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ELUCIDATION OF CHANGES IN THE MICROSTRUCTURE OF VEGETABLE LUBRICANTS BASED ON ANALYSIS OF RHEOLOGICAL PARAMETERS DETERMINED FROM THE MSD CORRELATION FUNCTION CARRIED OUT BY DWS DIFFUSION SPECTROSCOPY AND SPECTRA CARRIED OUT BY RAMAN SPECTROSCOPY

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Abstract: *This paper presents the results of a rheological and spectral study characterising the change in the microstructure of lubricants depending on the type of vegetable oil base. The three lubricating compositions were prepared based on vegetable oils (rapeseed, sunflower and abyssinian), where amorphous silica of a specific particle size was used as a thickener. These three lubricating compositions were then modified by introducing the AW/EP additive (BCH 351) into their structure. Rheological tests were performed for the prepared lubricating compositions on a DWS diffusion spectrometer. Based on the tests, the dependence of: ICF function values on time, MSD function values on time and G' and G'' modulus values on frequency were determined. From the collected data, rheological parameters such as elasticity coefficient, MSD curve slope factor, diffusion coefficients and the value at which the G' and G'' curves intersect were determined, which characterise the microstructure of the tested lubricants. Raman spectra were also performed to characterise the chemical structure of the compositions studied, and the intensity of integration of characteristic bands of vegetable greases was calculated. For vegetable greases made from different vegetable oils, a change in the value of the MSD function was observed, and the calculated value of the elasticity index indicates better viscoelastic properties for the grease made from rapeseed oil. Modification of vegetable greases with a multifunctional additive leads to a change in rheological parameters indicating a change in the structure of the greases studied. The results of tests of diffusion coefficients for vegetable greases show a change in microstructure for greases made with different vegetable oils. Such results testify to moderately strong viscoelastic properties, leading to the conclusion that the produced greases are substances stable to changes in chemical structure depending on the base oil and modifying additive used. Raman spectroscopy is a technique that enables changes in the chemical composition of vegetable oils to be assessed by analysing the degree of unsaturation of fatty acids in vegetable oils, making it a very good diagnostic method for quality control of lubricants based on vegetable oils. The results obtained make it possible to differentiate lubricants prepared with different vegetable oils and allow the chemical structure of the vegetable lubricants studied to be assessed on the basis of the intensity of integration of characteristic bands.*

Keywords: *vegetable greases, rheological tests on optical rheometer, mean square displacement, intensity correlation function, diffusion coefficient, elasticity index, slope coefficient of MSD function, Raman spectroscopy, integral intensity characteristics bands*

1. INTRODUCTION

The analysis of structural changes of colloidal systems determined by the interpretation of changes in viscoelastic properties during mechanical excitations is important due to the durability and stability of these systems. The explanation of the mechanisms of interaction of individual elements of the colloidal system and determination of the kinetics of structural changes under the influence of mechanical excitations will allow determination of rheological parameters characterizing structure changes and will contribute to acquiring new knowledge about the characteristics of structural changes of colloidal systems. Finding a correlation between lubricant components and changes in its structure as a result of interactions occurring under the influence of mechanical forces will contribute to the identification of mechanisms of these interactions. So far, the literature has described the interactions between the components of simple colloidal systems that characterize changes in their structure under the influence of small mechanical, temperature or variable chemical constraints. However, analysing and describing the mechanism of changes in the chemical structure of multi-component colloidal systems under the influence of high loads and large temperature changes can be an important contribution to the development of science about the chemical structure of colloidal systems. Identifying changes in the structure of lubricants will allow to broaden the knowledge about processes affecting the formation of the structure during mechanical excitations of substances with varied chemical composition [1,3].

It was assumed that the components of colloidal systems may be converted under the influence of mechanical excitations performed in tests carried out in the technological system, and the emerging new chemical compounds may change the chemical structure. Identification and description of mechanisms of changes in the chemical structure of the studied systems will be a research problem of this application. The full identification of changes in the structure of colloidal systems under the influence of mechanical excitations can only be realized through the use of complementary research techniques.

