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RHEOLOGICAL BEHAVIOR OF NANOPARTICLES IN NEWTONIAN FLUIDS

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Abstract. Nanofluids are colloidal suspensions comprising particles with nanometer-scale dimensions (less than 100 nm) dispersed within a base fluid. These nanofluids have demonstrated significant potential for a wide range of engineering applications, enhancing the thermomechanical properties of the base fluid. Naturally, the success of these applications hinges on a thorough understanding of their flow properties. Consequently, investigating the rheological behavior of nanofluids is of paramount importance, as it provides insights into the fluidic structure, which is crucial for engineering applications. In this particular study, we examined the influence of SiO$_2$ nanoparticles, present at various volumetric concentrations, in a Newtonian base fluid (mineral oil). The research explored the rheological characteristics of suspensions across three distinct regions: the liquid regime, solid regime, and the transition between solid and liquid behavior. Furthermore, the stability of these suspensions over a period of 60 days was assessed through sedimentation tests. This comprehensive investigation sheds light on the potential and behavior of SiO$_2$ nanofluids in a mineral oil base, offering valuable insights for practical applications in engineering.

Keywords: nanoparticles, nanofluids, rheological properties, colloidal suspensions

1. INTRODUCTION

The search for new technologies and the improvement of industrial processes, with the goal of aligning energy demands with environmental sustainability, has been humanity's primary challenge. It is not only a driving force behind research and the global economy but also a fundamental concern. Researchers contend that energy transport and conversion predominantly occur at atomic or molecular scales (Clyvedon, 2004).

In this context, nanoscience and nanotechnology play a pivotal role in rejuvenating traditional energy sectors and promoting emerging renewable energy industries. Over the last two decades, developments in nanoscale science and technology have provided efficient solutions to numerous industrial needs, particularly in the domain of heat transfer processes.

Recognizing that the size of a material profoundly influences its behavior has been a transformative breakthrough across various fields. When materials are scaled down to the nanometer level, their chemical and physical properties diverge significantly from those observed at micro and macro scales (Roduner, 2006; Tahir et al., 2020). Generally, nanomaterials are defined as those with at least one dimension ranging from 100 nm down to the atomic level (approximately 0.2 nm). It is within this range, especially at the lower end, that materials exhibit distinct or enhanced properties (Tahir et al., 2020). The principal drivers for this alteration in behavior are the increased relative surface area and the prevalence of quantum effects (Clyvedon, 2004).

Within the realm of nanotechnology, a novel category known as *"nanofluids"* has emerged. Nanofluids are innovative fluids created by dispersing nanometer-sized materials in conventional fluids (Li et al., 2009; Yu and Xie, 2012). In essence, nanofluids consist of colloidal suspensions at the nanoscale, incorporating concentrated nanomaterials. They are biphasic systems with one phase (solid) suspended in another (liquid). In recent years, nanofluids have gained increasing attention due to their diverse applications. Depending on the nanoparticle's characteristics, nanofluids offer tunable properties in terms of stability, thermal, optical, electrical, rheological, and magnetic attributes for various applications (Awais et al., 2021; Suleimanov et al., 2011). For example, in the petroleum industry, nanoparticles have been utilized in

drilling operations, wastewater treatment, corrosion prevention, production enhancement, heat transfer, and advanced oil recovery (Ali et al., 2020; Ali et al., 2020a; Abang et al., 2021; Mittal, 2022).

Although numerous papers have been published on the progress of nanofluid research in recent years, most of these studies have focused on experimental and theoretical aspects, particularly thermophysical properties or convection heat transfer. Consequently, the interaction mechanisms between nanoparticles and the base fluid matrices have not been extensively investigated. These interaction mechanisms have a strong connection to suspension rheology. Investigating the rheological behavior of nanofluids is crucial for comprehending fluidic structure and is of paramount significance for engineering applications. Understanding the properties of nanofluids presents a challenge, especially since suspended nanomaterials exhibit characteristics akin to liquid-solid mixtures.

The present work endeavors to address this gap in the research on the rheology of suspensions of SiO_2 nanoparticles in mineral oil. It aims to contribute to the fundamental knowledge related to the rheological behavior and microstructure of these materials. The research intends to develop a methodology for formulating colloidal suspensions of SiO_2 nanoparticles dispersed in mineral oil and to characterize the rheological properties of these suspensions in three distinct regions: the liquid regime, solid regime, and the solid-liquid transition.

