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Flow behaviour of suspensions of functionalized graphene nanoplatelets in propylene glycol–water mixtures

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ABSTRACT

The low thermal conductivity of the fluids usually used in heat exchange processes (water, oils, glycols…) has proved to be one of the limiting factors in improving their heat transfer performance. These traditional fluids enhance their thermal capabilities by dispersing nano-sized particles with high thermal conductivity, as many researches have revealed in the last decades. Although the thermal conductivity of nanofluids has centred the interest of the heat transfer community, the rheological behaviour of the resulting dispersions is very influential in the heat transfer process, pressure drops and pumping powers. In this work, different samples of functionalized graphene nanoplatelets dispersed into two different binary mixtures of propylene glycol and water at 10:90 wt% and 30:70 wt% have been analysed by using a DHR-2 rotational rheometer equipped with concentric cylinder geometry. Firstly, the flow curves for Krytox GPL102 oil, pure propylene glycol, and the two binary mixtures of propylene glycol and water used as base fluids were experimentally obtained. These values were used to check our experimental procedure finding a good agreement between them and those reported and well known in the literature, with an absolute average deviation of 2.0%. Then, the viscosity-shear rate curves in the temperature range from 278.15 to 323.15 K were obtained for the different graphene nanofluid sets. Furthermore, a new equation was proposed in this work to describe the viscosity dependence on both the temperature and the nanoparticles volume concentration of graphene nanoplatelet nanofluids with an absolute average deviation with respect to our experimental data lower than 2%. Additionally, oscillatory tests of the samples were performed observing pseudoplastic behaviour for the nanofluids at lower angular frequencies.

1. Introduction

The performance of the heat transfer processes is a key issue in the continuous searching of reducing operational costs in thermal facilities. The optimization of this parameter improving the boundary conditions of the fluid or the construction geometry of the heat exchangers has been extensively investigated in the last decades. However, the weak thermal conductivity of the working fluids usually used, like water, oil or glycolated mixtures, has been a limiting factor in convective heat transfer processes. Researchers have proved that the suspension of nano-sized solid particles in these conventional fluids enhances their thermal conductivity without the elevated pressures drops or clogging issues corresponding to dispersions with higher particle sizes [1,2]. As it is well known, since Choi [3] called for the first time “nanofluids” at the fluids with nanoparticles suspended in them, lots of experimental and theoretical investigations about their thermal conductivity improvements have been carried out. Metallic and non-metallic nanoparticles, like Al_2O_3, CuO, Cu, SiO_2 or TiO_2, were used at low concentrations (usually up to 5 vol%), resulting in remarkable increases in the convection coefficient of the obtained fluids [4–6].

Propylene glycol or 1,2 propanediol ($C_3H_8O_2$) is a non-toxic organic compound consisting of a three-carbon diol with a stereocenter at the central carbon atom. Its industrial synthesis is mainly produced by the hydration of propylene oxide at high temperatures and pressures. Propylene glycol is one of the chemicals with higher global production with applications like the creation of polyester resins, foods, cosmetics, personal care products, pharmaceutic products or detergents, among others. In heat transfer facilities, propylene glycol is widely used as working fluid, antifreezing protection and de-icing liquid. Among the applications as working fluid, their use in geothermal collection or as

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secondary fluids in indirect cooling systems deserves special attention. In this type of purposes, aqueous solutions of propylene glycol at 10–30 wt% are typically employed [7,8].

One of the families of nanoadditives that during last years has proved a great potential in heat transfer enhancement is that of carbon allotropes. Carbon-based nanoadditives achieve higher improvements at lower concentrations. However, different carbon structures entail dissimilar ranges of thermal conductivities. Carbon nanotubes and graphene show the highest values [9–11]. In particular, nowadays graphene is one of the most widely used materials in nanotechnology because of its exceptional mechanical, electrical and thermal properties (high mechanical strength, huge surface area and elevated thermal and electrical conductivity). Graphene, isolated and characterized in 2004 by Novoselov et al. [12], is theoretically conceived as a layer of a single-atom-thick composed by hexagonally organized carbon atoms, sp^2-bonded, into a honeycomb lattice. Nevertheless, nanopowder with multiple-layer structure, commertially known as graphene nanoplatelets, maintains the good properties of single-layer graphene in a few orders of magnitude while its synthetization cost is considerably lower. Otherwise, the use of graphene nanoplatelets like nanoadditives in nanofluids applied to heat transfer presents a major drawback because they are hydrophobic, and therefore the challenge of the stability must be confronted [13,14]. Graphene oxide, ideally conceived like two-dimensional oxidized graphene sheets, includes functional groups that contain oxygen and it is commercially available in the form of graphite oxide nanoplatelets. The cited polar groups allow its compatibility with polar solvents, like water. The disadvantage of functionalization through an oxidation process is that the thermal conductivity is reduced in relation to pristine graphene nanoplatelets [15,16]. To solve this effect, different types of reduction processes are currently used to partially restore graphene's properties maintaining the hydrophilicity [14,17–19]. A literature review evidences that the thermal conductivity of most conventional fluids can be significantly improved by mean of reduced graphene oxide additives [20–23], being able to obtain better convection coefficients. Nevertheless, the dispersion of nanoadditives also modifies other thermophysical properties, like viscosity. This change in the real processes of circulating fluids may lead to higher pressure drops, and consequently higher pumping powers [24,25]. Then, heat transfer performances lower even than those obtained for the base fluid can be achieved. Heat transfer is well known to depend on the flow regime of the fluid, in which viscosity plays a crucial role as inferred through the Reynolds number. Therefore, a comprehensive rheological characterization, e.g. determining Newtonian or non-Newtonian limits, of the supposed applied nanofluids in heat transfer processes is a key factor to understand and to develop their real application.

