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Research Article

Experimental Study on the Rheological Properties of Polymer Solutions and Solid Suspensions

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Abstract

This work deals with experimental study on the rheological behavior of polymer solutions, solid suspensions and the effect of adding polymers to solid suspensions. All polymers studied in this work are water soluble and used in industries as a rheology control additive (rheology modifiers), these are: Carboxymethyl cellulose (CMC), Xanthan Gum (XC), Hydroxyethyl cellulose (HEC), and Polyvinyl alcohol (PVA). Solid suspensions used are: Bentonite, Graphite and Corn starch. Experimens were performed with a concentration range of 4-40 g/L for CMC, HEC, XC, and 2-10 g/L for PVA, and the concentration range for solid suspensions were: Bentonite 50-120 g/L, Graphite 30-90 g/L and Corn Starch 300-800 g/L. It was found that as polymer concentration was increased, the flow behavior index (n) decreased, and the range of n was between 0.4 - 0.7 at 20°C. Increase the concentration of solid suspension causes the decrease of the flow behavior index (n), the range of n was between 1-1.3 at 35°C. The flow curves of polymer solutions and solid suspensions were studied using the power law model. By using the Solver Add-in in Microsoft Excel, the Bingham plastic model was found to be the best fits the experimental results of adding polymer to solid suspensions (PVA to Bentonite suspensions). The effect of adding PVA polymer on the rheological behavior of bentonite slurry was studied, it was found that the apparent viscosity of Bentonite/PVA decreases with increasing shear rate.

Keywords: *Rheology, Apparent viscosity, Flow curves, Polymer solutions, Solid suspensions.*

1. Introduction

Rheology is the branch of science that deals with the flow and deformation of materials. Rheological instrumentation and rheological measurements have become essential tools in the analytical laboratory for characterizing component materials and final products, monitoring process conditions, and predicting product performance and consumer acceptance (Dalwadi, *et al*, 2005).

Polymer molecules are long chain molecules composed of many repeating units. The bonds along the polymer backbone are continually rotating, and as a result, the molecule itself is continually changing orientation and configuration on a length scale much smaller than the equilibrium size. Polymer solutions can be considered as liquid mixtures made of long macromolecular chains, and small, light molecules of solvent (Gowariker, *et al*, 1986).

Polymer solutions, in general exhibit non-Newtonian pseudo plastic behavior i.e., its viscosity decreases with increasing shear rate. At rest, the chains of polymers are randomly entangled, but they do not set up a structure because the electrostatic forces and predominately repulsive when the fluid is in motion, the chains tend to align themselves parallel to the direction of flow, this tendency increases with increase in shear rate, so that the effective viscosity decreases (Gray, *et al*, 1981).

In dilute polymer solutions, the rheology of solution is depending solely on the dynamics of an individual chain and the number of chains (i.e. concentration) in the system. At high concentrations, interactions between polymer molecules impact the rheology in a significant way. As concentration further increases, polymer solutions exhibit a change from fluid-like to more elastic-like behavior (Kirk-Othemer, 1998).

The rheology of suspensions, colloidal dispersions and emulsions provide critical information for product and process performance in many industrial applications, and in order for them to give proper product performance, or to process efficiently, they must be stable. But these are often complex formulations of solvents (or fluids), suspended particles of varying size and shape, and various additives used to affect stability (Tadros, 1992).

The determination of rheological properties of bentonite-water systems is very important for its characterization. Bentonite dispersions have colloid

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structure. The control of the rheological properties of these systems is not only important from a technological but also from a scientific point of view (Kirk-Othemer, 1998).

Addition of polymer greatly changed the rheological properties of bentonite dispersion. The degree of interaction between polymer molecules and clay particles depended on the polymer concentration in the dispersion. The experiments carried out by İşçi, *et al* showed that the rheological properties of the sample can be brought to desired values by use of polymer concentrations. The polymers added to the bentonite dispersions interact with the clay particles, according to their ionic or non-ionic character. The ionic polymers induce electrostatic interactions, but the non-ionic polymers are adsorbed on the surface by steric interactions (PVA molecules attached on the net negatively charged clay particles) (İşçi, *et al* 2006).

