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Application of chokeberry biochar as a modified additive to the vegetable lubricants: the tribological and rheological properties

Rafal Kozdrach✉ & Pawel Radulski

Effect of modifying a vegetable grease with different amounts of chokeberry biocarbon on its tribological and rheological properties. The aim of the research was to investigate the effect of the incorporation of biochar derived from the pyrolysis of chokeberry biomass at 500 and 700 °C respectively, in lubricants formulated with vegetable oil, on their functional characteristics in terms of tribology and rheology. Fumed silicon dioxide was utilized as a thickening agent, ensuring the production of lubricants with a consistency class of II. The biochar was introduced into the lubricating formulations in concentrations of 1, 3, and 5%. A rapeseed-based grease with commercial activated carbon served as the reference sample. The research focused on assessing how this innovative additive influenced both the tribological and rheological behaviors of the resulting lubricants. The study evaluated the effects of chokeberry-derived biochar on the wear resistance and scuffing prevention properties of the vegetable-based greases. Additionally, the biochar's influence on various rheological parameters such as flow curves, viscosity profiles, hysteresis loops, and viscoelastic characteristics was analyzed. Results demonstrated that the biochar additive considerably enhanced the tribological and rheological performance of the tested rapeseed-based grease.

Properties of greases will be determined based on their formulation and production technology, with factors such as the choice of additives playing a significant role[1–3]. The functional properties of a lubricant are influenced not only by the presence of additives but also by the manner in which they are incorporated into the structure of the grease[4,5]. Introducing additives into grease formulations can present various technological challenges, as additive particles may adsorb onto the thickener's surface, potentially diminishing the performance of the component and even reducing the grease's overall stability[6–8]. The use of suitable, carefully selected additives in proper amounts is necessary to enhance the functional properties of the grease.

Lubricating greases tend to mix easily with dry lubricant agents, that help to decrease the coefficient of friction and increase the friction point's ability to withstand load and seizure. In demanding working conditions, these additives improve the performance of the lubricant by providing better protection against aggressive agents as well as increased thermal stability[9,10]. However, there is a growing trend towards developing more environmentally friendly lubricants without sacrificing their performance. In light of the increasing focus on environmental protection, lubricants should be free from toxic and dangerous substances in their composition[5,7,9].

In 2019, Poland was the largest producer of chokeberries and exporter of semi-finished products in the world. The national potential was then 60–70% entire world production. The area of chokeberry cultivation was approximately 4000 hectares, and the harvest ranged from 40,000 to 60,000 tons per year, which resulted in the problem of post-harvest waste management[11].

The solution of this problem may be pyrolysis-the process of heating biomass to a high temperature without oxygen in the present of inert gas. The resulting biochar can be used as an addition to grease to improve its tribological and rheological properties[12]. The produced carbonizate can be used as a replacement for activated carbon, which is produced from hard coal in the pyrolysis process[11–13]. There are different ways of working the pyrolysis cycle, which affects the production of syngas, bio-oil and also carbon residues. The pyrolysis process occurs at 400–1000 °C. Only the solid fraction (vegetable carbon) is recovered. Conventional or slow

Bioeconomy and Ecoinnovation Department, Lukasiewicz Research Network – Institute for Sustainable Technologies, 26-600 Radom, Poland. ✉email: rafal.kozdrach@itee.lukasiewicz.gov.pl

pyrolysis occurs at moderate temperatures around 500 °C at a rate of a few to several tens of degrees per minute, resulting in about three fractions in equal proportions. Fast pyrolysis occurs at moderately low temperatures (500–650 °C), increasing the production of the liquid fraction to 70–80% by weight of the biomass; this type of pyrolysis produces.

20% gas, 20% solid fraction (biochar) and 60% liquid fraction (bio-oil). The rate of temperature increase in this type of pyrolysis is 10–200 (°C/s). Flash pyrolysis is carried out at temperatures of 800–1000 °C and favours the production of a gas fraction (yields up to 80%) with a temperature rise rate of over 1000 (°C/s)[6].

The present study used a type of slow pyrolysis called cascade pyrolysis. By carrying out the process in this way, much more of the solid fraction can be obtained. Temperatures of 500 °C and 700 °C were used for the pyrolysis process. Below 500 °C, the resulting carbonate does not have a biochar structure, as the peak responsible for the disordered structure in the Raman spectrum is absent and only the G peak is present, indicating an ordered structure. Above 750 °C, commercial graphite lubricant additives are produced, meaning that pyrolysis below this temperature is more energetically viable and biochars with better lubricating properties can be obtained[14,15].

What is new on the market, however, is biochar, which in recent years has become a very important product that many believe could be one of the main factors in the sustainable development of our civilisation[16,17].

Biochar is a product made mainly from biomass residues from sawmills, forestry, fruit and vegetable processing and agricultural production. It is also sometimes produced from manure and residues from poultry production and palm oil pressing. Separated biodegradable municipal waste or sewage sludge is also used in its production[18–20].

It should also be mentioned that it is also used in the construction industry-as an additive in external insulation plasters and internal plasters to stabilise the indoor climate. It is also used in the metallurgy, clothing, food, electronics and various light industries: from packaging to cosmetics, and in the manufacture of lubricants as an additive that effectively modifies the tribological and rheological properties of plastic lubricants[17,21].

The specific characteristics of biochar depend on the type of biomass used to produce it and the conditions under which it is produced, and these determine its suitability for a particular biochar application. Biomass subjected to thermal treatment at different temperatures (400–800 °C) optimise mechanical and thermal behaviour of produced biochar[18,20,22].

Biochar production process at 600 °C results in a persistent form of biochar, whereas biochar produced at 400 °C retains volatile components and non-persistent compounds.Biochar from coalification processes carried out at relatively low temperatures has a high volatile content, contains readily degradable substances and can promote plant growth[20,23].

The structure of biochar produced at high temperatures is distinguished by high molecular weight due to the existence of aromatic carboxylic acids, thus increasing its absorptive capacity (bioremediation properties). Additionally, due to their stable composition, biochars are well-suited for carbon sequestration[24–26].

Shredded biochar is characterized by good sorption properties and a long decomposition period, so it can be used both to loosen heavy soils and improve the structure of sandy soils. The ground version is used as an additive in cosmetology. In this field, it is used, among others, thanks to its ability to remove unpleasant odors. Therefore, it works similarly to a deodorant. Increasingly, biochar is also being used effectively to increase the functional characteristics of lubricants. Biochar in pellet form can also be used to purify water and air and absorb odors[16,19,25].

In this study, chokeberry was selected for pyrolysis to create biochar for technological purposes, particularly for use in producing eco-friendly lubricants. In fact, Poland has become a leading producer of chokeberry, renowned for its high quality raw material, which is widely used for pharmaceutical and beauty products. Chokeberry has been primarily targeted for use in nutritional supplements and anti-aging cosmetics to support vision and boost the immune system[27–29].

In Poland, no special declaration is required for the legal cultivation of chokeberries for personal use or research purposes if the chokeberries are grown on a private plot and not intended for sale on a wider scale. Chokeberry is a crop that can be grown without the need for special permits or licences, as long as general land ownership and environmental regulations are respected.

In the context of scientific research, the statement that the chokeberry is privately grown is sufficient to meet the formal requirements.

Chokeberry is highly regarded for its wealth of active compounds with strong antioxidant properties. Among its bioflavonoids, the most notable are anthocyanins, flavonoids (such as quercetin and rutin), catechins, and leucocyanidins. These compounds serve various roles, including functioning as pigments that give the fruit its characteristic deep blue color. However, in medicine, their antioxidant activity is of greater significance—they help neutralize free radicals within the body. Chokeberry is also rich in essential vitamins, including B2, B3, B9 (folic acid), C, and E. These compounds have potent antioxidant capabilities, protecting cells from oxidative stress and reinforcing the body's defense mechanisms against free radical damage. This protective action helps slow the aging process and encourages cellular repair. Due to these powerful antioxidant properties, chokeberry-derived biochar can serve as an excellent additive to lubricants, particularly vegetable-based ones, significantly enhancing their tribological, rheological, and physicochemical characteristics[30–35].

In addition to its bioflavonoid content, chokeberry is also a wealthy supplier to the diet of some of the most important minerals, as well as important micro- and macronutrients such as calcium, magnesium, iron, potassium, phosphorus, sodium and zinc. These nutrients play a crucial role in minimizing wear and reducing friction in lubricants during prolonged use in frictional systems. They have the potential to greatly extend the operational life of lubricants and improve the degradation resistance of the plant-based oil components. Moreover, the biochar produced from chokeberry could offer new opportunities for enhancing the sustainability and performance of ecological lubricants, making it a valuable material for the future of green technology[36–41].

Increasingly, biochar produced by pyrolysis of waste biomass is being used as an additive to lubricants to improve their tribological and rheological properties. In work[42], the authors used biochar from sesame seeds as an additive to PAO oil to significantly improve its anti-friction and anti-wear properties. In paper[43], the possibility of using plant-derived biochar as an additive to polyurea lubricants was investigated; the applied additive influences the increase of parameters characterizing the anti-scuffing and anti-wear properties of the tested lubricant. Article[44] presents results of the application of biochar additives on tribological and rheological properties of lubricating oils. Paper[45] presents the results of using biochar from waste rice straw as an additive to plastic lubricants improving the tribological characteristics of the tested grease. Articles [14,15] describe the results of the use of biochar from vegetable waste as additives to lubricants, based on the results, it was concluded that the introduced additives improve the tribological characteristics in relation to the base lubricants.

Several important gaps have been noted in previous research on modified vegetable lubricants, which formed the basis of this paper. While much work focuses on the use of traditional additives such as graphite, molybdenum disulphide or commercial activated carbon, there is a lack of in-depth research on the use of biochar as an innovative modifying agent. In particular, there is a lack of comparative studies that assess the differences in tribological and rheological parameters between biochar produced during pyrolysis under different temperature and inert gas flow conditions and conventional lubricating additives.

An issue that has also not yet been sufficiently investigated is the effect of different biomass sources and pyrolysis process temperatures on lubricating properties. Many studies are limited to the use of single types of biochar, without considering specific raw materials such as, among others, chokeberry waste, which have unique physical and chemical properties.

In the context of increasing demand for green lubricants, there is a need to develop materials that combine high performance with low environmental impact. The use of biochar from chokeberries, a raw material rich in antioxidant compounds and minerals, represents an innovative approach to improve both the tribological and rheological properties of vegetable-based lubricants. Previous research has not considered the possibility of replacing activated carbon with biochar derived from waste biomass in a systematic way.

The aim of this study was to fill these gaps by assessing the effects of biochar produced from chokeberries on the tribological and rheological properties of vegetable lubricants. Particular emphasis was placed on evaluating the effects of modifying lubricants with biochar produced during the pyrolysis process carried out at different temperatures (500 and 700 °C), thus identifying the optimal process conditions. The results show that chokeberry biochar used as a lubricating additive not only matches the properties of commercial activated carbon, but in some cases exceeds them, especially in the context of protection against wear and seizure, and improves the rheological properties of vegetable greases.

Experimental work

Materials

A number of exemplary lubricants have been formulated containing natural ingredients, consisting of a liquid phase and a solid solution. Rapeseed oil was used as the dispersing agent[46–54], while the Aerosil® 300 was used as the solid agent[55–64]. These lubricants were further enhanced by incorporating varying amounts of chokeberry-derived biochar, which was produced via pyrolysis at temperatures of 500 and 700 °C. Temperatures of 500 and 700 °C were chosen as representative of the different types of pyrolysis and responsible for obtaining the optimal properties of the biochar produced.

A temperature of 500 °C is typical of conventional, slow pyrolysis, allowing the production of biochar with the desired physicochemical characteristics and an appropriate yield/quality ratio. A temperature of 700 °C, on the other hand, represents more advanced carbonisation, which allows the structure and properties of the biochar to be modified to suit specific applications.

Below the 500 °C, the formation of a structure corresponding to lubricating additives does not occur, as confirmed by results carried out using Raman spectroscopy. Such properties would not meet the objectives of the experiment and would significantly affect the quality of the test results.

In addition, above 700 °C, the amount of biochar obtained is very small, making the process economically unviable, and most of the biomass is converted into liquid and gaseous fractions, which were not the target of the study. The chosen temperatures of 500 and 700 °C therefore provide the optimum compromise between efficiency, structure of the resulting material and its properties, as envisaged in the experiment.

