Energy Conversion and Management 101 (2015) 767–777

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Synthesis of ethylene glycol-treated Graphene Nanoplatelets with one-pot, microwave-assisted functionalization for use as a high performance engine coolant

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ARTICLE INFO

Article history:
Received 27 March 2015
Accepted 5 June 2015
Available online 23 June 2015

Keywords:
Graphene Nanoplatelets
Microwave-assisted functionalization
Ethylene glycol
Coolant
Car radiator

ABSTRACT

An electrophilic addition reaction under microwave irradiation was developed as a promising, quick and cost-effective approach to functionalize Graphene Nanoplatelets (GNP) with ethylene glycol (EG). EG-treated GNP was synthesized to reach a promising dispersibility in the water–EG media without negative effects of acid-treatment. Surface functionality groups and the morphology of chemically-functionalized GNP were characterized by the vibration spectroscopies, temperature-programmed study, and microscopic method. Despite the fact that the main structures of GNP were remained reasonably intact, characterization results consistently verified the functionalization of GNP with EG functionalities. As new kinds of high-performance engine coolant, the EG-treated GNP based water–EG coolant (GNP-WEG) was prepared and its thermo-physical and rheological properties are evaluated. In particular, the thermal conductivity, viscosity, specific heat capacity, and density of all samples were experimentally measured to evaluate the thermal performance of the GNP-WEG coolant. The data showed insignificant increases in the pressure drop at different temperatures and concentrations, low friction factor, lack of corrosive condition, and the performance index larger than 1. In addition, no momentous change in the pumping power in the presence of GNP-WEG confirmed that it can be an appropriate alternative coolant for different thermal equipment in terms of economy and performance.

1. Introduction

Developing highly efficiency engines has been a major goal of automotive industries over the last several decades. Enhancing the thermal efficiency for optimizing the size of radiators or heat exchangers for decreasing the vehicle weight was reported in [1–3]. Different approaches such as addition of fins, use of micro-channels and high speed fans have been utilized [4]. However, many of the conventional methods for increasing the cooling rate by the above-mentioned approaches have faced certain limitations [5]. Furthermore, base-fluids such as water and ethylene glycol (EG), which are commonly used as coolant in engines, have poor thermal conductivity, that reduce the engine performance [6]. In order to enhance the heat transfer rate in car radiators, high-performance heat transfer fluids can be used. This approach can provide an innovative technology for solving problems that are caused by fluids that has poor thermal conductivity.

To improve the heat transfer properties of base-fluids addition of different particles has been suggested as a technique to enhance the heat transfer rate [7–12]. Since the thermal conductivity of metal and carbon based nano-particles are significantly higher than the conventional base-fluids, their suspension can significantly increase the effective thermal properties of the working fluids [13–15]. Recently along this line, a new class of fluid mixtures containing nanostructures has been introduced to overcome the issues caused by low thermal conductivity of coolants [16–18]. After introducing nanofluids by Choi [19], many scientists studied the effect of nanoparticles loading on the enhancement of effective thermal conductivity and heat transfer rates of various base-fluids. Numerous nanoparticles such as copper oxide (CuO), and aluminum oxide (Al_2O_3), TiO_2, and carbon based-nanostructures like graphene, fullerene and carbon nanotubes (CNTs) have been used to prepare nanofluids for enhancing thermal properties [20–24].

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http://dx.doi.org/10.1016/j.enconman.2015.06.019
0196-8904/

Nomenclature

C_p	specific heat (J/g K)
D	diameter (m)
h	heat transfer coefficient (W/m^2 K)
K	thermal conductivity (W/m K)
L	tube length (m)
m°	mass flow rate (kg/s)
Nu	Nusselt number
Pr	Prandtl number
q	heat flux (W/m^2)
Q	heat transfer rate (W)
Re	Reynolds number
T	temperature (°C)
U	velocity (m/s)
A	cross section of the tube (m^2)
f	friction factor
n	number of tube passes
G	mass velocity (kg/m^2 s)
W	pumping power

Greek symbols

ρ	density (kg/m^3)
μ	viscosity (Pa s)
ε	performance index
Δp	pressure drop (Pa)
η	efficiency of radiator

Subscripts

bf	basefluid
nf	nanofluid
p	particles
w	tube wall
in	inlet
out	outlet
b	bulkfluid

