Controlled ice nucleation under high voltage DC electrostatic field conditions

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ABSTRACT

The quality of frozen food and the preservation of the microstructure of the tissue depend on the nucleation rate. As the nucleation rate is related to supercooling, the control of supercooling is highly desirable. In this study, a novel approach is proposed to control ice nucleation using high electrostatic field. Distilled water has been considered as a model food. An original experimental set-up, consisting of pair of plate electrodes and cooling–heating system (Peltier element), has been designed. During sample cooling, high DC voltage was applied to a flat electrode located above the sample. The electrostatic field used in the experiments ranged from 0 V/m to 6.0×10^6 V/m. It was found that with the increase of applied voltage, nucleation temperature was shifted towards higher values. Other tests were conducted to clarify the capability of electrostatic field to induce ice nucleation at a desired supercooling degree. Our experimental results revealed that utilization of sufficiently high electrostatic field is a reliable method to control ice nucleus formation.

1. Introduction

Freezing is a commonly used method for food preservation. The quality of frozen products strongly depends on the nucleation rate which governs the number of ice crystals and also on the rate of heat transfer which governs the growth of existing ice crystals. Some limitation may also occur due to the fact that the growth of ice crystals is governed by the diffusion of free water molecules towards ice crystals. In the case of a slow cooling rate, the sample temperature remains close to the solid–liquid equilibrium curve for a long time, resulting in a reduced number of large ice crystals (Le-Bail, 2004). Formation of big crystals causes numerous undesirable changes in the food texture, such as: mechanical damage to food tissues, destabilization of emulsions, syneresis in gels, precipitation of proteins from solutions and drip loss during thawing (Fellows, 2000; Petersen, Schneider, Rau, & Glasmacher, 2006; Vaclavik & Christian, 2008; Wei, Xiaobin, Hong, & Chuanxiang, 2008). On the other hand ultra-rapid freezing may cause mechanical cracking, particularly in large samples with high water content and low porosity (Pham, Le-Bail, & Tremeac, 2006; Sanz & Otera, 2005; Tremeac, Datta, Hayert, & Le-Bail, 2007). Ideal situation can be attained at optimum cooling rate, when in the whole volume of the food matrix large number of small ice crystals is formed. Currently commercial food freezing is mostly realized by the use of conventional freezing processes such as blast air freezing, contact freezing, fluidised-bed freezing and cryogenic freezing.

A numerical value of the freezing rate can be proposed by calculating the cooling rate during the phase change phenomenon (usually in °C/min) or by calculating the velocity of the phase change front in the matrix (usually in cm/h) (Le-Bail et al., 2004). The reduced thermal conductivity of food material ranging typically between 0.5 and 1.5 W m^{-1} K^{-1} results in a reduced value of the freezing rate (Maroulis & Saravacos, 2003; Sun & Li, 2003; Vaclavik & Christian, 2008). Also, the geometry of the food and the convective heat transfer coefficient between the food and the surrounding media interact with the freezing rate. The apparition of the first ice crystals in the matrix occurs in the region close to the surface of the sample and is strongly dependent on the supercooling degree reached in this zone. The freezing rate is evoluting within a given product during the freezing process. In the case of slab geometry, the freezing rate is decreasing when the phase change front it traveling towards the centre of the geometry resulting in the growth of large ice crystals in its inner part (Sanz & Otera, 2005; Sanz et al., 1999). On the opposite, in the case of revolution geometry (sphere, cylinder), the freezing rate is increasing when the phase change front travels towards the centre of the geometry resulting in thinner ice crystals inside the geometry as shown by Chevalier, Le-Bail, and Ghoul (2000a). A high degree of supercooling (up to 10 °C) can be reached by using the pressure shift freezing process resulting in an improved microstructure and numerous and small ice crystals as described by Chevalier, Le-Bail, and Ghoul (2000b), Chevalier, Sequeira-Munoz, Le-Bail, Simpson, and Ghoul (2000), Zhu, Le-Bail, Ramaswamy, and Chapleau (2004), Zhu, Ramaswamy, and Le-Bail (2005a). Moreover as food portions are often large, considerable time period is taken for the centre of products to pass through the latent heat plateau. Long freezing times result in the weight

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Nomenclature

D	electric displacement field (C/m^2)
E	electrostatic field (V/m)
ΔG	Gibbs free energy (J)
ΔG_0	free energy of the system without applied electrostatic field (J)
ΔG_E	free energy of the system with applied electrostatic field (J)
ΔG_S	surface free energy (J)
ΔG_V	volume free energy (J)
ΔG_v	free energy of melting per unit volume (J/m^3)
$\Delta H_{m,f}$	molar enthalpy of fusion (J/mol)
p	pressure (Pa)
P	permanent polarization (C/m^2)
r	radius of the nuclei (m)
S	entropy (J/K)

ΔT	undercooling (K)
T	temperature (K)
t_C	crystallization time (s)
T_N	nucleation temperature (K)
T_f	temperature of fusion (K)
U	inner energy (J)
V	volume (m^3)
V_c	volume of the system subjected to electrostatic field (m^3)
V_m	molar volume (m^3/mol)
ε_0	vacuum permittivity, $\varepsilon_0 = 8.854187817 \times 10^{-12}$ (A^2 s^4 kg^{-1} m^{-3})
ε_r	relative permittivity of the system
γ	surface free energy of the crystal fluid interface (J/m^2)