These selected components have been used to develop second class consistency greases. The introduction of a modifying additive into the chemical structure of lubricating greases causes a significant improvement in the tribological and rheological properties of lubricants[65–81]. Biochar additive was introduced into the structure of the grease at concentrations with 1, 3 and 5% w/w.

The additive concentrations of 1, 3 and 5% were chosen to represent a wide range of possible applications of biochar as an additive. The 1% concentration corresponds to the minimum amount that can already have an effect on the properties of the modified vegetable grease, while 3% and 5% allow the effect of higher additive contents on tribological and rheological test results to be assessed. This range is in line with the literature, where similar concentrations are used in tests of lubricating greases modified with commercial additives.

In addition, it is assumed that above a certain limit (usually 5%) the substance used ceases to be considered an additive and starts to act as a lubricant thickener. The upper threshold chosen—5% -therefore preserves the status of biochar as an additive, which was in line with the experimental assumptions. This allows the study to focus on the effect of biochar as an additive rather than as a thickener. This choice of the concentration range of the additive used allows a comprehensive analysis of the effects at both low and higher concentrations, without crossing a boundary that would change the nature of the system studied.

The compositions were labeled as follows: R-0 (base grease), R-0 + 1% A500 (modified with 1% biochar from chokeberry produced via pyrolysis at 500 °C), R-0 + 3% A500 (modified with 3% biochar from chokeberry produced via pyrolysis at 500 °C), R-0 + 5% A500 (modified with 5% biochar from chokeberry produced via pyrolysis at 500 °C), R-0 + 1% A700 (modified with 1% biochar from chokeberry produced via pyrolysis at 700 °C), R-0 + 3% A700 (modified with 3% biochar from chokeberry produced via pyrolysis at 700 °C), R-0 + 5% A700 (modified with 5% biochar from chokeberry produced via pyrolysis at 700 °C), and R-0 + 3% WA (modified with 3% activated carbon).

The choice of 3% commercial activated carbon as a reference sample is due to its widespread use in lubricant modification and its availability as a standard additive. The commercial activated carbon is widely used in the lubricant industry due to its well-known sorption properties and its ability to improve anti-wear and anti-scuffing properties, as well as rheological properties. Its use as a reference additive allowed the results obtained for the grease modified with chokeberry biochar to be compared with greases modified with other additives, increasing the reliability and comparative value of the study.

In addition, the concentration of 3% of the additive in the grease was chosen because this is the average value used in research and industrial practice, which makes it possible to obtain clear effects of modifying characteristic tribological and rheological parameters without exceeding limit after which the additive could be treated as a thickener of the lubricating composition. The use of commercial activated carbon as a modifying additive made it possible to compare the effect of a novel additive in the form of chokeberry biochar with a well-established commercial additive such as activated carbon, while maintaining the consistency and uniformity of the experiment.

In the preliminary stage of the study, experiments were carried out to define the optimum level of additive used in the lubricating composition. Experiments were performed with levels ranging between 0.2 and 8% of modifier agent.

The concentration range of 0.2–8% for the modifying additive was chosen to take into account both minimum and maximum amounts of additives that can have a significant impact on the properties of the tested lubricants. The lower limit (0.2%) represents the minimum effective concentration that is often found in the literature. The upper limit (8%) was chosen to take into account the possible saturation with modifiers, above which further increases in the amount of additives are of no significant benefit and may even reduce the effectiveness of the lubricant in the tribosystem or significantly deteriorate the functional properties of the tested greases.

The formulated lubricants are then submitted to tribological & rheological tests. Information on the materials used is given in Table 1. The data were statistically analysed with t-Student tests.

A highly purified, refined rapeseed oil was utilized as the dispersing medium. This oil, characterized by its yellow–brown color and absence of free acids and organic particles, is odorless with very good physico-chemical properties. The rapeseed liquid was employed in various applications, including biofuel production, animal feed formulation, and the manufacturing of detergents, coatings, lacquers, pastes and bitumen dispersions. It has also been applied as a ingredient in the manufacture of plastic compounds, in flooring materials, as a lubricant to protect machinery in the food industry from wear and abrasion, and as a base oil for lubricants[46–51].

Hydrophilic colloidal silica, with particle sizes ranging from 7 to 40 nm, was utilized as the dispersed phase. It forms extended spatial networks where every Si atom is linked to four O atoms, while every O atom is linked with two Si atoms. The surface of silicon dioxide has added H atoms and OH functional groups. Thanks to its polar nature and van der Waals forces, it easily interacts with oil molecules. When modified with dimethyldichlorosilane, the tendency for silica particles to agglomerate is significantly reduced, facilitating their incorporation into the structure of the lubricant even under mild mixing conditions. This material boasts a high melting and boiling point, excellent chemical resistance, and non-toxicity—qualities particularly valuable in biodegradable lubricant formulations. It serves as an effective thickening agent and helps prevent sedimentation. The improved tribological properties of the lubricants are related to the high molecular size of silicon dioxide with its powerful interphase forces[56,58–64].

Methodology

Spectral characteristic of biochar from chokeberry

Chokeberry was subjected to pyrolysis at temperatures of 500 and 700 °C, using carbon dioxide as the inert gas. The carbonization process was conducted in cascade steps: Stage 1—temperature increase above 20 °C until 100 °C, for 5 min heat-up and 5 min hold time; Stage 2—increase in the operating range between 100 and 200 °C, also with 5-min heating period and a 5-min holding period; Stage 3—raising the operating heat level between 200 and 450 °C (500 °C for pyrolysis) or from 200 to 650 °C (for pyrolysis at 700 °C), with a 20-min heating time

Grease symbol	Type of base oil in lubricants	Kind of dispersed phase applied in lubricants	The type and amount of modifying additive
R-0	Vegetable	Modified silicon dioxide	Without modifier
R-0 + 1% A500	Vegetable	Modified silicon dioxide	1% of biochar from chokeberry produced in pyrolysis process in 500 °C
R-0 + 3% A500	Vegetable	Modified silicon dioxide	3% of biochar from chokeberry produced in pyrolysis process in 500 °C
R-0 + 5% A500	Vegetable	Modified silicon dioxide	5% of biochar from chokeberry produced in pyrolysis process in 500 °C
R-0 + 1% A700	Vegetable	Modified silicon dioxide	1% of biochar from chokeberry produced in pyrolysis process in 700 °C
R-0 + 3% A700	Vegetable	Modified silicon dioxide	3% of biochar from chokeberry produced in pyrolysis process in 700 °C
R-0 + 5% A700	Vegetable	Modified silicon dioxide	5% of biochar from chokeberry produced in pyrolysis process in 700 °C
R-0 + 3% WA	Vegetable	Modified silicon dioxide	3% of commercial active carbon

Table 1. Information about tested greases.

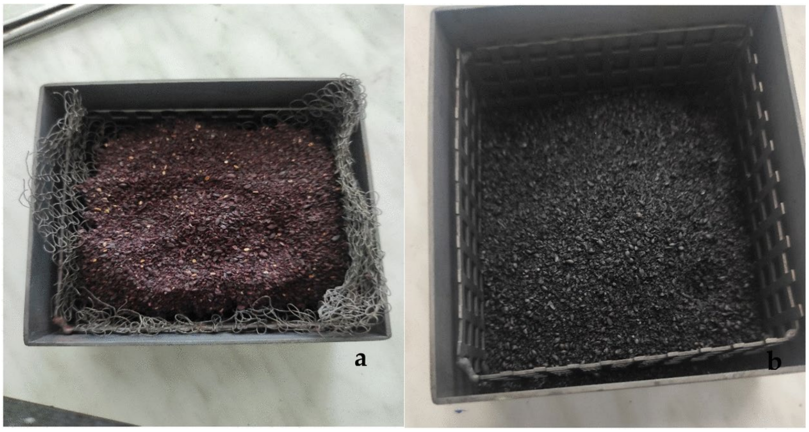

Fig. 1. (**a**) chokeberry before pyrolysis process, (**b**) biochar from chokeberry after pyrolysis process in 500 °C.

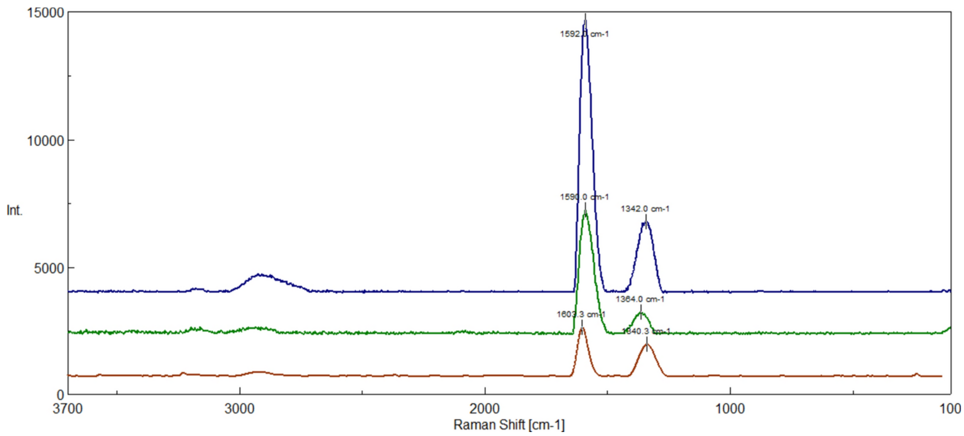

Fig. 2. The Raman spectra of biochar from chokeberry prepared in pyrolysis process in 500 °C (green line), 700 °C (blue line) and commercial active carbon (brown line).

and a 5-min holding period (Fig. 1); Stage 4—raising of heat level from 450 to 500 °C (for 500 °C pyrolysis) or from 650 to 700 °C (for the 700 °C pyrolysis), with a 5-min heating time and a 15-min holding period (Fig. 1). The pyrolysis was carried out in a Czylok chamber furnace, model FCF-V12RM, with an inert gas rate up to five litres per minute. After process, the sample was conditioned for 22 h using a sample volume of two litres per minute[14,15].

In biochars, the bands that occur in the 2000–1500 cm^{-1} range are also known as the G-band and are associated with stretching vibrations with E2g symmetry. They originate from the stretching vibrations of carbon bond pairs with sp^2 hybridisation, which occur in ring structures and correspond to ordered graphite-coal layers. On the other hand, the region between 1800 and 1600 cm^{-1} represents the GL region and indicates the presence of C = O carboxyl groups. The spectrum of biochar obtained from chokeberry at 500 and 700 °C (Fig. 2) contains a band at 1592 cm^{-1} associated with the appearance of ring structures and ordered carbon structure. The spectrum of chokeberry biochar contains a band at 1340 cm^{-1}, indicating a disordered structure and characterising the degree of amorphousness of the carbon structures. The bands occurring in the 1100–1500 cm^{-1} region are D1 defect bands corresponding to A1g symmetry. Bands occurring in this region are associated with planar defects, e.g. heteroatoms. The band in the 1400–1300 cm^{-1} region corresponds to the VR band and is indicative of the amorphous structure of carbon and the presence of metyl groups. In the products obtained, the presence of a D and G band was observed, indicating that the substances obtained are biochars[14,15,17,22,23].

Tribological tests

The tribological properties of the lubricants were assessed using a T-02 four-ball tester[50,54,78,80]. A Nikon MM-40 optical microscope[78,80] was employed to measure the dimensions of the wear scars on the surfaces of the test balls. These measurements were then used to calculate the LLW and LPS values, which evaluate the anti-wear and anti-scuffing characteristics of the lubricating greases tested in the tribological analysis. The lubricating performance of the tested compositions was determined by measuring the limiting load of wear (LLW), welding load (WL), scuffing load (SL), limiting load of scuffing (LLS), and limiting pressure of seizure (LPS) using the four-ball apparatus. The test elements were steel balls with a diameter of 12.7 mm, made of bearing-grade steel

H 15, featuring a surface roughness of Ra = 0.32 µm and hardness ranging between 60 and 65 HRC. The limiting load of wear (LLW) test was conducted under a tribosystem load of 392.4 N throughout the entire test duration of 3600 s, with a ball rotational speed of 500 rpm, following the conditions outlined in WTWT-94/MPS-025[82]. The welding load was measured according to the PN-76/C-04147 standard. This test involved running the four-ball assembly for 10 s under gradually increasing loads in the presence of the lubricant until the balls welded together. The lubricating properties under scuffing conditions, characterized by a continuously increasing load, were evaluated using a methodology developed by LRN-IST. The scuffing test was performed with a linearly increasing load from 0 to 7200 N over a duration of 18 s, at a spindle speed of 500 rpm and a load increment rate of 409 N/s. A sudden rise in frictional torque indicated the scuffing load (SL). The test was carried out until either a limiting frictional torque of 10 Nm or the maximum device load of 7200 N was reached, which defined the limiting load of scuffing (LLS). The final result was taken as the arithmetic mean of at least three measurements, with a deviation of no more than 10%. The Q-Dixon test was used for statistical analysis, with a 95% confidence level[83–85]. The limiting pressure of seizure (LPS) served as an indicator of the lubricant's anti-scuffing properties under severe scuffing conditions. The determination of this parameter consisted in calculating its value according to the formula:

$$LPS = 0,52 \cdot \mathrm{LLS}/d_{LW}^{2}$$

where LLS—limiting load of scuffing,

d_{LW}—the diameter of the defect formed on the steel balls used in the test.

