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Electric Properties of Sunflower Oil under Pressure

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ABSTRACT

This article presents the results of research on sunflower oil properties under high pressure. These properties have been investigated by the measurement of electric quantities like electric permittivity and electric resistivity and by constructing the impedance phase diagram. During the process of measurement sunflower oil has passed three long-time phase transitions. Processes in the period of this phase transitions have been well described by the electric quantities. Description of this phase transitions can be useful for oil producing and high pressure food preservation industry. Measuring setup presented in this work has simple construction so can be easy applicable in the food industry.

Key words: sunflower oil; electric permittivity; electric resistivity; impedance phase diagram; high pressure; phase transition

INTRODUCTION

Sunflower oil is one of the most widely used edible oils. It is a mixture of triglycerides of fatty acids, mainly unsaturated, which makes it an important component of healthy food [1]. Due to the triglyceride content, the oil can exist in three solid crystal forms [2-4], as shown in Figure 1. These forms are formed when pressure or temperature changes. The phase transitions between the liquid phase and the crystal forms are of a long-time nature. This means that they last much longer than phase transitions for typical substances, e.g. water. These transformations can take more than 100 hours [5]. Such long periods are due to the complicated structure of triglyceride molecules, their large size and the need to organize and change the shape of the molecules during phase transitions. Typically the temperature measurements are used to detect phase changes. However, due to the long phase transformation times in the case of oils, this method does not work. This paper presents electrical methods which are much better suited for studying such long-time phase transitions. Some of the methods based on the study of electrical physical quantities described in this paper have already been used in the study of other oils: castor oil [6], rapeseed oil [7] , soybean oil [8] and recently olive oil [9]. The review of such experiments and also other similar is given in the papers [10] and [11]. More information on solidification and the crystallization of lipids is presented in papers [12-15]. This allows us to believe that the electrical methods are an universal source of information about long-time phase transitions.. Recently, high-pressure methods of food preservation [16-18] have become more and more popular. Also vegetable oils are produced by using pressure methods. All this means that a good knowledge of the phase transitions taking place in vegetable oils (including sunflower oil) is very important for the food industry. Uncontrolled phase transformations rapidly changing the mechanical parameters of the substance may damage the equipment used in this industry blocking capillaries transmitting oil in the industrial installations. During phase transition viscosity of oil can rise even hundred times [19],[20].

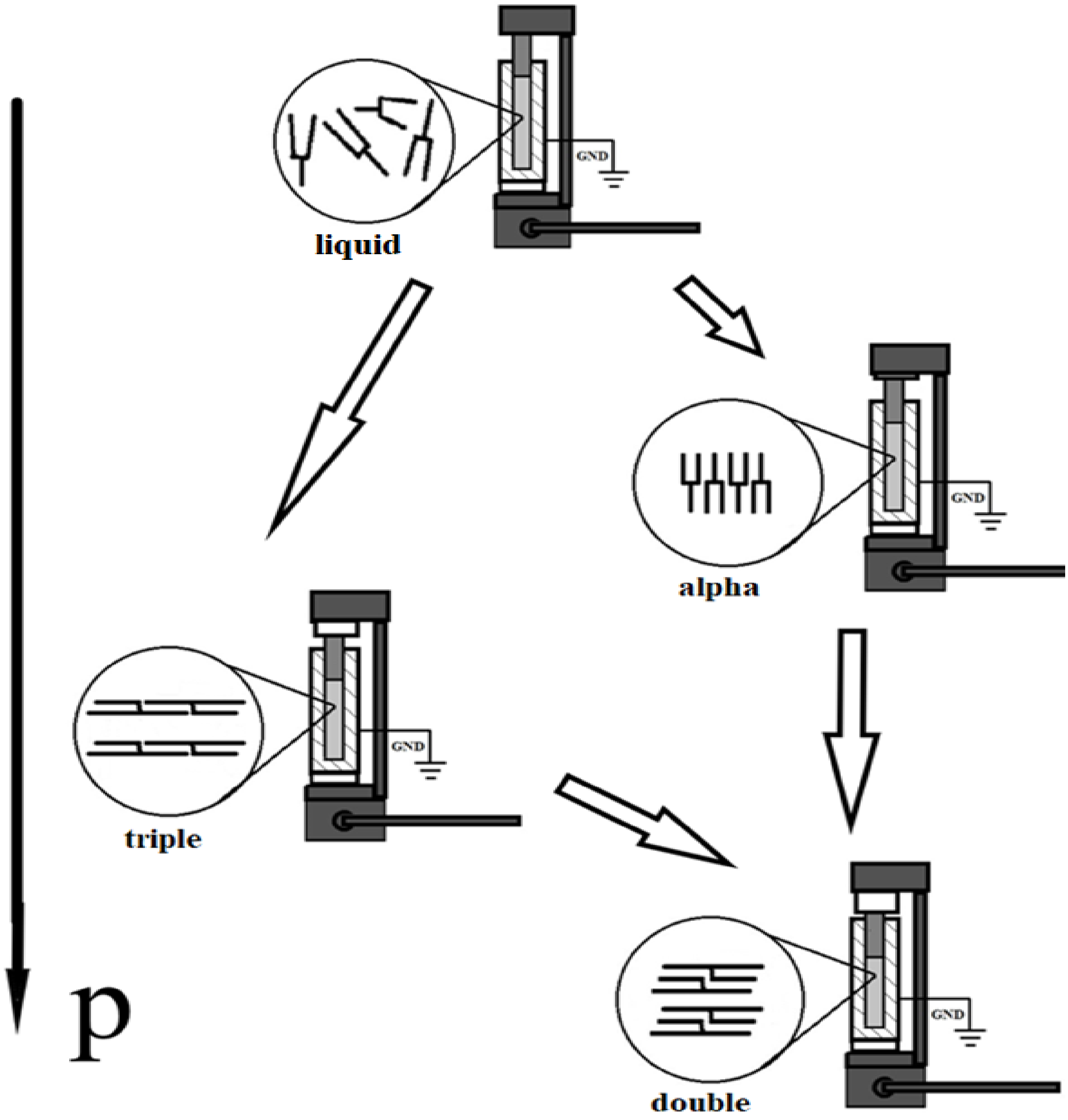

Figure 1. Sunflower oil phase transitions and its crystal forms

EXAMINED SUBSTANCE

The examined substance in this work was sunflower oil produced by A.C.E.F. Spa (Italy) with the molecular composition presented in Table 1.

