Impact of Water on the Rheology of Lubricating Greases

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ABSTRACT

The operational life of bearings is often determined by the performance of the lubricating grease. The consistency of the grease prevents it from leaking out of the bearing and provides good sealing properties. The possible ingress of water into the bearing will have a considerable impact not only on this consistency but also on the lubricating ability of the grease. There are numerous applications where water ingress may occur, such as in the food, pulp, and paper industries. Some greases are less sensitive to water than others. No specific guidelines are available to select the proper grease for bearings subjected to water ingress. The goal of the article is to contribute to the development of such guidelines for greases subjected to water ingress by studying the impact of water on grease rheology. Fully formulated, commercially available greases with the most common thickeners and base oils are used as model greases. It will be shown that water strongly influences rheological properties such as zero-shear viscosity, yield stress, and storage modulus. Calcium sulfonate greases were found to become stiffer after absorbing a considerable amount of water, leading to an increase in zero-shear viscosity and yield stress. However, lithium, lithium complex, and polyurea greases were found to soften, with appreciable changes in measured rheological properties.

Introduction

Lubricating greases are highly structured materials consisting of a dispersion of thickener material in mineral or synthetic oil (1). The consistency of the grease depends on the effectiveness of the Van der Waals and capillary forces (Bauer, et al. (2)). Lubricating greases serve as a convenient source of lubrication for a broad range of bearing applications. The service life and reliability of these bearings are often determined by the life of the grease (Begg, et al. (3); Lugt (4)) or by contaminants like solid particles or water (Cantley (5); Morales-Espejel, et al. (6)). Next to the possibility of corrosion caused by water ingress, any possible intrusion of water into the bearing may have a significant effect on the rheological properties of the lubricating grease, which depends on the properties of the materials (thickeners, base oil, additives; Lugt (7)) and the manufacturing process. Water may influence the rheological properties in several distinct ways. The grease may absorb considerable quantities of water, thereby forming a soft emulsion (Leckner (8); Mistry (9)), with a substantial reduction in adhesive and cohesive properties (tackiness). Alternatively, grease may become stiffer in the presence of water (Leckner (8); Mistry (9)), leading to a reduced ability to replenish the contacts due to a reduced oil bleed (Cann (10)). In the worst scenario, when water enters through the seals, free water is present when water-repellent grease is used (Mistry (9)). The “free water” may be detrimental for the bearing because it may lead to corrosion. Finally, water can cause additive depletion due to hydrolysis of antiwear, extreme pressure, and anti-oxidant additives. Possible solutions to prevent bearing failure due to the ingress of water could be improving the sealing system, flushing the bearing continuously with grease using a lubrication system, and/or using a more efficient grease. The selection of a more efficient grease may improve the lifetime but may also improve the sealing performance or reduce the required grease flow when flushing is applied. The effectiveness of sealing is given by the capability of a grease to maintain its stiffness if water has leaked through the seal, thereby forming a barrier for water to intrude further the bearing.

There is no compelling information on the performance of water-contaminated grease. Research has been conducted on the impact of water in lubricating oil (Echin, et al. (11); Liu, et al. (12); Kimura, et al. (13); Hamaguchi, et al. (14); Dalmaz and Godet (15)), and some of it can be applied to grease as well. It has been found that compounded oils tends to exhibit more water-repellent characteristics than straight mineral oils and are thus better at keeping moisture away from the bearing surfaces (16). Oils based on esters are more susceptible to water pickup because of their hygroscopicity. These oils are capable of forming associated groups with water through hydrogen bonding (Echin, et al. (11)), whereas mineral oils and poly alpha olefin (PAO) are hydrophobic, showing a very low affinity for water. Similar to oils, some greases perform well with
absorbed water, whereas others do not. In general, a grease shows high resistance to water if its individual components do not react with water and are soluble in water (Blanke and Bartz(17)). However, the phenomenon “grease and water” is more complex than the case of “oil and water” because the contribution of the thickener to this process is not known (Lugt(7)).

