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TEMPERATURE-DEPENDENT DIELECTRIC PROPERTIES OF FOODS DURING FREEZING AND THAWING

S. Isaksson[1], M. Sadot[2,3], A. Da Silva[4], S. Curet[2,3], O. Rouaud[2,3], A. Le-Bail[2,3], M. Havet[2,3], E. Xanthakis[1]

[1]RISE, Frans Perssons väg 6, Göteborg, Sweden
[2]ONIRIS Rue de la Géraudière, Nantes, France
[3]CNRS UMR GEPEA 6144, 37 bd de l'Université, France
[4]AGROSUP DIJON Boulevard Dr Petitjean, Dijon, France

sven.isaksson@ri.se

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Abstract

Dielectric properties of a variety of foodstuffs were measured during freezing and thawing conditions, and are presented here as functions of temperature. Measurements were done with the Agilent 85070 high temperature dielectric probe. The differences in characteristics of the graphs resulting from cooling and thawing are discussed. A specific model accommodating the amount of frozen water in the food sample as a function of temperature is used and compared to experimental results. The mass fraction of each component is coupled to the dielectric properties of each fraction to evaluate the effective dielectric properties based on a two phases Maxwell-Wagner model considering ice as a dispersed fraction and food as a continuous fraction. The unknown dielectric properties of dry matter and an adjusting coefficient are used to optimize the fitting between experimental data and calculated data.

Introduction

Microwaves have been used for the heating of foodstuffs since about the middle of last century. Over time, it has been applied in various kinds of processes e.g. blanching, cooking, thawing, drying and pasteurization. Microwave phenomena are generally described by Maxwell's equations. Specific solutions of these equations require knowledge about dielectric properties of materials involved. Hence, for design of equipment and understanding of resulting microwave heating, access to proper data on dielectric properties has always been important.

Due to the heating nature of microwaves, which have led to the applications listed above, the major focus has until now been on changes in dielectric properties during increase of temperature, especially in the positive temperature range. However, recently there have been a few studies regarding microwave assisted freezing processes, which gives rise to interest in changes of dielectric properties also in situations where temperature decreases, and especially below 0 °C.

In the freezing of food, formation of small ice-crystals is often preferred over large ones [1] if food quality is to be retained. The most common method to favor creation of small crystals is probably fast freezing [2]; however fast freezing methods, such as cryogenic freezing, are in general energy-demanding [3, 4]. Studies have indicated that microwave-assisted freezing also has the ability to result in creation of small ice-crystals [5], while probably being a more energy-efficient alternative to e.g. cryogenic freezing.

An important tool for understanding of microwave heating phenomena is numerical modelling; for this purpose a numerical model of microwave-assisted freezing was created by [6]. However, validity of any numerical model relies upon good data on physical properties. One objective of this study is to supply numerical modelling of microwave-assisted freezing with data on changes in dielectric properties of foods during freezing (crystallization).

The other objective is to present a theoretical model for dielectric properties below 0 °C. For this purpose, dielectric data during thawing was also measured, as well as dielectric properties at equilibrated temperatures. During freezing of food, the phase change of the free water occurs heterogeneously with the creation of dispersed ice crystals. The dielectric properties affect the microwave propagation which has a spatial behavior. In order to mimic the spatial ice crystal distribution, the dispersed Maxwell-Wagner model was chosen for this study. This theoretical model considers ice as a dispersed fraction and food as a continuous fraction. Here the model has been used to calculate effective dielectric properties by using the mass fraction of ice and food, together with the dielectric properties of each fraction.

In this study, the methylcellulose gel was chosen because it is a common food model system with certain properties close to some foodstuffs. The advantage of using a gel as a model is its homogeneity, which gives a better repeatability compared to a real food product.

Material and Methods

a) Materials and sample preparation

The food matrices used in this study were potato and chicken. They were purchased from local markets and stored at 4 °C until measurements were done. All measurements were carried out within two days from the purchase.

Potato samples were prepared by punching out 2.5 cm diameter and 1.1 cm height cylinders, each weighing 7.5±0.1 g. Chicken samples were prepared in a similar manner, punching out 2 cm diameter cylinders from chicken breast; each cylinder weighing 8 g.

For the comparison of experimental data to a theoretical model of dielectric properties, methylcellulose (Tylose) gel was used. The methylcellulose gel was stored at room temperature overnight, and measurements were carried out the following day.