Lee et al. [25] experimentally studied the thermal conductivity of alumina–water, alumina–EG and CuO–EG. They reported about 23% enhancement in the thermal conductivity of EG in presence of CuO. Murshed et al. [26] investigated the thermal conductivity of TiO_2-based water nanofluids. Their results suggested that there was a nonlinear trend between thermal conductivity and volume concentration of nanoparticles. Jha and Ramaprabhu [27] investigated the influence of well-dispersed copper nanoparticles-loaded multi-walled carbon nanotubes (Cu–MWCNTs) in deionized water (DI water) and Cu–MWCNTs in EG on the thermal conductivity and reported a marked enhancement at a very low volume fraction, which attributed to the homogeneous dispersion of Cu–MWCNTs in the base-fluids and formation of hydrophilic MWCNTs. In similar study, the thermal conductivity and heat transfer enhancements of MWCNTs-based water nanofluids were investigated and a noticeable enhancement was reported that was attributed to the thinning of the thermal boundary layer by MWCNTs and reducing the thermal resistance [28,29]. However, among various carbon-based nanostructures, graphene-family nano-materials (GFN) appears to over more potential due to their attractive thermal, electrical and mechanical properties [6,30,31]. In fact, GFN has found many applications including its use as high-performance coolant. A number of theoretical and experimental studies showed that GFN has a rather high thermal conductivity [32,33], indicating its superb potential for as an effective coolants for applications in thermal equipment such as thermosyphone and car radiators [6,30]. Recently, large-scale production of GNP via ball milling method provided the opportunity for their use in many industrial applications.

To fully utilize the thermal performance of GFN, it is essential to address the follow issues:

i. Lack and trivial interaction between GFN and other materials due to strong intertube van der Waals interactions.
ii. Generating highly dispersed GFN are quite expensive; therefore its usage may not be cost-effective.
iii. In order to synthesize highly dispersed GNF in the organic solvents, conventional covalent functionalization methods involves multiple steps and are generally time-consuming.
iv. Carboxylic groups have been commonly employed as the covalent functional group or bridge for attaching other functioned groups, but these linkages are a source of new problems such as corrosion (oxidation–reduction) and introducing defects.

To our knowledge, the earlier studies have not been able to address all of the aforementioned issues. Here, a promising, potentially industrially scalable, cost-effective functionalization approach is introduced for preparing ethylene glycol-treated Graphene Nanoplatelets (EG-treated GNP) as well as EG-treated GNP based water–EG coolant (GNP-WEG). Clearly EG is an organic compound, which has been primarily used as a cooling liquid in car radiators and employing it as functional groups decorated on GNP can provide some advantages such as lack of corrosion potential and excellent dispersibility in the radiator coolant mixture (both water and EG media). The EG-treated GNP samples are then analyzed from the viewpoint of functionality, and morphology. The introduced methodology also does not involve acid treatment, to avoid the issue of carboxylic acid formation and corrosion.

2. Material and methods

2.1. Chemical-assisted functionalization and preparation of EG-treated GNP based nanofluids

Fig. 1 illustrates the experimental procedure for chemical-assisted functionalization of GNP. In a typical experiment, the pristine GNP (0.5 g) and $AlCl_3$ (9.27 g) were first poured into a planetary ball-mill container, fixed and agitated at 500 rpm for 1 h. The resultant mixture was then transferred into a Teflon vessel filled with 80 ml of anhydrous EG and sonicated for 15 min with a probe-sonicator to attain a relatively homogeneous suspension. The concentrated hydrochloric acid (1 ml) was added drop by drop into the vessel over sonication time. The suspension was then sealed and placed in an industrial microwave (Milestone MicroSYNTH programmable microwave system), followed by irradiating at 150 °C for 15 min. The reaction mixture was then filtered through a PTFE membrane and followed by washing with abundant DI water to eliminate any unreacted materials and then dried for 48 h at 50 °C. The EG-treated GNP was much more soluble in both water and EG than the pristine GNP. The easily-miscible EG functionalities can explain a significant increase in dispersibility of the functionalized GNP with EG in both media of water and EG.

To synthesize the EG-treated GNP based water–EG coolant (GNP-WEG), the EG-treated GNP was sonicated with a volumetric ratio of 40:60 mixture of water and EG as a base-fluid for 10 min. The GNP-WEG was synthesized at the weight concentrations of 0.01%, 0.05%, 0.1% and 0.2%.