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# Rheology of new lubricating greases made from renewable materials

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**Abstract.** Lubricanting greases from waste frying vegetables oils with natural fibers additives could be the answer to the sustainable production of greases. Also, their biodegradability makes them more acceptable for the environment, having in view increasingly strict regulations in domain. In this experimental work, twenty lubricant formulae were created from waste sunflower oil and waste palm oil with calcium or lithium stearate as thickener and cellulose or lignin additives. All were rheologically tested and characterized as Bingham fluid with good consistency and plasticity. The penetration tests confirmed the good consistency, categorizing these products from normal to firm, very firm and hard lubricant greases comparable to those conventionally obtained from mineral oils.

***Keywords*:** lubricating greases; renewable materials; rheological properties; thickener.

## 1. Introduction

A lubricant is a material intended to reduce the effort in tools and equipment with moving parts [1]. It can be a mineral or a vegetable oil or animal fat, but in some applications, the structure of these is not able to meet all the requirements for a good lubrication. For heavier duties, modern lubricants are developed.

Lubricanting greases are viscoelastic semi-solids [1], classically made up of an oil and a thickener, usually a soap synthetized *in situ*. An additive is often added to modify the rheology of the grease, e.g. poliolefins, new or recycled [2, 3], microcrystalline cellulose [4] or nanoparticles [5, 6] or cellulose derivatives [7], lignin [8], polyurethanes [9], graphite nanoparticles or graphite derivatives of different morphology (bulky, sheets or tubular) [10], boron nitride [11], etc. To improve the rheology of lubricanting greases, more complex greases based on soaps were prepared [9, 12]. Some lubricanting greases don't even use a soap, but other thickeners in the oil, in the manufacture of oleogels with behavior comparable to classical lubricanting greases. The thickeners can be lignin [13, 14], polyurethane or bentonite [9, 15, 16]. Other lubricant "greases" are in fact gels made with aqueous solutions such as: cellulose microfibrils in triethyl citrate [6], cellulose acetate butyrate gel [7], lignin in polyethylenglycol [17]. However, classical lubricant greases can be improved forwards, especially considering renewable materials, for sustainability purposes [18].

For the characterization of lubricanting greases, the rheological study is an important step, thus measuring the fluidity and the deformation to evaluate the material's function. The rheologic behavior depends on the materials structure, the external stress acting on material, and temperature [19].

In the present work, new lubricanting greases made of renewable materials were prepared and characterized by rheometry. The aim of this study was to select the best formulae from rheological point of view, before scaling up the manufacture process for lubricant greases.

## 2. Experimental

Small batches of lubricant greases from waste cooking oil were prepared and characterized having in view the obtaining of sustainable products with the same quality as greases obtained from mineral oils.

### *2.1. Materials and methods*

*Materials.* For this experiment, two types of waste cooking oils were used: sunflower and palm oils. At 20 $^{o}$C, the sunflower oil has 0.9177 g/cm$^{-3}$ density and 78.8 cSt kinematic viscosity; the palm oil has 0.9168 g/cm$^{3}$ and 124.1 cSt. The density and the kinematic viscosity were measured with Anton Parr apparatus type SVM 3000, using the U-shaped vibrating tube method for density and the rotational viscometer for viscosity. The oils present high Marcusson flash points: 240 $^{o}$C for the sunflower oil and > 250 $^{o}$C for the palm oil, and a strong unsaturated character evident in high iodine numbers: 74.8 g $I_2$/100 g for sunflower oil and 60.2 g $I_2$/ 100 g for palm oil.

The thickener of the grease was a soap prepared from stearic acid from Merck and technical grade calcium hydroxide, $Ca(OH)_2$, from Carpat Var Ltd., or anhydrous lithium hydroxide, LiOH, from Merck.

In accordance with the purpose of the study, as additives, the microcrystalline cellulose-pharmaceutical grade and lignin Kraft/lignin sulfate were used in different proportions.

*Characterization methods.* First, the greases were characterized by optical microscopy, for concluding on

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their structure and texture. A digital Bresser 5201000 microscope was used, with a LCD screen MICRO 5 megapixel and magnifying by max. x 40.

The rheology of the greases was performed with a plate-to-plate rheometer Anton Parr, model MCR 72, with a measuring plate PP50 (d = 50 mm). The apparatus automatically draws the rheological curves and calculates the rheological parameters according to the Herschel-Buckley rheological model, but the experimental data can be also processed by the operator in another way, if this model is not considered satisfactory, which we did in this study.

The consistency of greases was checked with a digital penetrometer model APA-OA, made in China, by Cangzhou Oubeiruike Instrument and Equipment Co. Ldt., and adapted to Cone Standard Method STAS 42 – 68.