Table 1. Molecular composition of sunflower oil.

Fatty acid chain	C18:2	C18:1	C16:0	C18:0	C20:0	C16:1	C18:3	C14:0	C17:0	C17:1
Content [%]	57.0	30.7	6.8	4.0	0.3	0.1	0.1	0.08	0.05	0.05

EXPERIMENATAL SETUP

The experimental setup used in our research is shown in Figure 2. This system consists of two parts: the outer and the inner one located inside the pressure chamber.

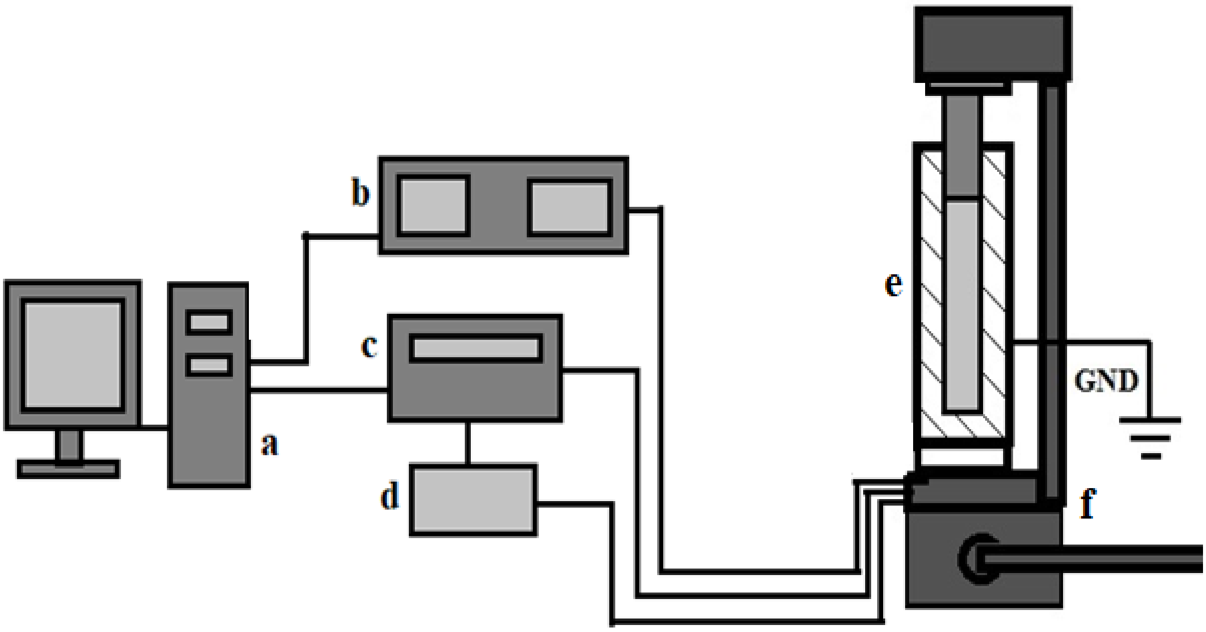

Figure 2. Data acquisition system: a – Computer with LabVIEW based acquisition system, b – RLC automatic bridge, c – multi-meter with multiplexer, d – temperature reference system, e – high pressure chamber, f – hydraulic press.

The external part of the measurement system consisted of properly connected and set measuring meters and a data acquisition computer with special software. This software was made in the LabView environment. The computer with the software is marked in Figure 2 with the letter a. The computer measured directly the duration of the experiment and collected data from measuring meters every three seconds. The first meter used in the experiments was the RLC model HP 4284a measuring bridge connected to a computer via GPIB bus, marked in Figure 2 with the letter b. This meter was used to measure the capacitance and the capacitor loss factor (DF). The second measuring device used in the experiments described in this work, connected to the computer also by means of the GPIB bus, was the HP 34970a digital universal meter. This device has been marked in Figure 2 with the letter c. Two measurements were made with this device. The first was to measure the electrical resistance of a special manganin coil. The second measurement performed on this device was the measurement of the voltage measured on the thermocouple, which the meter then automatically converted into temperature. In order to obtain precise measurements by means of a thermocouple, the temperature of its junction located outside the pressure chamber was stabilized with a specially designed temperature electronic reference system described in Figure 2 with the letter d. Another element of the measuring system used in the experiments described in this paper was a manual hydraulic press marked with the letter f in Fig. 2. Using this press, it was possible to regulate the pressure in the chamber by the means of a piston. The pressure chamber was located inside the hydraulic press, one of the jaws of which during compression extended and pressed through the pusher on the piston. The last element of the external part of the measuring system used in these tests was the pressure chamber marked with the letter e in Figure 2.

The inner part of the measuring system (located in the center of the pressure chamber) consisted of a thermocouple, a manganese coil and a capacitor. The thermocouple consisted of interconnected copper and constantan wires. One thermocouple junction was inside the pressure chamber and the other outside in a special electronic reference system. The thermocouple was used to measure the temperature inside the pressure chamber. A manganine coil (made of an alloy of copper, manganese and nickel) was used for indirect pressure measurement. Manganin is characterized by a negligible change in resistance as a result of temperature changes and a linear, within the range of interest to us, dependence of electrical resistance on pressure. The pressure-resistance characteristic for the manganin coil used was made using a load-piston manometer. The capacitor used in the study of sunflower oil was a cylindrical one. Its covers were made of brass. The centering of the covers and the spatial separation between them was achieved by means of plastic insulators placed at the ends of the capacitor.

RESULTS OF THE MEASUREMENT

Direct measurements

The physical quantities directly measured in the research on sunflower oil were: time, temperature, electrical resistance of a manganin coil converted into pressure, capacitance of the capacitor and its loss factor (DF). Graphs of the dependence of these physical quantities on time during compression are shown in Figure 3.

