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LONGITUDINAL AND SHEAR ULTRASONIC MEASUREMENTS IN VEGETABLE OILS

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In this paper the results of ultrasonic longitudinal and shear measurements in vegetable oils are presented and discussed. The run of the ultrasonic attenuation suggests a relaxation process at frequencies below 0.5 MHz. Another one is suggested at low temperature in the vicinity of 1 Hz.

1. Introduction

Vegetable oils play an important role in the diet because of their non-cholesterol nutrition properties. The chemical constituents of oils are triglycerides, i.e. esters of glycerol and three fatty acid molecules. The physico-chemical properties of oils are determined principally by the type and amount of triglycerides which they contain and by their thermal and shear histories.

A general chemical model of triglycerides is shown below:

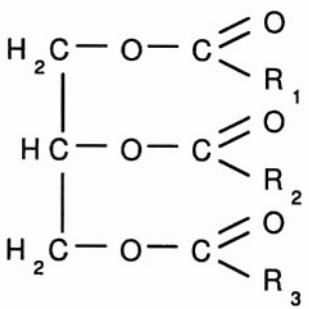

Fig. 1. General chemical model of triglycerides. R_1, R_2, R_3 are the carbon–hydrogen chains.

A variety of techniques have been used to characterise oils, including nuclear magnetic resonance (NMR), refraction measurements (RI), microscopy, X-ray diffraction, density measurements, neutron scattering and differential scanning calorimetry (DSC) [1, 5].

The ultrasonic method was used also to determine the rheological properties of vegetable oils [4, 6]. Ultrasonic spectroscopy has already proved to be a valuable tool for monitoring the dynamic rheology of oils [6] and may have many interesting applications in future in the oil industry. However, the latter is not much interested in the results until now.

The ultrasonic velocity, attenuation of sound and the dynamic viscosity or rheological properties as functions of temperature and frequency are usually measured in oils. The ultrasonic velocities in liquid oils can be related to the concentration of the constituent triglycerides [1]. By measuring the attenuation of longitudinal and shear waves over a wide range of frequencies, it is possible to determine the dynamic bulk and shear moduli as well the viscosities of the oils [6].

It has been proposed that the relaxation of the shear viscosity is due to molecular reorientational changes in the ultrasonic field, whereas the relaxation in the bulk viscosity is due to structural changes [1]. In general, there are two types of motion: viscous movements in which energy is dissipated and elastic deformations without dissipation of energy. In the simplest version of the viscoelastic theory, it is assumed that the viscous and elastic effects may be treated independently and that terms corresponding to the two effects may be added linearly in the equation of motion. Then each relaxation process occurs with a single relaxation time.

In highly viscous oils, such as castor oil, where the interaction between the triglyceride molecules is strong, the bulk and shear viscosities have similar relaxation frequencies, whereas in low viscosity oils, they have different relaxation frequencies [1]. This is probably due to the fact that a strong interaction occurs between the triglycerides in highly viscous oils.

The methods of ultrasonic measurements are typical [2, 4]. The results of ultrasonic measurements of some oils are given below.

2. Theory

The ultrasonic longitudinal waves can be considered as a superposition of pure compression and pure shear. If the period of the sound waves is much longer than the relaxation time of the liquid, the absorption coefficient is [2]

$$\alpha = \omega^2 \eta / 2\rho C^3, \tag{1}$$

where C is the velocity of sound, ω is the frequency, η is the viscosity and ρ is the density.

When the period of the applied stress becomes comparable to the structural relaxation time of the liquid, the attenuation increases rapidly. For a very high alternating stress, the molecules of the liquid do not have time enough to adjust their positions by inelastic (or viscous) movements in the period during which the force is applied, and the molecular motion is that of an elastic deformation. In this region, the viscosity consists of the shear viscosity, η_s, and the bulk one, η_v, and the absorption coefficient is:

$$\alpha = \omega^2 (\eta_s + 4/3\,\eta_v) / 2\rho C^3. \tag{2}$$

The velocity of ultrasonic waves C is connected with the physical properties of the liquid to be measured according to the following equation:

$$C^2 = E/\rho, \tag{3}$$

where E is the elastic modulus and ρ is the density of the liquid. For the longitudinal ultrasonic waves $E = K$, where K is the bulk modulus connected with the adiabatic compressibility. At low temperatures the liquid may have viscoelastic properties; then $E = K + 4G/3$, where G is the shear modulus. Usually all the moduli are complex, i.e. $E^* = E' + jE''$, $K^* = K' + jK''$ and $G^* = G' + jG''$. Shear waves propagate through most solids but they are highly attenuated in liquids and usually do not travel far enough to be detected and measured directly. The shear mechanical impedance is then measured in order to determine the shear modulus.

