RELATION BETWEEN SHEAR STRESS AND SHEARING TIME IN SELECTED LUBRICANT COMPOSITIONS

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Key words: greases, fillers, shear stresses, shearing time, machine lubrication systems.

Abstract
The paper presents the results of studies of the influence of fillers introduced into lubricating greases on changes in values of shear stresses in resulting lubricant compositions. These fillers were powders of graphite, molybdenum disulphide, and PTFE. They are added to grease to improve their tribological properties. They also impact the rheological properties of lubricating compositions, especially on the course of the shear stress, whose value decreases with the duration of the flow of these compositions. Knowledge of changes in the value of this stress is essential in designing central lubrication systems in which these compositions may be used. Tests were performed on lithium grease without fillers as well as on a composition of this grease with the fillers mentioned above. Measurements were carried out using a Rheotest 2.1 rheometer by changing the shearing time at selected gradients of shear rate. Test results have shown that both the kind of filler and the shearing time have an impact on the value of shear stress in the tested lubricant composition.

INTRODUCTION
The rapid development of the machine industry as well as the increasing requirements for modern machines and devices cause that they often cannot be lubricated with conventional lubricants. These requirements result from, among other things, the work of these machines in the conditions of very heavy loads, slow working motions, vibrations, and oscillatory motions. In these conditions, the lubricant is squeezed out of the contact area, and this leads to direct contact of cooperating surfaces. Then the increasing share of semi-dry and dry friction in the mixed friction process results in significant energy and material losses. In this situation, traditional greases were not sufficient and, as a result of searching for new lubricants, solid lubricants were “rediscovered.” It has been found that some solid lubricants can lubricate machine components functioning in the difficult conditions mentioned above. As a result of searching for lubricants suitable for these conditions, the aforementioned solid...
lubricants were gradually introduced as fillers into the structure of greases. It resulted in the improvement of tribological properties of compositions and ensured adequate lubrication of tribological nodes operating in these conditions [L. 10]. Recently, compositions consisting of oil or grease and fillers of carbon nanostructures, i.e. graphene, nanotubes, or fullerenes [L. 7, 8, 11], have also been increasingly used.

At present, along with the progressing automation of machines, the automation of their lubrication systems is also taking place. In the commonly used central lubrication systems, lubricant portions can be fed to a tribological node in optimum (often very small) amounts, which, besides economic benefits, is also important in terms of environmental protection. Moreover, a significant improvement is being achieved in the quality of these lubricants through introducing various additives into their structure, including fillers in the form of solid lubricants, considerably improving the effectiveness of lubrication.

OVERVIEW OF RESEARCH ISSUES

Besides ensuring that the compositions mentioned in the previous section have the desired tribological properties, it is important to assess their rheological properties. Rheological properties determine whether a grease will be delivered to surfaces being lubricated and whether the amount of grease will be suitable. As it is known, rheological properties of grease are influenced by the type of thickener, base oil, as well as various improvers introduced into the grease to provide properties required by operating conditions in a given tribological node. Often solid lubricants such as graphite, molybdenum disulphide, PTFE, as well as some coloured metals, are introduced into this structure [L. 9]. They are introduced in a suitably fragmented form. It is aimed at improving the lubricity of the resulting composition, which is particularly important at heavy loads and low slippage speeds, i.e. in conditions of mixed friction. Then, in places where there is no grease separating two contacting surfaces, the above-mentioned solid lubricants ensure boundary (semi-dry) friction.

From among the properties of such a lubricating composition, during its movement in a lubrication system, the rheological parameters such as structural viscosity and yield stress (the so-called flow limit) are of fundamental importance. These parameters determine the “pumpability” of lubricants. Solid lubricants introduced into the composition, due to their volume fraction, should cause an increase in the structural viscosity, and hence the shear stress in this composition. However, this is not always the case, because it is also necessary to take into account the impact of physicochemical interactions between the sets of particles of a thickener and base oil, as well as particles of solid lubricant introduced into a grease. The shape of the sets of thickener particles, their energy potential on the one hand, and the surface energy of the filler particles introduced on the other, can change the value of the structural viscosity of the resulting lubricant composition. The introduction of filler particles with appropriate surface energy results in such a modification of interactions between the sets of thickener particles that the value of the structural viscosity and the flow limit of the resulting lubricant composition decrease. If, on the other hand, low-active or inactive filler particles are introduced into the structure of grease, then the physicochemical interaction between these particles does not occur or is very small, and then the geometric factor is decisive. Then the concentration of the lubricant composition increases and the value of the structural viscosity increases.

