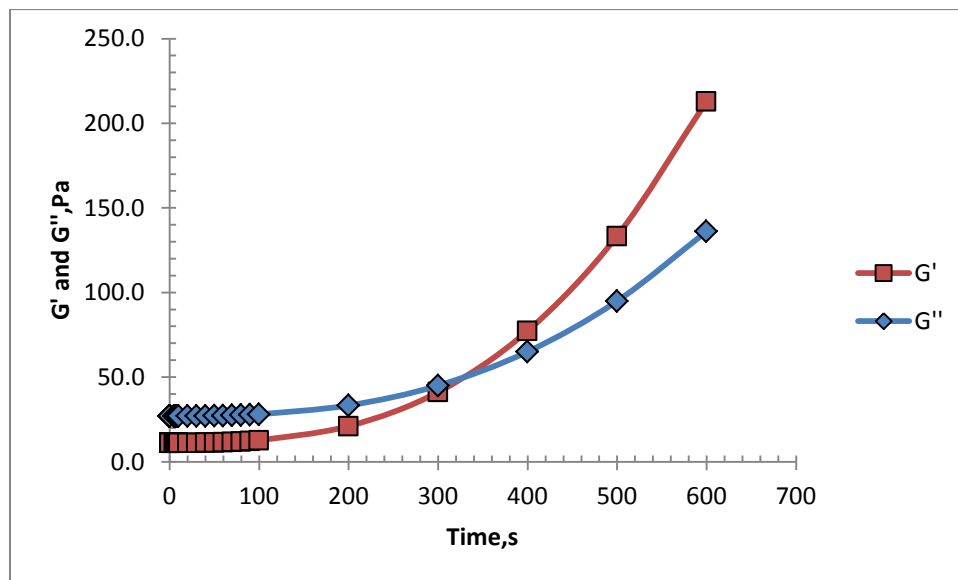


FIGURE 27 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 50 ppm of 5000 ppm master solution.

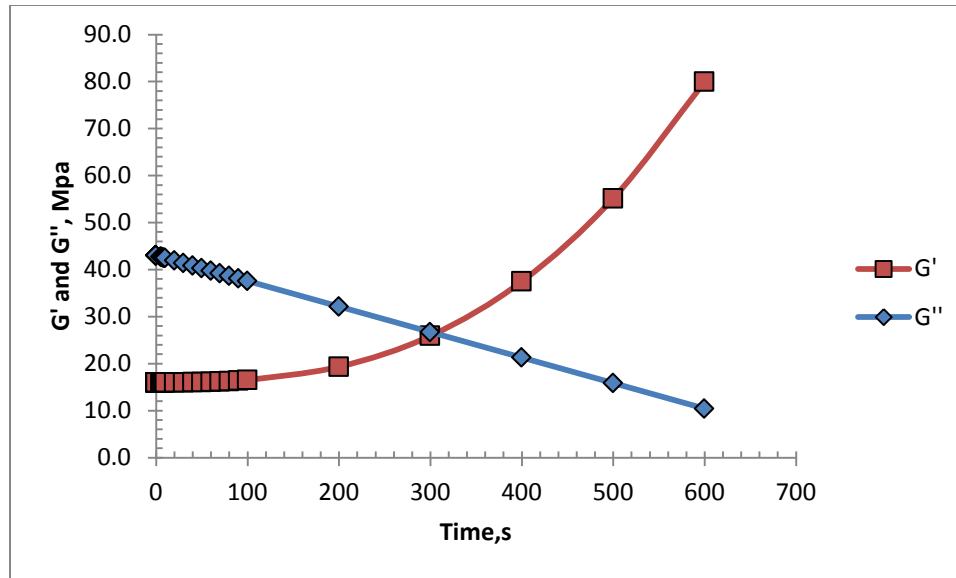


FIGURE 28 : Graph of  $G'$  and  $G''$  versus time for diluted HPAM solution of 50 ppm of 10,000 ppm master solution.

From figure 25 and 27, it is shown that the solution initially behaves like a viscous behavior and then after some time it behaves more toward the elastic behavior. For 50ppm diluted solution of 2000ppm, it has higher  $G''$  value which indicates that the solution behave towards the viscous behavior. Meanwhile from figure 28, it is shown that the value of  $G'$  is increasing however the value of  $G''$  is decreasing. This indicates that the solution behavior behave more towards the elastic behavior while the viscous part of the solution in being loss or decreasing through time.

