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On the Required Energy to Break Down the Thickener Structure of Lubricating Greases

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ABSTRACT

The rheology of a conventional lithium-12 hydroxystearate bearing grease changes significantly when it is subjected to mechanical shear. Often this shear energy–along with the consequent entropy–is measured and used in engineering and thermodynamic models, leading to grease life models for predicting bearing seizure due to insufficiently thick film or loss of lubricity of the base oil/grease. In this degradation process, the bonds between the individual molecules, consisting mainly of the fairly weak van der Waals bonds and/or hydrogen bonds, are broken during this shearing process. In this article, we show that only a very small portion of the shear energy is needed to break these bonds and that the vast majority is dissipated as heat due to the lubricant viscosity, also known as viscous dissipation. We model the thickener as rod-shaped fibers, wherein the grease viscosity is reduced by a factor of 5 when the length of a fiber is reduced by a factor of 2.5. The energy needed to break the bonds between the molecules to shorten these fibers is 6 to 7 orders of magnitude smaller than the energy applied by shear. Hence, it is very difficult to measure this fiber structure breakage energy from grease shear aging experiments directly.

Introduction

A lubricating grease is a mixture of oil, a thickener and various performance-improving additives. While there are many different types of chemical compounds which can be used as thickener, the most widely used materials are metal soaps which consist of fibers forming a network, giving the grease its viscoelastic properties.

When sufficient (external) mechanical shear is imposed on a volume of grease, such as a patch of grease entering a rolling bearing contact, the thickener fibers network will break down to a certain extent. This softens the grease, changing its rheology. Rheological changes can be measured in various tests such as a cone penetration test (1), indicating a decrease in consistency, or a rheometer, showing a change in yield stress, storage modulus and viscosity (2).

Via experiments with the grease worker (2, 3), Couette aging machine (4) and actual bearing data (2), it has been shown that, depending on grease type and temperature, the energy density required to significantly change the rheology of grease is large (in the order of 10 to 100 J/mm^3). In this work, we will show that the actual energy density to break the bonds between the thickener fibers, potentially changing the grease rheology, is in fact much smaller.

This leads to the hypothesis that the vast majority of the mechanical energy used to shear the grease is converted to heat, generated through viscous dissipation because of the shear flow of the oil-fiber matrix, and only a very small portion of this energy is needed to break down the actual thickener network structure. A similar view could be read in the 1951 article of Moore and Cravath (5) where it is stated that fiber breakage is a rare event, implying a large contrast in energies: 'The rate of breakage often varies exponentially with particle size because it is often the frequency of a relatively rare event that happens only when a number of randomly varying factors combine to cause a stress exceeding the breaking strength.'

This is most relevant for the development of grease life models for rolling bearings in which the end-of-grease-life is measured by the time until bearing seizure due to insufficiently thick film or loss of lubricity of the base oil/grease (6). This evolution of film thickness may be caused by multiple effects with the most common being thermo-mechanical degradation of the grease.

Thermodynamical degradation of grease has been studied by Kuhn, Osara, Khonsari, Lugt and co-workers (4, 7–11). In most of these studies, grease aging is obtained by shearing and heating/cooling the grease in a rheometer or as in the grease worker mentioned above. Degradation is then described using an entropy generation or energy transformation concept. In both cases, the mechanical work per unit volume of grease is calculated via the time integral of the product of the stress and strain rate on the grease. Energy is dissipated into degradation (via entropy generation) and