The rheological behaviour of suspensions of graphene nanoplatelets in water and in ethylene glycol-water mixtures has been experimentally analysed in the literature [2,26–32]. Tesfai et al. [26] reported the viscosity values at 293.15 K and at different shear rates for four dispersions in water of graphene oxide synthesized by themselves using the Staudenmaier method, finding increases from 2.5 to 48%. Dhar et al. [27] reported the viscosity values at 298 K of four dispersions of graphene oxide nanosheets in water, obtained by a two-step method. Their samples were prepared from commercial graphite powder, which was first oxidized following a modified Hummer's method and then reduced by using $NaBH_4$. In addition, for the 0.01 vol% sample they reported the viscosity values in the temperature range from 298 to 345 K. Sadeghinezhad et al. [28] analysed the viscosity at a shear rate of $500\ s^{-1}$ for distilled water and four aqueous dispersions of a commercial graphene nanoplatelet sample ($500\ m^2/g$) at several mass concentrations over the temperature range from 293.15 to 333.15 K, finding increases in viscosity of up to 38% compared to the base fluid. Merhali et al. [2,29] analysed the effect of nanoplatelet aspect ratio on aqueous nanofluid viscosity at shear rate of $500\ s^{-1}$ using graphene nanoplatelets of surface areas of 300, 500 and 750 m^2/g at various mass concentrations over the temperature range from 293.15 to 333.15 K. They found increases up to 44% compared to water for the highest concentration. Amiri et al. [30] reported the viscosity values at shear rate of $300\ s^{-1}$ for three mass concentrations (0.025, 0.050 and 0.10%) of two different graphene nanoplatelets-water dispersions in the temperature range from 293.15 to 353.15 K. They used two methods to increase the graphene nanoplatelets dispersibility in water, covalent and non-covalent functionalizations, feature in which lies the main difference between the two types of nanofluids. Non-covalent functionalization of graphene nanoplatelets was performed by employing sodium dodecyl benzene sulphonate (SDBS) and their covalent functionalization was performed by incorporating carboxyl groups (COOH). They found that the non-covalent nanofluids have significantly higher viscosities than covalent nanofluids, up to a 136% higher than water value at the same temperature for the 0.10 wt% non-covalent functionalized graphene nanoplatelets dispersion. Esfahani et al. [31] reported viscosity values from 298.15 to 333.15 K at different shear rates for two dispersions in water of commercial graphene oxide, finding increases at $100\ s^{-1}$ and the lowest temperature of 38 and 130% for the 0.01 wt% and the 0.5 wt% dispersions, respectively. They also found that these nanofluids present both Newtonian and non-Newtonian behaviours depending on concentration, and shear rate, finding that non-Newtonian behaviour at lower shear rates is significant at higher concentrations. Finally, we must point out our previous work [32] in which we reported dynamic viscosities for four nanofluids based on the dispersion of sulfonic acid-functionalized graphene nanoplatelets in water with maximum increases up to 80% compared to those of the base fluid. Nevertheless, up to our knowledge, no studies have been carried out analysing the base fluid influence or using propylene glycol-water mixtures as base fluids such as it is proposed in this work.

From the theoretical point of view, the first and more extended model to predict the viscosity of suspensions of spherical particles in base fluids is the Einstein's equation, developed in 1906 for concentrations lower than 2 vol% [33]. This model has some limitations because it is inconsistent for higher concentrations and for aspect ratios such as fibers or platelets and it does not consider interactions between particles [34], so many other models have been carried out. Models like those developed by Mooney [35], Krieger and Dougherty [36], Frandken and Acrivos [37], Nielsen [38] or Pak and Cho [39] estimate the viscosity of the suspension according to the viscosity of the base fluid and the volume fraction of suspended additives. In addition to the volumetric concentration, also the temperature plays an important role in the description of the behaviour of the viscosity modification. Some equations have been developed considering this variable, like those carried out by Kulkarni et al. [40], Namburu et al. [41,42] or Abu-Nada [43] for specific nanoparticles dispersed in various base fluids.

In this study, the flow behaviour of six graphene nanoplatelet propylene glycol/water nanofluids has been analysed by using a rotational rheometer with concentric cylinder geometry within the temperature range from 278.15 to 323.15 K. Two base fluids consisting of two binary mixtures of propylene glycol, PG, and water, W, at 10:90 and 30:70 mass ratio, in which were dispersed different mass concentrations of sulfonic acid-functionalized graphene oxide nanoplatelets formed the studied f-GnPs nanofluids. Moreover, a new relationship between dynamic viscosity, temperature and nanoparticles volume concentration is proposed in this work, which allows describing the temperature and concentration dependences on the viscosity of graphene nanofluids.

2. Material and methods

2.1. Samples preparation

Sulfonic acid-functionalized graphene oxide nanoplatelets were supplied by NanoInnova Technologies S.L. (Madrid, Spain). Propylene glycol was provided by Sigma-Aldrich with a mass purity of 99.5% and water was produced by a Milli-Q 185 Plus system (Millipore Ltd.,