

<https://doi.org/10.30678/ftj.84884>

© 2020 The Author

Open access (CC BY 4.0)

## The tribological properties of lubricating greases produced on vegetable base and modified of polytetrafluoroethylene

Rafał Kozdrach

Research Network Lukasiewicz – Institute for Sustainable Technologies, K. Pulaski 6/10, 26-600 Radom, Poland

rafal.kozdrach@itee.radom.pl, ORCID ID 0000-0001-7308-5496

### ABSTRACT

The article presents the results of research on the influence of polytetrafluoroethylene additive on the tribological and rheological properties of selected lubricant compositions.

Based on the obtained test results, it was found that the introduction of a modifying additive to the lubricant structure allows a significant reduction of the coefficient of friction, thus increasing the efficiency of tribological protection of the tribosystem.

All lubricating compositions modified with at least 1% polytetrafluoroethylene guarantee effective anti-wear protection under load conditions of the tribosystem. Modification of the tested lubricating compositions with the applied additive affects the increase of indicators characterizing the fatigue life of the examined lubricating greases based on sunflower oil. The introduction of the polytetrafluoroethylene into the structure of the tested lubricants changed the values of the MSD correlation function and the  $G'$  and  $G''$  modules, which significantly influenced the internal structure of the tested lubricant compositions.

**Keywords:** lubricating grease, modified additive, tribological properties, rolling contact fatigue, rheological properties, the correlation function MSD, the storage modulus  $G'$ , the loss modulus  $G''$

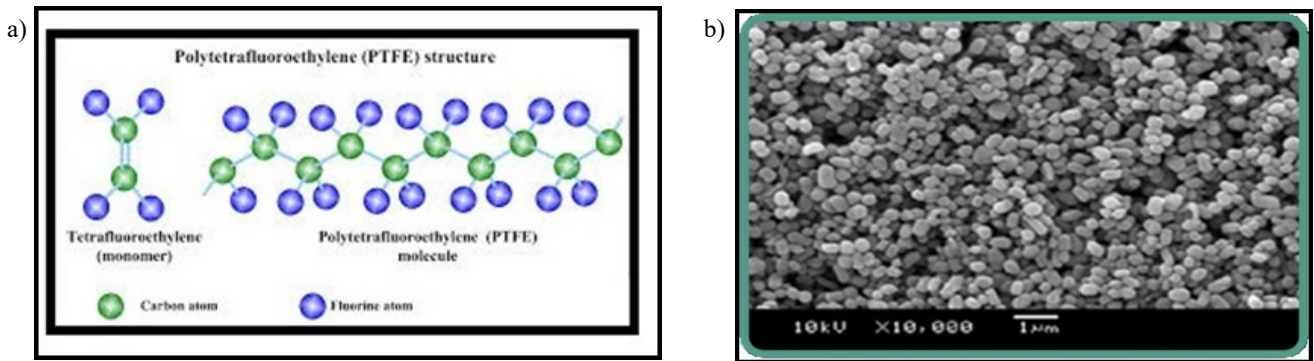
### Introduction

The properties of plastic greases depend on its composition and production technology and are shaped, among others, by appropriately selected refining additives [1-3].

Typical packages of additives improving plastic greases include, among others, antioxidants (increasing resistance to oxidation), anti-wear and anti-friction additives (improving tribological properties of the product) and anti-corrosion (reducing the aggressiveness of lubricants against metals), adhesives (improving adhesion of grease to machine components) and rheological (improving viscosity). Not only the presence of the additive decides about the usable properties of the lubricant, but also the way it is incorporated into the lubricating grease structure. Introduction of additives to lubricating greases causes many technological difficulties, because additive molecules adsorb on the surface of the thickener, which in consequence may lead to a reduction in the efficiency of such a component, and even to a decrease in the stability of the grease [2,4-5]. For lubricating greases, appropriate specially selected additives should be used in an amount that determines their improvement in performance. Lubricating greases mix very well with solid lubricating additives, which reduce the friction force and increase the resistance of the tribosystem to load and blurring. In difficult operating conditions, these

additives increase the efficiency of the lubricant due to resistance to chemical agents and better resistance to high temperatures. The most common thing among this type of additives are graphite, molybdenum disulphate, polytetrafluoroethylene, copper and chloroparaffins [5-7]. Nowadays, however, the aim is to make lubricants more and more environmentally friendly and at the same time not impair their lubricating properties. In connection with the increasing role of environmental protection, it is necessary to use means that do not contain heavy metals, halogens, sulphur or phosphorus [2,3,5]. Therefore, it was decided to use a polymer additive (PTFE), which is designed to improve the tribological and rheological properties of the lubricating compositions tested. The physicochemical properties of the applied additive allow to draw the thesis that the tribological and rheological properties of the tested compositions will improve after introducing the above-mentioned additive into the lubricant structure.

As a modifier of tribological and rheological properties of the lubricants tested, polytetrafluoroethylene was used (Fig.1.) [8,9]. Tarflen is a name used by the Nitrogen Plants in Tarnów-Mościce for polytetrafluoroethylene (PTFE), a fluorinated plastic with unique properties. It is used as an anti-corrosive and anti-adhesive material. It has a wide range of operating temperatures, is resistant to environ-



**Fig.1.** The chemical structure of modified additive: a) the chemical composition of polytetrafluoroethylene, b) SEM image of structure of polytetrafluoroethylene (magnification 10000x)

mental aging, physiologically inert, it has a low coefficient of friction and wear, therefore it is used in bearings and sliding coatings of machines used in the food industry [10,11]. Teflon is characterized by high heat resistance, low coefficient of friction, low mechanical strength and hardness, good dielectric and anti-adhesive properties, high resistance to chemical agents, is physiologically inert. PTFE is one of the most thermally resistant plastics (can work from -200 to +260°C). It is resistant to almost all elements and chemical compounds, it is not only resistant to alkali metals in the pure state, chlorine trifluoride and fluorine, it is not soluble in any solvent up to 300°C. Fluorine hydrocarbon compounds cause it to swell, and some fluorine oils above 300°C can dissolve PTFE to a certain extent. High-energy radiation can cause cracking of teflon's molecular chains, which is why its resistance to radiation is quite low. It is characterized by a low coefficient of friction (0,05-0,09) [8,11-13]. The static and kinetic friction coefficients are almost equal, therefore does not occur the stick-slip phenomenon, with increasing load. This parameters increases with increasing speed and don't depend on temperature.

