Rheological models for lithium and calcium greases

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1. Introduction

Lubricating greases is a solid or semi fluid two-phase system. It consists of a thickening agent (soap) in lubricating oil (the base oil). The 5-20% soap content acts like a sponge that retains the oil and gives the grease a more or less solid consistency. Besides the oil and the soap, normal grease also contains different additives, for example friction modifiers and EP additives. The influence of the rheological properties of the lubricant on the fluid film behavior is very important for all the grease lubricating bearings. To characterize a lubricant conclusively, the rheological properties at all working conditions, pressures and temperatures have to be known.

Rheometry of lubricating greases in viscometric motion is dominated by the existence of the yield state and the shear thinning behavior. At low strain rates, lubricating greases are modeled as time dependent viscoelastic fluids; for a critical value of the applied shear stress, the internal network becomes unstable and the deformation process within the material is suddenly transformed into flow.

Rotational rheometry in controlled stress mode is the most accurate technique for the investigation of lubricating greases behavior at low and medium strain rates, whereas the capillary rheometer is the only device able to give information about the rheology of lubricating greases at high strain rates.

This investigation presents an analysis of various rheological models (shear stress – shear rate relationships) for lithium and calcium greases, correlated with the microscopically structure of the greases.

2. Methodology

Two different Romanian greases have been investigated: lithium grease - UM 185 Li2 and calcium grease - U95Ca2. The main physical-chemical properties of the greases are presented in Table 1.

Table 1

Physical-chemical properties of lubricating greases

Symbol	Standard	Soap thickener	Soap content, %	Worked penetration, 1/10 mm^{-1}	Dropping point, ºC
UM185Li2	STAS 12721 - 89	Lithium	10	260-300	185
U95Ca2	NTR 3769 - 70	Calcium	15	270-330	95

The shear stress – shear rate relationship has been evaluated by measuring the torque needed to rotate a cone at a constant speed when the gap between the cone and the rigid plate is filled with the grease, Fig. 1. The gap angle between the cone and the plate has to be small compared to the cone diameter so that constant shear rate in the gap can be assumed.

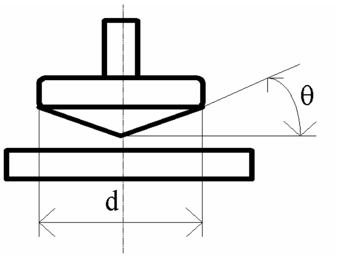

Fig. 1 Cone and plate rheometer

In this investigation, the cone and plate rheometer used was a STRESSTECH rheometer, produced by "REOLOGICA". It has the ability to measure shear stress with shear strain rates ranging from 0.007 to 3500 s^{-1} for different temperatures (4-95ºC) and atmospheric pressure.

All measurements have been carried out with ø40 mm cone and with 1ºgap angle. This gives the gap height of 0.1 mm at the circumference of the cone. The soap fibers are thus small compared to the gap high and the measurements can be referred to as bulk properties.

The stress controlled experiment was performed a, which is characteristic for the materials with yield stress like greases. For this case, the input is shear stress σ and the output is shear strain rate $\dot{\gamma}$.

3. Results and discussion

No single rheological constitutive relationship is able properly to model the entire rheological behavior and flow regime of lubricating grease. Currently, there is not an acceptable procedure to measure the elasticity of the samples in viscometric motions and the elongation motions have not even been investigated. Therefore, the current database is poor and there is not enough information to establish valuable criteria in the formulation of a proper constitutive relation for lubricating greases.

For the lithium and calcium greases, seven rheological models have been proposed to describe their behavior:

- Bingham model $\tau = \tau_0 + \mu\dot{\gamma}$ [1],
- Herschel – Bulkley model $\tau = \tau_0 + m\dot{\gamma}^n$ [1],
- Casson model $\tau^{1/n} = \tau_0^{1/n} + \left(\mu_\infty \cdot \dot{\gamma}\right)^{1/n}$ [2],

- Bauer model $\tau = \tau_0 + a(\dot{\gamma}) + b(\dot{\gamma})^n$ [3],
- Balan model $\tau = \tau_0 + \mu\dot{\gamma}\left(1 + \lambda_1\lambda_2\dot{\gamma}^2\right)/\left(1 + \lambda_1^2\dot{\gamma}^2\right)$ [4],
- Papanastasiou model $\tau = \tau_0\left[1 - exp(-m\dot{\gamma})\right] + \mu\dot{\gamma}$ [5],
- Dorier and Tichy model $\tau = (2/\pi)\tau_0\, arctan(\dot{\gamma}/\gamma_0) + \mu\dot{\gamma}$ [6].

