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**Effect of Nonionic Surfactant (X-100) on the
Rheological Properties of Aqueous
Polyacrylamide Solutions**

Ismail Jaghmani

**A Thesis
in
Department of Mechanical Engineering**

**Presented in Partial Fulfillment of the Requirements for
the degree of Master of Engineering at
Concordia University
Montreal, Quebec, Canada**

1999

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ABSTRACT

Effect of Nonionic Surfactant (X-100) on the Rheological Properties of Aqueous Polyacrylamide Solutions

Ismail Jaghmani

Polyacrylamide solutions are widely used in modern technology as thickening agent, for turbulent reduction and many other uses. They have been extensively used in enhanced oil recovery. In many cases, polyacrylamide comes into contact with surfactants which lead to a change in its rheological properties. In this study, an experimental work was carried out to investigate the effect of the nonionic surfactant (X-100) on the rheological properties of polyacrylamide, using cone-and-plate Rheometer. Polyacrylamide and the surfactant in the tested solutions ranged by weight from 0.02%-0.1% and 0.001%-0.05% respectively. The scope of the study includes the measurements of surface tension, steady-state behavior, yield stress, creep and recovery, thixotropy, transient shear stress response, and dynamic response.

Results have shown a dramatic decrease in the surface tension with increasing surfactant up to the critical concentration. Polyacrylamide solutions have shown three different behaviors, a first Newtonian region, then a region of dramatic shear thinning, and finally a shear thickening region. Dynamic viscosity have shown shear thinning up to a critical value above which the solutions gave a constant shear thickening behavior and also showed that Cox-Merz rule is not valid in this range of tested solutions. The viscoelastic and thixotropic responses of the tested solutions were small. The effect of surfactant was generally low.

ACKNOWLEDGMENTS

I wish to express my appreciation and gratitude to the thesis supervisor Professor M. Nabil Esmail, for his assistance, guidance and encouragement throughout the course of this research work.

Thanks are extended to Dr. Mamdouh Ghannam for his constructive suggestions regarding the laboratory work.

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CHAPTER 1

INTRODUCTION

Polyacrylamide is a brittle white material manufactured by radical Polymerization of acrylamide monomer. In water, high molecular weight polyacrylamide forms viscous homogeneous solutions, their viscosity increases with increase in the polymer concentration. In some cases polyacrylamide is partially hydrolyzed to give greater viscosity. Polyacrylamide molecules are very flexible and very long, with relatively small diameter, which makes the polymer susceptible to shear degradation or mechanical breakage. On the other hand, polyacrylamide is relatively immune to bacterial attack.¹ The average molecular weight of commercial polyacrylamide ranges approximately from very low 2×10^3 to high 15×10^6 . The fibrous nature of the polymer with its ability to extend and entangle gives great importance to its molecular weight. Higher molecular weight polymers exhibit a greater apparent viscosity than their low molecular weight polymers under similar conditions. The unique chemical and physical properties, the relatively low toxicity, and cost (as low as \$2/kg) give it the advantage to be widely used in practice.² Polyacrylamides are currently used as thickening agents in industrial processes of food industry, water treatment, pulp and paper industry. Its property to increase the solution viscosity substantially by the addition of quantities as small as a few parts per million gives it the ability to be used extensively in enhanced oil recovery in polymer flooding system. It is also has been used in enhanced oil recovery as surfactant- polymer injection.

Surfactants can be defined as the material exhibiting the characteristic of modifying interfacial interactions by way of adsorption at interfaces. One of the most fundamental characteristics of the surfactant is the presence of two structurally dissimilar groups within a single molecule, (1) molecular components that will have little attraction for the solvent or bulk material, called lyophobic group (tail), and (2) molecular components that have a strong attraction for the solvent or bulk phase, called lyophilic group (head). When a material exhibiting such behavior is dissolved in water, the presence of a lyophobic group causes a distortion of the solvent liquid structure, resulting in transport of surfactant molecules to the surface or interface. Such adsorption will effect the mechanical characteristics of the interface by, for example, lowering the interfacial tension between two liquids or changing the wetting characteristics of a solid surface. Although most of the surfactant can be characterized by the existence of a net electrical charge on the molecules, the situation is different in case of nonionic surfactants. The nonionic surfactant is electrically neutral, and the most important advantages of that neutrality are the lowering of the surfactant sensitivity to the presence of electrolytes in its system, the lessening effect of solution pH, and the flexibility in controlling its solubility into the molecule by controlling the size of lyophilic group.³

When the surfactant comes into contact with polymer solutions, its interaction mechanism leads to changes in polymer rheological, spectroscopic, and other physiochemical properties. Although some studies have published on some of the polyacrylamide rheological behavior, there was no complete study

on the behavior of the polymer when it mixed with a nonionic surfactant. In this work we present such study. It presents a comprehensive investigation of the effect of nonionic surfactant (X-100) on the rheological properties of aqueous polyacrylamide. Results have shown that at all concentrations the first Newtonian region is obtained. Also have shown that the effect of the X-100 on the rheological properties of the polymer is quite low.

CHAPTER 2

LITERATURE SURVEY

Polyacrylamide solutions and surfactants have been subjected separately or mixed to many rheological studies under different conditions. It has been reported that polyacrylamide can be used as a drag reduction agent and a vortex inhibitor. Although the mechanism producing the drag reduction is not clear, polyacrylamide is one of the most commonly used polymers for this purpose, due to its flexibility and long chain. The drag reduction mechanism is a substantial reduction in pressure drop for a given flow of a polymer solution, relative to the pressure drop of the pure solvent alone at the same flow rate.⁴ This result has been confirmed by Berwersdorff⁵ and Durst⁶ who have reported that polyacrylamide can be used as a drag reduction polymer. Tie-Qiang and McCathy⁷ have studied the pipe flow of aqueous polyacrylamide solutions by means of nuclear magnetic resonance imaging, and found that at a low bulk flow rate, steady laminar flow was observed for the solutions. As the bulk flow rate increases, unsteady motion appears and the mean velocity profile becomes more blunted. For fully turbulent flow, the 200 PPM polyacrylamide shows a typical velocity profile for drag reduction fluids. As a vortex inhibitor, polyacrylamide at a concentration of 3 PPM is one of the best polymers used for this purpose. On the other hand, at a concentration of 1.67%, aqueous polyacrylamide solutions exhibit a large toroidal vortex in the case of a sudden contraction flow from large reservoir into a small tube⁴. Flew and Sellin⁸ studied the non-Newtonian flow of polyacrylamide solutions in porous media and found

that polyacrylamide can be used as a viscosity enhancing agent in oil field injections. These authors also suggested that high molecular weight polyacrylamide could find applications in fracture treatment of oil wells.

Polyacrylamide has been used extensively in enhanced oil recovery as polymer flooding, a process that is usually applied after water flooding to increase the displacement efficiency. It is also commonly used in surfactant-polymer injection. In this case, the surfactant is injected into the oil reservoir and then polymer injection follows to push the oil out of the reservoir. The use of surfactants facilitates enhanced oil recovery through several mechanisms: (1) Production of low interfacial tension between the oil and the aqueous flooding solution, (2) The reduction of the interfacial rheological properties at the oil/aqueous solution interface, and (3) Optimizing the oil displacement by controlling the wettability of the rock pores.^{1,2} Nasr-El-Din and Taylor⁹ have studied the interfacial behavior of crude oil/alkali systems in the presence of partially hydrolyzed polyacrylamide and reported that at sodium carbonate concentrations less than 0.2 mass %, the interfacial tension slightly drops as a result of increasing the polymer concentration. At sodium carbonate 0.2 mass %, the addition of the polymer up to 2000 PPM had no effect on the interfacial tension. At concentrations greater than 0.2 mass % addition of the polymer resulted in lowering the interfacial tension. Lakatos and Lakatos-Szabo¹⁰ studied the effect of CO₂ on the properties and structure of polyacrylamide for the purpose of using them in enhanced oil recovery to improve simultaneously both the sweep and the displacement efficiencies. Their study has recommended that

higher molecular weight unhydrolyzed or slightly (5-10%) hydrolyzed polyacrylamide must be used if the polymer may have contact with CO_2 . The effect of salt on the viscosity of partially hydrolyzed polyacrylamide is reported to be much greater than the effect on the viscosity of unhydrolyzed polyacrylamide, for example, at CaCl_2 concentrations greater than 0.1% the hydrolyzed polyacrylamide displayed a lower viscosity than the unhydrolyzed polyacrylamide¹. The influence of salt concentration on the thixotropy of solutions of partially hydrolyzed polyacrylamide has been studied by Bradna et al.¹¹, who reported that the negative thixotropic effect in aqueous glycerol solutions of partially hydrolyzed polyacrylamide respond to NaCl in different manners. A slow increase in viscosity with time of shearing could be observed only at higher shear rates and its intensity decreased after addition of NaCl. On the other hand, the rapid increase in viscosity followed by viscosity oscillation did not depend on the salt concentration. Ait-Kadi et al.¹² have studied the rheological properties of partially hydrolyzed polyacrylamide solutions and reported that the salt (NaCl) has a stabilizing effect on the solutions' viscosity. This effect is characterized by lower viscosity level and less shear thinning behavior as salt concentration increased. Durst et al.¹³ have studied the flow of dilute partially hydrolyzed polyacrylamide solutions in porous media under various solvent conditions and concluded that as a result of the salt effect, hydrolyzed polyacrylamide is not considered a practical approach for increasing the viscosity of the flooding fluids employed in enhanced oil recovery. Shin and Cho¹⁴ have investigated the effect of temperature on aqueous polyacrylamide

solutions. They reported that at low shear rate of 0.001 s^{-1} , the viscosity was found to be very sensitive to temperature, whereas at a high shear rate 10 s^{-1} - 200 s^{-1} , the viscosity was almost independent of temperature. Accordingly, the time constant, the fluid behavior index, and the fluid consistency index were found to vary with temperature. On the other hand, Esmail and Ghannam¹⁵ have reported that the viscosity of polyacrylamide solutions significantly decreased with increasing the temperature. The temperature effect is more pronounced at the high shear rate of 100 s^{-1} . The flow behavior index n is found to be constant, whereas the fluid consistency index was found to be a function of temperature and polyacrylamide concentration. Durst et al.¹³ and Esmail and Ghannam¹⁵ have also reported the occurrence of shear thickening behavior at high shear rate. In the paper and pulp industry, polyacrylamide has been used to maintain the efficiency of operation and quality of products. It has been referred to as a beater adhesive, beater additive, or wet-end-additives. Polyacrylamide is effective in increasing fiber bonding, and in improving dry strength, filler retention, rosin sizing and drainage rate¹⁶. Polyacrylamide has been used in many additional applications, including water treatment, mineral processing, dust control, and sugar manufacturing.² In the case of mixing polyacrylamide with surfactants, a number of recent studies were carried out under different conditions. Biggs et al.¹⁷ have reported that in aqueous solutions of hydrophobically modified polyacrylamide with surfactant (SDS), they have seen a dramatic increase in viscosity below that of the critical micelle concentration (cmc). Examination of the viscosity, both as function of shear rate and time,

showed that the solutions have antithixotropic and thixotropic behavior. Wang and liu¹⁸ studied the effect of nonionic surfactant (Tween20) and associative thickener (Acrysol TT935) on the rheology of anionic polyacrylamide (Separan AP30) in aqueous glycerol solutions and their conclusion was that the nonionic surfactant in aqueous glycerol solutions with and without the presence of polymer and thickener reduced the surface tension and resulted in complex rheological behavior. The solution's viscosity increased initially with increasing surfactant concentrations to a maximum, followed by decrease to a minimum, and then increased again at very high surfactant concentration. Zhang et al.¹⁹ studied the oil/water interfacial viscosity of aqueous mixtures of partially hydrolyzed polyacrylamide in the presence of three different surfactants. The result showed that the oil/water interfacial viscosity without presence of polyacrylamide was independent of both shear rate and surfactant concentration. In the case of mixing with polyacrylamide, the interfacial viscosity decreased with ionic surfactant (sodium dodecyl sulfate, cetyltrimethylammonium bromide) and was independent of the nonionic surfactant (X-100).

Polyacrylamide and nonionic surfactant are less sensitive to the salt when they compare to hydrolyzed polyacrylamide and other types of surfactant respectively. That gives the advantage for both of them to be used whenever the solutions may come to contact with salt. The scope of this study is to investigate the effect of nonionic surfactant (X-100) on the rheological properties of aqueous polyacrylamide solutions. It includes the measurements of surface tension,

steady state flow behavior, yield stress, creep-recovery, thixotropy, transient shear stress responses, and dynamic responses.

CHAPTER 3

EXPERIMENTAL WORK

Polyacrylamide (PAM) with molecular weight of 5×10^6 purchased from BDH limited pool England was used in this study. The production number of the polymer is 29788. According to the supplier, the viscosity of 0.5% aqueous solution is about 280 mPas at 25 ° C. The surfactant employed in this study is biodegradable nonionic surfactant Triton X-100 (iso-octyphen oxypolethoxy-ethanol) containing approximately 10 moles of ethylene oxide. Triton X-100 is a trademark of Rohm and Hass Co. The polymer powder was always dissolved in double distilled water at room temperature . Sufficient time (10-15 days) was given to achieve the homogeneity of the solution without mixing or any external source of heat or power to avoid any pre-shear or change in the polymer molecular network. Five different concentrations of polyacrylamide in the range of 0.02-0.1 wt % were prepared. To study the effect of surfactant on these concentrations, nine different concentrations were added to every sample. The surfactant concentration is in the range of 0.001-0.05 wt %. Enough time was given (5-7 days) to ensure complete dissolution without using any external force. The rheological instruments used are a surface tensiometer and Haake Rheometer RS100. Surface tensiometer, model 21, designed by Fisher Scientific Company, has been used to determine the solutions' surface tension. The surface tension is determined by measuring the force per unit length required to detach a platinum ring from a liquid surface. When the wetted ring is lifted from the liquid surface, at a certain height the surface becomes unstable and the ring

separates from the liquid surface. The moment at which this separation appears, the value of the surface tension in dynes per cm is registered. This method has been used widely due to its simplicity and rapid determination of surface tension. The apparatus has to be calibrated using the known surface tension value of liquid. To increase accuracy, the tensiometer has been calibrated for every measurement. Several measurements have been taken for every sample and the average was calculated. Rheometer RS100 (figure 3.1) is a Searl type measuring system combined with a cone-and-plate sensor system. This system consists of flat plate, which carries a sample of the liquid, and a cone. It has a controlled variable lift speed to position the cone tip on the plate. The cone rotates at angular velocity " ω ". The gap between the cone and the plate is kept small to keep the angle " θ " between the flat plate and the conical surface small. It is preferred to keep the angle less than 5 degrees as the strain rate will be more uniform, the sample can be retained in the gap more easily, temperature rise is minimized, and a small sample is sufficient. Furthermore, a secondary flow which is radial outward flow, has been observed with larger angles. Rheometer RS100 has several operating modes, a controlled rate (CR) mode, a controlled stress (CS) mode, and oscillation (OSC) mode. Controlled rate mode is technically less complicated than controlled stress mode. In controlled rate mode, the cone is driven by a motor. Its speed is controlled for a programmed rotor speed while the plate is held at rest. To measure the resistance of the liquid being sheared between the stationary and rotating parts, a torque detector, normally a spring, is positioned between rotor and motor. When it rotates, it

provides the shear rate. The resistance of the sample causes a shear stress on the rotor that twists the detector accordingly. In controlled stress mode, the cone is driven by a special motor for which defined torque values exist. The torque input and the resulting motor speed act on the same rotor shaft axis. Torque data can then be mathematically transformed to shear stress and the rotor speed to shear rate. The drive shaft is centered by an air bearing that ensures an almost frictionless transmission of the applied stress to the test sample. The resulting shear rate registered into the sensor system is detected with a digital encoder which is able to measure a small yield value and low strain or shear rates. The oscillation mode relates the assigned angular velocity or frequency to the resulting oscillating stress or strain. The cone is no longer turning continuously in one direction, it is made to deflect with a sinusoidal time function alternatively for small angles to the left and to the right. The sample is forced to strain in similar fashion, causing resisting stress.^{20,21} The RS100 system can be easily switched between both the CR and CS modes. In oscillation mode, both stress and frequency sweeps can be applied. It is also designed to allow an easy exchange of a multitude of cone and plate systems characterized by their different active surface areas.

To avoid wear in the cone tip and plate, the plate is initially moved upwards until it makes contact with the cone. The plate is then moved downwards. When the test is running, the impinging tip of the cone touches the plate as is required for the cone-and-plate tests.

There are several advantages and disadvantages of using this kind of system to study the rheological properties of materials. Among the advantages, it has constant shear rate throughout the testing sample. The sample size is very small when compared with other systems, something that matters in the case when the sample is precious or only a few drops exist. It is also very easy to be cleaned after the test. The disadvantages of using this system are that when it is used for dispersions with sizable particles, these particles must be squeezed out from the tip region to allow cone contact. In thixotropy, the radial squeeze flow will cause some pre-shear and partial destruction of the thixotropic structure. When a visco-elastic material is subjected to shear, the normal force is able to draw some of the tested sample out of the gap. The fluid climbs upward on the outer rim of the cone, causing serious disturbance for the measurements. This phenomenon can be seen when one looks closely at the rotating cone.^{20,22}

In this study, the cone diameter, angle, and gap at the cone tip are respectively 35mm, 4°, and 0.137mm.

Seven types of measurements have been performed to investigate the effect of nonionic surfactant (X-100) on the rheological properties of polyacrylamide solutions: (1) Surface tension test, to study the effect of surfactant concentration on the solutions surface tension, (2) Steady-state flow test, to investigate the flow behavior. It is plotted in the form of viscosity-shear rate curves, (3) Yield stress test, (4) Transient test, to investigate the time dependent response, (5) Creep-recovery test, to investigate the visco-elastic response of the solutions, (6) Thixotropic test, to determine whether the material

behaves like a thixotropic or antithixotropic fluid or it has no time dependence of viscosity, and (7) Dynamic study, to measure the storage and loss moduli as well as complex viscosity as a function of angular velocity.

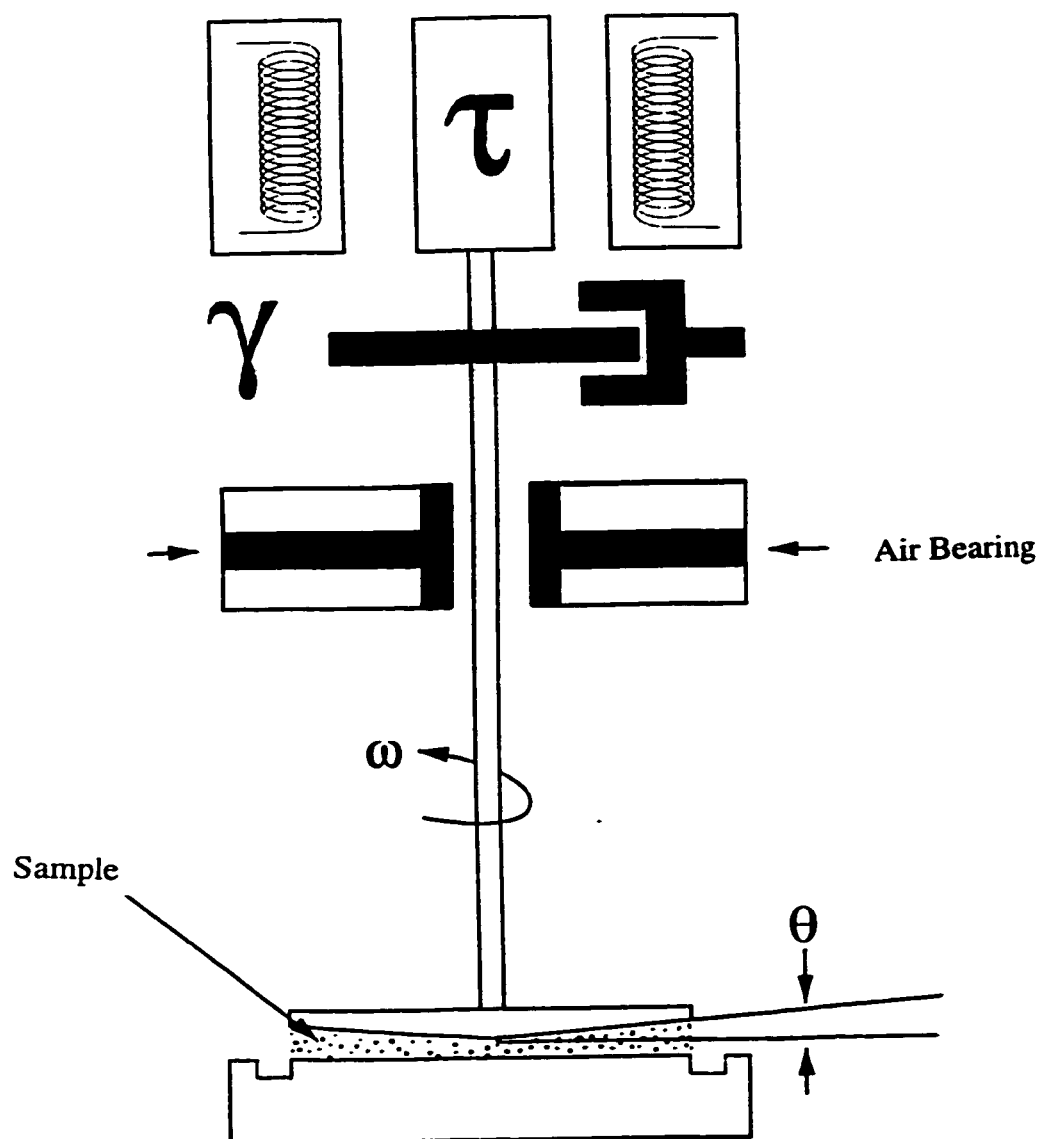


Figure 3.1 Schematic of the Cone and Plate System

CHAPTER 4

RESULTS

4.1 Surface Tension.

Molecules at the surface of any body experience a different force of interaction from its neighbors. In the interior of a liquid, the molecules are subjected to an equal force among each other; however, molecules at the surface of liquid which is in contact with an air or gas would be subjected to strong inward attraction and small outward attraction. This unbalanced attraction would cause as many molecules as possible to move into the bulk liquid, thus minimizing the surface area of a liquid. This attraction at the interface between the air and the liquid is called the surface tension. The concept of surface tension can be explained by the shape of a bubble or drop of liquid as it tends to have the smallest surface area by forming a sphere. The higher the surface tension, the higher the molecular attraction and the more nearly spherical is the drop.

The surface tension (liquid/air interface) and interfacial tension (liquid/liquid interface) between two phases usually have different physical properties from those of bulk material. Molecules at the surface or interface experience a different force of interaction, resulting in definite free energy because of different types and numbers of neighboring atoms and molecules. The surface tension and interfacial tension may vary dramatically by change in their bulk composition. In general, there is no direct relation between the change in surface tension and the change in interfacial tension; however, the change in

surface tension, for example as a result of addition of surfactant, can be an indication of changes in the interfacial tension³.

As surfactant is dissolved in a solvent, due to its unique chemical structure, its molecules tend to present in the interface or undergo an aggregation or micellization leading to reduction in the surface tension. The concentration at which the surfactant molecules start to form the micelles is called critical micelle concentration cmc. At this concentration, the rate at which the properties of surfactant solution vary with concentration changes dramatically.

Surface tension measurements have been carried out for all concentrations. The obtained data has been plotted in figure 4.1.1 in the form of surface tension-surfactant concentrations. The increase in polyacrylamide concentration has no meaningful effect on surface tension; however, increasing the surfactant concentration leads to a dramatic decrease in the surface tension. This decrease can be observed until the surfactant concentration reaches the cmc values, which are 0.02 for 0.02% PAM and 0.03 for the other polyacrylamide concentrations. Exceeding this value, increasing surfactant concentration has no effect on the solutions' surface tension. The surface tension at cmc for the tested polyacrylamide samples was in the range between 30-35 dynes/cm.

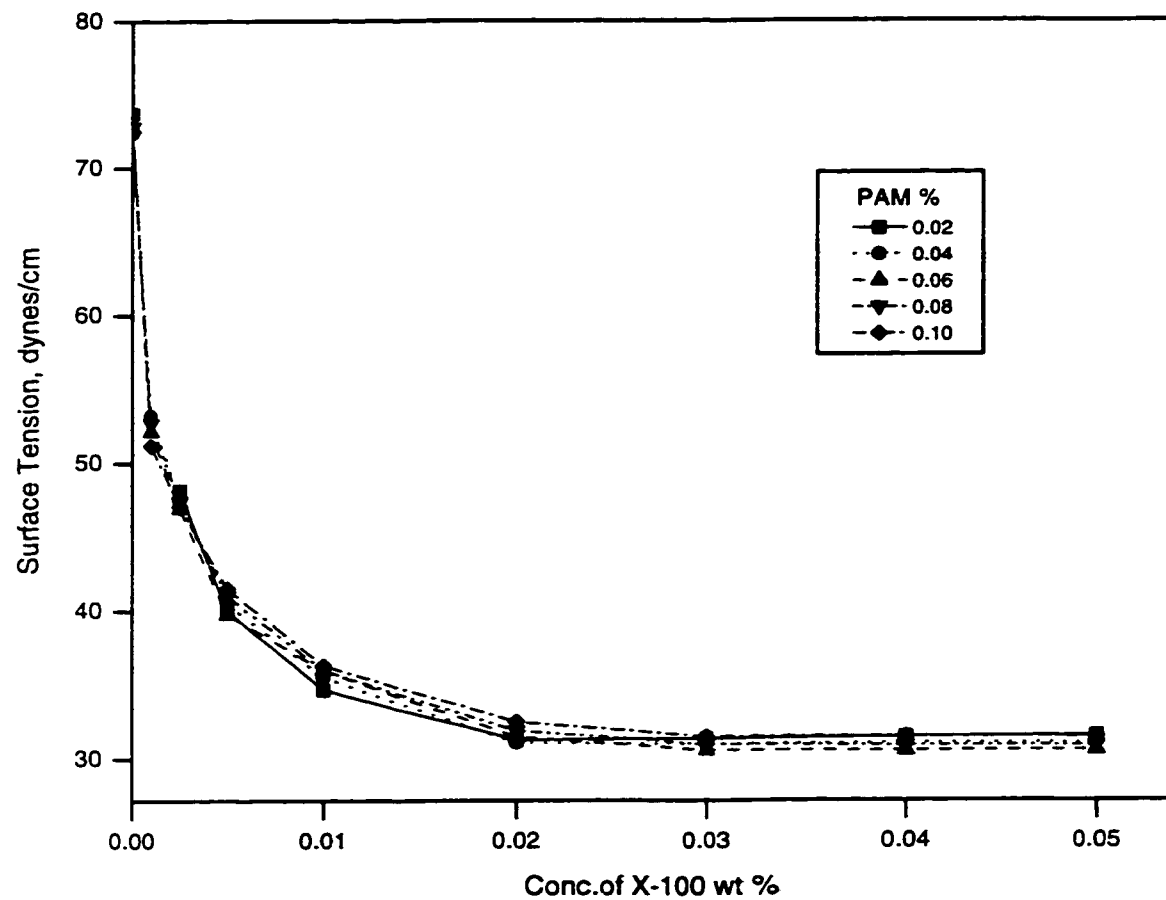


Figure 4.1.1 Effect of Surfactant on Surface Tension for PAM Solutions

4.2 Steady-state flow.

This test has been conducted under steady shear rate in CR mode, which means that the shear rate remains constant until constant steady shear stress is obtained. This represents one measuring point, then the selected shear rate rises to obtain a new value of the shear stress. This process repeats, based on the given values of the initial and final shear rate. In this study, the initial and final values were taken as 0.3 s^{-1} and 750 s^{-1} respectively. The data obtained describe the flow behavior of the solutions by providing the viscosity curves which present the behavior of the viscosity with increasing shear rate.

It is always necessary to know the viscous properties of a material to solve any hydrodynamic problem related to the flow of the material, such as calculation of flow rate and pressure drop in process equipment design, and predicting the conditions of its use in practice. It also reflects the chemical and physical structure of the material quality.

Figure 4.2.1 shows the viscosity curves at different concentrations of PAM solutions. The increase in polymer concentration results in an increase in the apparent viscosity of the solutions. This is clearly a mass effect because, as more polymer molecules are dissolved, the opportunity for intermolecular entanglement rises. These entanglements translate to an increase in the solutions' viscosity. The polymer solutions are Non-Newtonian in nature and they exhibit three different behaviors as a result of increasing shear rate. These three behaviors are Newtonian region at low shear rate, shear thickening at high shear rate, and region of dramatic shear thinning in between. In the range of shear rate

among 0.3 s^{-1} and 0.5 s^{-1} , the lower Newtonian region (zero-shear-viscosity) is observed at all PAM concentrations. This is related to the physical properties of the solutions. This region increases as the molecular weight decreases, molecular weight distribution narrows, and polymer concentration decreases. In this region, the rate of deformation is so slow that there is no change in the molecular shape or entanglements. The change in flow field is compensated by Brownian motion²³. In the range of shear rate among 0.5 s^{-1} and 200 s^{-1} , there is a sharp decrease in the viscosity pronounced at all concentrations. This pseudoplasticity is the most common phenomenon of non-Newtonian behavior²³ and it can be explained as the polymer solution with long entangled and looping molecular chain at rest, maintaining an irregular internal order and correspondingly characterized by a sizable internal resistance against the flow. When the shear rate is increased, the chain of the molecules can disentangle, stretch and orient themselves parallel to the driving force, which allow them to slip past each other more easily leading to the shear thinning. Another possible reason for the pseudoplasticity could be the solvent layers are being stripped from dissolved molecules which means that the intermolecular interactions causing resistance to flow become reduced²⁰. At shear rate above the critical shear rate 200 s^{-1} , the solutions are accompanied by shear thickening. This shear thickening is more visible at concentrations 0.02% and 0.1% PAM, but at the other concentrations, its intensity decreased to present nearly a second Newtonian region. Shear thickening phenomena have been reported under different conditions for both unhydrolyzed¹⁵ and partially hydrolyzed^{12,24,25,26}

polyacrylamide solutions. Dupuis et al^{24,25} and Ait-Kadi et al¹² have studied partially hydrolyzed polyacrylamide solutions under different conditions and reported that shear thinning was observed below the value of the critical shear rate, above which increase of the viscosity has been observed. Hu et al²⁶ have studied the shear thickening phenomenon and explained it, as the effect of simple shear flow reducing the number of interactions associated at low shear rate, leading to shear thinning, and, at sufficient high shear rates, stretching individual chains and generating interchain bonding by coagulation, leading to shear thickening and strong flow birefringence. It can also be explained that, at high shear rate, polymer degradation leads to rupture of the molecular chain, causing reduction in the chain length. At higher shear rate, connection between chains might occur, leading to shear thickening behavior.

The effect of surfactant on the solutions of polyacrylamide can be obtained from the viscosity curves, figures 4.2.2, 4.2.3, 4.2.4, 4.2.5 and 4.2.6 which describe the viscosity behavior in correlation between the viscosity-shear rate. Figure 4.2.2 shows the effect of surfactant on 0.02% PAM. Below shear rate 0.5 s^{-1} , complex behavior of the solutions is pronounced. At higher shear rate, decrease in viscosity with surfactant up to concentration 0.04% is followed by a slight increase at 0.05%. Figure 4.2.3 presents the effect of surfactant on 0.04% PAM. The effect of the surfactant on the solution at shear rate below 0.5 s^{-1} is random. At higher shear rate, the surfactant has no effect up to a concentration of 0.03%, at which point a sharp decrease in viscosity is followed by a gradual increase as the surfactant concentration increases. In figure 4.2.4,

the surfactant has almost no effect on 0.06% PAM solution. Figure 4.2.5 shows the effect of surfactant on 0.08% PAM, quite similar to the behavior of 0.06% PAM with a slight decrease in viscosity at surfactant concentration 0.03%. Figure 4.2.6 shows the effect of surfactant on 0.1% PAM, a relatively higher decrease in viscosity at concentration of 0.0025% followed by fluctuation as surfactant concentration increases to give an increase in the viscosity to the original value.

The critical shear rate has no dependence on the polymer or surfactant concentrations. Above the critical shear rate, surfactant concentrations higher than 0.03% enhance the viscosity for 0.02% and 0.04% PAM. Surfactant has almost no effect on concentrations of 0.06% and 0.08% PAM, while at the other concentration it leads to decrease in viscosity.

The flow behavior of PAM solutions with and without surfactant fitted to Ostwald-de Waele model (equation 4.2.1) and Carreau-Yasuda model (equation 4.2.3). These equations are just empirical fits of the experimental $\eta(\dot{\gamma})$ curves. It is a common practice in industry to use the Ostwald-de Waele model to describe a range of viscosity behavior of a sample. Because of its simplicity, a wide variety of flow problems have been solved analytically for it. ⁴

$$\tau = k \dot{\gamma}^n \quad (4.2.1)$$

Equation 1 can be written as:

$$\eta = k \dot{\gamma}^{n-1} \quad (4.2.2)$$

where τ is the shear stress and $\dot{\gamma}$ is the shear rate.

According to equation 4.2.2, the viscosity decreases with increasing of shear rate for $n < 1$ (shear thinning fluids) and increases with increasing of shear rate of

$n > 1$ (shear thickening fluids), where n is flow behavior index (dimensionless value) and, k -is consistency index (with units of $\text{Pa} \cdot \text{s}^n$).

$$(\eta - \eta_{\infty}) / (\eta_0 - \eta_{\infty}) = [1 + (\lambda \dot{\gamma})^a]^{(n-1)/a} \quad (4.2.3)$$

Where, η_0 is the zero-shear-rate viscosity, η_{∞} is the infinite-shear-rate viscosity. This viscosity is not usually measurable since polymer degradation becomes a serious problem before sufficient high shear rate can be obtained. λ is the time constant, and can be defined as the time at which polymer molecules change their configuration due to their motion⁴. a is a dimensionless parameter that describes the transition region between the zero-shear-viscosity region and the power law region. Their values are presented in Tables 4.2.1- 4.2.6.

Table 4.2.1 : Flow Parameters for PAM Solutions

PAM %	0.02	0.04	0.06	0.08	0.1
η_0	100	210	300	420	570
k	0.16	0.19	0.25	0.29	0.37
n	0.5	0.5	0.5	0.5	0.5
λ	0.084	0.084	0.084	0.084	0.084
a	2	2	2	2	2

Table 4.2.2 : Flow Parameters for 0.02% PAM Solutions

X-100	0%	0.0025%	0.005%	0.01%	0.02%	0.03%	0.04%	0.05%
η_o	100	99	120	100	110	89	100	120
k	0.16	0.13	0.15	0.13	0.15	0.12	0.12	0.15
n	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
λ	0.084	0.085	0.084	0.084	0.085	0.084	0.084	0.084
a	2	2	2	2	2	2	2	2

Table 4.2.3 :Flow Parameters for 0.04% PAM Solutions

X-100	0	0.001	0.0025	0.005	0.01	0.02	0.03	0.04	0.05
η_o	210	200	280	200	230	220	160	170	200
k	0.19	0.2	0.19	0.19	0.19	0.2	0.16	0.18	0.21
n	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
λ	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
a	2	2	2	2	2	2	2	2	2

Table 4.2.4 :Flow Parameters for 0.06% PAM Solutions

X-100	0	0.001	0.0025	0.005	0.01	0.02	0.03	0.04	0.05
η_o	300	330	320	340	300	320	310	320	310
k	0.25	0.24	0.24	0.23	0.24	0.26	0.24	0.26	0.27
n	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
λ	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
a	2	2	2	2	2	2	2	2	2

Table 4.2.5 :Flow Parameters for 0.08% PAM Solutions

X-100	0	0.001	0.0025	0.005	0.01	0.02	0.03	0.04	0.05
η_o	420	410	420	450	440	430	370	430	450
k	0.29	0.27	0.28	0.3	0.3	0.29	0.29	0.32	0.32
n	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
λ	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
a	2	2	2	2	2	2	2	2	2

Table 4.2.6 :Flow Parameters for 0.1% PAM Solutions

X-100%	0	0.001	0.0025	0.005	0.01	0.02	0.03	0.04	0.05
η_o	570	490	350	510	520	490	470	430	550
k	0.37	0.35	0.39	0.43	0.34	0.33	0.32	0.34	0.5
n	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
λ	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
a	2	2	2	2	2	2	2	2	2

From Tables 4.2.1 - 4.2.6, the flow behavior index $n=0.5$ presents the shear thinning region. The consistency index k goes through continuous increase as the polyacrylamide concentration increases. The parameter a is found to be 2 for all tested samples. The value of η_o is undetectable as some concentrations are accompanied by shear thickening behavior. The effect of surfactant on the consistency index is fluctuated in small values.

