THERMOPHYSICAL PROPERTIES OF FUNCTIONALIZED GRAPHENE NANOPLATELET DISPERSIONS FOR IMPROVING EFFICIENCY IN A WIND TURBINE COOLING SYSTEM

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ABSTRACT

A new generation of heat transfer fluids, nanofluids, can play a major role in the development of today’s renewable energies. In the particular case of wind turbines, an undesirable overheating of electrical and mechanical components can provoke a noticeable reduction of overall efficiency due to the temperature. The electricity generation or even very expensive repair cost can be expected. Hence, determining the thermophysical characteristics of these working fluids in heat transfer is the first step and key issue for analysing and optimizing the dispersions. In this sense, Scarce studies have been conducted using water-based graphene nanoplatelet nanofluids have been investigated and some correlations can be found in the literature. The purpose of this study is to carry out a thorough thermophysical characterization of different loaded samples of functionalized graphene nanoplatelet dispersions in an industrial heat transfer fluid, Havoline XLC Pre-mixed 50/50. Four different nanofluids at mass concentrations (0.25, 0.50, 0.75 and 1.0) wt.% of functionalized graphene nanoplatelets powder were produced. In order to obtain improved long-term stabilities, sodium dodecyl benzene sulphonate was added to the samples at a mass concentration of 0.125 % in relation to the base fluid without appreciable variations in the pH value. Stability was assessed through zeta potential and dynamic light scattering measurements. Tests for determining thermal conductivity were conducted with a transient hot wire technique in a wide temperature range. In addition, dynamic viscosities and specific heat capacities of the samples were experimentally determined at different temperatures in order to carry out further studies such as experimental convective heat transfer coefficients and pressure drops. Increases in thermal conductivity up to 7.3 % were found with not very high viscosity rises.

INTRODUCTION

Heat transfer fluids are involved in energy production, usage and storage. However, the limited thermophysical properties of conventional working fluids restrict the improvement of the heat transfer performance. Therefore, over the last two decades efforts have been focused on improving these thermophysical properties in an attempt to enhance energy efficiency. Solid particles have greater thermal conductivity than liquids and therefore dispersions that contain solid nano-sized particles in base fluids, known as nanofluids, represent an interesting solution. Since the concept of nanofluid was introduced by Choi et al. in 1995 [1], outnumbered studies have been carried out to determine their heat transfer performance. Several different nanoparticles such as oxides [2-3], metals [4], nitrides [5] and carbon allotropes [6-7] have been tested in nanofluids showing improved thermophysical properties. Likewise, graphene nanofluids have been proved to have the most desirable heat transfer performance in many applications due to their high thermal conductivity enhancement [8]. Water, ethylene glycol, propylene glycol and engine oil have been the most common base fluids tested [9-12]. Scarcely studies have been carried out using commercial antifreeze coolants as base fluids in nanofluids [13].

Nanofluids are breaking ground in the development of those renewable energies involving heat transfer processes. Overheating of wind turbines components inside the nacelles decreases energy efficiency and may require the power provided by the turbine to be reduced, leading to a significant energy loss. This situation may be caused by an undesirable combination of climatic and operation conditions and it is usually solved by air cooling, which forces outside air to flow through the nacelle [14]. However, the capacity of air cooling systems is sometimes not enough to dissipate the large amounts of heat generated by megawatt-size wind turbines and the service life of the components can be reduced. Furthermore, offshore wind turbines should not use air-cooling due to corrosion produce by the marine air [15]. Air-water cooling systems are much more efficient and can evacuate great amounts of heat. These more sophisticated systems can be improved by using nanofluids [14]. Regarding other renewable
energies, nanofluids have been tested in solar thermal panels, showing an excellent performance and high energy efficiency [16-17]. In addition, the use of nanofluids in heat transfer applications such as thermal management in compact electronic devices, transportation, industrial cooling and space and defence cooling systems, among others, has raised the attention of the scientific community [18].

Thermophysical characterization, which consists of the determination of density, heat capacity, thermal conductivity and viscosity, is essential to assess the heat transfer performance of nanofluids. In this study, the thermophysical properties of graphene nanoplatelets dispersions in an industrial heat transfer fluid have been thoroughly determined. Four different mass concentrations (0.25, 0.50, 0.75 and 1.0) % of functionalized graphene nanoplatelets dispersed in Havoline XCLPremixed 50/50, a working fluid widely used in wind turbine cooling, have been characterized. Sodium dodecyl benzene sulphonate has been added in a concentration of 0.125 wt.% with respect to the coolant in order to achieve long-term stability.