In these equations τ is shear stress.

The results from the cone-plate measurements are presented in Table 2 as results from fitting the rheological model to the measurements. In the same table, the correlation coefficient, equivalent to the significance of the fitting, is presented.

Table 2

Results from fitting equations 1-7 to the cone and plate measurements

Rheological model		Lubricating greases	
		UM185Li2	U95Ca2
Bingham	τ_0, Pa	671.58	663.34
	μ, Pa·s	0.138	0.131
	Correlation coefficient	0.971	0.964
Herschel-Bulkley	τ_0, Pa	611.26	563.24
	m, Pa·s^{-n}	3.201	6.703
	n	0.616	0.528
	Correlation coefficient	0.995	0.982
Casson	τ_0, Pa	608.74	568.40
	μ_∞, Pa·s	0.034	0.022
	n	1.768	2.016
	Correlation coefficient	0.992	0.982
Bauer	τ_0, Pa	595.21	570.59
	a, Pa·s	0.067	0.0095
	b, Pa·s^{-n}	11.792	5.258
	n	0.389	0.565
	Correlation coefficient	0.989	0.982
Balan	τ_0, Pa	671.29	663.33
	μ, Pa·s	0.286	0.19
	λ_1, s	0.061	0.212
	λ_2, s	0.029	0.145
	Correlation coefficient	0.971	0.964
Papanastasiou	τ_0, Pa	680.07	667.84
	μ, Pa·s	0.134	0.129
	m, s	2.379	2.151
	Correlation coefficient	0.977	0.968
Dorier and Tichy	τ_0, Pa	684.84	668.58
	μ, Pa·s	0.132	0.128
	γ_0, s^{-1}	0.194	0.182
	Correlation coefficient	0.983	0.968

Analyzing the values of the correlation coefficient for each of the rheological models, it can to observed that the most appropriate models for both greases are Herschel-Bulkley and Casson models. From the same point of view, the rheological models with the smallest correlation coefficient are the Bingham, Balan and Papanastasiou models.

Figs. 2 and 3 show the results from the measurements with the cone and plate rheometer and two extreme fitted models (Herschel-Bulkley and Bingham) according to the Table 2.

The rheological results for the two greases are not so obviously different. It can be observed that for the lithium grease, the viscosity and the shear yield stress are constant and greater than the same parameters for the calcium grease.

Another important remark is the fact that the rheological properties of the lithium grease are more stable comparatively to the calcium grease (see the values of the correlation coefficient for each rheological proposed model). These two important observations can be correlated with the microscopic structures of the greases.

