

## Jose Carlos Canazas Rodriguez

# Rheology of graphene oxide nanosheets in xanthan gum dispersions

Dissertação de Mestrado

Dissertation presented to the Programa de Pós–graduação em Engenharia Mecânica of PUC-Rio in partial fulfillment of the requirements for the degree of Mestre em Engenharia Mecânica.

Advisor : Prof. Mônica Feijó Naccache Co-advisor: Dr. Lorena Rodrigues da Costa Moraes

> Rio de Janeiro March 2025



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## Abstract

Canazas Rodriguez, Jose Carlos; Naccache, Mônica Feijó (Advisor); Rodrigues da Costa Moraes, Lorena (Co-Advisor). **Rheology of** graphene oxide nanosheets in xanthan gum dispersions. Rio de Janeiro, 2025. 107p. Dissertação de mestrado – Departamento de Engenharia Mecânica, Pontifícia Universidade Católica do Rio de Janeiro.

Xanthan gum (XG), a versatile biopolymer, is extensively utilized as a rheology modifier in diverse industries ranging from food and cosmetics to oil and gas. Then, the rheological response of XG under various thermophysical circumstances can be significantly influenced by the inclusion of nanomaterials like graphene oxide (GO). The goal of this work is to investigate how the rheology and microstructure of XG aqueous suspensions are affected by the addition of GO nanosheets. To assess the impact of GO concentration in an aqueous XG suspension at various pressures and temperatures, the rheological response was investigated using steady-state and oscillatory flow tests. Additionally, samples containing sodium chloride close to saturation were examined. The results indicate that addition of GO into XG suspension produces a more structured suspension with an increase in shear viscosity and viscoelastic moduli, as well as thermal stability at high temperatures, although at high pressure, a slight tendency to reduce viscosity has been observed. In contrast to GO, the addition of sodium chloride showed a decreased viscosity and viscoelasticity at low temperatures and a minor effect at high temperatures. A phenomenological model with two power-law regimes was used to fit flow curves. The cryomicrographs provided a visual representation of the microstructure of the suspessions and corroborated the rheological results. The noted improvements in shear viscosity, viscoelastic characteristics and thermal stability present encouraging avenues for the creation of sophisticated functional fluids.

#### Keywords

Graphene Oxide; Xanthan Gum; Rheology; Nanofluid; Cryomicrography;

#### Resumo

Canazas Rodriguez, Jose Carlos; Naccache, Mônica Feijó; Rodrigues da Costa Moraes, Lorena. **Reologia de nanofolhas de óxido de grafeno em dispersões de goma xantana**. Rio de Janeiro, 2025. 107p. Dissertação de Mestrado – Departamento de Engenharia Mecânica, Pontifícia Universidade Católica do Rio de Janeiro.

A goma xantana (XG), um biopolímero versátil, é amplamente utilizada como um modificador de reologia em diversas indústrias que vão de alimentos e cosméticos a petróleo e gás. Então, a resposta reológica da XG sob várias circunstâncias termofísicas pode ser significativamente influenciada pela inclusão de nanomateriais como óxido de grafeno (GO). O objetivo deste trabalho é investigar como a reologia e a microestrutura de suspensões aquosas de XG são afetadas pela adição de nanofolhas de GO. Para avaliar o impacto da concentração de GO em uma suspensão aquosa de XG em várias pressões e temperaturas, a resposta reológica foi investigada usando testes de fluxo oscilatório e em estado estacionário. Além disso, amostras contendo cloreto de sódio próximo à saturação foram examinadas. Os resultados indicam que a adição de GO na suspensão de XG produz uma suspensão mais estruturada com um aumento na viscosidade de cisalhamento e módulos viscoelásticos, bem como estabilidade térmica em altas temperaturas, embora em alta pressão, uma ligeira tendência a reduzir a viscosidade tenha sido observada. Em contraste com GO, a adição de cloreto de sódio mostrou uma diminuição da viscosidade e viscoelasticidade em baixas temperaturas e um efeito menor em altas temperaturas. Um modelo fenomenológico com dois regimes de lei de potência foi usado para ajustar as curvas de fluxo. As criomicrografias forneceram uma representação visual da microestrutura das suspensões e corroboraram os resultados reológicos. As melhorias observadas na viscosidade de cisalhamento, características viscoelásticas e estabilidade térmica apresentam caminhos encorajadores para a criação de fluidos funcionais sofisticados.

#### Palavras-chave

Óxido de Grafeno; Goma Xantana; Reologia; Nanofluido; Criomicrografia;

## Table of contents

1	Introduction	13
1.1	Motivation	13
1.2	Objective	19
2	Theoretical framework and literature review	20
2.1	Rheology and non-newtonian fluids	20
2.2	Colloidal dispersions	23
2.3	Aqueous polyelectrolytic dispersions	26
2.4	Drilling fluids	29
2.5	Xanthan Gum	33
2.6	Graphene Oxide	37
3	Materials and Methods	42
3.1	Synthesis of graphene oxide	42
3.2	Characterization of graphene oxide nanosheets	42
3.3	Base fluid and nanofluid preparation	43
3.4	Rheological characterization of the dispersions	44
3.5	Microstructure characterization of the dispersions	46
4	Results and Discussions	47
4.1	Physico-chemical aspects of graphene oxide nanosheets	47
4.2	Rheological response of the dispersions	50
4.2.	1 Base fluid and influence of nanofluid preparation method	50
4.2.	2 Influence of GO concentration and NaCl	54
4.2.	3 Influence of temperature	59
4.2.	4 Influence of pressure	66
4.2.	5 Phenomenological fitting	67
4.2.	6 Time temperature superposition	71
4.3	Microstructure of the dispersions	74
5	Conclusions	79
Bibliography		

# List of figures

Figure 1.1	Drilling fluids: basic constituents, main functions and	
classifi	cation	14
Figure 1.2	Molecular model of graphene	16
Figure 1.3	Molecular model of graphene oxide	17
Figure 2.1 fluids	Qualitative flow curves for some types of non-Newtonian	91
Figure 2.2	Stress sweep (right) and frequency sweep (left) curves	21
for a t	ypical polymers	22
Figure 2.3 within	Schematic description of the double layer model imposed the DLVO theory	24
Figure 2 4	Example of various linear branched and dendritic-type	24
polvele	ectrolytes	27
Figure 2.5	Scheme of a drilling fluid circulation system	30
Figure 2.6	Common drilling fluid problems: causes and solutions	31
Figure 2.7	General classification of drilling fluid additives based on	
the de	finitions of IADC.	32
Figure 2.8 Figure 2.0	Schematic representation of the xanthan gum mer.	34
Yanth	an gum	35
2001011	an gum.	00
Figure 3.1 metho	Scheme of the preparation of the base fluid (a), the d 1 (b) and method 2 (c) for nanofluid preparation.	44
Figure 3.2	Scheme of ARES G2 strain-controlled rheometer with	45
Figure 3.3	Scheme of Haake MARS III stress controlled rheometer	40
with si	mooth concentric cylinders geometry in the high-pressure	
cell.		45
Figure 4.1	FTIB spectra of GO	48
Figure 4.2	Baman Spectra of GO	48
Figure 4.3	XBD Spectra of GO	49
Figure 4.4	TGA Spectra of GO	49
Figure 4.5	UV-Vis spectra of GO.	50
Figure 4.6	Dispersed anisotropic phase phenomenon in XG observed	00
by per	forming ramp-down and ramp-up flow curves.	50
Figure 4.7	Steady-state shear stress as a function of shear rate.	
Prepar	cation method 1 (a) and 2 (b) for dispersion of GO at	
0, 1 ar	and 5 mg/ml concentration in XG at $T = 23^{\circ}C$ .	51
Figure 4.8	Storage and Loss moduli as a function of shear strain	
obtain	ed from strain sweep tests at a fixed frequency of 1 Hz.	
Prepar	cation method 1 (a) and 2 (b) for dispersion of GO at 0,1	
and $5$	mg/ml concentration in XG at $T = 23^{\circ}C$ .	52

Figure 4.9 Storage and loss moduli as a function of frequency obtained from frequency sweep tests at a fixed strain of 10%. Preparation method 1 (a) and 2 (b) for dispersion of GO at 0.1	
and 5 mg/ml concentration in XC at $T = 23^{\circ}C$	54
Figure 4.10 Steady-state shear stress as a function of shear rate	01
Influence of GO concentration (a) and NaCl (b) in XG at T	
$= 23^{\circ}C$	54
Figure 4.11 Flow curve comparison pure XG and dispersions with	01
10% and 20% sodium chloride	55
Figure 4.12 Storage and Loss moduli as a function of shear strain	00
obtained from strain sweep tests at a fixed frequency of 1 Hz	
Influence of GO concentration (a) and NaCl (b) in XG at $T =$	
$23^{\circ}C$	57
Figure $4.13$ (a) Complex modulus at $10\%$ strain (b) Viscosity at	51
$\dot{\alpha} = 0.01 \text{ s}^{-1}$ and (a) Viscosity at $\dot{\alpha} = 1000 \text{ s}^{-1}$ as a function of	
GO concontration at room tomporature	57
Figure 4.14 Storage and loss moduli as a function of frequency	51
obtained from frequency sweep tests at a fixed strain of 10%	
Influence of CO concentration (a) and NaCl (b) in XC at $T =$	
$23^{\circ}C$	59
Figure 4.15 Steady-state shear stress as a function of shear rate at	05
four temperatures: 4, 23, 50 and 80 °C. Pure XG dispersion (a)	
and influence of CO concentration $(h-d)$ in XC	60
Figure 4.16 Steady-state shear stress as a function of shear rate at	00
four temperatures: 4, 23, 50 and 80 °C. Pure XG dispersion (a)	
XG with NaCl (b) and XG with GO and NaCl (c)	62
Figure 4.17 Storage and Loss moduli as a function of shear strain	02
obtained from strain sween tests at a fixed frequency of 1 Hz	
and four temperatures: $4 23 50$ and $80 ^{\circ}\text{C}$ Pure XG dispersion	
(a) and influence of GO concentration (b-d) in XG	63
Figure 4.18 Storage and Loss moduli as a function of shear strain	00
obtained from strain sween tests at a fixed frequency of 1 Hz	
and four temperatures: $4, 23, 50$ and $80 ^{\circ}\text{C}$ . Pure XG dispersion	
(a) XG with NaCl (b) and XG with GO and NaCl (c)	64
Figure 4 19 Storage and Loss moduli as a function of frequency	01
obtained from frequency sweep tests at a fixed strain of 10%	
and four temperatures: 4–23–50 and 80 °C. Pure XG dispersion	
(a) and influence of GO concentration (b-d) in XG	65
Figure 4.20 Storage and Loss moduli as a function of frequency	00
obtained from frequency sweep tests at a fixed strain of 10%	
and four temperatures: $4 23 50$ and $80 ^{\circ}\text{C}$ Pure XG dispersion	
(a). XG with NaCl (b), and XG with GO and NaCl (c).	65
Figure 4.21 Shear stress as a function of shear rate of pure XG	
dispersion and XG dispersion with GO with concentration of	
5  mg/ml, at three pressures: 1, 100 and 400 bar. At 4 °C (a).	
23 °C (b) and 80 °C (c).	66
	- •

- Figure 4.22 Steady-state shear viscosity as a function of shear rate. Sold lines are the fits with the model proposed in Eq (4-1). Influence of GO concentration at (a) 4°C, (b) 23°C, (c) 50 °C and (d) 80 °C.
- Figure 4.23 First (a) and second (b) time coefficients as a function of the inverse of absolute temperature. Parameters A and B obtained through the Arrhenius equation in Eq. (4-2).
- Figure 4.24 Infinite shear rate viscosity (a), first power law coefficient (b), and effective second power law coefficient (c) as a function GO concentration. The symbol shape (related to GO concentration) and color intensity (related to temperature) follow the described in Fig. 4.15.
- Figure 4.25 Master curves of G' (solid symbol) and G" (hollow symbol). Reference temperature is 4°C. The symbol shape (related to GO concentration) and color intensity (darker colors represent higher temperatures) follow the described in Fig. 4.15.
- Figure 4.26 (a) Horizontal and (b) vertical shift factors. The symbol shape (related to GO concentration) and color intensity (darker colors represent higher temperatures) follow the described in Fig. 4.15
- Figure 4.27 Cryo-SEM micrographs of xanthan gum (XG) dispersions with varying graphene oxide (GO) concentrations. (a,d) Pure XG dispersion; (b,e) XG dispersion with 2 mg/mL GO; (c,f) XG dispersion with 5 mg/mL GO. Top row (a-c): 200  $\mu$ m scale; bottom row (d-f): 10  $\mu$ m scale.
- Figure 4.28 High-resolution micrographs of xanthan gum dispersions in various environments: (a, d, g) pure XG dispersion; (b, e, h) XG dispersion in 20 wt% NaCl brine; (c, f, i) XG dispersion with 2 mg/mL of GO in 20 wt% NaCl solution. Images were captured at three scales: 200  $\mu$ m (a-c), 20  $\mu$ m (d-f), and 10  $\mu$ m (g-i). Arrows in (f) indicate a distinct network structure observed in the GO-containing sample's microstructure. Arrows in (h) and (i) highlight XG lines and surfaces covering the pores. Elongated structures formed by densely packed solvated Na+ and Cl- ions are visible in (h) and (i).

69

70

71

72

73

74

77

## List of tables

Table 2.1	Estimated shear rates of drilling fluids	32
Table 2.2	Summary on some characterization techniques for GO	41

## List of Abreviations

- GO Graphene Oxide
- ${\rm GrO}-{\rm Graphite}$ Oxide
- XG Xanthan Gum
- XRD X-ray Difraction
- FTIR Fourier Transform Infrared
- TGA Thermogravimetric Analysis
- WBDF Water Based Drilling Fluid

## 1 Introduction

## 1.1 Motivation

Current and future oil and gas drilling and production operations are likely to face greater technical challenges, particularly due to increased operational depth [1]. Deepwater drilling is considered high-risk because of uncertainties and very complex operational conditions [2]. Among the most challenging conditions are the formation of methane hydrates, high pressures, high temperatures, and deep and extended-reach wells [3, 4]. Given these circumstances, drilling engineers, in collaboration with geologists and geophysicists, seek innovative materials and technologies for oil and gas exploration and production in difficult-to-access reservoirs [5, 6].

Currently, this industry is looking for chemical products, polymers or natural reagents that are mechanically strong, chemically and thermally stable, biocompatible and environmentally friendly, as well as cost-effective, to develop smart fluids for well drilling [4, 7]. It is worth noting that well drilling requires the use of different drilling fluid formulations, depending on the characteristics of the area to be drilled and conditions associated with the depth of the well [8]. Fluid selection and formulation depends primarily on geology, petrophysical data, previous field drilling data, and options for the drilling fluids disposal after their utilization [5, 9].

In addition to the characteristics of the well to be drilled, the efficiency of the process is also determined by the functions that the drilling fluids must perform during the operation. Drilling fluids are used to conduct numerous tasks, such as: carrying the produced cuttings from the bottom of the well to the surface, allowing the separation of cuttings in subsequent operations, cooling and cleaning the bit, promoting good lubrication to improve the penetration rate, maintaining the stability of the well, preventing fluid losses into the well, forming a thin and poorly permeable filter cake on the wellbore, not being dangerous to the environment and humans, and making it possible to obtain information related to the geology of formations drilled through cuttings [4, 7, 10, 11, 12]. Due to the multiple functions of drilling fluid, it is necessary to develop complex formulations to deal with different environments found in different geological situations.

Different types of drilling fluids, such as water-based, oil-based or synthetic-based, and air- or foam-based, are commonly used in various drilling circumstances [9, 11]. Among these types of fluids, water-based drilling fluids stand out for being low-cost, environmentally friendly and are the most used in onshore and offshore operations [10]. Approximately 80% of all wells in the world are drilled with water-based drilling fluids [13]. The formulations of these fluids are composed of several additives and constituents, among the most essential are additives for viscosity control, density control, filtration control and pH modifiers [7, 11, 5]. Figure 1.1 generically summarizes the basic constituents, main functions and classification of drilling fluids.



Figure 1.1: Drilling fluids: basic constituents, main functions and classification [7].

Among the constituents mentioned, viscosifiers play a very important role because they modify the rheological properties of drilling fluids [4, 14]. Viscosity-controlling agents, called viscosifiers, are added to drilling fluids to improve their ability to carry downhole cuttings and to increase their ability to suspend cuttings when fluid circulation is stopped [10]. Among the viscosifiers generally used are some clays, synthetic polymers, biopolymers and mixed metal viscosifiers [11, 15]. Synthetic polymers are generally stable at high temperatures and resistant to salts, but their cost can be higher and they are mainly derived from petroleum [16].