The uncertainty in the determination of the tested parameters (limiting load of wear LLW, welding load WL, scuffing load SL, limiting load of scuffing LLS and limiting pressure of seizure LPS) were estimated on the basis of the accuracy class of the used measuring device. The correlation of the individual results of the tested values, i.e. LLW, WL, SL, LLS and LPS with the data set was verified using the Q-Dixon test at the 95% probability level[50,54,78,80,82–85].

Rheological tests

An Anton Paar MCR-101 air bearing rotational rheometer was utilized to assess the rheological properties of the tested lubricants. The rheometer was controlled, and the data were analyzed using Rheoplus software. The rheological characteristics of the formulations were determined by obtaining flow curves, viscosity curves, and viscoelastic properties, such as the dependence of G′ (storage modulus) and G″ (loss modulus) on frequency and strain. The tests employed a cone-plate measuring system, which required a zero-gap adjustment at the test temperature. This adjustment was performed automatically by the instrument. Once the zero gap was set, approximately 5 g of the sample was placed at the center of the plate to ensure even distribution over the cone surface as the cone was lowered into the measuring position. The tests were conducted at ambient temperature, set at 20 °C, for flow curves, hysteresis loops, and the evaluation of viscoelastic properties based on frequency or strain. For viscosity curves, the tests were performed across a broader temperature range from – 20 to 180 °C. The shear rate range for the tests was set between 0.01 and 100 s^{-1}. Flow curves, hysteresis loops, and viscosity curves were measured at a shear rate of 100 s^{-1}, while the viscoelastic properties were analyzed within a strain range of 0.01–100% and a frequency range of 0.01–100 Hz. Additionally, the intervals for data recording, such as the number of measurement points, total test duration, and data collection frequency, were defined[53,78,86]. To describe the flow curves of the lubricants, three primary rheological models that account for yield stress were applied: Bingham, Casson, and Herschel–Bulkley models[87–94]. The Bingham model describes the dependence of shear stress on shear rate in a linear way:

$$\tau = \tau_0 + \eta_p \cdot \gamma$$

where:

τ—shear stress (Pa),

η_p—the structural viscosity of lubricant (Pa s),

τ_0—yield stress (Pa),

γ—shear rate (s^{-1}).

The Herschel–Bulkley model is the simplest model for describing the flow curves of non-linear plastic-viscous fluids:

$$\tau = \tau_0 + k \cdot \gamma_n$$

where:

τ—shear stress (Pa),

τ_0—yield stress (Pa),

k—consistency index (Pa s^2),

γ—shear rate (s^{-1}),

n—flow index (–).

The Casson model, which also describes the flow curves of non-linear plastic-viscous fluids, is as follows:

$$\tau_{1/2} = \tau_0^{1/2} + (\eta\infty \cdot \gamma)$$

where:

τ—shear stress (Pa),

τ_0—yield stress (Pa),
$\eta\infty$—the structural viscosity of lubricant (Pa s),
γ—shear rate (s^{-1}).

Spectral tests
A confocal dispersive Raman NRS 5100 microspectrometer (Jasco Corporation, Japan) was employed to analyze the chemical composition of the lubricating greases. The spectrometer was equipped with a 532.12 nm excitation laser and a CCD detector. The instrument's specifications included a diffraction grating with 600 lines/mm, laser power of 5.2 mW, a numerical aperture of 4000 µm, a spectral range of 3700–100 cm^{-1}, and a resolution of 4.2 cm^{-1}. The lens provided a magnification of 20×, and the exposure time for each measurement was set to 200 s. The samples were placed on glass slides for analysis.

Selected properties of greases, such as anti-wear properties, hysteresis loop and other tribological and rheological parameters, were included in the study, as they are crucial for assessing the functionality of greases under actual working conditions. Tribological parameters, such as the limiting load of wear, determine the wear resistance of the lubricants, which translates into their increased durability and effectiveness under different temperature and load conditions of friction node.

In turn, the rheological properties, such as the hysteresis loop, determine the ability of a lubricant to maintain its structure under varying mechanical and thermal loads.

The study of these parameters makes it possible to assess the synergies between lubricant components, such as the biochar additive obtained from chokeberries, and their effect on improving the capacity and efficiency of the lubricating composition under study in comparison with lubricants produced on other oil bases and modified with different additives. For example, the hysteresis loop provides information on the thixotropic properties of the grease, which are important in dynamic working conditions, and the anti-wear properties confirm the ability of the grease modified with the biochar additive to form a protective layer on friction elements, which increases resistance to wear and seizure.

Thanks to a detailed analysis of these properties, it was possible to gain a better understanding of the mechanisms of action of the chokeberry biochar additive and to assess its potential applications in green greases. The studied parameters allowed a comprehensive assessment of the grease in terms of its effectiveness and the possibility of using it in conventional friction nodes instead of commercial greases, as they are characterised by much higher values of individual tribological and rheological parameters.

Statement regarding plant guidelines

The use of plant parts in the study complies with international, national, and/or institutional guidelines. The source origin of Abyssinian oil from *Crambe Abyssinica* seeds. The Rapessed seed oil was purchased in Poland.

Results and discussion

Tribological tests

The data of tribology investigations (aimed at anti-wear & anti-seize characteristics) for lubricants formulated with rapeseed liquid and with carbon bioadditive are presented as follows. The welding load WL of the tested lubricants is shown in Fig. 3.

The anti-seize characteristics at a progressively higher stress of the tribological system are related to the level of the modifier ingredient, that has a substantial impact on the resistance of the lubrication layer (Fig. 3). The

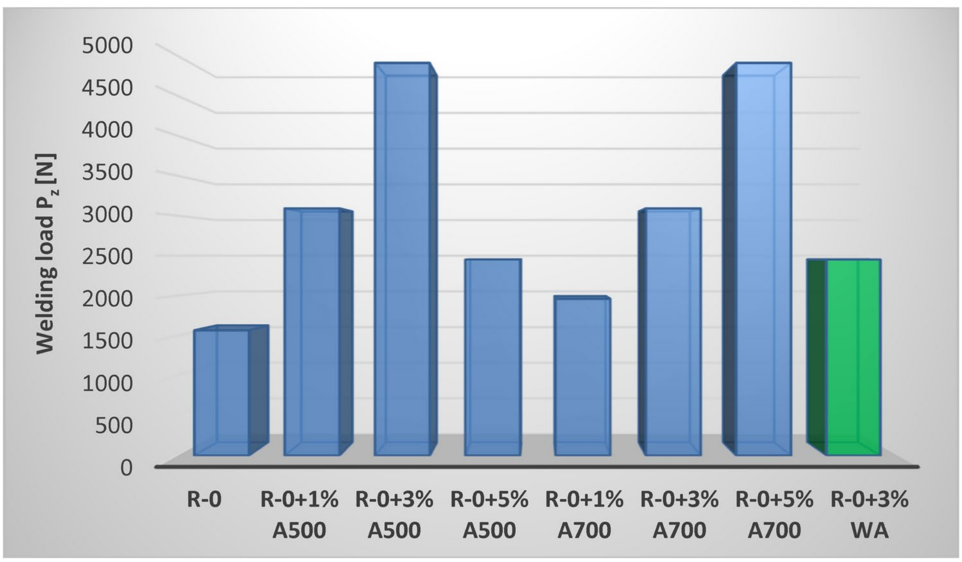

Fig. 3. The welding load of the tribological system with lubricants modified with different quantities of biochar agents.

best anti-seize behaviour was found for the lubricant containing vegetable base and modified with 3% biochar additive produced from chokeberry by pyrolysis at 500 °C (lubricant R-0 + 3% A500) and for the lubricant modified with 5% biochar additive produced from chokeberry at 700 °C—about 3 times higher value of welding load parameter than for the basic composition (lubricant R-0 without modified additive). The vegetable lubricating greases modified with smaller amounts of chokeberry biochar additive showed less favourable anti-stick properties, but more favourable than the basic grease. While the grease modified with activated carbon has weaker properties than those modified with 3–5% chokeberry biochar additive. These results confirmed that lubricating greases modified with a 3% chokeberry biochar additive produced by pyrolysis at 500 °C and a 5% additive produced at 700 °C had the most effective anti-scuffing properties.

The anti-seizure characteristics of the investigated lubricants were evaluated in the limiting pressure of seizure. The data of this parameter are shown in Fig. 4.

The anti-scuffing characteristics of the studied grease mixtures varied according to the results achieved for the scuffing limit pressure. According to the quantity of applied modifier additive, the anti-scuffing properties of evaluated lubricants vary significantly. The highest LPS value was characterized the composition modified of 3% additive from chokeberry at 500 °C (more than a four times improvement in LPS value in relation to base grease). It wasn't observe the improvement of the LPS parameter for the compositions modified with 1–3% of the chokeberry biochar additive produced at 700 °C and for the composition modified with the activated carbon additive. The anti-scuffing protection were characterised by compositions with 1–3% biochar additive produced at 500 °C and 5% additive produced from chokeberries at 700 °C.

Lubricating compositions modified with a biochar additive produced from chokeberries by pyrolysis process at 500 °C in an amount of 1–3% showed significantly more favourable anti-scuffing properties than the basic composition (Fig. 4). The limiting pressure of seizure data showed that applied biochar additive at 500 °C in an amount of 1–3% and additive at 700 °C in an amount of 5% significantly enhanced the superficial protection against seizure compared to the alternative lubricants applied in the study. This coefficient gives details of the pressure within the friction zone at the time of scuffing. From the presented data it was observed that the applied lubricant additive contributed to the formation of films with a high resistance to scuffing. The character of the layer formed favours an important decrease of scuffing.

For each formulated lubricant, the anti-seize characteristics were examined at progressively high levels of stress (represented by the scuffing load SL). The experimental data obtained are shown in Fig. 5.

Friction stress is a key indicator of the anti-seizure characteristics of lubricating greases in terms of a straight-line function of stress. Discussed parameter reflects the ability of lubricating film to bear the load. The addition of specific additives to the grease formulation affected the scuffing load value. The lubricant containing pure vegetable liquid (without additives) demonstrated the best anti-scuffing performance under the test conditions.

When biochar derived from chokeberry was added to the grease, the SL value decreased as the additive concentration increased, regardless of the pyrolysis temperature used to produce the biochar. This suggests that the amount of the biochar modifier in the lubricant has a direct impact on altering its scuffing resistance (Fig. 5). The longest film life was observed in grease without additives. Thus, it can be inferred that the effectiveness of scuffing protection is related to the texture of the interfacial zone created within the biochar additives. The vegetable oil molecules in the lubricant layer appear to be more highly concentrated, thus improving the reactions with the additives & their ability to carry heavier loads. In addition, tests were carried out to measure the limiting load of scuffing for friction node lubricated using biochar modified greases. The data from these tests are presented in Fig. 6.

