Ultrasound assisted nucleation of water during freezing

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ABSTRACT

Nucleation of ice during freezing is an important phenomenon affecting the probability distribution of the ice crystal size and crystal growth. Power ultrasound has been proved to be useful in promoting the nucleation of ice in water based solutions. In the present work, the use of ultrasound waves to induce dynamic nucleation was studied on deionized water, 8% sucrose solution, and agar gel samples; and the results were analyzed in regard to the theories suggested for ultrasound assisted nucleation. The samples were put into tubing vials and were frozen in an ethylene glycol - water mixture (-20°C) in an ultrasonic bath system. Ultrasound (25 kHz, 0.25 W cm-1) was applied continuously for 5 s at different sample's temperatures from just below 0ºC to -5ºC. For the water, sucrose solution and agar gel samples without ultrasound irradiation, their nucleation temperatures occurred stochastically and followed normal distributions with the values of -7.4 ± 2.4, -10.6 ± 1.7 and -7.5 ± 0.92 ºC, respectively. With 5 s ultrasound irradiation, the nucleation temperatures of water and sucrose solution exhibited repeatable results, and a linear relationship between the ultrasound irradiation temperature and the nucleation temperature was obtained. However, 5 s ultrasound irradiation could not obtain the linear relationship in the Tylose samples probably due to the state of water within the gel network or the heat produced as a result of cavitation and therefore, it was differently exposed to the influence of ultrasound.

Keywords: Nucleation; Freezing; Power ultrasound; Tylose; Sucrose solution; Water;

INTRODUCTION

The crystallization of water occurs during the phase transition stage of the freezing process and is a key step in determining the efficiency of the freezing process and the quality of final product. The crystallization of water consists of two stages namely nucleation and crystal growth. The morphology, size and distribution of ice crystals are strongly related to nucleation [5, 15]. 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. that in general cannot be easily monitored and manipulated [14]. Therefore, a method to control the nucleation phenomena and turn its stochastic behaviour towards a repeatable and predictable manner can be valuable and promising for the food freezing industry.

Ultrasound waves have been shown to initiate nucleation in different supercooled solutions [1] including aqueous solutions [2-4, 11]. Different theories have been proposed for the description of the mechanism of ultrasound induced nucleation. The first and the most commonly cited theory was provided by Hickling [8-10]. Based on this theory, vigorous collapses of cavitation bubbles produced by ultrasound can create local zones of high pressure during a very short period of time. The high degree of supercooling created by this local high pressure can act as a driving force resulting in instantaneous nucleation [11]. Nevertheless, some experiments have revealed that nucleation does not occur suddenly and there is a delay between the time of ultrasonic irradiation and the time that nucleation occurs indicating that sonocrystallisation is not necessarily initiated by the strong collapse of Hickling's theory [16]. The flow of the water due to the motion of the bubbles is probably the secondary cause of nucleation. Chow et al., [3] also confirmed the above mentioned results and by using microscopic observations concluded that stable cavitation can incorporate nucleation through the flow streams created by bubble movements.

Molecular segregation is another theory proposed for the description of ultrasound induced nucleation in the crystallization process of different solutions [6, 7]. According to this mechanism, the driving force for nucleation is the pressure gradient around the cavitation bubble which results in a pressure controlled diffusion of particles or embryos, which are composed of a number of molecules before they create a nucleus.

In conclusion, the exact mechanism of nucleation remains uncertain and probably a range of mechanisms act as the driving forces. In addition, as mentioned above, in the most of the experiments carried out on nucleation, fluid samples have been employed and solid foods have not been considered widely.
The aim of this article 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 Tylose at different temperatures.

MATERIALS & METHODS

An ultrasonic bath system was employed (CQBF-1025, 726 Research Institute, China Shipping Company, China). Unidirectional ultrasound waves were delivered to a freezing medium in the tank at the frequency of 25 kHz. The intensity of ultrasound in tubing vials (1.2 mL, 0.9 mm diameter) was calculated using the calorimetric method [13]. A mixture of ethylene glycol and water (50%:50% in volume) was used as the freezing medium, and its temperature was maintained at -20ºC by a low temperature circulator (Grant Instrument Ltd., Cambridge, UK).
Deionised water (Sigma-Aldrich, Dublin, Ireland), 8% sucrose (Fischer Scientific UK Ltd, Leicestershire, UK) solution in distilled water and a and Tylose (77% water and 23% methylhydroxyethyl cellulose powder; VWRInternational, Fontenay-sous-Bois, France), were prepared into tubing vials. In each freezing run, one sample in a tubing vial was frozen in the freezing medium (-20ºC) at the fixed chosen location in the tank, with a fixed sample holder. The freezing process was monitored precisely with a T-type thermocouple (Radionics Ltd., Ireland) at the centre of the vials. Continuous ultrasound was radiated for 1, 3, 5, 10 or 15s onto the samples at different temperatures (from just below 0 to -5 ºC). The ultrasound intensity was set at 0.25 W cm^{-2}. .
Minitab 16 software was employed for the statistical analysis of the data. ANOVA procedure and where applicable Duncan's mean comparison test was performed. Regression analysis was also carried out.