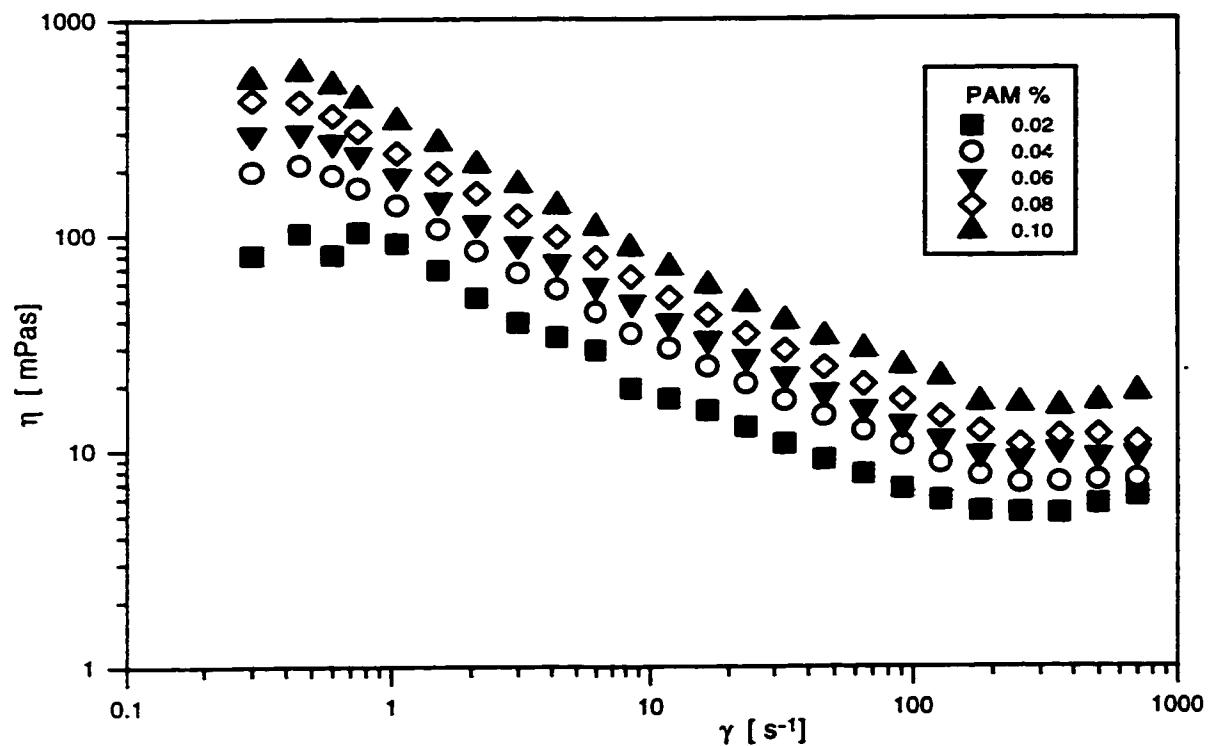


Figure 4.2.1 Viscosity Curves for PAM Solutions

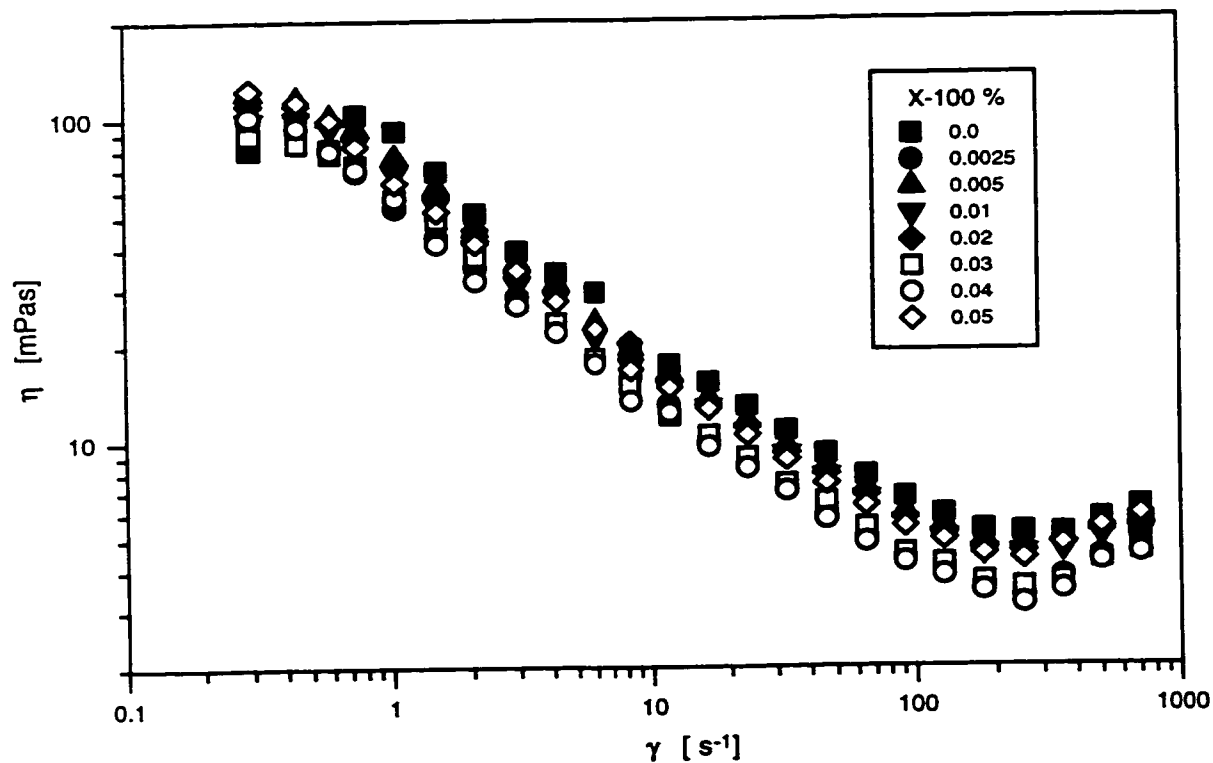


Figure 4.2.2 Effect of Surfactant on Viscosity Curves of 0.02%PAM

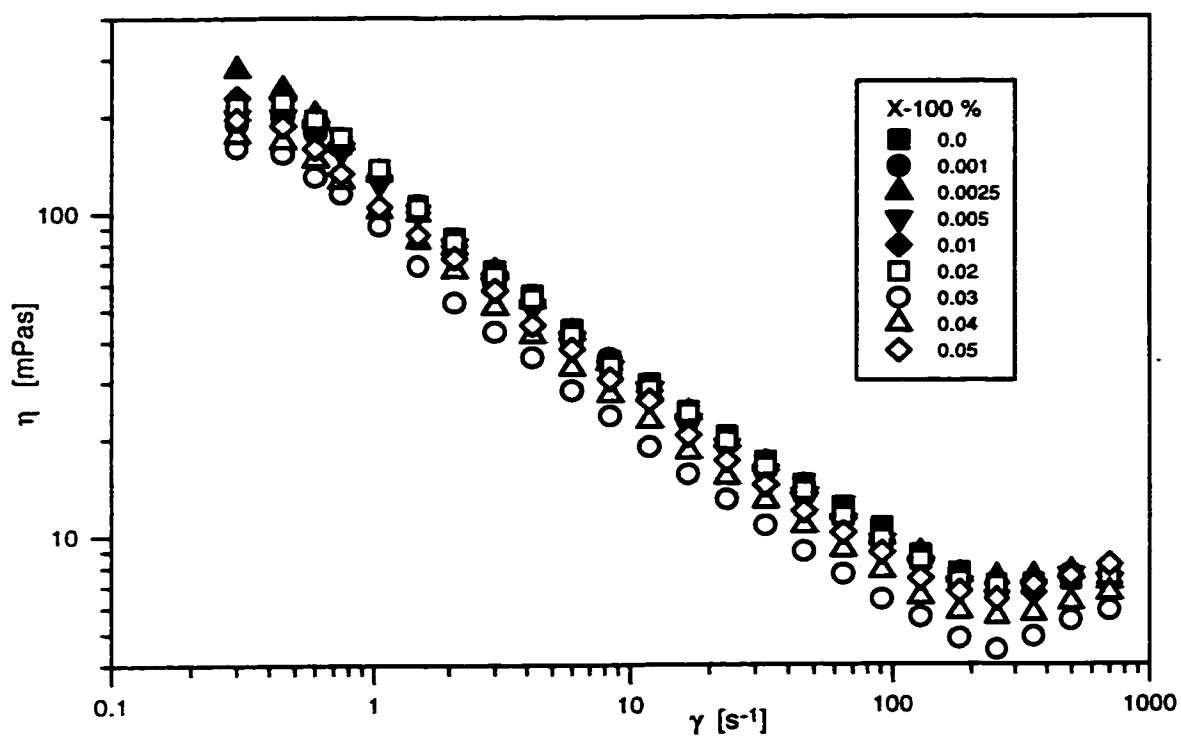


Figure 4.2.3 Effect of Surfactant on Viscosity Curves for 0.04%PAM

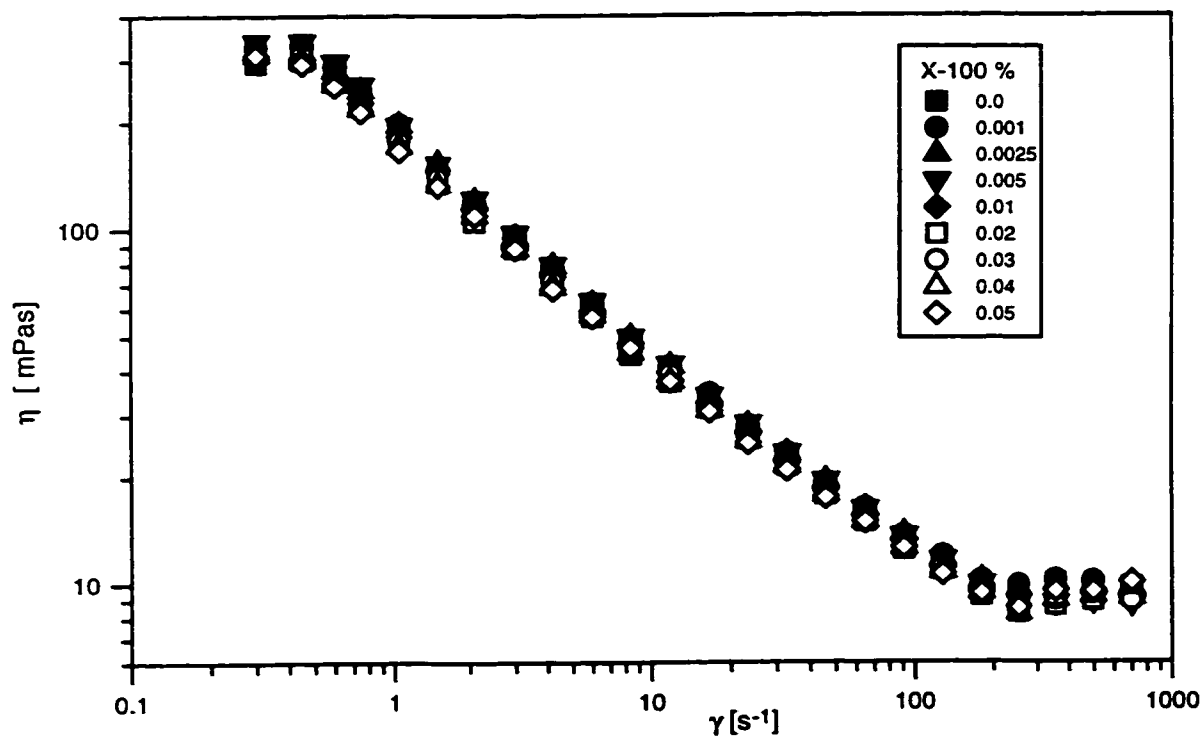


Figure 4.2.4 Effect of Surfactant on Viscosity for 0.06%PAM

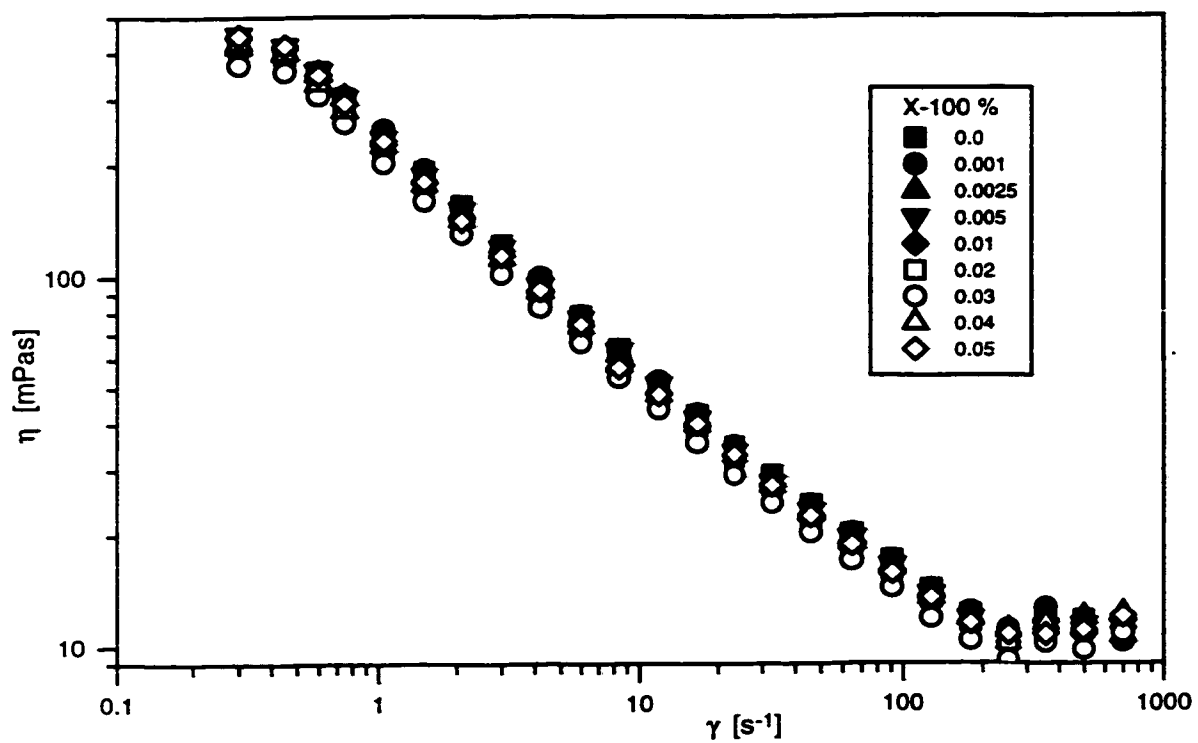


Figure 4.2.5 Effect of Surfactant on Viscosity for 0.08%PAM

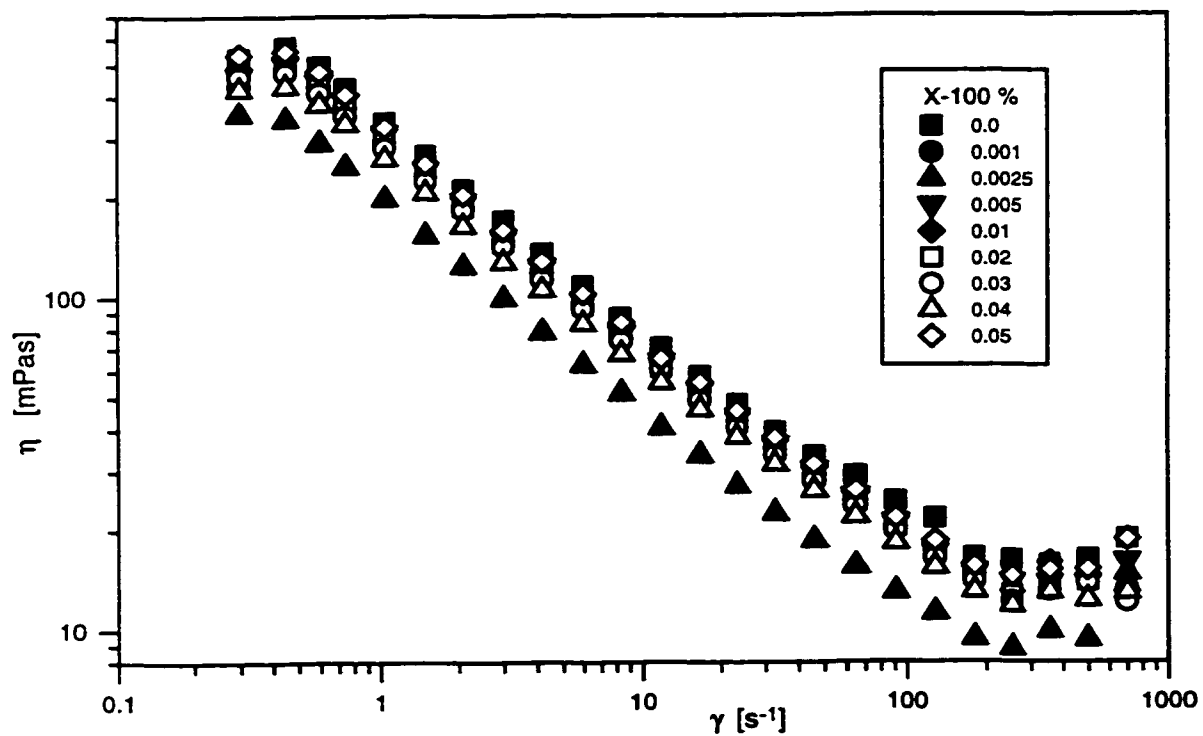


Figure 4.2.6 Effect of Surfactant on Viscosity for 0.1%PAM

4.3 Yield Stress.

Yield stress, (yield point) can be defined as the minimum stress required to cause a fluid to flow. Above the yield stress, the applied stress is proportional to the rate of the deformation, with viscosity as the proportionality factor, causing unlimited deformation and the material starting to flow. When the stress applied to a material is less than the critical value (yield stress), the material does not flow, but deforms elastically like a solid. In this case, the stress is linearly proportional to the strain and the material can recover its zero strain when the applied stress is removed. In this region, the material behaves like a Hookean solid with Young Modulus as the proportional factor.

$$\sigma = E \epsilon \quad (4.3.1)$$

Where σ is the stress, ϵ the strain and E Young modulus.

From a practical point of view, yield stress can be classified into two types, first: rigid Yield stress. This type is result of a three-dimensional-network which does not break down (no flow) until the stress reaches a particular value (yield stress)^{23,27}, and second: Dynamic yield stress. When a shear stress applied to a material which exhibits this behavior, it starts to vibrate with a small movement and the change in shear rate is relatively low compared to the change in shear stress.

Knowledge of the yield stress is essential in engineering design and operation where the handling and transport of such material is involved. The measurement of the yield stress is critical in understanding the flow properties of materials exhibiting this behavior. An important feature of this behavior is that if

the stress is not constant over a body, part of it may flow while the rest acts as a solid. Another characteristic of yield stress fluids is that they give rise to thick deposits on steep slopes while unyielding fluids go on flowing. They also determine the stability of suspensions and the appearance of coated material.²⁸ The mechanism behind the yield stress can be explained as the development of structure or net work. This net work can be formed by cross links, bridging or association through physical contacts or molecular weight effects. These structures can be deformed under an applied shear stress, but will be completely redeveloped upon cessation of the shear stress if the shear stress is below the yield stress without causing any kind of flow phenomenon. If the shear stress exceeds the yield stress, the structure may be partially redeveloped.²⁹

In order to determine the yield stress values of the polyacrylamide solutions with and without the surfactant, the hysteresis loop is used. Controlled stress mode is employed. In this mode, as controlled stress is applied, the shear stress is controlled, but it does not measure any meaningful shear rate as long as stresses are not high enough to cause the fluid to flow. The applied shear stresses are from 0.09 - 3 Pa to establish the up curve (ramped up), then the assigned stress is instantaneously reduced from 3 - 0.09 Pa to develop the down curve (ramped down).

The results of hysteresis loop measurements are plotted in figures 4.3.1-4.3.5. They indicate that polyacrylamide solutions with and without surfactant exhibit no rigid yield stress. Polyacrylamide at concentrations higher than 0.06% gave dynamic yield stress. For concentrations of 0.02% and 0.04% PAM in the

ramped down curve, the value of the shear stress appears to be a negative value at a very low value of shear rate, likely due to inertia . That is particularly apparent when measuring low viscosity (shear thinning) fluids with a control stress instrument. The rotor decreases dramatically with decreasing the shear stress, resulting in additional lower torque due to inertia.

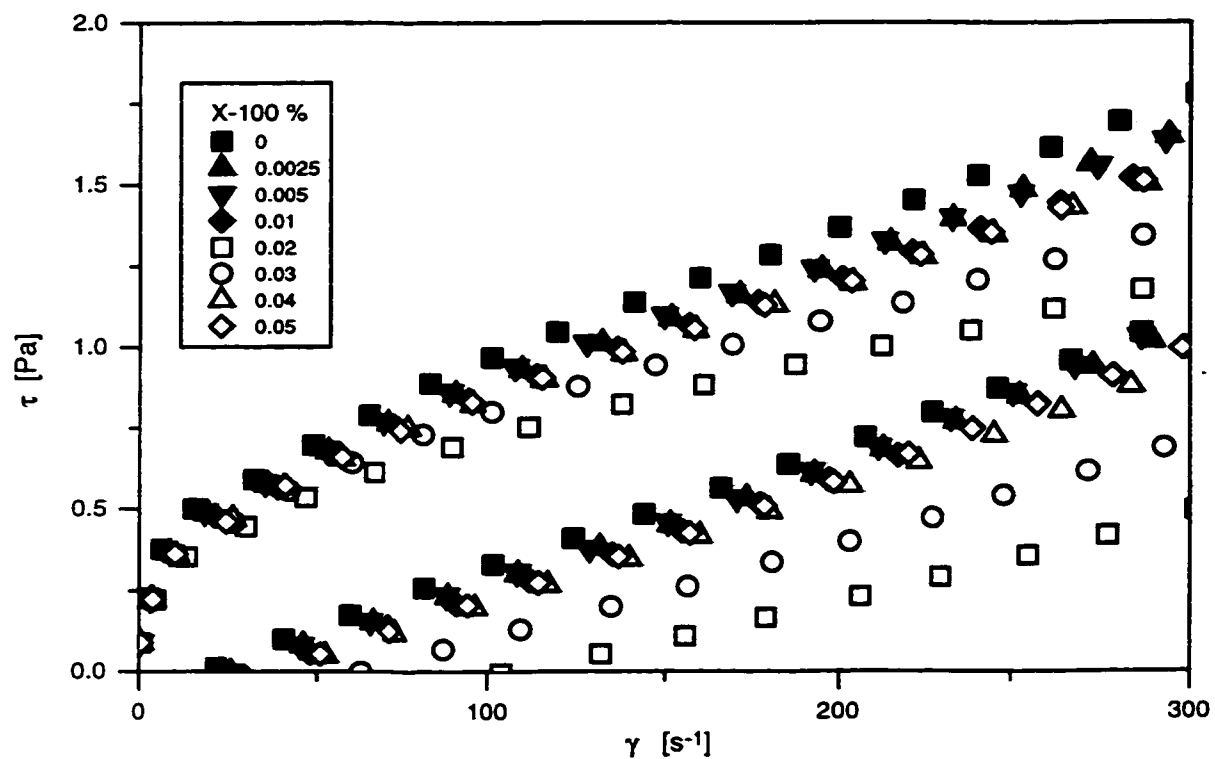


Figure 4.3.1 Yield Stress for 0.02% PAM

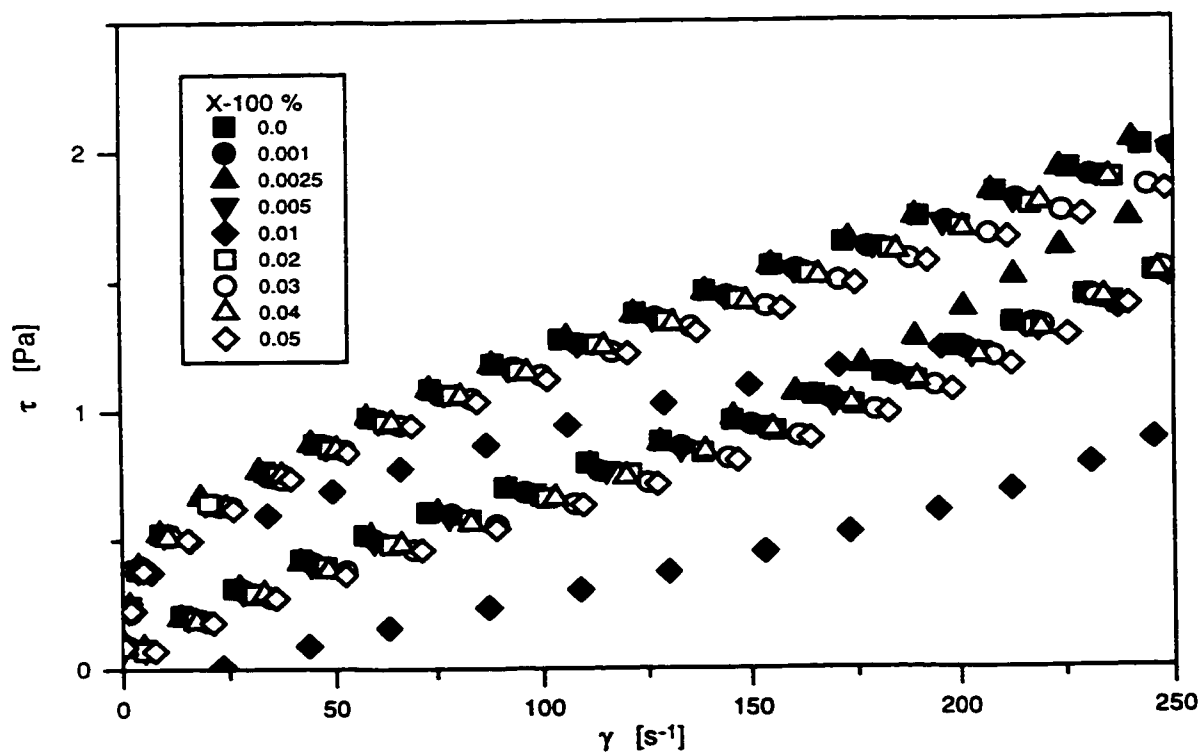


Figure 4.3.2 Yield Stress for 0.04% PAM

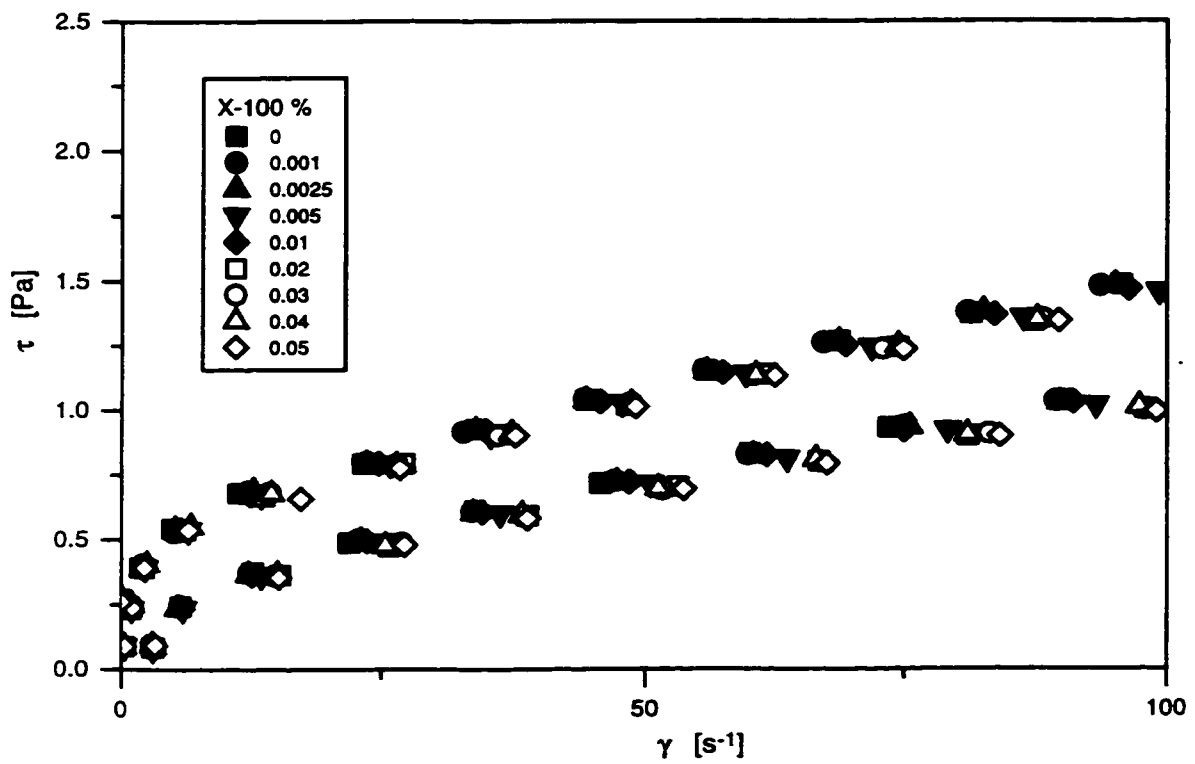


Figure 4.3.3 Yield Stress for 0.06% PAM

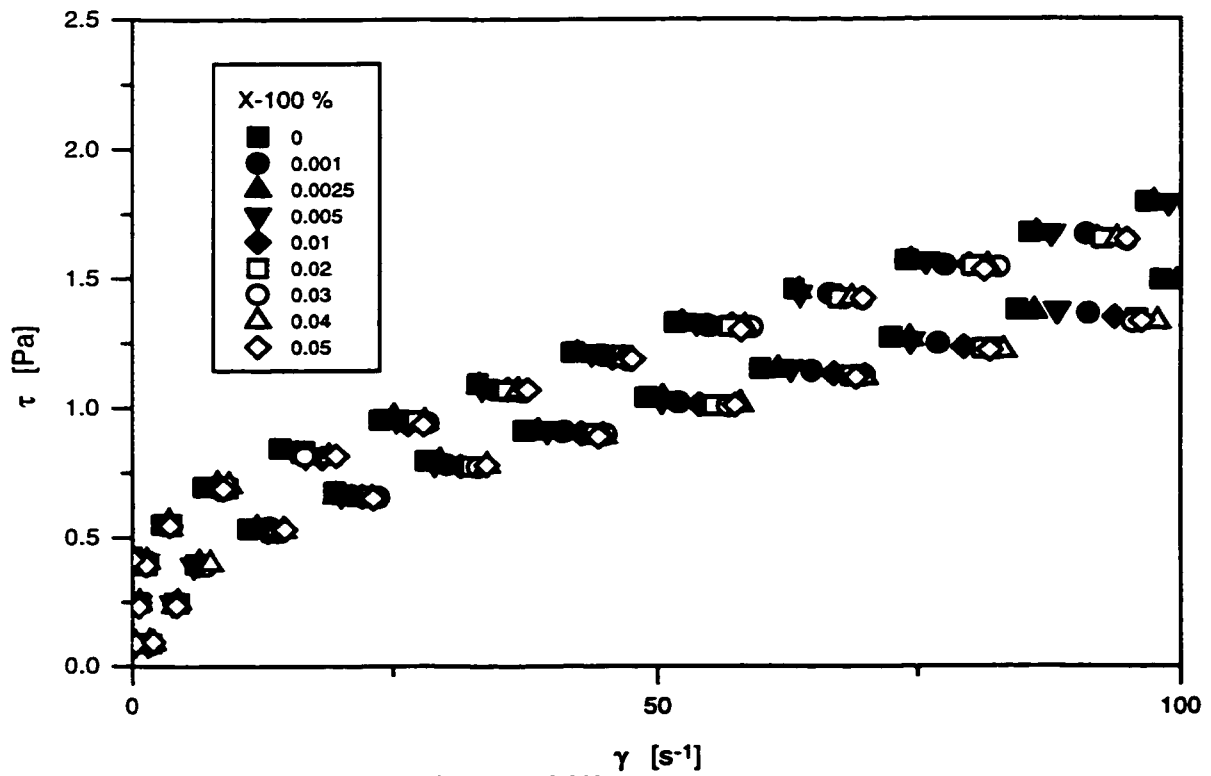


Figure 4.3.4 Yield Stress for 0.08% PAM

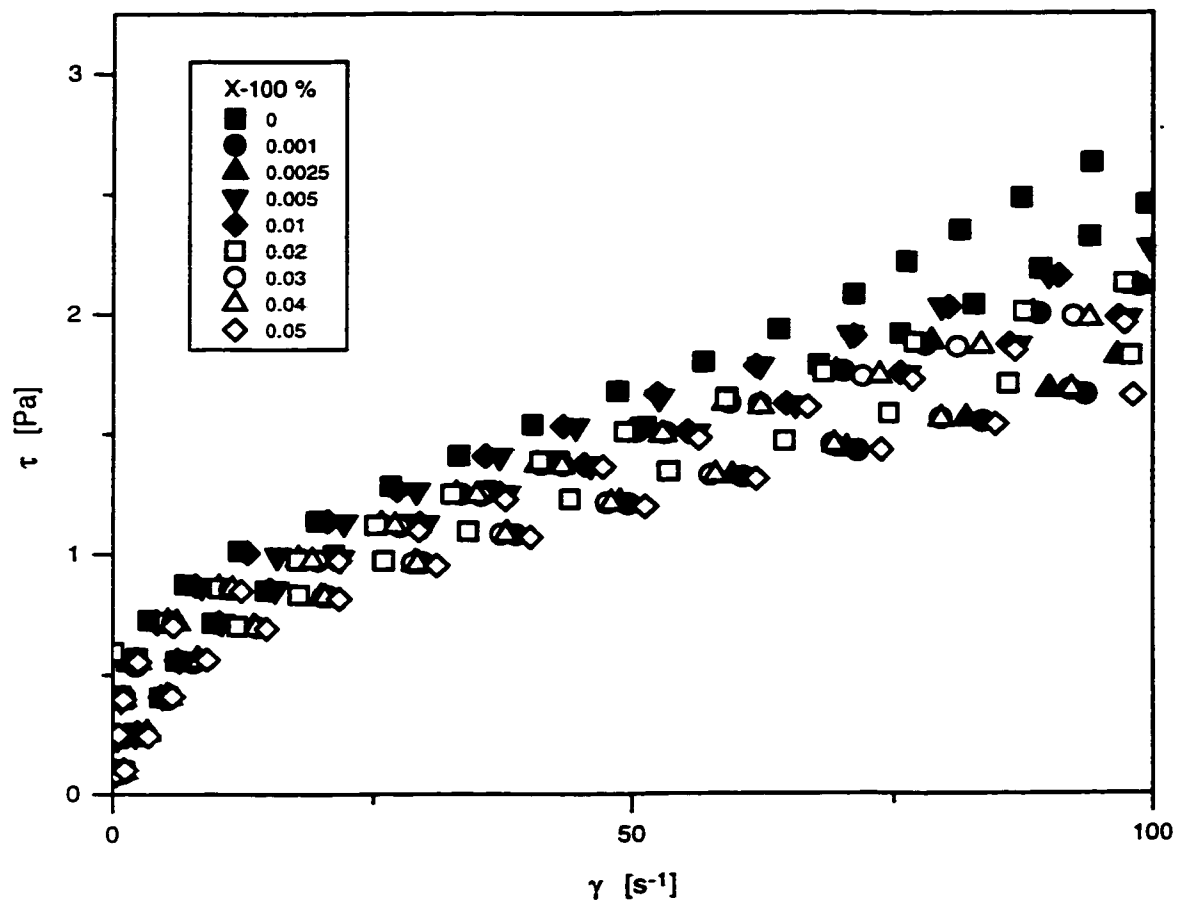


Figure 4.3.5 Yield Stress for 0.1% PAM

4.4 Creep-recovery.

The creep-recovery test has been used to investigate the viscoelastic response of material. Viscoelasticity is a combination of viscosity and elasticity, in other words, a material that exhibits viscous and elastic properties is called viscoelastic material. This kind of material is characterized by a certain level of elastic solid, but it flows and dissipates energy by friction as a viscous fluid. At constant stress, this material does not hold at constant deformation (react as solid), but it continues to flow with time. On removal of the applied stress, it does not react like viscous material (no recovery), but it recovers some of its deformation. This response of applied stress is a fundamental property of the material molecular structure. Flow of highly viscoelastic material leads to so-called vortex enhancement with strong recirculating region in the salient corner³⁰.

In this test, the undisturbed sample is subjected at time $t_0 = 0$, to constant stress $\tau_0 = \tau$, and the time related strain $\gamma(t)$ is measured. This can be mathematically related by:

$$\gamma(t) = J(t) \tau \quad (4.4.1)$$

Where $J(t)$ is the time related compliance, it is a material constant defining how compliant a sample is. The higher the compliance, the more easily the sample can be deformed. It has a unit of Pa^{-1} and can be defined as:

$$J(t) = \gamma(t) / \tau \quad (4.4.2)$$

The response of the tested viscoelastic material to the applied stress depends on whether it is tested in its linear or non-linear viscoelastic region. In linear viscoelastic range, the strain is proportional to the stress at any instant of time,

and doubling the stress will double the strain. Referring to equation 4.4.2, the compliance will be independent of the applied stress. In this case, if one plots the compliance as a function of time for different values of applied stress, the yielded curves will be curves falling on top of each other. This usually appears at low value of stresses in order to minimize the possibility of a breakdown in the structure of the tested material. As the strong bonds of the long chain molecules at rest loop and entangle with each other at minimum energy state, their response to the deformation is negligible at low stresses. The proportionality of the stresses and strains may be explained as the ability of the molecular network to elastically deform, but keep the network structure as such intact.

Determination of the linear limit of the tested sample is very important in engineering applications. The data obtained in this range is a material constant and repeating the test on the same sample will yield the same result, which makes it very useful to be used in quality control. When applying higher stresses, the molecules will start to disentangle and change position with respect to each other. The network is strained beyond its mechanical limits, which leads to structural breakdown, resulting in lower viscosity with little or no elasticity. The compliance curves will start to deviate from those which had fallen on the top of each other, indicating the dependence of the compliance on the applied stress. This means that the tested sample is in non-linear region and can be defined as:

$$\gamma(\tau, t) = J(\tau, t) \tau \quad (4.4.3)$$

where the dependence of the compliance $J(\tau, t)$ on the stress τ is indicated.

The data obtained in this region is no longer material constant as the material elastic structure is partially and irreversibly destroyed. It is affected by test condition and sensor system parameters. Repeating the test on the same sample may yield different values.

The process of using creep and recovery test to measure the viscoelastic response of a material can be divided into two sections. A constant stress is applied instantaneously for a fixed period of time. Instantaneous increase in the strain or compliance will appear. When the applied stress is removed, the response of the material (viscous, elastic) determines the profile of the compliance.

