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Assessing colloidal stability of long term MWCNTs based nanofluids

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ABSTRACT

This report presents an assessment on colloidal stability of functionalized multiwalled carbon nanotubes based nanofluids. To this end, an innovative technique that allows for measurement of settling velocity during centrifugation is applied. This method also enables measurements without dilution, inferring further accuracy to the experimental study. The results suggest that functionalization techniques enable the production of highly stable nanofluids. It is also found, that the colloidal stabilities of these nanofluids are characterized by hindered settling. The settling velocity decreases when the nanoparticles volume fraction rises from 0.25% to 1.50% due to the increase of interparticle interaction. Furthermore, a high aspect ratio of nanoparticles directly contributed to an increase in colloidal stability. It is expected that these results may significantly contribute to proper tailor of nanofluids engineering, ensuring a long term stable dispersion enhancing industrial application suitability.

1. Introduction

Nanofluids are suspensions of nanoparticles in base fluids with significantly improvements in their thermophysical properties. Among the various nanoparticles available, carbon nanotubes (CNTs) are those which have attracted the greatest interest due to their extraordinary properties [1–5]. However, it remains extremely difficult to prepare stable suspensions of pristine CNTs, since they easily tend to agglomerate. The aggregation of the CNTs will cause the settlement, clogging of the flow channels and the decay of their overall effective properties.

For the preparation of a stable dispersion, it is necessary to disentangle the pristine CNTs, which can be achieved by physical or chemical approaches. These approaches could cause the alteration of CNTs properties in different ways. Thus, the selection of appropriate methodologies for nanofluid preparation is detrimental [6]. Ultrasonication, ball milling and high-speed shearing are commonly used as physical methods [7–10]. Chemical methods include both surfactant and functionalization techniques [8,11].

Physical methods are recognized by the destruction they cause in the CNTs. When subjected to high ultrasonication periods, the CNTs average length could be reduced to 65% of its original [6]. Moreover, ball-milling and high-speed shear cause the opening in the sidewalls of the CNTs. The shorter CNTs are less suitable to entangle and agglomerate. However, the unique properties of CNTs are also modified by its geometry alteration.

The chemical methods, such as the use of surfactants act directly on the surface of the CNTs, creating a film that induces electrostatic or steric repulsions that counterbalance with the Van der Waals attraction forces [12]. Despite increasing the wettability of the CNTs, the use of dispersants influences the final properties of the mixture as it forms an interface between two phases [13,14]. Furthermore, for thermal nanofluids, the surfactant can degrade, since they are subjected to high variations of temperature, leading to agglomeration or formation of foams, [14]. Other chemical methods are through the covalent functionalization of the CNTs surface. The most commonly used covalent functionalization is through the oxidative treatment which attaches oxygenated functional groups on the CNTs surface, such as carboxylic groups [15–18]. This will increase the CNTs solubility, due to a more hydrophilic surface structure, reducing agglomeration by the increase of the electrostatic repulsions that counterbalance with the Van der Waals attraction forces [16]. Moreover, carboxylic groups have polar properties, contributing for the solubility of the CNTs in polar solvents, such as distilled water and ethylene glycol.

The settling velocity of the nanoparticles, suspended in a fluid at rest, can be used to quantify colloidal stability. Therefore, understanding the physico-chemical phenomena of the suspended nanoparticles is crucial for a better analysis.

In 1850, Stokes [19] verified that the settling velocity of a sphere suspended in a Newtonian fluid v_s, is directly proportional to the gravitational acceleration constant, g, mass density of the two phases (ρ_p and ρ for particle and fluid, respectively), to the

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diameter of the spherical particle, d_p, and inversely proportional to the fluid viscosity, μ:

$$v_s = \frac{g(\rho_p - \rho)d_p^2}{18\mu} \quad (1)$$

Later, Batchelor [20] found that a fluid containing 3% volume fraction of spheres has a settling velocity 20% lower than that predicted by Stokes. These results suggest that hydrodynamic interactions between particles play a decisive role on the settling velocity. During sedimentation, the particles displace liquid in the opposite direction to their movement, which affects the motion of the surrounding ones. Further, for elongated particles, the interactions become more pronounced even for lower concentrations. For these, the sedimentation rate also depends on its orientation, which is influenced by the fluctuations of the fluid viscosity resulting from the settling of the surrounding particles [21,22]. Brownian forces, collisions, agglomeration, and electrostatic repulsions between suspended particles are other factors influencing the settling velocity. Sedimentation with significant interactions is known as hindered settling. In this, the velocity becomes much slower than the Stokes-velocity [23–26].

It is expected that the interactions between CNTs become more significant when compared to spherical particles, even for small concentrations. The latter is believed to be due to its tubular geometry and its high aspect ratios that enable the formation of chains, as predicted by the excluded volume theory [27].

