

Article

Application of Raman Spectroscopy to Evaluate the Structure Changes of Lubricating Grease Modified with Montmorillonite after Tribological Tests

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Abstract: This study shows the experimental data obtained by Raman spectroscopy to evaluate the structural changes of vegetable lubricants modified with montmorillonite after tribological tests. The analysis of the friction factor and limiting load of wear in the test for the examined grease compound shows a substantial effect on this parameter for grease. A change in the evaluated tribo-parameter results in a modification of the structure of the tested lubricant and changes in the protection efficiency of the tribological system. The amount of thickener, oil base and additive in the grease structure has an influence on the value of anti-wear properties, as shown by the data obtained in the tribological test described in this paper. The Raman spectroscopy tests showed that, in the tribological processes, some of the ingredients undergo an oxidative reaction, which leads to the formation of oxygenated organic substances that form an organic layer on the metal surface and counteract the wear of the lubricated contact surfaces. Other compounds come into close contact with the tribological layer, which increases its ability to resist wear and shear. The efficiency of the used additive is based on the formation (during friction) of a low-shear and high-plastic-strength thin film which is chemically highly bonded to the material and has a high level of durability against wear processes. As a consequence of the thermal decomposition of the additive, chemical interactions occur among the ingredients of the material of the substrate and the lubricants.

Keywords: lubricant; montmorillonite; tribo-characteristics; coefficient of friction; wear limit; structural evolution; Raman spectroscopy



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1. Introduction

The structure of lubricating grease during work in variable test conditions is constantly degraded [1]. Therefore, an important problem is the observation of changes in the microstructure to determine the moment at which a significant change in the durability of tested grease occurs [2].

Raman spectroscopy is an important method of studying the rotational and oscillating spectra of molecules [3]. Thus, for example, in this respect, Raman spectroscopy complements infrared spectroscopy and vice versa. In addition, Raman spectroscopy enables the study of the movement of molecules which, by changing their position, make, for example, rotational movements, which in turn changes their orientation in relation to the incident radiation. This is manifested by a change in polarity in relation to the incident light. In addition, Raman scattering, like infrared spectroscopy, provides information about the structure of the molecule, the interatomic bonds that make it up and their polarizability. This allows the chemical reactivity and the course of chemical reactions to be predicted [4,5]. The structure of the lubricant undergoes continuous degradation under varying test conditions [6–9]. Therefore, an important problem is to observe changes in the microstructure and to determine the moment when a significant change in the durability of the tested lubricant has occurred.

The issue of analysing structural changes in lubricants as a function of the co-operation of different ingredients in grease has not been sufficiently considered, although it has been the subject of many studies. Experimental data describing the behaviour of heterogeneous and uniform greases with comparatively small amounts of solid solution can be found in the literature [10–12].

The elucidation of the influence of the individual components of the system and the determination of the kinetics of structural changes under specific physical loads allow the molecular structure of lubricants to be characterised by Raman spectroscopy [13–16].

The application of this analytical technique enables the elucidation of the behaviour of two-phase disperse systems subjected to mechanical and thermal loads [17–19]. The analysis of the previously described cases of application of Raman spectroscopy allows us to conclude that it is possible to identify and elucidate changes in the structure of lubricants [20–24].

Raman spectroscopy gives details of the material chemical behaviour of thermally and mechanically treated materials and allows its evolution to be monitored over long periods of time [25]. The evolution of the chemistry of the samples provides a full assessment of the effect of the experimental parameters on the structural condition of the material and a comprehensive characterisation of the strength of the sample at the molecular level [26]. Raman spectroscopy is a technique for investigating the vibration of chemical compound molecules. It gives details of the chemical nature of compounds through the identification of functional groups [27]. It also enables the quantitative or semi-quantitative determination of the amount of modifying additive in the lubricant [28].

Raman spectroscopy will be used as a complementary technique to study the structural changes in the studied lubricants subjected to variable stresses during the carried out tests.

Raman spectroscopy is a commonly applied analytical method used, for example, for molecular structure studies of polymer liquids [29], which have revealed a number of interesting structural changes at various altitudes. Similarly, changes in the chemistry of colloidal materials [30], paraffin waxes, and polymer suspensions at different conditions have been investigated [31]. Studies have also been carried out on phase transitions in hydrocarbons [32] or on the evaluation of the level of crystallization of polymer blends during thermal treatment [33]. The change in the chemical structure of water-based polymer suspensions, oil stocks and greases as a function of changing working conditions has been evaluated [29].

The elucidation of the effect of individual elements of a system and the determination of the kinetics of structural changes under the impact of specific physical stresses enables the characterization of the molecular structure of lubricants by Raman spectroscopy.

The use of this analytical technique will allow us to explain the behaviour of two-phase dispersion systems subjected to mechanical and thermal stresses [4]. The analysis of the previously described cases of Raman spectroscopy allows one to state that it is possible to identify and explain changes in the structure of lubricants [5]. Access to the equipment and the possibility of using it to explain changes in the structure under the influence of changing mechanical and thermal conditions will enable us to gain additional knowledge in the field of lubricating greases on biodegradable oil bases [7].

