

HEAT TRANSFER CAPABILITY OF FUNCTIONALIZED GRAPHENE NANOPLATELET DISPERSIONS IN PROPYLENE GLYCOL + WATER (30:70 WT.%)

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ABSTRACT

One of the most restricting factors in the performance of industrial heat transfer processes is the low thermal conductivity of the thermal fluids commonly used. Hence, dispersions of nanoparticles with high thermal conductivity in conventional fluids, nanofluids, have received increasingly interest over last decades in order to obtain improvements in heat transfer processes. The thermophysical properties are necessary to their flow behaviour characterization and they are not commonly available in the literature. Therefore, laboratories with wide experience in thermophysical characterization should call attention to this issue.

This study aims to determine those properties with a noticeable influence on the heat transfer capability for dispersions of functionalized graphene nanoplatelets in a propylene glycol:water mixture at (30:70) % mass ratio, usually employed in thermal facilities. Initially, nanofluid stabilities were investigated analyzing zeta potential measurements, optimizing the pH value. Tests for obtaining densities, heat capacities, thermal conductivities and dynamic viscosities were developed for different nanoadditive mass concentrations (0.25, 0.50, 0.75 and 1.0) wt.% over throughout the temperature range from (293.15 to 323.15) K. Thus, density values were obtained by using a pycnometric technique, a differential scanning calorimeter was utilized to measure heat capacities, thermal conductivities were determined with a transient hot wire technique while rheological tests were carried out by means of a rotational rheometer with cone-plate geometry. Secondly, thermal conductivity focused our attention due to its important role in the heat transfer process. Remarkable increases, up to 16 %, were found in this property.

INTRODUCTION

The low thermal conductivity of the heat transfer fluids often employed in industrial applications is one of the most restricting factors to obtain better efficiencies. Technological advances in the last century have led to an improvement in this area. Nevertheless, there is still scope for improvement in thermal conductivity of thermal fluids. Choi and Eastman proposed one of the most promising lines of investigation in this field, nanofluids [1]. A nanofluid can be defined as a stable dispersion

of solid nanoparticles with high thermal conductivity in a conventional fluid, which is known as base fluid.

The high thermal conductivity of nanoparticles is expected to raise the thermal performance of the base fluid. This property plays an important role in forced convection mechanisms, those with the highest weight in industrial heat transfer processes. Many researchers have studied the effect on the effective thermal conductivity of dispersing nanoparticles in different base fluids showing interesting results [2]. Notwithstanding, thermal conductivity is not the only important factor in heat transfer. Other thermophysical properties such as density, specific heat and dynamic viscosity influence the process [3-4]. As an example, the dispersion of nanoparticles in a fluid will especially modify its viscosity and flow regime, which would alter the heat transfer performance. A higher viscosity in nanofluids will increase pressure drops and, consequently, pumping powers required. Thus, it is also quite important to know the rheological behaviour of nanofluids. However, not all these properties necessary to characterize their flow behaviour and determine the convection coefficients of nanofluids are commonly available in the literature and so it is necessary to determine them experimentally.

Metallic, metal oxides and carbon allotropes have been commonly used as nanoadditives by many researchers in their studies obtaining good results in thermal conductivity enhancement [5-7]. Within the carbon allotropes, the discovery of graphene offered new possibilities [8]. Graphene is a layer of carbon atoms disposed in a plane hexagonal structure of sp² bonded atoms. This structure provides outstanding thermal, mechanical and electrical properties that make graphene an exceptional material [9]. Thus, graphene nanoplatelets have been utilized as nanoadditives in several works. Graphene is hydrophobic and so graphene nanoplatelets need to be functionalized to be suitable for a stable dispersion in aqueous fluids. Properties of functionalized graphene nanofluids based on water [4, 10-11] or ethylene glycol [2] have been reported in the literature. Nevertheless, up to our knowledge, no studies have been developed using a mixture of propylene glycol + water at (30:70) % mass ratio, fluid commonly employed in thermal facilities, as base fluid.

In this study, the thermophysical properties (density, specific heat capacity, thermal conductivity and dynamic viscosity) of four different mass concentrations (0.25, 0.50, 0.75 and 1.0) wt.% of commercial functionalized graphene nanoplatelets

dispersed in a propylene glycol:water mixture at (30:70) % mass ratio were experimentally determined in the temperature range from (293.15 to 323.15) K.

