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Influence of manufacturing temperature on the rheological behavior of some vegetable lubricating greases

Cyrille Alode VODOUNON,[1] Ancaelena Eliza STERPU*,[2] Iuliana Marlena PRODEA,[3] and Claudia Irina KONCSAG[2]

[1]*Universite de Parakou, BP:316, Fidjrosse, Cotonou, Benin*
[2]*Ovidius University of Constanta, 124 Mamaia Street, 900527, Constanta, Romania*
[3]*University "Politehnica" of Bucharest, 1-6 Polizu Street, Bucharest, 011061, Romania*

Abstract. Lubricant greases from renewable resources are considered as an alternative to those manufactured from mineral or synthetic oils, due to their close-loop supply chain. Low toxicity makes them prone for machinery in food industry. The goal of the present study was to find the optimum parameters for their manufacture from some vegetable oils and calcium stearate soap synthesized in situ. The effect of synthesis temperature (between 80-110 ºC) and soap concentration (between 15-25% wt.) on the rheology and consistency of the products was studied. The optimum manufacture resulted to be 100 ºC and soap concentration between 20-25% wt. The conclusions of these study can serve as a basis for improving the said greases through additivation.

Keywords: vegetable lubricating grease; lubricant grease rheology; grease penetration test.

1. Introduction

The use of renewable resources and the design of environmentally conscious products in close-loop supply chains [1] are of greatest importance due to their positive impact on the natural environment. Therefore, it is a challenge for industry not only to develop new products with good properties, but also to improve them from the environmental point of view [2, 3].

Common lubricating greases are suspensions of fatty acid soaps of Li, Ca, Na, Al or Ba in mineral or synthetic oil [4, 5] with improved structure due to specific manufacture conditions. According to some studies [6, 7], a more biodegradable lubricating greases formulation can be obtained just by replacing the mineral oil, which is the main component (70 – 95% wt.), with a vegetable one.

In comparison with mineral oils, traditionally employed in greases formulation, vegetable oils have different physical-chemical and tribological properties due to the presence of triglycerides in the chemical composition [8]. Vegetable oils have many advantages, such as low toxicity, low volatility (related to high flash points), good lubricity and ability for adhering to metal surfaces, and small viscosity–temperature variation [9]. But vegetable oils also present certain disadvantages, for instance poor oxidative stability, low-temperature bad performance, and high costs [9, 10]. Some of disadvantages can be mitigated through chemical or thermal modification [11-13] and by additivation [14-17].

A preliminary study [18], proved that some vegetable oils (corn oil and palm oil) are promising raw materials for lubricant greases but a more extensive study must be carried on to establish the effect of the manufacturing temperature on their rheological behavior and consistency. This was performed in the study presented in the following.

2. Experimental

2.1. Materials

For the preparation of lubricant greases, corn oil and palm oil were used as raw materials having the following characteristics:

- kinematic viscosity at 40 ºC: 32.108 cSt for corn oil and 35.41 cSt for palm oil, respectively (method SR ISO 3104/2002)
- density at 40 ºC: 905 kg/m^3 for corn oil and 880 kg/m^3 for palm oil, respectively (method SR EN ISO 3675/2003)

For the soap preparation, stearic acid from Merck and $Ca(OH)_2$ from Carpat Var SRL were used.

2.2. Synthesis of the greases

The vegetable oil, stearic acid and $Ca(OH)_2$ were loaded together in the vessel, heated up to 80 or 100 or 110 ºC, in proportions indicated in Table 1, to obtain batches of 100 g. The mixture is maintained under agitation for one hour, time enough to complete the saponification reaction, then it is allowed to cool slowly. This way, 18 samples of greases were prepared, corresponding to soap concentration of 15%, 20% and 25% wt. for each type of oil, at three different process temperatures: 80 ºC, 100 ºC and 110 ºC, respectively.

* Corresponding author. *E-mail address:* asterpu@univ-odivius.ro (Ancaelena Eliza Sterpu).