Many flow models have been proposed, which are useful for the treatment of experimental data or for describing flow behavior (Chhabra, *et al*, 2008). Such mathematical models range from the very simple to the very complex. Some of them merely involve the plotting of data on graph paper. Others require calculating the ratio of two numbers. Some are quite sophisticated and require use of computers.

The aim of this work was to study experimentally the rheological behavior of polymer solutions and solid suspensions in water, and the effect of adding polymers to solid suspensions. Also the aim was to obtain the best model that fits the rheological properties of solid suspensions and polymer solution, and to study the effect of temperature on the rheological properties of polymer solutions.

2. Materials and Methods

2.1 Materials

All solid suspensions (Bentonite, Graphite and Corn starch) studied in this work were suspended in distilled water. Corn starch used is a commercially available product supplied by Qingdao Shengda Commercial & Trade Co., Graphite powder is a commercially available product supplied by Panzhihua Panxi Graphite Co., Bentonite is a commercially available supplied by Comieco Company, Wyoming.

All polymers (XC, HEC, CMC, and PVA) studied in this investigation are water soluble and are used in industries as a rheology modifiers. XC polymer used is a commercially available product supplied by Yongkang Rig china Group Co., HEC is a commercially available product type Cellosize QP 4400H, supplied from DOW Chemical Company. CMC polymer is supplied by BDH chemicals Ltd. PVA supplied by Yongan Baohualin Industrial Development Co.

2.2 Materials Preparation

To prepare CMC, HEC, and XC polymer solutions, 500 ml of distilled water was measured in a volumetric flask and placed in the Hamilton Beach cup. A previously dried polymer powder was weighted to the nearest mg using electronic balance. The polymer was lightly sprinkled into the water while stirring. Stirring continued for 30 min to ensure complete polymer dissolution then poured into a properly labeled bottle and sealed and kept at rest at room temperature for 24 hr prior to conducting the rheological measurements.

Microwave heating method was used to prepare PVA solution. Dry PVA powder was weighted to the nearest mg, and then the polymer was added to 500 ml of distilled water in a Pyrex beaker with stirring. The beaker was covered with microwave plastic wrap and placed in a microwave oven. The microwave was turned on high for three minutes. The solution was stirred and heated for an additional three minutes. The prepared solution was allowed to cool, and then poured into a properly labeled bottle and sealed and kept at rest at room temperature for 24 hr prior to conducting the rheological measurements.

2.3 Rheological Measurments

Fann VG-Viscometer, Model 35A was used to measure the rheological properties. The cup was filled to the scribed line with the test sample and placed on the platform of the instrument. The platform was raised so that the surface of the test sample was level with the scribed line on the rotor. The instrument was set to rotate at 600 rpm until a steady reading was obtained (3 min). This reading was recorded as the 600 rpm reading to equalize the temperature of the bob, rotor and solid suspension and stopped the viscometer.

The above procedure was repeated for 300, 200, 100, 6 and 3 rpm.

To study the effect of adding PVA to bentonite suspensions, the prepared bentonite slurry at the concentration 40g/L was poured into a properly labeled jug. The PVA polymer was added, at different concentrations 2, 5, 7, and 10g/L. The samples were stirred for an additional 20 minutes using the Hamilton Beach mixer after PVA addition, interrupting briefly at 5 and 10 minutes to scrape any adhering material on the sides of the cup into the fluid. The samples were placed in closed containers (covered Hamilton Beach cups or equivalent) and were allowed to static age for 2 hours at room temperature. After all concentrations were prepared (Bentonite-PVA), the rheological properties were measured.

3. Results and Discussion

3.1 Effect of Polymer Concentration on Flow Curves

Figures 1, 2, and 3 shows the effect of polymer concentration on flow curves. These figures indicate that the shear stress increase with the increase in the shear rate. The fluid has been observed nonlinear (non-Newtonian) behavior.

At low concentration the flow curve of polymer solutions is approximately linear and the flow curves are close to each other. At high concentration the flow curves of polymer solution bends down and the flow curves are far from to each other.