heat development. Following the first law of thermodynamics, the energy used to break down the fiber structure–and thereby degrade the grease–is the difference between the heat generated by the grease through viscous dissipation and the total external energy imposed on the grease (via mechanical work and heating or cooling). In this paper, we will show that this energy required to break down the fiber structure is negligible, relative to the energy dissipated by viscous shear in the grease. It is therefore very difficult to measure this fiber structure breakage energy from grease shear aging experiments directly. Existing energy approaches for characterizing grease contain an 'engineering component', where the grease was considered as a homogeneous material. This is very valuable for the development of grease life models but does not provide insight into the physical mechanisms behind degradation. This needs to be improved in the future by considering lubricating grease as a mixture of base oil, which essentially does not degrade by shear, and thickener matrix with a structure that degrades significantly. This adds an extra layer of understanding to the existing thermodynamic models used to characterize grease degradation. A full mathematical description of the grease degradation process during aging in laboratory equipment of full bearings is beyond the scope of this paper. Here, we will estimate the energy required to break the thickener fibers of a good conventional lithium-12 hydroxystearate bearing grease and compare it to the total energy externally imposed on the grease to achieve this degradation. It will improve the interpretation of the results of models used to describe grease mechanical degradation.

Energy

The bond energy is estimated for a standard lithium grease, containing lithium 12-hydroxystearate (Li-12HSA) thickener molecules having the chemical formula $C_{18}H_{35}LiO_3$. As shown in SEM and AFM pictures in various papers (6, 12,13), these molecules form a twisted fiber having a typical diameter of 50-200 nm and a length of 1-25 micron.

The general view is that the thickener molecules forming these twisted fibers are held together mainly by weak intermolecular forces (non-covalent interactions). These forces are van der Waals forces (14), the hydroxyl groups can form hydrogen bonds (14–16) and the hydroxystearate molecules bond through the ionic lithium and the carboxylic group.

To estimate the order of magnitude of the energy required to form or break these bonds, several methods can be used. One of them is by taking the enthalphy of vaporization ΔH_{vap} of stearic acid, having a value of 195.4 kJ/mol (17). Another method is by quantum mechanics (QM) (16) calculations, where it is estimated that the intermolecular interaction energy ΔE_{int} for forming a dimer of two Li-12HSA molecules has a maximum value of 272.4 kJ/mol.

We can estimate the energy density e_e (in J/mm^3) to break all bonds by multiplying the enthalpy of vaporization by the molar mass of thickener per volume of grease

$$e_e = \Delta H_{vap} \frac{w\rho}{M} \tag{1}$$

A typical Li-12HSA grease has a density ρ of approximately 900 kg/m^3 and a thickener mass fraction w of approximately 0.1. For a molar mass M of Li-12HSA of 306.4 g/mol (18), this leads to a thickener molar density of 2.9×10^{-7} mol/mm^3. When the enthalpy of vaporization ΔH_{vap} is rounded to a worst-case value of 300 kJ/mol, the total energy density needed break all bonds and essentially 'evaporate' the Li-12HSA is 0.09 J/mm^3.

Viscosity

When a Li/M grease is degraded in a grease worker (3) up to an energy density of approximately 100 J/mm^3, the normalized viscosity η/η_{s1} is reduced by a factor of approximately 5, see figure 1. AFM images (19) suggest that the Li-12HSA grease micro-structure consists of fibers, and when the grease is degraded the fiber length is reduced. This was also shown by Hogenberk et al. (20) wherein working the grease in a grease worker softened the grease but did not significantly change the permeability. The permeability depends mainly on the fiber diameter and volume fraction, which do not change during grease working, whilst the softness/viscosity depends on the length of the fibers, which changes when fibers break.

