# Rheological Properties of Aqueous Polyacrylamide Solutions

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ABSTRACT: A comprehensive study of the rheological properties of aqueous polyacrylamide solutions was carried out. A RheoStress RS100 Haake rheometer was used in the measurements. The concentration of polyacrylamide ranged from 0.25 to 1.0% by weight. This range is sufficiently wide to cover many of the rheological features of polyacrylamide in the lower range of concentration. The study included measurements of steady shear flow parameters, transient shear stress response, yield stress, thixotropic behavior, creep recovery, dynamic responses, and temperature effects in the range 10−50°C. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1587–1597, 1998

Key words: polyacrylamide; viscosity; transient shear stress; yield stress; thixotropy; creep recovery; dynamic rheology

## INTRODUCTION

Polyacrylamide (PAA) is one of the most widely used and technically important water-soluble polymers. PAA is obtained by free-radical polymerization of acrylamide. It is widely used in modern technology as a thickening agent, suspending agent, turbulent reduction agent, and additive to adhesives. One of the important applications of PAA is in enhanced oil-recovery processes. Oil still remaining in the earth after a water flood can be recovered from the reservoir by improving sweep efficiency and/or reducing the interfacial tension between flood and oil. One effective technique to discharge oil at this stage is polymer flooding. Two major types of polymers currently employed in polymer flooding are the synthetically manufactured PAAs and the biologically produced polysaccharides.

A number of recent rheological studies on PAA

solutions were carried out under different conditions. These studies have shown along with earlier studies unusual and complex behavior by PAA solutions that could restrain their industrial uses. Chauveteau[1] and Durst et al.[2] reported significant pressure drops in porous media flows of PAA solutions compared to Newtonian liquids. Flew and Sellin[3] studied the non-Newtonian flow of PAA solutions in porous media. Li and McCarthy[4] studied the pipe flow of aqueous PAA solutions using nuclear magnetic resonance imaging. Mechanical degradation of PAA solutions was reported by Ghoniem et al.[5] and Chang and Darby.[6] Dupuis et al.[7] studied the rheological properties of solutions of high molecular weight partially hydrolyzed PAA in mixtures of glycerol and water. They reported 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. Shin and Cho[8] studied temperature effects on the non-Newtonian viscosity of an aqueous PAA solution. They reported that the viscosity of the PAA solu-

tion was very sensitive to temperature at low shear rates. However, it was almost independent of temperature at high shear rates. A significant laminar heat-transfer enhancement in a 2 : 1 rectangular duct occurs when a dilute aqueous PAA solution is used. This enhancement might be due to the effect of temperature on the viscosity of the PAA solution, particularly at low shear rates. Ait-Kadi et al.[9] carried out an experimental study to investigate the effect of salt on the viscoelastic properties of partially hydrolyzed PAA in aqueous solutions. They measured the viscosity and primary normal stress differences using a Weissenberg rheogonimeter and a Contraves low-shear viscometer. Ait-Kadi et al.[9] reported that the salt had a stabilizing effect on the solution viscosity. Numerous techniques based on continuum theories,[10] mechanical models,[11] and molecular theories[12–14] have been used to understand some of the reported phenomena. However, many of the reported observations are still not clearly understood. For more details on the preparation, characterization, solution properties, and rheological behavior of PAA, see Kulicke et al.[15]

Knowledge of the rheological properties of the PAA solutions is important for the design, selection, and operation involved handling, mixing, pumping, storage, and transportation processes. In this article, the rheological measurements in terms of steady, transient, creep, and oscillatory are reported for aqueous PAA solutions with a concentration range up to 1%. Also, the temperature effect on the behavior of the PAA solutions is discussed over the range of 10–50°C.

## EXPERIMENTAL

A Haake rheometer RheoStress RS100 was used to carry out all the rheological experiments of this study. The RS100 has several operating test modes, which are controlled rate (CR) mode, controlled stress (CS) mode, and oscillation (OSC) mode. The RS100 in the CS mode applies shear stresses to a test sample by means of extremely low inertia. The drive shaft is centered by an air bearing to deliver an almost frictionless transmission of the applied stress to the test fluid. The resulting deformation of the tested material is analyzed with a digital encoder that processes $10^6$ impulses per revolution. This resolution makes it possible to measure small shear rates, strains, or yield stress values. The RS100 can be easily switched between both the CS and CR modes, and

it can apply oscillating stress and frequency sweep. A controlled variable lift speed is used to position the cone on the plate. The cone diameter, the cone angle, and the gap at the cone tip are 35 mm, 4°, and 0.137 mm, respectively. A water bath is connected to the RS100 to control the applied temperature; all the experiments are carried out at 22°C unless mentioned otherwise. The Haake software package is used to operate and control the RS100, and is also used for data evaluation and analysis.

PAA is a white water-soluble solid material. PAA with molecular weight of $5(10)^6$ from BDH (Poole, England) was employed in this study. The production number of the sample used in the experiments is 29,788 and the viscosity of the 0.5% aqueous solution is about 280 mPa s at 25°C. Only fresh solutions were used in the experiments. The solutions were prepared by adding a known amount of polymer powder to 1 L of double-distilled water at room temperature. Sufficient time was given to achieve complete dissolution without an external source of heat or power to avoid any degradation on the polymer molecule network. This study investigated a concentration range of 0.25–1.0% PAA to cover a wide range of the rheological behavior of PAA solutions.

To study the many possible phenomena that could be observed in processes involving the use of PAA solutions, a wide range of tests was carried out. The tests conducted were steady shear flow, transient shear stress response, yield stress, thixotropy behavior, creep recovery, and dynamic behavior. The effects of temperature were studied in the range of 10–50°C.

