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# The Rheological Properties of Aqueous Polyacrylamide Solutions

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In

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# ABSTRACT

The Rheological Properties of Aqueous Polyacrylamide Solutions

Ali Kreiba

Polyacrylamide solutions are extensively used as chemical additives or processing aids in the manufacturing of paper and paperboard products. In addition, they have been widely used in enhanced oil recovery. In this thesis, an experimental work has been carried out to provide a complete and comprehensive study of the rheological properties of polyacrylamide solutions using cone-and-plate rheometery. Polyacrylamide concentrations in the tested solutions ranged by weight from 2 to 5%. The scope of the study includes the measurements of steady-state behavior, transient shear stress and yield stress response, thixotropic, creep recovery, and dynamic responses for each concentration.

The findings resulted in several conclusions regarding the rheological properties of polyacrylamide solutions. They have shown a strong shear-thinning behavior for all concentrations. The dynamic viscosity showed two different behaviors—shear-thinning region and shear-thickening region. Significant transient behavior has been observed for all concentrations of polyacrylamide solutions. The yield stress of PAM solutions increased with increasing concentrations. Three different behaviors of thixotropy test have been observed—thixotropy, antithixotropy, and time dependent. Finally, the viscous part of PAM solutions was always higher than the elastic part.

# ACKNOWLEDGMENTS

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

I also would like to thank my parents for their unconditional support regarding my studies. Their confidence in my ability to pursue my goal has provided immense inspiration.

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# CHAPTER 1

# INTRODUCTION

## 1-1: General introduction of Polyacrylamide:

Polyacrylamide is a brittle, white, odorless polymer, which can be manufactured by free radical polymerization of acrylamide monomer. It is versatile and synthetic, and is therefore, used worldwide to improve commercial products and processes. Furthermore, polyacrylamide is relatively immune to bacterial attack. It is water soluble at all concentrations, temperatures, and pH values. Polyacrylamide molecules are both very flexible and long with a relatively small diameter thereby making them susceptible to shear degradation or mechanical breakage[1]. The average molecular weight of commercial polyacrylamide ranges approximately from $2 * 10^3$ to high $15 * 10^6$. Polyacrylamides with molecular weights greater than $2 * 10^7$ are not unlikely. However, these large molecules greatly influence the products activity as a flocculant and rheology control agent[2].

## 1-2 Physical Properties:

**Dry polymer:** Solid polyacrylamide is hygroscopic, and the rate of moisture absorption increases with the increasing ionic character of the derivative. Dry polyacrylamide is available in several forms and particle size distributions depending on the type of polymerization, drying, and grinding processes employed. Polyacrylamide can be converted from a dry sheet to a powder by grinding, but only a small fraction of very small particles is desirable. These small particles can go into the solution and generate viscosity much too fast to get a good dispersion of the remaining polymer.

**Aqueous Solution:** Since most of the uses of polyacrylamide involve aqueous systems, the physical properties of aqueous solutions are important.

*Viscosity:* The viscosity of polyacrylamide in water increases dramatically with molecular weight while it decreases with increasing temperature. Higher molecular weight polymers exhibit a greater apparent viscosity than their low molecular weight polymers under similar conditions.

*Shear sensitivity:* At relatively low shear rates, aqueous solutions of polyacrylamide are pseudoplastic. However, at high shear rates rupturing the polymer chains can degrade the molecular weight.

*Solution Stability:* The stability of the polymer can be improved by the addition of sodium thiocyanate, thiourea, sodium nitrite, or nonsolvents. Adding of ferrous salts along with a ferric chelating agent can accelerate the degradation of aqueous solutions of polyacrylamide.

### 1-3 Chemical Properties:

Polyacrylamide has commercial value partly due to its ability to undergo chemical reactions. Reactions in the amide groups of polyacrylamides are often more complicated than reactions of simple amides. Postreactions of high molecular weight polyacrylamide can be difficult because of its high viscosity in even fairly dilute aqueous polyacrylamide solutions.

*Hydrolysis:* Polyacrylamide hydrolyzes rapidly under alkaline conditions at relatively low temperatures. However, higher temperatures are required to hydrolyze polyacrylamide under acidic conditions. The hydrolysis can take place in the solid polymer since polyacrylamide powders contain from 5 to 15 wt % moisture[2].

### 1-4 Uses:

Polyacrylamide is one of the most widely used polymers. It is used as a liquid-solid separator where the polymer is a flocculant. In this sense, it aids in the processing of minerals in mining, waste treatment, and water treatment for municipalities or industry. Polyacrylamides are extensively used as chemical additives or processing aids in the manufacturing of paper and paperboard products. The low molecular weight polymer acts as a binder to improve the various strength properties of paper; it reacts with glyoxal and paper to maintain paper's strength when wet. One of the important applications of polyacrylamide is in enhanced oil recovery.

Polyacrylamide is pumped into an oil well and the high viscosity solution pushes the oil from the rock formation—or reservoir—to another well where the oil can be recovered[2].

### 1-5 The scope of this study:

Knowledge of the rheological properties of the PAM solutions is important for the design, selection, and operation involved in handling, mixing, pumping, storage, and transportation processes. In this study, the rheological measurements in terms of steady-state behavior, transient shear stress response, yield stress, creep and recovery, thixotropy, and dynamic response are reported for aqueous polyacrylamide solutions with concentration ranging from 2% to 5%.

# CHAPTER 2

# LITERATURE SURVEY

A number of rheological studies on polyacrylamide have been carried out under different conditions. These studies have shown, along with earlier studies, that PAM solutions possess complex behavior that can restrain industrial uses. In the pulp and paper industry, polyacrylamide has been used to maintain the efficiency of operation and quality of products. It is effective in increasing fiber bonding and in improving dry strength, filler retention, rosin sizing, and drainage rate[3]. It has been used in many additional applications including water treatment, mineral processing, dust control, and sugar manufacturing. Polyacrylamide is one of the best polymers used as a drag reduction agent and a vortex inhibitor due to its flexibility and long chain. The drag reduction is defined by the reduction in pressure drop in the polymer solution relative to the pure solvent alone at the same flow rate[3]. F. Dust et al. and H. W. Bewersdorff[4,5], who reported that polyacrylamide could be used as a drag reduction polymer, have confirmed this point. A. AIT- Kadi et al.[6] have carried out an experimental study to investigate the rheological properties of partially hydrolyzed polyacrylamide solutions and reported that the salt had a stabilizing effect on the viscosity. This effect is characterized by lower viscosity levels and less shear thinning behavior as salt concentration is increased. Tie-Qiang Li. et al.[7] have studied the pipe flow of aqueous polyacrylamide solutions by means of nuclear magnetic resonance imaging. They found that, at a low bulk flow rate, steady laminar flow characterizes aqueous polyacrylamide solutions. As the bulk flow rate increases, unsteady motion appears and the mean velocity profile becomes more blunted. For fully turbulent flow, the 200 wt PPM polyacrylamide solution shows an atypical velocity profile for drag reduction fluids.

Polyacrylamide has been used in enhanced oil recovery processes. Oil still remaining in the earth after a water flood can be recovered from the reservoir by improving the sweep efficiency and/or reducing the interfacial tension between flood-oil. One effective technique to discharge oil at this stage is polymer flooding. Two major types of polymers currently employed in polymer flooding are the synthetically polysaccharides. I. Lakatos et al.[8] have studied the effect of carbon dioxide (CO2) on the rheological properties and structure of polyacrylamide solutions with the aim of using them in enhanced oil recovery. They concluded that high molecular weight unhydrolyzed or slightly (5-10%) hydrolyzed polyacrylamides must be used in order for the polymer to contact with CO2. Hisham A. et al.[9] have studied the interfacial behavior of crude oil/alkali systems in the presence of partially hydrolyzed polycrylamide and reported that, at sodium carbonate concentrations less than 0.2 mass %, the interfacial tension did not change with respect to time. Increasing polymer concentration caused a slight drop in interfacial tension. Using sodium carbonate 0.2 mass %, the addition of polymer up to 2000 PPM had no effects on the interfacial tension. At sodium carbonate concentrations greater than 0.2 mass %, adding of polymer resulted in the lowering of the interfacial tension. Sehyun. S.et al.[10] have studied temperature effect on the non-Newtonian viscosity of an aqueous polyacrylamide solution. They reported that the viscosity of the PAM solution was very sensitive to temperature at low shear rates. However, it was almost independent of temperature at high shear rates. Similarly, the time constant, the fluid behavior index, and the fluid consistency index were found to vary with temperature. M. Nabil Esmail et al.[11] have reported that the viscosity of polyacrylamide solutions significantly decrease with temperature. The temperature effect is more pronounced at high shear rates. The flow behavior index "n" is found to be constant for all the PAM concentrations and temperatures. However, the fluid consistency index "k" was found to be a function of temperature and PAM concentrations. S. Flew et al.[12] studied the non-Newtonian flow of polyacrylamide solutions in porous media and reported that polyacrylamide can be used as viscosifying agents in oil field injection, and even very high molecular weight polyacrylamides could find application in the fracture treatment of oil wells. F. Durst et al.[13] have studied the flow of dilute hydrolyzed polyacrylamide solutions in porous media under various solvent conditions and they found that the maximum increase in pressure drop is mainly dependent on the molecular weight of the polymer. Furthermore, the addition of salt ions to solutions of partially hydrolyzed polyacrylamide yields onset behavior previously observed for nonionic polymers. D. Dupuis et al.[14] demonstrated the rheological properties of solutions of high molecular weight partially hydrolyzed polyacrylamide in mixtures of glycerol and water. They concluded that its viscosity depends on time and displays a transient regime with strong instabilities followed by a steady state. The non-Newtonian viscosity of these solutions was affected by time and showed slight shear thickening. P.Bradna et al.[15] researched the influence of glycerol content and the degree of ionization on the negative thixotropy of solutions of partially hydrolyzed polyacrylamide. They reported that the character of negative thixotropy of partially hydrolyzed polyacrylamide in aqueous glycerol strongly depends on polymer concentration, glycerol content, and shear rate applied. At low polymer and glycerol concentrations, shear stress and viscosity slowly increase during shearing to a limited value. However, a steep increase in shear stress, as well as normal stress, followed by their pronounced oscillations occur at higher concentrations of both components and at higher shear rates.

# CHAPTER 3

# EXPERIMENTAL WORK

Polyacrylamide (PAM) of molecular weight ($5 * 10^6$) was purchased from "BDH Limited, Poole, England" and employed in this study. The production number of the polyacrylamide (PAM) is 29788. The viscosity of 0.5 % aqueous solution is approximately 280-mPa s at $25^0$ C. The solutions were prepared by adding a known amount of polymer powder (PAM) to half a liter of distilled water at room temperature. The solutions have been left at rest for at least 15 days to achieve complete dissolution without any stirring or external source of heat or power to initiate change in the polymer molecules network. This study investigates a weight concentration range of 2 - 5% PAM to cover the rheological behavior of PAM solutions.

The rheological measurements of this study were carried out using a Haake rheometer RheoStress RS100 which is a computer-controlled system. Rheometer RS100 is a searl-type measuring system combined with a cone- and-plate sensor system in which the sample is sheared between a flat plate and a broad cone whose apex contacts the plate. It has a controlled variable lift speed to position the cone tip on the plate. However, in practice, the tip of the cone is truncated and a small gap is maintained between the two surfaces. This is to prevent damage to either of the surfaces if they were to rub against each other. A schematic of the cone-and-plate geometry is shown in figure (3-1). The cone rotates at angular velocity "$w$". The angle ($\alpha$) between the cone and plate surfaces is less than $5^0$ (in this case $\alpha = 4^0$). Larger angles are not used because results for non-Newtonian fluids would be complex. Additional reasons for using small angles include the following; the shear rate and shear stress are uniform, the sample can be retained in the gap more easily, the temperature rise is minimized, and a small sample is sufficient. For any point within the gap from the cone tip to the outer (Rc), the constant ($\gamma$) can be assumed. It is also necessary to truncate the tip of the cone by grounding it off up to the truncation radius (Rt) to avoid wear in cone tip and plate. To prepare the sensor system for a test, the plate is initially moved upwards until it makes contact with the cone. As a result, the axial height of the cone is reduced by value (a). The plate is then moved downwards. When the test is starting, the cone's impinging tip touches the plate as is required for the cone and plate test.

An error occurs when measuring the shear stress or the torque because of the removal of the tip of the cone. The degree of this error is affected by the ratio of the cone surface area to the truncation area. Using parameters taken from measurements by the cone-and-plate sensor systems, the shear rate $\gamma$, shear stress $\tau$, and viscosity $\eta$ can be calculated as follows[16]:

- ***Shear rate ($\gamma$):***

$$\gamma = M.w$$

$$= \frac{1}{\tan\alpha}.w$$

$$= \frac{1}{\alpha}.\frac{2\pi}{60}n$$

$$= \frac{\pi.n}{30.\alpha}$$

Where: $w$ = Angular velocity [rad/sec].

$n$ = Rotor speed [min$^{-1}$].

$\alpha$ = Cone angle [rad].

$M$ = Shear rate factor.

- ***Shear stress ($\tau$):***

$$\tau = \left(\frac{3}{2\pi.Rc^3}\right).T$$

$$= A.T$$

Where: $\tau$ = Shear stress on the cone [Pa].

$Rc$ = Outer radius of the cone [m].

$T$ = Torque to be measured [N.m].

$A$ = Shear stress factor.

- ***Viscosity ($\eta$):***

$$\eta = \frac{T}{w} . \frac{A}{M}$$

Where: $\eta$ = Viscosity of the sample [Pa.s].

$T$ = Torque to be measured [N.m].

$w$ = Angular velocity [rad/sec].

$A$ = Shear stress factor.

$M$ = Shear rate factor.

Rheometer RS100 has several operating test modes. It has a controlled rate (CR) mode, a controlled stress (CS) mode, and an oscillation (OSC) mode.

In the controlled rate mode, a motor drives the cone. Its speed is at a controlled constant or programmed rotor speed while the plate is held at rest. The sample is sheared between the plate and the cone. The resistance of the sample being sheared between the stationary and rotating plate results in a viscosity related to the torque working on the cone which counteracts the torque provided by the drive motor. A torque detector (usually a spring that twists as a result of the torque applied) is placed between the rotor and motor. The twist angle of the torque spring is a direct measure of the viscosity of the sample.

In the controlled stress mode, a special motor, for which defined torque values may be preset, drives the cone. The electrical power input results in linearly related torque values on the motor shaft. The drive shift is centered by an air bearing that ensures an almost friction free transmission of the applied stress to the test sample. The resistance of the sample against the applied torque or shear stress will allow the rotor to rotate only at a speed and shear rate that inversely correlates to the viscosity of this sample. Torque input and resulting motor speed act on the same rotor shaft axis and, therefore, torque data can be mathematically transformed to shear stress and the rotor speed to shear rate.

In the oscillation mode, the cone is no longer turning continuously in one direction, but it is made to deflect with a sinusoidal time function alternatively for a small angle to both the left and right. The oscillation mode relates the assigned angular velocity or frequency to the resulting oscillating stress or strain. The sample placed into the shearing gap is forced to strain in a similar sinusoidal function causing resistance stresses in the sample[16]. Stress and frequency sweeps can be applied in the oscillation mode.

There are advantages of using this system to study the rheologcial properties of PAM solutions. First, only a small volume of sample is needed. Second, the mass and inertia of the plate held by the torsion bar are low. Third, both normal stress and oscillatory measurements are easily made. Fourth, the technique can be used for a wide range of fluids. Fifth, according to the uniform shear rate and shear stress, it is easy to observe if the fluid is behaving strangely. Finally, it is also very easy to clean at the end of the test[17].

While there are many advantages, there are only few disadvantages. The maximum shear rate is rather limited. A high viscosity sample will break down in laminar shear rate below $10S^{-1}$. At high shear rates, centrifugal effects can cause negative normal stresses to appear[17]. When this system is used, particles must be squeezed out from the tip region to allow for cone contact. The cone diameter, the cone angle, and the gap at the cone tip are 35 mm, $4^0$ and 0.137 mm, respectively.

In order to study the rheological properties of PAM solutions, a wide range of tests were carried out. They were the following: (1) Steady-state flow test in order to investigate the flow behavior; (2) Transient test in order to investigate the time dependent response; (3) Yield stress test in order to find the yield point of the solution; (4) Creep recovery test in order to investigate the visco-elastic response of the sample; (5) Thixotropic test in order to determine whether the material behaves like a thixotropic fluid or rheopectic fluid and if it is time-dependent on viscosity; and finally, (6) Dynamic test to measure the storage and loss modules, as well as, the complex viscosity as a function of angular velocity.

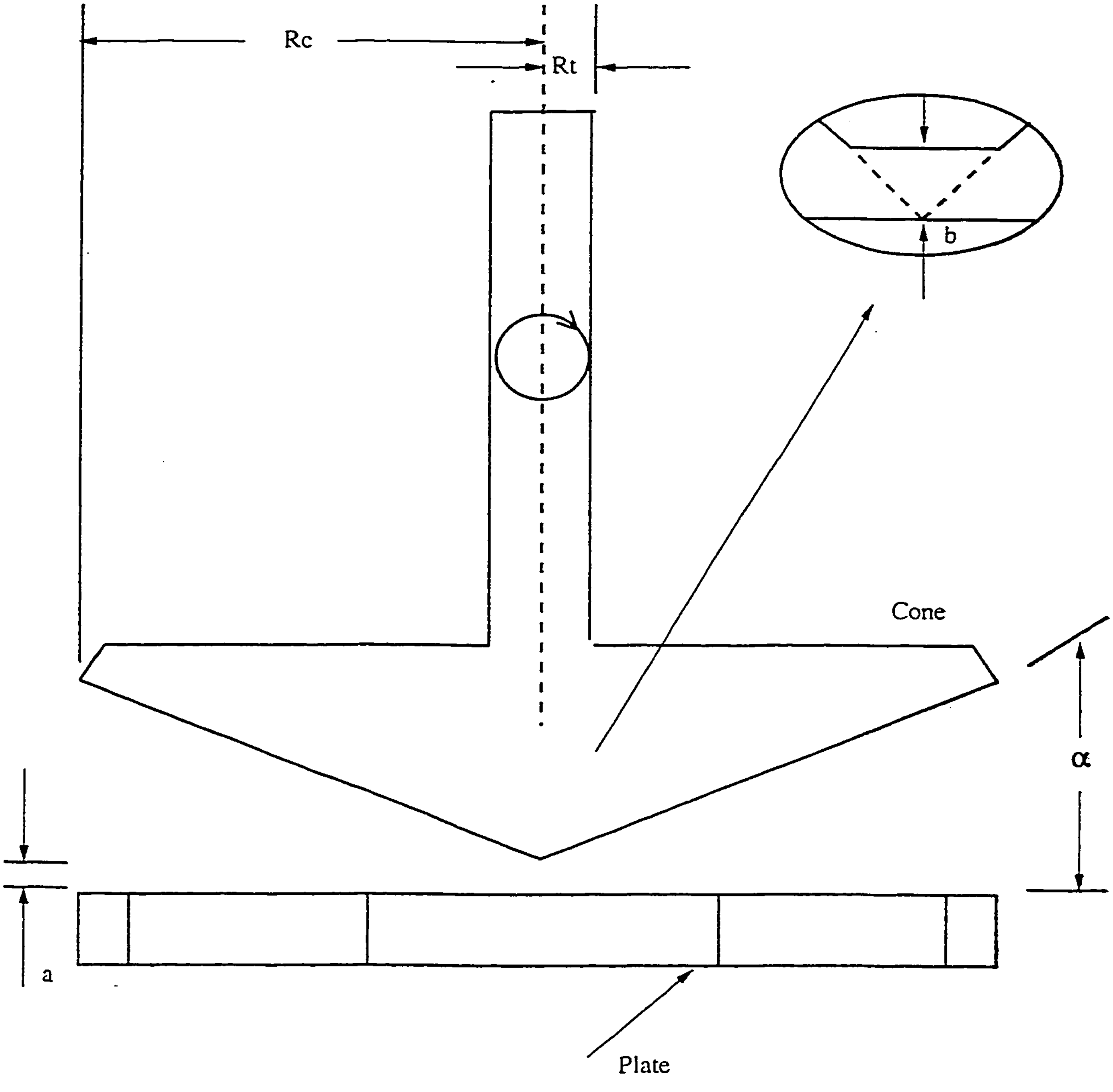


Figure 3.1 Schematic of the Cone and Plate System

# CHAPTER 4

# RESULTS

## 4.1 Steady-state flow test:

Viscosity is traditionally regarded as the most important material property of a liquid; therefore, any particular study requiring knowledge of material response would automatically turn to the viscosity in the first instance. The concept of viscosity was introduced through Newton's postulate in which the shear stress or shear rate was related to the viscosity. It is also necessary to know the viscosity of the material to solve any hydrodynamic problems related to the flow of the material; for instance, in calculating the flow rate and pressure drop in process equipment design, one can predict the conditions if it is used in practice. It also reflects the chemical and physical structure of the material. In addition, polymer viscosity plays a key role in almost all main commercial polymer processing or fabrication techniques. The most important characteristic of a thermoplastic is that its shear viscosity reduces with increasing shear rate; this is called shear thinning. The idea describes the decrease of the shear viscosity with increasing shear rate, which is due to the gradually progressive structural breakdown. In response, deformation of non-Newtonian systems has been developed since the first works in which this effect has been reported. The viscosity measurements are confined to be of a shear flow nature since the measurement of elongational viscosity is an extremely difficult task at actual low viscosities. In some specific application methods, strong elongational flow is involved. For example, in industrial roller coating the prevailing flow under the rollers will be approximately elongational. In hand rollers, the spatter is connected to elongational viscosity while strings of the coating are developing between the roller and the substrate, and are stretched to a point of breaking[18].

The steady state flow test has been conducted under controlled rate (CR) mode and, therefore, a certain shear rate is chosen. This shear rate, acting upon the sample, remains constant until a constant steady state stress is obtained. Since this represents only one data point, the selected shear rate is raised to obtain a new shear stress value. This process is repeated in order to arrive at flow and viscosity curves based on the given values of the initial and final shear rate. In this test, the initial shear rate is $0.15s^{-1}$ and the final shear rate is $700s^{-1}$. The data obtained describes the flow behavior of the sample by providing the viscosity curves, which present the behavior of the viscosity with increasing shear rate. The flow curve of the sample provides the correlation between the assigned shear rate and the resulting shear stress. The transformation of flow curves to viscosity curves was accomplished using computer software. Figure (4.1.1) shows the flow curves in terms of shear stress shear rate relationships for 2 - 5% PAM concentrations. These curves have been plotted over a log-log scale that includes four cycles of shear rate from 0.15 to 700$s^{-1}$. A consistent nearly linear pattern is recorded for all the PAM solution from 2 - 5%. Figure (4.1.2) shows the viscosity curves at different concentrations of PAM solutions. As the polymer concentration increases, the apparent viscosity of the solutions increases as well. This is due to the mass affect—as more polymer molecules are dissolved, the intermolecular entanglement rises. These entanglements translate to an increase in the solution's viscosity. The polymer solutions at various concentrations of PAM are non-Newtonian in nature and they exhibit strong shear thinning behavior. The majority of non-Newtonian materials are to be found in this category; this type of flow is typical for polymer solutions in which molecules are dissolved as statistical coils. This behavior (shear thinning) allows reduced pressure, and stretching at higher rates can be used to induce a preferred state of orientation in the direction of stretch in fiber spinning, thermoforming, or blow molding. The shear-thinning phenomenon is probably the most common rheological behavior for coating. Covering a sufficiently broad shear rate range, it will give a good picture of the influence of shear thinning at the different stages of the process.

In this phenomenon, the flow encounters less resistance at higher shear rate. It can be explained by the following: the polymer, at rest, has a long entangled and looping molecular chain, and maintains an irregular internal order, all the while it has a sizable internal resistance against the flow (higher value of viscosity). When the shear rate increases, the chains of the molecules can disentangle, stretch, and orient themselves parallel to the driving force which allows them to slip past each other more easily leading to the shear-thinning. Another reason for this phenomenon could be the progressive shearing away of solvated layers with increasing shear rate resulting in the decreasing interaction between the molecules (because of their smaller effective size) and consequent reduction in apparent viscosity. Linearity of the flow curve at very high shear rates might correspond to complete removal of the solvated layers[17].

The flow behavior of PAM solutions can be described by the flow curve, which is based on a measurement $\tau = f(\gamma)$ and is usually presented in the derived function $\eta = f(\gamma)$. The experimental measurements of the steady shear flow test were fitted by a nonlinear regression to Ostwald-de-Waele model (equation 4.1.2) rheologically, although the equation fits the data numerically. It is a common practice in industry to use the Ostwald-de-Waele model to describe the non-Newtonian flow properties of liquids in theoretical analysis as well as in practical engineering applications. Because of its simplicity, it has been used to solve analytically a wide variety of flow problems. However, care should be taken in the use of the model when employed outside the range of the data used to define it. The Ostwald-de-Waele model fails at high shear rates where the viscosity must ultimately approach a constant value; in other words, the local value of n must ultimately approach unity[19].

$\eta = k\,\gamma^{n-1}$ 4.1.1

Where "n" is the flow behavior index (dimensionless value).

"K" is the consistency index (Pa.s$^{n}$).

"$\eta$" is the apparent viscosity (Pa.s).

"$\gamma$" is the shear rate (s$^{-1}$).

According to equation (4.1.1), the viscosity decreases with increasing shear rate for n<1 (shear thinning).

$\tau = k * \gamma^{n}$ (the computer prints): $y = a * x^{b}$ 4.1.2

Where:

K= consistency as a viscosity related constant,

n(b)= exponent (flow index)

Table 4.1.1: Parameters for PAM Solutions

| PAM% | 2% | 3% | 4% | 5% |
|---|---|---|---|---|
| K | 16 | 66 | $1.1*10^2$ | $2.6*10^2$ |
| n | 0.27 | 0.18 | 0.14 | 0.11 |

Table 4.1.2: Parameters for PAM Solutions

| PAM% | 2% | 3% | 4% | 5% |
|---|---|---|---|---|
| a | 16 | 66 | $1.1*10^2$ | $2.6*10^2$ |
| b | -0.73 | -0.82 | -0.86 | -0.89 |

Tables 4.1.1 and 4.1.2 show that the Ostwald-de-Waele model is a suitable fit for the experimental data for all the polyacrylamide concentrations. Increasing the polyacrylamide concentration from 2 to 5% leads to a sharp drop in the flow behavior index from 0.27 to 0.11. This corresponds to a strong shear thinning behavior for the concentrations at

higher range. The consistency index “K” goes through a continuous increases as the polyacrylamide concentration increases. The parameter “a” is found to be equal to the consistency index “K”, and the parameter “b” decreases as the polyacrylamide concentration increases.

