Effect of concentration on the rheological behavior of aqueous non ionic polymer solutions

K. Benyounes[1], A. Benmounah[2], A.Mellak[1]

[1]Laboratoire Génie Physique des Hydrocarbures,Faculté des hydrocarbures et de la Chimie,Université M'hamed Bouguara de Boumerdes, 35000, Algeria

[2]Unité de Recherche Matériaux, Procédés et environnement, Université M'hamed Bouguara de Boumerdes, 35000, Algeria

Abstract

Rheological properties of aqueous derivative guar gum solutions at various concentrations (0.1%, 0.2%, 0.3%, 0.4%, and 0.5% w/w) were investigated in the rotational mode with a concentric cylinder using a controlled-stress rheometer over a wide range of shear rates (0-1000 s^{-1}). We had studied the rheological behaviour using shear stress / shear rate data. The effect of shear rate and polymer concentration has been analysed. The flow curves show that all polymer solutions exhibit an apparent viscosity which is dependent of shear-rate, no yield stress was detected. The rheogramms could be adequately described by several rheological models such, power-law and Williamson. It was found that the rheological parameters were greatly affected by polymer concentration. All polymer solutions have a shear-thinning behavior (n=0.35–0.85), the consistency index (k) and apparent viscosity increased with the increase in polymer concentration. The characterization of polymer solutions was completed with a time-dependent shear stress study that showed that the derivative guar gum dispersions don't exhibited thixotropic behavior.

Key words: Viscosity, rheology, polymer, shear rate

1. INTRODUCTION

The rheological properties of polymer solutions is of considerable technological importance in many domains, such as , food, pharmaceutical, textile, cosmetics, agricultural and petroleum industry(Kadajji and Betageri, 2011; Lapasin et al., 1995; Launay et al., 1997; Moraes et al., 2011; Singh and Sharma, 1991). Therefore, a good comprehension of rheological parameters of these polymers in aqueous solutions is required. Guar gum has been used in various formulations of food materials as emulsifier because it helps to prevent oil droplets from coalescing, as a stabilizer because it helps to prevent solid particles from settling. Guar gum is a natural polysaccharide composed of the sugars galactose and mannose. The backbone is a linear chain of β 1,4-linked mannose residues to which galactose residues are 1,6-linked at every second mannose, forming short side-branches. The guar gum polymer has a very high affinity for water. When the dry polymer is added to water, guar powders swell and hydrate, which means the polymer molecules become associated with many water molecules. Small quantities of guar powder in aqueous solution can exhibit high viscosity, which varies depending on the shear rate and temperature, showing a pseudoplastic behavior(Casas et al., 2000). The first fracturing fluids were oil-base, in the late 1950s, one of the first polymers used was guar gum for thickening the water-based fluids which is became more popular. The polymer molecules are cross-linked with metal ions to form fracturing fluid gels used to transport solid particles into fractures in subterranean oil formations in a process called hydraulic fracturing stimulation. The most common polymers used in fracturing processes are guar gums and guar gum derivatives.

Hydraulic fracturing is a technique of stimulating production of hydrocarbons from reservoir formations. Fracturing fluids are pumped into a well at sufficient rate and pressure to create a fracture in the reservoir formation. Proppants in the size range of 0.1-2.0 mm in diameter are carried down the wellbore and out into the fracture by the gel fracturing fluids. The guar polymer has several hydroxyl groups that will react with propylene oxide under basic conditions to form hydroxypropyl guar. The final quantity of propylene oxide attached to the polymer can be expressed in terms of *molar substitution,* frequently abbreviated as MS, which is defined as the moles of propylene oxide per mole of pyranose groups. The reaction changes some of the OH sites to $–O–CH2–CHOH–CH3$, effectively removing some of the crosslinking sites. The additional processing and washing removes much of the plant material from the polymer, so HPG typically contains only about 2% to 4% insoluble residue(Economides and Nolte, 2000). HPG was once considered less damaging to the formation face and proppant pack than guar, substitution makes HPG more stable at elevated temperatures than guar; therefore, HPG is better suited for use in high-temperature. Zhang et al.(2007) investigated the rheology of hydroxypropyl guar gum, he found that when the concentration of HPG increased from 1.5 to 2.5%, the thixotropic hysteresis area increased significantly, also, they have shown that the added salt (KCl and $CaCl_2$) to HPG lowers the zero-shear-rate viscosity and the thixotropy properties, especially at high concentration of the salt.

