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EFFECT OF THE CONCENTRATION AND TEMPERATURE ON THE RHEOLOGICAL PROPERTIES OF DIUTAN GUM

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Abstract. *Diutan Gum is a polysaccharide obtained through the fermentation of bacteria of the genus Sphingomonas, being thus classified as a biopolymer. Diutan gum has several applications of industrial interest, especially in oil industry. In the present article, aqueous solutions of diutan gum (2000, 6000 and 8000 ppm) were tested on a rotating rheometer, determining various rheological properties, especially shear viscosity, obtained through flow curves at 40°C and 60°C. Stationary and dynamic tests were performed to investigate the behavior of diutan gum. Diutan gum showed a pseudoplastic behavior on viscosity curves and the concentration modify apparent viscosity values. All the oscillatory tests were performed inside the linear viscoelastic range. The elastic component was predominant upon the viscous portion in the range investigated. In creep tests, diutan gum presented elastic recovery for all the investigated cases, showing viscoelastic behavior.*

Keywords: *biopolymer, diutan gum, rheological properties*

1. INTRODUCTION

According to (Katzbauer, 1998), gum or hydrocolloid is defined as any water soluble, high molecular weight polysaccharide from plants or microorganism metabolites, which have the ability to contribute to the viscosity and gelation of products.

As shown by (Xu et al., 2015a), diutan gum is a microbial exopolysaccharide, linear and anionic, secreted by the bacteria *Sphingomonas sp.* with high molecular weight, from about 2.88 to 5.18 million g / mol, developed by Kelco ®. (Cano – Barrita and Leon - Martínez, 2016) and (Schmidt et al., 2013a) affirm that diutan gum´s structure is composed by the repetition of 6 sugars, consisting of the repeated configuration of rhamnose, glucose, glucoronic acid, glucose units. Their chemical units consist of repeating units with - 1,3 - D - glucopyranosyl, β- 1,4 - D - glucuronopyranosyl, β - 1,4 - D - glucopyranosyl and β - 1,4 - L - rhamnopyranosyl and two sugars L - rhamnopyranosyl attached to the lateral chains. (Schmidt et al., 2013b) also emphasizes in their work that the side chains consist of one or two monosaccharides and its main chain contains carboxylate groups providing anionic charge. Diutan Gum acts as a thickening agent, suspender, binder, emulsifier and stabilizer. (Xu et al., 2015a) attest that diutan gum has distinct physicochemical properties, being able to be used in adverse conditions such as high temperature and salinity.

Among the applications of microbial polysaccharides cited by works from (Xu et al., 2015a) and (Xu et al., 2015b), two topics were selected as the object of application of gums: civil construction industry, with specific application in the composition of cement; and petroleum industry, as drilling fluids and EOR components.

According to (Plank, 2004), big amounts of bio mixtures are useful in construction civil industry, including natural biopolymers as diutan gum. In their works (Cano – Barrita and León – Martínez, 2016) and (Sonebi, 2006) says that, in most cases, natural polysaccharides added to cement are called viscosity modifiers agents (VMA), because they are soluble in water e increase retention of water in the. Systems. (Xu et al., 2015a) and (Xu et al., 2015b) established that the particulars of biopolymers make an huge influence on the performance of cement paste, especially in terms of viscosity, improving cohesion e stability of cement.

As reported by (Xu et al., 2015a) and (Xu et al., 2015b), the use of biopolymers on petroleum industry turns more attractive by its application on enhanced oil recovery (EOR) and in drilling fluids, by its ability of rheological modification, high resistance to thermal and mechanic degradation. However, they are suitable to degradation due to your chemical structure. In drilling operation, drilling fluids act removing and suspending cuttings from the bottom of the hole. The final aqueous solution must have similar apparent viscosity with oil-based fluids.

1.1 Non Newtonian Fluids

For (Freitas, 2002), fluids whose behavior of the shear stress as a function of the rate of deformation at a given temperature and pressure are not linear are called non-Newtonian fluids. Most solutions of macromolecules and suspensions belong to this category.