The use of additives with enhanced characteristics, which are tolerant to different well conditions, has become essential. However, their application has been constrained by the complex nature of the fluid formulations and the economic considerations of the project [15]. In contrast, biopolymers are less expensive and biodegradable, in addition to improving the properties of water-based drilling fluids even at low concentrations [11]. Nonetheless, some challenges still persist; for instance, drilling fluids containing biopolymers may undergo degradation when subjected to high temperatures, high pressures and critical shear conditions, leading to a reduction of viscosity and other properties of the fluid [16].

Among biopolymers, xanthan gum (XG) has proven to be a better option than other biodegradable polymers such as guar gum or wellan gum, due to its good solubility in water and brines due to its Hansen solubility parameters, as well as its rheological qualities such as increased viscosity and viscoelastic modules even at low concentrations [17, 18]. XG was developed by the United States Department of Agriculture in 1959 [19] and successfully produced in commercial quantities by Kelco in 1961 [20]. The dispersion of XG in an aqueous base results in a pseudoplastic fluid. This property meets a wide range of technical needs, ranging from low viscosity with high shear rate for simple pump circulation to high viscosity with low shear rate, required when the flow is stopped [17, 21].

In addition to biopolymeric additives, several studies in recent years have presented the significant potential of nanomaterials in applications with high temperatures and pressures, with the aim of improving physicochemical properties and having adequate performance under adverse conditions [22, 1]. Nanoparticle additives can affect almost all properties of modern drilling fluids used for oil and gas exploration [23] Nanomaterials began to be used as reagents in drilling fluids to regulate their rheological parameters, control filtration losses, and improve antifriction properties, among others [24]. Due to the unique characteristics of nanomaterials compared to standard additives and adaptability to perform specific functional tasks, nanoparticles are considered very promising candidates for creating high-performance drilling fluids [23, 1].

Among the nanomaterials developed to date, carbon-based ones have attracted attention due to their structural characteristics and different mechanical, electrical, thermal, optical, and chemical properties [25]. One of these nanomaterials, relatively recent and widely studied, is graphene. Graphene is a 2D material composed of a single layer of carbon atoms arranged in a hexagonal crystalline structure [26], as shown in figure 1.2. It was first isolated in 2004 [27] and has since been considered as a possibility for industrial, environmental, and biomedical applications due to the development of synthesis and functionalization procedures [28]. Furthermore, the hydrophobic properties of graphene limit its solubility in water and other organic solvents, limiting its potential applications in the production of nanofluids. To solve these issues, graphene oxide (GO), a graphene functionalization, has been extensively applied.

GO consists of a graphene nanosheet with oxygen-containing functional



Figure 1.2: Molecular model of graphene [29].

groups (particularly carboxyl, hydroxyl, and epoxy) attached to both sides of the carbon plane and edges [30], as shown in figure 1.3. Graphite oxide was first synthesized in 1859, decades later graphene oxide was obtained by exfoliating graphite oxide and has a wide range of applications in different fields, such as tissue engineering, photocatalysis, catalysis and biomedical applications [31]. In recent years, it has also been investigated as a potential additive in drilling fluids [7, 32].

GO can also be considered a rheological modifier, as it can convert a Newtonian fluid into a non-Newtonian one with increasing concentration [33]. Naficy et al. [34] found that GO in aqueous media exhibits four distinct conditions (moreover to newtonian liquid at low concentrations) as the concentration of nanosheets increases: viscoelastic liquid, a transition state consisting of viscoelastic liquid and soft viscoelastic solid, soft viscoelastic solid and viscoelastic gel. Kumar et al [35] reported that the aqueous dispersion of GO exhibits newtonian and non-newtonian behavior depending on the GO concentration; non-newtonian dispersion can exhibit pseudoplastic behavior with well-defined isotropic, isotropic-nematic, and liquid crystalline phases. Del Guidice & Shen [36] confirmed that the pseudoplastic behavior becomes more pronounced with increasing concentration; this response implies the existence of a yield stress since at low rates the viscosity values will tend to infinity. Recently, Malnaric et al [37] observed that in addition to the pseudoplastic behavior and yield stress at high concentrations, there is a thixotropic behavior, confirming the orientation of the nanosheets in the flow direction, followed by a buildup of the structure of GO when the shearing ceases [34, 36]. Therefore, it is evident that GO nanosheets can impart pseudoplastic behavior, characteristic of drilling fluids. But the effects of this nanosheet on other non-Newtonian water-based dispersions can present different behaviors, such as increasing or decreasing the viscosity or viscoelastic properties, caused by the interaction between the nanosheets and the dispersion [38, 39].

Among the main effects of adding GO nanosheets to drilling fluids for use in the petroleum industry, the reduction of filtration losses, modification of



Figure 1.3: Molecular model of graphene oxide [29].

rheological and tribological properties, and improvement of thermal conductivity can be highlighted [7, 32]. In the last decade, researchers have studied the effects of adding GO nanosheets on the rheological properties of drilling fluids. Xuan et al [40] studied the influence on rheological performance of GO in water and a bentonite suspension through a rotational viscometer. Concentration of 0.2, 0.4 and 0.6 wt% were considered. The results indicated that dispersions with higher concentrations of GO exhibited increased viscosity when dispersed just in water. Nevertheless, in the suspension, a small addition of GO led to a dramatic increase in viscosity in comparison with water-GO dispersion. It was concluded that in the suspension, the attraction between positively charged bentonite and negatively charged GO may cause nanosheets to connect to the clay and form a "physically" reticulated structure.

Studying a hybrid nanofluid formulation, Aramendiz and Imqam [41] reported the rheological response of silica and GO nanoparticles in a model water-based drilling mud at different aging temperatures up to 125°C by using a rotational viscometer. The optimal concentrations were considered 0.5 wt% and 0.25 wt% for silica and GO respectively. These concentrations were based on previous work done by them, considering technical characterizations for drilling fluids [42]. The effects of temperature on rheology were compared with a conventional fluid. Both fluids exhibited a very similar viscosity profile at ambient conditions. However, the conventional mud exhibited poor performance, having reduced viscosity at all other subjected temperatures due to the aging conditions. Conversely, the mud containing nanoparticles showed a stable viscosity for the studied range of temperatures. This stability was justified since nanoparticles could be capable of absorbing heat in order to preserve the rheological properties.

In a similar manner, Yang et al. [43] explored the influence of hybrid nanosilica (HNS), GO and HNS functionalized with GO (HNS-GO) in a waterbased drilling fluid. Three concentrations of GO, three concentrations of HNS, and a fixed concentration of HNS-GO were investigated. Tests were performed using a rotational rheometer under ambient conditions. The addition of GO and HNS led to an increase in viscosity, but GO had a higher influence in these results. The rheological response of HNS-GO produced an interesting rheological response, increasing its viscosity at low shear rates, which is important in the drilling process to suspend cuttings through the annular pipe region.

On the other hand, Gudarzifar et al. [44] studied the steady-state rheology of GO, polyacrylamide (PAM) and a GO/PAM nanocomposite in a bentonite-based mud. Up to 30 nanofluid formulations were prepared, first by simply adding and increasing the concentration of GO and PAM independently, then modifying the nanocomposite (with GO concentration on the polymer varying up to 2.0 wt%) and increasing the nanocomposite concentration on the mud. The tests were performed in a rotational rheometer at ambient conditions. Results showed that the addition of GO to the base mud led to a more pronounced shear-thinning behavior and higher viscosity. However, the higher concentration of GO (2.0 wt%) in the GO/PAM composite led to a slight decrease in viscosity, indicating that the higher increment was obtained with 1.5 wt% concentration. It was concluded that GO/PAM nanocomposites dispersed in the bentonite mud displayed higher viscosity, justified by the increment in electrostatic repulsive forces among bentonite, graphene oxide and polymer chains.

Similarly, Rafieefar et al. [45] examined the addition of GO in an aqueous dispersion of xanthan gum/carboxymethyl cellulose (XG/CMC) at ambient temperature. Tests were carried out in a rotational viscometer with GO concentrations of 0.05, 0.1, and 0.15 wt%. The addition of GO even at the lower concentration led to an increase in the shear stress response. This increase was explained by how the hydroxyl groups in XG/CMC interacted with the carboxyl and hydroxyl groups found in the edge and plane of GO sheets.

In addition to steady-state shear rheology tests, Medhi et al. [46] performed oscillatory shear tests (amplitude sweeps and frequency sweeps) to study the addition of GO in a water-based drilling fluid. The bulk rheological behavior was performed in a rotational rheometer at 30, 60 and 80 °C and the samples had GO concentrations of 0.2, 0.5 and 0.8% by weight. The steady-state results showed an increase in viscosity with the increment of GO until a specific concentration of 0.5 wt% from which was possible to identify viscosity reduction. The result of the amplitude sweeps exhibited a solid-like viscoelastic behavior in the linear viscoelastic region for all the samples. Although, a decrease in both viscoelastic moduli is identified as temperature increases, GO-containing samples showed good thermal stability of the moduli. Frequency sweeps of dispersion containing GO also displayed good stability in viscoelastic properties in comparison with the base dispersion.

In general, studies showed an evident increase in viscosity when adding and increasing GO concentration, displaying a more pronounced pseudoplastic behavior. However, these studies generally do not specify the level of oxidation and the number of layers, allowing for more precise comparisons between studies. Likewise, in some of these studies the effect of higher temperatures was analyzed, showing rheological stability when the fluid is heated. Rheological properties of drilling fluids can be influenced by the addition of GO; such formulations could have better performance compared to conventional fluids under adverse conditions during the drilling process. However, it is challenging to examine the interactions between the nanosheet and the base fluid to determine what led to the rheological alteration because of the numerous additives utilized in studies covering this subject. Therefore, understanding the influence of graphene oxide nanosheets in drilling fluids proves to be important knowledge. This type of study offers not only an analysis of the impact of nanomaterials on drilling fluids, but also a next step in the development of new research in the areas of non-Newtonian fluids and nanomaterials.

## 1.2 Objective

In the area of well drilling, the influence of incorporating nanomaterials on the properties of drilling fluids has been studied in a fragmented manner due to the numerous variables arising from the complexity of fluids and wellbores. Likewise, it is important to highlight that the results obtained in the laboratory can offer important indications about the impact of adding GO nanosheets to drilling fluids.

In this sense, the objective of this study is to analyze the effects of adding GO nanosheets on the rheology of aqueous dispersion of xanthan gum, as this is a biopolymer widely used as a viscosifier in the drilling industry [17]. Tests at different temperatures and pressures were developed to explore the potential effects on an offshore well. The presence of sodium chloride in the fluid was also analyzed in the study, as in pre-salt wells it is necessary to drill saline formations and for this purpose saturated fluids prepared with brine are generally used [10], so it is possible that the presence of salt affects the interaction dynamics between water, xanthan gum and graphene oxide.

## 2 Theoretical framework and literature review

In this chapter, some concepts of rheology and fluids with non-Newtonian behavior are presented. Then two sections are dedicated to discussing colloidal and aqueous polyelectrolyte dispersions. Next, some details regarding drilling fluids are presented, focusing on additives and their rheological response. Subsequently, general aspects of xanthan gum and its properties when dispersed in water are described. Finally, a brief introduction to nanomaterials are provided, followed by a comprehensive description of graphene oxide.

### 2.1 Rheology and non-newtonian fluids

Rheology is the science of deformation and flow of matter. Its main objective is the study of the deformation and flow of complex materials subjected to variable external stresses or strains [47, 48]. Rheology is also concerned with establishing a correlation between the molecular structure of materials and their properties during deformation or flow, which is of extreme importance in industrial processes. Examples include pulp and paper processing, food, paints, consumer products, pesticides and herbicides, polymer processing, drilling fluids, and biological fluids, among others [49, 48].

To understand the rheological properties of these materials, it is necessary to differentiate between Newtonian and non-Newtonian fluids. Newtonian fluids are fluids that obey Newton's law of viscosity, i.e. they present a linear relationship between shear stress and shear rate; some examples are water, air, oil or milk. Fluids that do not follow this law are called non-Newtonian [50]. In our daily lives, many of these non-Newtonian fluids appear, such as toothpaste, mayonnaise, ketchup, shampoo, blood, creams, and gels, among others. In general, these complex materials may be dependent on the shear rate, may also exhibit a mixture of viscous behavior similar to a liquid and elastic behavior similar to a solid, or have a dependence on the duration of shear and kinematic history [50, 51]. Over the years, researchers have developed constitutive rheological models to understand and predict the behavior of these materials under different circumstances [47, 52].

Currently, these fluids are largely characterized by simple shear flow, al-

though a wide variety of complex flows exist, as well as different environmental or boundary conditions. For example, there may be both shear and extensional components [53].

We can consider as a first class of non-Newtonian fluids those for which the shear stress at each moment is still fully determined by the instantaneous value of the shear rate but is not proportional to it anymore. These types of fluids are referred to as generalized Newtonian fluids [48]. A generalized Newtonian fluid is an idealized fluid for which the shear stress is a function of shear rate at the particular time, but not dependent upon the history of deformation. The ratio of shear stress to shear rate can still be used to describe apparent viscosity in this situation. This apparent viscosity now depends on the shear rate rather than being a constant. Figure 2.1 qualitatively illustrated the flow curves, also called rheograms, in linear coordinates for three categories of ideal fluid behavior that can represent generalized Newtonian fluids. On the one hand, pseudoplastic fluids, exhibit decreased viscosity with increasing applied shear stresses. Then dilatant fluids exhibit opposite behavior, increasing viscosity while increasing applied shear stress. Finally, viscoplastic fluids are a solid-like material that doesn't flow until critical stress is exceeded, after which it flows like a pseudoplastic fluid [49]. The typical linear relationship characteristic of Newtonian fluids is also included. Flow curves present the apparent viscosity and shear stress values as a function of shear rate; these quantities are obtained through a rheometer in steady-state shear flow.



Figure 2.1: Qualitative flow curves for some types of non-Newtonian fluids [51].

In addition to the flow curves, the stress (or strain) sweep and frequency sweep tests provide essential information for the rheological characterization of non-Newtonian fluids, which can have viscoelasticity. The characteristics of viscous fluids and elastic solids are combined in viscoelastic materials. Regardless of the length of time that the deformation occurs, the stresses in an elastic body are determined by the degree to which the actual shape of a material differs from the stressless, non-deformed one. Whenever stresses have been applied, even for a very long time, such a material always returns to the non-deformed state when the stresses are released. Consequently, perfect elastic materials can be thought of as possessing an ideal memory for their reference configuration that is not distorted. In contrast, a liquid has no memory at all; thus, even when the shear tension is relieved, it stays in its position [53].



Figure 2.2: Stress sweep (right) and frequency sweep (left) curves for a typical polymer [54].

In order to evaluate the viscoelasticity, experiments are performed in oscillatory shear flow where the stress or strain is imposed as an amplitude in a sinusoidal profile. In the case of the stress (or strain) sweep curve (Fig 2.2 (a)), at sufficiently low stresses, the microstructure of the material is preserved. This plateau region (the linear viscoelastic region) provides information regarding the resistance of the material to deformation (the stiffness of the material) [47, 54]. In the case of the frequency sweep curve (Fig.2.2 (b)), the dominant modulus, either storage (G') or loss modulus (G") at a given frequency indicates whether the material exhibits solid-like or liquid-like behavior. If the storage and loss moduli cross, this frequency ("crossover") marks the transition from elastic to viscous behavior or vice versa [51, 54]. Figure 2.2 shows qualitatively the stress sweep and frequency sweep curves for a typical polymer.

Complex fluids, which are composed of colloids, polymers, surfactants, and other supramolecular structures, exhibit intricate deformations in response to external stresses [49, 55]. Consequently, the stress-strain relationships are not merely defined by elastic and viscous components; rather, they are influenced by factors such as time, direction, extension, and thermophysical properties [47]. This allows for the quantification of rheological properties across a broad range of conditions and the potential to correlate these properties with the material's microstructure [52, 55]. In this work, we focus on the rheological behavior of two types of complex materials: colloidal dispersions and polyelectrolytic dispersions, specifically graphene oxide and xanthan gum in aqueous media.

## 2.2 Colloidal dispersions

According to IUPAC, a colloidal dispersion is a system in which particles of colloidal size of any nature (e.g. solid, liquid or gas) are dispersed in a continuous phase of a different composition (or state). The dispersed phase consists of particles that remain suspended in the continuous phase due to varios stabilizing interactions, rather than settling under gravity [56]. The dispersed phase is the one found in lesser proportion, and the continuous phase is liquid, but colloids can be found whose components are found in other states of aggregation of matter [53]. Colloidal chemistry studies the particle-liquid and particle-particle interactions that take place within a dispersion.