The innovative nature of the research will consist of assessing the change in rheological properties of lubricants determined using diffusion microrheology (DWS). On the basis of changes in rheological parameters, the change in the chemical structure of the tested lubricants will be assessed. The characteristics of changes in the chemical structure of the tested materials after mechanical and thermal excitations using rheological tests is an innovative method of assessing the quality of lubricants.

Diffusion spectroscopy DWS is used to study liquid and solid samples in a wide range of frequencies and viscoelasticity. It uses the technique of a diffusing wave to study optically turbid media. It allows the measurement of the dynamics of samples and local inter-molecular displacements. In transmission mode, scattered light is detected after passing through a L-shaped cuvette. While the time fluctuations of the detected intensity are measured using the ICF correlation intensity function. However, in the back-scattering mode, the light scatters towards the incident beam and its fluctuations are measured [3,4].

The module of elasticity and viscosity is calculated from the MSD function by means of a generalized Stokes-Einstein equation with the knowledge of the radius of the molecule/marker. The MSD correlation function is determined on the basis of coordinates of the phase particles dispersed at a given time and related to the value of the diffusion coefficient with the following relationship: $\langle \Delta r^2(t) \rangle = 4Dt$ [5-7]. Knowledge of the MSD correlation function allows to determine the diffusion coefficient in the tested liquid, and consequently to calculate the viscosity of the studied liquid. For non-Newtonian liquids, the dependence of the MSD correlation function on time is not a straight line. For samples exhibiting elastic properties, the MSD function is constant, i.e. independent of time. For Newtonian liquids, the correlation function is linearly time-dependent. While for viscoelastic liquids, the slope of the MSD function assumes intermediate

values between viscous and elastic properties, and the slope coefficient of the curve assumes the value of 0<n<1. The MSD function is characterized by the occurrence of the so-called *plateau,* for which the value of thermal energy is equal to the cumulated energy in the structure of the studied substance. The location of the plateau indicates the size of the elastic properties of the medium tests. The smaller the value of the plateau, the more elastic tested sample.

Studies conducted using optical microrheometry (DWS) give a lot of valuable information about the changes occurring in the dispersion microstructure, characterize its stability, allow monitoring of the quality of dispersion systems in changing conditions. They ensure not only the correlative knowledge of dispersion stability, but lead to a deeper understanding of the dispersion microstructure.

Changes in the physical properties of the emulsion are characterized by the diffusion spectroscopy [8-10]. There are many cases of using this technique to evaluate rheological properties to monitor and predict the dispersion stability and changes in the emulsion microstructure [11,12]. This technique can also be successfully applied to characterize ceramic sludges, colloidal suspensions and biopolymer gels, such as yoghurt [13-15]. Using diffusion spectroscopy, information on the quantitative transition of sol into gel, viscoelastic properties and characteristics of changes in the microstructure of aluminium oxide suspensions can be obtained [13]. It was also used to monitor changes in mechanical properties of soft composite materials, such as dispersions, latex polystyrene gels, casein gels and biopolymer solutions [16]. And also to study the movement of particles in concentrated fluids, such as colloids or microemulsions characterized by high dispersion of particles [17]. Using the DWS technique, research was also conducted, which gave a number of interesting pieces of information about the heterogeneity of biopolymer materials [18].

