

NANO GRAPHITE FLAKES AS LUBRICANT ADDITIVE

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The fundamental method of reducing friction and wear in metal to metal contact manufacturing processes like forging, extrusion, sheet metal forming etc. is based upon surface separation. The separation is usually obtained by adding different types of lubricants to the process. In this work, graphite nano platelets (GNp) powder has been used as a lubrication additive to explore and evaluate the influence on the frictional outcome. The experiments have been performed utilizing laboratory test equipment based on strip drawing. Three different lubricant systems are tested 'oil', 'oil-GNp' and GNp only. The result clearly shows that the specific type of nano-graphite used has a favorable effect of reducing the frictional forces both in mixture with a base oil and as a standalone coating.

Keywords: Nano graphite, Nano lubricants, Friction measurement, Tribotesting

1. INTRODUCTION

It is well known that lubrication can be classified into three different regimes according to Stribeck: boundary lubrication, mixed lubrication and hydrodynamic lubrication. The friction forces are particularly high in the boundary regime depending on the metal to metal contact which can give rise to harmful wear in many contact applications. To reduce the wear and improve the efficiency of these processes, better lubrication system must be developed.

Oil based lubricants are usually used in low- pressure/temperature applications and solid lubricants like graphite and molybdenum disulfide (MoS₂) are the predominant materials used during high pressure/temperature processes whereas liquid lubricants typically will not survive. The usage of solid lubricants can be directly as powder or thin films but it can also be used in bonded lubricants like in pastes or lubrication greases depending on application. The main advantages with solid lubricants are the high temperature properties and the high pressure resistance due to its lamellar structure which gives a high bearing load and a low shear stress during surface interaction. However, liquid lubricants are preferred or necessary in many manufacturing processes. In high friction processes like threading, hobbing, gear shaving etc. the lubricant acts not only as a friction reducer but also as a tool for removing chips and debris. The outcome of these processes is directly connected to the frictional state during processing and it is therefore important to find ways to improve the tribological process conditions to improve the efficiency of the processes.

Nanomaterials are attracting more and more attention within a wide range of applications including the use as an additive in industrial lubricants. Martin, *et al.* (2008) points out several potential applications in the tribological field and gives several examples of different nano-sized materials, for example carbon-based nanolubricants, boron-based solid nanolubricants and nanolubricants made of metal dichalcogenides. Tang, *et al.* (2014) have made an extensive review of the recent developments of friction modifiers and they stated that the combined

mechanisms of the friction modifier like excellent anti-wear, friction-reducing, extreme pressure and anti-oxidation properties will be the major focus areas in this field.

The interest in using carbon-based nanomaterials in tribological applications has drastically gained since the discovery of graphene, carbon nanotubes (CNTs) and fullerene. This is due to the materials excellent mechanical properties and their high chemical stability according to Stankovich, *et al.* (2006), Thostenson, *et al.* (2001) and Ku, *et al.* (2010). In this work, tribological evaluation in terms of frictional testing has been performed on graphite nanoplatelets (GNp) as an additive to oil based liquid lubricants. The friction tests have been carried out using a flat-die tribotester under different types of process conditions.

2. LUBRICANT MECHANISMS OF NANO ADDITIVE

The use of nanoparticles in lubricants for different applications has been thoroughly investigated in a number of papers, see (Lee, *et al.*, 1990; Huang, *et al.*, 2006; Shubrajit, *et al.*, 2013; Senatore, *et al.*, 2013, Kyung, *et al.*, 2011; Ingole, *et al.*, 2013; Flavio, *et al.*, 2014; Lou, *et al.*, 2014). Different materials, particle sizes and geometries have been used resulting in different influencing effects on the tribological system. The wear protective and friction reduction mechanisms during use of nano-sized additives can be addressed to mainly four different effects according to Figure 1, Tang, *et al.* (2014). The rolling effect, protective film build up, mending effect and polishing effect.

