

Effect of silica nanoparticles in xanthan gum solutions: Rheological behavior and preparation methods of nanofluids

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ABSTRACT

In this article, different methods are investigated for the preparation of nanofluids composed of hydrocolloid xanthan gum (XG) and hydrophilic silica nanoparticles (NP) dispersed in water. The rheological behavior of the XG solutions and NP suspensions was first characterized individually, for different concentrations. The effect of the presence of salt (NaCl) was then evaluated. The polymer dilution curves were established, delimiting the dilute and semi-dilute regimes. Different preparation methods of the nanofluids were then considered, testing different factors like the hydration time of the polymer, the sonication time, and the order of aggregation of the components (XG - NP). Characterization techniques such as dynamic light scattering (DLS) and rheological characterization at constant temperature and variable shear rate were used, providing a trend in the stability of the viscous profile of nanofluids. The simplest method providing a correct dispersion of the NP as well as the increase of the viscous profile was then selected. Finally, the evolution in time of the nanofluids was studied and it was observed that the presence of NP stabilized the polymer solution by maintaining its viscosity level in time. This study provides a better understanding of the interactions between XG and silica NP in solution, through the rheological behavior of fluids at low concentrations.

Introduction

The addition of polymer in a solvent causes an increase of the viscosity, due to inter- and intramolecular forces within the polymer and with the surrounding solvent molecules. The intensity of the viscosity increase both depends on the nature of the polymer and the nature of the solvent. Xanthan gum (XG) is an extracellular biopolymer (Sheng, 2011) which exhibits a shear thinning rheological behaviour when put in solution: the viscosity of XG solutions decreases with increasing shear rate. The presence of charged functional groups in its side chain (carboxyl groups (-COOH)) makes it an anionic polysaccharide (Camesano et al., 2001). The structure of XG undergoes conformational changes (rotation/coupling of the molecule) when it is in an aqueous solution and is exposed to conditions of temperature, salinity, and deformation stress (Pi et al., 2016). The intermolecular (COOH - water) and intramolecular (COOH - CCOH) bonds existing in the system, tend to weaken and then break, causing a viscosity loss and/or polymer precipitation (degradation) (Sheng, 2011). This phenomenon can be explained by the conformational structure of the polymer. Indeed XG exhibits two conformations: an ordered conformation (helix shape) and a disordered conformation (broken helix) (Carmona et al., 2015). The viscosity variations in xanthan solutions are caused by the transition from one conformation to another (ordered/disordered) (Moorhouse et al., 1977).

In the search for strategies to reinforce or maintain the inter / intra-molecular bonds that affect the viscosity and stability of solutions, the use of nanoparticles (NP) is considered a possible improvement for XG solutions (Abidin et al., 2012). The surface of silica NP allows an interaction with the carboxyl groups present in the

xanthan structure (- COOH), leading the polymer chains to link with the NP. Recent studies have suggested the reduction in the conformational transition of xanthan with the addition of silica NP (Jordan et al., 2014). The interaction of the polymer with the NP allows new cross-linked, three-dimensional and more rigid polymeric structures, which delay their conformational transition (Pi et al., 2016). However, it is necessary to establish the optimal conditions for the preparation of these nanofluids, composed of XG and NP dispersed in water. The present study describes and develops different methods for the elaboration of low viscosity nanofluids, evaluated through the viscosity profile as the response variable.

Materials and methods

2.1 Preparation of xanthan gum solutions and nanoparticles suspensions

The commercial XG used in this study was obtained from Sukin Industries. The silica NP, purchased from Evonik Industries, were fumed Aerosil 300 amorphous hydrophilic silica NP ($300 \pm 30 \text{ m}^2 / \text{g}$), with primary units of 12 nm. The sodium chloride was supplied by Sigma Aldrich 99.5 % (58.44 g/mol).