### *2.2. Synthesis procedure*

The greases were prepared in 100 g batches. The preparation started with *in situ* soap preparation in strictly stoichiometric proportions, so in the end, the soap constitutes theoretically 20% wt in the mixture with oil. The vegetable oil, stearic acid and the base ($Ca(OH)_2$ or LiOH) were mixed, then gradually heated up to 100 $^oC$, maintained at this temperature for an hour, for complete saponification, concomitant with resulted water removal. Towards the end of the saponification process, the additive was added in desired proportion (10%; 15%; 20% wt.), under mixing, then the batch was cooled by natural convection.

## 3. Results and discussion

### *3.1. Morphology of greases*

By free eye, the greases seem homogenous materials; in fact, their morphology is a complex one and influences their rheological behavior and consistency. The morphology of greases is usually observed by optical microscopy with relatively small resolution (x4 to x40). In Figure 1, captures through a x4 lens of a few greases based on sunflower oil are presented: greases *a* , *b* and *c* are prepared with 20% Li-soap; *d*, *e*, *f* with 20% Ca-soap; *a* and *d* are simple oil-soap systems, *b* and *e* are additivated with 20% cellulose; *c* and *f* are additivated with 20% lignin. Figure 2 contains captures for greases based on palm oil, in the same order. From the total of 20 greases created and examined, these 12 were considered representative to be shown since there are small differences from 10% additive to 15% and from 15% to 20%.

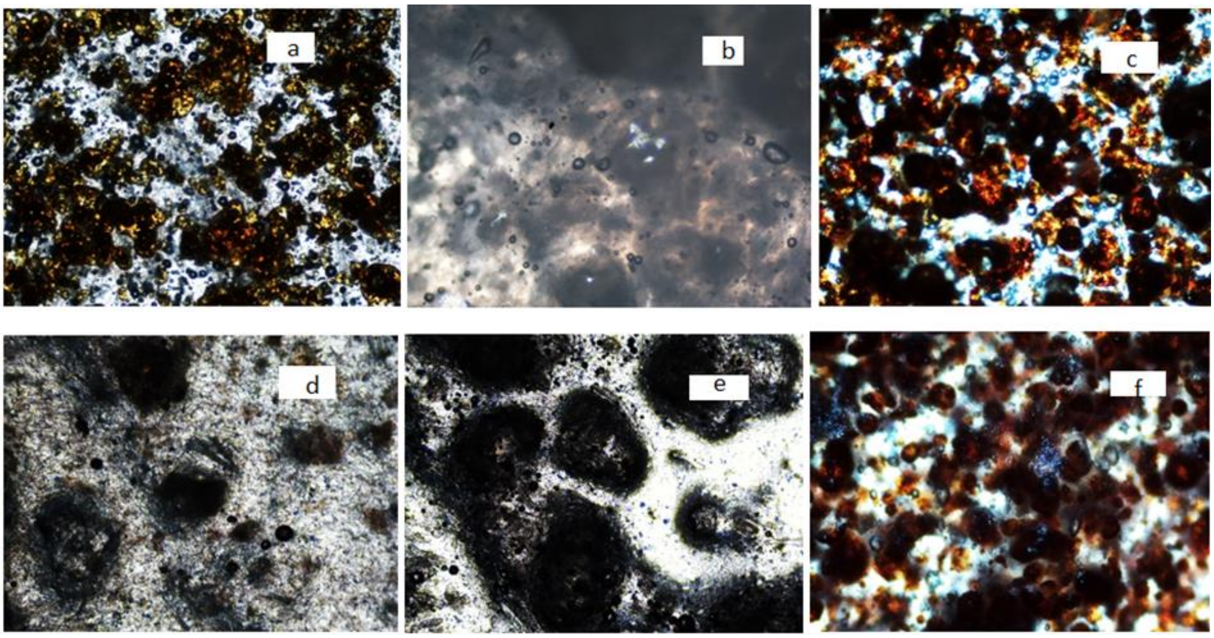


**Figure 1.** Captures with optical microscope (x4) for waste sunflower oil-based greases: a) sunflower oil - 20% Li-soap grease; b) sunflower oil - 20% Li-soap grease add. with 20% cellulose; c) sunflower oil - 20% Li-soap grease add. with 20% lignin; d) sunflower oil - 20% Ca-soap grease; e) sunflower oil - 20% Ca-soap grease add. with 20% cellulose; f) sunflower oil - 20% Ca-soap grease add. with 20% lignin.