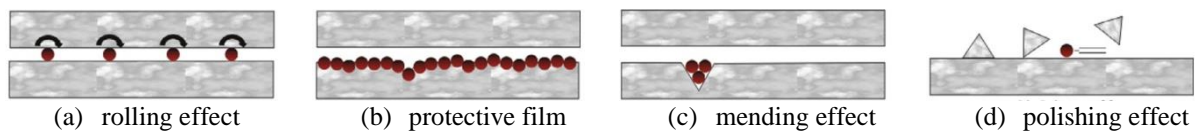
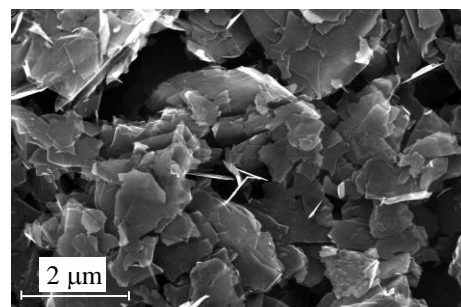
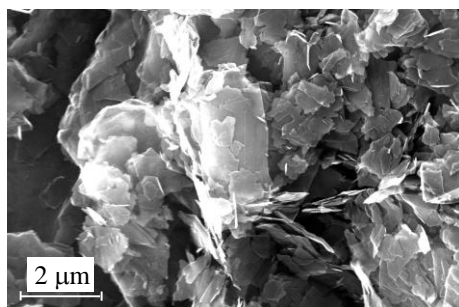


Fig. 1. Possible lubrication mechanisms of nanoparticles as friction modifiers according to Lee, *et al.* (2009), Tang, *et al.* (2014).

Two subgroups with similar resulting effects can be noted. The rolling- and protective effect, (a) and (b), can be extracted directly from the particles lubricant enhancement properties without chemical or mechanical surface reactions or modifications. The spherical nanoparticles are likely to roll between the friction surfaces and change the pure sliding friction to the mixed sliding-rolling friction. Regarding the protective film mechanism (b), the nanoparticles interact with the friction surfaces and forms a thin protective tribofilm, which have more favorable tribological properties compared to the base surface, and thereby reducing the friction and wear. The nanoparticles of mechanism (c) and (d) acts as surface enhancement. For the mending effect (c), the nanoparticles deposits on the friction surfaces and builds up physical tribo-layer to compensate for the loss of material. The polishing effect (d) improves the surface quality in terms of surface roughness due to the abrasiveness of the nano particles.

3. PREPARATION OF GRAPHITE NANO PLATELETS (GNp)

Graphite nanoplatelets preparation procedure was as follows. Natural flake graphite with an average diameter of 500 μm was used for preparing the exfoliated graphite. Concentrated sulfuric acid and potassium dichromate (chemically pure) were used as chemical intercalate and oxidizer to prepare graphite intercalation compounds GICs. The thermal expanded graphite (TEG) was obtained by the thermal shock of GIC powder in the oven at 1000°C during 15 sec. 95% (v/v) alcohol (chemical pure) and distilled water were used as solvents for preparation of graphite nanoplatelets (GNp). Then the mixture was subjected to ultrasonic irradiation by the ultrasonic dispenser with a power of 100, 250 and 350 W for the time of 4, 8 and 16 hours.