In this area, colloidal processing is the group of methods used to compact and shape particles that need to be prepared as colloidal dispersions first. This stage of preparation involves the chemical adaptation of the surface of the colloid, which occasionally calls for surface modification [53]. In our case, this is a part of the justification of the usage of graphene oxide instead of pristine graphene. Also, it is important to highlight that to prepare a dispersion containing a polymer it is essential to correctly mix and disperse the nanomaterial (filler) in the media, since the development of stable colloidal dispersions is important for the repeatability of the rheological measurements [57].

The stability of colloidal systems is governed by the balance between attractive and repulsive interactions among dispersed particles. The main attractive force, van der Waals interaction, arises from induced dipoles and is always present, regardless of surface charge. These forces become particularly relevant at short distances and can lead to particle aggregation if not counteracted. Repulsive forces, such as electrostatic interactions between like-charged surfaces, contribute to colloidal stability by preventing particle collisions. The overall stability of the system depends on the total energy profile resulting from the interplay of these forces [58, 57].

Electrostatic repulsion forces, together with van der Waals forces, constitute the double layer theory, or Derjaguin, Landau, Verwey, and Overbeek theory (DLVO). This theory establishes that when a particle is introduced into a polar medium, it becomes charged on the surface due to ionization, ion adsorption processes and/or dissociation of functional groups [59]. As a consequence of this, since it is a necessary condition for the system to maintain electroneutrality, a double ionic layer is formed to counteract the charge, as shown in Fig. 2.3. The first layer is called the rigid layer or Stern layer and is formed by the counter-ions adsorbed to the surface. A second parallel layer called the diffuse layer also appears, which does not fully compensate for the particle charge, but distributes ions in the medium to achieve a global electrostatic equilibrium [60, 61].



Figure 2.3: Schematic description of the double layer model imposed within the DLVO theory [59].

The colloidal stability of particles in aqueous media is a function of the different energies that act on the system, both repulsion and attraction, and by modifying and controlling these energies, stability and dispersion can be improved, as well as avoiding the formation of agglomerates and flocculation of the system.

For an understanding of the rheological response of colloidal systems, it is important to know that Brownian motion introduces an effective force that acts to keep particles well distributed. Every time there is a disturbance, this force generates a diffusive particle motion that returns the structure to its equilibrium condition. The corresponding time scale serves as a natural benchmark for determining whether the time scales of other deformation processes are "fast" or "slow," since it is a relaxation time for particle motion. It follows that reversible shear, time, and equilibrium phase behavior are all induced by Brownian motion and will show up in the rheology of colloidal dispersions [53].

Generally, theories to understand inherent properties related to colloidal dispersions arise from studying spherical particles, later with spheroids, fibers (rod-like) or platelets. A monodisperse colloidal dispersion can be defined by the particle volume fraction, particle size, medium viscosity, and temperature, among other parameters. However, particles can come in a wide range of shapes, not only rigid shapes [57, 62]. In our case, for example, the understanding of how graphene oxide behaves in aqueous media is more complex since it could not be considered a rigid platelet due to its flexibility to bend.

One of the properties of greatest interest when studying colloidal rheology is viscosity. In the case of colloidal dispersions, it is claimed that the presence of particles distorts the flow field and can therefore be expected to increase the energy dissipation during flow, and hence the viscosity. The work developed in this topic can be divided into three categories: dilute, semi-dilute and concentrated dispersions [53].

In dilute dispersions, particles move with the flow at the undisturbed velocity of their center of mass. Additionally, they rotate, but only at half the rate of the center of mass due to shear. Viscosity increases beyond that of the pure suspending medium as a result of local flow field disturbances caused by the particles and friction at their surfaces. This overall increase in viscosity is linearly related to concentration, being the sum of contributions from all particles [53]. One of the well-known viscosity relationships of rigid spherical particles was developed by Einstein [63].

In the semi-dilute regime, it is necessary to account for pairwise particle interactions. Calculating viscosity requires knowledge of the statistical nature of all possible interactions. Consequently, the microstructure has a direct impact on the dispersion viscosity, which is influenced by the method of sample preparation. Viscosity varies with particle size distribution and the type of flow being considered, as well as hydrodynamic interactions and electrostatic repulsion. Non-Newtonian effects and hysteresis during flow reversals are also anticipated, as surface roughness impacts the symmetry of trajectories and, consequently, the microstructure. If the relative arrangement of particles is known, it is possible to calculate the stress arising from hydrodynamic interactions [53]. For instance, in purely extensional flow, trajectories are not closed, allowing for the computation of viscosity and particle trajectories, as demonstrated by Batchelor and Green [64].

For concentrated dispersions, the average distance between particles decreases to the point where hydrodynamic and contact interactions (including friction and normal forces) are important. By scaling the packing fraction with the maximum packing fraction, this densely packed microstructure causes divergence in the shear viscosity, a principle that can be utilized to correlate data from various particle dispersions. Anisotropy with regard to the shear direction is seen in experiments instead of the fore-aft symmetry predicted for diluted dispersions, which has significant rheological implications. Surface roughness, repulsive or attractive interparticle forces, and challenges with experimental measurement led to deviations from expectations for idealized hard sphere dispersions. These effects are exacerbated at high particle concentrations due to the close proximity of particle surfaces [53]. Although semi-empirical relations like Krieger-Dougherty, Maron-Pierce, Eilers, Zarraga, and Cheng have been proposed and do a good job of describing the data, differences frequently only show up at high volume fractions, where sufficient general data for non-Brownian particles are either unavailable or not feasible [65, 66].

The rheological properties of colloidal dispersions are a topic of interest for many areas and applications. An interesting area is related to the response of nanomaterial dispersions, since the addition of nanoparticles can promote dramatic changes in the base fluids due to their unique properties.

# 2.3

#### Aqueous polyelectrolytic dispersions

From an international standard, a polymer dispersion is defined as liquid to semi-liquid material, containing the polymeric material in a stable condition finely dispersed in a continuous liquid phase, normally water [67]. When polymers are the dispersed material, it can be challenging to precisely determine whether they behave as liquids or solids, as variables such as temperature and stress amplitude play a crucial role. Polymers behave like glasses at temperatures below the glass transition temperature; while viscous or elastic materials are found beyond this temperature due to molecular rearrangement of the polymer. This behavior of polymers between liquid and solid is one another reason why, for instance, aqueous polymers are referred to as dispersions [68].

Specifically, polyelectrolytes are long-chain, linear, branched or reticulated polymers that have a charge throughout or in specific parts of their structure depending on the ionization of their functional groups. They become charged when the functional groups present in their repeating units dissolve in aqueous solutions due to the presence of an ionizable component. This kind of polymer would first be categorized according to the charge that their chain exhibits; if the groups in the chain have a propensity to charge positively, they are polycations, and if they do so negatively, they are polyanions. They are referred to as ampholytic polymers or zwitterions if they have groups with both charges [69]. The functional groups attached to the polymer chain can either be ionized or non-ionized. The charge of these groups fluctuates depending on their pKa and the medium pH. Thus, polyelectrolytes can be classified as strong or weak based on whether they fullybdissociate in solution for the majority of pH values or, conversely, if they partially dissociate at specific pHs and retain some charge in solution. This charge results from both the conformation and the kinds of functional groups that are present in the polyelectrolyte chain [70]. Despite their enormous prominence in many areas, polyelectrolytes were once described by nobel laureate P.G. de Gennes as "the least understood form of condensed matter", a designation that still holds true [71].

The three primary architectures that these polymers provide can be seen in Figure 2.4, which displays multiple ionized instances of polyelectrolytes: linear (like polyacrylic acid or polyvinylamine), branched (like branching polyethyleneimine), and dendritic (like polyamidoamine).



Figure 2.4: Example of various linear, branched and dendritic-type polyelectrolytes [72].

Similar to colloidal suspensions, the interaction and conformational structure of polyelectrolytes in a solvent (mostly water) are controlled to a large extent by electrostatic interactions. The two most frequently utilized approaches are a statistical thermodynamic approach based on the Debye-Hückel theory and the Flory-Huggins theory [73]. According to the Debye-Hückel approach, the ionic species form an ionic atmosphere structure rather than being randomly distributed in solution. It also states that thermodynamic properties, such as the heat of dilution, the mean activity coefficient of the solute, and the activity coefficient of the solvent, decrease linearly with the square root of concentration, in agreement with experimental observations; unfortunately, this approach only works at very low polyelectrolyte concentrations [70]. On the other hand, the Flory-Huggins theory is based on the so-called mean field approach, which is a theory that holds that fluctuations are ignored, no chain overlap is conceivable, and every component of the solvent-solvent and monomer-monomer interaction has the same energy [74]. This last theory presents several advantages, such as a clear distinction between entropic and enthalpic effects and a relatively simple and analytical set of equations [75].

The rheological response of polyelectrolytes lags behind that of neutral polymers because there are more parameters and length scales controlling the solution properties for charged polymers than for neutral ones [76, 77]. It is challenging to do experimental research on these complicated systems. For instance, observations altering the temperature, solvent quality, molar mass, and polymer concentration will typically be sufficient to comprehend the given system if we analyze the rheology of a neutral polymer in solution. On the other hand, for a polyelectrolyte, other physical parameters, including the charge density, the size and valence of the counterion, the concentration of added salt, and the dielectric constant of the solvent, all become significant experimental variables [78].

Furthermore, the chemical structure of the polyelectrolyte backbone, side-chain ions, and counterions must all be taken into account independently because it is impossible to define a single solvent quality. The dynamics of polyelectrolyte systems in concentrated solutions is intriguing, and its understanding is developing [79, 80, 81]. One of the primary focuses of polyelectrolyte study nowadays is their capacity to form complexes with oppositely charged materials, which makes them useful to many commercial formulations and biological systems [82, 83].

A pioneering attempt at construct a dumbbell model describing the rheology of polyelectrolyte solutions was developed by King and Eisenberg [84]. They looked at the behavior of a dumbbell model with two charged beads connected by a Hookean spring in weak shear flows to theoretically understand the rheology of these charged macromolecules. Dunlap and Leal [85] employed a similar micromechanical dumbbell model to simulate polyelectrolytes in strong flows. These models had conformation-dependent drag on the beads and finitely extensible springs.

In more recent studies, Shogin and Amundsen [86] presented a closedform stress tensor equation that explains the rheological behavior of dilute polyelectrolyte dispersions using the same charged dumbbell model as in the earlier experiments. With extremely high qualitative agreement with existing experimental data, their model predicted most of the steady and transient rheological features of a dilute polyelectrolyte dispersion in simple shear and extensional flows. By improving the previous work, Das et al. [87] developed a model using Onsager's variational principle to construct the diffusion equation for the probability distribution function governing the location and orientation of a charged dumbbell, representing a polyelectrolyte molecule. This approach was used to separately construct the free and dissipative energy contributions in a system before treating the combined effects. Free energy stands for other ionic species that contribute to the behavior of the polyelectrolyte in the solvent, such as salts.

Therefore, everything indicates that the rheological response of aqueous polyelectrolyte dispersions remains a subject of continuous development at the level of basic research. So, future experimental results could help to understand the behavior and structure under flow of different polyelectrolyte structures in different solvents and flows, with the aim of their use in everyday and industrial applications.

## 2.4 Drilling fluids

Drilling fluids are often classified as "complex" materials due to their wide range of rheological responses, such as elasto-visco-plasticity and thixotropy effects [88, 89, 90, 91, 92]. The importance of rheological properties and their effect on the performance of drilling fluids has been investigated by numerous authors over the years [93]. In a drilling fluid, shear-thinning behavior is a desirable property, since, given the high shear rates encountered in the drill pipe, the viscosity will be relatively low, which will reduce pumping pressure. Conversely, low shear rates in the annular region result in high viscosity values, which will increase the cuttings suspension capacity [89] as shown in Fig. 2.5. Likewise, these fluids generally have the ability to undergo a solid-liquid transition when subjected to sufficient stress, which is known as the yield stress [89, 91]. For good performance in the operation, the characteristics of the drilling fluid must be optimized, therefore, the rheological qualities must be regulated in order to minimize pumping costs, increase the penetration rate of the bit, efficiently lift the drilling cuttings, as well as separate the drilling solids at the surface [10, 23, 24].

In addition, the success of the drilling operation is significantly influenced by two elements that are strongly related to the rheological behavior in the annulus: cuttings lift and annular dynamic pressure. The first indicates the ability of the mud to retain and transport the cuttings. A low lifting capacity causes several problems, including altered rheological behavior and a greater chance of pipe sticking. On the other hand, the impact of the annular pressure loss on the downhole pressure regime is indicated by the annular dynamic pressure that depends on the rheological and tribological properties of the drilling fluid [93, 94, 91]. Likewise, all physico-chemical properties of the fluid are strongly influenced by the thermophysical properties of the well, such as pressure differentials, temperature gradients, complex geology, among others [95].



Figure 2.5: Scheme of a drilling fluid circulation system [96].

Due to the complexity of this process, several problems can occur and cause irreparable damage if sufficient care is not taken, such as drilling fluid filtration, which is one of the most common causes of formation damage [97]. In addition, wellbore instability is caused by the dispersion of clay deposits into ultrafine colloidal particles, and this has a direct impact on the properties of the drilling fluid [98]. Formation of a thin, low-permeability filter cake can mitigate these problems as it prevents the penetration of drilling fluid filtrate, which reduces hydration and excess cuttings formation [99]. Formation of an ultralow-permeability filter cake requires matching the pore size of the rock mass and the size of the screening/plugging particles. It is estimated that millions of dollars are lost each year due to wellbore instability problems resulting from drilling fluid penetration into shale [100]. Likewise, other problems such as corrosion or contamination are presented in Figure 2.6 in which the performance of drilling fluids takes on high relevance.

As already mentioned, there are currently different types of drilling fluids and each of them offers a different rheological response. The difficult task of choosing the right drilling fluid for each of the different drilling scenarios includes adjusting and monitoring the fluid properties to meet the well design, environmental regulations, logistical and financial constraints, in addition to performing multiple functions [16]. Density, viscosity, shear stress, alkalinity, filtration, solids content and chemical qualities are some of the characteristics which play a key role [10, 101]. Despite their environmental acceptance, conventional water-based drilling fluids present major challenges compared to oil-based drilling fluids with respect to their relatively poor shale inhibition, lubricity and rheological stability characteristics at high pressure and high temperature [12]. To overcome these shortcomings, specific additives can be added to water-based drilling fluid compositions to provide properties close to, although not as good as, the performance of oil-based fluids, while minimizing the environmental impact [90].



Figure 2.6: Common drilling fluid problems: causes and solutions [102].

Various materials, including clays, polymers, salts, inhibitors, and thickening agents, are added to water-based drilling fluids to improve their properties. Nowadays, there are numerous additives, and new additives are being developed in order to obtain high-performance drilling fluids [101, 12]. Rheological properties are influenced by all additives in the formulation, but some have a greater impact than others [93, 95, 101]. In this context, viscosifiers are mainly responsible for modifying the rheology of the fluid, providing a remarkable pseudoplastic behavior. Certain clays, synthetic polymers, biopolymers, and mixed metals are among the frequently used viscosifiers [11, 15, 16]. Other types of additives that may influence rheological behavior are densifiers (such as barite, hematite, limestone), inorganic salts (such as sodium and potassium chloride), lost circulation materials (such as fibers or granular materials), lubricants (such as esters, alcohols or particulate lubricants), shale control inhibitors (such as asphalts, polymers and humic acids), among others [103, 88, 104, 90, 15, 16, 23]. Figure 2.7 presents a general classification, functions and some examples of additives in drilling fluids based on the International Association of Drilling Contractors (IADC).

From a rheological point of view, the shear rate to which the drilling fluid is subjected is a relevant parameter. In the annulus, the flow may be subjected to a shear rate in the range of 10 to 150  $s^{-1}$ , while in the drill pipe there is a flow with an effective wall shear rate ranging from 150 to 10,000  $s^{-1}$ . It is also important to mention that when pumping is interrupted, even lower shear rates are experimented. Depending on the drill pipe and the extent of hole enlargement, the shear rate in each portion of the annulus can vary. In the bit, the fluid passes through the nozzle at very high velocities, equivalent to a shear rate of up to 100,000  $s^{-1}$ . In addition, the pseudo-helical flow produced by the eccentric rotation of the bit affects the velocity profile of the drilling fluid [11, 89]. Table 2.1 shows some estimated values of the shear rate to which drilling fluids are subjected.



Figure 2.7: General classification of drilling fluid additives based on the definitions of IADC. Adapted from [105].

Another important variable is that when drilling in a pre-salt layer, a saturated brine must be used to minimize the salt from dissolving and subsequently expanding the wellbore. The chemical composition and osmotic gradient of the brine and the salt bed must be fairly similar. If salinity remains saturated or slightly supersaturated, there may be less chance of salt leaching into the well [89].

