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## DRAFT

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### VISCOSITY AND TRIBOLOGY OF COPPER OXIDE NANOFLUIDS

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#### INTRODUCTION

Nanofluids, a term proposed by Choi in 1995 [1], are composites consisting of solid nanoparticles with sizes varying generally from 1 to 100 nm dispersed in a liquid. Numerous nanoparticles used as oil additives have been investigated in recent years [2-7]. Results show that they deposit on the rubbing surface and improve the tribological properties of the base oil, displaying good friction and wear reduction characteristics even at concentrations below 2% wt.

Although the viscosity of the nanofluids is a property of crucial importance for film forming, and hence friction and wear reduction, which are characteristic of lubricants, only Hwang et al. [8] have studied thermal characteristics, kinematic viscosity and tribological properties of nanofluids simultaneously. In this paper, we present measurements of dynamic viscosity of nanofluids formed by copper oxide nanoparticles dispersed in a polyalphaolefin, for temperatures and concentrations varying from 20 to 60°C and 0.5 to 2% wt., respectively. Dependence of the nanofluid viscosity to the solid fraction and temperature was compared with existing models and its influence on lubrication was also analysed.

#### **EXPERIMENTAL DETAILS**

In our experiments, we used copper oxide nanoparticles supplied by Nanostructured & Amorphous Materials Inc. [9]. The main properties of the nanoparticles are: purity of 99%, nearly spherical, and 30-50 nm in size. The polyalphaolefin has a viscosity of 5.90 cSt at 100°C and 31 cSt at 40°C. CuO nanoparticles were separately dispersed in the lubricant (polyalphaolefin, PAO6) in concentrations of 0.5-1.0-2.0% wt.

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using an ultrasonic probe for 30 minutes that ensures uniform dispersion of nanoparticles in the base fluid. Sample preparation was carried out using a very sensitive mass balance with an accuracy of 0.1 mg. The concentrations of 0.5, 1.0 and 2.0% wt. in the nanofluids correspond, using the apparent density of nanoparticles, with a volume concentration of 0.52, 1.04 and 2.09%.

The rheological property measurements of the nanofluids was done with a Physica RHEOLAB MC1 programmable rheometer controlled with a computer and using the software US200, which collects speed, torque, viscosity, shear stress, shear rate, temperature and time. All the viscosity measurements were recorded at steady state conditions. The rheological properties were determined over a shear rates and temperatures ranging 1-700 s<sup>-1</sup> and 20-60°C, respectively.

Wear testing was undertaken using a TE53SLIM friction and wear testing machine set for pure sliding contact, with a block-on-ring configuration. Test blocks of 12.7 mm AISI 1045 steel cubes with a hardness of about 31 HRC were run against a 60 mm-diameter AISI D3 steel counterface ring, hardened in the range 65-66 HRC. All tests were run for a total distance of 3066 m. at a sliding speed of 2 m/s and a load of 165 N applied via a cantilever. Through preliminary tests was proved that these test conditions correspond to the region of mixed lubrication on the Stribeck curve. Two tests were conducted for each suspension at this load, and wear was quantified by weight loss ( $\pm$  0.1 mg). The friction coefficient was recorded throughout each test and wear surfaces on blocks were characterised by SEM and EDS.

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#### RESULTS

The first step was to verify if the base oil and the nanofluids behave in a Newtonian or non-Newtonian manner. The equation governing Newtonian behaviour of a fluid is given by:

$$\tau = \eta \dot{\gamma} \tag{1}$$

where  $\tau$  is the shear stress,  $\eta$  is the coefficient of viscosity and  $\dot{\gamma}$  is the shear strain rate. All nanofluids and base oil demonstrate Newtonian behaviour for all nanoparticles concentration and temperatures.

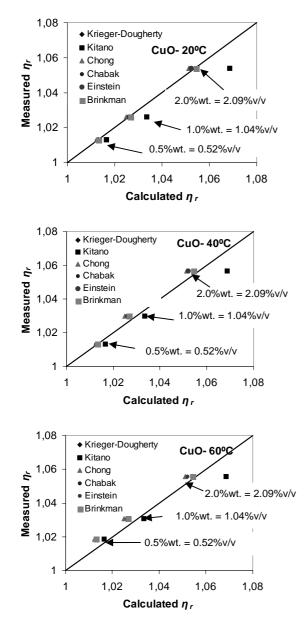


Fig. 1 The viscosity comparison of various models with the experimentally measured ones for copper oxide nanofluids.