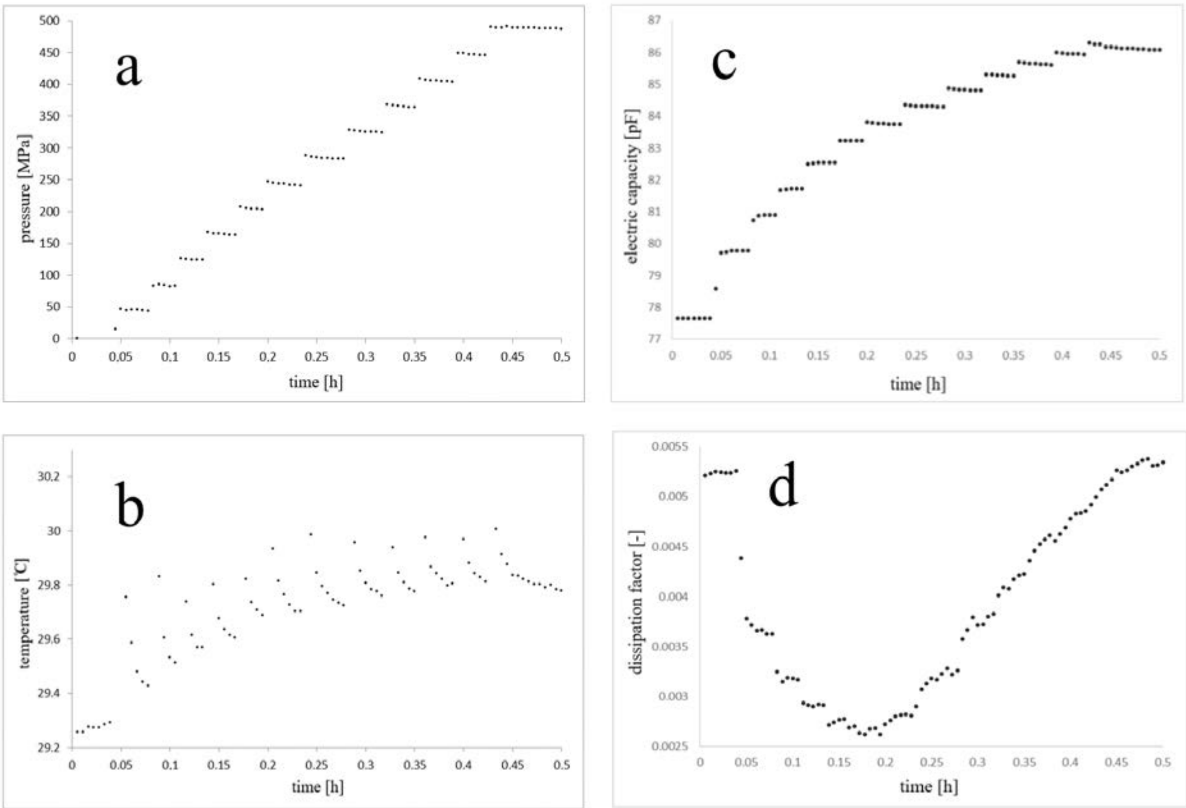

Figure 3. Quantities measured directly vs. time, a – pressure, b – temperature, c – capacitance, d – dissipation factor.

In the tests described in this work, the pressure in the pressure chamber was increased abruptly with periods of pause between these increases. This resulted in a pressure / time stepped plot shown in Figure 3a. It allowed to obtain the thermodynamic equilibrium during the research. As phase transformations in sunflower oil require not only appropriate pressure but also time to occur, after reaching the pressure of 500 MPa, the measuring system was left under constant pressure for about 170 hours. This compression method causes characteristic steps in the compression charts presented in this article. It also causes the characteristic temperature peaks formed during compression, visible in Figure 3b. The compression method used in this work gives time for the heat of compression causing these rapid changes in temperature to escape and the system to return to a stable thermodynamic state.

Impedance phase diagram

Since sunflower oil is a non-polar liquid, the conductivity of alternating current is determined by dispersion and induced electric moments, the source of which are oil particles. Apart from fatty acid triglycerides, the oil also contains traces of free fatty acids. These acids can be a source of ions that allow the flow of direct electric current. Despite this flow, due to the small amount of ions, sunflower oil is a very good electrical insulator.

Capacitive reactance modulus $|X_C|$ was calculated on the basis of the following formula:

$$|X_C| = \frac{1}{2\pi f C}$$

where: f is the frequency of the electric current of 1 kHz, and C is the electric capacity measured directly.

Resistance R was calculated on the basis of the following formula:

$$R = \frac{|X_C|}{DF}$$

where: DF is the dissipation factor measured directly.

Made on the basis of data on the capacitive reactance modulus and resistance, an impedance phase diagram showing the entire test process (both compression and the period after compression) is shown in the Figure 4. This plot is similar to the impedance phase diagram obtained in the previous article for olive oil [9]. It also takes a shape similar to a triangle.