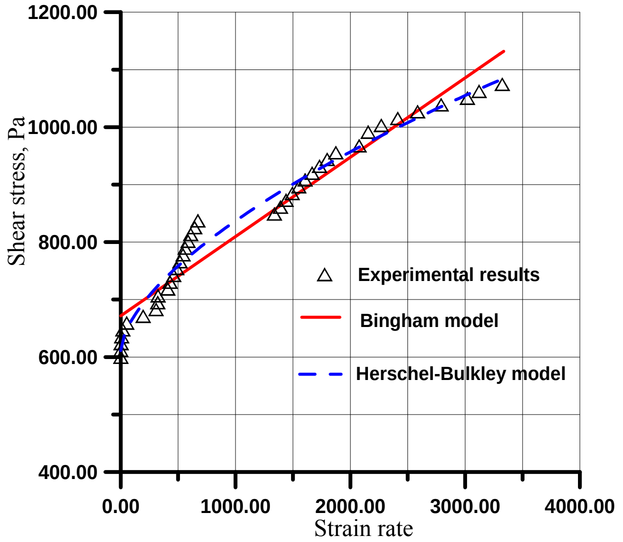

Fig. 2 Measurements and fitted models for the lithium grease UM185Li2

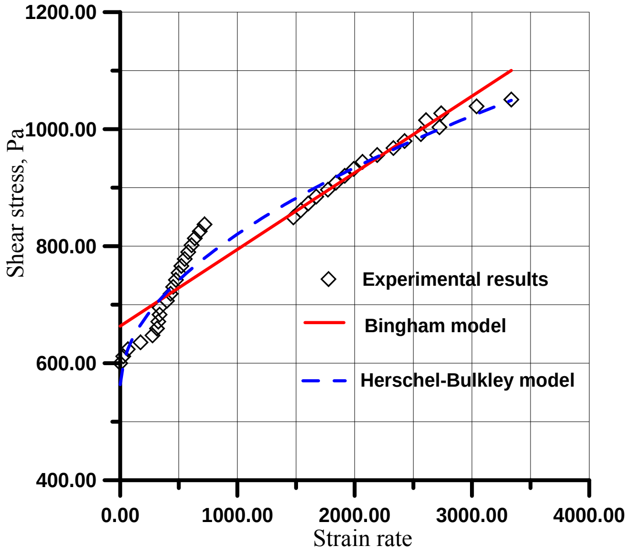

Fig. 3 Measurements and fitted models for the calcium grease U95Ca2

4. Grease microscopy

The greases quality and performances are essentially influenced by the dimensional and spatial soap fibers distribution. Using electronic microscopy it is necessary to examine the additives and the soaps, which concur to the high performance quality greases [7]. The most common micro structural theory is that the soap thickeners are forming a three-dimensional network structure built up by soap fibers.

Soap fibers are 80 nm thicknesses and consist in Ca and Li salt of hydrostearic acid. But the majority of solid insoluble elements are too small to visualize using optical microscope, the electronic microscope and its high resolutions necessary for morphological examination of the additives and thickening elements needed in the quality greases performance.

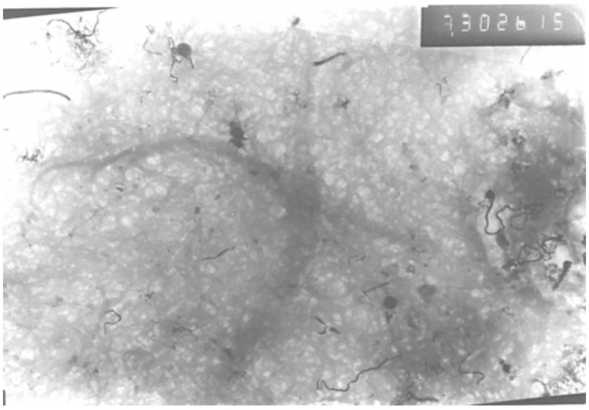

Fig. 4 Microscopic structure for UM185Li2 grease (x10000 magnitude)

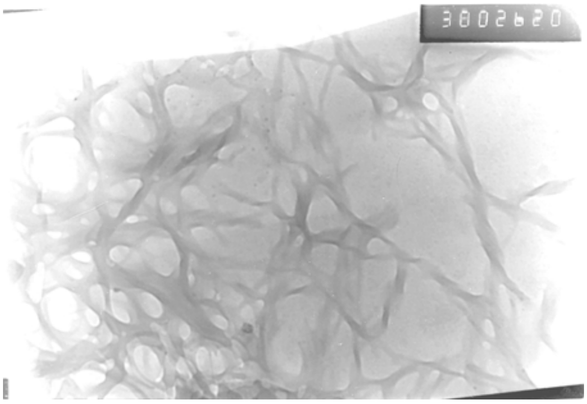

Fig. 5 Microscopic structure for UM185Li2 grease (x20000 magnitude)

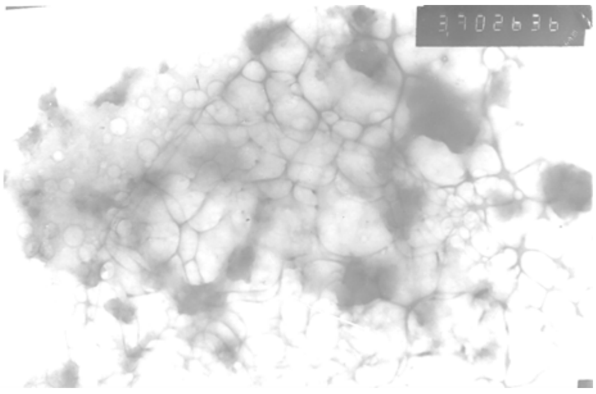

Fig. 6 Microscopic structure for U95Ca2 grease (x10000 magnitude)

Lubricating grease properties depend on both its composition and the manufacturing process used. Using SEM (Scanning Electron Microscopy) – or TEM (Transmission Electron Microscopy) - it is possible to obtain structural network images of the metallic soap into the grease. For the two investigated greases, Figs. 4-7 present the microscopic structures.