Generally, in the presence of water lithium and calcium soap greases are recommended (16). Lithium soaps are partially hydrophilic and contain traces of water from saponification. Lithium grease does not emulsify (18) and therefore provides good protection against corrosion at lower water concentration. At higher levels, lithium grease was found to soften, thereby losing its structural stability or consistency (Hobbs(19)). Calcium sulfonate complex greases may be preferred over lithium greases because they can absorb relatively large quantities of water (3–60 wt%) while retaining their structure. Leckner (8) noticed an increase in viscosity and flow resistance by incorporating water up to 30 wt% in calcium sulfonate complex grease. By contrast, the same grease that became thicker and more flow resistant when contaminated with water lost more grease in the water washout test when contaminated with 10 wt% water, giving contradictory expectations with the expected performance regarding water-contaminated bearings. An increase in cone penetration values and a significant reduction in apparent viscosity were found for polypropylene-thickened and lithium complex grease. Similar to calcium sulfonate complex grease, these greases exhibited poor performance during water washout tests.

Mistry (9) extensively studied the mechanical stability, consistency, and load-carrying capacity of greases used in an aircraft wheel bearing application using the following test methods: low-temperature torque (−54°C, IP 186 Test), cone penetration (25°C, ASTM 217), weld load (IP 239 Test), and roll stability (25°C, ASTM D1831). It was found that a grease consisting of hectorite (clay), lithium, or calcium soap as the thickener resulted in softening with increasing concentration of water, whereas an increase in consistency was observed for bentonite-based grease. It was found that the action of extended working with added water significantly affects the consistency of hectorite-based grease. On the other hand, calcium grease was found to exhibit no significant changes in consistency under the influence of added water and extended working in comparison to other greases.

Though a number of high-performance greases are available in the current market that offer durability even in the presence of water, a well-defined guideline to select the proper grease regarding bearings subjected to water ingress is not yet available. Therefore, currently, a pragmatic approach is to be followed based on experimental results. The goal of the present article is to contribute to the development of such guidelines by studying the impact of water on the changes in the rheology of commonly used rolling bearing greases varying the thickener–oil systems. Steady shear (flow curve) and dynamic (oscillatory strain and frequency sweep) measurements are performed at different temperatures to characterize the greases by varying the water concentration. The results are of practical significance in the bearing and lubrication industry because water can be encountered in many applications, such as steel, food, pulp, and paper industries. The change in the rheological properties of grease is one of the parameters that determines their suitability for use in such applications.

**Materials and methods**

Six commercially available greases consisting of the most common thickeners and base oils were tested, the important characteristics of which are summarized in Table 1. The shape and size of the thickeners in Table 1 were obtained using an atomic force microscope (AFM). AFM measurements (images not shown) were performed using a Multimode 8 AFM (Bruker Nano Surfaces, Santa Barbara, CA) with a Nanoscope V controller. Tapping mode AFM images were collected with commercially available silicon cantilevers (NCH and SSS-CH/PS, Nanosensors, Neuchatel) with a nominal spring constant of 42 N/m.

The mixing of grease and deionized water was carried out using an in-house-made grease worker (Fig. 1a) consisting of a 24-mm-diameter plate with 8 2.5-mm-diameter holes in a cylinder with a stroke of approximately 30 mm (Fig. 1b). This provided a thorough mixing of water and grease. An electronic counter controlled the number of strokes. All samples, including the samples without water, were similarly worked (1,000 strokes). The amount of water in grease is defined in terms of weight fraction (percentage). The saturation point of water in a given grease was obtained by observing with the naked eye and/or a confocal microscope if any visible droplets were formed, indicating the presence of free water.

Dynamic and steady-state rheology measurements were carried out using a controlled strain rheometer (MCR 501, Anton Paar, Austria). The measurements were carried out using a parallel plate setup with sandblasted surface finishing of the stainless steel plates ($R_s = 2.87 \mu m$) with a radius of 12.5 mm and a