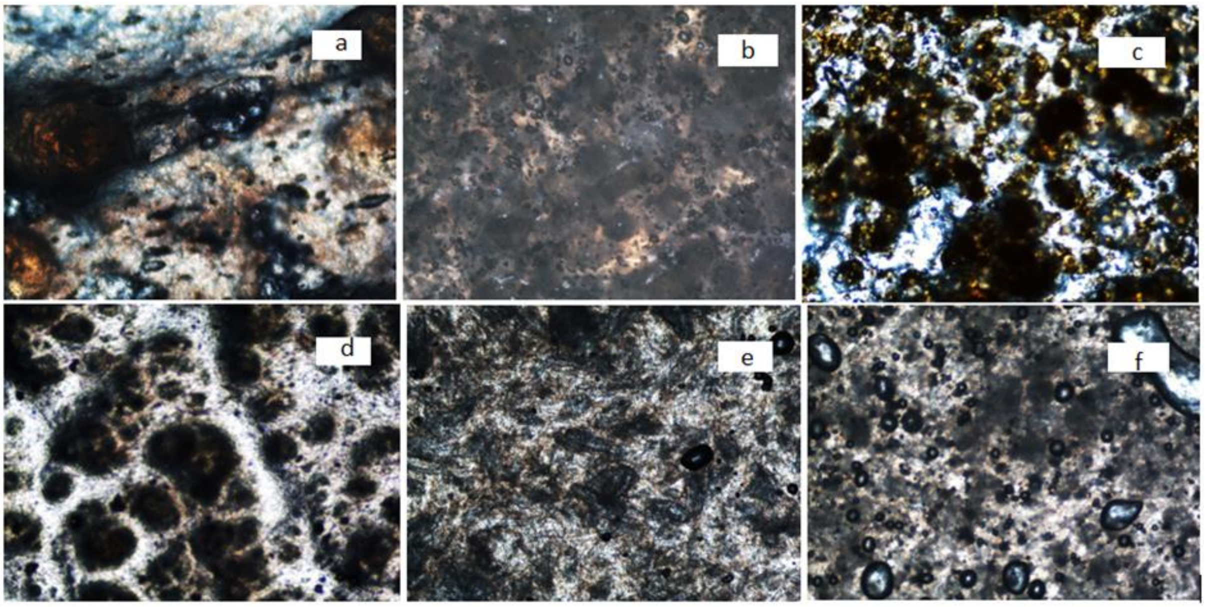


**Figure 2.** Captures with optical microscope (x4) for waste palm oil-based greases: a) palm oil - 20% Li-soap grease; b) palm oil - 20% Li-soap grease add. with 20% cellulose; c) palm oil - 20% Li-soap grease add. with 20% lignin; d) palm oil - 20% Ca-soap grease; e) palm oil - 20% Ca-soap grease add. with 20% cellulose; f) palm oil - 20% Ca-soap grease add. with 20% lignin.

In all pictures from Figures 1 and 2, the soap network is observed in white; in all cases, the network is well outlined, this confirming the accuracy of the preparation process. The cellulose fibers appear in grey, interpenetrated with the soap and oil drops; in case of Ca-soap greases, the cellulose forms agglomerates around the oil drops (clews of 0.7 - 1.5 mm diameter), since in Li-soap greases, the cellulose is more uniformly distributed. The lignin is black, and in Figures 1c, 1f, 2c and 2f, oil drops (0.07 - 0.14 mm diameter) stand out clearly from the soap network and lignin, this indicating that the dispersion of components in the grease may not be very good. But in general, the microscopic aspect of the samples leads us to the conclusion that the rheology and the consistency of the greases are expected to be those of good quality products.

### *3.2. Rheology*

The rheological curves of all greases were determined with the plate-to-plate rheometer Anton Parr, for the shear rate ($\dot{\gamma}$) in range of 0 - 100 $s^{-1}$ since the shear stress ($\tau$) was measured in Pa. The curves were determined at 20 ºC, 30 ºC, 40 ºC, 50 ºC and 60 ºC. Their appearance, as seen in Figure 3, reveals non-Newtonian fluids with initial tension ($\tau_0$) and hystheresis, with tixotropic behavior, as it is in the case of the majority of lubricating greases.

More than that, the correlation between the shear stress and the shear rate reveals a Bingham dependency, in the form of the Equation 1:

$$\tau = \tau_0 + \mu_p \cdot \dot{\gamma} \qquad (1)$$

where $\tau$ is the shear stress (Pa), $\tau_0$ is the initial tension, (Pa), $\mu_p$ is the plastic viscosity (Pa·s), and $\dot{\gamma}$ is the shear rate, ($s^{-1}$).

