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# Rheological study of partially hydrolyzed polyacrylamide-hexamine-pyrocatechol gel system

Upendra Singh Yadav\* and Vikas Mahto

## Abstract

**Background:** The cross-linked polymer gels exhibit non-Newtonian rheological behavior which can be described well by the different types of rheological models. This study investigates the onset of gelation behavior of partially hydrolyzed polyacrylamide-hexamine-pyrocatechol polymer gel system which may be used to control excessive water production in the oil fields. Rheological measurements of this system have been performed at different time intervals and pH at 90°C. Attempts have been made to validate the onset of gelation behavior with Bingham plastic, Herschel-Bulkley, Mizrahi-Berk, and Robertson-Stiff model.

**Results:** It was observed that the developed polymer gel system under the present study has better agreement with the Robertson-Stiff model.

**Conclusions:** The viscosity of cross-linked polymer gel solution increases with temperature with the passage of time. This increased viscosity leads to gel formation which in turn behaves as flow diverting agent or blocking agent for controlling excessive water production in the oil fields.

**Keywords:** Polymer gel system, Rheology, Excessive water production, Viscoplastic flow models

## Background

The excessive water production in association with crude oil is one of the major production difficulties for the oil industries worldwide. The costs of lifting, handling, separation, and disposal of large amounts of produced water increase the operating cost of the crude oil production and decrease the economic life of a well. Therefore, there is a need to reduce excessive water production [1-4].

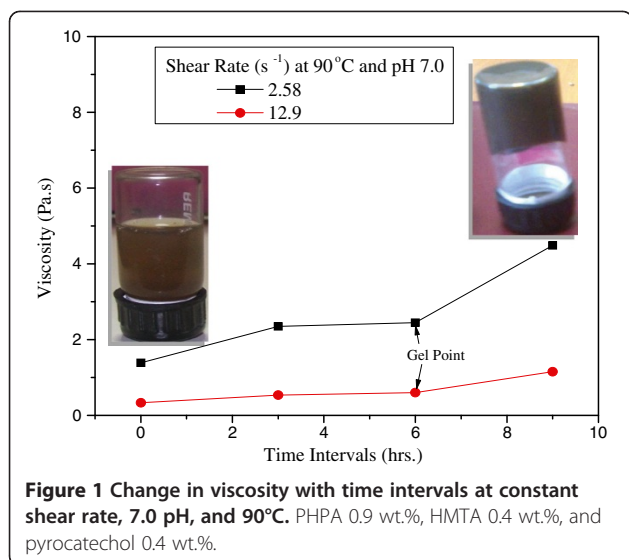
The polymer gel treatment is one of the most useful chemical methods to reduce water production [5-9]. Polymer gels are typically composed of a water soluble polymer and cross-linking agents which are dissolved in brine. After allowing sufficient time, the gelant solution sets into a semisolid mass and behaves as flow-diverting or blocking agent [10-12]. The selection of a polymer gel system for a given well treatment strongly depends on reservoir conditions such as temperature, salinity, hardness, and the

pH of the water used for the preparation of the gelant [13-19]. Other parameters to be considered for the proper selection of a given polymer gel system include salinity of the formation water, permeability of the target zone, and the lithology of the formation [20,21].

The different polymers used for the development of polymer gel in the oil fields are polyacrylamide with different degrees of hydrolysis (partially hydrolyzed polyacrylamide or PHPA) and polysaccharide such as xanthan biopolymer. These polymers can be cross-linked with metallic and organic cross-linkers to produce a three-dimensional polymer structure of the gel [22].

Gelation behavior is a fundamental parameter in oil-field application. The gelation behavior will determine the injection period and how deep into the formation the gel solution can be placed. For the study of gelation behavior, several methods like bottle testing method, sealed tube method, dynamic shear method (rheometer), and steady shear method (viscometer) are reported in the literatures [23]. Different equations have been used to describe the flow behavior of polymer gel system. The rheological behavior of polymer gel system is non-Newtonian, in which

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there is a nonlinear relationship between shear stress and shear rate. These polymer gel systems do not display simple behavior and require more complex models for their characterization [24].