## RESULTS AND DISCUSSION

### Steady Shear Flow

The first test in our study was the steady shear flow test. The test provides the flow behavior curve, displaying the relationship between the shear stress ($\tau$) and shear rate ($\dot{\gamma}$) (Fig. 1). The viscosity curve (Fig. 2) correlated changes in viscosity ($\eta$) with the shear rate. The polymer solutions at various concentrations of PAA are non-Newtonian in nature and they exhibit two different behaviors: The first behavior shows clearly that PAA aqueous solutions in concentrations between 0.25 and 1% exhibit strong shear-thinning behavior up to shear rate values of about 70–200 s$^{-1}$. This type of flow is typical for polymer solu-
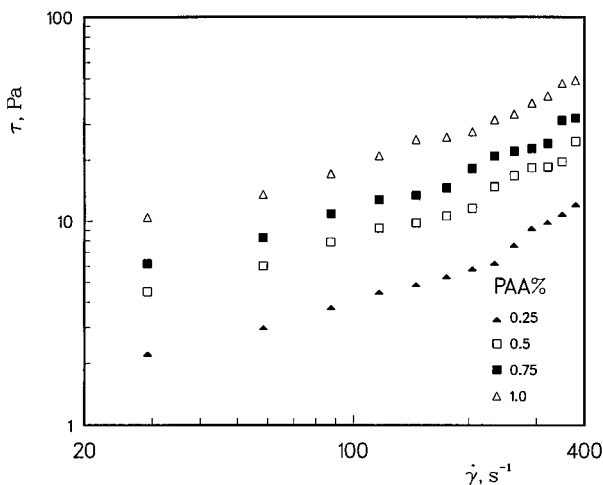
**Figure 1** Flow behavior curves of PAA solutions.

**Table I Zero Shear Viscosity ($\eta_0$), Flow Behavior ($n$), and Consistency Index ($k$) for PAA Solutions**

| % PAA Solution | $\eta_0$ | $n$ | $k$ |
|---|---|---|---|
| 0.25 | 78 | 0.5 | 410 |
| 0.50 | 150 | 0.5 | 840 |
| 0.75 | 210 | 0.5 | 1200 |
| 1.0 | 360 | 0.5 | 1800 |

rate could not be measured due to the limitations of the employed rheometer.

The flow behavior of PAA solutions can be described by the flow curve which, based on a measurement $\tau = f(\dot{\gamma})$, is usually presented in the derived function $\eta = f(\dot{\gamma})$. The experimental measurements of the steady shear flow test were fitted by a nonlinear regression to a Carreau and a power-law model equation. Table I shows the regression parameters of eqs. (1) and (2):

$$(\eta - \eta_\infty)/(\eta_0 - \eta_\infty) = [1 + (\lambda\dot{\gamma})^2]^{(n-1)/2} \quad (1)$$

$$\eta = k\dot{\gamma}^{n-1} \quad (2)$$

where $\eta_0$ is the zero shear rate viscosity (mPa s); $\eta_\infty$, the infinite shear rate viscosity (mPa s); $\lambda$, a time constant (s); $k$, the consistency index (mPa s$^n$); and $n$, the flow behavior index. The flow curve of the PAA solution generally is defined by two regions of limited viscosities $\eta_0$ and $\eta_\infty$. At low shear rate, the viscosity approaches a constant value of $\eta_0$. As the shear rate is increased beyond a certain value, viscosity departs from $\eta_0$ and becomes a decreasing function of $\dot{\gamma}$. At a very high shear rate, the molecules of the PAA solution are extended to a maximum limit and an upper limit viscosity value ($\eta_\infty$) should be reached. Using the Carreau model, the limiting values of the zero shear viscosity for this study are reported in Table I, which are in agreement with the values predicted by Kulicke et al.[15] On the other side, Kulicke et al.[15] mentioned that the existence of an upper limit viscosity of $\eta_\infty$ for solutions of flexible coils is still doubtful due to the shear heating and chain scission which occur at a very high shear rate. For the PAA solution, even at $\dot{\gamma} = 10^6$ s$^{-1}$, a limiting value of $\eta_\infty$ is not detectable.

Table I shows that PAA solutions experience strong shear thinning with a flow behavior index of $n = 0.5$ for all tested concentrations. The consistency index of $k$ went through significant in-

tions in which the polymer molecules are dissolved as statistical coils and can also be found for other polymer systems.[16] Their apparent viscosities decrease steadily with increase in the shear rate up to a critical value of $\dot{\gamma}_c$. The second behavior occurs when shear rate is higher than $\dot{\gamma}_c$: PAA solutions of 0.25–0.75% concentrations showed shear-thickening behavior. Above this value, $\dot{\gamma}_c$, the apparent viscosities for all the solutions increased with the shear rate and then started to fluctuate. This behavior is reversible and reproducible within the apparatus accuracy.[9] The apparent viscosity of a 1% PAA solution remained approximately constant past the critical shear rate. This critical shear rate depends on the concentration and is higher for lower concentrations. The complete flow curve at a lower shear
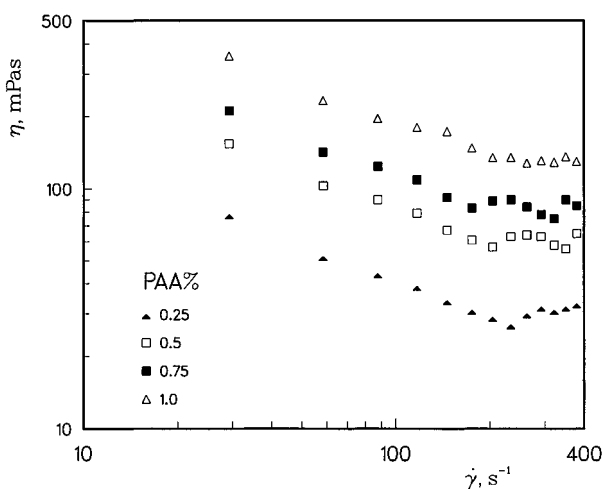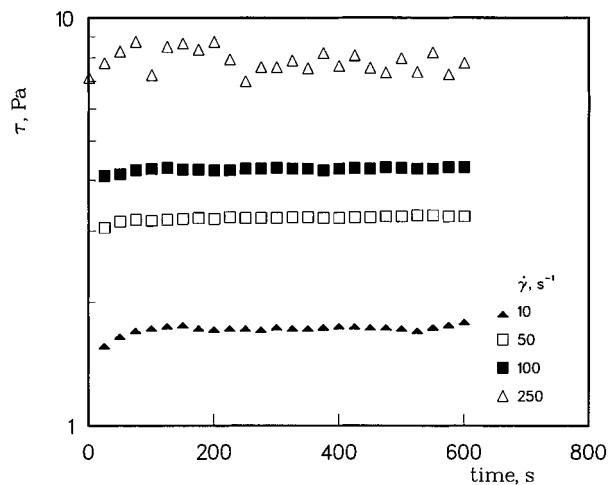