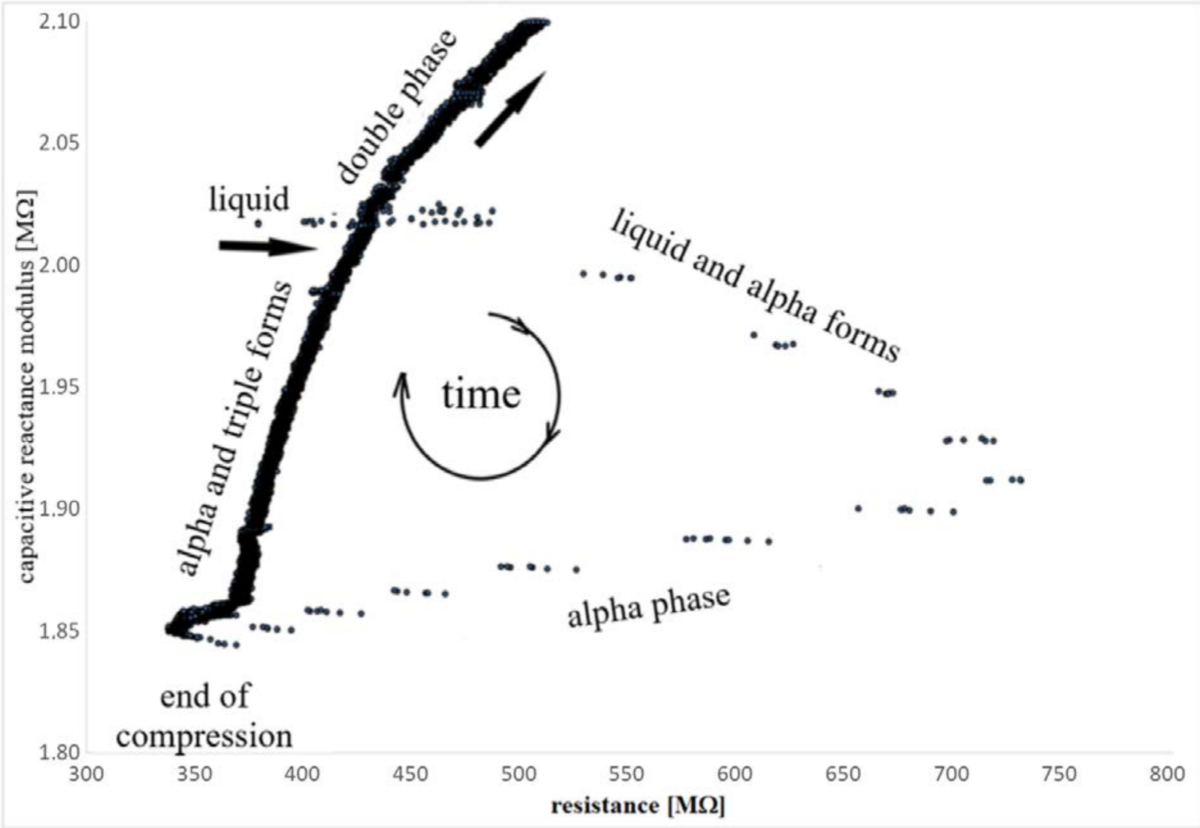

Figure 4. Impedance phase diagram for sunflower oil

At the beginning of the tests, compression takes place. As a result of this compression, the modulus of the capacitive reactance decreases and the resistance increases. This produces the upper side of the triangle. During the transition from the liquid phase to the alpha phase (when the alpha crystal forms begin to predominate over the liquid phase) the resistance reaches a local maximum. This produces the first corner of the triangle. Further, during the transformation to alpha phase, the resistance begins to decrease and the capacitive modulus drops further. This produces the bottom side of the triangle. Completion of the compression process is manifested in the form of the second vertex of the triangle. Upon completion of the compression, the conversion to the triple crystalline phase begins. During this phase transition, both the capacitive reactance modulus and the resistance begin to slowly increase. This creates the left side of the triangle. In the place where the left side of the triangle crosses the upper side (the third triangle vertex), the crystal double forms begin to gain advantage over the alpha and triple crystal forms. During the transformation to the double crystalline phase, the increase in both the modulus of capacitance and resistance rapidly accelerates. However, due to the fact that the change of pace for both electrical resistances is proportional, the angle of the side inclination undergoes only minor changes after passing through the apex.

Electric permittivity

The relative electric permittivity ε_r was calculated from the formula:

$$\varepsilon_r = \frac{C \ln \frac{r_z}{r_w}}{2\pi\varepsilon_0 l}$$

where: l is the length of the capacitor covers, r_z denotes the inner radius of the outer cover of the capacitor, and r_w denotes the outer radius of the inner cover of the capacitor, ĺ$_0$ is the permittivity in vacuum and C is the capacitance of the capacitor measured directly.

The graph of the dependence of the relative electric permittivity against time during compression for sunflower oil is presented in the Figure 5.

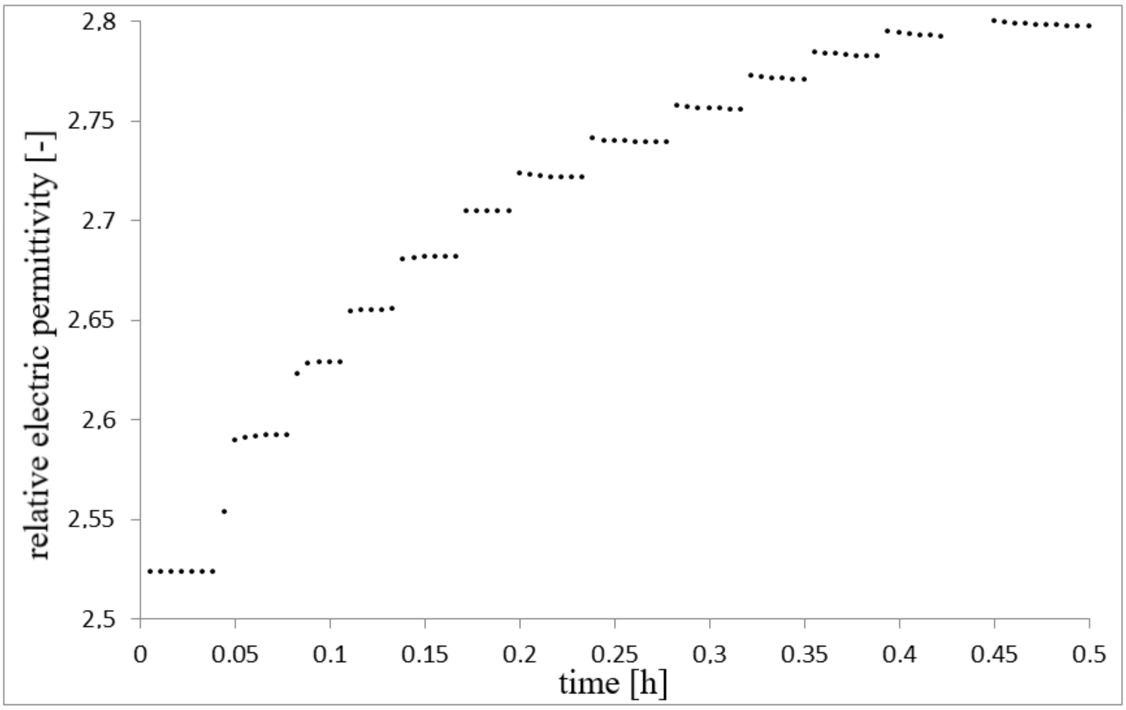

Figure 5. . Diagram of relative electric permittivity vs. time diagram during compression.