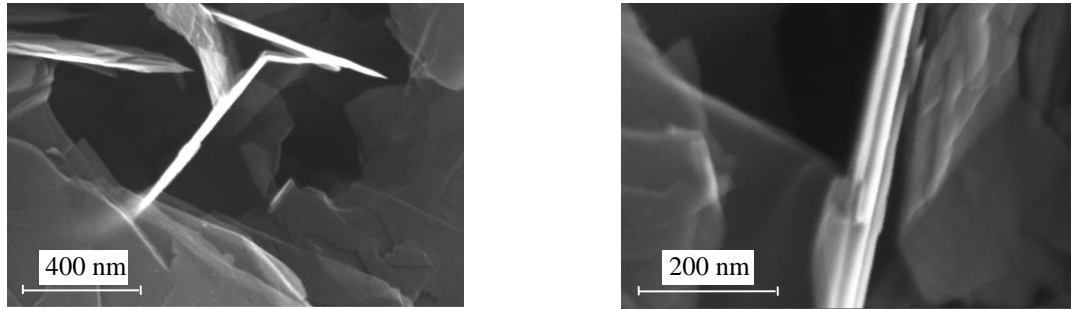


Fig. 2. SEM images of synthesized GNP at different magnifications.

After several hours of sonication, TEG particles were effectively fragmented into GNPs. Scanning electron microscopy analysis was performed with LEO-SEM 1530 microscope at accelerating voltage 10 kV. SEM images of nano-sized graphite powder produced by sonication at $P = 350$ W and duration 16 hours are represented in Fig. 2. Results of microscopy analysis have shown that the thickness of produced GNP particles was varied from 10 nm to 300 nm and the average particle diameter was in the range from 0.3 μm to 2 μm .

The distributions of the sizes of foliated graphite nanopowder were determined by a Shimadzu SA-CP3 (centrifugal particle size analyzer) from the measurements of GNP particles dispersed in alcohol. The analyzer, along with particle size distribution, allows the powder surface area to be estimated at once. The results of measurements the powder granulometry at different synthesis conditions are shown in Figure 3.

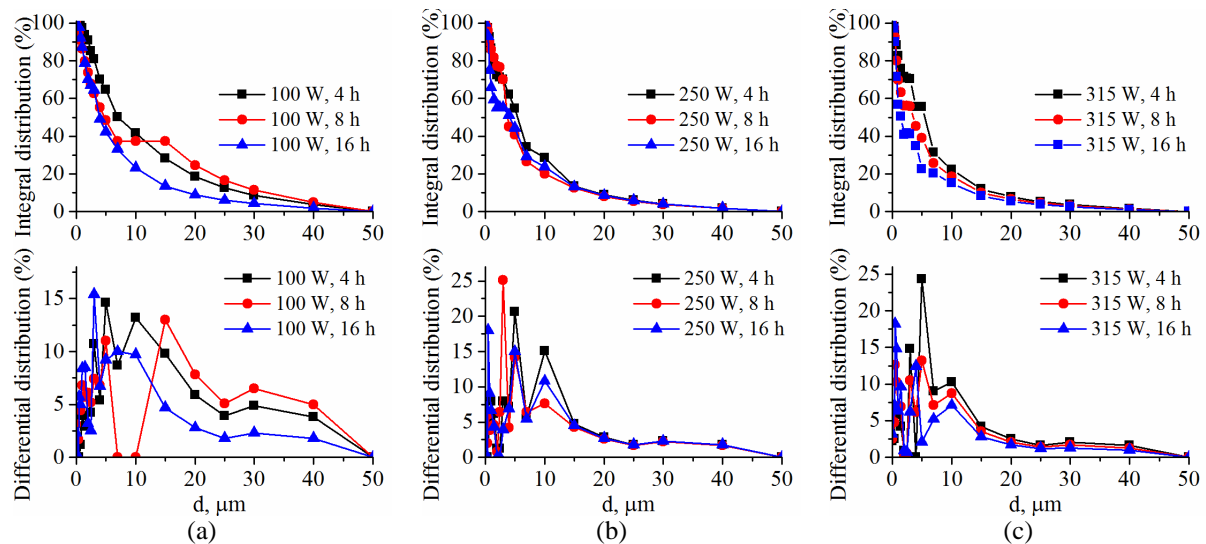


Fig. 3. Size distribution of particles after sonication at different conditions.