Previous publications written by the author or with the author’s participation contained the results of studies of the influence of graphite, MoS₂, and PTFE powders introduced into a grease on changes in shear stresses in resulting compositions [L. 1, 3, 6]. The results of tests conducted at different gradients of shear rate, at established temperatures, and in short shearing times were presented. These tests were carried out both in the “grease mass” as well as in the boundary layer. They demonstrated that the value of structural viscosity in the boundary layer is different than in the grease mass, because the type of wall material has a significant influence on changes in this value near the wall. These tests are carried out due to the increasing need to lubricate tribological nodes with these compositions using central lubrication systems.

Nevertheless, it should be emphasized that, in a central lubrication system, a lubricant must be relocated from a container to a tribological node, sometimes over considerable distances. It is then sheared (often intermittently) for a longer period, lasting several dozen and sometimes even several hundred minutes (in two-conduit systems). Therefore, it is important to study the changes in the values of shear stresses in a lubricating composition during its long-lasting (several hours) shearing. Experimental tests devoted to this issue are the subject of the work presented in this article.

SUBJECT, METHODOLOGY AND COURSE OF TESTS

Tests were carried out on a grease classified in the 1st class of consistency, produced from mineral oil thickened with lithium soap made of 12-hydroxy stearic acid. The samples for testing the grease were made with the use of the following ingredients: without fillers and with fillers in the form of graphite, MoS₂, and PTFE powders. Similarly as in tests presented in the previous publication [L. 6], here the oxidation and corrosion additives were also of the same quality and in
Only lubricating compositions with a concentration of 1% and 15% of filler were tested, because (as preliminary measurements had shown), at these concentrations of fillers, their impact on the rheological properties of tested compositions was the most noticeable and differences in the values of shear stresses were the greatest. In the case of intermediate values, the differences were also “intermediate.” Measurements were carried out using a rotary rheometer, Rheotest 2.1, whose measuring head is shown in Fig. 1 [L. 6]. It is a rheometer of the Couette type, in which the tested lubricant composition was placed between a stationary external cylinder and an internal cylinder rotating with a “pre-set” rotational speed. Knowing the diameter of the external cylinder and selecting an appropriate diameter of the internal cylinder, and thus fixing the thickness of the layer of the lubricant composition being tested between these cylinders, the average gradients of shear rate for this composition were determined. In the tests, two values of shear rate gradients were adopted, namely (the gradient is marked by “$D$”): $D = 0.05 \text{ s}^{-1}$, and $48.6 \text{ s}^{-1}$. The value $D = 0.05 \text{ s}^{-1}$ was adopted because, as it results from tests carried out earlier, at this value, the lubricant is sheared only in the boundary layer [L. 2, 4, 5]. As previous studies on greases without fillers have demonstrated, this layer has different rheological properties than layers situated further away from the wall. Therefore, tests on greases with the addition of fillers located near the wall were carried out, all the more so because such values of shear rate gradients occur during starting central lubrication systems; whereas, measurements at $D = 48.6 \text{ s}^{-1}$ were carried out because greases in lubricating systems flow with such intensity. Tests presented in the paper were carried out at $25^\circ\text{C}$.

The results of studies on the relationship between the shear stress and the shear rate gradient of lithium grease without fillers and compositions of this grease with graphite, MoS$_2$, and PTFE powders are presented in the figures below (from Fig. 2 to Fig. 14).