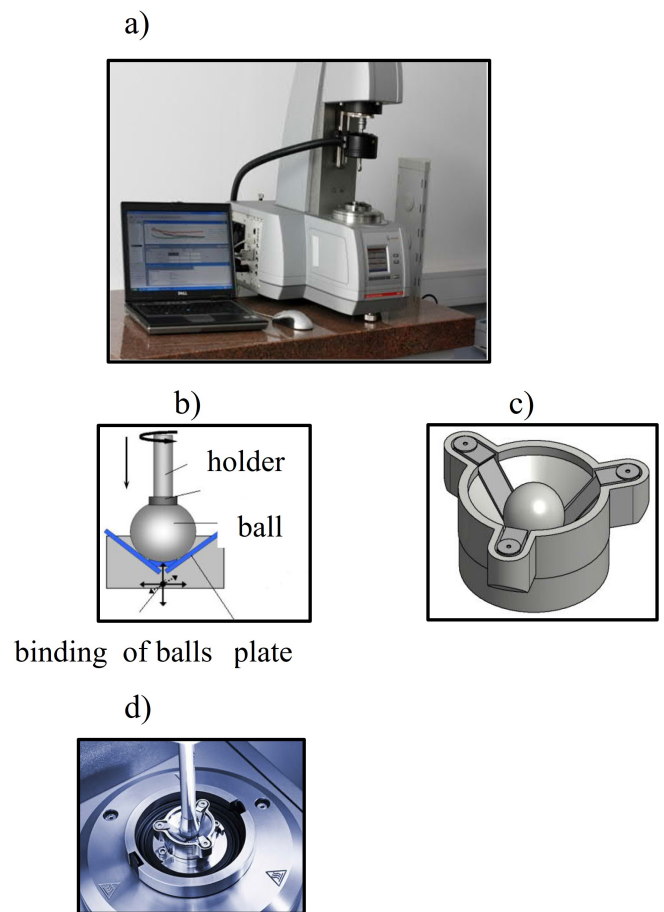
Molecular structure of PTFE makes its surface characterized by high anti-adhesiveness, it is also characterized by high wettability [9,11,14]. In order to improve the PTFE properties, fillers such as: glass fibre, carbon, bronze, graphite, molybdenum disulphate, metal powders, ceramics or metal oxides are added to it. Through the use of fillers, a significant increase in wear resistance, a reduction in thermal expansion coefficient, an increase in thermal and electrical conductivity, or a reduction in strain under load and an increase in creep resistance can be achieved. Teflon can be used in sealing elements, anti-corrosion and anti-adhesive coatings, elements of medical and chemical devices or in machine parts, e.g. in bearings [15-17].

The aim of the work was to examine the influence of different amounts of polytetrafluoroethylene on the change of tribological and rheological properties of lubricants based on plants and applicable in the food industry developed at the Research Network Lukasiewicz - Institute of Sustainable Technologies in Radom.

### Materials and methodology of studies

A group of model lubricating compositions was devel-

oped using non-toxic ingredients that are a dispersing and dispersed phase [18-20]. As a dispersing phase, vegetable oil (sunflower) with very good physicochemical properties was used. Lithium stearate was used as the dispersed phase. The lubricating compositions thus obtained were modified with 1%, 3% and 5% polytetrafluoroethylene. The following compositions were made of lubricants based on vegetable oil (sunflower): unmodified (A), modified 1% PTFE (B), 3% PTFE (C) and 5% PTFE (D). In the early phase



**Fig. 2.** The compact rotation rheometer MCR 102 (a) and the model of tribosystem (b,c,d)

of the experiment, research was carried out on the amount of the modifying additive that should be incorporated into the lubricating composition. Tests were carried out with compositions containing from 1 to 7% of a modifying additive. The lubricating compositions prepared in this way were subjected to tribological and rheological tests.

To determine the tribological (anti-wear) properties of the tested lubricating compositions, we used a compact MCR 102 rotational rheometer of the Anton Paar company with tribological seating T-PTD 200 (Fig.2.) with a concentric plate-ball contact point, in which three fixed cuboid steel plates were pressed with adequate force through a ball fixed in the spindle, rotating at the appropriate speed. The tribological device enables the execution of tests in the temperature range of  $-40\pm 200^{\circ}\text{C}$  [21-26]. The balls with a diameter of 12.7 mm and plates with dimensions of  $15 \times 5 \times 2$  mm were made of bearing steel LH 15 ( $R_a = 0,3 \mu\text{m}$ ; hardness 60-63 HRC). During the tests, immersion lubrication was used [21-23]. Tribological tests (measurement of wear limit -  $G_{oz}$ ) were carried out at the tribosystem at 39.24 N, rotational speed of 500 rpm, during 3600 s and temperature of  $20^{\circ}\text{C}$ . Before starting the tribological attachment, the plates were placed in the holder, pressed with springs, lubricant was introduced (approx.  $5 \text{ cm}^3$ ) and stabilized for 60 s at a set temperature. During the test, the friction force was recorded, which was automatically converted into a coefficient of friction at 36-second intervals. Three test runs were performed, and the final test results were averaged. The final result of the run was the value of 100 measurements registered during the test. The averaged results obtained during the tests were also given. For statistical processing of the results, the Q-Dixon test was used with a confidence level of 95%. After testing, the components of the tribosystem were dismantled, washed with n-hexane and dried.

The *limiting pressure (load) of wear* is a measure of the anti-wear properties of the lubricating compositions. The determination of this parameter consisted in calculating its value in accordance with the formula:  $G_{oz} = 0,52 \cdot P_n / d_{oz}^2$ , where  $P_n$  - load assigned of the tribosystem equal to 39.24 N, and  $d_{oz}$  - the diameter of the diathesis formed on the steel

plates used for the test.

The optical microscope was used to determine the size of the trace of wear of the surface of rectangular test plates. The obtained results were used to determine the value of  $G_{oz}$ , i.e. the evaluation of anti-wear properties of lubricating compositions subjected to tribological tests [27,28].

Fatigue wear test was carried out on the tribological T-03 tester (Fig.3) according to the IP 300/82 standard and consisted in determining the fatigue life of a rolling of tribosystem based on 24 test runs carried out at a constant friction load of 5886 N and a constant speed of 1450 rpm. The test elements were bearing balls made of 100Cr6 steel with a diameter of  $\frac{1}{2}$ " , surface roughness equal to 0.032 mm and hardness 60-65 HRC [29-32]. During the test, the measurement of vibrations of the tribosystem was carried out continuously, and the test was automatically interrupted after the node exceeded the permissible level of vibration caused by crushing the material on the upper ball. If the chipping occurred on one of the bottom balls, the run was discarded. The result of a single test run was the time expressed in minutes. The results obtained in individual runs have been ranked from the shortest to the longest. Each result was assigned a value that is a percentage probability of damage to balls [33-35].

In the Weibull coordinate system, in accordance with the procedure specified in the IP 300-82 standard, the dependence of the duration of the test run on the probability of damage was determined. The value of  $L_{10}$  and  $L_{50}$  was determined from the diagram, determining the durability of the tribosystem at 10% and 50% probability of tribosystem failure [29-30,36-37]. On the basis of obtained values of time to occurrence of pitting, the cumulative percentage of damage was calculated, expressed as:

$$\text{probability of damage} = i / (n+1) \cdot 100 [\%]$$

where:

$i$  - number of the run,

$n$  - number of runs ended with pitting ( $n=24$ ).

