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THE INFLUENCE OF TEMPERATURE ON THE RHEOLOGICAL PROPERTIES OF FIBROUS LUBRICATING COMPOUNDS WITH SELECTED SOLID ADDITIVES

WPŁYW TEMPERATURY NA WŁAŚCIWOŚCI REOLOGICZNE KOMPOZYCJI SMAROWEJ O STRUKTURZE WŁÓKNISTEJ ZAGĘSZCZACZA Z WYBRANYMI SMARAMI STAŁYMI

Key words: grease, solid grease, graphite, molybdenum disulphide, PTFE, copper, rheological properties, yield stress, cohesion energy.

Abstract The study evaluated the effect of temperature on the values of yield stress and cohesion energy of lubricating compounds thickened with calcium 12-hydroxystearate, prepared on the basis of mineral oil. Lubricating compounds without additives and with selected solid additives in the form of copper particles, graphite, molybdenum disulphide, and polytetrafluoroethylene were analysed. A rotational rheometer working with a plate-plate geometry was used for rheological studies. The influence of temperature on the rheological properties of lubricating compounds with additives was observed. Solid additives caused significant changes in the structure of the soap thickener, especially at negative temperatures.

Słowa kluczowe: smar plastyczny, smar stały, grafit, dwusiarczek molibdenu, PTFE, miedź, właściwości reologiczne, granica płynięcia, energia kohezji.

Streszczenie W pracy oceniono wpływ temperatury na wartości naprężenia stycznego granicznego i energii kohezji kompozycji smarowych zagęszczanych 12-hydroksystearynianem wapnia, wytworzonych na bazie oleju mineralnego. Analizie poddano kompozycje smarowe bez dodatków oraz z wybranymi dodatkami stałymi w postaci cząstek miedzi, grafitu, dwusiarczku molibdenu oraz politetrafluoroetylenu. Wyniki badań wskazały istotny wpływ temperatury i dodatków na właściwości reologiczne kompozycji smarowych.

INTRODUCTION

Greases are rheologically complex, two-phase fluids. These are polydisperse systems, chemically and physically heterogeneous **[L. 1]**. The dispersion phase in greases is the base oil (usually mineral, less frequently synthetic or plant), while the dispersed phase is the thickener and, depending on the needs, refining additives, including solid additives. The most common solid additives are those with a layer structure, mainly graphite and molybdenum disulphide. Polymers as well as soft metals, including tin and copper, are also popular **[L. 2]**. Soft metals show the ability to plate the collaborating surfaces of friction junctions. The main purpose of using solid additives is to extend the operation parameters (pressure, slip speed, temperature), which ensure the sliding node operation at normal friction with simultaneous minimization of friction and wear **[L. 3]**. The mass fraction of solid additives in greases is usually less than 5%. Compounds of greases with solid additives are, in most cases (according to Wo. Ostwald's division), systems subjected to mechanical grinding or phase colloids, and this division depends strictly on the instantaneous state of the thickener structure. Rheological properties of greases, including the ability to flow as a result of external forces, significantly influence their behaviour in rolling bearings. They determine, among others, the creation of permanent lubricating reservoirs in the bearing clearances, as well as the maintenance of the lubricating film between the rolling elements and the bearing race **[L. 4]**. The resistance of greases to delamination during their intensive exploitation, as well as to the separation of base oil from the thickener grid depend, among others, on the density of cohesion

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energy of these greases **[L. 5]**. Rheological properties, including, in particular, the yield stress of greases, also determine the starting torque of lubricated rolling and sliding bearings, especially of large sizes. It is essential to know these properties at low operating temperatures of lubricants. Improper selection of greases with respect to rheological properties may, in extreme cases, result in damage to the lubricated bearing **[L. 6]**. The yield stress of greases also determines their flow resistance through the structural elements of machine lubrication systems **[L. 7, 8]**. The aim of this study was to evaluate the influence of temperature on selected rheological properties of a fibrous lubricating compound with copper, graphite, molybdenum disulphide, and polytetrafluoroethylene additives. Particular attention will be paid to the analysis of structural changes in the thickener caused by solid additives.

TESTED MATERIAL

The tests were carried out on lubricating compounds with a fibrous structure (hereinafter referred to as Ca12HS) without solid additives and with solid additives. The thickener in the lubricating compounds was a complex calcium soap, i.e. calcium 12-hydroxystearate whose percentage by weight is 11%. Mineral oil with a kinematic viscosity of 36–59 mm²/s at 50ºC with a package of AW and EP additives was the dispersion phase. The basic properties of the grease, being the basis for all the lubricating compounds used in the tests, are presented in **Table 1**.