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**Table 1. Important properties of lubricating greases studied.**

| Grease | NLGI | Thickener | Thickener Concentration (%) | Shape and Size of Thickener | Base Oil | Viscosity of Base Oil (mm²/s) at 40°C/100°C | Water Resistance (DIN 51807/1, 3 h, 90°C) | Consistency (60 strokes, 0.1 mm) |
|--------|------|-----------|-----------------------------|-----------------------------|--------|---------------------------------|----------------------------------|---------------------|
| CaS/M  | 1–2  | Calcium sulfonate complex | 26                          | Spherical $D \approx 0.26 \mu m$ | Synthetic/PAO/mineral oil | 80/8.6 | 0                               | 300                 |
| CaS/M  | 2    | Calcium sulfonate complex | 27                          | Spherical $D \approx 0.26 \mu m$ | Mineral oil          | 420/26.5 | 0                               | 275                 |
| Li/M   | 3    | Lithium   | 15                          | Twisted fibers $L \approx 2 \mu m$ | Mineral oil            | 99.9/10 | NA                              | 207                 |
| Li/SS  | 2    | Lithium   | 17                          | Twisted fibers $L \approx 2 \mu m$ | Mineral oil            | 41.9/7.5 | 0–0                            | 270                 |
| LiC/PAO| 2–3  | Lithium complex | 20                          | Fibres $L \approx 0.4 \mu m$ | PAO                 | 191/22 | 1–0                            | 255                 |
| PU/E   | 2–3  | Polyurea  | 26                          | Platelets $L \approx 0.65 \mu m$ | Ester               | 70/9.4 | 1                              | 283                 |
gap setting of 1 mm. A small quantity of sample (≈ 0.5–1.5 g) was loaded onto the lower plate, after which the gap was set. After loading the presheared sample, a rest time of 20 min, which was sufficient for the normal force to relax, was introduced before performing the measurements. A maximum delay time of 24 h was employed between sample mixing and rheological characterization.

When bearings are running in the presence of water, problems such as grease softening or stiffening may occur. Therefore, the zero-shear viscosity from flow curve measurements and yield stress from oscillatory measurements were determined. Flow curve measurements were carried out in a range of shear rates in the order of $10^{-8}$ to $100 \text{ s}^{-1}$ for 1 h. The oscillatory strain sweep measurements were performed using a strain ranging from 0.001% up to 1,000% at a frequency of 1 Hz, without imposing a time constraint on measurement duration. All measurements were carried out at 10, 25, 50, and 75°C. Frequency sweeps between $10^{-2}$ and 100 Hz were also performed at 25°C to determine the sensitivity of the viscoelastic properties in the presence of water.

Temperature control was achieved to a precision of ±0.5°C. The experiments were replicated at least two times using fresh specimens to check for reproducibility. The difference in yield stress from oscillatory strain sweep after a rest times of 20 min and 10 h at elevated temperature was found to be less than 20%, from which it was concluded that severe evaporation of water during the course of the measurements could be neglected.

**Results**

First the maximum amount of water that can be absorbed in the different greases was determined. The results are summarized in Fig. 2. All of the greases were found to absorb considerable quantities of water. The lubricating oils have limited water absorbability, and the additives may play a role (Cantley (5)). However, even for fully formulated synthetic ester, which may take up more water than mineral oils, water absorbability is limited to approximately 0.36 wt% (Cantley (5)). Therefore, the absorption of a high concentration of water by the greases can be mainly attributed to their thickeners.

The tested calcium sulfonate complex greases were found to be able to absorb around 80 wt% water, irrespective of the difference in the base oil that constitute the grease matrix. The base oil (mixed mineral/synthetic [MS] and mineral [M] oil) is hydrophobic (water repelling). Therefore, the absorption of high concentrations of water must be due to the presence of the highly surface-active calcium sulfonate that covers the calcium carbonate core. The lithium-based greases were found to absorb a maximum of 10% water by weight. Similar to the calcium sulfonate complex greases, the base oil is hydrophobic. However, the lithium soaps are hydrophilic and therefore absorb water. Though PAO lubricants exhibit good hydrolytic stability among other synthetic lubricants and are hydrophobic (Lugt (7)), lithium complex grease based on PAO was found to absorb considerable quantities of water. The higher water absorbability (30%) of this grease compared to lithium greases can be due to the presence of complexing agents that are partially hydrophilic. The presence of esters in PAO formulations to improve additive solubility might also have resulted in its higher water intake in comparison to lithium greases. The polyurea grease based on synthetic esters was found to absorb 80 wt% water. Esters show water solubility due to their ability to participate in hydrogen bonding. To confirm that the high water absorption by this grease is due to its thickener, the maximum water absorbability was also measured for a polyurea grease based on PAO, which again showed a high, though
slightly lower, value (maximum water uptake of 70%), ascribed to the nonpolar base oil. The presence of additives that are polar by nature might also have played a role in the absorption of considerable quantities of water in all of the greases.