All the results shows that the existence of viscoelastic structure in HPAM can be detected quite sensitively by the apparatus. From the data gained, it is shown that the concentration does affect the viscoelastic behavior of the polymer solutions. It is proved that the elastic and viscous modulus increases when the concentration increases. These indicates that when the elastic modulus increases, the polymer solution have higher elastic recovery from deformation and when the viscous modulus increased, the polymer solution are more resistant on shear flow and strain linearly with time when stress is applied.



In the field of EOR, when the conventional pumping method can no longer recover the oil, the secondary technique is used which is to flood the oil well with water to displace the oil, the so-called water flooding technique. In order for the water flood to be efficient, the viscosity of the water injected must be higher than the oil so that it can push the oil and recovered. However after water flooding, residual oil still remains in the well for example as oil film on a rock surface. The yield of recovery oil can be improved by using polymer flooding technique in which a water-soluble polymer is used to be injected. Wang, D. et al. have describe that viscous-elastic polymer can increase microscale displacement efficiency. From the result it shows that HPAM possessed both the viscous and elastic part which indicates that it can be used in both the water flooding and the polymer flooding technique. In Water flooding technique, HPAM can be injected to the water in order to increase the viscosity so that it can displace the oil with more efficiency. For polymer flooding, the properties of both viscous and elastic part of HPAM can increase the recovery efficiency of the oil residue which is left after the secondary technique is applied. As a drag reducing agent used in pipelines, the solution which behave in between the viscous and elastic behavior is much more preferable to be injected in the pipeline because it can better enhance the flow of the fluid in the pipeline and also it can enhance the extensional flow of the fluids.

## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATION**

#### **5.1 Conclusion**

Rheology is very important as it explained the behaviour of a substance. Understanding the rheology of a polymer solution is critical as it is important for its applications as such for the design, selection, and operation involved in handling, mixing, pumping, storage, and transportation processes. In this study, the master concentration and diluted concentration is varied while the temperature and the hydration period is kept constant.

Based on the experiment done, the objective to study the polymer solution strength through the modulus behavior is achieved. From the data gained, it proves that the viscoelastic behavior does affect the strength of the polymer solution

All the polymer solutions exhibit both elastic and viscous behavior. As the polymer concentration increased, most of the elastic and shear moduli increases. Thus it indicates that the polymer solution strength is also increases.

#### **5.2 Recommendation**

The results of the laboratory works for this study are subjected to error affected by disturbances such as noise and vibration cause by human errors. To improve the results for the study, it is recommended to conduct the test in a closed room or equipped the rheometer with a sealed cell in order to minimize the disturbance from noise and avoid any vibration that could affect the test when running. The result for the all the diluted

Solutions are not totally accurate because of the improper preparation of the solution. Aside for the master solution, the diluted solutions should also left to rest for another hydration period of 24 hours for the solution to properly absorb water molecules. However the result may help to indicate the general trends for the diluted solution at a surface and thus give some information as a point to be studied in more details.

## REFERENCES

1. W.M. Kulicke; R. Kniewske; J. Klein. (1982). Preparation, Characterization, Solution Properties and Rheological Behaviour of Polyacrylamide. *Prog. Polym. Sci.*, Vol. 8 , 373-468.
2. W.M. Kulicke; R. Hass. (1984). Flow behaviour of dilute polyacrylamide solutions through porous media(1&2). *Ind. Eng.Chem.Fund* , 23:308.
3. Kreiba, A. (2000). The Rheological Properties of Aqueous Polyacrylamide Solutions.
4. Sehyun Shin, Young I. Cho. (1993). Temperature Effect on the Non-Newtonian Viscosity of an Aqueous Polyacrylamide Solution. 831-844.
5. Sehyun Shin, Young I. Cho. (1998). The effect of Thermal Degradation on the Non-Newtonian Viscosity of an Aqueous Polyacrylamide Solution. 267-273.
6. Glass, J. E. (1986). *Water-Soluble Polymers, Beauty with Performance*. North Dakota State University: American Chemical Society.
7. J. Chatterji, J.K. Borchardt. (1981). Applications of Water-Soluble Polymers in the Oil Field. *Journal of Petroleum Technology* , 2042-2056.
8. T. F. Al-Fariss; S. M. A-Zahrani. (1993). Rheological Behaviour of Some Dilute Polymer Solutions. *Eng. Sci.*, vol. 5 , 95-109.
9. Lewandowska, K. (2006). Comparative Studies of Rheological Properties of Polyacrylamide and Partially Hydrolyzed Polyacrylamide Solutions.
10. Mamdouh T. Ghannam; M. Nabil Esmail. (1998). Rheological Properties of Aqueous Polyacrylamide Solutions.
11. M. N. Esmail, Ghannam. (1998). *Applied Polymer Science*. 1587-1597.
12. Ait-Kadi, A. Cameau, P.J., Chauveteau. (1987). *Journal of Rheology*. 537.