RESULTS & DISCUSSION

Both deionised water and 8% sugar solution samples frozen in 1.2 ml tubing vials exhibited a supercooling period before they start to freeze. Supercooling is the process of lowering the temperature of a liquid material below its freezing point without solidification. The water samples nucleated at -7.4 ± 2.4ºC while the nucleation temperature of sugar solution was -10.6 ± 1.4ºC. The lower nucleation temperature detected for sugar solution samples was a result of depression of nucleation temperature by solutes, as has been reported widely [5]. Since the nucleation is a stochastic phenomenon, it can be expected that nucleation temperature follows a normal distribution. One of the statistical methods for examining the distribution of the data is to produce a normal cumulative probability plot and examine their distribution. If the plot follows a linear trend, it can be assumed that the data are normally distributed. The normal cumulative probability plot of the experimental nucleation data for deionized water is shown in Fig. 1.

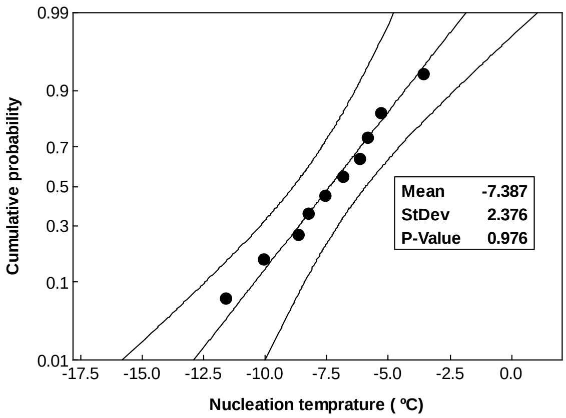

Figure 1. Normal cumulative distribution with 95% confidence interval of nucleation temperature of water frozen in plastic vials by immersion freezing.

The figure shows that a normal distribution with a mean of -7.39±2.4ºC appears to fit the data fairly well and the plotted points follow the fitted distribution line fairly closely. The p-value for the Anderson-Darling normality test was 0.98 confirming that the nucleation of water follows a normal distribution with a high p-value. The standard deviation for sugar solution samples (1.4) was lower than that of water and although the nucleation temperatures were normally distributed according to the Anderson-Darling test, the test resulted in a lower p-value (0.21). This might be arising from the less number of experiments carried out for sugar solution. It can be concluded that both water and sugar solution were randomly nucleated during freezing process exhibiting normally distributed nucleation temperatures over a supercooling range. Because of the large deviations, the nucleation temperatures could not be predicted precisely. This uncertainty of the nucleation temperature can cause complexities when dealing with the freezing process modelling and predictions.

The effect of ultrasound irradiation on the nucleation temperature of water and sugar solution is shown in Table 1 and Fig. 2. Table 1 indicates the effect of ultrasound irradiation (for 5 s at 0.25 w cm^{-2}) at different sample temperatures on the trigger of nucleation in water and sucrose solution samples frozen in plastic vials. As can be obviously detected from this table, at any temperature below the freezing point, nucleation occurred close to the ultrasound radiation temperature. Table 1 also illustrates that nucleation occurs after a delay from the onset of ultrasound irradiation. However, the delay was almost short and nucleation temperatures were close to the ultrasound irradiation temperatures. Even though the delay was short, these results do not support the Hickling's theory, which according to it nucleation occurs immidiately after cavitation. The results seemed to be in accordance with the data reported by Inada et al., [11] and Zhang et al., [16]. It should be noted that the effectiveness of ultrasound was improved at higher supercooling degrees as smaller delays was observed at higher ultrasound irradiation temperatures. This can be justified with the fact that at higher degrees of supercooling the material is much ready to be nucleated [12].