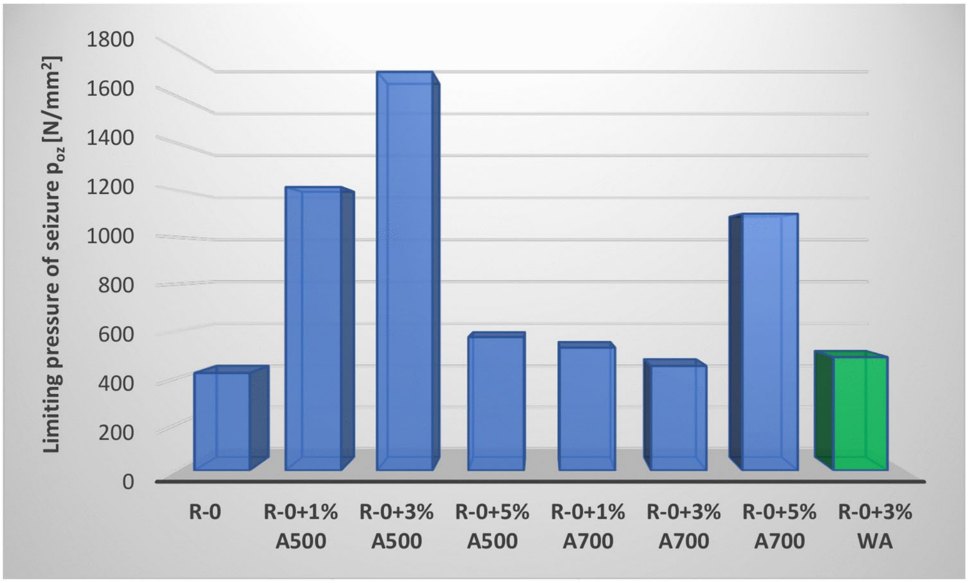

Fig. 4. The limiting pressure of seizure of friction node with greases modified of biochar additive.

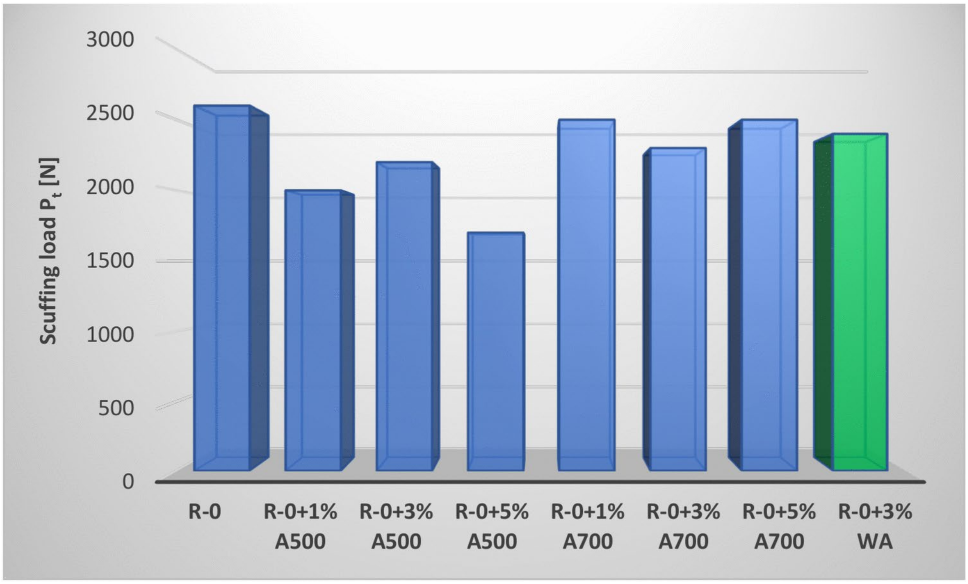

Fig. 5. Scuffing load of friction node lubricated with greases modified with biochar agent.

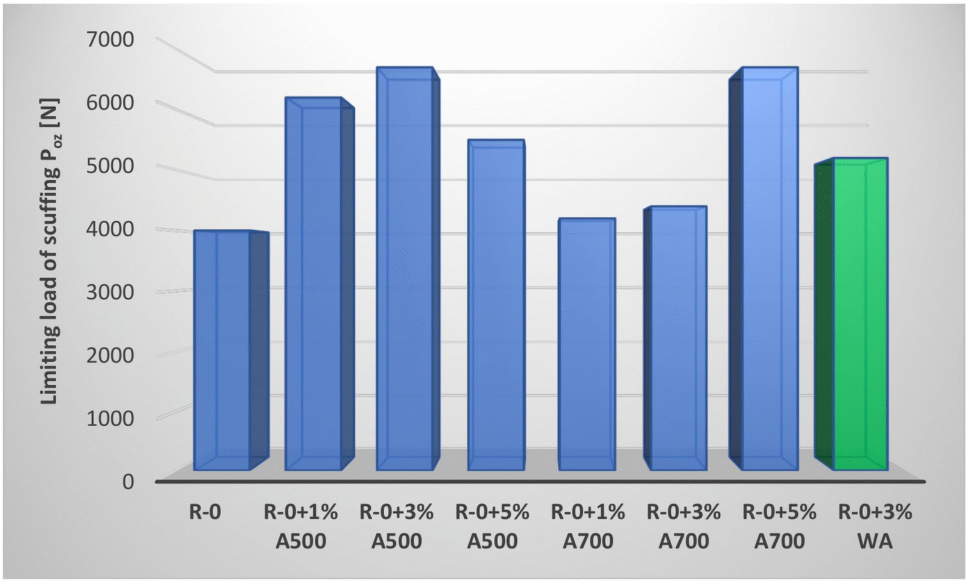

Fig. 6. Limiting load of scuffing of friction node with greases modified by biochar agent.

The limiting load of scuffing (LLS) determines the level of anti-scuffing protection provided by the investigated lubricants. The favourable anti-scuffing characteristics are observed in lubricant containing rapeseed oil modified with 5% biochar additive derived from chokeberry pyrolyzed at 500 and 700 °C. In both cases, the LLS value increased by approximately 67.5% compared to the base grease composition. Less favorable results were obtained for lubricating greases modified with 1 and 5% biochar from chokeberry produced at 500 °C. A smaller increase in LLS was noted for compositions modified with 1–3% biochar produced at 700 °C, showing an increase of around 5 and 10%, respectively, compared to the grease without additives (Fig. 6). The most effective performance after the disruption of the lubricating film was achieved with a 5% biochar additive produced at both 500 and 700 °C, which provided the highest LLS values. These values ranged from 4200 to 6700 N, indicating that variations in grease composition play a critical role under moderate force conditions. This demonstrates the significant protection offered by the grease in severe scuffing terms. The seizure reaction leads to an accumulation of pressure inside the seizure region, causing the removal of the friction layer on the contact areas. Protection from tribological immobility can be achieved by using lubricant formulations containing chokeberry biochar, which can interact with the friction pairing materials.

The antiwear characteristics of the greases were also evaluated through measurement of the limiting load of wear (LLW) on the tribological system. The obtained data is presented in Fig. 7.

Results of limiting load of wear tests demonstrate, in fact, that the addition of chokeberry derived biochar, produced by pyrolysis at 500 and 700 °C, enhances the wearing behaviour of the sliding contact points lubricated with tested compositions. Inclusion of this additive in rapeseed based grease resulted in an increase in the LLW parameter, highlighting the strong effect of chokeberry biochar on the anti-wear characteristics of vegetable based lubricants (Fig. 7). The higher LLW value, the more effective the lubricant is at reducing wear on machinery and equipment components. The highest LLW value was recorded for the formulation containing 3% chokeberry biochar produced at 500 °C, with a 121.6% increase compared to the base grease without additives. Biochar produced at 500 °C proved to be more effective in enhancing anti-wear performance. Most of the lubricating compositions modified with chokeberry biochar exhibited significantly better wear protection than those modified with activated carbon. The weakest anti-wear performance was observed in the rapeseed oil composition containing 1% chokeberry biochar produced at 700 °C.

It follows that the lower the temperature of pyrolysis during the production of chokeberry biochar, the more effective the incorporation of modifier into the chain of the vegetable lubricant and the more effective anti-wear effect of the produced lubricant. However, the obtained results show that the vegetable greases modified by the addition of chokeberry biochar provide better anti-wear protection in comparison to the base grease composition. Synergistic effect involving chokeberry biochar with the vegetable oil base could be attributed to the active agents included within the chokeberry, that interact effectively with rapeseed liquid. Incorporation of biochar into structure of lubricant leads to a modification of its structural composition by changing the spacing between the individual particles, resulting in a change in the lubrication efficiency of the tribosystem elements with the tested lubricant compositions.

The specific criteria for greases used in the grocery industry is defined individually for different types of equipment. Based on market research, lubricants are classified as follows: those with a LLW value greater than 600 N/mm^2 have excellent anti-wear characteristics; from 400 to 600 N/mm^2 have effective anti-wear characteristics; and those with a LLW value less than 400 N/mm^2 have inadequate anti-wear characteristics. Data presented herein clearly show that all tested compounds can be classified effective in their ability to provide anti-wear protection at constant stress states.

Rheological tests

The rheological characteristics investigated greases, including base grease and those modified with chokeberry biochar produced at 500 and 700 °C, and those modified with activated carbon, were analyzed using an Anton Paar MCR 101 viscometer. The effect of modified additives on the rheology behaviour of the rapeseed oil based greases is shown in Figs. 8, 9, 10, 11, 12, 13, 14, 15, 16 and 17. For each sample mixture, the flow curve was determined using Casson, Bingham and Herschel–Bulkley rheology equations. Results were shown in Table 2 is calculated yield stress values for studied lubricant greases.

Casson model provided the highest match of 98%, Bingham model provided a good match of 94% and Herschel–Bulkley model showed a similar correlation of 91% for the lubricant compositions produced. The yield point results from the Casson model were used for further consideration.

Graph eight illustrates flow characteristics with base lubricating composition and for compositions modified with various amounts of chokeberry biochar produced during the pyrolysis process at 500 °C and, for comparison, the composition modified with activated carbon. A very important rheological parameter, the yield point, was

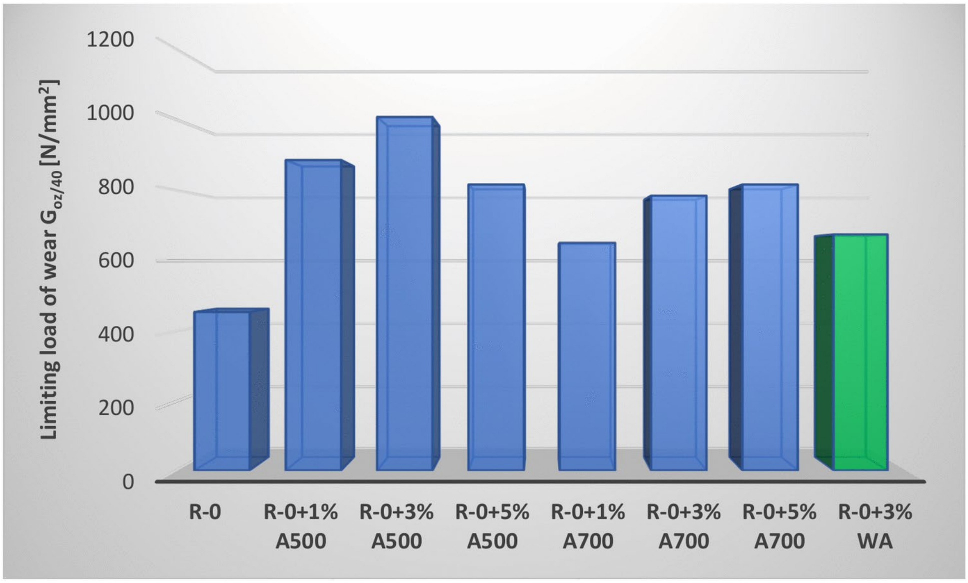

Fig. 7. Limiting load of wear of friction node lubricated with greases modified by carbon agent.

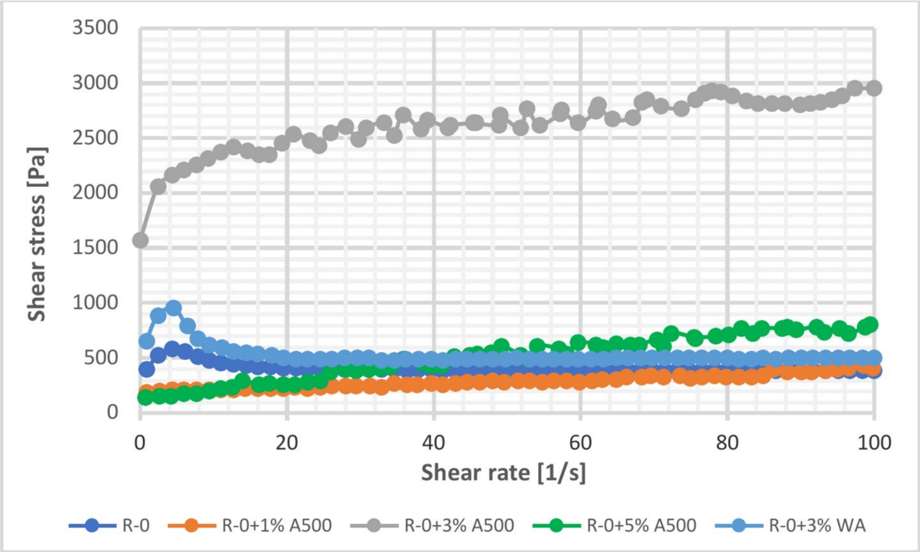

Fig. 8. Flow graphs of lubricating compositions modified with carbon additive.

