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Thermophysical and tribological properties of dispersions based on graphene and a trimethylolpropane trioleate oil

José M. Liñeira del Río [a], María J.G. Guimarey [a], María J.P. Comuñas [a], Enriqueta R. López [a,*], Alfredo Amigo [b], Josefa Fernández [a]

[a] Laboratory of Thermophysical Properties, Nafomat Group, Department of Applied Physics, Faculty of Physics, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain
[b] Laboratory of Thermophysical and Superficial Properties of Liquids, Department of Applied Physics, Faculty of Physics, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain

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ABSTRACT

The objective of this work is to study the tribological and thermophysical properties of nanolubricants composed by a trimethylolpropane trioleate (TMPTO) oil, and graphene nanoplatelets (GnP). For this aim, nanolubricants based on TMPTO with 0.05, 0.10, 0.25 and 0.50 wt% of graphene nanoplatelets were prepared. The dependence on temperature and concentration of the viscosity, density and speed of sound was determined by means of a rotational viscometer and two mechanical oscillation densimeters. Likewise, the antifriction and antiwear properties of these nanolubricants were analyzed. For this purpose, tribological tests were carried out at room temperature in a tribometer operating in ball on plate configuration and in reciprocating mode under a working load of 2.5 N. A 3D optical profilometer was used to analyze the wear track through the width of the scar. As regards thermophysical behavior of density and viscosity, both increase as the concentration of nanoparticles increases, whereas the speed of sound slightly diminishes when the GnP concentration increases. The best antifriction-antiwear performance was obtained for the nanolubricant containing 0.25 wt% in GnP.

1. Introduction

With the advent of nanotechnology, new nanomaterials have been the aim of research as lubricant additives because of their unusual properties [1–5]. There are many different types of nanomaterials with potentially interesting antifriction and antiwear properties [1, 2, 6–9]. Among them, different carbon-based nanomaterials are being subject of interest [2]. In this regard, in recent years graphene is object of research as lubricant additive because it has much better thermal conductivity, reduced friction capacity and anti-wear properties compared to those of other nanoadditives [10, 11]. The most remarkable progress on graphene based nanofluids and nanolubricants has been recently collected in a review [11]. The first conclusion of this review is that graphene nanoflakes can significantly enhance the thermophysical and tribological properties of base oils and coolants. Nevertheless, the authors point out that in order to understand the interaction of graphene flakes with contact surfaces, detailed tribological studies are required [11].

Graphene nanoplatelets (GnPs) are carbon nanostructures consisting of small stacks of graphene sheets, having thickness in the range from 1 nm up to a few tens of nanometers, and lateral linear dimensions varying from a few micrometers up to hundreds of micrometers [12]. Most of the research involving dispersions of GnPs are focusing in the field of heat transfer [11, 13], thus the property most studied is the thermal conductivity. Literature on viscosity is scarce. Moghaddam et al. [14] reported rheological properties of graphene-glycerol nanofluids, finding that the viscosity of the nanofluids rises with the increase of graphene mass fraction. These authors also found a very strong shear thinning behavior. Dhar et al. [15] found that the viscosity of nanosuspensions of graphene nanosheets in water increases with concentration and decreases with temperature. Mehrali et al. [10] studied the rheological behavior of dispersions of GnPs in distilled water. Sadeghinezhad et al. [16] analyzed the temperature and concentration dependences of the viscosity of aqueous dispersions of GnP; from their work it is shown that viscosity increases with the loading of the GnP nanoparticles due to the increase in friction and flowing resistance of fluids. Azman et al. [17] evaluated the effects of GnPs as additives in palm-oil trimethylolpropane (TMP) ester blended in polyalphaolefin, finding that the increase in the GnP concentration resulted in increasing values of viscosity, density and viscosity index. Vakili et al. [18] determined the viscosity of nanofluids containing GnP and deionized water from 20 to 60 °C, at concentrations ranging from 0.025 to 0.10 wt% of GnP finding also that viscosity increases when GnP concentration rises. Iranmanesh et al. [19] investigated the effect of GnP/distilled water nanofluids on the thermal performance of evacuated tube solar collector in solar-water heater systems. For this purpose, these authors measured physical and thermal properties of

* Corresponding author.
E-mail address: enriqueta.lopez@usc.es (E.R. López).

