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Formulation, rheology and thermal ageing of polymer greases—Part I: Influence of the thickener content

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ABSTRACT

The aim of this work is to show the correlation between polymer greases' rheology and its formulation. The tested polypropylene (PP) thickened greases were evaluated regarding their thickener content and its effect on the rheological properties. An artificial ageing procedure was performed by heating fresh grease samples in an oven to study the thermal degradation. The ageing evaluation was performed through rheological measurements, FT-IR spectra, oil loss, bleed-oil viscosity changes and bleed rate. The rheology measurements were performed on a rotational rheometer, emphasizing on the storage and loss moduli values at the Linear Visco-Elastic (LVE) region. The flow curve of each grease was also measured. A modified Herschel–Buckley model was applied and the data was correlated to the thickener content.

1. Introduction

Rolling bearings are very often grease lubricated. About 90% of the rolling bearings used are, in fact, lubricated with grease [1], therefore the importance of its study. New and innovative polymer based greases have been slowly introduced in the market, expected to perform with high efficiency and reliability.

Lubricating greases consist of mineral or synthetic oil which has been thickened by a thickener agent, typically a metallic soap, guaranteeing that it remains in place and in contact with the moving surfaces when needed. Although lithium soap is the most common grease thickener, polymers have been introduced not only as thickeners [2–5] but also, and primarily, as viscosity index improver and as dispersant [6,7]. When used as thickener, the polymers form short and thick elements connected to each other, which trap the oil and modify its rheology, generating the grease. On the other hand, when used as additive, the polymers are added to improve the viscosity index, promote the adhesion and cohesion characteristics of lubricating greases and also to improve mechanical and chemical stability at high and low temperatures [7]. A good review on different polymer types used in grease formulations and their effects can be seen in [8].

This study aims to evaluate the rheological properties and the effect of thermal ageing of polypropylene (PP) thickened greases with different thickener contents. The grease ageing is characterized by permanent changes in its properties and depends mostly on its own formulation, on the bearing type, geometry and material, the bearing house, the operating conditions (mainly speed and temperature), wear debris, water contamination and running time [9–12]. So far, it is impossible to accurately estimate grease life based only on the bulk properties of the fresh greases. It is known that during operation at high temperatures the grease is continuously stressed thermally and mechanically, leading to chemical and physical changes. However, the way these changes affect the lubricity and the capacity to maintain a lubricating film is still unknown. Therefore, this paper also intends to investigate and simulate the grease degradation in rolling bearings and its effect on the grease rheological and tribological properties, by artificially degrading fresh grease samples. Similar ageing methods have been used by other authors [13,14].

This paper is part of a larger work which aims to link the polymer greases formulation and rheology to the friction torque and film thickness formation in both the beginning and the later stages of grease life. This paper is divided into two parts where different grease formulation aspects are investigated. This first part reports the influence of the thickener content in the rheological and chemical properties, while the second part is focused on the effect of including an elastomer in the formulation. The thermal ageing

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Table 1
Tested greases properties.

Grease reference		M1	M2	M3	M4	MLi	Units
Thickener type		Polypropylene				Lithium complex	–
Thickener content		11	13	15	11[a]	17.5	%
Worked penetration (ISO 2137)		290	269	249	446	288	10^{-1} mm
NLGI		2	2	3	000	2	–
Shell roll stability 80 °C /50 h	Before	286	264	256	n.a.	284	10^{-1} mm
(mod. ASTM:D1831)	After	318	323	281	n.a.	324	
	Difference	32	59	25	–	40	
Flow pressure at −25 °C (DIN 51805)		320	390	670	30	370	hPa
Oil separation 100 °C /30 h (ASTM:D6184)		7.2	5.3	3.0	28.7	1.8	%
Oil separation 40 °C /168 h (IP121)		7.3	5.3	5.9	19.2	2.8	
Oil evaporation 100 °C /30 h (ASTM:D6184)		0.2	0.9	0.8	0.8	0.5	
Base oil viscosity (ASTM:D445)	40 °C	48				178.7	mm^2/s
	100 °C	8				21.4	

[a] Made with 15% but diluted to 11%.

and how it changes the greases' rheological properties are investigated in both parts.