Choi (2008) concluded that, the increased numbers of polymer molecules result in more interaction between polymer chains, which cause more friction effects to increase the shear stress. At very low concentrations there is no strong interaction between polymer molecules. In this region, the effect of concentration is not appreciable.

Increasing the polymer concentration decreases the distance between polymer particles and the slopes of the lines increase with increased polymer concentration. The apparent viscosity increases with increasing the concentration since the polymer solution with higher concentration has stronger intermolecular force.

Equations that describe the effect of polymer concentration on the flow behavior index (n) can be presented in a linear form as shown in equations 1-3, in the range of polymer concentrations between 4-40 g/L.

$$n_{CMC} = - 0.0063\, C_{CMC} + 0.6935 \qquad (1)$$

$$n_{XC} = - 0.0210\, C_{XC} + 0.5318 \qquad (2)$$

$$n_{HEC} = - 0.0021\, C_{HEC} + 0.5479 \qquad (3)$$

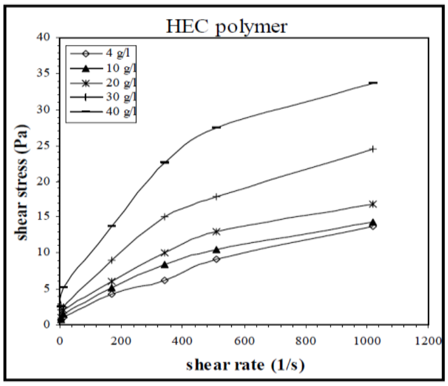

Fig.1 Effect of HEC polymer concentration on flow curves at 20°C

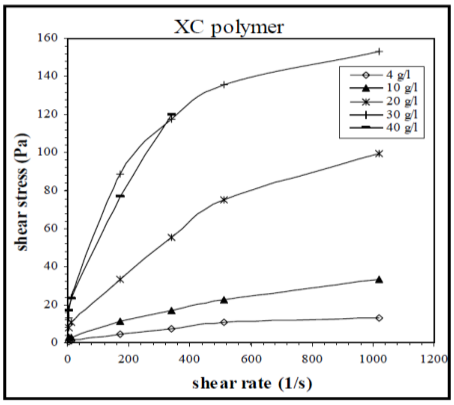

Fig.2 Effect of XC polymer concentration on flow curves at 20°C

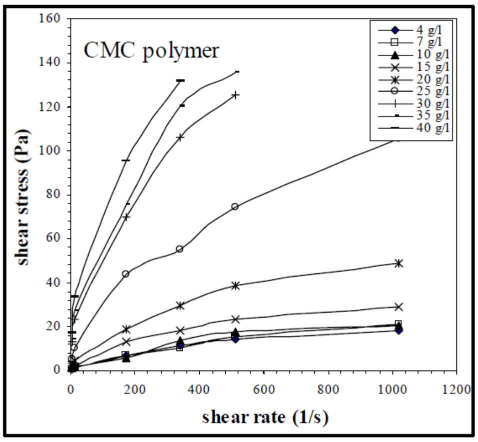

Fig.3 Effect of CMC polymer concentration on flow curves at 20°C

3.2 Effect of Temperature on Polymer Solution Viscosity

The effects of temperature on polymer solution viscosity are shown in figures 4, 5, and 6.