**Figure 2** Viscosity curves of PAA solutions.

**Figure 3**    Transient shear stress response, 0.25% PAA.

creases in the entire range of concentrations of 0.25–1%.

## Transient Shear Stress Response

It is necessary to carry out transient shear behavior for rheologically complex substances. Figures 3 and 4 show typical stress developments as a function of time for various concentrations of PAA solutions. The tests were carried out for 10 min for each applied constant shear rate in the range of 10–250 s$^{-1}$. At a low value of applied shear rate, the response stress increased rapidly within the first 50 s to a constant value for each shear rate applied. The steady response shear stress increased with shear rate. This conclusion is in agreement with the results of Dupuis et al.[7] This rheopexy behavior is reported for all the tested PAA solutions. At higher shear rate and higher concentration, the response stress rises beyond its steady value and passes through a maximum before approaching the steady value (i.e., this phenomenon is called overshoot). The onset of the overshoot occurs at different shear rates depending on the concentration of the PAA solutions. For a concentration range of 0.25–0.5% PAA, the onset of the overshoot occurs above 100 s$^{-1}$. For concentrations higher than 0.5, the overshoot starts to develop above 50 s$^{-1}$.

Rheopexy and stress overshooting are often observed for viscoelastic and thixotropic fluids. The observation of such complex transient flow behavior is attributed mainly to the fact that preshearing at a higher shear rate should break some structures, and a gradual increase in the shear

stress is due to the recovery and reformation of the molecule network structures.

## Yield Stress Measurements

The yield stress test was carried out for all the examined solutions of the range 0.25–1% PAA. This test employed a controlled stress mode to the ramp stress until the assigned stress surpasses the yield value and the sample starts to flow. In the first segment, the assigned stress was ramped from 0.09 to 5 Pa to establish the up curve. Then, the assigned stress was instantaneously reduced from 5 to 0.09 Pa to develop the down curve. In CS mode, the RS100 applies shear stress using an extremely low inertia, and the drive shaft of the RS100 is centered by an air bearing to deliver an almost frictionless applied stress. So, this system makes it possible to measure small yield stress. Figure 5 shows double logarithmic plots of the up and down curves for all the PAA solutions. A higher concentration of PAA produces higher cycles of up and down curves and, consequently, causes a higher resistance to flow. The solutions exhibited yield stress which was more significant for higher concentrations, according to the analysis of the Herschel–Bulkley model:

$$\tau = k\dot{\gamma}^n + \tau_0 \qquad (3)$$

Table II lists the parameters of this regression.

Samples of the PAA solutions show a higher up curve $\tau_{01}$ yield point than the yield point $\tau_{02}$ of the down curve. This means that the sample did
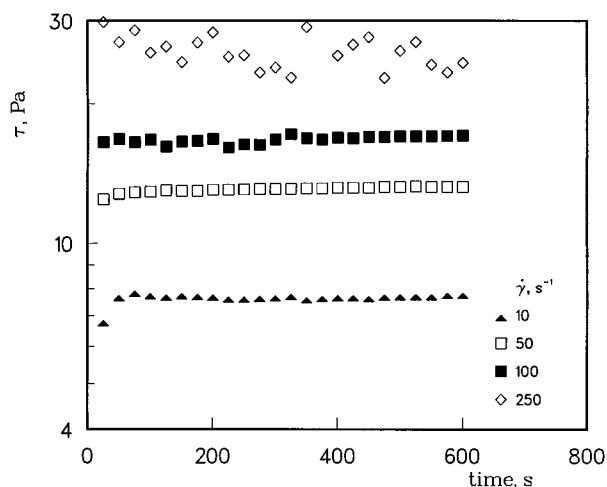


**Figure 4**    Transient shear stress response, 1.0% PAA.
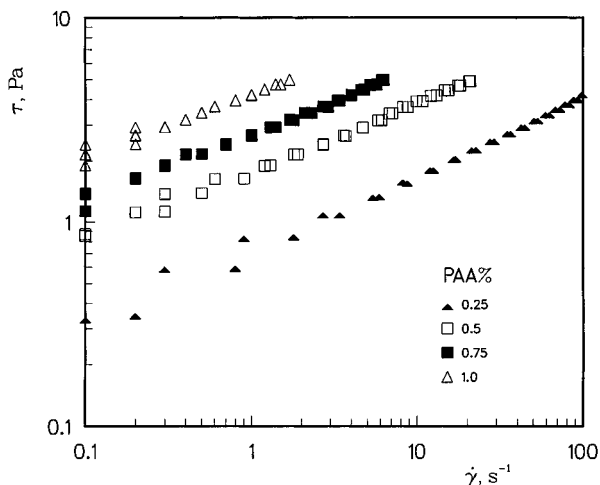
**Figure 5**  Yield stress response of PAA solutions.

not fully recover. It exhibits thixotropic behavior as it is sheared down from 5 to 0.09 Pa.