The problems involved with the analysis of structural changes have been the object of research works on pure chemical substances with a defined composition or model chemical compounds; however, the characterization of changes as a result of the interaction of individual components of lubricating greases in relation to the variable mechanical and thermal stresses has not been sufficiently recognized.

Raman spectroscopy gives detailed insight into the chemistry of samples undergoing thermal and mechanic treatments and provides the ability to monitor the evolution of the chemical structure over time. The evolution of the chemistry of samples gives a full assessment of the effect of process parameters on the nature of the material's chemistry, as well as a complete characterization of the strength of the sample at the molecular level.

Raman spectroscopy is a method that allows the study of the vibrations of molecules of chemical compounds. This provides information on the chemical structure of compounds by identifying functional groups [4]. It also allows quantitative or semi-quantitative determination of the content of the test substance in the sample [6]. It is used to control the course of reactions by analysing the spectra of products or their mixtures, as well as when investigating interactions between solution components (cation–solvent) or catalyst activity mechanisms [8]. Each substance gives a different and specific Raman spectrum, depending on its structure. Using the phenomenon of Raman spectroscopy, one can study compounds in all physical states, i.e., gases, liquids, solutions (including water), pastes, solids as micro-crystalline powders, or single crystals in a wide range of temperatures and pressures [10]. The measurement of Raman spectra does not require complicated sample preparation procedures, nor are special measuring vessels necessary. An important advantage of Raman spectroscopy is the possibility of using it for samples in aqueous solutions, because the low polarization of water is expressed by the low intensity of scattered light [33].

In my earlier work, I used amorphous silica to modify or produce lubricants that are used in the food industry and therefore have to meet safety requirements. The next step was to find a so-called safe additive and the choice was montmorillonite, which contains silicon atoms in its composition. The previous use of Aerosil amorphous silica had a positive effect on the properties of green lubricants.

The purpose of this study is to analyse the structural changes in vegetable lubricant compositions modified with montmorillonite after tribological tests carried out using a rheometer with a tribological cell using Raman spectroscopy.

2. Materials and Methods

The studied lubricating greases were prepared with non-toxic components [34], forming mixed solid/liquid phases [35–37]. The oil dispersant used was a vegetable base oil with good organoleptical and physicochemical characteristics. The linseed oil applied in the tribological tests is characterised by the following special parameters: density: 0.881–0.903 g/cm³; kinematic viscosity: 31.12 cSt at 40 °C; peroxide number: 3.11 meq O₂/kg; iodine index: 89.23 g I₂/100 g; saponification index: 184.63 mg KOH/g; and acid index: 0.46 mg KOH/g. The linseed base consists of over 60% alpha-linolenic acid (C22-1), which determines its properties. It is a low viscous liquid [38] with high absorption, anti-aging characteristics, high friction and wear [39] and very good thermo-mechanical performance [40]. Lithium stearate was used as the thickener. In the first phase of the experiment, the amount of thickening agent and the lubricant additive to be incorporated into the lubricating compound were examined. The thickener was applied to the vegetable base fluid at a rate of 8% *w/w*.

As a modifier, montmorillonite with the chemical formula M_x (Al_{4-x}Mg_x) Si₈O₂₀(OH)₄ and a grain diameter of 100–150 nm was used. It consists of a 2:1 triple-layer packing, with an octahedral phase located between two tetrahedral phases. The octahedral sheet is made of aluminium or magnesium oxide and is connected to two external silicium (tetrahedral) sheets by means of co-operative oxygen molecules. Modification with quaternary ammonium compounds makes it more hydrophobic and organophilic, enabling it to simultaneously extract organic fluids like oils. Activated montmorillonite has compatibility with lubricants and is added as an ingredient to change their lubricity and rheology parameters. The modified montmorillonite was incorporated into the plant lubricant at a concentration of 1.5% *w/w*. Selected ingredients were used to formulate lubricants for application in the agricultural and food industries [41].

The approved prepared lubricating greases were that with a linseed oil base (Grease A) and that with linseed oil base and modification of the additive (Grease B). The lubricant compounds obtained in this manner were submitted to tribology studies and to an assessment of the changes in the grease structure after tribology studies using Raman analysis (Table 1).

Table 1. The chemical compounds of used lubricating grease and used experimental methods.