The aim of the present study is to characterise the rheological properties of GGD solutions. The principal topics to be examined here are the shear-dependent viscosity behaviour under various conditions. Given the industrially important applications and relevant scientific interest, the investigations on the rheological behaviour of GGD are very few.

2. EXPERIMENTAL AND METHODS

2.1 Materials

The guar gum derivative used in this study is a commercial product, which is used by the oil companies. Its moisture content and the pH value of aqueous 0.5 wt.% solution (25°C) were of 8.0% and 7.0 respectively. Guar can be derivatized with propylene oxide to produce hydroxypropylguar (HPG). The structure of the repeating unit of guar derivatives is shown in Figure 1. Polymer solutions were prepared in different concentrations ranged from 0.1 wt. % to 0.5 wt.%. After mixing, each polymer dispersion was poured in a covered vessel and left for one day at room temperature.
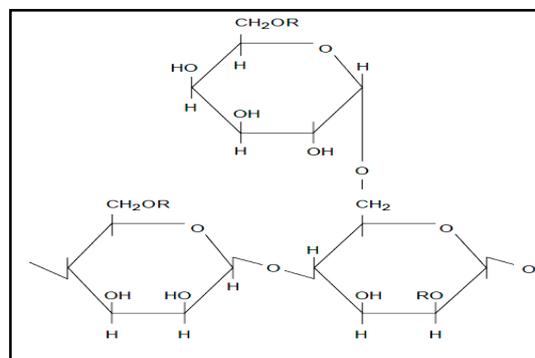

Fig.1 Molecular structure of guar
gum derivative showing the
mannose backbone structure

2.2 Apparatus

Rheological properties of prepared solutions s were measured with an AR 2000 rheometer (fig.2) from TA instruments using the concentric cylinder measuring system under various conditions.. The tests were performed at controlled temperature of 25 °C. Furthermore, to prevent water evaporation, a cover was placed around the geometry . Rheological parameters (shear stress, apparent viscosity and shear rate) were obtained from the software

Fig.2 Rheometer AR 2000

2.3 Rheological models

The flow curve of fluid will not only depend on its composition, but also on the protocol used in the flow test. Therefore, In the literature, there are many rheological models, the flow curves were fitted to the following equations:

2.3.1 Power law model

Power law is a two-parameter model indicating a non linear relationship between shear rate and shear stress(Ostwald, 1925), which is given as follows:

$$\tau = k\gamma^n \qquad\qquad (1)$$

where k is the consistency and n is the flow behavior index. The different values of n indicate the fluid behavior. For a Newtonian fluid, n = 1. If n < 1, the fluid is called pseudoplastic; if n > 1, the fluid is dilatant.

2.3.2 Williamson model

Williamson law is three-parameter model. The equation is:

$$\eta = \frac{\eta_0}{1 + (k\gamma)^n} \tag{2}$$

Where η_0 is zero-shear-rate viscosity

2.3.3 Vinogradov-Malkin model

Vinogradov-Malkin law is four-parameter model is given by the following is:

$$\eta = \frac{\eta_0}{1 + A\gamma^\alpha + B\gamma^{2\alpha}} \tag{3}$$

Where A,B and α are empirical constants.