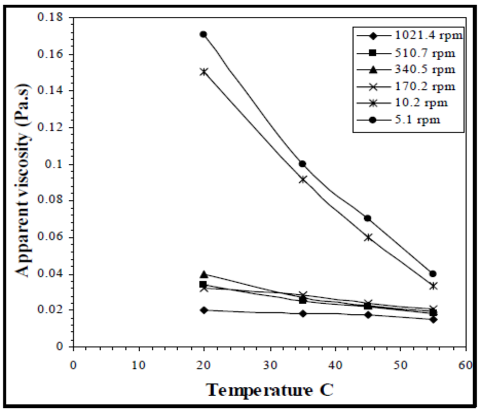

Fig.4 Effect of temperature on CMC polymer viscosity at concentration 10g/L

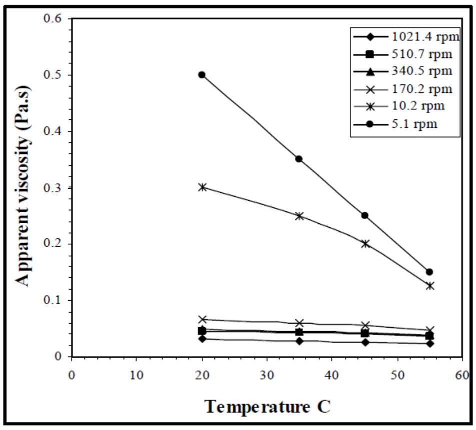

Fig.5 Effect of temperature on XC polymer viscosity at concentration 10g/L

The results show that the viscosities of the three polymers (CMC, XC and HEC) decreased with increasing shear rate and with increasing temperature, as expected. However, temperature effect was more significant at higher concentrations.

Liu, *et al*, (2007) concluded that, the viscosity of materials decrease as temperature increases. This is due to increase in the distances between particles of polymer causes low attraction forces. The increase in temperature destroys the bonding between particles. Practically, plot of Log η vs. T tend to be straight line over a considerable range of values.

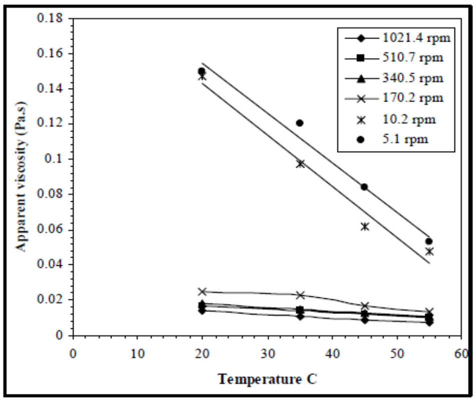

Fig.6 Effect of temperature on HEC polymer viscosity at concentration 10g/L

3.3 *Effect of Polymer Type on Viscosity*

The effects of polymer type on viscosity at the same concentration of 10 and 20 g/L are shown in figures 7 and 8. At same concentration, XC polymer solutions have higher viscosities than other polymer solution used in this work.

Barnes (1989) concluded that, the polymer that higher in molecular weight exhibits more pronounced viscoelastic behavior than the polymer which is lower in molecular weight. We can conclude that, in the range of polymer concentration used in this study, the apparent viscosity can be ordered as:

$$\eta_{XC} > \eta_{CMC} > \eta_{HEC}$$

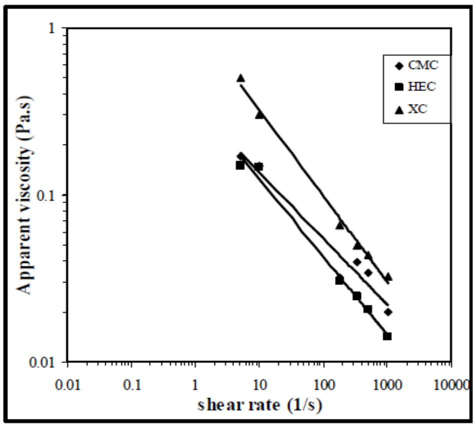

Fig.7 Effect of polymer type on viscosity at polymer concentration of 10g/L at 20°C

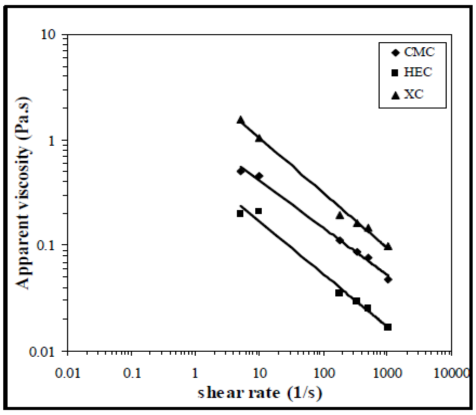

Fig.8 Effect of polymer type on viscosity at polymer concentration of 20g/L at 20°C

3.4 *Effect of Solid Suspension Concentration on Flow Curves*

The effects of suspension concentration on flow curves are shown in figures 9, 10, and 11. From these figures one can see that with increase in solid suspension content the shear stress gradually increase.