The Tested Lubricating Greases	The Chemical Compound of Tested Lubricating Greases	Experimental Methods Using to Tested of Lubricating Greases
Grease A	Linseed oil, lithium stearate	Tribological tests (anti-wear properties) on Anton Paar rheometer with tribological cell. Spectral test using Raman spectroscopy.
Grease B	Linseed oil, lithium stearate and montmorillonite	

To assess the anti-wear properties of the investigated lubricants, a compact Anton Paar MCR 102 rotating rheometer was provided with a T-PTD 200 concentrated plate–ball tester, in which the plate consists of three steel cuboids which are fixed in place and pressed with adequate load by a ball which is mounted in the shaft and spins at specified speeds. The tribological apparatus enables experiments to be performed in the temperature range of $-40 \div 200$ °C. The balls with a diameter of 12.7 mm and the plates with a dimension of 15 mm × 5 mm × 2 mm were manufactured from LH 15 bearing steel ($R_a = 0.3$ µm; hardness 60–63 HRC). The experiment was performed in an immersion chamber. Tribology tests (to establish the limiting load of wear— G_{oz}) were performed on the tribology apparatus at 1.00, 5.00 and 10.00 N, at a rotational speed of 500 rpm, for 3600 s and at a temperature of 20 °C. The test also measured the following parameters: the coefficient of friction, the work of friction, the force of friction and the power of friction. Before beginning the tribological process, the plates were inserted into the holder and fitted with springs, lubricants were introduced (approximately 5 cm³) and then the condition was stabilised at a specified temperature for a duration of 60 s. During the whole test, the tribology values were recorded and automatically converted into friction coefficients at a rate of 36 s. Three experimental runs were performed and the final results were recorded.

The final received value of the test run was the sum of the 100 measured values recorded during the experiment. The average of the test cycles was also obtained. The Q-Dixon test was used to evaluate the results statistically with a confidence limit of 95%. After the experiment, the parts of the tribological system were removed, washed in n-hexane and allowed to air dry [42].

The limiting load of wear is a characteristic parameter that describes the anti-wear behaviour of the lubricant. The estimation of this value was made by estimating its level according to the following equation:

$$G_{oz} = 0.52 \times P_n / d_{oz}^2 \quad (1)$$

where P_n —load of the tribological system amounting to 1.00, 5.00 and 10.00 N; d_{oz} —the diameter of the wear trace created on the steel sheets subjected to the experiment.

An optical microscope was used to observe the wear trace size on the upper layer of the squared test sheets. The received data were subsequently used to define the tribology index (G_{oz}), i.e., the assessment of the wear characteristics of the grease mixture under test [43].

The structural evolution of the grease was studied with a Raman spectrometer. The Raman analysis was applied to monitor the structural transformation of the lubricants subjected to mechanical and heat loads.

The evaluation of the Raman data includes the assessment of the decay of the vibration modes in the region of 1440–1470 cm^{−1} and around 1300 cm^{−1}, which correspond to the oscillations resulting from the modifications after the wear tests in the area of bands typical of non-saturated materials. The Raman spectra were recorded with a Raman NRS 5100 confocal microspectrometer (Jasco Corporation, Tokyo, Japan) fitted with a 532.12 nm excitation laser and a CCD detector. The operating parameters of the spectrometer are as follows: diffraction grating: 600 lines/mm; laser power: 5.0 mW; numerical aperture: 40 µm; resolution: 13.72 cm^{−1}; objective magnification: 20×; and exposure time: 200 s. The calibration of the Raman instrument was performed using a silicon standard plate [44].

3. Results

The evolution of the wear behaviour of the tested lubricating materials monitored in tests performed on the MCR 102 was validated by analytical measurements based on data from Raman spectroscopy.

The Raman spectral data of the plant lubricants before mechanical loading and after loading were compared in order to monitor the evolution of the surface structure of the investigated lubricants. In the Raman spectrogram of the initial vegetable lubricants, peaks were observed from plant oil and other components. The spectrum peak at 1306 cm^{-1} for the starting lubricant was caused by the vibration of the hydrocarbon groups present in the oil [8]. The occurrence of regions related to methylene and methyl chains was noted, together with regions typical of non-saturated chains (3010 , 1656 , 1444 and 1268 cm^{-1}). Furthermore, when studying the Raman spectrograms received from the lubricants after the fatigue experiment, the occurrence of groups at 802 cm^{-1} was found, which are representative of the stretching oscillations of the CH groups and the molecular oscillations of the carbon chain of the base oil (the dispersion mode) [33,45]. It was noted that the applied method made it possible to monitor the occurrence of modifications in the structure of the assessed greases when subjected to mechanical loads [18,46].

The performed tribological and rheological experiments for the studied lubricants were performed in three replicates and the obtained data are the means of three tests. The values were analysed using Q-Dixon statistical procedures.

3.1. The Wear and Friction Tests

The tribological properties of the studied vegetable greases were obtained [45], and then the evaluated experimental tribological values of the tested greases were assessed. The results are shown in Figure 1 and Table 2.