The shear mechanical impedance ($Z^* = R + jX$) is measured by applying transverse waves. The relation between the mechanical impedance $Z^*_{j\omega}$ and the complex modulus of shear elasticity of a liquid $G^*_{j\omega}$, for the frequency ω is expressed by the equation

$$(Z^*_{i\omega})^2 = \rho G^*_{i\omega}\,, \tag{4}$$

where ρ is the density of the liquid

$$Z^*_{i\omega} = R + iX, \qquad G^*_{i\omega} = G' + iG''. \tag{5}$$

The mechanical shear impedance is determined by measurements of the amplitude reflection coefficient, k, and phase, θ, of the ultrasonic wave on the boundary of two media, i.e. on the boundary between the solid body and the liquid. The mechanical shear impedance of a liquid in the case of a plane wave falling perpendicularly on the boundary surface is

$$Z^*_{i\omega} = Z_Q \frac{1 - k^2 + i2k\sin\theta}{1 + k^2 + 2k\sin\theta}\,, \tag{6}$$

where Z_Q is the impedance of the solid body.

For most of the liquids, the wave phase shift related to the reflection is small, as the impedance of the liquid is $|Z| < 0.1 < |Z_Q|$; therefore, it can be accepted that $\cos\theta = 1$. Then Eq. (6) has the following form:

$$Z^*_{i\omega} \cong Z_Q \left(\frac{1 - k^2}{(1 + k)^2}\right) + i\left(\frac{2k\sin\theta}{(1 + k)^2}\right) = R + iX. \tag{7}$$

The error caused by the assumption $\cos\theta \approx 1$ does not exceed 1%. Using Eq. (8), the real part of the impedance can be calculated if only the amplitude reflection coefficient is known:

$$R = Z_Q \left(\frac{1 - k}{1 + k}\right). \tag{8}$$

Having R and X, the components of the shear modulus of a liquid, $G^*_{i\omega}$, can be determined:

$$G'_\omega = \frac{R^2 - X^2}{\rho}\,, \qquad G''_\omega = \frac{2RX}{\rho} \tag{9}$$

while the dynamic viscosity is expressed by the equation

$$\eta'_\omega = \frac{2RX}{\omega\rho}. \tag{10}$$

The variations of the real and imaginary components of G^*, η^* and Z^* as functions of the normalised frequency are shown in Fig. 2.

