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Kramers-Kronig relationships application on master curves obtained on Honey from a few Hz to GHz: major interest of high frequency ultrasonic methods

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Viscoelastic properties of biological materials and food are of first interest on an academic point of view (internal structure evaluation) and on a practical point of view : link between rheological properties and macroscopic parameters : moisture, fat content… Since many years we are working on high frequency ultrasonic approaches dedicated to food and biological materials investigation. We have already shown that investigations of complex reflection coefficient at an interface (elastic solid) / (viscoelastic material) can give accurate information on alpha-transition or glass transition around room temperature for a typical biological material and food : honey. In this new communication we propose to investigate how high frequency methods can give interesting information for Kramers and Kronig relationships application.

1 Introduction

Measurement of material properties with ultrasonic waves has intensively been studied for decades. Many of these techniques have been demonstrated to be very efficient for non destructive examination. The advantage of such approaches is the direct coupling between ultrasonic quantities and mechanical properties. So, ultrasonic measurements can be considered as continuation of rheology for high frequencies. Hence, these high frequency mechanical vibrations can be used to perform "micro-rheometers". Some authors sometimes speak of piezo-rheometer. The most well known methods are : Ultrasonic Pulse Transmission technique, Thickness Shear Mode, Ultrasonic Shear Wave Reflection Method and are widely detailed in literature. In this paper we will not focus our attention on methods. They only will be rapidely presented.

After, we will present some results concerning measurement of the master curve of honey from a few Hz to hundreds of MHz. In fact, these master curves are of first interest because they are very sensitive to moisture content which is the major quality factor for honey [1-2].

Then we will focus our attention on the following question : how asymptotic behavior around glass transition (given with high frequency ultrasonic waves) can give fundamental information for Kramers- Kronig relationships application ?

2 Experimental methods

2.1 Low and medium frequency domain

The dynamic rheological properties at low frequencies were measured with a TA AR2000 rheometer (TAInstruments Inc.), using a parallel 40 mm diameter plate system at a gap of 1 mm. Temperature was regulated by a controlled Peltier system with an accuracy of ±0.2 °C. The rheometer has a transducer of 200 mN, allowing measurements of moduli above 0.2 Pa.

Dynamic rheological data were obtained from frequency sweep test. A strain sweep test was conducted to obtain the linear viscoelastic region at all the temperatures. A 10 % strain was found to lie within the linear viscoelastic region, and was used for the dynamic test.

The tests were done at 5, 10, 15, 20, 30 and 35 °C. TA rheometer Data Analysis software was used to obtain the experimental data and to calculate storage shear modulus G' and loss shear modulus G".

In order to apply the TTS principle, frequency sweeps were carried out at various constant temperatures, and then data on logarithmic scales were superimposed by simple horizontal shifting in order to obtain a single master curve. The temperature chosen as reference is 20°C.

With the frequency sweep and TTS, the frequency domain investigated was around 10^{-4} to 100 Hz.

Concerning the medium frequency domain (kHz to MHz) we used a well known technique already introduced by Ferry [3] and based on longitudinal vibrations of a plate which create a shear excitation in the viscoelastic medium. In [3], G' and G'' are deduced from the shear wavelength and attenuation evaluation with a stroboscopic system for wave visualization.

If the longitudinal excitation in ensured with a piezoelectric system, G' and G'' can be evaluated thanks to the electrical impedance measurement [2].

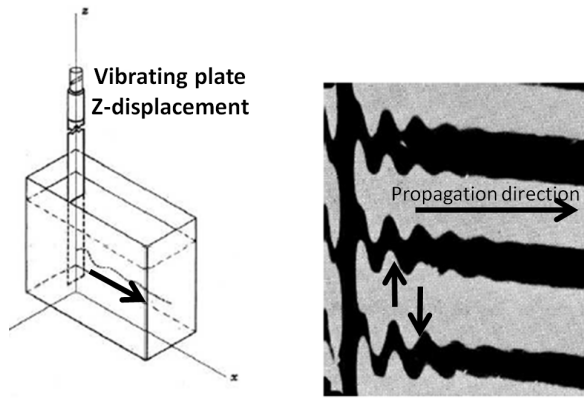

Fig 1. Vibrating plate and shear waves generated in the viscoelastic medium. Pictures extracted from reference [3]

2.2 High frequency range [4-8]

Several methods based on a single normal echo reflection have been developed to study the rheological behavior of wheat flour water systems, polydimethylsiloxane polymers, cementitous materials and curing epoxy systems. However, it has been shown that the measurements done via this reflection method are less accurate than those done with a transmission configuration .

