Tribological Performance of Graphene and Graphene Oxide Films as Solid Lubricant Layers on Tool Steel Surfaces

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Abstract. Some high productive processes induce a use of effective cooling and lubricating for forming and cutting tools today. Apart of various fluids, foams, oils and emulsions with EP (extreme pressures) additives some very effective means based on graphene or graphene oxide show excellent performance in their solid phase. In this study, a very effective way to enhance the tribological performance of graphene layers on tool steel surfaces is studied. The solid lubricants based on graphene and graphene oxide flakes showed a very good thermal stability, low coefficient of friction and high wear resistance. However, some technological conditions and topographies of surfaces for their successful applications should be made in advance as prerequisites. The research work deals with a high productive forming of metals and improving the mechanical and functional properties of special products. It contributes to finding the optimal internal varnishes, testing their resistance to stress and chemical resistance to the components, understanding all relevant mechanical properties especially of graphene (friction properties, adhesion and abrasion resistance). This research and development is concerned with a production of thin walled products, which will provide future customers with a more durable and safe products and also would have better properties compared to similar products already available on the market.

1. Introduction

Today’s scientific databases (WOS, Scopus) offer several thousand scientific works devoted to graphene and graphene oxide. About 1,000 papers deals with super friction properties, adhesion, superior strength, resistance to wear and the effect on mechanical properties of tribological systems. However, only a few of them with their behaviour at high speed deformation rates conditions used in industry, on real part surfaces. Right there the moving mechanical parts or work pieces undergoing severe plastic deformation consume a lot of energy also due to the friction. Therefore, investigations have been looking for innovative ways to minimize the friction and generation of heat via use of the advanced materials:

a. Graphene in general is a single-layered two-dimensional material, crystalline allotrope with a hexagonal lattice structure made from carbon atoms – Figure 1a. Graphene was first by the mechanical exfoliation of 3D graphite crystals. Nevertheless, the production costs for a mass use are still high.
b. Graphene-oxide (including the reduced graphene oxide) are also frequently referred to the perspective materials displaying extremal low friction mentioned also as super-lubricity, see Figure 1b. Graphene oxide (GO) is a similar material, made of carbon, hydrogen and oxygen molecules. GO seems to be a similar but cheaper product with some better mechanical properties compared to pure graphene. Through sonication, graphite adopts oxygen-containing functional groups that allow the material to be better dispersible in water that promote its use as a colloid. Despite all these research efforts and fundamental approaches, the super-lubricity has seldom been achieved at technological production systems. There are many theories and reasons for this fact, stemming from physical or chemical interactions that occur simultaneously at the sliding interfaces far away for hypothetical ideal planes, however, it is still a challenge for many engineers to realize them.

![Figure 1](image)

Figure 1. A single structure of graphene (a), and graphene oxide (b).

Graphene can have several morphological phases - spheres (hollow), of a size about 200 nm [1], flakes [2], wafers [3,4], ribbons [5], layers [6,7], nanotubes [8]. Its applications can take place on solid surfaces in the solid form, but also as a liquid (dispersed in water or oil) and even foam applications. In some cases, it can be mixed with MoS2 or nano-TiO2 [9], which are also excellent lubricants themselves. These nano-additives based on fullerenes (carbon beads) can be further filled inside with inorganic tungsten sulfide (IF-WS2) [10]. Such materials can be resistant to the extreme pressures, temperatures up to 500 °C. They have been developed for military purposes about 10 years ago in Israel and massively made in the U.S.A. later. The composition was based on IF-WS2/polymer and recommended for use in metalworking (drawing, forging, stamping, etc.) where provides excellent surface finishes also. The products were based on multifunctional closed spherical particles of inorganic tungsten bisulfide similar to fullerenes (IF-WS2), which provided unique properties due to exfoliation and tribological film formation on the metal surface. This product surpassed conventional synthetic and semi-synthetic fluids in its properties and did not contain chlorine, boron, formaldehyde or zinc.

