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Development of nanolubricant based on impregnated multilayer graphene for automotive applications: Analysis of tribological properties

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ABSTRACT

This paper shows novel formulations of nanolubricants added with multi-layer graphene (MLG), multi-layer graphene impregnated with copper (MLG-Cu), and multi-layer graphene impregnated with polyaniline (MLG-PANI) for applications in automotive engines. These nanofluids were prepared using commercial motor oil as the base fluid. The tribological properties were measured at 100 °C, and significant reductions were found in the coefficient of friction and wear. The concentrations used were 0.5% and 2% by weight, obtaining reductions in the friction coefficient and wear of up to 43% and 63%, respectively, in the case of motor oil with copper-impregnated graphene. All formulations of MLG, MLG-Cu, and MLG-PANI did not show any sedimentation when dispersed in engine oil, even three months after being produced.

1. Introduction

Lubricants are mainly used to eliminate contact between two parts in a sliding movement. The main applications of lubricants are focused in internal combustion engines, vehicle and industrial gearboxes, compressors, turbines, and hydraulic systems, where engine oil applications represent approximately 50% of the global market [1]. Engine oils contain many additives in order to effectively and efficiently accomplish their functions. Some commonly used additives are antioxidants, detergents, dispersants, friction modifiers, anti-wear, viscosity modifiers, pour point depressants, tackifiers and antimisting, corrosion inhibitors, etc. [2].

Because conventional additives fail at high temperatures (>200 °C) and pressures (>5000 psi), extreme pressure (EP) and anti-wear (AW) additives are needed. However, these types of materials are expensive and environmentally hazardous. In addition, EP additives have many technical limitations, such as ineffectiveness at slow speeds and low temperatures, high reactivity and corrosivity in contact with water, very limited operation at high temperatures, etc. [3] Due to the above reasons, there is a need to find new types of additives that are cost-effective and environmentally friendly [3]. Recently, it has been reported that metallic nanoparticles added to lubricant oils (nanolubricants) are able to act as anti-wear additives under extreme pressure [4]. These metallic nanoparticles are non-corrosive and are capable of working at very high temperatures. Therefore, they are very promising for establishing a new era of AW and EP additives [5,6].

The main advantage of using nanoparticles as additives is that they are not degraded or modified with the temperature. Moreover, due to the small size of these particles, clogging problems are avoided in lubrication systems [5].

Friction and wear, i.e., two of the main causes of material failure, have attracted more and more attention all over the world. Advances in nanotechnology have allowed the dispersion of nanoparticles in fluids without encountering sedimentation problems [5,7,8]. Numerous studies have been conducted on improving the tribological properties of certain lubricant fluids by the addition of nanoparticles. Nanoparticles that have been used include graphite [9,10]; nickel [5]; nanodiamond [11]; boron nitride [12]; CuO [13]; fullerene [14]; silica, titanium dioxide, alumina, tin dioxide, magnesium oxide, cerium oxide, zirconia, and mixtures thereof [15]; molybdenum disulfide, tungsten disulfide, and calcium oxide [16]. In particular, carbonaceous nanoparticles, such as graphene, CNTs, fullerenes, etc., are the most studied [9–11,14,15,17] due to large improvements in the wear and a friction coefficient reduction [18].

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Table 1
Nanofluids used in lubricant applications.

Nanoparticle	Base fluid	Size (nm)	Wear reduction (%)	Friction reduction (%)	Concentration	
CuO	GO, PAO	40		45	0.005–2 vol.%	[2,5,13]
Graphene	LO	500	20–68	40–70	0.001–30 wt.%	[18]
Graphite	LO	500			1–30 wt.%.	[9,10,16]
CNT MWNT, fullerene, diamond	EO, GO	200	40–50	10–55	0.001–30 wt.%	[9–11,14,15,17]
BN h-BN	PAO, GO	150	15	20	1 wt.%	[1,7,12,19]
TiO_2, Al_2O_3, SiO_2, MoO_2	LO, EO	40–100			0.01–10 wt.%	[10,15,16]

GO = gear oil; LO = lubricant oil; EO = engine oil; PAO = polyalphaolefine.

Some of the recently published articles and patents related to nanolubricants are listed in Table 1.

Gulzar et al. [6] improved the anti-wear (AW) and extreme pressure (EP) abilities of chemically modified palm oil (CMPO) by adding CuO and MoS_2 nanoparticles at low filler contents (1 wt.%). The morphology of the CuO nanoparticles was fairly spherical, with particle sizes between 50 and 300 nm. The particles of the MoS_2 powder had larger sizes, ranging from 50 to 2000 nm. The AW/EP properties of the formulations were evaluated by four-ball and sliding wear tests. The wear scar diameter reductions at 120 kg loading were 6.65% and 11% for CMPO + 1% MoS_2 and CMPO + 1% CuO, respectively. An average reduction of 16.6% at loads higher than 80 kg was achieved with the wear scar diameters. This reduction was higher than that achieved (10%) at a lower load range.