Sample preparation for measurement of dielectric properties of methylcellulose gel was done by mixing water with 13.04 % w/w Tylose powder. Sample size was 11 ml of gel, poured into a 12 ml plastic container after 1 hour of agitation. The plastic containers were manufactured by cutting off a Sarstedt 50 ml Polypropylene tube with flat/conical base at the 12 ml indication. The final shape of the samples hence became circular cylindrical, 28 mm in diameter, and with a conical base.

b) Methods of measurements

Dielectric properties

The Agilent 85070E dielectric probe was used for measurements on the substances during freezing and cooling. It is a method that is flexible and overall easy to use, but its default calibration procedure includes measurement on a shorting block, with which sufficiently good contact sometimes can be hard to establish.

An alternative, more repeatable and reliable calibration procedure is to use air, water and acetone as references, in which case however, acetone data for a dipole relaxation model needs to be manually entered into the measurement software. In this case we used the Debye model,

$$\varepsilon(f) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i2\pi f\tau}$$

where $\varepsilon(f)$ is the complex permittivity at frequency f, τ is the relaxation time, ε_∞ and ε_S are the dielectric constants as $f \to \infty$ and $f \to 0$ respectively. For acetone, the following parameter values can be used [7]: $\tau = 3.5 \cdot 10^{-12}$, $\varepsilon_\infty = 2.5$ and $\varepsilon_S = 21.5$.

Probe measurements were used both for measurement of dielectric properties at equilibrated temperatures for dynamic recording of changes in dielectric properties, during thawing or freezing of the sample.

In the dynamic case, recorded dielectric properties were paired with recorded temperature measurements. However, to avoid disturbance of the measurement of dielectric properties that any thermocouples placed in the sample for temperature measurements likely would cause, the thermocouples were instead placed in a parallel equivalent sample. Temperatures were measured at three positions: at the top of the sample (close to the probe), in the middle and close to the bottom of the sample. The equivalent sample was subjected to similar thermal conditions as that used for measurement of dielectric properties; hence it was placed in an identical sample holder and also set in contact with an identical dielectric probe, as was the sample for dielectric measurements.

In the dynamic measurements, air temperature within the climate chamber containing the sample was successively increased or decreased with the aim to keep the difference in temperature between air and sample within ±5 °C. Dielectric data measured over time was paired with temperature measurements recorded at the top of the sample, close to the probe. This gave resulting graphs, where dielectric properties can be read as a function of time at freezing and thawing. In the case of freezing however, dielectric data was aligned by a slight shift, relative to temperature data, in order to ensure that the nucleation point in both samples coincided.

To ensure good contact between samples and probes, the samples were placed in a plastic sample holder equipped with a spring that pushed the sample towards each probe.

Dry matter content

The dry matter content was measured by placing pre-weighted samples in a laboratory oven at 105°C during 48 h. They were then refreshed in a dryer during 30 min before weighting. The ratio of final mass on initial mass gives the percentage of dry matter.

Initial freezing temperature

Initial freezing temperature of methylcellulose gel was determined by measuring the temperature during slow freezing in a domestic static freezer. The temperature at the beginning of the crystallization temperature plateau due to the latent heat release is considered as the initial freezing temperature.

Freezable water and final freezing temperature

The amount of freezable water was measured using a DSC Q100, by freezing from 2°C to -40°C and thawing from -40°C to 2°C at 0.5°C/min. Assuming that the latent heat is only due to water, the ratio of product latent heat on water latent heat gives the freezable water content $x_{fw\%}$ as follows,

$$x_{fw\%} = (Q \cdot 100) / (H_f \cdot m_s)$$

$x_{fw\%}$ = percentage of freezable water
Q = enthalpy (J)
H_f = heat of fusion ice-water, equal to 333.50 J/g of ice or water
m_s = mass of sample.

The final freezing temperature is obtained from the thawing. At the temperature for which the derivative of the heat flux by the temperature is not constant anymore, the heat flux provided by the DSC does not only serve to decrease the temperature but starts to be due to the phase change. This temperature can be considered as the final freezing temperature.

c) Model of Dielectric properties

As mentioned above, the theoretical model used to describe the evolution of dielectric properties as a function of temperature during phase change is a two phase Maxwell-Wagner model. This model considers ice as a dispersed fraction and food as a continuous fraction. The continuous and dispersed fractions are respectively modelled as follows,

$$\begin{aligned} \varepsilon_c &= \varepsilon_w x_w + \varepsilon_{dm} x_{dm} \\ \varepsilon_d &= \varepsilon_{ice} x_{ice} \end{aligned}$$

ε_c an ε_d are the dielectric properties of the continuous and dispersed phases respectively. ε_w, ε_{dm} and ε_{ice} are the dielectric properties of water, dry matter, and ice respectively, while x_w, x_{dm}, and x_{ice} are the mass fractions of water, dry matter, and ice respectively. The dielectric properties of water and ice were taken from [8] and [9] respectively.