The commonly used techniques to evaluate sedimentation are the sedimentation photograph, zeta potential analysis and UV–visible spectrophotometry [28–31]. However, these techniques are quite slow and, in general require dilutions of the suspensions, changing the interaction between the nanoparticles, since the concentration is drastically reduced, which may affect the experimental measurements.

Amrollahi et al. [32] produced CNTs based nanofluids, with volume fractions ranging from 0.5% to 2.5%, for different ultrasonication periods. The evaluation of the stability of the particles (and of settling time) was observed at naked eye. They found that, for lower ultrasonication periods, where the CNTs clusters were not fully segregated, the settling time decreases with increasing volume fraction. However, by increasing the ultrasonication period, the clusters are totally separated and solutions with the higher volume fractions become the most stables, indicating that the settling velocity was significantly reduced. They have assumed that when the nanoparticles are entirely unbundled, collisions between each other increase with an increase of volume fraction, contributing for the hindered settling.

Other researchers [28,33] assessed the colloidal stability of CNTs based nanofluids by UV–visible spectrophotometry, and they used diluted suspension. Jiang et al. [28] produced CNTs suspensions with the addition of surfactant with a drop on concentration of 15% after 500 h. Chen et al. [33] also investigated the aggregation behavior of aqueous suspensions of CNTs. Continuous light scattering measurements made over 2 weeks have shown that CNTs create a percolation threshold with fractal-like structures.

The use of UV–visible spectrophotometry and zeta potential for evaluate the colloidal stability of the nanofluids is quite demanding, since it will take a large amount of time for a full sedimentation or flotation to occur, during the measurements.

A quite new method to evaluate the colloidal dispersion of suspensions is through the application of a centrifugal field. The analytical centrifuge is an effortless and undemanding method that allows for estimating the shelf life of suspensions [34]. A centrifuge field allows the acceleration of the demixing phenomenon, evaluating the change in concentration by detecting the transmission profiles along the entire height of the sample. Through the measurement of settling velocity at high Relative Centrifugal Force (RCF = centrifugal acceleration/earth acceleration), it is possible to find the constant of proportionality with the demixing phenomenon, and then extrapolate the results to gravity conditions (RCF = 1). With this is possible to estimate the shelf life of the colloid by a direct way. The methodology is described in detail in [34].

In this research study, the characterization of the colloidal stability of covalently functionalized multiwalled carbon nanotubes (MWCNTs) suspensions is achieved by the analytical centrifuge technique. Moreover, the expected shelf life of the nanofluids is estimated.

2. Materials and methods

The used multiwalled carbon nanotubes (MWCNTs), and the chosen base fluids are described below as well as the applied process to prepare the studied nanofluids. A description of the experimental analysis performed to all prepared samples is also described.

2.1. Materials

The multiwalled carbon nanotubes, obtained from Cheap Tubes, Inc., were produced by catalyzed chemical vapor deposition (CVD). The nominal purity of the nanotubes is reported by the manufacture as higher than 95 %wt. In Table 1, it is described the geometric properties of the nanoparticles studied. D = MWCNT diameter in nm; L = MWCNT length in μm.

Concerning to base fluids, were selected two mixtures of distilled water (DW) and ethylene glycol (EG), as the viscosity and density are identified as properties that cause impact on the results. The choice of these base fluids is consistent with their importance for industrial applications (as refrigerator fluids).

As mentioned before, the aim of this study is the evaluation of the settling velocity of MWCNTs based nanofluids. For that purpose, the effect of the viscosity of the base fluid, the geometry and volume fraction of nanoparticles in the colloidal stability was analyzed. It was studied two base fluids: the first one with a volume fraction of 30% of EG and the second one with a volume fraction of 60% EG. The volume fractions of MWCNTs were ranged from 0.25% to 1.5%. In Table 2, it is shown the control factors selected for the analysis and their respective degrees of freedom (DOF).

Applying a full factorial *design of experiments* to the identified control factors it is obtained a total of 12 samples (Table 3).

2.2. Nanofluids preparation

The MWCNT were covalently functionalized through the method described by Esumi et al. [15]. The pristine MWCNTs were refluxed at 413 K in nitric and sulphuric acid at 1:3 volume ratio for 30 min, followed by exhausting wash with DW until no signs of acidity and dried in an oven at 373 K, for at least 72 h, to evaporate the humidity. Other authors [16,33,35] used this method for the MWCNTs functionalization and reported good dispersion results.

The functionalized MWCNTs were dispersed in 50 ml of base fluid with a magnetic stirrer combined with ultrasonication for 60 min [36], to improve the dispersion of the MWCNTs into base fluid. The time elapsed since the finalization of sample preparation and the beginning of the measurements, needs to be taken into

Table 1
Geometric properties of the MWCNTs studied.

Nanoparticle designation	Aspect ratio	Particle volume (μm^3)
D > 50 L10–20	300	>29.452
D20–40 L10–30	667	14.137