Silica nanoparticles have garnered significant attention due to their physicochemical properties and diverse applications in industrial processes (Zulfiqar et al., 2016). They have found utility in applications such as process filtration, fluid rheology control, foam and emulsion stability for enhanced oil recovery, and drag reduction in porous media. Nanosilica suspensions have also been integrated into high-impact resistant structures within the aerospace, automotive, and energy sectors. In the past decade, SiO_2 nanoparticles have played a pivotal role in the development of new materials, leveraging specific properties like surface area, pore volume, and the potential for incorporating organic molecules into the silica network to form hybrid materials (Kochetov et al., 2011).

However, the rheological properties of suspensions of SiO_2 nanoparticles in non-polar fluids like mineral oil have received limited attention. Several factors influence the rheological behavior of these colloidal suspensions, including surface characteristics, nanoparticle concentration, temperature, interaction forces, and the suspension medium. While some studies have examined the rheological behavior of nanosilica suspensions, very few have delved into SiO_2 nanoparticles in non-polar fluids. To address this knowledge gap, the current work employs detailed rheological analysis, including steady-state and oscillatory techniques in linear viscoelastic regimes, to investigate the microstructural characteristics of suspensions formed at different volumetric nanoparticle concentrations. This research contributes to the understanding of the rheological behavior of SiO_2 nanoparticle suspensions in non-polar fluids and has potential applications in various technological and industrial processes.

2. EXPERIMENTAL METHODOLOGY

2.1 Materials

The experimental investigation was conducted using transparent paraffinic mineral oil (Sigma Aldrich-330779), with a specific mass of 0.838 g/mL and silica nanoparticles (Sigma Aldrich-381276). Silica nanoparticles are of the mesoporous type (pores between 2 and 50nm), have particle sizes smaller than 11nm and specific mass of 2.2 g/mL.

The concentrations of the suspensions were determined by means of the volumetric concentration (ϕv), which takes into account the specific mass of the nanoparticle, as well as the base fluid, for the calculation. Suspensions were formulated with five different concentrations, 0.25, 0.5, 1, 1.5 and 2.5% of SiO2.

For the rheometric tests, an Anton Paar MCR 702TD rotational rheometer was used, whose temperature at the base of the rheometer is controlled from a Peltier electronic system, with the aid of a thermostatic bath. To carry out the experiments, the geometries of parallel grooved plates with a diameter of 40 mm and a gap of 0.8 mm were used.

2.2 Experimental Procedure

The colloidal suspensions were prepared following these steps:
1. Measurement of base fluid volume;
2. Weighing of SiO_2 nanoparticles on an analytical scale, whose precision is 10^{-4} g;
3. Mix the nanoparticles in the fluid using a magnetic stirrer for 48 hours, at 150 rpm, forming a vortex in the center, taking special care not to introduce air bubbles into the suspension;
4. Defragmentation and dispersion of nanoparticles to attenuate agglomerations and improve stability in an ultrasonic bath, at a frequency of 35 kHz and 50 W for 30 minutes, at a constant temperature of 25 °C.

For the rheometric tests, the samples were pre-sheared for 1 min at -100 s^{-1} and for another 1 min at 100s^{-1}, and then left under a zero-shear stress condition for 10 min resting time. After the pre-test, the sample was submitted to different protocols: (i) measurement of the equilibrium viscosity curve in which plateaus of shear rate were applied until the steady-state shear stress determination; (ii) stress amplitude oscillatory sweep from 10^{-3} to 100 Pa and 1 Hz; (iii)Frequency oscillatory sweep from 0.1 to 100 Hz at a strain amplitude of 1%.

3. RESULTS AND DISCUSSION

Based on the visual inspection of the samples, the suspensions were classified into sol, pre-gel, and gel states, depending on the concentration of SiO_2 nanoparticles added. The appearance of the nanosilica suspensions depended on the silanol density on the surface: the suspensions were found in the sol state for volume fractions below $\phi v < 0.5\%$, in the pre-gel state for volume fractions between $1 < \phi v \leq 1.5\%$, and in the gel state for $\phi v > 2.5\%$. Figure 1 displays typical visual appearances in the sol, pre-gel, and gel states of the suspensions.

Figure. 1. Visual appearance of nanosilica suspensions in the sol, pre-gel, and gel states.

