

Characterisation of frozen orange juice by ultrasound and wavelet analysis[†]

Suyong Lee,¹ Laura J Pyrak-Nolte,² Paul Cornillon³ and Osvaldo Campanella^{4*}

¹Department of Food Science, Whistler Center for Carbohydrate Research, Purdue University, West Lafayette, IN 47907, USA

²Department of Physics, Purdue University, West Lafayette, IN 47907, USA

³Danone Vitapole, RD 128, F-91767 Palaiseau Cedex, France

⁴Department of Agricultural and Biological Engineering and Whistler Center for Carbohydrate Research, Purdue University, West Lafayette, IN 47907, USA

Abstract: Ultrasound technology was used to analyse the freezing behaviour of orange juice. The ultrasonic properties of orange juice, specifically velocity and attenuation coefficient, were characterised as the temperature was decreased from 20 to -50°C . The results were compared with NMR free induction decay data and correlated with the amount of unfrozen water present in the frozen sample. The velocities of longitudinal waves (P-wave) and shear waves (S-wave) in frozen orange juice were measured, yielding values of around 4000 and 2000 m s^{-1} respectively. They were related to the amount of unfrozen water in the frozen sample. The elastic moduli of the samples at different temperatures were obtained from the measured ultrasonic velocities. Significant changes in the attenuation of the ultrasonic waves propagated through the frozen sample were observed as a result of ice nucleation and growth. Information about the spectral behaviour of the ultrasound signal was obtained by means of wavelet analysis. The analysis provided a direct measure of the spectral content of the ultrasonic waves over time and showed the variation in the ultrasonic velocity dispersion with temperature. Significant velocity dispersions occurred for frequencies less than 1 MHz.

© 2004 Society of Chemical Industry

Keywords: frozen food; ultrasound; velocity; attenuation; elastic moduli; wavelet

INTRODUCTION

Food scientists have a growing interest in investigating and evaluating food quality non-destructively and non-invasively. Ultrasound not only satisfies this requirement but also lends itself to rapid, economical and in-line measurement. The velocity and attenuation of ultrasonic waves propagated through a sample provide information about physical properties of the sample such as composition, texture, density and rheology.¹ The ultrasonic method has been used to assess qualities such as fruit ripeness, solid fat content in oils and thickness of egg shells.^{2–4} However, there has been limited research on the application of ultrasound to frozen foods. Miles and Cutting⁵ studied changes in the ultrasonic velocity in beef during freezing. In that study a relationship between the enthalpy of lean meat and the velocity of sound was established by comparing measured ultrasonic velocities with estimates of unfrozen water determined from calorimetry. Another study investigated the attenuation of ultrasound waves in meat during

freezing, showing the differences in attenuation between frozen and unfrozen meat.⁶ Glazing, which is one of the methods used to protect frozen foods, was also examined by using ultrasound to measure the glazing thickness of frozen fish.⁷ The thickness measured by using ultrasound was similar to that measured with a caliper.

During freezing, two major events occur: (1) the formation of ice crystals (nucleation) and (2) the subsequent increase in size of the ice crystals (crystal growth). During frozen storage the number of ice crystals decreases and their average size increases. The increase in the size of ice crystals often damages food structure. Therefore the damage to food products caused by freezing, and consequently their quality, should correlate with the presence and size of ice crystals. Archer *et al.*⁸ monitored ice nucleation in water-in-oil emulsions and measured the proportion of ice by analysing ultrasonic velocities. They also showed that stirring a sample affects the ice nucleation rate. It was found that ultrasonic attenuation in ice crystals

* Correspondence to: Osvaldo Campanella, Department of Agricultural and Biological Engineering and Whistler Center for Carbohydrate Research, Purdue University, West Lafayette, IN 47907, USA

E-mail: camp@ecn.purdue.edu

[†]Approved as Manuscript No 16849 by the Agricultural Research Programs Division of Purdue University

Contract/grant sponsor: Purdue Research Foundation

(Received 24 July 2002; revised version received 17 January 2003; accepted 9 July 2003)

Published online 13 February 2004

increased rapidly at temperatures near the melting point.^{9,10} Thus ultrasound could be an important tool for monitoring the freezing process of food products.