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the GnP nanofluids including viscosity. The results showed Newtonian behavior. At constant temperature, viscosity rises with GnP concentration, which the authors attribute to the increase of the resistance of the fluid flow due to the high specific surface area of the GnP nanosheets. Rashmi et al. [20] have found viscosity increases up to 168% for dispersions of GnP in an additivated palm oil trimethylolpropane ester lubricant.

As regards the tribological behavior of nanolubricants containing GnPs, Eswaraiah et al. [21] prepared ultrathin-graphene based engine oil nanofluids evaluating their frictional characteristics, antiwear, and extreme pressure properties, obtaining improvements compared with the base oil of 80%, 33%, and 40%, respectively. Bernan et al. [22] found that small amounts of few-layer-graphene-containing ethanol solution strongly decreased wear and friction coefficients respect to neat ethanol. Guo and Zhang [23] investigated multi-layered graphene (5–8 layers) as additive of a polyalphaolefin (PAO_2), with a four-ball test method, finding that the friction reduction and anti-wear ability of pure lubricant was improved, showing the 0.05 wt% graphene dispersion the better tribological properties. Azman et al. [17] also obtained that the addition of 0.05 wt% GnP in blended lubricant resulted in both lowest coefficient of friction and wear scar diameter, with reductions of 5 and 15% respectively, comparing with the blended lubricant. Rasheed et al. [24] studied nanolubricants formulated using graphene nanoflakes and two engine oils found that the addition of 0.01 wt% graphene to one of these oils results in 23% enhancement and 21% reduction in thermal conductivity and in the friction coefficient, respectively. Wu et al. [25] investigated, using a four-ball testing machine, the tribological behavior of two types of tribopairs (Si_3N_4/GCr15, GCr15/GCr15) lubricated with an aviation lubricant with few layer graphene as additive. For the second tribopair these authors found that the friction coefficient and the wear scar diameter decreased 25% and 39%, respectively, with the addition of 0.05 wt% to the neat oil. The addition of 0.075 wt% in the same neat oil resulted in the reductions of friction coefficient and wear scar diameter of 27% and 43%, respectively. Rashmi et al. [20] achieved a maximum reduction of 7% and 16% for the coefficient of friction and the wear scar diameter, respectively, with the introduction of 0.05 wt% of GnPs in the additivated palm oil trimethylolpropane ester. Finally, Kiu et al. [26] studied the effect on tribological properties of the addition of carbon-based nanoparticles as lubricant additives of a vegetable oil; the nanoparticles investigated were graphene nanosheets (GN), carbon nanotubes, and graphene oxide. The results showed that the most positive effect in improving the tribological properties of the neat oil is obtained with the addition of 50 ppm GN.

In this paper we have characterized thermophysical properties of nanodispersions based on GnP and an ester type lubricant: a trimethylolpropane trioleate (TMPTO) based oil. This ester has excellent lubricating properties [27], high viscosity index [28], is nonflammable and biodegradable in an 80% or more [29]. For this purpose, densities, viscosities and the speed of sound in the different dispersions have been measured at atmospheric pressure as a function of temperature. In addition to evaluate the antifriction and antiwear properties of the dispersions, tribological test were performed under a load of 2.5 N.

2. Experimental section

2.1. Materials

The base oil used in this work was kindly provided by Croda. The sample was characterized by infrared spectroscopy (IR). This oil can be identified as trimethylolpropane trioleate (TMPTO, CAS: 57675-44-2), its chemical structure is shown in Fig. 1. The FTIR spectrum of TMPTO (Fig. 2) shows a strong peak at 1741 cm^{-1}, which can be assigned to the stretching vibration of ester carbonyl (C═O), a peak at 1157 cm^{-1} which corresponds to (C—O—C) single bond stretching vibration, a peak at 722 cm^{-1} due to the alkyl chains of TMPTO and peaks

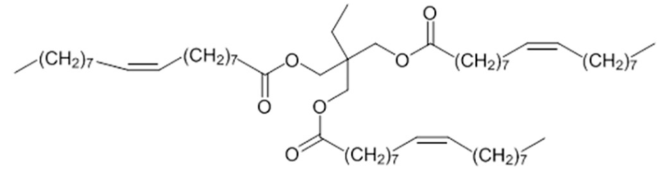

Fig. 1. Trimethylolpropane trioleate structure.

of carbon–hydrogen (C—H) stretching and bending which are observed at 2922–2853 cm^{-1} and 1463 cm^{-1} [30, 31].