Mewis, *et al* (2002) concluded that suspension rheology at low solids concentration is primarily dictated by the particle liquid interfacial interactions. Under shear, there is enough liquid phase between particles to lubricate them and the interaction between particles is mainly conducted by the liquid. With increasing solids content, however, the mean distance between particles decreases and drastic interactions such as particle-particle and hydrodynamic effects influence the flow.

Triantafillopoulos (1948) concluded that increasing the volume fraction seems to universally increase the tendency for shear thickening, where by the gradual shear thickening appears at lower volume fractions than the sudden variety. With increasing volume fraction the critical shear rate decreases and the subsequent viscosity increase becomes steeper and larger.

As shown in figure 11 (the flow curve of corn starch suspension), at low shear rate the flow curve behavior is shear thinning and the increasing gradually in shear rate cause the flow curve to become shear thickening.

Equations that describe the effect of solid suspension concentration on the flow behavior index (n) can be presented in a linear form as shown in equations 4-6.

In the range of Bentonite concentrations between 50-120 g/L :-

$$n_{Bentonite} = 0.0012\, C_{Bentonite} + 0.9549 \qquad (4)$$

In the range of Graphite concentrations between 30-90 g/L :-

$$n_{Graphite} = 0.0036\, C_{Graphite} + 0.9136 \qquad (5)$$

In the range of Corn starch concentrations between 300-800 g/L :-

$$n_{\text{Corn starch}} = 0.0001\, C_{\text{Corn starch}} + 0.9869 \qquad (6)$$

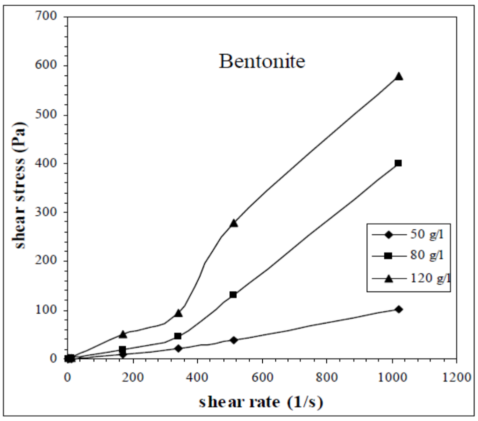

Fig.9 Effect of bentonite concentration on flow curves at 35°C

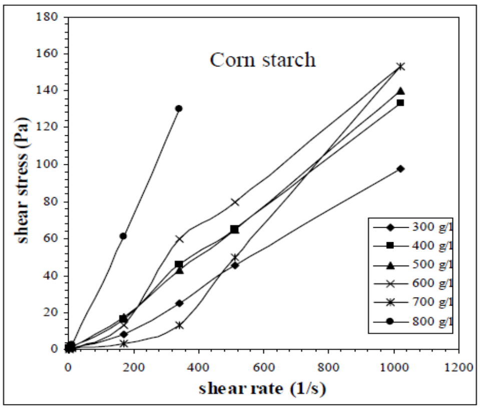

Fig.10 Effect of graphite concentration on flow curves at 35°C

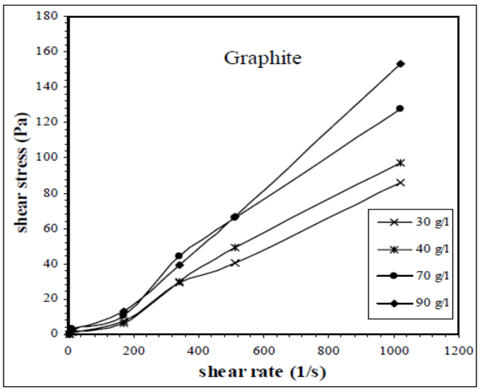

Fig.11 Effect of corn starch concentration on flow curves at 35°C

3.5 Viscosity of Solid Suspensions

In figures 12, 13, and 14 the shear rate variation with apparent viscosity are shown for Bentonite, Graphite and Corn starch suspensions. The apparent viscosity of a shear thickening solid suspensions increases as the shear rate increases.