Table 2.1: Estimated shear rates of drilling fluids. Reproduced from [11].

Drilling Fluid Region	Shear rate $(s^{-1})$
Interrupted	<1
Pits	1 - 10
Annulus	10 - 150
Suspension & Hole Cleaning	1 - 150
Solid Removal Equipment	150 - 10000
Inside Drill String	150 - 10000
Bit Region	10000 - 100000

In the drilling fluids area, the term flat rheology was created to address the operational problems associated with temperature and pressure control in deepwater and extended reach boreholes. In high-temperature, high-pressure wells, where conventional drilling fluids tend to exhibit excessive viscosity thinning, flat rheology formulations help mantain optimal viscosity for effective cuttings transport and wellbore stability. Then, fluids with flat rheology exhibit consistent rheological characteristics throughout a wide range of pressures and temperatures [92].

In Brazil, a lot of research is devoted to the description and study of the rheological properties of drilling fluids. It is important to preserve the structure of the fluid during its circulation under the influence of high temperatures, high pressures and different shear rates. Likewise, other variables are of high importance during the operation such as tribological behavior to increase the rate of penetration and reduce drag, or the study of drilling hydraulics, to evaluate the dynamics of the drill string, among others [94, 106, 103, 107].

#### 2.5 Xanthan Gum

In the 1950s, American scientists developed the polysaccharide B-1459, now known as Xanthan Gum, produced by the bacterium "Xanthomonas campestris" [19, 108]. The main application of xanthan gum is as a thickening and stabilizing agent in the food industry (sauces, ice creams, yogurts) and in personal care products (shampoo, gels, creams). Among other applications, it is also worth highlighting its use in petroleum extraction (filling agent), the pharmaceutical industry, etc. [109]. On an industrial scale, it is obtained through stage-by-stage fermentation processes in fermentation tanks with good oxygenation in the presence of glucose and other trace elements. Xanthan gum is soluble in cold water, and due to its structure and intermolecular interactions it gives rise to solutions with a high pseudoplastic character. Its viscosity is quite stable in a wide range of pH and temperature, and it is also resistant to enzymatic degradation [20, 110, 109]. The global market for xanthan gum is estimated to be approximately 500 million dollars and is expected to continue growing in the coming years [111, 112].

Numerous academic works have described Xanthan gum from many physico-chemical perspectives. Therefore, a few key points should be included in this dissertation to comprehend how morphology and chemical structure can impact rheological response. The main chain of xanthan gum (Figure 2.8) is made up of glucose units connected by carbons, whereas the side chains are made up of one glucuronic acid unit and two mannose units. A pyruvic



acid residue is present in half of the mannose units, whereas an acetyl group connected to an additional carbon is present in the other half [18, 113, 109].

Figure 2.8: Schematic representation of the xanthan gum dimer [114].

Temperature has a significant impact on the characteristics and actions of hydrocolloids such as xanthan gum. Optimizing the functioning and performance of hydrocolloids in a variety of applications requires an understanding of how temperature affects them. When subjected to high temperatures, hydrocolloids can become denatured or deteriorate, change their structure, or even thermally degrade, losing their useful properties. All things considered, one important property of hydrocolloids that should be taken into account when creating formulations with these materials that call for their utilization is their temperature sensitivity. Researchers can create novel and creative solutions to fulfill the demands of many sectors by using their understanding of how temperature influences the characteristics and behavior of hydrocolloids [112, 111].

The aqueous solutions of xanthan gum experience conformational changes as the temperature rises. This results in a transition from a stiff and ordered structure to a more flexible and disordered structure (Figure 2.9). The amount of pyruvic and acetic acid in the xanthan gum molecules, the gum concentration, and the ionic strength all affect the temperature transition [17, 115, 116]. The transition could happen between 50 and 60 °C when there is little salt present. When salt is added, on the other hand, the charge that stabilizes the gum's structure is screened, causing the transition to happen at 80 to 100 °C [110, 117]. The xanthan gum helix in solution can be thought of as a stiff chain that interacts with other chains to form a weak gel-like structure below the transition temperature [118, 119].



Figure 2.9: Schematic representation of conformal transitions of Xanthan gum [120].

Xanthan gum solutions exhibit strong pseudoplasticity, characterized by three distinct viscosity regions: (1) a Newtonian plateau at low shear rates ( $\eta_0$ ), where the intermolecular network remains intact; (2) a shear-thinning region, where molecular interactions weaken and viscosity decreases significantly; and (3) a second newtonian plateau at high shear rates  $(\eta_{\infty})$ , where molecules are aligned to the flow [121, 110]. This behavior is a consequence of the intermolecular associations between the xanthan gum chains that give rise to a network of rigid molecules. When shear rates are low, the viscosity stays constant because the rate of network breakup is less than the rate of formation. A noticeable pseudoplastic decrease indicates the weak bonding in the aggregates being broken as the shear rate rises. A consistent and low viscosity is obtained in the high shear rate zone due to the breaking of all the aggregates and alignment of the biopolymer chains in the direction of flow [17, 110, 122]. In the same way, the highly ordered structure of rigid molecules of xanthan gum confers very interesting viscoelastic properties to gum solutions, obtaining a weak gel-like behavior even at low concentrations [123].

The influence of electrolytes on the viscosity of xanthan gum depends on the concentration of the gum. It has been observed that below a certain concentration of xanthan gum, the addition of an electrolyte, such as sodium chloride, slightly reduces the viscosity, while at higher concentrations it causes the opposite effect. To explain this behavior, it must be taken into account the two different conformations mentioned before: an ordered helix-shaped conformation and a disordered one that is usually described as a broken or imperfect helix. The decrease in viscosity with the addition of salt is related to the screening of the electrostatic repulsion between the charged groups of the side chains, leading the molecule to adopt the ordered helical structure. This causes a significant decrease in molecular size and is the cause of the decrease in viscosity for low concentrations of xanthan gum. On the other hand, the change in behavior at high concentrations of xanthan gum (concentrations above the critical concentration of interaction between polymer molecules) is attributed to a greater capacity for interaction between the gum molecules in the ordered conformation, increasing the cross-linking of the chains and the gel-like character of the gum dispersions [124, 125, 110, 126, 127].

The viscosity values of xanthan gum are quite insensitive to pH variations. However, it is observed that xanthan gum solutions slightly decrease their viscosity at pH values below 4, with this viscosity reduction being more evident at low shear rates. This is a reversible process and if the pH increases again above 4 the solution recovers its original viscosity. This viscosity reduction could be caused by the suppression of the electrostatic repulsions between the side chains when the carboxyl groups change from their ionized form (COO-) to the deionized COOH. The decrease in pH has the same effect on viscosity as the addition of salt, but its influence is quantitatively less. On the other hand, at pH values above 9, xanthan gum gradually deacetylates, without this causing a large variation in the viscosity values [125, 128].

For xanthan gum to perform as best it can, it needs to be well-hydrated. Gum dispersion, agitation, solvent content, and gum particle size all affect hydration. Proper hydration necessitates a satisfactory gum particle dispersion. Aggregates, or microgels, are formed as a result of poor dispersion, which also lowers the functionality of the dispersion. High shear conditions are ideal for dispersing and hydrating xanthan gum. Use of various dispersants, such as sugar, starch, and salt, can enhance the hydration of the gum and dispersion process. Non-organic solvents including oils, glycerol, and alcohols can also be used for dispersion; they combine with the gum to create a slurry that dissolves readily in water. It is advised to hydrate the gum without excess salt since xanthan gum is less likely to hydrate when there is more than 1-2% salt present in the water. Salt can be added up to 10-20% after hydration without causing dramatic negative effects [111].

Pharmaceutical formulations, cosmetics, and agricultural products all use xanthan gum due to its ability to thicken aqueous solutions, disperse, and stabilize emulsions and suspensions. It is utilized in rust removers, slurry explosive compositions, ceramic glazes, and textile printing pastes. The petroleum industry has found significant uses for xanthan due to its high solution viscosity and water solubility. It is frequently utilized in enhanced oil recovery procedures and drilling fluids [129].

Xanthan gum is widely used as viscosifier in drilling fluids particularly for cuttings transport. This may be due to its high molecular weight, ranging from  $2.0*10^6$  to  $2.0*10^7$  g/mol, which can be influenced by fermentation conditions.
[130]. However, its performance at high temperatures is a limiting factor. Above 100°C, its molecular structure begins to degrade, and at 120°C, viscosity loss can exceed 80% [21, 131]. To mitigate this issure, the incorporation of nanoparticles has been explores as a potential strategy to enhance thermal stability

# 2.6 Graphene Oxide

For the oil and gas sector, nanotechnology is still a relatively recent breakthrough. Many of its applications, nevertheless, are now essential to some of its most important technological operations. Widespread use of nanotechnology is being seen, particularly in the improvement of wellbore fluids, drilling equipment performance, and improved/enhanced techniques for oil and gas recovery [132, 133].

In this context, a rapidly developing area of nanotechnology called carbon-based nanomaterials is making progress in a variety of applications, including tissue engineering, medication delivery, and transplantation. They are essential for improving a number of attributes, including surface area, immunogenicity, durability, multifunctionality, refractive index, and pharmacological delivery [134, 135]. This group includes a wide range of materials, such as fullerene and carbon foam, as well as single- and multi-walled carbon nanotubes, graphene oxide, graphene nanosheets, graphene quantum dots, nanodiamond, and nanocarbon [136].

Graphene is a material consisting of a single layer of a two-dimensional honeycomb lattice structure created by carbon atoms coupled by  $sp^2$  hybridization (Fig. 1.2). It is superhydrophobic and superlipophilic, as well as incredibly strong and ductile. Graphene's longer edges make it easier to dope and chemically modify than carbon nanotubes. Furthermore, it has significant potential applications in the fields of materials science, healthcare, energy, micro and nano processing, and aerospace [137, 138].

However, scalability is a major obstacle in the production of graphene [139]. Moreover, the hydrophobic nature of graphene makes it difficult for it to dissolve in water and other organic solvents, which restricts its usefulness in the creation of nanofluids. Graphene oxide (GO), a graphene functionalization, has been widely used to overcome these problems. However, the most common current synthesis produces many byproducts that generate chemical waste, making improving graphene oxide synthesis a topic of high research interest.

Graphene oxide is a graphene nanosheet heavily decorated with oxygencontaining groups such as epoxide, hydroxyl, and carboxyl, attached to both sides of the carbon plane and edges [30]. Although graphene oxide does not possess the same mechanical and physical characteristics as graphene [140], processes exist to improve and adjust the properties of graphene oxide based on the ratio of carbon to oxygen, nanosheet size, other functionalizations, etc.

In the dimensional structural model presented in Fig. 1.3, a GO nanosheet is characterized by the coexistence of two very different length scales. On the one hand, we find that the thickness of this material is in molecular order dimensions, with a measurement close to 1 nm [141]. On the other hand, the lateral dimensions of the sheet are similar to those of other more common particles. This feature allows us to characterize graphene oxide sheets either as molecules or as particles, depending on the dimension of greatest interest. Furthermore, the GO nanosheet has a delicate and flexible texture. These fascinating features of GO encourage a variety of application fields to use it [139, 142].

There is currently no widely recognized model for the precise chemical structure of graphene oxide, which has been the topic of continual discussion over the years. The complexity of the material (including sample-to-sample variability) resulting from its amorphous nature, its anisotropy, and the absence of precise analytical techniques for the characterization of these materials are the primary causes of the inability to apply a model universally [143, 144]. Despite these challenges, a great deal of work, much of which has been extraordinarily successful, has been done to try and understand the structure of graphene oxide.

Owing to its two-dimensional nature, GO has numerous features of considerable interest, and it is also used as a base material for the synthesis of graphene due to its flexibility in functionalization and reduction [144, 145]. GO has a high capacity to disperse in polar and nonpolar media because it is an amphiphilic material, which means that it has hydrophilic and hydrophobic ends. GO also has good properties to disperse in matrices of different characteristics, due to the oxygenated functional groups that abound on its surface. This property must be considered of utmost importance when mixing this material with ceramic or polymeric matrices [31].

In respect of stiffness, a monolayer of GO can have a Young's modulus to about 250 up to 430 GPa [146, 147], which indeed is lower than the modulus of a pristine graphene layer of about 1.0 TPa [148]. In terms of electrical conductivity, GO typically exhibits properties as an electrical insulator (with null or low electrical conductivity) [149, 150]. Regarding thermal conductivity, for a GO single layer at room temperature it can go up to 670 W/mK depending on oxidation degree [151], which is higher from common metallic oxides [152]. In order to approximately recover the hexagonal network shape of pristine graphene, and thus the properties, the reduction of graphene oxide is the process considered for this purpose. It is important to note that once most of the oxygenated functional groups are removed, the obtained reduced graphene oxide is more difficult to disperse due to its tendency to create aggregates and agglomerations [145, 153, 154].

There are currently two primary group techniques to synthesize GO. The "top-down" techniques in the first group rely on the oxidation and fragmentation of graphite. The modified Hummers method is the most often utilized of them [155, 156], however other approaches, like the classic Hummers method [157], the Brodie method [158], the Staudenmaier method [159], the Hofmann method [160], and their variants, are also less frequently employed. Strong acids and oxidation agents are typically used in these procedures to carry out the oxidation. The second category consists of "bottom-up" techniques, currently less investigated, which use heat treatment to carbonize organic precursors. Promissory results of precursors of graphene oxide have been examined, including tannic acid [161], glucose [162], and citric acid [163].

There are two main types of methods for preparing nanofluids that contain GO or other nanoparticles: one-step preparation and two-step preparation. The one-step method involves dispersing the particles into the base solution as the nanoparticles are being created, allowing for the simultaneous creation of the nanofluids and nanoparticles. On the other hand, the two-step method entails first manufacturing each nanometer powder and then distributing the nanoparticles in the base liquid [164]. The primary distinction between the two techniques is that produced nanoparticles from the two-step method must first be dried for a while before being added to the base solution; this procedure may have an impact on the characteristics of the nanoparticles [165, 166].

As well as polymeric dispersions, the rheological response of dispersions containing GO presents different responses as a function of the temperature, nanosheet dimensions, reactivity, among others variables. The rheology of graphene oxide in newtonian fluids, such as water-based [37, 35, 34, 167, 168, 169, 170, 171] and alcohol-based [172, 173, 174], has been the subject of numerous investigations. Due to GO 2D amphiphilic microstructure, the rheological behavior of GO suspensions is governed by attractive interactions arising from the unoxidized graphitic domains which compete with electrostatic interactions, primarily on the rims of the GO nanosheets [175, 176]. For instance, aqueous suspensions of GO have been categorized as isotropic liquids, nematic liquids, and liquids in arrested states (glasses or gels) as the concentration increases through dynamic and stationary shear rheological tests [35, 177, 34]. This behavior could be influenced by the previously mentioned criteria as well as intrinsic nanosheet features including the aspect ratio, functionalization technique, or even morphological defects of the nanosheets [37, 178].

In order to have a better understanding on properties and morphology of GO, characterization techniques are essential and critical when working with nanofluids since characteristics such as nanoparticles stacking, their dimensions, the functional groups contained, and the degree of disorder may be more important in some applications than in others [144]. Some characterization techniques used for GO are listed and described in table 2. The relevance of the characterization techniques relies not only on identifying if nanomaterials were successfully developed. These tools could also be carefully considered in each engineering result, as they would allow standardizing the description and characteristics of the nanosheets in each study.

It was mentioned in the introduction that literature shows the influence of GO in the rheological response in aqueous media, at moderate concentrations interesting behavior can be visualized. However, there is still a lack of understanding of the rheological response of GO dispersed in a wide range of aqueous non newtonian media such as cement pastes, polymeric or clay dispersions. Currently, there are some works addressing this topic [38, 184, 185, 186, 187, 188, 189, 190, 191, 192]. It can be identified that there is a high dependence on the physicochemical interactions at the molecular level that promote rheological modification in aqueous dispersions with GO nanosheets. In addition, since GO is a tunable nanomaterial, it would be optimal to standardize the specifications in terms of, for example, nanosheet size, oxidation level, or average number of layers, among other aspects in order to make better comparisons of the properties between studies.

GO nanosheets could have a significant impact on the rheological response of water-based drilling fluids formulations [32]. Additionally, they may have a direct and indirect impact on a number of their related properties, including filtration properties, lubricating properties, wellbore stability, cuttings removal (buoyancy), and wellbore strengthening [32]. For instance, the rheological characteristics of the mud are intimately associated with the lubricity or buoyancy, whereas the formation of a thin layer known as a "filter cake" at the surface of the formation to prevent leaks into or out of the formation and the viscoelastic response are closely related to the wellbore strengthening [7].