## Thixotropy

The time-dependent behavior due to structure changes at the microscopic and molecular levels is termed thixotropy. When a constant shear rate is suddenly applied on the fluid, the shear stress responses instantaneous and then decreases with time; consequently, viscosity decreases with time. A mathematical thixotropic model can be constructed using the idea that viscosity is a function of a structure parameter $\alpha$ and shear rate:

$$\eta = \eta(\dot{\gamma}, \alpha) \qquad (4)$$

The $(\tau, \dot{\gamma}, \alpha)$ relationship is described as the equation of state. The structure is considered to be shear-dependent, breaking down under high shear and recovering at low shear or at rest. The changes are governed by a rate equation as

$$d\alpha/dt = f(\dot{\gamma}, \alpha) \qquad (5)$$

Equations (4) and (5) make up the constitutive relationship for thixotropy.

Our measurements of thixotropy were conducted under the controlled-rate CR mode. 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, and the result was the up curve. After reaching the assigned maximum rate, a gradual decrease gave the down

curve. The down curve of a time-independent sample is identical to its up curve, while the down curve of thixotropic solutions is different from the up curve. The curves form a hysteresis loop that encloses an area $A$. The thixotropy of a solution is quantified by the solution ability to regain its gel structure when the liquid is allowed to rest for a longer period of 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, that is, the energy required to break down 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, a number of up and down cycles may be required before the 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.

Five tests were carried out for all PAA solutions using the two described techniques of studying the thixotropic behavior. Test 1 consisted of one cycle of an up curve from 0.15 to 700 s$^{-1}$ and a down curve back to 0.15 s$^{-1}$; each curve covered 2 min. Test 2 consisted of three cycles of test 1. Test 3 consisted of a three-part cycle of an up curve from 0.15 to 700 s$^{-1}$, a constant shear at 700 s$^{-1}$, and a down curve back to 0.15 s$^{-1}$. The duration of each part was 1 min. Test 4 repeated test 3 with time periods of 2 min instead of 1. Test 5 repeated the same sequence with 3-min parts. Results of the thixotropic analysis of all tested PAA solutions in terms of the hysteresis area for each test are listed in Table III. Under "cycles" in this table, $n_1-n_2-n_3$ indicates the number of cycles, the number of parts in a cycle, and the number of minutes in each part, respectively.

**Table II   Regression Parameters**

| % PAA Solution | $\tau_{01}$ (Pa) | $\tau_{02}$ (Pa) |
|---|---|---|
| 0.25 | 0.36 | 0.34 |
| 0.50 | 0.60 | 0.35 |
| 0.75 | 0.86 | 0.61 |
| 1.0 | 1.10 | 0.61 |

**Table III  Results of Thixotropic Analysis**

| Test No. | Cycles | PAA (%) | | | |
|---|---|---|---|---|---|
| | | 0.25 | 0.50 | 0.75 | 1.0 |
| 1 | 1–2–2 | N | 1211 | 2617 | 3139 |
| 2 | 3–2–2 | N | N | 1647 | 2476 |
| 3 | 1–3–1 | 44.1 | 1687 | 3885 | 4589 |
| 4 | 1–3–2 | 60.8 | 2077 | 5273 | 6111 |
| 5 | 1–3–3 | N | 3428 | 4430 | 5928 |

Some of the tests yielded a very small negative hysteresis area. A negative sign for the thixotropic area indicates that the down curve is positioned above the up curve, which is due to either the insignificance thixotropic behavior of those solutions or the difficulty of breaking down the thixotropic structure by the corresponding test. Such cases are marked in Table III by the letter "N." Table III shows that test 4 provides the highest thixotropic area for most samples of the PAA solutions. It also appears that a test according to the second technique which includes a constant shear time was essential to ensure that the structure of the PAA solutions has been completely destroyed.

Our conclusion is that the thixotropic behavior of PAA solutions builds up with increasing concentrations. For solutions with a concentration of 0.25%, the thixotropic behavior is barely noticeable.

**Creep-recovery Test**

To reveal the viscoelastic characteristics of a solution, a sample should be tested for its response to a constant stress over time. Liquids that exhibit viscoelastic behavior have long chain molecules, which at rest loop and entangle with each other at a minimum-energy state. Under deformation, these molecules stretch, increasing the bond vector angles and raising their energy state. If the cause of deformation is removed, molecules try to return to their original energy state. 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 $\tau_0$ 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. A viscoelastic response to an applied constant stress varies with the time of application.

Initially, the network of molecules undergoes deformation within the mechanical limits of the network. Continuous deformations lead to dismantling of the network and the liquid starts to flow. When the applied stress is removed, the total strain separates into a permanently maintained viscous part and a recovery elastic part. Viscoelastic behavior under lower values of stress usually has a linear response. In the range of nonlinear responses, at higher stress values, elasticity and viscosity data are usually dependent on the test conditions and the sensor system parameters.

Rheological systems that exhibit creep show a time-dependent strain $\gamma(t)$ under a constant stress $\tau$, where

$$\gamma(t) = \tau J(t) \qquad (6)$$

The compliance, $J(\mathrm{Pa}^{-1})$, of a sample is a material constant. The higher the compliance, the easier the sample can be deformed by a given stress. In the linear viscoelastic range, the compliance is independent of the applied stress. Consequently, the proper creep and recovery test conditions within the limit of linear viscoelasticity can be defined. In addition, linear viscoelasticity is a nondestructive test of measuring the rheological behavior of a sample. The deforming energy is recovered when the applied stress is released. This indicates the network ability to elastically deform while keeping the network intact.