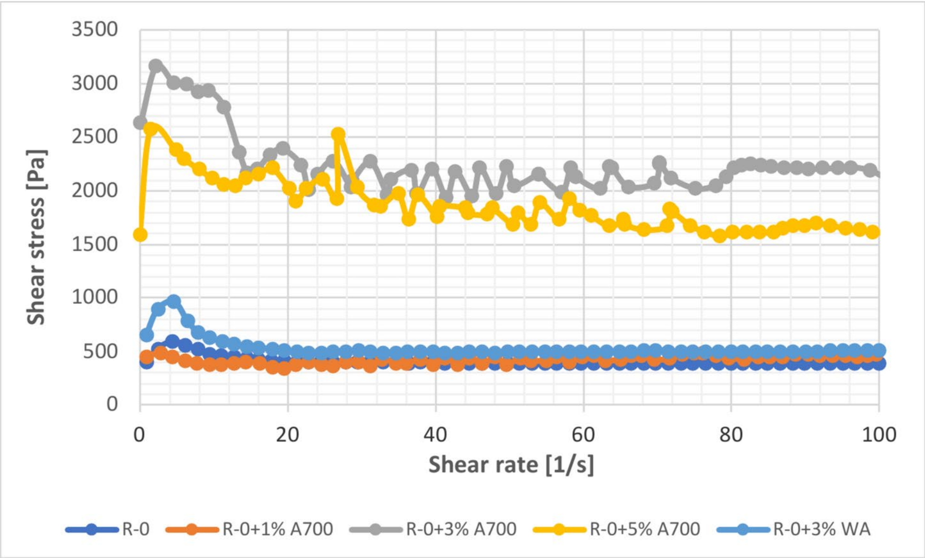

Fig. 9. Flow characteristics of the lubricating compositions modified of carbon additive.

determined from obtained curves. Lower worth of yield stress is more effective the rheological properties of the studied lubricants, as lubricant has to overcome less resistance and requires less force to start and operate the tribological system. The obtained test results show, that the most effective rheological properties are represented by lubricating compositions modified with 1 and 5% chokeberry biochar produced at 500 °C (characterised by the lowest values of the yield point, 180 and 230 Pa, respectively). For basic grease (with no modified agent) yield point value is 456 Pa and for the activated carbon modified composition it is 670 Pa. The highest value of yield point is characterised by the composition modified with 3% chokeberry biochar, in this case the yield point is 1550 Pa.

It follows, that the introduction of chokeberry biochar as modifier to vegetable lubricants considerably modifies the rheological properties of greases (lowest level of modifier in vegetable grease caused a decrease yield point value to a value lower than that of the base vegetable lubricant). Level of yield stress depends on how the biochar additive is incorporated into the structure of the vegetable grease, probably the mechanism of action the additive with the smallest and the largest amount of modifying additive is similar, this causes similar changes of the yield point and a significant reduction the value of yield point in relation to the base grease, which was not observed for the composition modified with 3% of biochar from chokeberry, which proves, that the mechanism of action the additive is different in this case.

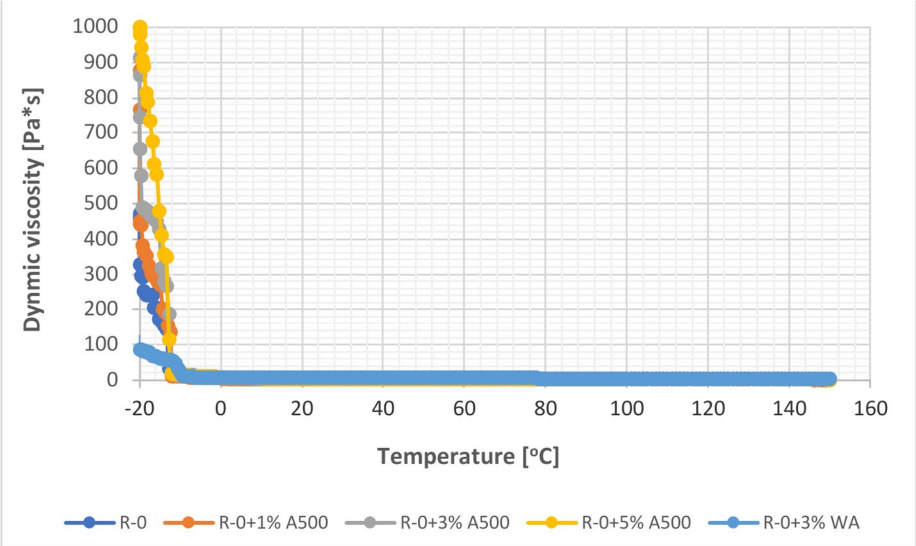

Fig. 10. Viscosity curve with heat for lubricating compositions modified with carbon additive.

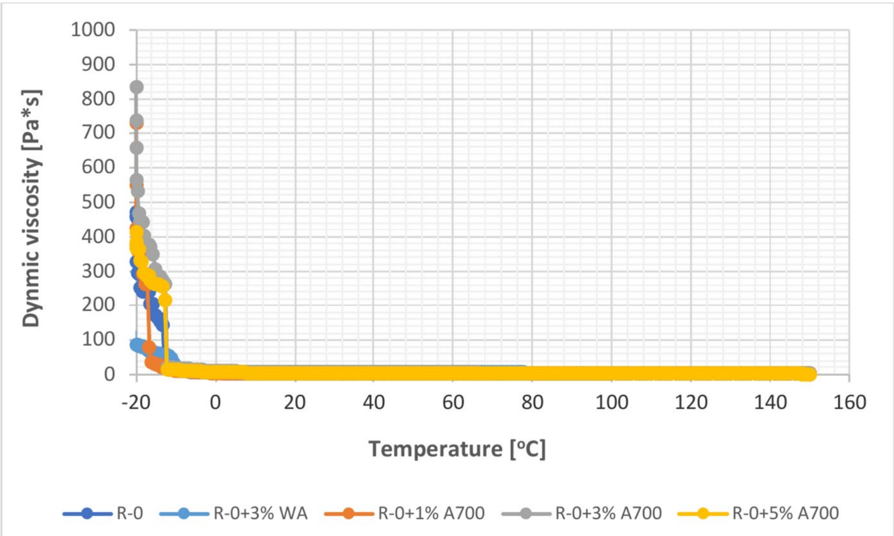

Fig. 11. The viscosity curve from temperature for lubricating compositions modified of carbon additive.

Under the same test conditions, the flow curves were determined for lubricating compositions modified with different amounts of chokeberry biochar produced at 700 °C, and again the yield point were calculated from the flow curves. The results of the tests were then compared and it was reported, which additive was the most effective rheologically.

The difference in the characteristics of the flow curves, especially for the grease modified with 3% chokeberry biochar additive, may be due to the unique interaction of the biochar with the base structure of the grease at this particular additive concentration in the grease structure. When the 3% chokeberry biochar is introduced, the internal structure of the grease is significantly strengthened, resulting in an increase in the value of the yield point, as shown in Fig. 8. This may be the result of a more intense interaction of the biochar with the spatial network of the grease, which leads to its stiffening. For additive concentrations of 1% and 5% in the vegetable grease, such effects do not occur to such a significant extent, indicating a different mechanism of action at these concentrations.

The results show, that the introduction of a 3% addition of chokeberry biochar induces more noticeable rheological changes, which may suggest that at this concentration the biochar used acts as a structural modifier, more so than at lower (1%) and higher (5%) concentrations. It was indicated, that the structure of the grease changes in a specific way at this amount of biochar, which significantly affects the value of the flow curves.

The mechanism of action of the additive in the vegetable plastic grease—biochar from chokeberries—at a concentration of 3% may be related to the optimal incorporation of biochar into the grease structure, leading to

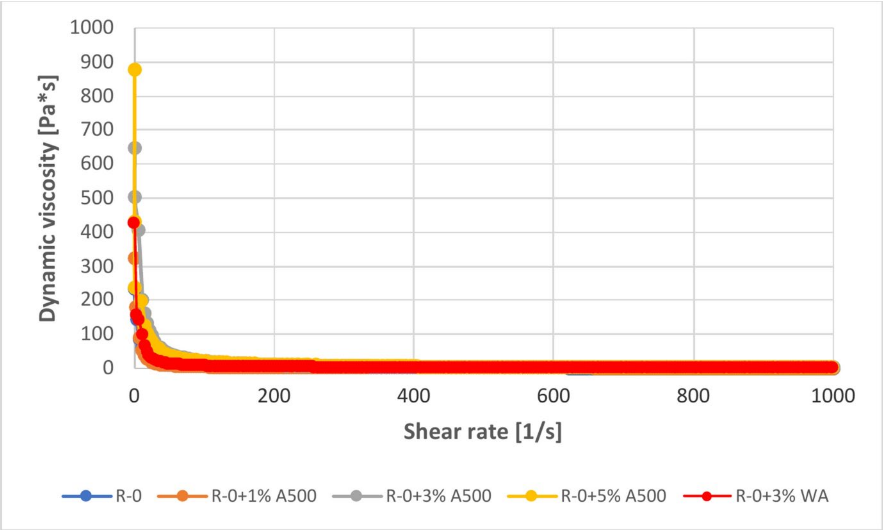

Fig. 12. The viscosity curve from temperature for lubricating compositions modified of carbon additive.

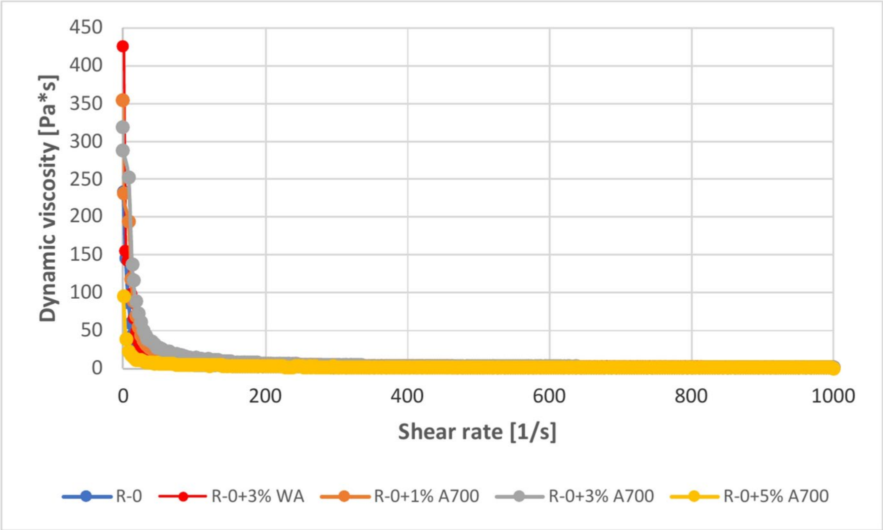

Fig. 13. The viscosity curve from temperature for lubricating compositions modified of carbon additive.

the formation of a more cross-linked and stable spatial network of the lubricating composition. The biochar acts as a reinforcing medium, increasing the resistance of the grease to deformation and giving it greater mechanical stability. For lower concentrations (1%) of the additive, this may not be enough to significantly affect the structure of the vegetable lubricating grease, and at higher additive concentrations (5%), supersaturation may occur, leading to a reduction in the reinforcing effectiveness of the additive on the tribological and rheological properties of the vegetable lubricants.

The mechanisms of action of the used additive at 1 and 5% concentrations may be similar, as in both cases the biochar introduces structural modifications to the grease under test, but not to the optimal range. The introduction of 1% of the additive into the structure of the grease may be too small to fully affect the structural network of the grease, while at a concentration of 5% of the additive in the grease, supersaturation may occur, leading to aggregation of the biochar particles and limiting its ability to modify the structure of the grease. As a result, although the results may be similar, their mechanism of action differs significantly, changing the intensity and effectiveness of the interaction of the used additive with the underlying lubricant structure.