Graphene and functionally deposited graphene are promising candidates as solid ultra-thin lubricants for solving adhesion and friction even in micro- and nano/electromechanical systems. Friction as a function of load shows a nonlinear characteristic [11] due to their strong adhesion. The phenomenon of increasing adhesion increases with increasing surface energy. Improvements in dynamic adhesion and friction are associated with associated hydrophilic properties. The beneficial effect of multilayer graphene in friction on M2 steel was demonstrated in [12], which confirmed the formation of shear layers with a low coefficient of friction.

Graphene is theoretically an excellent mechanical system with extreme flexibility [13], ultra-strong adhesion, and gas impermeability. For this two-dimensional material, the graphene interactions with the support substrate are unique. Amonton's first law states that macroscopic friction is proportional to the load applied, justified by the argument of increasing the load to increase the microscopic contact area between the two surfaces. However, due to its ultra-strong adhesion and low flexural stiffness, graphene does not require any higher loading to achieve an almost perfect fit to the nanoscale of the topography of its substrate. In contrast, the work [14] shows that damage to the graphene layers can
lead to mutual sliding and up to several times higher deterioration of friction, although micrometric graphene residues can continue to reduce friction, even if the connection of the graphene layer is damaged. Friction on multilayer graphene is known to be dependent on the thickness of the layer [15]. The exact role that this interface plays, especially its size, contact and substrate roughness, in the graphene friction dependence on the layer has not yet been fully elucidated, which is the subject of further research.

2. Materials and method
This Alumina alloy samples - AlCu4Mg according to the standards EN AW 6082 T6, EN 753-3 EN 755-2, in dimensions 30x6.6x100 mm (3x3 pieces, each tested 6 times) - Figure 2 - have been machined precisely, ground, polished and covered with three sorts of an epoxy lacquer and the same thickness 5.0±0.2 µm (measured via kalotest) marked as:

a) EP – a standard epoxy lacquer (a company know-how),

b) HP – the standard epoxy lacquer enriched by 0.02 wt.% of Graphene GNP HP F8/1 - nanoplatelets of size up to 26.5 µm, 73% ≤ 10 layers,

c) RGO – the standard epoxy lacquer enriched by reduced graphene oxide (10% dispersion in isopropanol, and the dose of 1.5 wt.% of the dispersion), with a low degree of oxidation, average size of particles 500 nm, 90% particles of dimensions less 800 nm with number of layers less 10.

All samples were set at the temperature 225 °C for 5 minutes in a laboratory heat oven Hoba 7940 (PPG, U.S.A.) The cylindrical tool was made from hardened steel 42CrMo4V - Table 1, turned precisely to a glossy surface with polycrystalline cubic boron nitride (PCBN) round cutting inserts SECO CCGW120408S-01020-L1-B CBN010 and ground by sapphire sandpapers of grit sizes FEPA 120, 240, 480 and 600 to suppress turning surface morphology without any releasing or re-fastening of the tool. The morphology of surfaces, roughness and other geometrical parameters were evaluated with Alicona IF G5 (Bruker Alicona, Austria), some selected parameters with Zeiss Stemi 2000C (Carl Zeiss AG, Germany) also. The surface temperature of the tool was measured with the thermal camera Flir 2000 (Flir, U.S.A.).

Table 1. Steel 42CrMo4V CSN EN 10083-1: 1991+A1: 1996; DIN 17200 – hardened state.

| Chemical composition (weight %) | C    | Cr    | Mo    | V    | Si    | P     | S     | Fe    |
|---------------------------------|------|-------|-------|------|-------|-------|-------|-------|
|                                 | 0.38 | 0.15  | 0.15  | 0.15 | 0.22  | 0.013 | 0.017 | balance |

| Mechanical properties            | HRC Hardness* | Yield point Re [MPa] | Tensile strength Rm [MPa] | Young modulus [GPa] |
|----------------------------------|---------------|----------------------|--------------------------|---------------------|
|                                 | 35-36         | 920                  | 1103-1137                | 224                 |

*Zwick/Roeller Rockwell hardness tester ZHR 4045/4150/8150, loading 150 kg, diamond indenter.