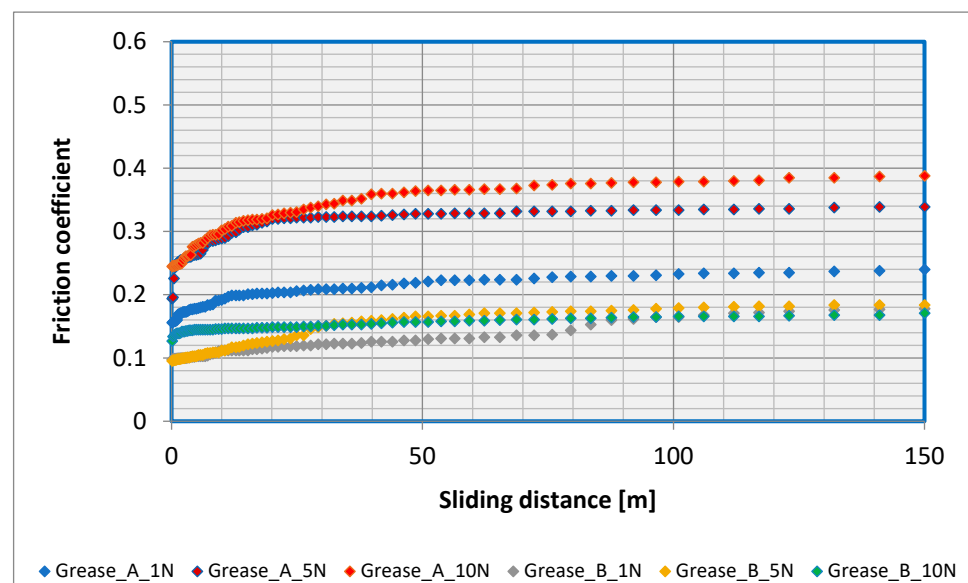


Figure 1. The correlation results between the coefficient of friction and the sliding distance of plant lubricants.

Table 2. The tribological characteristics of the studied lubricants.

The Studied Greases	The Limiting Load of Wear G_{oz} [N/mm ²]	The Mean Friction Factor	The Mean Dynamic Viscosity [Pa * s]
Grease A_1 N	411.34 ± 28.79	0.201 ± 0.012	1.973 ± 0.158
Grease A_5 N	374.73 ± 26.23	0.298 ± 0.018	2.237 ± 0.178
Grease A_10 N	311.43 ± 21.80	0.321 ± 0.019	2.713 ± 0.217
Grease B_1 N	542.81 ± 37.99	0.122 ± 0.009	0.878 ± 0.070
Grease B_5 N	513.12 ± 35.92	0.135 ± 0.008	1.123 ± 0.089
Grease B_10 N	497.23 ± 34.81	0.151 ± 0.009	1.474 ± 0.118

The tests performed on the lubricity behaviour of the vegetable greases produced showed that the modifier has a significant influence on the variation in the values of the friction factor [47,48], as well as on the wear stability of the tribosystem of the produced lubricants in comparison with the mixtures with different oil-dispersing systems [49] and with various modifying agents [50]. For all studied lubricating greases, stable values of the coefficient of friction were observed after the first increase step. There were no significant fluctuations in this parameter over time. When measured at a tribological system load of 1 N, the value of the friction coefficient was in the interval of 0.17–0.22.

As the load on the tribological system increased to 5 N, the friction coefficient changed to 0.26–0.31, while the experiment performed at a 10 N load indicated that the friction coefficient was larger than at smaller loads, so the value of the indicator describing the degree of wear protection was substantially decreased. The evolution of the viscosity of the studied lubricants was also assessed when performing the tribological experiments by increasing the stress levels of the tribology equipment. An improvement in the dynamic viscosity of the vegetable lubricant mixtures without the modifier was noted as the tribological load was progressively increased.

In the case of the lubricating composition containing 1.5% of a modifier called stratified silicate, the values of the friction coefficient were not as stable. The lower values of this factor were observed in relation to Grease A, which confirms the effectiveness of the applied modifier. The variation in the friction factor for Grease B at a load of 1 N of the tribological apparatus is in the range of 0.09–0.14. Increasing the load of the tribological friction junction to 5 N resulted in a significant growth of the friction factor to the level of 0.11–0.15 and, consequently, in a reduction in the G_{oz} factor, which characterises the degree of lubricating properties of the tested grease under test. The greater value of the G_{oz} parameter was associated with an increase in the dynamic viscosity of the tested lubricant, i.e., an undesirable phenomenon in the workings of the tribological system. The instability of the values of this wear index for this kind of lubricant may be related to the uneven distribution of the additive in the structure of the grease.

Experiments performed with a tribological load of 10 N for this grease showed a continued growth in the friction factor and dynamic viscosity in relation to the values recorded with smaller tribological stresses. The factor describing the degree of wear protection was reduced in comparison with the data recorded for the 1 N and 5 N stresses.

Nevertheless, there is a significant reduction in the friction value and an improvement in the G_{oz} index, together with a reduction in the dynamic viscosity, for the stratified silicate-modified mixture compared with compositions not containing this additive.