In this work, the rheological behavior of PHPA, hexamine, and pyrocatechol gel solution was studied and was simulated using different rheological models. The rheological and gelation behaviors of polymer solution due to the effect of temperature and pH were evaluated using the equipment of Physica Rheolab MC1 (Anton-Paar GmbH, Stuttgart, Germany).

## Methods

### Materials

The materials used in this work are partially hydrolyzed polyacrylamide, hexamine, pyrocatechol, sodium chloride, hydrochloric acid, and sodium hydroxide. Partially hydrolyzed polyacrylamide in the form of white crystalline powder (procured from Oil and Natural Gas Corporation Limited, Mumbai, India) was used as the water soluble polymer in carrying out the experimental work. The organic cross-linkers hexamine and pyrocatechol were obtained in solid form from renowned manufacturers: Otto Kemi Pvt. Ltd., Mumbai, India and Central Drug House (P) Ltd., New Delhi, India, respectively. Sodium chloride is used to maintain the salinity of polymer gelant, purchased

from Nice Chemical Pvt. Ltd., Kerala, India. Hydrochloric acid (Central Drug House Ltd.) and sodium hydroxide (S. D. Fine-Chem Ltd., Mumbai, India) are used for the adjustment of pH.

### Equipment

All rheological measurements were performed in a stress-controlled Physica Rheolab MC1. It is a rotational rheometer based on the Searle principle. It features a DC motor drive and optical encoder which provides excellent speed regulation, dynamic range, and transient response. These features provide superior performance in comparison with rheometers using gear-driven (indirect) or stepper motor drives. It enables precise measurements of fluid viscosity over the widest range of conditions available today. This machine is not equipped with a high pressure cell, and measurement at high temperature is not allowed. Hence, the gel had to be cured in hot air oven. The cured samples were transferred to the rheometer, and tests were conducted at 30°C. If these experiments were done at higher temperature, the viscosity of the polymer gel may have increased. Viscosity measurement tests were performed at different shear rates ranging from 1 to 1,200 s<sup>-1</sup> using cone-and-plate geometry with a logarithmically increasing scale. Gelled samples were placed on the lower plate, and the upper spindle was brought slowly to the 0.2-mm gap. The reasons why a cone-and-plate sensor configuration was chosen as a test geometry are (1) cleaning is very easy after each measurement, (2) the cone and plate can be easily covered with tissue paper, and (3) there is a relatively smaller gap error due to a larger gap size between the cone and plate (0.2 mm in this experiment) compared to a cone-and-plate sensor (50-mm diameter, 1° angle).

### Rheological measurements

The steady shear flow properties of prepared partially hydrolyzed polyacrylamide-hexamine-pyrocatechol gel solutions were measured using a stress-controlled Physica Rheolab MC1. All measurements were performed at a fixed temperature of 30°C over a wide range of shear rates from 1 to 1,200 s<sup>-1</sup> with a logarithmically increasing scale. The 2 ml of the sample was used for each measurement of the polymer gel solution. The cone and plate were covered with tissue paper in order to remove a wall

**Table 1** Viscoplastic flow models used in this study and their characteristics

| Flow model       | Equation                                      | $n_1$ | $n_2$ | $\gamma_\infty$      | Shear-thinning condition |
|------------------|---|-------|-------|----------------------|--------------------------|
| Bingham plastic  | $\tau = \tau_o + k\dot{\gamma}$               | 1     | 1     | $k$                  | -                        |
| Herschel-Bulkley | $\tau = \tau_o + k\dot{\gamma}^n$             | 1     | $n$   | $0 k$ , if $n = 1$   | $0 < n \leq 1$           |
| Mizrahi-Berk     | $\tau^{1/2} = \tau_o^{1/2} + k\dot{\gamma}^n$ | 0.5   | $n$   | $0 k^2$ , if $n=0.5$ | $0 < n \leq 0.5$         |
| Robertson-Stiff  | $\tau = k(\dot{\gamma} + C)^n$                | 1     | $n$   | $k$ , if $n = 1$     | $0 < n \leq 1$           |