Table 1. The formula for different concentration of calcium soap in the grease

Soap concentration, wt.	Oil, [g]	Stearic acid, [g]	$Ca(OH)_2$, [g]	Obtained soap, [g]	Grease batch, [g]
15%	85	14.05	1.83	15	100
20%	80	18.74	2.44	20	100
25%	75	23.43	3.05	25	100

2.3. *Characterisation of greases*

Greases were characterised through their density vs. temperature variation, rheological behaviour and consistency, as follows:

2.3.1. Density determination. Greases density determination was carried out according to NYE CTM003 cup method for density and specific gravity of lubricating greases. In this case, the standard method, with standard determination at 25 °C was adapted for determinations at different temperature: 20 °C, 30 °C, 40 °C, 50 °C. The density measurements were necessary for dynamic viscosity calculations.

2.3.2. Rheological measurements. Rheological measurements were carried out with a rheoscope Haake VT 550, Germany, with plate-cone geometry.

The samples were characterized at temperature in range 20 – 50 °C, both with increasing and decreasing shear rate (in range of 9.97 – 4500 s^{-1}, corresponding to 2 - 964 rotations per minute).

The rheological reports containing the variation of shear stress vs. shear rate were provided by the software included in the rheological system. Every curve was built in 100 points.

2.3.3. Penetration tests. The penetration indexes of greases samples were determined with Romanian standard STAS 42 – 68, using a Richardson Cone Standard Penetrometer and converted to NLGI grades [19] this system classifying the consistency of greases in rank from 000 to 6 grade.

3. Results and discussion

The base greases were obtained by the procedure described in Section 2.2 at 80 °C, 100 °C and 110 °C, in order to observe the influence of synthesis temperature on their characteristics.

3.1. Variation of greases density with temperature

The density at different temperatures is required for dynamic viscosity calculations [20]. Also, the variation of grease density with temperature indicates the degree of soap dispersion in the final product.

In Table 2, the densities at 40 °C of greases manufactured at 100 °C from corn oil and palm oil are compared, for soap dispersion estimation.

Table 2. Density at 40 °C of base greases manufactured at 100 °C.

Soap concentration, % wt	Density of corn oil greases, $kg{\cdot}m^{-3}$	Density of palm oil greases, $kg{\cdot}m^{-3}$
0	905	880
15	890	832
20	853	812
25	832	829

In Table 2, one can observe the decrease of density with soap concentration increasing, indicating that the crystalline soap net formed during synthesis has a lower density than the base oil. The exception from this tendency is the density of the palm oil grease containing 25% wt. soap which is higher than that of grease containing 20% soap. This indicates that the soap net suffered a compaction because the soap concentration may be too large.

All greases density was measured at 20 °C, 30 °C, 40 °C, 50 °C and 60 °C. As expected, all greases samples exhibit a decrease in density values with the increase of temperature. For all manufacture temperatures and all soap concentrations, the slopes of the density variation curves were distinctly higher for the grease made of corn oil. For example, the slope of the density variation curve for the corn based grease with 20% wt. soap was -2.03 $kg{\cdot}m^{-3}{\cdot}{}^oC^{-1}$ and that for similar palm based grease was -0.65 $kg{\cdot}m^{-3}{\cdot}{}^oC^{-1}$. Low slope indicates a good dispersion of soap in oil during the manufacture process. Therefore, one can conclude that the soap is better dispersed in palm oil than in corn oil.

3.2. Rheological study

The rheological study was performed for all 18 base greases because the viscosity and its variation with temperature are the main properties counting for a good lubricant.

The appearance of rheological curves (shear stress vs. shear rate) is exemplified in Figure 1, for the grease made of corn oil with 20% wt. calcium stearate, at 20 °C, 30 °C, 40 °C and 50 °C; all the greases in this study had a similar behavior.