Just as (Jain et al., 2016) says, rheological models were created in order to describe mathematically the relationship between stress - shear rate for non - Newtonian fluids. According to (Steffe, 1996), the Power Law or Ostwald model encompasses a reasonable number of fluids, and can be described in terms of shear stress through Eq.(1):

$$\tau = K.\dot{\gamma}^{n} \quad (1)$$

And in terms of shear viscosity, through Eq.(2):

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

For the ideal case, for both cases, n = 1, that is, the fluid is Newtonian. When n < 1, it is determined as shear thinning or pseudoplastic behavior. For n > 1, it is called shear thickening or dilating behavior.

1.1.1 Viscosity Curves

According to (Neto, 2006), stationary tests are used to obtain flow curves or viscosity curves. For the author, these curves are used to set the curves as Newtonian or Non – Newtonian Fluids and it respectively subclasses. These tests also analyze other factors as temperature and concentration.

(Shah et al., 2010) says that these tests are able to show the apparent viscosity behavior as a shear rate function. Besides this, the authors also named that the tests can be repeated any time as necessary, which allows analyze the fluid degradation.

1.2 Viscoelastic Behavior

Conforming to (Gunasekaran & Ak, 2000), materials that display elastic and viscous behavior simultaneously are called viscoelastic. An elastic solid stocks mechanic energy during the strain process and recovery it is to the original shape (before the imposed strain). On the other hand, viscous fluid lost this energy in the strain process. The simplest viscoelastic behavior is called linear viscoelasticity. This behavior follows Hook model (elastic behavior) and Newtonian model (viscous behavior). This kind of behavior is observed when the strain is very small, so the structure of the material is not affected. As showed by (Gunasekaran & Ak, 2003), the Equations (3),(4),(5),(6) show some viscoelastic parameters:

$$G' = G_0 \frac{\omega^2\lambda^2}{1+\omega^2\lambda^2} \quad (3)$$

$$G'' = G_0 \frac{\omega\lambda}{1+\omega^2\lambda^2} \quad (4)$$

$$|G^*| = \sqrt{(G')^2 + (G'')^2} \quad (5)$$

$$|\eta^*| = \frac{|G^*|}{\omega} \quad (6)$$

Where G' is called storage/elastic modulus; G'' is called loss/viscous modulus; $|\eta^*|$ is called complex viscosity; $|G^*|$ is called complex modulus; λ is the relaxation time of a Maxwell fluid and ω is the angular frequency.

1.2.1 SAOS tests

As cited by (Mezger, 2014), (Gunasekaran & Ak, 2000) and (Gunasekaran & Ak, 2003), SAOS methods must begin by amplitude sweep test or amplitude sweep. This test indicates the maximum stress or strain that the material hold without suffering any break in your structure. This value must be inside the linear viscoelasticity range. Only by determining this value it will be possible to perform other SAOS tests as for example, frequency sweep or frequency ramp, because they are dependent of the strain or stress values obtained on the amplitude test. Dynamic moduli, in this range, respect both Newtonian´s law and Hooke´s law.

Small amplitude oscillation shear (SAOS) tests consists on submitting the sample to small strains or stress to investigate the structure of the material and its development during different processes.

SAOS measures allow finding storage modules, loss modules and complex modulus as frequency function in the linear viscoelastic range. The storage modulus $G'(\omega)$ is the measure of the storage and recovery energy per cycle. The loss modulus $G''(\omega)$ is the measure of the lost or dispersed energy by heat per strain cycle.

There are four types of SAOS tests: amplitude sweep, frequency sweep, temperature sweep and time sweep. In this paper, the frequency sweep was used to investigate the behavior of the dynamic moduli and a possible existence of a crossover point. Before using the frequency sweep, an amplitude sweep test was used to determine the linear viscoelasticity of the material.