This graph shows a marked increase in the relative electric permittivity during compression. The permittivity increases because the volume of the substance decreases with increasing pressure. With the same number of molecules confined in the pressure chamber, this means an increase in the concentration of the molecules and the electric moments they produce. Additionally, during compression, the liquid phase transforms into the alpha crystal forms. The ordering of molecules as part of this phase transition creates new spaces between the molecules, allowing (with constantly increasing pressure) for an additional increase in the concentration of electric moments.

The graph of the dependence of the relative electric permittivity on the time after compression for sunflower oil is presented in the Figure 6.

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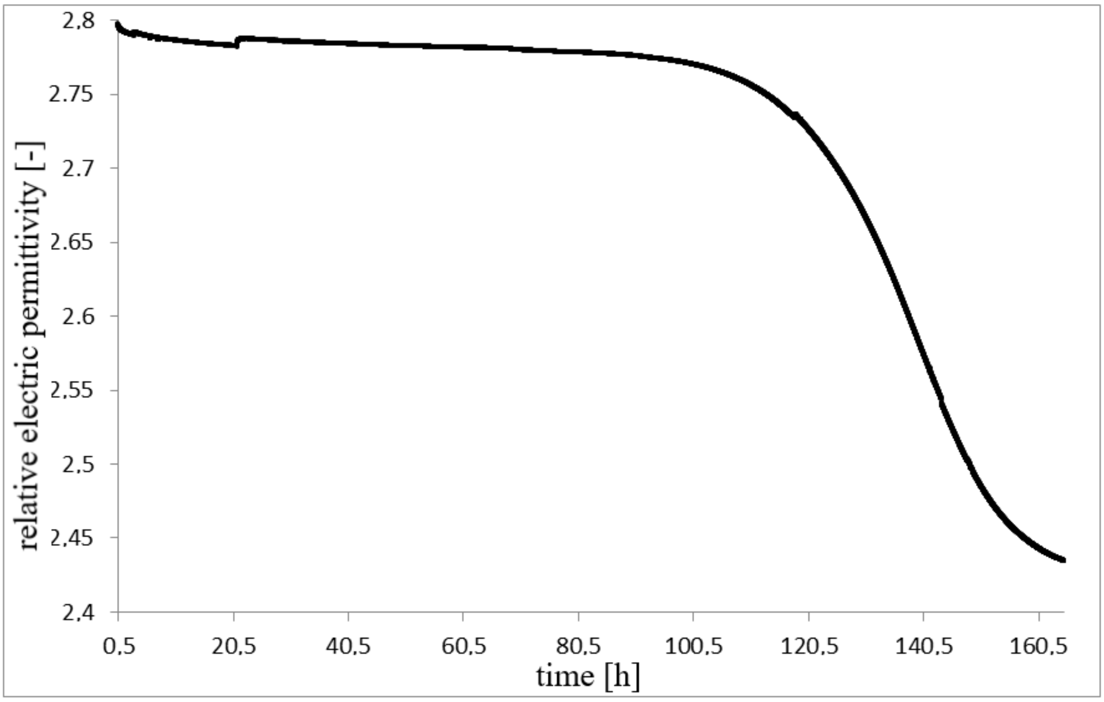

Figure 6. Diagram of relative electric permittivity vs. time after compression.

After compression, the transformation of the alpha crystalline forms into the triple form began. As the electric moments produced by the molecules were partially neutralized, due to pairing up of the "chair" forms, the relative permittivity began to decline. However, since the transformation into the triple crystal phase occurs very slowly (due to the necessary deformation of the shapes of the molecules) and is a transformation that takes place only partially, the decrease in relative electric permittivity is almost linear and very slow. For sunflower oil, this process takes almost a hundred times longer than for olive oil [9] due to the proportion of different content of triglycerides in their molecular composition. Once a sufficient fraction of the oil molecules have taken the triple form, the remaining alpha crystal forms and the triple crystal forms are transformed into double forms. Since some of the molecules have already been deformed into a chair-like phase as a result of the phase transformation of the alpha crystal phase into the triple phase, the conversion to the double phase is much faster. Due to the fact that during the transformation into a crystal form, the double “chair” forms of the paired molecules begin to adhere to each other practically along their entire length, so almost complete neutralization of the electric moments generated by the molecules occures. This in turn causes an intense decrease in the electric permittivity of the oil.

Figure 7 shows the dependence of the relative electric permittivity on pressure during the entire measurement. This diagram clearly shows a sharp decrease in permeability resulting from the phase transition to the double phase.

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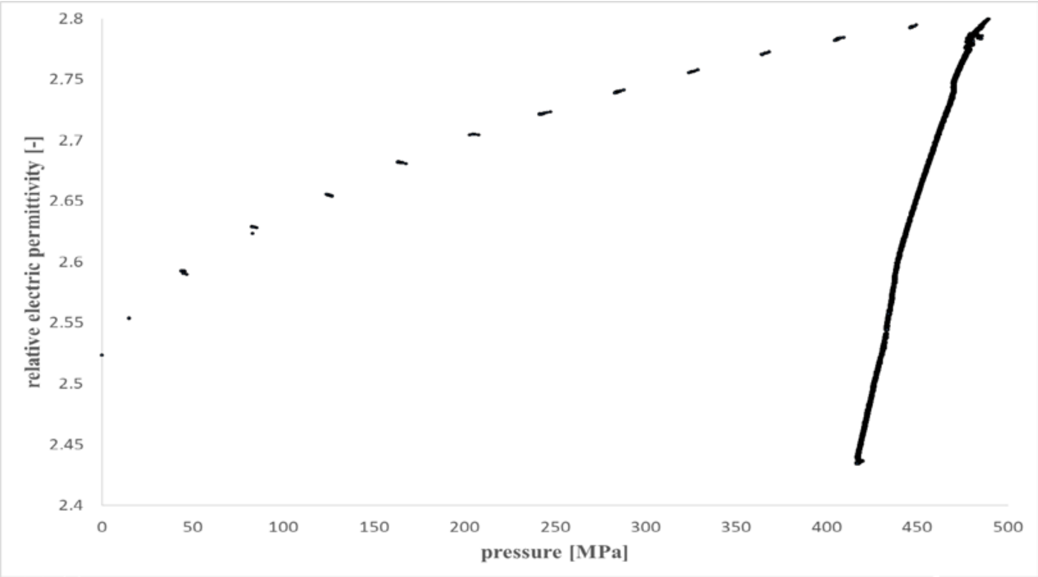

Figure 7. Diagram of relative electric permittivity vs. pressure during and after compression.