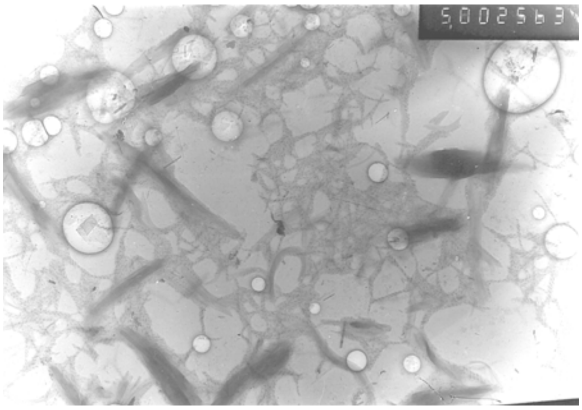

Fig. 7 Microscopic structure for U95Ca2 grease (x20000 magnitude)

It can be observed an important difference between the microscopic structure of the lithium and calcium greases. Lithium grease presents a more regulate network structure, with long fibers, which confers the rheological stability. The structure of the calcium grease presents short fibers, with all the inconvenient involved.

5. Conclusions

1.The grease bulk rheology can be described in optimum conditions by the Herschel-Bulkley model, for both lithium and calcium greases.

2.The rheological behavior of the lithium and calcium greases corresponds to the microscopic structures observed.

3.Calcium soap greases shear more easily than lithium soap greases, as can be seen from the model fittings in Table 2.

4.The experimental procedures showed the importance of the correlation between rheological methods and the microscopic investigations.

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REOLOGINIS LIČIO IR KALCIO TEPALŲ MODELIS

Reziumė

Straipsnyje pristatomi dviejų dažniausiai naudojamų plastinių tepalų (UM185Li2 ir U95Ca2) reologinių savybių tyrimai. Reologinės savybės tirtos kūginio disko tipo tyrimų įrenginiu, mikroskopinė dilimo paviršių analizė atlikta elektroniniu mikroskopu.

Rezultatai, gauti kūginio disko areometru, buvo palyginti su septyniais reologiniais modeliais: Bingham, Herschel – Bulkey, Casson, Bauer, Balan, Papanastasiou bei Dorier ir Tichy modeliais.

Mikroskopinės plastinių tepalų plėvelių struktūros buvo susietos su reologinėmis savybėmis.

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RHEOLOGICAL MODELS FOR LITHIUM AND CALCIUM GREASES

Summary

This paper presents the investigation of the rheological properties and the microscopic structures of two common greases: UM185Li2 - lithium grease and U95Ca2 - calcium greases, with NLGI grade two.

The experimental apparatus used were a cone-and-plate rheometer for the rheological properties of the greases and an electronic microscope for the microscopic structures.

The results from the cone-and-plate rheometer have been fitted to seven different rheological models: Bingham, Herschel – Bulkley, Casson, Bauer, Balan, Papanastasiou and Dorier and Tichy models.

Finally, the microscopic structures of the greases have been correlated with their rheological properties.

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РЕОЛОГИЧЕСКАЯ МОДЕЛЬ ДЛЯ СМАЗОК ЛИТИЯ И КАЛЬЦИЯ

Резюме

В статье представлены результаты исследований реологических свойств и микроструктуры двух чаще всего применяемых смазок UM185Li2 ir U95Ca2 (2-ого класса по NLGI).

Для исследования реологических свойств был использован реометр типа диск – конус. Для исследования микроструктуры смазочной пленки применялся электронный микроскоп.

Результаты, полученные реометром, были сопоставлены с семью реологическими моделями Bingham, Herschel – Bulkey, Casson, Bauer, Balan, Papanastasiou, а так же Dorier и Tichy. Была установлена связь между микроструктурой и реологическими свойствами.

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