**Table 2** Calculated flow model parameters for polymer gel solution (PHPA 0.9 wt.%, HMTA 0.4 wt.%, and pyrocatechol 0.4 wt.%) at 0 h, pH 7.5, and 30°C

| Flow models      | Parameters    |                                   |          |                       |
|------------------|---------------|-----------------------------------|----------|-----------------------|
|                  | $\tau_0$ or C | $k$ (Pa·s <sup><i>n</i>-1</sup> ) | <i>n</i> | <i>R</i> <sup>2</sup> |
| Bingham plastic  | 4.6845        | 0.0068                            | -        | 0.8671                |
| Herschel-Bulkley | 2.130         | 0.2704                            | 0.5018   | 0.7942                |
| Mizrahi-Berk     | 2.4372        | 0.0994                            | 0.4136   | 0.8510                |
| Robertson-Stiff  | 205.32        | 0.136                             | 0.631    | 0.8788                |

slippage between the test material and the cone and plate. Through a preliminary test using a direct visualization technique in which a straight line marker was drawn from the cone to the lower plate passing through the free surface of the sample solution, it was confirmed that a wall slip effect could almost be eliminated over a shear rate range tested by covering the plate surfaces with tissue paper. Special care was taken to minimize the effect of work softening when the sample solution was initially loaded on the plate each time. In all measurements, a fresh sample solution was used and rested for 20 min after loading to allow material relaxation and temperature equilibration. It was found from a preliminary test that 10 min of resting time is enough for all sample solutions to be completely relaxed and to be thermally equilibrated. All measurements were made at least three times for each test, and highly reproducible data were obtained within the coefficients of variation of ±5% in all cases.

### Results and discussions

In the partially hydrolyzed polyacrylamide structure, the amide group (CONH<sub>2</sub>) is converted to hydrophilic carboxylate group (COONa<sup>+</sup>) by hydrolysis reaction, and further cross-linking agent builds up a complex network with carboxylate groups of polymer and forms a three-dimensional gel network structure.

The gel point is defined as the time needed to reach the inflection point on the viscosity vs. time curve (Figure 1). This method has been widely used by several authors [7,16]. Before the gel formation, the viscosity of the gelling solution is relatively low; therefore, it can be measured accurately. After the gel formation, it will be hard to get an

**Table 3** Calculated flow model parameters for polymer gel solution (PHPA 0.9 wt.%, HMTA 0.4 wt.%, and pyrocatechol 0.4 wt.%) after 3 h at 7.5 pH and 90°C

| Flow models      | Parameters    |                                   |          |                       |
|------------------|---------------|-----------------------------------|----------|-----------------------|
|                  | $\tau_0$ or C | $k$ (Pa·s <sup><i>n</i>-1</sup> ) | <i>n</i> | <i>R</i> <sup>2</sup> |
| Bingham plastic  | 7.1737        | 0.0146                            | -        | 0.9563                |
| Herschel-Bulkley | 4.5052        | 0.1399                            | 0.6937   | 0.9285                |
| Mizrahi-Berk     | 4.8104        | 0.0561                            | 0.5399   | 0.9512                |
| Robertson-Stiff  | 218.571       | 0.111                             | 0.747    | 0.9631                |

**Table 4** Calculated flow model parameters for polymer gel solution (PHPA 0.9 wt.%, HMTA 0.4 wt.%, and pyrocatechol 0.4 wt.%) after 6 h at pH 7.5 and 90°C

| Flow models      | Parameters    |                                   |          |                       |
|------------------|---------------|-----------------------------------|----------|-----------------------|
|                  | $\tau_0$ or C | $k$ (Pa·s <sup><i>n</i>-1</sup> ) | <i>n</i> | <i>R</i> <sup>2</sup> |
| Bingham plastic  | 7.2198        | 0.0181                            | -        | 0.9544                |
| Herschel-Bulkley | 2.5593        | 0.3632                            | 0.5882   | 0.8785                |
| Mizrahi-Berk     | 3.4865        | 0.1097                            | 0.4828   | 0.9313                |
| Robertson-Stiff  | 155.268       | 0.131                             | 0.751    | 0.9554                |

accurate viscosity value. Generally speaking, the strength of the cross-linking polymer solution is hard to measure and also hard to define. When the gel has reached a certain high strength, the gel will deform and is easily transferred in various mechanical viscometers, which will bring some damage to the gel performance. Unless this gelling solution allows gelation in the viscometer, the value of the measurement cannot represent its real strength.