As related by (Mezger, 2014), (Steffe, 1996) and (Gunasekaran and Ak, 2003), frequency sweep or frequency ramp consists submitting the material to a sinusoidal strain or stress. Besides this, an increasing frequency range is imposed to the material. The stress or the strain must be selected carefully, to ensure that the behavior of the sample stays at the linear viscoelastic range The Equation (7) shows the sinusoidal stress that is submitted to the sample in SAOS tests:

$$\tau(t) = \tau_0 \sin(\omega t) \tag{7}$$

Where: $\tau_0 \rightarrow sinusoidal\ shear\ stress$
$\omega \rightarrow Angular\ Frequency\ [rad/s]$

1.3 Creep & Recovery

The main goal of creep & recovery tests is to define the viscoelastic behavior of the materials. A constant shear stress is imposed and it induces a resultant strain. Other aim of the test is to estimate if the material will show an elastic recovery when it suffers a deformation. Materials that don´t show any recovery are called viscous. On the other hand, materials that recovers totally are called elastic. Viscoelastic materials shows an intermediary behavior, i.e., it recovers partially of the deformation.

2. EXPERIMENTAL PROCEDURE

Diutan Gum was supplied by Kelco ®. The tests were performed at a Haake MARS III rheometer, with a cone and plate geometry C35/2°Ti. The maximum deviation allowed was ± 0.1 °C.

Dynamic and oscillatory tests were performed at temperatures of 40°C and 60°C, yielding the following rheological properties: apparent viscosity; dynamic modulus (storage, loss and complex) and complex viscosity.

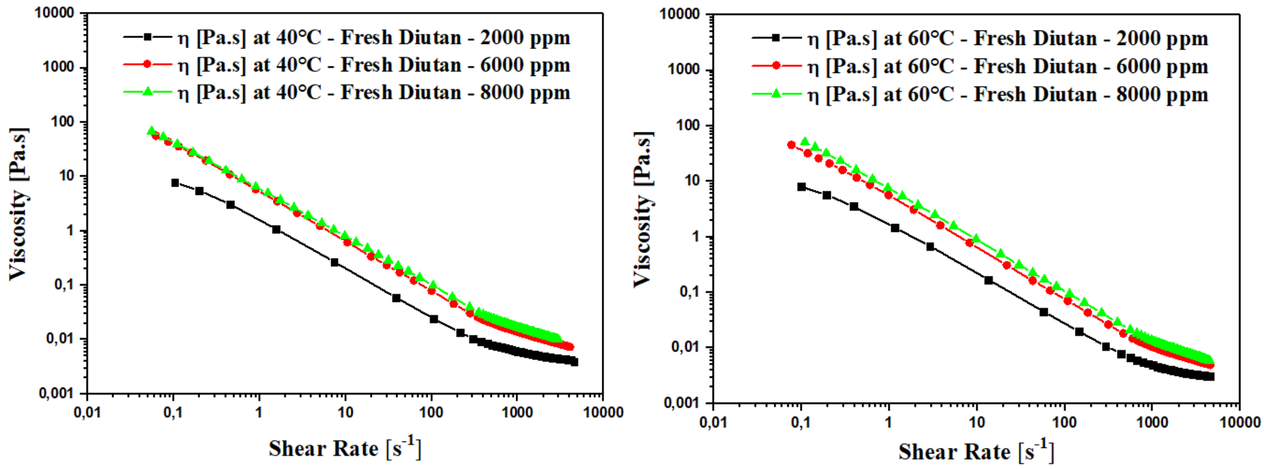
2.1 Sample Preparation

The solutions were prepared by mechanical stirring, diluting the specific concentrations in deionized water at room temperature of 25°C, with the angular velocity of the mixer at 500 rpm for ten minutes. As suggested by (Melo et al., 2013) and (Xu et al., 2015a), samples were kept resting for 12h before measurements to ensure the absence of bubbles and a correct hydration of the solution. After respecting resting time, before performing the tests, the samples were stirred to ensure that it was homogeneous as cited by (Ma et al., 2018) and (Melo et al., 2013).

3. RESULTS AND DISCUSSION

3.1 Viscosity Curves

Figure 1 (a-b) shows the viscosity behavior as a function of the shear rate of the aqueous solution of fresh diutan gum (2000, 6000 and 8000 ppm) at 40°C and 60°C



(a) (b)

Figure 1. (a) Viscosity Curve at 40°C – 2000 ppm, 6000 ppm and 8000 ppm, (b) Viscosity Curve at 60°C – 2000 ppm, 6000 ppm and 8000 ppm

The results on Figure 1 (a-b) show a typical pseudoplastic behavior. This shape is common for polysaccharides solutions with a high molecular weight. The apparent viscosity decreases when the shear rate increases. As described by (Chagas et al., 2004) and (Xu et al., 2015b), this behavior is related with the orientation of molecules along the flow line.