Electric resistivity

The electric resistivity was calculated from the formula:

$$\rho = \frac{2\pi R l}{\ln \frac{r_z}{r_w}}$$

where: l is the length of the capacitor covers, r_z denotes the inner radius of the outer cover of the capacitor, and r_w denotes the outer radius of the inner cover of the capacitor.

Graph of the dependence of electric resistivity on time during compression for sunflower oil is shown in the Figure 8.

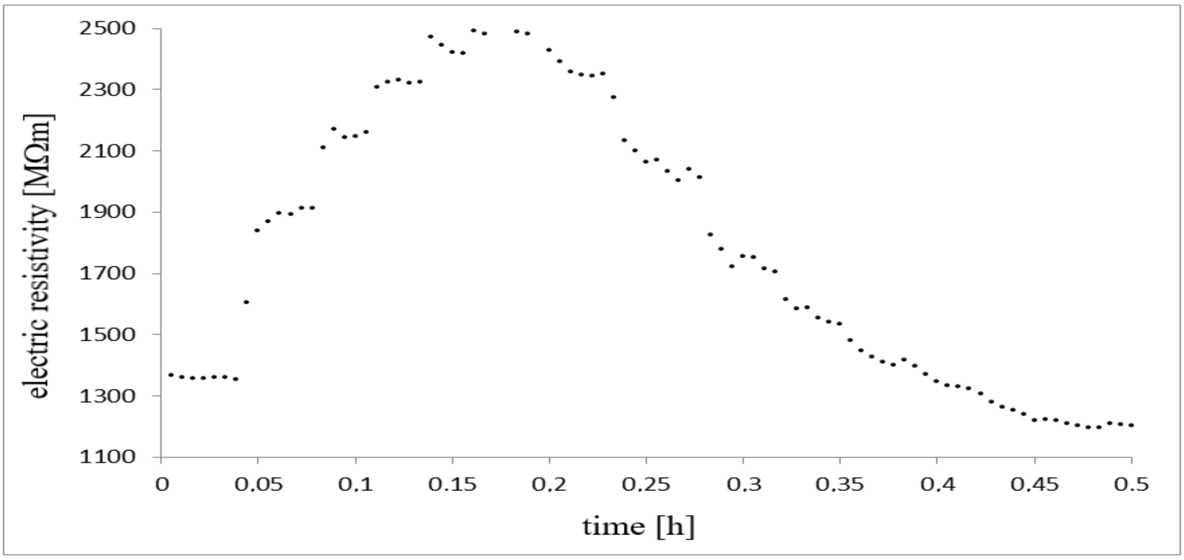

Figure 8. Diagram of electric resistivity vs. time during compression.

Initially, the tested oil is in the liquid phase. Chaotic triglyceride system of its structure hinders the flow of ions (much lighter than triglyceride molecules). As pressure increases, the gaps between molecules and the number decrease and ion channel patency decreases. Hence the initial increase in oil resistivity. When the transformation to the alpha crystal phase begins, the molecules begin to organize themselves, creating new ion channels. The ordering of the molecules also creates additional free space between them. This increases the throughput and patency of the ion channels. All these processes cause that when the alpha crystalline form begins to dominate over the liquid phase (characteristic maximum of the graphs), the resistivity of the oil begins to decrease.

The graph of the dependence of electric resistivity on time after compression for sunflower oil is shown in the Figure 9.

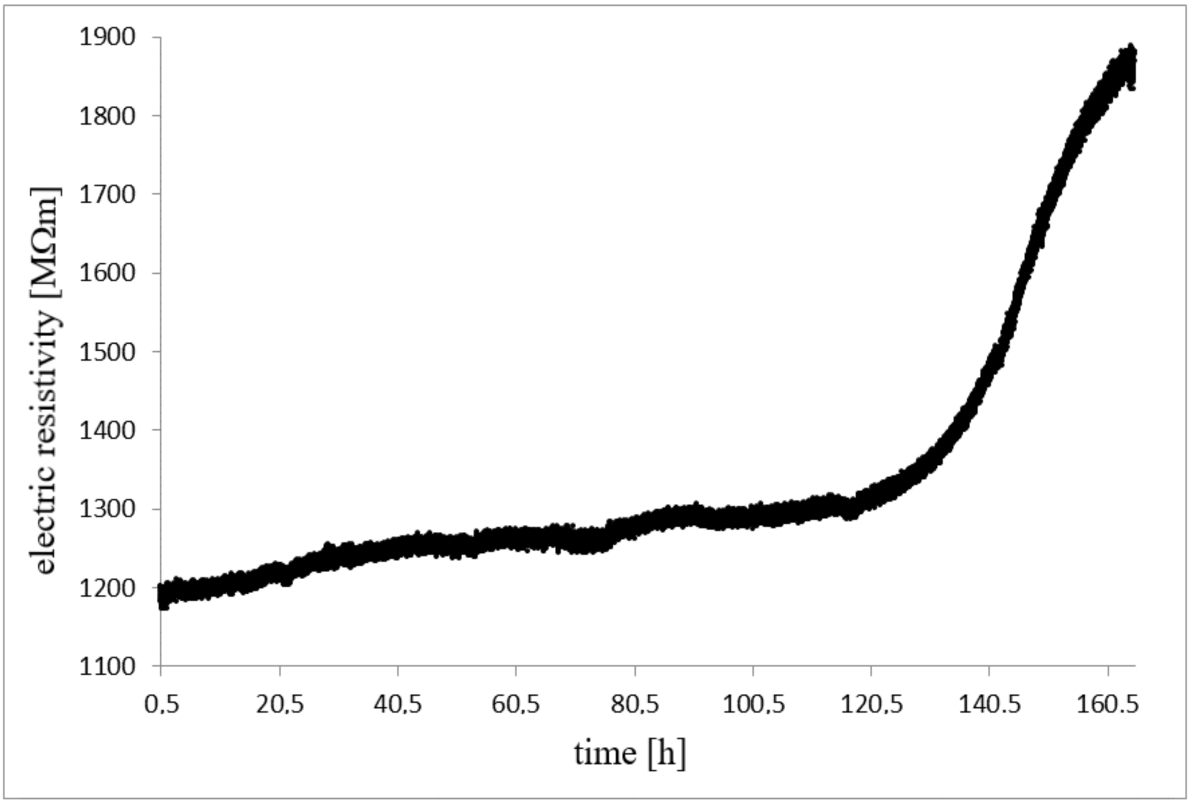

Figure 9. Diagram of electric resistivity vs. time after compression.