**Flow curve measurements**

In steady-state flow and low shear rates, the viscosity of lubricating greases shows a Newtonian plateau region. Application of shear rates beyond a critical value will result in a reorientation of the fibers within the microstructure that leads to shear thinning (Vinogradov and Sinitsyn (20)). The viscosity drops monotonically, and a power law behavior is often observed (Barnes and Walters (21)). At high shear rates, the fibers will be reduced in width and length (Forster, et al. (22)), and the grease viscosity is assumed to approach the base oil viscosity.

Figure 3 shows flow curves obtained for lithium and lithium complex greases at different temperatures and water concentrations. The decrease in viscosity with shear rate extends over a few decades of shear rate. An anomaly was found at intermediate shear rates where the viscosity increased with increasing shear rate in a narrow range around a shear rate denoted by \( \dot{\gamma}_{ch} \) in this article. In the absence of water, this only occurred at a higher temperature (Fig. 2a). In the cases where water was present, this effect became more pronounced, and at higher shear rates—that is, beyond \( \dot{\gamma}_{ch} \)—the flow curves converged, irrespective of the concentration of water, as shown in Fig. 3b.

A minimum in the stress versus shear rate is evident with an increase in temperature (Fig. 3c). This effect was found to be more pronounced for greases contaminated with water (Fig. 3d). The nonmonotonous increase in stress versus shear rate is attributed to a nonhomogeneous velocity flow field in the gap between the measuring plates in which a part of the sample is fluidized while the rest remains semisolid. This effect is called shear banding (Delgado, et al. (23); Britton and Callaghan (24)). If the global shear rate increases above \( \dot{\gamma}_{ch} \), the fluidized region will grow until a uniform flow is obtained in the gap between the rheometer plates. Apparently, water has an effect on the semisolid fraction and enhances this effect.

The viscosity versus shear rate was fitted using the Cross model; see Fig. 4. The Cross model reads

\[
\eta = \frac{\eta_0 - \eta_\infty}{1 + \frac{\dot{\gamma}}{\dot{\gamma}_c}^m + \eta_\infty},
\]

where \( \eta_0 \) is the zero-shear-rate viscosity, \( \eta_\infty \) is the viscosity at very high shear rates, \( \dot{\gamma}_c \) is the critical shear rate at which the fluid changes from Newtonian to power law behavior, and \( m \) is the shear thinning index. Unfortunately, it is not possible to measure the high shear rate viscosity with the cone plate/parallel plate rheometer. A good approximation is to use the base oil viscosity (Lugt (7)), which is assumed to be unaffected by water.

The viscosity of the base oil at a given temperature was obtained using Walther’s equation (Walther (25)). The equation is defined as

\[
\mu = 10^{A/B - B \log_{10}(T)} - 0.7,
\]

where \( \mu \) is kinematic viscosity (mm²/s), \( T \) is the temperature (K), and \( A \) and \( B \) are unknown constants calculated from the
Irrespective of the thickener and base oil type, the zero-shear viscosity and critical shear rate were primarily found to be influenced by the presence of water. At higher shear rates, the water had a negligible effect on the viscosity. The influence of water on the fitting parameters obtained from the Cross model is summarized in Table 2.

The zero-shear viscosity of the calcium sulfonate complex greases was found to increase with water, which was most pronounced at lower temperatures (Figs. 5a and 5b). This is in agreement with the findings of Leckner (8). He showed an increase in apparent viscosity at a shear rate of 1 s\(^{-1}\) for a calcium sulfonate complex thickened grease in mineral oil. However, his study was restricted to a maximum water content of 30 wt%. Giasson, et al. (26) performed Small Angle X-ray Scattering (SAXS) analysis on hydrated and nonhydrated overbased calcium sulfonate dispersions. By using the square-well potential model, they showed an increase in attractive potential in the presence of water and related it to agglomeration of micelles, which is the cause of the stiffening. At higher temperatures (50 and 75°C), the zero-shear viscosity of calcium sulfonate greases was found to decrease, especially for greases with higher water content.

