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Study regarding enhancement of antiwear properties of a grease, by using carbon nanomaterials based additives

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This study focuses on the improvent of antiwear properties of two categories of greases, sodium grease and lithium grease. Additives such as nanomaterials are essential to improve the properties of greases. Graphene, MWNT and fullerene are used in different quantitites (0.5 wt.%, 1.5 wt.% and 3 wt.%) to improve the antiwear properties. Non-added samples were analyzed from density (ASTM D 1298), drop point (ASTM D 566), cooper strip test (ASTM D 130) and water resistance (DIN 51807) perspective. Also, non-added and added greases were analized tribologicaly with HFRR test, and the results showed that all types of carbon nanomaterials investigated improve the tribological properties of the greases, but in the case of grease based on Li soap it can be observed an important decrease of friction coefficient for 3 wt.% graphene and MWNT. The most important decrease in the friction coefficient was recorded by Li35 with graphene additive. In case of grease based on Na soap, it was not notices important changes.

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1. Introduction

According to ASTM standard, a lubricating grease is semi-fluid to solid of a thickening agent mixed with a liquid lubricant. Other ingredients that convey special properties may be included in its composition. In the context of this definition, few authors, such as R.M. Martin and S.T. Orszulik argues that in some places it is diffuse, but it still establishes that grease is a multi-phase system consisting of at least 2 well-defined compounds, a thickening agent and a lubricating fluid [1]. Therefore, a lubricating grease has in its composition a mineral, vegetable or synthetic lubricating oil. From the beginning of industrialization, since the field of lubricants has grown exponentially, use of mineral oil was preferred, given the performance offered to the grease and the relatively low cost compared to synthetic oil. Aromatic and/or naphthenic oils have been predominantly used in the past due to their high degree of polarity. However, it has been shown that these oils can contain considerable amounts of polycyclic aromatic, with carcinogenic potential. Paraffin oils are preferred today, although highly refined naphthenic oils meet the health and environmental requirements of the European Union [1]. Still, fossil resources provide 86% of the energy needed and 96% of organic chemicals. However, future oil production is unlikely to meet the growing needs of our society [2]. Therefore, in the last few decades, alternative energy resources try replacing fossils based resources. Lubricants based on vegetable oil are also emerging as substitutes for conventional lubricants, especially in the automotive industry [3]. Even if the vegetable oil has certain properties that do not excel (hydrolytic stability, thermo-oxidation), in the case of greases, the incorporation of additives in their composition, significantly improves the final product.

Thus, “the image” of 21st century grease has a new concept, different from the original one, of a relatively simple and cheap product. So, the grease should be an exceptionally complex product, which requires chemical, physical, rheological and tribological performance, but should also be environmentally friendly. A grease with superior properties has in its composition performant additives, that play a crucial role in the lubricant industry. To be a performant additive, it must improve the existing properties of the base oil through antioxidants, corrosion inhibitors, anti-foaming agents and demulsifiers, or to suppress the undesirable properties of the base oil by

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using depressants of the pour point and ameliorators of the viscosity index, or to provide new properties to base oils through extreme pressure agents, detergents, metal deactivators and gelling agents [4].

Nowadays, nanoadditives try to find their own space in the additive industry.

Recently, carbon-based nanomaterials (fullerene and carbon nanotubes) have been used as additives for lubricating oil, but have not been widely used in this industry due to their high cost [5-7].

However, graphene, boron nitride (BN) and molybdenum disulfate (MoS_2) are two-dimensional (2D) nanomaterials, which offer excellent anti-friction and anti-wear properties due to their structure. Graphene, due to its very small size has a high mechanical strength and thermal conductivity. BN and MoS_2 offer superior lubrication (low coefficient of friction) due to the ultra-thin layers of the 2D material, thus providing extremely low shear strength between layers. These features help prevent direct contact between friction surfaces [5, 9].

Also, the 2D materials used as nanoadditives, not only offer excellent anti-wear and anti-friction properties, but also a reasonable price of preparation in the field of lubrication. Therefore, 2D materials are classified as high performance and, most importantly, environmentally friendly additives [5].