As can be seen from the course of the curve presented in Fig. 2, at a very small gradient of the shear rate, the shear stress is small, because the flow takes place only in the boundary layer. In this layer, the structure of lithium lubricant is thinned as a result of the deposition of active particles of the thickener on the wall. Therefore, the maximum shear stress during the measurements had a small value of about 250 Pa (this very small value was also caused by the very small gradient of shear rate). Afterwards, a slow decrease of this stress to the value of 130-140 Pa occurred after 316 minutes of shearing. During the shearing of the layer of grease (thinned at the wall), the remaining bonds between individual sets

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**Fig. 1.** The measuring head of the rheometer Rheotest 2.1: 1 – internal cylinder, 2 – external cylinder, 3 – clutch, 4 – thermometer, 5 – drive shaft, 6 – lubricant being tested, 7 – thermostatic agent [L. 6]


**Fig. 2.** Change in the shear stress during the shearing of lithium grease without fillers in a rotary rheometer, at the shear rate gradient $D = 0.05 \text{ s}^{-1}$

**Rys. 2.** Zmiana naprężenia stycznego podczas ścinania w reometrze rotacyjnym smaru litowego bez wypełniaczy przy gradiencie prędkości ścinania $D = 0.05 \text{ s}^{-1}$

**Fig. 3.** Change in the shear stress during the shearing of lithium grease without fillers in a rotary rheometer, at the shear rate gradient $D = 48.6 \text{ s}^{-1}$

**Rys. 3.** Zmiana naprężenia stycznego podczas ścinania w reometrze rotacyjnym smaru litowego bez wypełniaczy przy gradiencie prędkości ścinania $D = 48.6 \text{ s}^{-1}$
of thickener particles are destroyed, which results in the decrease in the value of structural viscosity and the shear stress in this area. In relation to the value of initial stress, this is almost a two-fold drop, which proves that, after 316 minutes of shearing, the initial structure of the grease layer changed significantly. The curve depicting the course of this process indicates its mild progress, because, in the structure of grease in this area, there are no strong bonds between individual sets of particles of lithium soap, and if they still exist, they are rare, whereas loose sets of particles of this thickener prevail, suspended in the base oil.

The course of the curve depicting the changes in the shear stress in the lubricant sheared with greater intensity, namely at $D = 48.6 \, \text{s}^{-1}$, looks slightly different. Fig. 3 shows, for the same grease, the relationship between the shear stress and the time of shearing with the intensity mentioned above. The maximum value of stress at the beginning of the shearing, reaching approximately 950 Pa, fell after 330 minutes to approximately 700 Pa, i.e. by approx. 24%. This decrease is noticeably smaller than in the previous case. However, it should be remembered that here the flow also took place in layers located further away from the wall, where the concentration of the thickener was significantly greater. Here, the decrease in the shear stress during the first 15 minutes was quite large, because, within this time, fairly significant destruction of bonds occurred in the space network of the thickener, and reconstruction of its structure by newly created bonds was insignificant. Over time, the process of destruction in the structure “weakened” and more and more frequent cases of new bonds appeared in the structure as a result of the thixotropic phenomena occurring in this lubricant.

Fig. 4. Change in the shear stress during the shearing of lithium grease with the addition of 1% of graphite filler powder in a rotary rheometer, at the shear rate gradient $D = 0.05 \, \text{s}^{-1}$

Rys. 4. Zmiana naprężenia stycznego podczas ścinania w re-ometrze rotaacyjnym smaru litowego z dodatkiem 1% wypełniacza grafitowego przy prędkości ścinania $D = 0.05 \, \text{s}^{-1}$

Figure 4 shows the course of the relationship between the shear stress and the shearing time for lubricating grease filled with 1% of graphite powder and sheared (similarly as in Fig. 2) in the boundary layer. Here the intensity of structural destruction was slightly different, because the shear stress value declined from 225 Pa at the beginning of the shearing to 175 Pa after 330 minutes. In this case, during the first almost one hundred minutes of shearing, the value of shear stress was almost unchanged. The shape of this curve indicates that, in the boundary layer, there was actually no spatial network of the thickener. The bonds appearing between the thickener particles in this layer are destroyed very quickly during its flow, and the flow takes place in the oil in which only sets of these particles are dispersed.

Figure 5 shows the course of the decline in the value of shear stress in the same lubricating grease composition (with 1% content of graphite powder) during shearing with intensity $D = 48.6 \, \text{s}^{-1}$. The shear stress in this composition fell from the initial value of approx. 930 Pa to 635 Pa after 330 minutes of shearing. The course of the curve is similar to the curve in Fig. 3 showing the decrease in the shear stress with the passage of shearing time in the grease without graphite filler.