In contrast to calcium sulfonate complex greases, the zero-shear viscosity of lithium and lithium complex greases was found to decrease with water content (Figs. 6a, 6b, and 7a). A similar finding was reported by Leckner (8) for lithium complex grease with 10 wt% water but for apparent viscosity measured at a shear rate of 1 s\(^{-1}\). The lithium and lithium complex greases showed an almost linear relation between zero-shear rate viscosity and water concentration. The decrease in zero-shear viscosity for these greases can be the result of a reduction in particle interactive forces in the presence of water. The zero-shear viscosity of polyurea grease showed a slight decrease with water at lower temperatures (10 and 25°C). However, the zero-shear viscosity was found to increase at higher temperatures. An increase in zero-shear viscosity, which is an order of magnitude higher compared to the viscosities at lower temperatures was exhibited by this grease at 75°C (Fig. 7b). The increase in consistency at this temperature may be attributed to the reinforcement of the thickener network, induced by chemical or phase change.

### Oscillatory strain sweep measurements

At low deformations, lubricating greases are viscoelastic materials. The viscoelastic properties are quantified using storage \(G'\), elastic component) and loss modulus \(G''\), viscous component), which are measured in oscillating shear. The stress at which the grease loses its elastic properties is called the yield stress (De Graef, et al. (27); Hunt and Zukoski (28)). There is no sharp transition from elastic to plastic behavior, which makes determination of the yield stress a subject of debate and results in various methods to determine its value. The authors have evaluated these methods in an earlier paper (Cyriac, et al. (29)). From this study, it was concluded that the yield stress exhibits a frequency dependence, which can be illustrated using the Maxwell model. This general model for viscoelastic materials constitutes of a spring and dashpot in series and reads

\[
\tau = \eta \frac{d\gamma}{dt} + \eta G \gamma.
\]

in which \(\tau\) is the stress, \(\gamma\) is the shear rate, \(\eta\) is the viscosity, \(G\) is the elastic modulus, and \(\frac{d\gamma}{dt}\) is the stress rate.

It is assumed that yielding takes place at the onset of nonlinearity in the stress–strain relation, which is influenced by the properties of the dashpot (the viscosity). The viscous properties make the system and, therefore, measured yield stress time dependent (Eq. [3]); the reader is referred to Cyriac, et al. (29) for more details on this method. In the present article, the yield stress is reported as the stress level at which a predefined (0.5%) deviation from the linear relation between stress and strain is observed for a frequency of 1 Hz. The yield stress (Figs. 8–10) can be used as a parameter to quantify the ability to provide the bearing with a grease reservoir and for predicting the flowability of grease in lubrication systems.

The yield stress of the two measured calcium sulfonate complex greases was in general found to increase with increasing concentration of water (Figs. 8a and 8b). Leckner (8) found an increase in yield stress for a calcium sulfonate complex grease with a maximum of 30 wt% water for measurements performed at 25°C. However, his definition of yield stress is different from the one used in this article. The yield stress in Leckner (8) was taken as the stress corresponding to the crossover of storage and loss modulus.

The yield stress can be fitted with

\[
\tau_y = \tau_{yo} + b \times x^c,
\]

where \(\tau_{yo}\) is the yield stress without water (Pa), \(x\) is the wt% water in the grease, and \(b\) and \(c\) are fitting parameters. Equation [4] can be used to capture the evolution of yield stress for all of the greases studied and the parameters \(b\) and \(c\) obtained are listed in Table 3.
Table 2. Influence of water on various parameters obtained using the cross model for the studied greases at $T = 25^\circ C$.