It should be noted that the particle size analyzer is calibrated on spherical particles with given density which are sedimenting in a liquid with known properties. Therefore the obtained results show overrated data regarding the size of particles because of the specifics of particles' geometry and behavior in liquid under gravitation as compared to spherical particles with same physical properties. But the effect of procedure conditions (power and duration) on the powder granulometry is clearly seen. Both the differential and integral distributions show the clear shift of experimental curves to the area of small diameters of particles with increase of sonication power and time (see Fig. 3).

The measured by the employed technique surface area of the obtained graphite nanopowder is varying in range 0.3-1.2 m^2/g and linearly increases with increase of both sonication duration and power. The results of measurements are presented in Figure 4 which partially confirm the mentioned above conclusions.

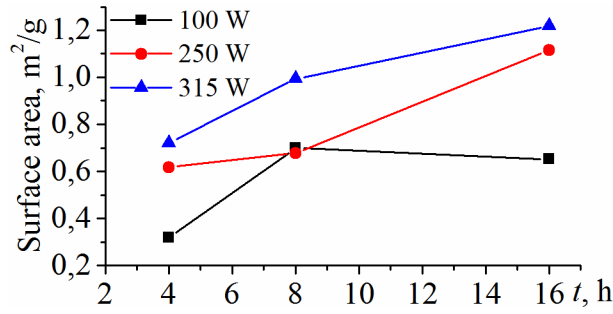


Fig.4. Surface area of synthesized GNp powder depending on sonication time.

4. EXPERIMENTAL DETAILS

4.1 Tribotester

The tribological experiments are performed in a tribotester based on strip drawing (Kirkhorn, *et al.*, 2004). The schematics of the tribotester can be seen in Fig. 5. The specifications for the test apparatus are:

- Maximum normal force $F(t)$: 10 kN
- Maximum push/pull force (shear direction): 6 kN
- Maximum velocity $v(t)$: 2 m/s
- Travel distance: max 600 mm
- Maximum acceleration: 5 m/s^2

The forces are measured with a 3-axis Kistler piezo-electric transducer (9275B). A linear encoder measures the position of the strip synchronously with the force signals. The acquired encoder signal is then being processed to obtain the actual velocity.

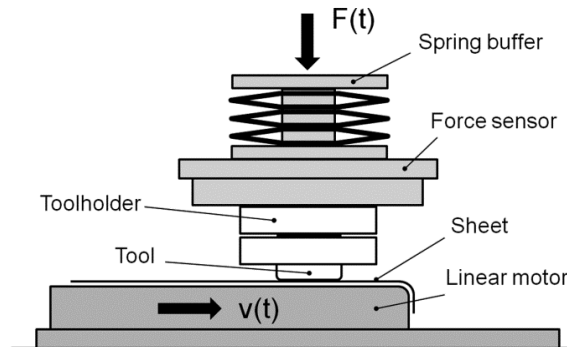


Fig. 5. Schematics of the tribotester.

4.2 Tools

The tool materials used in this work is Caldie tool steel produced by Uddeholm Tooling. The material is developed with main focus on severe cold work applications. Its well balanced chemistry and advantageous heat treatment properties make it a good substrate material for different coatings. The chemical composition of the tool material can be seen in Table 1.

Table 1. Chemical composition (wt. %) of Caldie.

C	Si	Mn	Cr	Mo	V
0.7	0.2	0.5	5.0	2.3	0.5

Initial testing with different process- and contact conditions revealed that coated tools were preferable to reduce the adhesive wear. The tool geometry used in the experiments can be seen in Figure 6. The tool/sheet interface is based on a flat contact and has an active contact area of 112 mm^2 (diameter 12 mm). A radius of 1.5 mm was machined at the edges and a small chamfer was polished at the edges to reduce edge effects during experimenting. The active surface was prepared by surface grinding to an average surface roughness S_a of

approximately 0.08 μm with subsequent polished to S_a 0.4 μm . The tools were hardened to 62 HRC before surface preparation.