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loss of unwrapped products as well as cause potential risk of food spoilage (Aparicio, Otero, Guignon, Molina-García, & Sanz, 2008). Therefore to ensure the maximum attainable quality of frozen foods new methods, e.g. the high-pressure assisted freezing (Le-Bail, Chevalier, Mussa, & Ghoul, 2002; Van Buggenhout, Grauwet, Van Loey, & Hendrick, 2007; Zhu, Ramaswamy, & Le-Bail, 2005b), power ultrasound assisted freezing (Sun & Li, 2003; Zheng & Sun, 2005), dehydrofreezing (Sun & Zheng, 2006; Wu, Orikasa, Tokuyasu, Shiina, & Tagawa, 2009) and most recently electrofreezing (Petersen et al., 2006; Wei et al., 2008), are being proposed and developed.

The electrofreezing phenomenon is based on the ability of strong electric field to induce the crystallization of supercooled water. Process of crystallization is initiated by nucleation, related to formation of small stable molecular aggregates, called nuclei. In liquid water there are clusters of molecules linked by hydrogen bonds, which are in solid-like configuration. Since the free energy of a cluster is higher than the sum of the energies of the molecules making up the cluster, there is natural tendency for them to disintegrate, leading to a very short life-times. As water is cooled, cluster formation is in favor and embryos become larger. Once the critical size has been reached, the energy decrease associated with an increasing volume makes the probability of growth more likely, but still not absolutely certain (Vali, 1995). Nucleation occurs spontaneously when associated change in the Gibbs free energy for the system is negative ($\Delta G < 0$). The free energy of a spherical crystallite in a solution without applied electrostatic field, ΔG_0, is equal to the sum of the surface free energy, ΔG_S, i.e. the energy between the surface of the particle and the bulk of the particle, and volume free energy, ΔG_V, i.e. free energy between a very large particle ($r = \infty$) and the solute in solution (Mullin, 2001). Thus ΔG_0 is given by:

$$\Delta G_0 = \Delta G_S + \Delta G_V = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \Delta G_v \tag{1}$$

where r is the radius of the sphere, γ is the surface free energy of the crystal fluid interface. ΔG_v is the free energy change of the transformation per unit volume:

$$\Delta G_v = \frac{\Delta H_{m,f}(T_f - T)}{T_f V_m} \tag{2}$$

where $\Delta H_{m,f}$ is the molar enthalpy of fusion, V_m is the molar volume and ($T_f - T = \Delta T$) is the undercooling.

In the presence of an electric field E, the free energy G_E for a linear system having permanent polarization P, is defined by:

$$G_E = U - TS + pV - V_C E \cdot D \tag{3}$$

where V_C is the volume of the system that is subjected to the field, and D is the electric displacement field (Guggenheim, 1967; Marand, Stein, & Stack, 1988). D is related to E by:

$$D = \varepsilon_0 \varepsilon_r E + P \tag{4}$$

where ε_r is the relative permittivity of the system and ε_0 is the vacuum permittivity.

By complying with the scheme of calculations of Marand et al. (1988) we can write the expression for the free energy of formation of a spherical nucleus in the presence of an electric field as follows:

$$\Delta G_E = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 (\Delta G_v + PE) \tag{5}$$

From comparison of Eqs. (1) and (5) it follows that application of an electrostatic field can modify the free energy and in consequence the nucleation process. Molecular dynamics simulations performed by several authors (Jung, Yang, & Jhon, 1999; Shevkunov & Vegiri, 2002; Sun, Chen, & Huang, 2006; Svishchev & Kusalik, 1994; Vegiri, 2004a; Vegiri, 2004b; Zangi & Mark, 2004) revealed that the structure of water clusters can be changed by applying a DC external electric field. The structural changes of water by the external electric field are mainly due to the permanent electric dipole moment of a water molecule. Because of the dipole moment, the external electric field aligns the dipole of water molecules from random directions to the direction of the electric field vector. Due to the reorientation of water molecules, hydrogen bonds are stronger along the field than along orthogonal directions (Shevkunov & Vegiri, 2002; Vegiri, 2004a; Vegiri, 2004b; Wei et al., 2008). Shevkunov and Vegiri (2002) calculated that the cluster transforms into an almost aligned state with the dipoles pointing in a direction less than 90° to the direction of the field, as the electric field strength reaches 1.5×10^7 V/m. Sun et al. (2006) performed a set of molecular simulations at −15 °C under an extensive strengths of the external electric field varying from 0 V/m to 8.0×10^9 V/m. Authors reported that with increasing field strength, water system has a more perfect structure, which is similar to ice-like structure. The possibility of obtaining liquid water with more structural regularity by applying an electric field was also suggested by Jung et al. (1999), who calculated the diffusion coefficients of 1000 water molecules under the field strength of 5.0×10^9 V/m and at −30 °C. Obtained values of diffusion coefficients under the electric field were 10 times smaller than diffusion coefficient for liquid water not subjected to electrostatic field, and at the same time significantly greater than diffusion coefficient of ice I. Therefore Jung