The different models were fitted to measured rheograms using rheological data analysis software, which also estimated the standard error and correlation coefficient, for the various rheological models using Eq. (4) and Eq. (5) respectively. In a general way, an acceptable fit gives a standard error <20% and a correlation coefficient > 0.90.

$$ES = \left[\frac{\left[\frac{\sum(X_m - X_c)^2}{n-2} \right]^{1/2}}{X_m^{max} - X_m^{min}} \right] \times 1000 \tag{4}$$

$$R^2 = 1 - \frac{\sum(X_m - X_c)^2}{\sum X_m^2 - \frac{\sum X_C^2}{N}} \tag{5}$$

where X_m is the measured value, X_c is the calculated value, n is the number of data points and range is the maximum value of X_m—the minimum value.

3. Results and discussion

All rheograms were obtained by applying a slow rising ramp of stress, in order to take account of the relaxation time of the solutions. The rising ramp of imposed stress was 0.03 Pa/s. Figures 3 and 4 illustrate the effects of guar gum derivative concentration (0.1 to 0.5%) on the shear stress and apparent viscosity of aqueous GGD solutions under diverse shear rates. These curves are traced over a log–log scale that contains four cycles of shear rate from 0.1 to 1000 s^{-1}. For all concentrations, the apparent viscosity was observed to decrease with the increase of shear rate showing that these solutions behaved as typical non-Newtonian shear-thinning fluids. This is due to network disentanglement. Variations in the apparent viscosity of non Newtonian solutions with

shear rate can be ascribed to the orientation and the deformation of molecular network in the direction of flow

Analogous behaviour has also been observed for aqueous solutions of guar gum,(Casas et al., 2000; Whitcomb et al., 1980), anionic guar gum(Zhang et al., 2007), cationic guar gum(Zhang et al., 2007),amphoteric guar gum(Zhang et al., 2005), and other polysaccharides(Benyounes and Benmounah, 2012; Casas et al., 2000).
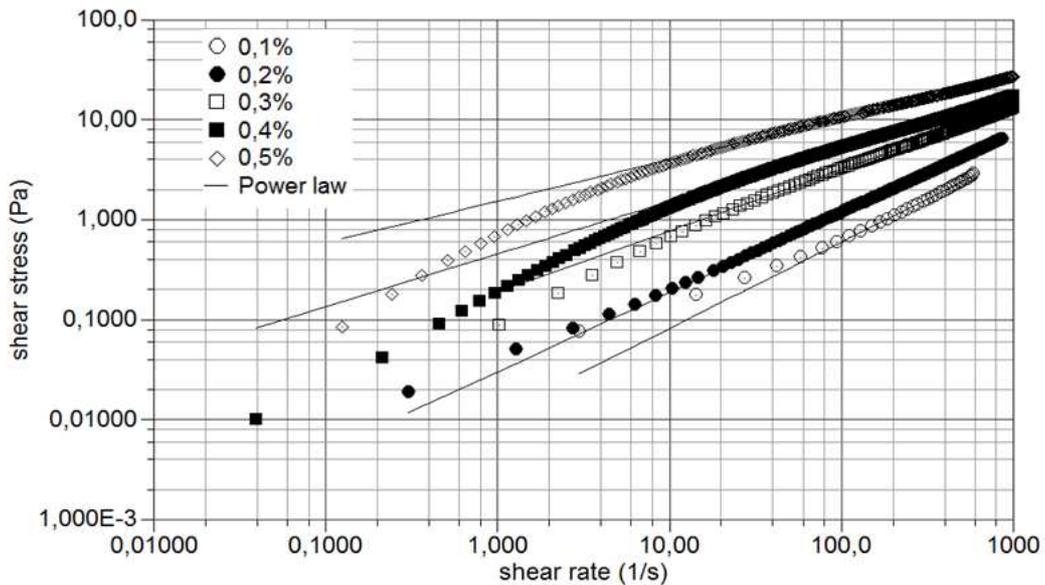