At low shear-rates, slight shear-thinning can be observed because antiparticles repulsion forces delay shear thickening. The low level of viscosity at these shear rates reflects the non-flocculated nature of the system. At a gradually increase shear rate the viscosity begins to increase steeply. The viscosity rise by nearly an order of magnitude in the process.

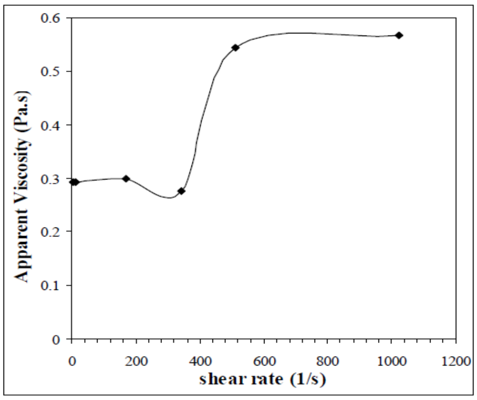

Fig.12 Apparent viscosity of bentonite suspension at concentration 120 g/L at 35°C

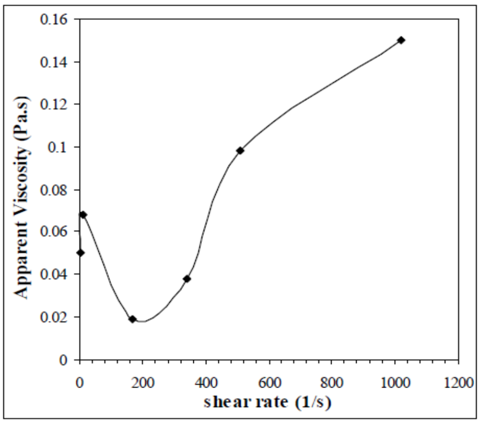

Fig.13 Apparent viscosity of corn starch at concentration 700g/L at 35°C

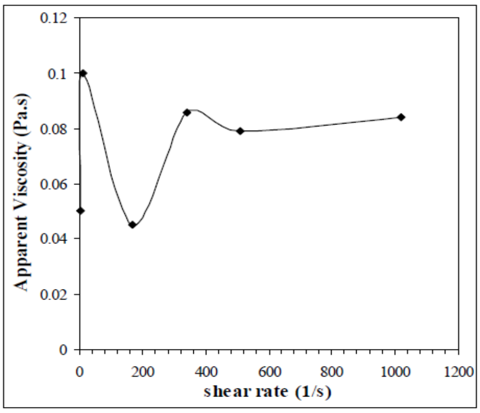

Fig.14 Apparent viscosity of graphite at Concentration of 30 g/L at 35°C

3.6 Effect of Adding PVA to Bentonite

Figures 15 and 16 show the effect of adding PVA to bentonite suspensions. The determination of rheological properties of bentonite slurry (bentonite/ water) systems is very important for its characterization. Bentonite dispersions have colloid structure, the control of the rheological properties of these systems is not only important from a technological but also from a scientific point of view.

The rheological property of the bentonite in water is shear thickening (dilatants) and the apparent viscosity increases with increased shear rate. This characteristic property is not desired in many applications but can be changed to gain the desired property with the addition of various polymers.

PVA is a polymer with non-ionic structure, which is dissoluble in water. Non-ionic polymer does not interact electrostatically with charged bentonite particles. The polymer molecules can attach or anchor on the particle surfaces and into the interlayer. Adsorption of the polymer on charged surface of the clay particles leads to significant modification of the charge distribution in the electrical double layer.