Table 2.2. Summary on some characterization teeninques for GO		
Technique	Description	Ref.
Scanning	SEM is used to analyze the topology and lateral	[179,
electron	dimensions of samples. Typical SEM images of GO	141]
microscopy	show 2D nanosheet morphologies with wrinkled and	
(SEM)	folded textures.	
Transmission	TEM uses electrons that pass through the sample	[179,
electron	with contrast resulting from differences in electron	180,
microscopy	density. It is useful to identify single-layer and few-	181]
(TEM)	layer graphene oxide sheets. Also to see detailed	
	morphology of the nanosheets as wrinkles and de-	
	fects on surfaces.	
Atomic force	AFM is performed to determine the number of GO	[182,
microscopy	layers. The image obtained at AFM relates the	141,
(AFM)	thickness and size of the sample to a color scale.	180,
		183]
Fourier	FTIR is utilized to get an infrared spectrum of ab-	[182,
transform	sorption or emissions of a solid, liquid or gas. It re-	180,
infrared	veals the chemical bonds present in the materials.	181,
spectroscopy	For GO, oxygenated functional groups such as car-	183]
(FTIR)	boxyl, hydroxyl, alkoxy and epoxy can be identified.	
Raman spec-	Raman permits analyzing the quality of the GO.	[141,
troscopy	The G band is related to the stretching of the $sp^2$	180,
	band between carbon pairs. The D band appears due	183]
	to the presence of structural defects. The high inten-	-
	sity ratio of D and G bands reveal large quantities	
	of defects in the GO due to the oxygen functional	
	groups on its surface.	
Ultraviolet-	UV-Vis has been used to measure optical absorption	[182,
visible spec-	properties. Spectrum of GO has two features: a	181]
trometer	maximum corresponding to transition of aromatic	
(UV-Vis)	bonds and a shoulder attributed to carbonyl bonds.	
X-ray diffrac-	XRD is used to evaluate the influence of oxygenated	[179,
tion analysis	groups on the interplanar distance of the GO layers.	181,
(XRD)	By applying Bragg's Law, spacing between layers	183]
	can be calculated from the incident angle.	
X-ray pho-	XPS is used to analyze the elemental composition	[182,
toelectron	on the surface by measuring the number and kinetic	179,
spectroscopy	energy of photon-emitted electrons produced. For	141,
(XPS)	GO, peaks with related functional groups can be	181]
	visualized.	
Thermo-	TGA measures the mass loss versus temperature. It	[182,
gravimetric	can indicate the oxidation degree of GO. For GO can	141,
analysis	be identified three stages: moisture evaporation, dis-	181]
(TGA)	integration of oxygen containing bonds and degra-	
	dation of graphitic structure.	

Table 2.2: Summary on some characterization techniques for GO

# 3 Materials and Methods

This chapter presents the materials and procedures used for the synthesis and characterization of graphene oxide nanosheets, as well as the preparation of the base fluid and the nanofluid. The rheological and microstructural characterization techniques of the dispersions that were carried out are also described.

## 3.1 Synthesis of graphene oxide

The modified Hummers method, as previously reported in the literature [155, 193, 194], was used to synthesize graphene oxide. For the synthesis, 360 mL of  $H_2SO_4$  was utilized at 5°C under low agitation. Next, 4.5 g of synthetic graphite (graphite powder 99%  $\leq 20\mu m$  - SigmaAldrich) was added while the mixture was still being shaken, after which 40 mL of  $H_3SO_4$  was added. The system was heated to 50°C and kept under continuous agitation for 12 hours after the dispersion had been homogenized for an hour. After cooling the reaction to 0 °C, 1.0 L of deionized water was added. Subsequently, hydrogen peroxide ( $H_2O_2$ ) was added until a color change was observed.

The graphite oxide (GrO) was washed with a 10% hydrochloric acid (HCl) solution, and after a 24-hour rest period, the supernatant was extracted. There were two more iterations of this procedure. After removing the supernatant, the substance was once again suspended in deionized water. Following precipitation during rest, the material was centrifuged in a DT 4500 Daiki centrifuge at 4500 rpm for 20 cycles, of 2 minutes each cycle. After the supernatant was extracted from each centrifugation, the precipitate was resuspended in deionized water until its pH fell between 4 and 5. The materials were then prepared for usage in the nanofluid production process after being lyophilized in a Liotop lyophilizer (L101).

### 3.2

### Characterization of graphene oxide nanosheets

In order to characterize graphene oxide (GO), numerous analyses were carried out. We used Fourier transform infrared spectroscopy (FTIR) to examine the vibration modes between the carbon and oxygen atoms in the dried GO sample, and the spectrum of 500-4000  $cm^{-1}$  was recorded using a Burker Vertex 70 spectrometer with resolution 4  $cm^{-1}$  and scan time of 32 s. X-ray diffraction (XRD) tests were performed with dried samples in sample holder equipment. The diffractograms were acquired on Rigaku Miniflex II equipment with a copper filament tube ( $\lambda = 1.5406$ Å), with steps of 0.001° and a scan rate of 2°/min. The thermogravimetric analysis (TGA) quantitatively indicates the oxidation level of GO. It was performed using the SDT-Q600 from TA Instruments, with a temperature range of 25°C to 1000°C and a variation rate of 10°C/min in a nitrogen ( $N_2$ ) atmosphere. Raman spectra were obtained using a Witec Alpha300 system with a 600 g/mm grating, BLZ = 500 nm, and a laser exitation wavelength of 532 nm. UV-Vis absorption spectra were measured over the wavelength range of 200–600 nm using a Shimadzu UV-3600 Plus spectrophotometer.

## 3.3 Base fluid and nanofluid preparation

The base fluid was prepared by following the procedure done by [195]. XG powder (F200, Plury Química Ltda) was dispersed in deionized water in order to obtain a concentration of 0.86 wt%. Mechanical stirring was initially performed at 300 rpm for 15 minutes, followed by the addition of bactericides (sodium benzoate and potassium sorbate, both from Sigma-Aldrich) at 0.5 wt% each. The dispersion was then stirred for an additional 60 minutes and subsequently allowed to rest undisturbed for 24 hours under ambient conditions. Fig. 3.1(a) shows the scheme of this process.

Two preparation methods were evaluated to prepare the dispersion of GO in xanthan gum. In preparation method 1, the nanofluid was prepared by first exfoliating lyophilized graphite oxide in deionized water for two hours in an ultrasonic bath to form a GO aqueous suspension with the desired concentration of GO. Subsequently, the same procedure for the preparation of the base fluid was followed. Fig. 3.1(b) shows a scheme of this process.

In method 2, the nanofluid was prepared by first exfoliating the GO (with the mass quantity for the desired global concentration) in 30% of the total water mass to be used in the system for two hours in an ultrasonic bath. Subsequently, homogenization of xanthan gum in the remaining deionized water (70% wt.) was performed for 45 minutes (Adding the bactericides after 15 minutes of starting the agitation), then both systems were mixed and mechanically stirred for another half hour. Figure 3.1(c) shows the scheme of this process.



Figure 3.1: Scheme of the preparation of the base fluid (a), the method 1 (b) and method 2 (c) for nanofluid preparation.

Nearly saturated dispersions with sodium chloride (99%, Labsynth Ltd.) were prepared by adding salt to a concentration of 20 wt%, 30 minutes before finishing preparation. Only base fluid and GO dispersion with the optimal preparation method were prepared with the addition of sodium chloride. All the dispersions were left to rest for 24 hours before any test, for the complete hydration of the polymer molecules [195].

# 3.4 Rheological characterization of the dispersions

Rheological tests at ambient pressure were performed on the ARES-G2 (TA Instruments) strain-controlled rheometer. Smooth concentric cylinders geometry was used, with a titanium bob having an external diameter of 32 mm and a length of 47 mm and a cup with an internal diameter of 34 mm. This geometry was used in all tests because xanthan gum at the concentration used and with the addition of graphene oxide did not show wall slip. A scheme of the rheometer and the sample in the geometry is shown in Fig. 3.2. All tests were carried out at atmospheric pressure and four different temperatures (4, 23, 50, and 80 °C). These temperatures are analogous to the working temperatures of a drilling fluid in a well, 4 °C represents the seabed temperature, and 80 °C when the fluid passes through the drill bit. The rheology of the suspensions was analyzed for steady-state and oscillatory flow tests. Flow curves were obtained with shear rates ranging from 1000 to 0.01  $s^{-1}$ . Each point was obtained considering that a comparison point is obtained every 30 seconds, which must have a difference of less than 0.1% in relation to the previous two,

or with a time limit of 1000 seconds (this last value was never reached in the experiments). The responses of storage (G') and loss (G") modulus were also evaluated through oscillatory tests. In order to visualize the linear viscoelastic region (LVR), strain sweep tests were carried out, varying the strain amplitude from 1 to 1000% with a frequency of 1 Hz. To obtain a reasonable value in these experiments, 3 cycles per point were considered. A constant strain amplitude obtained in the LVR was used as input data in frequency sweep tests performed from 0.1 to 10 Hz.



Figure 3.2: Scheme of ARES G2 strain-controlled rheometer with smooth concentric cylinders geometry.

Rheological measurements at higher pressures were performed on the Haake MARS III (Thermo Fisher Scientific) stress-controlled rheometer equipped with a high-pressure cell shown in Fig. 3.3. Smooth concentric cylinders geometry was used, with a cup diameter of 35 mm, a bob diameter and length of 32 mm and 80 mm, respectively. Steady-state flow measurements at three pressures (1, 100, and 400 bar) and three temperatures (4, 23 and 80 °C) were performed in Haake MARS III. Flow curves were obtained with shear rates ranging from 1000 to 10  $s^{-1}$ ; measurements at lower shear rates were not performed due to technical limitations (the minimum sensible torque of the equipment was reached).



Figure 3.3: Scheme of Haake MARS III stress controlled rheometer with smooth concentric cylinders geometry in the high-pressure cell.

It is important to note that all flow curves in this study were obtained from the highest to the lowest shear rate in order to ensure that a fluid with a homogeneous structure was measured. An anisotropic phase was seen in the dispersion when tests were run from the lowest to the maximum shear rate for the investigated concentration of XG. This phenomenon is associated with the shear orientation behavior of XG chains [196], that is shown in Fig. 4.6 in the results section. Also, to remove any remaining stresses and keep the quiescent state constant during each oscillatory test, they were carried out following a pre-shear followed by a rest period [197].

## 3.5 Microstructure characterization of the dispersions

Cryo-scanning electron microscopy (cryo-SEM) was used to visually inspect the microstructures of the base fluids and suspensions using the TESCAN CLARA field-free Ultra High Resolution (UHR) electron microscope in conjunction with a Quorum PP3000T cryogenic system. In order to prevent the formation of ice crystals, the samples were prepared by rapidly immersing them in liquid nitrogen for 30 seconds at -210°C under vacuum conditions. To exclude water, the samples were subsequently sublimated for 15 minutes at -60°C in a preparation chamber set at -170°C. According to tests, this can remove water to some extent without altering the structure of the liquid. After that, the samples were sputter-coated with a thin coating of platinum for 120 seconds at 10 mA. This coating is used to improve image quality and resolution. Following their transfer to the microscope chamber, the samples were photographed at a 5 kV acceleration voltage while being kept under a high vacuum at -140°C.

# 4 Results and Discussions

# 4.1 Physico-chemical aspects of graphene oxide nanosheets

The dispersion must be morphologically and structurally characterized in order to better understand the characteristics of GO and its possible interactions with xanthan gum. Moreover, the characteristics of the nanomaterial may be directly related to its thermal and rheological characteristics. Through a deeper comprehension of the molecular structure of the material and behavior under various situations, these techniques offer insightful information about the structural characteristics and interactions of GO.

Fig. 4.1 shows the FTIR spectrum, where the vibrations related to the presence of functional groups in GO can be observed [38]. The stretching modes of the O-H bonds in the structure, which may originate from water molecules or tertiary alcohols, are responsible for the strong band at about  $3314 \text{ cm}^{-1}$ . The band that corresponds to the stretching of O=C=O bonds, which is commonly linked to adsorbed carbon dioxide, is seen at  $2355 \text{ cm}^{-1}$ . This is most likely connected to the presence of atmospheric  $CO_2$ . Either carboxylic acids, ketones, or aldehydes on the GO surface are responsible for the band at 1726  $\rm cm^{-1}$ , which is linked to the stretching of C=O bonds from carboxyl groups. It is easy to confuse the band at  $1613 \text{ cm}^{-1}$  for C=C stretching. This stretching would need the presence of extra bands between 1575 and 1590  $cm^{-1}$ , which correspond to C=C bonds. It can be inferred from the lack of these bands that the bending of the water molecules in the GO is associated with the band at  $1613 \text{ cm}^{-1}$ . C–O bond stretching vibrations from alcohols and epoxides are responsible for the bands at  $1165 \text{ cm}^{-1}$  and  $1040 \text{ cm}^{-1}$ . The apparent band overlap in the fingerprint region makes identification a little trickier. The stretching of epoxy groups, however, is responsible for the bands at 960 cm<sup>-1</sup> and 680 cm<sup>-1</sup> [198, 199, 200].

The characteristic spectrum of GO as determined by Raman spectroscopy is shown in Fig. 4.2. The G band, which corresponds to the intense band at about 1600 cm<sup>-1</sup>, is an in-plane vibrational mode that is linked to the structural integrity of GO and is related to the stretching of  $sp^2$  bonds between



Figure 4.1: FTIR spectra of GO.

pairs of carbon atoms. However, the D band, which is located at 1350 cm<sup>-1</sup>, shows that there are flaws in the GO structure. These defects can occur at the edges and in the basal plane and include, among other things, the creation of sp<sup>3</sup> carbon and Stone-Wales defects [193]. Furthermore, the 2D band, which corresponds to an overtone vibration and is associated with the degree of disorder in the material, is found in the range of 2700 to 2930 cm<sup>-1</sup>. The introduction of oxygenated groups at the margins and on the basal surface of GO results in a significant number of defects in the structure, as indicated by the  $I_D/I_G$  ratio of 1.0. This may also be connected to the degree of oxidation of the material [38, 201].



Figure 4.2: Raman Spectra of GO.

Fig. 4.3 shows the X-ray diffraction analysis (XRD) of GO, displaying an intense peak at 9.2°, which corresponds to the (001) plane, a somewhat wider peak at 21.7°, which corresponds to the (002) plane, and a peak at 42.8°, which corresponds to the (100) plane. Because of the (002) plane's suppression, the latter shows low intensity. The interplanar distance of 9.6 Å (or 0.960 nm) for the (001) plane can be determined using Bragg's Law. The gap between the GO layers, which results from the addition of functional groups during the

oxidation process, is represented by this distance [38, 202].



Figure 4.3: XRD Spectra of GO.

Thermogravimetric analysis (TGA) of GO indicates its degree of oxidation, as well as the temperature at which mass loss events occur. In the analysis shown in Fig. 4.4, it is possible to identify three separate mass loss events, each of which is connected to a different material phenomenon. At about 100°C, the initial mass loss event takes place, and at 41°C, the peak evaporation rate is observed. This shows that a portion of the material, estimated at about 17 weight percent, has been lost as water or another kind of adsorbed organic solvent. The second event, which is linked to the breakdown of oxygen-containing groups within the GO structure, takes place at about 350°C. This gives the oxidation degree of the material, which was found to be about 39%. The burning of carbon is the third event. The third mass loss, which is 44%, is caused by the burning of the graphitized carbon in the GO structure at about 580°C [193, 38, 203]. Based on the observed mass losses and the achieved degree of oxidation, it can conclude that the material was successfully synthesized and exhibits a good level of oxidation [38, 199, 204].



Figure 4.4: TGA Spectra of GO.

In Fig 4.5, unique electronic transitions of GO are emphasized in its UV-Vis spectrum. The  $\pi \to \pi^*$  transition, which is characteristic of aromatic C=C bonds, is represented by the major absorption peak in the UV area at 230 nm. Furthermore, the  $n \to \pi^*$  transition of the carbonyl (C=O) groups in the GO structure is responsible for a shoulder seen at about 300 nm. This distinct spectrum profile represents the electrical characteristics of GO in addition to confirming the existence of these functional groups [198].



Figure 4.5: UV-Vis spectra of GO.

### 4.2 Rheological response of the dispersions

As described above, the phenomenon of dispersed anisotropic phase is shown in Figure 4.6, as well as the ramp-up and ramp-down flow curves.



Figure 4.6: Dispersed anisotropic phase phenomenon in XG observed by performing ramp-down and ramp-up flow curves.