Diffusion microrheology was used to assess the quality changes of dextran solutions. The G' and G'' modules were determined from frequency. The results of the discussed parameters were used to assess changes in the structure of the tested solutions [19]. The DWS technique was used to assess the temperature-dependent gelling process in colloidal dispersions. The change in the structure of colloidal dispersions from temperature was determined, the gelation point was determined and the rate of aggregation of particles suspended in the dispersion was studied. The viscoelastic properties were discussed using the Maxwell and Kelvin-Voigt model [20]. Optical microrheology can be used to determine the dynamics of particle motion, changing the structure and mechanical properties of dual emulsions based on the value of MSD function in time, and changes in the G' and G'' module values from frequency in order to facilitate the understanding of emulsion destabilization processes [1]. Optical microrheology was used to assess the rheological and microstructural characteristics of submicron emulsions deposited on a modified matrix based on waxy maize starch. Based on the results of the MSD curve in time and the G' and G'' modules on frequency, the change of structure of the studied emulsion was assessed and the structure destabilization mechanism was confirmed [21]. Optical microrheology is also used to study the dynamics and structure of complex fluids. Based on the changes in the G' and G'' module values on frequency, the changes of the structural properties of the colloidal dispersions, polymers and biomaterials were assessed. Dynamic phenomena related to the tested fluid were evaluated, and relaxation modes of the adsorbed polymers were also studied [22]. Microrheology properties of complex fluids and gels can be characterized using optical microrheology. Structural changes were evaluated based on the results of the G' and G'' modules. It was found that the results of the MSD function can be used to characterize the technological process and to monitor changes in structure over time [23]. Optical microrheology was used to study the viscoelastic properties of soft materials. Changes in the structure over time were evaluated based on the results of the G' and G'' modules. The DWS technique allows to obtain information about the medium quickly and in a wide frequency range,

which is fundamental for characterizing and monitoring structural changes over time [16].

The DWS technique has also been used to evaluate structural changes in paraffin emulsions [24] and vegetable greases after tribological tests in which silicon-containing substances were used as thickener or as an additive [25-27].

The Raman spectroscopy will be used as a complementary technique to tests carried out using DWS diffusing rheometry. This technique will be used to determine the structural changes of the tested lubricating greases subjected of variable extortions during the carried out tests.

The 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. It also allows quantitative or semi-quantitative determination of the content of the test substance in the sample. It is used to control the course of reactions, by analyzing the spectra of products or their mixtures, as well as when investigating interactions between solution components (cation-solvent) or catalyst activity mechanisms. 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 microcrystalline powders, or single crystals in a wide range of temperatures and pressures. 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 [28-29].

The Raman spectroscopy is a widely used analytical technique, which is used, among others, for structural studies of polymer solutions [30], which gave an information on a series of interesting changes in structure at different temperatures. Changes in the chemical structure of colloidal systems [31] as well as paraffin waxes and polymer microemulsions at variable temperatures were also studied [32]. Studies on phase transitions in hydrocarbons [33] or the assessment of the degree of the crystallinity of polymer mixtures under the influence of heating [28] were also conducted. The change in the chemical structure of aqueous polymer solutions, oil bases, and lubricants, under the influence of changing operating conditions, was also assessed [29].

In summary, the Raman spectroscopy technique allows one to obtain information on the chemical structure of materials subjected to temperature and mechanical excitations in the processes of their operation and enables monitoring of structural changes over time. Observation of changes in the chemical structure of materials allows one to comprehensively assess the impact of process conditions on the state of their structure and allows for a comprehensive characterization of the stability of the examined systems at the microscopic level.

So far, no reports have been reported on the comprehensive assessment of lubricant microstructures using DWS diffusion spectrometry enriched with Raman spectroscopy. The use of these two analytical techniques will allow explaining the behaviour of multicomponent dispersion systems subjected to mechanical and thermal excitations. Analysis of the previously described cases and own works of Raman spectroscopy allows one to state that it is possible to identify and explain changes in the structure of lubricants and correlate them with changes in rheological properties investigated by means of DWS diffusing rheometry.

On the basis of changes in rheological parameters, including the correlation function MSD, the microstructure of the tested lubricants will be evaluated in relation to the different content of thickener in the dispersed phase, having an influence on the consistency of tested systems. The obtained results will be the basis for finding a correlation between the stability of the

microstructure and the parameters determined from the correlation function MSD - the diffusion coefficient and the modules characterizing the viscoelastic properties of tested dispersion systems.

2. METHODOLOGY OF RESEARCH

The three lubricating compositions were prepared based on vegetable oils (rapeseed, sunflower and abyssinian), where amorphous silica of a specific particle size (7-40 nm) was used as a thickener. These three lubricating compositions were then modified by introducing the AW/EP additive (BCH 351) into their structure [34-38].