Investigations on the wear and friction behaviour of the prepared greases confirmed that the addition of the modified additive changed the ability of the assessed lubricants to protect the tribosystem against wear. The introduction of montmorillonite into the lubricant structure had a positive effect on its tribological properties. The degree of stabilisation of the interfacial system is indicated by the value of the wear parameter (G_{oz}). The higher the level of this index, the more stable the film and the lower the rate of wear. It was found that the use of montmorillonite as a modifying agent in the lubricating grease blends

investigated had a positive effect on the lubricating properties of the tested blends. In practice, the lubricants containing stratified silicate showed higher tribological stability against wear than those not containing the modifier when the tribosystem was submitted to a constant load. The amount of the modifier in the grease structure affects the level of its tribological properties, as the above tribological test data show. On the basis of the obtained experimental data, it has been established that the additive used affects the growth of the factors describing the tribological characteristics of the investigated lubricants [51]. The size of the changes in the lubricating properties of the tested greases will depend not only on the type of chemical configuration of the solid/liquid components and of the applied modifying agent, but also on the relation between the various ingredients of the lubricating grease mixture [52]. The chemical nature of the applied additive leads to the assumption that the lubricating performance of the tested lubricants is a consequence of the properties of the modifier's physicochemical particles, i.e., the dispersed phase [53] and the liquid dispersion phase [54].

Based on this theory, it can be assumed that there is a relationship between the interactions of the dispersant with the dispersive phase and the modified agent at the microscopic scale [55] and the operational effectiveness of the grease [56]. The application of a layered silicate as an additive was selected due to its ability to create strong films on interaction surfaces and adhere to metallic surfaces [57].

This lubricating grease contains active agents that provide micro-scale lubrication of the cooperating areas with no film formation. The powerful action of the nano-scale modifier is due to the incorporation of active components such as phosphorus and nitrogen into the lubricant matrix, thus increasing the wear protection of the investigated lubricating grease [58]. The introduction of this substance into the lubricant structure generates a powerful plastification effect on the contact surface, which is associated with a significant reduction in the stresses generated by the impact of the irregularity of the contact surface and increases the degree of the lubricity of the lubricant [59].

3.2. Raman Spectroscopy for the Study of Structural Change

The changes in the lubricant structure were studied by means of a Raman spectrometer. Using Raman spectroscopy, the qualitative evolution of the studied lubricants was observed in relation to the combination of mechanical and thermal stress. The interpretation of the Raman spectra involves the assessment of the decrease in bands in the region of 1440–1470 cm^{-1} and around 1300 cm^{-1} , which correspond to the oscillations resulting from the modifications after the tribological experiments in the group of bands typical of non-saturated systems.

The Raman spectra of the unmodified plant lubricant and the montmorillonite-modified lubricant were compared to monitor the evolution of the molecular structure of the studied lubricants (Figure 2a). The spectrum of montmorillonite is shown in Figure 2b. In the Raman data of the starting lubricant, bands of plant oil and other ingredients were observed. The peak at 1306 cm^{-1} for the starting lubricant was due to twist vibrations of the hydrocarbon chains existing in the base oil. The occurrence of peaks related to methylene and methyl groups was observed, similar to peaks typical of non-saturated groups (3010, 1656, 1444 and 1268 cm^{-1}).