Fig. 5. Change in the shear stress during the shearing of lithium grease with the addition of 1% of graphite filler powder in a rotary rheometer, at the shear rate gradient: $D = 48.6 \, \text{s}^{-1}$

Rys. 5. Zmiana naprężenia stycznego podczas ścinania w re-ometrze rotaacyjnym smaru litowego z dodatkiem 15% wypełniacza grafitowego przy prędkości ścinania $D = 48.6 \, \text{s}^{-1}$

The difference is only in these values of this stress, which turned out to be slightly smaller compared to the corresponding values relating to the grease without filler. One per cent of graphite powder introduced into the lubricant did not cause a significant decrease in the value of shear stress in the lubricant composition. A significant decrease in the shear stress was found after the introduction of 15% of graphite powder into this grease. The course of the decline in the value of shear stress for this composition is shown in Fig. 6. As can be seen from the course of the curve in this drawing, the value of shear stress of approx. 780 Pa at the beginning fell after 330 minutes to approx. 500 Pa. Compared to the corresponding values for compositions containing 1% of graphite, these values are approx. 150 Pa lower. Thus, the graphite filler powder weakened the structure
of the composition so that its viscosity declined by about 20%. When analysing the course of this curve, one can divide it into four stages, namely: the destruction of the structure, some stabilisation resulting from the partial reconstruction of broken bonds in the thickener (the phenomenon of thixotropy), again increased destruction, and subsequent stabilisation.

D = 0.05 s\(^{-1}\). The shearing took place in the boundary layer; whereas, the values of stresses at the beginning and after 330 minutes of shearing were slightly smaller than in the corresponding compositions of this lubricant with 1% of graphite powder. Moreover, the course of the decline in these values with the passage of shearing time was steady and similar to the course of the decline in the stress as observed in the case of grease without filler.

The course of the shear stress during the shearing of this composition at a more intense shearing, i.e. at the gradient D = 48.6 s\(^{-1}\) was less steady. It is shown in Fig. 8.

Similarly as in the case of graphite filler, MoS\(_2\) powder filler introduced into the lithium grease also influences the rheological properties of the resulting lubricant composition; however, the extent of the influence depends on the percentage of this filler. Fig. 7 shows the change in the shear stress value in the composition of lithium lubricant with the one-percent content of MoS\(_2\) powder during the shearing of this composition with a very small gradient of shear rate:

Values of shear stress at the beginning of shearing were slightly lower (approx. 880 Pa), and after 330 minutes of shearing, they were the same as in the case of compositions with graphite filler. The course of the curve describing the changes in the structure of this composition during shearing is quite diversified. In the beginning, during the first 36 minutes, there was a fairly rapid breakdown of the structure, which resulted in a fairly intense decline in the shear stress value to around 700 Pa. In the next stage, until about 110 minutes, a change occurred and, apart from the process of structural decay, the bonds of previously ruptured elements of the structure appeared (due to the phenomenon of thixotropy), i.e. besides the degradation, there was also a reconstruction of this structure. Then a (less intense) process of degradation and stabilisation appeared.

With the increase in the content of MoS\(_2\) powder in the composition with lithium grease, the structural viscosity was decreasing, and the curve of the structural breakdown was stabilising. This can be clearly seen in Fig. 9, where, during the shearing of the composition of lithium-based grease with a fifteen-percent content of MoS\(_2\) powder within the first 50 minutes, a (relatively steady) breakdown of the composition occurred, and then
for the remaining time up to the 330 minute the value of shear stress was stable. Thus, the process of structural decay in this lubricant composition was balanced by the process of its reconstruction, which means that, in this case, the stabilising role of the MoS$_2$ filler should be emphasised. After the introduction of the MoS$_2$ powder as a filler, the shear stress value in the resulting lubricant composition was about 20% lower than the shear stress value in the identical composition, but with graphite filler. The value of stress after stabilisation was, similarly as in the case of graphite, about 520 Pa. It means that, in the case of MoS$_2$ powder, the stabilisation of stresses in the flowing lubricant composition takes place faster than in the case of graphite and the course of the curve of changes in the shear stress is also more stable.