The compositions prepared in this way, which were marked with the symbols: 1A (based on rapeseed oil), 1B (based on rapeseed oil and modified of BCH additive), 2A (based on sunflower oil), 2B (based on sunflower oil and modified of BCH additive), 3A (based on Abyssinian oil) and 3B (based on Abyssinian oil and modified of BCH additive) carried out the rheological and spectral tests.

Next, the prepared compositions will be evaluated using Raman spectroscopy and the structure of the tested lubricants by DWS diffusion spectroscopy and Raman spectroscopy.

The tests of rheological properties of lubricants will be carried out by means of the optical rheometer of DWS RheoLab Swiss Company LS Instruments AG. The device uses the Diffusing Wave Spectroscopy (DWS) to determination of the rheological characteristics of the media, such as suspensions, emulsions, and foams. The working principle of the DWS rheometer is based on the assumption, that light transport can be treated as a diffusion process in optically turbid samples. The apparatus provides microrheological measurements of materials in conditions of static intermolecular displacements in a wide range of frequencies and viscoelasticity.

The optical rheometer provides tests in two different geometries, i.e. transmission and backscattering [EU Patent 1720000]. In the transmission mode, scattered light is detected after passing through the sample, and intensity fluctuations are measured. However, in the backscattering mode, light is collected that is scattered back towards the incident beam and its fluctuations are measured.

The correlation function MSD (mean square displacement) under static conditions will be appointed. The rheological measurements will be carried out at temperatures of 293 K. On the base of the analysis of appointed rheological parameters, the change in viscoelastic characteristics of the starting lubricant samples will be appointed. In order to carry out correct tests, the experiments affecting the calibration of the device, the selection of the measurement mode and the thickness of the cuvette, will be carried out. Before starting the measurements, the device will be calibrated using a standard, which is an emulsion of polystyrene with a particle size of 222 nm in water. Next, the refractive indices for the oil bases of particular lubricants will be appointed, the time of the measurement will be appointed, and the temperature and size of the spectrometer cuvette in which the samples will be placed and which will be prepared by added of marker (titanium dioxide with a particle size of 360 nm). The selection of the cuvette for the tested media is very important, because the correct measurements require fulfilling the condition, that the ratio of the cuvette thickness (L) to the mean free path of particle (l*) must be greater than 7 and less than 30, otherwise the measurement is not possible. The measurements will be carried out in the transmission mode and the backscattering mode in order to determine the best optical path and to obtain correct results. Then the samples will be homogenized and placed in a measuring cuvette. The rheological tests will be carried out in a measuring cuvette with an optical path equal to 1 mm.

The structural changes of the lubricants will be investigated using a Raman spectrometer. The Raman spectroscopy will be used to monitor the qualitative changes occurring in tested materials. Analysis of Raman spectra will consist in evaluation of band decay in the range of 1440-1470 cm^{-1} and approximately 1300 cm^{-1}, corresponding to the vibrations coming from changes in the range of bands characteristic of unsaturated systems derived from vegetable base oil (3010, 1656 i 1268 cm^{-1}). The Raman spectra will be obtained using a Raman NRS 5100 confocal Raman micro-spectrometer (Jasco Corporation, Japan) equipped with an excitation laser with a wavelength of 532.12 nm and a CCD detector. The working conditions 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, lens magnification 20 ×, and exposure time 200 s. The calibration of the Raman spectrometer will be carried out using a silicon reference plate.

3. THE TEST RESULTS AND DISCUSSION

Spectral tests with a Raman spectrometer were carried out for all lubricating compositions made with different vegetable oils. The results obtained are shown in Figure 1.