NOMENCLATURE

AAD	[%]	Absolute Average Deviation
pH	[-]	pH value
PG		Propylene glycol
c_p	[J·kg ⁻¹ ·K ⁻¹]	Specific heat capacity
T	[K]	Temperature
k	[W·m ⁻¹ ·K ⁻¹]	Thermal conductivity
W		Water
wt.%	[%]	Nanoadditive mass concentration

Special characters		
ρ	[kg·m ⁻³]	Density
η	[Pa·s]	Dynamic viscosity
ϕ_m	[-]	Nanoadditive mass concentration
ζ	[mV]	Zeta potential

Subscripts	
nf	Nanofluid
bf	Base fluid
GnP	Graphene nanoplatelets

EXPERIMENTAL

Materials and nanofluid preparation

Graphene nanoplatelets were supplied by IoLiTec - Ionic Liquids Technologies GmbH (Heilbronn, Germany) with a purity level of 99.5 % and a thickness of 11-15 nm as commercial parameters. The base fluid is a mixture of propylene glycol and water at (30:70) % mass ratio. Propylene glycol was purchased from Sigma-Aldrich with a mass purity of 99.5 % and water was produced by a Milli-Q 185 Plus system (Millipore Ltd, Watford, UK) with a resistivity of 18.2 M Ω ·cm.

Nanofluid samples were designed following a two-step method. Firstly, the amounts of each component of the base fluid and the amounts of needed powder to obtain the desired nanoparticle mass concentrations (0.25, 0.50, 0.75 and 1.0) wt.% were weighted in a Sartorius electronic balance model CPA225 (Sartorius AG, Goettingen, Germany). Then, after mixing the components, the samples were sonicated for 240 minutes with a maximum sonication power of 200 W and a frequency of 20 kHz by using an Ultrasounds ultrasonic bath (JP Selecta S.A., Barcelona, Spain).

Nanopowder characterization

The nanopowder was characterized by atomic force microscopy (AFM). Analyses were carried out through a Scanning Probe Microscopy Multimode 8 (Veeco Instruments Inc., New York, United States) using Peak Force Tapping measurement mode. The silicon tip has a radius of curvature (Tip ROC) less than 10 nm, a force constant of 0.4 N·m⁻¹ and a resonance frequency of 50–90 kHz. The studied nanopowder sample was first dispersed in water and then deposited on mica substrate.

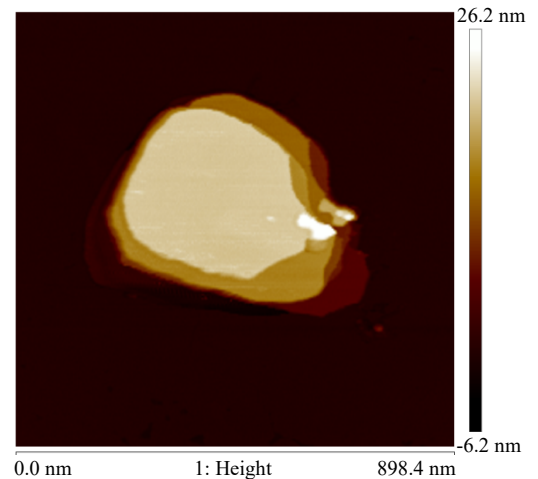


Figure 1 AFM image of 900x900 nm² of the functionalized graphene nanoplatelets dispersed in water and deposited on mica substrate.

The obtained images show groups of graphene flakes with total thicknesses up to 20 nm and total lengths and widths between 400 and 550 nm. An example is presented in Figure 1, where it can be observed up to five stacked graphene plates of 2–5 nm confirming the expected nanoplatelet-shape.

Samples stability

The preparation of a homogenous suspension is a critical parameter to ensure the heat transfer enhancement. The formation of aggregates, favoured by the existence of van der Waals interactions forces between nanoparticles, should be especially taken into account. Different variables such as the surface treatment of nanoparticles, the method of nanofluids preparation, the addition of surfactants or the pH control are relevant to obtain stable samples.

The zeta potential, ζ , of the studied dispersions were analyzed through a dynamic light scattering technique by using a Zetasizer Nano ZS (Malvern Instruments Ltd, Malvern, United Kingdom). According to the literature, high absolute values of the zeta potential, usually larger than 30 mV in aqueous solutions, indicate strong electrostatic repulsions among nanoparticles and so better suspension stabilities [12]. Since the pH value of the sample is one of the variables with a higher influence on nanofluid stability, a study of the zeta potential variation with the pH was carried out. pH values were modified by the addition of very small quantities of aqueous solution of ammonia. The measurements of this indicator were performed by a PHM 210 standard pH meter (Radiometer Analytical S.A., Lyon, France) with a pH electrode code 5208 (Crison Instruments S.A., Alella, Spain).