**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>AAD</td>
<td>[%]</td>
<td>Absolute Average Deviation</td>
</tr>
<tr>
<td>GnP</td>
<td>-</td>
<td>Functionalized graphene nanoplatelets</td>
</tr>
<tr>
<td>Hav. XLC 50/50</td>
<td>-</td>
<td>Havoline XLC Pre-mixed 50/50</td>
</tr>
<tr>
<td>pH</td>
<td>[-]</td>
<td>pH value</td>
</tr>
<tr>
<td>SDBS</td>
<td>-</td>
<td>Sodium dodecyl benzene sulphonate</td>
</tr>
<tr>
<td>cp</td>
<td>[J·kg⁻¹·K⁻¹]</td>
<td>Specific heat capacity</td>
</tr>
<tr>
<td>k</td>
<td>[W·m⁻¹·K⁻¹]</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>wt.%</td>
<td>[%]</td>
<td>Nanoadditive mass concentration</td>
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**Special characters**

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<thead>
<tr>
<th>Symbol</th>
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<th>Description</th>
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<tbody>
<tr>
<td>ρ</td>
<td>[kg·m⁻³]</td>
<td>Density</td>
</tr>
<tr>
<td>η</td>
<td>[Pa·s]</td>
<td>Dynamic viscosity</td>
</tr>
<tr>
<td>ϕw</td>
<td>[-]</td>
<td>Nanoadditive mass fraction</td>
</tr>
<tr>
<td>ζ</td>
<td>[mV]</td>
<td>Zeta potential</td>
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**Subscripts**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>bf</td>
<td>Base fluid</td>
</tr>
<tr>
<td>GnP</td>
<td>Functionalized graphene nanoplatelets</td>
</tr>
<tr>
<td>nf</td>
<td>Nanofluid</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL**

**Materials**

Functionalized graphene nanoplatelets, GnP, were supplied by NanoInnova Technologies S.L. (Madrid, Spain). This nanopowder is supplied with the commercial reference of graphenit-HYDRO. It is described as polycarboxylate chemically modified graphene nanoplatelets, specially designed to obtain useful good performances and high stability in aqueous mediums. These nanoplatelets consist of few layers (5-10 layers) of stacked graphene (2-3 nm high per layer) with the largest dimensions higher than 200 nm.

The base fluid is a commercial antifreeze coolant, widely used in the engine industry, consisting of a premixed solution of Havoline XLC and water from Chevron Products UK Limited (London, United Kingdom) and sold under Texaco brand with the reference Havoline XLC Pre-mixed 50/50, abbreviated us Hav. XLC 50/50. According to the supplier, pure Havoline is a mixture of up to 93 wt.% of ethylene glycol, up to 0.5 wt.% of other glycols and up to 5 wt.% of water; with 5 wt.% of inhibitor content and 1.1 wt.% of ash content. For the commercial solution Havoline XLC Pre-mixed 50/50, that includes 50 vol.% of Havoline XLC and 50 vol.% of water, it is ensured freezing protection above -40 °C. Other properties of both products, according to the manufacturer, are reflected in Table 1.

**Table 1** Properties of Havoline XLC and Havoline XLC Pre-mixed 50/50, according to the manufacturer.

<table>
<thead>
<tr>
<th></th>
<th>Specific gravity, 20 °C</th>
<th>Equilibrium boiling temperature</th>
<th>pH, 20 °C</th>
<th>Refractive Index, 20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Havoline XLC</td>
<td>1.113</td>
<td>180 °C</td>
<td>8.6</td>
<td>1.430</td>
</tr>
<tr>
<td>Havoline XLC Pre-mixed 50/50</td>
<td>1.068</td>
<td>108 °C</td>
<td>8.6</td>
<td>1.385</td>
</tr>
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</table>

Sodium dodecyl benzene sulphonate, SDBS, dispersant added to obtain durable stability of the nanofluids, was provided by Sigma-Aldrich (Louis, Missouri, USA).