The results show the influence of the concentration on diutan gum. As long as concentration gets higher, the apparent viscosity also increases. The amount of entanglements formed is directly linked with the increase of the concentration explaining higher values of apparent viscosity for higher concentrations. According to (Bretas and D´Ávila, 2005), the presence of entanglements makes the flow process harder, and then the apparent viscosity increases.

3.2 SAOS curves

Figure 2 shows the amplitude sweep at 40°C and 60°C for a concentration of 8000 ppm. The tests were performed at the range of 0,01 Pa – 2 Pa, with an constant frequency of 1 Hz, as suggested by (Gunasekaran and Ak, 2000).

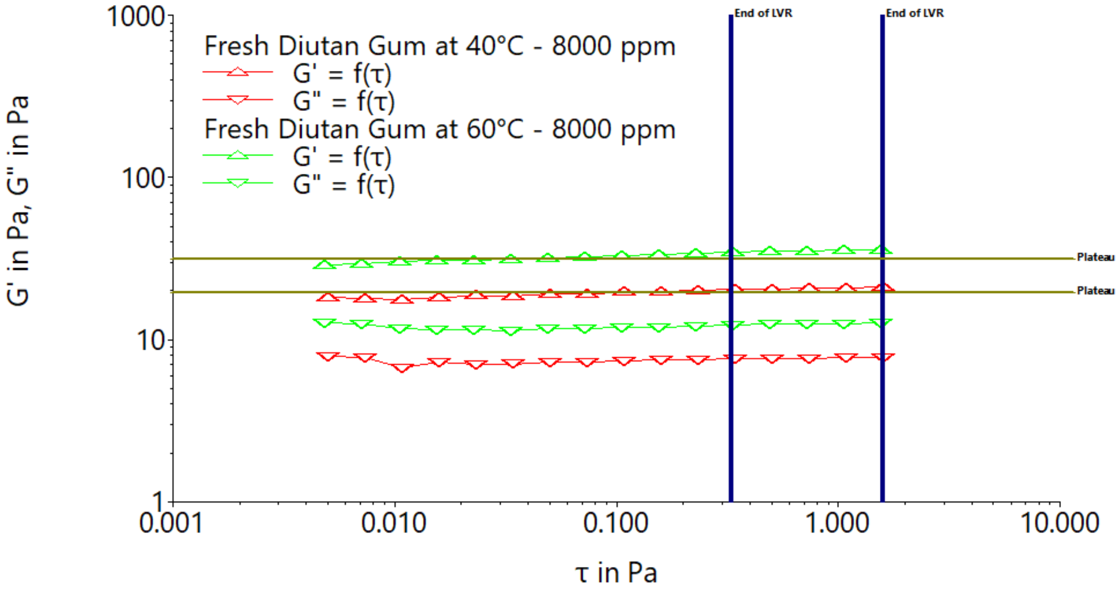
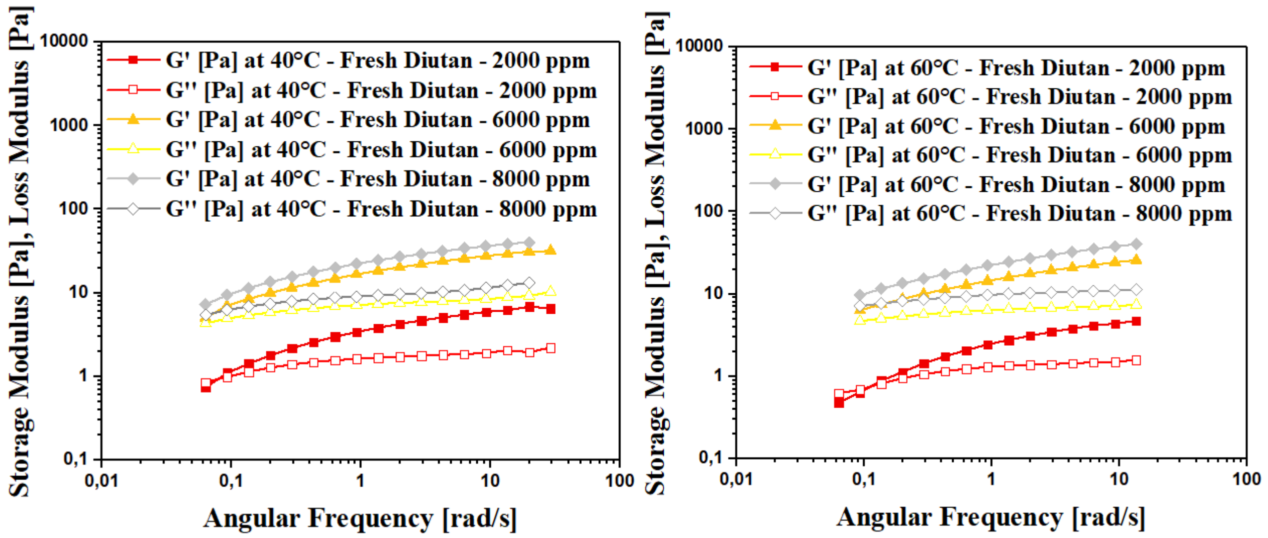