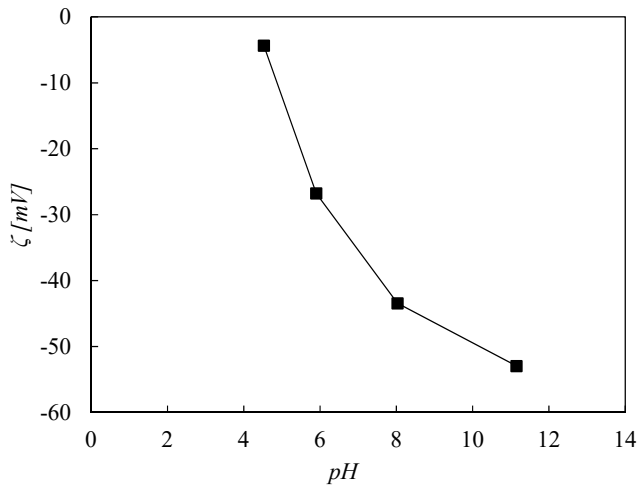


Figure 2 pH dependence of the zeta potential for 0.25 wt.% GnP/PG:W 30:70 wt.% nanofluid at 298.15 K.

Figure 2 shows the zeta potential values obtained at 298.15 K for dispersions of 0.25 wt.% in GnP/PG:W 30:70 wt.% at different pH values. The original sample presents a pH value of 4.5 and its zeta potential is around -15 mV. Similar results for the rest of the studied mass concentrations were found. As we can see, zeta potential exceeds -30 mV for pH values higher than 5.9. Values higher than 8.0 entail negative zeta potentials higher than -45 mV. Similar trends were observed for the other analysed GnP mass concentrations.

Experimental methods

Densities, ρ , were experimentally measured in the temperature range from (293.15 to 323.15) K using a Gay-Lussac pycnometer for liquids of borosilicate glass provided by Hermanos Alamo (Spain) with a volumetric capacity of 25 ml. The mass data were obtained through a Sartorius electronic balance model CPA225 (Sartorius AG, Goettingen, Germany). In order to control the temperature, samples were immersed in a Grant GP200 (Grant Instruments, Cambridge, UK) oil bath.

Specific heat capacity, c_p , was experimentally determined for the nanopowder and for the base fluid in the temperature range from (293.15 to 323.15) K using a quasi-isothermal temperature-modulated differential scanning calorimetry method (TDMSC) through a heat-flux differential scanning calorimeter, DSC, Q2000 (TA Instruments, New Castel, USA) [13]. The specific heat capacities of the nanofluids were obtained using the following equation:

$$c_{p\,nf} = \phi_m \cdot c_{p\,GnP} + (1 - \phi_m) \cdot c_{p\,bf} \quad (1)$$

where c_p is the specific heat capacity, ϕ_m is the nanoadditive mass concentration and the subscripts bf, GnP and nf stand for base fluid, graphene nanoplatelets and nanofluid, respectively.

Effective thermal conductivities, k , were experimentally measured in the temperature range from (293.15 to 323.15) K using a KD2 Pro thermal analyzer (Decagon Devices, Inc., Pullman, USA) with a KS-1 probe (1.3 mm diameter and 60 mm

long). To control the samples temperature, they were immersed in the previously cited oil bath [14].

Dynamic viscosities, η , in the temperature range from (293.15 to 323.15) K were experimentally determined by a rotational Physica MCR 101 rheometer (Anton Paar, Graz, Austria) equipped with a cone-plate geometry with a cone angle of 1° and a diameter of 25 mm [15].

RESULTS AND DISCUSSION

Figure 3 shows the obtained experimental density values of the studied nanofluid samples over the temperature range from (293.15 to 323.15) K as a function of the nanoadditive mass concentration.

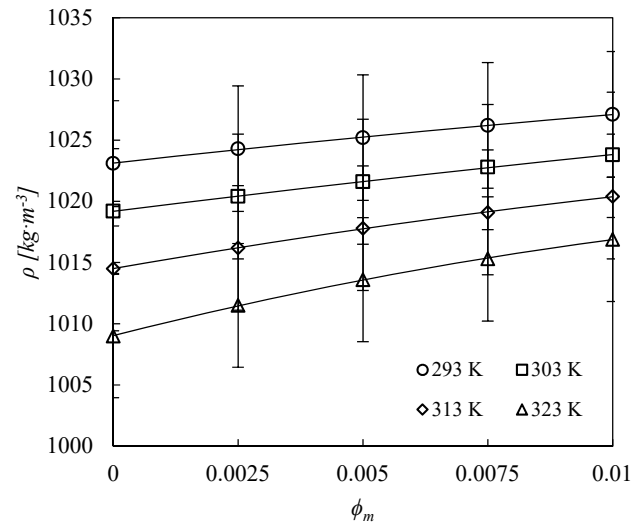


Figure 3 Density of the graphene nanoplatelets glycolated water nanofluids as a function of nanoadditive mass concentration at different temperatures.