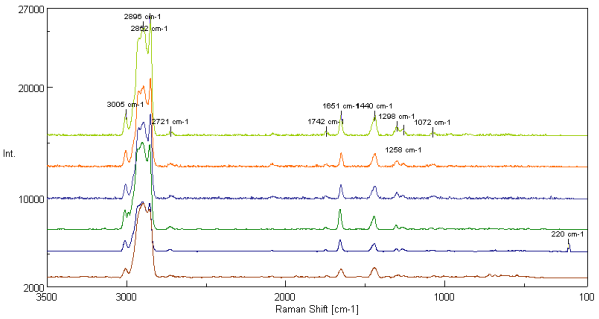

Figure 1. Raman spectra of lubricating compositions prepared on vegetable oil bases, (composition 1A - brown, composition 1B - blue, composition 2A - green, composition 2B - blue, composition 3A - red, composition 3B - light green)

For tested lubricating compositions, characteristic bands occurring in the fatty acids of vegetable oils were plotted, such as: bands excited by stretching vibrations of C=C groups, CH_2 scissor vibrations at 1654 and 1444 cm^{-1}, respectively; and bands of stretching vibrations =C-H and C-H of CH_3 and CH_2 groups occurring near 3003 and 2859 cm^{-1}. In order to analyse the changes occurring in the structure of the tested lubricants, bands excited by stretching vibrations of unsaturated C=C groups occurring at 1654 cm^{-1} and saturated CH_2 groups occurring at 1444 cm^{-1} were chosen, as these bands are definitely separated and their boundaries clearly marked. The intensity of the peak integral was determined as the value of the integral corresponding to the area under the peak. The ratio of the number of C=C double bonds to C-C single bonds present in the fatty acids of the vegetable oils was determined. For composition 1A, the intensity ratio of the I_{1654}/I_{1444} bands was 0.545; for composition 2B, 0.530; for composition 1B, 0.550; for composition 3A, 0.590; for composition 2A, 0.540; and for composition 3B, 0.620.

Then, for the produced lubricating compositions, the rheological properties were tested using a DWS diffusion spectrometer. The results of the tests are presented in Fig.2-4.

The carried out tests made it possible to determine the dependence of the correlation function ICF on time, the dependence of the mean square displacement - MSD on time, and the dependence of the modules G' and G'' on frequency. On the basis of the determined dependencies, the diffusion coefficients D_0 and D_m characteristic for determining the changes in viscoelastic properties of tested lubricating greases were calculated. The elasticity index, the slope coefficient of the MSD curve, and the point at which G'“ and G”'' modulus equalise were also calculated. The values of these parameters indicate a change in the structure of the tested lubricating compositions. The results of the tests of the rheological properties of lubricating compositions produced on the rapeseed oil basis are presented in Fig.2.

The application of the DWS technique was aimed at proving that it is possible to determine a change in the chemical structure of tested lubricating compositions on the basis of calculated values of ICF, MSD functions and G'

and G'' modules, as well as on the basis of calculated values of parameters determined from these functions, which, in connection with spectral tests carried out on a Raman spectrometer, will make it possible to explain that changes in rheological parameters are related to changes in the struture of the tested lubricating compositions.