Figure 2. Amplitude Sweep – 8000 ppm

The results of Figure 2 show that the elastic component is higher than viscous portion. This phenomenon indicates that the elastic component occupies a larger proportion of the solution compared to viscous component at the low applied stress. Then, the value of the dynamic modulus decreases sharply when the applied stress exceeds the maximum stress, and slopes of both curves are not equal as described by (Xu et al., 2013).

Figure 3 (a-b) shows the frequency sweep for fresh diutan gum at 60°C for 2000, 6000 and 8000 ppm. The frequency range was from 0,01 Hz – 100 Hz. The shear stress was within the linear viscoelastic range.



(a) (b)

Figure 3. (a) Frequency Sweep at 40°C, (b) Frequency Sweep at 60°C

Figure 3 (a-b) shows that the dynamic modulus of fresh diutan gum increases with increasing the concentration. For 6000 and 8000 ppm concentrations, the storage modulus is higher than loss modulus in all the range investigated. For 2000 ppm, there is a crossover point at a low frequency. Both results indicate that the elastic modulus is dominant in the viscoelasticity, so it concludes that a gel structure may be formed, converging with the results of (Nitta et al., 2009), (Oh et al., 1999) and (Xu et al., 2013).

For (Mezger, 2014), the advantage of the storage modulus against the loss modulus is related with the increasing values of frequency. As soon as the frequency increases, the entanglement structure turns more inflexible and stiff. At this point, more energy can be storage by the friction between the molecules, lifting the storage modulus. However, this phenomenon induces a reduction on the mobility of the molecules, decreasing your power of mobility and the importance of the viscous portion and the decrease of the complex viscosity.