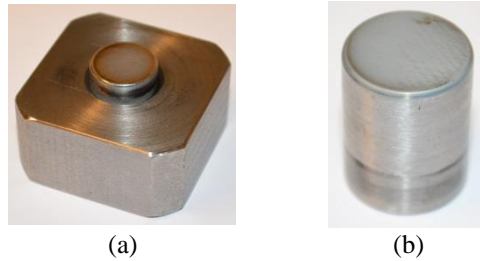


Fig. 6. Tool holder (a) and tool geometry (b). The active area of the tools are 112 mm².

The operational surface of tools was electrochemically coated by chromium. The procedure of chromium deposition was as follows:

- Preparation of the Cr-containing solution: distilled water, CrO₃ (150 g/l) and activator H₂SO₄ (1.5 g/l) were mixed at 70°C.
- The solution was ‘trained’ at temperature 50°C with current density 4-6 A/dm² during 6 hours, anode material – lead, cathode material – steel plate.
- Chromium-plating was started after settling the solution during one day. The operational conditions were: temperature 50°C, anode – steel plate, cathode – workpieces (tools), current density – 20 A/dm², duration – 8 hours.
- The plated tools were boiled during 2 hours and dried at 130°C during 5 hours in a drying oven.

To ensure as stable process conditions as possible during testing, the tools were used before the sharp tests. The break-in of the tools was performed by 10 repetitions on a lubricated sheet, to stabilize the frictional measurement, with a pressure of 40 MPa.

4.3 Sheet material

The sheet material used throughout this study was an uncoated high strength steel from SSAB, Docol 600DP. Properties and composition of the sheet material are presented in Table 2. The sheet surface has an average surface roughness S_a of approximately 1.4 μm . The sheet strips were prepared according to: cutting to size, deburring of edges, cleaning with acetone and lubrication. Each strip was thoroughly optically inspected. All strips with irregularities on the surface like scratches or indents of any kind were removed.

Table 2. Mechanical properties and chemical composition (wt. %) of Docol 600DP.

Yield strength	Tensile strength	Elongation A80	C	Si	Mn	P	S	Al
350-450 N/mm ²	600-700 N/mm ²	16 %	0.11	0.40	0.90	0.015	0.005	0.04

4.4 Lubricants

To compare the frictional influence of the nano graphite additive, three different lubrication systems were used during the tests: ‘oil’, ‘oil-GNp’ and solely GNp. The lubricant oil used was Ensis PQ 144 and it is normally used as a delivery oil to protect hot- and cold rolled steel during transportation and storage but has some advantageous properties as a forming lubricant. The kinetic viscosity at 40°C is 32 mm²/s.

The amount of lubricant (oil) was determined by weigh. The test specimens were thoroughly cleaned with acetone and dried before the lubricant was added. A cloth was used to apply the lubricant and thus a uniform distribution could not be guaranteed but was optically controlled. A scale with a resolution of 0.1 mg was used to measure the amount of applied lubricant. The amount was 0.1 g/m² which correspond to a thin film. The nano-graphite was manually applied using a roller in two layers with drying in between. The amount of applied nano-graphite was approximately 1.8 g/m² and the distribution was inspected visually and with electron microscopy (in case of only GNp coated strips). The images of plain-steel strips, coated only with graphite nano-powder, are depicted in Figure 7.