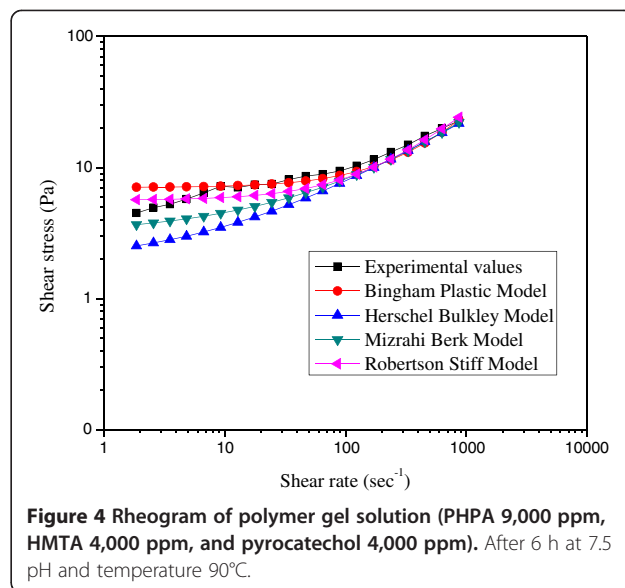
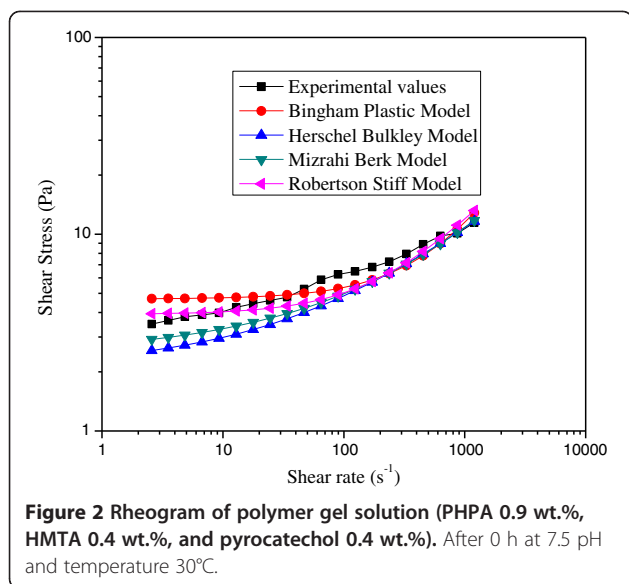
The change in shear stress with shear rate at different reaction time intervals and pH was studied using Physica Rheolab MC1. It was observed that the polymer gel solution is non-Newtonian, and the values of shear stress increase with increasing shear rate which indicates that the viscosity of solution is shear rate-dependent. Also, it was observed that the values of shear stress increases with temperature at constant shear rate, which reflects that the viscosity of cross-linked polymer gel solution increases with temperature with the passage of time. This increased viscosity leads to gel formation which in turn behaves as flow-diverting agent or blocking agent for controlling excessive water production in the oil fields. There is no strong effect of pH on the rheological behavior of HMTA and pyrocatechol cross-linked partially hydrolyzed polyacrylamide gel system. Different polymer gel systems have different ranges of pH over which they can maintain their stability. All the experiments were carried out at pH 7.5.

### Gelation mechanism

The general mechanism involved in the polymer gel formation at any gelation temperature and pH (in this

**Table 5** Calculated flow model parameters for polymer gel solution (PHPA 0.9 wt.%, HMTA 0.4 wt.%, and pyrocatechol 0.4 wt.%) after 9 h at pH 7.5 and 90°C

| Flow models      | Parameters    |                                   |          |                       |
|------------------|---------------|-----------------------------------|----------|-----------------------|
|                  | $\tau_0$ or C | $k$ (Pa·s <sup><i>n</i>-1</sup> ) | <i>n</i> | <i>R</i> <sup>2</sup> |
| Bingham plastic  | 14.118        | 0.0224                            | -        | 0.9398                |
| Herschel-Bulkley | 7.0577        | 0.7382                            | 0.5172   | 0.8368                |
| Mizrahi-Berk     | 8.1910        | 0.1232                            | 0.4640   | 0.8939                |
| Robertson-Stiff  | 232.539       | 0.33                              | 0.664    | 0.9489                |