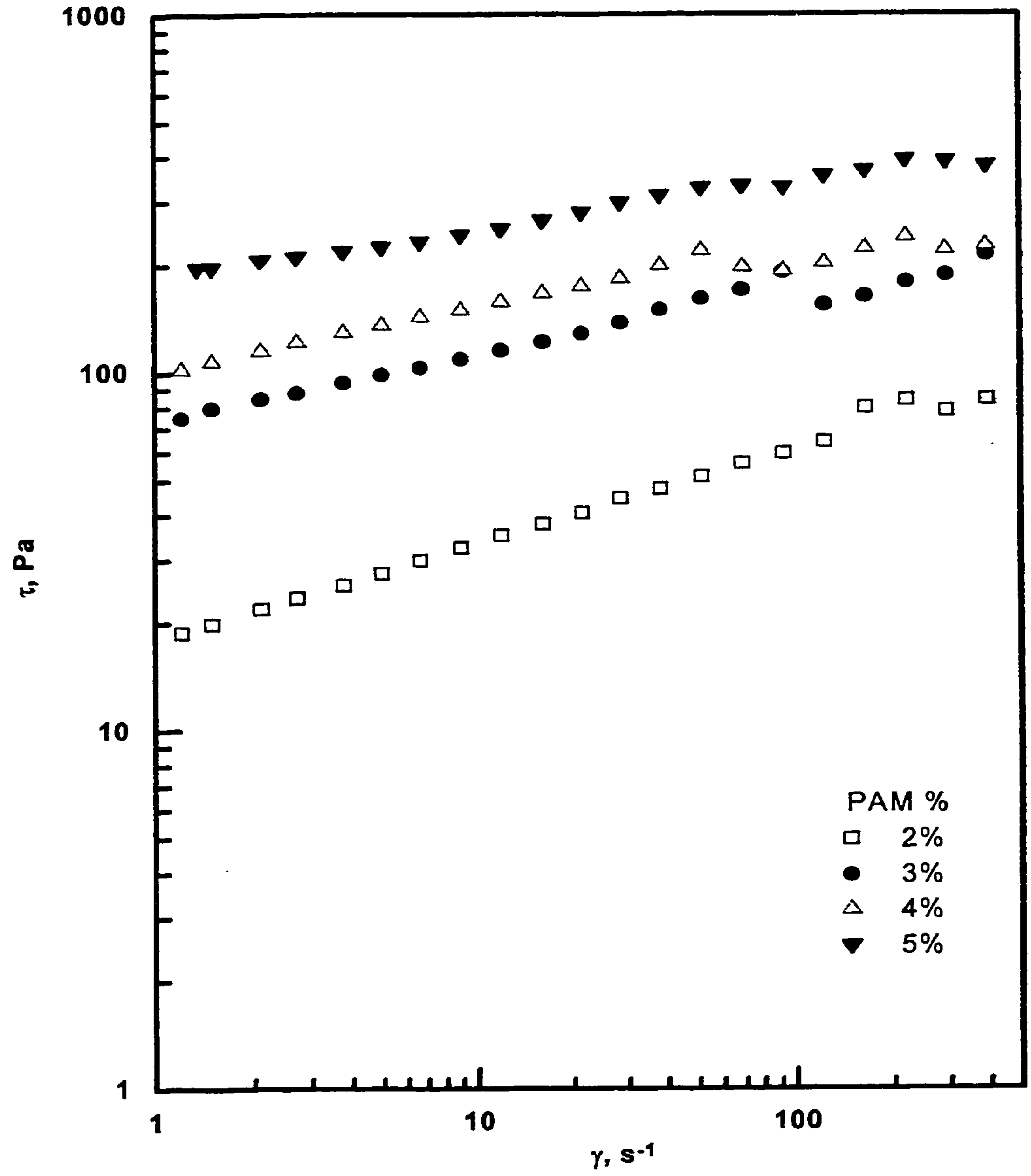


Figure 4.1.1 Flow Behavior Curves of PAM Solutions.

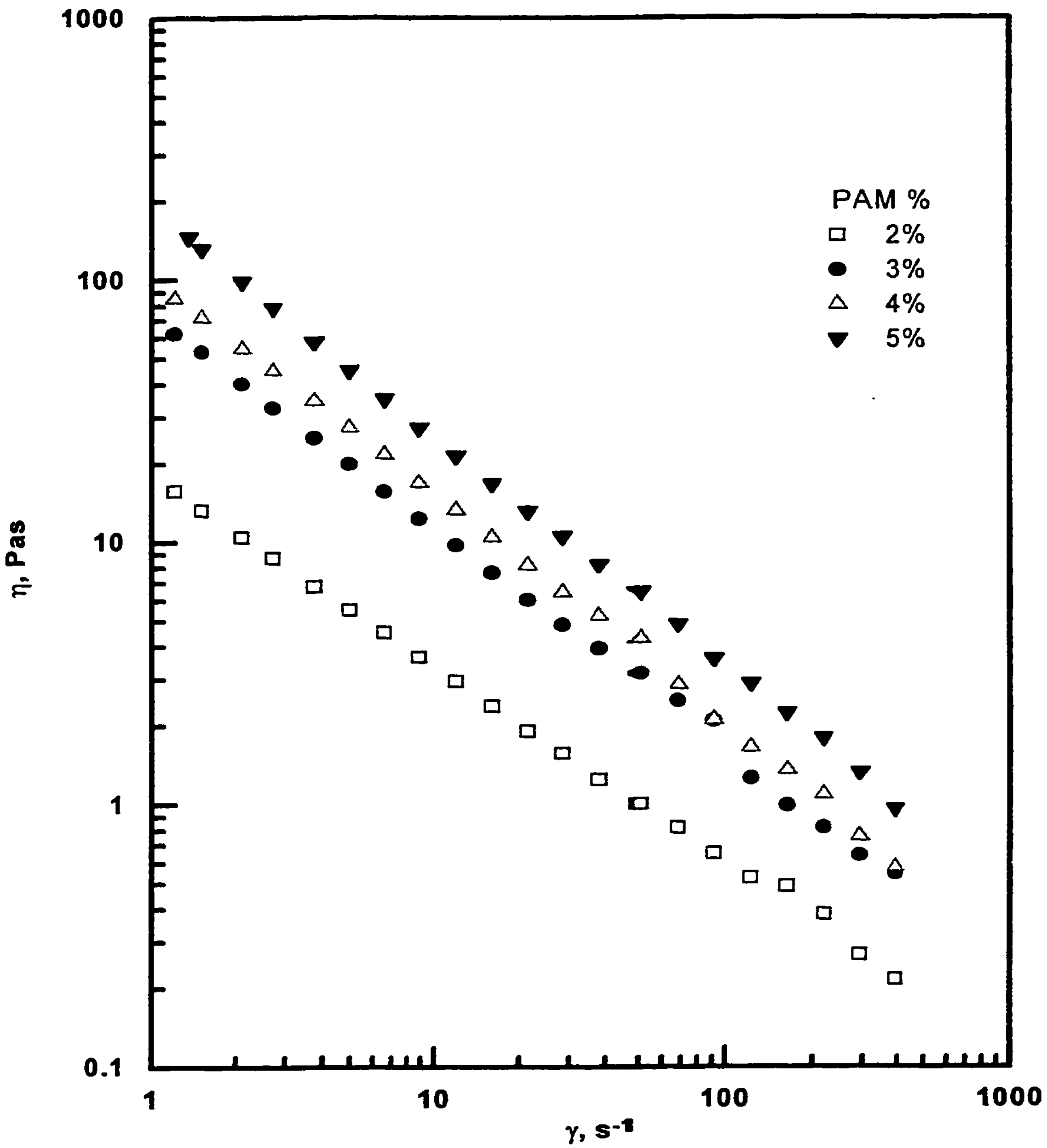


Figure 4.1.2 Viscosity Curves of PAM Solutions.

## 4.2: Transient Shear Stress Response:

It is important to study the transient shear behavior for rheologically complex materials. This test is characteristic of the time effect, which leads to a relationship between shear rate and shear stress. It is also verifies any existence of structure build up behavior at different ranges of shear rates. The shear stress response of polyacrylamide was measured as a function of shear rate and time in order to examine the transient behavior of PAM solutions.

In an effort to reveal the transient characteristics of polyacrylamide, transient tests were conducted for the concentrations 2 to 5%. The tests were carried out for 300 s for each of the following applied constant shear rates, 10, 50, 100 and $500 s^{-1}$. Figures (4.2.1,4.2.2,4.2.3, and 4.2.4) show the effect of different shear rates on shear stress for polyacrylamide solutions. Figure (4.2.1), at shear rate $10 s^{-1}$, demonstrates that the response stress increased rapidly within the first 3 seconds which represents the overshoot phenomenon. This phenomenon is typical of a semidilute polymer solution. The stress overshoot arises in non-associative polymer solutions because the polymer chains initially respond affinely to the start-up shear; however, the imposed strain on the chains, as well as the stress produced by the chain retraction force, grows with time. Beyond the characteristic relaxation time of the solution, the chains contract to a configuration and the shear stress decreases, resulting in a retraction force. For a semidilute solution such as PAM, the overshoot may arise from breakup of interchain associations while the individual PAM chains remain essentially undeformed[20]. From 3 to 5 seconds, the thixotropic behavior (i.e. decreasing shear stress or viscosity with time at a fixed shear rate) was observed after which there was a steady-state response. Although a thixotropic behavior was observed for the shear rates 50, 100s$^{-1}$, there was a significant scatter in the shear stress-time date at 500s$^{-1}$, followed by steady-state behavior. At shear rate 10s$^{-1}$, a steady-state response was observed since start-up time. Figure (4.2.2), at shear rate 10s$^{-1}$, illustrates a slight increase in shear stress at time less than 50s (overshoot phenomenon) followed by a steady-state response at shear rate 50s$^{-1}$. In addition, a thixotropic behavior was observed within 10s followed by a slight increase in shear stress from 10 to 50s. After 50s, the sample started to lead off steady-state response. At shear rate 100s$^{-1}$, a thixotropic behavior again was observed within the first 10s. Next, the sample started to exhibit a little scatter in the shear stress-time. At shear rate 500s$^{-1}$, the sample exhibited fluctuation in the time evaluation of shear stress; those fluctuations are more stable after 200s. Figure (4.2.3), demonstrates that, at low shear rate 10s$^{-1}$, an almost steady-state response was observed. The trixotropic behavior was observed within the 10s at shear rate 50s$^{-1}$. Following this behavior, the sample levels off to steady-state value. A steady-state response, with a little scatter, was exhibited at shear rate 100s$^{-1}$. At shear rate 500s$^{-1}$, a slight fluctuation was observed within 100s, and then the sample almost lead off to steady-state response. Figure (4.2.4), shows that from the start-up time, the sample demonstrated an almost steady-state response at shear rate $10s^{-1}$. The thixotropic behavior was observed within the first 10s at shear rate $50s^{-1}$, and then the sample lead off to a steady-state behavior. At shear rate $100s^{-1}$, a slight fluctuation was observed within 175s, and then a steady-state response. However, the sample exhibited high fluctuations within 175s at shear rate 500 $s^{-1}$, followed by an almost steady state response for the rest of the time.

Therefore, the transient test results indicate that time evaluation shear stress is dependent on both shear rate and polyacrylamide concentration. The overshooting phenomenon is often observed for viscoelastic and thixotropic fluids. The observation of such complex transient flow behavior is mainly attributed to the fact that pre-shearing at a higher shear rate may break some structures. The increase in the shear stress is due to the recovery and reformation of the molecule network structures. Thixotropic behavior (i.e. decreasing shear stress with time) is believed to be due to a limited structure breakdown.

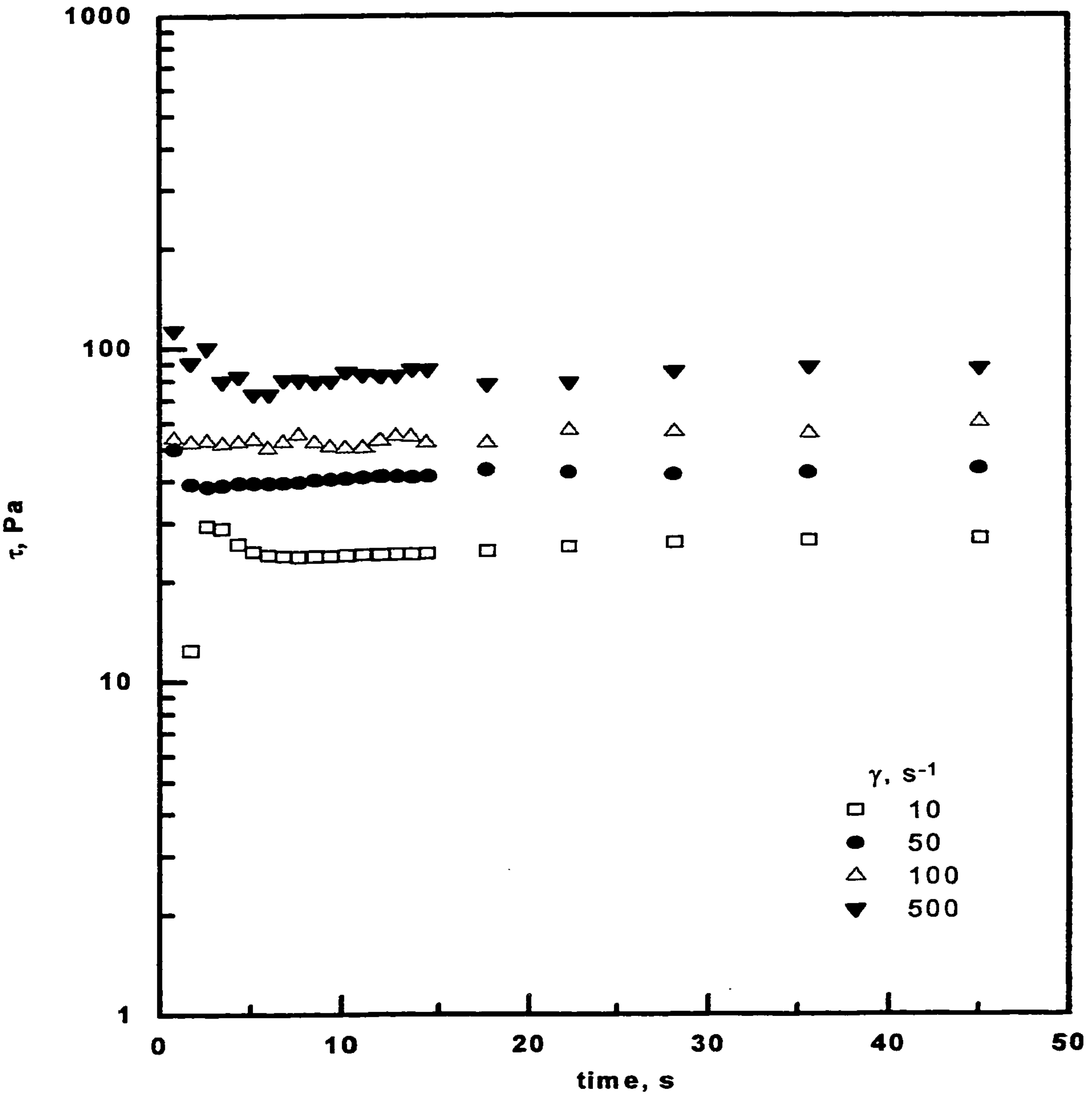


Figure 4.2.1 Transient Shear Stress Response, 2% PAM

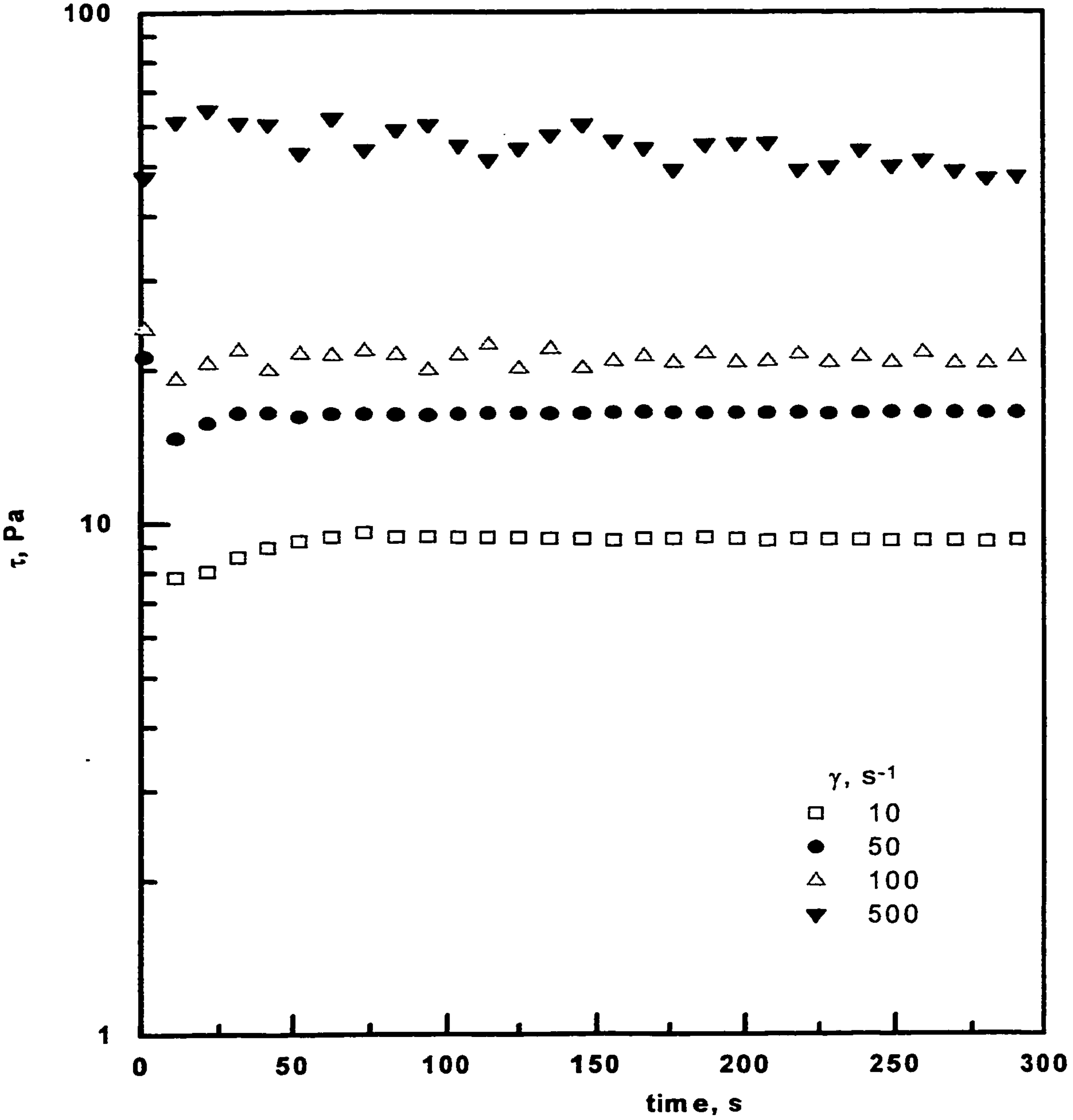


Figure 4.2.2 Transient Shear StressRresponse, 3% PAM

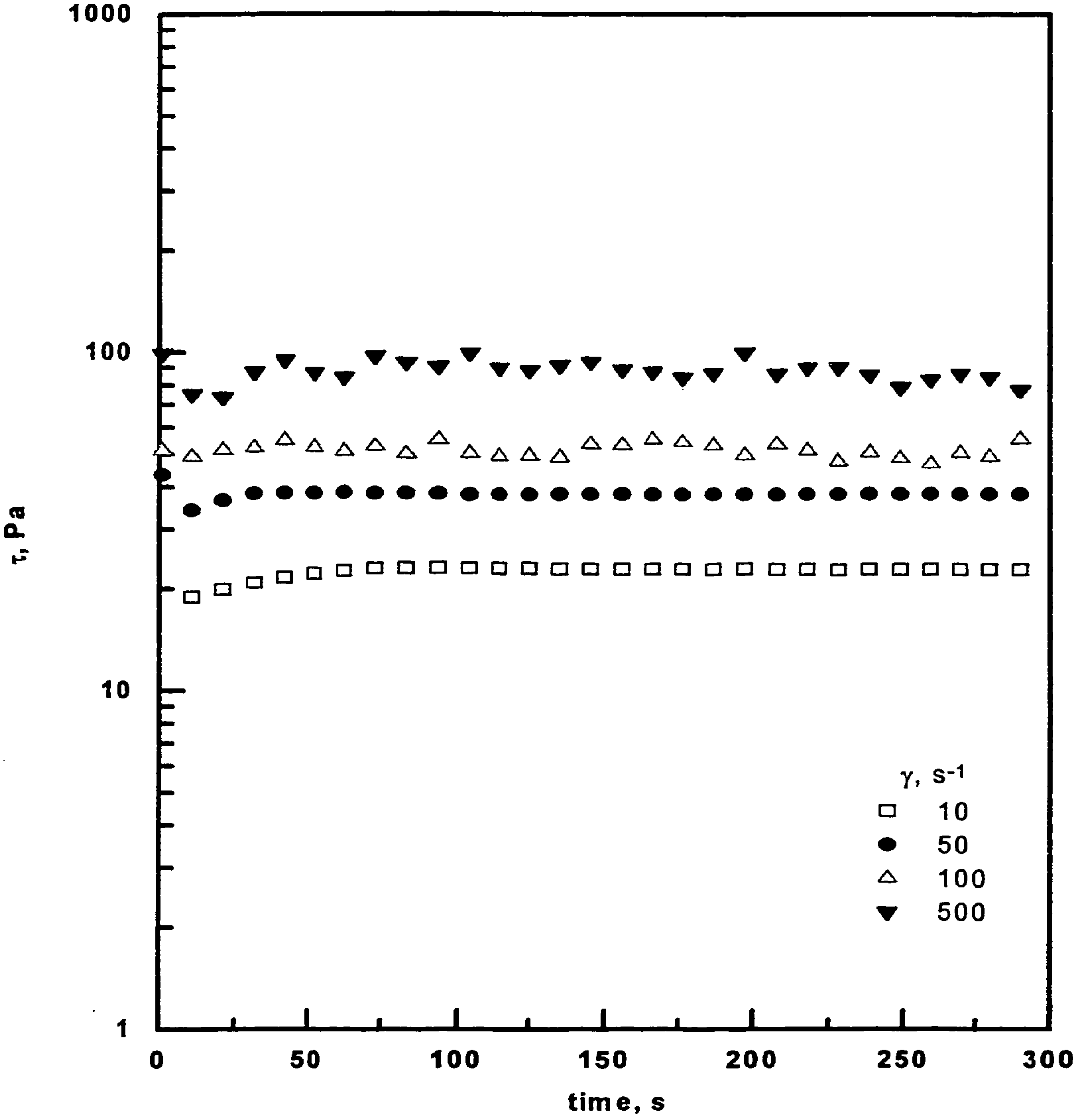


Figure 4.2.3 Transient Shear Stress Response, 4% PAM

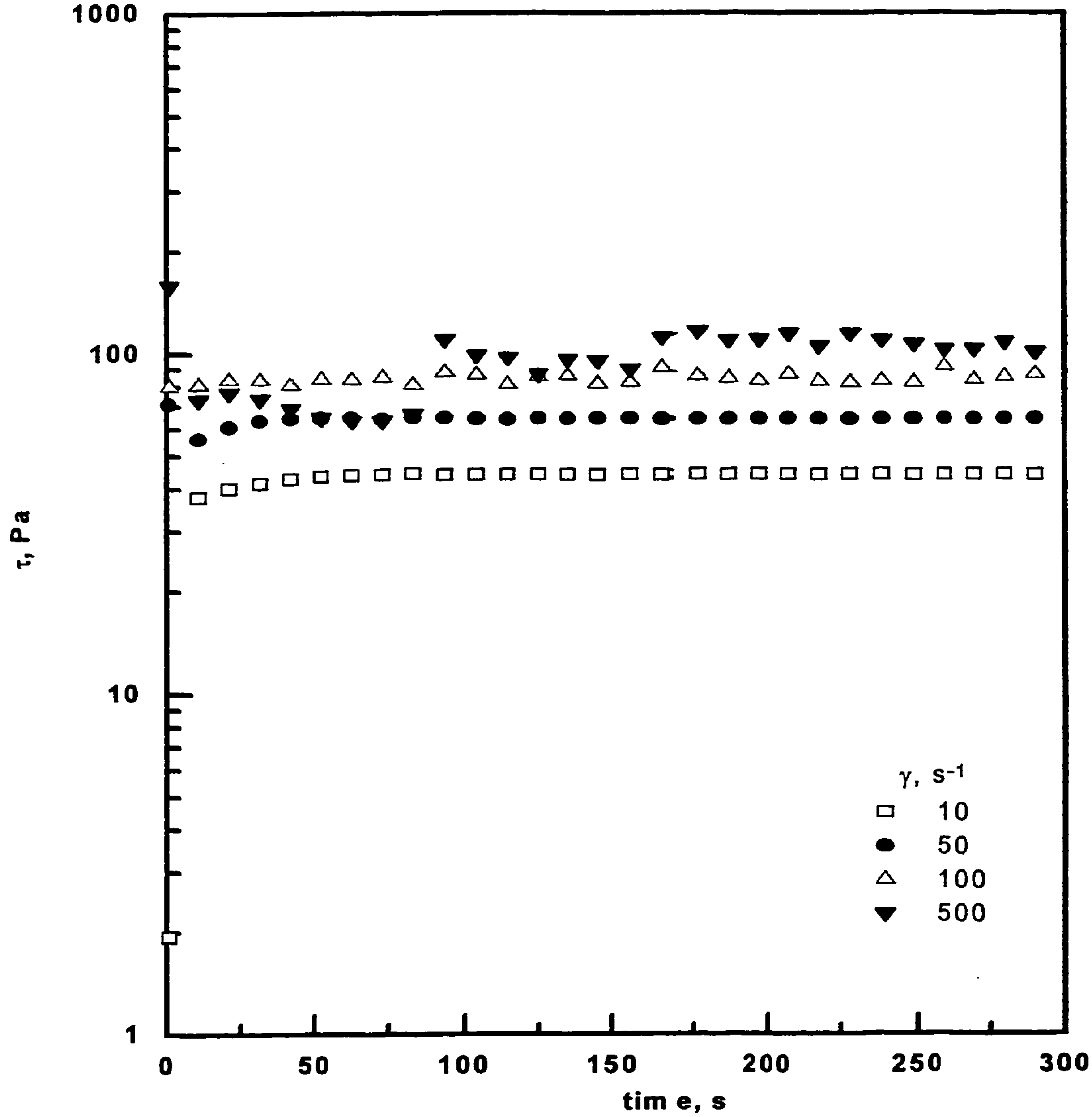


Figure 4.2.4 Transient Shear Stress Response, 5% PAM

## 4-3: Yield Stress Test:

The yield stress, or yield point, as it is often called, can be defined as the force required to make a material flow. A lower stress causes an elastic deformation that elastically disappears when the applied stress is released. The elastic deformation is linearly proportional to the applied stress. Above the yield point, the applied stress causes unlimited deformation, and the sample starts to flow. Under flow conditions, the applied stress is correlated to the rate of deformation with viscosity as the correlating factor. In this region, the material behaves like a Hookien solid with the Young's Modulus as the proportional factor,

$$\sigma = \mathrm{E}\varepsilon \qquad 4.3.1$$

Where $\sigma$ is the stress, $\varepsilon$ the strain, and $\mathrm{E}$ is Young's modulus.

Yield stress is a particularly important rheological property. It is characteristic of many materials which are widely used in industry. It controls the thickness of coating layers, ensures storage stability and inhibits free flow, and it gives a very good approximation for practical purposes, such as in characterizing the ability of grease to resist slumping in a roller bearing. In addition, it affects mass and heat transfer and introduces constraints in manufacturing processes and quality of the final product. Determining the yield stress can be essential for predicting flows.

The main characteristic of yield stress fluids is that they give rise to thick deposits on steep slopes while unyielding fluids go on flowing as long as surface tension effects remain negligible. It also determines the stability of suspensions and the appearance of coated material[21]. Most researchers agree that the mechanism behind a yield stress is the development of a structure or network. Crosslinks, bridging or association through physical contacts or molecular weight effects can form this structure or network. These structures can be broken down under an applied shear field, but will partially redevelop upon cessation of the shear rate[22].

Yield stress can be classified into two types: dynamic yield stress and static yield stress. Dynamic yield stress is strongly dependent on the shear rate prior to the measurement and to the decrease of the applied stresses when the shearing ceases. The latter relationship occurs since the plasticity is related to the structure in the material. Dynamic yield stress can only be expected to give a first estimate of the yield stress in a storage period. Static yield stress is a result of a three-dimension of network, which does not break down until the stress reaches the yield point.

The concept of yield stress is sometimes a very good approximation for practical purposes, such as in characterizing the ability of grease to resist slumping in a roller bearing. The measurement of the yield stress is critical in understanding the flow properties of materials, which can be used in engineering and operations where the handling and transport of such materials are involved. If the stress is not constant over a body, part of it may flow while the rest acts as a solid.

The yield stress test was carried out for all the examined solutions for the range 2 - 5% PAM, using the hysteresis loop. This test employed controlled stress mode (CS). In CS mode, the RS100 applies a shear stress by means of an extremely low interia. An air bearing that delivers an almost frictionless applied stress centers the drive shaft of the RS100. Therefore, this system makes it possible to measure a small yield stress. In this mode, as a controlled stress is applied, the shear stress is controlled, but it does not produce any meaningful shear rate as long as stresses are not high enough to cause the fluid to flow. For the concentration of 2 %, in the first segment, the assigned stress ramped from 0.09 to 50 Pa to establish the up curve. Then, the assigned stress instantaneously reduced from 50 to 0.09 Pa to develop the down curve. For concentrations of 3% and 4%, the first segment was ramped from 0.09 to 100 Pa to establish the up curve. Then the segment ramped down from 100 to 0.09 Pa to develop the down curve. Finally, for the 5% concentration, the first segment, was ramped up from 0.09 to 250 Pa, and then ramped down from 250 to 0.09 Pa.

The results of hysteresis loop measurements have been plotted down in figures (4.3.1-4.3.2-4.3.3,and 4.3.4). All the solutions exhibited a static yield stress which was higher for higher concentrations. It has been pointed out that the static yield stress is a result of a three-dimension of network. This network 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 a viscous fluid[17]. Yield stress has no influence on the material flow at higher shear rates. Higher concentrations of polyacrylamide solutions produce higher cycles of up and down curves and, consequently, cause higher resistance to flow.