**Nanofluid preparation**

The analysed nanofluids were designed following a two-step method. Firstly, the amounts of each component of the base fluid, the solution Hav. XLC 50/50 and the surfactant SDBS, and the amounts of the required GnP to get the desired nanoadditive mass concentrations (0.25, 0.50, 0.75 and 1.0) wt.% were weighted in a CPA225 Sartorius electronic balance (Sartorius AG, Gottingen, Germany). Then, the mixtures were mechanically stirred and afterwards sonicated by using an Ultrasounds ultrasonic bath (JP Selecta S.A., Barcelona, Spain) for 240 minutes, with a maximum sonication power of 200 W and a frequency of 20 kHz.

**Sample stability**

Two of the most important improvements that the dispersions of nanoparticles have introduced are both the lower sedimentation and the aggregates formation obtained, in comparison with those of dispersions of larger particles. Nevertheless, stability of nanofluids, which plays a main role in heat transfer performance, is not ensured by the nanometric size of particles. There are various methods to try to improve their stability such as include a surface treatment of the nanoparticles, subject the mixtures to ultrasounds, modify the pH of the resulting sample or the addition of surfactants, among others. Surfactants or dispersants are substances with a hydrophobic tail and a hydrophilic polar head group, which increase the contact of nanoparticles and the base fluid [18]. Zeta potential is a measurement of the dispersion stability. According to the literature, absolute values of the zeta potential higher than 30 mV are a sign of good sample stability in liquids of low ionic strength [19].

With the aim of designing stable nanofluids, a first study analyzing the zeta potential of different samples by a Zetasizer Nano ZS (Malvern Instruments Ltd, Malvern, United Kingdom)
was carried out. A dispersion of 0.25 wt.% of GnP in Hav. XLC 50/50 presented a zeta potential around -24 mV at 298.15 K just after preparation. That value was increasingly approaching the isoelectric point as time progressed. For this reason, it was decided to include a surfactant to improve stability. According to a literature survey, SDBS is expected to improve stability in all cases with the least possible modification of the base fluid of the different concentrations of GnP (0.25, 0.50, 0.75 and 1.0) wt.% to determine the dispersion stability. It was selected a mass concentration of 0.125 % in Hav. XLC 50/50 + 0.125 wt.% SDBS as the stability in all cases with the least possible modification of the base fluid. A dispersion of 0.25 wt.% of GnP in Hav. XLC 50/50 + 0.125 wt.% SDBS presents a zeta potential around -33 mV at 298.15 K just after preparation and after several days, without evident signs of sedimentation. That value was increasingly approaching the isoelectric point as time progressed. For this reason, it was decided to include a surfactant to improve stability. According to a literature survey, SDBS is expected to improve stability in all cases with the least possible modification of the base fluid of the different concentrations of GnP (0.25, 0.50, 0.75 and 1.0) wt.% to determine the dispersion stability. It was selected a mass concentration of 0.125 % in Hav. XLC 50/50 + 0.125 wt.% SDBS as the stability in all cases with the least possible modification of the base fluid. A dispersion of 0.25 wt.% of GnP in Hav. XLC 50/50 + 0.125 wt.% SDBS presents a zeta potential around -33 mV at 298.15 K just after preparation and after several days, without evident signs of sedimentation.

The pH variation due to the addition of GnP was measured by a PHM 210 standard pH meter (Radiometer Analytical S.A., Lyon, France) with a pH electrode code 5208 (Crisson Instruments S.A., Alella, Spain). The obtained results are gathered in Table 2.

### Table 2 pH value for pure Hav. XLC 50/50, for the base fluid and the different analysed mass concentrations of GnP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
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<tbody>
<tr>
<td>Hav. XLC 50/50</td>
<td>8.45</td>
</tr>
<tr>
<td>Hav. XLC 50/50 + 0.125 wt.% SDBS</td>
<td>8.44</td>
</tr>
<tr>
<td>Hav. XLC 50/50 + 0.125 wt.% SDBS + 0.25 wt.% GnP</td>
<td>8.63</td>
</tr>
<tr>
<td>Hav. XLC 50/50 + 0.125 wt.% SDBS + 0.50 wt.% GnP</td>
<td>8.76</td>
</tr>
<tr>
<td>Hav. XLC 50/50 + 0.125 wt.% SDBS + 0.75 wt.% GnP</td>
<td>8.93</td>
</tr>
<tr>
<td>Hav. XLC 50/50 + 0.125 wt.% SDBS + 1.0 wt.% GnP</td>
<td>9.09</td>
</tr>
</tbody>
</table>

No significant increments in the pH value were found in the range of analysed loadings. The obtained pH values are gathered in Table 3.

