Experimental Researches on Additivated Biodegradable Greases

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Abstract. In the recent years, the lubricating market is demanding new biodegradable products based on renewable resources as a consequence of progressively more strict environmental regulations. This work is focused on the rheological study of biodegradable greases based on rapeseed oil and beeswax, additivated with graphene or graphite nanoparticles. For this study, different grease samples have been prepared and each of them were thermal analysed in the range of 20 °C … 50 °C. The rheological tests indicate that the greases have non-Newtonian behaviour, which are rheological described by the Bingham model. Finally, the thermal variation of the rheological parameters (yield stress and viscosity) was obtained, in the mentioned temperature range.

1. Introduction

Lubricating greases are highly structured suspensions, usually consisting of a thickener (5–30% wt) dispersed in mineral, synthetic oil, vegetable, animal fats (70–95% wt). Vegetable oils usually possess attractive properties like biodegradability, low volatility and good rheology compared to the conventional base oils without functional additives. Moreover, vegetable oils stand out for its low friction and anti-wear property [1]. The thickener is a key component, added to increase the consistency-temperature relationship of the lubricant, in order to solve some difficulties that lubricating grease cannot cover properly in specific applications [2], [3]. The thickener forms an entanglement network, which traps the oil and confers the appropriate rheological and tribological behaviour to the grease [4]. Fatty acid soaps of lithium, calcium, sodium, aluminium or barium are most commonly used as thickener agents.

Greases generally cannot satisfy the requirements of high performance lubricants without using the benefits of modern additive technology. Additives are natural or synthetic chemical substances that can improve lots of different parameters of lubricants such as anti-wear and extreme pressure [5]. Nanoparticles as additives shine new properties that differ from the properties of bulk materials, because of size they can penetrate into all places of friction surfaces especially in places where the surface deformations appear due to tribocontacts, local temperature increase or microcracks formation.

Graphite is a mineral that naturally occurs in metamorphic rock. It is formed as a result of the reduction of sedimentary carbon compounds during metamorphism. Contrary to common belief, the chemical bonds in graphite are actually stronger. So, graphene is fundamentally one single layer of graphite; a layer of bonded carbon atoms arranged in a honeycomb (hexagonal) lattice. However, graphene offers some impressive properties that exceed those of graphite as it is isolated from its “mother material” [6], [7].
Greases for lubricating machines used in food processing or in drinking-water systems, in which incidental and unavoidable contact between food and lubricant can occur, must fulfill specific requirements relating to food legislation, human health protection, taste, and odour [5]. Researchers are mainly focused on the replacement of mineral base oils by vegetable oils, whereas new types of thickeners, additives, carbon nanoparticles are seldom studied [8]. Lubricating grease produced from rapeseed oil and beeswax can be useful in applications where strict non toxicity and biodegradability are required. In this case, rapeseed oil is used as a base oil and beeswax as a thickener.

Beeswax presents good characteristics for the lubrication purposes, because it is a non-toxic material, it is non-corrosive and has chemical stability for a long period of time and reduced fabrication costs. The greatest disadvantage of beeswax is the very low melting point, in the range of 60 °C … 70 °C, which diminishes the field of use [9], [10].

2. Experimental methodology

Biodegradable greases used for experiments were prepared using rapeseed base oil with thickener beeswax in concentration of 30% (wt). Four different types of samples have been tested, with the following composition:

- Pure grease (Figure 1);
- Additivated grease, with antioxidant (1%) and antiwear (2%) additives (Figure 2);
- Graphene grease, with antioxidant (1%), antiwear (2%) and graphene powder (0.5%) (Figure 3);
- Graphite grease, with antioxidant (1%), antiwear (2%) and thermal expanded graphite (0.5%) (Figure 4).

Figures 5 and 6 presents the SEM micrograph for commercial products of graphene [11] and graphite [12], in order to understand the difference between their microstructure.
Rheological tests were performed using a Brookfield viscometer CAP 2000+, with a cone and plate geometry. A “velocity imposed gradient” test was used, with the temperature range between 20°C and 50°C and cone geometry number 8 [13]. The experimental results were numerically treated assuming the validity of Bingham rheological model:

\[ \tau = \tau_0 + \eta \frac{\partial u}{\partial y} \]  

where: \( \tau \) – shear stress  
\( \tau_0 \) – yield stress  
\( \eta \) – dynamic viscosity  
\( \frac{\partial u}{\partial y} \) – shear rate

3. Results

The experimental test consists of a load from the 10 s\(^{-1}\) to 2000 s\(^{-1}\) shear rate gradient, followed by an unload in order to highlight the thixotropy of the lubricant - "shear memory". The test is repeated three times for each temperature (20°C, 26°C, 32°C, 38°C, 44°C, 50°C) and the duration of homogenization (soaking time) of the sample at a certain shear rate was 1 min. The rheograms (Figures 7, 8, 9 and 10) are obtained by plotting shear stress as a function of the shear rate, as an average of three points, using the software Capcalc 32 specific for the viscometer. At the end of the tests, in the case of the temperature 20°C, the rupture of the grease film was visualized (Figure 11 a, b, c, d), in order to characterise properties such as adherence, cohesion, and tackiness (ability to form threads before separation) [14].