In order to obtain complete information on the physicochemical properties of materials from ultrasonic measurements, it is desirable to apply a frequency-based ultrasound analysis. In practice, fast Fourier transform (FFT) is often used because of its rapid and simple application. Recently, a technique called wavelet analysis¹¹ has been developed and used in the areas of mathematics, engineering and physics. Wavelet analysis is a time-frequency localisation of ultrasound properties. It is capable of extracting information from a signal that is not possible to solve with the traditional FFT. It can provide a direct measure of spectral ultrasound content over time¹¹ and has been used to investigate the velocity dispersion in interface waves.^{12,13}

The main objective of this research was to characterise the physical properties of frozen orange juice using ultrasound and wavelet analysis. A secondary objective was to demonstrate that an ultrasonic sensor can be used to evaluate the physical quality of frozen foods.

MATERIALS AND METHODS

Ultrasonic measurement

Experimental set-up

Changes in the physical properties of orange juice during freezing were determined using measurements of ultrasonic velocity and attenuation. The experimental set-up consisted of a pulse generator-receiver (model 5800, Panametrics, Waltham, MA, USA), 5 MHz piezoelectric transducers (V609 and V155, Panametrics), a delay line (Panametrics), a custom-made measurement cell and a PC with appropriate acquisition hardware and data analysis software (LABVIEW for Windows, National Instruments, Austin, TX, USA). Samples were frozen by connecting a cooling unit with a temperature controller (FTS Systems, Stone Ridge, NY, USA) to the measurement cell. A thermocouple was placed inside the sample cell. A delay line was used to produce a time delay between the emission of the pulse and the reflection of a signal from the top of the sample (Fig 1).

When a transducer is placed on the surface of a sample, a contact gel is usually used to achieve good contact between the transducer and the sample. Since the gel could penetrate into the sample during the experiment, no gel was used and instead the sample was frozen along with the delay line. As a result, there was good contact between the delay line and the sample. Orange juice without pulp made from concentrate and with 90% moisture content was purchased at a local grocery store. A 30 ml portion of orange juice was placed in the measurement cell, which was held at the test temperatures for 1 h prior to analysis. All experiments were performed in triplicate.

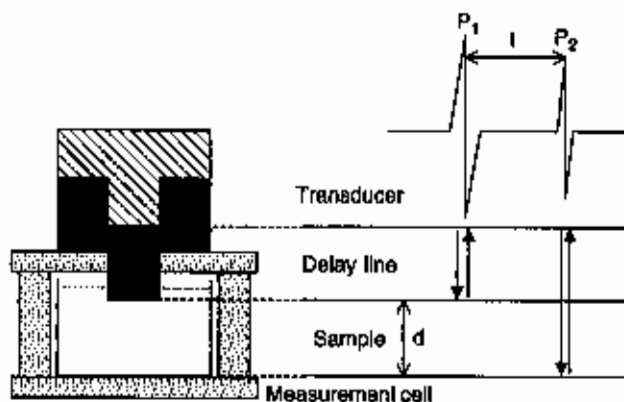


Figure 1. Schematic diagram of sample set-up and ultrasound response.

The pulse-echo method, the most widely used technique for ultrasonic measurements, was used to investigate the effect of freezing on the orange juice. In this method a pulse generator-receiver produces electrical signals, which are converted into ultrasonic waves by the piezoelectric transducer. The ultrasonic waves (Fig 1) travel across a delay line. When a wave reaches the interface between the delay line and the sample, a portion of the energy is reflected and a portion of the energy is transmitted. The reflected waves travel back to the transducer and are converted back into electrical signals which are recorded. The transmitted waves propagate through the sample until they reach the boundary between the sample and a measurement cell, where they are reflected back to the transducer. At the receiver the transducer now converts the reflected waves back into electrical signals which are displayed and recorded.

