Predicting rheological properties of water-based polymer mixtures from their component properties – Poly-Anionic Cellulose and Xanthan gum

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ABSTRACT

When designing drilling muds for the petroleum industry, polymers can be combined to obtain desirable rheological properties, different from those of the components individually. The effect of Xanthan gum (Xg) on rheological properties of Poly-Anionic Cellulose (PAC) has been investigated. A comprehensive description of shear viscosity is presented together with viscoelasticity of combined PAC and Xg polymers. An empirical correlation has been developed to predict the overall non-Newtonian behaviour of mixtures over a range of PAC and Xg concentrations. Higher Xg concentrations lead the polymer mixtures to be more elastic while the shear viscosity seems less dependent on shear rate at high shear region.

INTRODUCTION

The drilled cuttings are usually transported up to the ground with drilling fluids ("drilling muds"). In addition to the transportation of drilled cuttings, drilling fluids play an important role in controlling the formation pressure, cooling and cleaning the drill bit, reducing the friction and in avoiding the loss of fluids to the formation, etc.^{1,2,3}. In particular, for directional drilling, drilling fluids must be reached the rock reservoir with high permeability in order to achieve a higher well productivity⁴. To fulfil these tasks, drilling fluids need to be designed; so that they perform efficiently.

Water-based drilling muds are the most widely used drilling fluid type in oil industry due to many reasons, including less environmental issues^{1,4}. They are usually non-Newtonian, exhibiting both viscous and elastic properties under deformation; referred to as viscoelasticity, which helps in suspending proppants within the well. Rheology of the drilling fluid is a governing factor in consideration of proppant settling as well as achieving the aforementioned tasks.

Rheological models such as power-law model, Bingham Plastic model, Casson model, Carreau model, Herschel-Bulkley model, etc. generally characterize drilling fluids. The parameters of any particular drilling fluid can then be derived from the appropriate rheological model.

The complexity of the water-based drilling mud is mainly due to the different additives such as viscosifiers, shale inhibitors, weighting material, etc. Today, there are many types of polymers and viscosifiers, which are added to the drilling mud in order to enhance the capacity of colloidal and rheological properties of drilling fluids¹. That means the interaction between different polymers has been considered to achieve different properties of drilling fluids. Poly-Anionic Cellulose (PAC) and Xanthan gum (Xg) are two such types of polymers, which in some cases are used as viscosifiers too. In the literature, there are many scientific articles which have been addressed the rheological properties of

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individual polymers^{3,5,6,7}. But, the studies that have addressed the combined effect of the polymers mentioned above are very limited.

Nowadays, researchers^{8,9} have paid attention to investigate whether the shear viscosity of the fluid or its elasticity is more dominant in controlling the suspended solids when viscoelastic drilling fluids are used. In such a situation, accurate measurement of rheological properties is vital in understanding the non-Newtonian fluid behaviour of drilling fluids together with its structure¹⁰. physics and Viscoelastic properties of the drilling fluids strongly influence the gel strength, solids controlling, transportation, solids filtration loss characteristics, etc.¹¹. Therefore, the study of elasticity and the relative importance of shear viscosity together with elasticity of the drilling fluid has become very important where the possibility of predicting the rheological properties of polymer mixtures would make the decision easier.

In summary, there is an extensive amount of scientific work related to studies on rheological properties of different fluid systems individually, but the section on predicting the rheological properties of combined polymers in order to achieve the intended use is not as complete. This paper incorporates a comprehensive description of shear rate dependent viscosity together with viscoelasticity of PAC and Xg combined polymers and an empirical correlation to predict the non-Newtonian behaviour of the polymer blend. Furthermore, the results of this study provide quantitative information about the dynamic properties of the concerned biopolymers.