In order to investigate the viscoelastic response of polyacrylamide solutions, creep and recovery test were carried out for all tested samples. To determine the linear viscoelastic range, various stress levels (0.1 Pa-0.4 Pa) were carried out instantaneously for 120 s to the samples. The obtained data was plotted in form of compliance-time. Figures 4.4.1-4.4.5 show that the compliance curves deviate from one another, indicating the dependence of compliance on the shear stress. That means the tested samples are in nonlinear viscoelastic region. To determine the recovery part, shear stress 0.1 Pa has been applied to all tested samples for 300 s, following this period of time, the applied stress was brought to zero for the same period of time.

Figure 4.4.6 shows creep and recovery test of 0.02% PAM with different concentration of X-100. Polyacrylamide at this concentration with and without surfactant shows pure viscous behavior. The effect of surfactant is complex,

increasing in compliance values as surfactant concentration increases up to 0.005%, followed by decrease until it reaches 0.02%, then increasing again up to 0.05%. In figure 4.4.7, the solutions of 0.04%PAM still behave like viscous material, increasing in compliance as the surfactant concentration increases up to 0.01%, then slightly decreasing up to 0.02%, followed by an increase up to concentration of 0.05%. At higher concentration of 0.06% PAM, figure 4.4.8 shows that the solution behaves as viscoelastic material, with slight decrease in compliance at concentration 0.001%, followed by increase up to concentration of 0.0025%. Then the compliance value decreases again at concentration of 0.005%, followed by increase to a constant value for higher concentrations. Figures 4.4.9 and 4.4.10 show the effect of surfactant on polyacrylamide at concentration of 0.08% and 0.1% respectively. Both of the solutions behave like viscoelastic materials. The change of the compliance as a function of surfactant is still complex.

From the figures mentioned above, the surfactant has no effect on the viscoelastic response of the tested samples. Polyacrylamide solutions behave like viscous material at low concentrations and as viscoelastic material at higher concentrations. In all tested samples, the viscous part was always higher than the elastic part. Surfactant increases the compliance value which increases the response of the material to flow. For PAM solutions, except 0.02%, the highest compliance appears at surfactant concentration of (cmc) 0.03% or higher. For polyacrylamide solutions, the higher the concentration, the lower is the compliance.

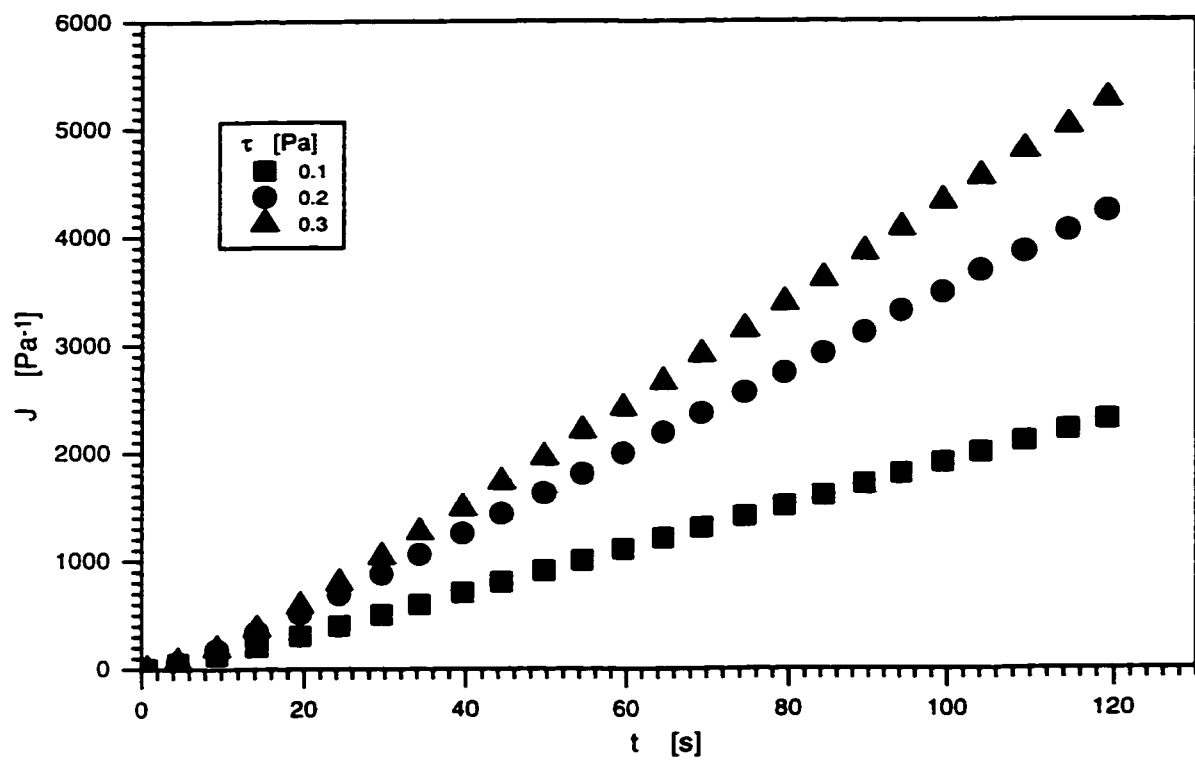


Figure 4.4.1 Nonlinear Viscoelastic Response for 0.02% PAM

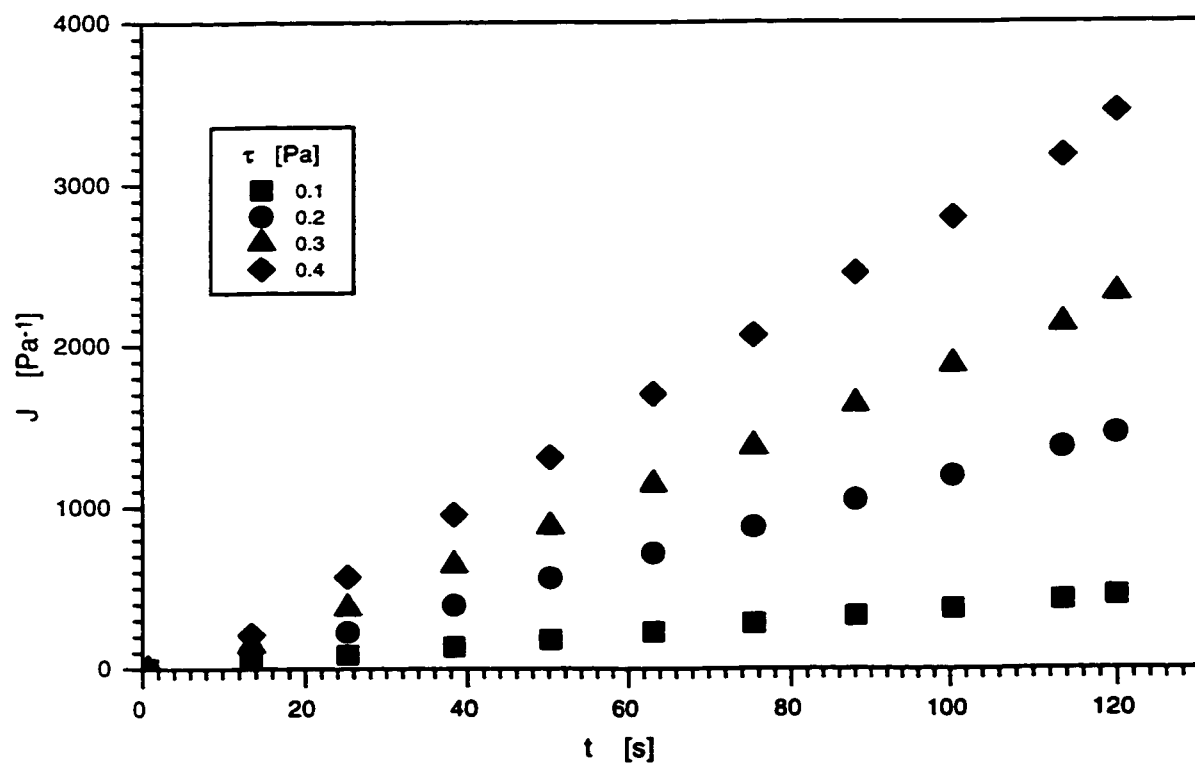


Figure 4.4.2 Nonlinear Viscoelastic Response for 0.04% PAM

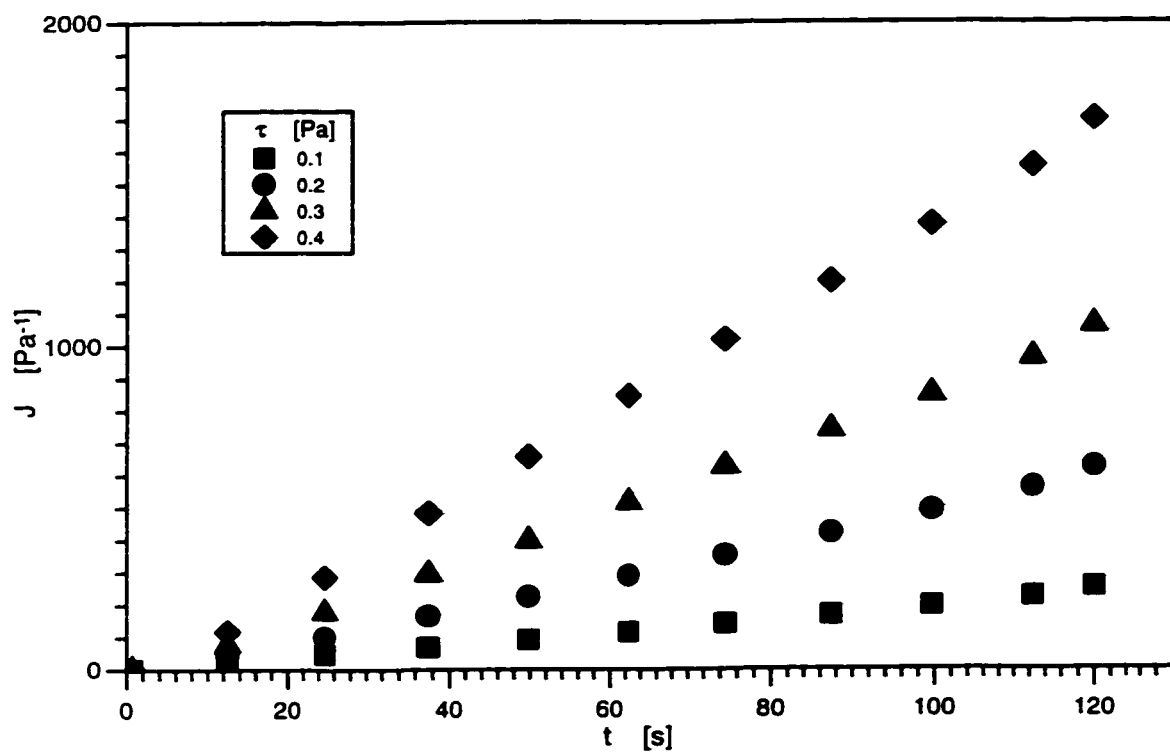


Figure 4.4.3 Nonlinear Viscoelastic Response for 0.06% PAM

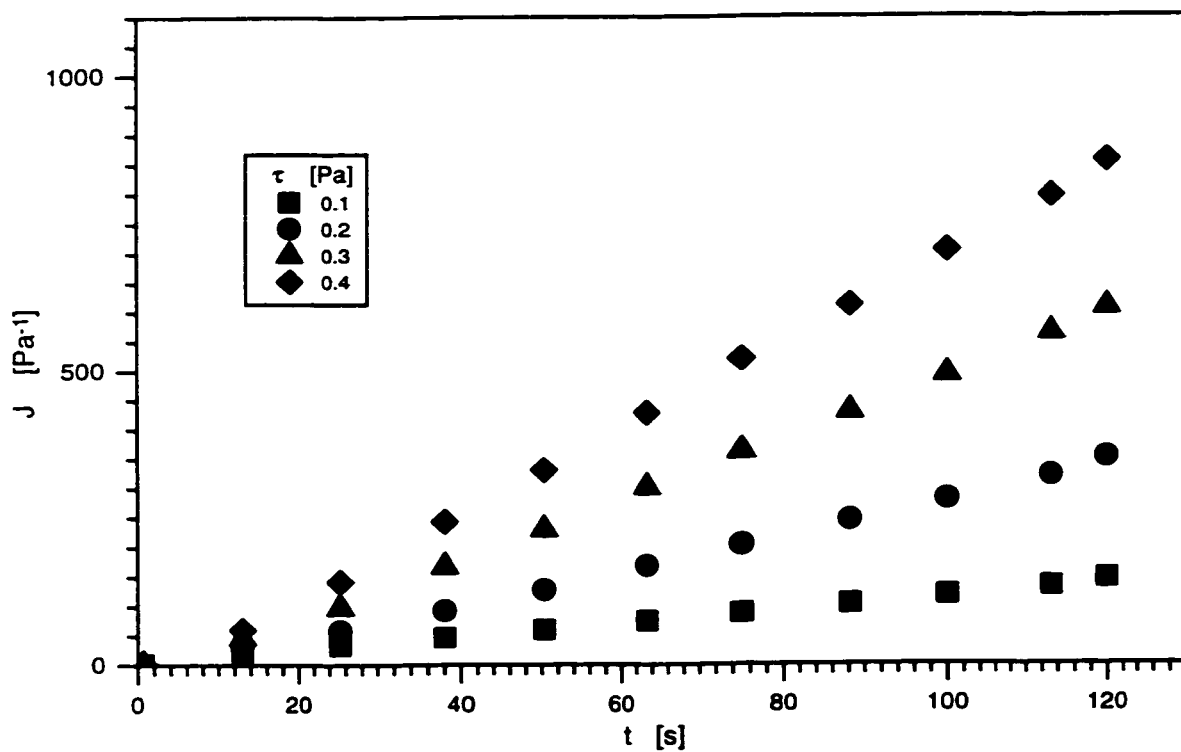


Figure 4.4.4 Nonlinear Viscoelastic Response for 0.06% PAM

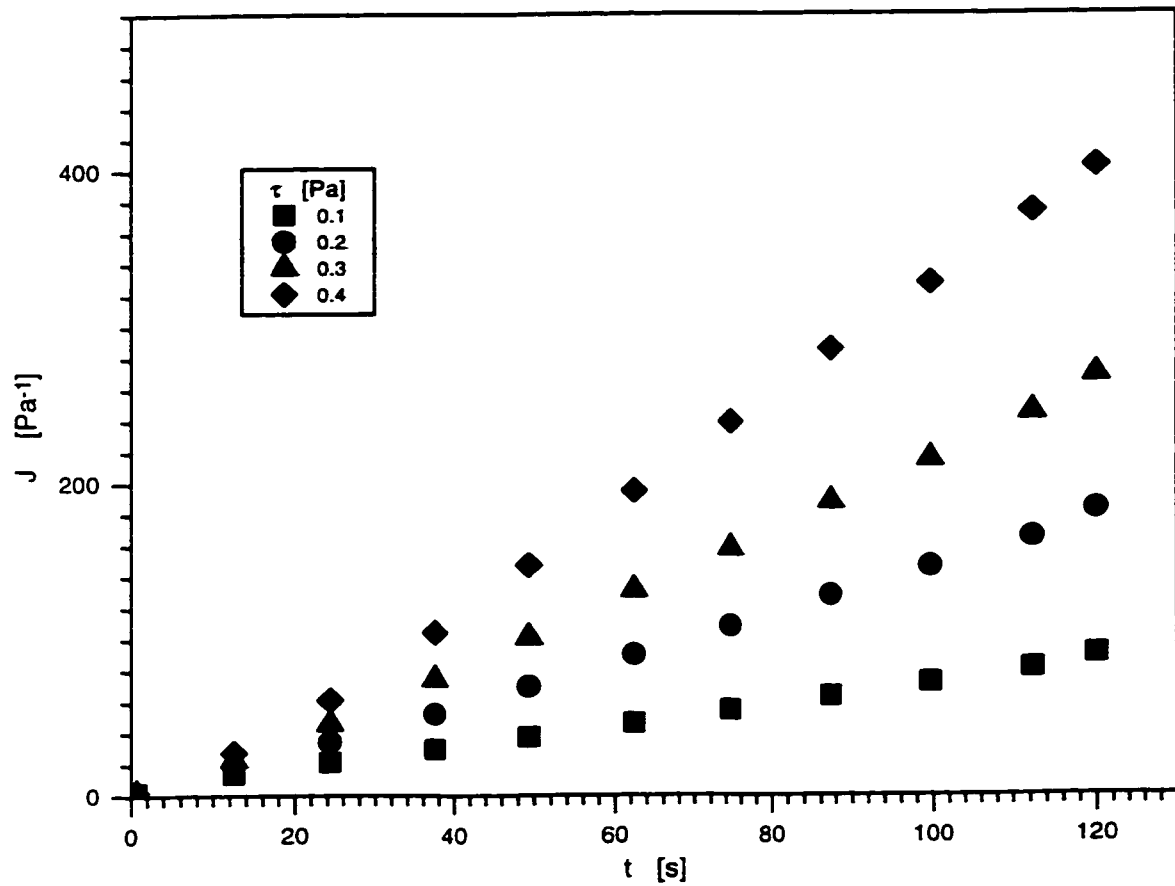


Figure 4.4.5 Nonlinear Viscoelastic Response for 0.1% PAM

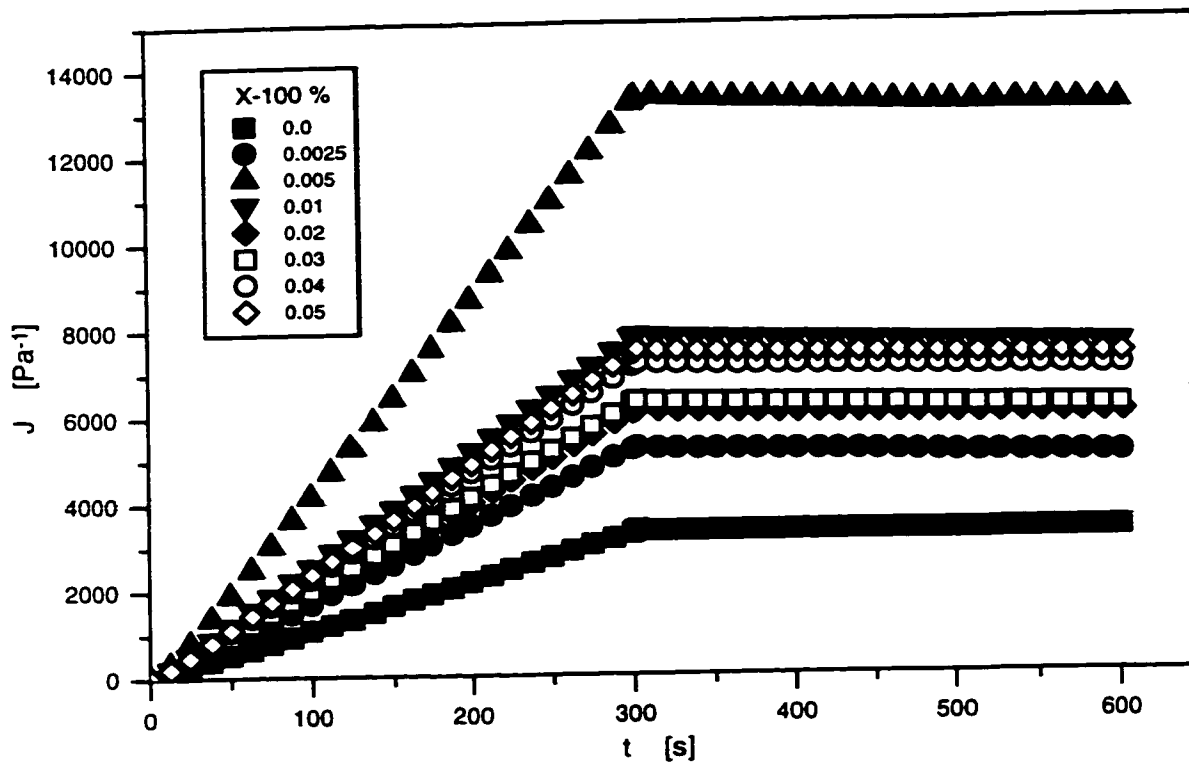


Figure 4.4.6 Effect of Surfactant on Viscoelastic Response for 0.02%PAM

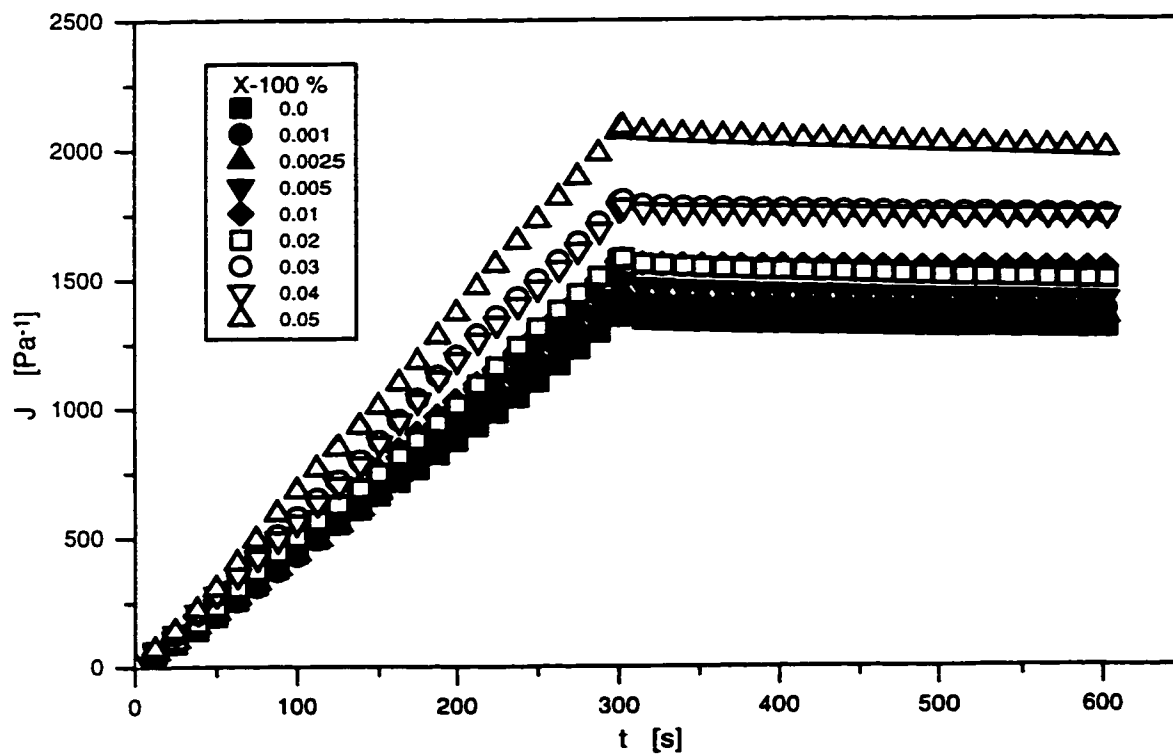


Figure 4.4.7 Effect of Surfactant on Viscoelastic Response for 0.04%PAM

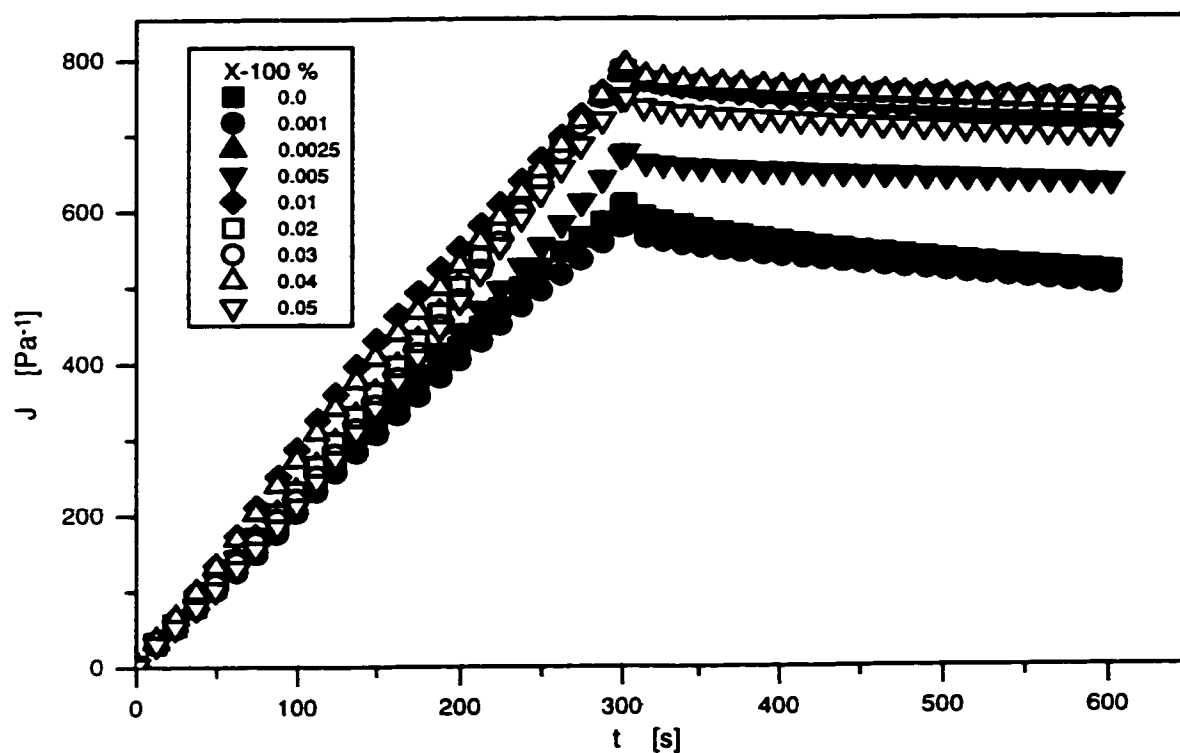


Figure 4.4.8 Effect of Surfactant on Viscoelastic Response for 0.06%PAM

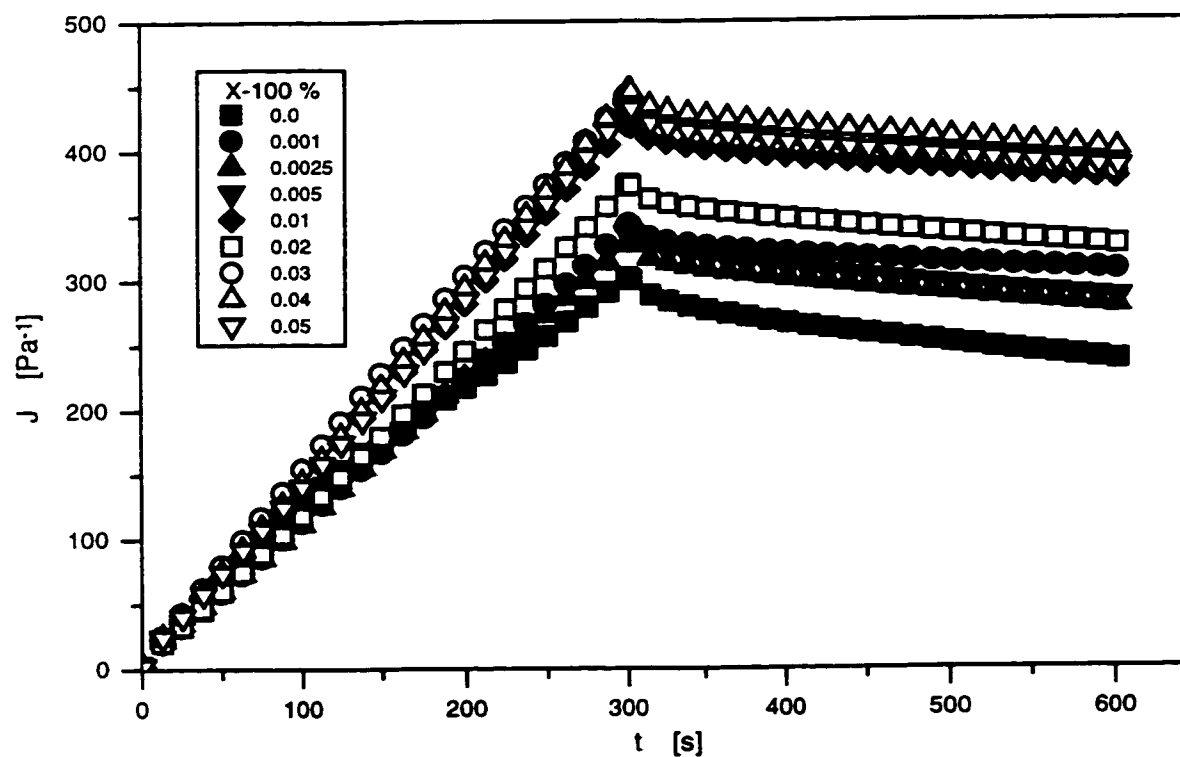


Figure 4.4.9 Effect of Surfactant on Viscoelastic Response for 0.08%PAM

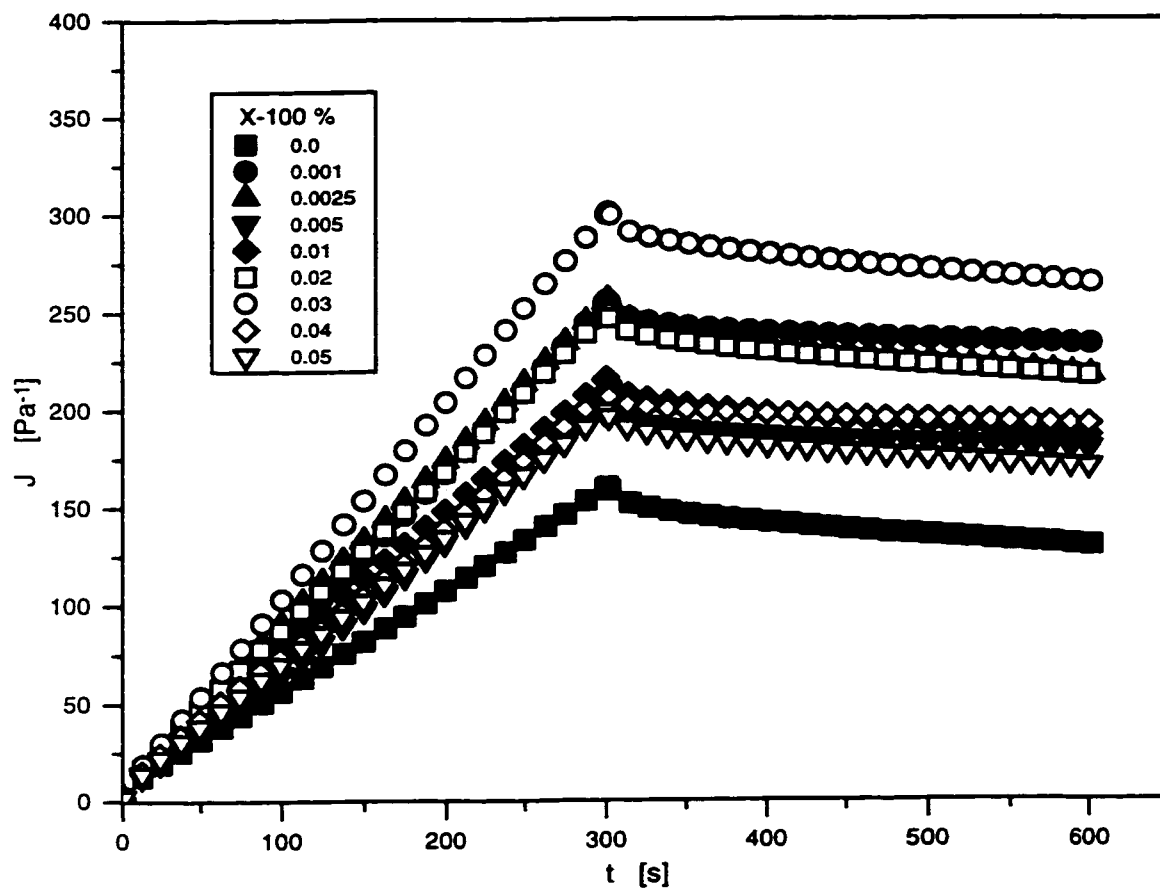


Figure 4.4.10 Effect of Surfactant on Viscoelastic Response for 0.1%PAM

4.5 Thixotropy.

Thixotropy can be defined as the ability of a material to change from gel state to sol state and back again to gel as a result of applying and removing an external force. This processes is completely and endlessly reversible, that can be defined as: $\tau = \eta \dot{\gamma}$, $\eta = \eta(t)$.

Thixotropic materials exhibit a shear thinning behavior as a result of gradually applying external force from low to high values. This state of liquid is called sol state. On removing or reducing this force, the material will regain most or all of its original viscosity (gel state), on the other hand antithixotropic materials exhibit a behavior opposite to that of thixotropic fluids. Such a phenomenon occurs less frequently³¹. A single material can show both shear thinning or thixotropy and antithixotropy. In that case, antithixotropy will appear at higher rates than the other effect³². Thixotropic materials have a structure that can be destroyed by application of shear and redeveloped by letting it to rest. The process of destroying and rebuilding the structure is isothermal and reversible. If an applied shear rate is maintained constant for a sufficient time, shear stress will approach an equilibrium value and the response of shear stress to a sudden change of shear rate is immediate. Those time dependent phenomena are referred to as the microstructure of the liquid system. The driving force for microstructure change in flow results from competition between breakdown due to flow stresses and build-up due to in-flow collisions and Brownian motion. Brownian motion is the random thermal agitation of atoms and molecules that results in elements of the microstructure being constantly

bombarded, which causes them to move to a favorable position³³. At this position they can bond themselves to other parts of the microstructure. It can also be described as the stability of the system depending upon the existence of a potential energy barrier that prevents the particles from approaching close to one another. In this way, the comparatively weak physical bond between the particles gives rise to aggregation. If the fluid is at rest, the particles' aggregation can form a network and the fluid develops an internal structure. If a shear is applied, the weak physical bonds are ruptured and the network breaks down into separate aggregates that can disintegrate further into smaller fragments causing reduction in viscosity. As a result of removing the stresses, the small fragments start to bond with each other due to collision and Brownian motion²³. Very rarely, a situation arises where existing weakly attached microstructure elements brought together by collision during shear are torn apart by constant action of the random Brownian motion, in which case, the antithixotropic is seen.

Thixotropy is neither good nor bad, but for certain applications such as paint, ink and coating, it can be favorable. For example, paint that thins fast by strokes of brush can be easily painted. When the applied paint layer rethickens fast, it prevents sagging. In other applications such as process control design, it can be very challenging for engineers. For example, when thixotropic fluid enters a long pipe from a large vessel where it has been allowed to rest, the development of the velocity and pressure field in the pipe is very complicated. The large pressure involved in the start-up of flow of a thixotropic liquid can cause significant problems in terms of the necessary pump performance. Cavitation

can be caused because, although a pump could cope with the sheared material, it might be unable to initiate flow of material that has been at rest. Cavitation in the liquid within the pump can then ensue ³³ .

There are many techniques used to determine the measurements of thixotropy. One of the most common techniques used is the hysteresis loop test ^{15,33,34,35} , that is, to linearly increase the shear rate from low value to maximum value which can be held for some time, then to return at the same rate to the minimum value over the same prescribed time period. This process can be repeated again and again. When plotting shear stress against shear rate, the up-curve will be separated from the down-curve and the area between these two curves defines the magnitude of the thixotropy. It has the dimension of energy related to volume of the sheared sample indicating the energy required to break down the thixotropic structure. If the fluid is antithixotropic, the down-curve will be above the up-curve. In case of time independent fluids, the upper and lower curves will be identical. ²³

In this study, 5 different hysteresis loop measurements have been used to investigate the thixotropic behavior of polyacrylamide solutions. Test 1 consists of one cycle of ramped up from 0.15 s^{-1} to 700 s^{-1} in 120 s and then ramped down from 700 s^{-1} to 0.15 s^{-1} in the same period of time. Test 2 consists of three cycles of ramped up from 0.15 s^{-1} to 700 s^{-1} in 120 s and then ramped down to 0.15 s^{-1} in the same period of time. Test 3 consists of three-part cycle, ramped up from 0.15 s^{-1} to 700 s^{-1} in 60 s, constant shear rate at 700 s^{-1} for 60 s, and ramped down to 0.15 s^{-1} in 60 s. Test 4 consists of three-part cycle,

ramped up from 0.15 s^{-1} to 700 s^{-1} in 120 s, constant shear rate at 700 s^{-1} for 120 s, and ramped down to 0.15 s^{-1} in 120 s. Test 5 repeats the same sequence with tests 3 and 4 with change of time to 180 s.

Figures 4.5.1-4.5.5 and Table 4.5.2 present the thixotropic behavior at various regions of shear rate and thixotropic value respectively. Referring to Table 4.5.1, the five tests being used yield different values. For all used tests, polyacrylamide gives antithixotropic under some conditions, which is denoted with a minus sign. Test 3 in general shows the highest thixotropic values for all tested samples. Figures 4.5.1-4.5.5 indicate that thixotropic behavior of polyacrylamide solutions changes as a function of concentration and shear rate. It is relatively higher at low shear rate and it decreases as concentration increases. At higher shear rate and low concentration, time independent behavior occurs; however, at higher concentration, a fluctuation between thixotropy and antithixotropic behavior is seen.

Test 3 has been used to investigate the effect of surfactant on thixotropic behavior of polyacrylamide solutions. Figures 4.5.6-4.5.10 and Table 4.5.2 present that at concentrations of 0.02%, 0.04% and 0.08% PAM, surfactant has positive values indicating that at all surfactant concentrations, the solutions behave like thixotropic material. At concentrations of 0.06% and 0.1% PAM, surfactant has fluctuation between thixotropic and antithixotropic behavior. From above, at higher polyacrylamide concentrations, one can expect lower thixotropic or anti-thixotropic behavior than in low concentrations. Also by comparing tests 3, 4 and 5, time has the major effect of changing the solution

behavior from thixotropic to antithixotropic which is more noticeable at polyacrylamide concentration higher than 0.04%.