Fig. 1 shows the comparison of the predictive  $\eta_r$  and the experimentally measured  $\eta_r$  for each nanofluid at different temperatures and volume concentrations.  $\eta_r$  is the relative viscosity and can be calculated as  $\eta_s/\eta_f$ , where  $\eta_s$  is the suspension viscosity and  $\eta_f$  is the viscosity of base fluid.

All the used models give a reasonable approximation of the rheological data for uniform-sized colloidal suspension with spherical geometry of the particles over the studied volume concentration range  $\phi = 0.5-2.0\%$ . The deviation observed for Kitano's model for 2% volume concentration is only of 1.2% with regard to measured value. It can be also observed that nanofluid viscosity rise between 1.8% for  $\phi = 0.5\%$  and 5.5% for  $\phi = 2.0\%$  with regard to base oil at a temperature of 60°C, so we can expect a positive viscosity contribution of these nanofluids on tribological behaviour at that temperature.

Although the rheological measurements were made up to shear rates of 700 s<sup>-1</sup>, the results of recent similar works [10], where nanofluids were tested up to  $10^4$  s<sup>-1</sup>, showed that in semidilute nanofluids (volume concentration up to 5%) appear some degree of nanoparticles aggregation, the shear viscosity fits the modified Krieger–Dougherty equation and there is no obvious shear-thinning behaviour. So, we can also insure that our results are valid up to these shear rates ( $10^4$  s<sup>-1</sup>).

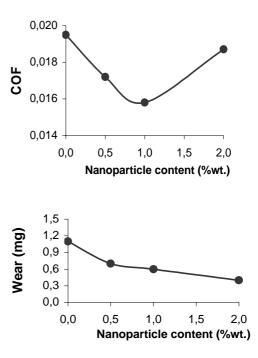


Fig. 2 Friction coefficient and wear behaviour as a function of nanoparticle concentration for all tested nanofluids.

The tribological results obtained with a block-on-ring tribometer using the same base oil and nanoparticles

concentration [11] showed that an increase of copper oxide concentration diminishes friction and wear. These results were attributed to nanoparticles deposition on wear surfaces but now we can state the viscosity contribution as well. Fig. 2 illustrates how all nanoparticle concentrations in PAO6 diminished the friction coefficient and wear compared to pure PAO6.

The antiwear mechanism of nanoparticulate additive can follow three different processes: the nanoparticles may be melted and welded on the shearing surface, reacted with the specimen to form a protective layer, or tribo-sintered on the surface [12]. This last option is the most likely one here and was also verified by Kato et al. [4] using nanometer-sized oxide nanoparticles as solid lubricant. In addition, Zhou et al. [13] showed that, when very fine metallic particles are employed, sintering starts as soon as the temperature increases above room temperature. However, the nanoparticles can also act as nano-bearings on the shearing surfaces. The above cited deposition mechanisms take place especially under mixed and boundary lubrication.

Analysis of the wear surfaces was done in order to detect a possible tribofilm formation. Although copper was detected in a percentage similar to nanoparticle concentration in the nanofluid, agglomeration or a uniform deposition of nanoparticles were not found on the wear surfaces.

#### CONCLUSIONS

- The additivation of a polyalphaolefin (PAO6) with copper oxides nanoparticles enhance the base oil viscosity even at low nanoparticles volume concentration. This enhanced viscosity, and not only the nanoparticle deposition on wear surfaces, can contribute to better tribological results.
- All the used models appear reasonably predicting the relative viscosity for uniform-sized colloidal suspension with spherical geometry of the particles over a concentration range  $\phi = 0.5-2.0\%$ .
- All nanofluids and base oil demonstrate Newtonian behaviour for all nanoparticles concentration and temperatures. Although the rheological measurements were made up to shear rates of 700 s<sup>-1</sup>, these results are also valid up to 10<sup>4</sup> s<sup>-1</sup>.
- All nanofluids exhibited friction and wear reduction compared to the base oil. However, friction and wear behaviour should both be taken into account when designing lubricants because both parameters can exhibit different tendencies depending on additive content.
- The antiwear mechanism of nanoparticulate additive was produced by tribo-sintering of nanoparticles on the wear surfaces, reducing metal-to-metal contact and acting as load

bearing areas. An increase of nanoparticle concentration in the base oil increases their deposition on wear surfaces.

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