Table 1. Characteristics of the grease, which is the base for all lubricating compounds used in the tests

Tabela 1. Charakterystyka smaru plastycznego stanowiącego bazę dla wszystkich kompozycji smarowych użytych do badań

Dropping point, ºC ≥	80
Penetration number (acc. to NLGI)	300–350
Free base content, % NaOH ≤	0.2
Free organic acid content	does not contain
Solid foreign matter content, % ≤	0.5
Water content, % ≤	2.5

The solid additives used as the dispersed phase in the lubricating compounds were copper particles of a medium granulation size of 63 µm, graphite of a granulation size of 20 to 200 µm, molybdenum disulphide (MoS_2) of a granulation size of 2 to 25 µm and polytetrafluoroethylene (PTFE) of a granulation size of 20 to 40 µm. Copper powder was obtained by cathodic deposition of aqueous solutions of copper sulphate in the electrolysis process. The powder grain structure was dendritic. PTFE powder is a suspension Tarflen with a density of 2.185 g/cm³, produced by the Polskie Zakłady Azotowe (Polish Nitrogen Works) in Tarnów. The percentage by weight of solid additives in the lubricating compounds for all samples was equal and amounted to 5%. Lubricating compounds used in the tests were prepared in such a way that a weighed portion of solid additives was added to the base grease and the whole was homogenized for 30 minutes. The base grease without solid additives was also intensively mixed to obtain a similar degree of fineness of the thickener fibres. Mixtures of lubricating compounds with solid additives were prepared in the laboratory of the Department of Fundamentals of Machine Design and Tribology of the Wrocław University of Science and Technology.

TEST METHOD

Rheological properties of lubricating compounds were investigated using a Physica Anton-Paar MCR rotational rheometer with a torque range from 0.1 µNm to 150 mNm. The rheometer was equipped with an air bearing and connected to an oil-free reciprocating compressor with a set of filters and air dryers. During the tests, the rheometer worked with a plate-plate geometry at a constant height of the measurement gap of 1 mm. The accuracy of the measurement gap height setting was ±0.001 mm. The rheometer also included a Peltier P-PTD200 thermostatic system and a H-PTD200 insulating and thermostatic flange with air circulation inside the measuring head. A measuring spindle in the form of a sanded 316L steel plate with a diameter of 40 mm was used. The use of a sandblasted plate with a roughness Ra = 2 µm was aimed at limiting the slip of lubricating compounds. The diagram of the measuring head of the rheometer is shown in **Fig. 1**.

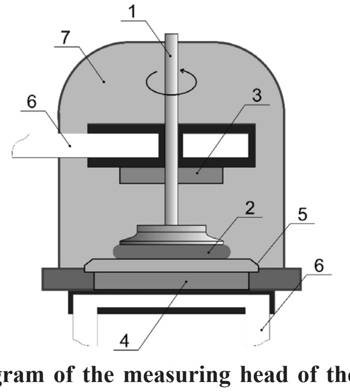

Fig. 1. Diagram of the measuring head of the rotational rheometer used in the tests: 1 – measuring spindle(with sanded top plate of diameter 40 mm); 2 – lubricating compound; 3, 4 – Peltier module (P-PTD200); 5 – bottom plate; 6 – cooling system; 7 – insulating and thermostatic flange (H-PTD200)

Rys. 1. Schemat głowicy pomiarowej reometru rotacyjnego użytego do badań: 1 – wrzeciono pomiarowe (z płytką górną piaskowaną o średnicy 40 mm); 2 – kompozycja smarowa; 3, 4 – moduł Peltiera (P-PTD200); 5 – płytka dolna; 6 – układ chłodzenia; 7 – kołnierz izolująco-termostatujący (H-PTD200)

Samples of lubricating compounds were temperature controlled in the rheometer head at a constant temperature of -20, -10, 0, 20, and 60ºC (with an accuracy of ±0.01ºC). Each sample was cooled/heated for 5 minutes (after the desired temperature had stabilised). After this time, the measurement automatically took place. In order to avoid temperature changes and to obtain a higher precision, an insulating and thermostating flange was used during the measurement to control and monitor the temperature of the samples. The RHEOPLUS/32 program (version 3.4) was used to acquire the measurement data. The tests were repeated five times and bilateral confidence intervals were determined at the confidence level of 0.95. In order to examine the normality of individual distributions, a non-parametric Shapiro-Wilk test was performed.