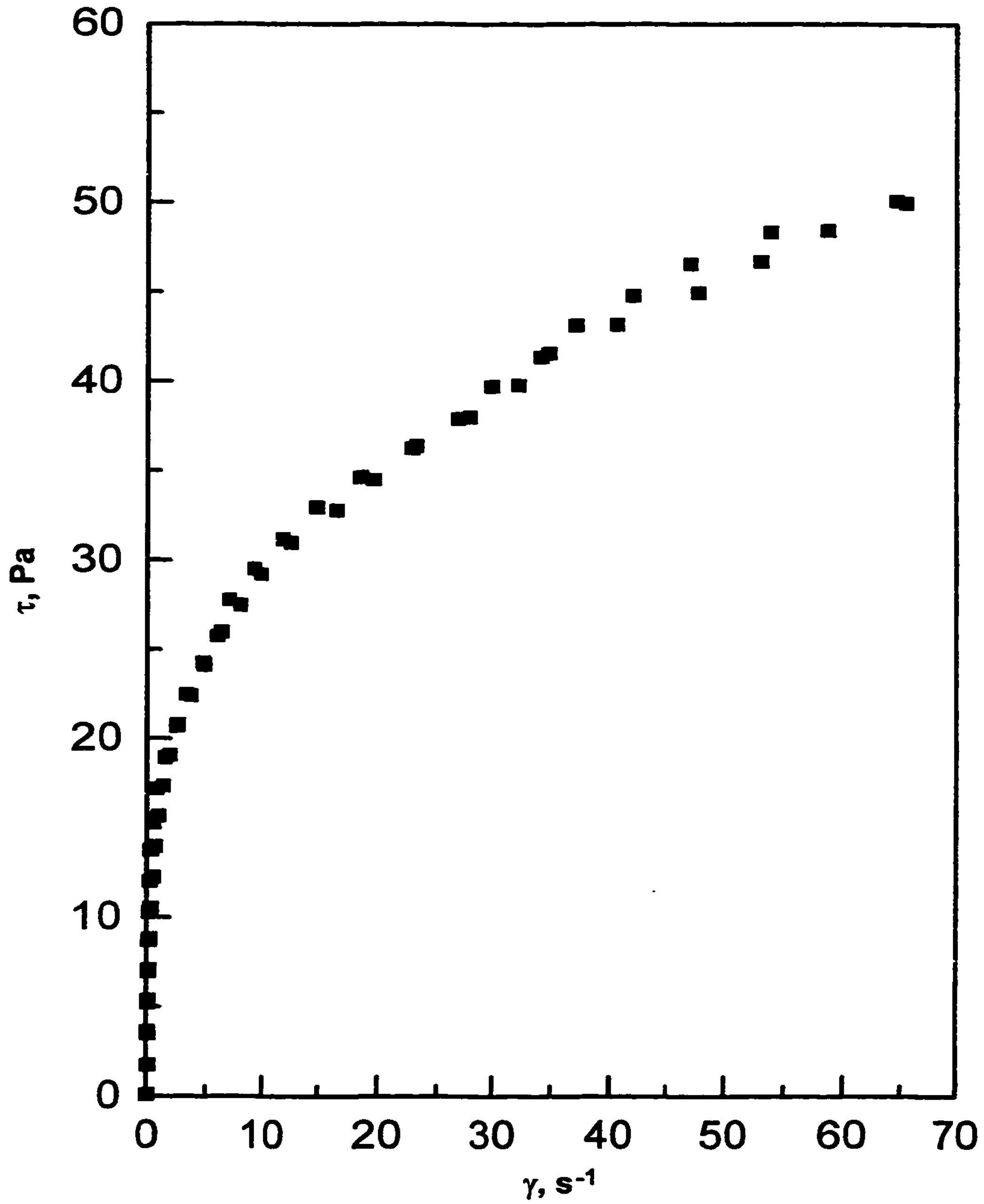


Figure4.3.1 Yield Stress Response of 2 % PAM.

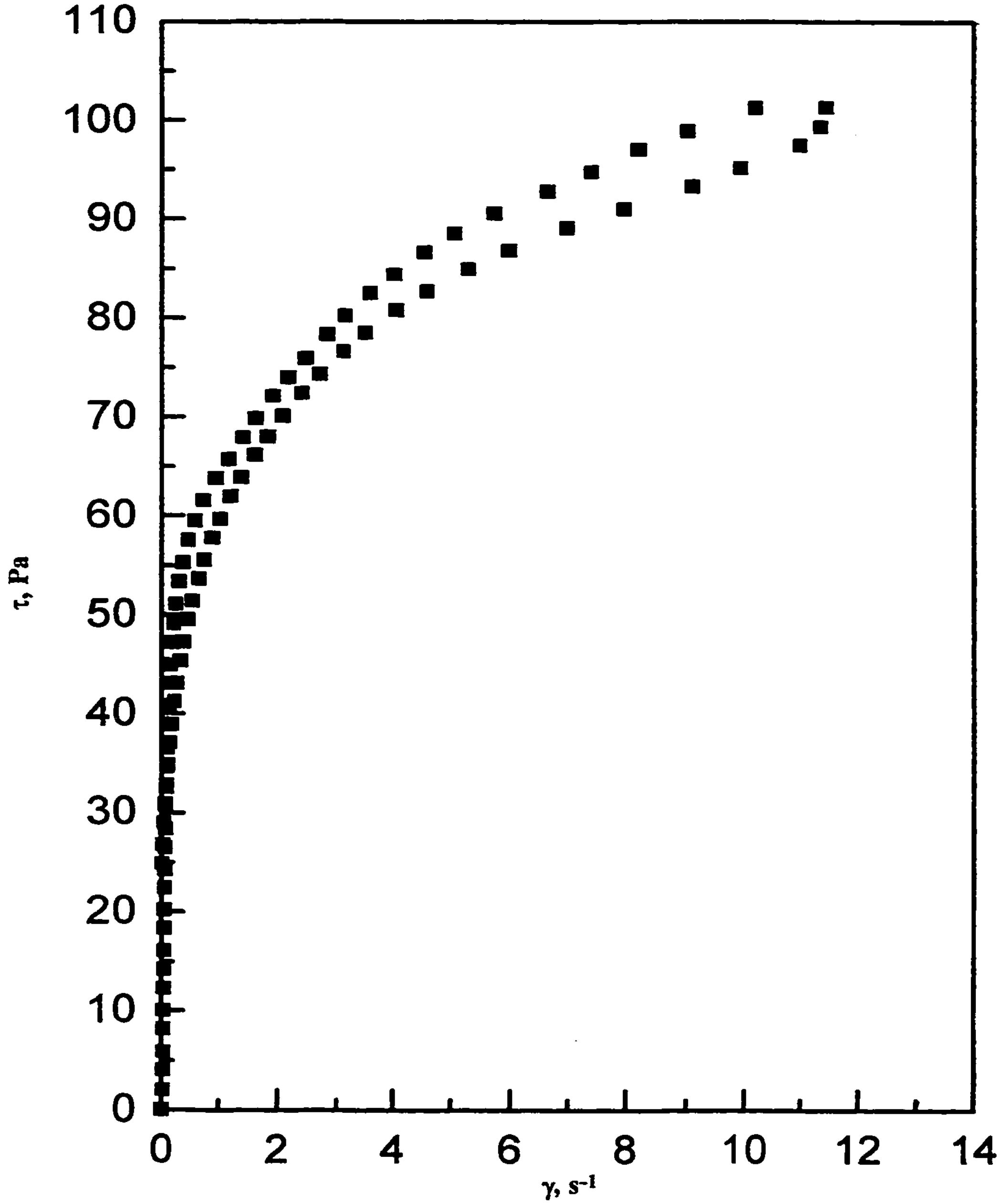


Figure 4.3.2 Yield Stress Response of 3 % PAM.

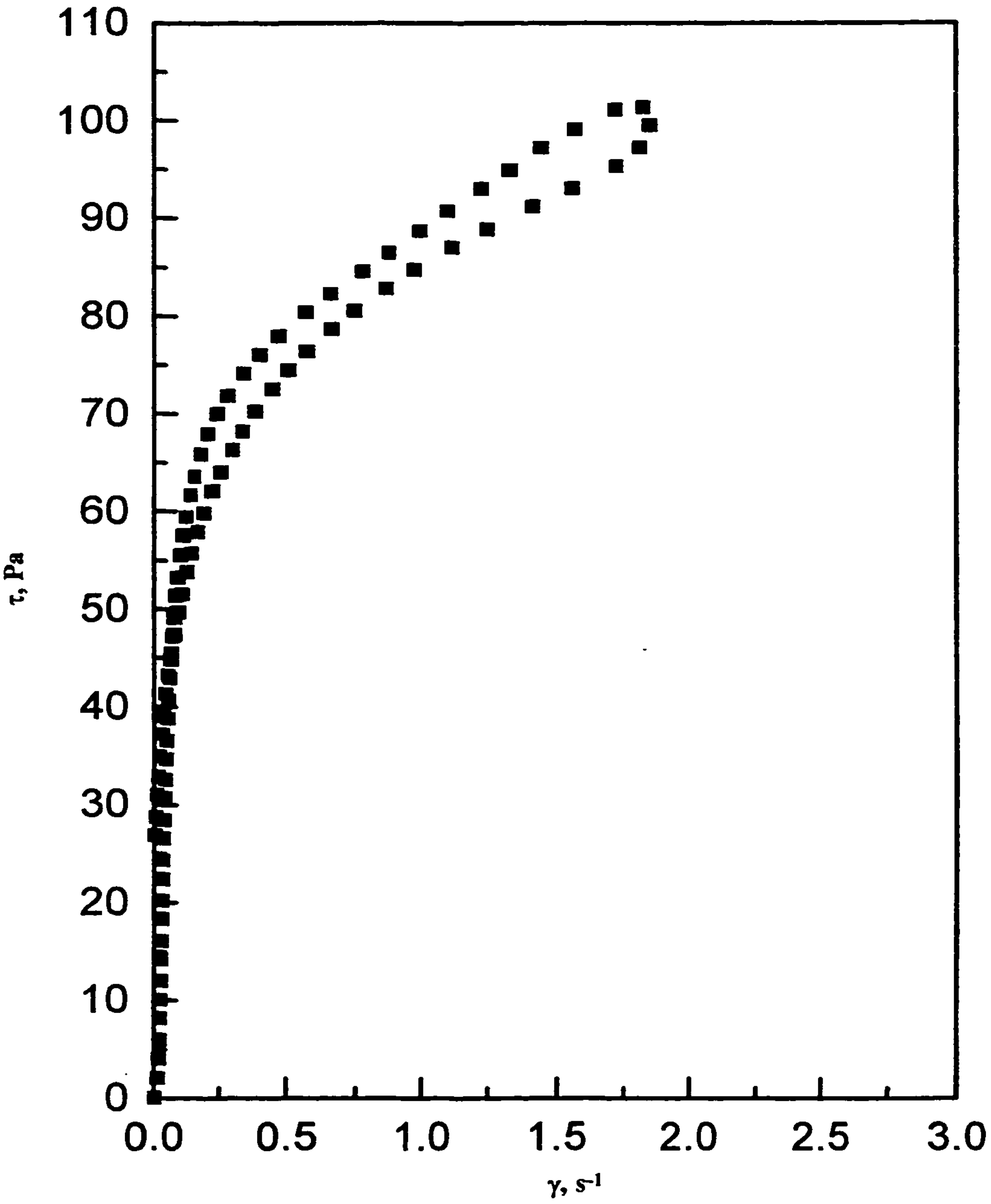


**Figure 4.3.3 Yield Stress Response of 4 % PAM.**

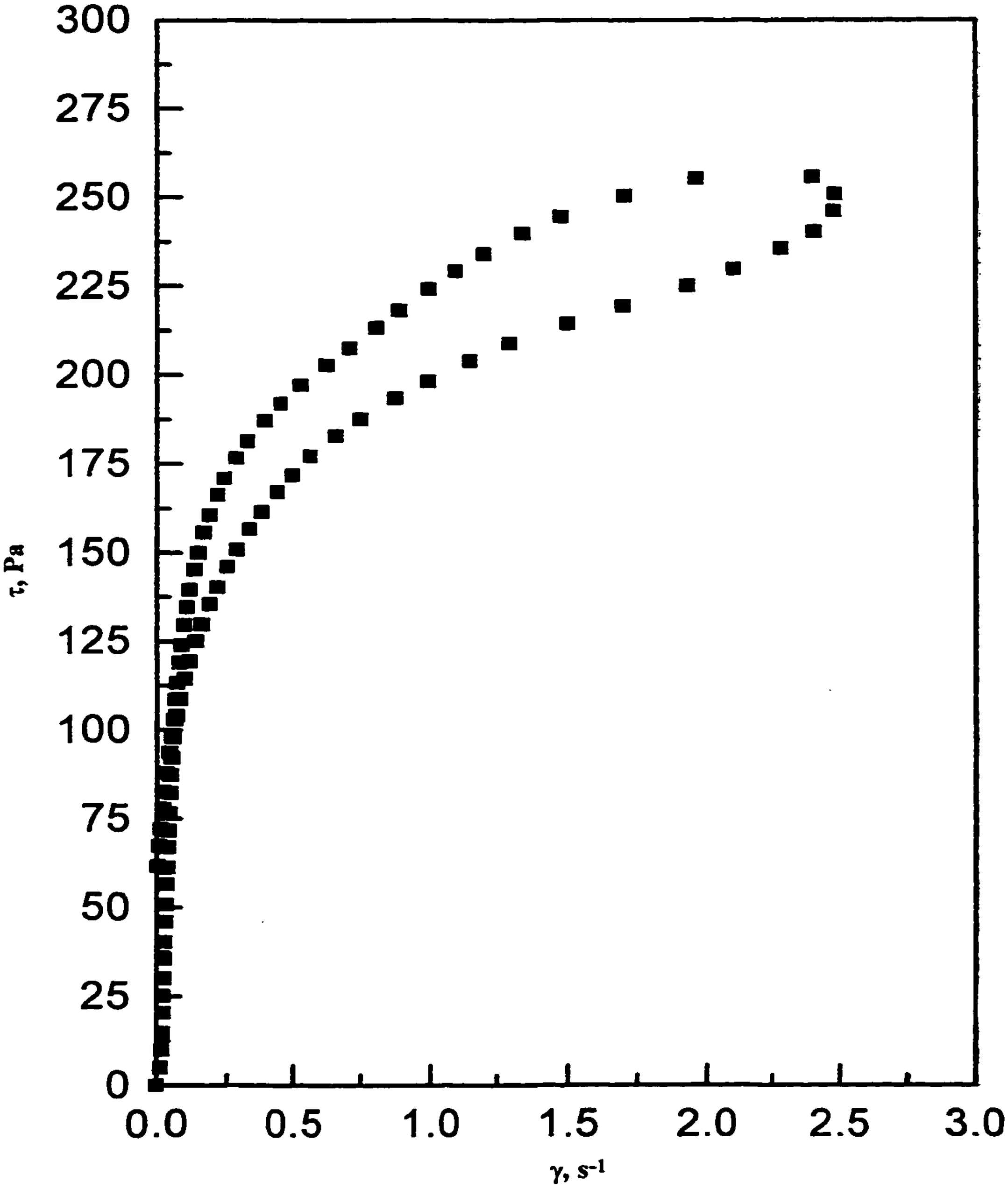


**Figure 4.3.4 Yield Stress Response of 5% PAM.**

## 4-4: Thixtropic test:

Thixotropy is defined as the decrease of the apparent viscosity under constant shear stress or shear rate, followed by a gradual recovery when the stress or shear rate is removed. The effect is time dependent[19]. As a result of removing the stresses, the small fragments start to bond with each other due to collision and Brownian motion.

Thixotropy reflects the finite time taken to move from any one state of microstructure to another, and back again, which results from an action of an external force that can be defined as:

$$\tau = \eta \, du/dy \qquad \eta = \eta(t) \qquad 4.4.1$$

The driving force for microstructure change in flow is the result of the competition between breakdown due to flow stresses, 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, causing them to move to a favorable position where they can, given the necessary attractive force, attach themselves to other parts of the microstructure[23]. 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 one another. If the material is at rest, the particles aggregation can form a network, and the material develops an internal structure. The weak physical bonds are ruptured and the network breaks down into a separate aggregate by applying a shear force. The term microstructure pertains to the alignment of fibers, favorable spatial distribution of particles or drops, and the entanglement density or molecular associations in polymer solutions. All these determine the level of viscosity and elasticity, and they all take time to change from one state to another under the action of shear and/or Brownian forces.

Thixotropy is neither good nor bad, but for certain applications it can be favorable or negative. For example, paint that thins fast by strokes of a brush can be easily painted. Or, when the applied paint layer on a vertical wall re-thickens fast, this viscosity recovery will help prevent sagging. In other applications, such as process control design, thixotropy can be very challenging for engineers. For example, the behavior of a range of thixotropic materials in a series of mixers is quite easy to characterize if one assumed that the mixer behaved in the same way as a viscometer running at the same shear rate as the average shear rate in the mixer. Furthermore, where a thixotropic liquid enters a long pipe from a large vessel, where it has been allowed to rest, the development of the velocity and pressure fields in the pipe is very complicated; they are very difficult to measure. 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. Often cavitation can be caused because, although a pump could cope with sheared material, it might be unable to initiate flow of material that has been at rest for some time. Cavitation in the liquid, within the pump, can then ensue[23]. Thixotropic fluids are stiff and do not flow under relativity small stresses. However, they can be made to flow with less and less viscosity as the shearing stress is increased. This continues to be the case as long as the low viscosity persists, even under reduced stress; however, when the materials are stress-free, they return to their high stiffness state with time.

These kind of fluids can be classified in two ways: Thixotropic or anti-thixotropic. Thixotropic fluids: These fluids exhibit a shear-thinning behavior as a result of gradually applying an external force from low to high values. On removing this force, the fluid will regain most or all of its original viscosity. The lower viscosity state of a liquid is called the Sol state. However, anti-thixotropic fluids exhibit a behavior opposite to that of thixotropic fluids. Anti-thixotropy can be defined as: an increase of the apparent viscosity under constant shear stress or shear rate, followed by a gradual recovery when the stress or shear rate is removed. This phenomenon can arise because flocs (i.e. small fragments called flow units) can become looser, more open under the action of shear, and thus, the viscosity increases. A single material can show both shear thinning or thixotropy, and antithixotropy. In that case, antithixotropy will appear at higher shear rates than the other effects[24].

Thixotropic materials have a structure that can be destroyed by the applications of shear stress and rebuilt by letting them rest. The process of destroying and rebuilding the structure is isothermal and reversible transformation occurs from a higher to a lower viscosity. This transformation can be brought about either by an increase in the shear rate followed by a rest period, or by the application of a constant shear rate over a period of time followed by a rest period. Those time dependent phenomena are referred to as the microstructure of the liquid system.

There are many tests used to determine the measurements of thixotropy. One of the most common way of measuring thixotropy is the hysteresis loop test[11,23,25,26], which is characterized by a linear increase in the shear rate from low to a maximum value, followed by a return, at the same rate, to the minimum value. This test could then be repeated again and again.

Our measurement of thixotropy was conducted under the controlled-rate CR-mode using the hysteresis loops test. The apparatus was programmed to gradually increase the assigned shear rate from a given initial value to a terminal value. The stresses and the shear rates of flow were recorded. The results are marked by an up-curve reaching the assigned maximum rate followed by a gradual decrease as demonstrated by the down curve. The down curve, of a time independent sample, is identical to its up-curve; however, the down curve of a thixotropic solution is different from the up-curve. The area (A) between the up and down curve defines the magnitude of the thixotropy. If the fluid is antithixotropic, the down curve will be above the up curve. A solution's thixotropy is quantified by the solution's ability to regain its gel structure when the liquid is allowed to rest for a longer period time after attaining the Sol phase. The hysteresis area A (Pa/s) of a sample is taken to be a measure of the degree of thixotropy. It has the dimensions of energy over volume, i.e. the energy required to breakdown the thixotropic structure of the solution.

A linearly ramped shear rate cycle, with a certain period of upward and downward shear change, is often used to carry out the thixotropic test. The total breakdown of the thixotropic structure may not be completely attained in a single cycle. To completely destroy the thixotropic structure, the test is repeated until a number of up and down curves coincide. In a different approach, the sample is kept under the upper limit shear rate for a certain period of time. If the structure has been completely destroyed during this period, ramping down the applied rate establishes the full hysteresis area.

In this study, two different hysteresis loop tests have been used to investigate the thixotropic behavior of polyacrylamide solutions. In the first test, one cycle of 60, 120, and 180s for each of the up and down curves has been carried out. The shear rate was ramped up from 0.15 to 700 $s^{-1}$ for the specified period, and then immediately ramped down from 700 to 0.15 $s^{-1}$ in equal time. In the second test, a three part cycle occurred consisting of an up curve from 0.15 to 700 $s^{-1}$ in 60s, a constant shear rate at 700 $s^{-1}$ for 60s, and a down curve back to 0.15 $s^{-1}$ in 60s. The second test was repeated two more times with different times; 120 and 180s.

Polyacrylamide exhibits different thixotropic behaviors throughout the two above-mentioned tests. Figures (4.4.1 to 4.4.23) and tables (4.4.1-4.4.2-4.4.3-4.4.4) present the thixotropic behavior at various regions of shear rate and thixotropic value, respectively. They indicate that the thixotropic behavior of polyacrylamide solutions change as a function of concentrations and shear rate. Concentration 5% shows the highest thixotropic values.

In general, polyacrylamide has low time dependent behavior and gives both thixotropic and antithixotropic responses depending on concentration and shear stress, as well as the technique that is used.

Table 4.4.1: Thixotropic Behavior of 2% PAM

| Time(s) | First Test | Second Test |
|---|---|---|
| 60 | 11.5 Ps/s | 10.6 Ps/s |
| 120 | 8.5 Ps/s | -9.7 Ps/s |
| 180 | 5.2 Ps/s | 10.5 Ps/s |

Table 4.4.2: Thixotropic Behavior of 3% PAM

| Time(s) | First Test | Second Test |
|---|---|---|
| 60 | 3.4 Ps/s | 5.2 Ps/s |
| 120 | 4.4 Ps/s | 8.3 Ps/s |
| 180 | 5.3 Ps/s | -7.7 Ps/s |

Table 4.4.3: Thixotropic Behavior of 4% PAM

| Time(s) | First Test | Second Test |
|---|---|---|
| 60 | 7.2 Ps/s | 16.5 Ps/s |
| 120 | -8.9 Ps/s | 12.8 Ps/s |
| 180 | 9.4 Ps/s | -12.3 Ps/s |

Table 4.4.4: Thixotropic Behavior of 5% PAM

| Time(s) | First Test | Second Test |
|---|---|---|
| 60 | 38.5 Ps/s | 37 Ps/s |
| 120 | 33 Ps/s | 35 Ps/s |
| 180 | 32 Ps/s | 26 Ps/s |