The experimental data obtained for the base fluid are in agreement with the values reported by Melinder [16], with an AAD% lower than 0.10 %. As it can be observed in Figure 3, density rises with increasing graphene nanoplatelets mass concentration. The reported increases with respect of the base fluid reach up to 0.78 % for the 1.0 wt.% nanofluid. Moreover, density decreases with the increasing temperature, as shown in Figure 3. Density reductions throughout the studied temperature range go from 1.4 % for the base fluid to 0.99 % for 1.0 wt.% nanofluid.

Figure 4 plots the obtained heat capacities of the studied nanofluids at different temperatures in the range from (293.15 to 323.15) K as a function of the nanoadditive mass concentration.

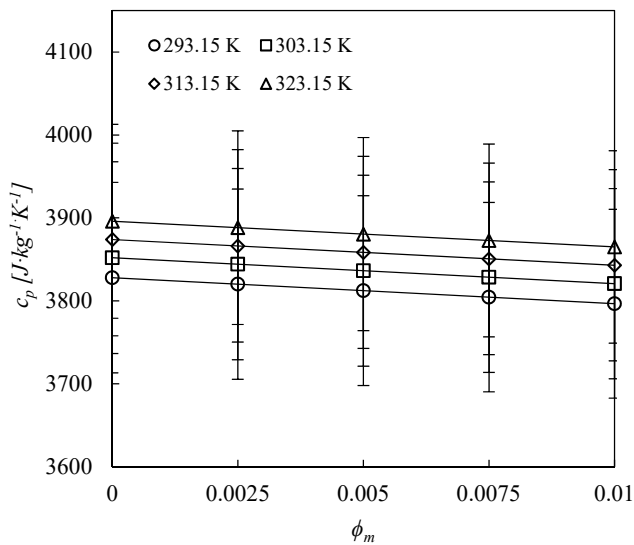


Figure 4 Specific heat capacity of the graphene nanoplatelet glycolated water nanofluids as a function of nanoadditive mass concentration at different temperatures.

The obtained experimental heat capacities of the base fluid present an AAD% lower than 0.85 % in relation to those previously reported in the literature [16]. As it can be observed in Figure 4, obtained heat capacity decreases with the loading of nanoadditive for all the analysed temperatures. Decreases range between 0.2% for the 0.25 wt.% concentration and 0.8 % for the 1.0 wt.% nanofluid, without a clear temperature effect. Furthermore, it is shown as the experimental heat capacities increase when the temperature rises, reaching maximum increments of up to 1.8%.

Figure 5 shows the obtained thermal conductivities of the studied nanofluid samples as a function of the temperature.

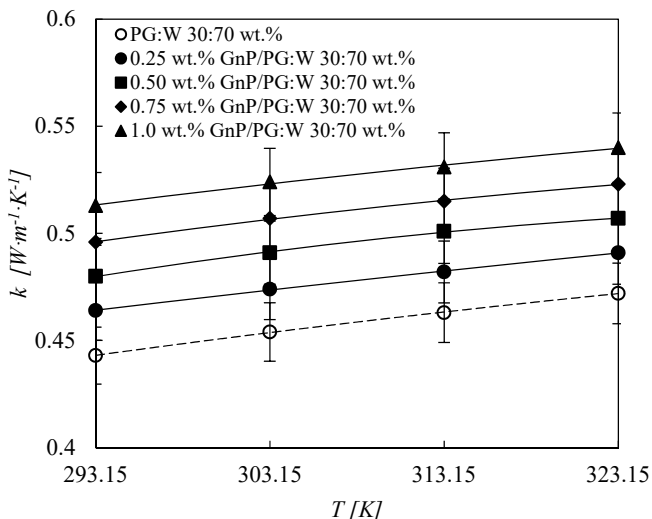


Figure 5 Thermal conductivity of the graphene nanoplatelet glycolated water nanofluids as a function of temperature for different nanoadditive mass concentrations.

The experimental thermal conductivities of the base fluid are in good agreement with the ones reported in the literature [16], with an AAD% lower than 0.44 %. Figure 5 shows the improvement trend of the thermal conductivity with the increasing temperature for the studied samples. Maximum enhancements in the temperature range vary from 6.5 % for the base fluid to 5.3 % for the 1.0 wt.% concentration. Furthermore, it can be seen how this property improves as the nanoadditive concentration rises, being for the 1.0 wt.% GnP nanofluid up to 16 % greater than for the propylene glycol:water mixture.