The rheological properties study of the tested lubricating compositions was performed by means of the DWS

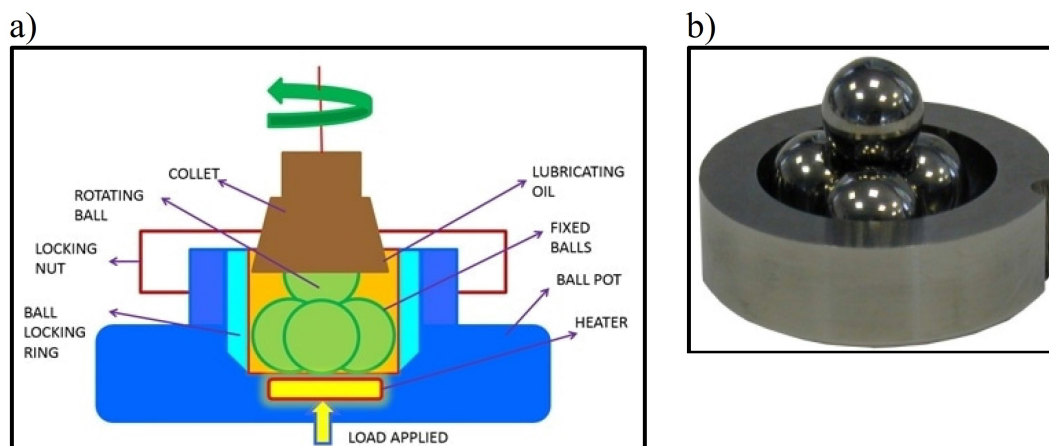


Fig. 3. The tribosystem of four-ball tester for the investigation of rolling contact fatigue of lubricants: a) the schematic view, b) the image

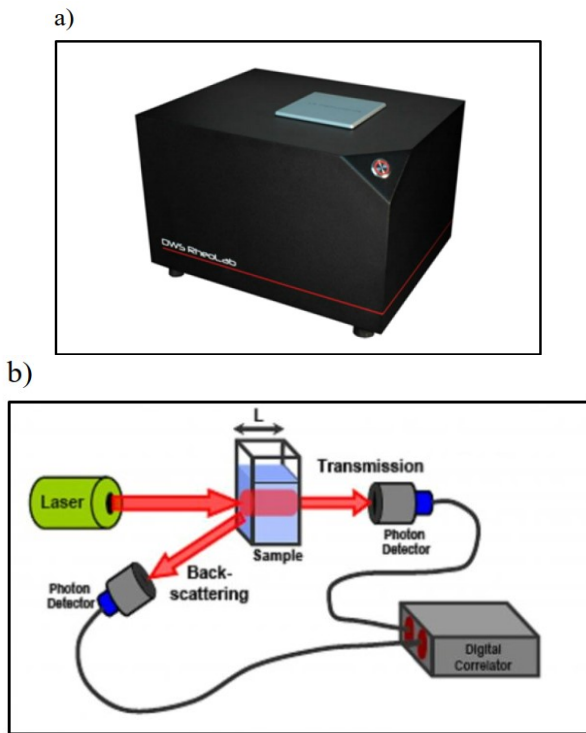


Fig. 4. The optical rheometer DWS (a) and rule of measurements of rheological properties (b)

RheoLab optical rheometer of the Swiss company LS Instruments AG (Fig.4). This device uses *Diffusing Wave Spectroscopy* (DWS) for rheological characteristics of media, both solid and liquid, such as suspensions, emulsions, foams, lubricants, etc.[38-42]. The principle of operation of the DWS rheometer is based on the assumption that light transport can be treated as a diffusion process in optically turbid samples. The apparatus enables micro-rheological measurements of materials under static inter-molecular displacements in a wide range of frequencies and viscoelasticity. The optical rheometer enables testing in two different geometries, i.e. transmission and backscattering. In the transmission mode, scattered light is detected after passing through the sample, and intensity fluctuations are correlated using the correlation intensity function (ICF). In contrast, in the backscattering mode, the light that disperses back towards the incident beam is collected and its fluctuations are measured [43-45].

Before the measurements were commenced, the apparatus was calibrated using a model, i.e. emulsion of polystyrene with a particle size of 222 nm in water. Then, the refractive indices for the oil bases of the individual lubricating compositions, the duration of the measurement, the temperature and the size of the spectrometric cuvette in which the sample was placed were determined. The tested lubricating greases were prepared by adding a titanium dioxide marker with a particle size of 360 nm to their structure. The test sample was then homogenized and placed in a measuring cuvette. Rheological tests were carried out using a measuring cuvette with an optical path equal to 1 mm [46-48]. The duration of the measurement was 90 s.

During the rheological tests, the correlation function of the MSD (mean square displacement) from the time of delay, the storage module  $G'$ , the loss module  $G''$  in static conditions were determined, depending on the frequency. Rheological measurements were carried out at the temperature of 20°C. Based on the analysis of the determined rheological parameters, the change in viscoelastic properties of the investigated lubricating compositions was determined [38-40,48,50].

### Results of testing the tribological properties

The results of the tribological properties of lubricating greases formed on vegetable base oil and modified with different amounts of polytetrafluoroethylene are presented below.

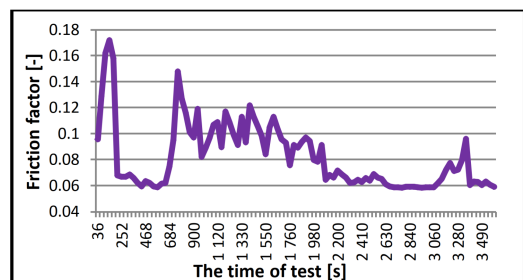
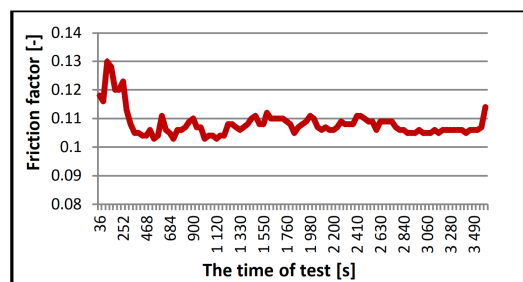
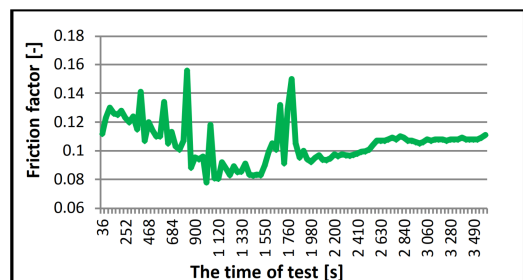
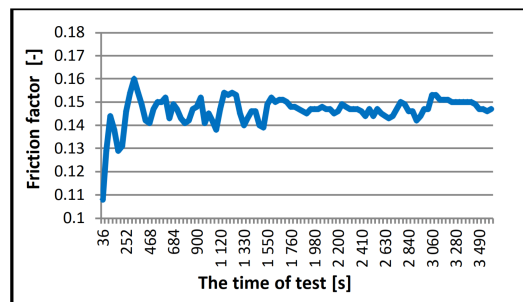
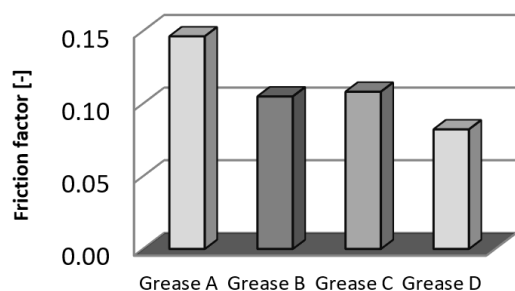
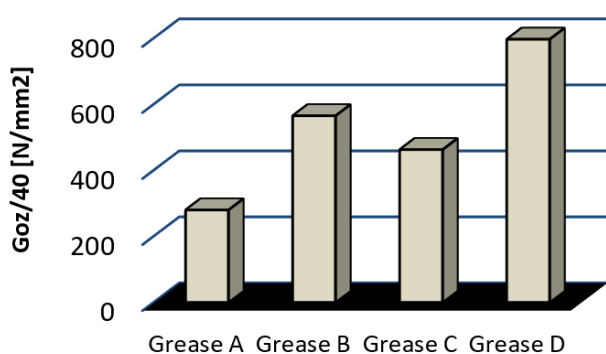