In general, polyacrylamide has low time dependent behavior and gives both thixotropic and antithixotropic response. That depends on polymer concentration, shear stress, and the test being used. Surfactant has an oscillation effect on thixotropic values of polyacrylamide concentrations.

Table 4.5.1 Thixotropic Values (Pa/s)

PAM conc.	test. 1	test. 2			test 3	test 4	test. 5
		1st cycle	2nd cycle	3ed cycle			
0.02%	233	232	184	191	568	184	150
0.04%	164	162	146	115	312	81	-45
0.06%	131	130	32	-42	335	-5	-262
0.08%	68	67	41	-60	281	-313	-156
0.10%	25	27	-123	36	202	-28	-103

Table 4.5.2 Effect of Surfactant on Thixotropic Values

surfactant wt%	Polyacrylamide concentration wt %				
	0.02	0.04	0.06	0.08	0.1
0	568	312	335	281	202
0.001	x	156	39	67	276
0.0025	454	389	-11	95	125
0.005	531	334	79	78	13
0.01	371	338	-38	17	-52
0.02	381	460	197	40	52
0.03	412	460	16	448	-68
0.04	410	172	615	280	496
0.05	416	139	532	463	-253

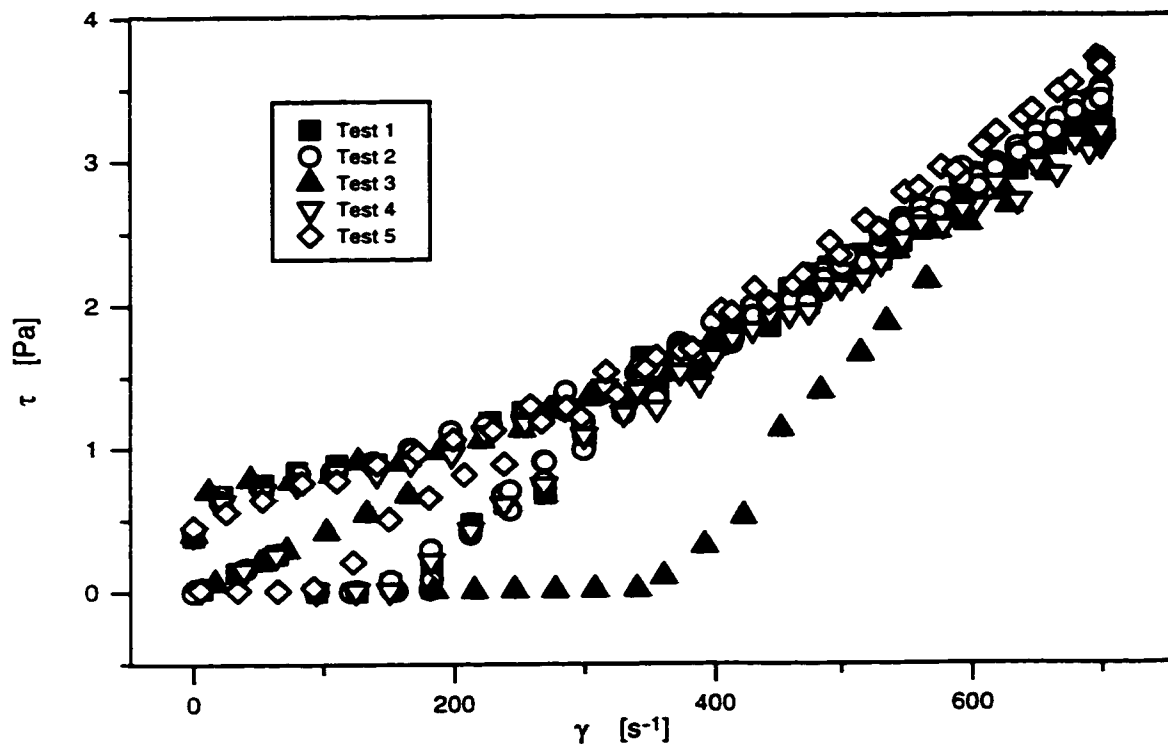


Figure 4.5.1 Thixotropic Behavior for 0.02% PAM

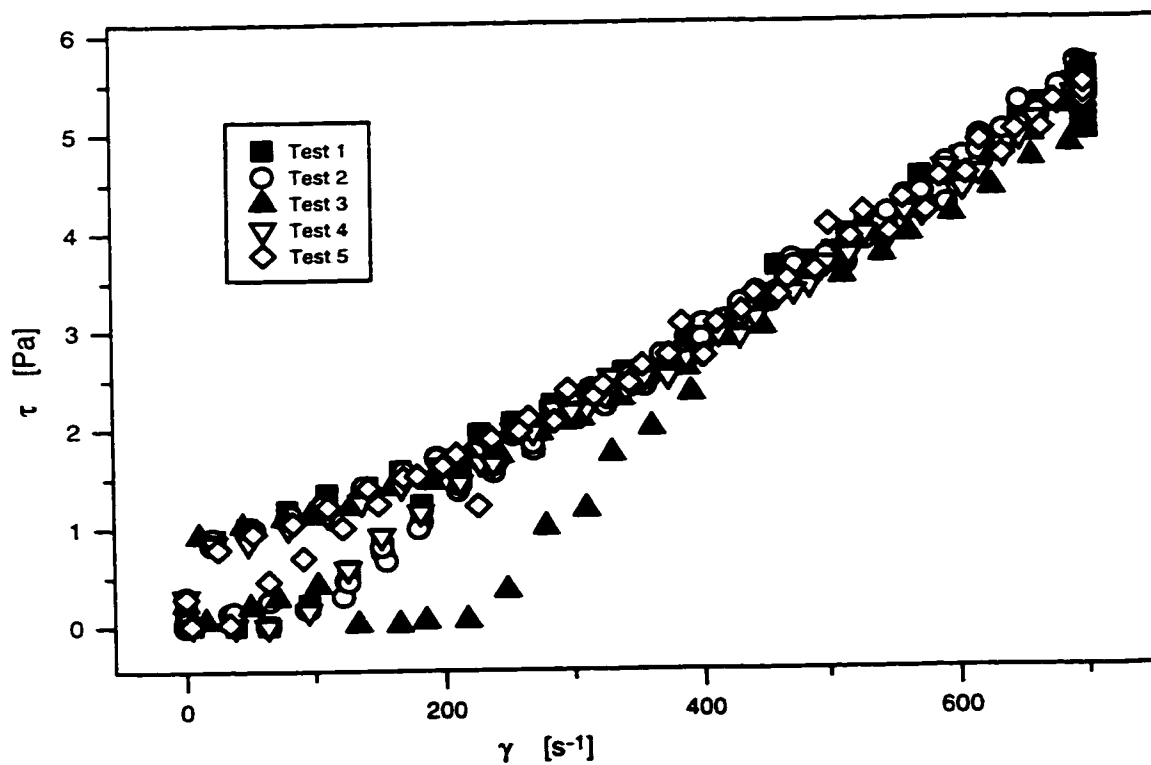


Figure 4.5.2 Thixotropic Behavior for 0.04% PAM

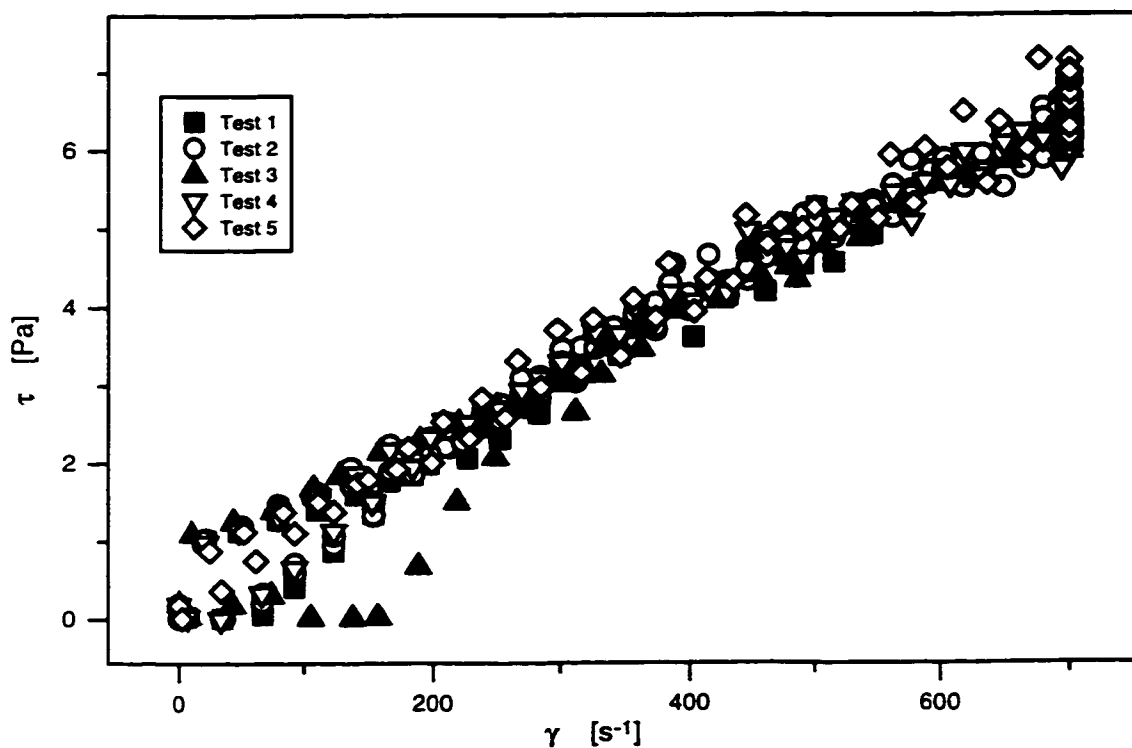


Figure 4.5.3 Thixotropic Behavior for 0.06% PAM

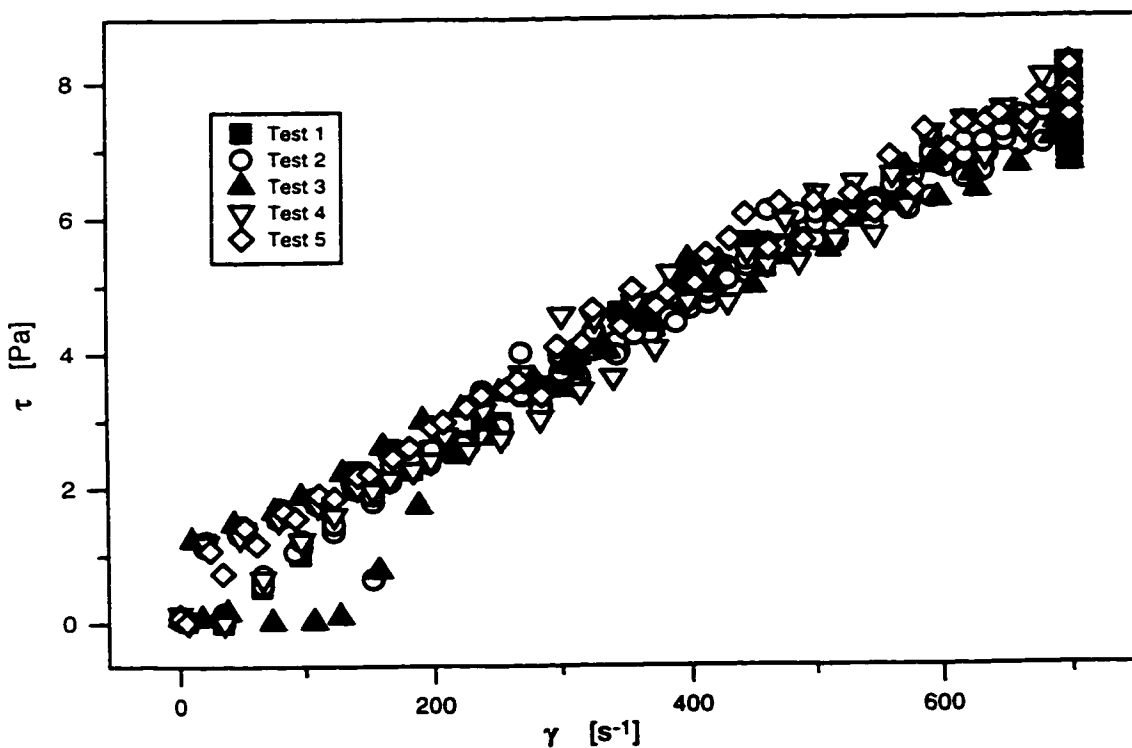


Figure 4.5.4 Thixotropic Behavior for 0.08% PAM

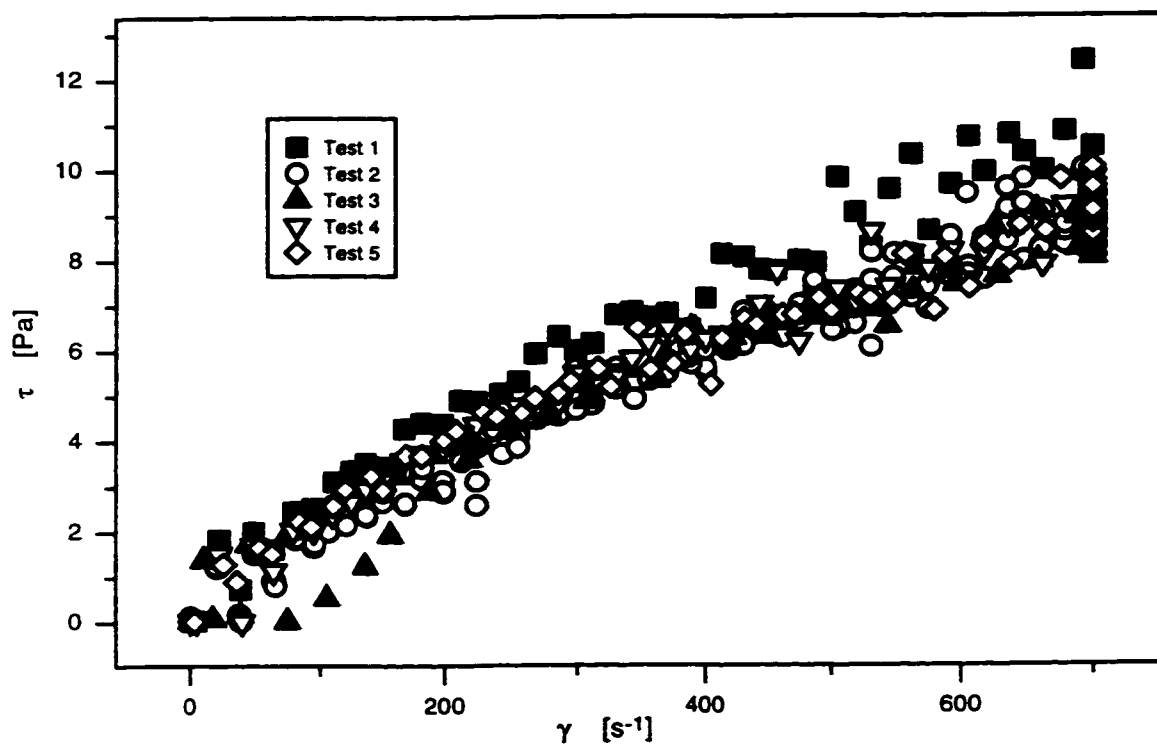


Figure 4.5.5 Thixotropic Behavior for 0.1% PAM

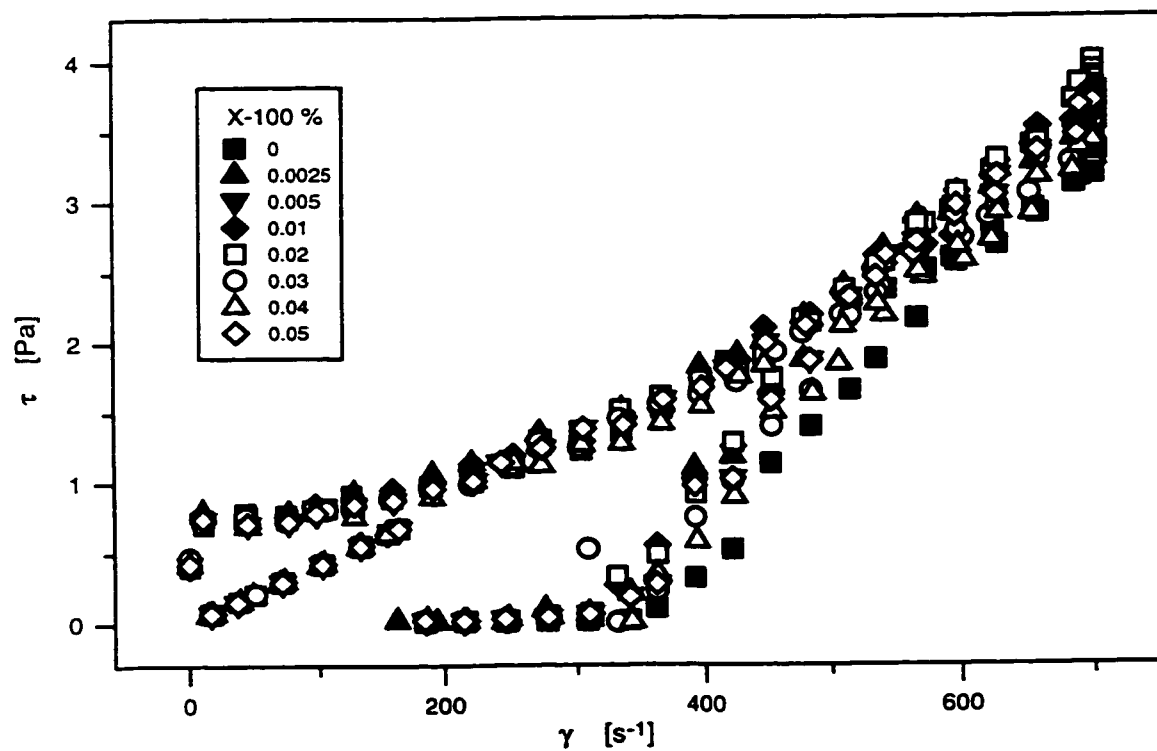


Figure 4.5.6 Effect of Surfactant on Thixotropic Behavior for 0.02% PAM

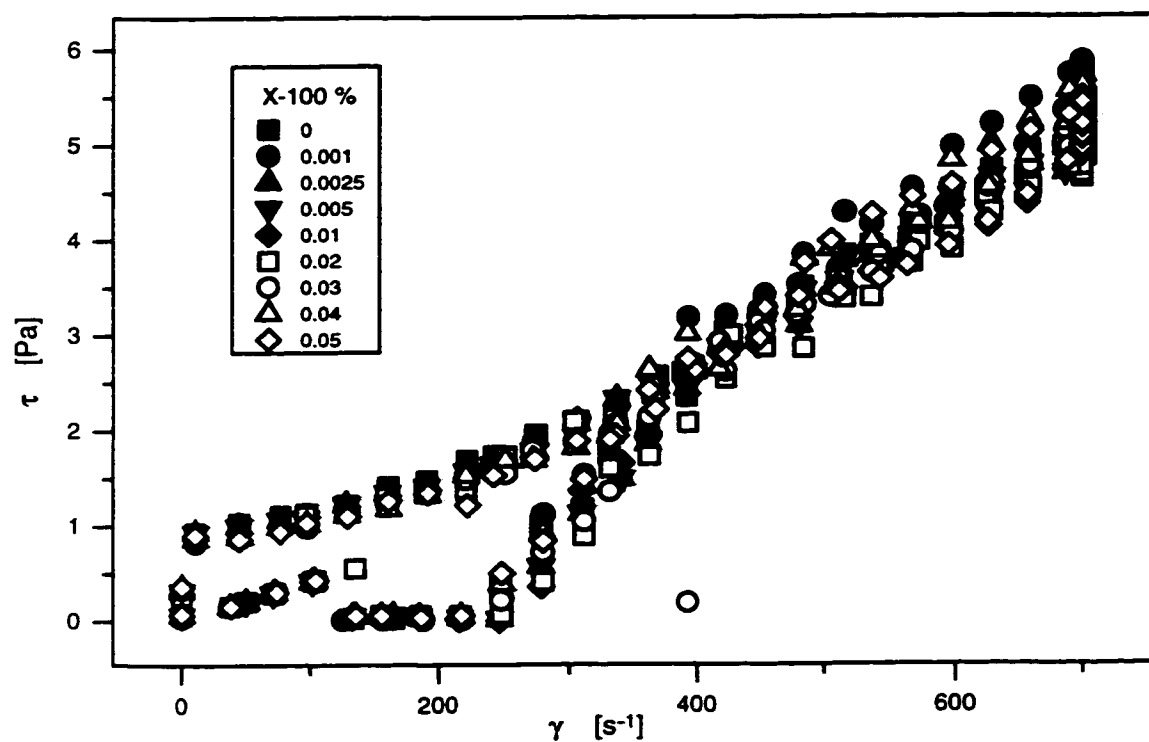


Figure 4.5.7 Effect of Surfactant on Thixotropic Behavior for 0.04% PAM

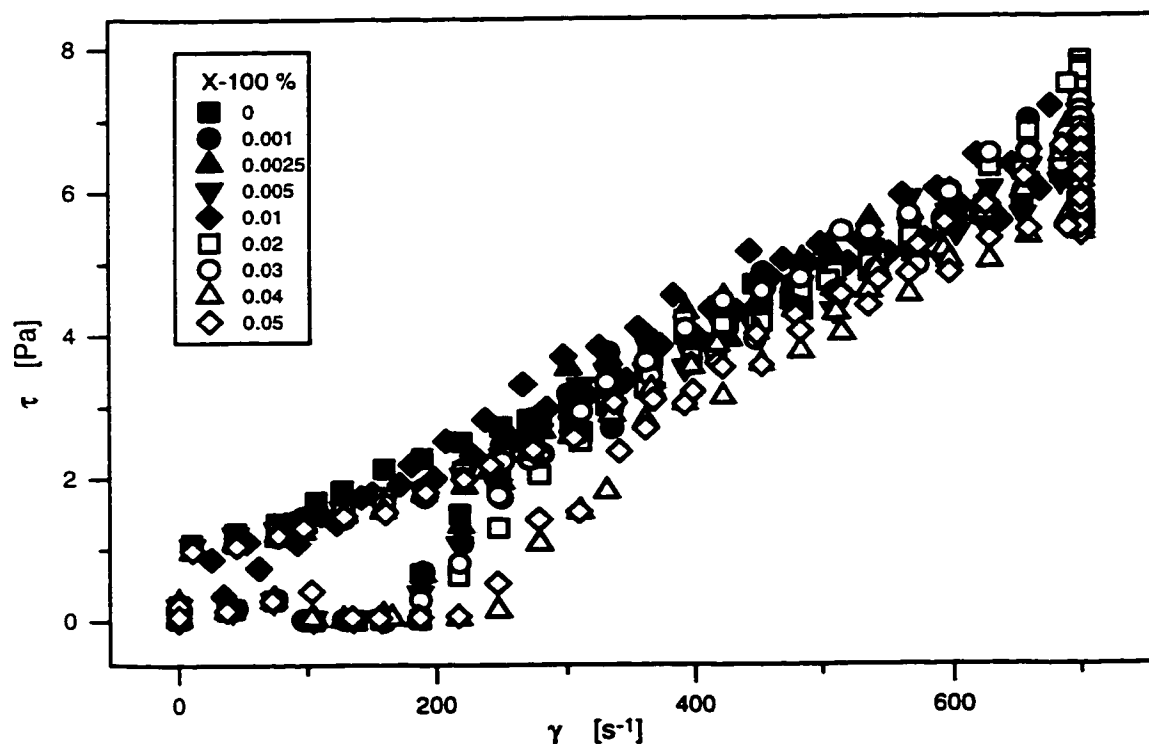


Figure 4.5.8 Effect of Surfactant on Thixotropic Behavior for 0.06% PAM

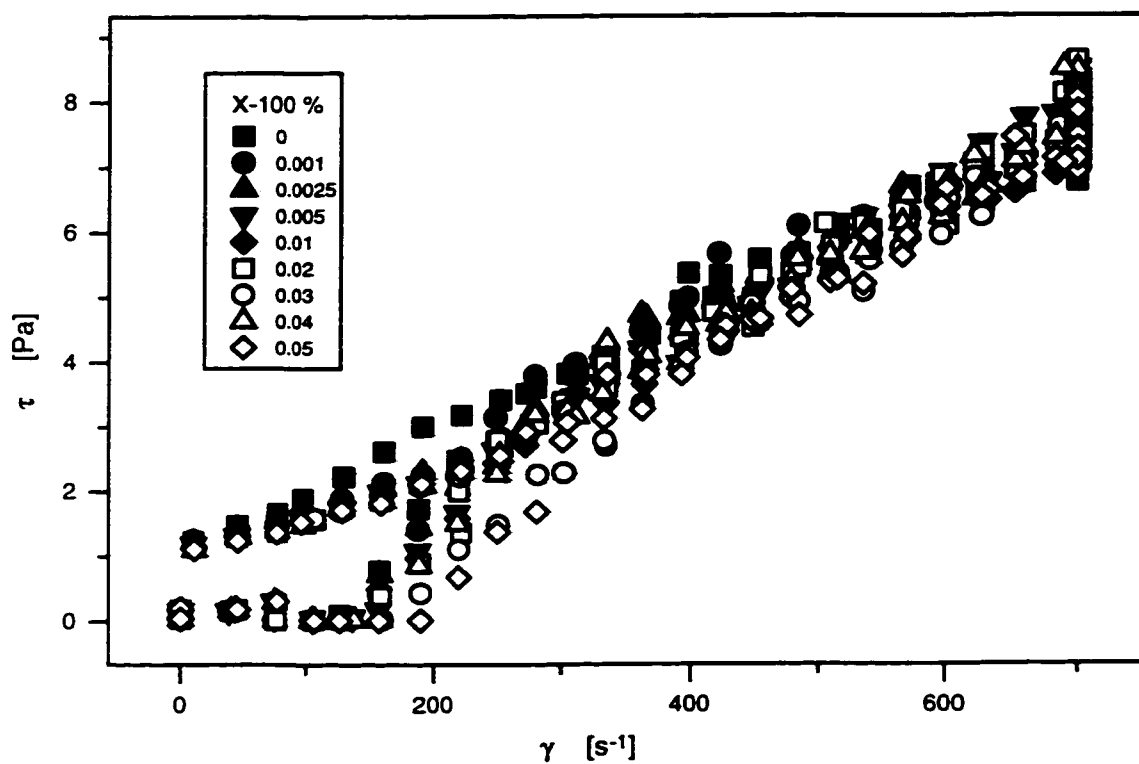


Figure 4.5.9 Effect of Surfactant on Thixotropic Behavior for 0.08% PAM

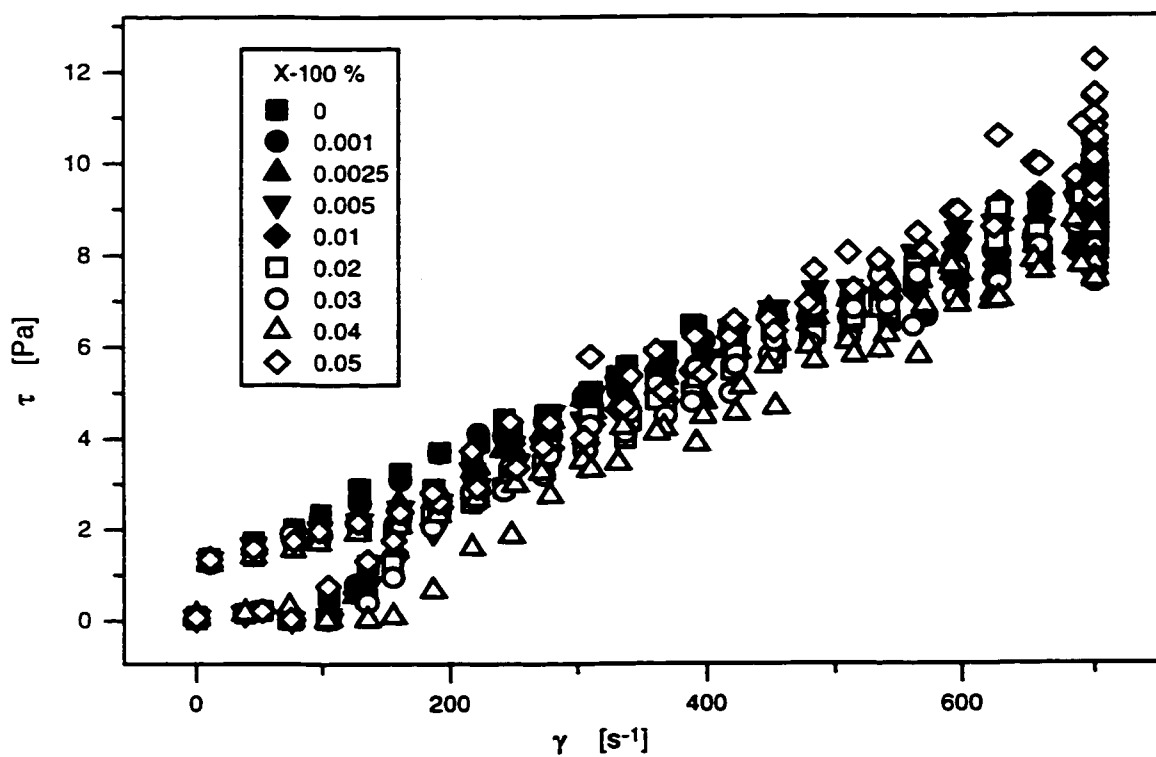


Figure 4.5.10 Effect of Surfactant on Thixotropic Behavior for 0.1% PAM

4.6 Transient Flow Behavior.

Transient test is a characteristic of time effect, leading to a relationship between shear stress and shear rate. This test is a study of the stress growth at shear rates 10 s^{-1} , 50 s^{-1} , 100 s^{-1} , and 500 s^{-1} for 300 s. Figures 4.6.1-4.6.5 show the effect of different shear rates on shear stress response for polyacrylamide solutions. At shear rate 10 s^{-1} , a slight decrease in shear stress value at time less than 15 s results from structure breakdown. This behavior decreases with concentration to reach time independent behavior at concentration of 0.08% and antithixotropic behavior at concentration of 0.1%. Beyond this critical time 15 s, all tested solutions level off to steady state value representing time independent response. At shear rates 50 s^{-1} and 100 s^{-1} , decrease in shear stress value at time below the critical time points out the existence of the structural breakdown. This adjustment is relatively concentration independent. Exceeding the critical time steady state response arises. At shear rate 500 s^{-1} , different behavior is observed. At start-up, concentrations of 0.02% and 0.04% show a decrease in shear stress value; however, higher concentrations give an increase in shear stress. After the start-up, all the tested samples exhibit fluctuation in the time evaluation of shear stress. Those fluctuations are more stable at lower concentrations.

The effect of surfactant on shear stress response is demonstrated in figures 4.6.6-4.6.25. Figures 4.6.6, 4.6.10, 4.6.14, 4.6.18 and 4.6.22 indicate that at shear rate of 10 s^{-1} , the surfactant has no effect on shear stress for all polyacrylamide solutions. For shear rate 50 s^{-1} , figures 4.6.7, 4.6.11, 4.6.15,

4.6.19 and 4.6.23 show that polyacrylamide is associated with slight decrease in shear stress with increasing surfactant concentration; however, concentration of 0.04% is associated with dramatic decrease in shear stress value at surfactant concentration of 0.0025%, and at concentration of 0.1% PAM, there is a sudden increase to its original value at surfactant concentration of 0.05%. Figures 4.6.8, 4.6.12, 4.6.16, 4.6.20 and 4.6.24 show the effect of surfactant at shear rate 100 s^{-1} for 0.02% PAM, a decrease in shear stress value with increasing surfactant concentration up to 0.1%, then increasing with increasing surfactant concentration to reach the primary shear stress value at surfactant concentration of 0.05%. For 0.04%PAM, figure 4.6.12 indicates a slight decrease in shear stress with increasing surfactant concentration. At 0.06% PAM, surfactant has no effect up to 0.001%, followed by decrease in shear stress to slightly lower constant value for the other surfactant concentrations. For 0.08% PAM, figure 4.6.20 indicates a slight decrease in shear stress with increasing surfactant concentration, associated with dramatic decrease at surfactant concentration of 0.02%. Figure 4.6.24 shows the effect of surfactant on 0.1% PAM, a slight decrease in shear stress response with increasing surfactant up to concentration 0.04% followed by increase to the original value. At shear rate 500 s^{-1} , figures 4.6.9, 4.6.13, 4.6.17, 4.6.21 and 4.6.25 show a complex fluctuation effect of surfactant on the shear stress response of polyacrylamide solutions.

From the above results, the transient test indicates that time evaluation shear stress is dependent on both shear rate and polyacrylamide concentration. Surfactant has no effect at low shear rate, it decreases the shear stress value at

shear rates of 50 s^{-1} and 100 s^{-1} , and it leads fluctuation of shear stress at shear rate 500 s^{-1} . For shear rates less than 500 s^{-1} and time higher than 15 s, shear stress response is time independent for all tested samples.