The influence of different concentrations of silica nanoparticles on the rheological behavior of mineral oil was analyzed in three regions: the liquid regime, the solid regime, and the solid-liquid transition. First, we analyzed the net regime, which means examining the influence of nanosilica concentration on the material's apparent viscosity. Figure 2 illustrates the equilibrium viscosity curve of the material at a constant temperature of 25 °C. In these experiments, each shear rate was applied for a sufficient duration (a minimum of 10 minutes) until the material reached a steady state for each condition.
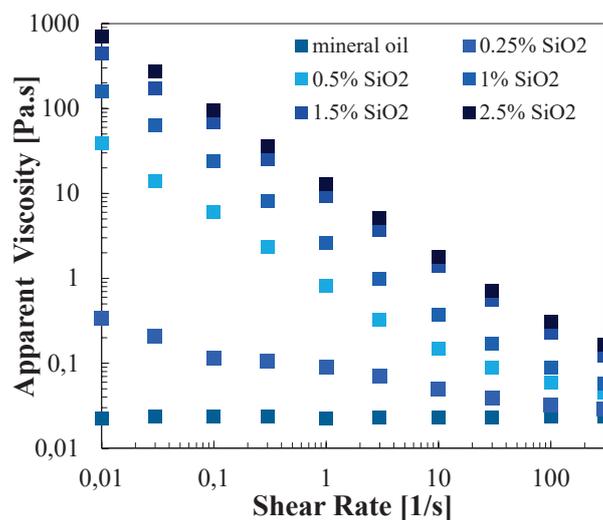

Figure 2. Viscosity curves as a function of shear rate at 25 °C.

When analyzing Figure 2, we observe that as the concentration of SiO_2 nanoparticles increases, the mineral oil no longer exhibits Newtonian behavior and instead displays typically non-Newtonian behavior. Moreover, a significant increase in apparent viscosity becomes evident as the concentration of silica nanoparticles increases. We observed that the apparent viscosity values varied minimally when comparing the concentrations of suspensions with 1.5% and 2.5% of SiO_2 nanoparticles. This result is supported by other authors (Chen et al., 2001; Warren et al., 2015; Sugino et al., 2017; Gómez-

Merino et al., 2020; Alaee et al., 2022), who used different types of mineral oil as a base fluid and different fluids for suspension formation.

Oscillation measurements were conducted to gain further insight into the microstructure of the suspensions. Stress amplitude experiments were carried out at a frequency of 1 Hz to define the linear viscoelastic region. Figure 3 presents the results of oscillatory stress scans for mineral oil and nanosilica suspensions formed with various concentrations.
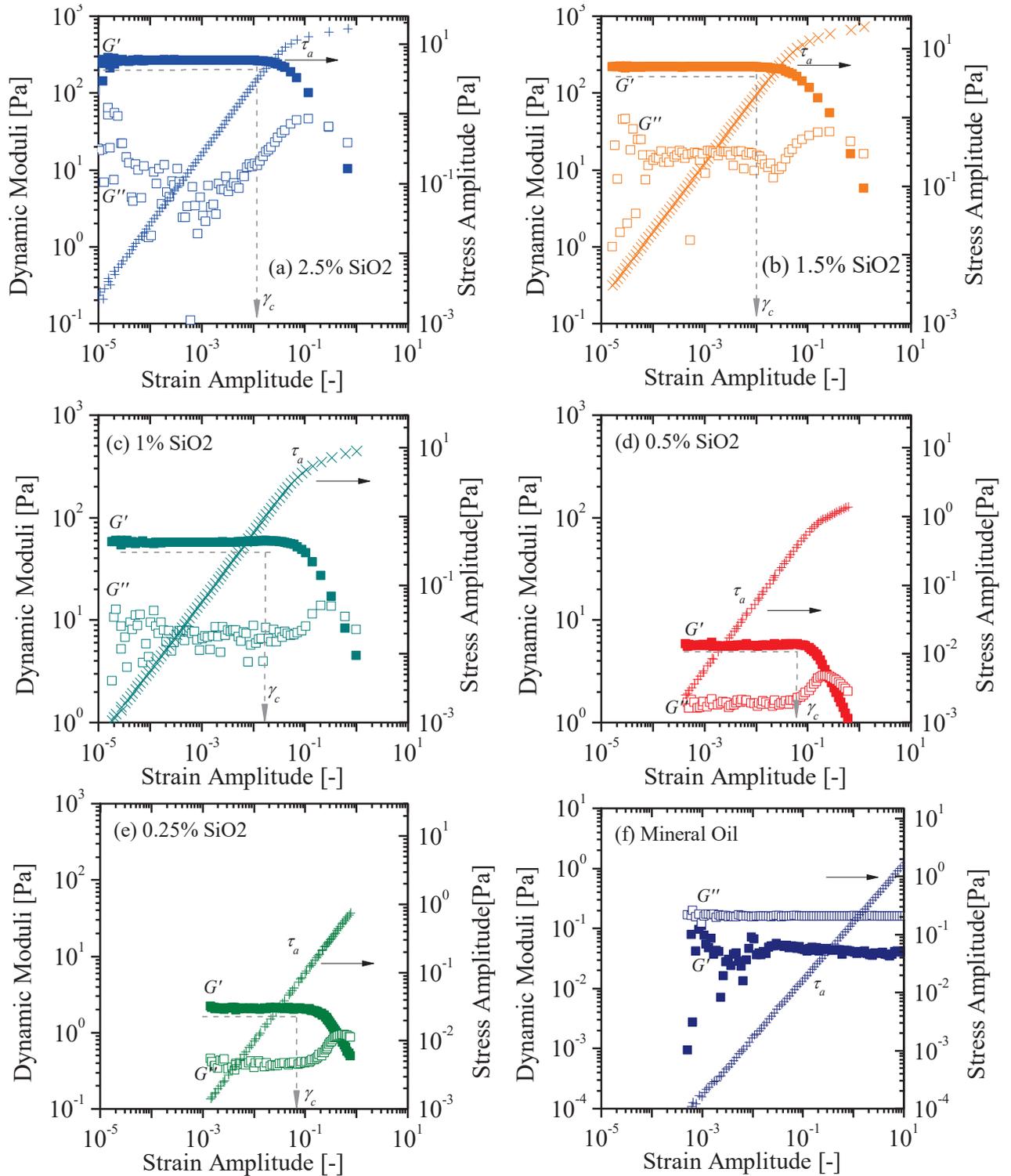