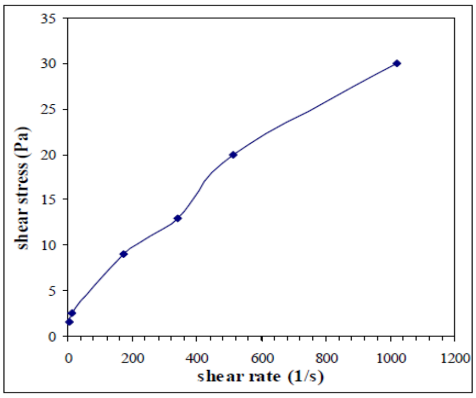

Fig.15 Flow curve of bentonite/PVA (concentration of PVA=2 g/L) at 35°C

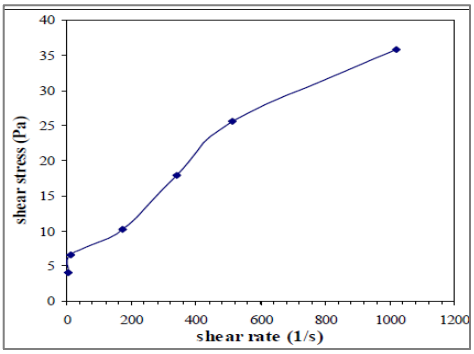

Fig.16 Flow curve of bentonite/PVA (concentration of PVA=10 g/L) at 35°C

4. Flow Model Selection

The selection of the flow model that best fit the rheological behavior is useful for treating experimental data or for describing flow behavior. In this work a method which was proposed by Morrison (2005) is used. This method uses the Solver Add-in in Microsoft Excel to optimize the solution.

The solver allow us to put constrains on the ways in which it manipulate the cells it is changing. For our work we know that none of the model parameters may be negative, so we put this as a constraint. The results for using the add-in in Microsoft excel for the Bentonite/PVA are shown in tables 1 and 2. From these tables, one can conclude that the Bingham plastic model best fits the experimental results (lower value in sum of square error). So this model will be considered in the following section.

Figures 17 and 18 illustrate the results of using the solver add-in in Microsoft Excel for adding different concentrations of PVA (2 and10) g/L to bentonite at concentration of 40 g/L.

Table 1 Flow equations for flow models

Flow model	Flow equation	Eqn. no.
Newtonian	$\tau = \eta\,\gamma$	(7)
Bingham Plastic	$\tau - \tau_o = \eta\,\gamma$	(8)
Power law	$\tau = \kappa\,\gamma^n$	(9)
Modified power law	$\tau - \tau_o = \eta\,\gamma^n$	(10)
Robert-Stiff	$\tau = A\,(\gamma + C)^B$	(11)

Table 2 Model selection for Bentonite/PVA using Add-in in solver Microsoft Excel

Bentonite conc. (g/L)	PVA conc. (g/L)	Sum of square error **Equation no.**				
		7	**8**	**9**	**10**	**11**
40	2	1.911	0.172	0.403	0.224	0.483
40	5	1.858	0.489	0.500	0.859	0.856
40	7	1.850	0.377	1.283	1.977	1.450
40	10	1.928	0.131	0.298	0.440	0.383

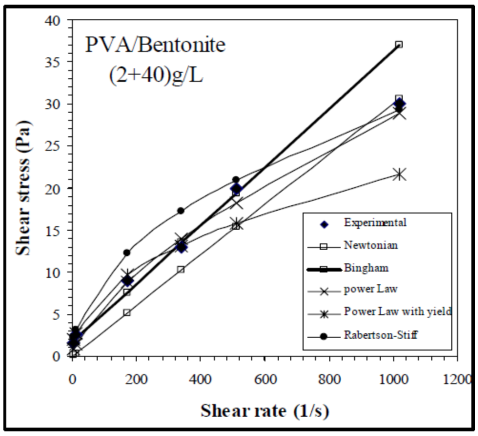

Fig.17 Experimental results and flow models representation For PVA (2 g/L) / Bentonite suspensions (40 g/L) at 35°C

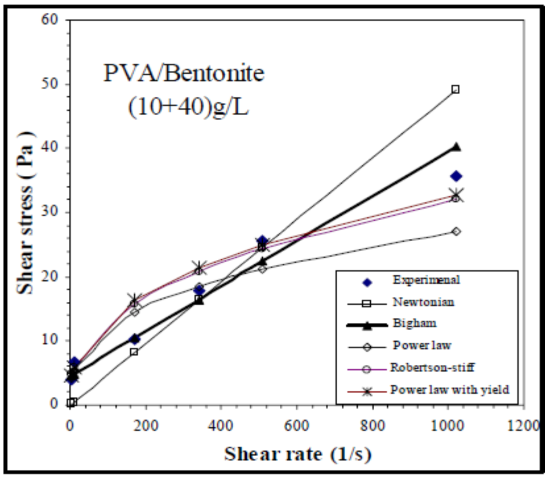

Fig.18 Experimental results and flow models representation For PVA (10 g/L) / Bentonite suspensions (40 g/L) at 35°C