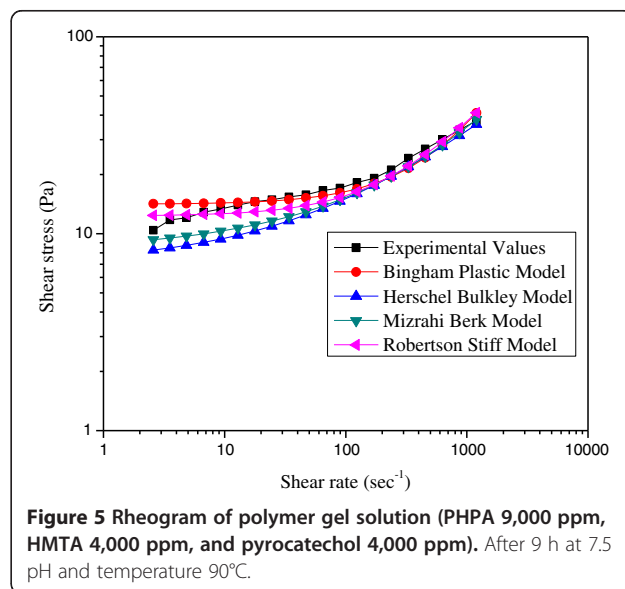
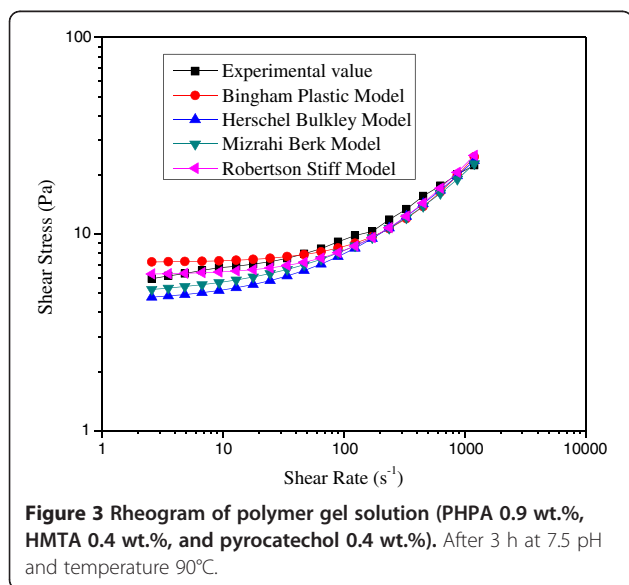
study, the temperature is 90°C and pH 7.5) is the cross-linking of polymer solution with organic or inorganic cross-linkers. In this case, the hexamethylenetetramine cross-linker is produced by the condensation reaction of formaldehyde with ammonia which then hydrolyses to form an unstable compound methanediol which dissociates to yield formaldehyde at room temperature. The hexamine cross-linker on hydrolysis yields formaldehyde which then combines with pyrocatechol cross-linker and forms 3, 4, 5, 6-tetramethylol pyrocatechol. Further, partially hydrolyzed polyacrylamide reacts with 3, 4, 5, 6-tetramethylol pyrocatechol and forms three-dimensional networks of polymer gel [25].

#### Applicability of viscoplastic flow models

The developed polymer gel behaves like a non-Newtonian fluid; hence, viscoplastic flow models may be applied in this system. Here, four inelastic-viscoplastic flow models including a yield stress parameter were employed to make a quantitative evaluation of the steady shear flow behavior of polymer gel solution, and then the applicability of these models was also examined in detail.

A general viscoplastic flow model having a yield stress term may be expressed by the following form:

$$\tau^{n_1} = \tau_o^{n_1} + k\gamma^{n_2} \quad (1)$$



where  $\tau$  is the shear stress,  $\tau_0$  is the yield stress,  $\gamma$  is the shear rate,  $k$  is the consistency index, and  $n_1$  and  $n_2$  are material parameters related to the material's flow behavior, and consequently, each flow model is determined according to the conditions of  $n_1$  and  $n_2$ .