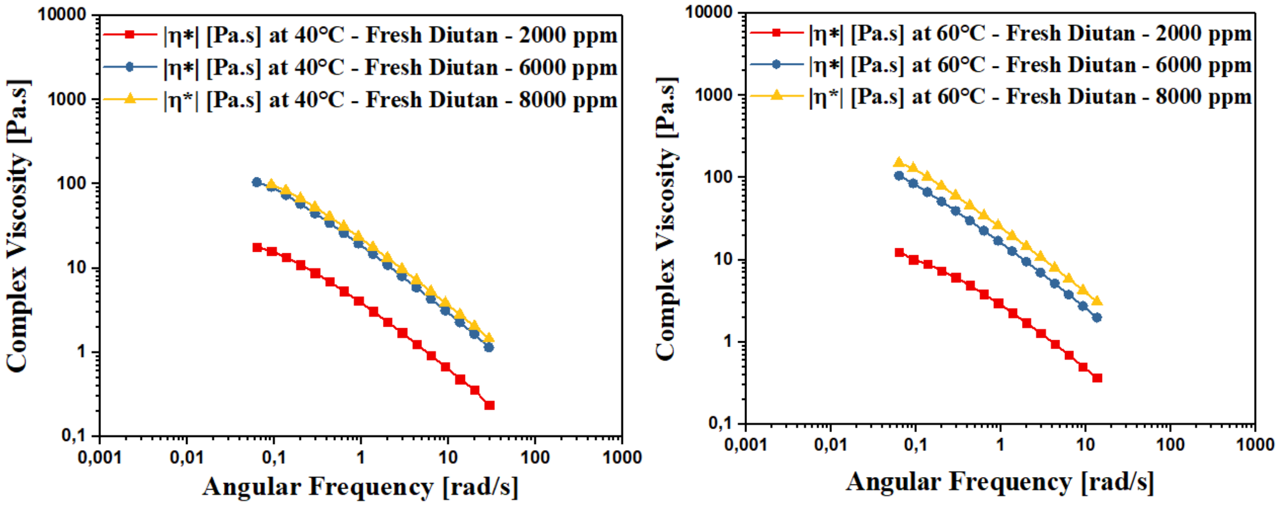
Table 1 presents the crossover points of Fresh Diutan gum, i.e., the point where the elastic modulus is equal to viscous modulus ($G' = G''$).

Table 1. Crossover points for different concentrations of diutan gum

Samples	Angular Frequency (rad/s)	
	40°C	60°C
Fresh Diutan Gum - 2000 ppm	0.068	0.113
Fresh Diutan Gum - 6000 ppm	0.063	0.029
Fresh Diutan Gum - 8000 ppm	0.024	0.029

Table 1 shows the results of crossover points for diutan gum at 40°C and 60°C at different concentrations. The crossover points occurred in the frequency range investigated, showing that the elastic portion is predominant for all the established temperatures. The crossover points outside the range were found by extrapolation in Rheowin Data software.

Figure 4 (a-b) shows the complex viscosity of Diutan gum at 40°C and 60°C at different concentrations. The chosen range for frequency was 0,01 – 100 Hz and the shear stress was in the linear viscoelastic range.



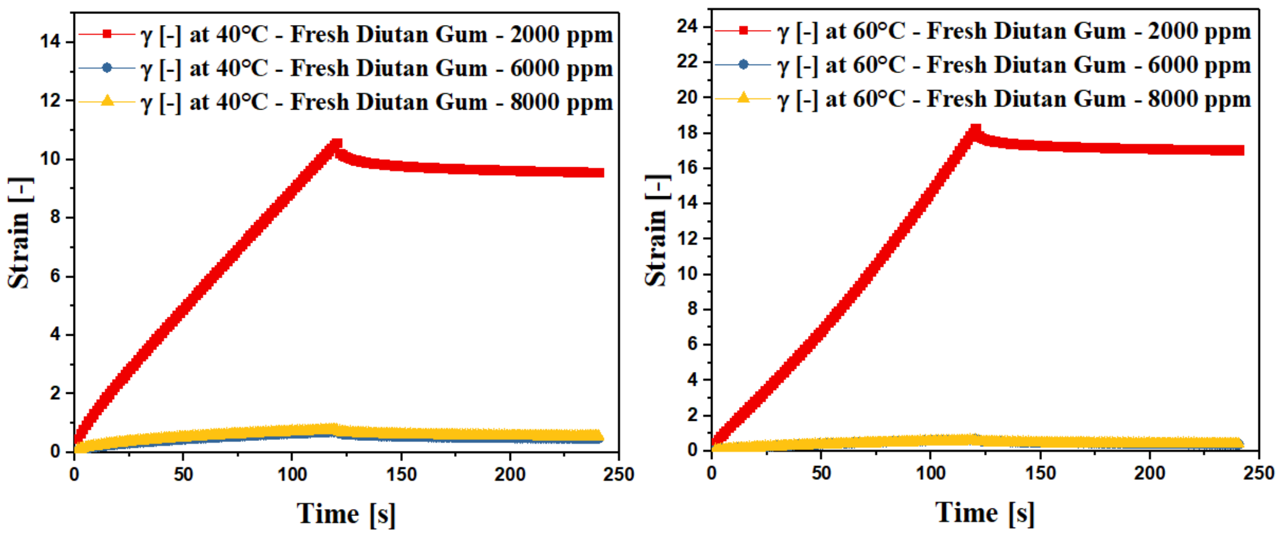
(a) (b)

Figure 4. (a) Complex Viscosity at 40°C, (b) Complex Viscosity at 60°C

The results of Figure 4 (a-b) show that an increase of concentration also increases complex viscosity values, indicating the dependence of complex viscosity and concentration. The temperature didn´t influence so much the complex viscosity, indicating a good thermal stability.