The influence of solid additives on yield stresses in fibrous lubricating compounds was evaluated using two independent rheological tests. During the first test, the flow curves of lubricating compounds in the range of shear rate from 0 to 50 s^{-1} were determined within temperature range under examination and described by the Casson equation (1):

$$\tau^{\frac{1}{p}} = \tau_0^{\frac{1}{p}} + \left(\eta_\infty \cdot \dot{\gamma}\right)^{\frac{1}{p}} \tag{1}$$

where τ – shear stress [Pa], τ_0 – yield stress [Pa], $\dot{\gamma}$ – shear rate [s^{-1}], η_∞ – limiting viscosity, i.e. viscosity at a very high shear rate [Pa · s], p – power exponent [-].

Thanks to the flow curves, rheological parameters of the Casson equation were determined, including the value of yield stress τ_0 of the tested lubricating compounds. In the second test, the oscillation method was used to determine the yield stress. During the tests, changes in storage modulus G' and loss modulus G'' were analysed as a function of the strain of the grease, at a constant oscillation frequency f = 1 Hz. Storage modulus G' represented the ability of the lubricant to store energy, while the loss modulus G'' the ability to dissipate energy. A material's ability to dissipate energy (damping) is tantamount to the ratio of loss modulus to storage modulus, called the damping factor. It is equal to the tangent of the phase shift angle δ. When the value of tan δ = 1, grease starts to flow. The value of shear stress recorded at the point at which $G' = G''$ is equal to the value of the yield stress. This method is currently one of the most accurate rheological methods for determining the yield stress of greases. The results obtained with this method are reliable and reproducible. It is the least sensitive to grease slip near the measuring plate of the rheometer, as well as to its roughness and material **[L. 9]**.

The next step was to evaluate the cohesion energy of lubricating compounds. Changes in cohesion energy E_{coh} (J/m³) have been determined on the basis of the critical strain value γ_c and the storage modulus G'_{LVR} at a critical point:

$$E_{coh} = \int_0^{\gamma_c} \gamma_c \cdot G'_{LVR} d\gamma = \frac{1}{2}\gamma_c^{\,2} \cdot G'_{LVR} \tag{2}$$

Values γ_c and G'_{LVR} were the upper limit of linear viscoelasticity (LVR) of the grease. The LVR upper limit is the amplitude of the strain γ in the range from 10-2 to 102%, for which the deviation of the storage modulus values G' from its maximum value is 5% **[L. 10]**. The cohesion energy density is used for quantitative evaluation of the degree and strength of flocculation of phase particles dispersed in the heterogeneous system. It is a measure of the sum of all physicochemical interactions between these particles. The higher the value of cohesion energy, the more cross-linked is the microstructure **[L. 11]**.

RESULTS

Figure 2 shows exemplary curves of shear stress change as a function of shear rate, obtained experimentally together with model curves for lubricating compound with Cu63 shear in the temperature range from -20 to 60°C. The highest values of yield stress were recorded at temperatures below 0°C and the lowest at a temperature of 60°C, mainly due to a decrease in the viscosity of the base oil. This tendency was observed in all of the tested lubricating compounds with additives, and the shape of the flow curves for individual compounds was very similar.

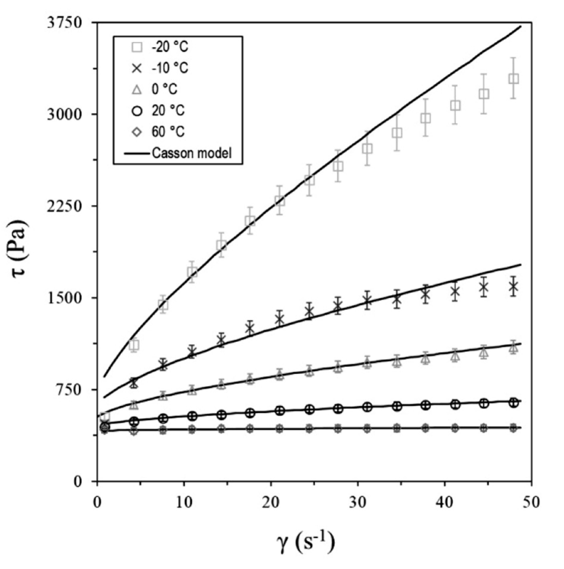

Fig. 2. Changes in shear stress as a function of the shear rate for fibrous grease with Cu63 obtained at different temperatures

Rys. 2. Zmiany naprężenia stycznego w funkcji gradientu prędkości ścinania dla smaru o strukturze włóknistej z dodatkiem Cu63 uzyskane w dla różnych wartości temperatury

Significant differences were noted, however, when comparing the values of yield stress determined from the Casson model for all the tested lubricating compounds with additives as a function of temperature of these compounds, as shown in **Fig. 3**. The results obtained indicate a significant influence of solid additives. Particularly large differences between the individual greases can be observed at -20°C. For soap grease without additives, the yield stress at this temperature was 1018 Pa, and for the grease with Cu63, this value was 487 Pa, i.e. more than half as much. The addition of copper powder causes significant changes in the fibrous structure of the thickener. It should also be emphasized that the addition of Cu63 caused a decrease in the yield stress value in the whole accepted temperature range. The lowest influence on the value of yield stress at temperatures below 0°C was observed for polytetrafluoroethylene and graphite. It is also interesting that, for higher temperatures, soap greases with PTFE and graphite showed slightly higher yield stress values compared to greases without additives.