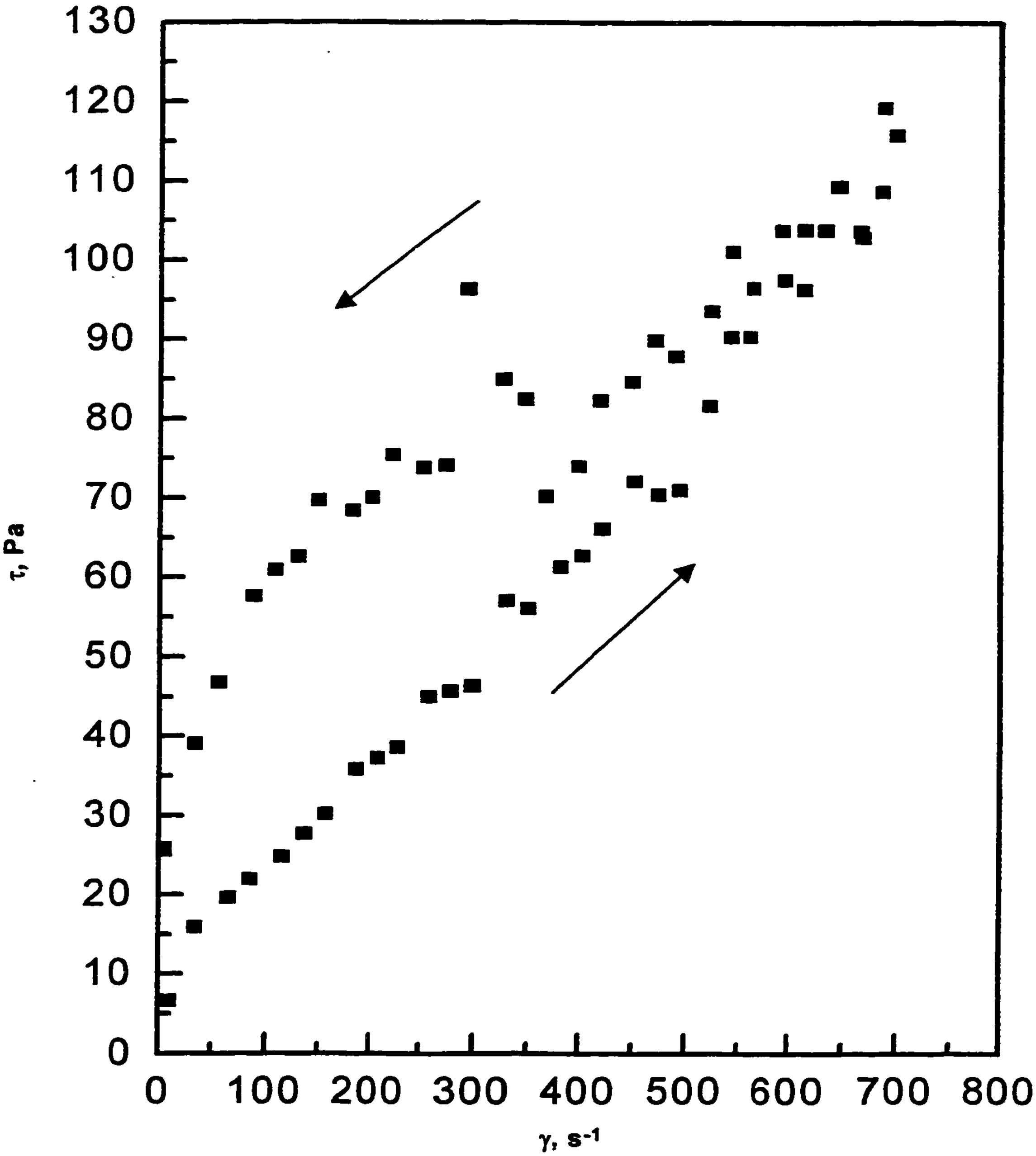


Figure 4.4.1 First Test for 2% PAM, One Cycle at 60s

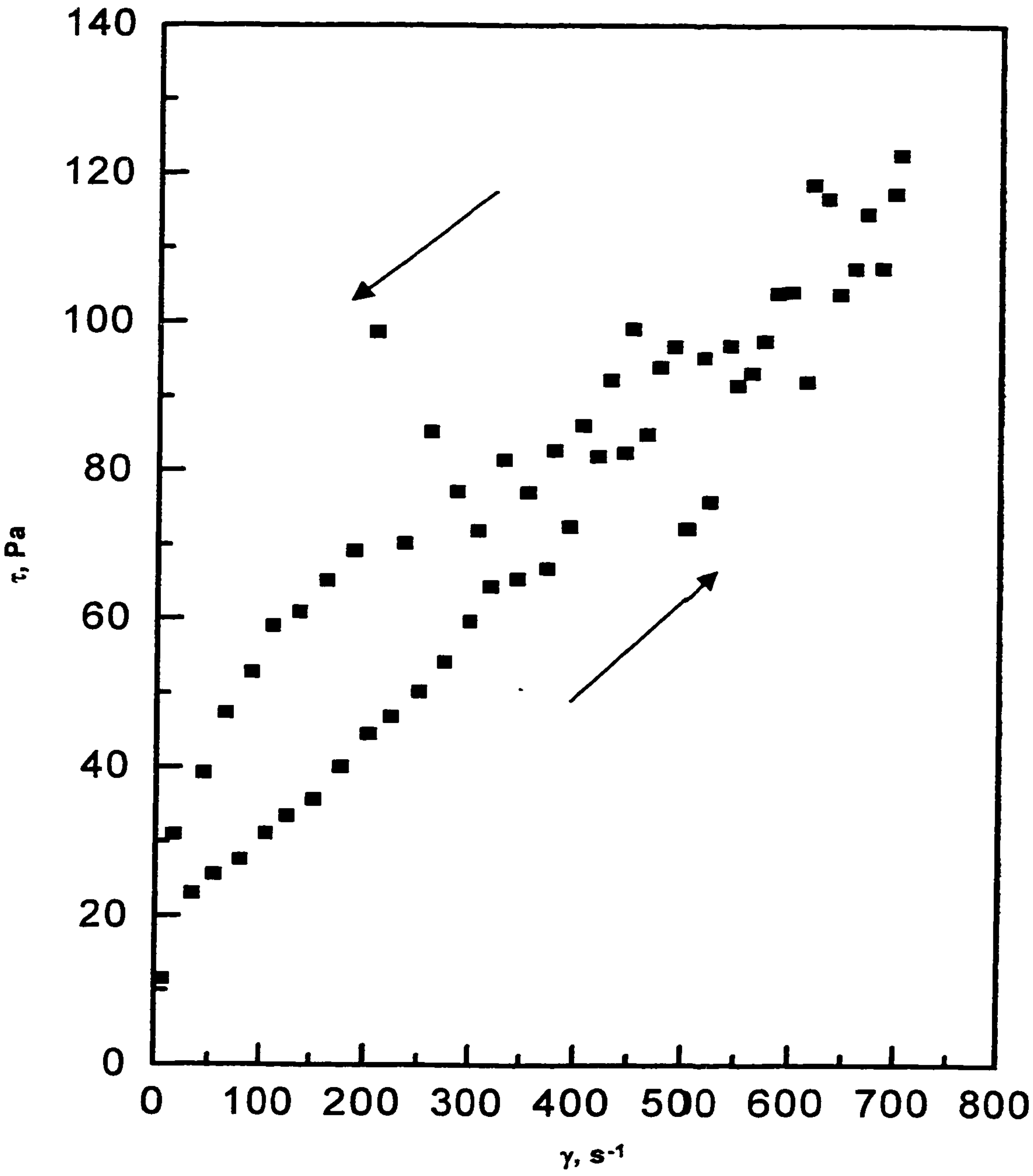


Figure 4.4.2 First Test for 2% PAM, One Cycle at 120s

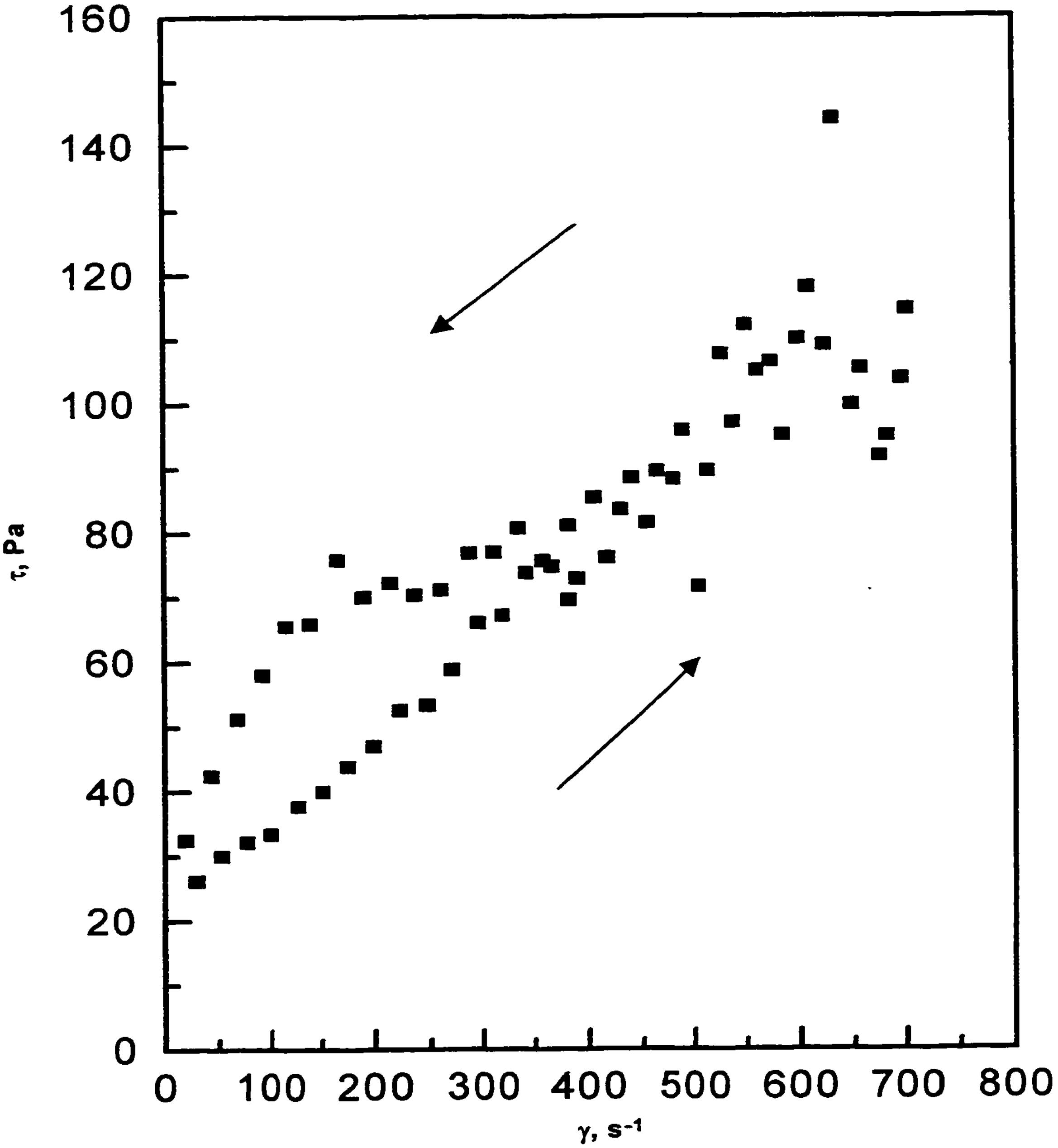


Figure 4.4.3 First Test for 2% PAM, One Cycle at 180s

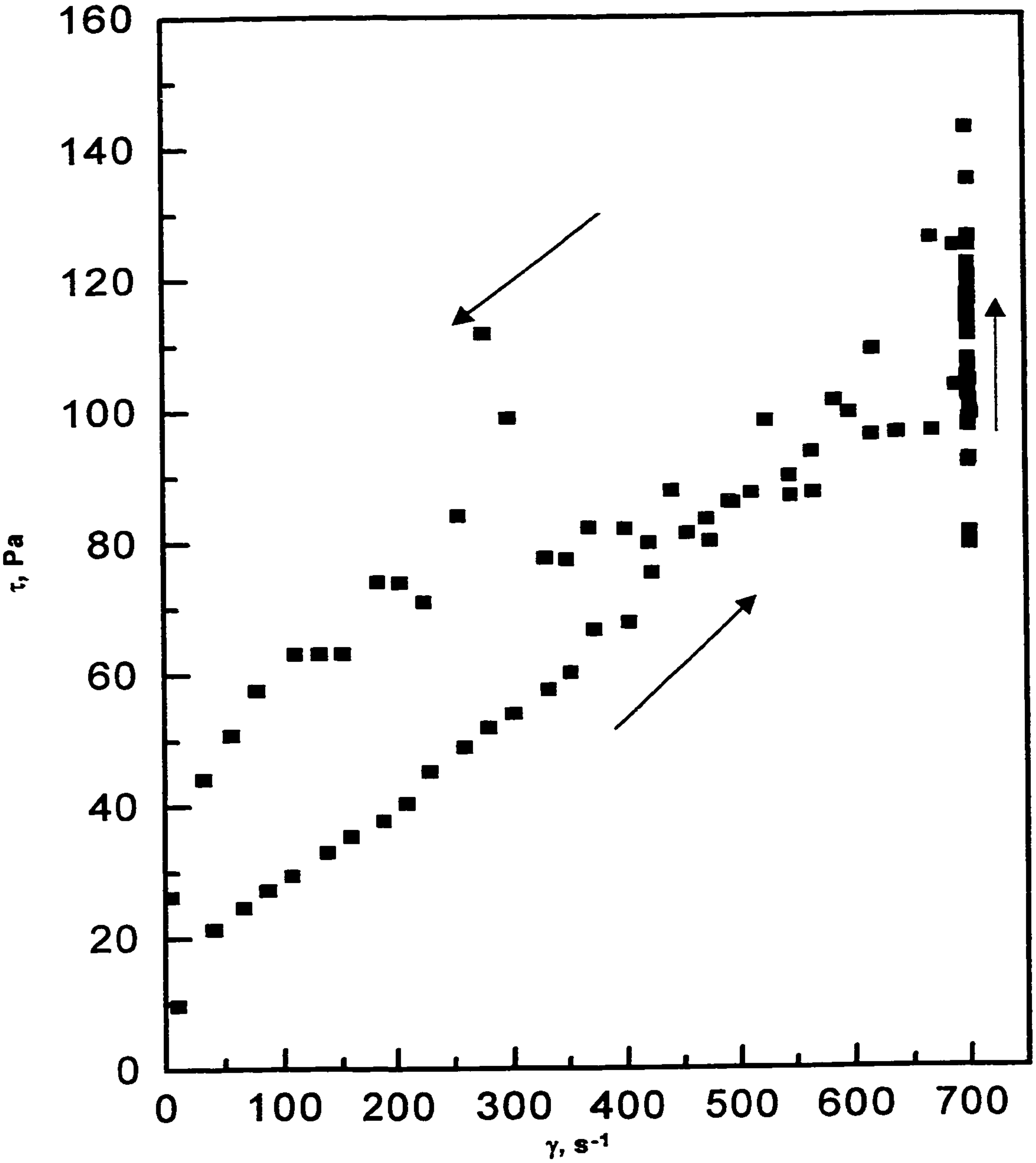


Figure 4.4.4 Second Test for 2% PAM, (Up-Time-Down Curves) at 60s

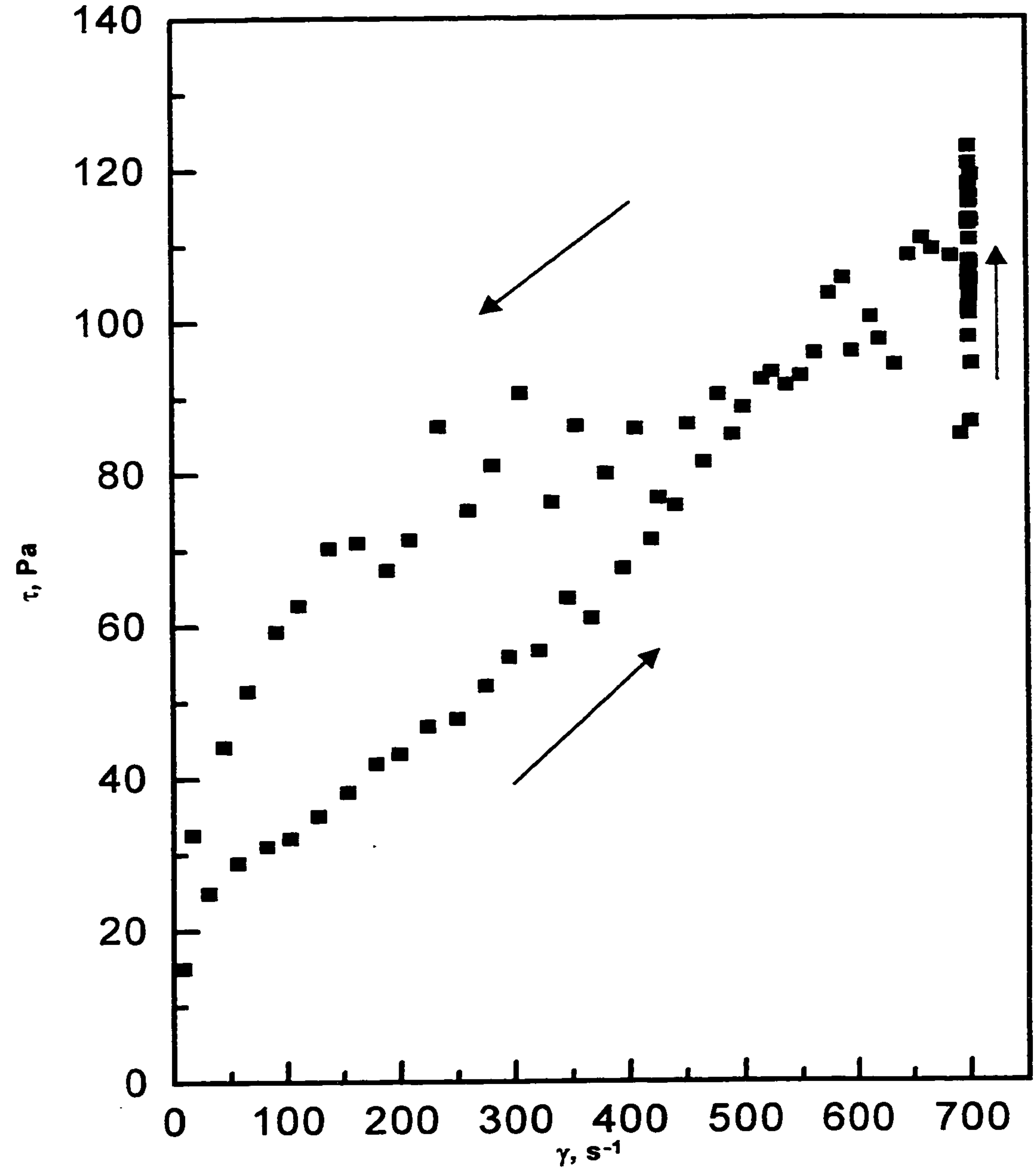


Figure 4.4.5 Second Test for 2% PAM, (Up-Time-Down Curves) at 120s

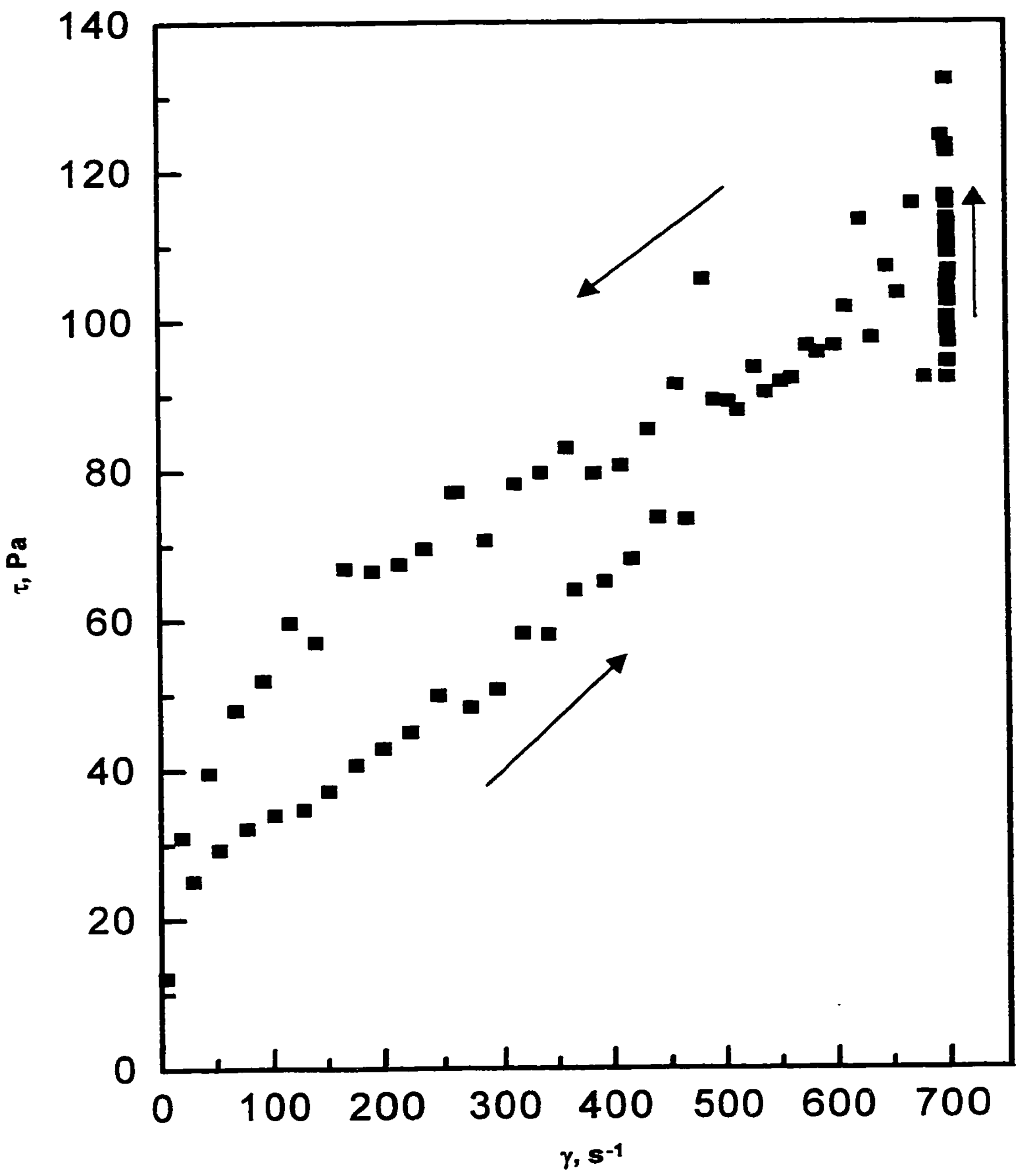


Figure 4.4.6 Second Test for 2% PAM, (Up-Time-Down Curves) at 180s

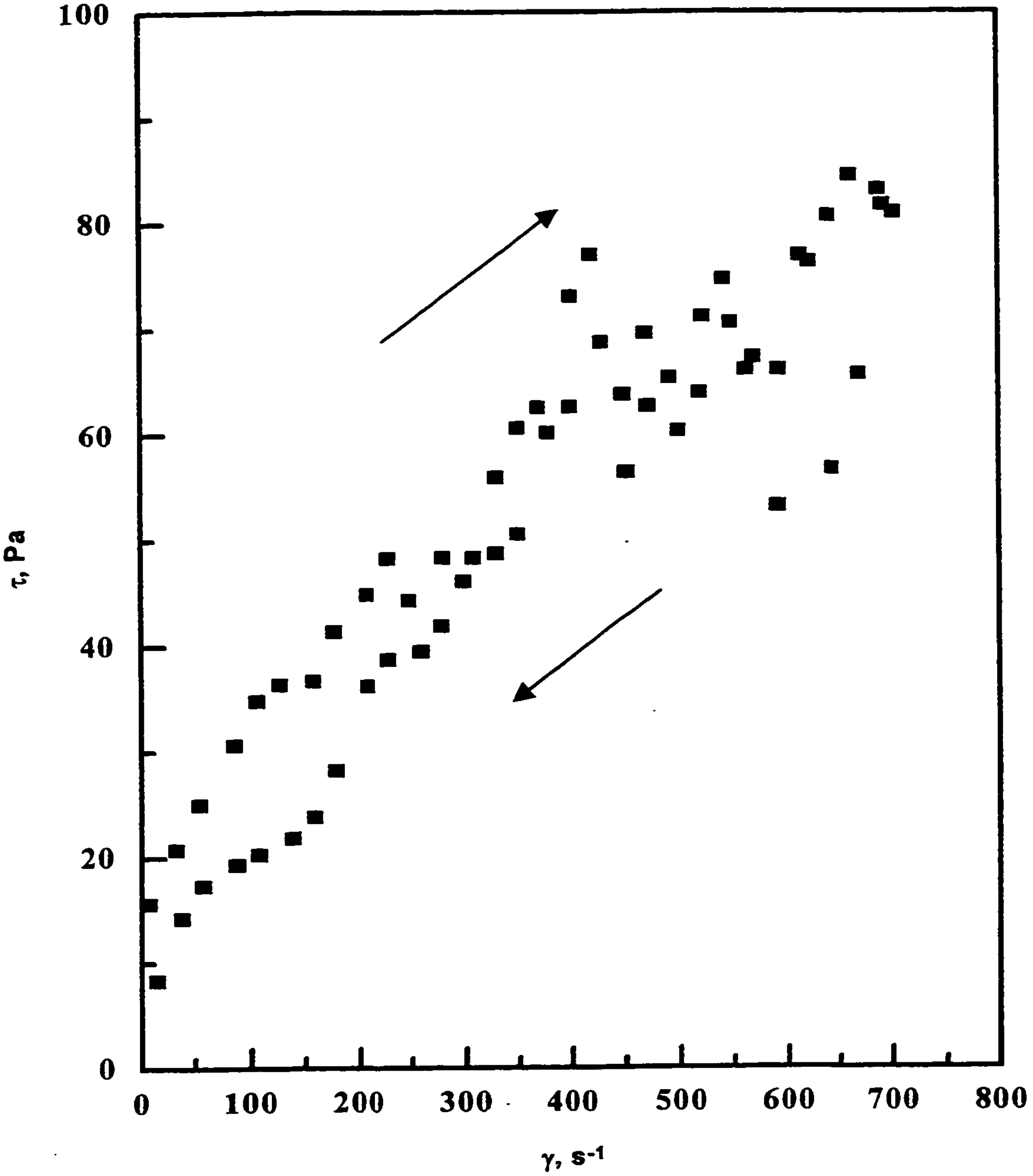


Figure 4.4.7 First Test for 3% PAM, One Cycle at 60s

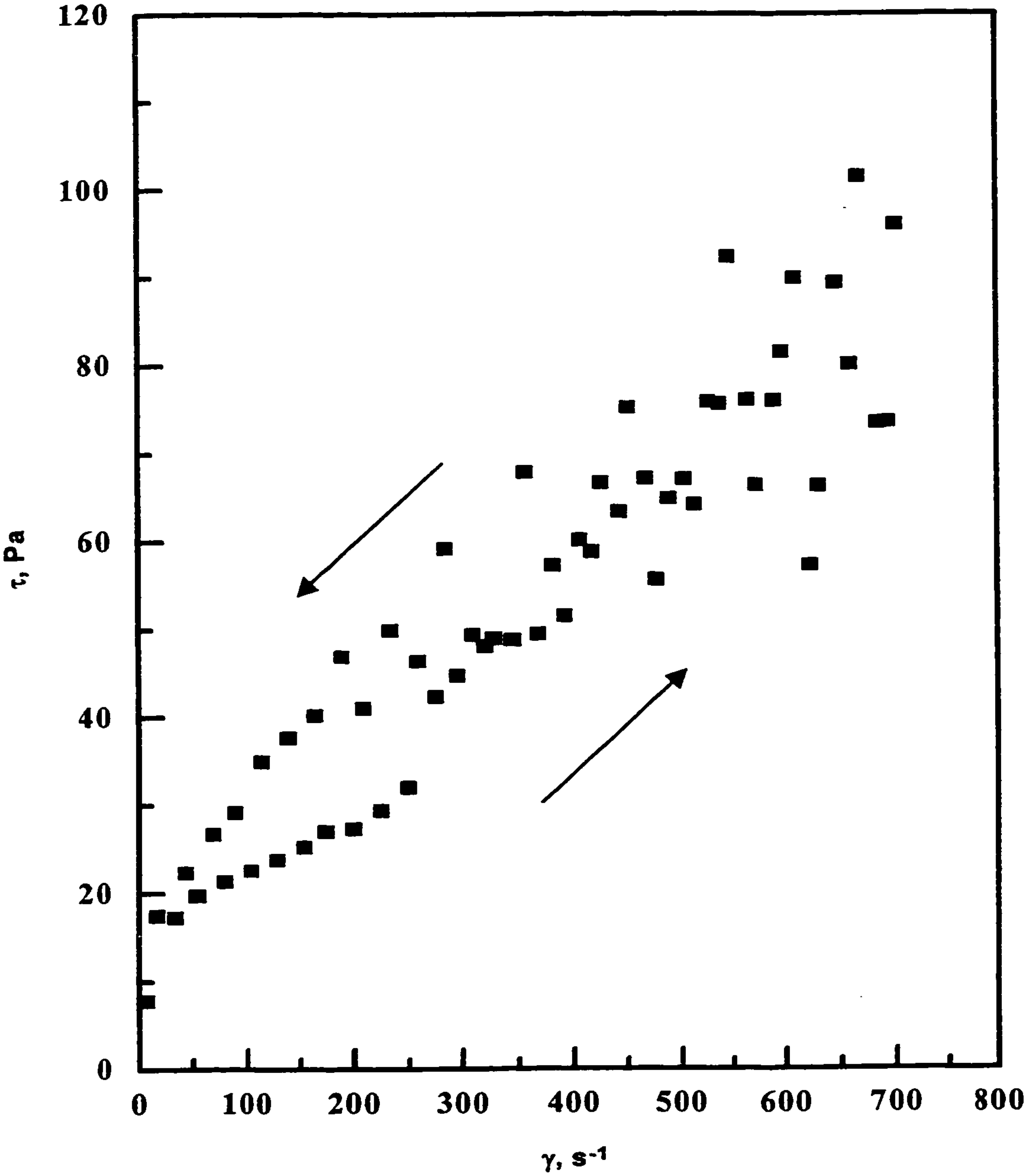


Figure 4.4.8 First Test for 3% PAM, One Cycle at 120s

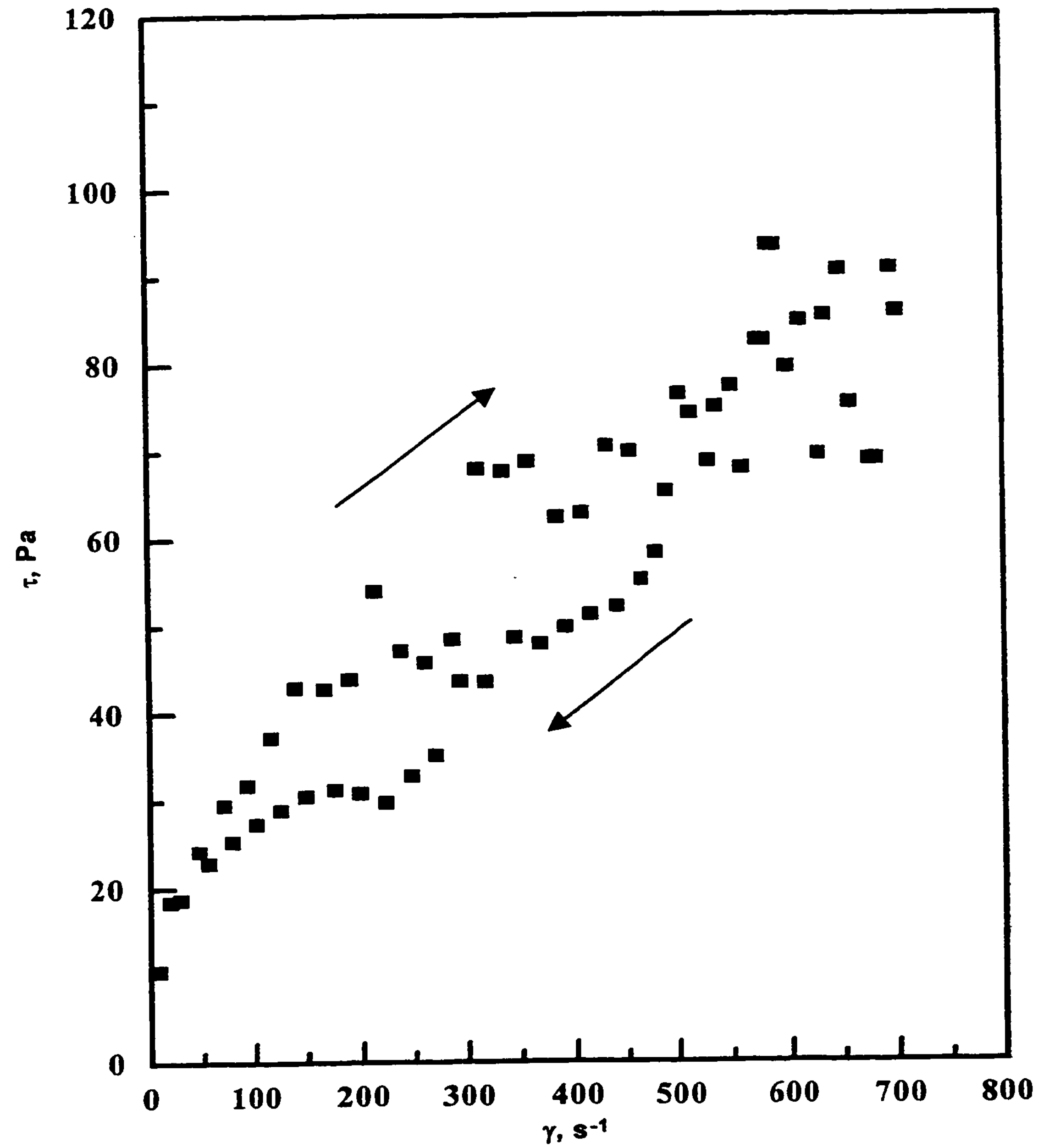


Figure 4.4.9 First Test for 3% PAM, One Cycle at 180s

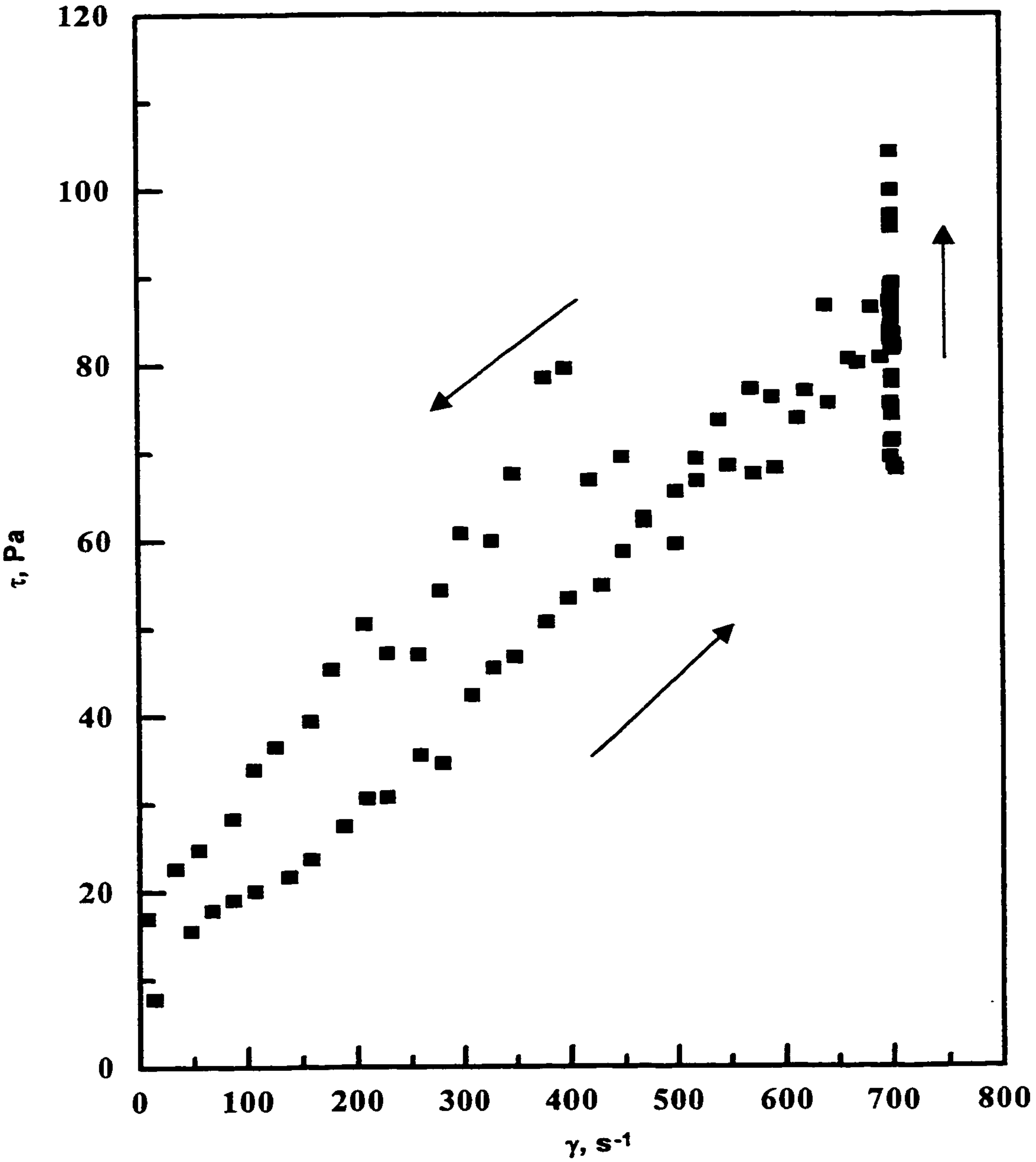


Figure 4.4.10 Second Test for 3% PAM, (Up-Time Down Curves) at 60s

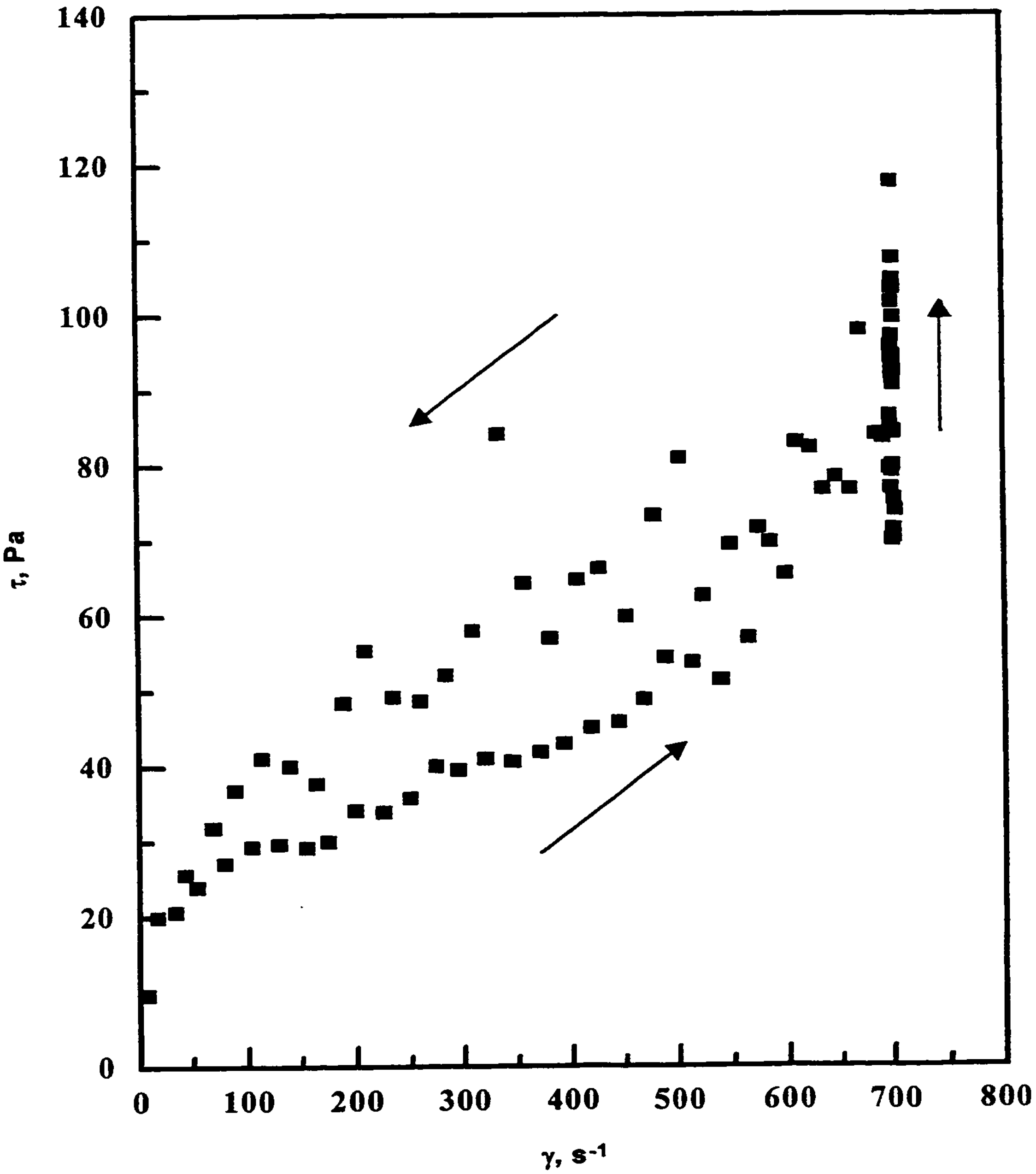


Figure 4.4.11Second Test for 3% PAM, (up-Time-Down Curves) at 120s

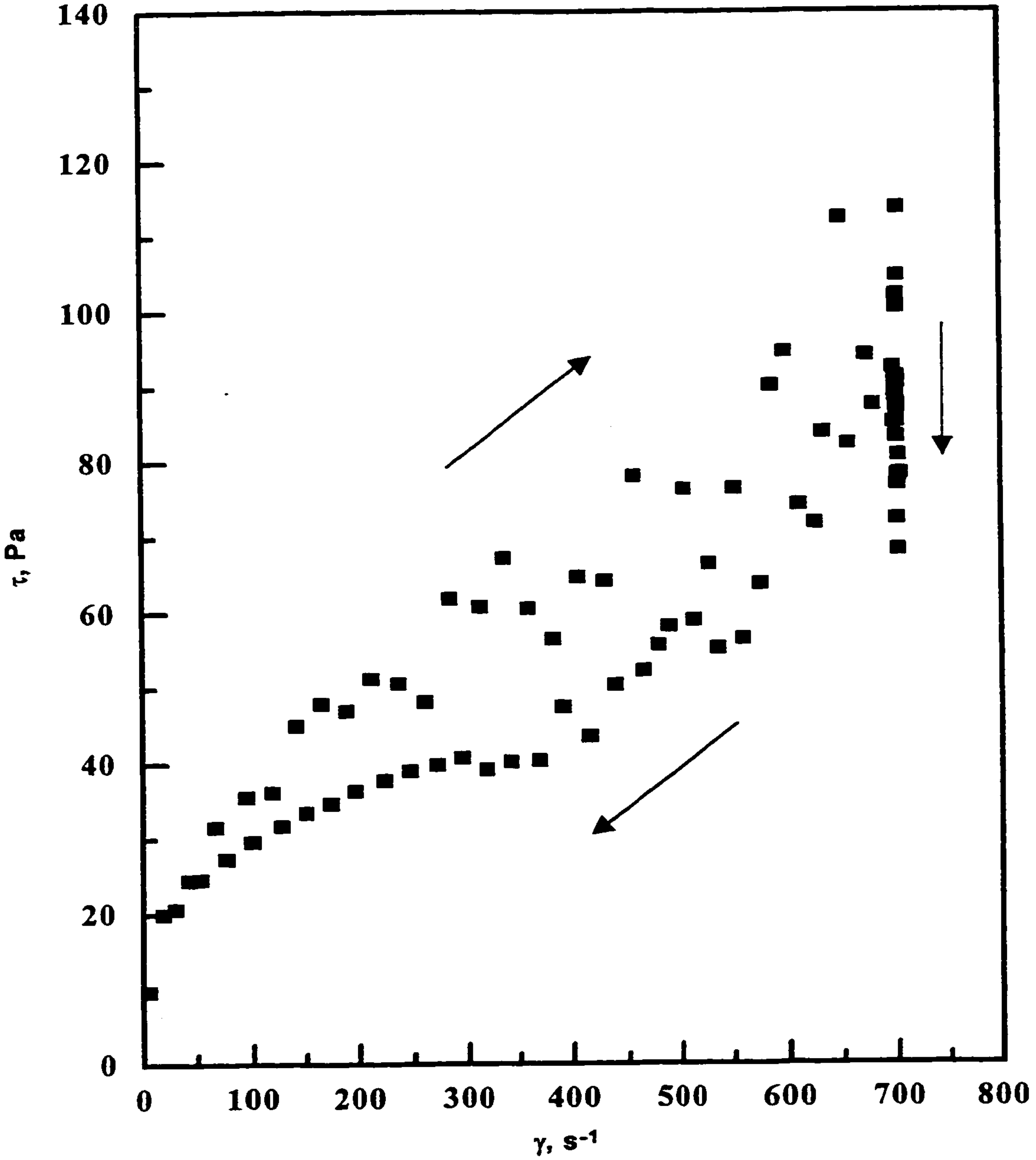


Figure 4.4.12 Second Test for 3% PAM, (up-Time-Down Curves) at 180s