In this paper are presented the preliminary results on the friction behavior of different carbonaceous materials as potential antiwear additives for greases based on mineral oil and palm oil.

A HFRR High Frecvency Reciprocating Rig equipment was used to evaluate the tribological properties of the carbonaceous materials.

2. Materials and experimental methods

The first part of the study was focused on the synthesis of greases from different raw materials, while the second part was dedicated additivation greases with different concentrations of carbonaceous nanomaterials such as: graphenes, multiwall carbon nanotubes and fullerenes, to improve the anti-wear properties.

2.1. Materials

2.1.1. Carbonaceous nanomaterials

Graphene platelets (6 – 8 nm, 99.5 %), multiwall carbon nanotubes (outer diameter: 10 – 20 nm, length: 1 – 2 μm, 95+ %) and fullerene (structure C60, 99%) used as antiwear additives in our investigations were provided by Iolitec Ionic liquid.

2.1.2. Chemicals

Sodium hydroxide 98%, stearic acid >98% and lithium carbonate 96% were provided by Sigma Aldrich and Merck.

2.1.3. Mineral oil and vegetable oil

Mineral oil, SN 500, was provided by Lukoil Lubricants Romania, palm oil is a food grade product and their physical - chemical characteristics are depicted in Table 1.

Table 1. Physical-chemical characteristics of SN 500 mineral oil and palm oil.

Properties	SN 500	Palm oil	Methods
Density (kg/m^3)	885	910	ASTM D-1298
Kinematic viscosity (40°C, cSt)	101.32	44.35	ASTM D-445
Kinematic viscosity (100°C, cSt)	10.89	8.73	ASTM D-445
Viscosity index	90	184	ASTM D-2270
Flash point (°C)	243.9	>290	ASTM D-92
Pour point, (°C)	-16	13	ASTM D-97
Biodegradability Test CEC (%)	20…40	90…98	ASTM D-5864 95

2.2. Synthesis and characterization

2.2.1. Grease synthesis

In this study, two categories of greases were synthesized, with different concentrations of two types of soap.

The first category is represented by a sodium grease, which was synthesized by mixing sodium soap with base oil SN500. The sodium soap was prepared by dissolving 19 g NaOH in distilled water, and heated up to 40 ^{0}C. In the same time, 150 g palm oil was heated up to 40 ^{0}C. When the sodium solution reached 40 ^{0}C, it was mixed with palm oil and heated for 30 min. at 100 ^{0}C. In the second phase, 50 wt.% of mineral oil and the soap were mixed for 30 min., at 100 ^{0}C, to evaporate the water. After 30 min., the other 50 wt.% oil was added in the mixture, and the temperature was raised to 150-160^{0}C and kept constant for 15 min. In this stage, the bonds and structure of grease are formed. Then, the temperature is raised again to 185-190^{0}C, for another 30 min. Finally, the grease cools down to 90^{0}C and is additivated under gentle stirring for 30 min.

The second category is represented by lithium grease [8].

First, the lithium soap was prepared by adding 50 g of stearic acid to 125 g distilled water. The mixture was stirred and heated up to about 92 - 95 ^{0}C, until the acid was fully dissolved in the water, forming an oil solution. Then, the lithium carbonate was dissolved in warm water to the concentration of m(Li_2CO_3): m(water) = 1: 6.7 and slowly added into the first mixture and maintained under stirring and heating to about 95 – 100 ^{0}C for 1h, to ensure complete saponification. After full saponification, the solution was heated to about 110 ^{0}C and maintained for 1 h to remove the additional distilled water, leaving a white semi-solid paste. Subsequently, the paste was introduced into an oven and dried for 30 h at 65 ^{0}C. The dried paste was ground into white solid powder for further use.