The ideal Bingham material is an elastic solid at low shear stress values and a Newtonian fluid above a critical value called the Bingham yield stress, τ_B. The plastic viscosity region exhibits a linear relationship between shear stress and shear rate, with a constant differential viscosity equal to the plastic viscosity, η_p. If subjected to shear stress smaller than the yield stress, they retain a rigid structure and do not flow. It is only at stresses in excess of the yield value that flow occurs. In the case of a Bingham plastic model, the shear rate is proportional to shear stress in excess of the yield stress.

$$\tau = \tau_B + \eta_p \ \gamma \qquad (12)$$

The experimental results are shown in figures 19 and 20, which are plot of shear stress versus shear rate in Bingham plastic model at PVA concentrations of 2 and 10 g/L added to 40 g/L bentonite slurry.

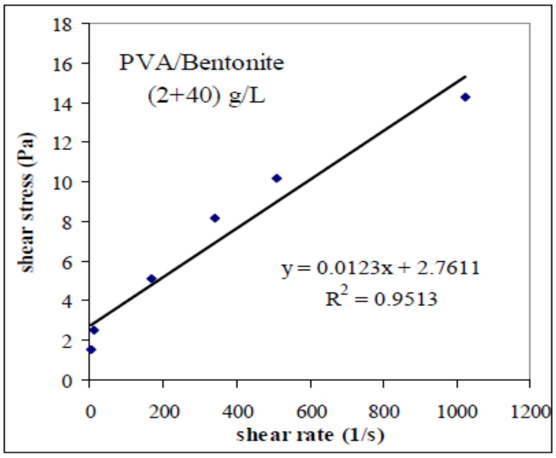

Fig.19 Rheogram for PVA (2 g/L) / Bentonite suspensions (40 g/L) at 35°C

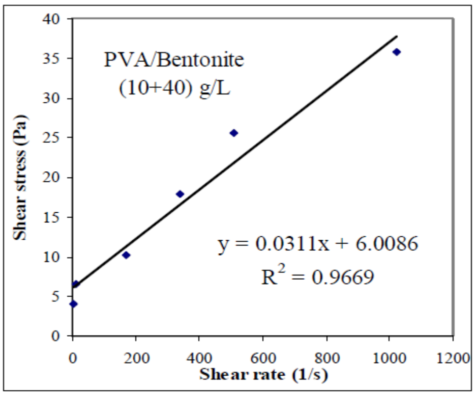

Fig.20 Rheogram for PVA (10 g/L) / Bentonite suspensions (40 g/L) at 35°C

Conclusions

1. All polymer solutions used in this work (XC-polymer, Carboxymethyl cellulose and Hydroxyethyl cellulose) behave as shear-thinning fluid, in which the viscosity decrease as the shear rate increase and all solid suspensions used in this work (Bentonite, Graphite and Corn starch) behave as shear-thickening fluid, in which the viscosity increase as the shear rate increase.
2. As the polymer and solid suspension concentrations are increased, the flow behavior index (n) are decreased and increased respectively. This behavior reflects the fact that as the polymer concentration increases the solution become far from Newtonian behavior. Correlations were developed, which describe the effect of polymer and solid suspensions concentration on the flow behavior index (n) for each polymer and solid used in this study.
3. XC-polymer solutions have a higher viscosity, and its viscosity decreases much more, when subjected to same shear rate, than other polymer solutions used in this study.
4. By using the Solver Add-in in Microsoft Excel, the Bingham plastic flow model was found to be the best fit to the experimental results of added PVA/Bentonite.
5. By adding PVA to bentonite suspension, the suspension turned from shear thickening behavior to shear thinning behavior.

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