In the creep-recovery test, it was important to initially define the linear viscoelastic range by applying different values of constant shear stress for 300 s. The compliance data $J(t)$ at different values of applied shear stress should coincide within the linear viscoelastic range. However, in the nonlinear viscoelastic range, the compliance data curve separates significantly from the linear viscoelastic data. So, a creep test was carried out to define the linear viscoelastic range for all the PAA solutions. It was determined that the linear viscoelastic ranges for 0.25, 0.5, 0.75, and 1.0% PAA were 0.5, 1.0, 1.5, and 2.0 Pa, respectively.

The creep-recovery experiments were conducted by applying a constant known value of shear stress to the sample using cone-and-plate geometry. The resulting compliance was monitored as a function of time. The imposed stress was suddenly removed after 300 s, and recovery was monitored for another 300 s. Figures 6 and 7 show the compliance data $J(t)$ for PAA 0.25 and 1.0% solutions at different values of applied shear
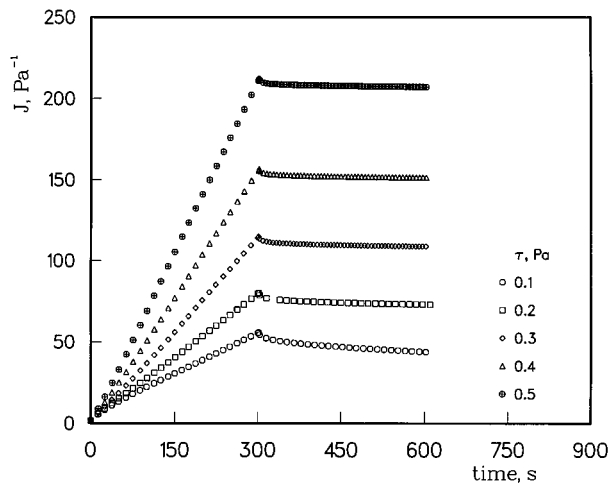
**Figure 6**    Viscoelastic response of 0.25% PAA.



**Figure 8**    Viscous response of PAA solutions in non-linear viscoelastic range.

stress. For all concentrations of PAA, a noticeable time-dependent response is evident in the creep and recovery phases at lower applied shear stress. Therefore, all PAA solutions show an elastic recovery in addition to their viscous response at lower applied shear stress. However, at higher applied shear stress, the time dependence in the creep phase is diminished and is significantly reduced in the recovery phase. The response of the compliance $J$ to the instantaneous removal of stress can be summarized into three steps: Initially, a step reduction occurs as a pure elastic response, followed by an exponential decrease related to a viscoelastic response. Finally, the compliance values approach a constant limit corresponding to the nonrecovered deformation of the
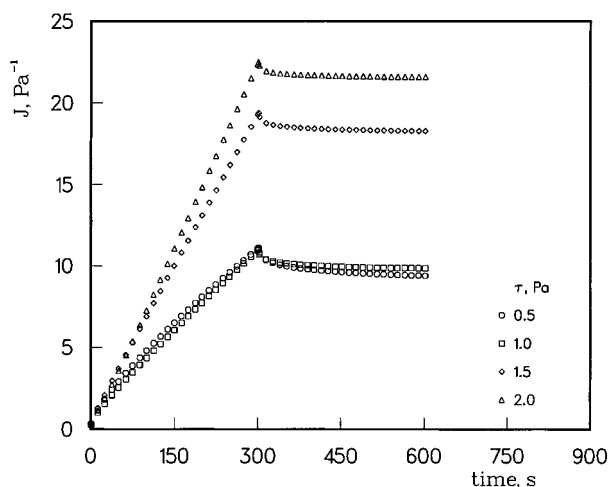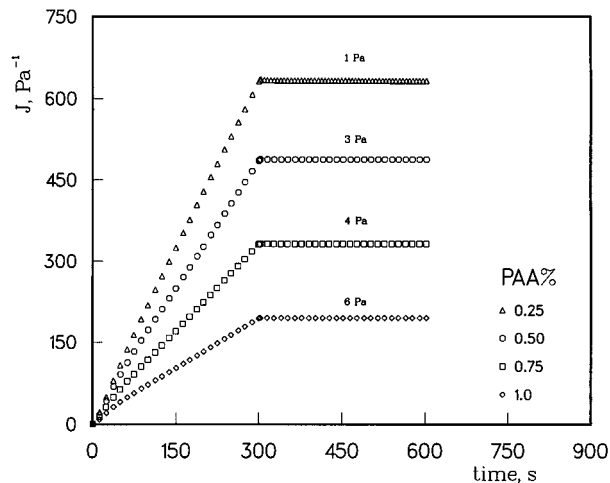
viscous flow. For comparison, Figure 8 shows the compliance values of all the PAA solutions at shear stress values in the nonlinear viscoelastic range. Each PAA solution shows time-independent behavior in the creep and recovery phases. Also, a pure viscous response of nonrecovered deformation can be seen. This is significantly different from the behavior recorded within the linear viscoelastic range in Figures 6 and 7.

**Dynamic Test**

The dynamic test is another tool of the rheological study of viscoelastic behavior. In this test, the effect of oscillating stresses or strains on the behavior of the sample is studied. In the controlled stress mode, the stress may be applied as a sinusoidal time function:

$$\tau = \tau_0 \sin(wt) \qquad (7)$$

The approach taken in the dynamic test to study the viscoelastic behavior is different from the approach of the creep-recovery test. The two tests complement each other, since some features of viscoelasticity are better described in a creep-recovery test and others in a dynamic test.

The complex modulus $G^{\bullet}$ (Pa) represents the substance total resistance against the applied strain and can be calculated from

$$G^{\bullet} = \tau_0 / \gamma_0 \qquad (8)$$

where $\tau_0$ and $\gamma_0$ are the stress and strain ampli-



**Figure 7**    Viscoelastic response of 1.0% PAA.

tudes, respectively. On the other hand, it can be defined as

$$G^* = G' + iG'' \qquad (9)$$

where $G'$ and $G''$ are the storage modulus and loss modulus, respectively. Complex viscosity represents the total resistance to a dynamic shear as

$$\eta^* = G^*/w \qquad (10)$$

where $w$ is the frequency (rad/s) and $\eta^*$ is the complex viscosity (mPa s). To determine the linear viscoelastic range in a dynamic test, a fixed frequency of 1 Hz is used while a stress sweep is performed. 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 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 equations 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. The linear viscoelastic range for the 0.25–1.0% PAA solutions was found to be in the neighborhood of 4 Pa.