Regarding the analysis of the rheological behaviour of the analysed samples, various rotational tests were performed maintaining constant different shear rates between 1000 and 4000 s^{-1} for at least 500 seconds. Once steady state was reached, no dependence of viscosity with respect to time was observed for any mass concentration. In addition, viscosity values obtained at different shear rates did not show significant differences. Thus, it can be concluded that nanofluids are Newtonian in the range of study.

Figure 6 plots the obtained dynamic viscosities of the studied nanofluids in the temperature range from (293.15 to 323.15) K.

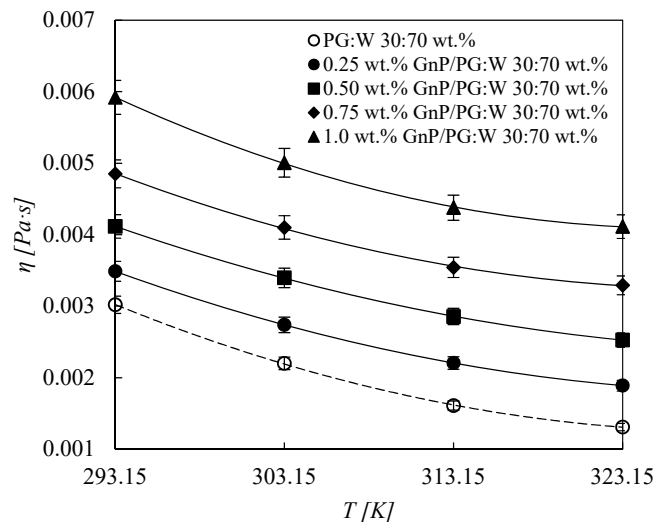


Figure 6 Dynamic viscosity of the graphene nanoplatelet glycolated water nanofluids as a function of temperature for different nanoadditive mass concentrations.

The experimental dynamic viscosities of the propylene glycol:water mixture at (30:70) % mass ratio used as base fluid are in accordance with those reported by Melinder [16], finding an AAD% of 2.5 %. The dynamic viscosity decreases when the temperature rises for all the nanoadditive mass concentrations. As it can be seen, the decreases become smaller with the nanoadditive loading rises. Thus, the highest drop, up to 57 %, is achieved with the base fluid. For the nanofluids, the decreases reach 46 % for the 0.25 wt.% concentration and 31 % for the 1.0 wt.% nanofluid.

The behaviour of the dynamic viscosities when nanoplatelets concentration rises for the same temperature is clear, higher values are reached with higher loadings of nanoparticles. As an example, the 0.50 wt.% nanofluid reaches increases in viscosity

up to 93 % in relation to the base fluid value at the same temperature.

CONCLUSIONS

In this work, the thermophysical properties necessary to characterize the heat transfer processes and the flow behaviour of four nanofluids were experimentally determined in the temperature range from (293.15 to 323.15) K. The analysed nanofluids consist of different concentrations of stacked graphene plates of 2-5 nm with total thicknesses up to 20 nm in a propylene glycol:water mixture at (30:70) % mass ratio.

Density increases with the loading of graphene nanoplatelets reach values of 0.78 % and density decreases with the temperature rises, reductions achieving values between 1.4 % and 0.99 %. For the heat capacities, it was found a decreasing trend with the nanoadditive loading between 0.2 % and 0.8 % depending on the temperature of analysis. The increases with the temperature rises reach up to 1.8 % in the studied temperature range.

Regarding the thermal conductivity, noticeable improvements with respect to the base fluid were found. These enhancements reach a maximum of 16 % for the 1.0 wt.% graphene nanoplatelet mass concentration while the found increases with the temperature achieve 6.5 %.

Dynamic viscosity values were measured in the shear rate range from 1000 s^{-1} to 4000 s^{-1} , showing a Newtonian behaviour. The decreases in viscosity when the temperature rises reach up to 46% for the nanofluids. Moreover, expected clear increases in viscosity with the nanoplatelets concentration were determined. As an example, the 0.50 wt.% nanofluid reaches increases in viscosity up to 93 % with respect of the base fluid values.

The obtained results encourage the testing of the designed nanofluids in forced convection processes of real installations. The determination of the convection coefficients and the pressure drops associated to various working conditions will allow detecting the real extent of the improvements that the observed increases in thermal conductivity allow to glimpse.

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