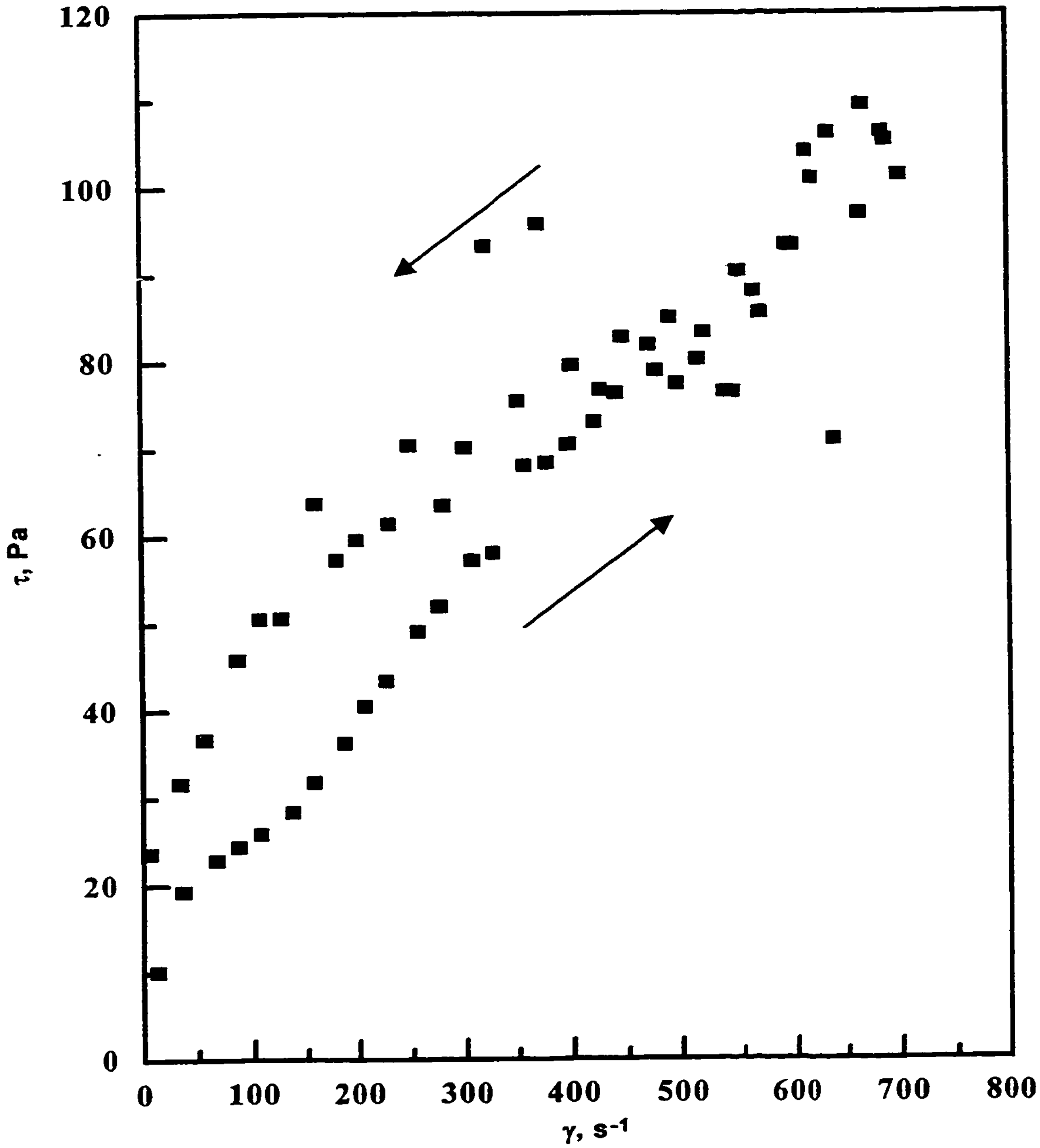


Figure 4.4.13 First Test for 4% PAM, One Cycle at 60s

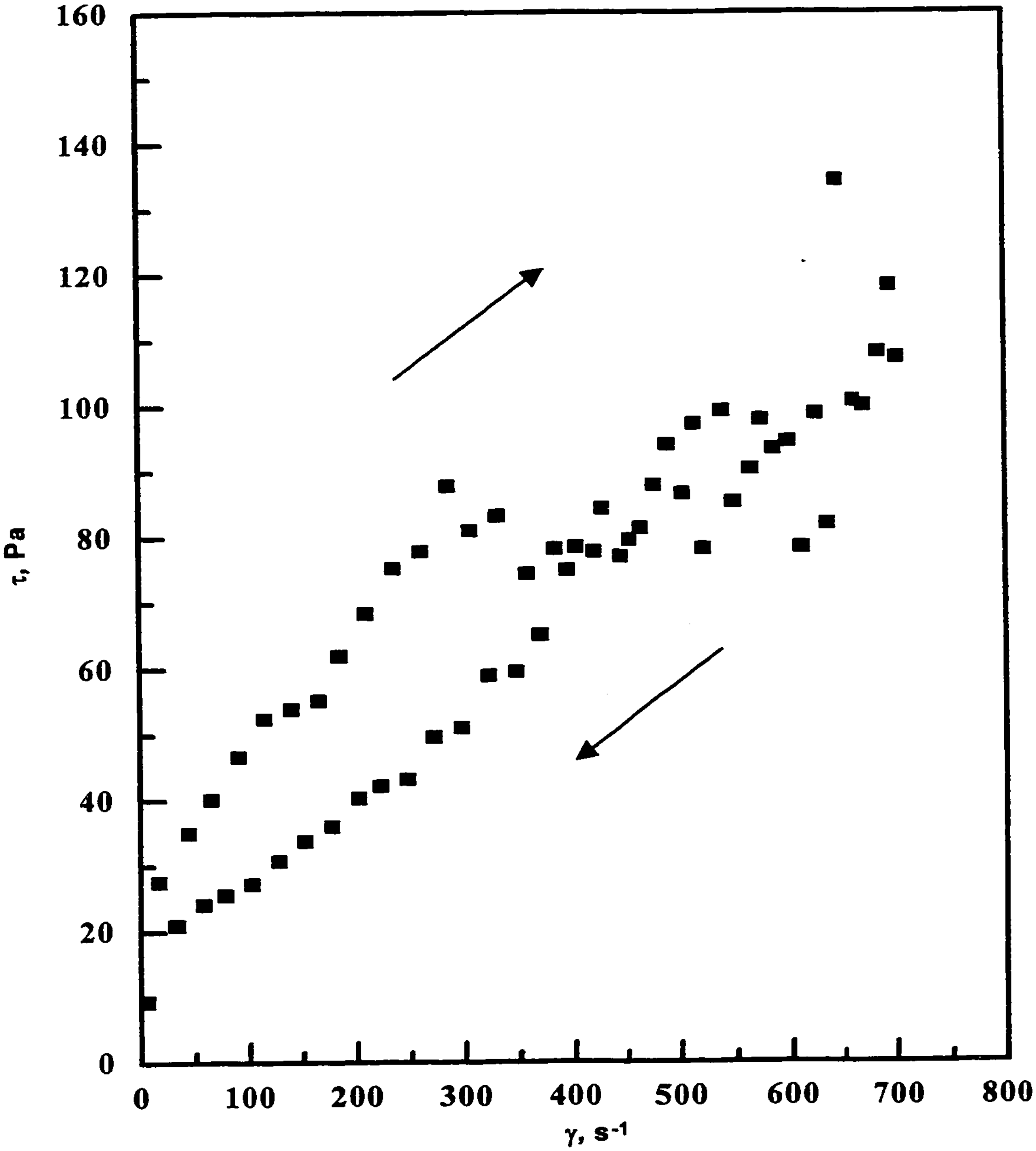


Figure 4.4.14 First Test for 4% PAM, One Cycle at 120s

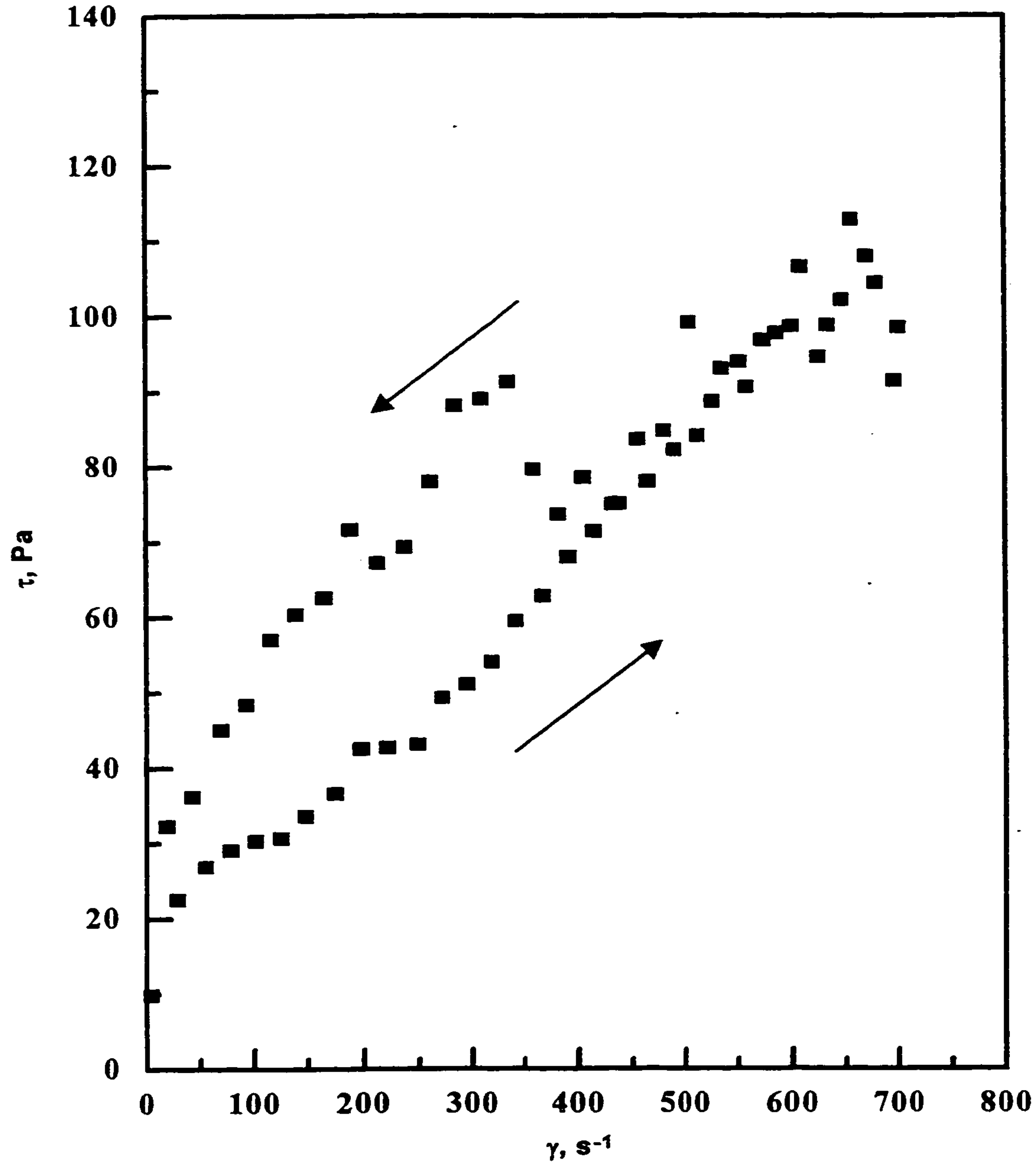


Figure 4.4.15 First test for 4% PAM, One Cycle at 180s

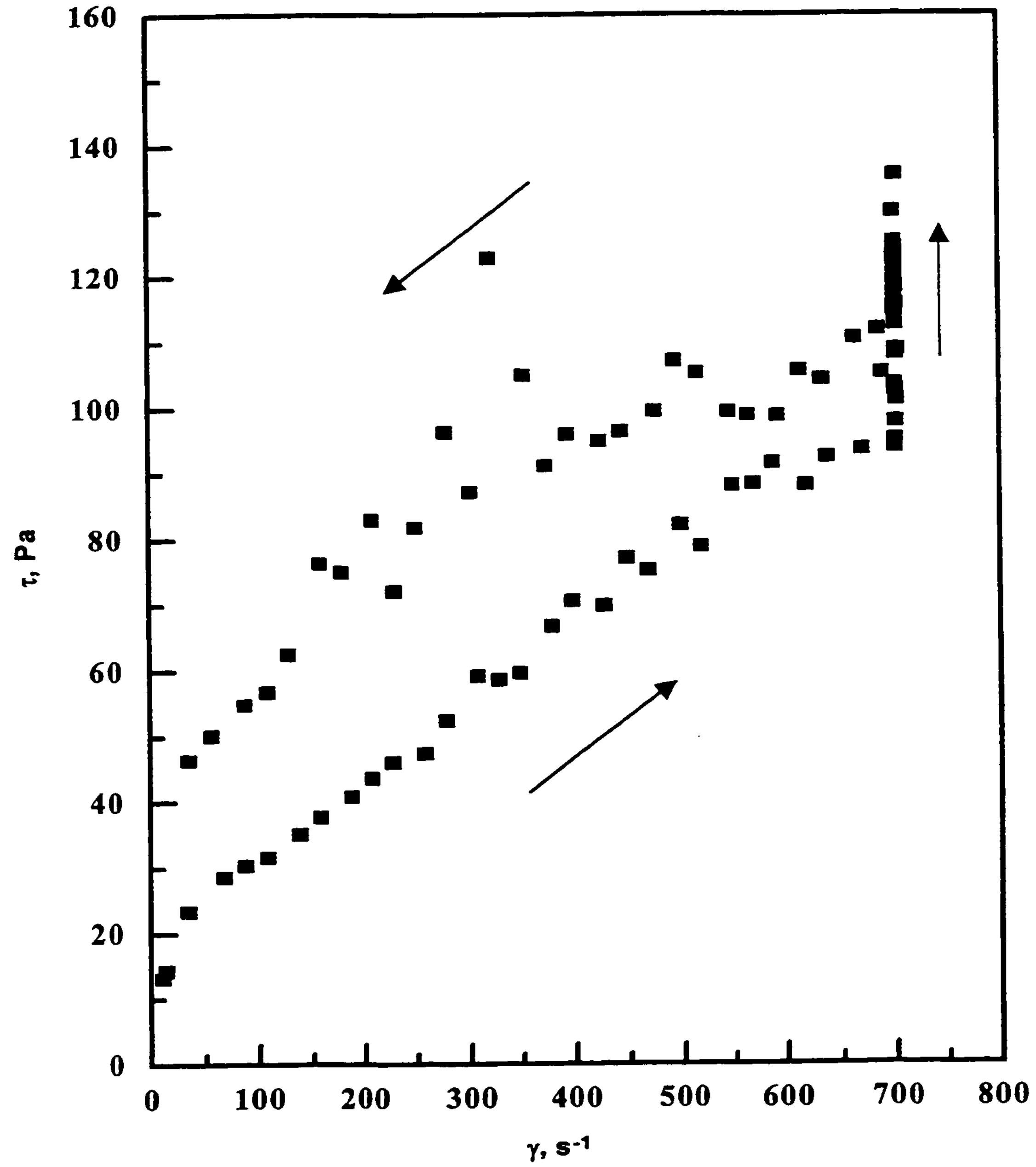


Figure 4.4.16 Second Test for 4% PAM, (Up-Time-Down Curves) at 60s

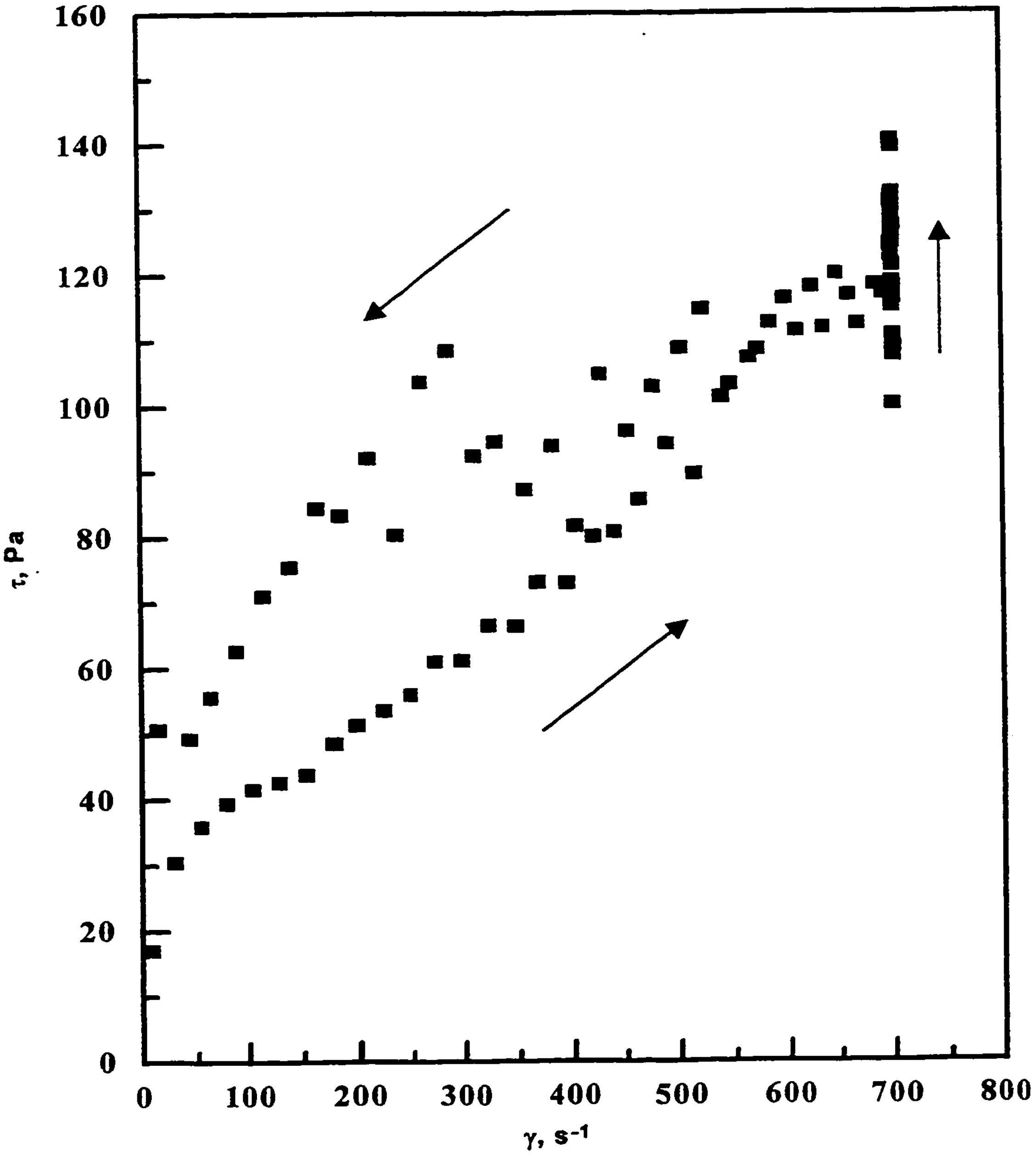


Figure 4.4.17 Second Test for 4% PAM, (Up-Time-Down Curves) at 120s

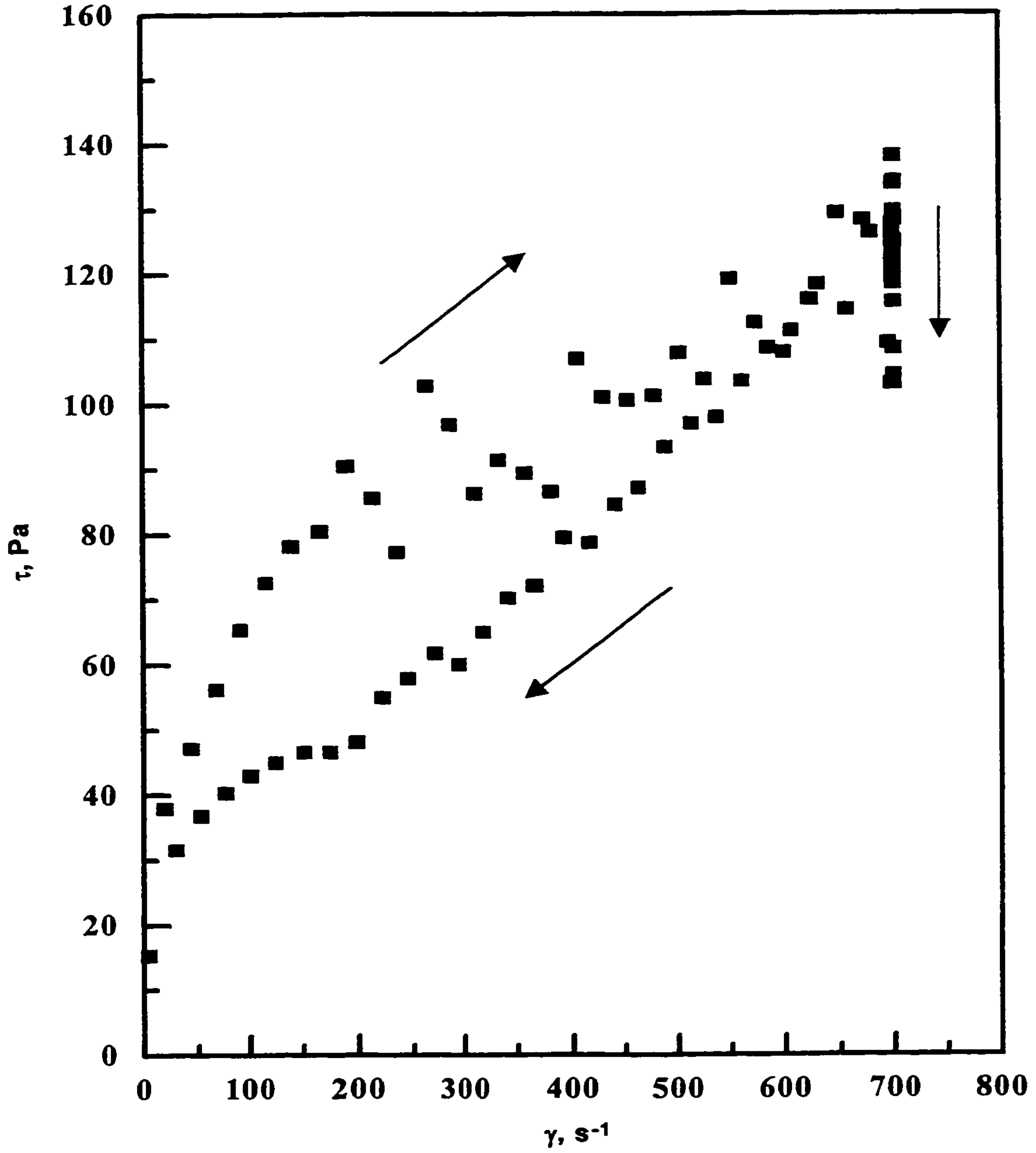


Figure 4.4.18 Second Test for 4% PAM, (Up-Time-Down Curves) at 180s

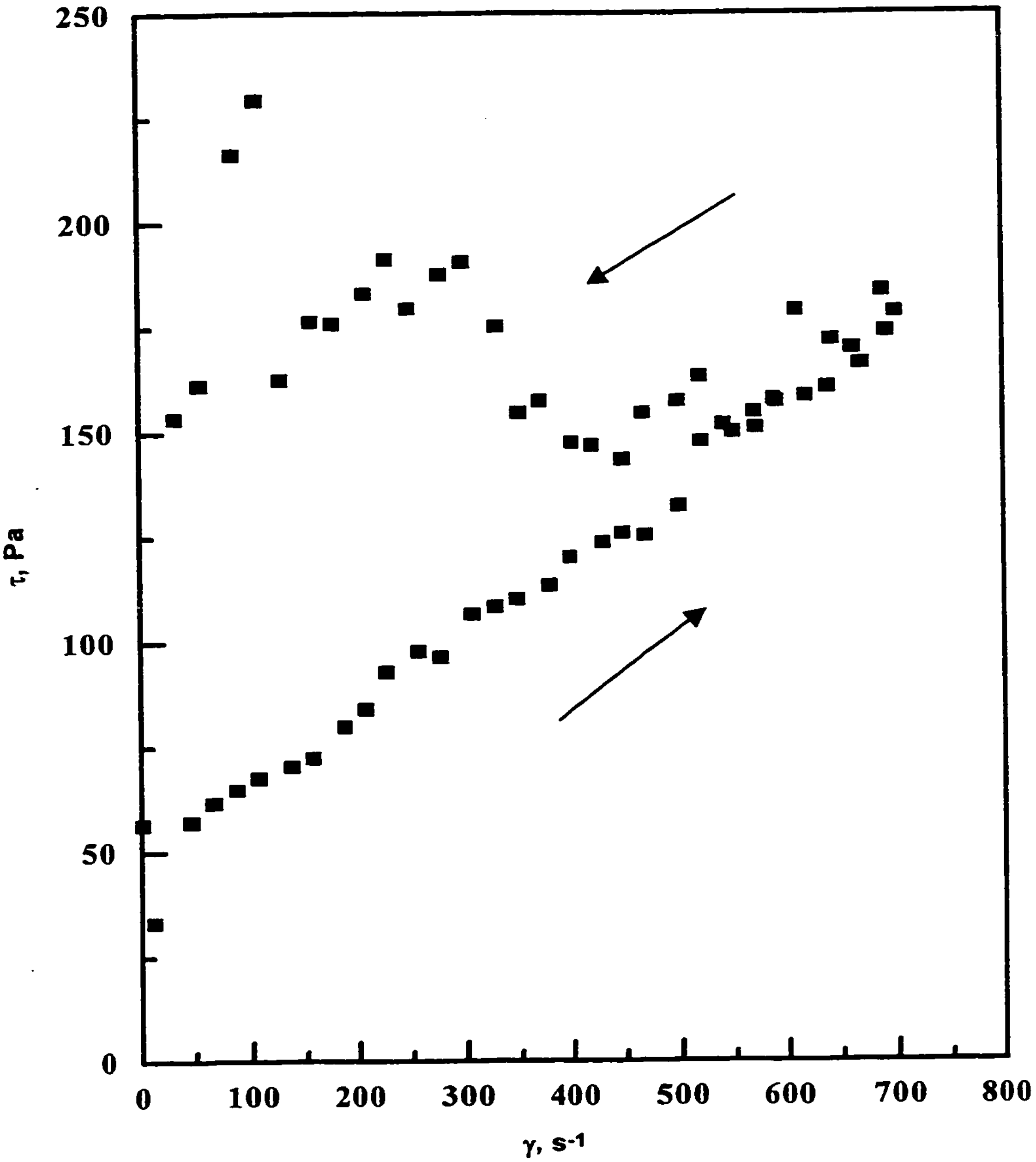


Figure 4.4.19 First Test for 5% PAM, One Cycle at 60s

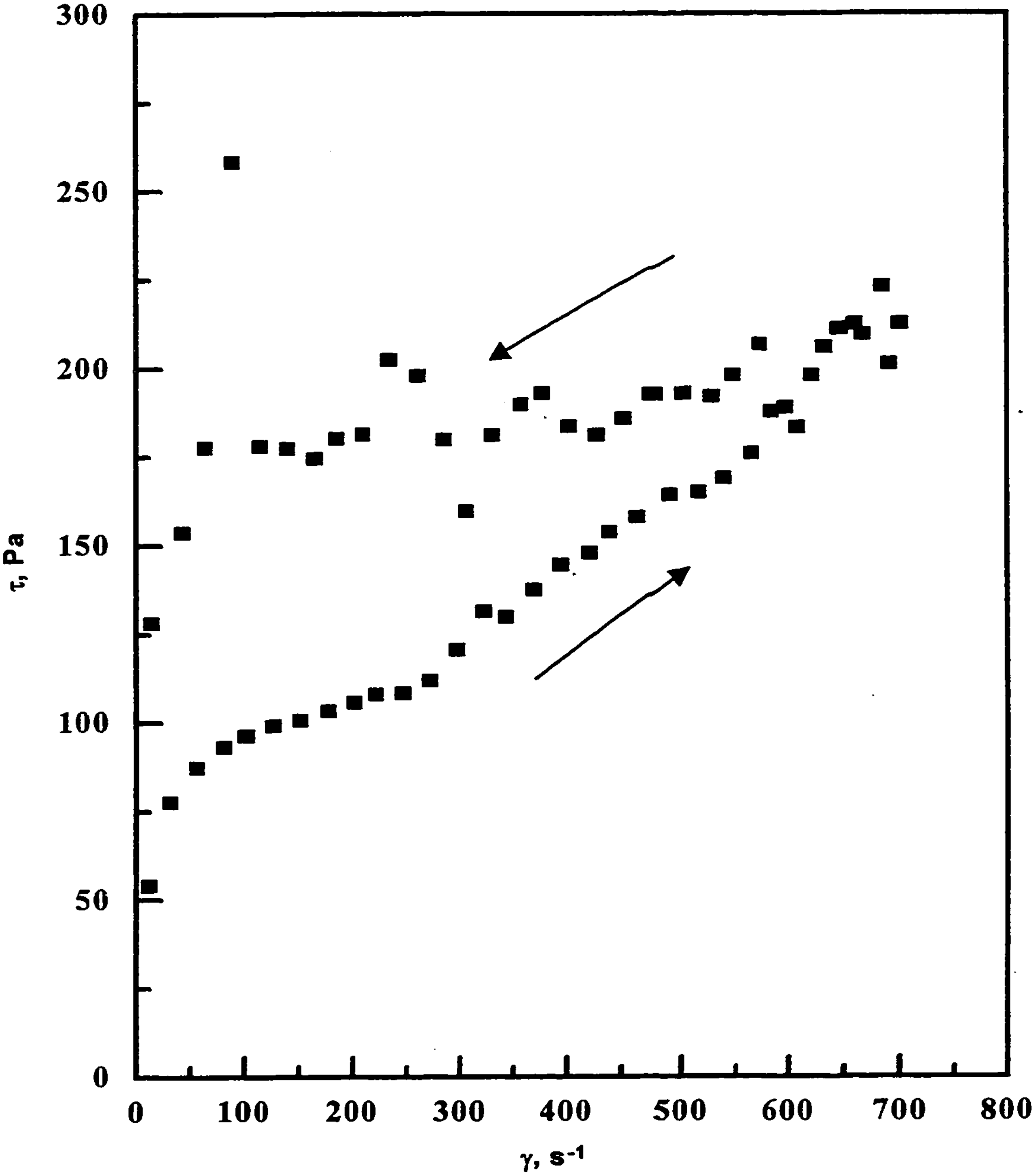


Figure 4.4.20 First Test for 5% PAM. One Cycle at 120s

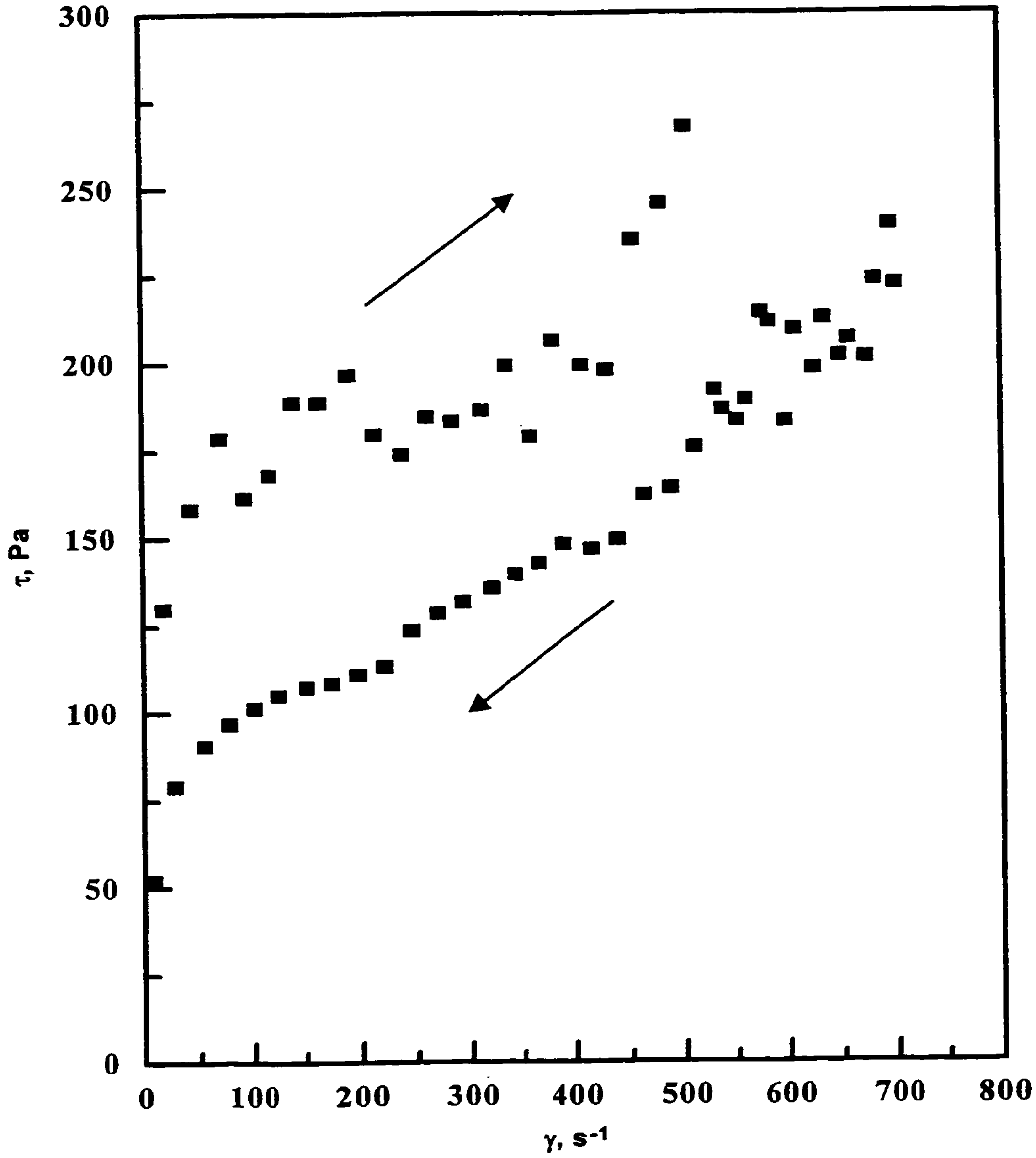
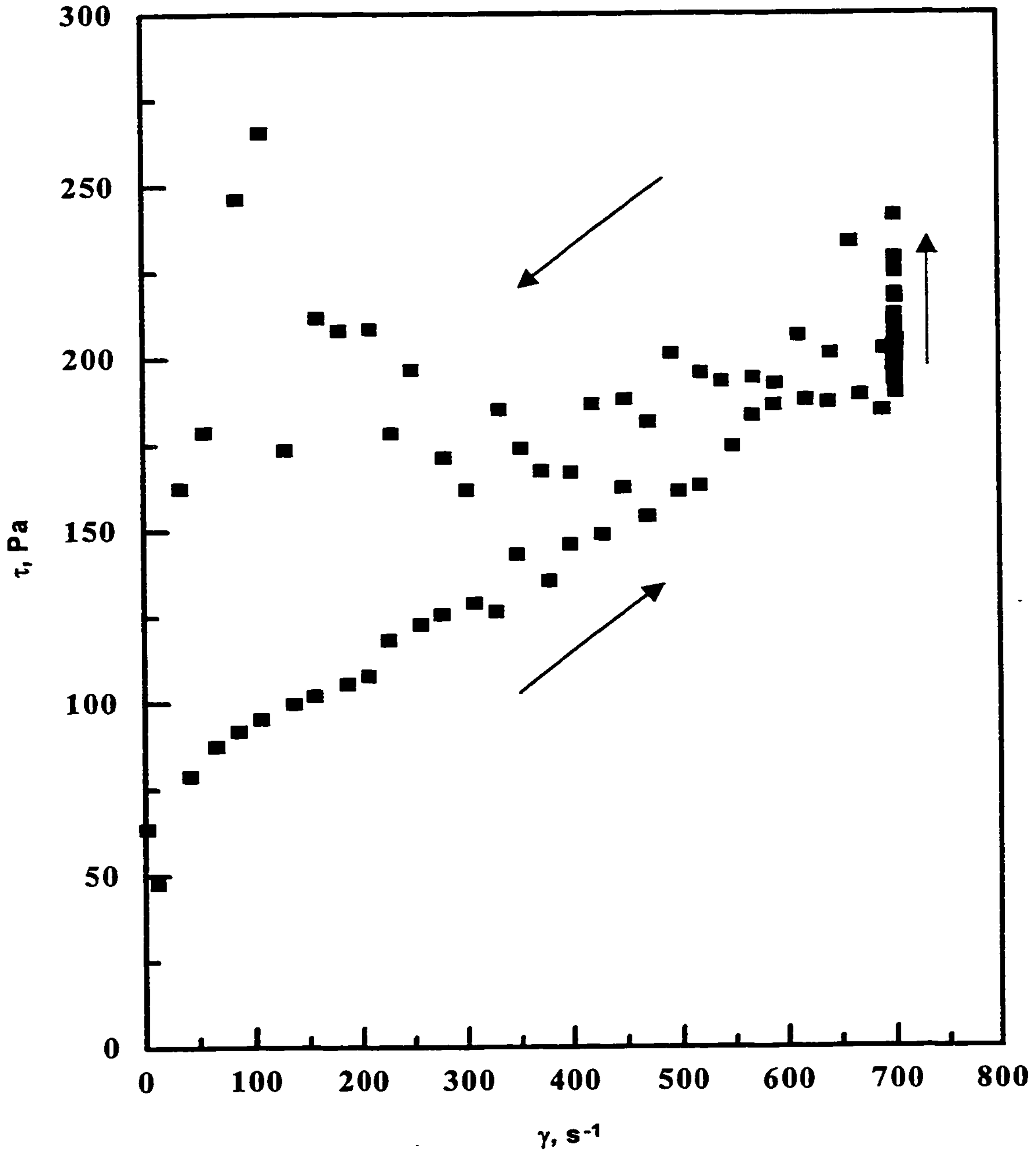


Figure 4.4.21 First Test for 5% PAM, One Cycle at 180s



Figue 4.4.22 Second Test for 5% PAM, (Up-Time-Down Curves) at 60s

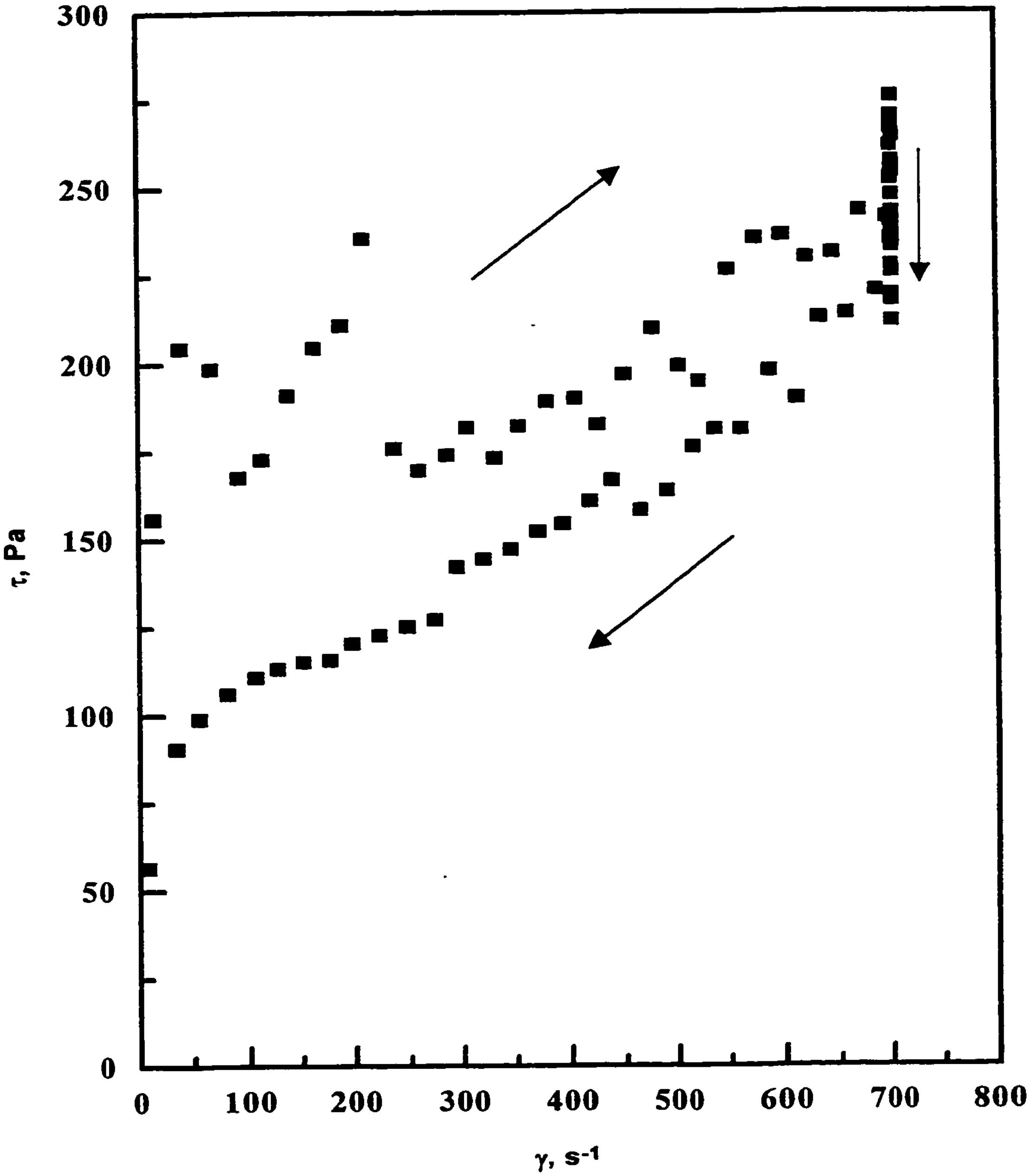


Figure 4.4.23 Second Test for 5% PAM, (Up-Time-Down Curves) at 120s

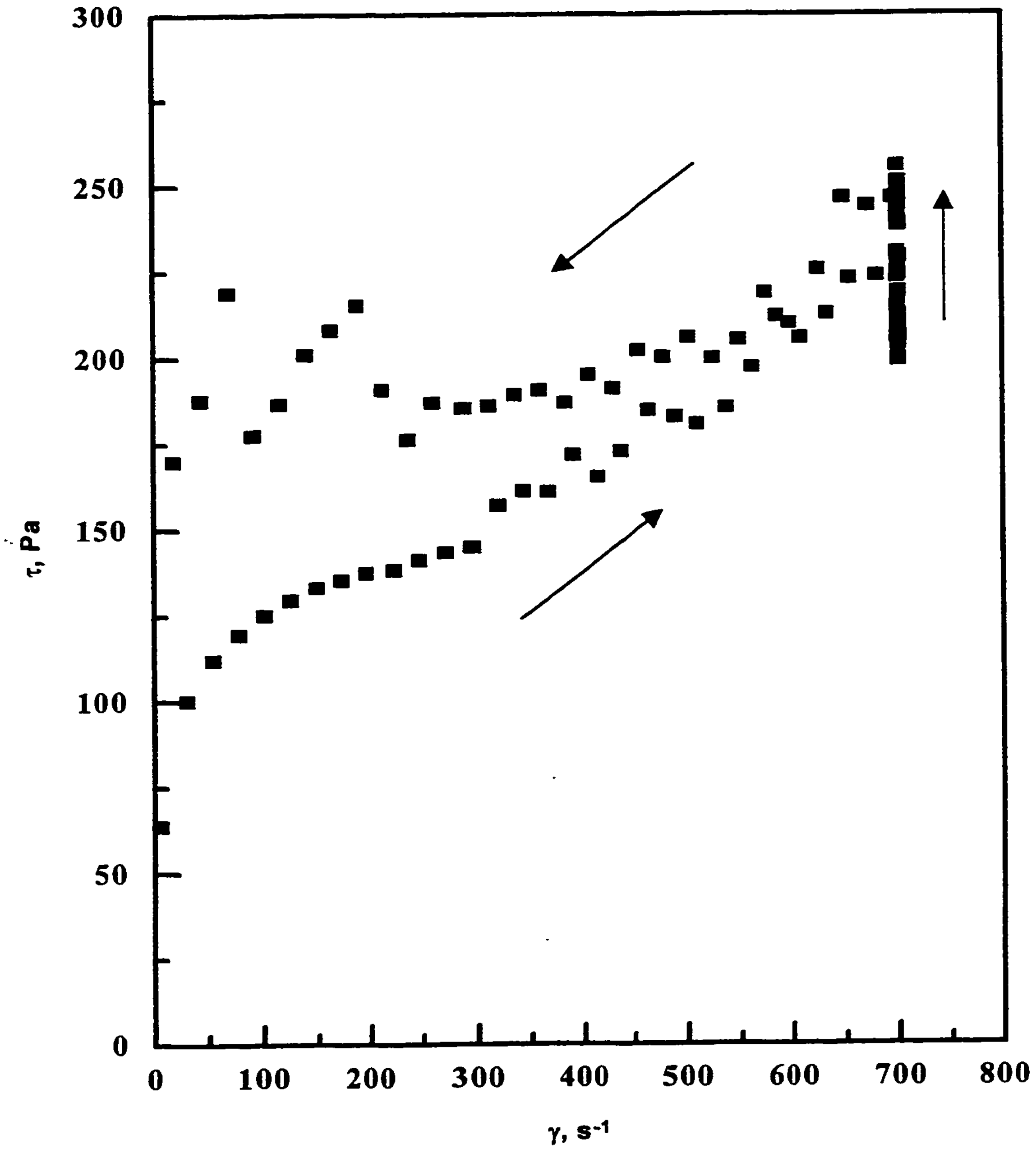


Figure 4.4.24 Second Test for 5% PAM, (Up-Time-Down Curves) at 180s

## 4-5: Creep-Recovery test:

The creep-recovery test can be performed to investigate the viscoelastic response of a material. Viscoelasticity is a combination of viscosity and elasticity. In general, the term viscoelastic refers to a material that exhibits viscous and elastic properties. This kind of material has an element of flow in its response to an applied stress, and the extent of this flow varies with time. Materials that exhibit viscoelastics behavior have long chain molecules which, at rest, loop and entangle with each other at a minimum energy state. At a constant stress, these materials do not hold at a constant deformation, and their molecules stretch thereby increasing the bond vector angles and raising their original energy. When applied stress is removed, they do not react like viscous materials (no recovery), but instead, recover some of their deformation. In addition, their molecules try to return to their original energy state. The deformation response, in the viscoelastic material to an applied stress, is a function of time. Initially, the network of molecules undergoes deformation within the mechanical limits of the network. Continuous deformation leads to the dismantling of the network, and the liquid starts to flow.