After each test a re-polishing and cooling of the circumferential contact surface to 20-25 °C followed. Tribological tests have been running at a precise turning machine (SV18RD, TOS Trencin, a.s., overhauled by the M-MOOS Ltd., Lipnik nad Becvou in 2020) and use of a special friction facility that enabled many advantages – Figure 2:

- production of symmetrical and coaxial cylindrical steel surface aligned to the axis of its rotation, with high quality of the surface (Ra<0.4 µm) - Figure 3 and Figure 4,
- repeatable setting of the same loading conditions for the tribological tests,
- an adjustable sample positioning, dry and wet testing conditions etc.
Figure 2. Principle of the friction test - measurement of normal force $\mathbf{F}_n$ and tangential force $\mathbf{F}_t$ for angular speed $\omega$ and circumferential speed $v$ according to tool radius $r$.

Figure 3. The surface of the steel tool and its quality; (a) – the morphology after the final polishing, (b) the typical selected surface amplitude characteristics.

The polished tool surface – see Figure 4 – exhibited a very low fraction of peaks above the core of material with surface texture aspect ratio over 88°, so a very good alignment of the circumferential speed to the machined surface was set to avoid a tangential removal of particles by micro-cutting due to a helix path that had been made by the cutting insert in the turning operation.

The laboratory tests were performed at a circumferential speed of 100 m/min (resp. 1.67 m/s), with a constant pressing force of 40 N, derived mechanically by means of a weight. The speed was set using a frequency converter and read by the digital chronometer (TESLA, a.s., Czech Republic). The piezoelectric system KISTLER 9575B (Kistler, Switzerland) was mounted on an axial bearing with
virtually zero friction along the motion axis. The basic scanning frequency was 100 Hz, with a long
time constant and a low-pass filter of 10 Hz. The apparatus was calibrated using a laboratory
mechanical weights in the scale 10–60 N with a high linearity (a statistical correlation over 98%).
Testing was performed under dry conditions.

![Bearing Ratio/Firestone-Abbott Curve of Roughness Profile](image)

| Name  | Value | Unit | Description                                                                 |
|-------|-------|------|-----------------------------------------------------------------------------|
| Rk    | 1.077 | μm   | Core roughness depth, Height of the core material                           |
| Rpk   | 0.448 | μm   | Reduced peak height, mean height of the peaks above the core material       |
| Rvk   | 0.453 | μm   | Reduced valley height, mean depth of the valleys below the core material    |
| Rmr1  | 10.370| %    | Peak material component, the fraction of the surface which consists of peaks above the core material |
| Rmr2  | 80.490| %    | Peak material component, the fraction of the surface which will carry the load|
| L    | 5.800 | mm   | Profile Length                                                             |
| Lc    | 800.000| μm  | LambdaC: cut off wavelength                                                |

![Figure 4. The bearing ratios of the polished steel tool surface.](image)

The actual course of a test started with a gradual motion of the sample forward the rotating tool
until the full force thrust was reached. Then the constant engagement continued until the first traces of
adhesion appeared on the surface, when the testing was stopped, and sample was released – Figure 5.
All the time the force data were measured and downloaded. Their evaluation was performed using the
Data Processing module in Microsoft Excel v. 10, U.S.A., which was based on a statistical evaluation
of instantaneous Coulomb friction $\mu_i$ according to the relation of instantaneous tangential force $F_{ti}$
and normal force $F_{ni}$:

$$
\mu_i = \frac{F_{ti}}{F_{ni}} 
$$

![Figure 5. A typical pattern of wear at the end of testing (Zeiss Stemi 2000C).](image)
3. Results and discussions
This method of testing resulted in very consistent files for the friction evaluation with normal Gaussians distributions (assessed with the test $\chi^2$). The range of statistically processed data captured a steady, stable phase of the friction see Figure 6 and Figure 7 and did not include either the first moments of the tool contacts with the lacquers, or a formation of the metal contacts between the tool and the aluminum base of the samples in the end of the test.

Figure 6. Selected measured force data from tribological tests, limits for a statistical assessment.