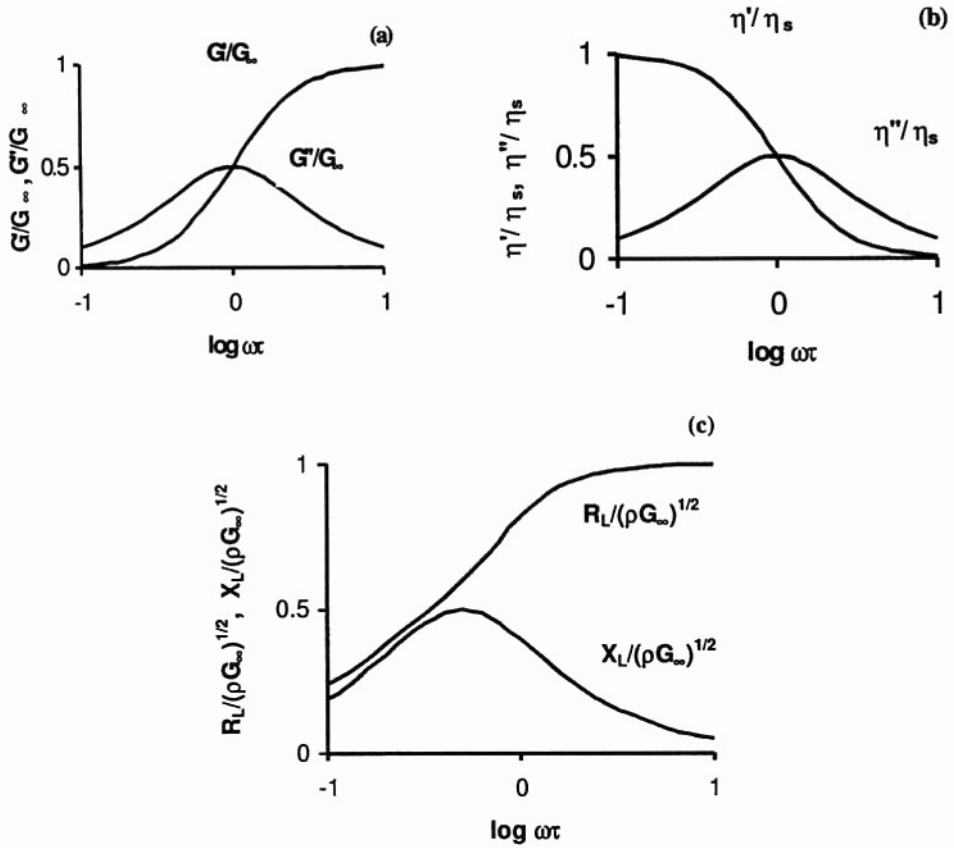

Fig. 2. Variation with frequency of the normalised components of a) the rigidity modulus, b) the dynamic viscosity, and c) the shear mechanical impedance for a single relaxation process [2].

3. Results

Vegetable oils are an interesting object for the investigation of the dynamic viscosity properties because the absorption of longitudinal ultrasonic waves in them has been studied over a wide frequency range, so that with the available data on the shear viscosity it is possible to separate the pure bulk viscosity from the attenuation coefficient.

Our measurement results are reported below and compared with the results of other authors. The chemical components of the rapeseed oil produced by Polish refinery [3] are:

acid	formula	contents in rapeseed oil, % raw	refined
Palmitic	$CH_3(CH_2)_{14}COOH$	5.1	4.9
Oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	61.8	61.4
Linoleic	$CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_7COOH$	19.9	20.6
Linolenic	$CH_3(CH_2{-}CH{=}CH_2)_3CH_2(CH_2)_6COOH$	9.2	9.0

The chemical components and specific gravities for edible oils are shown in Table 1 [4].

Table 1. Chemical components (%) and specific gravity (g/cm^3) of edible oils.

	Oil			
Acid	Safflower	Soybean	Peanut	Rapeseed
Myristic	trace	trace	trace	trace
Palmitic	8.8	12.1	13.2	11.3
Palmitoleic	trace	trace	trace	trace
Stearic	3.1	3.7	4.1	4.0
Oleic	14.0	21.0	30.1	21.8
Linoleic	73.6	53.2	44.9	53.4
Linolenic	0.3	7.7	3.8	8.0
Arachidic	—	—	0.7	—
Others	0.2	2.2	3.2	1.5
Specific gravity	0.914	0.913	0.912	0.915

The viscosity of the rapeseed oil measured with an Ubbelohde viscometer as a function of temperature is shown in the Fig. 3. The changes in the ultrasonic velocity for rapeseed oil as a function of frequency are shown in Fig. 4.

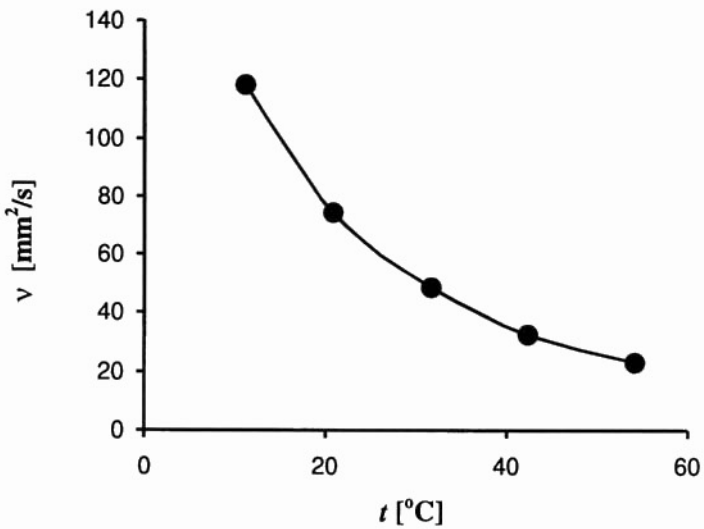

Fig. 3. Viscosity of rapeseed oil vs temperature.