Both ε_c and ε_d are dependent on the ice fraction, which in turn depends on temperature. This study compared two ice fraction models to fit the experimental data. The first one has been used in [10],

$$x_{ice}1 = \frac{1 - \frac{T_{if}}{T}}{1 - \frac{T_{if}}{T_{ff}}} x_{fw}$$

where, x_{fw} is the mass fraction of freezable water, T_{if} is the initial freezing temperature and T_{ff} the final freezing temperature. The second ice fraction model is based on a volume ice crystal growth dependant of temperature [6]:

$$x_{ice}2 = \frac{4.\pi}{3}.r(T)^3.N.\frac{\rho_{ice}}{V_t.\rho_t}$$

$$N = \frac{V_t.\rho_t}{\rho_{ice}}.x_{fw}.\frac{3}{4.\pi.r_{fin}^3}$$

$$r(T) = \left(1 + \frac{a}{T - T_{if} - a}\right).r_{fin}$$

with *r(T)* being the radius of ice crystals, *N* the number of crystals, and ρ_{ice} and ρ_t respectively the density of ice and that of the total substance. V_t is the volume of the product, r_{fin} is the final radius of crystals and *a* is an adjusting coefficient specific to the system.

Dielectric properties are described by the following equation [11]:

$$\varepsilon = \varepsilon_c\left(\frac{2\varepsilon_c + \varepsilon_d - 2v_d(\varepsilon_c - \varepsilon_d)}{2\varepsilon_c + \varepsilon_d + v_d(\varepsilon_c - \varepsilon_d)}\right)$$

where, v_d is the volume fractions of dispersed phase.

Results and Discussion

Graphs showing the dynamically measured relationship between temperature and dielectric properties for chicken, potato and Tylose gel during thawing and freezing are shown in figures 1 – 3.

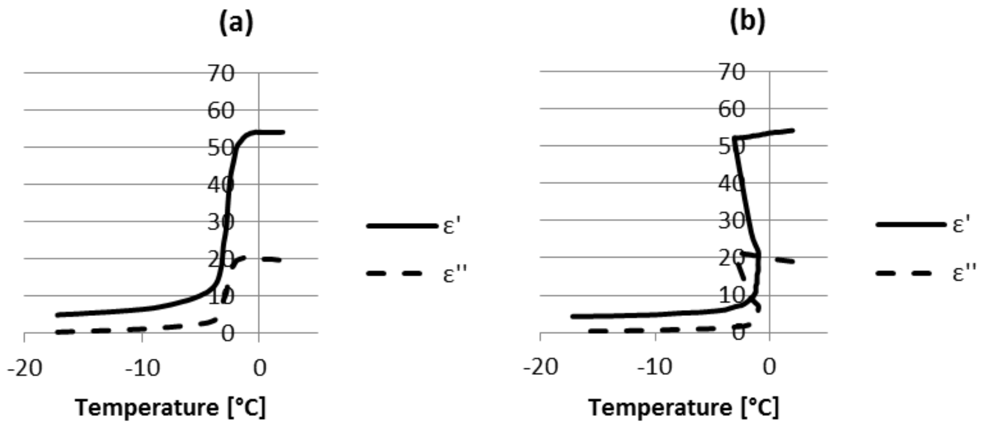

Fig. 1. Dielectric properties of chicken as a function of temperature, recorded under dynamic change of temperature, (a) thawing (b) freezing.

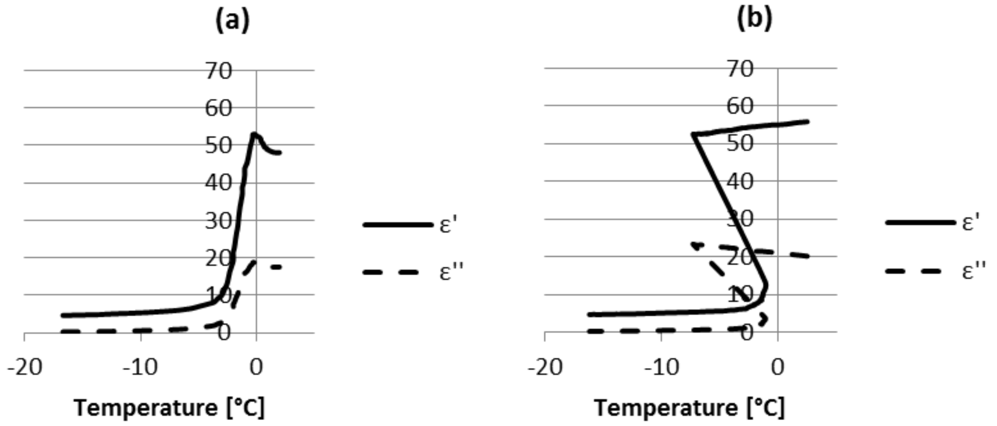

Fig. 2. Dielectric properties of potato as a function of temperature, recorded under dynamic change of temperature, (a) thawing (b) freezing. The drop in the graphs in (a) for temperatures above 0 °C is probably due to reduced contact between the probe and the potato as a result of softening of the matrix when thawing.