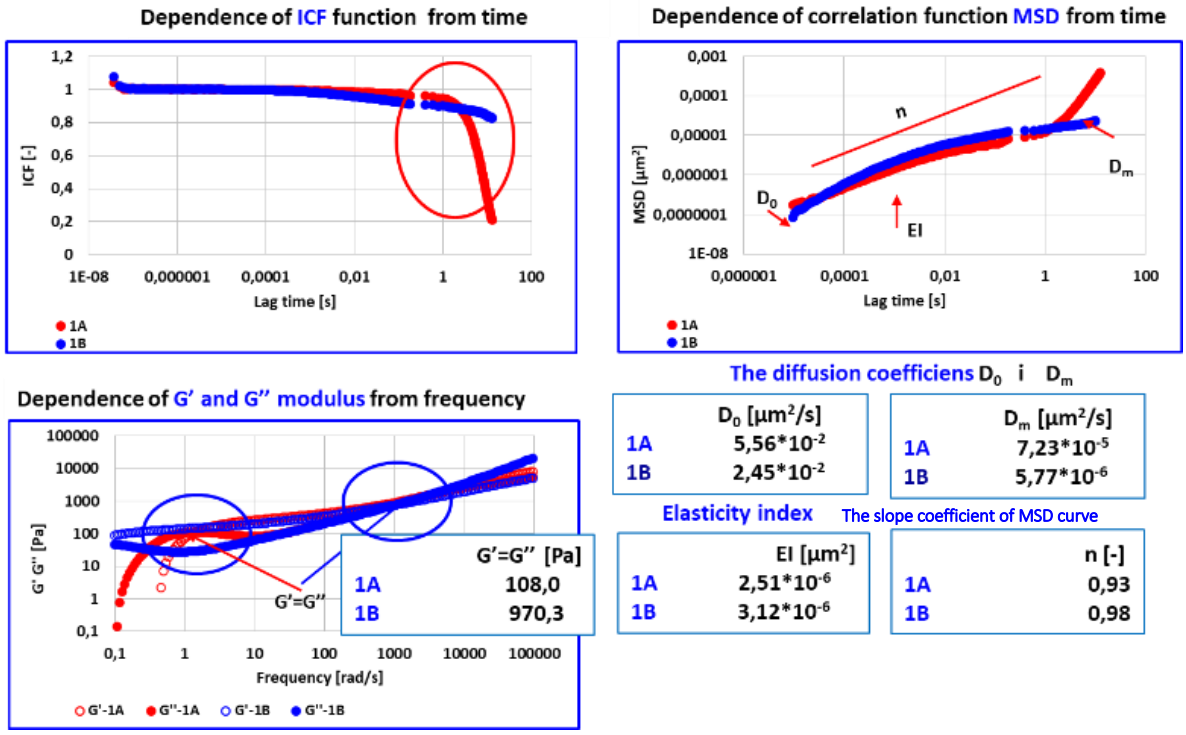

Figure 2. Test results of rheological properties together with determined values of characteristic parameters for composition 1A (based on rapeseed oil) and composition 1B (based on rapeseed oil modified with BCH additive)