# 4.2.1 Base fluid and influence of nanofluid preparation method

The steady-state and dynamic measurements for the suspensions of 1 mg/ml and 5 mg/ml of GO in XG dispersion obtained for the two preparation methods described in the methodology are presented in Fig. 4.7, 4.8 and

4.9. These concentrations were considered a reasonable range for observing the influence of graphene oxide on rheology, since the ideal when using nanomaterials is to use the smallest amount possible in order to reduce costs. The outcomes of the rheological response of the dispersions as the concentration of GO increases will be described in the next section. In this section, pure XG in water and nanofluid preparation method rheological response will be discussed.

Fig. 4.7 shows the flow curve (orange) of XG aqueous dispersion at room temperature. The concentration of XG used in this study is in the semidilute regime [205]. It shows shear thinning behavior, which means that at lower shear rates, relatively high viscosity results from the difficulty of the macromolecules to slide past one another. While at higher shear rates, the polymer chains become more aligned, making it easier for the molecules to pass by their neighbors [206]. A comprehensive understanding of the rheological behavior of aqueous polymer dispersions can be achieved by examining the energy dissipation processes that arise from molecular interactions within the system [207]. In the case of XG, due to its high molecular weight and double-stranded helix configuration in the semidilute regime [208, 209], the rheology is governed by polymer-solvent and polymer-polymer interactions [196, 210]. That is, the formation of hydrogen bonds between its hydroxyl groups and water molecules, as well as glycosidic oxygen atoms; and the electrostatic repulsion among charges on the side chains, which causes chain extension and subsequently increases viscosity [211]. Although the chains are quite rigid in this stage, they still have some flexibility [196, 212].



Figure 4.7: Steady-state shear stress as a function of shear rate. Preparation method 1 (a) and 2 (b) for dispersion of GO at 0, 1 and 5 mg/ml concentration in XG at  $T = 23^{\circ}C$ .

In addition to pseudoplastic behavior, XG dispersions also have a viscoelastic behavior that is commonly represented through strain sweep curves. For aqueous polymers, these curves are divided into three regions: a linear viscoelastic region (LVR), a transitional region, and a non-linear region [213]. In Fig. 4.8, the strain sweep curves are shown through the storage (G') and loss (G") moduli as the strain amplitude increases. The storage modulus represents the elastic or energy storage component of the response, while the loss modulus represents the conformational, loss, or entropic component [206].



Figure 4.8: Storage and Loss moduli as a function of shear strain obtained from strain sweep tests at a fixed frequency of 1 Hz. Preparation method 1 (a) and 2 (b) for dispersion of GO at 0,1 and 5 mg/ml concentration in XG at T =  $23^{\circ}$ C.

The rheological behavior in the LVR is described at small strains, allowing the molecules to remain in their equilibrium condition and maintaining a constant microstructural level of material. This region is characterized by having constant modules, that is, G' and G" are independent of the strain amplitude [213]. It can be observed that XG dispersion has a higher G' than G" in LVR, which may indicate the behavior as a weak gel since it flows at sufficiently larger deformations [214]. This behavior is explained by the fact that this predominantly elastic behavior is maintained in the linear viscoelastic region. Furthermore, as seen below, there is a variation in both viscoelastic moduli with changing frequency without any crossover. Likewise, we did not observe yield stress in the steady-state results. However, additional tests can be performed to better evaluate the structure. So, at ambient temperature, it seems that the conformation of XG dispersion studied behaves as a solid-like viscoelastic material with a helical ordered structure reported in the literature [215, 116]. The increase in the strain drives to the transition region, where the strain amplitude is high enough to disrupt the interactions of the dispersion at its quiescent state and a greater relative movement occurs. The value of G' remains larger than G" within this strain amplitude, indicating that the level of structuring is still sufficiently high to maintain a percolated microstructure and a significant elastic response [197]. An increase in the strain amplitude after the crossover between G' and G" forces the molecules to depart from their equilibrium condition, where the viscoelastic properties depend on the kinematics of the deformation and the shear rate, as well as the structural level changing as the fluid deforms [206].

Frequency sweep curves also display the viscoelastic mechanical response of the material microstructure in its quiescent state. In order to guarantee that the experiment is carried out in this state over the frequency range, a strain amplitude is kept constant and low enough during the test. A strain amplitude of 10.0% corresponding to the LVR, as seen in Fig. 4.8 was chosen to perform the dynamic measurement. In polymeric dispersions, these curves are commonly divided into four regions: terminal, rubbery, transition, and glassy [216, 217]. The studied dispersions seem to lay in the rubbery region, as reported by other studies with XG [205, 218]. On these timescales, the polymer chains do not have sufficient time to disentangle, causing a stress raise in the chain segments between the coupling points and resulting in an elastic-dominant behavior. The extent of this region can be related to polymer molecular weight and concentration, which impart to the number of entanglements and hence relaxation time [219]. It can be seen from Fig. 4.9 that for the XG dispersion, as the frequency is lower, both moduli decrease. It is also observed that for the range of frequencies studied no crossover  $(\tan \delta = 1)$ was observed, the material response below this crossover behaves as liquidlike material. The reciprocal of this crossover frequency of the two moduli is interpreted as the characteristic relaxation time of the material. The higher the G' relative to the G" as well as the longer rubbery region could indicate a good stability as a weak gel that promotes its resistance to flow, this indeed depends on the concentration and structure of the polymer, temperature, and other physicochemical variables.

From these results, it is observed that the rheological response is highly influenced by the preparation method of the dispersion. The results show that the dispersion prepared by method 2, with greater emphasis on the more concentrated dispersion, has lower rheological properties: viscosity and viscoelastic moduli across all parameters used as input. Since in method 2, XG was hydrated in a more concentrated dispersion, it is possible that the polymer chains did not open in the same way as for the preparation method 1 leading to weaker viscosity and viscoelasticity [220]. Also, because more concentrated dispersions of graphene oxide were prepared in method 2, the exfoliation of graphite oxide may not have been as good compared to method 1. Therefore, method 1, which is also the simpler preparation method, was chosen to be used



Figure 4.9: Storage and loss moduli as a function of frequency obtained from frequency sweep tests at a fixed strain of 10%. Preparation method 1 (a) and 2 (b) for dispersion of GO at 0,1 and 5 mg/ml concentration in XG at  $T = 23^{\circ}C$ .

in all the following dispersions presented in this work.

### 4.2.2 Influence of GO concentration and NaCl

Fig. 4.10(a) illustrates the results from adding and increasing the GO concentration in the base XG dispersion. It is observed a notable increase in shear stress response, especially at 5 mg/ml, it may be explained by the numerous oxygen-containing functional groups of GO, which actively interact with the polymer chains [186, 45]. A stronger microstructure and thus higher shear stress are the results of increased chemical and physical interactions within the system, such as hydrogen bonding, ionic repulsion, and van der Waals forces [221].



Figure 4.10: Steady-state shear stress as a function of shear rate. Influence of GO concentration (a) and NaCl (b) in XG at  $T = 23^{\circ}C$ .

Furthermore, it is noteworthy that at shear rates above  $10 \text{ s}^{-1}$ , the 5

mg/ml suspension showed a similar rheological profile (with shifted values) to the other dispersions. However, at shear rates below this threshold, a characteristic stress decay was observed. The dissipation through plastic rearrangements, which explains concentrated colloidal systems, may be connected to this phenomenon [222]. Therefore, when GO concentration increases, there is a propensity for a transition from merely shear-thinning behavior to the appearance of an apparent yield stress, suggesting that the GO strengthens the space-spanning network [223]. Moreover, the consistency in shear stress profiles at shear rates above 10 s<sup>-1</sup> shows that nanosheet orientation, generally observed in aqueous GO suspensions [35, 224], does not significantly affect the response of the system at higher shear rates. However, a discernible shift in the shear stress curve profile is seen, especially in the system with a higher GO content at lower shear rates. This suggests that GO has a greater impact on rheological behavior in these conditions.

On the other hand, as Fig. 4.10(b) illustrates, the shear stress response was somewhat reduced when salt was added to the XG dispersion, the shearthinning behavior is preserved, though. The NaCl ions, which buffer the charges on the XG chains [212, 118], are probably the reason for this decline. As a result, the negatively charged pyruvate groups in xanthan gum wrap around the main chain [225]. Accordingly, it is thought that the folding of the polymer chains causes molecular curling, chain shrinkage, and a subsequent reduction in the hydrodynamic radius [226, 227, 114]. A stress response that is very similar to that of pure XG is observed when exposed to greater shear rates (>  $500 \text{ s}^{-1}$ ); this could be due to the breakup of polymer clumps [228, 229]. A critical salinity threshold (CST), over which salinity has little to no influence on viscosity, is also believed to have been reached by XG with this very high salt concentration [184]. To visualize this, a flow curve with an intermediate salt concentration (10 wt%) in XG was tested and is shown in Fig. 4.11.



Figure 4.11: Flow curve comparison pure XG, and dispersions with 10% and 20% sodium chloride

When GO was added to this near-saturated dispersion, the flow curve resembled the profile of the NaCl-XG dispersion but had slightly higher stress levels. This behavior makes sense because the CST most likely sets a limit on the amount of molecules that the salt cations could protect. The addition of GO increases the amount of interactions in the system, as was previously mentioned. Additionally, some of the ions produced when NaCl dissolves stop interacting with XG macromolecules and start to protect the charges on the suspended nanosheets. The observed increase in shear stress is probably caused by these combined factors.

The GO suspended in the XG-NaCl dispersion counteracts the effect of NaCl at lower shear rates when compared to the pure XG dispersion, producing comparable shear stress levels in both flow curves. But at greater shear rates, the interactions between GO and XG likely make it harder for polymer aggregates to rupture and for chains to align, which increases the shear stress. Therefore, GO continues to interact well with the solvent and polymer even in this highly ionic environment.

It can be seen in Fig. 4.12(a) that both moduli increase with increasing GO concentration, with the 5 mg/ml GO suspension showing noticeably increment in both moduli. Additionally, the crossover point, and the start of the transition phase occur with a little smaller strain amplitude as the concentration of nanosheets increases; this behavior is more noticeable for the suspension with the highest concentration of GO. Under higher strains, these more structured materials tend to break non-covalent bonds and interactions, which induce a higher stress dissipation [214]. The dispersion flows at a higher stress but a lower deformation amplitude because of the shape of GO, which does not allow for entanglements, and the greater number of interactions within the system. Stated differently, suspensions with higher GO concentrations tend to behave like brittle materials. The G<sup>"</sup> curve profiles also show a different behavior; pure XG dispersion appears to exhibit strain overshoottype behavior, with G<sup>"</sup> slightly increasing before decreasing; however, strain thinning behavior becomes more noticeable as GO concentration increases, as both moduli simply decrease as strain increases [230]. Due to side electrostatic repulsion, the stretched xanthan structure in the case of pure XG aqueous dispersion creates a weakly structured material that at first resists deformation, increasing G<sup>"</sup>, but is ultimately destroyed by high strains, aligning polymer chains and lowering G<sup>"</sup> [230]. Given the 5 mg/ml GO suspension, it might be argued that the morphology of GO makes it easier to align the chain with the direction of deformation [231].

According to the examination of the moduli values at the LVR region, the



Figure 4.12: Storage and Loss moduli as a function of shear strain obtained from strain sweep tests at a fixed frequency of 1 Hz. Influence of GO concentration (a) and NaCl (b) in XG at  $T = 23^{\circ}C$ .

loss factors (tan  $\delta = G''/G'$ ) for the pure XG dispersion, 1 mg/ml, 2 mg/ml, and 5 mg/ml GO suspensions are, respectively, 0.302, 0.299, 0.301, and 0.264. The first three dispersions that are quoted have nearly identical loss factor values. According to these observations, as shown in Fig. 4.13, the complex modulus increases linearly at decreased GO concentrations. This indicates a linear increase in the stiffness of these dispersions. On the other hand, the loss factor for the 5 mg/ml suspension drops by about 12% in comparison to the other samples, suggesting that the material's elastic component has increased more. Because of this behavior, the complex modulus increases nonlinearly for suspensions with larger concentrations, resulting in an exponential shape for the G<sup>\*</sup> against the GO concentration.



Figure 4.13: (a) Complex modulus at 10% strain, (b) Viscosity at  $\dot{\gamma}=0.01 \text{ s}^{-1}$  and (c) Viscosity at  $\dot{\gamma}=1000 \text{ s}^{-1}$ , as a function of GO concentration at room temperature

Some underlying mechanisms may account for the observed increment in shear stress as well as in elastic and viscous moduli with increased GO concentrations. First, as previously mentioned, adding GO nanosheets to the suspension increases the quantity of interactions in the system. A more percolated network is created as a result, and this raises the solid-like behavior. Furthermore, the nanosheets start interacting more widely with the xanthan gum and water as well as with one another as the GO concentration increases. The electrostatic repulsions at the margins of the nanosheets, which arise from the deprotonation of carboxylic acid groups, require a certain degree of structural organization [232]. A greater shear stress is needed to shatter such extra nanosheet configurations. The system is therefore affected by these two processes after a specific GO concentration, which explains the trend of yield stress emergence as the GO content increases as well as the exponential growth in complex modulus and viscosity at low shear rates.

It is clear from comparing Figures 4.13(b) and 4.13(c) that the behavior of the dispersion is greatly affected by an increase in GO content at low shear rates, while this influence lessens at higher shear rates. The suspension with 5 mg/ml of GO shows a significant increase in viscosity at a shear rate of 0.01 s<sup>-1</sup>. Its viscosity values are 80% greater than those of the xanthan gum dispersion, hence increasing by an order of magnitude. At this low shear rate, the viscosity curve exhibits an exponential growth pattern as the GO concentration increases, mirroring the G<sup>\*</sup> curve. On the other hand, the viscous behavior seems to be primarily impacted by the elongation and alignment of polymer chains at a shear rate of 1000  $s^{-1}$ . The viscosity values stay low, within the same order of magnitude, even though the apparent viscosity of the suspension with the maximum concentration of nanosheets is 33% higher than that of the XG base dispersion. The viscosity increases linearly with increasing GO concentration in this high shear rate condition. These results imply that the rheological response of suspensions under low to intermediate shear rates is more significantly influenced by the orientation and arrangement of the GO nanosheets.

As shown in Figure 4.12(b), adding salt to the basic XG dispersion causes a minor decrease in the elastic and viscous moduli, which is consistent with the steady-state test results. The dispersion with higher ionic strength shows a more pronounced drop in elastic modulus under oscillatory strain amplitude. The interactions between XG and water may be affected by the ions in the system partially neutralizing the anions on the polymer chain, which could lower the macromolecule's hydrodynamic radius. Nonetheless, it is likely that xanthan gum preserved its weak gel behavior by maintaining an entangled, partially ordered conformation even at high salinity [122]. Both the storage and loss moduli increased with the addition of GO. The GO nanosheets promoted the creation of hydrogen bonds in the system, which ultimately resulted in an increase in viscoelastic moduli, even if the higher salt concentration would have encouraged partial neutralization of the anions on the GO nanosheets and the polymer chains.

From Fig. 4.14(a), higher GO concentrations were associated with improved suspension rigidity, as evidenced by the increased viscoelastic moduli observed across all timescales examined when GO was added to XG dispersions. Furthermore, the results indicate that because of the stronger macromolecular interactions and more robust network structure, these dispersions show an extended rubbery area at higher time scales when compared to pure XG [184].



Figure 4.14: Storage and loss moduli as a function of frequency obtained from frequency sweep tests at a fixed strain of 10%. Influence of GO concentration (a) and NaCl (b) in XG at  $T = 23^{\circ}C$ .

The addition of salt to the XG base dispersion caused a minor drop in both viscoelastic moduli during frequency sweep, as seen in Fig. 4.14(b), similar to the outcomes of strain sweep results. It is evident, therefore, that the moduli of the base and brine XG dispersions tend to be closer at higher frequencies, with the loss moduli equalizing at 10 Hz. Conversely, the inclusion of GO in the brine dispersion increased both moduli maintaining a rheological response very similar to the base fluid in the frequency range studied.

### 4.2.3 Influence of temperature

The rheological behavior of the dispersions at different temperatures (4°C, 23°C, 50°C, and 80°C) is thoroughly examined in this section. Aqueous polymeric dispersions may undergo physical or chemical changes as a result of rising temperatures, which may decrease viscosity or result in irreversible molecular degradation like chain scission [184, 233].