In addition, the base oil was also characterized by means of high performance liquid chromatography, HPLC, coupled to a *quadrupole orthogonal acceleration time*-of-*flight mass spectrometer* (*micrOTOF-Q*™) equipped with an electrospray ionization source (ESI). The sample was dissolved in isopropanol (5:200) and analyzed by isocratic mode, being the injection volume 5 μL. The time of the analyses was 30 min, with a flow of 0.7 mL/min and using methanol and isopropanol in 0.1% like aqueous phase. The chromatogram (Fig. 3) shows three identified peaks that correspond to the components of the sample, and others that correspond to the pattern sample analysis. The mass spectrum (Fig. 4) of the majority compound, corresponding to peak 3, shows that the mass of the molecular ion coincides with that of TMPTO (molecular mass 927.51 $g \cdot mol^{-1}$). The mass spectra of the other two components of the oil (Figs. S1 and S2 of the Supplementary Information) indicate that their molecular masses are around 925 and 923 $g \cdot mol^{-1}$. Taking into account these results and the FTIR spectrum we can conclude that the second and third compounds of the base oil have the same structure as TMPTO but with two and four hydrogen atoms less, this fact could correspond to one (peak 2) or two (peak 1) C═C bonds instead C—C bonds. Therefore, our base oil is composed by 68.3% of TMPTO, 27.6% of a compound with a C═C bond more than TMPTO and a 4.1% of a compound with two C═C bonds more than TMPTO.

Graphene nanoplatelets (GnP, CAS number 1034343-98-0) of a purity of 99.5% with an average particle diameter of 15 μm and of 11–15 nm of thickness, were provided by Iolitec. In order to analyze their morphology and size, the nanoplatelets were characterized by both transmission and scanning electron microscopy (TEM and SEM). SEM micrographs were taken with a Zeiss Ultraplus Field Emission Scanning Electron Microscope, FESEM. TEM images were carried out with a JEOL JEM-2010 equipment; for this purpose, nanoparticles were dispersed in 1-butanol. Detailed images of the specimen are shown in Figs. 5 and 6. The appearance of GnP shows that platelets are bended and wrinkled.

The FTIR spectrum (Fig. 7) shows a peak at 3333 cm^{-1} which is attributed to O—H stretching vibrations, an absorption peak at 2920 cm^{-1} indicating the C—H stretching, and a weak peak at 1658 cm^{-1}, which refers to C═O stretching vibrations. A quite wide and intense peak appears at 1453 cm^{-1} which corresponds to O—H bending vibrations. Several absorption peaks were observed at around 1152 to 1024 cm^{-1}, indicating the presence of C—O stretching of alcohol [32, 33]. Therefore, due to the nature of the graphene borders, one of the major impurities are oxygen-containing groups. Carbonyl and hydroxyl groups are usually impurities due to the reaction synthesis of GnP [33]. EDX analysis shows an atomic composition of GnP with more than 95% carbon.

Raman spectroscopy in the visible range, specifically at a wavelength of 514 nm, was used in order to characterize the graphene nanoplatelets (Fig. 8), since this technique is a powerful non-destructive tool to characterize carbonaceous materials. The typical characteristics for graphene carbon in Raman spectra for visible excitation are the D-band which lies at 1350 cm^{-1}, the G-band around 1580 cm^{-1} and the second order of the D-band (2D) which is also called G′-band and appears around 2700 cm^{-1} (Fig. 8). All of these bands can change in shape, position, or relative intensity and so reflect the evolution of the