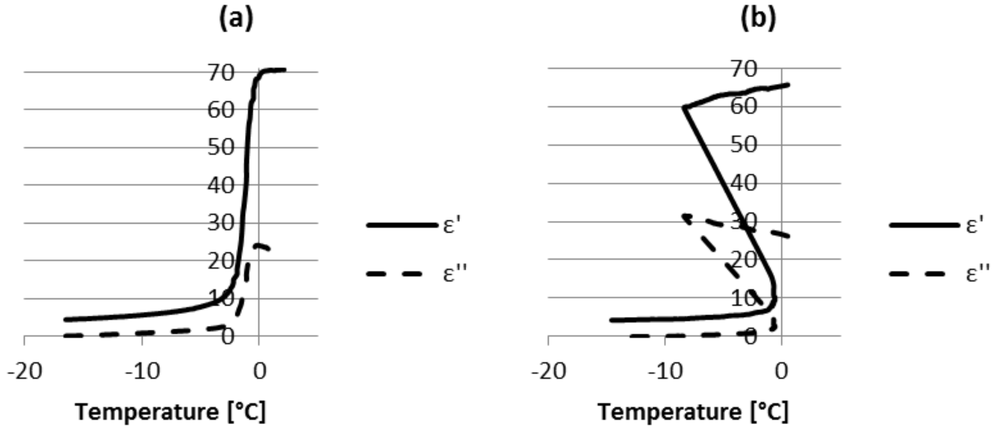

Fig. 3. Dielectric properties of Tylose gel as a function of temperature, recorded under dynamic change of temperature, (a) thawing (b) freezing.

The dynamic measurements of dielectric properties were primarily done for the purpose of catching the moment when nucleation occurs in the sample. This is a phenomenon that occurs within the course of a few seconds; hence recording if the event with ensured homogeneous temperature distribution within the sample is difficult to accomplish in a sample of considerable size.

Bearing this aspect in mind, plus the fact that also tempering graphs in Figures 1 – 3 were measured under dynamic conditions, it may be interesting to compare these results to measurements carried out at conditions with homogeneous temperature distribution within the sample. This is done in Figures 4 – 5, where results are also presented through the Maxwell-Wagner two-phase models.

As mentioned above, the two-phase models were based upon measurements of initial and final freezing temperature, as well as the amount of freezable water. These measurements resulted in initial and final freezing temperature of -0.7 °C and -12.5 °C respectively, as well as 84% freezable water. Also dry matter had to be measured, which resulted in a value of 12.9% (w/w).

The models were developed by changing the value of the unknown dielectric properties of dry matter, together with an adjusting coefficient (only for the second model 'xice2'), in order to optimize their fitting to experimental data. As seen in Figures 4 – 5, the model used in [10] could be adjusted to coincide quite well with the equilibrated measurements, while that of [6] fit better the data of the dynamic measurements.