2. Methods and materials

2.1. Tested greases

Five greases were tested in this work: M1, M2, M3, M4 and MLi. The greases' main properties are shown in Table 1.

Experimental batches of polymer greases were specifically manufactured for this work. These batches were processed so they should reflect the differences in their composition. The samples have been melted and quenched in 1 kg batches using the same settings for each batch. The milling has been done in a colloidal mill where each grease has passed through the mill exactly the same number of times with decreasing gap size. The process is kept as uniform as possible.

All the polymer greases were formulated with the same poly-alpha-olefin (PAO) base oil. Grease MLi was formulated with a mixture of two different grades of PAO and some ester to facilitate the saponification reaction.

Regarding the thickener, greases M1–M4 were formulated with polypropylene (PP) while MLi was formulated with lithium complex (LiX). Greases M1, M2 and M3 were formulated with different thickener contents, respectively, 11%, 13% and 15%. Grease M4 is a batch of grease M3 which was diluted to 11% thickener content, after the milling process. These greases are not additized, which means that this study relies only on the influence of the thickener content on the performance of these polymeric greases.

Since lithium thickened greases are the most common lubricating greases in the market, MLi was tested as a benchmark grease for high temperature greases. Grease MLi was retrieved from a production batch prior to the addition of additives and therefore, it has no polymer or additives in its formulation.

2.2. Ageing process

The ageing process was performed on a sample of each fresh grease. The sample was manually spread over a steel disc forming a film thickness of approximately 1 mm. The steel disc was chosen on purpose to replicate the ageing on rolling bearings. Both the polymer and the LiX thickened greases were thermally aged in the oven for five consecutive days at 120 °C which is the maximum working temperature of the polymer greases, indicated by the manufacturer for continuous use (the corresponding temperature for the LiX thickened grease is 150 °C). The temperature of the oven was adjusted manually through a potentiometer, using a thermometer for the atmosphere temperature evaluation. Although there was no forced convection mechanism, the oven had a breathing hole on the top, allowing the chamber atmosphere to be refreshed. Care was taken to keep the temperature constant at all times. After the ageing process, the disc was removed from the oven to the room temperature and the grease was immediately collected in a container to avoid further ageing.

From here on, the aged samples will be referred to with the suffix "a" for aged.

2.3. Infra-red spectroscopy

The grease molecular alterations were evaluated through Infra-red (FTIR) spectroscopy. The spectra were obtained on an Agilent ® Cary 630 FTIR device, using an ATR (Attenuated total reflectance) accessory. The samples were analysed through direct comparison of height of the characteristic oxidation peaks between the samples spectra. All the spectra shown in this work were taken directly from the device's software without smoothing and a very good reproducibility was achieved. All spectra were normalized to the same peak's height at 1460 cm^{-1} [13], allowing the comparison between samples.

The spectra of grease M2, its bleed-oil (equal spectrum to the PAO base oil) and the PP thickener can be seen in Fig. 1, on the fingerprint region. This region is of the utmost importance, since it is where most of the substance's characteristic peaks are located. There are several relevant aspects in these spectra:

1. The presence of several peaks in the thickener spectrum which are not present in the bleed-oil. Some of these peaks are also visible in the grease spectrum but with smaller intensity.
2. The absorbance band at 721.5 cm^{-1} is mainly due to the base oil.
3. The height ratio between the absorption peaks at 1378/1461 cm^{-1} for the bleed-oil and the corresponding pair at 1376/1453 cm^{-1} for the thickener are due to the CH_2 and CH_3 deformation vibration. This CH_3/CH_2 ratio is larger in the thickener.

The differences among the fresh and aged spectra allow us to characterize the grease ageing and correlate that information to the oil loss and the bleed-oil viscosity changes.