Analysis methods

The ultrasonic velocity and attenuation coefficient of the sample were determined by analysing the reflected signals which are designated P_1 and P_2 in Fig 1. The ultrasonic velocity was determined from the length of the sample, d , and the time difference, t , between the signal (P_1) reflected from the delay line/sample interface and the signal (P_2) reflected from the sample/measurement cell interface (Fig 1). This time difference (t) represents the two-way travel path through the sample. The equation $v = 2d/t$ was used to calculate the ultrasonic velocity (v) of the sample.

The velocity at which the longitudinal (v_1) and shear (v_2) waves travel through a material depends on its density (ρ) and the elastic moduli of the material, including the bulk modulus (K) and rigidity (G).¹⁴ For a solid medium

$$v_1 = \left(\frac{K + 4G/3}{\rho} \right)^{1/2} \quad (1)$$

$$v_2 = \left(\frac{G}{\rho} \right)^{1/2} \quad (2)$$

while for a liquid medium

$$v_1 = \left(\frac{K}{\rho}\right)^{1/2} \quad (3)$$

A longitudinal wave can propagate in both a liquid and a solid. In a liquid this velocity depends on the bulk modulus, whereas in a solid it is associated with both the bulk modulus and the shear modulus. Sound can propagate through a solid material faster than through a liquid material, because a solid material resists shearing. Although a shear wave (transverse wave) can propagate through most solid materials, it is highly attenuated in a fluid. In general, the shear velocity is less than that of a longitudinal wave.

The attenuation coefficient (α) of the sample was determined by using wave analysis of peaks P_1 and P_2 . The equation for the attenuation coefficient is¹⁵

$$\alpha(f) = \frac{1}{2d} \ln \left(\frac{A_1 R_{23}}{A_2 R_{12}} (1 - R_{12}^2) \right) \quad (4)$$

where A_1 and A_2 are the amplitudes of the waves reflected from the end of a delay line and the bottom of a sample respectively (Fig 1). Both A_1 and A_2 are functions of frequency. Wavelet analysis can be used to determine the change in frequency of a signal as a function of time. In this investigation we used the wavelet analysis to determine the maximum amplitude of signals P_1 and P_2 at a given frequency. The interfaces between the delay line and the sample and between the sample and the measurement cell have reflection coefficients R_{12} and R_{23} respectively. They were calculated from the equations

$$R_{12} = \frac{(Z_2 - Z_1)^2}{(Z_1 + Z_2)^2}, \quad R_{23} = \frac{(Z_3 - Z_2)^2}{(Z_2 + Z_3)^2} \quad (5)$$

where Z_1 , Z_2 and Z_3 are the impedances of the delay line, the sample and the measurement cell respectively. The impedance (Z) was calculated from the density and phase velocity of each system using the relationship $Z = \rho v$. The values of density of orange juice in the range of temperatures studied necessary to calculate the elastic moduli and impedance were determined through the measurement of volume and weight of the sample contained in a graduated cylinder which was placed in the freezer. The densities of the delay line and the cell were 1225 and 2700 kg m⁻³ respectively.

Wavelet analysis was also used to investigate velocity dispersion, which is the change in ultrasound velocity as a function of frequency. The analysis was performed using the method described in previous research.^{12,13}