The rheological properties of a series of PAA solutions in the range of 0.25–1.0% were measured using an oscillatory shear rheometer with cone-and-plate geometry in the frequency range
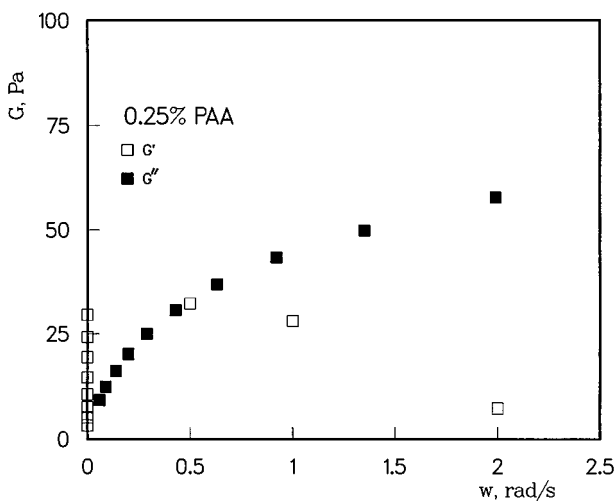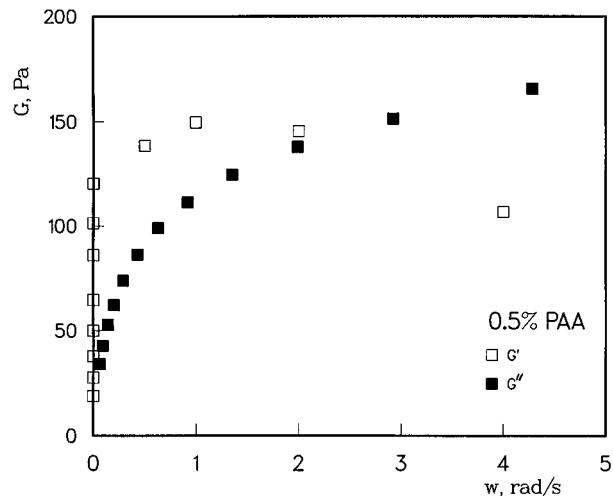


**Figure 10**  $G'$ and $G''$ for 0.5% PAA.

of 0.01–10 rad/s. The storage modulus ($G'$) and loss modulus ($G''$) for 0.25–1.0% PAA in the linear viscoelastic range are plotted in Figures 9–12. First, Figures 9–12 reveal that the storage modulus is higher than the loss modulus over a definite range of frequency, indicating that the elastic behavior is more predominant at a lower range of frequency. However, at a higher range of frequency, the PAA solutions show only viscous behavior up to 10 rad/s. Second, Figures 9–12 show that the frequency range responsible for elastic behavior increases with PAA concentration. This conclusion is in very much agreement with the behavior of the creep-recovery response.

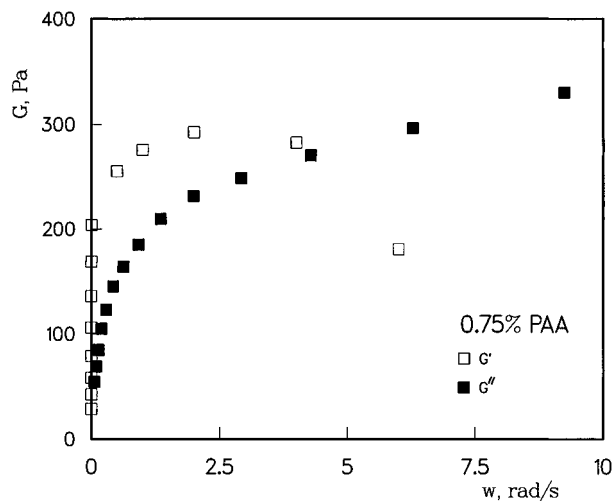The complex viscosity of PAA solutions is shown in Figure 13 versus the frequency in the



**Figure 9**  $G'$ and $G''$ for 0.25% PAA.



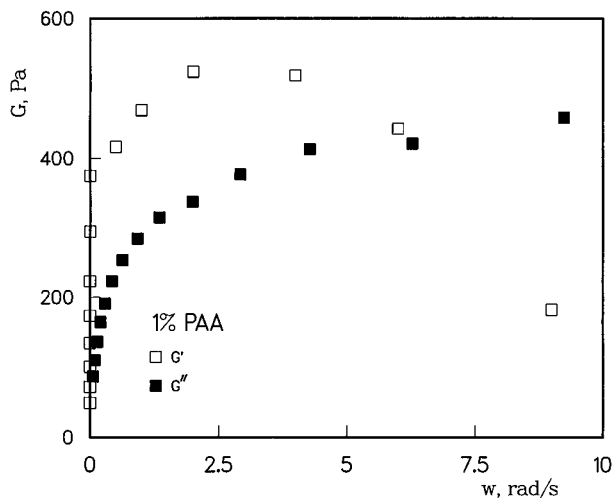**Figure 11**  $G'$ and $G''$ for 0.75% PAA.

