RHEOLOGICAL STUDY OF BIODEGRADABLE LUBRICATING GREASES

ANCA IULIANA DUMITRU[1], CLAUDIA IRINA KONCSAG[1], NICOLETA TEODORESCU[2], IULIANA MARLENA PRODEA[2], CYRILLE ALODE VODOUNON[3], ANCA ELENA ELIZA STERPU[1]

[1] *OVIDIUS University of Constanta, 124 Mamaia Street, 900527Constanta, Romania, asterpu@univ-ovidius.ro*

[2] *Politehnica University of Bucharest, 313 Splaiul Independentei, 060042 Bucharest, Romania*

[3] *Universite de Parakou, BP:316, Fidjrosse, Cotonou, Benin*

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 some dispersions, potentially applicable as biodegradable lubricating greases obtained by dispersing calcium soap in vegetable base oils. The calcium soap is obtained during the grease preparation by saponification reaction between stearic acid, CH_3-$(CH_2)_{16}$-COOH, and calcium hydroxide, $Ca(OH)_2$. The vegetable oils were olive, palm and corn oil. For this study 15 grease samples have been prepared and each of them was analyses at 20, 30, 40, 50 and 60°C. The effects that concentration of calcium soap and temperature exert on the rheological properties of these greases were studied. The evolution of shear stress with shear rate was very similar to that found for traditional lubricating greases. The rheological curves indicate that the greases have non-Newtonian behaviors which are better described by the Bingham model. In general, the values of plastic viscosity increase with calcium soap concentrations and decrease with temperature.

Keywords: calcium soap, biodegradable greases, rheological properties

INTRODUCTION

Lubricating greases are highly structured suspensions, usually consisting of a thickener (5–30% wt) dispersed in mineral or synthetic oil (70–95% wt). Fatty acid soaps of lithium, calcium, sodium, aluminium or barium are most commonly used as thickener agents. Although the lubricating component is the base oil, the thickener is a key component, added to increase the consistency of the lubricant, in order to solve some difficulties that lubricating oils cannot cover properly in specific applications (Sanchez *et al.*, 2011; NLGI, 2006). The thickener forms an entanglement network, which traps the oil and confers the appropriate rheological and tribological behaviour to the grease (Mas and Magnin, 1994).

The main consumer market of lubricating greases is the automotive market. The grease used is conventional lithium greases, conventional calcium greases, and often sodium greases. This type of greases usually has very good water resistance, adhesive properties, corrosion resistance and oxidation stability. 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 odor (Mang and Dresel, 2007).

Researches concerning the effects of compositions and texture of thickeners agents on the greases wear and friction properties have been reported on many studies (Franco *et al.*, 2005; Martin-Alfonso *et al.*, 2011; Nunez *et al.*, 2012; Sanchez *et al.*, 2011). These studies demonstrated that the greases composition and processing conditions have a great influence on their microstructure and rheology.

Because of increasingly stringent environmental regulations, most of the last years studies (Adhvaryu *et al.*, 2005; Dresel, 1994; Nunez *et al.*, 2012) are mainly focused on the replacement of mineral oils by vegetable ones. Even the vegetable oils present poor oxidative stability, in comparison to some of the mineral oils, they have good lubricity and ability for adhering to metal surfaces, low volatility, small viscosity–temperature dependence and, of course, non-toxicity and high biodegradability (Adhvaryu and Erhan, 2002; Adhvaryu *et al.*, 2004; Dicken, 1994; Erhan and Asadauskas, 2000; Erhan *et al.*, 2006).

Taking into account these considerations, the main goal of the present work is focused on the development of new renewable and biodegradable lubricating greases, using calcium stearate soap as thickener agents dispersed in vegetables oils like corn, olive and palm oils. The effects that temperature and concentration of the thickener agent exert on the rheological properties of the corresponding biolubricating greases have been analyzed.