Table 1 summarizes the viscoplastic flow models adopted in this study and their flow characteristics. Here,  $\tau_0$  is the yield stress of each model, and  $k$  is the consistency index related to a high-shear limiting viscosity, and  $\gamma_\infty$  as the shear rate is increased towards infinity.  $n$  is the flow behavior index, a material parameter that determines the shear-thinning nature of a material. In order that the models summarized in Table 1 could predict a shear-thinning behavior, both  $n_1$  and  $n_2$  must be positive values, and  $n_1$  should be larger or equivalent than  $n_2$ .

In order to determine the polymer gel solution parameters of each model, a linear regression analysis was used for the Bingham model, while a nonlinear regression analysis method was used for the Herschel-Bulkley, Mizrahi-Berk, and Robertson-Stiff models. The calculated values of the polymer gel solution parameters from the viscoplastic flow models along with those of the determination coefficients and its comparison with the experimental values are reported in Tables 2, 3, 4, and 5 and Figures 2, 3, 4, and 5.

All the polymer gel solutions exhibit a marked shear-thinning behavior regardless of their pH. As expected, both the yield stress and consistency index values are not the same for the flow models. The value of the flow behavior indices provides a reference for the assessment of a shear-thinning nature, and it was observed that developed gelant is shear-thinning in nature.

The Bingham plastic, Herschel-Bulkley, Mizrahi-Berk, and Robertson-Stiff models give an excellent ability to describe the flow behavior of polymer gel solution. All of these four models have the values to determine coefficients near to 1 and show a clear tendency that the yield stress values remain unchanged with change of pH of the polymer gel solution.

The similar values of the determination coefficients are obtained for different flow models. The Bingham plastic, Herschel-Bulkley, Mizrahi-Berk, and Robertson Stiff models are all in good agreement with the experimentally measured data over a whole range of shear rates tested. But Robertson stiff model has better agreement with the experimental values of shear stress and shear rate data of the developed polymer gel system than the other models tested.

## Experimental

Initially, the stock solution of partially hydrolyzed polyacrylamide in brine solution (1.0 wt.%) was prepared and kept for aging at ambient temperature for 24 h. Further, fresh solutions of hexamine and pyrocatechol were pre-

pared in brine ahead of mixing the polymer and cross-linkers to form gelant. The appropriate solution of partially hydrolyzed polyacrylamide, hexamine, pyrocatechol, and brine were thoroughly mixed at room temperature by magnetic stirrer. The pH of the gelant solution was measured by Century CP-901 digital pH meter (Century Instruments Private Limited, Chandigarh, India). The pH of the gelant was maintained using 1N sodium hydroxide and 1N hydrochloric acid. Finally, the solution was transferred into small glass bottles and kept at the desired temperature in the hot air oven (90°C). At regular intervals of time, rheological behavior at different shear rates was measured using Physica Rheolab MC1. The concentration of polymer was 0.9 wt.%, whereas those of the cross-linkers, i.e., pyrocatechol and HMTA, were 0.4 and 0.4 wt.%, respectively.

## Conclusions

The following conclusions are drawn from the present study:

- The developed polymer gel solution behaves like a non-Newtonian shear-thinning fluid.
- The rheological behavior of polymer gel varies with time as the gelation time increases; the gel solution will be more viscous, and the increase in viscosity is due to the cross-linking reaction.
- The nonlinear rheological models like Herschel-Bulkley, Mizrahi-Berk, and Robertson-Stiff models are found to be more suitable compared to the linear rheological model like the Bingham plastic flow model.
- Out of the three nonlinear rheological models (Herschel-Bulkley, Mizrahi-Berk, and Robertson-Stiff), the Robertson-Stiff model has better agreement with the experimental values of shear stress and shear rate data of the developed polymer gel system.

## Competing interest

The authors declare that they have no competing interests.

## Authors' contributions

USY carried out the experiments using the Physica Rheolab MC1 and analyzed the data with non-Newtonian viscoplastic flow models using nonlinear regression method. VM has supervised the research work. USY and VM participated in the interpretation of results and drafted the manuscript. All authors read and approved the final manuscript.

## Author' information

USY is a Ph.D. student of the Department of Petroleum Engineering, Indian School of Mines. VM is an associate professor of the same department.

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