Following the appearance, the greases are non Newtonian fluids, the curves presenting a hysteresis, so they are tyxothropic, as normal for lubricating greases. The tyxothropy is more emphasized at lower temperature (20 °C), it decreases with temperature increasing and almost balances out at 50 °C. Also, there is a threshold for taking up fluidization. The rheological curves, at shear rate increasing (ascending curves) or decreasing (descending curves) are best described by Bingham law (Eq. 1):

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

where: τ_0 is the threshold (Pa), μ_p- the plastic viscosity ($kg{\cdot}m^{-1}{\cdot}s^{-1}$ or $N{\cdot}s{\cdot}m^{-2}$) and $\dot{\gamma}$ is the shear rate (s^{-1}); these can be determined from the rheological curves, graphically or by linear regression, as seen in Table 3.

The viscosity is a function of the shear rate, and the apparent viscosity (μ_a) at a certain value of shear stress, can be calculated with Eq. 2:

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

The parameters: τ_0 and μ_p for the descending rheological curves and the apparent viscosities μ_a calculated at $\dot{\gamma}$ =4500 s^{-1} are presented in Table 3 for the corn oil based and in Table 4 for the palm oil based greases.

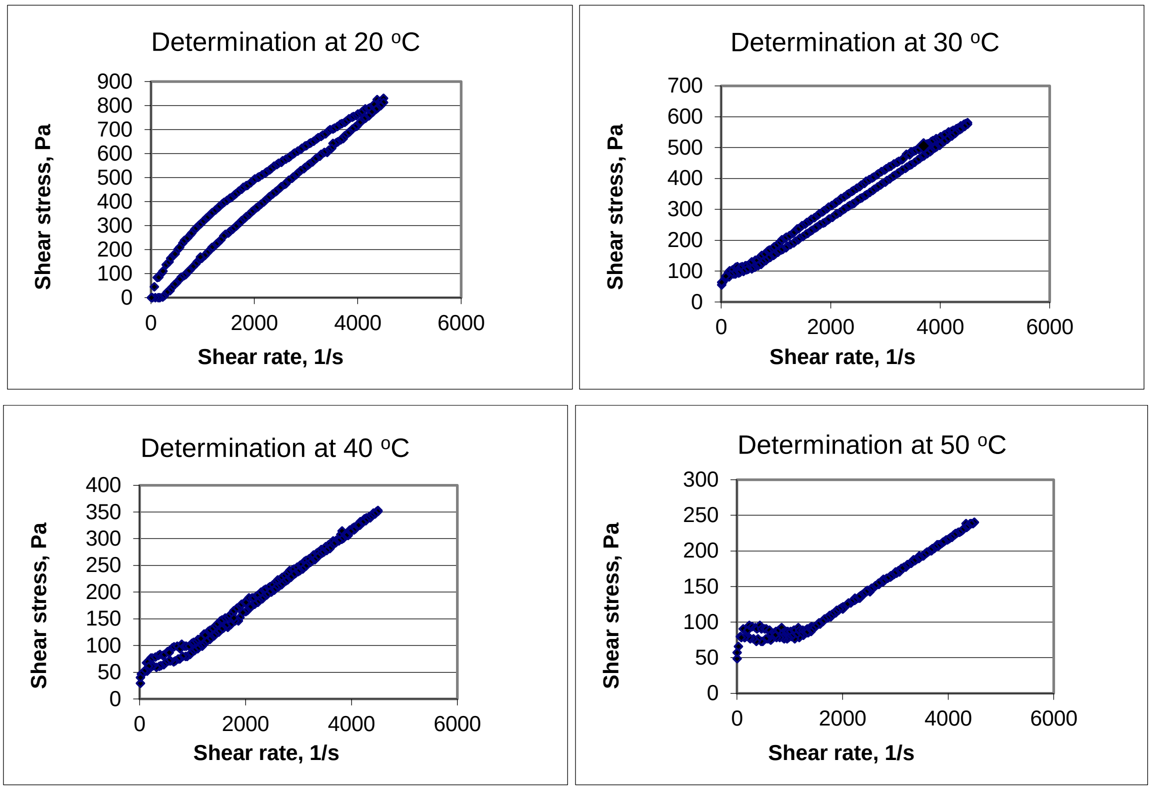

Figure 1. Rheological curves of greases made of corn oil with 20% wt calcium stearate. Determinations were performed at 20 °C, 30 °C, 40 °C and 50 °C