The steady-state measurements of XG dispersions at 4, 23, 50, and 80°C with the addition of GO and NaCl are shown in Fig. 4.15. The polymeric chains in XG aqueous dispersions may experience an order-disorder transition as the

temperature increases, changing from a double helix shape at lower temperatures to a disordered coil structure at higher temperatures [120]. Because of the increased kinetic energy and thermal mobility of the dispersion molecules, the shear stress response for pure XG dispersion significantly reduces with increasing temperature, as shown in Figure 4.15(a). Furthermore, since bond strength may decrease with heat, this behavior is probably caused by the weakening of bonds and interactions in the dispersion at high temperatures [184, 234]. The shear stress profile is relatively stable at higher shear rates (> 100 s<sup>-1</sup>), and it decreases with increasing temperature. There is a noticeable temperature impact at lower shear rates, however, since a more substantial decrease in shear stress is shown as temperatures increase. This implies that the stress response has a steeper slope at higher temperature of XG contributes more to the viscosity of the system. As the temperature increases, this structure destabilizes, reducing the viscosity more significantly.



Figure 4.15: Steady-state shear stress as a function of shear rate at four temperatures: 4, 23, 50 and 80 °C. Pure XG dispersion (a), and influence of GO concentration (b-d) in XG.

Fig. 4.15(b-d) illustrates the impact of GO concentration at various temperatures. The shear stress response gradually increases as the concentration of nanosheets increases. At lower shear rates, with GO concentration increasing, the shear stress shows a different decay pattern as the temperature increases, with the most pronounced effect observed in the 5 mg/ml dispersion. The stress curve tends to flatten gradually with increasing GO concentration, especially in the 5 mg/ml GO dispersion, and the decrease in shear stress becomes smaller with rising temperature. This implies that the nanosheets aid in stabilizing the XG dispersion, leading to a nearly flat rheological behavior where the shear response is less susceptible to temperature variations, signifying enhanced suspension thermal resistance. This behavior is explained by the physicochemical interactions between GO and XG, which limit the thermal mobility of the polymer chains and stabilize the system. Compared to XG, the sheet-like shape of GO seems less susceptible to temperature fluctuations in the temperature range under study, which probably makes conformational adjustments in the polymeric chains more challenging. It's important to notice that, despite a distinct trend, a dynamic yield stress had not yet appeared in the most concentrated dispersion (5 mg/ml) at 4°C.

Fig. 4.16(b) illustrates how the addition of NaCl affects the rheological response of XG dispersion at various temperatures. In comparison to the pure XG dispersion, a minor reduction in shear stress is noted for the NaCl-containing dispersion, primarily for lower shear rates. At 80°C, there is no discernible change in shear stress, but as the temperature increases, the difference becomes even less noticeable. Two phenomena that overlap may be the cause of this behavior. First, the hydration of xanthan may be affected by the presence of salt in the dispersion; any interference with this process may lead to a viscosity that is lower than expected [211, 111]. Second, an ordered polymer shape gradually changes to a disordered one as the temperature increases [116]. This disordered conformation becomes the primary factor affecting the rheological behavior of the dispersion as the temperature increases. This explains why, as temperature increases, the shear stress curves of the saline and pure xanthan aqueous dispersions become closer.

The impact of adding GO to the salt-containing XG dispersion is seen in Fig. 4.16(c). The outcomes once more demonstrate how well GO nanosheets and XG work together, even in a salty environment. Across all assessed temperatures, the flow curves of the GO-salt-XG dispersion show greater shear stress values than the XG-salt dispersion. Furthermore, the shear stress values of the GO-salt-XG dispersion start to converge with those of the 2 mg/ml GO-XG sample, as shown in Figure 4.15(c), as the temperature increases. This implies that, similar to the XG-salt system, the polymer chain conformational change is mostly responsible for the decrease in shear stress and thus viscosity at higher temperatures. GO, on the other hand, improves hydrogen bonding



Figure 4.16: Steady-state shear stress as a function of shear rate at four temperatures: 4, 23, 50 and 80 °C. Pure XG dispersion (a), XG with NaCl (b), and XG with GO and NaCl (c).

in the system, which lessens the magnitude of the stress drop and partially offsets these conformational alterations.

Fig. 4.17(a) displays the strain sweep results of pure XG dispersion at various temperatures at 1 Hz. As the temperature increased, it was found that both moduli decreased. The dispersion retains its solid-like viscoelastic behavior in this quiescent condition, despite being very temperature dependent.

Both viscoelastic moduli in the LVR increase when GO is added to the XG dispersion, as shown in Fig. 4.17(b-d). Indicating a greater oscillatory shear stress response in contrast to the base dispersion. G' and G" declines with increasing temperature become less noticeable as GO concentration increases, particularly for the loss modulus. Between 4°C and 80°C, the G' reduction in the sample containing 5 mg/ml of GO is roughly 33.3%, while the pure XG dispersion shows a reduction of 61.8% across the same temperature range. This result demonstrates once more how suspensions with larger concentrations of GO tend to show a more stable rheological response to changes in temperature.

The impact of adding salt on the rheological behavior of the base dispersion at different temperatures is seen in Figure 4.18(b). G' and G" moduli often decrease when the hydrodynamic radius of xanthan chains decreases [116]. For the saline XG dispersion, the moduli also exhibit a discernible temperaturedependent trend in the linear viscoelastic region (LVR). In comparison to the pure XG suspension, the decreases in G' and G" are marginally more noticeable at 4, 23, and 50°C. Both moduli, however, are greater than the base dispersion at 80°C, suggesting a change in the reaction of the dispersion to the increased temperature. Because of the greater concentration of Na+ counterions in the dispersion, the addition of salt has a shielding effect on the XG chains, which is associated with the drop in moduli values at lower temperatures [212, 118]. Conversely, other writers have noted that in situations with intermediate salinity, the decrease in XG viscosity with temperature is less noticeable [122]. The



Figure 4.17: Storage and Loss moduli as a function of shear strain obtained from strain sweep tests at a fixed frequency of 1 Hz and four temperatures: 4, 23, 50 and 80 °C. Pure XG dispersion (a), and influence of GO concentration (b-d) in XG.

precise processes causing this unusual behavior are still unknown, though. It is important to note that a similar effect was seen for G' within the LVR in the current investigation; in other words, this uncommon phenomena happens under dynamic conditions without shear.

The effect of adding GO on the dispersion of XG and NaCl at different temperatures is shown in Figure 4.18(c). Strong interactions between the nanosheets and the system are further depicted in the LVR, where the moduli of the GO suspended in the saline XG dispersion are larger than those of the pure XG and XG with salt. Salt has an impact on the system because, at lower temperatures, the moduli of the GO solution with salt are lower than those of the suspension with the same GO concentration (2 mg/ml) but without salt. Nevertheless, the difference in moduli between the two samples decreases with increasing temperature. The moduli of the dispersion containing GO with and without salt converge at 80°C, indicating that xanthan is the primary target of the impact of GO at high temperatures. This pattern is consistent with the flow curve findings and lends credence to the idea that, even in the presence of salt or when temperatures fluctuate, the GO nanosheets and the xanthan



Figure 4.18: Storage and Loss moduli as a function of shear strain obtained from strain sweep tests at a fixed frequency of 1 Hz and four temperatures: 4, 23, 50 and 80 °C. Pure XG dispersion (a), XG with NaCl (b), and XG with GO and NaCl (c).

gum system interact effectively.

The relationship between the G' and G" moduli of the XG dispersion and frequency at various temperatures is displayed in Figure 4.19(a). All samples generally showed G' values bigger than G", with both moduli rising with frequency. This suggests that all systems behave more elastically when deformations are applied more quickly. At lower frequencies, a discernible drop in moduli is seen as temperature increases. In particular, a value around the crossover point can be found at 80 °C and 0.1 Hz, the lowest frequency. This implies that the terminal zone may become noticeable at lower frequencies, or below 80 °C and within a low-frequency range. Polymer chains in this situation can detangle and pass through one another through a process called reptation, because they have enough time to do so [219].

The crossover point at 80 °C tends to occur at lower frequencies than those examined as the GO content increases, as seen in Fig. 4.19(b-d). It is also observed that because of its thermal stability in the moduli, the dispersion with a concentration of 5 mg/ml was less temperature-sensitive than other dispersions. GO and XG interaction, then, causes polymer relaxation to slow down and shows more elastic behavior in low-frequency regions [235, 236].

Both moduli at 4, 23, and 50°C decrease when salt is added to the base dispersion, preserving the base dispersions' rheological profile as seen in Fig. 4.20(b). In comparison to the base fluid, a small increase in the oscillatory shear stress response was seen at 80 °C previously discussed for the strain sweep results. Figure 4.20(c) illustrates how the addition of GO preserved the rheological profile with greater moduli in comparison to brine dispersion.



Figure 4.19: Storage and Loss moduli as a function of frequency obtained from frequency sweep tests at a fixed strain of 10% and four temperatures: 4, 23, 50 and 80 °C. Pure XG dispersion (a), and influence of GO concentration (b-d) in XG.



Figure 4.20: Storage and Loss moduli as a function of frequency obtained from frequency sweep tests at a fixed strain of 10% and four temperatures: 4, 23, 50 and 80 °C. Pure XG dispersion (a), XG with NaCl (b), and XG with GO and NaCl (c).

## 4.2.4 Influence of pressure

The impact of pressure on the shear stress measurements of pure XG and XG with GO (5 mg/ml) dispersions at 4, 23, and 80  $^{\circ}$ C and at three pressures (1, 100, and 400 bar) is depicted in Fig. 4.21. The rheological response of the pure XG dispersion is not substantially affected by increasing pressure at the tested temperatures. Hydrogen bonding and Van der Waals forces between the polymer and solvent, which have been shown to be influenced by pressure, can be influenced by the high incompressibility of water in aqueous polymer dispersions [237, 238]. Furthermore, a weak gel is probably formed by the semidilute concentration used, in which the polymer chains take up a large portion of the free volume of water while just slightly increasing the excluded volume. As a result, even at higher pressures, the rheological response remained constant because intermolecular interactions diminished in importance. Under high pressures below 33 °C, water viscosity can show anomalies, but overall, the variance is less than 5% when compared to the viscosity at atmospheric pressure [239, 240]. Thus, the rheological behavior of XG dispersion is hence mostly insensitive to variations in pressure in comparison to the contribution of the polymer interactions.



Figure 4.21: Shear stress as a function of shear rate of pure XG dispersion and XG dispersion with GO with concentration of 5 mg/ml, at three pressures: 1, 100 and 400 bar. At 4  $^{\circ}$ C (a), 23  $^{\circ}$ C (b) and 80  $^{\circ}$ C (c).

As seen in Figures 4.21(a) and 4.21(b), the dispersion containing GO shows a different rheological tendency in comparison to pure XG, especially at low temperatures and high shear rates. When exposed to higher shear rates under rising pressures, the GO-containing sample shows a decrease in shear stress and, as a result, in viscosity at these lower temperatures. However, as the observed variances are within the error range of the equipment, it should be highlighted that they represent a trend rather than absolute differences.

It is interesting to note that these results deviate from the typical pressure effects for complex fluids that have been documented in the literature.

According to earlier studies [241, 242], higher pressures usually leads to greater intermolecular contacts by reducing free volume and mobility at the microscopic molecular level, in contrast to temperature effects. These circumstances typically encourage higher intermolecular friction, which raises viscosity. The observed behavior in our GO-containing systems, however, points to a different mechanism.

This phenomenon of reduced viscosity can be explained by the sliding between GO nanosheets that retained some residual layers after being partially exfoliated during ultrasonic treatment. Also, turbulence could become significant, but more detailed velocity profile studies should be performed at high pressure. Low temperatures provide increased shear stresses in the dispersion, which are inherently linked to the onset of sliding between nanosheets in the system. Thus, these nanosheets might work as solid lubricants as pressure and shear rate increases.

The rheological response at higher temperature, as shown in Fig. 4.21(c), has no appreciable changes in the stress curve slope throughout the three pressures under investigation. This finding suggests that, within the investigated shear rate range, the GO dispersion does not experience significant rheological changes as a result of pressure at high temperatures. The polymeric chains undergo conformational changes as a result of the temperature increment, which weakens intermolecular connections and increases mobility. Sliding between the potential stacked GO layers is not favored by this reduction in contacts, which results in a lower viscosity.

Importantly, shear stress measurements at lower rates could not be carried out due to technical limitations in the experiment. The intricate relationship between temperature, pressure, and nanosheet behavior is demonstrated by this thorough grasp of the interaction dynamics, which also offers important new information about the rheological characteristics of these dispersions. It is necessary to look into the underlying mechanisms further because the apparent departure from conventional pressure-viscosity correlations emphasizes the special characteristics of GO-containing dispersions.

### 4.2.5 Phenomenological fitting

According to Figure 4.15, neither temperature nor GO concentration induced the formation of a dynamic yield stress in the material. Also, viscosity functions such as the Cross or Carreau-Yasuda models are frequently used to empirically fit flow curves for shear-thinning fluids. Nonetheless, two observations from the experimental results should be made. First, it is observed that Newtonian plateaus at both high and low shear rates were not experimentally obtained by measuring the steady-state shear viscosity (shown in Fig. 4.22). Second, distinct rheological behavior was observed. For instance, pure XG at 80°C tends to approach a zero-shear rate viscosity at low shear rates, as defined by the empirical models, while at 4°C, the viscosity keeps increasing as the shear rate decreases.

Some factors can be taken into account in order to utilize a model that enables comparison of the behavior of the dispersion at different temperatures. The difficulty of achieving zero-shear rate viscosity in some fluids with large relaxation times is being discussed [243], as controlling very low shear stress or strain rates requires highly precise equipment, or very long extensions of time should be required. Therefore, estimating the order of magnitude of the zero-shear rate viscosity appears to be challenging. However, as water is the continuous medium in the dispersions under study, it makes sense to assume that the order of magnitude of the infinity shear rate viscosity might be closer to the order of magnitude of viscosity of water at the specified temperature. However, even at high shear rates, polymer interactions can be important and influence this value. Additionally, a time coefficient and a powerlaw index should appear when this regime begins and how prominent it is because of shear thinning behavior. These factors allow us to capture the rheological response of the experimental data, which is why we are using a viscosity function with two power-law regimes and the infinity shear-rate viscosity in our work. An additional relaxation is provided by conventional diffusion due to thermal motion [244], this may be connected to the addition of a second power-law regime. As a result, an intermediate relaxation area is not entirely insignificant, and the Newtonian plateau at zero shear rate is most likely delayed to longer time scales.

$$\eta(\dot{\gamma}) = \eta_{\infty} [1 + \lambda_1 \dot{\gamma}^{(n_1 - 1)}] [1 + \frac{1}{\lambda_2 \dot{\gamma}}]^{(n_2 - 1)}$$
(4-1)

The five-parameter model suggested in Eq. (4-1) is a reorganization of previously proposed viscosity functions [245, 246, 247]. The primary distinction with the models found in the literature is that the viscosity at zero shear rate was used to be the beginning point for describing the rheological behavior of the material. The infinity shear rate viscosity, denoted by  $\eta_{\infty}$ , serves as the initial value in this case. Two shear thinning regimes are then governed by their power law coefficients, denoted by n, and time coefficients, denoted by  $\lambda$ . The first and second regimes, which follow the infinity shear rate Newtonian region, are denoted by the subscripts 1 and 2, respectively.

It should be noted from this model that if  $n_2=1$ , the suggested model

reduces to the Sisko model. Additionally, it can forecast the behavior of a yield stress material if  $n_2=1+n_1$  and a comparable behavior of the Carreau model if  $n_2=n_1$ . To get a better fit, transition indexes could be added and changed, however this might not present a clear physical behavior. Lastly, as previously stated, the derivative of the logarithmic part of the viscosity with respect to the logarithmic part of the shear rate could be calculated because our experimental data does not provide the infinite shear rate viscosity. Thus, this parameter can be estimated and extrapolated using the four-parameter formula that is obtained through that derivation [246].

The flow curves with the phenomenological fit of the suggested model of XG dispersions with varying GO concentrations at the four temperatures under investigation are shown in Figure 4.22(a-d).



Figure 4.22: Steady-state shear viscosity as a function of shear rate. Sold lines are the fits with the model proposed in Eq (4-1). Influence of GO concentration at (a) 4°C, (b) 23°C, (c) 50 °C and (d) 80 °C.

Due to the complex nature of a five-parameter model, and in order to better compare the fitting parameters, an additional condition was considered which is to keep the time coefficients fixed for each temperature and impose that they follow an Arrhenius-like equation shown in Eq. (4-2)

$$\lambda = A e^{\frac{B}{T_a}} \tag{4-2}$$

Where A and B are constants and Ta is the absolute temperature in K. The time coefficients for the first and second regimes are plotted against the reciprocal of the absolute temperature in Fig. 4.23(a-b). The transition from infinite shear rate viscosity to the first power law regime is taken into account by the first-time coefficient. The first-time coefficient grows as the temperature increases, because the viscosity of the continuous phase decreases with increasing temperature, so it approaches the Newtonian plateau more quickly at lower temperatures where the viscosity of the continuous phase is larger. While, the change from the first to the second power law regime is indicated by the second time coefficient. This characteristic time can be linked to an intermediate quasi-terminal relaxation time where physicochemical interactions may still be important and the internal motions of the dispersions are most likely not entirely caused by the thermal motions of the macromolecules. This second time coefficient reduces with temperature considering that the theoretical reptation time decreases for higher temperatures [248].