### Experimental methods

To determine the thermophysical profile of Hav. XLC 50/50, inside the temperature range from (293.15 to 343.15) K, the rheological behaviour and the dynamic viscosity under different flow conditions were experimentally determined by a rotational rheometer Physica MCR 101 (Anton Paar, Graz, Austria) with a cone-plate geometry (25 mm of diameter and 1° of cone angle) in the temperature range from (293.15 to 323.15) K [24].

Specific heat capacities, \( c_p \), were experimentally obtained for GnP, for Hav. XLC 50/50 and for Hav. XLC 50/50 + 0.125 wt.% SDBS through a heat-flux differential scanning calorimeter, DSC, Q2000 (TA Instruments, New Castel, USA) by means of quasi-isothermal temperature-modulated differential scanning calorimetry method (TDMSC) in the temperature range from (293.15 to 343.15) K [22]. The specific heat capacities of the different nanofluids were determined through the following expression:

\[
c_p, nf = \phi_m \cdot c_p, GnP + (1 - \phi_m) \cdot c_p, bf
\]

where \( c_p \) is the specific heat capacity, \( \phi_m \) is the nanoadditive mass ratio and \( nf, bf \) and GnP stand for nanofluid, base fluid and graphene nanoplatelets, respectively.

Effective thermal conductivities, \( k \), were experimentally determined through a KD2 Pro thermal analyzer (Decagon Devices, Inc., Pullman, USA) provided with a KS-1 probe (1.3 mm diameter x 60 mm long) in the temperature range from (293.15 to 343.15) K [23]. The sample temperature was set by means of the previously cited oil bath.

The rheological behaviour and the dynamic viscosity values, \( \eta \), under different flow conditions were experimentally determined by a rotational rheometer Physica MCR 101 (Anton Paar, Graz, Austria) with a cone-plate geometry (25 mm of diameter and 1° of cone angle) in the temperature range from (293.15 to 323.15) K [24].

### RESULTS AND DISCUSSION

The nanopowder at 298.15 K presents a density of 2250 kg·m\(^{-3}\) [25], a specific heat capacity of 0.887 J·kg\(^{-1}\)·K\(^{-1}\), and a thermal conductivity of 4.54 W·m\(^{-1}\)·K\(^{-1}\).

The experimental density data obtained for Hav. XLC 50/50 are in agreement with the values reported by Melinder for an ethylene glycol–water mixture at 50:50 vol.% [26], with an AAD lower than 0.32 %. The density values obtained by adding 0.125 wt.% of SDBS are practically the same that those of Hav. XLC 50/50, with deviations within the experimental uncertainty. In all cases, it was observed a slight increase of around 0.05 %.

Figure 1 plots the percentage density increases for the four different GnP mass concentration samples regarding the density of the base fluid, Hav. XLC 50/50 + 0.125 wt.% SDBS, over the temperature range from (293.15 to 323.15) K.
As it can be seen, the reported increases grow slightly with the increasing temperature in most cases for all the analysed nanoadditive concentrations. For instance, density rises go from 0.18% at 293.15 K to 0.33% at 343.15 K for the 0.50% GnP mass concentration sample. Increases in the nanoadditive mass concentration lead to increases in density rises over all the temperature range. As an example, density increase grows from 0.13 % for the 0.25 wt.% GnP nanofluid to 0.40 % for the 1.0 wt.% GnP nanofluid at 293.15 K.

Specific heat capacity values obtained for Hav. XLC 50/50 are in accordance with those reported in the literature for the ethylene glycol–water mixture at 50:50 vol.% [26], with an AAD of 0.34 %. The specific heat capacity values obtained for Hav. XLC 50/50 + 0.125 wt.% SDBS are very similar to those of the fluid without SDBS, with deviations within the experimental uncertainty that reach up to 0.06 %.

Figure 2 plots the obtained heat capacities of the studied nanofluid samples as a function of temperature.

As it can be observed, heat capacity increases when temperature rises, reaching maximum increments of up to 7.7 % in the studied temperature range. Furthermore, it can be seen that the increasing loading of nanoadditive causes decreases in heat capacity for all the analysed temperatures. Decreases range between 0.2 % for the 0.25 wt.% concentration and 0.7 % for the 1.0 wt.% nanofluid.