The polymer solutions were prepared by incorporating polymer powder in deionized water at different concentrations (150, 300, 600, 1200, and 2400 ppm). The solutions were then left under magnetic stirring during 24 h or 48 h. The influence of ionic forces on the viscous behavior of fluids was studied by adding NaCl with varying concentrations (0, 0.1, 0.5, 1 and 3%). Nanoparticle suspensions of different fractions (100, 200 and 300 ppm) were prepared by dispersing NP in water with different ionic charges (0, 0.1, 0.5, 1 and 3% NaCl) under magnetic stirring for 1 h.

The XG solutions and the nanoparticle suspensions were subjected to ultrasound during different times (0, 3, 6, 9, and 30 min) with a Fisher Scientific 550 Sonic Dismembrator Ultrasonic Processor. The amplifier frequency was set to 40 Hz, and the amplitude to 20 %, which corresponds to a power of approximately 300 W. An ice-water bath was used to control the temperature of the dispersions in the cell. After the sonication treatment, the formulations were analyzed through rheological tests and through qualitative observations to detect the possible appearance of precipitates or agglomerates in the fluid. For the nanoparticle suspensions, agglomerate size measurements were made through Dynamic Light Scattering (DLS) for each sonication duration.

Table 1: Preparation methods of the nanofluids

Method	Step 1	Step 2	Step 3	Step 4	Step 5
Method 1	Addition of XG and NP in water at the same time	Magnetic stirring for 24 h	-	-	-
Method 2	Addition of XG in water and magnetic stirring for 24 h	Addition of NP powder to the XG solution	Magnetic stirring for 24 h	-	-
Method 3	Addition of NP in water and magnetic stirring for 1 h	Sonication of NP suspension for 30 min	Addition of XG to the NP suspension	Magnetic stirring for 24 h	-
Method 4	Addition of XG in water and magnetic stirring for 24 h	Addition of NP in water and magnetic stirring for 1 h	Sonication of NP suspensions for 30 min	Mixing of the XG solution and NP suspension (under sonication)	Magnetic stirring for 24 h

2.2 Rheology measurement

The rheological characterization at each stage of the study was performed using a Rheometric Scientific RFS II rheometer equipped with a rotating helical ribbon of 17.95 mm radius in a tank of 27.5 mm internal radius and 42 mm inner height. This helical geometry is adapted to low viscosity fluids since it generates higher torques than classical geometry, like plate/plate cells. The tests were executed at a constant temperature (25°C) and for variable shear rate (0.1 - 100 [s⁻¹]), with sensitivities of 1 Pa.s for the viscosity and 0.002 N.m for the torque. The effect of salinity on the rheological behavior of the generated formulations (NP suspensions and polymer solutions) was evaluated. The dilution curve of the polymer in brine was established at the arbitrary shear rates of 6.3 s⁻¹ and 10 s⁻¹ at temperature 25°C. The rheology of the dispersions obtained with the different methods was then characterized.

2.3 Nanofluids preparation

Four different methods to prepare the nanofluids (XG and NP in water) were considered, by varying the hydration time of the polymer, the order of addition of the components, the sonication time applied to the NP suspensions, and the time of interaction between the components (Table 1). In this part of the study, the concentrations of NP and XG were kept constant (200 ppm and 600 ppm respectively), as well as the temperature and pressure of the process.

Results and discussions

3.1 Characterization of the polymer solutions

The effect of the mixing time applied to the polymer solutions was evaluated for 4 concentrations. Very close viscosity profiles were obtained after 24h and 48h mixing. Therefore, the shortest mixing time, 24 h, was considered sufficient for a complete hydration of the polymer at the given concentrations.

Ultrasonic energy was enforced to the polymer solutions for different durations (figure 1). For all considered polymer concentrations, a viscosity reduction of around 50-69% was measured after the first 3 min and 87-96% after 30 min, at a shear rate of 10 s⁻¹. This indicates a degradation of the polymer due to sonication, even for the shortest sonication time. This is attributed to the implosion of microbubbles generated by cavitation under high pressure and high temperature acoustic waves, leading to the breakdown of the polymer molecules. Sonication promotes depolymerization and reduces the polymer molecular weight, with accelerated cleavages in the middle of the polymer chain (Saleh et al., 2017). In order to prevent this effect, no sonication was applied in the presence of the polymer for most of the methods (methods 1, 2 and 3).