Free induction decay (FID) measurement using NMR

Nuclear magnetic resonance (NMR) was used and compared with the ultrasonic method. Because the

free induction decay (FID) measurements in NMR are able to determine the amount of unfrozen water present in frozen samples,¹⁶ the comparison is useful to investigate whether the ultrasonic properties can be used to characterise frozen samples in regard to the amount of unfrozen and frozen water present in the sample. The measurements were made with a 15 MHz Maran benchtop NMR spectrometer with a variable temperature (VT) controller (Resonance Instruments, Inc, Witney, UK) connected to a cooling unit (FTS Systems). The FID curve for orange juice was obtained as a function of temperature at -50, -40, -30, -20, -10, 0, 10 and 20 °C and the FID curves were separated into two components (solid- and liquid-like). The liquid signal intensity was extrapolated to time zero and divided by the average FID value at the temperatures above freezing point to obtain an estimate of the proportion of liquid-like components in the frozen samples. A more detailed description of the NMR test and the method utilised to separate the FID curves into solid- and liquid-like components is given in a previous paper.¹⁶

RESULTS AND DISCUSSION

Propagation of ultrasonic waves through orange juice

Fig 2 shows the longitudinal waves propagated through orange juice at 20, -20 and -50 °C. As mentioned previously, P_1 and P_2 are the peaks reflected from the delay line/sample interface and the sample/measurement cell interface respectively. The difference in arrival times between P_1 and P_2 indicates how long it took for ultrasonic waves to propagate through the sample. This difference decreased with decreasing temperature, indicating that the ultrasonic velocity increased. Also, the amplitude of the peaks changed significantly as the temperature changed. Specifically, an abrupt decrease in peak amplitude was observed at -20 °C and the P_2 amplitude increased again at -50 °C. The changes in signal velocity and amplitude indicate a change in the physical properties of the sample upon freezing.

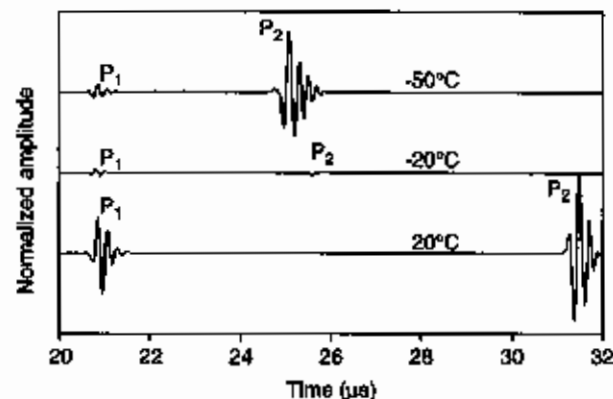


Figure 2. Waveforms for the propagation of ultrasonic waves through orange juice.

Ultrasonic velocity and elastic modulus

The velocities of longitudinal and shear waves in frozen orange juice were measured as a function of temperature to investigate the effect of freezing on ultrasonic properties (Fig 3). As orange juice was cooled to -10°C (ie the orange juice was still in a liquid state), the velocity of the longitudinal wave in the juice decreased slightly from about 1500 m s^{-1} to about 1400 m s^{-1} . However, below -10°C the velocity first rose abruptly as ice crystals formed. Then, as the temperature continued to decrease, the P-wave velocity increased more gradually, reaching approximately 4000 m s^{-1} at -50°C . Fig 3 is also illustrating the proportion of unfrozen water measured by the NMR technique in order to show any possible correlation between results obtained by the two methods. NMR data are showing that about 85% of the water was frozen at -20°C , while at -50°C 95% was frozen. Also, a transition in the same range of temperature between -10 and -20°C and a gradual decrease in the amount of unfrozen water at temperatures below -20°C were observed. Therefore the figure is also clearly showing the high correlation between the ultrasonic velocity and the amount of unfrozen water. As the water was converted into ice crystals, the ultrasonic velocity increased, because the velocity of ultrasound in ice (3940 m s^{-1} at -26°C) is higher than its velocity in water (1482 m s^{-1} at 20°C).^{17,18} Therefore ultrasonic velocity measurements can be used to estimate the amount of ice and unfrozen water in frozen foods.