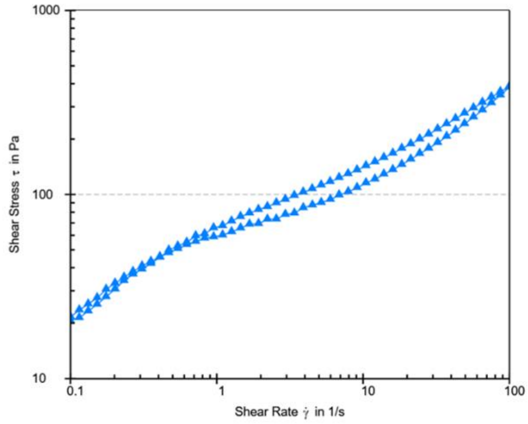


**Figure 3.** Rheological curve at 20 ºC for the palm oil-based grease with 20% wt. Ca-soap and 10% wt. lignin added.

From the rheological curves, the parameters $\tau_0$ and $\mu_p$ were graphically determined; the experimental data are presented in the Tables 1-8. These parameters allow to make interpretations on the consistency and plasticity of the greases, as follows. Tables 1-4 present the results obtained for sunflower oil-based lubricanting greases.

**Table 1**. Rheological parameters for sunflower oil- based greases with 20% Ca soap and cellulose

| Cellulose concentration (% wt) | Rheological test temperature (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$ (Pa) | $\mu_p$ (Pa·s) |
| 0 | 20 | 9.0 | 1.10 |
| | 30 | 5.2 | 0.70 |
| | 40 | 2.3 | 0.20 |
| | 50 | 1.2 | 0.09 |
| | 60 | 0.6 | 0.08 |
| 10 | 20 | 18 | 2.20 |
| | 30 | 10 | 1.00 |
| | 40 | 2.50 | 0.30 |
| | 50 | 0.75 | 0.10 |
| | 60 | 0.70 | 0.09 |
| 15 | 20 | 25 | 3.50 |

| Cellulose concentration (% wt) | Rheological test temperature (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$ (Pa) | $\mu_p$ (Pa·s) |
| | 30 | 13 | 2.00 |
| | 40 | 6 | 0.70 |
| | 50 | 2.2 | 0.20 |
| | 60 | 1.5 | 0.15 |
| 20 | 20 | 70 | 6.0 |
| | 30 | 42 | 5.0 |
| | 40 | 15 | 1.0 |
| | 50 | 1.2 | 0.4 |
| | 60 | 1.3 | 0.25 |

**Table 2.** Rheological parameters for sunflower oil- based greases with 20% Ca-soap and lignin

| Lignin concentration (% wt) | Rheological test temperature, (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$ (Pa) | $\mu_p$ (Pa·s) |
| 0 | 20 | 9.0 | 1.10 |
| | 30 | 5.2 | 0.70 |
| | 40 | 2.3 | 0.20 |
| | 50 | 1.2 | 0.09 |
| | 60 | 0.6 | 0.08 |
| 10 | 20 | 16 | 2.2 |
| | 30 | 13 | 1.5 |
| | 40 | 12 | 1.3 |
| | 50 | 6.5 | 1.0 |
| | 60 | 3.1 | 0.7 |
| 15 | 20 | 18 | 2.0 |
| | 30 | 15 | 1.3 |
| | 40 | 12 | 1.1 |
| | 50 | 11 | 0.8 |
| | 60 | 5 | 0.7 |
| 20 | 20 | 20 | 4.0 |
| | 30 | 18 | 2.8 |
| | 40 | 17 | 2.0 |
| | 50 | 12 | 1.8 |
| | 60 | 5.5 | 0.85 |

**Table 3.** Rheological parameters for sunflower oil-based greases with 20% Li-soap and cellulose

| Cellulose concentration (% wt) | Rheological test temperature (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$ (Pa) | $\mu_p$ (Pa·s ) |
| 0 | 20 | 30 | 2.5 |
| | 30 | 26 | 2.0 |
| | 40 | 20 | 1.8 |
| | 50 | 14 | 1.6 |
| | 60 | 11 | 1.4 |
| 10 | 20 | 40 | 4 |
| | 30 | 18 | 2 |
| | 40 | 6.8 | 1 |
| | 50 | 5.5 | 1 |
| | 60 | 4 | 1 |
| 15 | 20 | 32 | 5.0 |
| | 30 | 17 | 2.8 |
| | 40 | 5 | 1.2 |
| | 50 | 3.8 | 1.2 |
| | 60 | 3.5 | 1.1 |
| 20 | 20 | 63 | 6.0 |
| | 30 | 27 | 3.7 |
| | 40 | 12 | 1.3 |
| | 50 | 9 | 1.2 |
| | 60 | 8 | 1.2 |