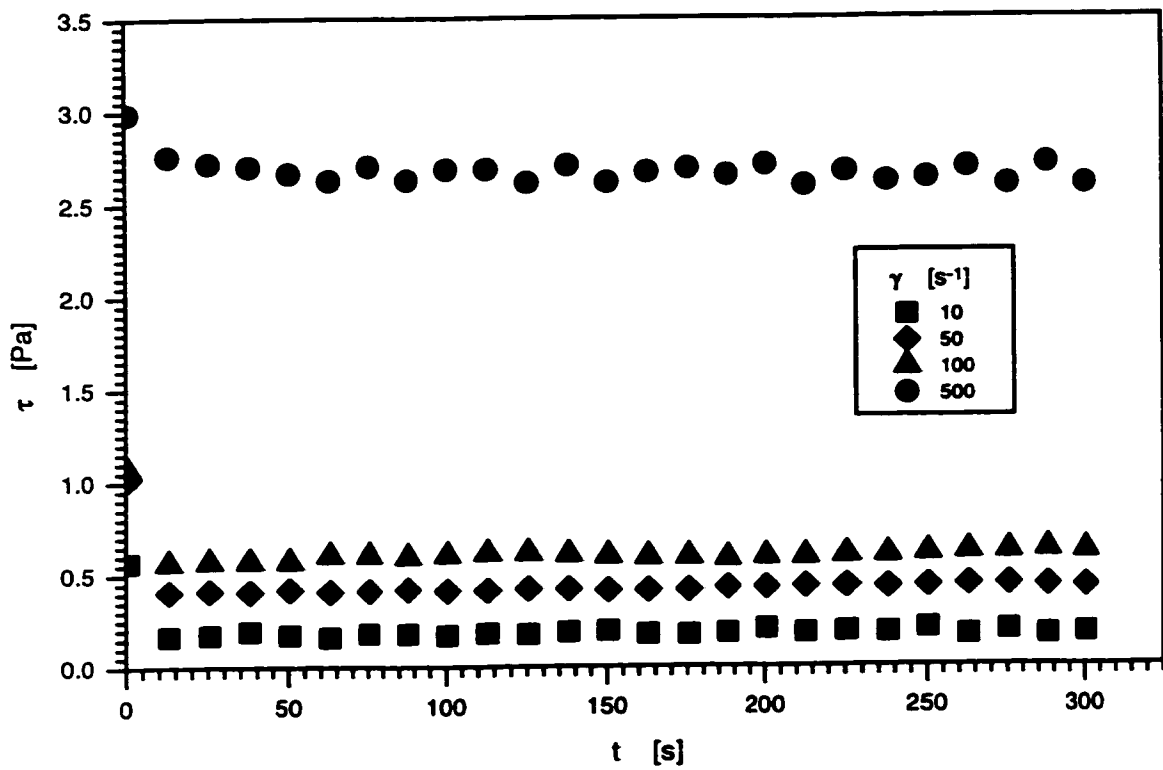


Figure 4.6.1 Transient Shear Stress Response for 0.02% PAM

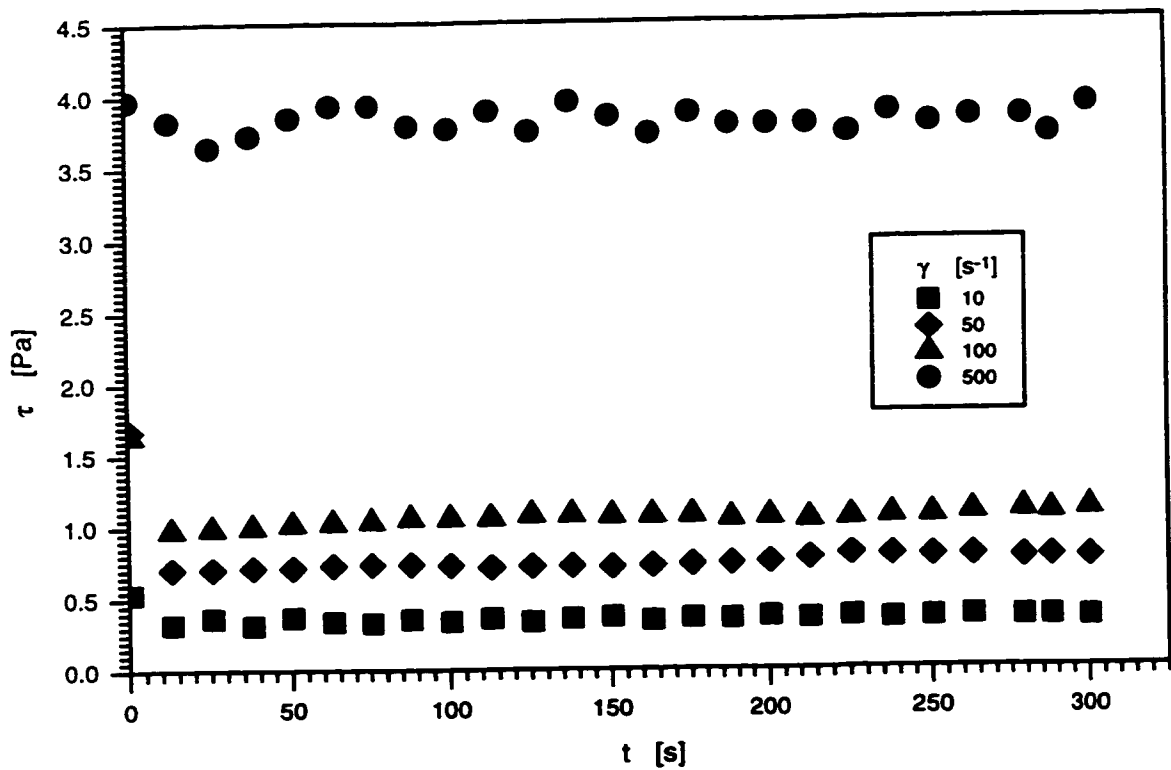


Figure 4.6.2 Transient Shear Stress Response for 0.04% PAM

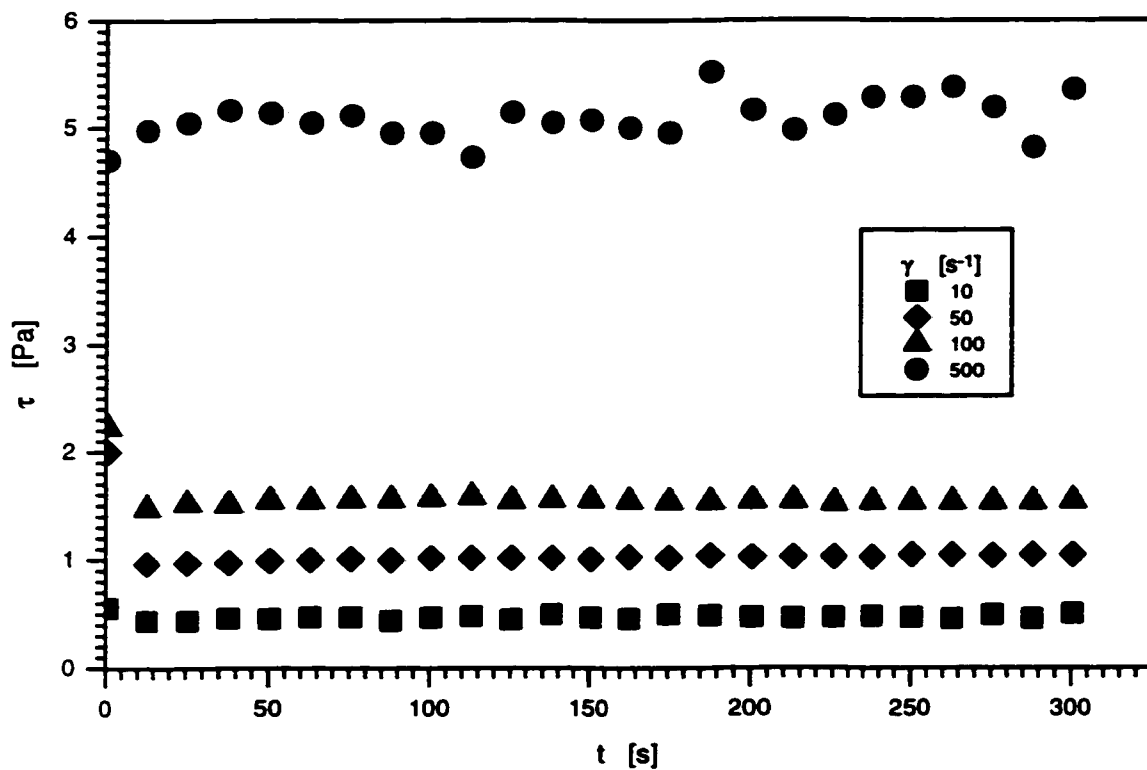


Figure 4.6.3 Transient Shear Stress ResponseFor 0.06% PAM

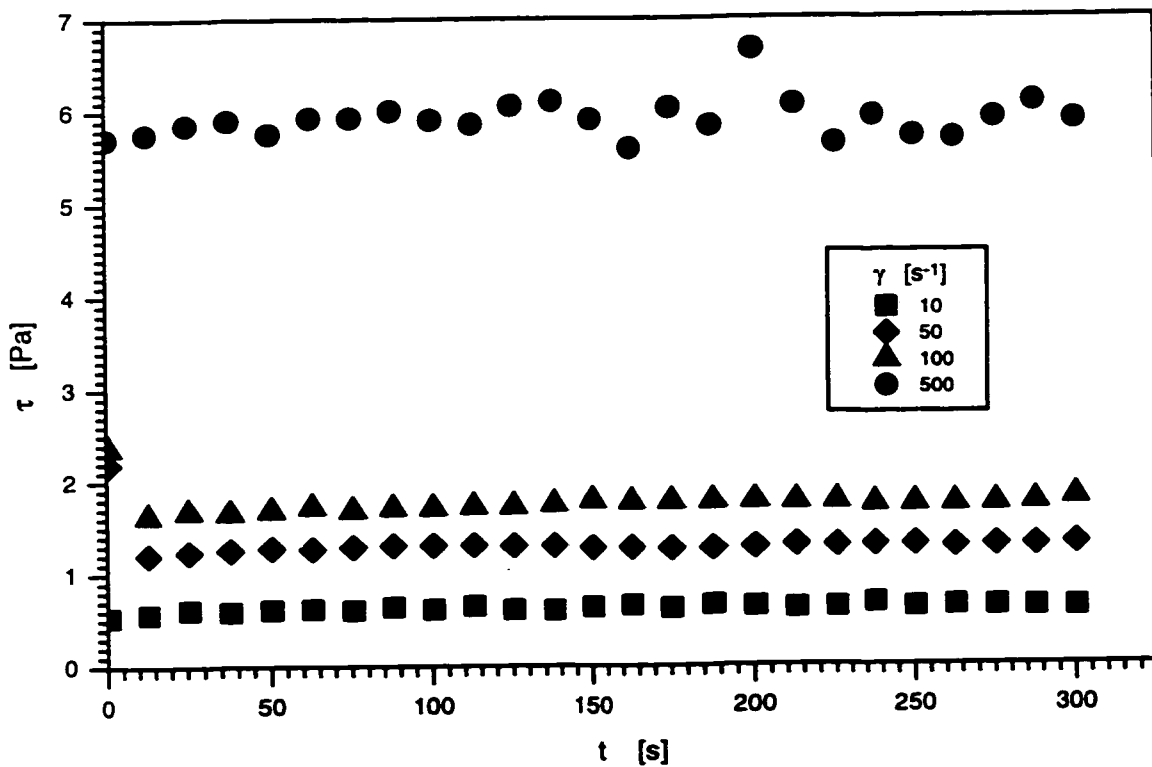


Figure 4.6.4 Transient Shear Stress Response for 0.08% PAM

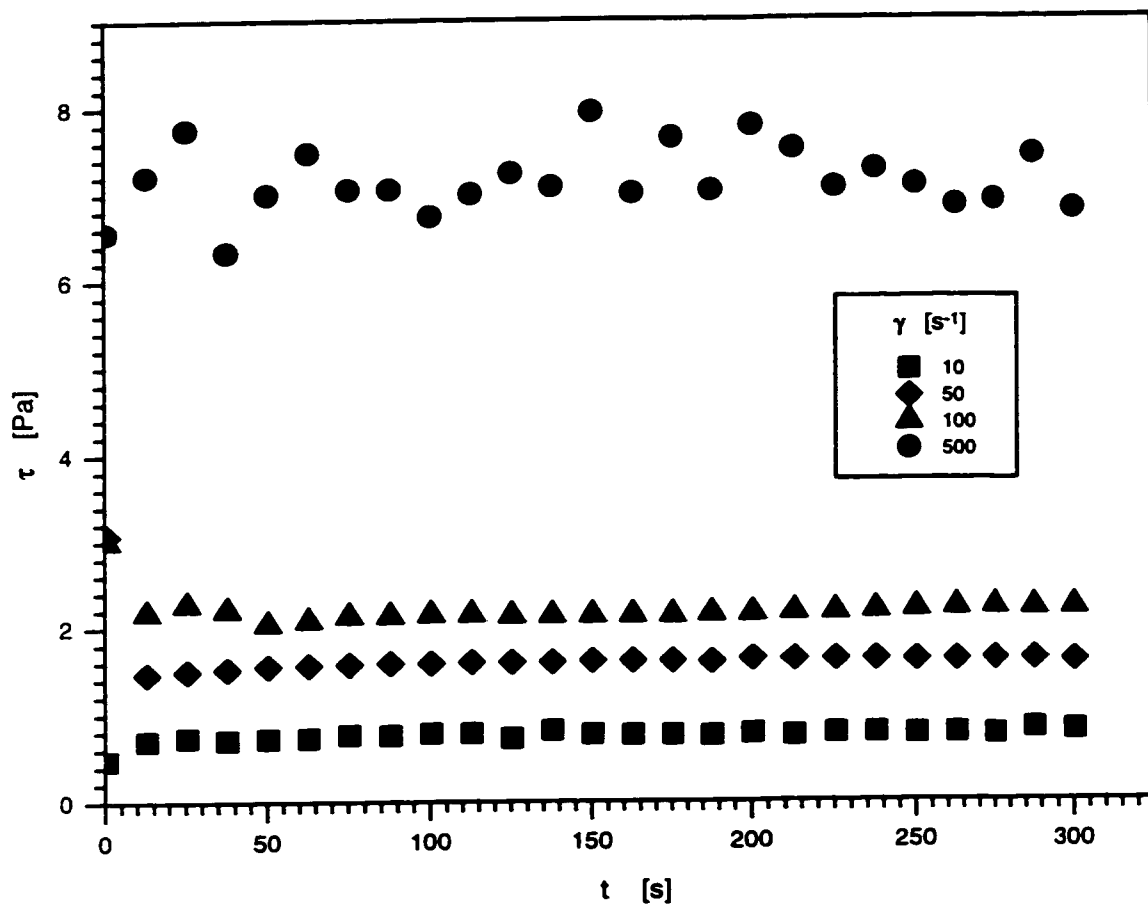


Figure 4.6.5 Transient Shear Stress Response for 0.1% PAM

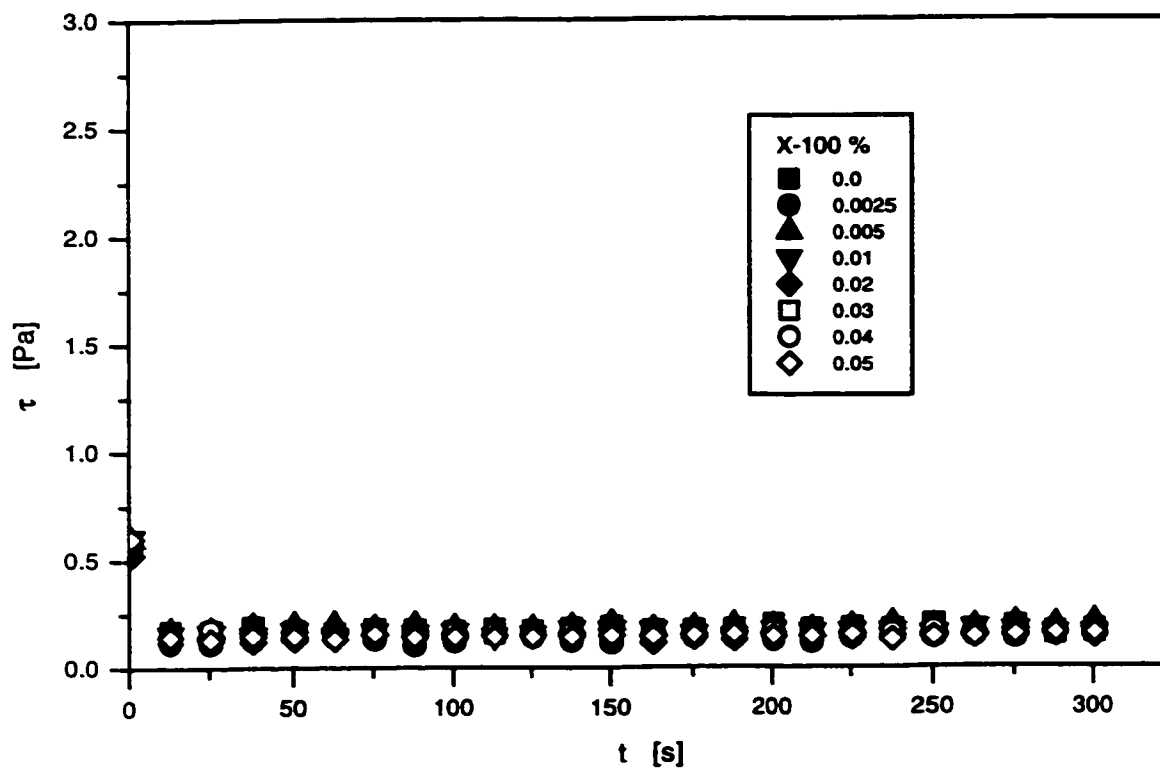


Figure 4.6.6 Effect of Surfactant on Transient Shear Stress Response for 0.02%PAM at 10 1/s

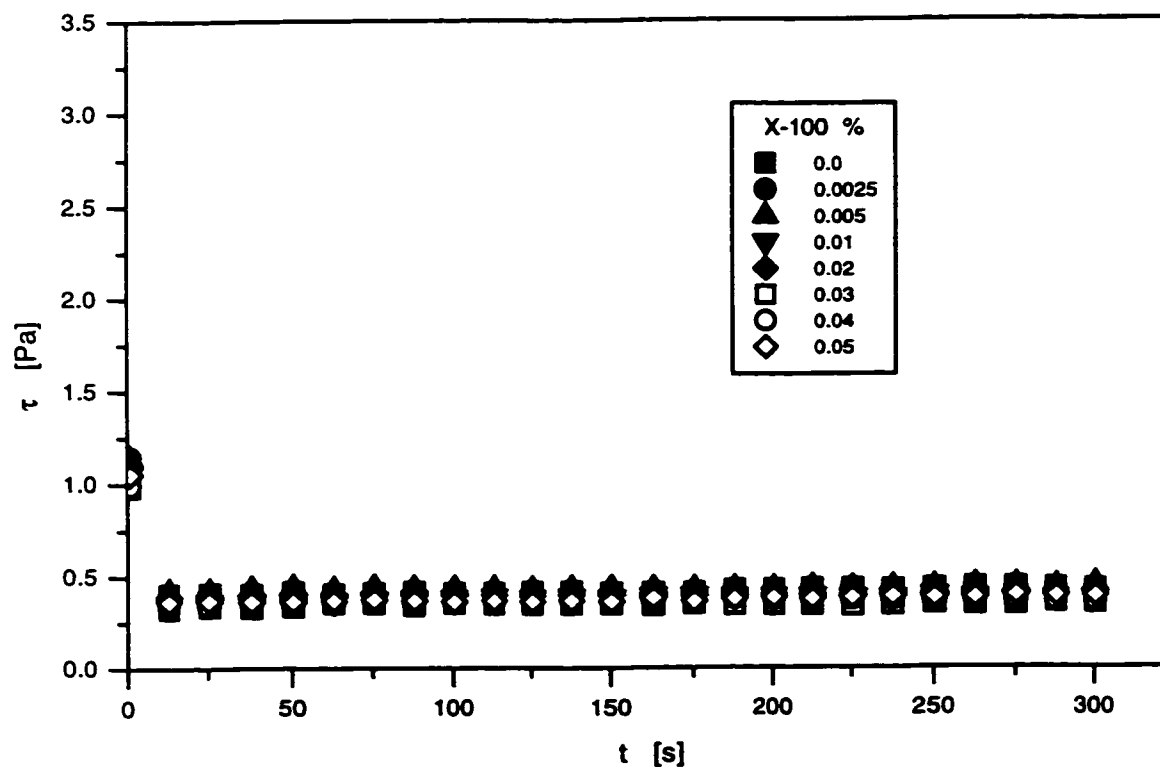


Figure 4.6.7 Effect of Surfactant on Transient Shear Stress Response for 0.02%PAM at 50 [1/s]

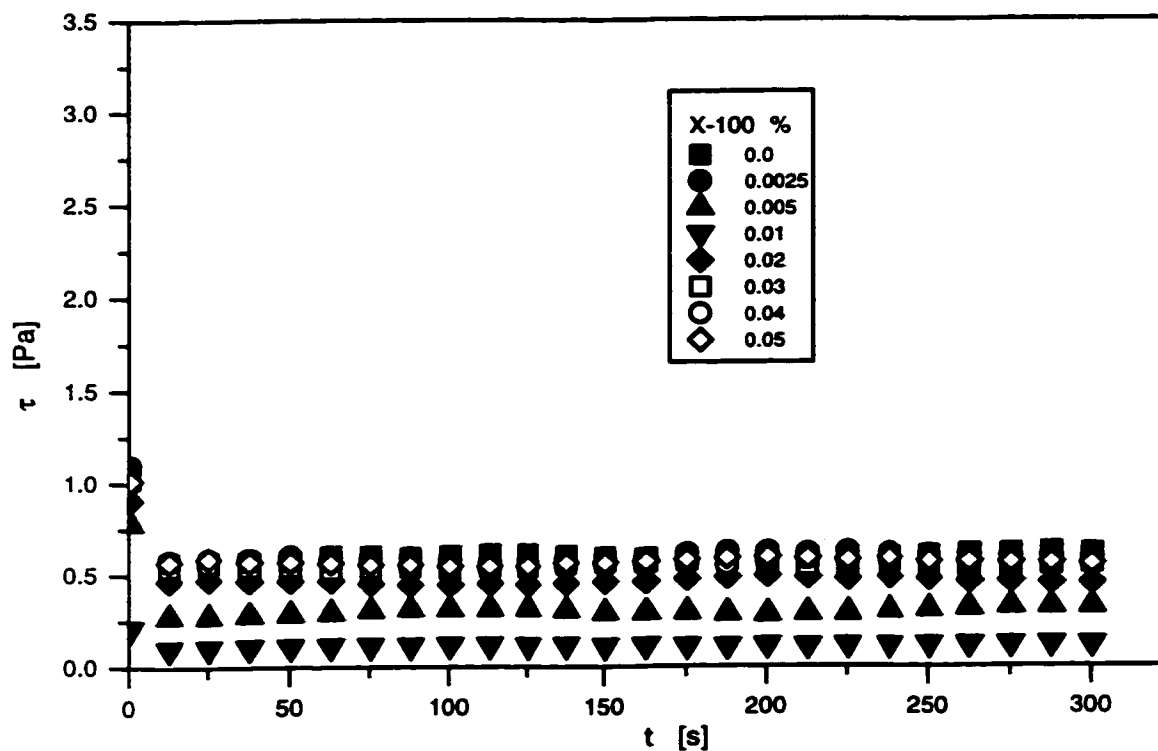


Figure 4.6.8 Effect of Surfactant on Transient Shear Stress Response for 0.02%PAM at 100 [1/s]

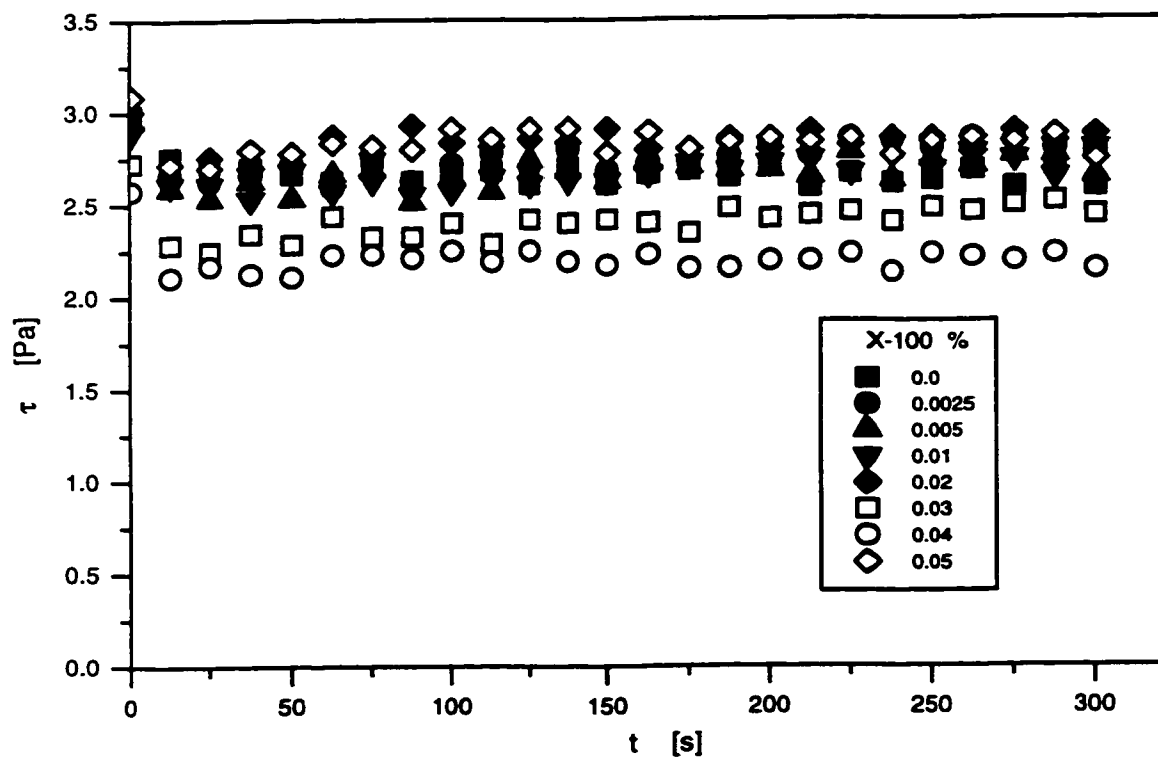


Figure 4.6.9 Effect of Surfactant on Transient Shear Stress Response for 0.02%PAM at 500 [1/s]

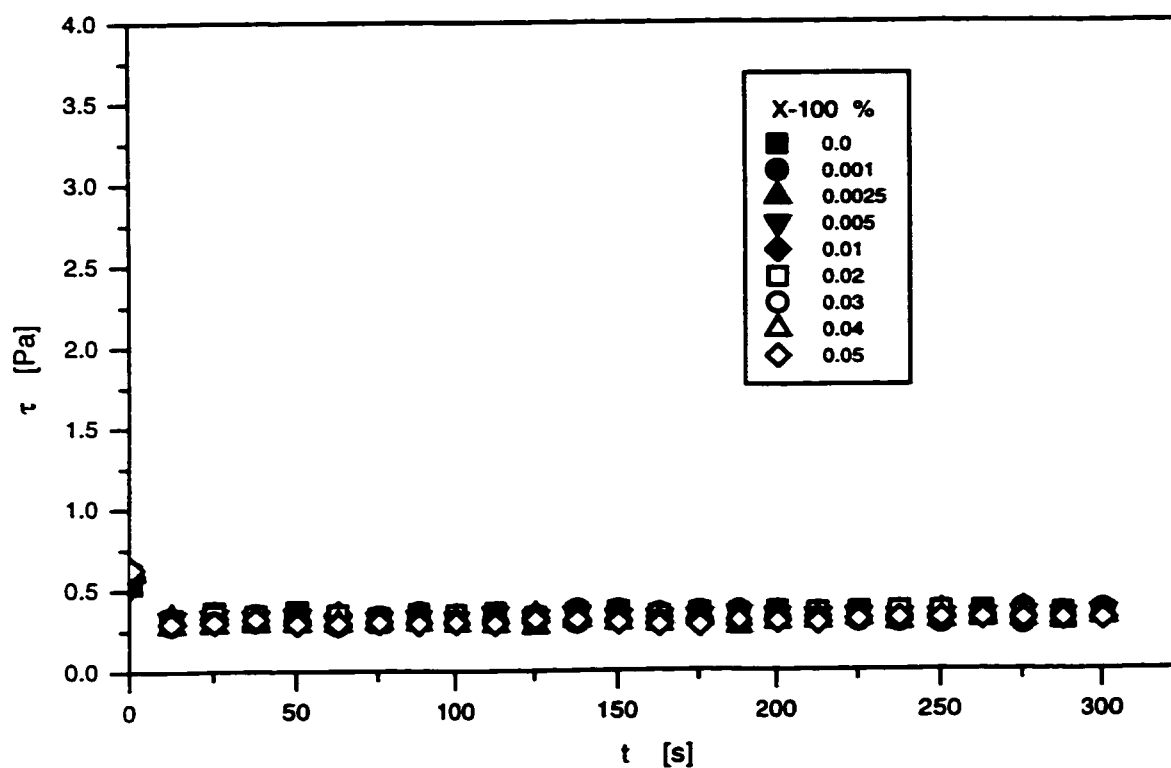


Figure 4.6.10 Effect of Surfactant on Transient Shear Stress Response for 0.04%PAM at 10 [1/s]

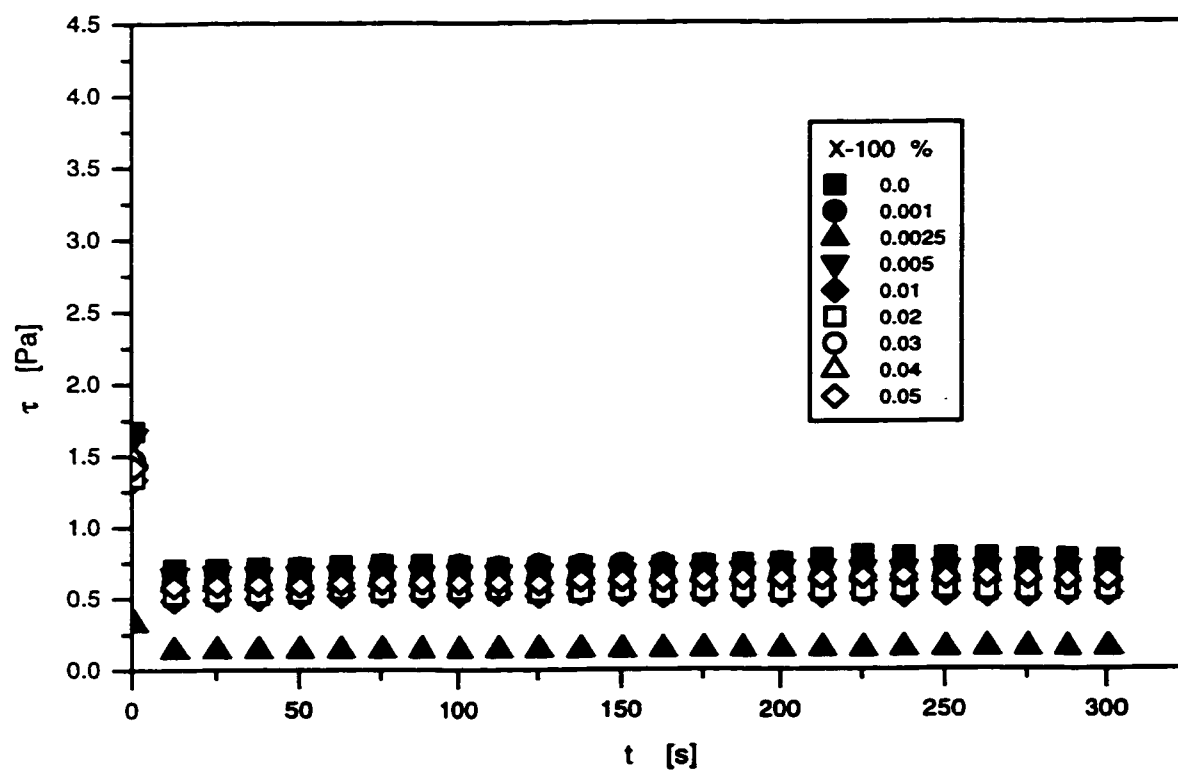


Figure 4.6.11 Effect of Surfactant on Transient Shear Stress Response for 0.04%PAM at 50 [1/s]

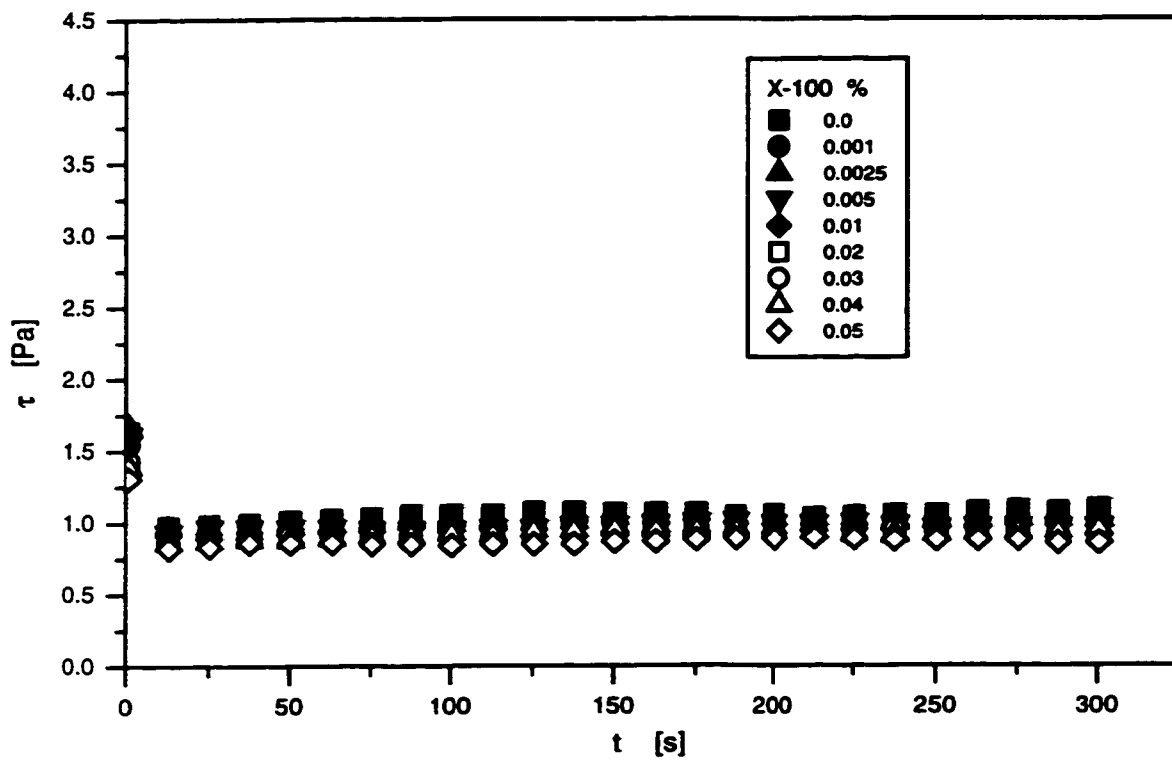


Figure 4.6.12 Effect of Surfactant on Transient Shear Stress Response for 0.04%PAM at 100 [1/s]

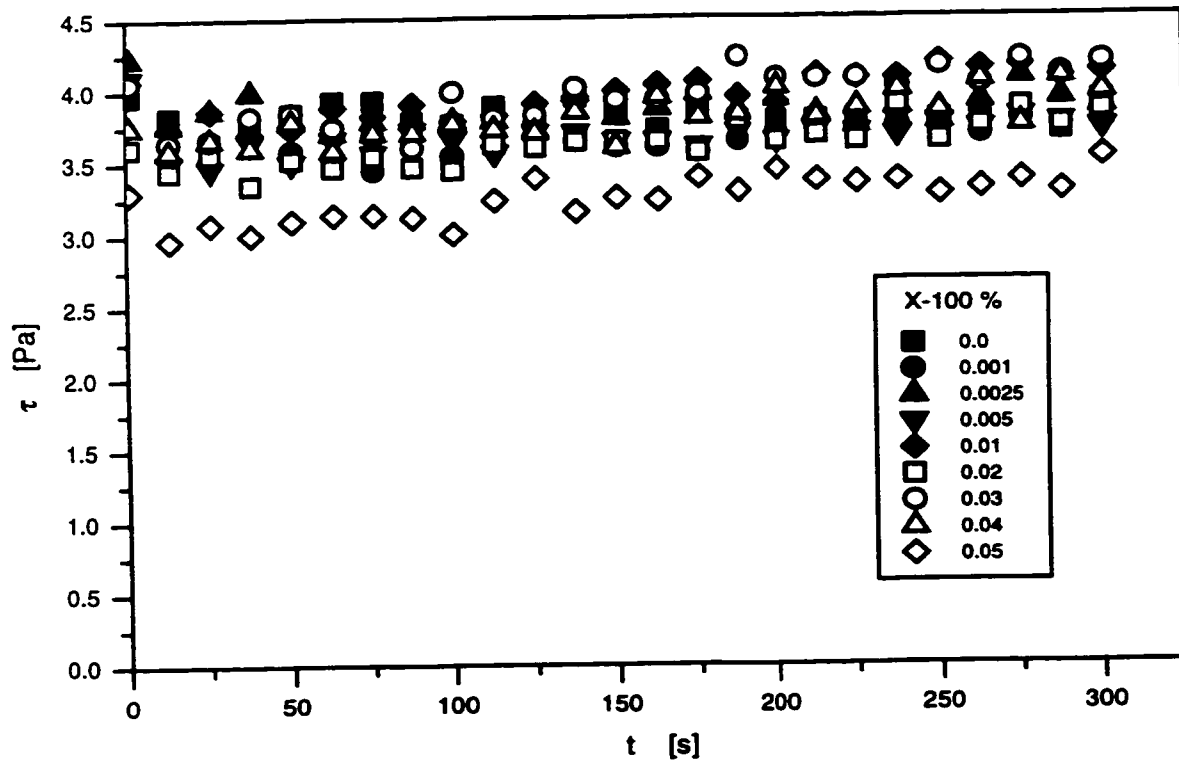


Figure 4.6.13 Effect of Surfactant on Transient Shear Stress Response for 0.04%PAM at 500 [1/s]

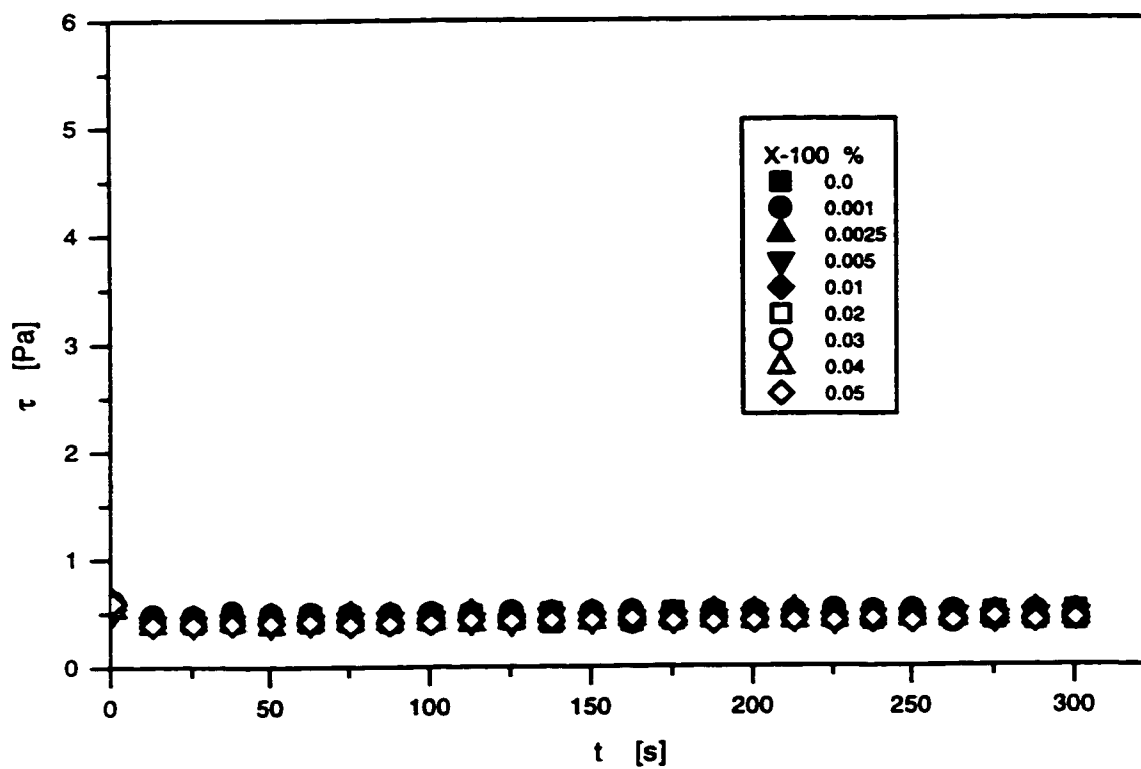


Figure 4.6.14 Effect of Surfactant on Transient Shear Stress Response for 0.06%PAM at 10 [1/s]