**Figure 12**  $G'$ and $G''$ for 1.0% PAA.

range of 0.01–10 rad/s. Steady shear viscosity or oscillating viscosity can be used for polymer fluids characterization. Similarities between steady shear viscosity and dynamic viscosity exist as reflected by

$$\lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma}) = \lim_{w \to 0} \eta'(w) \qquad (11)$$

where $\eta'$ is the real component of the dynamic viscosity. This relation was predicted by a molecular study.[17] Many polymer fluids have been found to follow eq. (11) experimentally. At a high shear rate, deviations from eq. (11) are usually observed (i.e., $\eta'$ decreases more rapidly with $w$ than $\eta$ decreases with $\dot{\gamma}$). Cox and Merz[18] 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 $\dot{\gamma}$:

$$\eta^*(w) = \eta(\dot{\gamma}) \qquad (12)$$

Kulicke et al.[15] found that the experimental results of PAA–formamide are in a good agreement with the Cox–Merz relationship for a concentration range of 1–2% PAA and a molecular weight of $2.53 \times 10^6$ and $4.7 \times 10^6$. However, for PAA–$H_2O$ solutions, they mentioned that the experimental results do not coincide with the Cox–Merz relationship. Kulicke et al.[15] suggested that intra- and intermolecular hydrogen bonds may be the reason for this behavior. Hydrogen bonds influence the internal structure of the dissolved PAA molecules in water so strongly that they differ

in their rheological behavior in contrast to other polymer fluids.

Figure 13 shows that the dynamic viscosity decreases with the frequency for all the PAA solutions displaying a shear-thinning behavior. The PAA concentration has a significant influence on the dynamic viscosity of the PAA solutions. Figures 2 and 13 reveal that the complex dynamic viscosity is higher than the shear viscosity for all the tested concentrations due to the energetic interactions of hydrogen bonds on the internal structure of the PAA molecules.

## Temperature Effect

Temperature has a significant influence on viscosity and viscous behavior. The rheological behavior of a liquid plays an important role in heat-transfer operations. Shin and Cho[8] mentioned that the temperature-dependent viscosity of a Newtonian solution could increase the convective heat-transfer performance by 70–80% over its value in a laminar flow in a 2 : 1 rectangular duct. Hartnett and Irvine[19] reported that the heat-transfer coefficients for an aqueous PAA solution in the laminar flow of a rectangular duct are about 300–400% higher than those of a constant property fluid value. Therefore, it is important to study the flow behavior of the PAA solutions over a wide range of shear rate and temperature.

Figures 14 and 15 show typical examples of the apparent viscosity as a function of shear rate for aqueous PAA solutions of 0.5 and 0.75% at the temperature range of 10–50°C. There is a signifi-
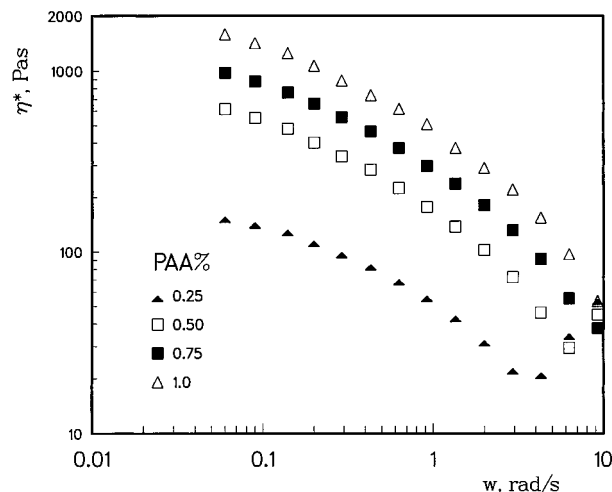


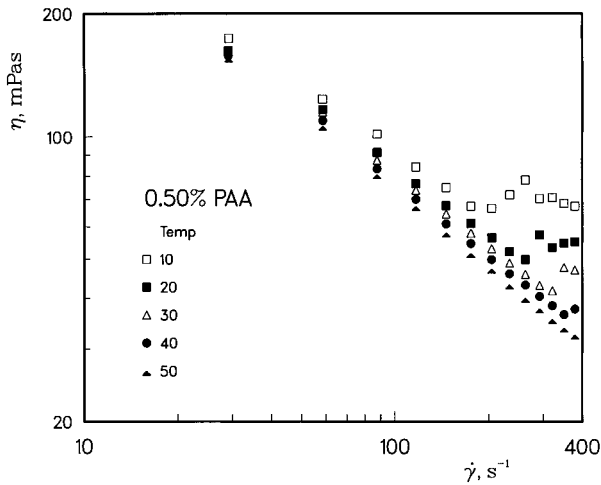**Figure 13**  Complex viscosity–frequency of PAA solutions.

**Figure 14**   Viscosity curve of 0.5% PAA as a function of temperature.

cant decrease in the apparent viscosity of the PAA solutions with temperature. The effect of temperature is more pronounced at higher shear rates of about $100$ s$^{-1}$ compared with its effect at lower shear rates of about $20$ s$^{-1}$. This could be due to the shear-thickening behavior of the PAA solution at a higher shear rate. Apparently, for higher concentration, 1% of the PAA solution exhibits more dramatic changes with temperature.

The objective now is to report the viscosity data which depend on both shear rate and temperature and to develop a correlation among viscosity, shear rate, and temperature. Mahalingam et al.[20] measured the viscosity of carbopol-934 [poly-(acrylic acid)] solutions and methocel (methyl
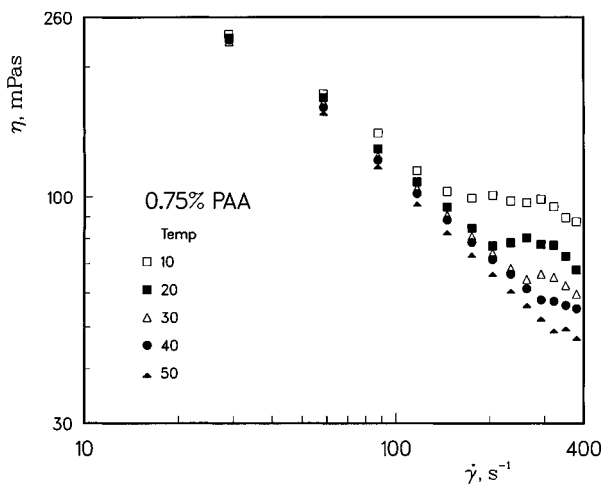
**Table IV   Parameters $a$ and $b$ of Eq. (13) for PAA Solutions**