The chart in graph nine illustrates flow characteristics of the lubricating compositions modified with the chokeberry biochar produced at 700 °C and, for comparison, for the composition modified with activated carbon. The lowest level of yield stress (460 Pa) was characterised by composition modified with 1% chokeberry biochar. Higher value of yield point are characterised by compositions modified with 3 and 5% of chokeberry biochar produced at 700 °C with yield point of 2650 and 1525 Pa respectively. The values of yield point for

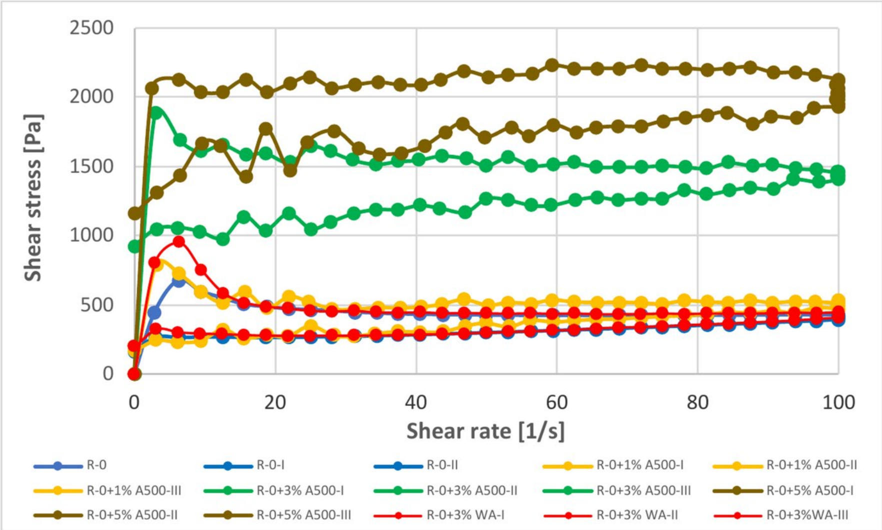

Fig. 14. The loop hysteresis for lubricating compositions modified of carbon additive.

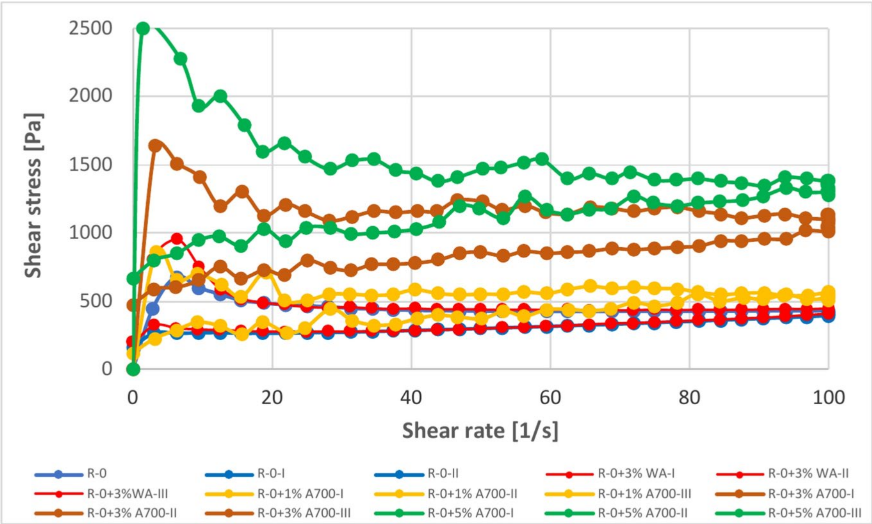

Fig. 15. The loop hysteresis for lubricating compositions modified of carbon additive.

compositions modified with chokeberry biochar at 700 °C are higher than those for biochar produced at 500 °C, which proves, that chokeberry biochar produced at 500 °C is rheologically more effective.

The maximum shear stress (yield point) is influenced by the percentage of modifier additive up to an optimum level. This indicates that incorporation of additive into the grease will not cause a weakening of its spatial structure, and in fact will strengthen it. This finding has significant implications for the selection of design parameters in the development of central lubrication systems using chokeberry biochar modified lubricants produced by pyrolysis at 500 and 700 °C. Yield point evaluation by means of Herschel–Bulkley regression gave better yield point results than the Casson model, although latter had a higher correlation coefficient. The best fit was obtained with the Casson model, while the Bingham model gave lower yield strength values and a lower correlation coefficient than Casson equation It is evident from the obtained curves of flow that there is a significant variation in the rheological characteristics (yield stress) of the lubricant as a function of the quantity and pyrolysis temperature of the modifying additive. The extent of these variations in yield stress values is a function of the chemical nature and physico-chemical characteristics of component base fluids, which are governed by strong mutual forces—primarily van der Waals interactions—as well as the amount, method and production conditions of the chokeberry biochar used as an additive in the vegetable-based lubricants.

In the next phase of the study, viscosity curves were analysed to determine the relationship between shear viscosity and thermal expansion for the grease compositions. The data is illustrated in Figs. 10 and 11.

The addition of chokeberry biochar as a modifying additive to vegetable based lubricants resulted in a noticeable change in shear viscosity at reduced heat. Higher concentrations resulted in a decrease in dynamic

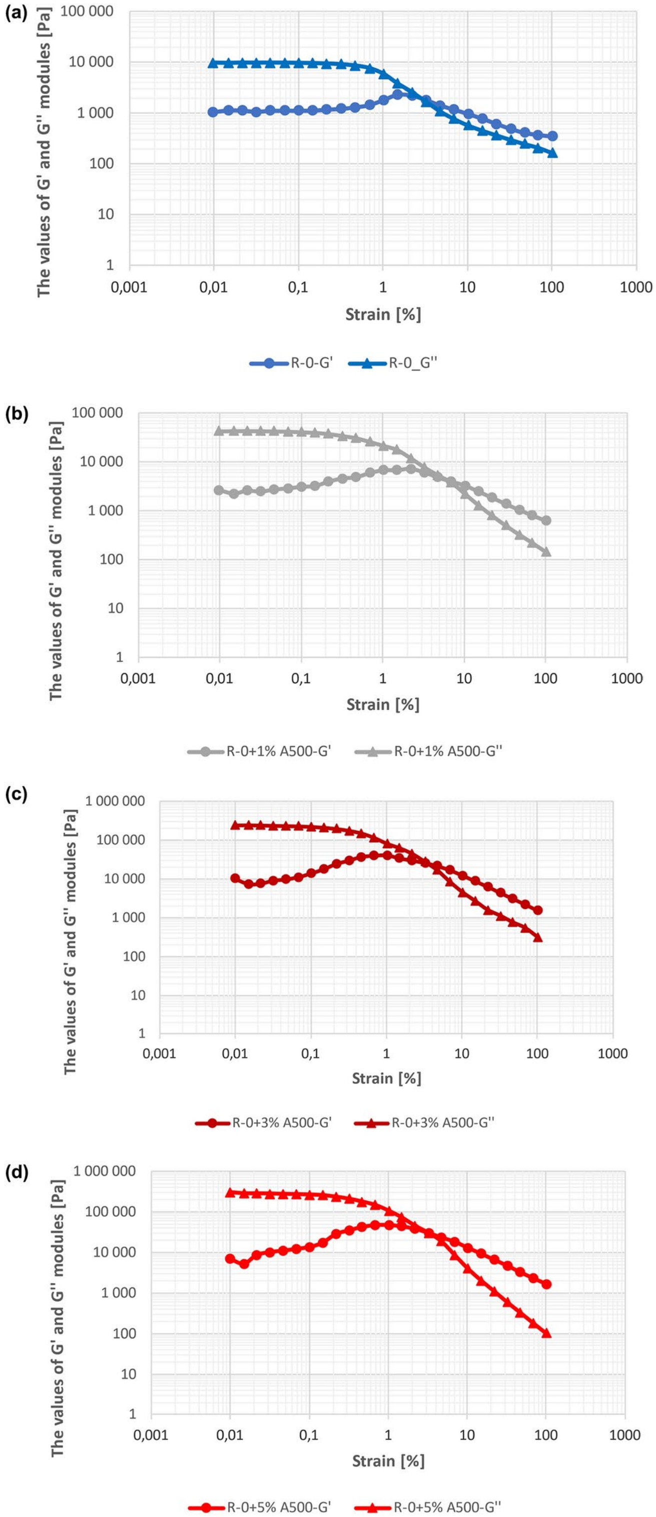

Fig. 16. (**a**) Storage and loss modules as a function of strain in greases without carbon additive. (**b**) Storage and loss modules as a function of strain in greases modified of 1% A500 carbon additive. (**c**) Storage and loss modules as a function of strain in greases modified of 3% A500 carbon additive. (**d**) Storage and loss modules as a function of strain in greases modified of 5% A500 carbon additive. (**e**) Storage and loss modules as a function of strain in greases modified of 1% A700 carbon additive. (**f**) Storage and loss modules as a function of strain in greases modified of 3% A700 carbon additive. (**g**) Storage and loss modules as a function of strain in greases modified of 5% A700 carbon additive. (**h**) Storage and loss modules as a function of strain in greases modified of 3% active carbon additive.

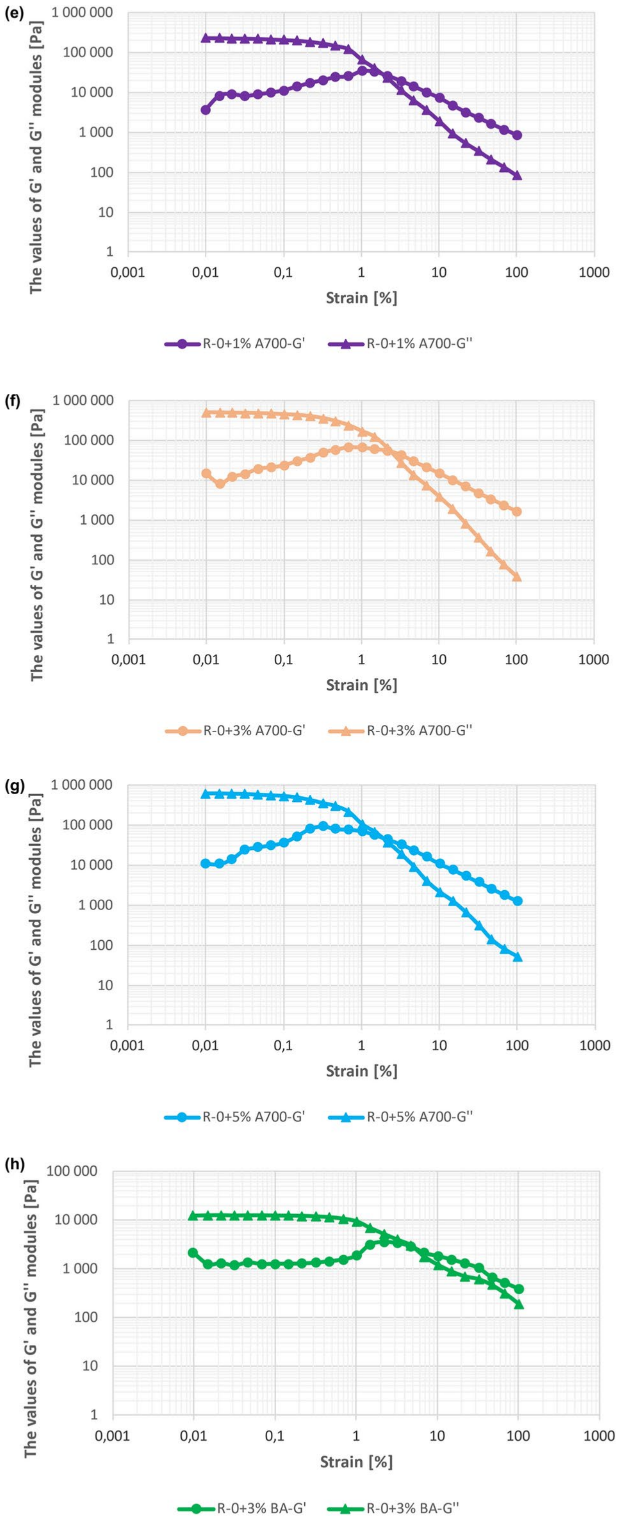

Figure 16. (continued)

viscosity at these lower temperatures. However, within the temperature regime of 0–160 degrees C, viscosity was not significantly affected by the amount of biochar added to the lubricant and the viscosity remained stable around 20 (Pa*s). When assessing the variation of shear viscosity at different temperatures, the inclusion of chokeberry biochar had a significant effect on the viscosity especially at lowest temperatures. Dynamic viscosities for the studied lubricants were not linear with the levels of modifiers. The maximum viscosity levels occurred in sample containing five percent chokeberry biochar, while the low viscosity levels were found in sample containing one percent additive.