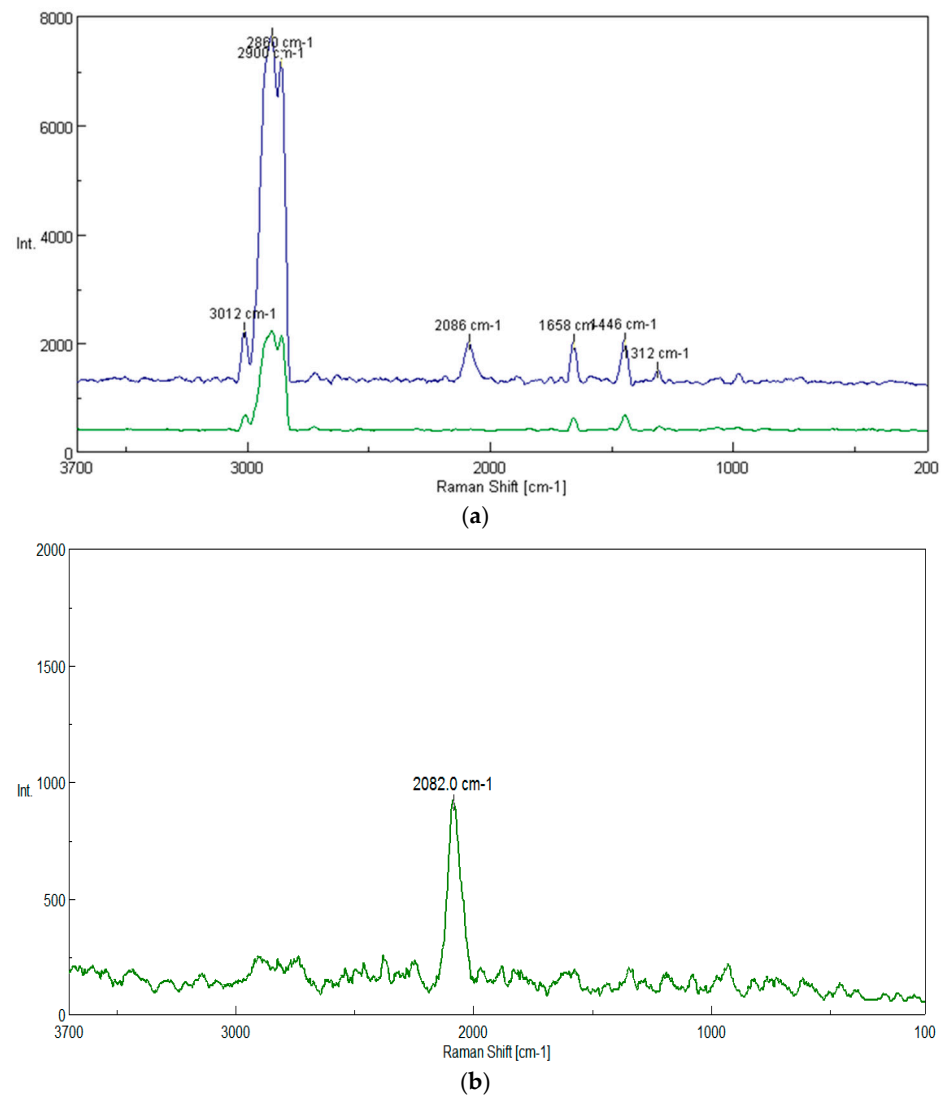


Figure 2. (a) The Raman spectra for lubricating grease without additive—Grease_A (green curve)—and for lubricating grease modified with montmorillonite—Grease_B (blue curve). (b) The Raman spectra of montmorillonite—the additive for vegetable lubricating grease (green curve).

In the analysis of the received Raman spectra of the lubricating greases prepared from stratified silicate, the presence of characteristic peaks was noticed at 802 cm^{-1} , corresponding to the stretching vibrations of the CH_2 chains and to the covalency oscillations of the carbon atom of the base oil (the dispersion layer), while the peaks at 710 cm^{-1} correspond to the stretching vibrations of the SiO_4 chain, the peaks at 2730 cm^{-1} correspond to the stretching vibrations of the structural OH chains in stratified silicate, and the peaks at 200 cm^{-1} correspond to the stretching vibrations of the AlO_6 group. It was concluded that the applied method made it possible to monitor the conformational evolution of the investigated lubricating greases.

For lubricating greases submitted to tribological tests, Raman spectroscopy was carried out after the tribological tests. The impact of the used additive and the stress of the tribosystem on the structure of the investigated lubricants is presented in Figures 3 and 4.

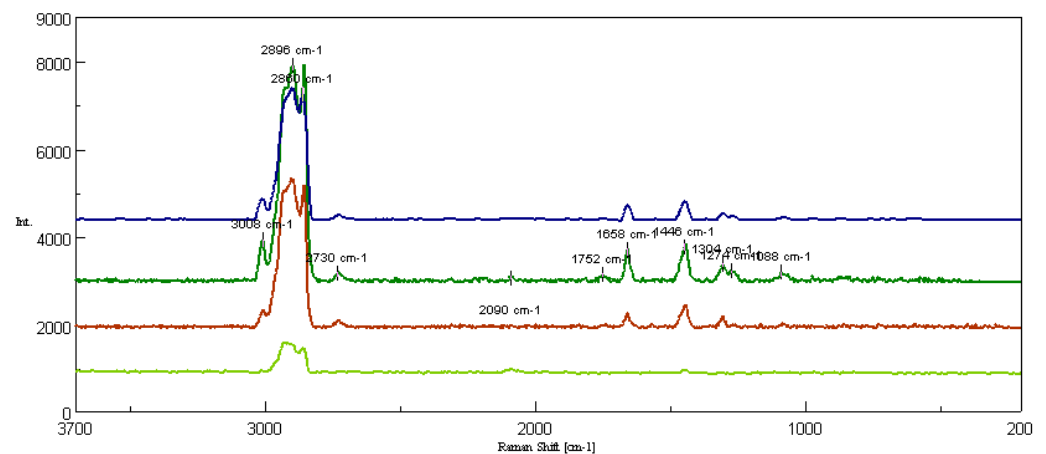


Figure 3. The Raman scans of the investigated lubricants after tribology testing within the frequency range of the Raman peak at $3700\text{--}200\text{ cm}^{-1}$: the lubricant with the addition of hydrogenated soap thickener (A, green), with the addition of hydrogenated soap thickener after tribological test at 1 N load of tribosystem (A_1 N, brown), thickened with of lithium stearate after tribological test at 5 N load of tribosystem (A_5 N, dark green) and thickened of lithium stearate after tribological test at 10 N load of tribosystem (A_10 N, blue).