Figure 3. Oscillatory stress sweep tests performed at different configurations at 1 Hz after pre-shearing the sample for 1 min at -100s⁻¹ and 1 min 100 s⁻¹ and then left it under a zero-shear stress condition for 10 min. Figures (a)–(f) show the results at different concentrations nanoparticles SiO₂.

In this work, the transition from linear to nonlinear viscoelastic behavior is referred to as a critical strain, γ_c. It's important to note that while G′ and G″ are typically shown in MAOS and LAOS regimes, and the yielding point is defined in the G′-G″ crossover, this analysis must be approached with caution. The dynamic moduli can be accurately determined only in the SAOS regime (Hyun et al., 2011).

As seen in Figure 3, SiO_2 nanoparticle suspensions consistently exhibit a storage modulus value greater than the loss modulus, and as the concentration of nanoparticles increases, these moduli also increase. This suggests that the formed colloidal suspensions behave like viscoelastic solids. It is noteworthy that the linear region of the suspensions diminishes as the SiO_2 concentration rises. According to Chen et al. (2007), the suspension structures of SiO_2 in oil are stronger and more resistant to breaking, and the dynamic modulus in the linear region increases with the concentration of nanoparticles. The presence of the linear region also indicates that the suspensions behave like a gel network, formed by the coalescence of aggregates of silica particles (i.e., a flake). This process is facilitated by bonding interactions between silica particles, occurring through hydrogen bonds in the mineral oil. The formation of the gel network in silica suspensions can be analyzed by examining the dependence of the silica concentration on the value of G' in the linear region and the critical strain at which the linear region ends, using scale models based on fractal analysis (Shih et al.,1990; Wu et al., 2001; Genovese, 2012). The strain at which the G' and G″ curves intersect decreases with increasing SiO2 nanoparticle concentration, indicating that suspensions become more brittle with higher concentration.

Furthermore, it was observed that the magnitudes of G' values are significantly greater than those of G″ values for samples with 2.5%, 1.5%, and 1% SiO_2, indicating that these suspensions are predominantly in a gel-like state. In contrast, samples with 0.5% and 0.25% SiO_2 suggest that the viscoelastic response can be attributed to the formation of a non-flocculated sol in the mineral oil.

The rheological study conducted with hydrophobic nano-silica suspensions in mineral oil can assist in determining the most relevant heat transfer mechanisms. Additionally, rheological studies can provide insights into the most effective microstructure for heat transport. Therefore, the rheological results obtained in this study, along with thermal conductivity measurements already available in the literature and those we plan to conduct in the future, will enable us to infer the impact of the liquid layer surrounding the particles on heat transmission in SiO_2 suspensions in mineral oil. This information will be valuable for engineering applications involving energy transfer.

4. CONCLUSIONS

The rheological characteristics of SiO_2 mineral oil nanofluids were investigated. In addition to the base fluid, five different nanoparticle concentrations (0.25%, 0.5%, 1%, 1.5%, and 2.5% by volume) were examined. The following observations were made in this study:

a. The addition of SiO_2 nanoparticles imparts non-Newtonian fluid characteristics to the mineral oil.
b. The viscosity of the nanofluids increased with higher particle concentrations.
c. Within the linear viscoelastic region, the nanofluids exhibited viscoelastic behavior akin to solids.
d. The point of intersection for G' and G″ occurred at lower deformations as the SiO_2 nanoparticle concentration increased.

In summary, understanding the flow properties of these nanofluids is crucial for industrial applications and provides valuable insights for property studies related to nanofluid applications.

5. ACKNOWLEDGEMENTS

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