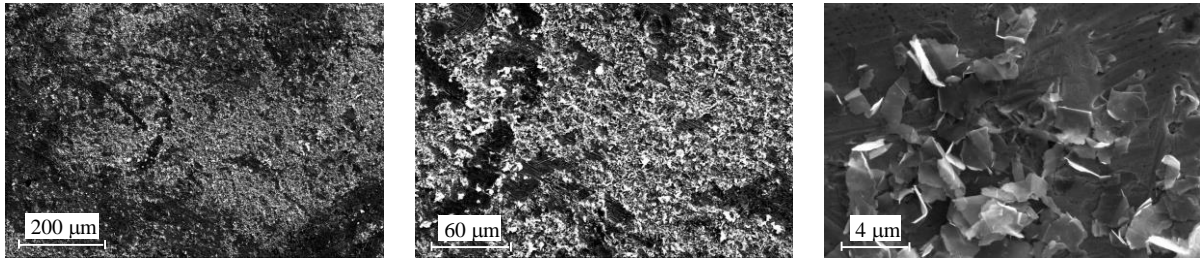


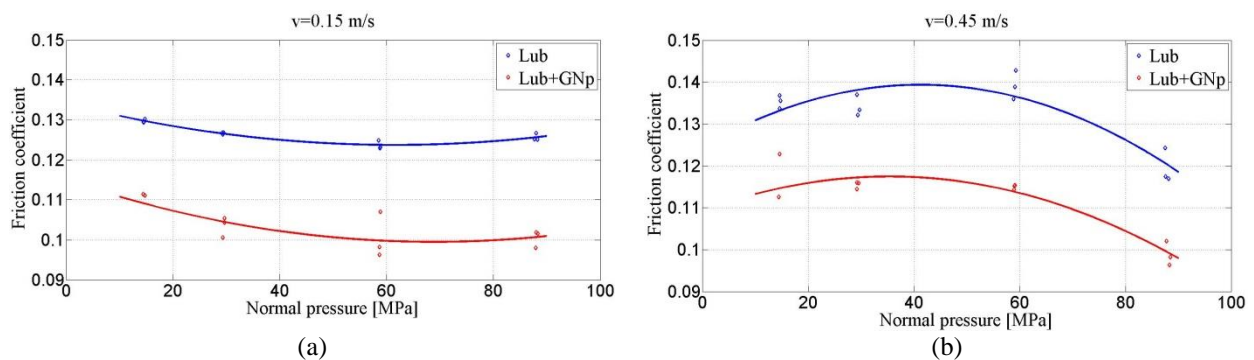
Fig. 7. SEM images of plane steel coated with graphite nanoplatelets.

5. RESULTS AND DISCUSSION

The main objective for this work was to study the influence on friction if nano platelets were used as an additive to a base oil or used by itself as a lubricant. Three different lubricant systems are tested: ‘oil’, ‘oil-layer GNP’ and ‘graphite nano-platelets’ only. The test conditions covered a wide range of relative velocities (0.15-0.9 m/s) and normal pressure (15-90 MPa) between the tool and the workpiece materials. When using the speed of 0.9 m/s, the normal pressure was maximized to 60 MPa due to machine control limitations.

It is found out that the process of synthesis of GNP powder has nonlinear and ‘stepped’ nature. It is evident the shift of maxima of particle size distribution to the area of smaller size with increase of both power and duration of sonication. On the other hand there are constant “size phases” of 10 and 4 μm (Fig. 3) which leave after hours of sonication but their amount nonlinearly decreases with process progress. At the same time new picks on the distribution diagrams appear during the synthesis in the vicinity of small particle sizes 0.5, 1.5, 3 μm percentage of which increases with increase of process parameters. It should be noted that the diagrams of size distributions presented in Fig 3 show the distribution of effective sizes of equivalent spherical particles which sediment in the liquid. The size of GNP particles was estimated by electron microscopy and vary from 10 nm to 300 nm and the average particles diameter was in the range from 0.3 μm to 2 μm . The surface area of synthesized GNP may be a most important and demonstrative factor of reliability and applicability of such kind of nano-materials and has to be investigated much carefully in future studies. In our case the mentioned factor was in the range 0.3-0.7, 0.6-1.1 and 0.7-1.2 m^2/g for sonication power 100, 250 and 315 W respectively.