METHODOLOGY

Materials and sample preparation

The two polymer solutions of PAC and Xg were prepared individually by mixing with clean tap water. The white/off-white colour PAC granular powder with a bulk

density of $400 - 880 \text{ kg/m}^3$ was provided by M-I Swaco, England. The Xg was provided by M-I Swaco, Norway and appeared as a cream-to-tan powder with a bulk density of 800 kg/m^3 . The water-polymer solutions were mixed using the Silverson L4RT-A mixer at low shear conditions for 15 - 20 minimize shear-induced minutes to degradation. The individual concentrations of PAC were prepared as 0.2 and 0.4 w/w% while the individual concentrations for Xg were prepared from 0.05 to 0.4 w/w%. The prepared individual samples were kept still for 48 hrs, for complete hydration and for the eventual release of any trapped air bubbles. After a sequence of calculation and dilutions, nine different samples were prepared to be used in the experiments and kept still for 24 hrs more to enable relaxation of the sample and to reduce possible still existing prestresses deriving from the preparation of the sample. The two PAC solutions were analysed for hysteresis to find out the most stable PAC concentration. Based on the results, PAC 0.4 w/w% was selected as the base fluid to be mixed with different Xg concentrations (see steady-state results section). The combined polymer concentrations used for the experiments are mentioned below in Table 1.

Table	1:	Test	samples	with	their	com	ponents
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Sample	PAC	Xg
number	concentration	concentration
1	0.4 w/w%	0 w/w%
2	0.4 w/w%	0.05 w/w%
3	0.4 w/w%	0.10 w/w%
4	0.4 w/w%	0.15 w/w%
5	0.4 w/w%	0.20 w/w%
6	0.4 w/w%	0.25 w/w%
7	0.4 w/w%	0.30 w/w%
8	0.4 w/w%	0.35 w/w%
9	0.4 w/w%	0.40 w/w%

The nine samples shown in Table 1 were tested for steady-state and dynamic-state rheological properties using an Anton Paar

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MCR 302 apparatus at a constant temperature of 21 °C and ambient pressure. The geometry with concentric cylinder mode (CC27 - bob radius 13.327 mm and cup radius 14.455 mm) was employed to have a high measuring accuracy and low liquid evaporation. The solutions were gently stirred for few minutes before loading into the cylinder cup to sample uniform for achieve а the experiments. After pouring the required amount of sample to the measuring cup, the bob was lowered at a very slow speed in order to prevent the disruption of the solution It is assumed that the samples structure. have sufficient adhesion to the measuring bob and the cylinder cup without any wallslip effects and the samples are deformed homogeneously throughout the entire shear gap in order to achieve accurate rheological parameters.

RESULTS AND DISCUSSION

The results of the experimental series to investigate the effect of Xanthan gum (Xg) concentration on the rheological properties of Poly-anionic Cellulose (PAC) are presented in this section.

Steady state results

The two PAC solutions were tested separately under the hysteresis mode in order to find the most stable solution/concentration to be mixed with Xg. The hysteresis mode was conducted for two repeated cycles in order to check the repeatability of the results. In the hysteresis curves drawn in Fig. 1, the upper curve represents the ramping up process from low shear rate to high shear rate, and lower curve represents the ramping down process from high to low. A representative method of calculating the relative hysteresis was adopted using Eq. 1¹².

Hys = Hysteresis %
=
$$\frac{|\mu_{max} - \mu_{min}|}{\mu_{average}} \cdot 100\%$$
 (1)

Based on Eq. 1, the relative hysteresis for the two PAC solutions are mentioned in Fig. 1, itself. The relative hysteresis in the lowest shear region is higher compare to that in high shear region. This is due to the lower accuracy of measurements at very small angles of torque and angular displacement within the very low shear region, which could be attributed to the start-up and timedependent transient effects.



Figure 1: Hysteresis (Hys) analysis for PAC

Based on the result, PAC 0.4 w/w% showed the least relative hysteresis and therefore, PAC 0.4 w/w% sample was selected to proceed with the study by mixing with different concentrations of Xg.

Viscosity at steady shear conditions

Typical curves for the shear viscosities of the combined polymers measured at constant temperature are shown in Fig. 2. All the test runs were carried out four times in order to check the repeatability and reproducibility.