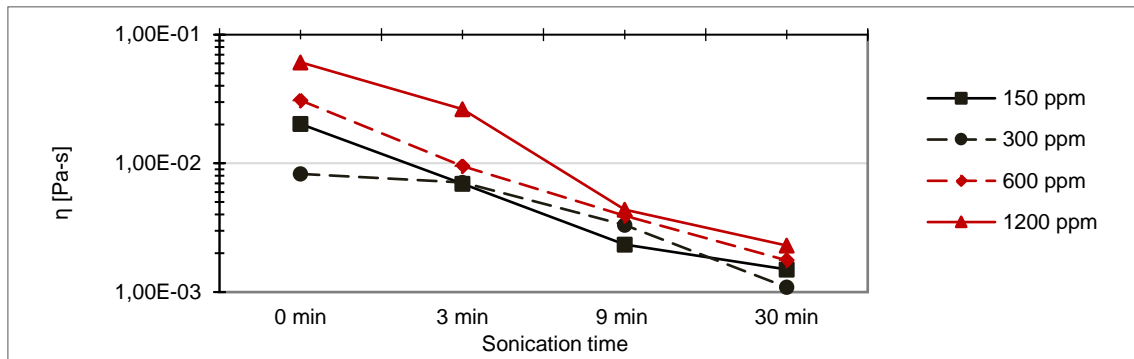


Figure 1: Effect of sonication on viscosity curves for xanthan gum solutions at a shear rate of 10 s⁻¹

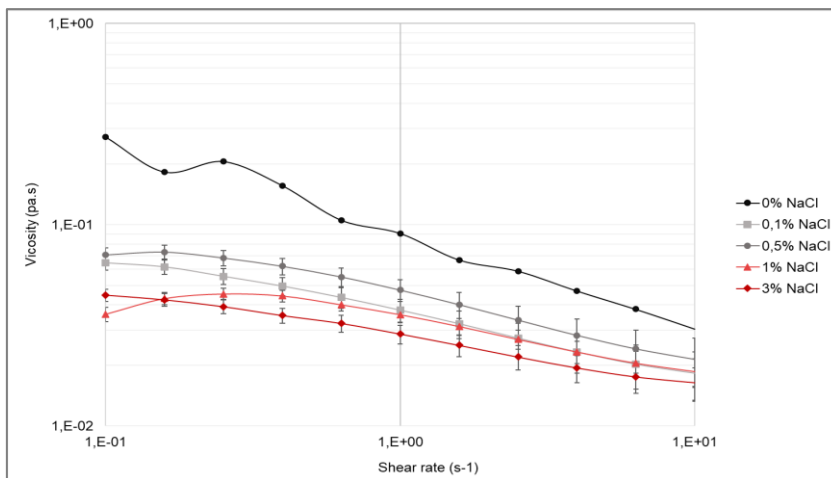


Figure 2: Effect of NaCl on the rheology for xanthan gum solutions.