| Water (%) | CaS/MS (Calcium Sulfonate Complex/Synthetic (PAO)/Mineral) | CaS/M (Calcium Sulfonate Complex/Mineral Oil) | Li/M (Lithium/Mineral Oil) | Li/SS(Lithium/Mineral Oil Semisynthetic) | LiC/PAO (Lithium Complex/Synthetic PAO) | PU/E (Polyurea/Synthetic Ester) |
|-----------|-----------------------------------------------------------|---------------------------------|-----------------|---------------------------------|-----------------------------|-----------------|
| 0         | $\eta_0$ (Pa.s) 1.9 x 10^6 2.10 x 10^6 2.15 x 10^6 2.20 x 10^6 2.23 x 10^6 | $\eta_0$ (Pa.s) 1.85 x 10^6 2.10 x 10^6 2.30 x 10^6 2.83 x 10^6 2.91 x 10^6 | $\eta_0$ (Pa.s) 5.20 x 10^6 5.08 x 10^6 4.10 x 10^6 4.08 x 10^6 3.8 x 10^6 | $\eta_0$ (Pa.s) 3.8 x 10^6 3.5 x 10^6 3.2 x 10^6 3.05 x 10^6 2.9 x 10^6 | $\eta_0$ (Pa.s) 5.1 x 10^6 4.4 x 10^6 4.31 x 10^6 4.18 x 10^6 3.14 x 10^6 |
| 20        | m 0.18 0.18 0.18 0.18 0.18 | m 1.083 1.083 1.083 1.083 1.083 | m 0.231 0.231 0.231 0.231 0.231 | m 0.91 0.93 0.93 0.93 0.93 | m 0.265 0.265 0.265 0.265 0.265 |
| 40        | $\gamma_0$ (s^{-1}) 4.8 x 10^{-4} 4.8 x 10^{-4} 5.7 x 10^{-4} 6.6 x 10^{-4} 6.4 x 10^{-4} | $\gamma_0$ (s^{-1}) 3.1 x 10^{-4} 3.8 x 10^{-4} 4.1 x 10^{-4} 4.1 x 10^{-4} 4.2 x 10^{-4} | $\gamma_0$ (s^{-1}) 1.6 x 10^{-4} 1.4 x 10^{-4} 1.3 x 10^{-4} 1.2 x 10^{-4} 1.2 x 10^{-4} | $\gamma_0$ (s^{-1}) 1.4 x 10^{-4} 1.1 x 10^{-4} 1.3 x 10^{-4} 1.2 x 10^{-4} 1.2 x 10^{-4} | $\gamma_0$ (s^{-1}) 1.2 x 10^{-4} 1.8 x 10^{-4} 1.6 x 10^{-4} 2.1 x 10^{-4} 3.9 x 10^{-4} |
| 60        | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} |
| 80        | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} | $\gamma_0$ (s^{-1}) 2.1 x 10^{-4} 2.6 x 10^{-4} 3.9 x 10^{-4} 3.6 x 10^{-4} 3.6 x 10^{-4} |

Figure 5. Zero-shear-rate viscosity from the Cross model as a function of percentage water for calcium sulfonate complex greases at different temperatures.
Figure 6. Zero-shear viscosity from the Cross model versus percentage water for lithium greases at different temperatures.

Figure 7. Zero-shear viscosity from the Cross model as a function of percentage water for (a) lithium complex and (b) polyurea grease at various temperatures.

Figure 8. Yield stress from oscillatory strain sweep measurement as a function of percentage water for calcium sulfonate complex greases at different temperatures, at a frequency of 1 Hz. The dotted lines are the fitting curves obtained using Eq. [4].

Figure 9. Yield stress as a function of percentage water for lithium greases at a frequency of 1 Hz. The dotted lines are the fitting curves obtained using Eq. [4].
The decrease in yield stress occurs if negative values of \( b \) are found. The yield stress of lithium greases showed a reduction within increase in water concentration (Fig. 9), whereas the yield stress of the representative lithium complex grease was in general found to increase in the presence of water (Fig. 10a). This is contrary to what has been reported in the literature. Leckner (8) found a decrease in yield stress for a lithium complex grease. This may be ascribed to the different definition of yield stress. The yield stress of polyurea grease showed a very moderate, almost stable, decreasing trend (Fig. 10b). Similar to the observations on the zero-shear viscosity (Fig. 7b), the behavior at 75°C was very different from that at lower temperatures. Initially, the yield stress increased with increasing water concentration, whereas it decreased again at very high water concentration. This behavior cannot be described by Eq. [4].