The shear wave velocity was only measured for temperatures at which ice crystals are produced, because a shear wave cannot propagate through a liquid medium. At -20°C the shear wave velocity was around 1700 m s^{-1} and it increased gradually with a decrease in temperature, reaching a value of about 2000 m s^{-1} at -50°C . The velocity of the longitudinal wave was almost twice the velocity of the shear wave. Previous studies reported that longitudinal and shear wave speeds in ice were 3940 and 1990 m s^{-1} at -26°C respectively.^{18,19} The ultrasonic velocities for frozen orange juice at -26°C obtained in this study were slightly lower. Orange juice has a composition that is different from that of pure water. Therefore this

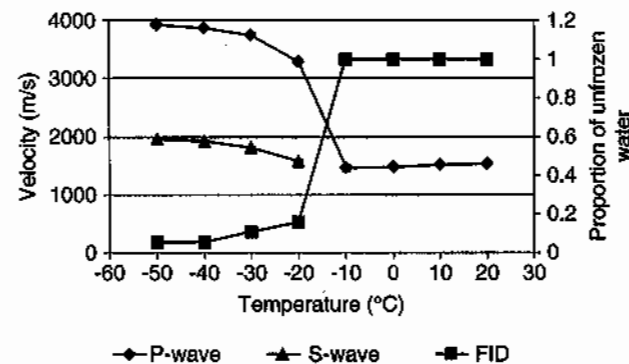


Figure 3. Comparison of ultrasonic velocities with the proportion of unfrozen water over temperature.

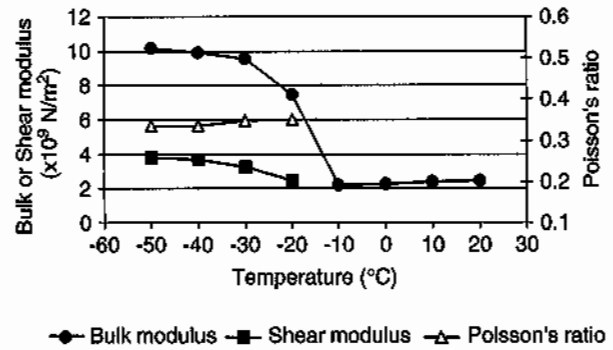


Figure 4. Elastic moduli of orange juice over temperature.

could be due to differences in the frozen matrix caused by the differences in composition. Furthermore, in our experiments, freezing began at the outside of the measurement cell. This could create a non-uniform distribution of ice and unfrozen water, with less ice at the centre where the transducer was located.

The elastic moduli (Fig 4) of the sample as a function of temperature were calculated from the velocities of the longitudinal and shear waves. The ultrasonic velocity is related to the density and elastic moduli of the material, such as Young's modulus, bulk modulus and rigidity, by eqns (1)–(3). The physical characteristics of frozen orange juice are dependent on temperature. Therefore the elastic moduli should also be different. The production of ice crystals caused an increase in bulk modulus. For temperatures below -20°C the bulk and shear moduli increased gradually. Finally, the Poisson ratio for frozen orange juice was determined from the bulk and shear moduli. It was approximately 0.35 at -20°C and decreased slightly with a decrease in temperature, corresponding to the increase in rigidity of the sample.

Attenuation

As an ultrasonic wave propagates through a material, the amplitude of the wave changes because of absorption and scattering.²⁰ Absorption is generally caused by a physical phenomenon that converts ultrasound into heat, while scattering occurs in inhomogeneous materials such as emulsions and suspensions. The attenuation coefficient is often used to quantify the decrease in amplitude of an ultrasonic wave. Fig 5 presents the attenuation coefficient of frozen orange juice as a function of temperature at 5 MHz. The attenuation coefficient was constant before freezing. However, ultrasonic waves were attenuated significantly at -20°C . It is hypothesised that the high attenuation at -20°C is a result of the nucleation of ice crystals. It appears that, at temperatures between -10 and -20°C , orange juice undergoes a transition from liquid phase to solid phase which is detected by both NMR and ultrasound (Fig 3). At the onset of freezing, the formation of ice crystals begins and accelerates with a reduction in temperature, resulting in a mixture of ice and unfrozen water. This heterogeneity would scatter the ultrasonic