The influence of NaCl at five different concentrations on 600 ppm XG solutions was evaluated through rheograms (figure 2). It appears that an increase of the NaCl concentration leads to a viscosity decrease. It has been suggested that, in the absence of ionic charges in the dilution medium, the XG chain is disordered and extended due to electrostatic repulsions between the charges within the polymer. (Stokke et al., 1992). This conformation provides relative flexibility to polymer chains and increases the viscous response of the solution. In the presence of Na⁺ and Cl⁻ ions, the XG backbone becomes stiffer and less stretched, while electrostatic repulsions affect the solubility of the polymer and therefore the viscosity of the solution. However, higher viscosities were observed at a concentration of 0.5% than at 0.1%. This paradoxical effect can be explained by previous studies (Li et al., 2015), which reported that in XG solutions with low NaCl concentration, the polymer may rotate to a slightly messier and more extended conformation. In contrast, when NaCl ions are present in a solution with a higher salt concentration, the ordered conformation is favoured. The XG chains in this conformation become more rigid and stable, decreasing the viscosity of the solution. Formulations with 3% NaCl showed the most dramatic viscosity reduction. Therefore, the polymer dilution curve was constructed at this salinity concentration for constant shear rates of 6.3 s⁻¹ and 10 s⁻¹ (figure 3). The dilute zone corresponds to XG concentrations inferior to 600 ppm while the semi-dilute zone ranges between 600 ppm and 4800 ppm. The concentrated zone was not determined in the present work

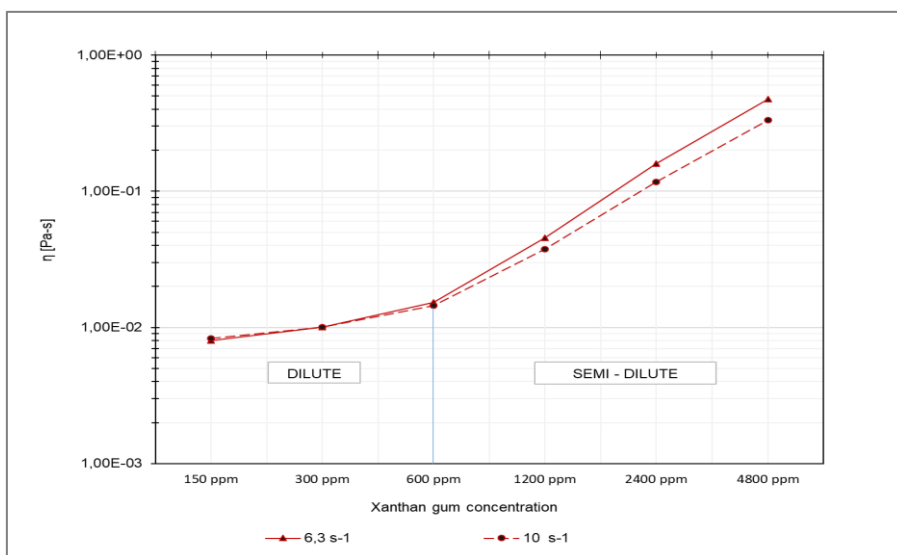


Figure 3: Dilution curve of xanthan gum with 3% NaCl. Shear rates of 6.31 s⁻¹ and 10 s⁻¹.

3.2 Characterization of nanoparticle suspensions

The rheological behavior of NP suspensions is also analyzed to determine the degree of dispersion of the NP. For a smaller agglomerate size or a better dispersion of the NP, the suspensions tend to be more viscous and to adopt a Newtonian behavior (viscosity independent of the shear rate) (Mondragon et al., 2012). However, the flow profiles obtained in the present study for 3 different NP concentrations did not show a significant difference: there was no apparent viscosity change between suspensions of 100 ppm and 300 ppm NP. This possibly due to the low and close concentrations evaluated.

Particle size measurements showed initial agglomerates average size (before sonication) of 598 nm and 690 nm for 100 ppm and 300 ppm NP concentrations respectively. During sonication, the agglomerates size decreased progressively due to their fracturing. For smaller agglomerates, the NP dispersion improves in an isotropic distribution of the particles, thus increasing the viscosity. Therefore, a sonication time of 30 min was chosen to prepare the nanoparticle suspensions. Figure 4 shows the decrease of the agglomerates size (dotted line) and the viscosity curves (solid line) at a shear rate of 10 s⁻¹.