Viscoelasticity is also observed in untangled solutions due to the conformational entropy of single chains. In pure elastic behavior, the deformation response to a constant shear stress is linearly linked to its value, and is maintained as long as the stress is applied. The deformation will disappear completely and simultaneously when the stress is removed. Furthermore, the total strain separates into a permanently maintained viscous part and a recovered elastic part. The proportionality of the stresses and strains may be explained as the ability of the molecular network to elastically deform, while keeping the network structure intact. Flow of highly viscoelastic material leads to so-called Vortex enhancement with a strong re-circulating region in the salient corner[27]. Rheological systems that exhibit creep show a time-dependent strain $\gamma(t)$ under a constant stress $\tau$, where:

$$\gamma(t)=\tau J(t) \qquad 4.5.1$$

Where J(t) is the time related compliance—a parameter for describing how compliant a test sample is. The greater the compliance, the easier it is to deform the sample. The compliance has units of $\mathrm{Pa}^{-1}$, and can be defined as:

$$J(t)=\gamma(t)/\tau \qquad 4.5.2$$

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 the case of linear viscoelastic range, it is required that the applied stress leads to a proportional strain response; for example doubling the stress will double the strain. From equation 4.5.2, the compliance will be independent of the applied stress when plotting the compliance curves as a function of time for different values of applied stress; the compliance curves will fall on top of each other. In the Creep-recovery test, it was important to initially define the linear viscoelastic range by applying different values of constant shear stress. Determining the linear limit of the tested sample is very important in engineering applications. The material is constant in the linear viscoelastic range and repeating the test on the same material will yield the same result, which makes it useful to be used in quality control. In the non-linear viscoelastic range, the curve representing compliance separates significantly from the curves produced in the linear range; the data obtained in the non-linear viscoelastic range is no longer constant as the material elastic structure is partially and irreversibly destroyed. The non-linear viscoelastic range can be defined as:

$$\gamma(\tau,t)=J(\tau,t)\tau \qquad 4.5.3$$

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

The benefits of creep and recovery tests are to investigate the viscoelastic response of a material, as well as checking samples for sedimentation, sagging, and slumping. For example, testing paints with different levels of stresses will indicate how thick a coat, on a vertical wall must be before this coat will start to sag off the wall. On the other hand, a paint that resists sagging will not level well on horizontal surfaces (brush marks may still be seen in many years). In this case the creep and recovery tests will be very useful for the conflicting requirements of minimal sagging and maximum leveling.

In order to investigate the viscoelastic response of polyacrylamide solutions, creep-recovery experiments were conducted by applying a constant known value of shear stress to the sample using rheometer RS100 that has an almost frictionless air bearing for its rotor shaft. This feature is extremely important to the creep-recovery test. The stress in the recovery phase of this test must be set to zero for full recovery to reach a final permanent strain level. For creep-recovery tests, constant shear stresses were carried out instantaneously for 300s on the samples. Following this period of time, the applied stress was brought instantaneously to zero. The obtained data was plotted in form of compliance-time. Figure (4.5.1) shows the creep and recovery test for 2% PAM solution at different values of applied stresses. The compliance curves for stresses 0.3, 0.4, and 0.5 Pa fall on top of each other indicating that the sample is in linear viscoelastic range. However, when the stress goes up to 1.0 Pa the compliance curve starts to deviate from the other curves. This indicates the dependence of compliance on the shear stress which means the tested sample is in non-linear viscoelastic range. In figure (4.5.2), the solutions of 3% PAM still behaves like a viscoelastic material with an increase in compliance. The linear viscoelastic range for this concentration was 3.0, 3.5, and 4.0 Pa. At 4.0 Pa, the compliance curve deviated from the other curves, which means the sample is in non-linear viscoelastic range. In figure (4.5.3), the compliance curves of 4% PAM under the stresses 6.0, 6.5, and 7.0 Pa fall on top of each other which demonstrates that the sample is in linear range. The non-linear range for 4% PAM started at 7.5 Pa. Figure (4.5.4) shows the creep and recovery results for the 5% PAM solutions. In the creep phase, there is a linear viscoelastic range for the stresses 8.5, 9.0, and 9.5 Pa; however, there is a non-linear viscoelastic range as well which started at 10.0 Pa. In the recovery phase, the response shows a viscoelastic behavior.

Illustrated in the figures mentioned above, polyacrylamide solutions behave like viscoelastic material in all concentrations. The viscous part is always higher than the elastic part in all tested samples. For polyacrylamide solutions, the higher the concentration the lower is the compliance.

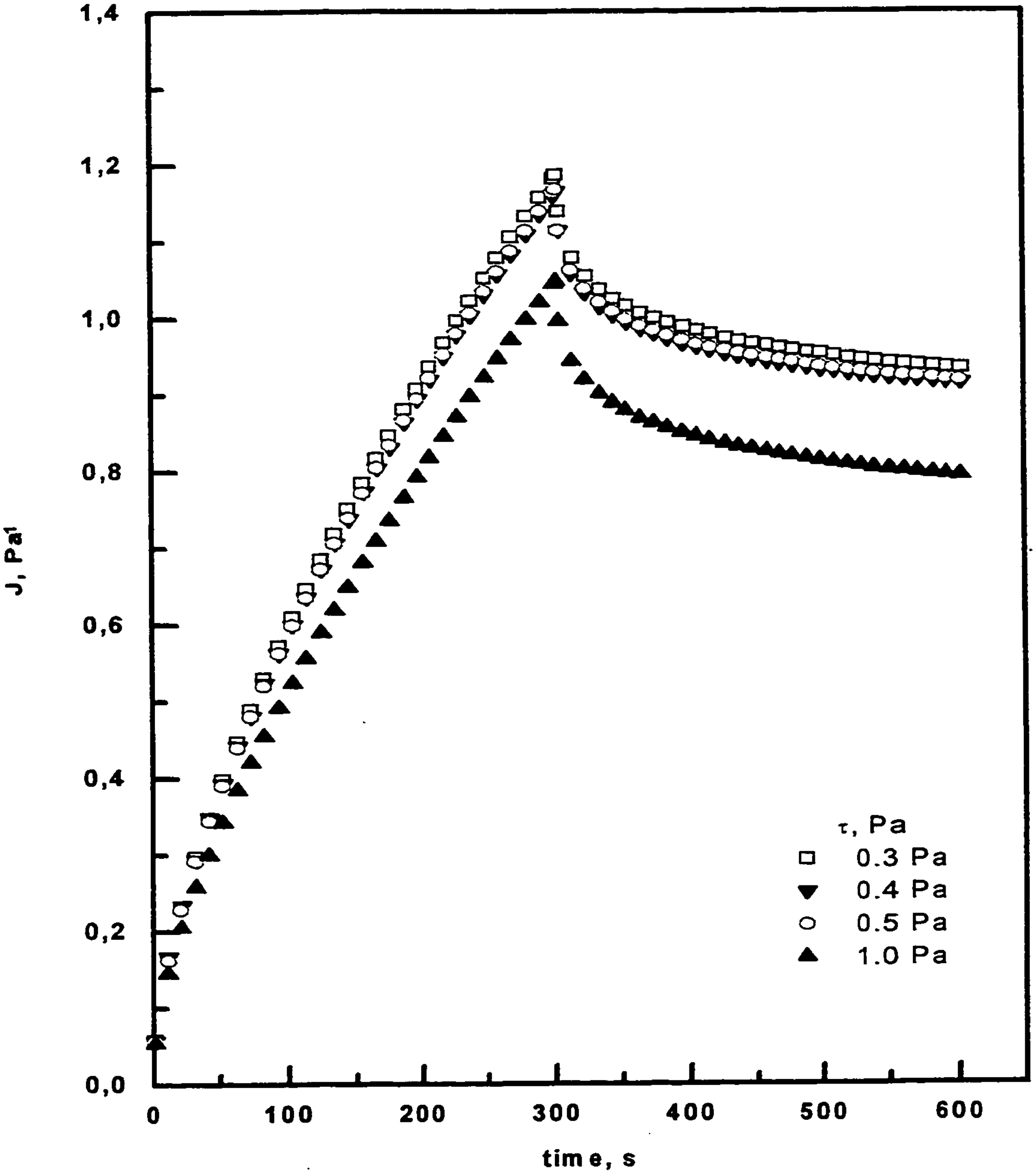


**Figure 4.5.1 Visco-elastic Response of 2% PMA.**

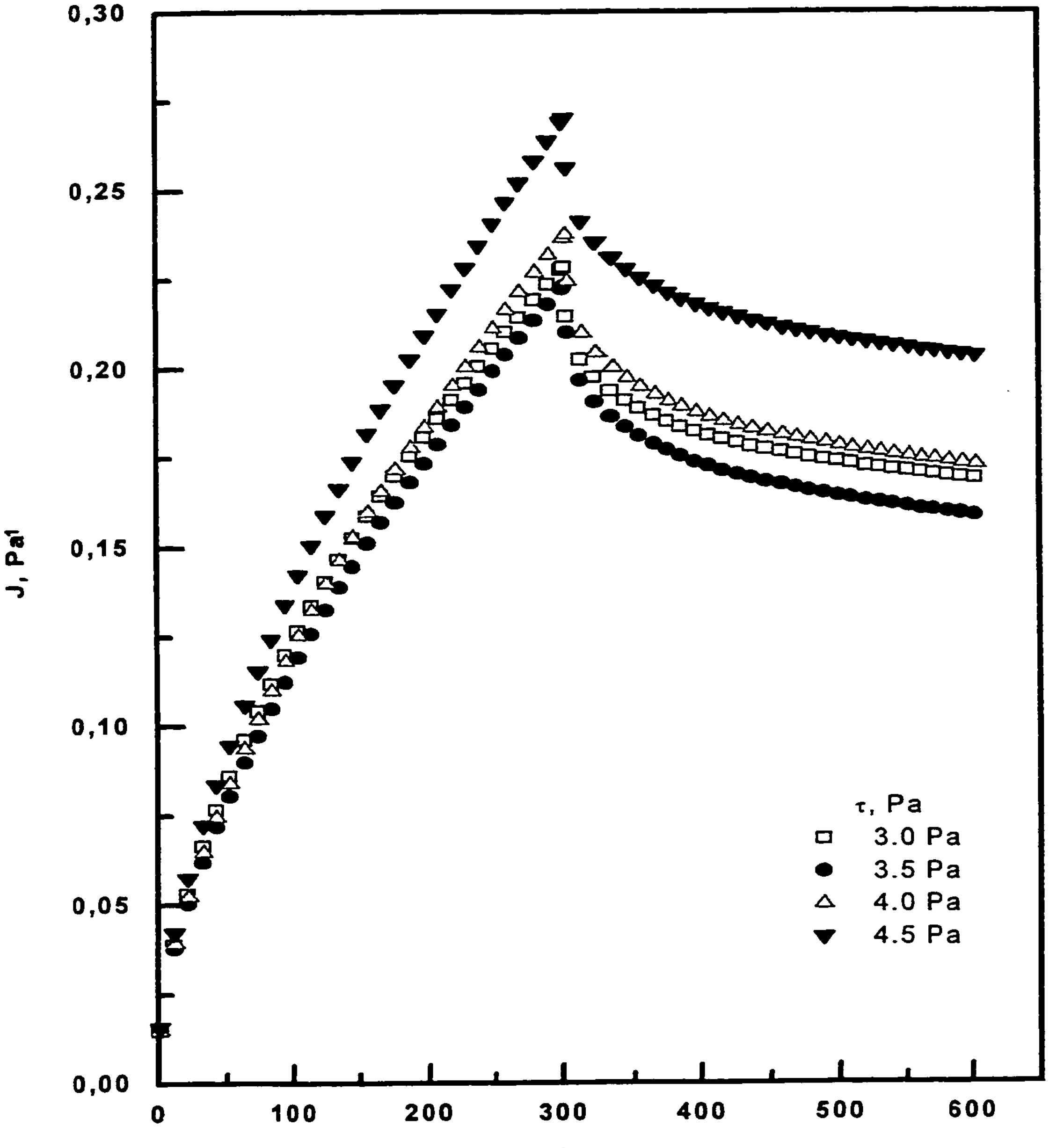


Figure 4.5.2 Visco-elastic Response of 3% PMA

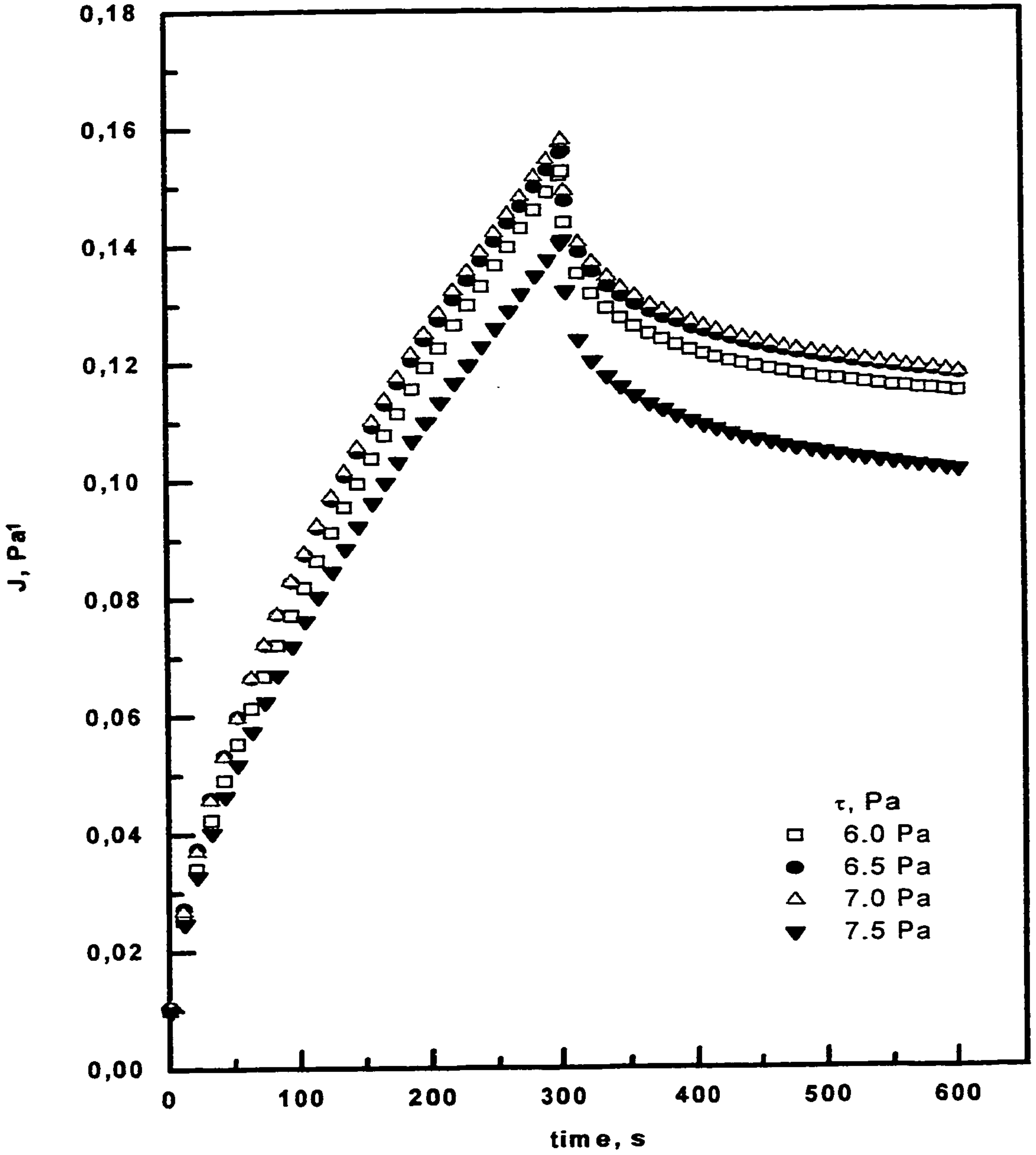


**Figure 4.5.3 Visco-elastic Response of 4% PMA**

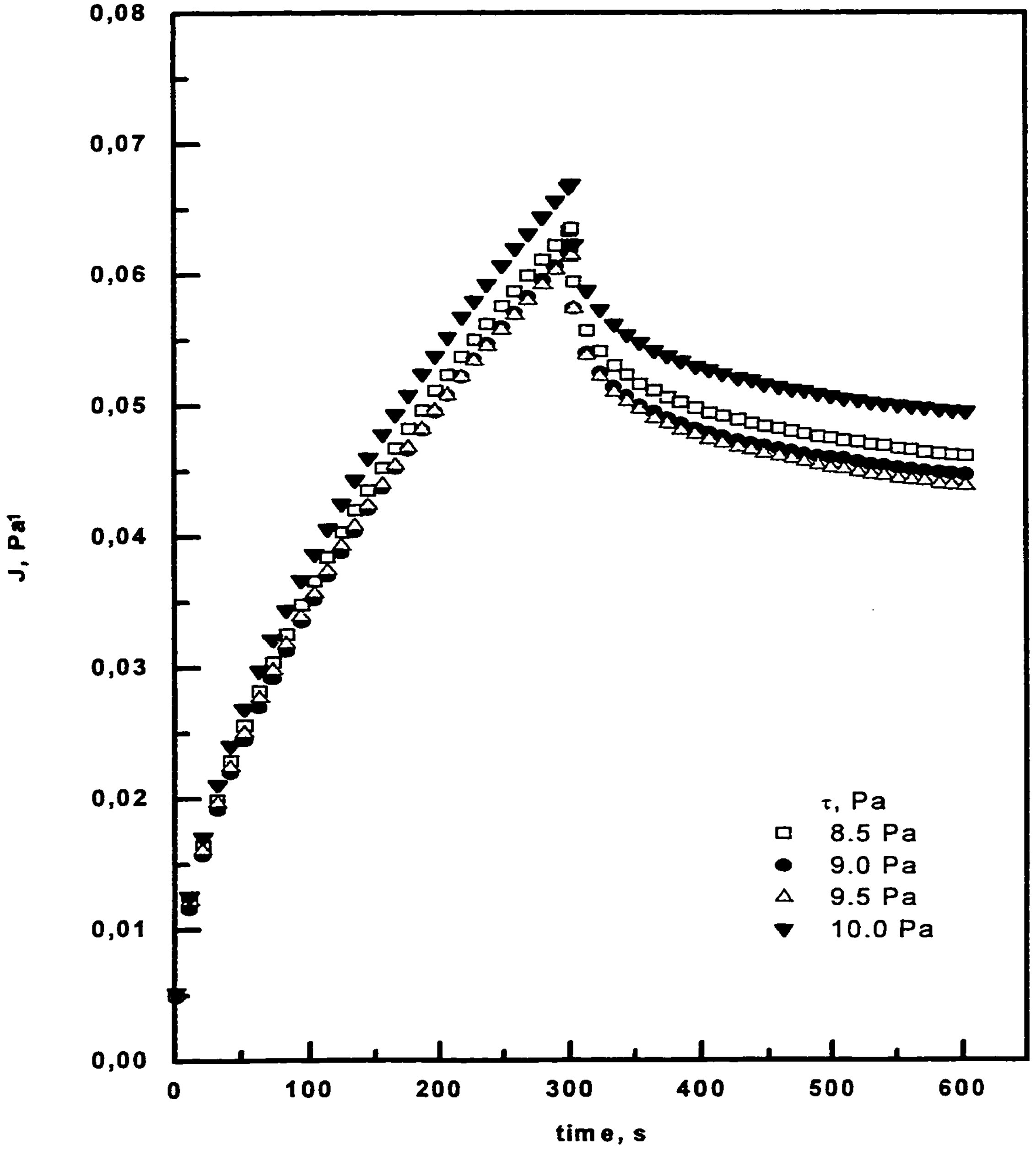


Figure 4.5.4 Visco-elastic Respose of 5% PMA

## 4-6: Dynamic test:

The dynamic test is another tool for the rheological study of viscoelastic behavior. The approach taken in the dynamic test to study the viscoelastic behavior is different from the approach of the creep-recovery test. Both tests complement each other because some features of viscoelasticity are better described in a creep-recovery test and others in a dynamic test. In a dynamic test, instead of applying a constant stress, which leads to a steady state flow, an oscillating stress or oscillating strain is applied with an assigned frequency and amplitude. In a rheometer, such as RS100 in the controlled stress (CS) mode, the stress may be applied as a sinusoidal time function.

$$\tau = \tau_0 . \sin(w.t) \qquad 4.6.1$$

Where $\tau_0$ is the amplitude or maximum stress.

$w$ represents the angular velocity.

In the dynamic test, the upper plate or the cone is no longer turning continuously in one direction, but it is made to deflect with a sinusoidal time function alternatively at a small angle to the left and to the right. The tested sample is placed in a similar sinusoidal function causing resisting stresses in the tested sample. Those stresses follow a sinusoidal pattern, the amplitude of which reflects the nature of the tested sample.

Dynamic test provides data on viscosity and elasticity related to their time response. By measuring how the stress behaves as a function of time, the magnitude of the elastic and viscous components of the material can be readily evaluated. The elastic part is called the storage modulus $G'$, and it indicates that the stress energy is temporarily stored during the test, but that it can be recovered afterwards. The viscous part is called the loss modulus $G''$, and it hints at the fact that the energy which has been used to initiate flow is irreversibly lost having been transformed into shear heat. The total resistance of a substance against the applied strain is called complex modulus $G^*$, which is defined as:

$$G^* = {}^{\tau_0}\!/_{\gamma_0} \qquad 4.6.2$$

Where:

$\tau_0$ is the stress magnitude.

$\gamma_0$ is the strain magnitude.

Or as:

$$G^*(w) = G'(w) + G''(w) \qquad 4.6.3$$

In purely viscous materials, the stress follows the rate of the deformation. This means that in an oscillatory flow the viscous parts of the rheology will respond totally out of phase, and the phase difference between stress and strain is equal to 90°.

$$G' = 0, \qquad G'' = G^*.$$

In purely elastic materials the stress depends on the deformation. This means that in an oscillatory flow the elastic parts of the rheology will respond totally in phase with the oscillation, and the phase difference between stress and strain is equal to zero.

$$G'' = 0, \qquad G' = G^*.$$

Alternatively to the complex modulus $G^*$, one can define a complex viscosity $\eta^*$ as:

$$\eta^* = G^* \big/ w = \left( \tau_0 \big/ \gamma_0 \right) w. \qquad 4.6.4$$

It describes the total resistance to a dynamic shear. To determine the linear viscoelastic range in a dynamic test, stress sweeps are performed at a fixed frequency. The stress is automatically increased to cover a wide range. The linear viscoelastic range is the range where $G^*$ is constant with the stress $\tau$. At a higher stress, the sample structure is deformed to the point that the internal temporary bonds are destroyed. Shear thinning will take place and a major part of the introduced energy will irreversibly be lost as heat. In the linear range of viscoelasticity, the relevant equations are linear differential with constant coefficients.

Dynamic tests must start with a stress sweep to determine the linear viscoelastic range; then, further tests can be performed to determine features of the viscoelastic behavior.

Polyacrylamide samples have been subjected to stress sweep at a fixed frequency of 0.1 Hz, and the linear viscoelastic range has been found to be in the neighborhood of 4 Pa, as shown in figure (4.6.1). The rheological properties of a series of PAM solutions in the range of 2 -5% have been measured by means of using the oscillatory shear rheometer with cone and plate geometry in the frequency sweep from 0.01 to 10 Hz. Figures (4.6.2-4.6.3-4.6.4,and 4.6.5) reveal the storage modulus $G'$, and loss modulus $G''$ for 2 - 5% PAM. For concentrations 2, 3, and 4%, the storage and loss modulus values increase as a result of increasing the concentrations and frequency. However, the loss modulus in comparison to the storage modulus is more predominant up to a critical frequency; the value is the same for each concentration. Above the critical frequency, the three concentrations behave like pure viscous material ($G' = 0$). For the concentration 5 %, the frequency responsible for the elastic behavior increases; however, the viscous and elastic parts are nearly equal. This conclusion is in good agreement with the behavior of the creep recovery test. The complex viscosity of PAM solutions is shown in figure (4.6.6).

Two different behaviors can be recognized. First it is clear those polyacrylamide aqueous solutions in concentrations between 2 - 5% exhibit strong shear thinning behavior up to the critical frequency. Their complex viscosity decreases steadily with an increase in frequency. Secondly at a frequency higher than the critical one, polyacrylamide solutions of 2, 4, and 5 concentrations show shear thickening behavior. Above the value of critical frequency, the complex viscosity increased with frequency. The shear thickening phenomenon can be explained as the following: the effect of simple flow reduces the number of interactions associated with low frequency, leading to shear thinning at a sufficient high frequency. In addition, individual chains stretch and generate inter-chain bonding by coagulation leading to shear thickening and strong flow birefringence. It can also be explained that, at high frequency, polymer degradation leads to the rupture of the molecular chain causing reduction in the chain length. At a higher frequency, connection between chains might occur leading to shear thickening behavior. Steady shear viscosity or dynamic viscosity can be used for polymer fluids characterization. Similarities between steady shear viscosity and dynamic viscosity exist as reflected by:

$$\lim_{\gamma \to 0} \eta(\gamma) = \lim_{w \to 0} \eta'(w) \qquad 4.6.5$$

Where:

$\eta'$ is the real component of the dynamic viscosity.

Many polymer fluids have been found to follow this relation experimentally. At a high shear rate, deviations from this relation are usually observed (i.e. $\eta'$ decreases more rapidly with $w$ than $\eta$ decreases with $\gamma$). Cox and Merz[29] found a useful empirical relationship which predicts that the complex dynamic viscosity, $\eta^*$, should be identical to the steady shear viscosity at equal values of $w$ and $\gamma$.

$$\eta^*(w) = \eta(\gamma) \qquad 4.6.6$$

Where:

$\eta^*$ is complex viscosity at frequency of $w$ (rad / s).

$\eta$ is the shear rate viscosity at shear rate of $\gamma(s^{-1})$.

By comparing the dynamic complex viscosity with shear rate viscosity, one can find that the complex dynamic viscosity is higher than the shear viscosity for all the tested concentrations.