Table 1. The ultrasound irradiation temperature and nucleation temperature of deionised water and sucrose solution frozen in plastic vials by immersion freezing and the delay between the two mentioned temperatures.

Water			**Sucrose solution**		
Irradiation temperature (ºC)	Nucleation temperature (ºC)	Delay (s)	Irradiation temperature	Nucleation temperature	Delay (s)
-0.34±0.02	-1.21±0.15	5.00±1.41	-0.56±0.08	-1.71±0.32	5.50±0.71
-1.00±0.10	-1.38±0.35	4.67±0.58	-0.93±0.06	-2.09±0.23	5.50±0.71
-1.43±0.05	-2.10±0.06	4.00±0.00	-2.08±0.05	-2.68±0.10	5.50±0.71
-1.97±0.08	-2.54±0.19	3.50±0.71	-2.89±0.02	-3.37±0.02	4.50±0.71
-3.02±0.08	-3.54±0.26	3.67±0.58	-5.07±0.04	-5.36±0.37	4.00±0.00
-5.03±0.10	-5.30±0.00	3.00±0.00			

Statistical analysis of the nucleation temperatures for different ultrasound irradiation temperatures revealed that there was a significant difference between different nucleation temperatures ($P < 0.05$). The nucleation temperature seemed to be a function of irradiation temperature with a linear trend and nucleation temperature increased with increasing ultrasound irradiation temperature. Fig. 2 illustrates the relationship between the nucleation temperature and the ultrasound irradiation temperature for water and 8% sucrose solution samples. This figure indicates that samples that irradiated at different temperatures exhibited different nucleation temperatures. To evaluate this linear trend, regression analysis of nucleation temperature versus the ultrasound application temperature was carried out resulting in very good fits (R2 = 0.99 for both water and sugar solution) to the linear equations (Fig. 2).

As observed in the above mentioned results, nucleation followed a probabilistic behaviour. The application of ultrasound, however, turned this stochastic behaviour towards a controllable manner with reasonable standard deviation. It can be concluded that nucleation of both water and sucrose solution samples were effectively controlled by ultrasound irradiation. The slope of the linear fits was near to one, confirming that the nucleation temperature was linearly controlled by ultrasound irradiation. Since the slopes were a little bit lower than one, as compared to the sub-line represented for y=x in Fig. 2, it can be suggested that ultrasound irradiation was more effective at higher supercooling degrees resulting in closer nucleation temperature to irradiation temperature while at lower supercooling degrees the difference between irradiation temperature and nucleation temperature was higher. This behaviour was more significant in sugar solution samples so that the detected differences for the mentioned samples at the higher ultrasound irradiation temperatures were higher than that observed for water. However, at lower irradiation temperatures, the nucleation points for sugar solution coincided with the points observed for water. This caused the curves to have a noticeable space between each other at higher irradiation temperatures while they tend to close to each other and finaly cross one another at lower irradiation temperatures. As a conclusion remark, water was more susceptible to ultrasound irradiation at higher temperatures (lower supercooling degrees) than the sugar solution samples while both sugar solution and water exhibited a similar sensitivity to irradiation at lower temperatures (higher supercooling degrees). It can be implied that differences between the initial freezing points and possibly ultrasound transmission properties have resulted in the above mentioned behaviour.

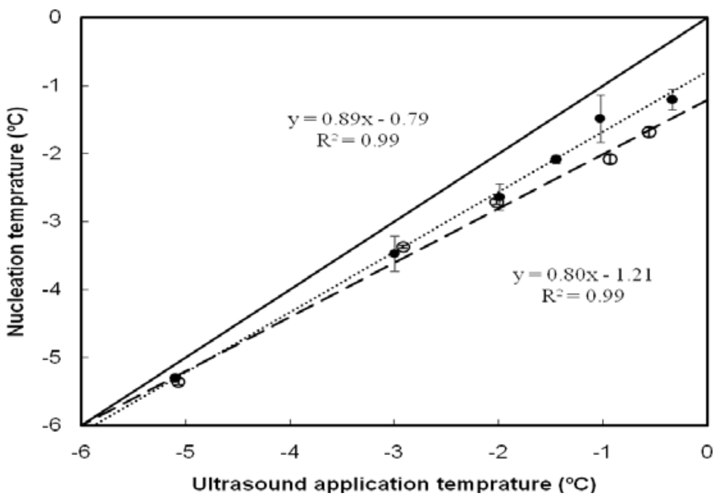

Fig. 2: Nucleation temperature of water (●) and sucrose solution (○) samples frozen in plastic vials, versus the temperature at which ultrasound was applied for 5 s at 0.25 W cm^{-2}. The continuous line represents the sub-line for y=x. Ultrasound can control nucleation of water with a good predictability.