In the second step of the synthesis, lithium soap and 50 g base oil SN500 were added to a reaction kettle. During the addition, the mixture was heated and stirred for 10 min. at 120 ^{0}C, and after that at 170 ^{0}C for another 10 min. Then, the mixture was slowly heated to 200 ^{0}C for 40 min. After that, 50 g base oil SN 500 was added to quench the solution to 170 ^{0}C under stirring. The temperature was kept constant for 5 min., before the mixture was cooled naturally to room temperature [10].

The mass percentage of thickener (soap) was 25 wt. % and 35 wt.%. The grease samples were labeled depending on the soap wt. % and type. For the preparation of nano-greases, different weight percentages of graphene, multiwall carbon nanotubes (MWNT) and fullerene were used (0.5, 1.5 and 3). The carbon nanomaterials have been dispersed into the greases by ultrasonication, in the presence of ethanol. After dispersion, the greases have been heated up to 85 ^{0}C, to remove ethanol.

2.2.2. Greases characterization

Greases without additives were characterized by density, drop point, corrosion on copper strips and water resistance [11-14]. These results are presented in Table 2 and Fig. 1.

Table 2. The result of the analysis of non-added greases.

Analysis	**Na25**	**Na35**	**Li25**	**Li35**	**Methods**
Density (kg/m^3)	0.8917	0.8884	0.9241	0.9369	ASTM D 1298
Drop point (°C)	126	138	194	194	ASTM D 566
Cooper strip test	1b	1b	1a	1a	ASTM D 130
Water resistance*	3	3	0	0	DIN 51807

**Evaluation stages: 0 = no change to 3 = major change.*

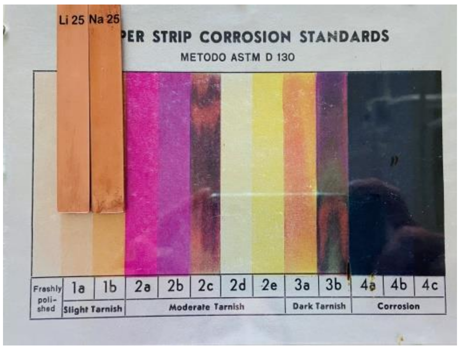

Fig. 1. Corrosion of Li 25 and Na 25 greases

2.2.3. Tribological investigations

A High Frequency Reciprocating Rig (HFRR) equipment endowed with a friction couple from class 1 was used to evaluate the friction coefficient and the wear scar diameter imprinted on the stainless ball. The test consist of rubbing a steel ball (AISI-E 52100/535A99 with roughness of Ra=0.050µm and hardness of RC 58-66) against a steel disk (AISI-E 52100/535A99 with 10 mm diameter and roughness of Ra=0.020µm and a hardness of RC 76-79), in the presence of few grams of grease. The HFRR investigations have been performed at a frequency of 50 ± 1 Hz, 1000 um stroke, 200 ± 1 g load and 60 ± 2°C (according to ASTM D-6079), while the relative humidity was kept between 40 and 60% and the ambient temperature between 24 and 26°C. After tribological investigations, the wear scar imprinted on the steel ball was measured and the friction coefficient was recorded.

3. Results and discussion

To investigate the effect of carbonaceous materials as antiwear additives, it was investigated the variation of friction coefficients and wear scar diameters with different percentages of additives. The results were compared to those without additives and are presented in Table 3 and Figs. 2 and 3.

Table 3. HFRR results for Na 25 and Li 25 greases.

	No additives				**3 wt.% Graphene**				**3 wt.%MWNT**				**3 wt.% Fullerene**			
	Na25	Na35	Li25	Li35	Na25	Na35	Li25	Li35	Na25	Na35	Li25	Li35	Na25	Na35	Li25	Li35
Friction coefficient	0.132	0.130	0.138	0.206	0.116	0.121	0.118	0.116	0.120	0.106	0.137	0.128	0.107	nd	0.127	nd
WS, µm	265	265.5	157	290	164.5	203	175.5	219.5	157.7	198.5	195.5	203.5	151.5	nd	135.5	nd

From these results it is obvious that all type of carbon nanomaterial investigated improve the tribological properties of the greases, but for the grease based on Li soap, the best results, respectively the lowest friction coefficient was recorded for the sample additivated with graphene, while for the grease based on Na soap, fullerene are the best candidate to improve the tribological properties.