Fig.5. The dependence of the coefficient of friction on the time of test run for tested lubricating greases: unmodified vegetablegrease (A) and vegetable lubricants modified respectively 1% (B), 3% (C) and 5% (D) polytetrafluoroethylene



**Fig.6.** The average value of the coefficient of friction for tested lubricating greases: unmodified vegetable grease (A) and vegetable lubricants modified respectively 1% (B), 3% (C) and 5% (D) polytetrafluoroethylene

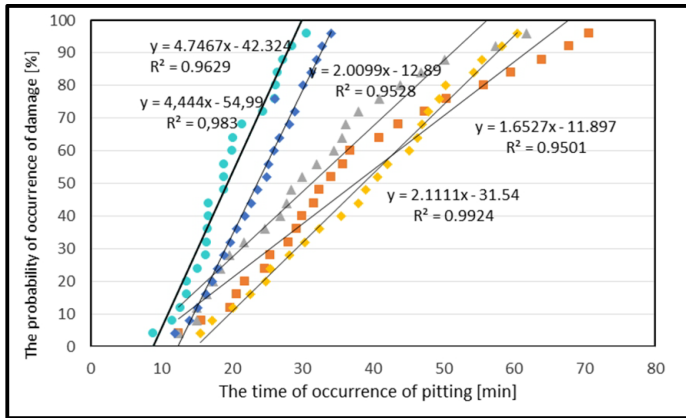


**Fig.7.** The value of limiting load of wear for tested lubricating greases: unmodified vegetable grease (A) and vegetable lubricants modified respectively 1% (B), 3% (C) and 5% (D) polytetrafluoroethylene

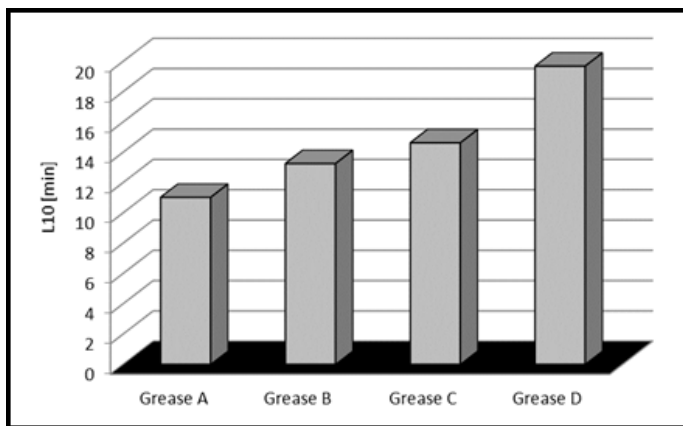
Tests of tribological properties of lubricating compositions produced showed that the used modifying additive has a positive effect on changes in the coefficient of friction and the ability of obtained lubricants to anti-wear protection of the tribosystem in relation to compositions made on other plant bases and modified with other additives [51-52]. For the additive-free composition A, stable friction coefficient values were observed after the initial increase. No rapid changes in this parameter were observed over time. During the measurement, the coefficient of friction ranged between 0.14-0.15 [-]. The composition labelled B, which has been modified by introducing 1% polytetrafluoroethylene is characterized by less stable friction coefficient values. Lower values of this parameter were observed in the case of composition A, which confirms the belief in the effectiveness of the additive used. Changes in the coefficient of friction over time range from 0.08-0.16 [-] suggest that polytetrafluoroethylene was insufficiently homogenized in the lubricant structure. Only after more than half of the test, the value of the discussed parameter is stabilized at the level of 0.10-0.11 [-]. The graph of changes in the coefficient of friction for composition C, which has been modified with 3% of the additive, looks different. In this case, after the initial increase over time, the value of

the friction coefficient stabilizes at the level of 0.10-0.11 [-]. For the composition being discussed, similar results were obtained as for composition B, clearly better than for composition A without a modifier. For this composition very good homogenization of the additive was achieved in the structure of the grease, which is evidenced by stable friction coefficient values during the test. However, composition D, which has been modified with 5% polytetrafluoroethylene is characterized by very unstable friction coefficient values. In the initial phase, the value of the discussed parameter was quite high and was at the level of 0.18 [-], later it dropped to 0.06 [-] to increase again to 0.1-0.14 [-]. In the further phase of the test, the value of the friction coefficient ranged from 0.06-0.10 [-]. Such unstable values of this parameter for this composition may be caused by uneven distribution of the modifying additive in the structure of the examined lubricant. However, the average friction coefficient for this composition is the lowest of all the lubricating compositions tested. The introduction of this amount (5%) of the grease additive works effectively, but variations in the coefficient of friction between 0.06 and 0.18 [-] are unacceptable. Therefore, lubricating compositions containing 1-3% of a modifying additive characterized by a lower value of coefficient of friction lower than the initial composition and stable changes of this parameter over time determine effective tribological protection.

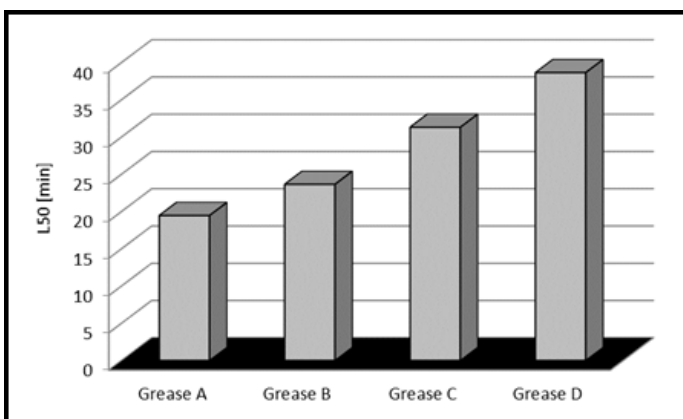
The anti-wear properties of the lubricating compositions tested were verified by determining the limiting load of wear  $G_{oz}$  of the tribosystem. The results obtained are presented in Fig. 7. The tests of tribological properties of the lubricating compositions produced have shown that the modifying additive used has changed the ability of the tested lubricants to anti-wear protection of the tribosystem. The introduction of polytetrafluoroethylene to the lubricant structure has beneficial effects on their anti-wear properties. The limit value of the boundary layer is confirmed by the limit value of wear  $G_{oz}$ , the higher the index, the greater the durability of the boundary layer and the reduction of wear. The highest value of the ultimate wear load is characterized by composition D modified with 5% polytetrafluoroethylene, while the lowest value of this parameter is characterized by lubricant A without a modifying additive. The lubricant composition modified with 1% polytetrafluoroethylene (B) has more than twice the value of the  $G_{oz}$  parameter than composition A. While composition C modified with 3% of the additive is characterized by a lower limit value of wear on composition B and D, but higher by 65% from the composition to which no modifiers were introduced. It has been found that the use of polytetrafluoroethylene as a modifying additive in the tested lubricant compositions has a positive effect on their anti-wear properties. All modified polytetrafluoroethylene compositions guarantee effective anti-wear protection of the tribosystem under constant load conditions, which cannot be said of a composition without an additive. The content of the additive in the lubricant structure affects the level of their anti-wear properties, as evidenced by the results obtained during the tribological tests presented in this article.