To estimate the number of bonds to be broken to significantly reduce the viscosity, a basic Einstein model for rod-shaped particles may be sufficient. We note a few limitations stemming from our simplification: a thickener mass fraction
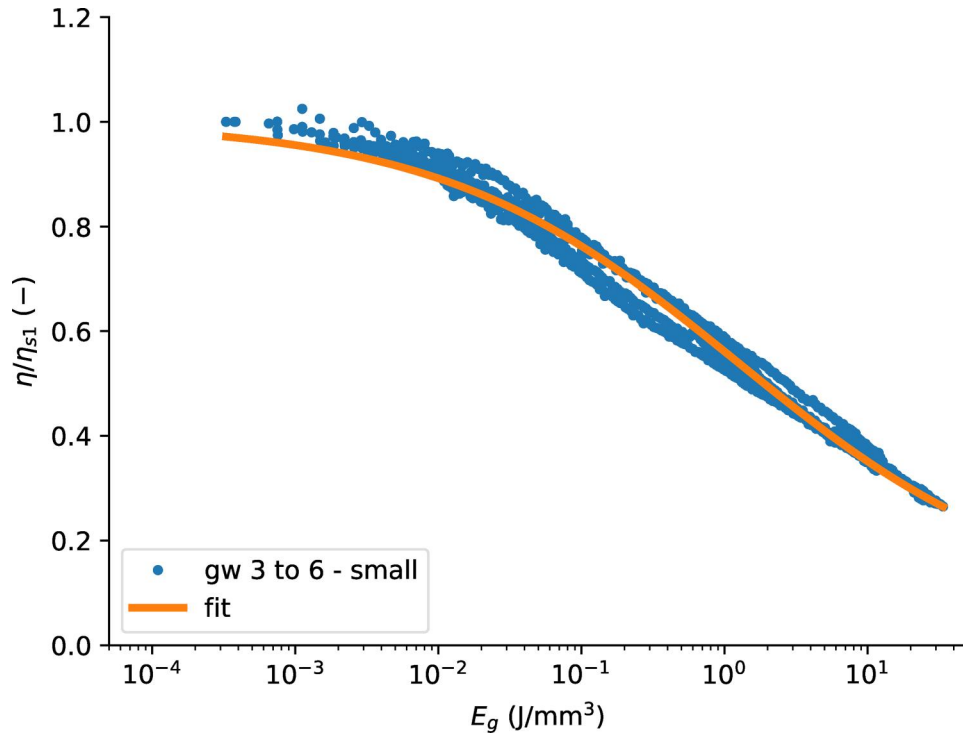
Figure 1. Normalized viscosity as a function of cumulative energy density, reprinted with permission from (3).

of 0.1 does not result in the very dilute solution required by the Einstein model; stiff rod-shaped particles do not represent the flexibility of the grease thickener fibers or fiber network well; and a change in the zero-shear viscosity upon mechanical degradation is not necessarily the same as the change in viscosity in the shear-thinning region. Nevertheless, this model can be used as a first estimation for energy required to break the fibers in order to change the viscosity significantly.

The well-know Einstein equation (21, 22) reads:

$$\eta = \eta_0(1 + [\eta]\phi), \tag{2}$$

where η is the viscosity, η_0 is the continuous-phase viscosity, $[\eta]$ the intrinsic viscosity and ϕ the volume fraction of hard spherical particles. For rod-like particles, Barnes (21) derived

$$[\eta] = \frac{7}{100}p^{5/3} \tag{3}$$

where $p = l/d$ is the length to diameter ratio. Then the normalized viscosity η/η_{s1} can be defined in a similar way as for the grease worker, where η_{s1}, p_i and l_i are the viscosity, length-diameter ratio and fiber length of the initial stroke. Combining equations 2 and 3, assuming that the diameter does not change when mechanically degrading a grease and that the viscosity is much larger than the continuous-phase viscosity, as shown in appendix A.1, gives

$$\frac{l}{l_i} = \left(\frac{\eta}{\eta_{s1}}\right)^{\frac{3}{5}}. \tag{4}$$

Equation 4 shows that when the normalized viscosity η/η_{s1} is reduced by a factor of 5, as shown in Figure 1, the length of the rod-shaped particles is reduced by a factor of 2.5.

Estimates

To calculate the number of molecules in a rod-shaped fiber, we assume that the fiber consists of parallel-oriented molecules as shown in figure 2.