EXPERIMENTAL

Greases Synthesis

The oil (three types: olive oil, corn oil and palm oil) stearic acid and $Ca(OH)_2$ were loaded from the beginning in the mixing vessel in proportions shown in Table 1. During the preparation of the grease, the soap was obtained by reaction between stearic acid and calcium hydroxide:

$$2\ CH_3\text{-}\ (CH_2)_{16}\text{-}COOH + Ca(OH)_2 = (CH_3\text{-}(CH)_{16}\text{-}COO)_2Ca + 2\ H_2O$$

The manufacture methodology was reported elsewhere (Sterpu *et al.*, 2010) and consisted briefly of the warming up and mixing at 120^{o}C for an hour to eliminate the water from the product in order to improve its viscosity. There were prepared 15 greases corresponding to soap concentrations of 10%; 15%; 20%, 25% and 30% for each type of oil, according to the formulas in Table 1. At the end of the preparation, the mixture was cooled down by natural convection. The benchmark grease was prepared from the paraffin oil with 20% calcium soap, in the same conditions and was characterized in a previous work (Sterpu *et al.*, 2010).

For simplification, the greases were named after the base oil name and the concentration of calcium soap: O10%; O15%; O20%, O25% and O30% for grasses produced from olive oil, P10%; P15%; P20%, P25% and P30% for grasses produced from palm oil and C10%; C15%; C20%, C25% and C30% for grasses produced from corn oil.

Table 1. The greases preparation formula for different concentration of calcium soap

Soap concentration	Stearic acid, [g]	$Ca(OH)_2$ [g]	Obtained soap, [g]	Oil, [g]
10%	46.86	6.11	50	450
15%	70.29	9.15	75	425
20%	93.73	12.21	100	400
25%	117.15	15.26	125	375
30%	140.59	18.32	150	350

Viscosity Determination

The preparation of the lubricant greases was performed in an open vessel with a helix agitator provided by Petrotest, Germany, in batches of 0.500 kg. For the rheological behavior determination of the grease G20% at different temperatures a rheoviscometer, HAAKE VT 550, Germany with cone and plate geometry was utilized. The grease samples were analysed at 5 different temperatures: 20^{o}C, 30^{o}C, 40^{o}C, 50^{o}C and 60^{o}C, with both increasing and decreasing shear rate, in the range of 9.97– 4500 s^{-1}.

RESULTS AND DISCUSSIONS

The reports containing two variation curves (ascending and descending) of shear stress with shear rate (rheograme) were provided automatically by the software included in the rheoviscometer system. Every variation curve was built in 100 points. The rheograms of the grease samples at different temperatures are presented in Figs.1-3. To simplify the diagrams of this work, only the descending curves were represented.