Figure 7. Time series of friction coefficients: (a) epoxy lacquer, (b) epoxy lacquer with graphene, (c) epoxy lacquer with reduced graphene oxide.
Table 2. Statistical evaluation of the data - mean and standard deviation of friction coefficient for all tested materials.

| Statistics                  | EP       | HP       | RGO      |
|-----------------------------|----------|----------|----------|
| mean [N]                    | 0.1988   | 0.1853   | 0.1648   |
| standard deviation [N]      | 0.0482   | 0.0404   | 0.0280   |

Figure 8. A typical pattern of the wear.

Figure 9. Three types of wear.

A typical pattern of the wear can be seen in Figure 8, where the morphology of a worn surface in the moment of tool penetration into the alumina surface is shown. In this case, the whole thickness of the lacquer was removed from the contact area in the deepest distance. Anyway, three types of wear have been watched at the cross-section of the surface and analysed - Figure 9, each with different material areas and volumes removed by the rotating tool. The prevailing mode of plastic flow was observed for the pure epoxy lacquer. The dominant abrasive mode was rare, but it has been found a few times for the lacquers enriched with graphene and graphene oxide. The dominant mechanism of wear for lacquers with graphene and graphene oxide resulted in the mixed mode.

Figure 10. Statistical data of the coefficient of friction for individual coatings and given loading conditions.
All wear patterns and morphologies were analysed and classified in details. The analyses showed that the initial abrasion mechanism for all layers was similar. First, there was an abrasive removal of the contacting lacquer irregularities, then an increase in the contacting area and in temperature also due to friction and plastic flow of the loaded lacquer layer. The material flow at the leading edge was usually lower than the one at the running edge. However, it was found that:

- the intensity of wear for the various materials was different with respect to the time,
- the tests were, among other facts, sensitive to a corrugation or some irregularities of the samples at the microscopic level (a careful preparation of the flat surfaces had to be guaranteed),
- a partial problem can be an unknown orientation of the graphene or graphene-oxide flakes exerted to the loading, so a little plastic flow or a suitable ordered particle orientation with a convenient sliding planes can help to low friction [17,18],
- the mechanical loading (40 N) seemed to be optimal, because higher loadings (50 N and more) caused a quicker testing, but followed with a higher dispersion of data and a lower loading (30 N) prolonged the testing and some “burnt” micro-particles begun to appear at the frictional areas.

Based on statistical processing of the results - Table 2, Figure 10 - the RGO type coating was found to be the superior coating for the given loading conditions, showing the lowest value of the friction, low data dispersion (expressed with standard deviations) and the longest time of its performance. There is the statistically significant difference between the mean values of the epoxy lacquer with reduced graphene oxide compared to the epoxy lacquer and epoxy lacquer with addition of graphene (α=0.05) also.

The effect of heating of the lacquer when loaded can be important, because it can soften the hardness and mechanical properties of the layer, its dynamic viscosity. Nevertheless, all tests started from the surface temperature 20±1°C and ended in the range of 50–62°C. However, the values are moreless informative, because it was difficult to define the surface emissivity exactly. The deeper analyses of the mechanisms continue.

4. Conclusions, future prospects
This application of graphene and graphene oxide can be beneficial for a wide range of applications in technical and medical practice. These phases, in a wide range of morphologies and dimensions, have been shown to reduce friction at the point of contact and protect technical components, forming and cutting tools from wear. These layers work theoretically from a single atomic layer, but provided perfectly flat and smooth contact surfaces. This is difficult to achieve in the common technical practice, and therefore it is necessary to determine the type of phase applied, its concentration and possibly the size of the layering. Experimental tests have shown very promising results for reduced graphene oxide, which could be used for application to the technological surfaces.

Next research with use of Raman spectroscopy would be oriented to a study of the induced dominant particle orientation and a technology of its deposition. A tiled composition of the flakes with very strong covalent bonds in the hexagonal structures, situated perpendicularly to the expected loading, and the weak Van der Waals bonds within the layers might yield in a significant lubrication effect and other benefits.

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