**Fig.8.** The probability of damage of the upper ball of the tribosystem lubricated unmodified vegetable grease and vegetable lubricants modified respectively 1% (B), 3% (C) and 5% (D) polytetrafluoroethylene from time of pitting



**Fig.9.** The comparison of fatigue live bearing - L<sub>10</sub> - probability of failure of bearing for tested lubricating greases: unmodified vegetable grease (A) and vegetable lubricants modified respectively 1% (B), 3% (C) and 5% (D) polytetrafluoroethylene



**Fig. 10.** The comparison of fatigue live bearing - L<sub>50</sub> - probability of failure of bearing for tested lubricating greases: unmodified vegetable grease (A) and vegetable lubricants modified respectively 1% (B), 3% (C) and 5% (D) polytetrafluoroethylene

Lubricating compositions based on sunflower oil and modified with 1-5% of polytetrafluoroethylene exhibited a much more favourable level of anti-wear properties compared to the unmodified additive composition. The highest resistance to wear was noted for lubricants containing more than 1% of the modifying additive, which was reflected in the results of the G<sub>02</sub> parameter test. The best results were obtained with grease modified with 5% polytetrafluoroethylene.

The Fig. 8 presents the Weibull distributions obtained for lubricant compositions prepared on a vegetable oil base thickened with lithium stearate and modified with a different amount of polytetrafluoroethylene. The equation of curves and correlation coefficients R<sup>2</sup> were also given.

On the basis of the obtained relationships, the time was determined, after which 10% and 50% of the tested tribosystem lubricated with lubricating compositions participating in the experiment would be damaged - L<sub>10</sub> and L<sub>50</sub>. The results obtained are shown in Fig. 9-10.

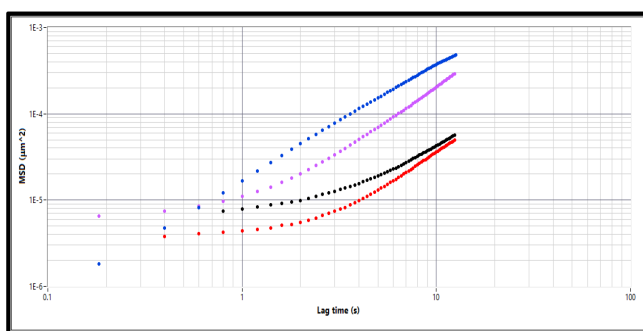
Analysing the graphs presented above, it should be noted that the surface fatigue life of the tribosystem lubricated with the tested lubricating compositions underwent significant changes depending on the amount of the modifying additive used. With a failure probability of 10% (L<sub>10</sub>), the time of the occurrence of pitting for the lubricant compositions to which the modifying additive was introduced, was, respectively: 11.02 min. for compositions without a modifier, 13.25 min. for grease modified with 1% polytetrafluoroethylene, 14.62 min. for grease modified with 3% polytetrafluoroethylene and 19.68 min. for a composition modified with a 5% of the additive. An increase of tribosystem durability was observed within 10% probability of damage occurring for modified lubricating compositions: 1% of a modifier (by 20.23%), 3% of a modifier (by 32.7%) and 5% of a modifier (by 78%) in relation to composition devoid of a modifying additive.

However, at 50% probability of damage (L<sub>50</sub>) the time after which the pitting occurred was: 19.45 min. for a composition devoid of a modifying additive, 23.63 min. of grease modified with 1% polytetrafluoroethylene, 31.30 min. for a composition modified with 3% of a modifier and 38.63 min. for a composition modified with 5% of an additive. The level of fatigue life expressed by the L<sub>10</sub> and L<sub>50</sub> coefficients for the tested lubricating compositions varies and depends on the amount of modifying additive introduced into the lubricating grease structure. The analysis of the graphs indicates that the increase in the surface fatigue life of the tribosystem at 50% damage probability for lubricating compositions modified with the additive used is, respectively: 21.5% in the case of grease modified with 1% polytetrafluoroethylene, 60.9% in the case of a composition modified with 3% of a modifier and 98.6% in the case of a composition modified with 5% of the additive in relation to the grease composition, which was not modified with polytetrafluoroethylene.

Based on the obtained results, it was found that the applied modifying additive affects the increase of indicators

characterizing the fatigue life of the examined lubricating greases based on sunflower oil. The size of surface changes of fatigue life of the lubricating compositions tested depends on the chemical structure of the dispersing, dispersed phase and a modifying phase used, as well as interactions between the individual phases that by combining create lubricating compositions. The chemical structure of the used modifying additive allows to state that in the case of the lubricating compositions tested, the effectiveness of counteracting pitting is derived from the parameters characterizing the physicochemical properties of the modifying additive, the dispersed phase and the dispersing phase. Based on this assumption, the relationship between the intermolecular interaction of the dispersing phase (oil base) with the dispersed phase and the modifying additive, and the tribological efficiency of lubricating compositions, including the protection against surface fatigue, the so-called pitting. As an additive, an electrically neutral polytetrafluoroethylene has been used, which has the ability to form films with high durability on cooperating surfaces and adsorbs well to metal surfaces. He friction occurs in the metal-teflon-metal combination. This relation protects the lubrication with the teflon layer of the micro-areas of the cooperating surfaces of the film-free lubricating film. High efficiency of polytetrafluoroethylene results from the low temperature of its decomposition, and the easier the distribution, the greater the improvement of fatigue life. The introduction of this additive to the structure of the tested lubricating compositions results in a significant plasticity of the surface, which is associated with a large reduction in stresses resulting from the interactions of surface unevenness and increases the fatigue life. The use of polytetrafluoroethylene ensures the creation of boundary layers capable of regeneration and a high degree of protection against wear.

A more detailed explanation of the mechanism of action of polytetrafluoroethylene in vegetable lubricating compositions on surface fatigue requires the study of the condition of the surface layer and changes occurring after tribological tests in the deeper layers of the test lubricating compositions on the XPS photoelectron spectrometer.



**Fig. 11.** The dependence of correlation function MSD from lag time for tested lubricating compositions: unmodified vegetable grease (blue) and vegetable lubricants modified respectively 1% (red), 3% (violet) and 5% (black) polytetrafluoroethylene

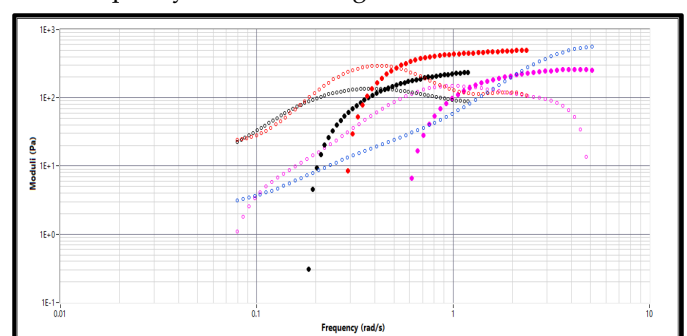
## Results of rheological research

The selected lubricating compositions were examined for rheological properties on the optical rheometer DWS RheoLab. The influence of various amounts of the modifier on the rheological properties of lubricating greases were presented on Fig.11-12.