It can be seen that the viscosity of PAC has increased due to the addition of Xg as expected. The shear viscosities of the combined polymer samples are in the range of $10^2 - 10^4$ mPa.s at low shear rates while the viscosities of all samples being tested, approach a value around 30 mPa.s as the shear rate reaches to 1000 s⁻¹. This rise of shear viscosity is linked to the separate contribution of Xg itself, but quite likely also



due to the intermolecular interactions between PAC and Xg molecules. However, it is quite important to see the significance at different shear regions. There is a significant influence of Xg concentration on the shear viscosity of PAC at low shear region. Even at low shear rates such as 0.1 s⁻¹, many of the combined polymer samples have not reached the constant shear viscosity or the zero-shear region. This observation is much more significant when the added Xg concentration is increased where the combined polymers tend to be more inter-linked and elastic (or gel type) rather than being viscous. The influence of Xg concentration on the PAC viscosity is less significant at high shear region, where the shear rate is somewhat similar to that within the drilling pipe according to Bui et al.¹¹.

It can be noted that the shear-thinning behaviour (seen from the slope of the curves) is more prominent with high concentrations of Xg. At high shear rates, this is more visible since the flow encounters less resistance. The disentanglement of the polymer coils in solution or the increased orientation of the polymer coils in the direction of flow could have influenced this behavior of the samples at higher shear region. It is of primary importance to check the influence on shearthinning behaviour of the polymer mixtures based on the power-law rheological model compared to that of the individual polymers. Since the experimental data show a nonlinear pattern for the viscosity curves at very low shear region, power-law model was used over a selected shear rate domain to visualize how the experimental results fit with rheological models. This selected shear rate domain consists of medium to high shear rates ranging from 1 to 1000 s⁻¹. The medium to high shear region represents the most relevant shear rates which is experienced by drilling fluids inside the annulus and drilling pipe respectively¹¹. See Table 2 for the results.

	Samula	K	n
	Sample	[mPa.s ⁿ]	[-]
	PAC 0.4 w/w%	174.2	0.73
ers	Xg 0.05 w/w%	26.2	0.64
, m	Xg 0.10 w/w%	120.9	0.48
lo	Xg 0.15 w/w%	175.8	0.46
al I	Xg 0.20 w/w%	323.4	0.38
Individua	Xg 0.25 w/w%	784.4	0.29
	Xg 0.30 w/w%	1141.4	0.26
	Xg 0.35 w/w%	1685.5	0.22
	Xg 0.40 w/w%	2249.8	0.19
S	PAC 0.4 + Xg 0.05 w/w%	261.3	0.68
ombined Polymer	PAC 0.4 + Xg 0.10 w/w%	336.8	0.64
	PAC 0.4 + Xg 0.15 w/w%	427.7	0.61
	PAC 0.4 + Xg 0.20 w/w%	536.5	0.58
	PAC 0.4 + Xg 0.25 w/w%	692.2	0.54
	PAC 0.4 + Xg 0.30 w/w%	909.9	0.51
	PAC 0.4 + Xg 0.35 w/w%	1280.8	0.46
С	PAC 0.4 + Xg 0.40 w/w%	2047.6	0.39

 Table 2: Power-law parameters for the individual and combined polymers

The values presented in Table 2 also confirm the fact that the added Xg concentration has increased the shearthinning behaviour of the polymer mixture. However, when the consistency index (K) is considered, it can be noted that the individual K for Xg has been greatly enhanced at low concentrations of polymer mixtures while at higher concentrations, the enhancement is somewhat controlled by the PAC molecules. Similarly, the behaviour index (n) keeps reducing with added Xg concentration by making the polymer mixtures more shearthinning but, at higher concentrations, the mixture is unable to become more and more shear-thinning since it has to obey the effects of PAC molecules.

As mentioned before, for this particular study the approximation with power-law rheological model is limited from medium to high shear region since it fails to predict the rheological properties at very low shear region. This may be due to the viscoelastic properties of the polymer mixture¹¹, which will be discussed in the later sections.