Chen et al. [17] presented a study of a nanofluid based on multi-wall carbon nanotubes (MWCNTs) dispersed in pure liquid paraffin at a concentration of 0.45 wt.% MWCNTs, where the nanotubes were surface modified by means of oxidation via refluxing in stearic acid (SA). The maximum friction and wear reduction reported were approximately 10% and 40%, respectively.

Madhusree et al. [20] experimented with a nanofluid in order to improve the viscosity behavior. They used spherical CuO nanoparticles with diameters of 40 nm and gear oil as the base fluid. The CuO volume fraction was between 0.005 and 0.025, and the prepared nanofluids were stabilized by adding oleic acid (surfactant). The prepared nanofluids did not show any visual sedimentation of CuO nanoparticles, even after keeping the fluids stationary for >30 days. By increasing the CuO nanoparticle content to >0.025 wt.% at 30 °C, the nanofluid viscosity was enhanced by nearly three times compared to the gear oil viscosity.

Chou et al. [21] presented a study of a nanofluid based on Ni nanoparticles dispersed in polyalphaolefin (PAO6) as the base oil. Ni nanoparticles were dispersed in the lubricant at concentrations of 0.5, 1, and 2 wt.%. The suspension with 0.5 wt.% exhibited the best tribological behavior, i.e., 54% wear reduction, and the worst performance was found for the 2 wt.% suspension, which gave a 5% wear reduction.

Hernández et al. [13] and Madhusree et al. [22] reported a nanofluid formulation using spherical CuO nanoparticles dispersed in gear and PAO oil for improving lubrication properties. CuO nanoparticles were evaluated in the range between 0.005 and 2 wt.% of the filler content.

Zhamu et al. [18] patented a nanolubricant-based multi-layer graphene (MLG) dispersed in the lubricant fluid. The content of MLG ranged from 0.001 to 75 wt.%, with an average thickness <10 nm and length or width <500 nm. Compared with graphite or carbon nanotube-modified lubricants, MLG-modified lubricants exhibited much better thermal conductivity, friction-reducing capability, anti-wear performance, and viscosity stability.

Most of the earlier studies focused on thermophysical properties of nanofluids based on single nanoparticles, and in particular, graphene-based nanofluids provided the best results [23]. However, the synthesis of hybrid nanofillers and the preparation of nanofluids based on hybrid nanofillers to evaluate their synergistic effects are still very new areas of research. Two examples of the preparation of water-based nanofluids with hybrid nanofillers are the addition of graphene-copper oxide (GNP-CuO) [23] and graphene-silver (GNP-Ag) [24]. In both types of nanofluids, water was the base fluid, and only thermal and rheological properties were evaluated. Therefore, it will be interesting to analyze the behavior of hybrid nanofillers dispersed in oil to evaluate their capabilities as nanolubricants.

In this work, the tribological properties of metallic nanoparticles with a spherical shape (Cu) and polymer nanoparticles with a tubular shape (PANI), in synergy with multi-layer graphene, dispersed in a commercial engine oil (EO), were evaluated. All experiments were conducted at 100 °C because this is very close to the temperature at which vehicle engines work. Morphology analyses of multi-layer graphene (MLG), multi-layer graphene impregnated with copper (MLG-Cu), and multi-layer graphene impregnated with polyaniline (MLG-PANI) were conducted. Moreover, characterization of worn surfaces using MLG and hybrid nanofillers (MLG-PANI and MLG-Cu) was conducted. Finally, the stability of nanoparticles in the base fluid was analyzed.

2. Experimental details

2.1. Materials

Commercial graphite powder (<20 μm) was utilized as the graphene precursor. The base fluid was a commercial engine oil (SAE 25 W-50).

Sulfuric acid with a purity of 95–98%, nitric acid with a purity of 68.0–70.0%, potassium chloride with a purity ≥99.0%, aniline with a purity of 99.5%, ammonium persulfate with a purity of >98%, hydrochloric acid with a purity of 37%, tetraamminecopper (II) sulfate monohydrate, and ammonium hydroxide solution were used as reagents.

2.2. Materials preparation

2.2.1. Synthesis of MLG

Graphite powder was oxidized using a modified Staudenmaier's method to produce graphite oxide (GO) [26–28]. In this work, graphite

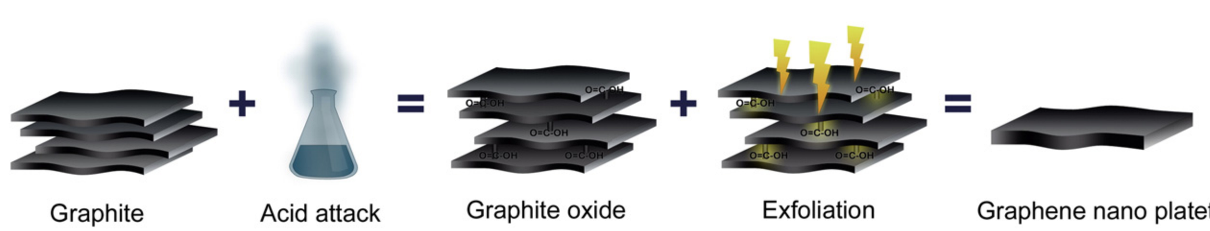

Fig. 1. MLG chemical exfoliation process.