The MSD correlation function characterizing the displacement of particles in the tested sample and the modules of elasticity and viscosity depending on the frequency, which characterize changes in viscoelastic properties, were determined for all lubricating compositions subjected to the tests. The determination of these rheological parameters made it possible to assess the structural changes of the lubricating grease tested, depending on their chemical composition.

The experimentally measured values of the MSD correlation function and the  $G'$  and  $G''$  modules of the tested lubricating compositions confirmed the different nature of each of the samples. It was found that the introduction of a modifying additive to the lubricating grease structure significantly changes the course of both the MSD correlation function, as well as the frequency-dependent  $G'$  and  $G''$  modules.

Analysing the shape of the MSD function for the tested lubricating compositions at 20°C, it should be stated that the function is characterized by two phases, i.e. the plateau phase, where the value of the MSD function is constant and the growth phase. For the composition to which no modifier additive (A) was added, only the growth phase was observed. The growing nature of the MSD curve may indicate the predominance of diffusion features with the predominance of elastic properties over a wide frequency range. These assumptions are confirmed by the graph of  $G'$  and  $G''$  modules from the frequency for this composition. The presence of only a spring module indicating the elastic properties of this lubricant was noted. The introduction of a 1% modifying additive to the structure of the vegetable lubricant (B) has changed the nature of the test composition. The presence of a plateau phase and growth phase was observed. The existence of a plateau phase at low time values indicates the predominance of elastic properties at low frequency values. At higher times, the value of the



**Fig. 12.** The dependence of modulus  $G'$  and  $G''$  from frequency for tested lubricating compositions: unmodified vegetable grease (blue) and vegetable lubricants modified respectively 1% (red), 3% (purple) and 5% (black) polytetrafluoroethylene

MSD correlation function increases, which indicates the prevalence of viscous features at higher frequency values. These considerations seem to confirm the graph depicting the dependence of the  $G'$  and  $G''$  module on the frequency. Above 0.5 [rad/s], the viscous character of the test sample is observed, while below 0.5 [rad/s], the tested sample is characterized by a predominance of elastic properties. However, the introduction of 3% polytetrafluoroethylene to the grease structure (C) gave similar results. From the graph of correlation function between MSD and time, the existence of plateau phase and growth phase was found, but with higher values than for composition B. The presence of the plateau phase at lower times indicates the predominance of elastic properties at lower frequency values. With increasing time, the values of the MSD function increase for the tested sample, which proves the prevalence of viscous features at higher frequency values. These considerations are confirmed by the graph of elastic and viscous modulus on the frequency for composition C. The  $G'$  and  $G''$  modules intersect at the frequency of 0.45 [rad/s]. Above this frequency value, the test sample is characterized by viscous features, while below this value the elastic features dominate. The lubricating composition modified with 5% polytetrafluoroethylene (D) is characterized by the presence of a short plateau phase and the growth phase of the MSD correlation function. Below 1[s], the MSD function assumes constant values, which proves the advantage of elastic features at low frequency values, whereas at higher values of the delay time the value of the MSD function increases, which results in viscous features dominating at higher frequency values. These considerations are confirmed by the graph of the dependencies of the  $G'$  and  $G''$  modules on the frequency of this lubricating composition. An advantage of elastic features was observed at low frequency values (to 1.2 rad/s), then along with the increase in frequency, the viscous module begins to prevail. Above 1.2 rad/s, the nature of the sample is changed and viscous features begin to dominate.

The tests conducted have shown that the introduction of a modifying additive to the lubricating compositions significantly changes the internal structure of the tested lubricants. The reason for this is the chemical structure of the additive used. The interaction between the individual phases forming the lubricant compositions affects changes in the rheological stability of the produced lubricants. It was found that the introduction of polytetrafluoroethylene to the structure of the tested lubricants changed the value of the MSD correlation function and the  $G'$  and  $G''$  modules, which indicates the movement of the particles and their location in time, which significantly affected the internal structure of the lubricating compositions tested.

Based on the test results, it can be concluded that the applied modifier significantly influences the microstructure of the lubricating compositions, and thus the viscoelastic characteristics of the lubricants tested are changing.

## Conclusion

The conducted research showed different influence of applied modifying additive on changes of coefficient of friction, limiting load of wear as well as fatigue durability, and rheological properties of tested lubricating compositions.

The analysis of friction coefficient values during the test for the tested lubricating compositions indicates a significant change in this parameter for lubricants modified with various amounts of additive. The values of the coefficient of friction have a significant scattering and abrupt changes during the test. The introduction of a modifying additive to the lubricant structure allows for a significant reduction of the coefficient of friction, thus increasing the efficiency of tribological protection of the tribosystem.

The determined limiting load of wear values ( $G_{oz}$ ) for the tested lubricating compositions showed that the greases modified with polytetrafluoroethylene are characterized by effective anti-wear protection of the tribosystem under constant load conditions, which cannot be said of a composition without an additive. The content of the additive in the lubricant structure affects the level of the anti-wear properties, as evidenced by the results obtained during the tribological tests presented in this article.

The applied modifying additive affects the increase of indicators characterizing the fatigue life of the lubricating greases tested on the basis of sunflower oil. The chemical structure of the used modifying additive allows to state that in the case of the lubricating compositions tested, the effectiveness of counteracting pitting is derived from the parameters characterizing the physicochemical properties of the modifying additive, the dispersed phase and the dispersing phase. On the basis of this assumption, the relationship between the intermolecular interaction of the dispersing phase with the dispersed phase and the modifying additive and the tribological efficiency of lubricating compositions, including protection against surface fatigue, can be assumed. The introduction of this additive to the structure of the tested lubricating compositions results in a significant plasticity of the surface, which is associated with a large reduction in stresses resulting from the interactions of surface unevenness and increases the fatigue life.

The interaction between the individual phases forming the lubricating compositions affects changes in the rheological stability of the produced lubricants. It was found that the introduction of polytetrafluoroethylene to the structure of the tested lubricants changed the value of the MSD correlation function and the  $G'$  and  $G''$  modules, which indicates the movement of the particles and their location in time, which significantly affected the internal structure of the lubricating compositions tested. Based on the test results, it can be concluded that the applied modifier significantly influences the microstructure of the lubricating compositions, and thus the viscoelastic characteristics of the lubricants tested are changing.



## Funding

Project co-financed from the European Fund of Regional Development as part of the POIR Intelligent Development Program 04.01.02-00-0004 / 16.

