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Ultrasound assisted nucleation of some liquid and solid model foods during freezing

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ABSTRACT

Power ultrasound has been proven to be useful in promoting the nucleation of ice in water-based solutions, and different mechanisms have been proposed to describe this phenomenon. In the present work, the use of ultrasound waves to induce dynamic nucleation in deionised water, sucrose solution, and agar gel samples was studied, and the mechanism of ultrasound assisted nucleation was discussed. The samples were frozen in an ethylene glycol–water mixture (−20 °C) in an ultrasonic bath system after putting them into tubing vials. Ultrasound irradiation (25 kHz, 0.25 W cm^{-1}) was applied continuously for 1, 3, 5, 10 or 15 s at different sample's temperatures in the range of 0 °C to −5 °C. The nucleation temperatures of the water, sucrose solution and agar gel samples without ultrasound irradiation, occurred stochastically at -7.4 ± 2.4 °C, -10.6 ± 1.7 °C and -7.5 ± 0.92 °C, respectively and followed normal distributions. Unlike agar gel samples, the nucleation temperatures of water and sucrose were induced by applying ultrasound for 5 s at different temperatures after a short delay, and linear relationships between the ultrasound irradiation temperatures and the nucleation temperatures were observed. Evaluation of the effect of different durations of ultrasound application on agar gels indicated that 1 s was not long enough to induce nucleation, 3 s was optimal, 5 s and 10 s produced heat and inhibited nucleation, and 15 s did not exhibit significant differences from 3 s and 10 s. It was concluded that longer irradiation durations (especially 5 s and 10 s) caused the sample to heat up, which interrupted or delayed the nucleation. Ultrasound irradiation for 3 s induced nucleation in agar gel samples at different temperatures resulting in a linear relationship between irradiation and nucleation temperatures. The observations indicated that the Hickling's theory, according to which vigorous collapses of bubbles are the only driving mechanism of nucleation, is not adequate to describe the ultrasound assisted nucleation. The results, however, were in agreement with results of some other researchers suggesting that secondary phenomena such as flow streams are also important for the initiation of nucleation. In conclusion, the use of ultrasound as a means to control the crystallisation process offers promising application in food freezing, though further investigations are needed for understanding the mechanisms, especially in solid foods.

1. Introduction

Crystallisation of water occurs during the phase transition stage of the freezing process and is a key step in determining the efficiency of the process and the quality of a frozen food product. Crystallisation of water consists of two stages, namely nucleation and crystal growth. Nucleation is defined as the formation of a new crystal and is considered as a critical factor for the optimization of industrial processes related to freezing (Nakagawa, Hottot, Vessot, & Andrieu, 2006). In addition, the morphology, size and distribution of ice crystals are strongly related to nucleation (DeMan, 1999; Petzold & Aguilera, 2009). However, ice nucleation occurs spontaneously and stochastically within a wide range of temperature and is affected by several factors such as impurities, asperities, surface properties, etc., which in general cannot be easily monitored or controlled (Nakagawa et al., 2006). Based on this statement, a probability distribution is used to describe the nucleation temperature (Hofmeister, Morton, & Bayuzick, 1998). In other words, precise prediction of the nucleation temperature is difficult due to its probabilistic occurrence. However, repeatability of a process is very important for controlling and prediction purposes. Therefore, a method to control the nucleation phenomena and turn its stochastic behaviour into a repeatable and predictable manner can be valuable and promising for the food freezing industry.

It is known that nucleation of water can be induced by irradiation of power ultrasound waves, a kind of ultrasound wave with frequencies in the range from 20 to 100 kHz and high sound power or sound intensity (generally higher than 1 W cm^{-2}), which can improve or alter the freezing process due to different mechanisms (Li & Sun, 2002; Sun & Li, 2003; Zheng & Sun, 2005). Since nucleation, as an important stage of the crystallisation process, can be induced, the freezing process can be strongly affected by ultrasound irradiation. Ultrasound irradiation has shown its ability to initiate nucleation in different supersaturated solutions (Chalmers, 1964) and supercooled aqueous solutions (Chow,

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Blindt, Chivers, & Povey, 2003, 2005; Chow, Blindt, Kamp, Grocutt, & Chivers, 2004; Inada, Zhang, Yabe, & Kozawa, 2001). Power ultrasound has also been employed to trigger nucleation in industrial crystallisation processes of organic molecules (Ruecroft, Hipkiss, Ly, Maxted, & Cains, 2005; Saclier, Peczalski, & Andrieu, 2010a). In fact, ultrasound can be considered as a means to manipulate and control nucleation and then improve the process.

Different theories have been proposed for the description of the mechanism of ultrasound induced nucleation. The first and the most commonly cited theory was developed by Hickling (1965a, 1965b, 1994). Based on his theory, vigorous collapses of cavitation bubbles produced by ultrasound can create local zones of high pressure (5 GPa or more) during a very short period of time (nano-seconds), resulting in high degrees of supercooling. The supercooling can act as a driving force for instantaneous nucleation (Inada et al., 2001; Zhang, Inada, Yabe, Lu, & Kozawa, 2001). This theory seems to be qualitatively reasonable but has not been evaluated quantitatively (Saclier et al., 2010a; Saclier, Peczalski, & Andrieu, 2010b). In addition, according to this theory, nucleation is expected to occur immediately after the collapses of cavitation bubbles. Nevertheless, some experiments have revealed that nucleation does not occur immediately, although cavitation exists, and there is a delay between the cavitation and the occurrence of nucleation (Chow et al., 2005; Zhang, Inada, & Tezuka, 2003).