Fig.3 flow curve of of guar gum derivative at various concentrations
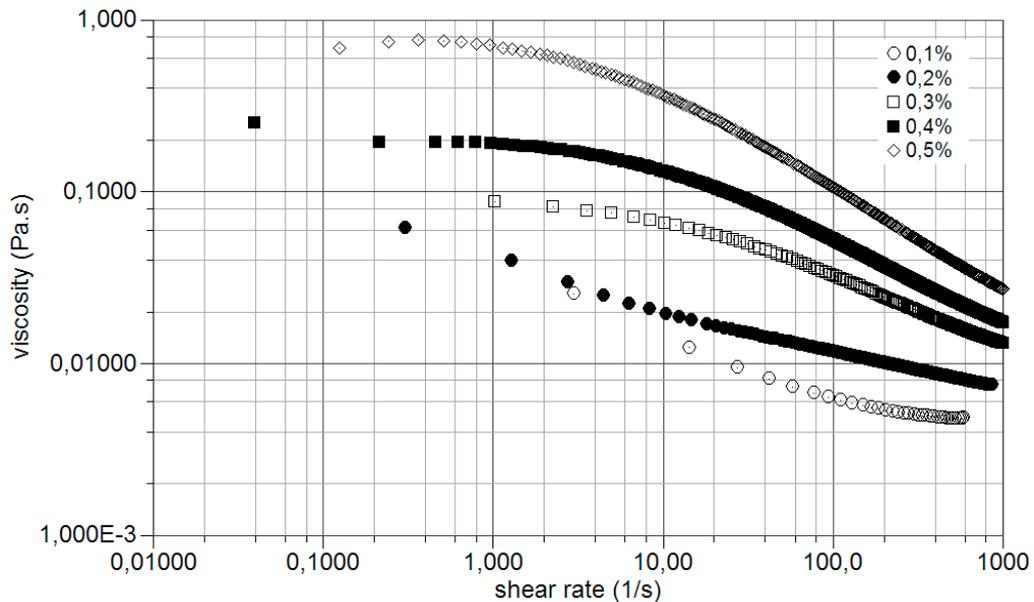

Fig.4 Viscosity as a function shear rate at different concentrations

The analysis of the curve(fig.5) marking the change of apparent viscosity as a function of the stress shows that the viscosity decreases slowly as the increase of shear rate, this indicates that the polymer solutions do not exhibit yield stress
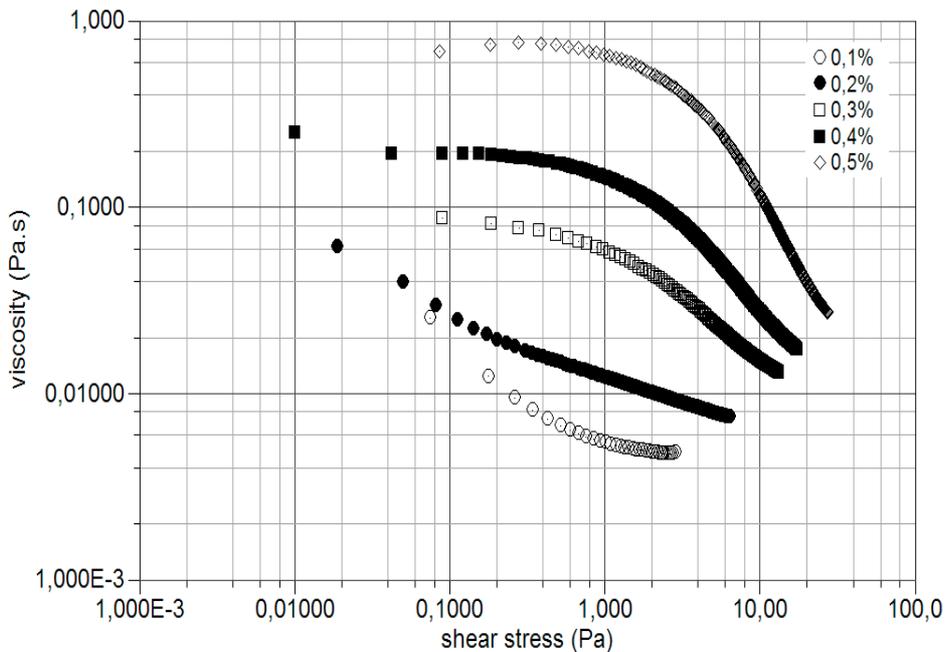

Fig.5 Variation of viscosity as a function shear stress of polymer solutions

For all the rheological models presented in the experimental section, the best-fit parameters were obtained by minimizing the standard error and maximizing the correlation coefficient of the absolute deviations between experimental and calculated values.