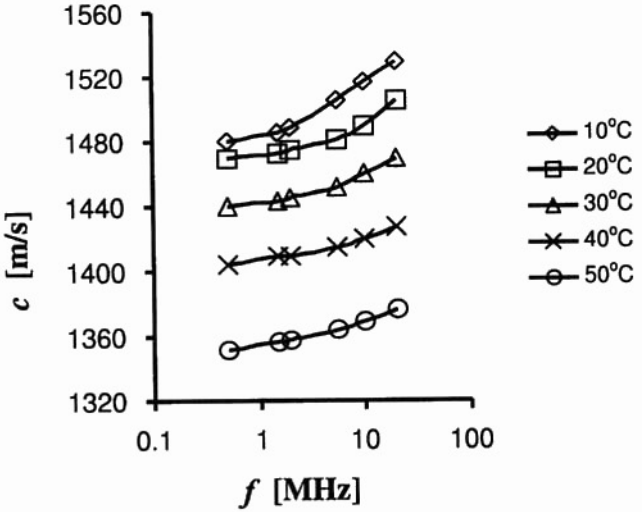

Fig. 4. Velocity of rapeseed oil vs. frequency.

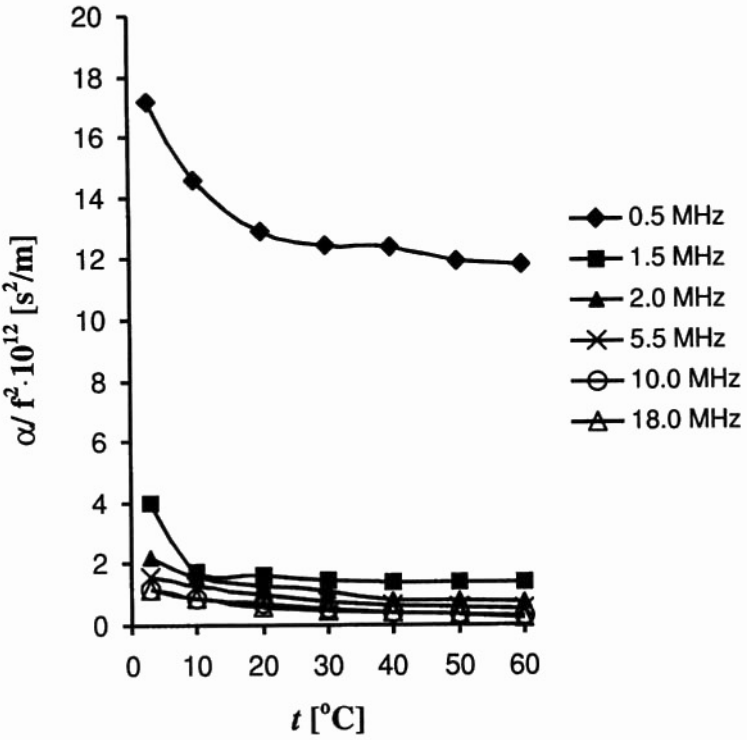

Fig. 5. Ultrasonic attenuation of rapeseed oil vs. temperature.

Many measurements of the ultrasonic velocity in liquids and their temperature dependencies have been reported [7]. In a wide range of liquids, the ultrasonic velocity decreases linearly with increasing temperature over a considerable range of temperature. Deviations from this linear relation occur near the boiling points and the melting points of the liquids, so that an extrapolation of the measured ultrasonic velocities from higher temperatures to the melting point can lead to errors of the order of -2 to -6%. In most of the edible oils, the coefficient dC/dT is close to -3 to -3.4 [1]. The same linear dependence was found for the rapeseed oil.

Considerable changes in ultrasonic attenuation with frequency between 0.5 and 18 MHz are observed in rapeseed oils (Figs. 5 and 6).

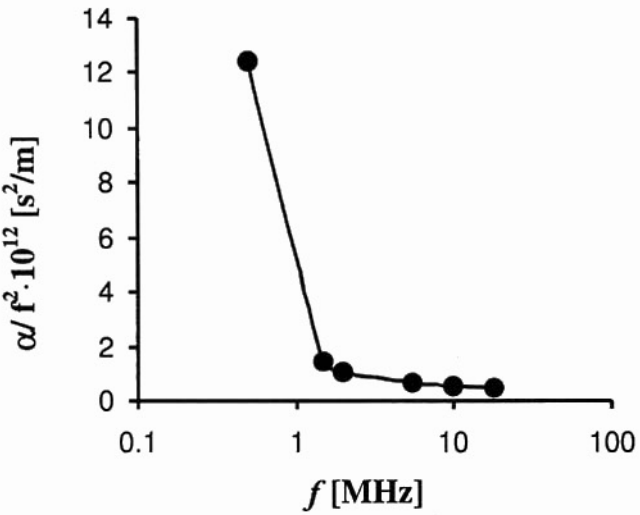

Fig. 6. Ultrasonic attenuation of rapeseed oil vs. frequency. Temperature 30° C.

