



# Mechanical properties of sunflower oil under pressure

L. T. Pawlicki<sup>1</sup> · A. J. Rostocki<sup>1</sup> · D. B. Tefelski<sup>1</sup> · R. M. Siegoczyński<sup>1</sup> · S. Ptasznik<sup>2</sup>

Received: 17 July 2021 / Revised: 18 September 2021 / Accepted: 2 October 2021 / Published online: 15 November 2021  
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## Abstract

This article presents the results of research on the influence of high pressure on the mechanical properties of sunflower oil. The pressure value was changed by the stepwise method to obtain thermodynamic equilibrium. Dependencies of changes in the volume and compressibility of sunflower oil on pressure were investigated. A discontinuous (step) change was observed indicating the appearance of the first order phase transformation. The phase transition for sunflower oil was observed in the pressure range from 450 to 500 MPa after about 170 h. Most likely, then, there was a change to the double crystal phase. The time after which this transformation took place was the longest of all times that the authors have observed so far for the study.

**Keywords** Sunflower oil · High pressure · Compressibility · Phase transition

## Introduction

The development of high pressure food preservation (HPP) methods in many laboratories around the world has initiated, the intensive research into changes in the physical properties of edible oils under the influence of high pressure. In this method (HPP), food is stored for 5–20 min in a pressure chamber under a pressure of about 600 MPa [1–6]. The effect of pressure on the properties of edible oils is of interest as they are one of the main ingredients in high pressure preserved foods. On the other hand, phase transitions caused by high pressure occur in vegetable oils and then require a fairly long keeping of the oil under high pressure above a certain minimum pressure value characteristic for each type of oil. This time can be up to several hundred hours. For the first time such a transformation was observed in the case of castor oil [7]. Transitions caused by the increase in pressure are analogous to the changes caused by lowering the temperature and constitute a transition to a crystalline or amorphous solid state. Phase transitions caused by temperature changes in oils have been known for quite a long time [8–12]

while the influence of pressure was mainly reduced to the study of PVT characteristics [13, 14]. Recently, the significant progress has been made [15, 16] by the optical observation of pressure-induced crystallization of triglycerides. The properties of edible oils were also tested in the high pressure laboratories. These experiments were a continuation of previous studies on pressure changes of the physical properties of castor oil [17]. The measurements of optical properties of triglycerides [18] showed the occurrence of the first order phase transformations. This phenomenon in the formation of a pressure-induced phase transition has been investigated with multiple methods, showing discontinuous changes in volume [19], refractive index [18], dielectric permittivity [20] and viscosity [21–23] during the phase transition. Most of these effects have been summarized in the paper [17]. Further, progress was achieved thanks to the study of pressure changes of triolein [14, 22, 24, 25] showing similar phase transformations as in castor oil. Both these substances are the mixtures of fatty acids triglycerides. On this basis, the authors predicted the occurrence of a phase change in a wide class of edible oils with the above properties [26–28]. These predictions were confirmed by observations of the phase change in rapeseed oil [26]. Further, the measurements of the  $V(p)$  and  $\varepsilon(p)$  dependences were performed for soybean oil [27] and lately in olive oil [28], showing a similar behavior. Therefore, it is expected that sunflower oil should have a similar relationship between volume and pressure. So the authors have tested sunflower oil under high pressure. All the described oils are mixtures of triglycerides,

✉ L. T. Pawlicki  
leszek.pawlicki@pw.edu.pl

<sup>1</sup> Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662, Warsaw, Poland

<sup>2</sup> Department of Fat and Meat Technology, Institute of Agricultural and Food Biotechnology, ul. Jubilerska 4, 04-190 Warsaw, Poland

which causes phase transitions between the liquid phase and the alpha, triple and double crystal forms [29].

## Experimental arrangement

Sunflower oil produced by A.C.E.F. Spa (Italy) was used for the experiments. The molecular composition of the sunflower oil which was used in this research is presented in Table 1.