The analysis of the various flow curves by rheological models of Power Law, Williamson and Vinogradov- Malkin allowed us to calculate the rheological parameters namely: the flow index, the consistency index, viscosity at zero shear rate and the empirical constants.

Table 1 gives the values of rheological parameters obtained for aqueous GGD solutions using non-linear curve fittings which corresponding to correlation coefficients (R^2) and error standard (ES). The values of the correlation coefficient which are shown in table 1 for the three rheological models are higher than 0.99, at least we can say that the flow curves can well be represented by these rheological models.

The values of error standard in table I shows that the power law model is a adequate fit for the concentrations in GGD < 0.5% . The flow behavior index for 0,1% GGD shows that the flow is not close to Newtonian behavior (n=0.87). the williamson model appears to be superior to the

power law and Vinogradov- Malkin equations in that it furnished better results for the concentration in polymer of 0.5%.

From Table 1, it was found that the ηo value increased with the increase of polymer concentration when the temperature was kept constant.

Table 1: Rheological parameters of GGD at various concentrations for several rheological models

Rheological model		Concentration(%)				
		0.1	0.2	0.3	0.4	0.5
Power law	$k(Pa.s^n)$	0,01	0,03	0,19	0,46	1,53
	n(-)	0,87	0,79	0,61	0,53	0,42
	R^2	0,999078	0,999988	0,999798	0,99970	0,99937
	ES	14,16	1,67	5,87	19,64	15,56
Williamson	$\eta_0(Pa.s)$	0,01	0,03	0,13	0,3	1,75
	k(s)	0,01	0,05	0,12	0,19	0,88
	n(-)	0,23	0,3	0,46	0,53	0,62
	R^2	0,999026	0,999982	0,999608	0,9995	0,999655
	ES	15,22	3,54	8,67	25,73	10,99
Vinogradov- Malkin	$\eta_0(Pa.s)$	0,02	0,05	0,25	0,54	1,73
	A(s)	1,11	1,04	1,01	0,95	0,91
	B(s)	0	0	0	0	0
	α(-)	0,17	0,25	0,42	0,5	0,62
	R^2	0,999048	0,999973	0,999747	0,99969	0,999653
	ES	14,6	2,61	6,89	20,91	11,01

As illustrated in Fig. 6, the dependence between the concentration of GGD and the power law parameters(k,n) can be properly described with the exponential-law and linear law relationship for k and n as follows:

$$k = a.e^{b.C_{GGD}}$$ (6)

$$n = a'.C_{GGD}^b + b'$$ (7)

Where a, a',b and b' are empirical constants, a=0.00456; b=11.62462; a'=1.18062; b'=0,9975

A correlation between consistency index and flow index can be established (eq.8) from equations (6) and(7).

$$k = 0.00456e^{9.84n-9.82}$$ (8)

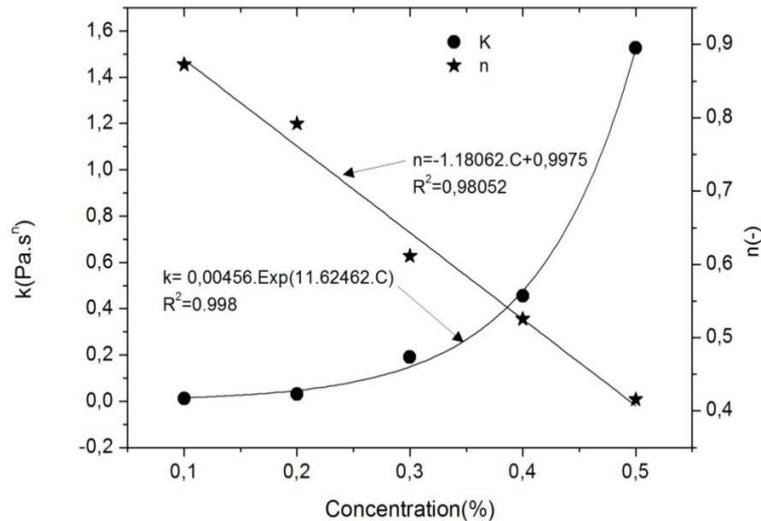Fig.6 Plot of k and n versus polymer concentration