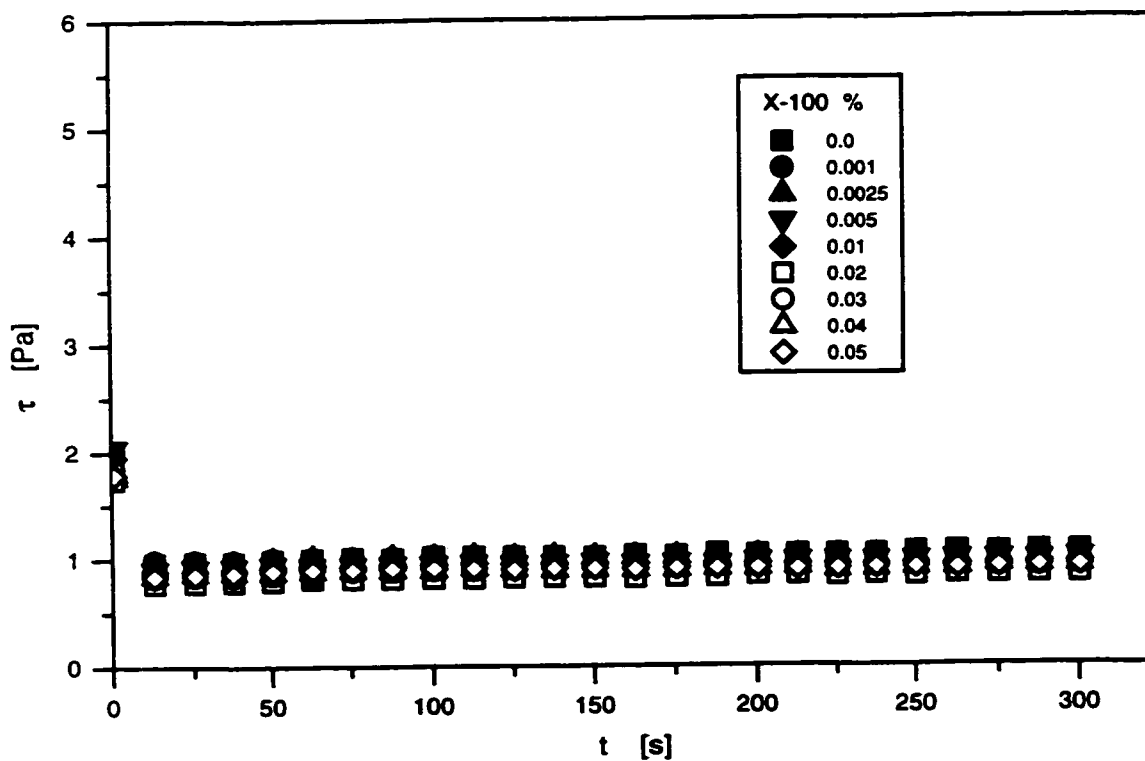


Figure 4.6.15 Effect of Surfactant on Transient Shear Stress Response for 0.06%PAM at 50 [1/s]

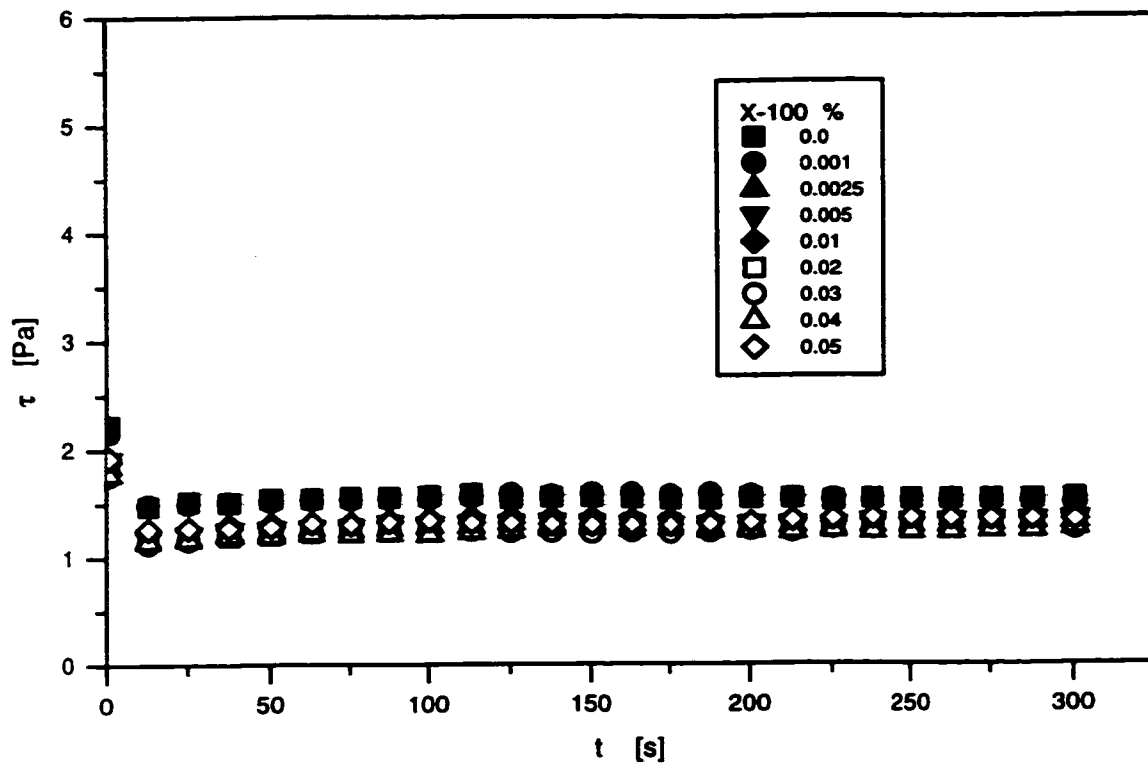


Figure 4.6.16 Effect of Surfactant on Transient Shear Stress Response for 0.06%PAM at 100 [1/s]

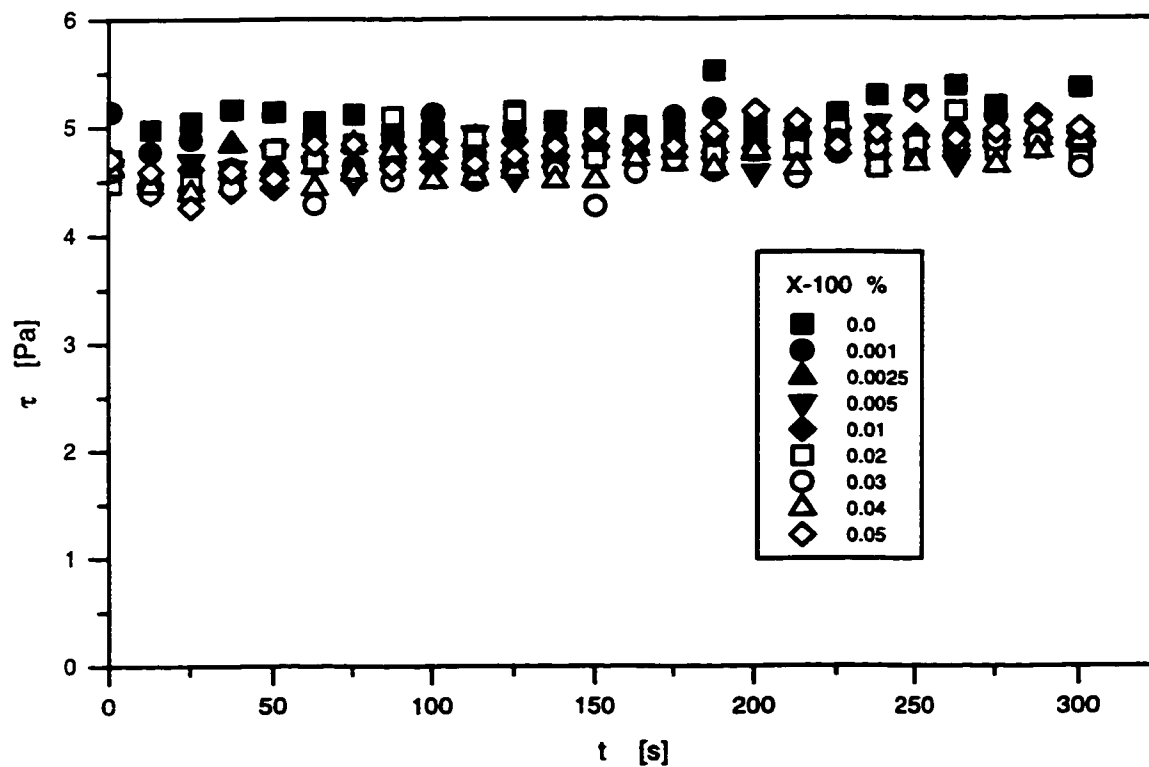


Figure 4.6.17 Effect of Surfactant on Transient Shear Stress Response for 0.06%PAM at 500 [1/s]

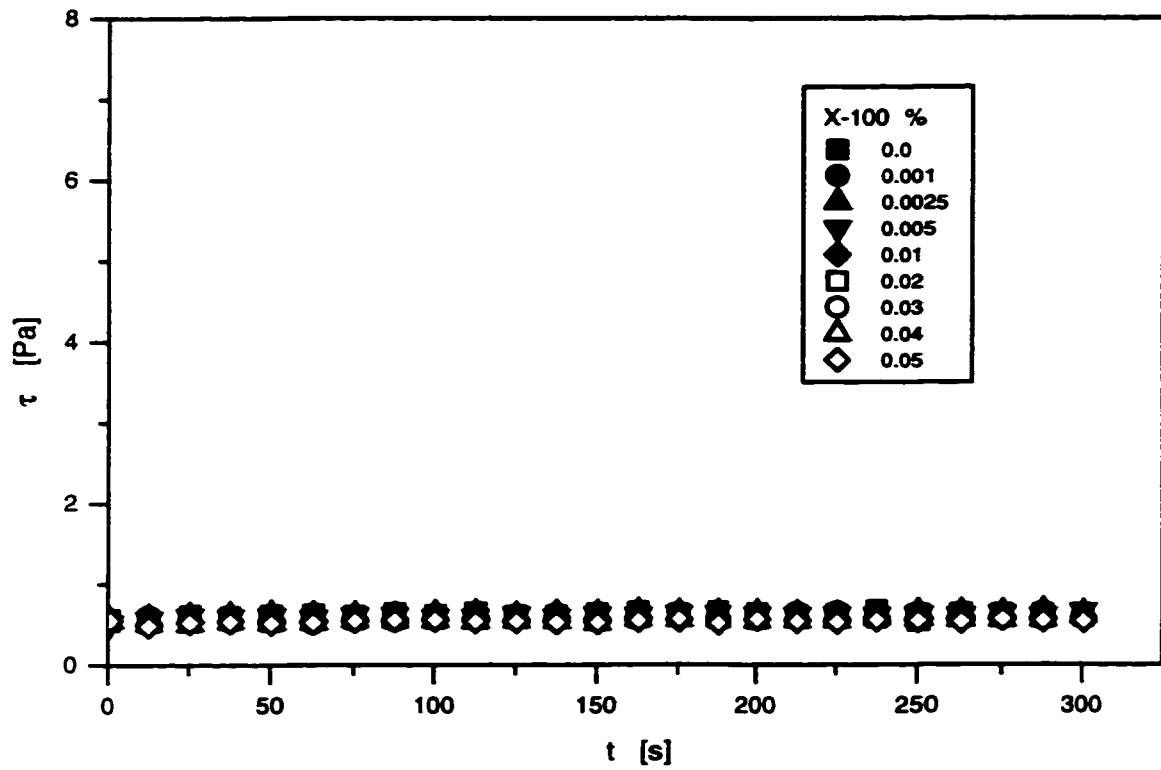


Figure 4.6.18 Effect of Surfactant on Transient Shear Stress Response for 0.08%PAM at 10 [1/s]

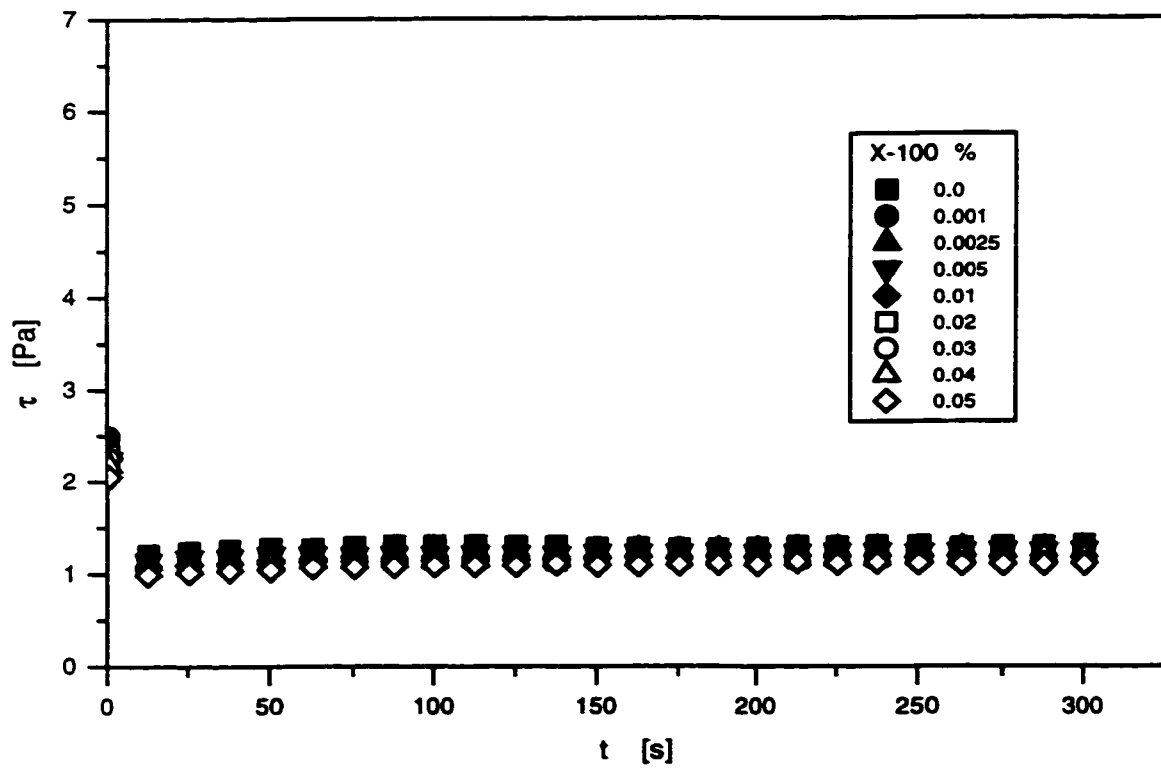


Figure 4.6.19 Effect of Surfactant on Transient Shear Stress Response for 0.08%PAM at 50 [1/s]

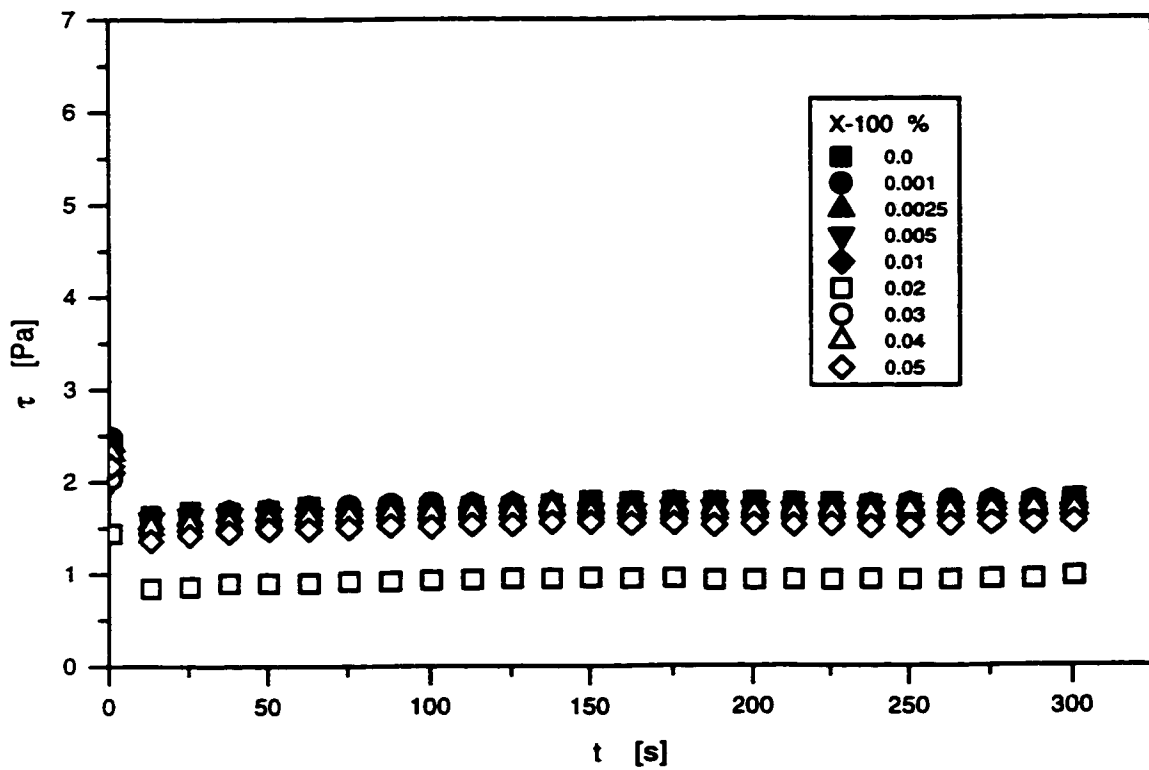


Figure 4.6.20 Effect of Surfactant on Transient Shear Stress Response for 0.08%PAM at 100 [1/s]

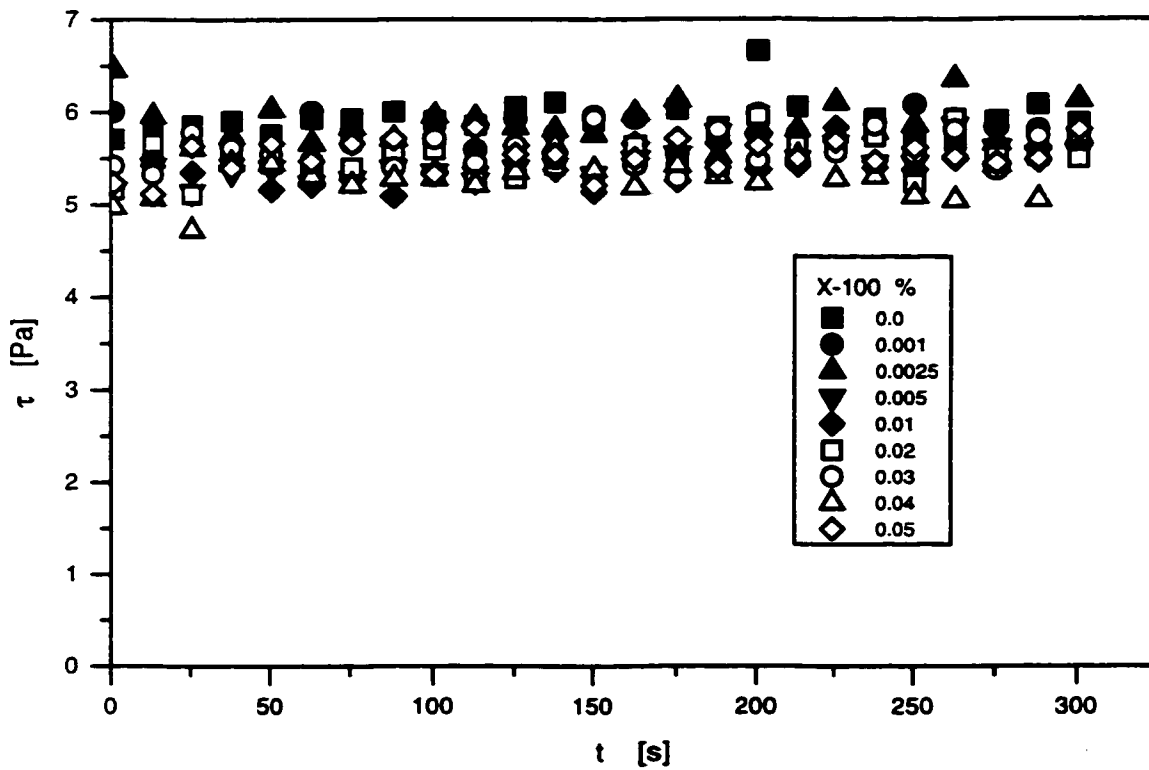


Figure 4.6.21 Effect of Surfactant on Transient Shear Stress Response for 0.08%PAM at 500 [1/s]

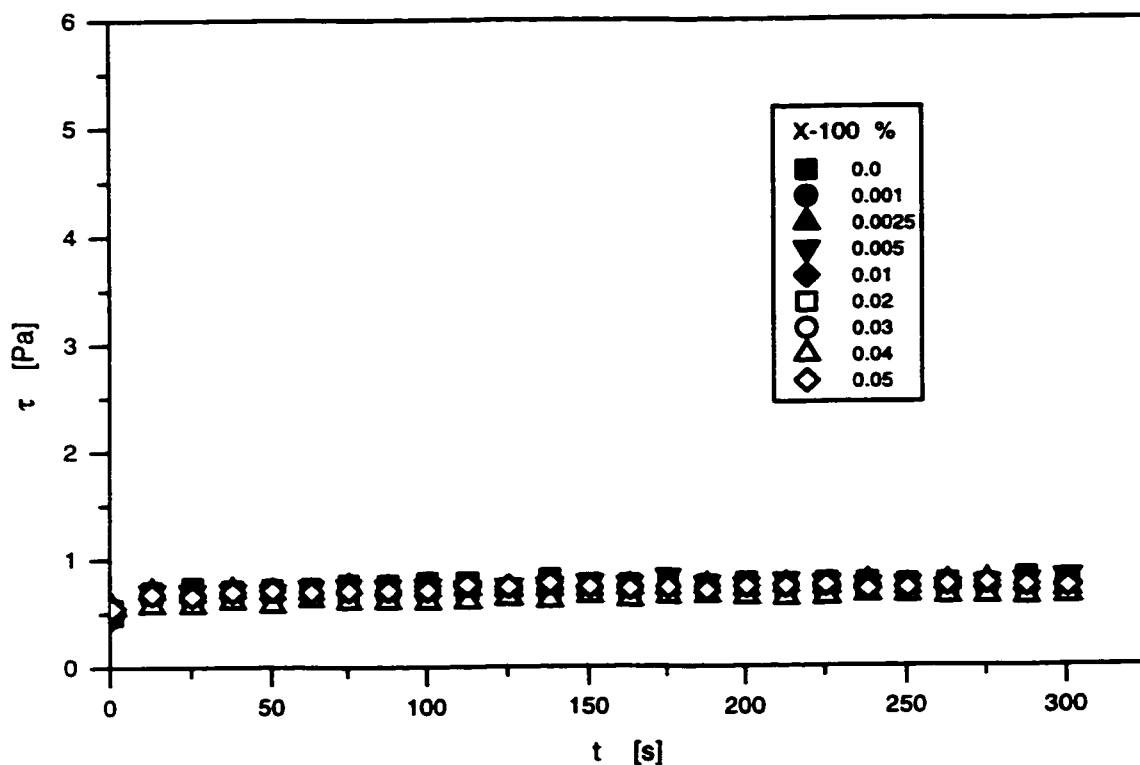


Figure 4.6.22 Effect of Surfactant on Transient Shear Stress Response for 0.1%PAM at 10 [1/s]

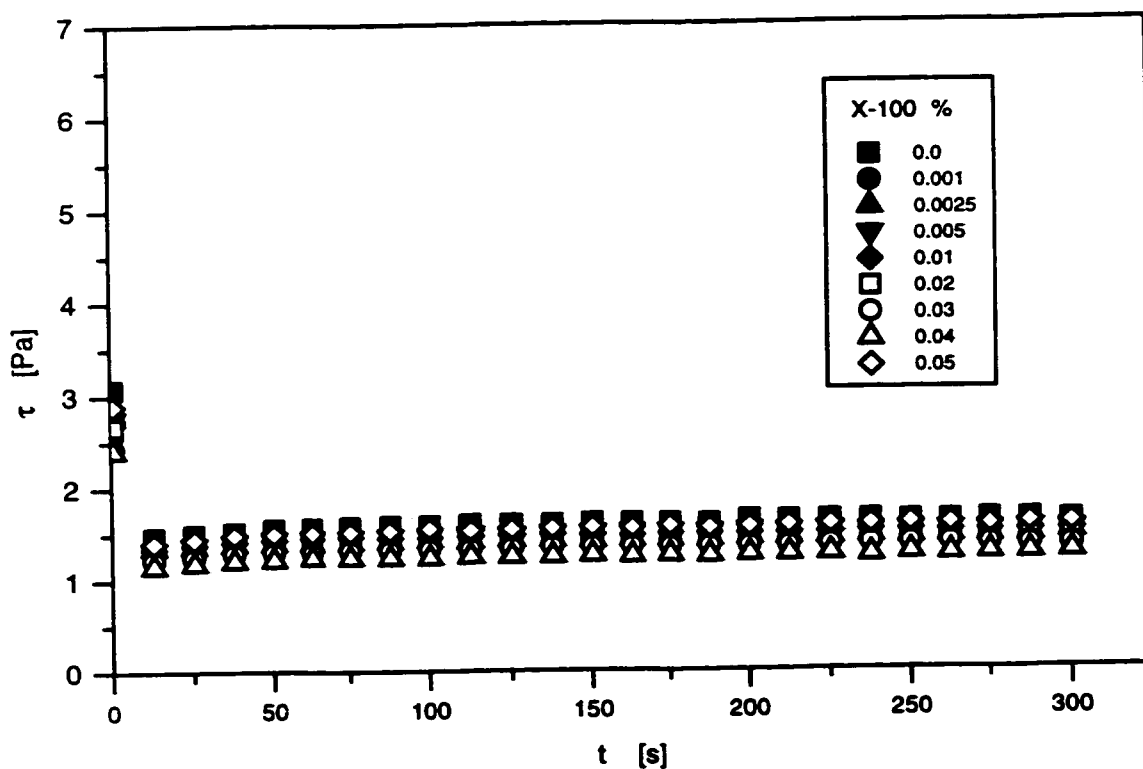


Figure 4.6.23 Effect of Surfactant on Transient Shear Stress Response for 0.1%PAM at 50 [1/s]

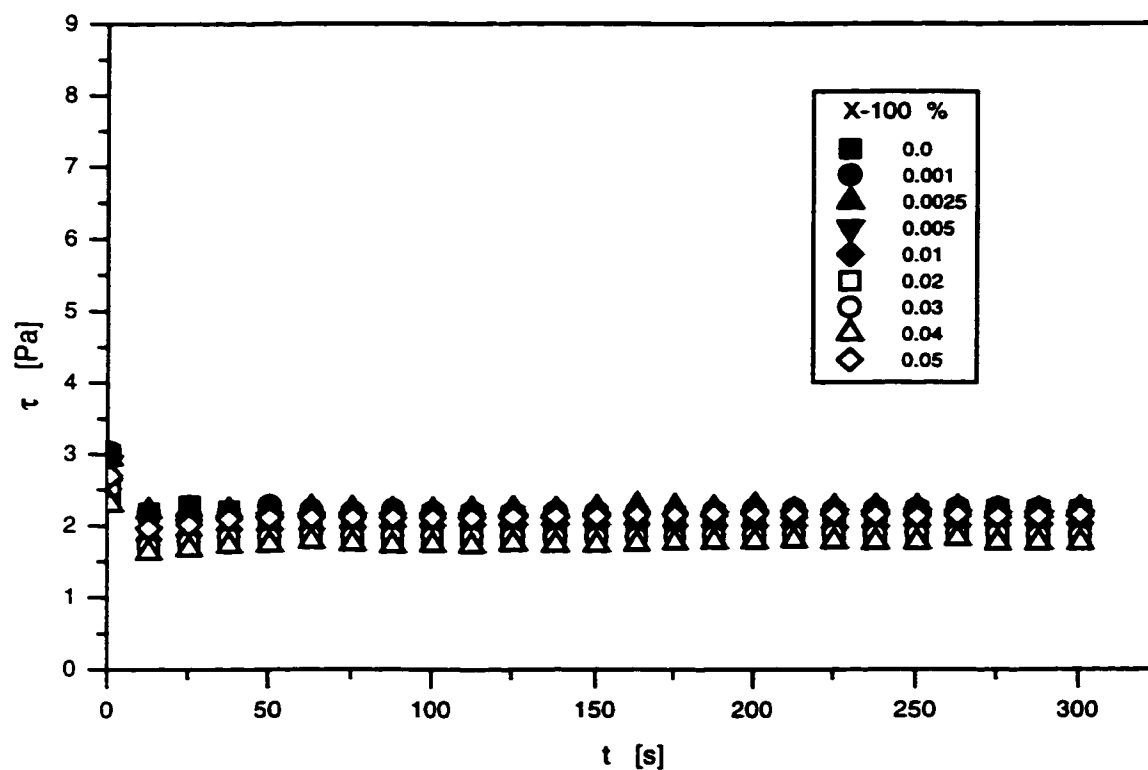


Figure 4.6.24 Effect of Surfactant on Transient Shear Stress Response for 0.1%PAM at 100 [1/s]

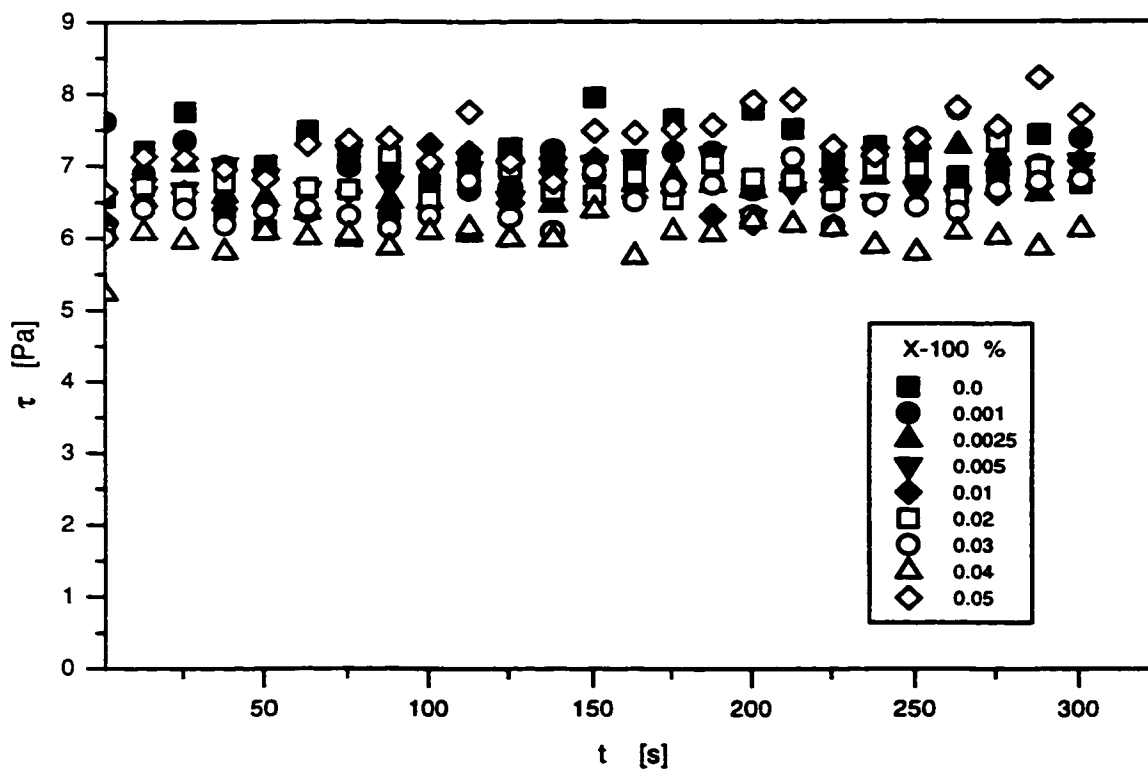


Figure 4.6.25 Effect of Surfactant on Transient Shear Stress Response of 0.1%PAM at 500 [1/s]

4.7 Dynamic Study.

This study includes the measurements of dynamic viscoelastic response and complex viscosity. The definition of viscoelasticity has been mentioned in the creep recovery test. In the dynamic test, instead of applying constant stress leading to steady state shear rate, an oscillating stress or strain is applied with assigned frequency (ω) and amplitude. In this case, the cone no longer turns continuously in one direction, but is made to deflect with a sinusoidal movement for small angle to the left and right. The tested sample is thus forced to stress in a similar sinusoidal function, causing resisting strain in the sample. Those strains follow sinusoidal pattern, the amplitude of which is the nature of the tested sample. The deforming stress occurs within a short time and changes rapidly in magnitude and direction. As this process appears rapidly, there is not enough time for any kind of flow phenomena. Samples are just probed rheologically for their molecular structure and interactions²⁰.

The viscous and elastic parts of the material are very important factors of the material response. By measuring how the strain or stress behaves as a function of time, the magnitude of the elastic and viscous components of a material can be evaluated. The elastic part is called the storage modulus $G'(\omega)$ and it is a measure of the energy stored and recovered per cycle. The viscous part is called the loss modulus $G''(\omega)$ which is a measure of the energy dissipated or lost as heat per cycle. In applying a sinusoidal stress, a material returning less elastic energy will show more energy loss, leading to a retardation in the material response to a periodic force. This retardation can be expressed

as a phase difference between force (applied stress) and deformation (resulting strain). The total resistance of a material against the applied stress is called complex modulus G^* , defined as:

$$G^* = \tau_0 / \gamma_0 \quad (4.7.1)$$

where

τ_0 is the stress magnitude

γ_0 is the strain magnitude

or as

$$G^*(\omega) = G'(\omega) + G''(\omega) \quad (4.7.2)$$

All materials are situated between two extremes.

-The purely elastic material where all the energy is returned elastically and the phase difference between stress and strain is equal to zero. On the molecular basis, this would correspond to the absence of any molecular movements capable of dissipating energy within the period of deformation.

$$G'' = 0, \quad G' = G^*$$

- The purely viscous materials where all the energy is dissipated into heat and the phase difference between stress and strain is equal to 90.

$$G' = 0, \quad G'' = G^*$$

As an alternative to the complex modulus, one can define the complex viscosity (η^*) as

$$\eta^* = G^* / \omega \quad (4.7.3)$$

It is a measure of magnitude of total resistance to a dynamic shear.

All tested materials have been subjected to frequency sweep at constant stress amplitude in order to characterize the material response. The stress amplitude usually lies within the linear viscoelastic range so that the measurements are stress independent. To determine the limit of linear viscoelastic range, stress sweep performs at a fixed frequency. The results of such a test are plotted as G^* against stresses amplitude. The linear viscoelastic range is limited to the amplitude range for which G^* is constant.

Polyacrylamide samples have been subjected to stress sweep at fixed frequency of 0.1 HZ and the linear viscoelastic range has been found to be less than 5 Pa. Frequency sweep from 0.01 HZ to 10 HZ has been carried out to characterize the sample's degree of viscoelasticity and the change of complex viscosity. Figure 4.7.1 shows the stress sweep test results. At all concentrations, the linear viscoelastic range has been determined. Figures 4.7.2-4.7.6 reveal the storage and loss modulus as function of frequency and concentration, their values increasing as a result of increasing the concentration and frequency while the loss modulus is more predominant up to critical frequency which depends on concentration, however, above this frequency, all tested solutions behave like pure viscous material ($G'=0$). The frequency responsible for the elastic behavior increases with concentration, and there are frequency values at concentrations of 0.08% and 0.1% where the viscous and elastic parts are nearly equal. These results shows that the behavior of polyacrylamide solutions do not match neither Voigt model nor Maxwell model²⁰. The effect of surfactant on the elastic part is plotted in figures 4.7.7-4.7.11 and its effect decreases with concentration. At

concentration of 0.02%, surfactant concentration less than 0.005% has almost no effect on the storage modulus. Higher surfactant concentration leads to random decrease in the module. At polyacrylamide concentration of 0.04%, there is a slight irregular decrease in the storage modulus at surfactant concentrations of 0.0025% and 0.01%. At polyacrylamide concentrations from 0.06%-0.1%, the surfactant has no effect on the storage modulus. The effect of surfactant on the viscous part of the tested samples plotted in figures 4.7.12-4.7.16. At polyacrylamide concentration of 0.02%, there is a slight decrease in loss modulus up to a frequency of 1 rad/s where the surfactant has no effect. Above this frequency there is a slight increase in the loss modulus. At higher concentrations of polyacrylamide, the surfactant has almost no effect.

Figure 4.7.17 reveals the complex viscosity at different concentrations of polyacrylamide. Two regions can be recognized, decrease in viscosity as frequency increases and concentrations decrease up to critical value which depends on concentration. Above this value, the viscosity is equal for all concentrations and its value increases with frequency. The effect of surfactant on the complex viscosity is shown in figures 4.7.18-4.7.22. At polyacrylamide concentration of 0.02% and low frequency, the surfactant has complex effects on the sample. Above the critical value, three effects appear. They are: 1) no effect up to concentration 0.0025%, 2) slight decrease up to concentration 0.01%, and 3) sharp decrease at 0.02% followed by increase to the same value observed at concentration 0.01% . At higher polyacrylamide concentration and below a critical frequency value, the effect of surfactant leads to a decrease in complex

viscosity. This effect decreases with increasing polyacrylamide concentration up to concentrations of 0.08% and 0.1% where surfactant has almost no effect. Beyond the critical frequency, the surfactant has no effect on polyacrylamide solutions.

By comparing the dynamic complex viscosity with shear rate viscosity, one can find that at a certain range of frequency, the complex viscosity tends to follow the same pattern as shear rate viscosity (shear thinning up to critical value above which the tested solutions are associated with shear thickening). Applying Cox-Merz rule³⁶, that is

$$\eta(\dot{\gamma}) = \eta^*(\omega) \big|_{\omega=\dot{\gamma}} \quad (4.7.4)$$

Where:

η is the shear rate viscosity at shear rate of $\dot{\gamma}(\text{S}^{-1})$

η^* is complex viscosity at frequency of ω (rad/s)

shows that the Cox-Marz rule is invalid for all tested samples.