3.3 Creep & Recovery

Figure 5 (a-b) shows the results for creep & recovery tests at 40°C and 60°C for concentrations of 2000, 6000 and 8000 ppm:



(a) (b)

Figure 5. (a) Creep & Recovery at 40°C – 2000 ppm, 6000 ppm and 8000 ppm, (b) Creep & Recovery at 60°C – 2000 ppm, 6000 ppm and 8000 ppm

For all the temperatures investigated, the concentration of 2000 ppm suffered a higher deformation comparing with 6000 and 8000 ppm. When the sample is submitted to a constant shear stress, higher concentrations resists more than lower concentrations due the presence of more. The strain turns higher for lower concentrations, especially at 2000 ppm. Temperature increases molecular stirring, breaking the chains, turning easier the strain process of diutan gum.

The Equation 8 estimates the recovery rate in a creep & recovery test:

$$Recovery\ Rate\ [\%] = [(\gamma_t - \gamma_P)/\gamma_P] \times 100 \quad (8)$$

Where: $\gamma_t \rightarrow Total\ Strain$
$\gamma_P \rightarrow Permanent\ Strain$

Table 2 indicates the recovery rate for fresh Diutan Gum. The shear stress used in the creep & recovery test was inside the linear viscoelastic range

Table 2. Recovery Rate – Fresh Diutan Gum

		Temperature [°C]	
		40	60
Fresh Diutan Gum - 2000 ppm	Recovery Rate [%]	9.64	6.71
Fresh Diutan Gum - 6000 ppm	Recovery Rate [%]	32.79	39.74
Fresh Diutan Gum - 8000 ppm	Recovery Rate [%]	29.28	32.58

The results show that the recovery rate of diutan gum is deeply influenced by the temperature. The recovery rate at 60°C is always higher when compared with 40°C, except for 2000 ppm. In terms of concentration, 6000 ppm showed more recovery rate compared, respectively, with 8000 ppm and 2000 ppm. It can be inferred that the concentration has a bigger influence than the temperature.

4. CONCLUSIONS

Diutan gum showed a pseudoplastic and viscoelastic behavior for all the temperatures and concentrations investigated. The viscosity curves showed that the concentration influence the value of viscosity. An increase in the concentration increases viscosity values for all the temperatures investigated.

In terms of oscillatory tests, the SAOS tests were performed in the linear viscoelastic range. The frequency sweep showed that the crossover between the storage modulus and loss modulus turns lower when the concentration increases. These results are valid for all the temperatures investigated. The complex viscosity showed a huge influence of concentration. Increasing the concentration causes an increase of complex viscosity values for all the temperatures.

In terms of creep tests, lower values of concentration make it easier to deform the samples. Therefore, concentrations of 2000 ppm showed more deformation for all the temperatures. When the temperature increases, the recovery rate of diutan gum also increases, except for 2000 ppm. The concentration of 6000 ppm showed more recovery rate comparing with the other concentrations.

5. REFERENCES

Bretas, R.E.S., D`Ávila, M.A.,2005. “Reologia de Polímeros Fundidos”. EdUFSCar, 2ª edição, São Carlos.

Cano – Barrita, P.F.J., Léon – Martínez, F.M.,2016. “Biopolymers with viscosity – enhancing properties for concrete”. *Biopolymers and Biotech Admixtures for Eco – Efficient Construction Materials*, pp.221 – 252.

Chagas, B. S., Machado, D. L. P., Haag, R. B., De Souza, C. R., Lucas, E. F., 2004. ”Evaluation of hydrophobically associated polyacrylamide-containing aqueousfluids and their potential use in petroleum recovery”. *Journal of Applied Polymer Science*, Vol.91, pp. 3686 – 3692.