In order to confirm the results of tests obtained under shear conditions of lubricating compounds with variable shear rate, a dynamic-oscillatory test was additionally carried out. **Fig. 4** shows examples of the curves obtained during these tests, showing changes in the values of the storage and loss moduli and the damping factor. The values of shear stress at the point of intersection of the curves G' and G'', which is the yield stress of the tested lubricating compound, were read on the basis of the curves. The shape of the curves obtained for other greases was similar.

Independent dynamic-oscillatory tests also confirm significant differences in yield stress values for lubricating compounds with solid additives **(Fig. 5)**. Again, the greatest differences could be observed for monitored greases at temperatures below 0°C. The highest value of the yield stress was recorded for soap grease without solid additives and amounted to 794 Pa, the lowest value for the grease with copper powder,

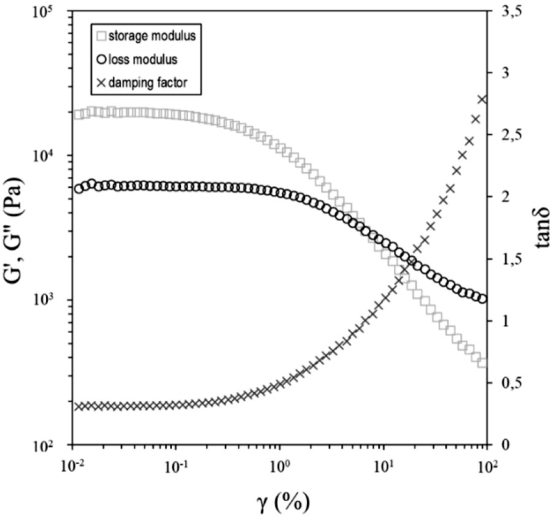

Fig. 4. Changes in storage and loss moduli as a function of strain for fibrous grease with Cu63 obtained at -20°C

Rys. 4. Zmiany modułów zachowawczego oraz stratności w funkcji odkształcenia dla smaru o strukturze włóknistej z dodatkiem Cu63 uzyskane w temperaturze -20°C

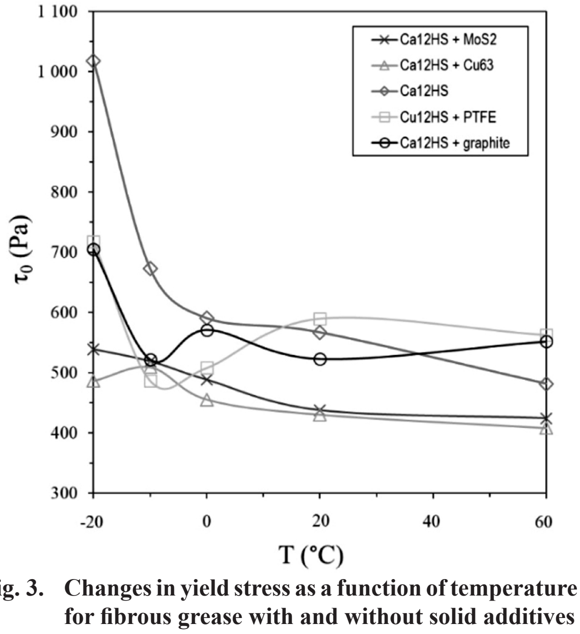

Fig. 3. Changes in yield stress as a function of temperature for fibrous grease with and without solid additives

Rys. 3. Zmiany naprężenia stycznego granicznego w funkcji temperatury dla smaru o strukturze włóknistej z dodatkami w postaci smarów stałych i bez dodatków