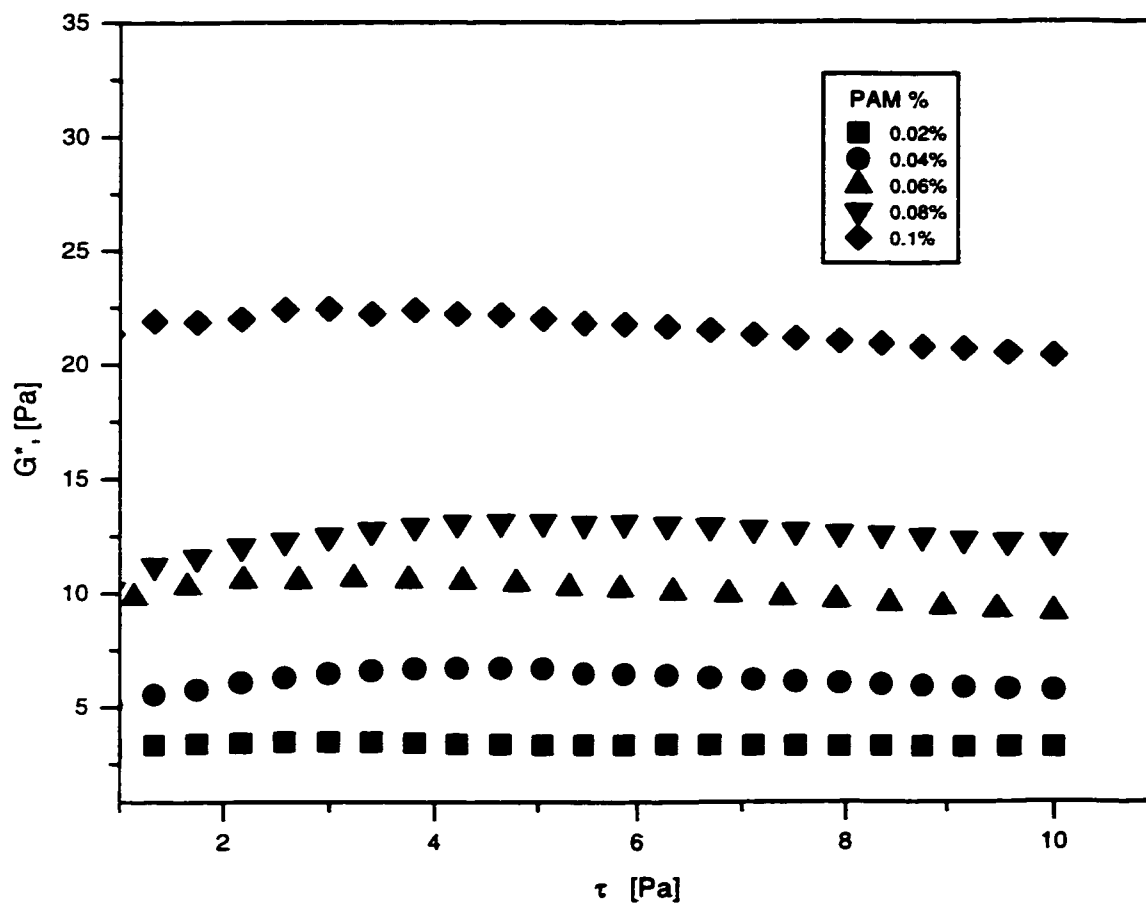


Figure 4.7.1 Dynamic Linear Viscoelastic Range for PAM Solutions

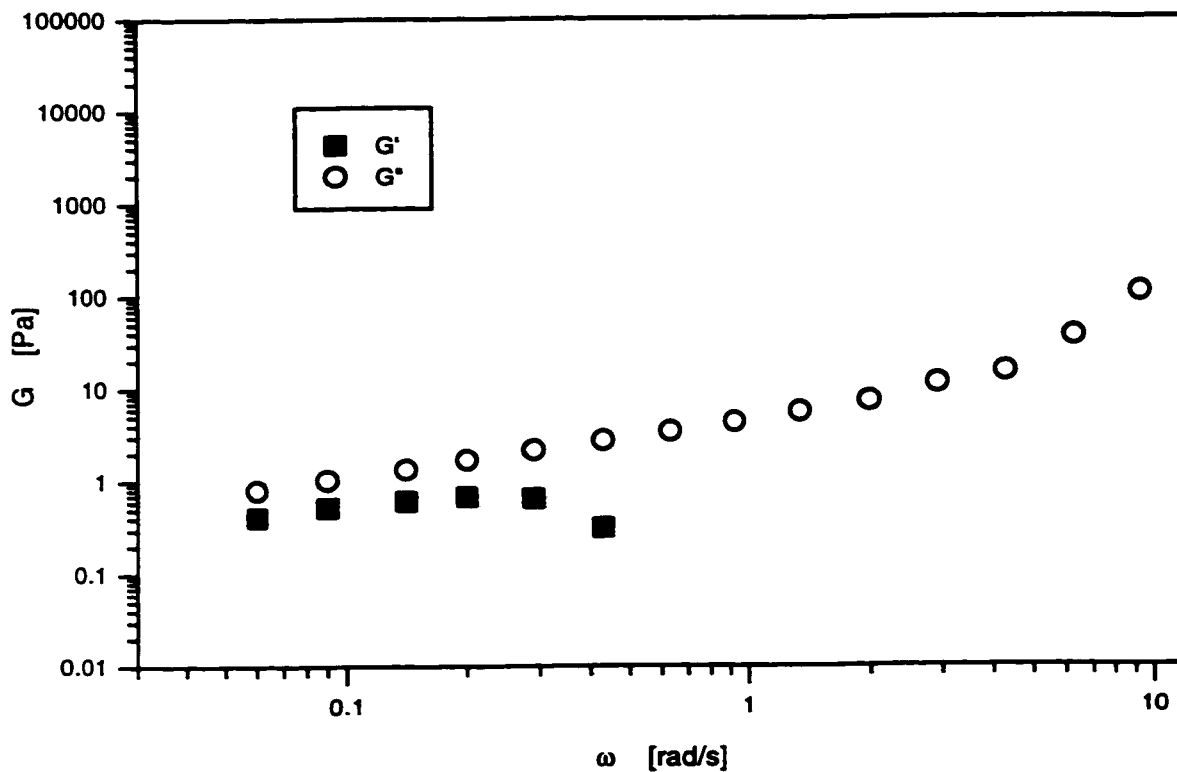


Figure 4.7.2 Storage and Loss Modulus for 0.02% PAM

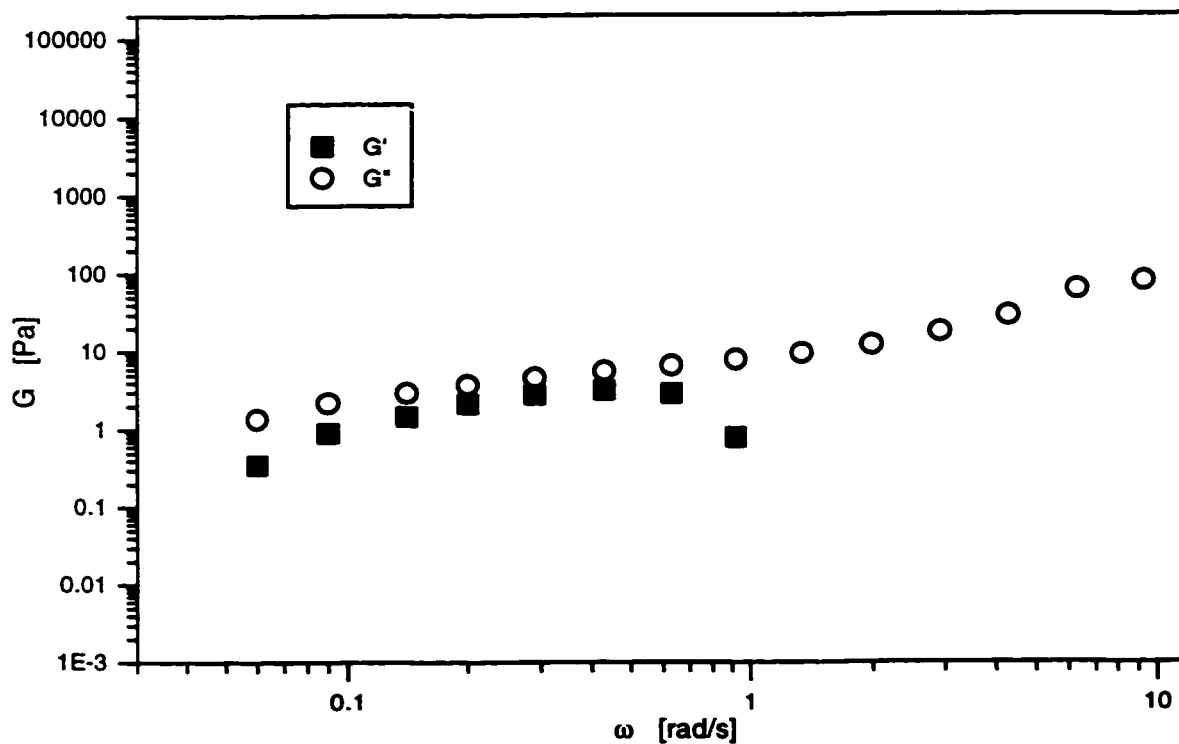


Figure 4.7.3 Storage and Loss Modulus for 0.04% PAM

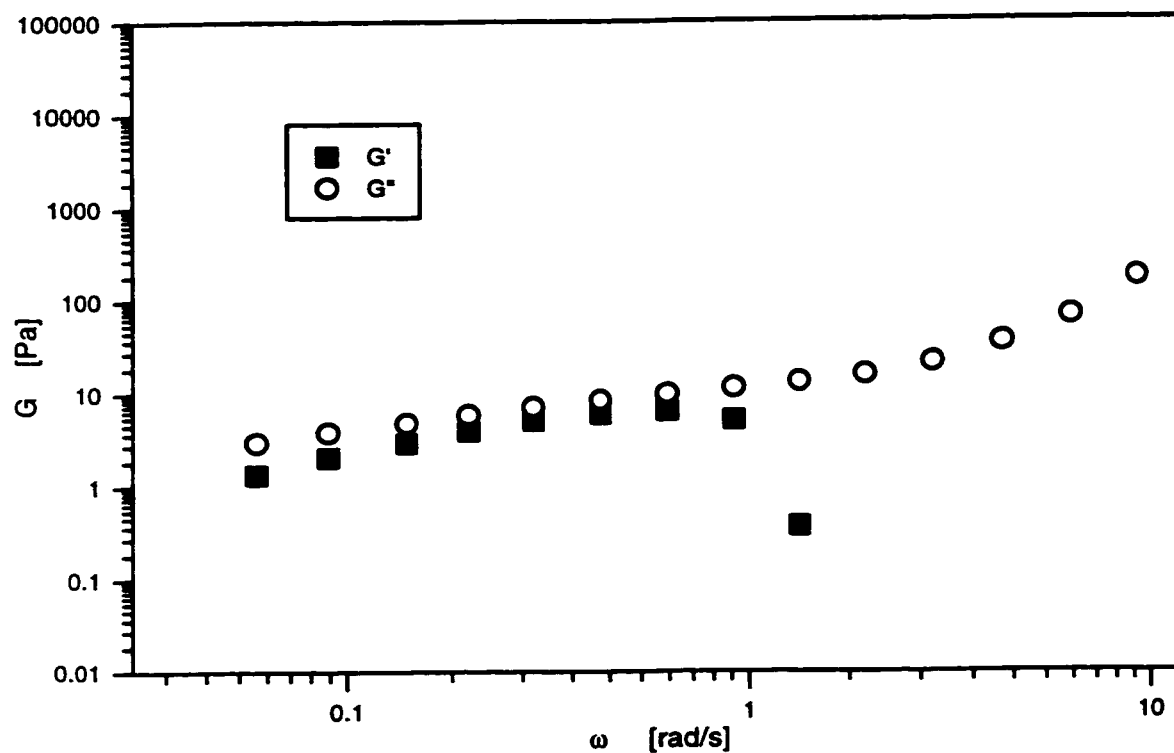


Figure 4.7.4 Storage and Loss Modulus for 0.06% PAM

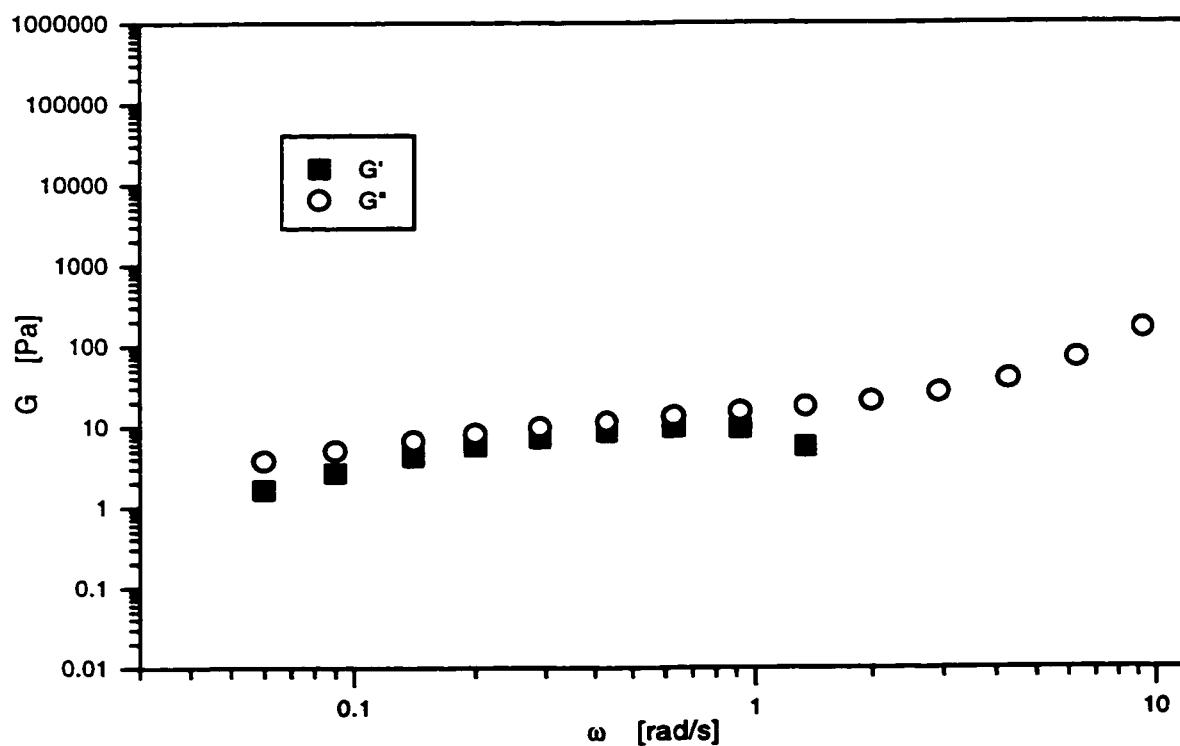


Figure 4.7.5 Storage and Loss Modulus for 0.08% PAM

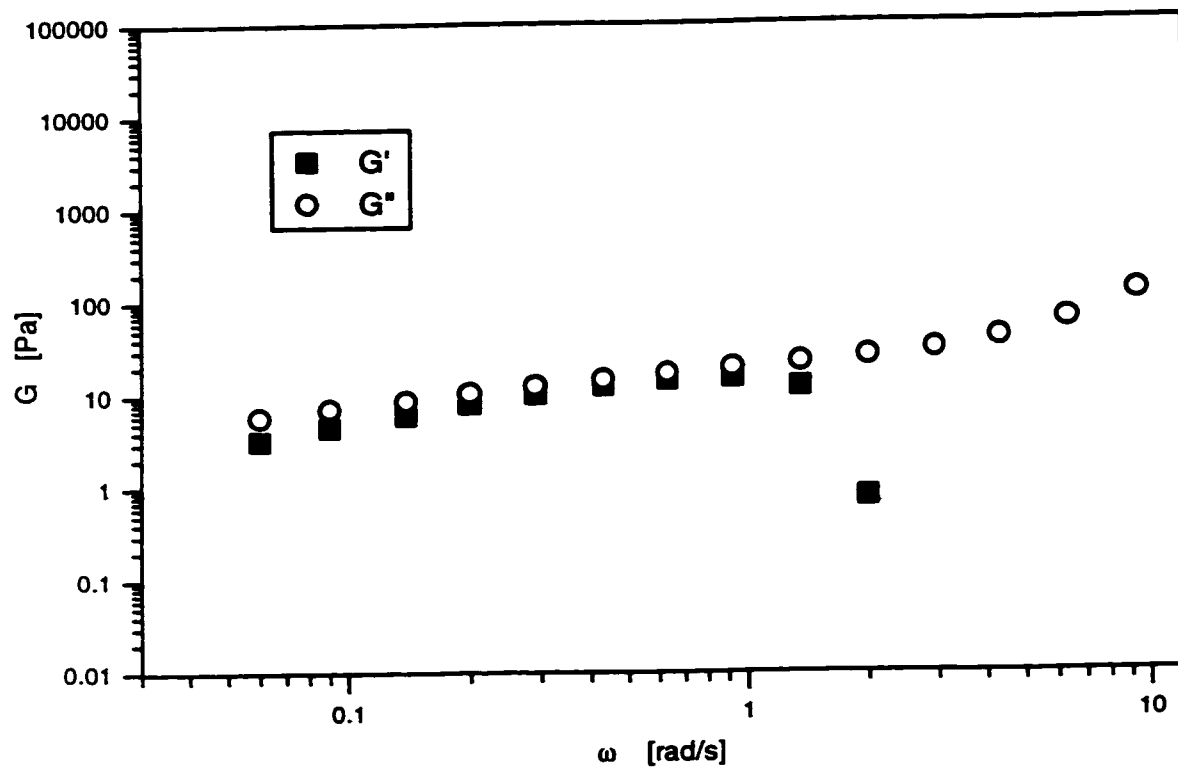


Figure 4.7.6 Storage and Loss Modulus for 0.1% PAM

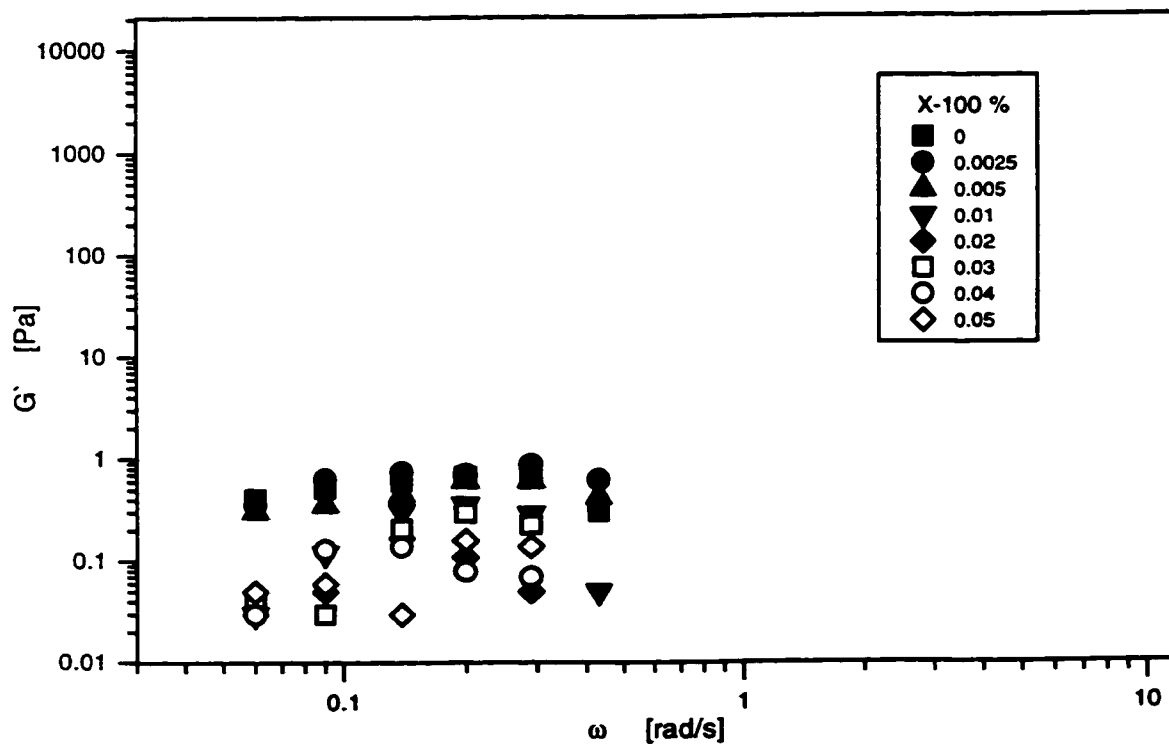


Figure 4.7.7 Effect of Surfactant on Storage Modulus for 0.02% PAM

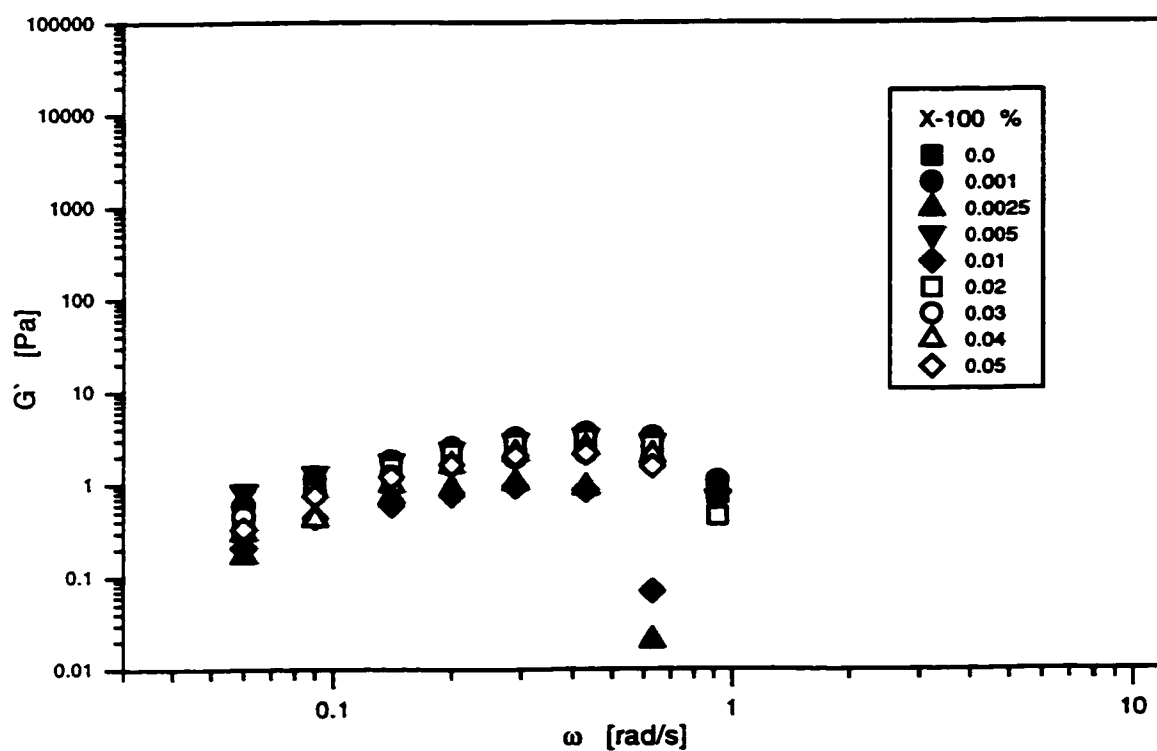


Figure 4.7.8 Effect of Surfactant on Storage Modulus for 0.04% PAM

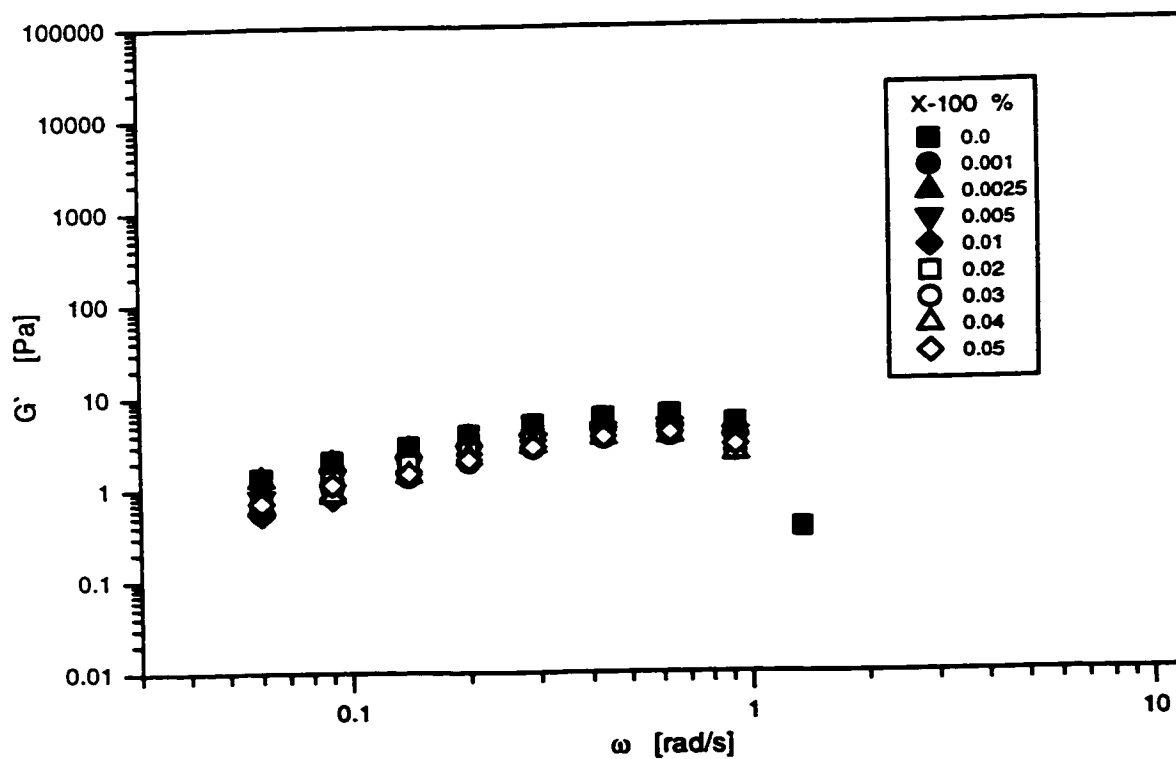


Figure 4.7.9 Effect of Surfactant on Storage Modulus for 0.06% PAM

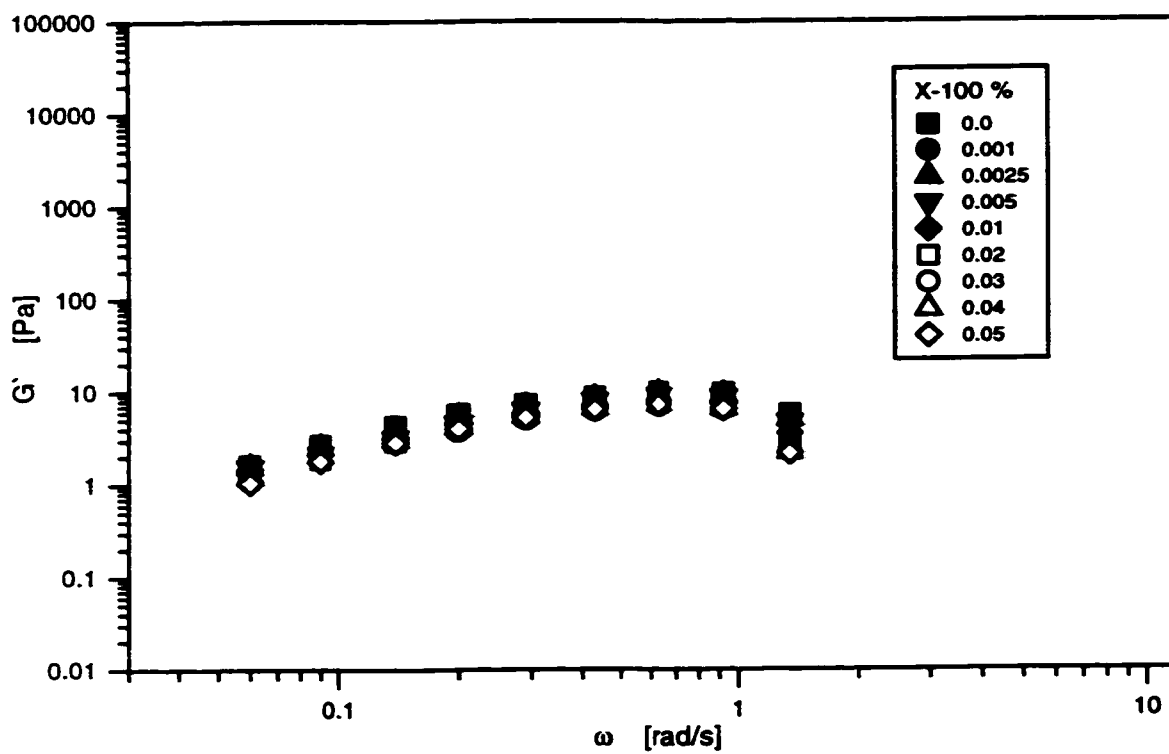


Figure 4.7.10 Effect of Surfactant on Storage Modulus for 0.06% PAM

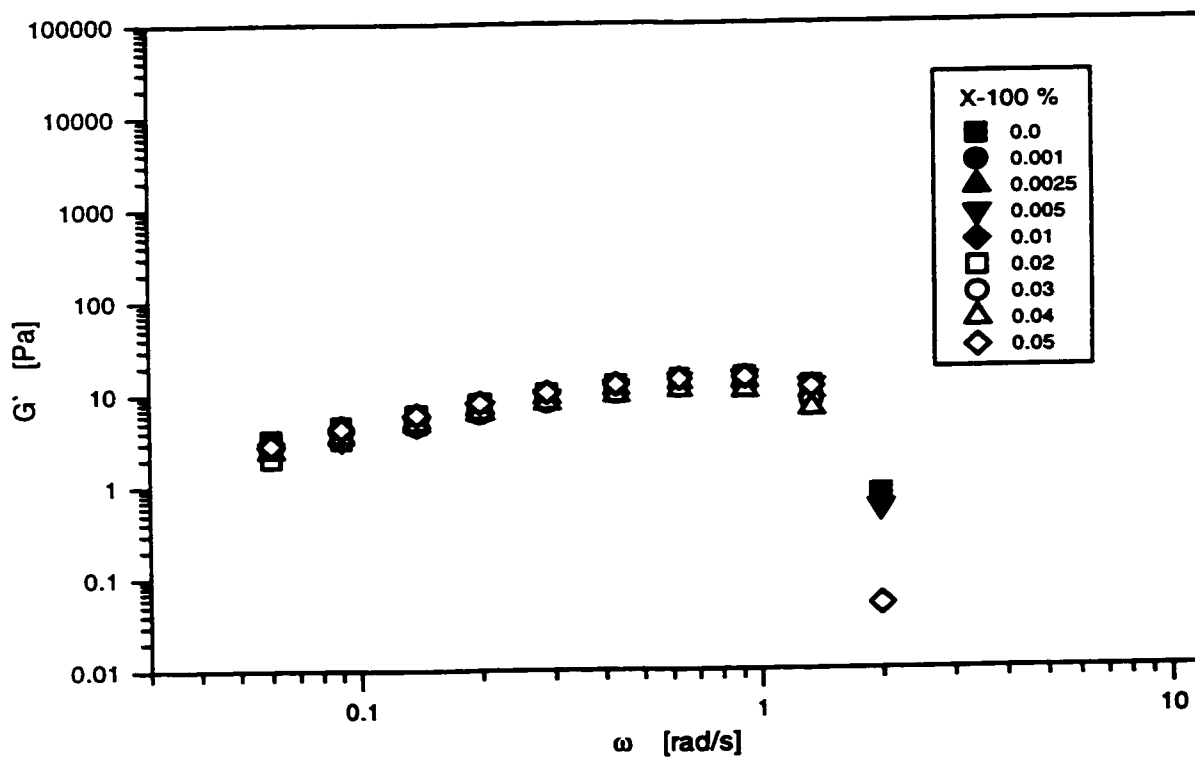


Figure 4.7.11 Effect of Surfactant on Storage Modulus for 0.1% PAM

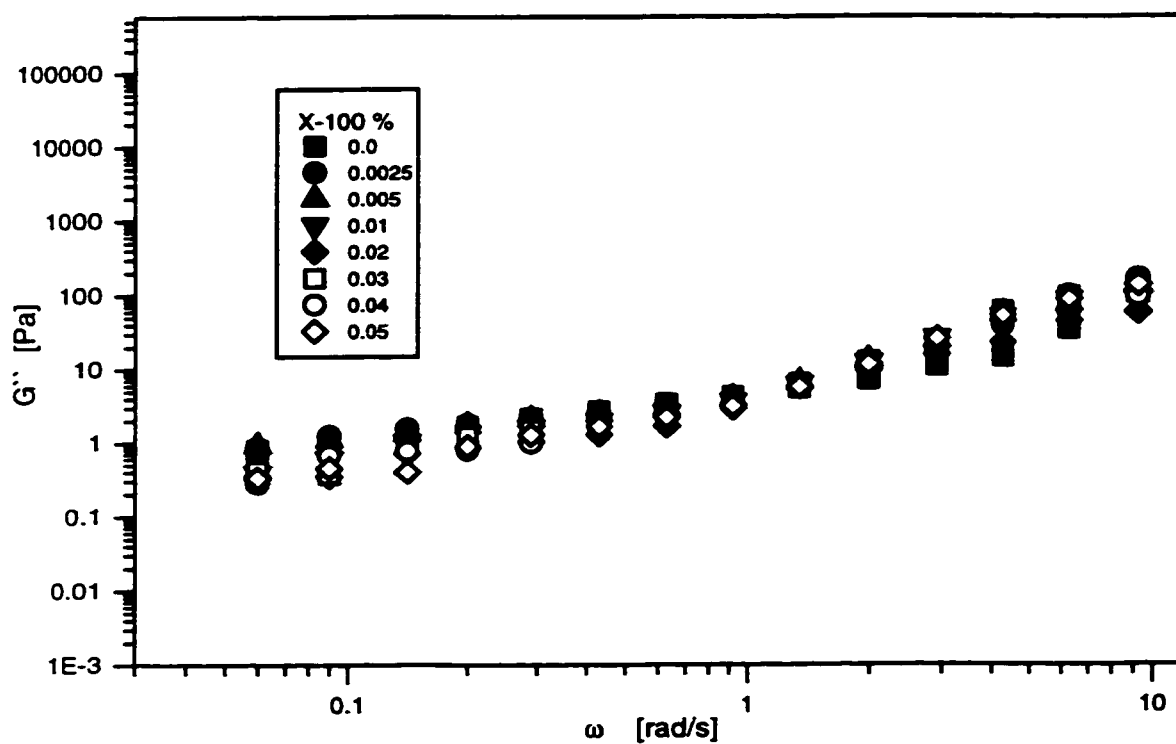


Figure 4.7.12 Effect of Surfactant on Loss Modulus for 0.02% PAM

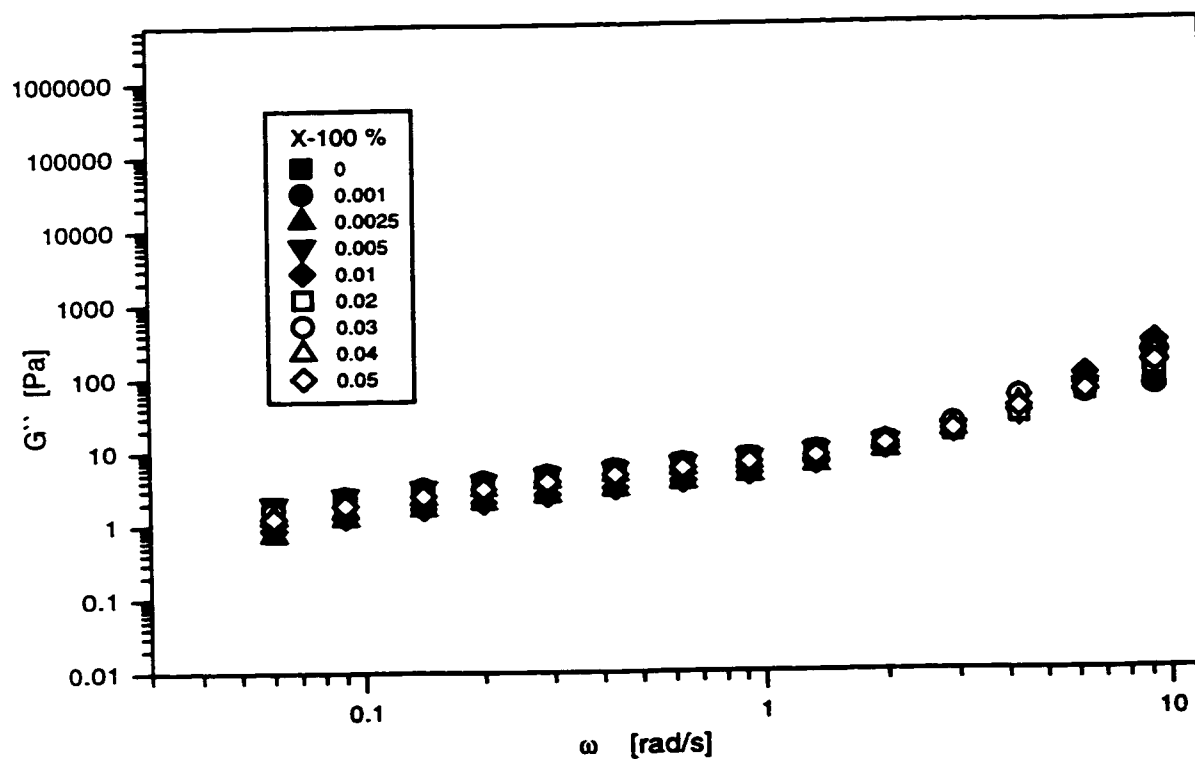


Figure 4.7.13 Effect of Surfactant on Loss Modulus for 0.04% PAM

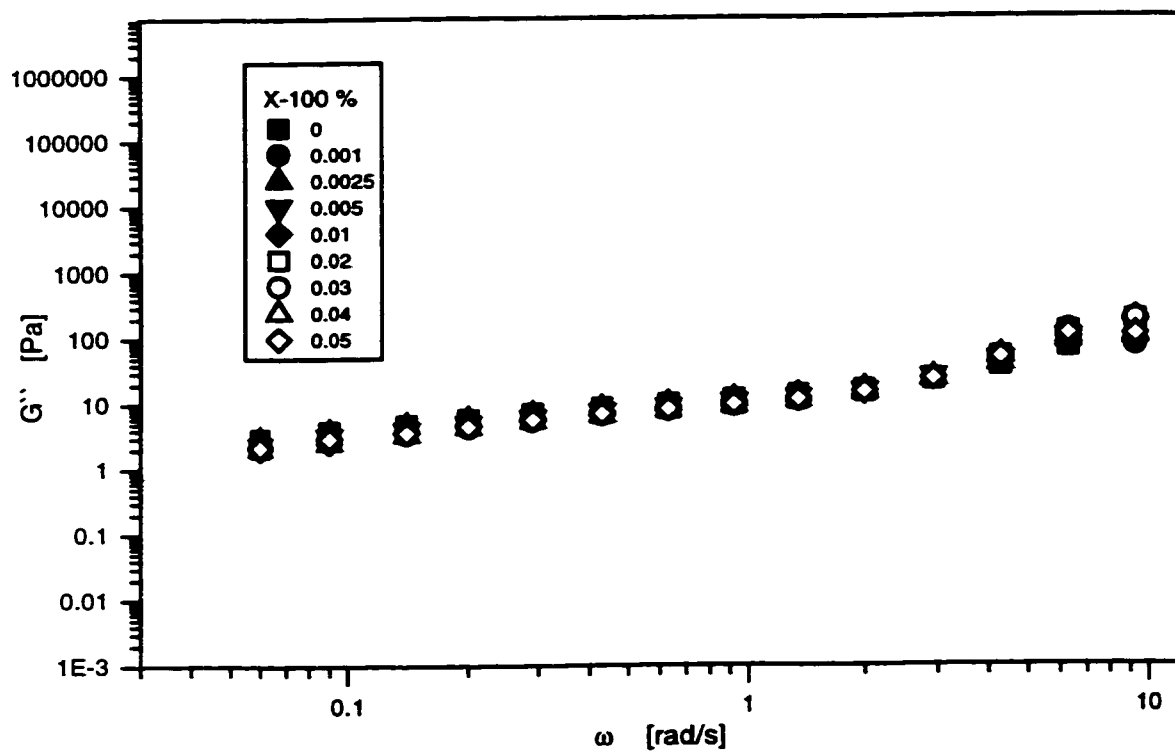


Figure 4.7.14 Effect of Surfactant on Loss Modulus for 0.06% PAM

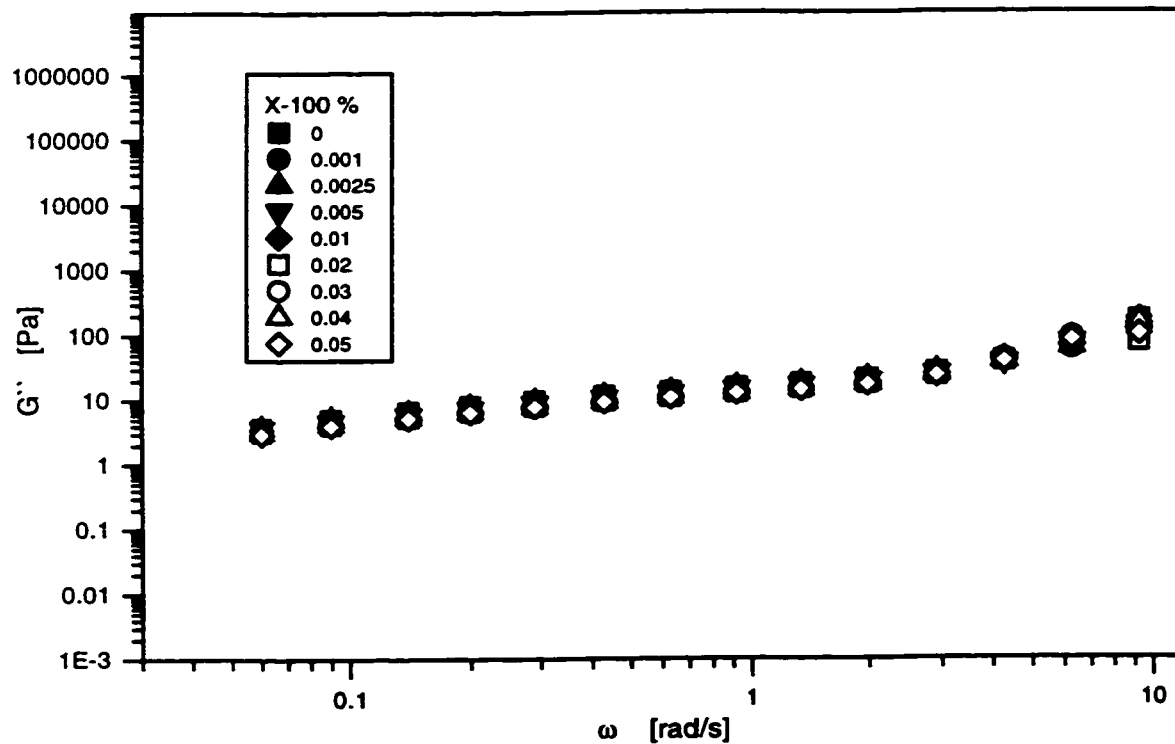


Figure 4.7.15 Effect of Surfactant on Loss Modulus for 0.06% PAM

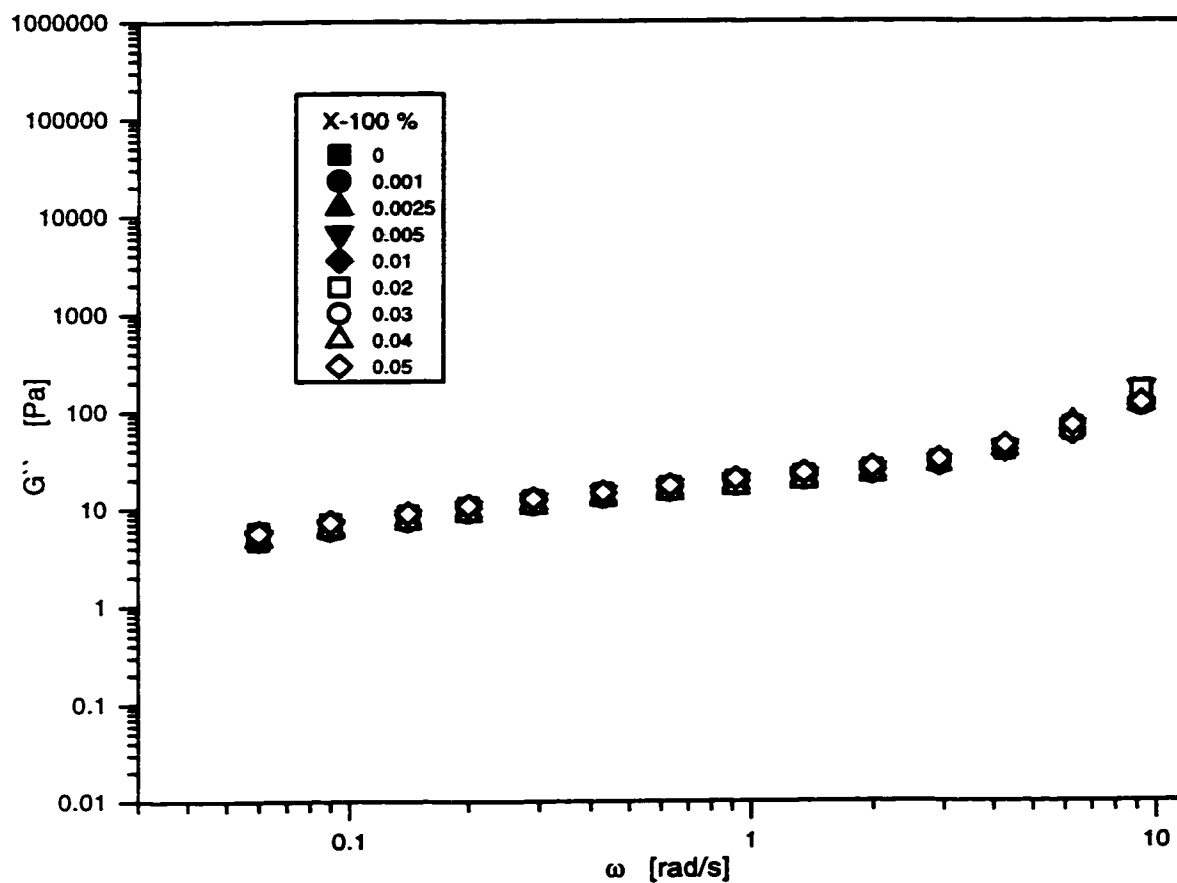


Figure 4.7.16 Effect of Surfactant on Loss Modulus for 0.1% PAM

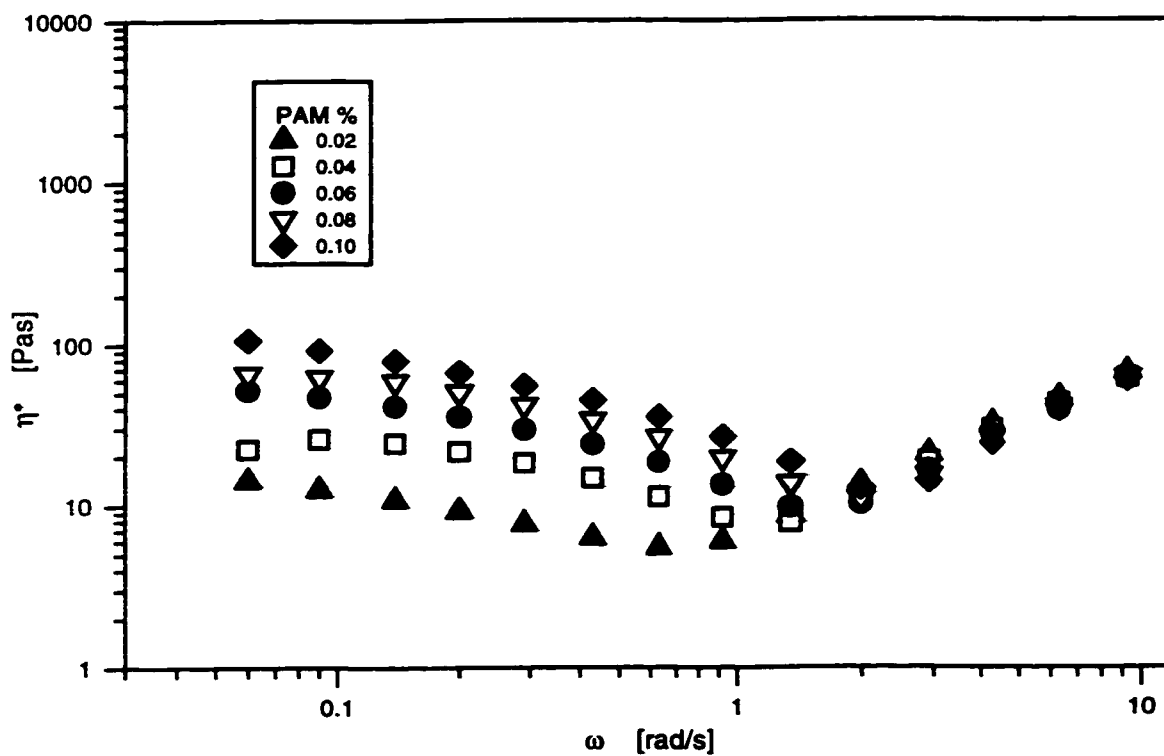


Figure 4.7.17 Complex Viscosity for PAM Solutions

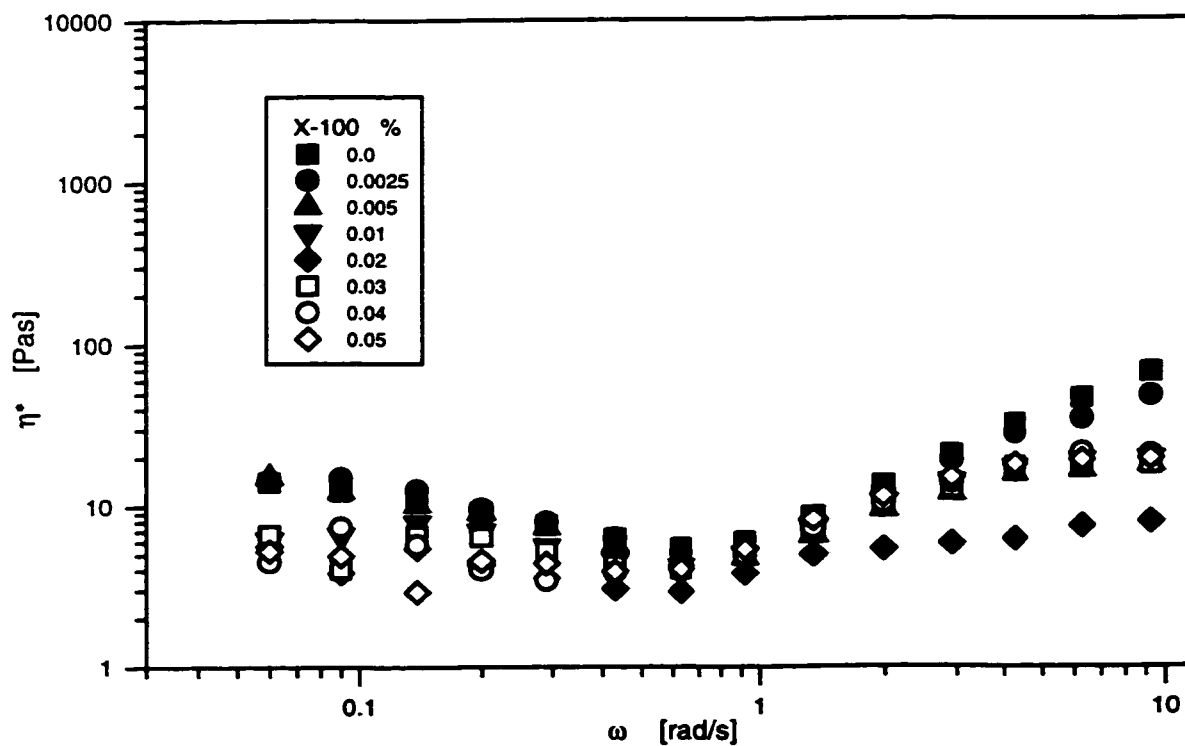


Figure 4.7.18 Effect of Surfactant on Complex Viscosity for 0.02%PAM

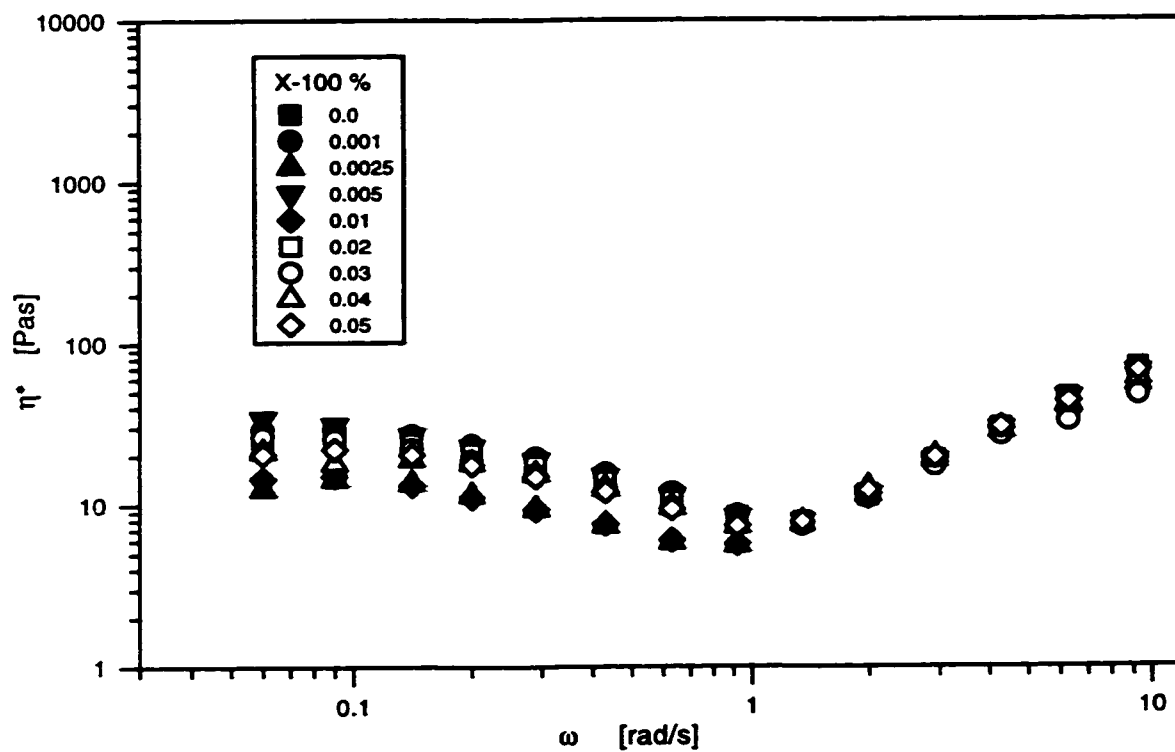


Figure 4.7.19 Effect on Surfactant on Complex Viscosity for 0.04% PAM

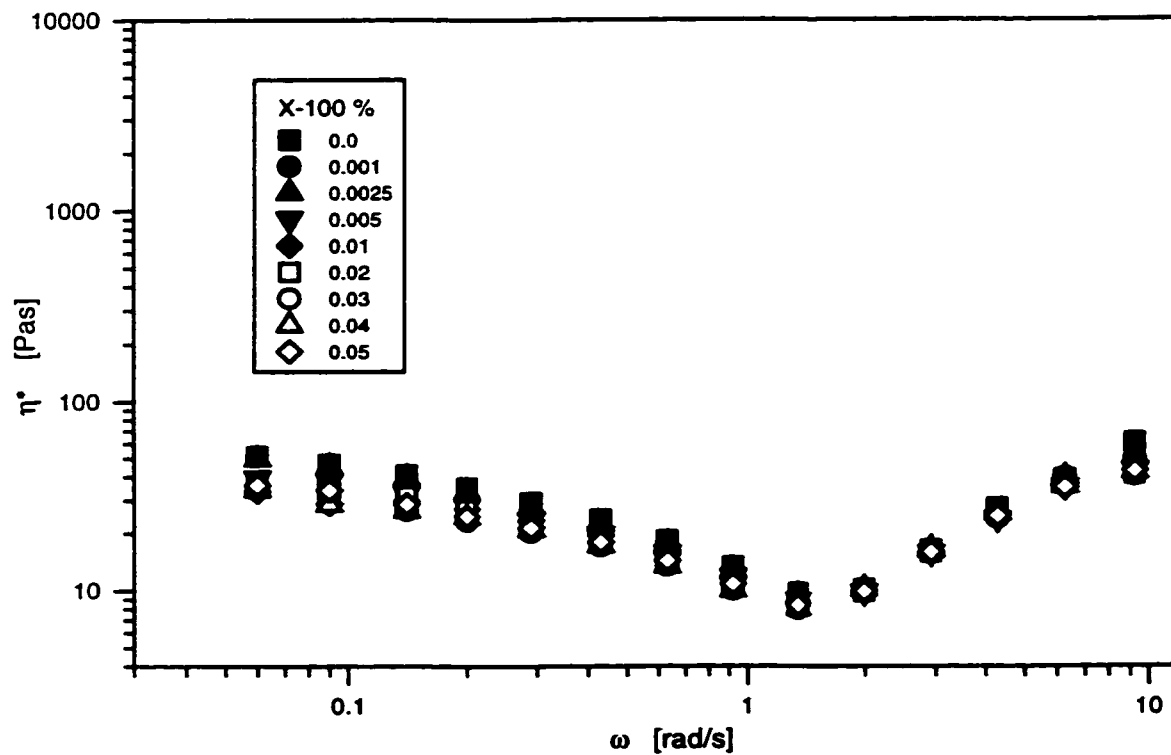


Figure 4.7.20 Effect of Surfactant on Complex Viscosity for 0.06% PAM

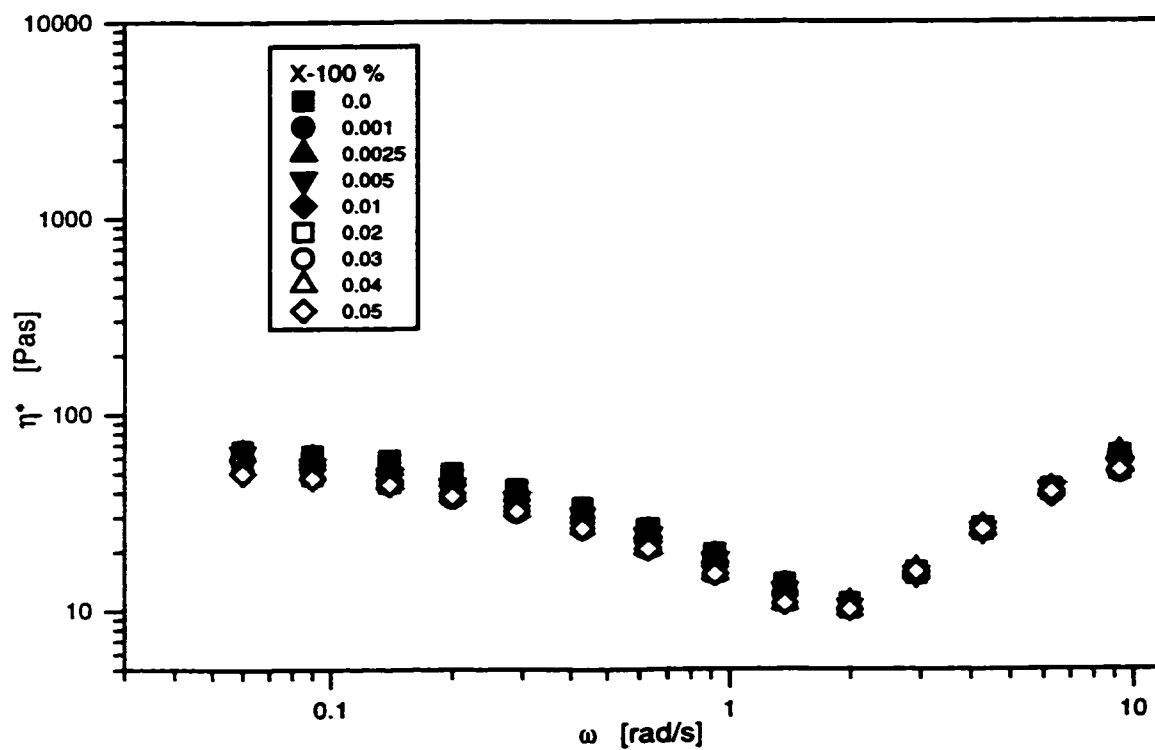


Figure 4.7.21 Effect of Surfactant on Complex Viscosity for 0.06% PAM

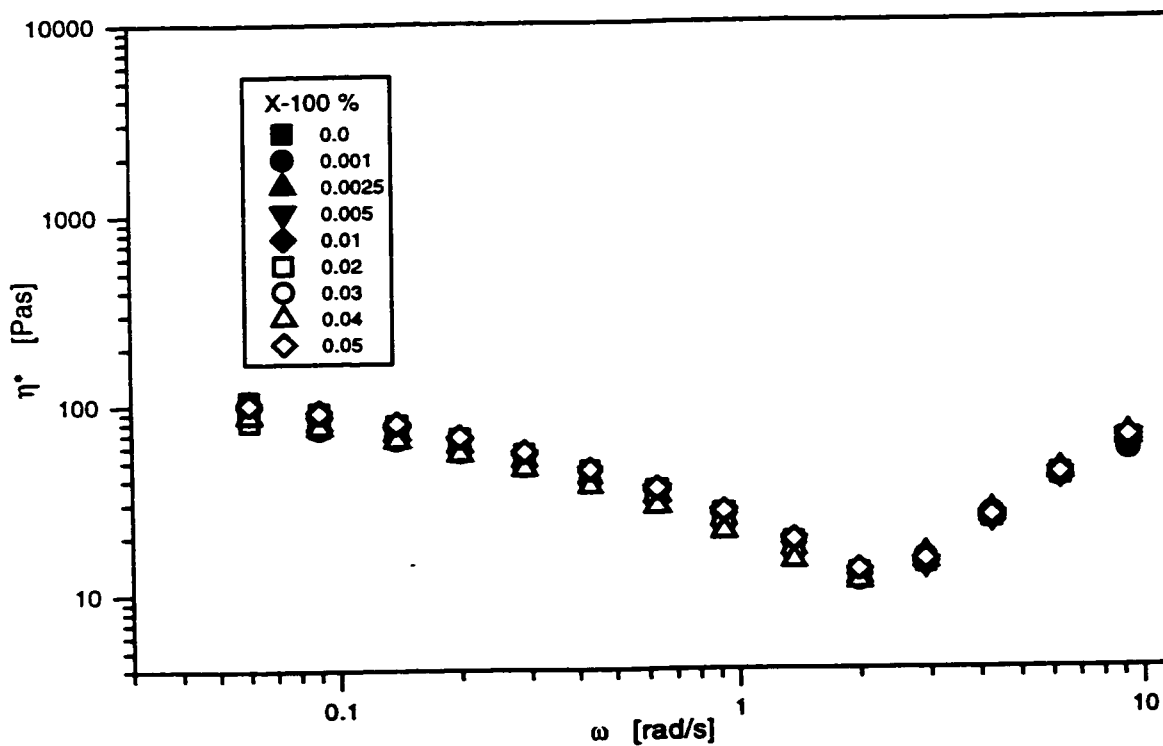


Figure 4.7.22 Effect of Surfactant on Complex Viscosity for 0.1% PAM

CHAPTER 5

DISCUSSION OF RESULTS

The rheological properties of a material in general are all interrelated. This interrelation refers to the nature of the molecules' interactions and their responses to the applied stresses. The response of the material depends on the condition of the test and the value of the applied force.

In the steady state flow test, an increase in viscosity as polymer concentration increases was observed. In this test, polyacrylamide solutions behave in different manners, either as a function of shear rate or concentration. Three different regions were seen, first Newtonian region (zero shear viscosity), shear thinning region, and shear thickening region. The first Newtonian region is related to the physical properties of the polymer and gives an indication of its molecular weight and molecular weight distribution. It is also an indication of the absence of the rigid yield stress, which will be discussed later on. The second region is the shear thinning region, which is the most common behavior in polymer solutions. It has practical importance and usually depends on whether the fluid is time dependent or not. Finally is the region above the critical shear rate. This region exhibit two different behaviors, almost a Newtonian region at concentrations of 0.04%, 0.06% and 0.08% and shear thickening at the other concentrations. The concentrations at which the response is nearly a second Newtonian region result from an almost complete breakdown of the material structure and any further stresses will not lead to significant changes in the molecular configuration. In the case of shear thickening concentration, buildup in

viscosity occurs. This buildup in viscosity has a critical effect on flow behavior of the solution, and has been subjected to many studies in case of partially hydrolyzed polyacrylamide. These studies have shown that the shear thickening effect is characterized by the occurrence of drastic pressure drops during flow in porous media^{13,37}, this excess pressure drop is mostly due to entrance effects. This response is very unfavorable if the polymer may be used in enhanced oil recovery as the porous of the rock is a combination of different sizes.

In the dynamic test, there was a decrease in complex viscosity as frequency increased and concentrations decreased up to critical value which depends on the concentration. Above this value, the viscosity is equal for all concentrations and its value increases with frequency. Comparing that with shear viscosity shows that even though at a certain range of frequency, the complex viscosity tends to follow nearly the same pattern of the shear viscosity, the Cox-Merz rule is invalid.

In the yield stress test, the result showed the lack of rigid yield stress. On the other hand, the dynamic yield stress has been observed and it increases with concentration. That is predictable, as the solutions behave like Newtonian fluids at the low shear rates in steady state test. The relation between the yield stress and the zero shear viscosity is a finite structural relaxation time, meaning that the network structure which is deformed by stress will always relax in a finite time to an undeformed state. In other words, the structure of this temporary network is of finite extent or the network is constantly forming, breaking and reforming by Brownian motion or both. Bubbles or particles dispersed in this kind

of solution will always rise or sediment. Coating this kind of fluid on a vertical wall will result in sagging. On the other hand, viscosity of a material that exhibits a rigid yield stress, their viscosity goes toward infinity at zero shear rate. That is the result of a three dimensional network. This network is permanent and under the applied stress, it will not flow until the yield stress is reached. If it exceeds the yield stress, the structure of the material breaks down instantaneously and completely and the material starts to flow as viscous fluid^{23,27}. Systems exhibiting this behavior may find application in coating, suspension, and drilling mud. Yield stress has no influence on the material flow at higher shear rates.

In the creep recovery test, the viscoelastic response was measured in non linear viscoelastic region. The results showed that at low concentration, there was no elastic response, while at higher concentration, the material exhibited a little elastic response. In general, the elastic response was quite low, agreeing well with the results obtained by dynamic test.

Thixotropy test is also used to investigate time dependence of the material. The results of this test have shown that polyacrylamide responded in different manners, exhibiting three different behaviors, thixotropy, antithixotropy, and time independent. That depended on shear rate, the test being used, and the concentration. Polyacrylamide in general gave weak time-dependent behavior, especially at higher concentration and higher shear rates.

As thixotropy and viscoelasticity both deal with a similar effect, the relative position of both approaches can be confused. Whereas thixotropy is related to viscosity, viscoelasticity is related to elasticity. The complication arises because

in non linear viscoelasticity, the microstructure of material changes in response to the imposed stress, but does so reversibly. Similar behavior appears in thixotropy. The mechanism of viscoelasticity arises from the fact that some materials can store part of the mechanical energy and as a result, there is some delay in their response. In the thixotropy mechanism, there is a complete dissipation of the mechanical energy, and the memory for recovery results from a delayed adjustment of the internal structure of the fluid to actual shearing condition.