## Literature

- [1] Ge X., Xia Y., Cao Z.: Tribological properties and insulation effect of nanometer TiO<sub>2</sub> and nanometer SiO<sub>2</sub> as additives in grease, *Tribology International*, vol.92, 2015, pp. 454-461, <https://doi.org/10.1016/j.triboint.2015.07.031>
- [2] Rizvi S.Q.A.: *A Comprehensive Review of Lubricant Chemistry, Technology, Selection, and Design*, ASTM International, Baltimore, 2009, USA, <https://doi.org/10.1520/mnl59-eb>
- [3] Mortier R.M., Fox F.M., Orszulik S.T.: *Chemistry and Technology of Lubricants*, Springer, Dordrecht, 2010, <https://doi.org/10.1007/978-1-4020-8662-5>
- [4] Rudnick L.R.: *Chemistry and Applications: Lubricant Additives*, CRC Press, Boca Raton, 2017, <https://doi.org/10.1201/9781315120621>
- [5] Lugt P.M.: *Grease Lubrication in Rolling Bearings*, Wiley, 2013, USA, <https://doi.org/10.1002/9781118483961>
- [6] Mohamed A., Osman T.A., Khattab A., Zaki M.: Tribological Behavior of Carbon Nanotubes as an Additive on Lithium Grease, *Journal Of Tribology*, 137(1), 2014, pp. 011801-5, <https://doi.org/10.1115/1.4028225>
- [7] Zhao G., Zhao Q., Li W., Wang X., Liu W.: Tribological properties of nano-calcium borate as lithium grease additive, *Lubrication Science*, 26(1), 2014, pp. 43-53, <https://doi.org/10.1002/ls.1227>
- [8] Yuan X.D., Yang X.J.: A study on friction and wear properties of PTFE coatings under vacuum conditions, *Wear*, 269, 2010, pp. 291-297, <https://doi.org/10.1016/j.wear.2010.04.014>
- [9] Rico E.F., Minondo I., Cuervo D.G.: The effectiveness of PTFE nanoparticle powder as an EP additive to mineral base oil, *Wear*, 262, 2007, pp. 1399-1406, <https://doi.org/10.1016/j.wear.2007.01.022>
- [10] Su F.H., Zhang Z.Z., Liu W.M.: Study on the friction and wear properties of glass fabric composites filled with nano and micro particles under different conditions, *Mater Sci Eng A*, 392, 2010, pp. 359-365, <https://doi.org/10.1016/j.msea.2004.09.036>
- [11] Hou X., Deem P.T., Choy K.L.: Hydrophobicity study of polytetrafluoroethylene nanocomposite films, *Thin Solid Films*, 520(15), 2012, pp.4916-4920, <https://doi.org/10.1016/j.tsf.2012.02.074>
- [12] Khedkar J., Negulescu I., Meletis E.I.: Sliding wear behavior of PTFE composites, *Wear*, 252(5), 2002, pp.361-369, [https://doi.org/10.1016/S0043-1648\(01\)00859-6](https://doi.org/10.1016/S0043-1648(01)00859-6)
- [13] Bijwe J., Sharma M.: Nano and micro PTFE for surface lubrication of carbon fabric reinforced polyethersulphone composites, In: Davim J. (ed) *Tribology of nanocomposites materials forming machining and tribology*, Springer, Berlin Heidelberg, 2012, pp 19-39, [https://doi.org/10.1007/978-3-642-33882-3\\_2](https://doi.org/10.1007/978-3-642-33882-3_2)
- [14] Chen J.: Tribological Properties of Polytetrafluoroethylene, Nano-Titanium Dioxide, and Nano-Silicon Dioxide as Additives in Mixed Oil-Based Titanium Complex Grease, *Tribology Letters*, vol. 38, issue 3, 2010, pp. 217-224, <https://doi.org/10.1007/s11249-010-9593-5>
- [15] Czarny R., Paszkowski M.: The influence of graphite solid additives, MoS<sub>2</sub> and PTFE on changes in shear stress values in lubricating greases, *Journal of Synthetic Lubrication*, 24(1), 2007, pp. 19-29, <https://doi.org/10.1002/jsl.26>
- [16] Krawiec S.: On the mechanism of the synergistic effect of PTFE and copper in a lithium grease lubricant, *Industrial Lubrication and Tribology*, vol. 63 issue: 3, 2011, pp.171-177, <https://doi.org/10.1108/00368791111126590>
- [17] Blanchet T.A., Kennedy F.E.: Sliding wear mechanism of polytetrafluoroethylene (PTFE) and PTFE composites, *Wear*, vol. 153, issue 1, 1992, pp. 229-243, [https://doi.org/10.1016/0043-1648\(92\)90271-9](https://doi.org/10.1016/0043-1648(92)90271-9)
- [18] Iłowska J., Chrobak J., Grabowski R., Szmatoła M., Woch J., Szwach I., Drabik J., Trzos M., Kozdrach R., Wrona M.: Designing lubricating properties of vegetable base oils. *Molecules*, 23(8), 2018, pp. 2025-2032, <https://doi.org/10.3390/molecules23082025>
- [19] Nowicki J., Drabik J., Woszczyński P., Gębura K., Nowakowska-Bogdan E., Kozdrach R.: Tribological characterisation of plant oil derived fatty acid esters of higher polyols: Comparative experimental study, *Lubrication Science*, 31, 2019, pp. 61-72, <https://doi.org/10.1002/ls.1448>
- [20] Drabik J., Kozdrach R., Wolszczak M., Wrona M.: The proecological base oils of highly specialized lubricants, *Przemysł Chemiczny* 9/2018, pp. 1538-1541, <https://doi.org/10.15199/62.2018.9.30>
- [21] Moreira-Izurieta F., Jabbarzadeh A.: Tribological Studies in Cartilaginous Tissue of Lamb Synovial Joints Lubricated by Distilled Water and Interstitial-Fluid-Like Solution, *Tribology in Industry*, 39 (3), 2017, pp. 319-328, <https://doi.org/10.24874/ti.2017.39.03.06>
- [22] Gilardi R.: Tribology of Graphite-Filled Polystyrene, *Lubricants*, 4 (2), 2016, pp. 20-25, <https://doi.org/10.3390/lubricants4020020>
- [23] Cyriac F., Lugt P.M., Bosman R.: The Impact of Water on the Yield Stress and Startup Torque of Lubricating Greases, *Tribology Transactions*, 60(5), 2017, pp. 824-831, <https://doi.org/10.1080/07420114.2017.1375000>