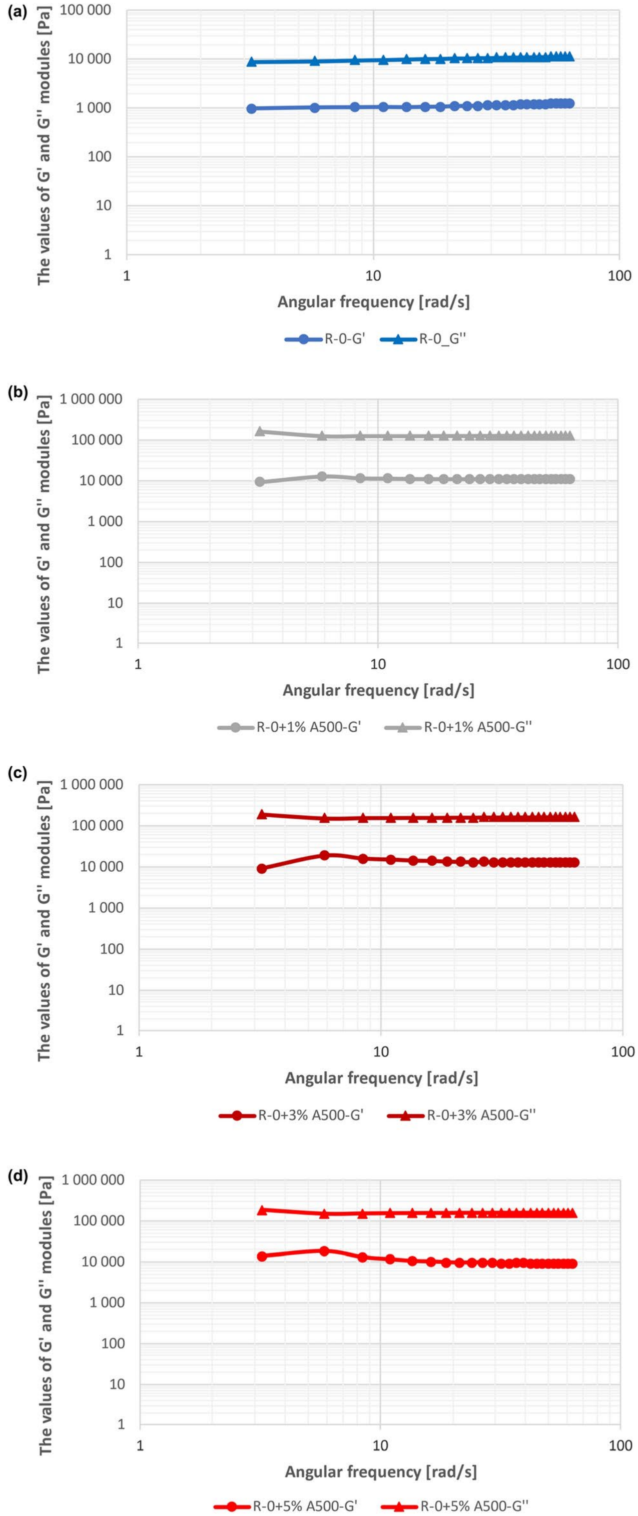

Fig. 17. (**a**) Storage and loss modules as a function of frequency in greases without carbon additive. (**b**) Storage and loss modules as a function of frequency in greases modified of 1% A500 carbon additive. (**c**) Storage and loss modules as a function of frequency in greases modified of 3% A500 carbon additive. (**d**) Storage and loss modules as a function of frequency in greases modified of 5% A500 carbon additive. (**e**) Storage and loss modules as a function of frequency in greases modified of 1% A700 carbon additive. (**f**) Storage and loss modules as a function of frequency in greases modified of 3% A700 carbon additive. (**g**) Storage and loss modules as a function of frequency in greases modified of 5% A700 carbon additive. (**h**) Storage and loss modules as a function of frequency in greases modified of 3% active carbon additive.

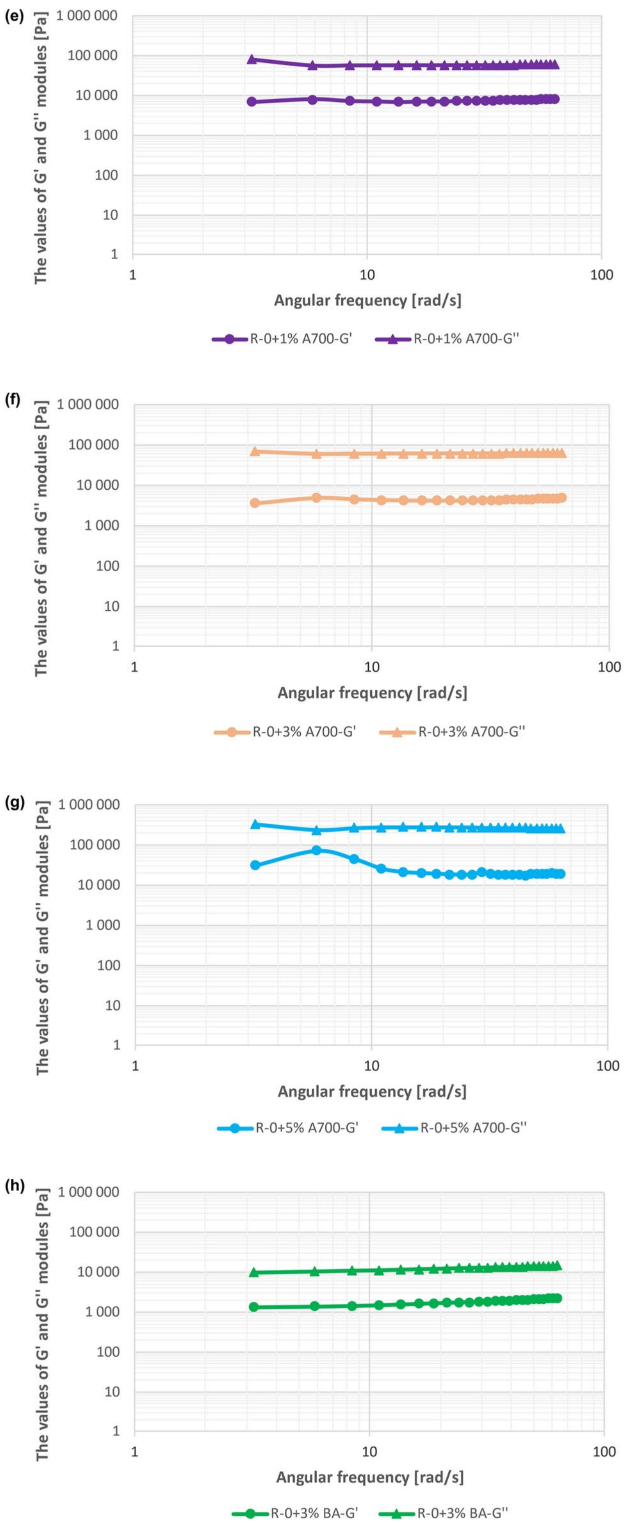

Figure 17. (continued)

The chokeberry biochar particles, which are only a few nanometres in size, have a significant effect on dynamic viscosity changes, particularly at low temperatures, due to their interaction with the colloidal structure of the vegetable-based grease.

In addition, tests were carried out to evaluate viscosity curves illustrating the correlation in shear rate and dynamic viscosity of the grease formulations. The results are shown in Figs. 12 and 13.

The introduction of a vegetable modifier in the form of chokeberry biochar into the lubricant structure resulted in an improvement in shear dynamic viscosity at relatively small shear speeds, particularly up to a shear

The symbol of lubricating greases	The value of yield point—Casson model (Pa)	The value of yield point—Bingham model (Pa)	The value of yield point—Herschel–Bulkley model (Pa)
R-0	456	413	474
R-0 + 1% A500	180	167	195
R-0 + 3% A500	1550	1516	1589
R-0 + 5% A500	230	211	261
R-0 + 1% A700	460	421	488
R-0 + 3% A700	2650	2576	2711
R-0 + 5% A700	1525	1483	1587
R-0 + 3% WA	670	633	714

Table 2. Calculated yield stress values for studied lubricant greases.

rate of 200 s^{-1}, above which no significant viscosity changes were observed. The lubricant compositions tested are non-Newtonian fluids whose viscosity decreases with increasing shear speed. The dynamic viscosity value of the examined lubricant mixtures increased as the quantity of applied modifier progressed. The highest viscosity is recorded in lubricant containing five percent of chokeberry biochar produced by pyrolysis at 500 °C and 1% of chokeberry biochar produced at 700 °C, while the minimum viscosity is recorded in lubricant containing 1% of biochar produced at 500 °C and 5% of biochar produced at 700 °C. Variations in shear viscosity, particularly at small shear rates, are important in selection of design parameters for machinery and equipment in various industries, such as the design of central lubrication systems. It is very important that the dynamic viscosity at low shear rates is as low as possible, as this is of great technological importance when starting up machinery. It is important not to overcome high resistances; higher forces mean higher energy and economic costs, which is important in industry. The use of biochar additives in vegetable-based lubricants makes it possible to obtain low viscosities, which is a positive phenomenon for many industries.

For tested lubricants, tests were carried out to determine the fluidity characteristics at varying shear speeds (hysteresis loops). Results are shown in Figs. 14 and 15.

The thixotropy capacity of the lubricating composition modified with 3% chokeberry biochar produced at 700 °C is higher than that of the base composition due to the specific structural and physicochemical properties of the biochar formed at high temperature. The pyrolysis at 700 °C leads to create a biochar with higher structural stability and increased specific surface area, allowing more efficient incorporation of biochar particles into the lubricant structure.

During the thixotropy test, it was observed, that the addition of biochar from chokeberries creates a more stable spatial network in the lubricant matrix. With 3% of the additive introduced into the grease, its concentration is optimal for creating a three-dimensional structure that effectively rebuilds itself once the applied stresses cease. The higher temperature of biochar production (700 °C) further promotes the elimination of volatile substances and heterogeneous components, enhancing the ability of the resulting additive to interact synergistically with the base lubricating composition.

In addition, the biochar produced at high temperature has a higher number of functional groups, such as carboxyl and hydroxyl groups, which increase its ability to interact with the liquid phase (base oil) of the lubricating composition. This explains the more efficient reconstruction of the lubricant structure after the destruction of its structure following the application of stresses, which directly translates into stronger thixotropic properties of the composition modified with the addition of chokeberry biochar compared to the results for the basic lubricating composition without the modifier.

The region of hysteresis curve, defined by the space enclosed by the shear-rate increasing and shear-rate decreasing flow profiles, has been estimated by the interval procedure. These calculated results have been used to evaluate the thixotropy behaviour associated with studied lubricants[60].

Thixotropy refers to a process in which the interior conformation of the grease becomes disrupted, resulting in a decrease in viscosity as the shear rate decreases, followed by a gradual recovery of the grease's original conformation over time. The area of the hysteresis loop is an indicator of the thixotropic properties of the grease. Thixotropy is closely related to shear thinning and is understood as a function of the coagulation of particles in a viscous liquid.

In a quiescent state, the droplets have the tendency to agglomerate and form an interior configuration similar to that of a dispersion. Under shear stress, this structure may break down partially or completely. After a period of time, the system reaches equilibrium, reflecting a different status of the internal atomic chain within the lubricant.

Each of investigated plant-based greases that have been changed using chokeberry biochar produced at 500 and 700 °C have shown varying degrees of thixotropic behaviour, as indicated by the non-coincidence of shear flow characteristics with changing shear stress. Hysteresis loop areas for the lubricants tested are shown in Table 3.

The modification of vegetable grease with additive of chokeberry biochar produced by pyrolysis at 500 and 700 °C caused in most cases an increase of the hysteresis loop, i.e. a deterioration of the thixotropic properties, which can have a negative influence in technological processes in many industries. However, the lubricating

The symbol of lubricating greases	The value of loop hysteresis (Pa*s)
R-0	44 786,7
R-0 + 1% A500	52 443,2
R-0 + 3% A500	66 868,1
R-0 + 5% A500	212 184,0
R-0 + 1% A700	57 298,5
R-0 + 3% A700	39 924,9
R-0 + 5% A700	155 440,6
R-0 + 3% WA	48 104,5

Table 3. The measured hysteresis curves values for selected lubricants.

composition modified with 3% of chokeberry biochar produced at 700 °C showed better thixotropic properties than the base composition without modifying additives, which indicates, that the used additive can be an effective thixotropic agent. And the phenomenon of thixotropy is of great industrial importance.