The relatively low viscoelasticity and thixotropy give the solution the advantage of flowing easily either in pipe line or porous media; however, they exclude them from the use in applications such as coating and drilling mud.

In the transient flow behavior test, polyacrylamide gave stable behavior for shear rates less than 500 s^{-1} and time beyond 15 s. For time less than 15 s, the solutions were accompanied by either a decrease or increase in shear stress response, depending on both concentration and shear rates. For shear rate higher than 500 s^{-1} , the shear stress response fluctuated, this fluctuation being higher at higher concentrations.

The surfactant had a complex effect under some conditions and not under others, and the change in cmc was random.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions.

1. All tested samples showed a sharp decrease in the surface tension with increasing surfactant up to the critical concentration, above which surfactant had no effect on the surface tension of the solutions.
2. Polyacrylamide solutions showed three different behaviors, a first Newtonian region, region of dramatic shear thinning, and finally a shear thickening region.
3. The intensity of the shear thickening region is found to be lower at concentration of 0.06% and 0.08% and almost a second Newtonian region at 0.04% .
4. Surfactant led to decrease in viscosity for concentrations of 0.02%, 0.04%, and 0.1% PAM, but no effect on other concentrations.
5. All tested solutions exhibit no rigid yield stress; however, dynamic yield stress had been observed for concentrations higher than 0.06% PAM.
6. Polyacrylamide solutions behaved like pure viscous material at low concentrations and viscoelastic material at high concentrations, and the viscous part is always higher than the elastic part.
7. Surfactant had no effect on the viscoelastic response; however, it led to increase in the compliance values.

8. Thixotropy test showed three different behaviors, thixotropic, antithixotropy, and time independent, depending on the polyacrylamide concentration, shear rate, and the test being used.
9. Transient test showed that the time evaluation of shear stress depends on both shear rate and polyacrylamide concentration, and for shear rate less than 500 s^{-1} and time higher than 15 s, shear stress response revealed a time dependent behavior for all tested solutions.
10. The surfactant has no effect on shear stress response at low shear rate, decrease at shear rates 50 s^{-1} and 100 s^{-1} , and fluctuation at shear rate 500 s^{-1} .
11. Dynamic test showed that the value of storage and loss modulus increased with increasing the polyacrylamide concentration and frequency, with the loss module was more predominant and there was a frequency value at concentrations of 0.08% and 0.1% PAM, where the viscous and elastic parts are almost equal.
12. The range of frequency for elastic behavior increases with concentration; however, at higher frequency, all tested solutions behaved like pure viscous material.
13. The effect of surfactant on loss and storage modulus was generally low however it led to a noticeable decrease in storage modulus at 0.02% PAM.
14. Complex viscosity decreases as frequency increases and concentration decreases up to critical frequency value, above which the complex viscosity is equal for all solutions and increases with increasing the frequency.

15. Below the critical frequency the surfactant decreases the complex viscosity, this effect decreasing with increasing the polyacrylamide concentration to reach no effect at concentrations of 0.08% and 0.1% PAM; however, above the critical frequency, surfactant has no effect on the tested solutions except, for 0.02% PAM which was accompanied by a decrease in complex viscosity.

6.2 Recommendations.

1. Polyacrylamide at concentrations of 0.04%, 0.06%, 0.08% can be used as viscofied agent in polymer flooding in enhanced oil recovery.
2. If the polymer might come in contact with nonionic surfactant(X-100), concentrations of 0.06% and 0.08% must be used.
3. further study can be done to investigate the behavior of the solutions at shear rate higher than 700 s^{-1} .
4. To study the behavior of the molecules at the critical shear rate, microscopic study is required.

REFERENCES

- 1- Van Poolen, H. K. and Associates, Inc. *Fundamentals of enhanced oil recovery*. Tulsa, Oklahoma. 1981
- 2- Kirk-Othmer. *Encyclopedia of Chemical Technology*, vol.1, John Wiley and Song Inc., New York. 1991
- 3- Myers, D. *Surfactant Science and Technology*. VCH, New York. 1988
- 4- Bird, R. and Armstrong, R. *Dynamics of polymeric liquids 1*. John Wiley and Song Inc., New York. 1987
- 5- Bewersdorff, H. W. *Rheol. Acta*, 21, 587. 1982.
- 6- Durst, F., Haas, R. and Interthal, W. *Rheol. Acta*, 21, 572. 1982
- 7- Tie-Qiang, L. and McCathy, K. L. *J. Non-Newtonian Fluid Mech.*, 57, 155. 1995
- 8- Flew, S. and Sellin, R. H. *J. Non-Newtonian Fluid Mech.*, 47,169 .1993
- 9- Nasr-El-Din, H. A. and Taylor, K. C. *Colloid and Surfaces A: Physicochemical and Engineering Aspects*, 75, 169. 1992
- 10- Lakatos, I. and Lakatos-Szabo', *J. Colloid Polym. Sci.*, 274, 959. 1996
- 11- Brandna, P. Quadrat, O. and Dupuis, D. *Colloid Polym. Sci.*, 273, 421. 1995
- 12- Ait-Kadi, A. Comeau, P. J. and Chauveteau, G. *Journal of Rheology*, 31(7),537. 1987
- 13- Durst, F. Hass, R. and Kaczmar, B. U. *J. Applied Polym. Sci.*, 26, 3125-3149. 1981
- 14- Shin, S. and Cho, Y. I. *Int. Comm. Heat Mass Transfer*, 20, 831. 1993
- 15- Esmail, M. N. and Ghannam, M. T. *J. Appl. Polym. Sci.*,69,1587-1597. 1998

- 16- Casey, J. P. *Pulp and Paper: Chemistry and chemical technology*. Intersence Publisher, New York. 1960
- 17- Biggs, S., Selb, J. and Candua, F. *Langmuir*. 8, 833. 1992
- 18- Wang, L. Tiu, C. and Liu, T. J. *Colloid Polym. Sci.* 274, 138. 1996
- 19- Zhang, J. Y., Wang, X. P., Liu, H. Y., Tang, J. A. and Jiang, L. *Colloid and surfaces, A: Physicochemical and Engineering Aspects*. 132, 9 .1998
- 20- Schramm, K. *A practical Approach to Rheology and Rheometry*. Gebrueder Haake GmbH, Karlsruhe , Germany. 1994
- 21- Whorlow, R. W. *Rheological Techniques*. Ellis Horwood Limited, West Sussex, England. 1992
- 22- Nielsen, L. E. *Polymer rheology*. Marcel Dekker, New York. 1977
- 23- Ferguson, J. and Kemblowski, Z. *Applied Fluid Rheology*. Elsevier Applied Science, New York. 1991
- 24- Dupuis, D., Lewandowski, F. Y., Steiert, P. and Wolff, C. J. *Non-Newtonian Fluid Mech.* 54, 11. 1994
- 25- Brandna, P., Quadrat, O. and Dupuis, D. *Colloid Polym. Sci.* 273, 642. 1995
- 26- Hu, Y., Wang, S. Q. and Jamieson, A. M. *Macromolecules*. 28, 1847. 1995
- 27- Kornum, L. O. *Rheol. Acta*. 18, 178. 1979
- 28- Collyer, A. A. and Utracki, L. A. *Polymer Rheology and Processing*, Elsevier Science Publishers LTD, Essex, England. 1990
- 29- Padolewski, J. P., Collins, E. A. and Chen, C.H. *J. Rheol.* 36 (1), 117. 1992
- 30- Lodge, A. S., Renardy, M. and Nohel, J. A. *Viscoelasticity and Rheology*, Academic Press Inc., London. 1984

- 31- Stokes, R. J. and . Evans, D. F. *Fundamental of interfacial Engineering*.
Wiley-VCH, Inc., New York. 1997
- 32- Mewis, J. *J. Non-Newtonian Fluid Mech.* 6,1-20. 1979
- 33- Barnes, H. A. *J. Non-Newtonian Fluid Mech.* 70, 1-33. 1997
- 34- Esmail, M. N. and Ghannam, M. T. *J. Appl. Polym. Sci.* 64,289-301. 1997
- 35- Esmail, M. N. and Ghannam, M. T. *Ind. Eng. Chem. Res.* 37,1335-1340.
1998
- 36- Cox, W. P. and Merz, E. H. *J. Polym. Sci.* Vol. XXVIII, 619. 1958
- 37- Hass, R. and Durst, F. *Rheol. Acta.* 21,566. 1982