Initial tests with uncoated tools showed a distinct tendency of galling. Chromium coated tools create a more chemically stable process in the contact between the tool and sheet with no adhesion problems. Each parameter setup was repeated 3 times during the tests to capture the dispersion of the acquired data. Figure 8 and 9 shows the calculated friction coefficients for the different tests. The solid lines are the least square approximation of the collected data points for each experiment. The sub plots in figure 8 and 9 shows different velocity conditions during testing. The lubricant system used during the tests in figure 8 is solely oil (blue) and a mixture of oil + GNP (red). The lubricant used in figure 9 is GNP only.



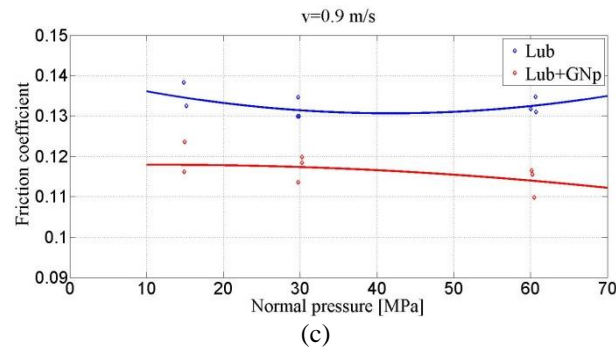


Fig. 8. Friction coefficient as a function of the applied normal pressure, lubrication system and velocity.

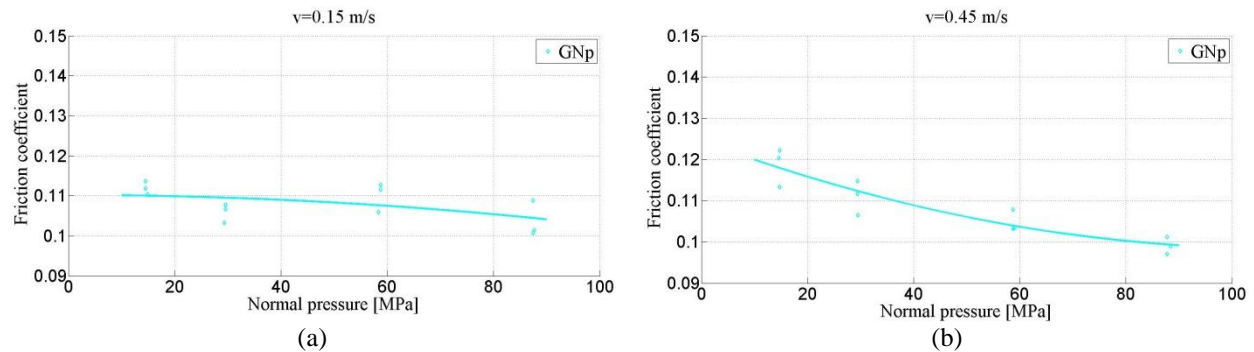


Fig. 9. Friction coefficient as a function of the applied normal pressure, velocity and lubrication (GNp).

6. CONCLUSIONS

Tribological testing in terms of friction measurement has been performed in this work. Graphite nano platelets (GNp) has been used as a lubrication additive to explore and evaluate the influence on the frictional outcome. A large number of tests have been done under different conditions. The applied normal pressure was in the range of 15 to 90 MPa. Velocities used were between 0.15 to 0.9 m/s. The following conclusions could be made:

- Ultrasound treatment of chemically oxidized and thermally expanded natural graphite powder was used for synthesis of graphite nanoplatelets and gives good results of yielding and quality of the GNp. The thickness of as-synthesized particles-platelets was nano-sized and varied from 10 to 300 nm and the diameter was in the range 0.3-2.0 μm .
- Three different lubricant systems are tested: 'oil', 'oil-GNp' and nano-graphite only. The result clearly shows that the specific type of nano-graphite used has a favorable effect of reducing the frictional forces both in mixture with oil and as a standalone coating. The tribotester generates consistent results with high repeatability independently of lubricant system.
- Coated tools must be used to eliminate the adhesion between tool and sheet when using pure GNp as a lubricant.

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