As it can be seen in Table 1 the sunflower oil is a molecular mixture mainly of triglycerides of linoleic acid (57.0%) and oleic acid (30.7%). The physical properties of sunflower oil with high oleic acid content were described in [30–32]. It was all the more interesting to compare the pressure transitions from this publication with the changes

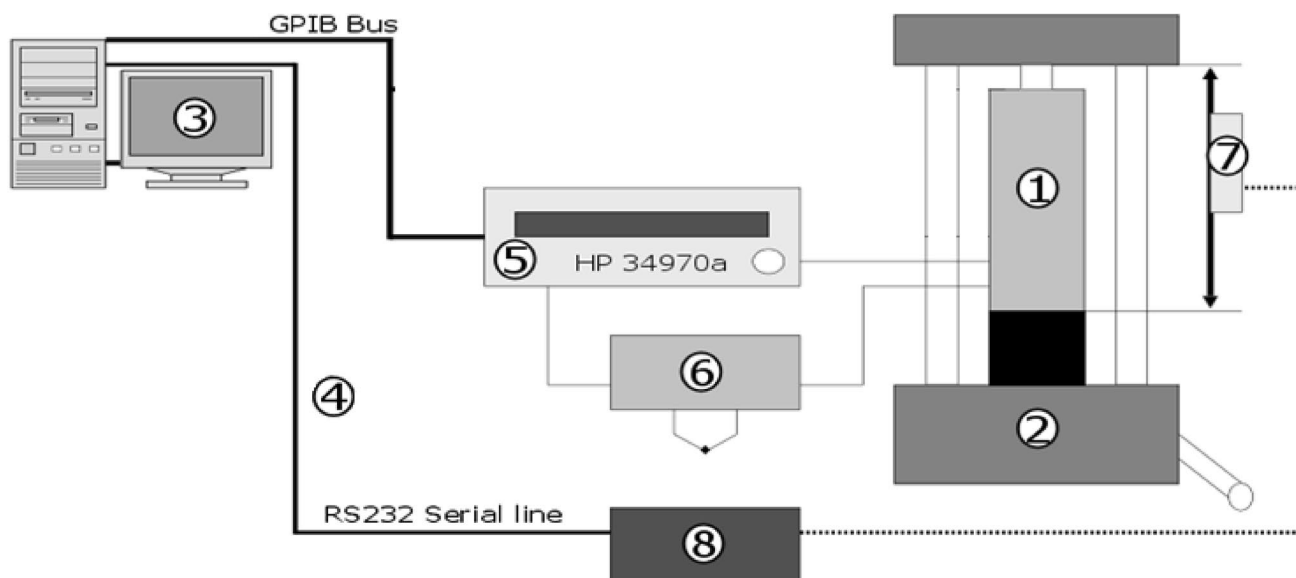
observed by the authors of this article, and also whether there is no phase transition at a slightly higher pressure, which was not shown in the work [31].

The experimental setup used in our research is shown in Fig. 1.

The samples were placed under high pressure in the chamber (1) in the form of a thick-walled cylinder with an internal diameter of 17 mm with a straight piston [26]. The force on the piston was exerted by means of a hydraulic press with a pressure of up to 20 tons (2). All this mechanical system was connected with the electronic system, which consisted of a set of electronic meters and a multi-channel data acquisition system operating in the LAB VIEW environment by National Instruments. The maximum pressure has been limited to about 1.2 GPa due to the maximum pressure of the hydraulic press (2). The displacement of the piston was measured using an electronic caliper (7) with a resolution of 0.01 mm which was also connected to the data acquisition system via the RS232 interface (8). A manganine transducer with a resistance of 500  $\Omega$  was used to measure the pressure. The resistance of this transducer was measured with a precision HP 34,970 multimeter (5). The pressure measurement resolution was better than  $\pm 0.5$  MPa. The sensor was calibrated using a MT 6000 weight and piston pressure gauge having class 0.05.