In order to improve the accuracy of the measurements done by reflectometry, one can work with multiple reflections instead of simple one.

The method is essentially based on the measurement of the complex shear reflection coefficient at an interface between an elastic solid and a viscoelastic material. This means that when an ultrasonic wave is reflected on such an interface, its amplitude decreases and the wave undergoes a phase shift.

Experimentally, an ultrasonic transducer made of a piezoelectric crystal and a delay line (DL) in silica or glass, for instance, is used. As the ultrasonic attenuation is small in the DL, multiple reflections are possible leading to many echoes.

Then, the complex reflection coefficient, $R^* = r_o e^{j\Phi}$, is calculated with the following relationships :

$$r_o = \left(\frac{B_i}{A_i}\right)^{\frac{1}{i}} \quad (1)$$

$$\Phi = -2\pi f\left(\frac{\Delta t_i}{i}\right) \quad (2)$$

where A_i is the amplitude of the echo n° i, in the case of the interface (DL)/air, B_i is the amplitude for the interface (DL)/material, Δt_i is the time shift between these two echoes, and f is the operating frequency.

With R*, G* = G' + j G'' is calculated with (3) and (4), where ρ is the density of the studied material, ρ_{DL} is the density of the DL, and V_{DL} is the shear ultrasonic velocity in the DL.

$$G' = (\rho_{DL} V_{DL})^2 \frac{(r_0^2 - 1)^2 - 4r_0^2 \sin^2 \Phi}{\rho(2r_0 \cos\Phi + 1 + r_0^2)^2} \quad (3)$$

$$G'' = -4(\rho_{DL} V_{DL})^2 \frac{(r_0^2 - 1)4r_0 \sin\Phi}{\rho(2r_0 \cos\Phi + 1 + r_0^2)^2} \quad (4)$$

3 Kramers-Kronig relationships

3.1 Calculation validation

Kramers and Kronig relationships are well known in physics to link the real and imaginary parts of susceptibility. Concerning rheology, such relationships exist for G' and G'' and can be formulated as follows according to H.C.Booj [9] with ω=2πf, f being the frequency in Hz :

$$G'(\omega) - G'(\infty) = -\frac{2}{\pi}\int_0^\infty \frac{uG''(u) - \omega G''(\omega)}{u^2 - \omega^2}\,du \quad (5)$$

$$G''(\omega) = \frac{2\omega}{\pi}\int_0^\infty \frac{G'(u) - G'(\omega)}{u^2 - \omega^2}\,du \quad (6)$$

Such a formulation is very interesting because the fonctions discontinuities can be easily completed. In order to test the integrals calculation, we have simulated a multiple Maxwell system expressed in relations (7) and (8) :

$$G'(\omega) = \frac{G_{\infty 1}\omega^2\tau_1^2}{1+\omega^2\tau_1^2} + \frac{G_{\infty 2}\omega^2\tau_2^2}{1+\omega^2\tau_2^2} + \frac{G_{\infty 3}\omega^2\tau_3^2}{1+\omega^2\tau_3^2} + \frac{G_{\infty 4}\omega^2\tau_4^2}{1+\omega^2\tau_4^2} \quad (7)$$

$$G''(\omega) = \frac{G_{\infty 1}\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{G_{\infty 2}\omega\tau_2}{1+\omega^2\tau_2^2} + \frac{G_{\infty 3}\omega\tau_3}{1+\omega^2\tau_3^2} + \frac{G_{\infty 4}\omega\tau_4}{1+\omega^2\tau_4^2} \quad (8)$$

The parameters of the model are summarized in table 1.

i	$G_{\infty i}$ in Pa	τ_i in s
1	1e3	1e3
2	1e9	0.5e-7
3	5e3	1e-3
4	8e4	1e-5

Table 1. Parameters of the fourth order Maxwell model

Then, using (5) and (6), G' has been estimated with G'' and G'' has been calculated with G'. The results are presented in Figure 2 and validate the numerical calculation.

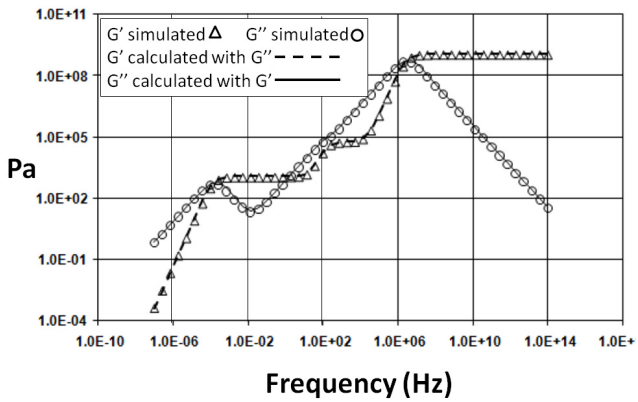

Fig 2. Fourth order Maxwell model for Kramers-Kronig numerical calculation validation

Remark : we have chosen such a fourth order Maxwell model in order to reproduce the general master curve morphology observed for honey.