Figure 4.23: First (a) and second (b) time coefficients as a function of the inverse of absolute temperature. Parameters A and B obtained through the Arrhenius equation in Eq. (4-2).

Fig. 4.24 displays the remaining parameters, power law coefficients, and infinity shear rate viscosity that were used for the fit. As previously stated, it is not possible to confirm that the values obtained for the infinite shear rate viscosity displayed in Fig. 4.24(a) represent the second Newtonian plateau of this material because they were extrapolated from the power law fitting and the time coefficients. These values, however, enable us to spot a pattern that varies with temperature and GO concentration.

Conversely, when the temperature increases, the power law coefficients are higher, but when the GO concentration increases, they fall. This is to be expected because in this instance, the shear thinning behavior of the dispersions increases with a smaller power law coefficient. Figure 4.24(b) shows that the first power law coefficient appears to have a linear dependence on



Figure 4.24: Infinite shear rate viscosity (a), first power law coefficient (b), and effective second power law coefficient (c) as a function GO concentration. The symbol shape (related to GO concentration) and color intensity (related to temperature) follow the described in Fig. 4.15.

GO concentration, but not on temperature. The effective second power law coefficient, a normalized second coefficient that preserves the first power law coefficient's axis reference, is shown in Fig. 4.24(c). When both the first and effective second coefficients are equal, the rheological behavior shifts from a shear thinning behavior to a model with a certain amount of viscoplasticity. This second coefficient does not clearly follow any trend with both temperature and GO concentration. It should be noted that a yield stress limit appears when this effective second power-law coefficient is zero.

### 4.2.6

#### Time temperature superposition

Thermorheologically simple materials, that is, those which are absent of temperature-dependent structural changes, phase transition, or side reactions, could be allowed for time-temperature shifting [249]. The TTS technique is helpful in real-world applications because it enables the exploration of various time scales without being constrained by large testing periods (very low frequencies) or equipment frequency restrictions. Thus, among other factors, the so-called master curves of complex viscosity, loss factor, and dynamic moduli can be obtained.

The TTS approach was used to establish the master curves of G' and G" for the GO dispersions at a reference temperature of 4°C, as shown in Fig. 4.25. As seen in Fig. 4.25(b), a master curve of the loss factor was first obtained in order to determine the horizontal shift factor, denoted by  $a_T$ . Since all of the dispersions have a very similar tendency at various temperatures, it can be seen that the master curve obtained is independent of the GO concentration. However, the curves are not superimposed since additional adjustment is required in relation to the resulting viscoelastic modules. This is explained by

the fact that the dispersions can also follow the concentration superposition [236], which exhibits a different stress response (different structural stiffness) but a very similar viscoelastic response for various time scales. Likewise, G' and G" were vertically displaced to get  $b_T$ , the vertical displacement factor, as shown in Fig. 4.25(a).



Figure 4.25: Master curves of G' (solid symbol) and G" (hollow symbol). Reference temperature is 4°C. The symbol shape (related to GO concentration) and color intensity (darker colors represent higher temperatures) follow the described in Fig. 4.15.

The current study employed the Williams-Landel-Ferry (WLF) equation, which is based on the free volume theory presented in Eq. (4-3) and has been applied in earlier studies involving XG dispersions [205, 218], to evaluate the temperature dependence of the horizontal shift factor. Since the WLF equation [250] is obtained by relating the first constant to an empirical constant and a dimensionless volume fraction at a reference temperature, the first constant in this formulation was left fixed. For low concentration suspensions, adding GO can make this dimensionless volume fairly equal; but, for high concentration suspensions, this strategy may result in shifting challenges because of varying viscoelastic responses (e.g. agglomeration). The second constant, on the other hand, was thought to vary for every GO dispersion since it is defined by the dimensionless volume and the thermal expansion coefficient, both of which are influenced by temperature in aqueous dispersions.

$$log_{10}a_T = \frac{C_1(T - T_r)}{C_2 + (T - T_r)}$$
(4-3)

The vertical displacement factor may occasionally be disregarded and taken to be one [251]. This value, however, cannot be neglected in more intricate thermorheological materials. A vertical shift factor that is influenced by temperature and GO concentration must be added because a master curve could not be obtained by merely applying the horizontal shift factor. By
using an empirical model and taking into account the thermal density ratio, a vertical shift may be estimated [250, 252]. This model can be rearranged to get a quadratic polynomial expression if the mass of the specimens is assumed to remain constant [253]. A third-order polynomial equation was taken into consideration as an approximation in other research [254, 255]. A second-order polynomial expression shown in Eq. (4-4) in a manner akin to that of earlier publications used in this work.

$$b_T = 1 + x_1(T - T_r) + x_2(T - T_r)^2$$
(4-4)

The horizontal shift factors derived using the TTS method are displayed in Fig. 4.26(a). Because the frequency sweeps were logarithmic, this shift factor is increasing logarithmically when the temperature is lowered and the GO content is raised, approaching unity. As previously said, polymer relaxation is slowed down by a higher solid-like viscoelastic behavior. Additionally, as can be shown from the steady state data, a dynamic yield stress may be reached by increasing the GO concentration to 5 mg/ml; in this case, the horizontal shift factor will be extremely low or insensitive to temperature changes. Also, the concave down tendency of the horizontal shift was visualized [256].



Figure 4.26: (a) Horizontal and (b) vertical shift factors. The symbol shape (related to GO concentration) and color intensity (darker colors represent higher temperatures) follow the described in Fig. 4.15

Figure 4.26(b) displays the vertical shift factors as a function of GO concentration. As the GO concentration increases, this horizontal shift factor gets closer to the reference temperature values. Negative constants can be obtained in the usage of Eq.(4-4), since when obtaining the quadratic polynomial expression with the mass remaining constant, the coefficient arrangements have subtractions that contain the absolute temperature and an empirical thermal expansion coefficient. Given the low order of magnitude of the thermal expansion coefficient, these coefficients may be extremely sensitive to even little changes and provide negative values.

## 4.3 Microstructure of the dispersions

The examination of the fluid microstructure resulting from the addition of graphene oxide offers important new information on the processes that cause the dispersion to change rheologically. The pure xanthan gum dispersion and the GO-containing samples at concentrations of 2 and 5 mg/mL are shown in cryogenic scanning electron microscopy images in Fig. 4.27. These microstructures can be examined in greater depth thanks to the display of micrographs at two different scales: 200  $\mu$ m and 10  $\mu$ m. We were able to view the various microstructures of the dispersions under study thanks to the images that the cryo-SEM provides.



Figure 4.27: Cryo-SEM micrographs of xanthan gum (XG) dispersions with varying graphene oxide (GO) concentrations. (a,d) Pure XG dispersion; (b,e) XG dispersion with 2 mg/mL GO; (c,f) XG dispersion with 5 mg/mL GO. Top row (a-c): 200  $\mu$ m scale; bottom row (d-f): 10  $\mu$ m scale.

A honeycomb-like structure is revealed by the examination of the pure XG dispersion microstructure, which is shown in Fig. 4.27(a) and 4.27(d). This structural arrangement is suggestive of the creation of a network microstructure and has already been documented in the literature [257, 258]. The observed network structure supports the findings of the strain sweep experiments, which show that G' is greater than G" within the linear viscoelastic zone for the XG dispersion, because the cryo-SEM imaging was conducted on the dispersion at rest. The very high viscosity seen at lower shear rates may be related to the existence of this network microstructure even if XG dispersion does not show a yield stress. The interconnectedness of the honeycomb structure probably helps

the dispersion retain its integrity at rest while permitting flow when stress is applied, which is an essential characteristic in many xanthan gum industrial applications.

It is important to note that the use of cryo-microscopy for fluid microstructure study is still relatively new, and as such, there is still debate on how to interpret the results of this method. The hypothesis that the observed honeycomb structure could be an artifact of ice crystal development during sample freezing is one such argument. Nonetheless, a number of elements support the validity of the structures found in this investigation. In order to reduce the production of ice crystals, the samples were first frozen at a high rate of cooling while being vacuumed. The development of physical cross-linking points in aqueous xanthan dispersions has also been independently confirmed by complementary research employing different methodologies, such as atomic force microscopy [259]. The network structure seen by cryo-SEM is further supported by our results.

By comparing Fig. 4.27(a), (b), and (c), which show pictures of pure XG dispersions and those with 2 and 5 mg/mL of GO, respectively, it is possible to determine how the addition of GO affects the microstructure of XG dispersions. The number of physical crosslinking locations inside the network increases noticeably as the concentration of GO nanosheets increases, even though GO-containing dispersions retain a network structure just as well as pure XG. During this structural evolution, the average size of individual pores decreases while the overall number of interstices in the system increases, creating a more complex network structure. The enhanced capacity of GO to promote ionic interactions and hydrogen bond production is responsible for this reconfiguration. Furthermore, it is worth saying that this increase is possible due to the formation of aggregates or percolated networks. To put it another way, the GO nanosheets probably act as extra network formation nucleation points, resulting in a structure that is more complex and densely connected. Furthermore, a more effective space-filling configuration of the network is suggested by the increase in pore number, even though the overall volume has decreased. The rheological behavior of GO-XG dispersions, specifically with regard to their viscoelastic qualities and flow characteristics under various shear conditions, may be influenced by this structural adaptation as shown in Fig 4.13.

The adsorption of GO nanosheets to the "walls" of the microstructure is shown in Fig. 4.27(e) and 4.27(f), which also show that there are strong interfacial contacts between the nanosheets and the polymer chains. This fact, which is closely related to the increment of the rheological properties, indicates once more that the microstructure of the dispersion is reinforced as the concentration of GO increases.

A greater density of nanosheets is visible in the microstructure of the more concentrated sample, together with a discernible decrease in internanosheet distances. This closeness implies that GO nanosheets start to interact with the polymer matrix and with other nanosheets at greater concentrations. The exponential increment in viscous and elastic moduli with increasing GO content is probably caused by these inter-nanosheet interactions. The observed rheological behavior can be explained at the molecular level by the dual interaction mechanism, which consists of GO-polymer and GO-GO. Overall structural integrity is improved by adherence of nanosheets to the polymer network, and at larger concentrations, sheet-to-sheet contacts produce more resistance to deformation, which shows up as a non-linear increment in viscoelastic properties.

Fig. 4.28 shows the microstructural properties of XG dispersions with the addition of NaCl. The microstructures seen in three different samples are qualitatively compared in this figure: pure XG dispersion (Figs. 4.28(a), (d), and (g)), XG dispersion in 20 wt% NaCl brine (Figs. 4.28(b), (e) and (h)), and XG dispersion with 2 mg/ml of GO in 20 wt% NaCl brine (Figs. 4.28(c), (f), and (i)). The micrographs were taken at three distinct scales: 200  $\mu$ m (Figs. 4.28(a)-(c)), 20  $\mu$ m (Figs. 4.28(d)-(f)), and 10  $\mu$ m (Figs. 4.28(g)-(i)) to enable both general and in-depth structural analysis. The microstructure of the dispersions is significantly impacted by the addition of NaCl, as these high-resolution pictures demonstrate.

Upon examining the micrographs shown in Fig. 4.28(b-c), (e-f), and (h-i), significant microstructural changes in the samples are observed. The two most noticeable characteristics are the increased material density in the specimens and the structural change from a honeycomb-like configuration to a porous architecture. The walls of this new dispersion are noticeably thicker and have interior linear frames. It is important to identify that the concentration of NaCl added to the system significantly surpasses that of both GO and XG in the brine-prepared samples. The observed structural reconfiguration is probably mostly due to this concentration difference.

In a thorough cryo-SEM examination of NaCl solutions in water, Ivashchenko [260] identified microstructural characteristics that closely match the results of our investigation. That research clarifies a universal structural paradigm in which wall-like structures are formed by the interconnection of lamellar forms in NaCl solutions. Ionic content and structural resilience appear to be directly related, as seen by the positive correlation between the



Figure 4.28: High-resolution micrographs of xanthan gum dispersions in various environments: (a, d, g) pure XG dispersion; (b, e, h) XG dispersion in 20 wt% NaCl brine; (c, f, i) XG dispersion with 2 mg/mL of GO in 20 wt% NaCl solution. Images were captured at three scales: 200  $\mu$ m (a-c), 20  $\mu$ m (d-f), and 10  $\mu$ m (g-i). Arrows in (f) indicate a distinct network structure observed in the GO-containing sample's microstructure. Arrows in (h) and (i) highlight XG lines and surfaces covering the pores. Elongated structures formed by densely packed solvated Na+ and Cl- ions are visible in (h) and (i).

thickness of the wall and salt concentration. Densely packed solvated Na+ and Cl- ions are thought to make up these walls. The complicated interaction between solute and solvent at increasing ionic strengths is reflected in these ionic assemblies, which transform into elongated threads as the concentration of salt increases. These threads then arrange themselves into complex patterns, and the system forms holes or discrete domains made of free water molecules at high salt concentrations [260].

Both with and without GO, the microstructural pattern typical of aqueous NaCl solutions is clearly visible in our results of NaCl in XG dispersion. Nonetheless, these systems display an extra structural element inside the solvation walls, which might be attributed to the XG chains. A more robust material may be present if there are finer linear structures that occasionally pass through pores that were once occupied by free water. A smoother surface texture material covers some of the pores, resembling XG aqueous dispersion microstructures. This discovery reveals a change in the interactions of the XG chains, which now interact with the solvated ion walls instead of just each other. However, the three-dimensional arrangement of XG is still visible in the microstructure. The XG dispersion microstructure seems to be weakened by this new organizational paradigm, as seen by a decrease in rheological characteristics like storage modulus.

The microstructures of samples generated in brine with and without GO do not differ significantly, by visually comparing the micrographs shown in Figures 4.28 (b, e, and h) and (c, f, and i). Although XG is present in the microstructure of GO-containing materials, the GO nanosheets are not visible, most likely because they are encircled by solvated ions. However, a small but important detail in the top left corner of Fig. 4.28(f) shows a different network structure from the solvated ion walls. In contrast to salt-based structures, this structure seems to be made of XG and/or GO, indicating more durability. This special formation would suggest that XG dispersions in brine with GO have a stronger network, supporting the greater viscosity and storage modulus values in saline XG dispersions with GO than in those without nanosheets. These results point to a complicated interaction between XG, GO, and the saline environment that affects the final rheological response.

## 5 Conclusions

This study assessed how adding and increasing the concentration of graphene oxide affected the aqueous xanthan gum matrix under changes in pressure and temperature. The study provided chemical characterization of GO nanosheets, then a thorough analysis of the rheological response and analysis of the microstructures of the GO in XG dispersions.

Significant rheological improvements, including a propensity for yield stress development and notable increases in both storage and loss moduli, were obtained when GO was added to XG dispersions. Both brine-based and aqueous XG matrices showed these enhancements in their viscoelastic properties. The thermal stability is notable, which can be useful in hightemperature conditions. In turn, the rheological behavior of the dispersions was barely affected by pressure changes. A phenomenological model with two power law regimes was taken into consideration when fitting the flow curves in order to describe the rheological behavior of these dispersions. The suggested model makes it possible to depict the change from shear thinning material to one with yield stress. In addition, a time-temperature superposition analysis was performed, identifying the low temperature sensitivity of the GO-containing dispersions.

Cryogenic scattering electron microscopy microstructural research showed that the addition of GO results in a more complex network topology with more physical crosslinking locations. The microstructure significantly reorganizes in saline conditions, with GO and XG assimilating into the solvated ion walls while retaining some degree of structural independence. These observations offer a visual depiction of the structural alterations that underlie the improved characteristics and support the rheological findings.

The application of GO in non-Newtonian matrices is significantly impacted by the findings obtained through this study. The complicated rheological behavior and improved thermal stability of GO-XG dispersions present potential benefits for creating more robust and effective fluids for hightemperature and high-pressure settings. By achieving "flat rheology" with GO addition, fluids may function more consistently under a variety of harsh circumstances, potentially increasing stability and efficiency in a range of industrial applications.

Future studies on this subject might be related to rheological and chemical developments. On the one hand, it might be feasible to functionalize graphene oxide nanosheets to create nanomaterials for more specific applications and develop more complex fluids by adding components, for instance, those used in drilling fluid formulation. On the other hand, to gain a better understanding of the effects of graphene oxide under different conditions, rheological studies in extensional flows or experimental visualization tests via complex geometries might also be helpful.

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