Table 3. The parameters of Bingham law model for greases made of corn oil (curve for decreasing shear rate) and apparent viscosities at $\dot{\gamma}$ = 4500 s^{-1}

Soap concentration, % wt	**Rheological test temperature, °C**	**Manufacture temperature, 80 °C**				**Manufacture temperature, 100 °C**				**Manufacture temperature, 110 °C**			
		τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s
15	20	52	0.1222	0.9978	0.1338	86	0.1457	0.9969	0.1648	52	0.1456	0.9981	0.1572
	30	45	0.0737	0.9877	0.0837	64	0.1052	0.9991	0.1194	46	0.0953	0.9932	0.1055
	40	96	0.0184	0.9050	0.0397	68	0.0667	0.9970	0.0818	70	0.0550	0.9897	0.0706
	50	316	0.0184	0.8654	0.0886	85	0.0436	0.9809	0.0625	77	0.0370	0.9700	0.0541
20	20	86	0.1389	0.9994	0.1580	127	0.1619	0.9959	0.1901	107	0.0543	0.9930	0.0781
	30	82	0.0916	0.9982	0.1098	98	0.1092	0.9982	0.1310	74	0.0400	0.9838	0.0564
	40	75	0.0531	0.9781	0.0698	102	0.0739	0.9986	0.0966	114	0.0374	0.9822	0.0627
	50	76	0.0347	0.9396	0.0516	137	0.048	0.9673	0.0784	66	0.0283	0.9682	0.0430
25	20	97	0.1452	0.9989	0.1668	115	0.1776	0.9990	0.2032	136	0.0538	0.9264	0.0840
	30	121	0.0826	0.9964	0.1095	67	0.1306	0.9995	0.1455	37	0.0694	0.9988	0.0776
	40	160	0.0384	0.9739	0.0740	91	0.0751	0.9959	0.0953	65	0.0405	0.9760	0.0549
	50	359	0.0286	0.8244	0.1084	43	0.0341	0.9930	0.0437	43	0.0341	0.9935	0.0437

Table 4. The parameters of Bingham law model for greases made of palm oil (curve for decreasing shear rate) and apparent viscosities at $\dot{\gamma}$ = 4500 s^{-1}

Soap concentration % wt	**Rheological test temperature, °C**	**Manufacture temperature, 80 °C**				**Manufacture temperature, 100 °C**				**Manufacture temperature, 110 °C**			
		τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s
15	20	72	0.1445	0.9996	0.1605	0	0.1664	0.9992	0.1664	0	0.1639	0.9989	0.1639
	30	46	0.0856	0.9937	0.0958	38	0.1024	0.9954	0.1108	20	0.1006	0.9995	0.1050
	40	73	0.0454	0.9541	0.0616	51	0.0558	0.9817	0.0671	11	0.0599	0.9986	0.0623
	50	25	0.0327	0.9764	0.0383	39	0.0440	0.9987	0.0527	22	0.0428	0.9920	0.0477
20	20	42	0.1511	0.9989	0.1604	127	0.1619	0.9959	0.1901	0	0.1914	0.9950	0.1914
	30	82	0.0916	0.9982	0.1098	97	0.1092	0.9982	0.1308	0	0.1244	0.9948	0.1244
	40	75	0.0531	0.9781	0.0698	102	0.0739	0.9986	0.0966	0	0.0707	0.9822	0.0707
	50	76	0.0347	0.9396	0.0516	117	0.0542	0.9970	0.0802	21	0.0463	0.9980	0.0510
25	20	98	0.2656	0.9989	0.2874	44	0.1139	0.9990	0.1237	90	0.2032	0.9953	0.2232
	30	85	0.1485	0.9964	0.1674	39	0.1247	0.9995	0.1334	0	0.1280	0.9864	0.1280
	40	91	0.0789	0.9739	0.0991	26	0.0710	0.9959	0.0768	22	0.0766	0.9997	0.0815
	50	384	0.0235	0.5395	0.1088	46	0.0412	0.9971	0.0514	23	0.0490	0.9933	0.0541

As seen in Table 3 and Table 4, the apparent viscosity μ_a always increases with the concentration of the soap and it is maximal at 100 ºC manufacture temperature, for both types of greases. The synthesis at 110 ºC produced less consistent greases, probably because of higher loss of water during manufacturing; a small concentration of water is necessary in the grease for better "oiliness" of the dispersed system. This is why manufacture at 100 ºC is preferable in order to obtain base greases of good quality.