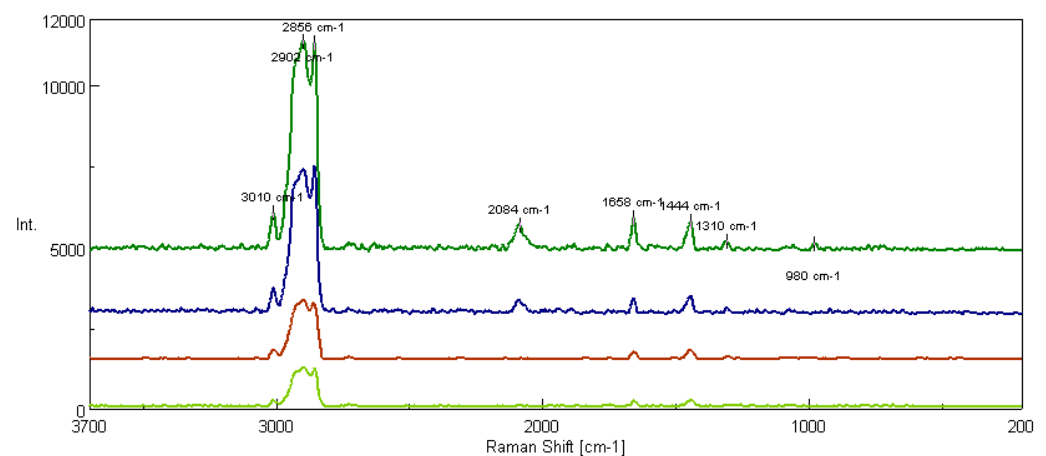


Figure 4. The Raman scans of the investigated lubricants after tribology testing within the frequency range of the Raman peak at $3700\text{--}200\text{ cm}^{-1}$: the lubricants with the addition of hydrogenated soap thickener and with the addition of phyllosilicate (B, green), with the addition of hydrogenated soap thickener after tribological test at 1 N load of tribosystem (B_1 N, brown), thickened with lithium stearate and modified with montmorillonite additive after tribological test at 5 N load of tribosystem (B_5 N, dark green) and thickened with lithium stearate and modified with montmorillonite additive after tribological test at 10 N load of tribosystem (B_10 N, blue).

According to tribological tests of plant lubricating greases with stratified silicate modifier [60], the occurrence of organometallic compounds in the surface material has been the topic of research, and these signals show the presence of organometallic materials on the steel ball's top layer.

Studies of lubricants after tribological experiments performed at different tribological system stresses resulted in significant changes in the chemical structure of the lubricating greases. The greater the stress on the tribological system, the lower the stability of the chemical structure of the tested lubricating greases. A substantial decomposition of the modifier takes place, resulting in the elimination of the band derived from the modifier. As the tribological stress was higher, the strength and size of the peaks derived from the base oil were reduced.

The environment in the tribological system, i.e., the stress on the tribological system and the temperature, are crucial in altering the chemical structure of the dispersion phase. Variations in the dynamic viscosity of the dispersion phase have also been monitored, and this behavioural pattern has helped to identify the tribological mechanisms that have a strong impact on the structural modifications occurring in the tribological tests.

The higher stress on the tribological regime during the test causes the strength of the peaks in the Raman spectra to decrease, which is relevant to the state of the dispersion phase and has a major effect on the changes in the useful characteristics of the investigated lubricating materials.

The appearance of oxidation compounds may be interpreted in terms of the excellent anti-wear characteristics of the lubricants, as indicated by the size of the wear scar. The signals at 3010 and 3008 cm^{-1} were assigned to the hydrocarbon group (-CH), which contributes to the formation of both internal and external hydrogen bonds in the dispersion phase chain. The signals at 2902, 2895, 2860 and 2856 cm^{-1} are the peaks resulting from the overlapping of the signals typical of the symmetric and asymmetric vibrations of the -CH₃ and -CH₂- chains derived from the aliphatic carbon chain of the plant components of the analysed lubricant.

The band at 2730 cm^{-1} represents stretching vibrations of the hydroxyl functional species of the stratified silicate. In the spectra modified by the addition of montmorillonite, especially after tribological tests at 5 N and 10 N loading, peaks at 2080–2090 cm^{-1} became apparent, which originate from the stretching vibrations characteristic of the Si-O group in montmorillonite. The signal at 1752 cm^{-1} may be caused by vibrations of the carbon oxide group, which are typical of molecules such as oligomers. The signal at 1658 cm^{-1} is probably associated with the elongation motions of -C=O- that are characteristic of aerobic oxidation reaction compounds.

These changes are due to the interaction of low-energy electrons in the frictional contact zone with acids or esters, forming carboxylate anions. However, the regions at 1444 and 1446 cm^{-1} are due to the oscillations of ester groups or to the symmetrical and asymmetrical transformations of the -C=C-H group(s) found in the hydrocarbon sequence of the vegetable oil base. The peaks at 1310, 1304 and 1274 cm^{-1} observed in the modified montmorillonite additive are characteristic of the structural vibrations of the -Al=O group present in the montmorillonite. The region at 1088 cm^{-1} is typical of the distortion mode of the carbon chain in the organic solvent and the peak at 980 cm^{-1} is characteristic of the skeletal distortion mode of the oxysilicone group in the montmorillonite.