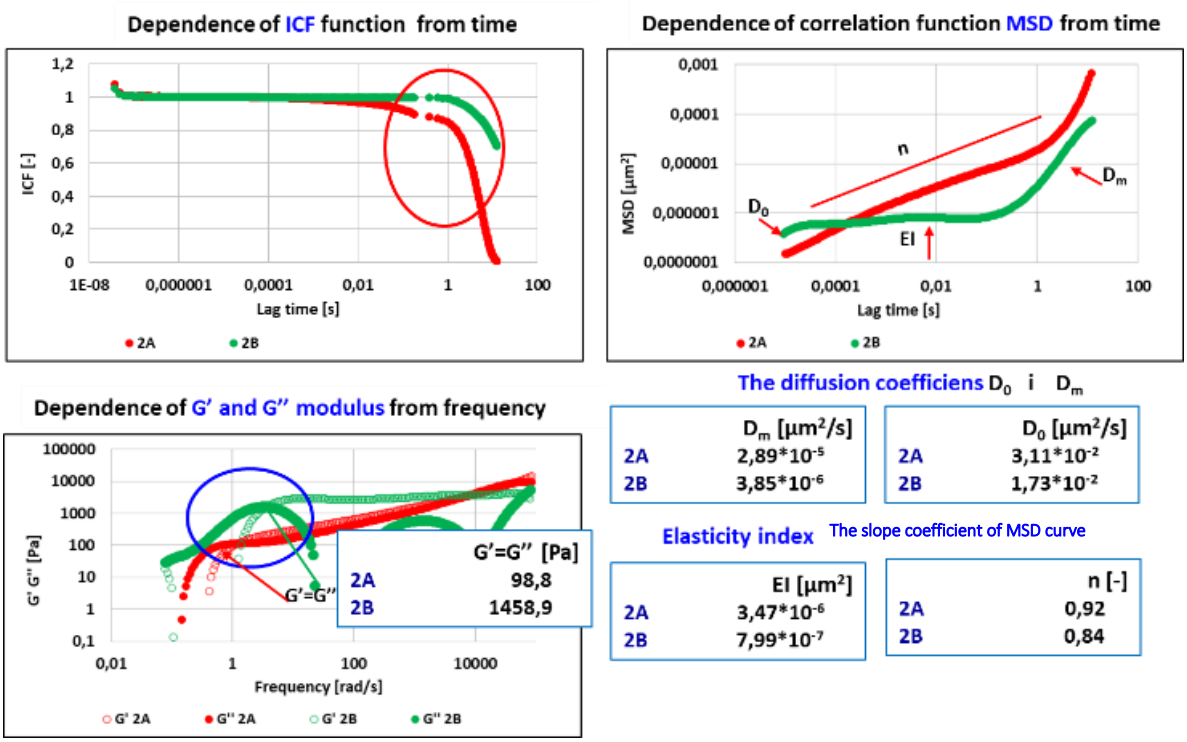

Figure 3. Results of testing of rheological properties together with determined values of characteristic parameters for composition 2A (based on sunflower oil) and composition 2B (based on sunflower oil modified with the addition of BCH)

The introduction of a multifunctional additive into the chemical structure of a lubricating greases produced on the basis of rapeseed oil leads to a change in the rheological properties of the tested grease. Much higher values of the ICF function were observed for the grease modified with the BCH additive compared to the base grease at higher values of lag time, which indicates a change in the microstructure of the tested lubricant. The calculated values of diffusion coefficients assume lower values for the additive-modified grease, indicating a different chemical structure to the base grease. A much steeper slope of the MSD correlation function is observed in relation to the base grease, indicating a change in structure towards a higher viscosity substance. The higher value of the elasticity index for the grease modified with the additive, indicates a change in structure and stronger viscoelastic properties for this grease, resulting in a stronger structure and less degradability.

This behaviour is also evidenced by the results of the G' and G'' modulus, the intersection occurs at a much higher value, resulting in a strengthening of the structure and an increase in resistance to changes under mechanical forcing.

The results of rheological tests on the grease produced from sunflower oil are shown in Fig.3.

The introduction of a multifunctional additive into the chemical structure of a sunflower oil-based grease leads to a change in the viscoelastic properties of the tested grease. Higher values of the ICF function were observed for the lubricant modified with the BCH additive compared to the base lubricant, especially at deceleration times above 1 s, which indicates a change in the microstructure of the tested lubricant. The calculated values of diffusion coefficients assume a higher value at low delay time values and a lower value of diffusion coefficient at higher delay time values, for the grease modified with the additive, indicating a change in chemical structure over time. A much lower slope coefficient of the MSD correlation function was observed in relation to the base lubricant, indicating a change in structure towards a lower viscosity fluid. The lower value of the elasticity index for the additive-modified grease indicates a change in structure and weaker viscoelastic properties for this grease, resulting in a weaker structure and greater degradability under applied load, tending towards a Newtonian fluid structure.