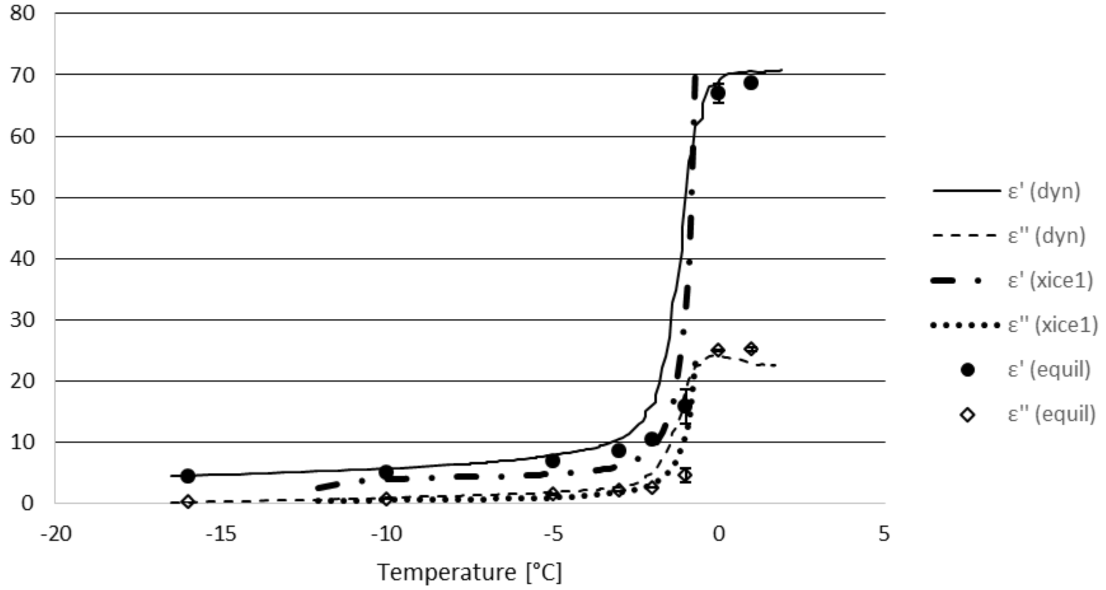

Fig. 4. Dielectric properties of Tylose gel as a function of temperature. The figure shows both the experimental values for dynamic measurement (index 'dyn') and the equilibrated temperatures (index 'equil'), as well as the calculated values (index 'xice1'), based on the model proposed in [10].

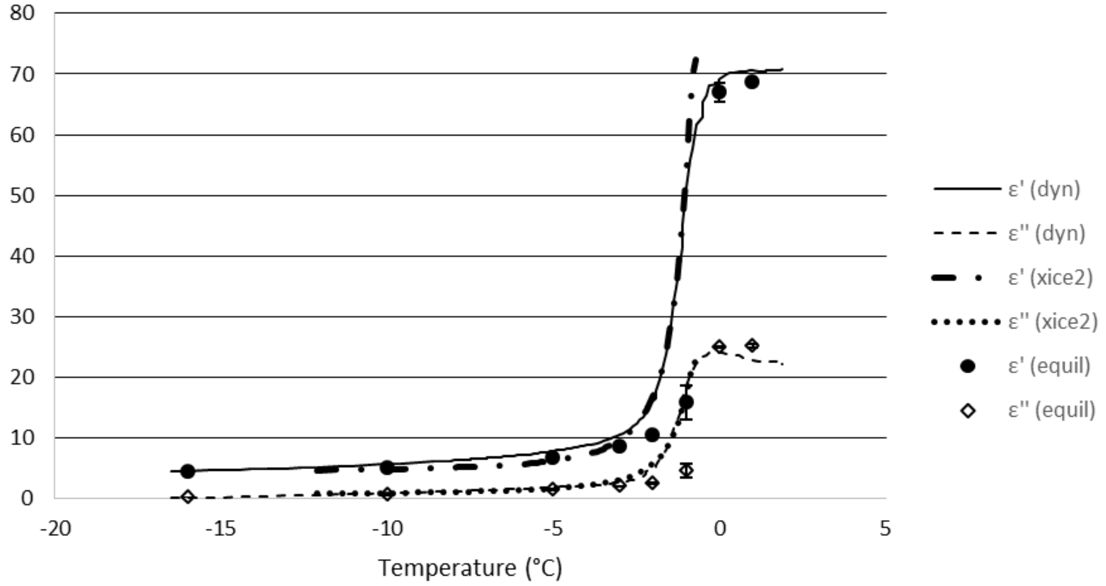

Fig. 5. Dielectric properties of Tylose gel as a function of temperature. The figure shows both experimental values for dynamic measurement (index 'dyn') and equilibrated temperatures (index 'equil'), as well as calculated values (index 'xice2'), based on the model developed in [6].

In the ideal case, dynamic measurements would have been carried out on a sample with size small enough to allow for homogeneous temperature at each point in time.

However, given the probe method used here, there is a minimum sample size according to specifications provided by the manufacturer. The sample sizes used in this study (approximately 8 - 11 g) were close to this minimum size; nonetheless the resulting maximal temperature gradient within the sample was around 5 – 6 °C, depending on the substance under investigation. Even if we would assume correctly measured temperatures at the contacting point of the probe, this temperature difference may have a significant impact on the measurement results, especially for temperatures just below zero. This is also confirmed by comparison to measurement at equilibrated temperatures, as seen in Figures 4 – 5. Nonetheless the dynamic measurements seem to provide a qualitative picture of the changes occurring during freezing and thawing. These results may provide valuable input to the development of theoretical models, such as Multiphysics modelling, describing the interaction between physical phenomena during the impact of microwave heating in freezing or thawing processes of foodstuffs.

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