3.2. Application on Honey master curves

Using both classical rheology, vibrating plates and ultrasonic high frequency reflectometry, master curves have been obtained on Honey (Lune de Miel ©) for G' and G'' (figures 3 and 4). These master curves have been built for T=20°C.

With classical rheology, the beginning and the end of the rubbery plateau are clearly visualized. With reflectometry, the glass transition is well observed. Regarding this master curve it is clear that honey, generally studied with very low frequencies and which is sometimes said to be Newtonian is clearly non Newtonian and appears as an entangled polymer.

Then relationships (5) and (6) have been used to deduced G' from G'' and G'' from G'. The results are presented in figure 3 and 4. The agreement between experimental moduli and re-calculated moduli is perfect.

It constitutes an important validation of experimental approaches for low, medium and high frequency domains. In the next paragraph we will discuss about the major role of high frequency behavior knowledge.

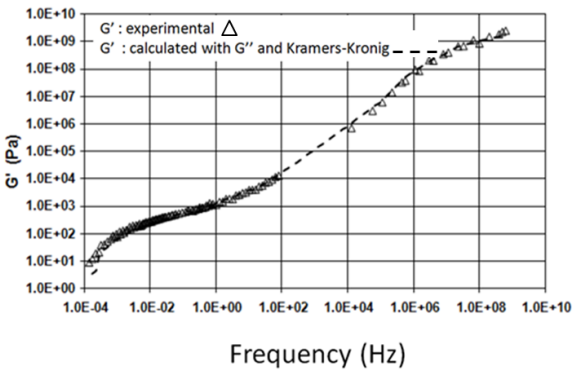

Fig 3 : comparison between experimental G' and G' evaluated with G'' and Kramers-Kronig relationships

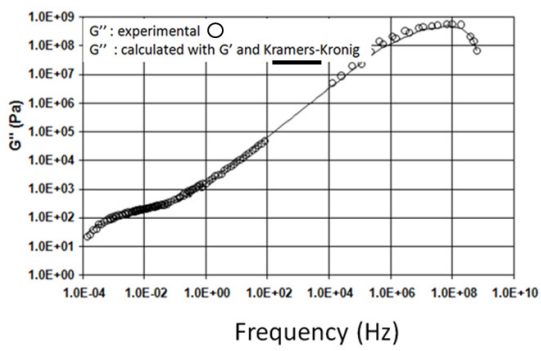

Fig 4 : comparison between experimental G'' and G'' evaluated with G' and Kramers-Kronig relationships

3.3. Discussion and conclusive remarks

In order to test the impact of high frequency behaviour on Kramers-Kronig relationships application, we have tried to calculated G' with G'' and G'' with G' for less and less points in high frequency domain. Hence we have taken G'(f) and G''(f) and suppressed progressively points in high frequency domain before applying relations (5) and (6)

The result remains correct if the master curve is known up to the glass transition (point where G'=G''). In fact, such a result is not very surprising because Kramers-Kronig relationships are theoretically integrals from 0 to infinity. So, asymptotic behaviour for very high frequency has to be known. After glass transition G'' decreases rapidely and G' remains constant : the viscoelastic material appears as a solid for high frequencies.

As a conclusion, if ones wants to deduce G' or G'' with Kramers-Kronig relationships, the high frequency behaviour has to be known up to glass transition. Hence high frequency ultrasonic approaches are very usefull.

In particular for materials for which applying TTS for very low temperatures is impossible because of phase transition for instance, we recommend the following approach :

- Classical rheology with TTS around room T°C.
- Medium and high frequency investigation with ultrasonic and vibrating systems and TTS around room T°C.
- Application of Kramers-Kronig relationships in order to validate the measurement consistency.

In fact the Kramers-Kronig relationships application can go further : in many cases we have observed that high frequency G'' is more sensitive to phase shift for shear reflectometry than G'. As this phase shift is very small and more difficult to evaluate than the real part of the complex reflection coefficient, the measurement of high frequency G' is more precise than the measurement of G''. Then one can use Kramers-Kronig relationships to deduce G'' with G'

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