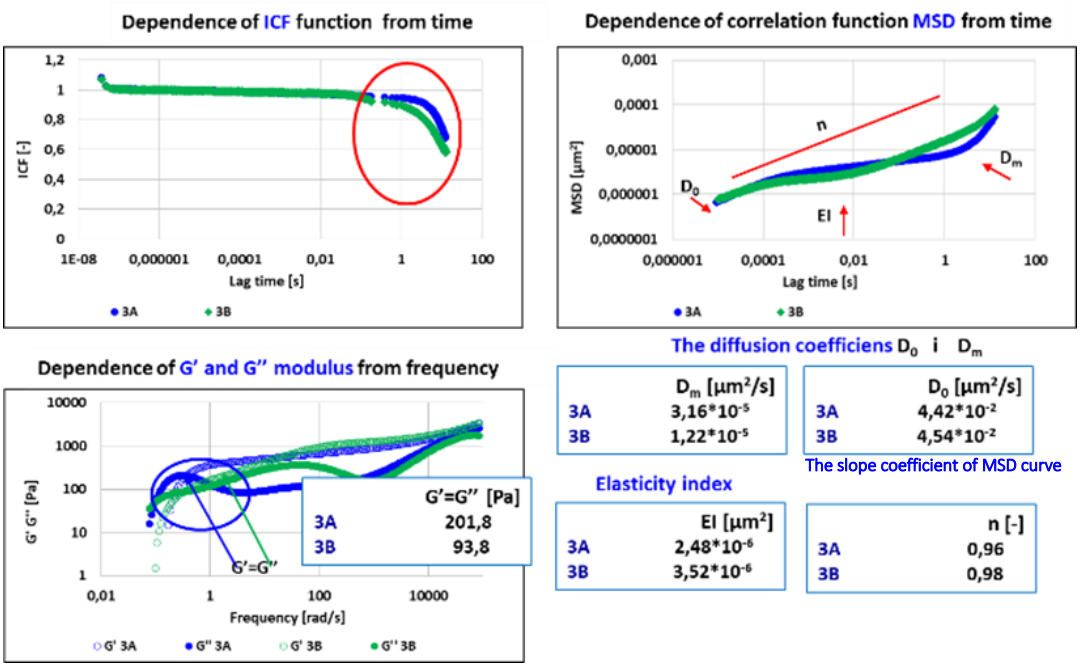

Figure 4. Results of testing of rheological properties together with determined values of characteristic parameters for composition 3A (based on abyssinian oil) and composition 3B (based on abyssinian oil modified with the addition of BCH)

This behaviour is also evidenced by the results of the G' and G'' modulus, in this case the low stability of the sample is observed on the graph, the shape of the graph of both modulus assumes variable values, first increasing, then decreasing, to increase again, which indicates a change in the structure and low stability of the tested sample, even though the intersection occurs at a much higher value of the G' and G'' modulus.

The results of the rheological tests of the grease produced with abyssinian oil are shown in Fig.4.

The introduction of the multifunctional additive to the chemical structure of the abyssinian oil-based grease caused a change in the rheological characteristics of the tested grease. Lower values of the ICF function were observed for the lubricant modified with the BCH additive compared to the base lubricant, especially at higher lag times of the ICF correlation function, which indicates structural changes in the tested lubricant caused by the introduction of the modifying additive. The calculated values of the diffusion coefficients assume a higher value in a wide range of lag times of the MSD function. Such values are indicative of a change in the chemical structure of the lubricant to which the multifunctional additive was introduced and a weakening of its structure, characterised by lower values of the MSD correlation function. The weaker structure is susceptible to change when mechanical forces are applied. A higher slope coefficient of the MSD correlation function was observed for the additive-modified grease compared to the base grease, indicating a change in structure towards a higher viscosity fluid. The higher value of the elasticity index for the additive-modified grease indicates a change in structure and weaker viscoelastic properties for this grease, resulting in a weaker structure and greater degradability under applied load, tending towards a Newtonian fluid structure.

This behaviour is also evidenced by the results of G' and G'' modulus, the point of intersection of G' and G'"" modulus occurs at lower values of both modulus, which indicates a change in structure and lower resistance of the lubricant to degradation of its structure during applied mechanical forcing.

Comparison of obtained results of rheological tests of tested lubricating compositions with spectral tests indicates that the parameters determined from rheological tests may constitute the basis for assessing changes in the chemical structure of vegetable lubricants.

4. CONCLUSION

The DWS technique is a rapid measurement technique that is non-invasive and spares the material under test. This method can be used as an instrument for monitoring lubricant quality. In contrast to other methods, data from the MSD function not only provides knowledge about the stability of the lubricant, but also leads to a deeper understanding of the microstructure of the dispersion.

A change in the calculated rheological parameters was observed for lubricating compositions produced on different vegetable oils and modified with a multifunctional additive, resulting in a change in the microstructure of the tested lubricating compositions. The determined values of rheological parameters, obtained from the data analysis of MSD, ICF functions and G', G'' modules, showed a correlation with the corresponding values determined during spectral tests characterising the chemical structure of vegetable lubricants, i.e. the calculated ratio of the number of C=C double bonds to C-C single bonds occurring in fatty acids of vegetable oils. On the basis of the obtained values of the rheological parameters, it is possible to assess changes in the structure of tested lubricants.

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