In general, the viscosity decreases with testing temperature, however there are some greases manufactured at 80 ºC, with viscosity decreasing between 20 ºC and 40 ºC, then slightly increasing at 50 ºC. This could be due to the model's parameter errors which, in some cases are higher at 50 ºC.

By comparing greases obtained from corn oil (Table 3) with those proceeding from palm oil (Table 4), it results that palm oil greases are more viscous than corn oil greases obtained in the same conditions (soap concentration and manufacture temperature).

3.3. Cone penetration and consistency

Hardness of lubricating greases was determined using the cone penetration method. According to NLGI classification, softer grades 0 and 1, are sometimes used in low-temperature applications in order to improve pumpability, while higher consistency indexes (4-6) are proper for high-speed bearings.

Table 5 collects the penetration values of greases samples and the corresponding NLGI grades.

Table 5. Penetration values of greases samples and the corresponding NLGI grades

Grease sample	Unworked Penetration [x 10^{-1} mm]	NLGI Grade
Grease from palm oil, c= 15% at t= 80 ºC*	> 400	00
Grease from palm oil, c= 15% at t= 100 ºC	> 400	00
Grease from palm oil, c= 15 % at t= 110 ºC	> 400	00
Grease from palm oil, c=20%, t= 80 ºC	330	1
Grease from palm oil, c= 20%, t=100 ºC	140	5
Grease from palm oil, c= 20% at t= 110 ºC	> 400	00
Grease from palm oil, c= 25%, t=80 º C	160	5
Grease from palm oil, c= 25%, t=100 ºC	150	5
Grease from palm oil, c= 25% at t= 110 ºC	> 400	00
Grease from corn oil, c=15%, t= 80 ºC	220	3
Grease from corn oil, c= 15% at t= 100 ºC	> 400	00
Grease from corn oil, c=15%, t= 110 ºC	> 400	00
Grease from corn oil, c=20%, t= 80 ºC	290	2
Grease from corn oil, c= 20%, t= 100 ºC	230	3
Grease from corn oil, c= 20%, t=110 ºC	155	5
Grease from corn oil, c= 25% at t= 80 ºC	> 400	00
Grease from corn oil, c= 25%, t= 100 ºC	85	6
Grease from corn oil, c= 25%, t= 110 ºC	150	5

* *c* is the soap concentration (%wt) and *t* = manufacturing temperature

The penetration values in Table 5 are low for all greases obtained with 20% or 25% wt. soap, at 100 ºC (grade 3-6) this indicating that they are pretty hard. Greases with 15% wt. soap are soft, in general. For all products made at 80 ºC and 110 ºC, the consistency is pretty mutable (from 00 to 5), this indicating that the manufacture process can't be firmly controlled: at 80 ºC because too much water remains in the grease, or at 110 ºC because too much water was removed from the composition.

4. Conclusions

A study was performed to find the optimum manufacturing conditions for the corn oil and palm oil based lubricating greases with calcium stearate produced *in situ*. More precisely, the influences of the manufacturing temperature (80-100-110 ºC) and soap concentration (15-20-25% wt) were studied.

Low density variation with temperature and rheological determinations as well as penetration values (3-6 NLGI grades) indicate that the optimum temperature for greases manufacturing is 100 ºC and concentration of the soap should be 20-25% wt. Also, the rheological study suggests that palm oil based greases are superior having the apparent viscosity at $\dot{\gamma}$ =4500 s^{-1} from 1.2 to 2.6 times higher than corn oil based greases, at the same soap concentration and testing temperature.

This study is to be continued with additivation, in order to improve the hardness of the greases without affecting oiliness.

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Conflict of interest

The authors declare no conflict of interest.

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