In the next stage of the work, tests were carried out on the rheological characteristics for lubricant compositions to determine the dependence of elastic modulus and stress modulus on strain and frequency. Results are shown in Figs. 16 and 17.

For base lubricant made from vegetable liquid and containing modified silicone dioxide, value of viscous modulus is 10,000 Pa at low levels of strain, then the value of this parameter decreases with increasing strain, which is particularly noticeable at strain levels above 1%. While, the value of elastic modulus G′ is 1000 Pa at low strain values, then value of this parameter increases with strain and then decreasing significantly to 650 Pa at strain values above 10%. In the range of deformations up to 2%, the viscous modulus dominates, indicating high viscous characteristics for studied lubricant; when deformation increases above 2%, the elastic characteristics start to dominate, indicating low elastic characteristics, and we can speak about the change of structure of the studied lubricant, the sample diluting towards characteristics characterised by liquid.

The introduction of 1% chokeberry biochar produced by pyrolysis at 500 °C into the structure of rapeseed lubricant caused a change in the visco-elastic characteristics of selected lubricating compositions. The level of the viscous modulus G″ reached 40,000 Pa, which is more than four times higher than that of the base composition. As the elongation increased, the level of this characteristic decreased, reaching the equivalent of 100 Pa at 100% elongation. Elastic module for low strain amounts to 2000 Pa, with increasing strain the value of this parameter increases to 8000 Pa for a strain of 3%, after reaching the maximum the value of G′ modulus starts to decrease rapidly to 600 Pa. Up to a strain value of 5% for this composition, the viscous modulus dominates, indicating strong viscous properties. After exceeding 5% strain, the elastic modulus begins to dominate, indicating poor elastic properties of the sample tested. Modification with biochar—the lubricating composition is characterized by stronger viscous properties than the base composition excluding modifier agent.

Increasing the amount of modifier in the form of chokeberry biochar in the vegetable lubricant to 3% caused a difference in the viscoelastic properties of studied lubricant composition. At small deformation values, the level of viscous modulus G″ was 200 000 Pa, which is more than 20 multiples greater than the level of this quantity for the basic mixture. As the strain progressed, the level of this characteristic decreased until 300 Pa at highest strain value. However, the value of the modulus of elasticity G′ reaches the value of 10,000 Pa, which is more than 10 × greater than that obtained for the unmodified sample with additive used at low strain values. Up to 1% strain, the value of the G′ modulus increases to 40,000 Pa, after exceeding 1% strain, the value of this parameter decreases to 200 Pa. In the deformation range of 0–3% for the tested sample, the viscous modulus G′′ dominates, which indicates strong viscous properties, when the amount of deformation exceeds 3%, the elastic modulus begins to dominate, which indicates weak elastic properties aiming at liquid properties. This behaviour proves that the tested lubricant composition changes its structure under the influence of deformation and undergoes shear thinning.

Modification of rapeseed grease with 5% chokeberry biochar produced at 500 °C did not cause any significant changes compared to the results of viscoelastic properties obtained for the mixture changed by three percent of applied modifier. Value of G′′ modulus at low strain values was 250,000 Pa, with increasing strain the value of this parameter decreased up to 100 Pa. However, the value of the modulus G′ was 10,000 Pa, then with the increase of the strain its value increased up to 40,000 Pa. When the deformation value exceeded 3%, the value of this parameter decreased to 1700 Pa. Up to the deformation value of 4% the strong viscous properties dominate, after exceeding the deformation value of 4% the G′′ modulus dominates, which characterizes the weak elastic properties characteristic for liquids. From the results obtained, it can be concluded that the texture of grease has been transformed with increase of deformation, which proves that the tested grease composition undergoes shear thinning.

Modification of vegetable grease with 1% addition of chokeberry biochar produced by pyrolysis process at 700 °C caused modifications of viscoelastic characteristics of rapeseed lubricant. The level of loss module at low strain levels was 200,000 Pa, then as the stress level increased, the amount of discussed parameter decreased to 80 Pa. The level of elastic module with low strain amounted to 4000 Pa, then it increased to 30,000 Pa, and after exceeding the strain of 1.5% it started to decrease to the level of 800 Pa. In the range of low deformations, the viscous modulus G′′ dominates, indicating strong viscous properties, while when the deformation exceeds 1.5%, the modulus G′ dominates, indicating weak elastic properties of the tested lubricant composition. The above data show evidence of shear thinning of the tested mixture. Greater deformation, the larger change in viscoelastic properties towards those characteristic of fluids.

For rapeseed grease modified with 3% chokeberry biochar produced at a temperature of 700 °C, the changes in its viscoelastic properties were observed. The value of the viscous modulus G′′ at low strain values was 400,000 Pa, then with increasing strain the level for viscous modulus is reduced to 40 Pa. Level of elastic modulus G′ reaches 10,000 Pa and decreases to 2000 Pa at 100% strain. Up to the value of 3% strain the viscous properties dominate in the tested lubricant, then the type of investigated lubricant has been changing and the elastic properties starts to be more important, which proves that with increasing elongation of the test lubricant the viscosity reduces and the structure of the test lubricant changes in the direction of a Newtonian fluid.

For grease modified with 5% of carbon additive produced in the pyrolysis process at 700 °C, the changes of viscoelastic properties were observed in relation to the basic grease (without modifier), but no significant changes were observed in relation to the composition modified with 3% of additive. The level of loss module reaches 500,000 Pa at very low strain levels and decreases to 50 Pa as the strain increases. However, the value of the modulus G′ was 10,000 Pa at low strain values and decreases to 1000 Pa at the highest strain values. Up to 2% of deformation, the viscous properties characteristic of the non-Newtonian fluid dominate, then the character of probe has been modified allowing the elastic properties to be established, indicating that with increase of deformation, the sample tested tends towards the properties represented by the non-Newtonian fluids. Therefore, under the influence of deformation, the tested sample changes its structure, which is a characteristic feature of lubricating greases.

For comparison, the test results for rapeseed composition modified with the additive of 3% activated carbon were presented. In this case, the change of viscoelastic properties was also observed in relation to the results obtained for the basic composition. Magnitude of viscous module at small deformation amounts to 10,000 Pa, which was several times lower than for compositions modified with the additive of chokeberry biochar, which proves about much stronger viscous properties for compositions modified with chokeberry biochar. The value of the viscous modulus decreases with increasing strain to the value of 200 Pa. However, the value of the G′′ modulus is 1000 Pa, which is approximately ten times lower than for the compositions modified with chokeberry biochar, which indicates about much weaker elastic properties for the composition modified with activated carbon compared to the compositions modified with the additive of chokeberry biochar. It was observed, that with increase of deformation, the value of elastic modulus G′ decreases to 200 Pa. Up to deformation value of 4%, the viscous features characteristic of solid dominate, then the elastic features characteristic for liquid begin to dominate. This behavior indicates about the change of structure with increasing strain. Comparing the obtained test results, it should be stated, that the structure of lubricating compositions created by the addition of activated carbon is much weaker on changes than in the case of modification with chokeberry biochar, this is demonstrated by the values obtained for the viscoelastic properties for selected lubricants.

For tested lubricating compositions, tests of viscoelastic properties were also carried out, i.e. the frequency function of storage & loss modulus at a constant deformation of 1%. The value of the viscous and elastic modulus did not depend on the frequency.

For base composition without the modifier, the value of viscous modulus G′′ was 10,000 Pa and the value of elastic modulus was 1000 Pa. Modification of vegetable lubricating compositions with the addition of chokeberry biochar were changed the value of both modules clearly. The introduction of 1% of the biochar modifier produced in the pyrolysis process at 500 °C into the structure of rapeseed grease increased the value of both modules ten-times, the viscous G" to 100,000 Pa and the G' modulus to 1000 Pa, which indicates about the change of the structure composition modified with biochar additive. The use of the additive changed the strength of configuration of studied composition, making it more resistant to changes under the influence of deformation.

Adding 3% of biochar modifier to the rapeseed lubricant increased the elastic module to 150,000 Pa and the viscous modulus G' to 15,000 Pa, which further strengthened the texture of investigated sample and made it more resistant to deformation due to external stress. Addition with 5% of chokeberry biochar to the structure of rapeseed fat increased the value of viscous modulus G′′ to 170,000 Pa and the elastic modulus to 17,000 Pa, which caused of strengthening the structure and increasing its resistance to changes caused by mechanical and thermal forces. Modification of vegetable lubricating composition with 1% of biochar additive obtained as a result of chokeberry pyrolysis process at 700 °C showed a lower rheological effectiveness and lower structure stability to changes than the additive produced at 500 °C, but much higher than the basic composition without the modifying additive. In this case, the value of viscous modulus G′′ is 60,000 Pa and the elastic modulus G′ is 6000 Pa. The introduction of 3% biochar additive produced at 700 °C into the grease structure caused the change of the viscoelastic properties. The value of viscous modulus was 55,000 Pa and the elastic modulus was 4000 Pa, which caused a change the stability of the structure towards its weakening on changes caused by mechanical forces in relation to the compositions modified with the additive produced at 500 °C.

However, the introduction into the structure of rapeseed fat of the biochar additive produced from chokeberries during the pyrolysis process at 700 °C in an amount of 5% caused a significant strengthening of the structure in the changes subjected to mechanical and thermal stresses[95], as shown by results of storage & loss modulus. Microstructure was much stronger than for the compositions modified with the biochar additive prepared at 500 °C. The value of the viscous modulus G′′ was 250,000 Pa, which was 25 times higher than that of the base mixture with no modifier. However, the value of the elastic modulus G′ ranged from 20,000 to 70,000 Pa. Such high values of both modules indicate a positive change in the structure's resistance to changes caused by variable working conditions of greases in different industries.

For comparison, tests were also carried out on a vegetable lubricant containing 3% activated carbon. In this case, no such favorable changes of stability and resistance of the structure of tested lubricants on changes caused by mechanical-thermal forces were observed. The obtained test results for this composition were comparable to the lubricating composition without modifiers, and much weaker than the compositions modified with a biochar additive produced from chokeberry (in some cases even a several times).

Conclusion

The results of tribological and rheological tests carried out on vegetable lubricants and containing modifier with different amounts of biochar additive produced from chokeberry during pyrolysis process at 500 and 700 °C allowed to conclude that:

- Carried out tests showed a strong relationship between the content of biochar additive produced from chokeberry in rapeseed lubricants on the parameters characterizing the anti-wear and anti-seizure characteristics of tested lubricating compositions,
- The experimental data validates the positive effect of the chokeberry biochar ingredient on the tribological and rheological characteristics of rapeseed greases,
- Lubricants containing 3% of chokeberry biochar produced at 500 °C and 5% of biochar produced at 700 °C showed the most effective anti-seizure characteristics with gradually growing stress on the friction node,
- The most significant anti-seizure activity occurred with lubricating composition modified with 3% chokeberry biochar additive at 500 °C and 5% biochar additive at 700 °C,
- The best anti-wear properties has a lubricating composition modified with 3% of chokeberry biochar, produced at a temperature of 500 °C,
- Used biochar additive creates a lubricating film, that protects the elements of tribosystem against wear,
- The introduction of 3% chokeberry biochar in the matrix of vegetable lubricants increases the value of yield stress, thus strengthening the three-dimensional structure of the lubricant and increasing its resistance to mechanical and thermal forces,
- The introduction of 1% biochar additive caused a decrease of dynamic viscosity at low temperatures, which have a decisive importance when working in many technological processes,
- The lowest viscosity value at low shear rates was observed for compositions modified with 1% biochar produced at 500 °C and 5% additive produced at 700 °C, which have a great importance when designing machine and equipment components and in central lubrication systems,
- The introduction of 3% chokeberry biochar, produced at a temperature of 700 °C, into the structure of the vegetable grease caused a reduction of the hysteresis area, which caused an optimization of the thixotropic characteristics, having a major technological meaning,
- Introduction of chokeberry biochar additive into the lubricant microstructure increases level of G′ and G′′ modules, which results in increased stability of the lubricant microstructure and increased resistance to mechanical and thermal forces.

Data availability

The data that support the findings in the present study are available from the corresponding author upon request.

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Author contributions

Conceptualization, R.K. and P.R.; methodology, R.K. and P.R.; software, R.K.; validation, R.K. and P.R.; formal analysis, R.K.; investigation, R.K and P.R.; writing—original draft preparation, R.K., and P.R.; review and editing, R.K.; supervision, R.K. and P.R.; project administration, R.K.; All authors have read and agreed to submit the manuscript.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to R.K.

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