From Williamson and Vinogradov- Malkin models, the four parameters (n, k, α and η_0) increased when concentration rosen. By cons, the parameter B is zero and the parameter A is nearly constant. Among these parameters the most sensitive one was the zero-rate viscosity η_0.

4.Conclusion

The rheological behavior of 0,1 to 0,5% guar gum derivative solutions were measured using a rheometer at room temperature of 25°C. With the increase of GGD concentration from 0.1 to 0.5%, the zero shear-rate viscosity increased. The influence of shear rate on rheological behaviour shows that all polymer solutions are non Newtonian, when guar gum is subjected to large shear conditions, a shear-thinning behavior is observed in the shear rate range of 0–1000 s^{-1}. All polymer solutions don't exhibit yield stress. The apparent viscosity of polymer in aqueous phase increases with the increase in the volume fraction of the polymer. When GGD concentration varies in the range of 0.1–0.5.0% (w/w), the K value increases while the n value decreases.

References

Benyounes, K., Benmounah, A. 2012. Rheological and electrokinetic properties of carboxymethylcellulose-water dispersions in the presence of salts. International Journal of the Physical Sciences.

Casas, J.A., Mohedano, A.F., García-Ochoa, F. 2000. Viscosity of guar gum and xanthan/guar gum mixture solutions. Journal of the Science of Food and Agriculture 80(12): 1722-1727.

Economides, M.J., Nolte, K.G. 2000. Reservoir Stimulation: Wiley.

Kadajji, V.G., Betageri, G.V. 2011. Water Soluble Polymers for Pharmaceutical Applications. Polymers 3(4): 1972-2009.

Lapasin, R., De Lorenzi, L., Pricl, S., Torriano, G. 1995. Flow properties of hydroxypropyl guar gum and its long-chain hydrophobic derivatives. Carbohydrate Polymers 28(3): 195-202.

Launay, B., Cuvelier, G., Martinez-Reyes, S. 1997. Viscosity of locust bean, guar and xanthan gum solutions in the Newtonian domain: a critical examination of the log ([eta]sp)o-log c[[eta]]o master curves. Carbohydrate Polymers 34(4): 385-395.

Moraes, I.C.F., Fasolin, L.H., Cunha, R.L., Menegalli, F.C. 2011. Dynamic and steady-shear rheological properties of xanthan and guar gums dispersed in yellow passion fruit pulp (*Passiflora edulis f. flavicarpa*). Brazilian Journal of Chemical Engineering 28(03): 483 - 494.

Ostwald, W. 1925. About the rate function of the viscosity of dispersed systems. Kolloid-Z. 3699–117.

Singh, P.K., Sharma, V.P. 1991. Effect of Additives and Aging on the Rheological Properties of Water-Based Drilling Fluid. Energy Sources 13(3): 369-387.

Whitcomb, P.J., Gutowski, J., Howland, W.W. 1980. Rheology of guar solutions. Journal of Applied Polymer Science 25(12): 2815-2827.

Zhang, L.-M., Kong, T., Hui, P.S. 2007. Semi-dilute solutions of hydroxypropyl guar gum: Viscosity behaviour and thixotropic properties. Journal of the Science of Food and Agriculture 87(4): 684-688.

Zhang, L.M., Zhou, J.F., Hui, P.S. 2005. Thickening, shear thinning and thixotropic behavior of a new polysaccharide-based polyampholyte in aqueous solutions. Colloids and Surfaces A: Physicochemical and Engineering Aspects 259(1–3): 189-195.