The number of molecules in the cross-section of a fiber is approximated by

$$N_c = \frac{d^2}{D^2} \tag{5}$$

where d is the fiber diameter and D the molecule diameter. The width of two 12-hydroxystearate molecules connected by hydrogen bonds is, according to Abraham et al. (23), about 4 Å. The thickness of a single hydroxystearate molecule, according to Forster et al.(24), is about 5 Å. If we assume 6 Å, then a cross-section of a fiber having a diameter of 0.1 μm consists of 2.8×10^4 molecules. The length L of a Li-12HSA molecule, with 18 carbon atoms having a distance of 150 pm between each C-C bond, is approximately 2.7 nm. If we assume an initial fiber length l_i of 10 microns, then we have approximately 3700 Li-12HSA molecules in the longitudinal direction. Multiplied by the number of molecules in the cross-section of a fiber yields 1×10^8 molecules per fiber.

Although figure 2 shows two positions with bonds, as a worst-case estimate we assume that each Li-12HSA molecule has only one bond. In addition we assume that the number of bonds is equal to the number of Li-12HSA molecules in a fiber, which is a good approximation when the amount of molecules in a fiber is large.

The fiber number density, or number of fibers in 1 mm³ of grease, can be calculated as the total number density of Li-12HSA molecules divided by the number of Li-12HSA molecules in a fiber
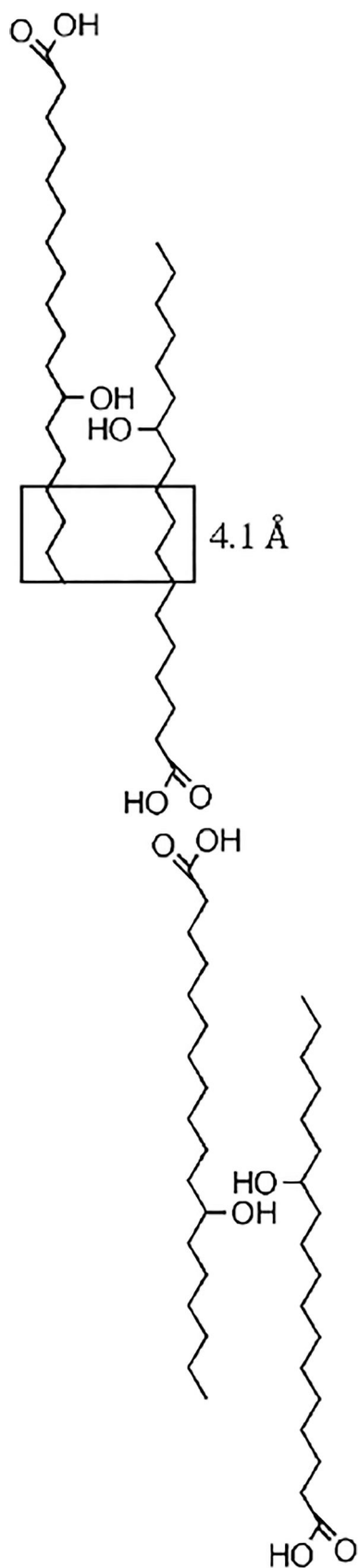
Figure 2. Packing arrangement of 12-hydroxystearate, reproduced from Abraham et al. [23].

$$n_f = \frac{N_A w \rho / M}{N_c l_i / L} \qquad (6)$$

Then the energy density to considerably break up the fibers can be calculated as

$$e_f = \frac{\Delta H_{vap}}{N_A} N_c n_f \frac{l_i}{l} \qquad (7)$$

where $\Delta H_{vap}/N_A$ is the bond energy per Li-12HSA molecule, $N_c n_f$ is the amount of molecules per mm^3 which need to be broken to separate all the fibers in the volume into two parts and l_i/l is the number of parts into which the fibers are broken. Combining and rearranging equations 7, 6 and 1 and assuming that the length of a fiber is large relative to the length of a Li-12HSA molecule, $l \gg L$, gives

$$e_f = e_e \frac{L}{l} \qquad (8)$$

In the example of section 3, where the fiber length is reduced by a factor 2.5 to a length l of 4 μm, the energy density to break the fibers is only 6×10^{-5} J/mm^3, which is between 6 to 7 orders of magnitude less than the shear energy density measured in typical grease shearing experiments as discussed in section 2. In energy balances characterizing these experiments, this study shows that the shear energy density is almost entirely dissipated by viscous interactions. The contribution of viscous dissipation to grease degradation is beyond the scope of this study. Here, we only show that the energy required to break the thickener fibers is relatively negligible.