**Table 4.** Rheological parameters for sunflower oil- based greases with 20% Li soap and lignin

| Lignin concentration (% wt) | Rheological test temperature, (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$, (Pa) | $\mu_p$, (Pa·s) |
| 0 | 20 | 30 | 2.5 |
| | 30 | 26 | 2.0 |
| | 40 | 20 | 1.8 |
| | 50 | 14 | 1.6 |
| | 60 | 11 | 1.4 |
| 10 | 20 | 12 | 2.20 |
| | 30 | 10 | 1.80 |
| | 40 | 6 | 1.15 |
| | 50 | 4.8 | 0.90 |
| | 60 | 4.2 | 0.80 |
| 15 | 20 | 13 | 3.00 |
| | 30 | 12 | 1.19 |
| | 40 | 10 | 1.15 |
| | 50 | 5 | 1.18 |
| | 60 | 5 | 1.00 |
| 20 | 20 | 18 | 3.00 |
| | 30 | 12 | 2.00 |
| | 40 | 11 | 1.18 |
| | 50 | 10 | 1.15 |
| | 60 | 10 | 1.10 |

Tables 5-8 present the results obtained for palm oil-based lubricanting greases.

**Table 5.** Rheological parameters for palm oil-based greases with 20% Ca-soap and cellulose

| Cellulose concentration (% wt) | Rheological test temperature (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$ (Pa) | $\mu_p$ (Pa·s) |
| 0 | 20 | 15.5 | 1.3 |
| | 30 | 5.5 | 0.7 |
| | 40 | 4.8 | 0.5 |
| | 50 | 4.2 | 0.4 |
| | 60 | 3.5 | 0.3 |
| 10 | 20 | 6.5 | 1.90 |
| | 30 | 3.0 | 0.90 |
| | 40 | 2.0 | 0.21 |
| | 50 | 1.9 | 0.17 |
| | 60 | 1.8 | 0.15 |
| 15 | 20 | 12 | 3.00 |
| | 30 | 5 | 1.30 |
| | 40 | 2.5 | 0.65 |
| | 50 | 2 | 0.40 |
| | 60 | 1.5 | 0.32 |
| 20 | 20 | 14 | 4.50 |
| | 30 | 6.5 | 2.10 |
| | 40 | 3.2 | 0.85 |
| | 50 | 2.5 | 0.50 |
| | 60 | 2 | 0.40 |

**Table 6.** Rheological parameters for palm oil- based greases with 20% Ca-soap and lignin

| Lignin concentration (% wt) | Rheological test temperature (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$ (Pa) | $\mu_p$ (Pa·s) |
| 0 | 20 | 15.5 | 1.3 |
| | 30 | 5.5 | 0.7 |
| | 40 | 4.8 | 0.5 |
| | 50 | 4.2 | 0.4 |
| | 60 | 3.5 | 0.3 |
| 10 | 20 | 14 | 2.30 |

| Lignin concentration (% wt) | Rheological test temperature (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$ (Pa) | $\mu_p$ (Pa·s) |
| | 30 | 8 | 1.10 |
| | 40 | 5 | 0.60 |
| | 50 | 4 | 0.55 |
| | 60 | 3.2 | 0.50 |
| 15 | 20 | 18 | 3.7 |
| | 30 | 8 | 2.0 |
| | 40 | 4.5 | 0.9 |
| | 50 | 3 | 0.4 |
| | 60 | 2.5 | 0.35 |
| 20 | 20 | 18 | 4.5 |
| | 30 | 7.5 | 2.7 |
| | 40 | 4.5 | 1.4 |
| | 50 | 3.5 | 0.5 |
| | 60 | 1.8 | 0.4 |

**Table 7.** Rheological parameters for palm oil- based greases with 20% Li-soap and cellulose

| Cellulose concentration (% wt) | Rheological test temperature, (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$, (Pa) | $\mu_p$, (Pa·s) |
| 0 | 20 | 35 | 3.00 |
| | 30 | 18 | 2.00 |
| | 40 | 13 | 1.10 |
| | 50 | 8 | 1.05 |
| | 60 | 6 | 0.85 |
| 10 | 20 | 51 | 5.0 |
| | 30 | 21 | 2.0 |
| | 40 | 11 | 1.1 |
| | 50 | 8 | 0.8 |
| | 60 | 5 | 0.5 |
| 15 | 20 | 47 | 6.0 |
| | 30 | 20 | 3.0 |
| | 40 | 11 | 2.0 |
| | 50 | 8.5 | 1.3 |
| | 60 | 5 | 0.9 |
| 20 | 20 | 38 | 7.0 |
| | 30 | 18 | 3.0 |
| | 40 | 12 | 2.0 |
| | 50 | 9 | 1.3 |
| | 60 | 8 | 1.2 |