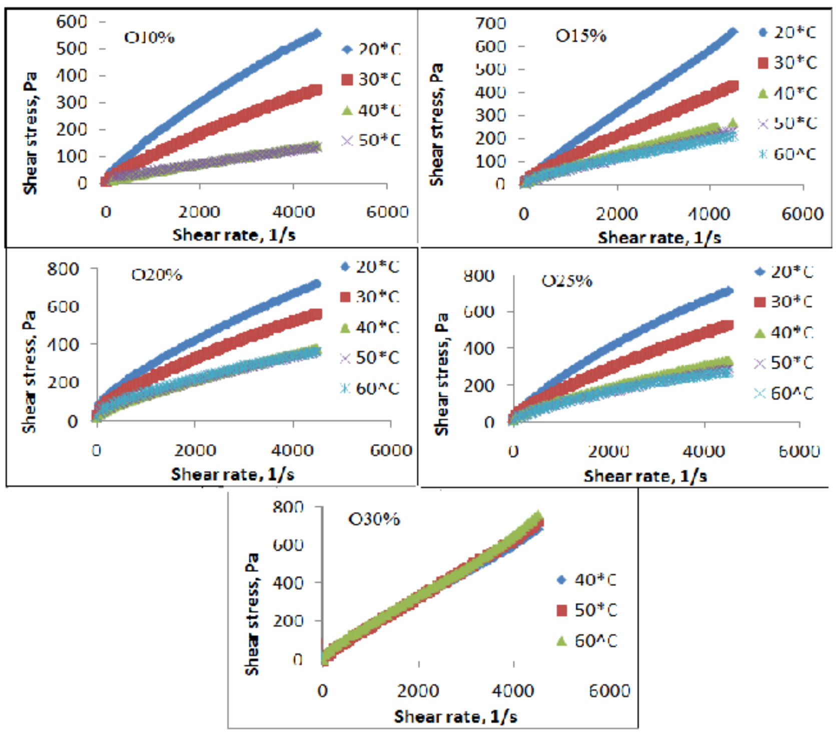

Figure 1. Variation of shear stress *vs.* shear rate of greases based on olive oil at different temperature

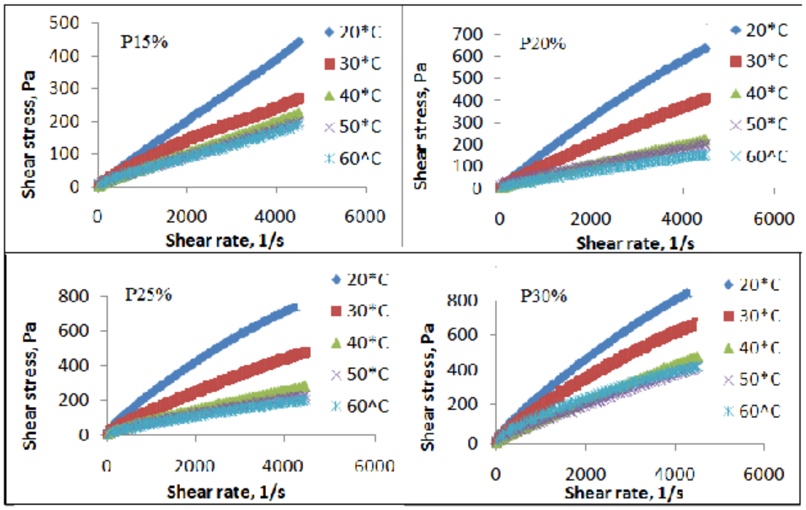

Figure 2. Variation of shear stress *vs.* shear rate of greases based on palm oil at different temperature

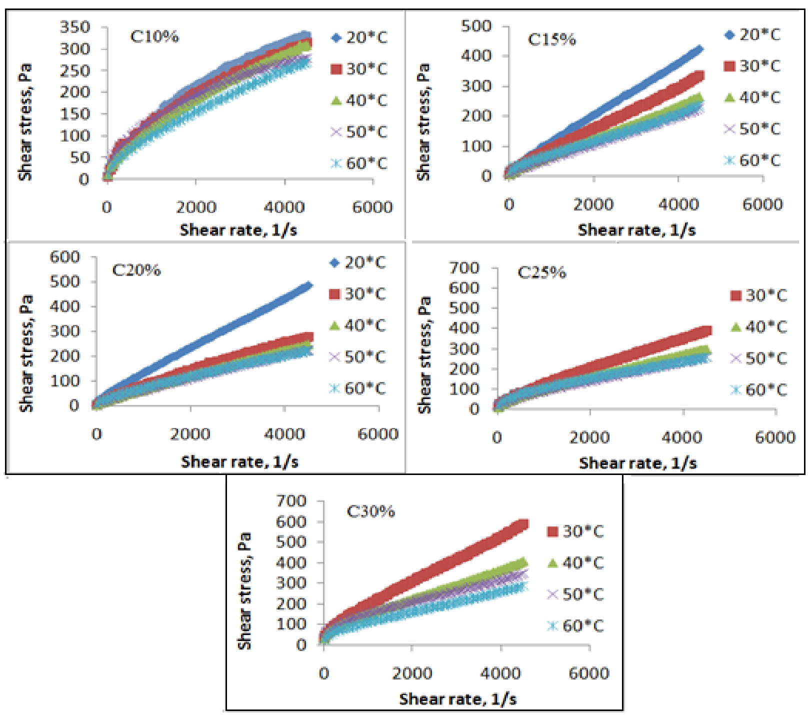

Figure 3. Variation of shear stress *vs.* shear rate of greases based on corn oil at different temperature