As per the intention of this study, the impact of Xg on the rheological properties of PAC solutions is illustrated in Fig. 3,

concerning the K and n values obtained from power-law. It is to find out the relationship of K and n values together with the individual sample concentrations and how far it is possible to predict the properties of polymer mixtures.



The K and n values have been fitted into third order polynomials as shown in Fig. 3. The experimental results are in good agreement with the fitted polynomial having R^2 values for both the curves better than 99%. This means that, it is possible to predict the behaviour of any combined polymer with PAC 0.4 w/w% and Xg, using the below mentioned two correlations.

$$n = -6.061 C_{Xg}^{3} + 3.199 C_{Xg}^{2} - 1.157 C_{Xg}$$
(2)
+0.7303

$$K = 6.236 * 10^4 C_{Xg}^3 - 2.302 * 10^4 C_{Xg}^2 +3871C_{Xg} + 148.3$$
(3)

Here C_{Xg} is the Xg concentration in w/w%. Furthermore, the authors have supplemented the current study with some other experimental results which have been obtained by them to develop a more generalized correlation for predicting the *K* value as presented in Eq. 4.

$$K' = \frac{K}{M} \tag{4}$$

Where, $M = 2.47. (10 C_{PAC})^{-0.65}$, C_{PAC} is

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the PAC concentration in w/w% and K' is the generalized consistency index of any blended polymer solution in mPa.sⁿ which contains PAC and Xg.

Model validation

A separate rheological investigation was carried out to validate the presented correlations for K and n of a polymer mixtures. See Fig. 4 for the experimental and predicted shear viscosity curves based on the developed correlations.



The K and n values for the combined polymers were calculated using Eq. 2 and Eq. 4 based on their respective C_{PAC} and C_{Xg} . According to Fig. 4, it can be seen that the predicted viscosity curves well represent the viscosity curves for combined polymers with errors less than 14% within the shearthinning range. Shahi & Kuru¹³ observed that there exists a strong correlation of 'n' and 'K' of the shear-thinning fluids with the percent error of settling velocity. This dependency is higher for highly shear-thinning fluids and decreases for the fluids close to Newtonian. highly This means that accurate measurement of fluid properties is required to determine the required amount of viscosifiers in order to achieve the intended degree of solids separation and other functions associated to drilling fluids. Therefore, such correlations presented in Eq. 2 and Eq. 4 are indeed helpful in predicting the rheological characteristics and then to design the blended polymers which contain PAC and Xg.

The error bars presented with shearviscosity curves in Fig. 2 illustrate the accuracy (in terms of the standard deviation) of viscosity measurements. It can be noted that, the error associated with the viscosity measurements is higher at low shear region ($\gamma < 1 \text{ s}^{-1}$) compared to that at high shear region. The main reason for this behaviour is the start-up effects or the time-dependent transient effects.

Dynamic state results

Oscillatory Amplitude Sweep Test

Determination of the Linear Viscoelastic (LVE) range is one of the main goals of performing oscillatory rheological experiments where the structural characteristics of any polymer or sample can be investigated. See Fig. 5 for the storage modulus (G') and loss modulus (G'') curves for PAC 0.4 + Xg 0.35 w/w% and PAC 0.4 + Xg 0.4 w/w% mixtures at an angular frequency of 10 rad/s and at 21 °C.



Figure 5: Storage Modulus (SM) & Loss Modulus (LM) for Amplitude Sweeps

Both G' and G'' curves display constant plateau values within the LVE range at low amplitude values and G' is used to determine the limiting value of shear strain (γ_L), since it is the first to deviate from the constant plateau value. In a similar manner, the LVE range in terms of γ_L has been determined for all the samples and the results are tabulated in Table 3.