**Table 3.** Parameters of Eq. [4] at different temperatures for yield stress versus percentage water for all the greases studied.

| Grease  | \( \tau_{yo} \) (Pa) | \( b \) | \( c \) | \( \tau_{yo} \) (Pa) | \( b \) | \( c \) | \( \tau_{yo} \) (Pa) | \( b \) | \( c \) | \( \tau_{yo} \) (Pa) | \( b \) | \( c \) |
|---------|---------------------|------|------|---------------------|------|------|---------------------|------|------|---------------------|------|------|
| CaS/MS  | 215.3               | 1.49 | 0.92 | 176.8              | 3.95 | 0.64 | 147.1               | 0.62 | 0.79 | 82.3                | 0.06 | 1.16 |
| CaS/M   | 246.7               | 13.12| 0.59 | 177.6              | 26.9 | 0.46 | 124.1               | 40.1 | 0.30 | 78                  | 20.2 | 0.26 |
| Li/M    | 95.2                | -0.30| 1.06 | 81.5               | -0.08| 1.30 | 64.6                | -0.14| 1.10 | 59.9                | -1.07| 0.66 |
| Li/SS   | 87.1                | -3.29| 0.55 | 63.4               | -0.57| 0.79 | 52.4                | -0.59| 0.75 | 45.8                | -1.28| 0.55 |
| LIC/PAO | 167.8               | 0.016| 2.34 | 131.6              | 0.006| 2.03 | 94                  | 2.53 | 0.62 | 60                  | 9.68 | 0.39 |
| PU/E    | 26                  | -1.34| 0.21 | 23.16              | -1.58| 0.46 | 17.1                | 0.096| 0.27 | —                   | —    | —    |

**Frequency sweep measurements**

Frequency sweep measurements were performed to determine the sensitivity of the viscoelastic properties (\( G' \) and \( G'' \)) in the presence of water within the linear viscoelastic (LVE) regime. The results of these measurements can be used for quantifying the elastic behavior, \( \tan \delta = \frac{G''}{G'} \), and plateau modulus, \( G_N^{0} = [G']_{\tan \delta \rightarrow \text{minimum}} \). The latter is a measure of the aggregation of the dispersed structural phase (Delgado, et al. (30) and therefore related to the strength of the microstructural network.

These measurements were carried out after carefully establishing the boundaries of the linear viscoelastic regime from the oscillatory strain sweep measurements. The frequency sweep tests were performed at constant strain within this regime. The results are shown in Fig. 11 for CaS/M and Li/SS. Regardless of the quantity of water, the storage modulus was found to be an order of magnitude higher than the loss modulus in the whole...
frequency range studied for all of the greases. For the calcium sulfonate complex greases, the storage modulus ($G'$), complex modulus $G'' = \sqrt{(G')^2 + (G'')^2}$, and complex viscosity $\eta^* = \frac{G'}{\omega}$ (not shown in figure) were found to increase with water, similar to what was shown for the zero-shear viscosity. In contrast, for lithium, lithium complex, and polyurea greases, $G'$ was found to decrease with water.

In the presence of water, the loss tangent, $\tan \delta$, was found to decrease with an increase in water concentration for calcium sulfonate greases, whereas it showed an increase for the rest of the greases studied (Fig. 12). This indicates that calcium sulfonate greases become more elastic and the other greases become more viscous in the presence of water. The plateau modulus as a function of water at $25^\circ C$ is shown in Fig. 13 for all of the studied greases. The plateau modulus was found to increase with water for the calcium sulfonate complex greases, whereas it was found to decrease for the rest of the greases.

**Discussion**

In the case of lubricating oils, the water uptake depends on its composition and physicochemical properties (Echin, et al. (11)). The water solubility of pure base oil is small but may increase significantly with the use of additives. In comparison to oils, lubricating greases can absorb larger quantities of water due to the polar nature of its thickeners. This applies to lithium–hydroxyxystearate (10% water) and even more to lithium complex grease (30% water). The polyurea grease based on ester was found to absorb 80% of water. To confirm that this high value was indeed caused by the properties of the polyurea thickener, the maximum water absorbability was also measured for a polyurea grease based on PAO, which again showed a high, though slightly lower, value (maximum water uptake of 70%), ascribed to the nonpolar base oil. Calcium sulfonate complex grease based on mineral oil was found to absorb the most water (80%). This is caused by the very strong polar nature of the calcium sulfonate that covers the calcite core. The presence of additives, which are polar by nature, may further facilitate the absorption of large quantities of water in all these greases.