When the compression is complete, the alpha phase transition begins to triple crystal forms. This transformation takes place very slowly and only partially. During this transformation, the molecules deform each other's shapes and take the form of "chairs". Such molecules combine in pairs closing the ion channels between them. For this reason, the resistivity of the oil increases very slowly (almost linearly). After the appearance of a sufficient amount of triple crystal forms, their phase transition (and the remaining alpha crystal forms) to the double crystal phase begins. As a result of this transformation (and the associated pairing of the "chair" forms), subsequent ion channels are closed. Additionally, when switching the triple from to double form, the "chair" shapes of the molecules in each pair overlap, causing the entire pair to expand effectively. This causes a narrowing and reduction of the throughput of the remaining ion channels. This in turn causes a marked and rapid (compared to the transformation into the triple form) increase in the value of the resistivity.

Figure 10 shows the dependence of electrical resistivity on pressure during the entire measurement. The graph clearly shows the resistivity maximum associated with the alpha phase conversion and the rapid increase in resistivity resulting from the phase transition to double phase.

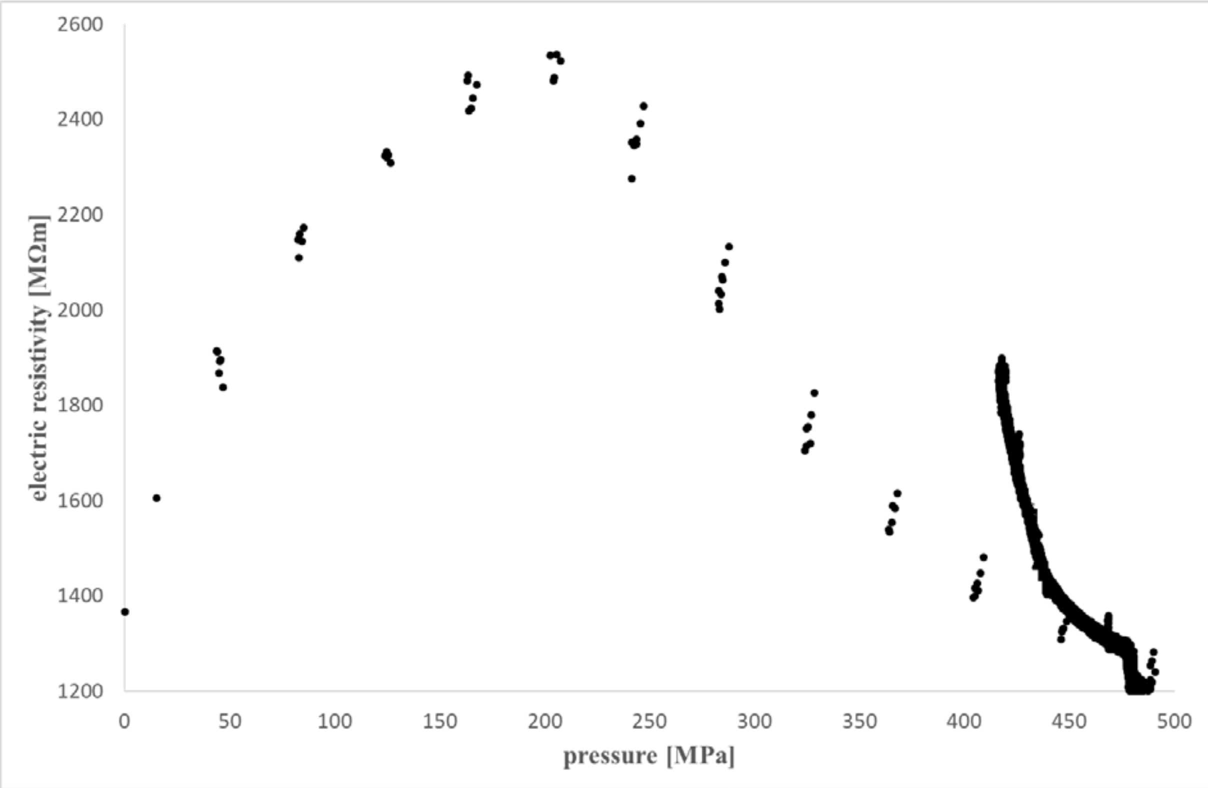

Figure 10. Diagram of electric resistivity vs. pressure during and after compression.

SUMMARY AND CONCLUSIONS

In this work, three phase transitions in sunflower oil were investigated. The first is from liquid phase to alpha phase. Second from partially alpha to triple crystal forms. The third from the triple and alpha crystal forms to the double phase. These transformations were investigated using electric methods including testing the values of electric permittivity, electric resistivity and constructing the impedance phase diagram. These parameters turned out to be very sensitive to the changes in the distribution and shape of sunflower oil molecules. They allowed for a detailed description of the condition of the tested oil. They are also much more sensitive to changes in oil properties and simultaneously much more resistant to external conditions than temperature. This is especially important during processes in sunflower oil that last more than 150 hours. It can be seen in the Figure 11 and Figure 12.