Ultrasound irradiation was able to control the nucleation temperature of water and sucrose solution effectively. However, nucleation occurred after a short delay from the irradiation time. The deriving mechanism of ultrasound assisted nucleation has known to be the cavitation phenomenon and in order to produce cavitation bubbles, stable ultrasound waves are required in the fluid [17]. According to the Hickling's theory, transient cavitation, in which cavitation bubbles collapse suddenly and there is a very short duration from their creation to their collapse, have been suggested to induce the nucleation of ice as the result of ultrasound irradiation. This theory, is based on the fact that vigorous collapses of cavitation bubbles can create local zones of high pressure during a very short period of time resulting in supercooling of the solution [10]. The supercooling created by the local high pressure can act as the driving force for nucleation[10]. According to the mentioned statement, the nucleation should occur immediately after cavitation. However, the delays observed in this study and other studies [11, 16] are not entirely in accordance with this theory. The delays observed by Zhang et al., [16], were around 0.5 seconds between the onset of ultrasonic irradiation and the commencement of ice nucleation. In the present work, as shown in table 1, the delays were generally higher than that observed by Zhang et al., [16] and were around 3-6 seconds. Zhang et al., [16] suggested that ultrasonic-induced nucleation of ice in water samples is explained not only by the conventional Hickling's model, but also by secondary effects. As mentioned before, they also showed that the rate of nucleation is not constant during the sonication period and two distinguishable zones with different nucleation rates were detected. They attributed the second zone, which had a lower nucleation rate, to the rates that can be created by the Hickling's theory. However, the first zone, in which the rate of nucleation was considerably higher, could not be explained only by the Hickling's model. Their investigations with particle image velocitometery indicated that cavitation results in the flow streams in the

water due to the motion of the bubbles, and these flow streams are probably the secondary cause of nucleation. Results obtained in this study are also in accordance with the above mentioned observations.
Moreover, Chow et al., [2] showed that stable cavitation, in which bubbles do not collapse suddenly and remain stable for a number of ultrasonic cycles, can also incorporate in ultrasound induced nucleation of water. Their results indicated that the bubble oscillations in the ultrasonic field exhibited a ratio of maximum to minimum radius of approximately 3–1, indicating that the sonocrystallisation is not necessarily initiated by the strong collapse of Hickling's theory. They concluded that ultrasonic streaming and flow patterns are certainly present and may also be significant causing the nucleation to occur.
When recalling the mechanism proposed by Dodds et al., [6] and Grossier et al., (2007), the molecular segregation theory, in which stable bubble oscillations in terms of compression and rarefaction are important, the observations mentioned above seems to be also in accordance with this theory. Since a number of oscillations are needed to aggregate the embryos and build a nucleus, the detected delays are also meaningful. However, more investigation is needed to demonstrate this idea. Generally, all of the mentioned mechanisms can incorporate in the ultrasound induced nucleation.
Table 2 shows the effect of ultrasound irradiation on the nucleation of ice in Tylose samples. As it can be observed in this table, ultrasound waves seemed to not directly affect the nucleation and there was big delays between ultrasound irradiation temperature and nucleation temperature.

Table 2. The ultrasound irradiation temperature and nucleation temperature of Tylose frozen in plastic vials by immersion freezing and the delay between the two mentioned temperatures.

Irradiation temperature (ºC)	Nucleation temperature (ºC)	Delay (s)
-0.5	-2.02	56
-1	-2.01	30
-1.5	-1.99	13.5
-2	-3.01	45
-3	-3.37	4

CONCLUSION

Ultrasound was irradiated into water, sucrose solution and agar gel which were being frozen. Results indicated that ultrasound can be used to trigger with high repeatability and further to control the nucleation of ice. Results also revealed that nucleation of ice assisted by ultrasound, commenced at a temperature close to the irradiation temperatures. Since the nucleation is a stochastic phenomenon and its control is difficult, these results can be of great value in the freezing industry and other related processes. Nucleation occurred more repeatedly in fluid samples but for solid samples ultrasound did not affect the nucleation directly. More investigation is needed to study the effect of ultrasound in nucleation of ice in solid samples.
The results implied that the conventional theory of ultrasound assisted nucleation, the Hickling's theory, is not enough to explain the effect of ultrasound on the nucleation of ice.

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