By processing the rheological data, it resulted that the curves are best described by the Bingham model (Eq.1):

$$\tau = a \cdot \dot{\gamma} + b \qquad (1)$$

where τ is the shear stress, γ is the shear rate and a, b are constants. In Eq.1, *a* represents the plastic viscosity (η_p) and *b* is the yield stress (τ_0). These are the two rheological properties describing the flow behavior of a Bingham plastic fluid. This type of fluid acts like a solid for small values of shear stress and then as a fluid at higher shear stress.

The Bingham model described with Eq.1 has positive constants a and b and always $0 < a < 1$. The rheological curves are accurately described by the linear function taking into account that the values of correlation factors (R^2) are between 0.949 and 0.999, as seen in Table 2.

Table 2. The values of coefficients *a*, *b* and the correlation coefficients R^2 of the Eq.1

Soap conc.	Temp. °C	Greases based on olive oil			Greases based on palm oil			Greases based on corn oil		
		a	b	R^2	a	b	R^2	a	b	R^2
10%	20				-	-	-			
wt		0.116	55.29	0.993				0.088	50.26	0.998
	30	0.074	28.36	0.995	-	-	-	0.058	44.52	0.996
	40	0.028	15.23	0.997	-	-	-	0.053	36.94	0.994
	50	0.026	14.91	0.997	-	-	-	0.047	36.06	0.994
	60	-	-	-	-	-	-	0.044	54.82	0.984
15%	20									
wt		0.139	79.80	0.999	0.135	10.12	0.999	0.108	27.39	0.999
	30	0.089	48.10	0.998	0.076	21.98	0.991	0.072	21.15	0.995
	40	0.056	31.87	0.998	0.044	6.152	0.999	0.055	11.58	0.998
	50	0.046	29.12	0.997	0.035	8.666	0.999	0.049	14.15	0.997
	60	0.042	46.00	0.993	0.03	10.81	0.998	0.045	25.1	0.995
20%	20									
wt		0.137	91.86	0.990	0.14	30.15	0.996	0.13	24.63	0.999
	30	0.107	66.43	0.990	0.089	15.31	0.998	0.077	18.2	0.999
	40	0.067	47.92	0.992	0.046	8.931	0.998	0.06	12.29	0.999
	50	0.058	40.27	0.990	0.039	23.1	0.998	0.05	12.42	0.999
	60	0.054	67.08	0.985	0.033	9.224	0.997	0.046	24.21	0.997
25%	20							-	-	-
wt		0.147	112.9	0.988	0.161	81.29	0.990			
	30	0.108	80.30	0.993	0.101	37.78	0.996	0.096	63.77	0.972
	40	0.074	59.45	0.991	0.058	26.83	0.995	0.065	52.11	0.983
	50	0.069	55.80	0.989	0.046	25.84	0.993	0.052	43.93	0.989
	60	0.068	77.03	0.972	0.041	23.02	0.993	0.049	80.86	0.949
30%	20	-	-	-				-	-	-
wt					0.183	51.76	0.993			
	30	-	-	-	0.11	37.16	0.991	0.119	104.8	0.985
	40	0.059	14.51	0.998	0.063	14.94	0.998	0.089	77.37	0.996
	50	0.057	8.898	0.999	0.054	19.44	0.998	0.074	71.31	0.995
	60	0.056	13.18	0.997	0.048	40.02	0.986	0.058	86.19	0.998

The grease proceeding from palm oil containing 10% wt soap wasn't analysed because it was unstable and the oil was separated after a week. Also, the grease with 10% soap proceeding from olive oil wasn't analysed at 60°C, because it was too soft and started to leak. The greases with 30% soap from olive oil and with 25% and 30% from corn oil, which are solid at room temperature, couldn't be analysed at 20 ^{o}C and/or 30^{o}C.