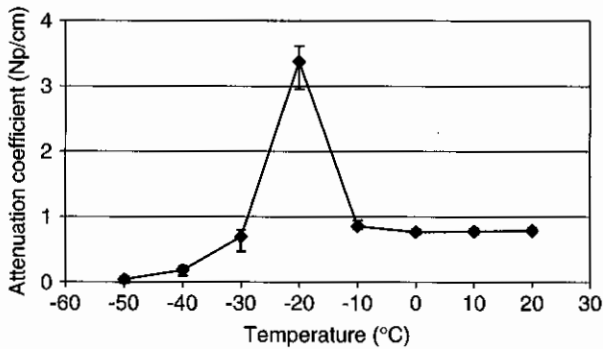


Figure 5. Attenuation coefficient of ultrasonic waves over temperature (attenuation coefficients were calculated from wavelet transforms at 5 MHz).

waves as they pass through the orange juice sample. The attenuation coefficient would decrease abruptly at temperatures below -20°C because of the decrease in unfrozen water and the growth of ice crystals, ie an increase in the ratio of solid phase (ice) to liquid phase (unfrozen water).

Frequency dependence

The results of wavelet analysis of ultrasonic waves, which enable the study of the ultrasonic frequency-dependent properties in orange juice at different temperatures, are shown in Fig 6, which presents the group wavelet transformations at 20, -20 and -50°C . The peak labelled P_1 is the reflected signal from the interface between the delay line and the sample, and the peak labelled P_2 is the signal from the interface between the sample and the measurement cell (Figure 1). The wavelet transformation is presented in two dimensions and the grey scale indicates the strength or energy of transform, ie white is high energy and black is low energy. The Y axis in this two-dimensional wavelet transform is time and the X axis is frequency. It suggests that the wavelet analysis provides information on time localisation as well as frequency localisation of the ultrasonic wave. There are several distinct features of these transformations. Frozen orange juice, especially at -20°C , had a more complicated waveform than unfrozen orange juice. The frequency of the dominant energy for P_2 shifts from 5 MHz for unfrozen juice to 1 MHz at -20°C and then to 4 MHz at -50°C . The energy for P_2 advances in time with decreasing temperature and has the smallest amplitude at -20°C . At -20°C the energy in P_2 as a function of time and frequency is different from that at the other temperatures. At -20°C the energy at low frequencies arrives later than that at high frequencies.

The wavelet transform gives information on the variation in frequency content as a function of time; therefore the velocity dispersion can be calculated. Dispersion means that the group velocity is not equal to the phase velocity, ie the velocity is a function of frequency. To investigate whether the waves propagated through frozen foods were