**Table 8.** Rheological parameters for palm oil-based greases with 20% Li-soap and lignin

| Lignin concentration (% wt) | Rheological test temperature, (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$, (Pa) | $\mu_p$, (Pa·s) |
| 0 | 20 | 35 | 3.00 |
| | 30 | 18 | 2.00 |
| | 40 | 13 | 1.10 |
| | 50 | 8 | 1.05 |
| | 60 | 6 | 0.85 |
| 10 | 20 | 100 | 7.5 |
| | 30 | 50 | 4.3 |
| | 40 | 32 | 3.0 |
| | 50 | 25 | 3.3 |
| | 60 | 21 | 2.0 |
| 15 | 20 | 50 | 5.3 |
| | 30 | 25 | 3.0 |
| | 40 | 15 | 1.9 |
| | 50 | 10 | 1.2 |
| | 60 | 9 | 1.1 |
| 20 | 20 | 60 | 6.5 |
| | 30 | 31 | 4.0 |

| Lignin concentration (% wt) | Rheological test temperature, (ºC) | Rheological parameters | |
|---|---|---|---|
| | | $\tau_0$, (Pa) | $\mu_p$, (Pa·s) |
| | 40 | 18 | 2.5 |
| | 50 | 12 | 1.8 |
| | 60 | 10 | 1.5 |

From data in Tables 1-8, it becomes noticeable that the greases prepared with Li-soap have higher initial tension $\tau_0$. For example, the grease prepared with palm oil with Ca-soap and without other additive has $\tau_0$ = 15.5 Pa at 20 ºC, and that prepared with Li-soap has $\tau_0$ = 35 Pa at the same temperature.

Also, the greases based on palm oil are tougher than those prepared based on sunflower oil with 20% Ca-soap, without other additive, e.g. $\tau_0$ = 9 Pa at 20 ºC, since the grease made with palm oil has $\tau_0$ = 15.5 Pa at the same temperature.

As a rule, increasing the temperature of the greases leads to the decrease of the $\tau_0$, for all the greases prepared in this experiment, as seen in Tables 1-8.

In general, more additive added, cellulose or lignin, will lead to the increasing of $\tau_0$. Exceptions occur for some greases additised with lignin, whose $\tau_0$ may vary in a particular way, with a decrease from 0% to 10%, and a so-called stabilization of the $\tau_0$ values for 10, 15, and 20% additive. This may arise from a poorer stability of greases with lignin added.

The plastic viscosity $\mu_p$ of all greases decreases with increasing temperature and, in general, palm oil-based products have higher plasticity than those based on sunflower oil. Also, adding more cellulose or lignin leads to higher plasticity of the products.

The apparent viscosity ($\mu_a$, Pa·s), at 20 ºC and $\dot{\gamma} = 100\ s^{-1}$, was calculated with Equation 2, for all greases formulations, in order to compare values among them and with other data in literature:

$$\mu_a = \mu_p + \frac{\tau_0}{\dot{\gamma}} \quad (2)$$

The values of the apparent viscosity $\mu_a$, at 20 ºC and $\dot{\gamma} = 100\ s^{-1}$, also extrapolated at 4500 $s^{-1}$, are presented in Table 9.

**Table 9.** Apparent viscosity of greases at 20 ºC, $\dot{\gamma} = 100\ s^{-1}$ and $\dot{\gamma} = 4500\ s^{-1}$

| Sample | Grease formulation | $\mu_a$ at $\dot{\gamma} = 100\ s^{-1}$ (Pa·s) | $\mu_a$ at $\dot{\gamma} = 4500\ s^{-1}$ (Pa·s) |
|---|---|---|---|
| **1** | **SOC*** | **1.19** | **1.10** |
| 2 | SOC+10% cellulose | 2.38 | 2.20 |
| 3 | SOC+15% cellulose | 3.75 | 3.51 |
| 4 | SOC+20% cellulose | 6.70 | 6.01 |
| 5 | SOC+10% lignin | 2.36 | 1.1 |
| 6 | SOC+15% lignin | 2.18 | 2.00 |
| 7 | SOC+20% lignin | 4.20 | 4.00 |
| **8** | **SOL*** | **2.80** | **2.51** |
| 9 | SOL+10% cellulose | 4.4 | 4.00 |
| 10 | SOL+15% cellulose | 5.32 | 5.01 |
| 11 | SOL+20% cellulose | 6.63 | 6.01 |
| 12 | SOL+10% lignin | 2.32 | 2.20 |
| 13 | SOL+15% lignin | 3.13 | 3.00 |
| 14 | SOL+20% lignin | 3.18 | 3.00 |
| **15** | **POC*** | **1.46** | **1.31** |