A similarly stabilising effect on the course of shear stresses during the flow of the lithium lubricant composition is achieved by using PTFE powder as a filler; however, it applies only to small amounts of this filler. The results of tests with a small, only one-percent share of PTFE powder filler, are presented below. The decrease in shear stresses after using PTFE was not as significant as in the case of MoS$_2$ powder, but the structure degradation process in the case of this filler also runs in a stabilised manner. This applies both to the boundary layer (at the gradient of shear rate $D = 0.05$ s$^{-1}$) as well as layers more distant from the wall (at $D = 48.6$ s$^{-1}$). This is shown by means of the graphs presented in Figures 10, 11 and 12. Figure 10 shows the decline in the shear stress over the time of shearing in the composition of lithium grease with PTFE powder (1%) at the shear rate gradient $D = 0.05$ s$^{-1}$, and thus at the flow in the boundary layer.

The course of the curve in this figure is similar to the course of the curve shown in Fig. 7, concerning the flow of the same lubricant composition with the addition of 1% of MoS$_2$ powder. The difference is only in the value of stress, which, in the case of PTFE filler, was about 8% lower. Presumably, this slightly lower value of stress was caused by the addition of PTFE, a material characterised by very low surface energy, which weakened the interaction forces between the grease composition and the wall material. It is visible in the analyses of the stress value in this grease composition with a 15% addition of PTFE (Fig. 11).

![Fig. 10. Change in the shear stress during the shearing of lithium grease with the addition of 1% PTFE filler in a rotary rheometer at the shear rate gradient: $D = 0.05$ s$^{-1}$](image)

Here, even an increase in the shear stress value was observed over a period of about 70 minutes. It can be assumed that, at a high concentration of PTFE powder, in the boundary layer, or actually on the surface of the steel wall, the PTFE fraction initially “slipped” on the wall and afterwards the flow occurred in the boundary layer. PTFE is a substance with very low surface energy, which means that its impact on the steel surface is small, and thus the increase in the shear stress in the boundary layer is slow. It seems that this can explain the properties of the lithium grease composition with a greater amount of PTFE.

Moreover, at a greater gradient of the shear rate, the lithium grease composition with a higher (15%) content of PTFE filler shows lower shear stresses than with a smaller (1%) content of this filler. It can be observed by analysing the curves in Figures 12 and 13. At a lower percentage of PTFE powder, the value of shear stress during the flow of this composition is higher; whereas, at the beginning of the flow, this value was about 780 Pa, and after 40 minutes of shearing in the rheometer, it fell to about 620 Pa. During the remaining nearly 300 minutes of shearing, the value of this stress remained at the same level. The curve in Fig. 13 shows the course of the shear stress value in the composition of the same lithium grease with a 15% share of PTFE filler.
The addition of 15 per cent of PTFE powder should (through its "mass") "thicken" the structure of lithium grease; whereas, the introduction of a larger amount of PTFE powder with very low surface energy caused the "weakening" of this structure. This was revealed by smaller values of shear stress during the shearing of the resulting lubricant composition. The value of this stress at the beginning of shearing in the rheometer was slightly above 700 Pa, and after 330 minutes, it fell to about 500 Pa.

Figure 14 shows, for comparison, the course of changes in the shear stress in the composition of lithium grease with MoS$_2$ filler at concentrations of this filler amounting to 1% and 15%. In the figure, the "upper" curves refer to the concentration 1%, and the "lower" curves refer to the concentration of 15%. As can be seen in Figure 14a, at a very small gradient of shear rate $D = 0.05$ s$^{-1}$, and thus during the flow of the lubricant composition, the shear stress in the boundary layer of this composition containing 15% of MoS$_2$ is lower by about 35% than the corresponding stress with 1% share of MoS$_2$. When the gradient increases to $D = 48.6$ s$^{-1}$, this difference declines to approximately 20%. The nature of the differentiation of shear stress values at different shear rate gradients, i.e. the shearing of lubricating compositions at different distances from the wall, indicates various mechanisms which cause this state of stresses. Molybdenum disulphide, which is part of the lubricant composition in the film situated...
close to the metal wall, is presumably due to its surface activity, attracted to this metal wall, and entering in its predominant part besides lithium soap into the composition of the surface layer. Lithium soap, being also a polar substance and depositing on the surface, also enhances this MoS₂ deposition process.