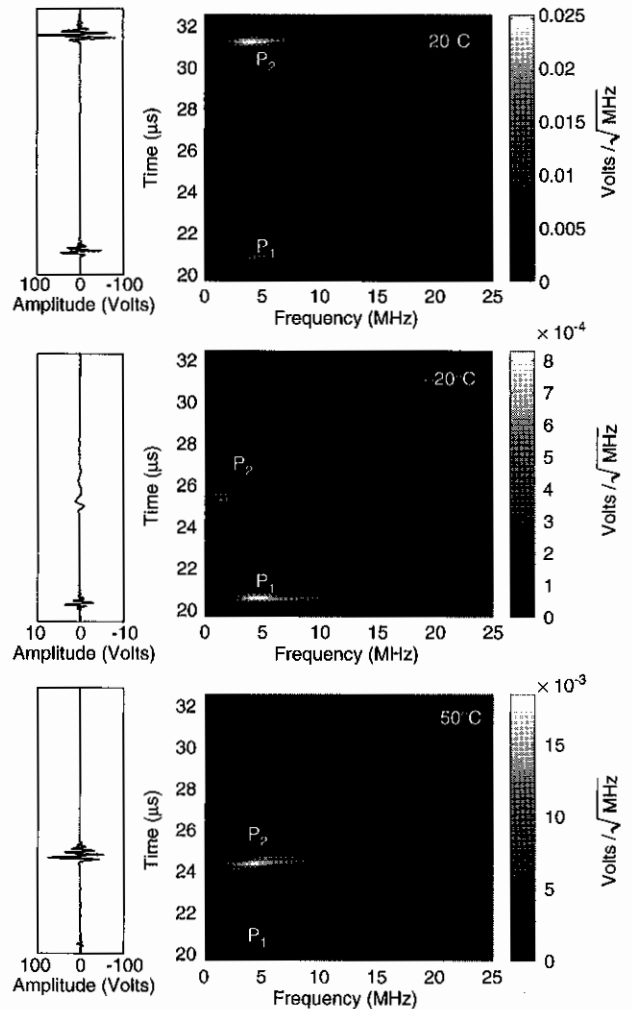


Figure 6. Wavelet analysis of ultrasonic waves in orange juice at (from top to bottom) 20, -20 and -50°C .

dispersive, the time during which the waves travelled twice the length of a sample over frequency was calculated quantitatively using wavelet analysis. For constant length this time is inversely proportional to the dispersive velocity. The experimental results for orange juice are plotted in Fig 7. For frequencies greater than 2.5 MHz the time or velocity is constant for a given temperature, ie the waves are non-dispersive. However, significant velocity dispersion is observed at frequencies less than 1 MHz.

The interpretation of the dispersive properties obtained from the wavelet analysis requires fundamental knowledge of the samples being tested. In Fig 7 the greatest dispersion (large time or smallest velocity) is observed at -20 and -30°C and the dispersion decreases as the temperature is decreased to -50°C . As mentioned previously, the proportion of water that is frozen increases as the temperature drops. That is, the source of dispersion can be related to the physical structure of the food and subsequently to its quality. Therefore wavelet analysis can be used to evaluate different physical structures such as the amount and distribution of ice and unfrozen water in frozen

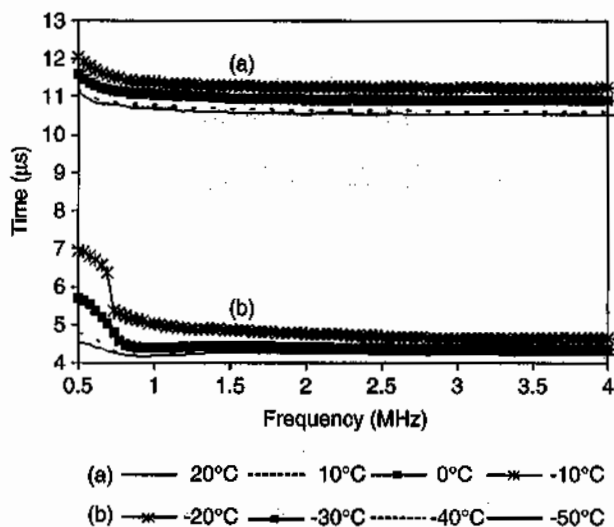


Figure 7. Experimental time calculated from wavelet transform over frequency ((a) and (b) indicate before and after freezing respectively).

foods, by showing how dispersive frozen foods are to ultrasonic waves.

CONCLUSIONS

Ultrasonic measurements can be used for non-destructive and non-invasive evaluation of the percentage of water that is frozen in frozen foods. Moreover, it appears to be less expensive and faster than NMR, which is also a non-destructive method of monitoring freezing. Ultrasonic velocity and attenuation varied as the temperature was decreased from 20 to -50°C . These changes could be interpreted on the basis of changes in the physical properties of frozen samples, such as the rheology and the proportion of ice and unfrozen water. The authors are not aware of any previous studies that have applied wavelet analysis to frozen food systems. The frequency change as a function of time provided information on how dispersive frozen samples were, indicating the different physical properties of the samples at the different freezing temperatures. It seems likely that wavelet analysis can be a promising method for analysing ultrasound signals obtained from frozen foods as well as other types of food. However, additional research is needed on how ultrasound can be used to evaluate the quality of frozen foods and how it depends on freezing and storage conditions such as temperature, time and freezing rate.