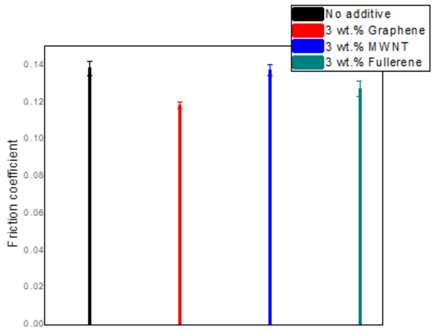

Fig. 2. Friction coefficient of Li 25 greases with 3 wt.% nanomaterials

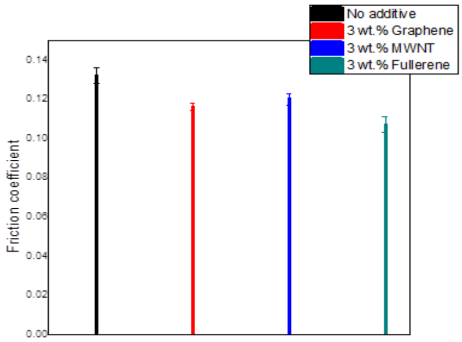

Fig. 3. Friction coefficient of Na 25 greases with 3 wt.% nanomaterials

The biggest improvement in the friction coefficient with increasing percentage of graphene was recorded by Li35, who recorded the lowest value for 3 wt.% graphene. Also, we can see in Fig. 4 that Li 25 has a decrease in friction coefficient, but not as important as observed for Li35. For sodium greases, we can see that by adding graphene, the friction coefficient does not have a significant improvement. The same situation can be seen in Fig. 5, where the additive was MWNT, lithium greases had obtained a better friction coefficient for 3 wt.% additive. In the case of sodium greases, MWNT did not have any important effect on friction coefficient.

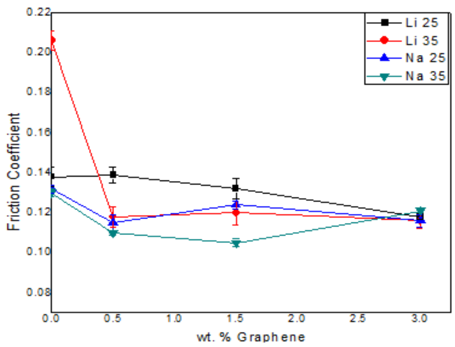

Fig. 4. Friction coefficient of nanoaditivated greases with graphene

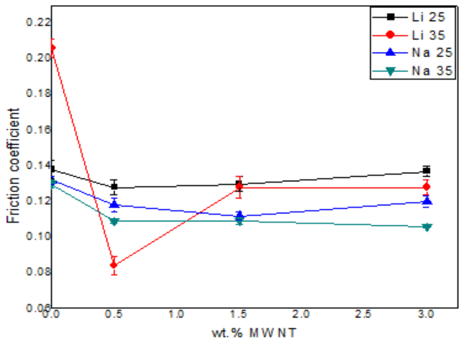

Fig. 5. Friction coefficient of nanoaditivated greases with MWNT

4. Conclusions

Well-formulated greases are semi-solids products which have a higher ability to stay in place and can provide superior film thickness than lubricating oils. Greases are crucial to the function of industrial equipment. The tribological properties of the greases such as friction coefficient and wear scar are the most important. For this reason, this study shows how friction coefficient is influenced by grease type and by additive used. Nanomaterials used as additives played an important role in this research, graphene had the biggest impact on the friction coefficient, and greases based on lithium soap gave better results than greases based on sodium soap. Also, the utilization of 3 wt.% of fullerene leads to the lowest wear scar diameter imprinted on the steel ball. Also, for greases based on lithium soap, fullerene is more suitable anti-wear additive rather than graphene.

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