The presence of water has an impact on all greases. The zero-shear viscosity of the calcium sulfonate complex greases was found to increase with water, whereas it was found to decrease for the rest of the greases. The yield stress for lithium complex and calcium sulfonate complex greases showed an increase with water. This points to a strengthening of the shear-resistant structures in the presence of water. For smaller amounts of water (up to 10%) this increase is subtle and will most likely not have an impact on the flow and lubricant reservoir formation. Other than in the case of calcium sulfonate grease, which displays a fine dispersion of agglomerated particles, lithium greases consist of an agglomerated fibre network (Sánchez, et al. (31)). The decrease in yield stress in the presence of water for lithium grease is therefore likely due to a reduction in interactive forces between fibers caused by water absorption, giving rise to a less stable network. The yield stress of the studied polyurea grease exhibited a contradictory behavior in the presence of water. The yield stress showed a very

Figure 12. Loss tangent versus frequency for different concentrations of water within the LVE regime for (a) calcium sulfonate complex and (b) lithium grease.

Figure 13. Plateau modulus versus percentage water for the studied greases at $T = 25^\circ C$. 
Table 4. Trend of rheological properties for water-contaminated greases at different temperatures.

| Grease       | 10    | 25    | 50    | 75    | 10    | 25    | 50    | 75    |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|
| CaS/MS       | ↑     | ↑     | ↑     | ↓     | ↑     | ↑     | ↑     | ↑     |
| CaS/M        | ↑     | ↑     | ↑     | ↓     | ↑     | ↑     | ↑     | ↑     |
| Li/M         | ↓     | ↓     | ↓     | ↓     | ↓     | ↓     | ↓     | ↓     |
| Li/SS        | ↓     | ↓     | ↓     | ↓     | ↓     | ↓     | ↓     | ↓     |
| LiC/PAD      | ↓     | ↓     | ↑     | ↑     | ↓     | ↓     | ↓     | ↓     |
| PU/E         | ↓     | ↓     | ↑     | ↑     | ↓     | ↓     | ↓     | ↓     |

moderate, almost stable, decreasing trend up to 50°C, whereas this grease exhibited an increase in yield stress, which was at least twice as large as the yield stress at lower temperatures at 75°C. For calcium sulfonate complex greases the viscoelastic parameters (\(\eta_s\), \(G^*\), and \(G'\)) quantified within the LVE were found to increase with water, similar to what was shown for the zero-shear viscosity. Apparently water enhances the strength of the microstructural network, giving rise to a stiffer grease. In contrast, for lithium, lithium complex, and polyurea greases, the viscoelastic parameters were found to decrease with water. The plateau modulus, which is a measure of the aggregation of the dispersed structural phase, was found to increase with water for calcium sulfonate greases. This is in line with the observations for the zero-shear viscosity. For lithium, lithium complex, and polyurea greases, the plateau modulus was found to decrease with water. This is similar to what was seen for zero-shear viscosity for these greases.

Conclusions

The impact of water on the rheology of the most common types of lubricating greases that are used in rolling bearings was studied in this article. All of the studied greases, irrespective of their chemical composition and microstructure, were found to absorb considerable quantities of water. This can be mainly attributed to the polarity of the thickener. Water resulted in the formation of either a softer or a stiffer grease with appreciable changes in rheological properties as suggested in earlier work (Leckner (8); Mistry (9)). The general trend of different rheological parameters for water-contaminated greases with respect to the temperature is shown in Table 4.

Water was found to influence the evolution of the flow curve but only at low shear rates. Shear banding was found to occur for all greases characterized by a local increase in viscosity at the intermediate shear rate. This shear banding was found to occur at higher shear rates with an increase in water concentration and temperature. The zero-shear viscosity from the Cross model was also found to be influenced by the presence of water. The zero-shear viscosity of calcium sulfonate complex greases increased with increasing water concentration. On the contrary, lithium, lithium complex, and polyurea greases gave rise to a softened matrix in the presence of water. For the studied polyurea grease, an increase in zero-shear viscosity, which is an order of magnitude higher compared to the viscosities at lower temperatures, was observed at 75°C.

The yield stress from oscillatory strain sweep and plateau modulus from frequency sweep measurements were also found to be influenced by water. For calcium sulfonate complex grease, an increase in yield stress and plateau modulus was found. The yield stress of the studied lithium complex grease showed an increase, whereas its plateau modulus was found to decrease with water. The rest of the greases exhibited a decrease in yield stress.

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