Evidence indicated that flow streams caused by the movement of stable cavitation bubbles, which do not collapse immediately after their generation, can also act as a potential driving mechanism for the nucleation of water during freezing. Zhang et al. (2003) analysed the rate of nuclei formation during sonication and showed that the rate of nucleation is not constant during the sonication period. In the studied period of sonication, the authors (Zhang et al., 2003) detected two separate zones with different nucleation rates. In the first zone, a high rate of nuclei formation was observed, whereas the nucleation rate was much lower in the second zone. The second zone with the lower nucleation rate could be explained by the Hickling's theory. However, the nucleation rate observed in the first zone was much higher than the rates that would be achievable with the Hickling's theory. Therefore, another mechanism should exist to boost the nucleation rate in the first zone. Zhang et al. (2003) suggested that flow streams, which resulted to the motion of the bubbles, are probably the secondary cause of nucleation. Chow et al. (2005) also confirmed these results and based on microscopic observations, concluded that stable cavitation, in which bubbles do not collapse suddenly and remain stable for a number of ultrasonic cycles, can induce nucleation by means of the flow streams. Thus, ultrasound induced nucleation is not necessarily caused by the bubble collapses, but bubble movements can also induce nucleation.

In addition to the mentioned mechanisms, molecular segregation is another approach proposed for the description of ultrasound induced nucleation in the crystallisation process of different solutions (Dodds et al., 2007; Grossier, Louisnard, & Vargas, 2007) and can be potentially applied to water. In this approach, the driving force for nucleation is the pressure gradient around the cavitation bubbles, which results in a pressure controlled diffusion of particles or embryos that are composed of a number of molecules before they form a nucleus. Following the diffusion theory (Bird, Stewart, & Lightfoot, 2002; Hirschfelder, Curtiss, & Bird, 1964), when a mixture of two species is submitted to a pressure gradient, the lighter of the two is pushed toward low pressure regions (Dodds et al., 2007). Since the outward acceleration of the bubble at the end of its collapse is much higher than gravity, it is conceivable that the corresponding huge pressure gradient would segregate very efficiently the species present in the liquid (Archibald, 1938). Therefore, as Dodds et al. (2007) described, a cavitation bubble can promote nucleation by acting as a cluster attachment reactor. Solute molecules and small clusters would remain un-segregated, and medium clusters would be periodically over-concentrated near the bubble wall once the bubble collapses. This would enhance the direct aggregation between two clusters, thus considerably increasing the overall nucleation rate. Large clusters would be pushed far away from the bubble, which favours nucleation kinetics.

Therefore, the exact mechanism of ultrasound induced nucleation remains uncertain and probably various mechanisms contribute to the nucleation process. In addition, fluid samples have been employed widely for studying ultrasound assisted freezing, while solid samples have not yet been considered in the studies related to nucleation. Since flow streams cannot be generated in solid foods as they are produced in fluid samples, studying the effect of ultrasound on the nucleation of water in solid samples can be valuable for the investigation of the nucleation mechanism.

The aim of the current research is to study the effect of ultrasound waves on the nucleation of ice in fluid and solid model food samples including deionised water, sucrose solution, and agar gel at different temperatures, and to compare the nucleation behaviour in solid and fluid model foods. This can be valuable for the evaluation of the different mechanisms of ultrasound induced nucleation.

2. Materials and methods

2.1. Ultrasound assisted immersion freezing equipment

An ultrasonic bath system (CQBF-1025, China Shipping Company, China) consisting of a stainless steel tank with six transducers attached to its base, and operating at 25 kHz was used.

A mixture of ethylene glycol and water (50%:50% in volume) was used as the freezing medium, and its temperature was maintained at −20 °C by using a low temperature circulator (FP50, Julabo, Germany). The flow rate of the coolant was measured using a flow metre (H612S-001-RF, Hedland, USA).

2.2. Measurement of local ultrasonic intensity

The ultrasound intensity dissipated to the freezing medium could be adjusted at different levels by varying the power output of the ultrasonic generator (0–300 W). However, due to energy conversion and losses that occur in the ultrasonic system, the actual ultrasonic power that dissipated into the medium is lower than the nominal output power provided by the equipment manufacturer (Li & Sun, 2002; Thompson & Doraiswamy, 1999). Although the transducers are evenly located at the bottom of the bath, the intensity of the ultrasound waves delivered to the medium is different at different positions in the tank. This may arise from the non-uniformity in power outputs from the sonic transducers and the interference between incident and reflected waves in the tank. Moreover, the transducers cannot fully cover the whole tank (Li & Sun, 2002; Lima & Sastry, 1990). Therefore, different positions within the sonication area of the bath were tested by using aluminium foils.

A map of cavitation zones was obtained when aluminium foils, placed at the bottom of the tank, were irradiated for 30 s. The locations of high cavitation intensity were then identified based on holes created by cavitation in the aluminium foils, an example is shown in Fig. 1. Afterwards, 1.2 ml sealed tubing vials containing distilled water were placed on the bottom of the tank at the different locations of high ultrasound intensity previously identified and were irradiated for 120 s. The temperature of the water in each vial was recorded by a T-Type thermocouple (Radionics, Ireland) and a data logger (Squirrel 2040, Grant Instrument Ltd., UK). Heat generated by ultrasound was assumed to be proportional to the acoustic energy dissipated in each vial and was evaluated by the following equation:

$$P_{diss} = mc_p\left(\frac{dT}{dt}\right)_{t=0} \tag{1}$$