**Table 1** Sunflower oil molecular composition

Fatty acids		%
Miristic acid	C14:0	0.08
Palmitic acid	C16:0	6.8
Palmitoleic acid	C16:1	0.1
Margaric acid	C17:0	0.05
Margaroleic acid	C17:1	0.05
Stearic acid	C18:0	4.0
Oleic acid	C18:1	30.7
Linoleic acid	C18:2	57.0
$\alpha$ -linolenic acid	C18:3	0.1
Arachidic acid	C20:0	0.3



**Fig. 1** Data acquisition system. 1—high pressure chamber, 2—hydraulic press, 3—computer with LabVIEW based acquisition system, 4—RS232 line, 5—multimeter with multiplexer, 6—thermocou-

ple with temperature reference system, 7—digital calliper, 8—RS232 interface for digital calliper

## Results of the measurement

The pressure was generated by a hand pump in steps of 40 MPa and then held constant for approximately 2 min. To make sure that the occurring changes result from the examined phenomenon and not from the random changes of individual parameters, changes of all measured values as a function of time were observed simultaneously in individual windows on a common screen. This allowed the pressure drop to be distinguished resulting from a first order phase transition from ordinary leakage. It also allowed the system to achieve the thermodynamic equilibrium. During this time, the temperature, which was increasing due to the stepwise compression of the oil, could return to its original value and the system reached the thermodynamic equilibrium.

### $p$ – $V$ dependence

On the basis of  $p(t)$  dependence and  $V(t)$  dependence, the  $V(p)$  dependence was calculated and presented in Fig. 2. For the analysis of results, the modified Tait equation [33–35] was adopted in the form of:

$$\frac{V}{V_0} = 1 - C \ln \left( 1 + \frac{p}{B} \right)$$

where  $V$  is the volume of oil,  $V_0$  is the initial volume of oil,  $p$  is pressure,  $C$  and  $B$  are fitting factors. The Tait equation curve fitting was done using the Levenberg–Marquard optimization method. The obtained fitting coefficients were:  $C=0.079$ ,  $B=0.077$  GPa. On this basis, the isothermal compressibility can be calculated from the following expression:

$$\beta_T(p, V) = \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

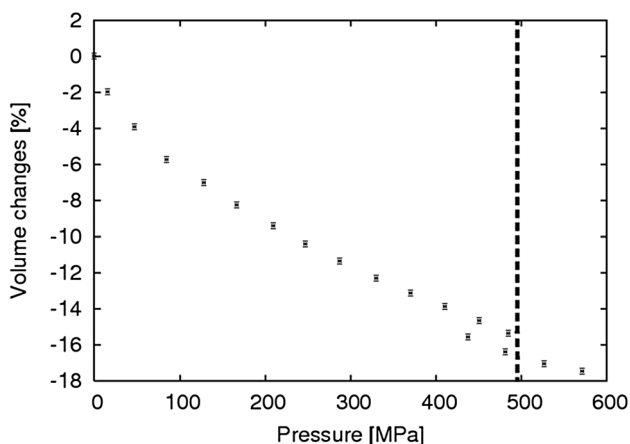


Fig. 2 Volume change as a function of pressure of sunflower oil

By differentiating the Tait equation we can get an expression enabling to calculate the compressibility of the compress liquid:

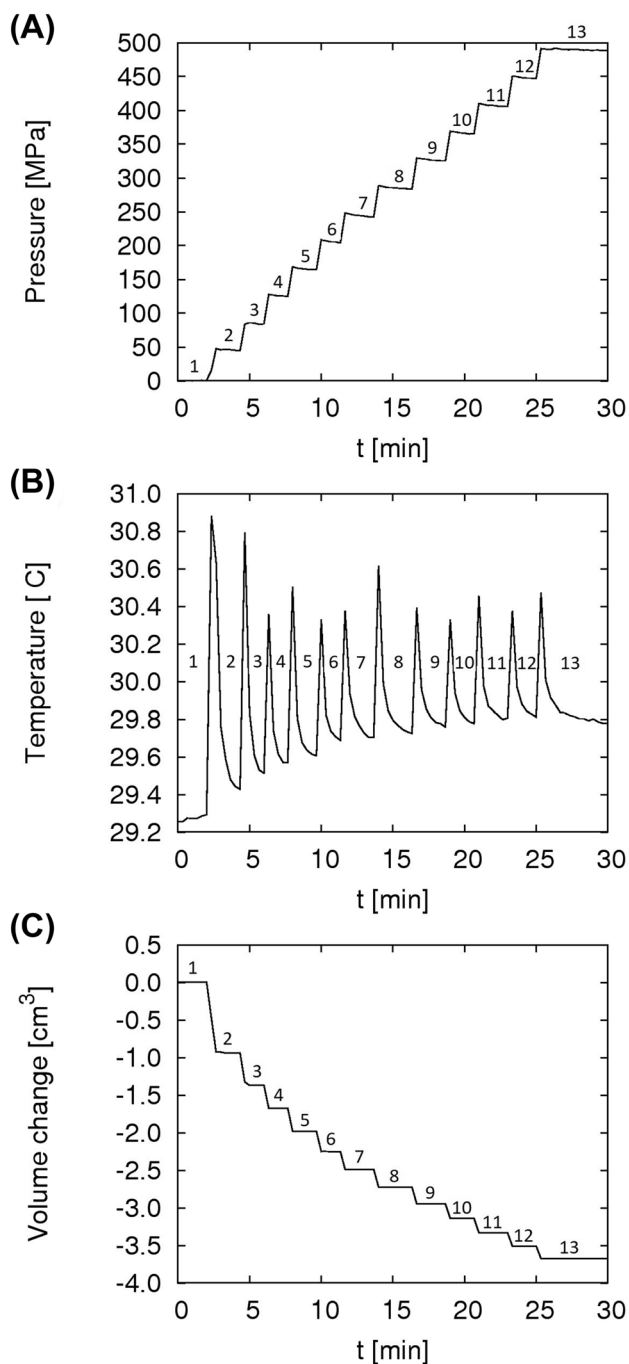
$$\beta_T(p, V) = \frac{C \cdot V_0}{V(p + B)}$$

The above relationship between  $p$  and  $V$  and the respective values of the  $C$  and  $B$  coefficients was correct in the range of pressures lower than the phase transition pressure. In Fig. 2, each of the steps in Fig. 3 is marked with a corresponding point. At a pressure of about 0.47 GPa, a sharp drop in volume can be seen as the oil solidifies. Above this point, the relation  $V(p)$  is similar, but slightly shifted downwards. In this range, the changes in volume depended not only on pressure but also on time, which suggests the coexistence of two phases and the ongoing phase transition process. In other words, the pressure was decreasing for about 2–3 h after repositioning the piston (no oil leakage was observed). This means that during this time some of the oil changed its structure to the new one with much smaller volume (higher density) probably double. The results of the first part correspond very well with the results presented by Guignon [31]. Above the phase transition, the pressure range was too short to find the matching factors for the next phase of sunflower oil.

The PVT dependence can also be determined alternatively on the basis of the free-volume theory [36, 37].

## Discussion

It is clear, that a phase transition was observed for the sunflower oil. This transformation is very similar to the one previously found in castor, rapeseed [26] and soybean oils [27]. Both the pressure range and the direction of changes (rapid volume decrease) are similar to the changes observed in castor oil [21, 22]. The difference appeared in the form of the dynamics of the phase transition and the relaxation time. The phase transition time was longer than in other oils. Although the optical properties have not been tested under pressure, in the oil removed from the high pressure chamber after the end of the experiment the abnormal lateral scattering of the laser beam transmitted through this oil was observed. This phenomenon lasted for about 2–3 days and then it gradually disappeared. A similar phenomenon was previously observed in rapeseed oil. The phase transformation presented in this paper should be further investigated using other pressure methods. It seems that it is very important for the food preservation process because the pressure of this transformation is in the range of HPP technology working pressures.



**Fig. 3** The simultaneous run of the 5 measuring channels of the acquisition system. **A** Pressure in the chamber, **B** the temperature inside chamber, **C** volume change

## Declarations

**Conflict of interest** We do not have any conflicts of interest.

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