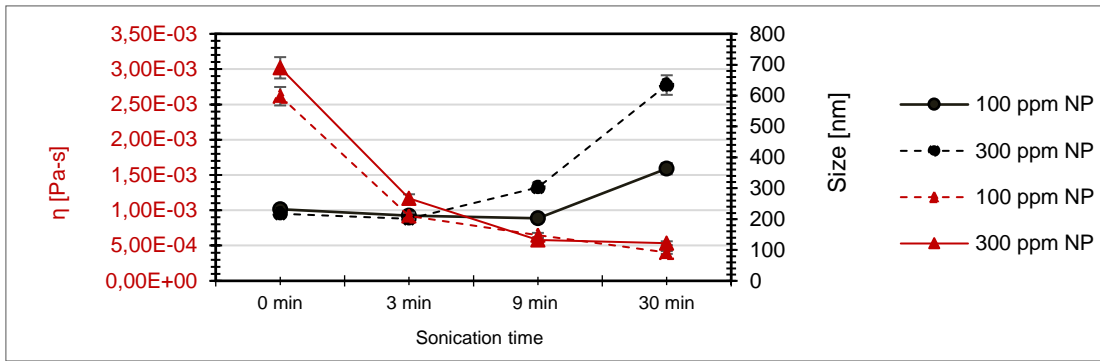


Figure 4: Viscosity at 10 s^{-1} and particle size of NP suspensions as a function of sonication duration. Left axis: viscosity η (red); Right axis: nanoparticles size (black).

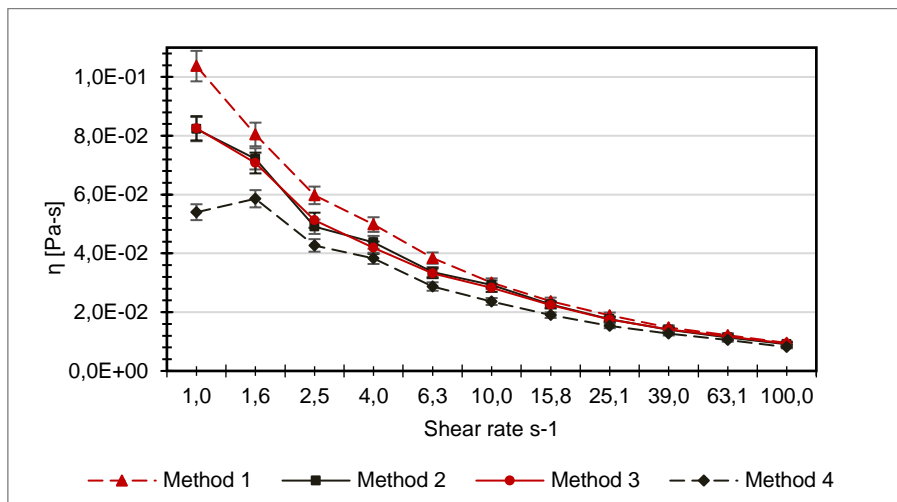


Figure 5: Viscosity as a function of the shear rate of nanofluids prepared according to the 4 different methods.

3.3 Nanofluids preparation

The four methods proposed for the preparation of nanofluids (table 1), ensured the same interaction time between the components (24 h). From the polymer dilution curve (figure 3), the intermediate concentration between the dilute and semi-dilute zone of 600 ppm of XG was selected and kept constant for the preparation of all nanofluids. Since the suspension rheology was little influenced by the NP concentration, the NP fraction was fixed to 300 ppm. In figure 5 are plotted the viscosity curves of the nanofluids prepared according to the 4 different methods. No notable difference is observed in the rheological response. This indicates that the preparation process (addition order of the components, preliminary sonication of the nanoparticle suspensions) has little incidence on the final viscosity of the nanofluid. Therefore, method 1 was selected for the preparation process, since it yielded the highest viscosity profile with a minimum number of steps.