![Figure 5. Graphene microstructure [11]](image1)

![Figure 6. Graphite microstructure [12]](image2)

![Figure 7. Lubricant rheogram for pure grease, at different temperatures](image3)
Figure 8. Lubricant rheogram for additivated grease, at different temperatures

Figure 9. Lubricant rheogram for graphene grease, at different temperatures

Figure 10. Lubricant rheogram for graphite grease, at different temperatures
4. Discussions

Analyzing the experimental results concerning the variation of the rheological parameters with the temperature (Table 1), it can be observed the influence of the additives and nanoparticles on the grease behavior. The grease in pure state has a homogenous structure at low temperatures (below $38^\circ$C), but with the increasing of the temperature the structure is completely destroyed and no measurement can be performed (Figure 7). The yield stress of this grease increases with the temperature until the threshold of $26^\circ$C (probably because of the internal structure of the beeswax) and above this temperature, the yield stress decreases (Figure 12). Regarding the viscosity of the pure grease, it decreases on the whole range of temperatures (Figure 13), whithout any threshold.

It has to be mentioned that above $50^\circ$C the melting process of the grease starts, independent of the presence or absence of additives or nanoparticles. This phenomenon was also observed in other studies regarding the use of beeswax as thickener [9], [10], which reduces the field of application of this kind of greases.

The addition of antioxidant and antiwear additives to the grease decreases the homogenity only at the room temperature ($20^\circ$C). This fact implies the curve fluctuations at the mentioned temperature (Figure 8), while the grease becomes more stable at medium temperatures (until $44^\circ$C). At temperatures above $44^\circ$C, the structure of this grease is also destroyed (Figure 8). The yield stress and viscosity of the additivated grease are smaller than the same values for the pure grease (Figures 12 and 13), having the same behavior until the threshold of $26^\circ$C.

If the grease is additivated supplementary with nanoparticles (graphene or graphite), the structure is very stable for the whole range of investigated temperatures, until the melting point of the beeswax, above $50^\circ$C (Figures 9 and 10). The addition of the graphene nanoparticles decreases the values for yield stress by comparison with pure grease and increases the threshold at $38^\circ$C (Figure 12). Above
this threshold, the yield stress increases by comparison with pure grease. The same observation is
valid for the viscosity, but the threshold is at 32°C (Figure 13).

The greatest values for the rheological parameters are obtained for grease additivated with graphite
particles (Figures 12 and 13), with the particularity that the threshold is missing in this case.

**Table 1. Rheological parameters for the biodegradable grease.**

| Type of grease      | Temperature, 0°C | Yield stress ($\tau_o$), Pa | Viscosity ($\eta$), Pa-s |
|---------------------|------------------|------------------------------|--------------------------|
| Pure grease         | 20               | 355                          | 0.400                    |
|                     | 26               | 427                          | 0.359                    |
|                     | 32               | 258                          | 0.194                    |
|                     | 38               | 159                          | 0.077                    |
| Additivated grease  | 20               | 462                          | 0.191                    |
|                     | 26               | 212                          | 0.228                    |
|                     | 32               | 179                          | 0.097                    |
|                     | 38               | 92                           | 0.048                    |
|                     | 44               | 59                           | 0.039                    |
| Graphene grease     | 20               | 241                          | 0.383                    |
|                     | 26               | 205                          | 0.307                    |
|                     | 32               | 121                          | 0.339                    |
|                     | 38               | 176                          | 0.155                    |
|                     | 44               | 59                           | 0.039                    |
|                     | 50               | 43                           | 0.014                    |
| Graphite grease     | 20               | 459                          | 0.556                    |
|                     | 26               | 389                          | 0.407                    |
|                     | 32               | 205                          | 0.338                    |
|                     | 38               | 191                          | 0.147                    |
|                     | 44               | 95                           | 0.041                    |
|                     | 50               | 29                           | 0.019                    |

![Figure 12. Variation of the yield stress versus temperature, for all the greases](image-url)
Figure 13. Variation of the viscosity versus temperature, for all the greases

Regarding the property of tackiness (ability to form threads before separation), it can observe that pure grease and grease with graphite nanoparticles have a more reduced degree of adherence by comparison with additivated grease and grease with graphene nanoparticles.

5. Conclusions
In this paper was performed the study of the rheological properties (yield stress and viscosity) of biodegradable greases based on rapeseed oil and beeswax, additivated with graphene or graphite nanoparticles.

The rheological properties were investigated in the range of temperature of 20°C … 50°C and the results were fitted according to Bingham model.

It can be observed that the addition with nanoparticles increases the homogeneity of the grease and enlarges the field of use of biodegradable lubricants until the melting point of the beeswax.

The greatest values for the yield stress and viscosity are obtained for the grease additivated with graphite nanoparticles, by comparison with the one additivated with graphene nanoparticles.

From the point of view of the adherence, the grease with graphene nanoparticles is more appropriate than the grease with graphite nanoparticles.

6. References
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