| Sample | Grease formulation | μa at $\dot{\gamma}$ = 100 s-1 (Pa·s) | μa at $\dot{\gamma}$ = 4500 s-1 (Pa·s) |
|---|---|---|---|
| 16 | POC+10% cellulose | 1.97 | 1.90 |
| 17 | POC+15% cellulose | 3.12 | 3.00 |
| 18 | POC+20% cellulose | 4.64 | 4.50 |
| 19 | POC+10% lignin | 2.44 | 2.30 |
| 20 | POC+15% lignin | 3.88 | 3.70 |
| 21 | POC+20% lignin | 4.68 | 4.50 |
| **22** | **POL*** | **3.35** | **3.01** |
| 23 | POL+10% cellulose | 5.51 | 5.01 |
| 24 | POL+15% cellulose | 6.47 | 6.01 |
| 25 | POL+20% cellulose | 7.38 | 7.01 |
| 26 | POL+10% lignin | 8.5 | 7.52 |
| 27 | POL+15% lignin | 5.8 | 5.31 |
| 28 | POL+20% lignin | 7.10 | 6.51 |

*Abbreviations: SOC - Sunflower oil-based grease with Ca-soap 20%; SOL - Sunflower oil-based grease with Li-soap 20%; POC - Palm oil-based grease with Ca-soap 20%; POL - Palm oil-based grease with Li-soap 20%.

As noticed in Table 9, at $\dot{\gamma} = 100$ s$^{-1}$ and 20 ºC the apparent viscosities have values between 1.19 Pa·s and 8.5 Pa·s, indicating viscous fluids prone for use as lubricants. The palm oil-based greases and Li-soap are the most viscous, and those with sunflower oil and Ca-soap are more fluid. In general, increasing the concentration of additives leads to increasing the viscosity. Small deviations from this rule can be observed. By comparing with data in literature for lubricant oleogels obtained from castor oil with epoxidated lignin [20], our lubricant greases are less viscous since their lubricants had viscosities between 5 and 11 Pa·s.

By calculating $\mu_a$ at $\dot{\gamma} = 4500$ s$^{-1}$, in order to compare the present greases with similar greases previously prepared [18] from fresh palm oil with Ca-soap 20% thickener and the same additives, cellulose and lignin, much viscous greases were obtained by using waste fried oil, with apparent viscosity in range 1.31 - 5.5 Pa·s, comparing with former greases with $\mu_a$=0.19 ÷0.47 Pa·s. This difference can be explained by more polar character of waste oil comparing with fresh oil, due to hydrolysis reactions and alkenes, oxopropylesthers, and ketones formed during the frying process.

### *3.3. Consistency of greases*

Even though $\tau_o$ is a hint in appreciation of grease consistency, the penetration test is defining for the quality of the grease from consistency point of view.

All the fresh greases were tested at 20 ºC, and their penetration value in tenth of mm are shown in Table 10.

**Table 10**. The penetration test results for the prepared greases

| Sample | Grease formulation | Penetration, tenth of mm | NLGI** grade |
|---|---|---|---|
| **1** | **SOC*** | **268** | **2** |
| 2 | SOC+10% cellulose | 216 | 3 |
| 3 | SOC+15% cellulose | 208 | 4 |
| 4 | SOC+20% cellulose | 212 | 4 |
| 5 | SOC+10% lignin | 341 | 1 |
| 6 | SOC+15% lignin | 327 | 1 |
| 7 | SOC+20% lignin | 256 | 2 |
| **8** | **SOL*** | **298** | **2** |
| 9 | SOL+10% cellulose | 205 | 4 |
| 10 | SOL+15% cellulose | 213 | 3 |
| 11 | SOL+20% cellulose | 165 | 4 |
| 12 | SOL+10% lignin | 334 | 1 |
| 13 | SOL+15% lignin | 316 | 1 |
| 14 | SOL+20% lignin | 322 | 1 |
| **15** | **POC*** | **170** | **4** |
| 16 | POC+10% cellulose | 126 | 5 |
| 17 | POC+15% cellulose | 117 | 6 |
| 18 | POC+20% cellulose | 117 | 6 |
| 19 | POC+10% lignin | 128 | 5 |
| 20 | POC+15% lignin | 152 | 5 |
| 21 | POC+20% lignin | 136 | 5 |
| **22** | **POL*** | **210** | **3** |
| 23 | POL+10% cellulose | 186 | 4 |
| 24 | POL+15% cellulose | 171 | 4 |
| 25 | POL+20% cellulose | 138 | 5 |
| 26 | POL+10% lignin | 135 | 5 |
| 27 | POL+15% lignin | 128 | 5 |
| 28 | POL+20% lignin | 104 | 6 |