| % PAA Solution | $a$ | $b$ | $r$ |
|---|---|---|---|
| 0.25 | 759 | −0.012 | 0.87 |
| 0.50 | 1580 | −0.019 | 0.99 |
| 0.75 | 1844 | −0.014 | 0.96 |
| 1.0 | 2378 | −0.012 | 0.87 |

ether of cellulose) at different temperatures. They proposed a correlation for the fluid consistency index, $k$, with temperature in the form

$$k = ae^{bT} \qquad (13)$$

Regression analysis was carried out using eq. (2) for the temperature range 10–50°C for each PAA solution. The result shows that the fluid behavior index $n$ is 0.5 for all PAA solutions for all temperatures. However, the fluid consistency index $k$ is found to be a function of temperature for each PAA solution. Table IV shows the parameters $a$ and $b$ of eq. (13) for each solution.

The second part of the temperature-effect study was concerned with the effect of temperature on the thixotropy of the PAA solutions over the range of 10–50°C. Test 4 in the thixotropy study was employed to establish the up curve from 0.15 to $700$ s$^{-1}$ for 2 min, a constant shear of $700$ s$^{-1}$ for 2 min, and a down curve from 700 to 0.15 s$^{-1}$ for 2 min. Figure 16 shows the thixotropic area in Pa/s versus temperature in the range $T = 10$–50°C for all the PAA solutions. In the case of 0.25



**Figure 15**   Viscosity curve of 0.75% PAA as a function of temperature.
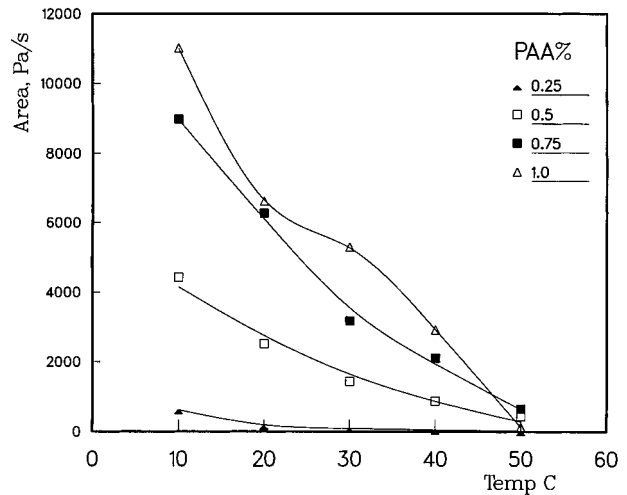


**Figure 16**   Effect of temperature on thixotropy of PAA solutions.

and 0.5% PAA solutions, a gradual reduction for the thixotropic area is shown over the 10–50°C range. However, for higher concentrations of PAA, there is a sharp reduction in the thixotropic area. The effect of PAA concentration on the thixotropic area is more pronounced at lower temperatures. At the high temperature of 50°C, the effect of concentration is almost insignificant.

## CONCLUSIONS

A comprehensive rheological study for aqueous PAA solutions of weight concentrations 0.25–1.0% was carried out. The PAA solution showed shear-thinning behavior for all concentrations of 0.25–1.0% up to a critical shear rate value, which depended on the concentration. For higher shear rates, all tested concentrations showed shear-thickening behavior except for the 1% PAA solution. Its apparent viscosity remained constant. PAA solutions experienced a significant transient behavior over the range of $10-50$ s$^{-1}$, an indication of a structure breakdown and recovery process within the first 50 s.

PAA solutions showed yield points for the up and down curves. The yield points of the up curve were slightly higher. The yield point increased with the PAA concentration. PAA solutions showed a thixotropy behavior which increased with concentration from 0.25 to 1.0%. A three-part test with 2 min time periods in the thixotropy study provided the closest conditions for destroying the PAA thixotropic structure. A creep test was carried out to define the linear viscoelastic range as 0.5, 1.0, 1.5, and 2.0 Pa for the 0.25, 0.5, 0.75, and 1.0% PAA solutions, respectively. A time-dependent response was found for the creep and recovery phases at a lower applied shear stress. However, at higher shear stress, the creep and recovery phases are time-independent.

Dynamic tests were carried out to reveal the viscoelastic behavior of the PAA solutions. The linear viscoelastic range for all tested PAA solutions according to these tests were 4 Pa. PAA solutions showed elastic behavior at a low range of frequency and viscous response at a higher range of frequency. The viscoelastic behavior of the PAA solutions depends strongly on the concentration in the range of 0.25–1.0%. The complex viscosity is measured over 0.01–10 rad/s and showed a shear thinning with frequency and concentration dependence. The dynamic viscosity is higher than the shear viscosity due to the energetic effect of the hydrogen bonds on the internal structure of the dissolved PAA molecules.

The apparent viscosity of the PAA solutions significantly decreased with temperature. The temperature effect is more pronounced at the high shear rate of 100 s$^{-1}$. Regression analysis of experimental measurements showed that the flow behavior index $n$ is 0.5 for all the PAA concentrations and temperatures. However, the fluid consistency index $k$ was found to be a function of temperature and PAA concentration. There seemed to be a gradual reduction of the thixotropic area for lower concentrations of PAA with temperature. However, a sharp reduction in that area was evident for higher concentrations ($>$0.5% PAA). The effect of concentration is more pronounced at lower temperatures. However, at 50°C, the effect of concentration is almost insignificant.

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