CONCLUSIONS

In this work we evaluated some dispersions formulated with calcium stearate as thickener agent in olive oil, palm oil and corn oil to be applied as lubricating greases. The evaluation was made from the rheological point of view.

The said greases can be characterized as soft, and they rheological behaviour is non-newtonian, described with accuracy by the Bingham model (R^2 = 0.949 - 0.999).

The highest values of plastic viscosity (a or η_p) are those of greases from palm oil and the lowest values are those of greases from corn oil; this indicates that palm oil greases are the most consistent and corn oil greases are the softest.

The finding of rheological equation for every grease at different temperatures is important for the study of mixing with applications in the processing of these products.

REFERENCES

Adhvaryu, A., Sung, C., Erhan, S.Z. (2005), "Fatty acids and antioxidant effects on grease microstructures", *Industrial Crops and Products*, 21, 285–291.

Adhvaryu, A., Erhan, S.Z. (2002), "Epoxidized soybean oil as a potential source of high temperature lubricants", *Industrial Crops and Products*, 15, 247–254.

Adhvaryu, A., Erhan, S.Z., Perez, J.M. (2004), "Tribological studies of thermally and chemically modified vegetable oils for use as environmentally friendly lubricants", *Wear,* 257, 359–367.

Dicken, T.W. (1994), "Biodegradable greases", *Industrial Lubrication and Tribology*, 46, 3–6.

Dresel, W.H. (1994), "Biologically degradable lubricating greases based on industrial crops", *Industrial Crops and Products,* 2, 281–288.

Erhan, S.Z., Asadauskas, S. (2000), "Lubricants base stocks from vegetable oils", *Industrial Crops and Products*, 11, 277–282.

Erhan, S.Z., Sharma, B.K., Perez, J.M. (2006), "Oxidation and low temperature stability of vegetable oil-based lubricants", *Industrial Crops and Products*, 24, 292–299.

Franco, J.M., Delgado, M.A., Valencia, C., Sanchez, M.C., Gallegos, C. (2005), "Mixing rheometry for studying the manufacture of lubricating greases", *Chemical Engineering Science*, 60, 2409–2418.

Hurley, S., Cann, P.M. (1999), "The influence of grease composition on film thickness in rolling contacts", *NLGI Spokesman*, 63, 12-22.

Mang, T., Dresel, W. (2007), *Lubricants and Lubrication. Second ed.,* WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Martin-Alfonso, J.E., Nunez, N., Valencia, C., Franco, J.M., Diaz, M.J. (2011), "Formulation of new biodegradable lubricating greases using ethylated cellulose pulp as thickener agent", *Journal of Industrial Engineering Chemistry*, 17, 818–823.

Mas, R., Magnin, A. (1994), "Rheology of colloidal suspensions: Case of lubricating greases", *Journal of Rheology*, 38, 889.

NLGI, (2006), *Lubricating Greases Guide*, National Lubricating Grease Institute, Kansas.

Únez, N., Martín-Alfonso, J.E., Valencia, C., Sánchez, M.C., Franco, J.M. (2012), "Rheology of new green lubricating grease formulations containing cellulose pulp and its methylated derivative as thickener agents", *Industrial Crops and Products,* 37, 500–507.

Sánchez, R., Franco, J.M., Delgado, M.A., Valencia, C., Gallegos, C. (2011), "Thermal and mechanical characterization of cellulosic derivatives-based oleogels potentially applicable as bio-lubricating greases: influence of ethyl cellulose molecular weight", *Carbohydrate Polymers*, 83, 151–158.

Sterpu, A.E., Teodorescu, N., Prodea, I.M., Popescu, E., Niţă, I., (2010), "Mathematical models for power consumption at the mixing of some lubricating greases" *Environmental Engineering and Management Journal,* 9, 1063-1068.