*Abbreviations: SOC- Sunflower oil-based grease with Ca-soap 20%; SOL- Sunflower oil-based grease with Li-soap 20%; POC- Palm oil-based grease with Ca-soap 20%; POL- Palm oil-based grease with Li-soap 20%.
**NLGI (National Lubricating Grease Institute) consistency number.

As seen in Table 10, the sunflower oil-based greases with Ca-soap as well as with Li-soap are in "normal grease" category (grade 2) and the addition of cellulose increases the consistency up to grade 4 ("very firm") at 20% wt. soap concentration. The additive lignin in sunflower oil-based greases leads to "soft" greases, grade 1. This indicates that, for sunflower oil- based formulae, the lignin added didn't form homogeneous mixtures with the grease, affecting its stability. The most probable reason for this behavior is the quality of lignin which was Kraft lignin in the case of sunflower oil-based lubricants.

Palm oil forms "firm" (grade 3) and "very firm" (grade 4) greases with Li-soap and Ca-soap, respectively, in absence of any additive. Adding cellulose or lignin has as an effect, without exception, the hardening of greases, to grades 4, 5 (“hard”), and 6 (“very hard”). More additive in the formula leads to harder products. In case of palm oil-based lubricants, lignin sulfate was used, and the consistency of the grease increased spectacularly with the lignin added. This led us to the conclusion that lignin sulfate is more compatible with the system’s components that the alkali lignin Kraft.

There are three sets of available penetration data to be compared between palm oil-based greases prepared from fresh oil in our previous study [18] and those from waste oil in the present work. These data can be compared in Table 11.

**Table 11.** Comparation of penetration data for fresh palm oil-based greases and waste oil-based greases

| Sample | Grease formulation | NLGI grade (Fresh oil formula) | NLGI grade (Waste oil formula) |
|---|---|---|---|
| 1 | Palm oil with 20% Ca soap + cellulose 10%) | 4 | 5 |
| 2 | Palm oil with 20% Ca soap + cellulose 20%) | 6 | 6 |
| 3 | Palm oil with 20% Ca soap + cellulose 20%) | 4 | 5 |

As seen, the waste palm oil-based greases are at least as consistent as those based on fresh oil and this can be realized by the same more polar character of waste oil.

The greases obtained in the present study, with NLGI grades in range 3-6, are clearly very good by comparing with other bio-lubricants obtained in literature. The oleogels prepared by Sánchez et al. [21] from vegetable (castor, rapeseed, and soybean) oils with sorbitan monostearate have NLGI between 2 and 3 which are considered pretty good since they are superior to standard lithium 12-hydroxystearate lubricant greases (NLGI:1-2).

## 4. Conclusions

In this work, new formulae of sustainable greases made-up of waste vegetable oils were prepared and characterized. The waste vegetable oils were sunflower and palm oils, the most used as frying oils in our region, so they are available at a scale large enough for the industrial production of some lubricating greases. The additives, cellulose and lignin, are also sustainable components of vegetable origin.

The quality of the greases depends on the materials used but equally it is due to the synthesis correctness.

The rheological study disclosed that the prepared greases are non-Newtonian fluids with initial tension $\tau_o$ and hysteresis, with thixotropic behavior, as lubricant greases are, in majority of cases.

In addition, from the rheological results it can be observed that apparent viscosity of greases measured at the same shear rate (100 $s^{-1}$) decreases with the increasing temperature but preserves the type of non-Newtonian behavior.

The palm oil-based greases are more consistent (higher initial tension, $\tau_0$) then those sunflower oil-based and the consistency increases with the concentration of the additives in the lubricant. The greases prepared with Li-soap are more consistent than those prepared with Ca-soap.

Moreover, these conclusions are sustained by the penetration tests. The quality of the lubricant greases is visible in the classification (NLGI grade) which denotes that they are comparable with those obtained from mineral oils.

This study will be continued by scaling-up the preparation to 500 g batches, when the processes can be challenging for the quality of the greases, and using the best formulae obtained here.

## Conflict of interest

Authors declare no conflict of interest.

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