As a result, the composition layer near this layer undergoes a significant thinning, i.e. the so-called “thinned layer” is being created. Consequently, next to the surface layer thus formed, the lubricant composition layers, situated further away and located in the thinned layer, relocate easier. With the rise in the value of the shear rate gradient, the lubricant composition flows in layers situated further away and at the shear rate gradient $D = 48.6 \text{ s}^{-1}$ the difference in values of shear is about 20% (Fig. 14b). The latter difference results from the fact that, as other tests have shown, the MoS₂ filler, being surface-active, weakens the structural bonds of the lithium thickener and thereby the value of structural viscosity in the lubricant composition declines.

Smaller differences occur during the shearing of lithium grease composition containing PTFE powder. The results of tests of this composition show that, at the gradient of shear rate $D = 0.05 \text{ s}^{-1}$, these differences are around 20%, and, at a higher gradient of shear rate $D = 48.6 \text{ s}^{-1}$, the difference declined but remained at the level of a dozen or so percent. In the author’s opinion, the mechanism of slippage at the wall of a lubricating composition containing PTFE is a consequence of the very low surface energy of this filler. As a result, the PTFE powder does not deposit on the metal surface, and the composition containing PTFE “slides” on this surface.

**SUMMARY**

The results of tests presented in the paper, being a continuation of previously published papers [L. 3,6], prove that the type of filler introduced into grease and aimed at improving its tribological properties also has a significant impact on rheological properties of the resulting composition. The grease thickened with polar lithium soap displays, depending on the amount of this thickener, certain values of structural viscosity and shear stresses corresponding to the viscosity. As the previously published studies have shown, the introduction of a filler in the form of graphite, MoS₂, or PTFE powder caused a decrease in the shear stress value during the flow of the resulting lubricant composition; however, these values declined with the rise in the percentage share of the filler.

Test results presented in Figures 2 to 13 have shown that the type of filler introduced into the lithium grease has a significant impact on rheological properties of a resulting composition. These results show that all fillers, especially graphite and molybdenum disulphide, primarily change the rheological properties of their composition with lithium grease. It applies both to the boundary layer of this composition as well as the layers more distant from the metal wall. In all of these cases, both graphite and molybdenum disulphide cause that values of shear stresses in these compositions significantly decline in comparison with pure grease. The decline in the values of these stresses is the greatest at the beginning of shearing but still lasts (generally at a lower level) during shearing.

**Figure 14** shows (as an example) a comparison of the decline in the value of shear stress over the time of shearing in the lithium grease composition with MoS₂ powder. The difference is visible between the stresses in the boundary layer and layers more distant from the steel wall. The difference in the boundary layer at the beginning of shearing was about 35%, and, after 330 minutes of shearing, it fell to about 20%. In the case of shearing the layers more distant from the wall (at the gradient of a shear rate equal to $48.6 \text{ s}^{-1}$), the difference at the beginning of shearing was about 20%, and after 330 minutes it fell by several per cent.

In the case of graphite filler, the course of the curves was similar, but differences in values of shear stresses were smaller. This is shown in Figures 5 and 6.

Smaller decline and differences in values of shear stresses occurred in the composition of lithium grease with PTFE, where these stresses in the boundary layer are not as small as in the case of graphite or MoS₂. Also, during the shearing of the composition at a higher value of gradient ($D = 48.6 \text{ s}^{-1}$) the differences in values of shear stresses were smaller.

Results of these tests are of crucial importance in assessing the flow resistances of individual compositions in automated central lubrication systems and may be helpful when selecting a suitable lubricant composition for a specific pump and other components while designing such a system.

In the author’s opinion, it might be interesting to study rheological properties of grease compositions with fillers in the form of nanostructures. Interesting studies on tribological properties of such compositions are presented in the latest publications, examples of which are indicated below in the list of literature. It would also be advisable to do research into rheological properties of these compositions.
REFERENCES