ACKNOWLEDGEMENTS

This research was supported by Purdue Research Foundation. Thanks also go to Dr Richard Strohshine

for reviewing the manuscript and providing very valuable comments.

REFERENCES

- McClements DJ, Ultrasonic characterization of emulsions and suspensions. *Adv Colloid Interface Sci* 37:33–72 (1991).
- Sarker N and Wolfe RR, Potential of ultrasonic measurements in food quality evaluation. *Transactions of the ASAE* 26:624–629 (1983).
- McClements DJ and Povey MJ, Solid fat content determination using ultrasonic velocity measurements. *Int J Food Sci Technol* 22:491–499 (1987).
- Voisey PW and Hamilton RMG, Ultrasonic measurement of egg shell thickness. *Poultry Sci* 55:1319–1324 (1976).
- Miles CA and Cutting CL, Technical note: changes in the velocity of ultrasound in meat during freezing. *J Food Technol* 9:119–122 (1974).
- Miles CA and Shore D, Changes in the attenuation of ultrasound in meat during freezing. *Proc 24th Eur Meet of Meat Research Workers*, pp D4:1–D4:6 (1978).
- Jonassen O, Frozen fish glazing thickness measurement by ultrasonic sound method. *Proc 9th Int Congr of Refrigeration*, Vol 1, pp 176–183 (1995).
- Archer GP, Kennedy CJ and Povey MJ, Investigations of ice nucleation in water-in-oil emulsions using ultrasound velocity measurements. *Cryo-Lett* 17:391–396 (1996).
- Hiki Y and Tamura J, Ultrasonic attenuation in ice crystals near the melting temperature. *J Physique* 42(C5):547–552 (1981).
- Tamura J, Kogure Y and Hiki Y, Ultrasonic attenuation and dislocation damping in crystals of ice. *J Phys Soc Jpn* 55:3445–3461 (1981).
- Morlet J, Arens G, Gourgeau E and Giard D, Wave propagation and sampling theory—Part II: Sampling theory and complex waves. *Geophysics* 47:222–236 (1982).
- Pyrak-Nolte LJ and Nolte DD, Wavelet analysis of velocity dispersion of elastic interface waves propagating along a fracture. *Geophys Res Lett* 22:1329–1332 (1995).
- Nolte DD, Pyrak-Nolte LJ, Beachy J and Ziegler C, Transition from the displacement discontinuity limit to the resonant scattering regime for fracture interface waves. *Int J Rock Mech Min Sci* 37:219–230 (2000).
- Povey MJ and McClements DJ, Ultrasonics in food engineering. Part I: Introduction and experimental methods. *J Food Eng* 8:217–245 (1988).
- McClements DJ and Fairley P, Frequency scanning ultrasonic pulse echo reflectometer. *Ultrasonics* 30:403–405 (1992).
- Lee S, Kim Y and Cornillon P, Spatial investigation of the non-frozen water distribution in frozen foods using NMR SPRITE. *J Food Sci* 67:2251–2255 (2002).
- Bilaniuk N and Wong GSK, Speed of sound in pure water as a function of temperature. *J Acoust Soc Am* 93:1609–1612 (1993).
- Smith AC and Kishoni D, Measurement of the speed of sound in ice. *AIAA J* 24:1713–1715 (1986).
- Hansman Jr RJ and Kirby MS, Measurement of ice accretion using ultrasonic pulse-echo techniques. *J Aircraft* 22:530–535 (1985).
- McClements DJ, Ultrasonic characterization of foods and drinks: principles, methods, and applications. *Crit Rev Food Sci Nutr* 37:1–46 (1997).