The run of the attenuation of ultrasonic waves in the rapeseed oil (Fig. 6) measured as a function of frequency suggests a relaxation process at frequencies lower than 0.5 MHz, for which our measurement method can not be applied. The measurements of rapeseed oil performed with DMTA technique [5, 8] using a torsional rheometer signal suggest the possibility of a relaxation process at frequencies around 1 Hz within the temperature limit — 30°C and 0°C.

The shear modulus measured in those temperatures is rather low (circa 30 MPa) and in this range the scale of the equipment was not very accurate. The change of the shear modulus as a function of frequency is shown in Fig. 7a. The curve in Fig. 7b shows the change of the loss angle ($\tan\delta = G''/G'$) and supports the suggestions of a second relaxation process in this range.

The frequency dependence of the dynamic shear viscosity, shear elasticity and effective viscosity in castor oil is shown in Fig. 8.

The shear elasticity measurements of castor oil as a function of frequency show also rather low values and have not been determined within the low frequency range [6].

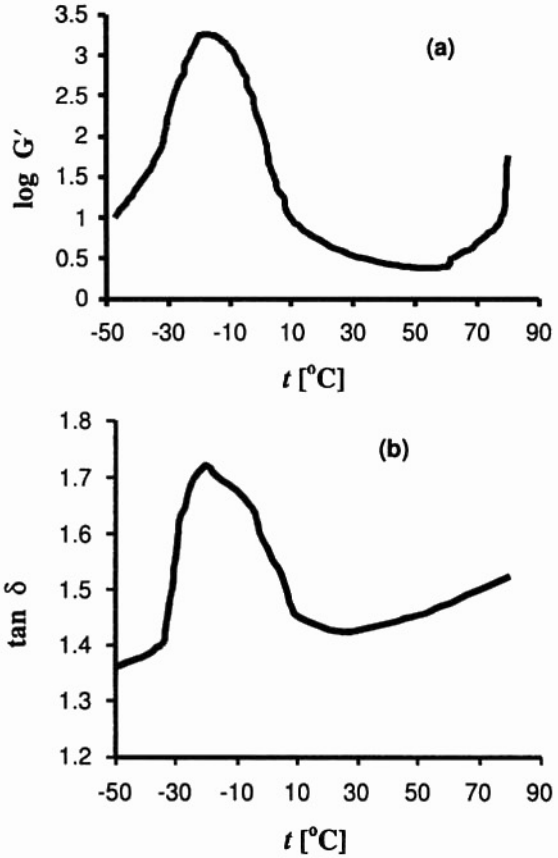

Fig. 7. Changes of the shear modulus (a) and the tan of loss angle (b) vs. temperature for rapeseed oil.

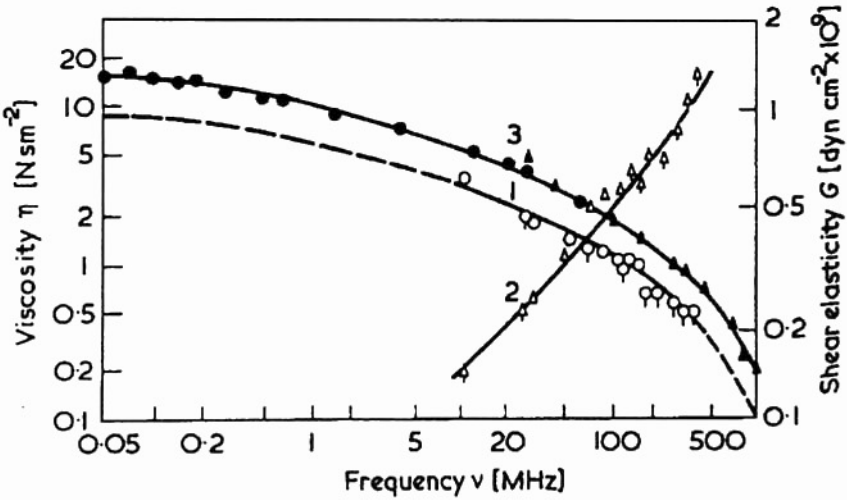

Fig. 8. Frequency dependence of the dynamic shear viscosity (1), shear elasticity (2) and effective viscosity (3) in castor oil [6].

4. Conclusions

The ultrasonic measurements increase the information on vegetable oils because they allow to determine the shear modulus and its changes as a function of temperature, while the attenuation measurements allow to determine the dynamic shear and bulk viscosities and the relaxation processes in oils, and to measure its frequency. Thus the ultrasonic measurements allow to determine the physico-chemical and dynamic properties of vegetable oils.

References

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