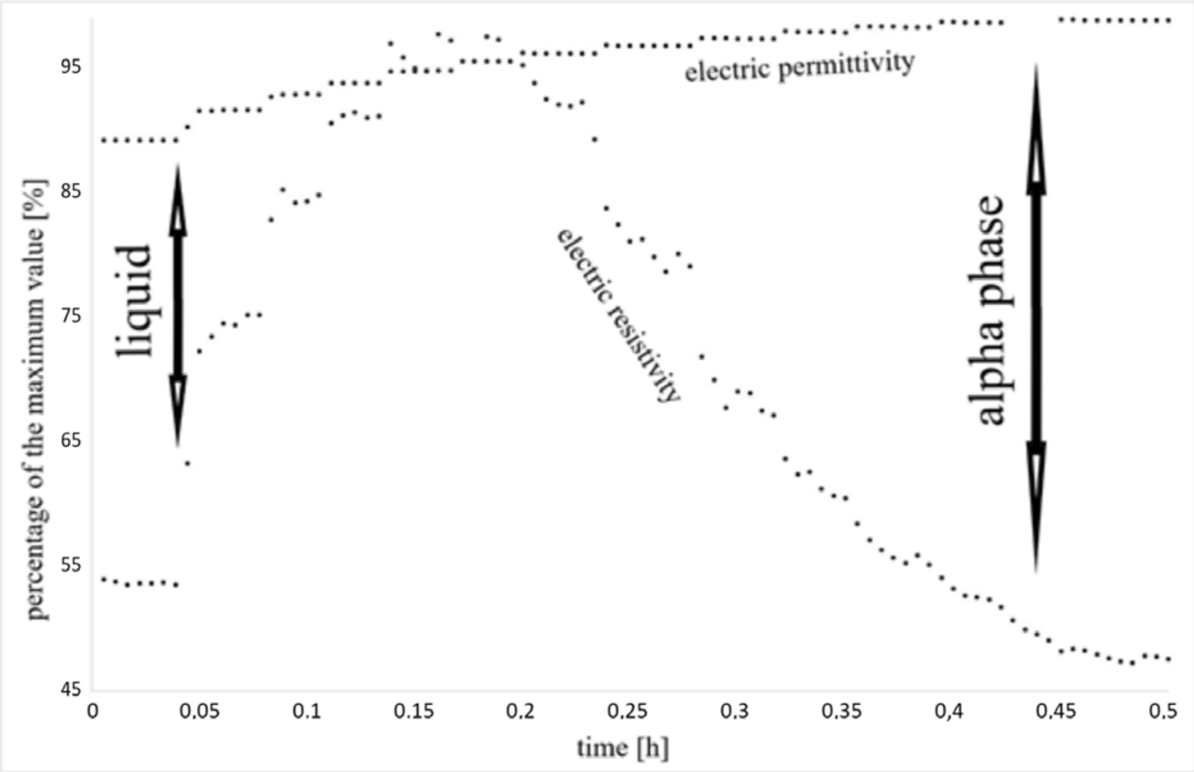

Figure 11. Comparison of the dependence of electric permittivity and electric resistivity on time during compression.

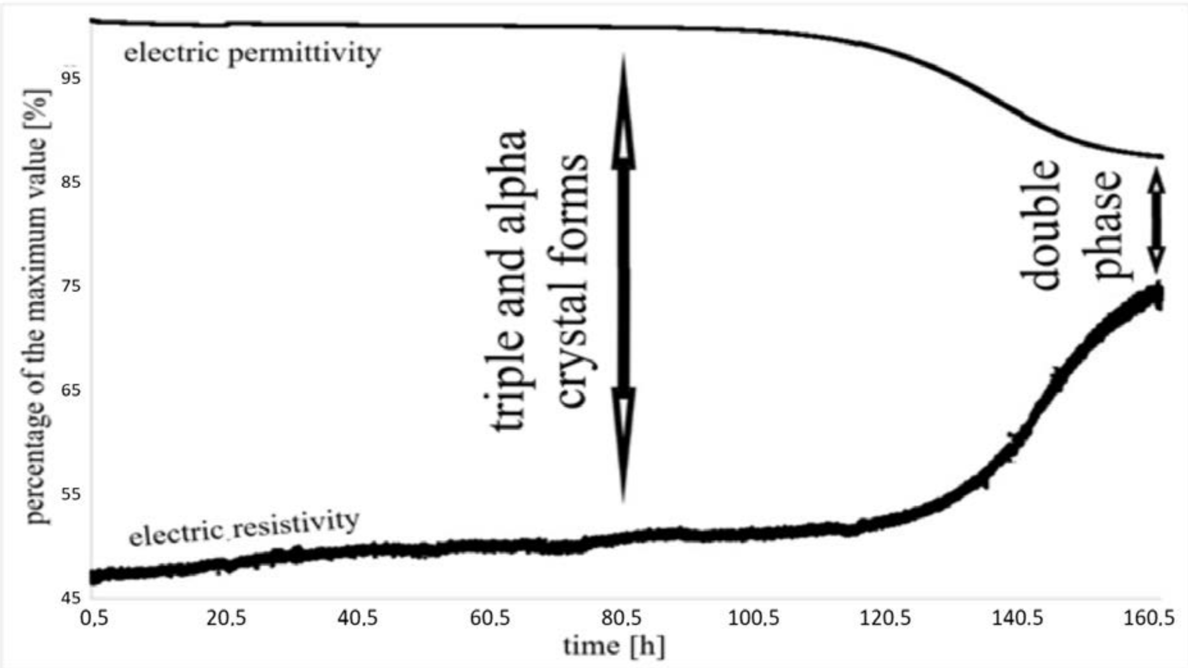

Figure 12. Comparison of the dependence of electric permittivity and electric resistivity on time after compression.

The impedance phase diagram and the diagram of the electric resistivity versus time show a similar shape to the graphs of the same quantities for the olive oil presented in the paper [9]. A similar shape of the electric permittivity diagrams to the one presented in this work can also be observed in earlier works [6-9]. All this proves that the research methods based on electrical parameters selected in this work are universal in the study of long-time phase transitions occurring in vegetable oils and other mixtures of fatty acid triglycerides. Additionally, the simple-design measuring equipment presented in this paper allows for easy application of these methods in industries related to the production of oils or high pressure food preservation. The determination of the dielectric properties of edible oils is the basis for the study of their electrical parameters. Due to the complex composition of various chemical compounds, it is necessary to study not only the changes in capacity but also the entire impedance [21].

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