Conclusion

In most grease degradation studies (4, 7–11), the change of a rheological property is a function of the energy applied to (or entropy resulting from) the grease under mechanical shear and this energy is used as a measure of its state of degradation. Apparently it works quite well in practice, which is surprising because the energy required to break down the fiber structure itself is many orders of magnitude smaller. As an upper limit for this energy, the enthalpy of vaporization for Li-12HSA can be used. With this crude approach, all molecules are essentially 'evaporated', leading to an energy level 3 to 4 orders of magnitude below the measured shear energy. A more refined approach is to model the grease as rod-like particles, where degradation involves shortening of those particles by breaking the bonds at the cross-section of the fiber. This gives good insight into the orders of magnitude involved, leading to the following results and conclusions:

- Using a rod-shaped fibers model, it is shown that grease viscosity is reduced by a factor of 5 when the length of these rod-shaped fibers is reduced by a factor of 2.5.
- The energy density required to break bonds is 6 to 7 orders of magnitude smaller than the energy measured when working the grease, for instance, in a grease worker. It also shows that it would be very difficult, if not impossible, to measure this energy directly.
- This supports the hypothesis from the introduction: the vast majority of the mechanical energy used to shear

the grease is indeed converted into heat. It suggests that the mechanical coupling between the external process and the fiber structure is very weak and that the energy measured externally to shear this structure is very dependent on the physical state, e.g. the viscosity of the base oil, the temperature, and the fiber type, fraction, structure and strength.

- In the thermal energy balance governing grease working experiments and bearing grease operation, the heat generation–via viscous dissipation–can be estimated as the mechanical shear energy (the product of volume, shear stress and strain), because the energy needed to break the thickener fibers is so small that it can be neglected.

At the moment the implications on the development of grease life models are unclear, but in our opinion it is valuable to have notion of the enormous difference in magnitude of the energies involved when developing these models. One of the consequences of this dominant heat generation could be that, when developing engineering models for grease degradation, special care should be given to the thermal design of degradation experiments: Isothermal conditions are desirable because any temperature change during the experiment will influence the base oil viscosity and perhaps could influence the fiber structure. The model with rod-like particles presented here is basic and will have its limitations in describing the complex grease thickener micro-structure and rheology. Quantum mechanics and molecular dynamics calculations could help to capture this complexity better and perhaps provide better understanding of how the micro structure degrades under shear on a molecular level. This could include phenomena like cross linking, fiber alignment/ reorientation (19) and thixotropy (25).

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Disclosure Statement

No potential conflict of interest was reported by the author(s).

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Appendix

(A.1). Derivation of equation 4

The normalized viscosity η/η_{s1} can be written as

$$\frac{\eta}{\eta_{s1}} = \frac{\eta_0\left(1 + 0.07p^{\frac{5}{3}}\phi\right)}{\eta_0\left(1 + 0.07p_i^{\frac{5}{3}}\phi\right)} \tag{9}$$

where p_i is the initial length to diameter ratio. For Li-12HSA $\eta \gg \eta_0$, so the normalized viscosity can be approximated as

$$\frac{\eta}{\eta_{s1}} \approx \frac{\eta_0 0.07p^{\frac{5}{3}}\phi}{\eta_0 0.07p_i^{\frac{5}{3}}\phi} \tag{10}$$

Then rearranging gives

$$\frac{p}{p_i} = \left(\frac{\eta}{\eta_{s1}}\right)^{\frac{3}{5}} \tag{11}$$