The properties of lubricants are determined by the base oil, which usually accounts for more than 80% of the weight of the grease. There are many scientific publications in which scientists evaluate the behaviour of oils under the influence of various conditions, such as temperature or load. Raman spectroscopy provides an assessment of the chemical structure based on the analysis of the characteristic peaks of the Raman spectrum.

Under the influence of mechanical forces, including those prevailing in the tribological tests, the oil base undergoes changes in its chemical structure [61]. Under constantly increasing temperature, the thermal stability of the vegetable oil base is constantly changing, leading to its degradation, as confirmed by the research described in this publication [62]. The analysis of changes in the degree of unsaturation of the unsaturated fatty acids in vegetable oils is the basic method of monitoring the quality of vegetable oils and, therefore, vegetable greases [63,64].

The intensity level of the characteristic bands (1658 cm^{-1} and 1440 cm^{-1}) in the tested vegetable greases with linseed oil as the main component of the composition was changed, which proves that the mechanical forces to which the grease was subjected during the extortions in the tribological system had a significant importance for the evaluation quality of the grease after the tribological tests and may indicate unfavourable changes in the properties of the grease and its further suitability for lubrication purposes. The obtained results and their analysis, as well as the results presented by other scientists [65,66], show

that Raman spectroscopy is a fast and effective technique for assessing the quality of vegetable lubricants.

Raman spectroscopy is a technique that enables the evaluation of changes in the chemical composition of vegetable oils by analysing the degree of unsaturation of fatty acids in vegetable oils, which makes it a very good diagnostic and quality control method for lubricants based on vegetable oils [63–65], including linseed oil, which was used by the author of this publication to prepare vegetable lubricant compositions that were subjected to tribological tests. On the basis of the publications of other authors, it was possible to obtain information allowing the quality of vegetable lubricants subjected to tribological tests to be evaluated.

The tests carried out showed that, as a result of the tribological effects, some components are oxidised, producing organic and oxygenated substances that form an internal layer on the metal surface, counteracting the anti-wear effect of the lubricant combination. Other substances form intimate bonds with the top layer, improving its resistance to scuffing and sliding. The interpretation of the test data, together with the observation of the change in the structure of the grease, makes it possible to see that lubricity is not only the effect of the applied additive, while the effect of the oxide and the tribochemistry react with the working area of the tribological system. The effect of the additive is caused by the formation (at the time of mechanical stress) of a small film closely associated with the working surface and characterised through low shear stability, good elasticity and high tolerance to tribological processes. As a consequence of the heat decomposition of the dispersed phase and additive, thermal processes cause a chemical reaction between the components of the matrix and the lubricant. The resulting combinations migrate into the working zones of the tribosystem and create antifriction films. The interfaces are created by the transformation of grease components into radical oxygenated polar particles and their consequent exposure to metal oxides and metals. The thermal reactions lead to the breakdown of hydrogen bonds in the oil, resulting in the formation of organic polydisperse products [63,66]. The end result of the reactions in the tribological zone is the formation of barriers on the tribological system surface.

4. Conclusions

The data from the research on the impact of the modifier and load on the tribosystem for plant lubricants indicated the following:

- The modification of the lubricity life influenced the studied lubricants due to the specific chemistry of the solid phase, the liquid phase and the applied additive, as well as the interdependence between the components of the grease mixture;
- The tribochemical reactants between the components of the lubricant mixture and the tribological film had a major impact on the tribological characteristics of the studied lubricants;
- The extremely effective activity of the phyllosilicate is due to the unique structure of the additive used, which contains substances capable of increasing the lubricity of selected greases;
- In the upper zone of the steel tribological scar, according to the wear and friction tests with vegetable lubricants containing phyllosilicate, the presence of organic and inorganic substances was detected, which modify the tribological effect of greases on the tribological system;
- The occurrence of oxidation compounds can be attributed to the excellent anti-wear characteristics of the lubricants, as measured by the size of the wear marks;
- The interpretation of the results of the friction and wear studies, together with the evaluation of the modification of the structure of the lubricant after the friction and wear studies, shows that the lubricity is a function not only of the addition of the modifier, but of oxidation compounds that protect the tribological system;
- The action of the additive used is based on the mechanism that assumes that, as a consequence of the interference of low-energy photons with the acid or ester particles

adsorbed in the friction contact zone, carboxylate anions are formed, which react with the contact area of the tribosystem to create wear-protective boundary layers;

- The mechanism of the formation of boundary layers in lubricating conditions is based on the oxidation reactions of the composition ingredients to polar organic species and then to interactions of functional groups of these species with atoms or metal oxides of the working tribosystem surface.

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