Experimental thermal conductivity values for Hav. XLC 50/50 present a deviation of 0.47 % with respect to those reported by Melinder for a mixture at 50:50 vol.% of ethylene glycol and water [26]. Regarding the comparison between the experimental thermal conductivities of Hav. XLC 50/50 and Hav. XLC 50/50 + 0.125 wt.% SDBS, no appreciable variations were found. The differences obtained are lower than 0.5 %.

Figure 3 shows the experimental thermal conductivity values of the studied nanofluid samples over the temperature range from (293.15 to 343.15) K as a function of nanoadditive mass concentration.

As it can be seen, there exists a clear improving trend in thermal conductivity with the increasing nanoadditive concentration. Reported enhancements reach up to 7.3 % for the 1.0 wt.% GnP concentration. It can also be observed that the increase in temperature contributes to improve the thermal conductivity for all the studied concentrations. In the analysed temperature range, enhancements go from 5.3% for the base fluid to 6.1 % for the 1.0 wt.% GnP concentration.

The rheological behaviour of the studied samples was analysed in the temperature range from (293 to 323) K. Dynamic viscosity was obtained through several rotational tests in which shear stresses at values ranging from (0.245 and 2.45) Pa were held constant for at least 500 s⁻¹. After achieving the steady state, the viscosity of none of the samples exhibits any time-dependence. Furthermore, once the steady state was reached, the viscosity values obtained for the same sample at
the different shear stress, which cover the shear rate range between (50 and 900) s⁻¹, are very similar. Both behaviours allow us to conclude that the analysed samples are Newtonian in the range of study.

In contrast to what happens with the rest of properties, obtained dynamic viscosity values of Hav. XLC 50/50 show significant differences with those reported by Melinder for an ethylene glycol–water mixture at 50:50 vol.% [26]. The differences reach 21%. The additional additives of the commercial sample, which reach a minimum of 7 wt.%, affect the viscosity values more significantly than the rest of thermophysical properties.

On the contrary, a comparison between the experimental values of Hav. XLC 50/50 and Hav. XLC 50/50 + 0.125 wt.% SDBS indicates that the addition of surfactant leads to slight increases in dynamic viscosity at all studied temperatures. In any case, the rises are not particularly significant since differences between the viscosity values of both fluids are lower or equal to 0.8%. Figure 4 plots the obtained dynamic viscosities of the studied nanofluid samples as a function of the temperature.

As it can be observed, dynamic viscosity decreases when the temperature increases for all the nanoadditive mass concentrations. In this case, the decreases reach up to 40% for the base fluid and 32% for the 1.0 wt.% GnP concentration in the analysed temperature range. Furthermore, as expected dynamic viscosity increases with nanoadditive concentration. The aforementioned increments reach maximum values of 20% for the 1.0 wt.% concentration. However, it should be noted that these increases are much lower than those achieved with other types of graphene nanoplatelets [9].

**CONCLUSIONS**

In this work it is experimentally determined the thermophysical profile of different loaded samples consisting of polycarboxylate chemically modified graphene nanoplatelet dispersions, up to 1.0 wt.%, in an industrial antifreeze coolant, Havoline XLC Premixed 50/50, widely used in wind turbines for the cooling of generators. To ensure the samples stability, SDBS at 0.125 wt.% with respect of the coolant was added. Densities, heat capacities and thermal conductivities were experimentally determined in the temperature range from (293.15 to 343.15) K, whereas the rheological behaviour was studied in the temperature range from (293.15 to 323.15) K.

Regarding the base fluid without surfactant, all the thermophysical properties are similar to those of a mixture of ethylene glycol and water at 50:50 vol.%, with the exception of dynamic viscosity, more affected by the additional additives of the commercial mixture.

Apropos of nanofluids, density increments rise with the increasing temperature up to 0.58% in the analysed temperature range. Furthermore, heat capacity increases with the increasing temperature up 7.7%. Regarding the rheological analysis, nanofluids showed Newtonian behaviour in the analysed shear rate range. Viscosity increments with the increasing loading of nanoplatelets reach up to 20%. Thermal conductivity enhancements reach up to 7.3% with the loading of nanoadditive, pointing to good expectations for the improvement of the performance of forced convection processes in wind turbine cooling systems.

**ACKNOWLEDGEMENTS**

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