	-	
Sample	γ_L	$\dot{\gamma} = \gamma_L * \omega$
PAC 0.4 + Xg 0.05 w/w%	15.8 %	1.58 s ⁻¹
PAC 0.4 + Xg 0.10 w/w%	13.8 %	1.38 s ⁻¹
PAC 0.4 + Xg 0.15 w/w%	11.9 %	1.19 s ⁻¹
PAC 0.4 + Xg 0.20 w/w%	10.1 %	1.01 s ⁻¹
PAC 0.4 + Xg 0.25 w/w%	9.0 %	0.9 s ⁻¹
PAC 0.4 + Xg 0.30 w/w%	7.9 %	0.79 s ⁻¹
PAC 0.4 + Xg 0.35 w/w%	7.1 %	0.71 s ⁻¹
PAC 0.4 + Xg 0.40 w/w%	6.0 %	0.6 s ⁻¹

Table 3: Limiting value of shear strain and its corresponding shear rate

According to the γ_L values in Table 3, it can be seen that the linear viscoelastic (LVE) range of the individual PAC and the combined polymers is generally very low at an angular frequency of 10 rad/s. According to Ferry¹⁴, this could be due to the entanglement of long chain molecules in a concentrated polymer solution results in a transient network structure, which can lead to the viscoelasticity of the samples. It is noted that when the Xg concentration is increased, the LVE range of the combined polymer is reduced. The LVE range of the polymer mixture is shorter than that of pure PAC solution revealing the fact that by adding Xg. the combined mixtures become more viscous, confirming the viscosifier properties of Xg. However, it is interesting to see the effect at higher Xg concentrations. Two cross over points can be observed for the added Xg concentrations 0.35 and 0.40 w/w%, denoting that those two mixtures are having more or less gel type properties. For these two higher concentrations of added Xg, elastic behavior dominates the viscous, and they exhibit a gel-like consistency in the low shear range where the transient viscoelastic response is quick. But, for the low concentrations, the loss modulus curve is lying on top of the storage modulus curve indicating that the transient viscoelastic response is stronger compared to that of higher concentrations.

Oscillatory Frequency Sweep Test

The viscoelastic property of any polymer solution in its LVE range is reflected in the frequency sweep data which can be used to investigate the time-dependent deformation behavior of any sample. Fig. 6 shows the frequency sweep experiment results for PAC 0.4 + Xg 0.35 w/w% and PAC 0.4 + Xg 0.4 w/w% polymer mixtures at constant shear strain of 1% and at 21 °C.



Figure 6: Storage modulus (SM) and Loss modulus (LM) for Frequency Sweeps

In a frequency sweep test, high frequency corresponds to a fast deformation and a low frequency corresponds to a slow deformation. From such a test, it can thus be determined whether the response of the sample to deformation is viscous or elastic. The crossover points for the moduli curves are important since it quantifies the relaxation time for the sample and hence the viscoelasticity. Out of all the nine samples, only the added Xg concentrations of 0.35 and 0.40 w/w% showed the crossover points and that confirms their elastic properties with compared to the results obtained from amplitude sweeps. Since the reciprocal of the crossover frequency represents the relaxation time of any particular viscoelastic fluid, the polymer mixtures of PAC 0.4 + Xg 0.35 w/w% and PAC 0.4 + Xg 0.4 w/w% have their relaxation times of 15.8 ms and 10 ms respectively. Knowing such properties is of paramount importance in order to determine

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and keep the required degree of particles in suspension. A larger viscoelastic range and gel formation is desired to prevent the settling of particles and enhance the cuttings carrying capacity. Therefore, viscoelasticity is a desired property in drilling operations and thus, the possibility of predicting the behaviour in advance would be an advantage.