After establishing the preparation method, the stability in time of the nanofluid was evaluated compared to a reference polymeric solution without NP (control blank). The viscosity of both fluids were measured just after preparation (initial time) and after 2 weeks (figure 6). At initial time, the viscous curves of the nanofluid and the control blank are very close, showing that the presence of the NP in the freshly prepared nanofluid does not have a strong impact on the viscosity, possibly due to the low NP mass concentrations in the formulation. After 2 weeks however, the control blank fluid showed a viscosity decrease while the nanofluid showed no evolution. The presence of NP thus promotes the stability of the fluid, maintaining the viscous profile. This indicates that a physicochemical equilibrium was reached in time within the nanofluid. The more components in the fluid, the more interaction points and the higher the electrostatic interactions. The surface charge of the NP could interact with the charges present in the xanthan structure ($-\text{COOH}$), leading the polymer chains to join with the NP (Min-Ho et al., 1999); the interaction of the polymer with the nanoparticles allows new crosslinked, three-dimensional, and more rigid polymeric structures that delay their conformational transition when deformation stresses are applied (Pi et al., 2016).

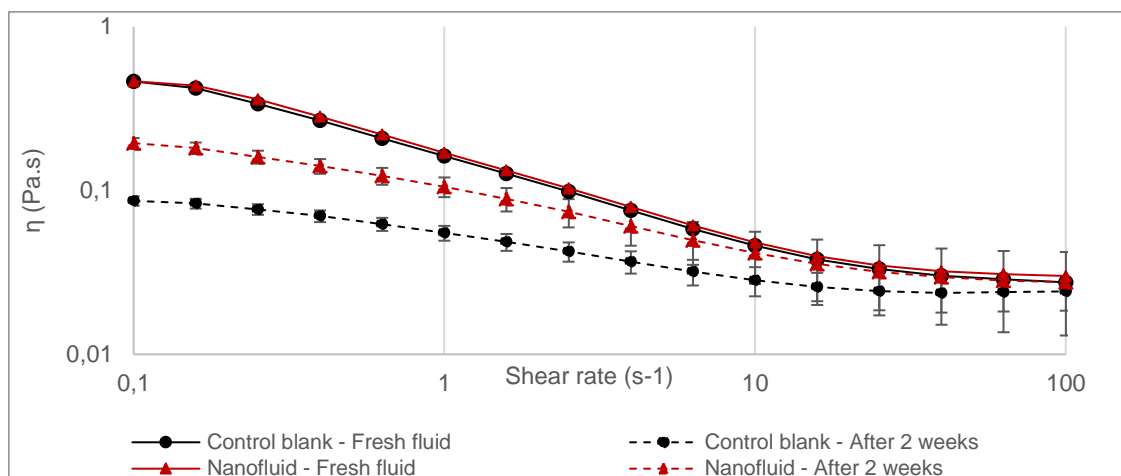


Figure 6: Rheological behaviour of nanofluids and control blank freshly prepared and after 2 weeks

Conclusions

In this paper, 4 different methods (with varying ingredient incorporation order, sonication, polymer hydration time) were evaluated to prepare nanofluids composed of xanthan gum (XG), silica nanoparticles (NP) and NaCl salt dispersed in water. First, an analysis of the individual fluids composing the nanofluid was performed. A hydration time of 24h was found sufficient to prepare the polymer solution. Sonication, which produced deagglomeration of the particles, was shown to damage the polymer and was thus only applied to the nanoparticle suspensions (without XG). The ionic strength provided by NaCl was observed to decrease the viscosity of the polymer solutions. Then, the properties of the final nanofluids were analyzed. It appears from rheological measurements that all 4 methods provided similar rheological behavior and viscosity levels, showing little impact of the preparation method. The simplest method, also yielding the highest viscosities, was thus selected. Finally, the evolution in time of the nanofluids was studied: after 2 weeks of aging, the nanofluids registered higher rheological profiles than a polymer solution without nanoparticles. This proves the interest of the addition of nanoparticles, into xanthan gum solutions to enhance and maintain their viscosity in time.

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