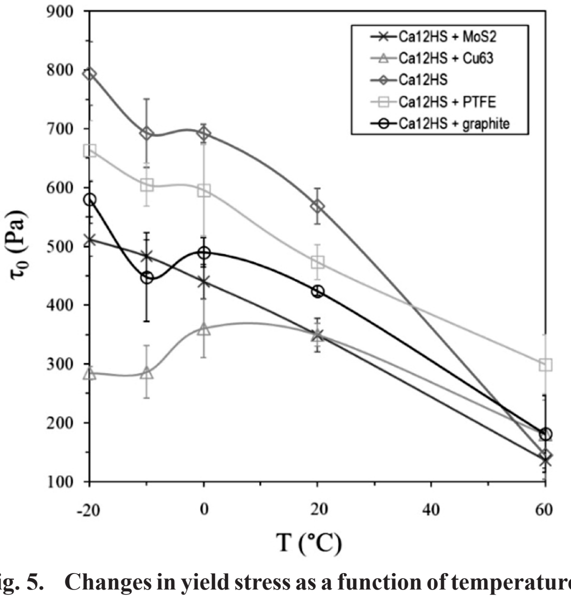

Fig. 5. Changes in yield stress as a function of temperature for fibrous grease with and without solid additives

Rys. 5. Zmiany naprężenia stycznego granicznego w funkcji temperatury dla smaru o strukturze włóknistej z dodatkami w postaci smarów stałych i bez dodatków i.e. 285 Pa. As with the rheological tests conducted at a variable shear rate, the low values of yield stress were recorded for greases with the popular additive of molybdenum disulphide. The lowest effect on the value of yield stress of the lubricating compound had powdered polytetrafluoroethylene. This is most likely due to the fact that PTFE has the lowest surface energy among all the solid additives tested. The value of this energy is almost half as much as the surface energy of graphite, molybdenum disulphide, and copper. The addition of PTFE did not, therefore, cause any significant weakening of the physicochemical interactions between the soap floccules in comparison with the other solid additives.

In order to evaluate the influence of solid additives on structural changes of fibrous thickener in the lubricating compound, the cohesion energy of these compounds was determined. The studies showed a significant influence of the additive of powdered copper on the weakening of physicochemical interactions between soap particles. At a temperature of -20°C, the cohesion energy of the lubricating compound without additives was 805 mJ/m^3. The addition of powdered copper caused the reduction of this energy to the value of 294 mJ/m^3. Polytetrafluoroethylene, in turn, significantly increased the cohesion energy of lubricating compounds. Particularly significant differences in comparison to the grease without additives can be observed at 60°C. For example, the cohesion energy of the grease with PTFE in this case was 558 mJ/m^3 and that of the grease without additives was 280 mJ/m^3.

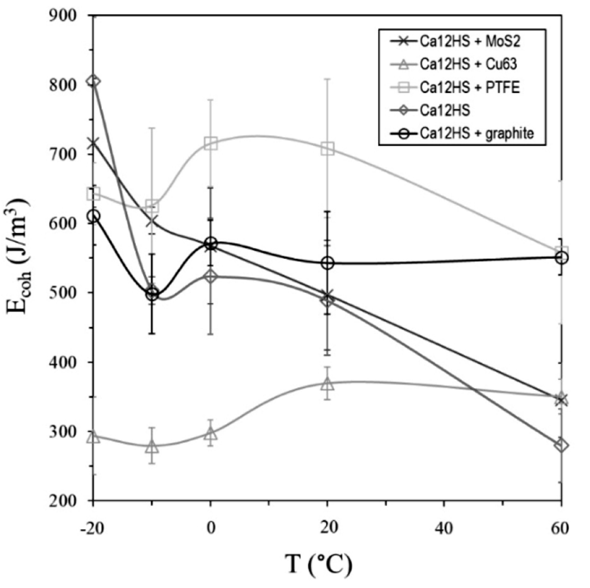

Fig. 6. Changes in cohesion energy as a function of temperature for fibrous grease with and without solid additives

Rys. 6. Zmiany energii kohezji w funkcji temperatury dla smaru o strukturze włóknistej z dodatkami w postaci smarów stałych i bez dodatków

SUMMARY

The results of tests of greases thickened with calcium 12-hydroxystearate without and with solid additives indicate a significant influence of the latter on the value of yield stress and cohesion energy of lubricating compounds. There is a strong correlation between changes in the yield stress and the weakening or strengthening of physicochemical interactions between soap particles in the grease. The addition of powdered copper caused the greatest decrease in the value of yield stress among all the tested lubricating compounds. Particularly large differences in rheological properties between the lubricating compounds could be observed at negative temperatures. In order to clarify these differences, further studies into the microstructure of greases, including spectroscopic studies, are necessary.

The practical aspect of the work is the possibility of qualitative assessment of the influence of solid additives on the flow resistance of greases thickened with metal soaps in structural elements of central lubrication systems of machines, as well as energy losses resulting from the start-up of lubricated friction junctions. This is particularly true for large-sized bearings operating at high thermal amplitudes.

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