CONCLUSION

A set of experiments were carried out to determine the influence of Xg on the rheological properties of PAC, using a rheometer with the option for both rotating and oscillatory testing. Both steady and dynamic tests were performed to investigate the flow behavior and viscoelastic properties of the combined polymer. Results confirm that, when the added Xg concentration to the PAC is increased, the combined polymer or the solution gets increasingly elastic relative to viscous loss properties. Polymer-polymer interaction is the reason for the higher viscosity at higher concentrations. The experimental results were well represented by the power-law rheological model. The behaviour of the combined polymers can be predicted from the correlation developed from the study. It can be used for calculation of non-Newtonian behavior of mixtures which contains PAC and Xg. The dynamic oscillatory tests were employed to investigate the LVE region of the polymer mixtures. It is found that the mixture becomes more elastic with increasing amounts of Xg, even if the LVE range itself is less influenced. Mixed PAC and Xg solutions show that both the shear-thinning non-Newtonian behaviour and the viscoelastic properties are much more pronounced at higher polymer concentrations. Therefore, optimal drilling performance depends strongly on the optimum dosage of different polymers into the drilling fluids. As a total outcome, it can be clearly said that the addition of Xg into water-based drilling mud should be carried out carefully in order to achieve the required properties of the drilling fluid.

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REFERENCES

- Caenn, R., & Chillingar, G. V. (1996). "Drilling fluids: State of the art". *Journal* of Petroleum Science and Engineering, 14(3), 221-230.
- Omland, T. H. (2009). "Particle Settling in non-Newtonian Drilling Fluids". (*PhD Thesis*), University of Stavanger, Norway.
- Saasen, A., & Løklingholm, G. (2002).
 "The Effect of Drilling Fluid Rheological Properties on Hole Cleaning". Paper presented at the IADC/SPE Drilling Conference, Dallas, Texas, 26–28 February 2002.
- Baba Hamed, S., & Belhadri, M. (2009).
 "Rheological properties of biopolymers drilling fluids". *Journal of Petroleum Science and Engineering*, 67(3), 84-90.
- Edali M, Esmail M.N. and Vatistas G.H. (2001). "Rheological properties of high concentrations of carboxymethyl cellulose solutions", *Journal of applied polymer science*, 79(10), 1787-1801.
- Herraez-Dominguez J, De León F.G.G., Diez-Sales O. and Herráez-Domínguez M. (2005). "Rheological characterization of two viscosity grades of methylcellulose: An approach to the modeling of the thixotropic behaviour", *Colloid and Polymer Science* 284(1), 86-91.

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- Benchabane A. and Bekkour K. (2008).
 "Rheological properties of carboxymethyl cellulose (CMC) solutions", *Colloid and Polymer Science* 286(10), 1173.
- Arnipally, S. K., & Kuru, E. (2017a). "Effect of Elastic Properties of the Fluids on the Particle Settling Velocity", Paper presented at 36^a International Conference on Ocean, Offshore and Arctic Engineering, Trondheim, Norway, 25–30 June, 2017
- Arnipally, S. K., & Kuru, E. (2017b). "Settling Velocity of Particles in Viscoelastic Fluids: A Comparison of the Shear Viscosity vs Elasticity Effect", Paper presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, 9-11 October, 2017.
- Time, R. W., & Rabenjafimanantsoa,
 A. H. (2013). "On the Relevance of Laboratory Scale Rheometric Measurements for Calculation of Complex Large Scale Flows in Well Drilling and Pipe Flows", Annual Transactions of Nordic Rheology Society, (21), 69-79.
- Bui, B., Saasen, A., Maxey, J., Ozbayoglu, M. E., Miska, S. Z., Yu, M., & Takach, N. E. (2012). "Viscoelastic properties of Oil-based drilling fluids", *Annual Transactions of the Nordic Rheology Society*, (20), 33-47.
- 12. Khatibi M., Potokin N. and Time R.W. "Experimental investigation of effect of salts on rheological properties of non-Newtonian fluids", *Annual Transactions of the Nordic Rheology Society*, (24), 117-126.
- Shahi, S., & Kuru, E. (2016).
 "Experimental investigation of the settling velocity of spherical particles in Powerlaw fluids using particle image

shadowgraph technique". International Journal of Mineral Processing, 153, 60-65.

14. Ferry J.D. (1948). "Viscoelastic properties of polymer solutions", *Journal* of research of the National Bureau of Standards, (41), 53-61.