Freitas, I.C.,2002. *Estudo da interação entre biopolímeros e polpas de frutas tropicais em cisalhamento estacionário e oscilatório*. Ph.D. thesis, Universidade Estadual de Campinas, Campinas, Brasil.

Gunasekaran, S., Mehmet Ak, M., 2000. “Dynamic oscillation shear testing of foods – selected applications”. Trends in food science & technology, Vol. 11, pp. 115 – 127.

Gunasekaran, S., Mehmet Ak, M., 2003. “Cheese Rheology and Texture”. CRC Press. Boca Raton.

Katzbauer, B., 1998. " Properties and application of xanthan gum".*Polymer Degradation and Stability*, Vol. 59, pp. 81-84.

Melo, K.C., Dantas, T.N.C., Barros Neto, E.L., 2013 "Influência da temperature na reologia de fluidos de perfuração preparados com carboximetilcelulose, goma xantana e bentonita". *Holos*, Vol. 5.

Ma, S., Qian, Y., Kawashima, S., 2018. " Experimental and modeling study on the non – linear structural build – up of fresh cement pastes incorporating viscosity modifying admixtures". *Cement and Concrete Research*, Vol. 108, pp. 1 – 9.

Mezger, T.G. The Rheology HandBook, 4ª edição, Vincentz – Hannover, Germany, 2014.

Neto, J.C.Q., 2006. *Redução na pressão de rompimento da torta de filtração através de melhorias na composição do fluido de perfuração à base de polímeros*. Ph.D. thesis, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brasil.

Nitta, Y., Takahashi, R., Nishinari, K., 2009."Observation of gellan gum by scanning tunneling microscopy". *Carbohydrate Polymers*, Vol. 30, pp. 77 – 81.

Oh, M.H., So, J.H., Yang, S.M., 1999. "Rheological evidence for the silica – mediated gelation of xanthan gum." *Journal of Colloid and Interface Science*,Vol. 216, pp. 320 – 328.

Plank, J., 2004."Applications of biopolymers and other biotechnological products in building materials". *Applied Microbiology and Biotechnology*, Vol. 66, pp. 1 – 9.

Schmidt, W., Sonebi, M., Brouwers, H.J.H., Kühne, H., Meng, B.,2013a. "Rheology Modifying Admixtures: The Key of Innovation in Concrete Technology – A General Overview and Implications for Africa". *Chemistry and Materials Research*, Vol. 5.

Shah, S.N., Shanker, N.H., Ogugbue, C.C., 2010. "Future Challenges of Drilling Fluids and Their Rheological Measurements". American Association of Drilling Engineers, Houston, Texas.

Schmidt, W., Broouwers, H.J.H., Kühne, H., Meng, B.,2013b. "The working Mechanism of Starch and Diutan Gum in Cementious and Limestone Dispersions in presence of Polycarboxylate Ether Superplasticizers". *Applied Rheology*, Vol. 23, Issue 5.

Sonebi, M., 2006. "Rheological properties of grouts with viscosity modifying agents as diutan gum and welan gum incorporating pulverised fly ash". *Cement and Concrete Research*,Vol. 36, pp. 1609-1618.

Steffe, J.F.,1996. Rheological Methods in Food Process Engineering, 2ª edição, Freeman Press, Michigan – USA.

Xu, L., Xu,G., Liu, T., Chen, Y., Gong, H., 2013. "The comparison of rheological properties of aqueous welan gum and xanthan gum solutions". *Carbohydrate Polymers*, Vol. 92, pp. 516 – 522.

Xu, L., H. Gong, M. Dong, Y. Li.,2015a. "Rheological properties and thickening mechanism of aqueous diutan gum solution: Effects of temperature and salts". *Carbohydrate. Polymers*, Vol. 132, pp. 620-629.

Xu, L., Dong., Gong, H., Sun, M., Li, Y.,2015b. "Effects of innorganic cátions on the rheology of aqueous welan, xanthan, gellan solutions and their mixtures". *Carbohydrate Polymers*, Vol. 121, pp. 147 – 154.

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