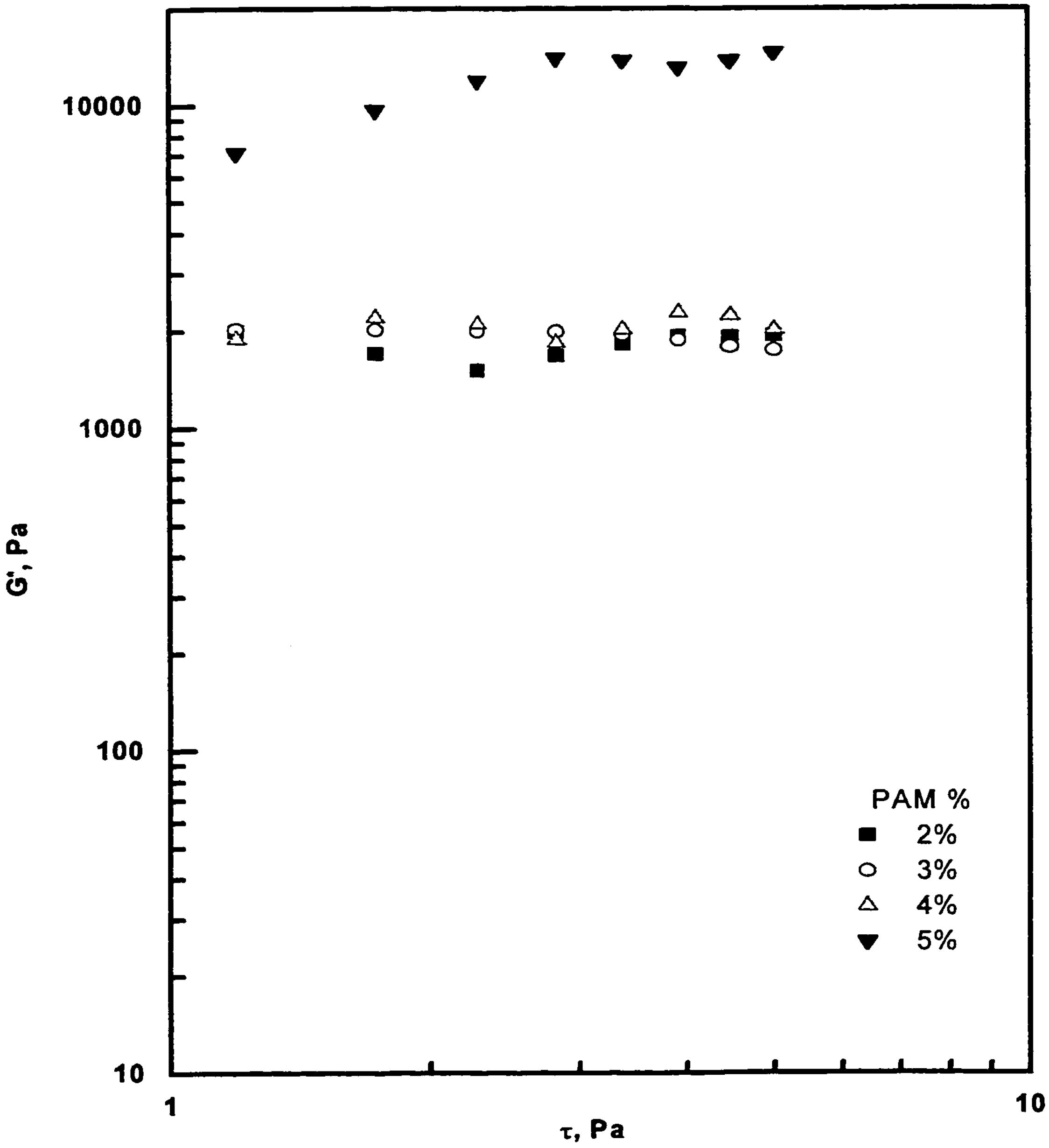


Figure 4.6.1 Dynamic linear visco-elastic range for PAM solutions.

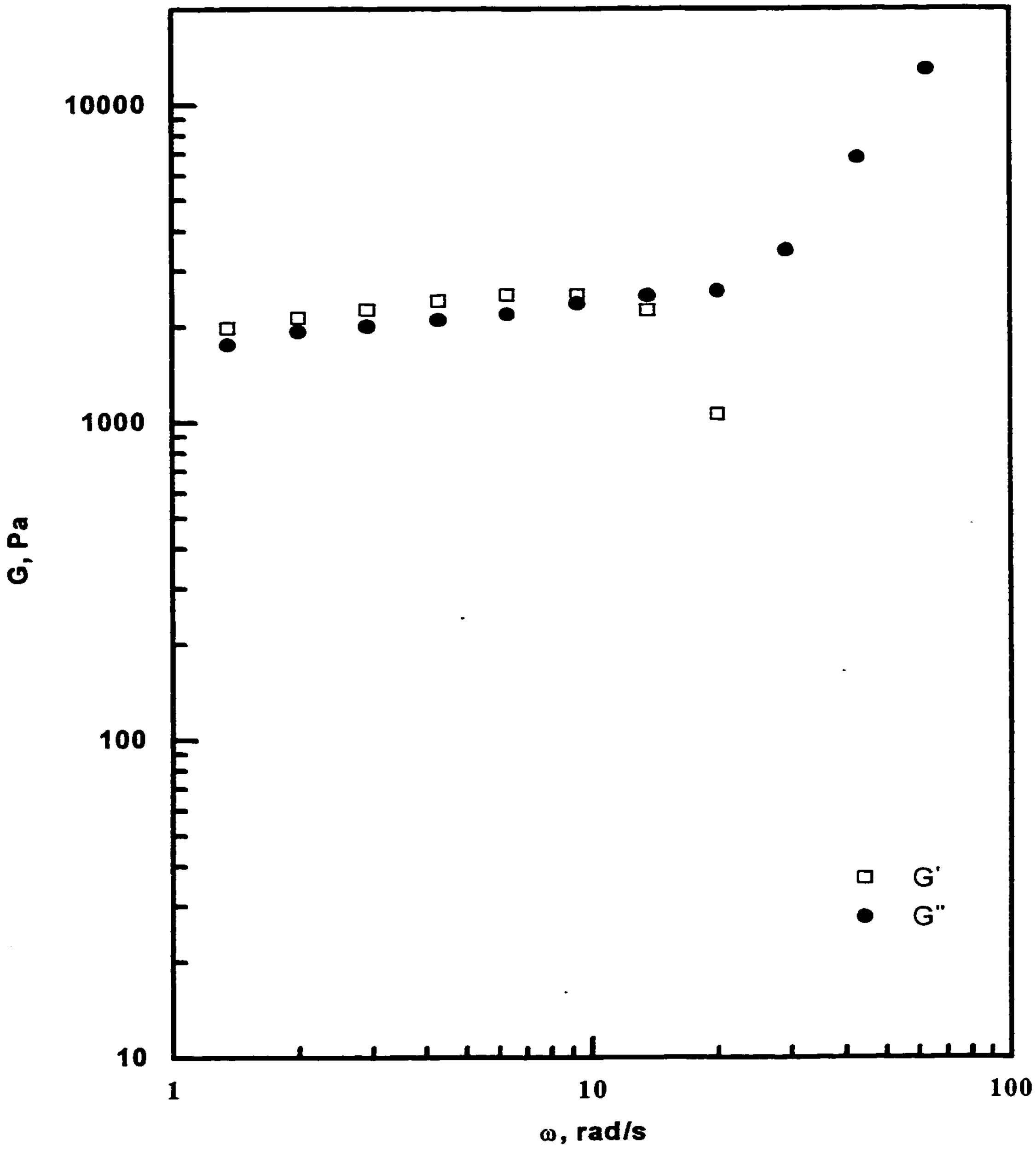


Figure 4.6.2 G' and G" for 2% PAM.

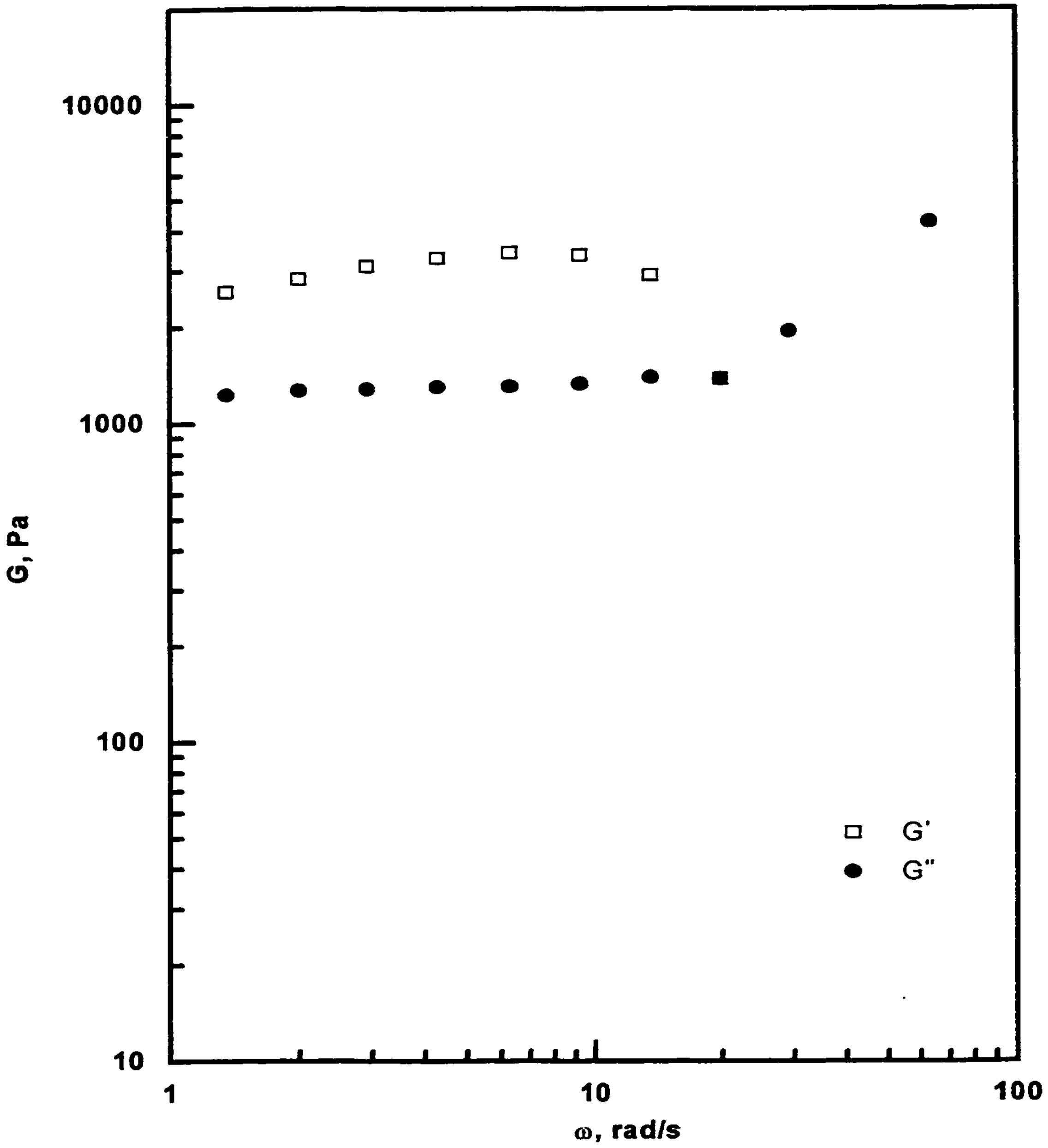


Figure 4.6.3 G' and G" for 3% PAM

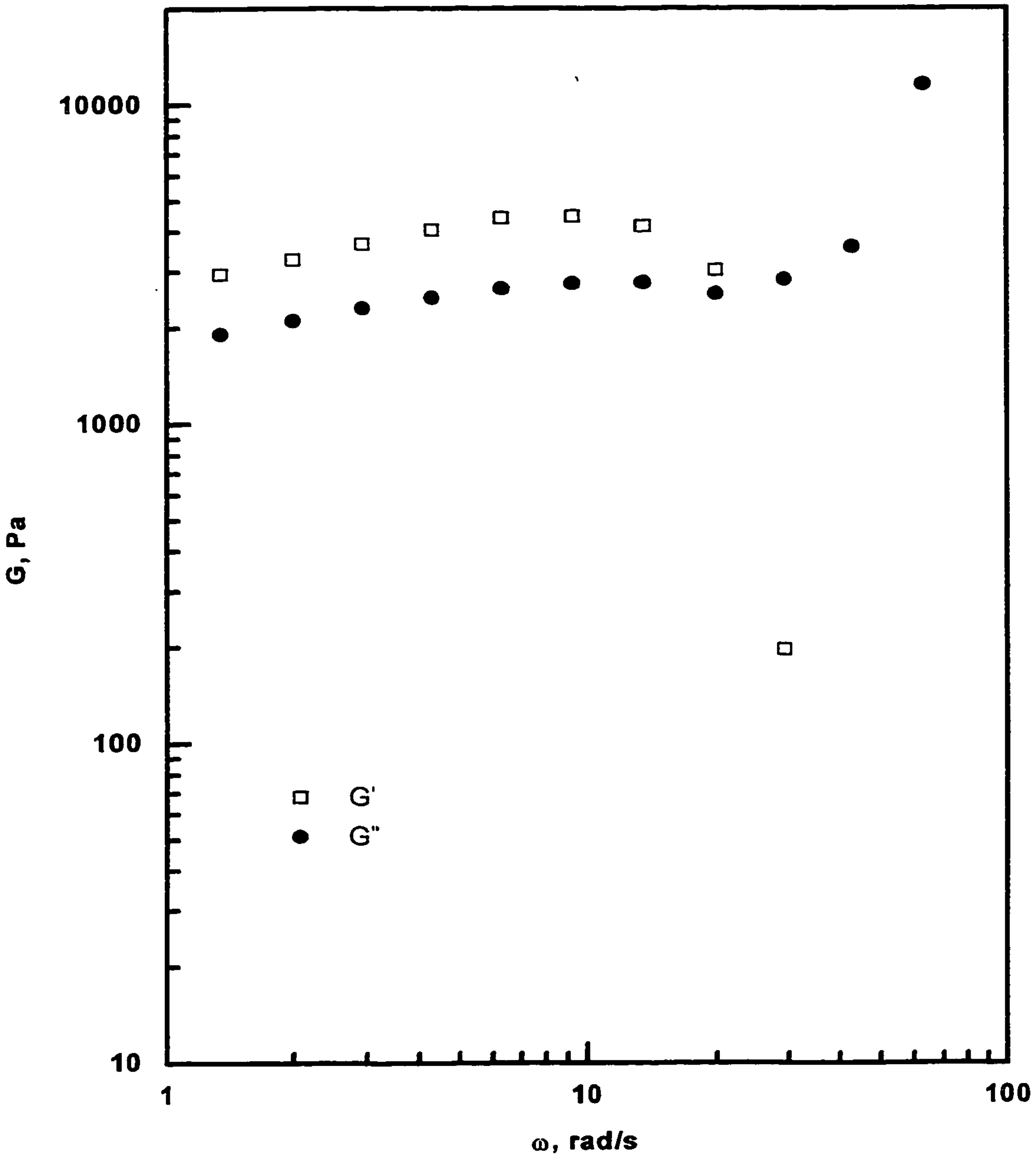


Figure 4.6.4 G' and G" for 4% PAM

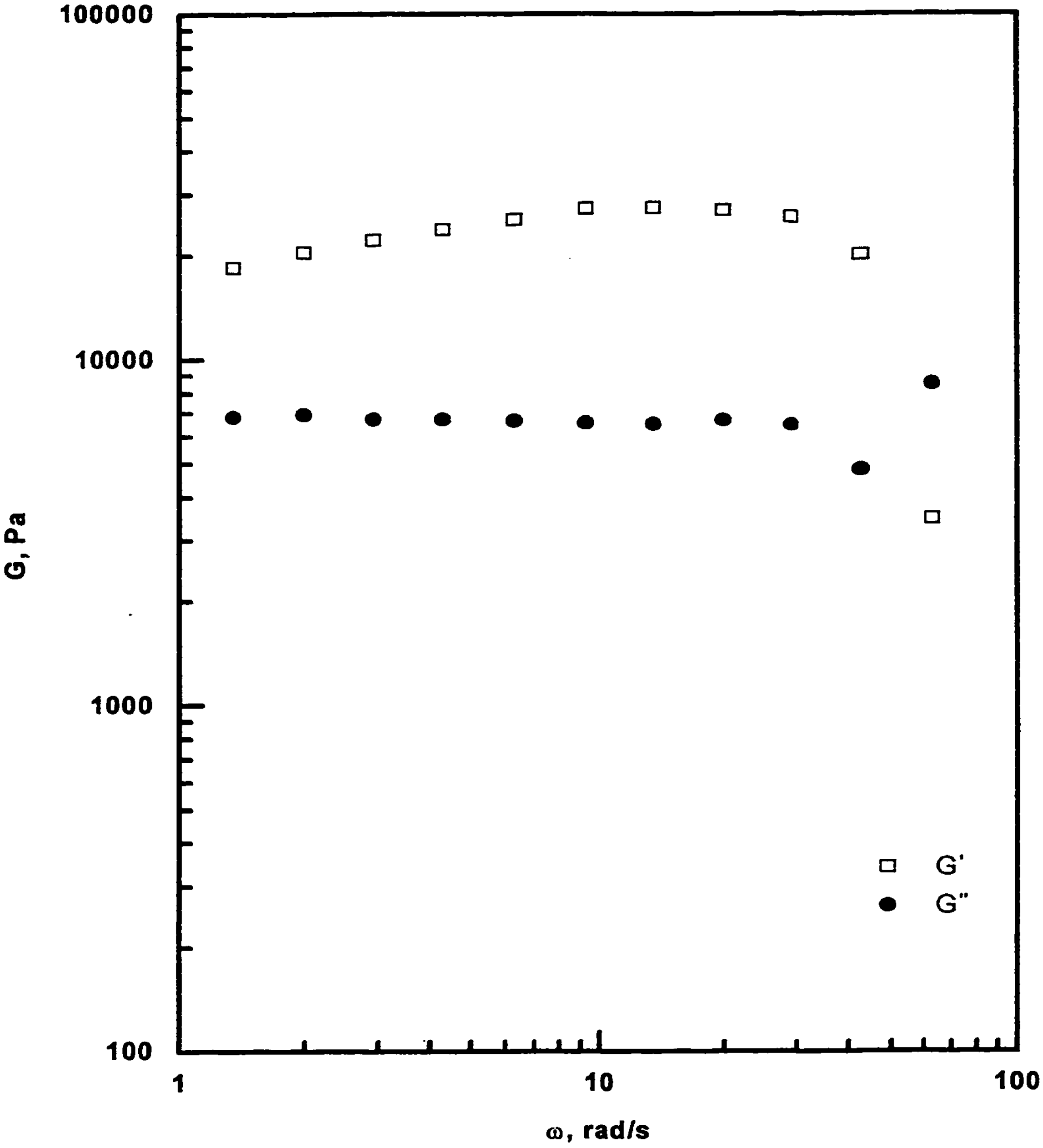


Figure 4.6.5 G' and G" for 5% PAM

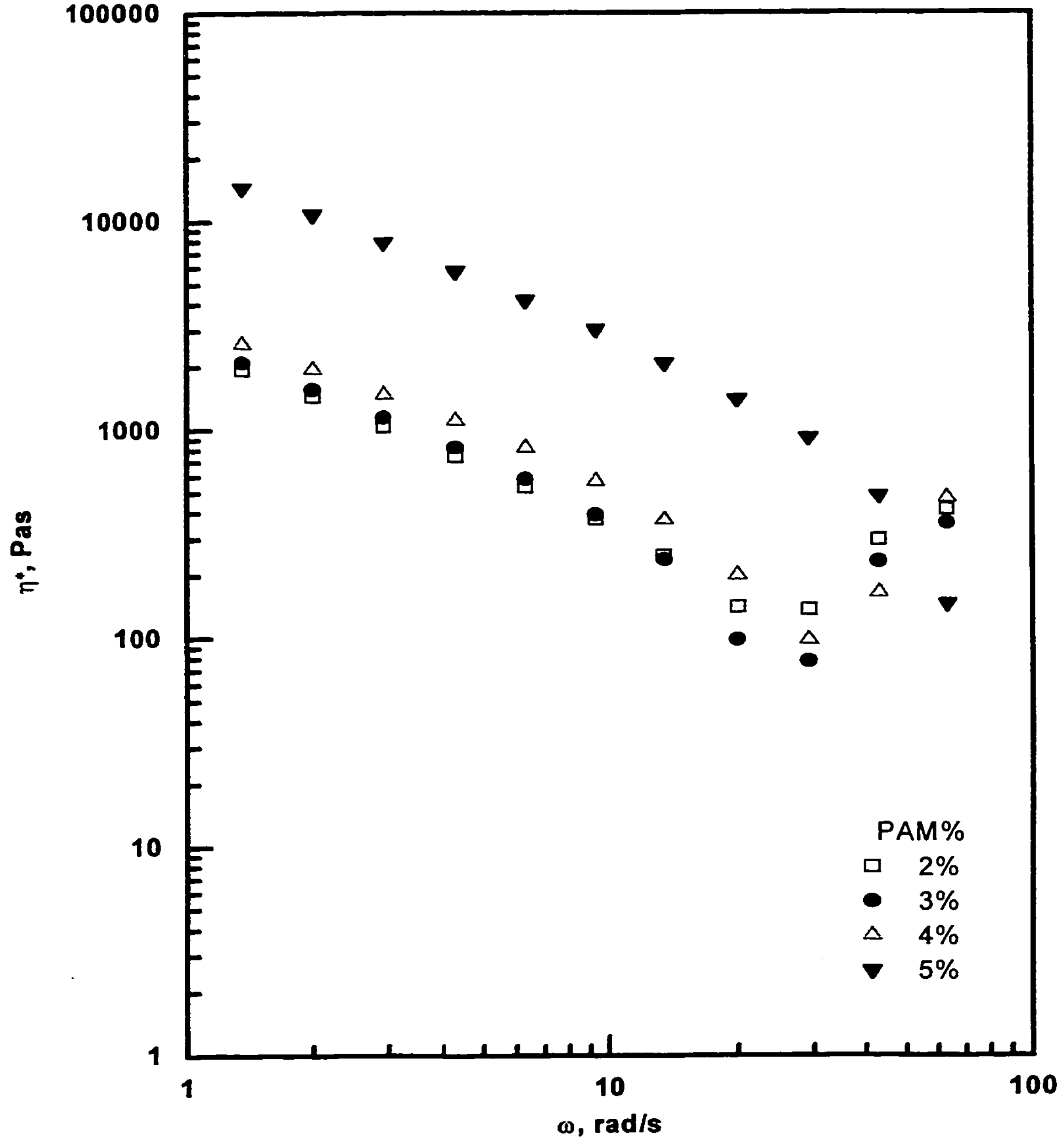


Figure 4.6.6 Complex viscosity - ferquency of PAM solutions.

# CHAPTER 5

# DISCUSSION OF RESULTS

The rheological properties of a polymer solution are the consequence of the deformation and orientation of the molecules interactions and their response to the applied stresses in the flow. The response of the polymer depends on the test condition and the value of the applied stress. In general, the rheological properties of a material are all interrelated with each other.

The first test in our study was the steady-state flow test. A nearly consistent linear pattern is recorded for the flow curves of all PAM solutions. However, there is some scatter for 2 and 3 % concentrations of polyacrylamide in the range of shear rates 100 - 130$s^{-1}$. This is due to the relatively low concentrations of there solutions. An increase in viscosity as polymer concentration increases has been observed. In this test, polyacrylamide solutions behave in different ways, either as a function of shear rate or concentration. A strong shear thinning behavior for all PAM concentrations has been shown which is the most common behavior in polymer solutions. In practice, this means that the flow encounters less resistance at higher shear rates. Polyacrylamide solutions contain long entangled and looping molecular chains which have irregular internal order that forms a high resistance against flow (higher value of viscosity). With increasing shear rates, chain type molecules in PAM solutions are disentangled, stretched, and reoriented parallel to the driving force. Molecular aligning allows molecules to slip past each other which reduces the viscosity of the polyacrylamide solution.

In the transient behavior test, polyacrylamide solutions behave in different manners, either as a function of shear rate or time. Polyacrylamide demonstrated stable behavior for time less than 15s. Beyond this time, the solutions showed both the overshoot and thixotropy phenomenon. For shear rate $500s^{-1}$, solutions gave a slight fluctuation for 3 and 4% concentrations and high fluctuation for the 5% concentration.

In the yield stress test, the solutions exhibited yield stress which became more significant for higher concentrations. When the applied stress exceeded the yield stress value, an unlimited deformation ensued and the material started to flow. In this case, the applied stress was proportional to the rate of deformation, with viscosity as the proportionality factor. All polyacrylamide solutions showed a cycle of up and down curves. This cycle was found to increase according to the concentration.

The thixotropy test is used to investigate time dependence of a material. The time dependent behavior results from reversible changes in fluid structure. The results of this behavior have shown that polyacrylamide exhibits three different behaviors—thixotropy, antithixotropy, and time-dependent. In general polyacrylamide, gave weak time-dependent behavior.

While thixotropy deals with similar effects as viscoelasticity, the relative position of both approaches comes into question. Thixotropy is related to viscosity only while viscoelasticity is related to viscosity and elasticity. On the other hand, the time scale of thixotropy seems not to be necessarily associated with time scale for viscoelastic relaxation. For non-linear viscoelastic, not only does the microstructure take time to respond to the flow, but it is also changes by the flow, and this change will itself take time. This is the essential difference between linear viscoelasticity and thixotropy. Both are time effects; the former is in the linear region where the structure responds but remains unchanged, while the latter takes place in the non-linear region where the structure is broken down by deformation as well as responding to it. Thixotropy is always to be expected from any shear thinning mechanism. However, thixotropy becomes significant when the time scale over which it is seen becomes significantly longer than the response times of instruments used to measure rheology or longer than some flow time in a process (e.g., the average time a liquid takes to flow through a pipe).

In the creep-recovery test, it was important to initially define the linear viscoelastic range by applying different values of constant shear stress for a period of time. When the applied stress is removed, the total strain separates into a permanently maintained viscous part and a recovery elastic part. The results showed that all concentrations of polyacrylamide solutions behave like viscoelastic material, and the linear viscoelastic range for all concentrations has been determined. The viscous parts were higher than the elastic parts, agreeing well with the results obtained by the dynamic test.

In the dynamic test, there was a decrease in dynamic viscosity as frequency increased up to critical value which was almost equal for all concentrations except the 5% concentration; it showed shear thinning only. Above this value, the viscosity started to increase as frequency increased indicating the shear thickening behavior. In comparing dynamic viscosity with shear viscosity one will find that the dynamic viscosity is higher than shear viscosity for all concentrations. The concentrations 2, 3, and 4% showed that the loss modulus is higher than storage modulus up to critical frequency. Above this frequency, the three concentrations behave like pure viscous material. For concentration 5 %, the viscous and elastic parts are almost equal.

# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

## 6-1 Conclusion:

An experimental study has been conducted to examine the rheological properties of aqueous polyacrylamide solutions of weight concentrations 2 - 5%. The following conclusions have been made:

1- The polyacrylamide solutions showed strong shear thinning behavior for all concentrations.

2- As the polymer concentration increases, the apparent viscosity of the solution increases.

3- Significant transient behavior has been observed for all concentrations of polyacrylamide solutions which shows that the time evaluation of shear stress depends on both shear rate and polyacrylamide concentration.

4- The increase in the shear stress is due to the recovery and reformation of the molecule network structures.

5- Polyacrylamide solutions exhibit yield stress. The yield stress increases with an increase in the concentration.

6- Two different techniques have been used to investigate the thixitropic behavior of polyacrylamide solutions.

7- Three different behaviors of thixotropy test have been observed--thixotropy, antithixotropy, and time-dependent; the latter is dependent on the used technique, shear rate, and polyacrylamide concentration.

8- Polyacrylamide solutions behave like viscoelastic material in all concentrations. However, the viscous part was always higher than the elastic part.

9- For concentrations 2, 3, and 4%, the storage and loss modulus values increase as a result of increasing the concentrations and frequency.

10- Loss modulus is more predominant up to a critical frequency which was almost the same for the 2, 3, and 4% concentrations.

11- Above this critical frequency, the 2, 3, and 4% concentrations behave like pure viscous material.

12- The viscous and elastic parts are nearly equal for the 5% concentration.

13- The complex viscosity of polyacrylamide solutions is shown by two different behaviors—shear thinning region and shear thickening region.

14- The dynamic viscosity is higher than the shear viscosity for all polymer concentrations.

## 6-2 Recommendations:

1- Further study can be done to investigate the behavior of the solutions at shear rates higher than $700s^{-1}$.

2- Temperature has a significant influence on viscosity; therefore, a heating circulator with powerful pumps can be connected to the rheometer RS100 to provide a tool to study the temperature effect on the rheological properties of polyacrylamide solutions used in this work.

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