13. Yanfang Zhang; Pin Gao; Mengmeng Chen; Guangsu Huang. (2008). Rheological Behavior of Partially Hydrolyzed Polyacrylamide Hydrogel Produced by Chemical Gelation.
14. L. Tie-Qiang; K.L.J. McCathy . (1995). Non-Newtonian Fluid Mech. 155.
15. Hidejiro Tanaka;Akio Sakasishi;Jiotozo Kakeko;Jiro Buruichi. (1966). Dynamic Viscoelastic Properties of Dilute. *Journal of Polymer Science: Part C* , 317-330.
16. Bouldin M; Kulicke W.M.; Kehler H.;. (1988). Prediction of the Non-Newtonian Viscosity and Shearstability of Polymer Solutions. *Colloid Polymer Sci* , 266: 793-805.
17. Ferry, J. D. (1948). Viscoelastic Properties of Polymer Solutions.
18. G. Marin; J. P. Montfort; Ph. Monge. (1982). Viscoelastic properties of concentrated polymer solutions and melts:a reduced form of linear viscoelasticity. 449-451.
19. Ghaithan A. Al-Muntasheri; Ibelwaleed A. Hussein; Hisham A. Nasr-El-Din; Mohamed B. Amin. (2007). Viscoelastic properties of a high temperature cross-linked water shut-off polymeric gel. *Journal of Petroleum Science and Engineering* 55 , 56–66.
20. Huai Tian BU; Zhen Zhong YANG; Li HUANG. (2002). Effect of Thermal History on Rheological Properties of Partially Hydrolyzed Polyacrylamide/Anionic Surfactant SDS Complex Systems. 456 – 459.
21. Francis W. Wang; Bruno H. Zimm. (1974). The Viscoelasticity of Polymer Solutions:Comparison of Theory and Experiment. *JOURNAL OF POLYMER SCIENCE* , VOL. 12, 1639-1648.
22. Ahmad Ramazani Saadatabadi; Meysam Nourani; Mohammad Ali Emadi. (2010). Rheological Behaviour and Hydrodynamic Diameter of High MolecularWeight, Partially Hydrolyzed Poly(acrylamide) in High Salinity and Temperature Conditions. *Iranian Polymer Journal* , 105-113.

23. Ahmad Rabiee; M. Ebrahim Zeynali; Habibollah Baharvand. (2005). Synthesis of High Molecular Weight Partially Hydrolyzed Polyacrylamide and Investigation on its Properties. *Iranian Polymer Journal* .
24. A.S. Lodge; M. Renardy; J.A. Nohel. (1984). *Viscoelasticity and Rheology*.
25. Ivonete da Silva; Elizabete Lucas; Francisca de Franca. (2010). Study of conditions for Polyacrylamide use in Petroleum Reservoir: Physical Flow simulation in Porous media.
26. J. Ferguson; Z. Kemandowski. (1991). *Applied Fluid Rheology*.
27. Jirui Hou; Zhongchun Liu; Shufen Zhang; Xiang'an Yue; Jinzong Yang. (2005). The role of viscoelasticity of alkali/surfactant/polymer solutions in enhanced oil recovery. *Journal of Petroleum Science and Engineering* 47 , 219– 235.
28. S. Oluranti; R.M. Emmauel; T.A. Adesola; F.B. Olusesan. (2011). Rheological Properties of Polymers: Structure and Morphology of Molten Polymer Blends. *Materials Sciences and Applications* , 30-41.
29. Schramm, K. (1994). *Practical Approach to Rheology and Rheometry*.
30. Witten, T. A. (1998). *Polymer Solutions: a Geometric Introduction*.
31. Dr. Hans M Wyss, Ryan J. Larsen, David A. Weitz. (2007). *Oscillatory Rheology*. 68-67.