- [doi.org/10.1080/10402004.2016.1215583](https://doi.org/10.1080/10402004.2016.1215583)
- [24] Miller M.K., Khalid H., Michael P.W., Guevremont J.M., Garelick K.J., Pollard G.W., Whitworth A.J., Devlin M.T.: An Investigation of Hydraulic Motor Efficiency and Tribological Surface Properties, *Tribology Transactions*, vol. 57, issue 4, 2014, pp. 622-630, <https://doi.org/10.1080/10402004.2014.887167>
- [25] Cyriac F., Lugt P.M., Bosman R.: Yield Stress and Low-Temperature Start-Up Torque of Lubricating Greases, *Tribology Letters*, 63 (6), 2016, pp. 1124-1131, <https://doi.org/10.1007/s11249-016-0693-8>
- [26] Oppermann A.K.L., Verkaik L.C., Stiegera M., Scholten E.: Influence of double (w1/o/w2) emulsion composition on lubrication properties, *Food and Function*, 8, 2017, pp. 522-532, <https://doi.org/10.1039/c6fo01523a>.
- [27] Kozdrach R.: The influence of mechanical forces on the change of the tribological properties of mineral based lubricating greases, *Nafta-Gaz*, 1/2016, pp. 50-57, <https://doi.org/10.18668/NG2016.01.07>
- [28] Kozdrach R.: The influence of dispersed type phase on tribological properties of lubricating greases to form on the linseed oil, *Nafta-Gaz* 6/2018, pp. 471-478, <https://doi.org/10.18668/NG.2018.06.08>
- [29] Kozdrach R.: The influence of vegetable dispersion phase on rolling contact fatigue of biodegradable lubricating greases, *Tribologia*, no. 6, 2016, pp. 57-67, <https://doi.org/10.5604/01.3001.0010.6716>
- [30] 30. Kozdrach R., Molenda J.: The testing of exploitation properties of ecological greases modified with polymer-silica additive, *Tribologia*, no. 6, 2012, pp. 99-111
- [31] Rico J.E., Battez A., Cuervo D.G.: Rolling contact fatigue in lubricated contacts, *Tribology International*, no. 36, 2003, pp. 35-40, [https://doi.org/10.1016/S0301-679X\(02\)00097-X](https://doi.org/10.1016/S0301-679X(02)00097-X)
- [32] Łubiński J., Śliwiński P.: Multi parameter sliding test result evaluation for the selection of material pair for wear resistant components of a hydraulic motor dedicated for use with environmentally friendly working fluids, *Solid State Phenomena*, no. 225, 2015, pp. 115-122. <https://doi.org/10.4028/www.scientific.net/SSP.225.115>
- [33] Pawelec E., Drabik J.: The change of fatigue life of rolling bearings as effect of an interaction between grease components and friction elements surface, *Tribologia*, no. 1, 2007, pp. 115-125
- [34] Piekoszewski W., Szczerek M., Tuszyński W.: The modification of four-balls tribological tests, *Tribologia*, no. 5, 6, 1997, pp. 818-825
- [35] Michalczewski R., Piekoszewski W., Wulczyński J.: The method for investigation of rolling contact fatigue of coated elements, *Tribologia*, no. 4, 2003, pp. 91-99
- [36] Mota V., Ferreira L.A.: Influence of grease composition on rolling contact wear: experimental study, *Tribology International*, vol. 42, issue 4, 2009, pp. 569-574, <https://doi.org/10.1016/j.triboint.2008.04.002>
- [37] Zhao P., Hadfield M., Wang Y., Viellard C.: The influence of test lubricants on the rolling contact fatigue failure mechanisms of silicon nitride ceramic, *Wear*, vol. 257, issues 9-10, 2004, pp. 1047-1057, <https://doi.org/10.1016/j.wear.2004.07.015>
- [38] Mason T. G., Weitz D. A.: Optical measurements of frequency-dependent linear viscoelastic moduli of complex fluids, *Physical Review Letters* 1995, 74, pp. 1250-1253, <https://doi.org/10.1103/PhysRevLett.74.1250>
- [39] Dziubiński M.: Microrheology: review of methods and applications in microtechnological processes, *Przemysł Chemiczny*, 93, 10/2014, pp. 1767-1772, <https://doi.org/10.12916/przemchem.2014.1767>
- [40] Corredig M., Alexander M.: Food emulsions studied by DWS: recent advances, *Trends in Food Science and Technology*, 2008, 19(2), pp. 67-75, <https://doi.org/10.1016/j.tifs.2007.07.014>
- [41] Lopez-Diaz D., Castillo R.: Microrheology of solutions embedded with thread-like supramolecular structures, *Soft Matter*, 7 (13), 2011, pp. 5926-5937, <https://doi.org/10.1039/C1SM05274H>
- [42] Alexander M., Dagleish D. G.: Interactions between Denatured Milk Serum Proteins and Casein Micelles Studied by Diffusing Wave Spectroscopy, *Langmuir*, 21, 2005, pp. 11380-11386, <https://doi.org/10.1021/la0519958>
- [43] Alexander M., Corredig M., Dagleish D.G.: Diffusing wave spectroscopy of gelling food systems: The importance of the photon transport mean free path ( $l^*$ ) parameter, *Food Hydrocolloids*, 20 (2-3), 2006, pp. 325-331, <https://doi.org/10.1016/j.foodhyd.2005.02.021>
- [44] Carinaux F., Cipelletti L., Scheffold F., Schurtenberger P.: Microrheology of giant-micelle solutions, *Europhysics Letters*, 57 (5), 2002, pp. 738-744, <https://doi.org/10.1209/epl/i2002-00525-0>
- [45] Marze S., Choimet M., Foucat L.: In vitro digestion of emulsions: diffusion and particle size distribution using diffusing wave spectroscopy and diffusion using nuclear magnetic resonance, *Soft Matter*, 8 (42), 2012, pp. 10994-11004, <https://doi.org/10.1039/C2SM26334C>
- [46] Oelschlaeger C., Suwita P., Willenbacher N.: Effect of Counterion Binding Efficiency on Structure and Dynamics of Wormlike Micelles, *Langmuir*, 26 (10), 2010, pp. 7045-7053, <https://doi.org/10.1021/la9043705>
- [47] Dasgupta B. R., Tee S. Y., Crocker J. C., Frisken B. J. & Weitz D. A.: Microrheology of polyethylene oxide

- using diffusing wave spectroscopy and single scattering, *Phys Rev E Stat Nonlin Soft Matter Phys* 65, 2002, pp. 051501-10, <https://doi.org/10.1103/PhysRevE.65.051505>
- [48] Galvan-Miyoshi J., Delgado J., Castillo R.: Diffusing wave spectroscopy in Maxwellian fluids, *Soft Matter*, 26 (4), 2008, pp. 369-377, <https://doi.org/10.1140/epje/i2007-10335-8>
- [49] Scheffold F., Diaz-Leywa P., Reufer M., Brahm N.B., Lynch I., Harden J.L.: Brushlike Interactions between Thermoresponsive Microgel Particles, *Phys. Rev. Lett.*, 104 (12), 2010, pp. 128304-08, <https://doi.org/10.1103/PhysRevLett.104.128304>
- [50] Drabik J., Kozdrach R., Wrona M., Iłowska J.: Use of diffusing wave and Raman spectroscopy for evaluation of paraffinic emulsions formed by homogenization, *Przemysł Chemiczny*, 12/2017, pp. 2544-2549, <https://doi.org/10.15199/62.2017.12.31>
- [51] Kozdrach R., Skowroński J.: The Application of Polyvinylpyrrolidone as a Modifier of Tribological Properties of Lubricating Greases Based on Linseed Oil, *Journal of Tribology*, 140(6), , 2018, pp. 061801-07, <https://doi.org/10.1115/1.4040054>
- [52] Drabik J., Trzos M., Kozdrach R., Wrona M., Wolszczak M., Duszyński G., Piątkowski M.: Modeling and evaluation of properties of lubricants used in the food industry, *Przemysł Chemiczny* 12/2018, pp. 2200-2204, <https://doi.org/10.15199/62.2018.12.39>