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Effects of micro-nano bubbles on the nucleation and crystal growth of sucrose and maltodextrin solutions during ultrasound-assisted freezing process

Zhiwei Zhu[a,b,c], Da-Wen Sun[a,b,c,d,*], Zi Zhang[a,b,c], Yifei Li[a,b,c], Lina Cheng[a,b,c]

[a] *School of Food Science and Engineering, South China University of Technology, Guangzhou 510641, PR China*
[b] *Academy of Contemporary Food Engineering, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou 510006, PR China*
[c] *Engineering and Technological Research Centre of Guangdong Province on Intelligent Sensing and Process Control of Cold Chain Foods, Guangzhou Higher Education Mega Centre, Guangzhou 510006, China*
[d] *Food Refrigeration and Computerized Food Technology (FRCFT), Agriculture and Food Science Centre, University College Dublin, National University of Ireland, Belfield, Dublin 4, Ireland*

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ABSTRACT

The effects of micro-nano bubbles (MNBs) on the ultrasound-assisted freezing process of sucrose and maltodextrin solutions were investigated and different freezing characteristics of both nucleation period and crystal growth period were analyzed. Results showed that the introduction of MNBs was effective for the acceleration of freezing process, including the ice nucleation and crystal growth of both sucrose and maltodextrin solutions. Under optimal combination conditions, both sucrose and maltodextrin solutions with MNBs achieved a remarkable reduction in the supercooling degree and freezing time ($T_n = -1.24 \pm 0.09$ °C, $t_p = 92 \pm 3.88$ s and $t = 230 \pm 4.82$ s for sucrose solution, and $T_n = -1.97 \pm 0.13$ °C, $t_p = 102.9 \pm 8.62$ s and $t = 240.2 \pm 3.72$ s for maltodextrin solution) as compared with conventional immersion freezing ($T_n = -7.87 \pm 4.65$ °C, $t_p = 126 \pm 17.86$ s and $t = 303 \pm 28.12$ s for sucrose solution without MNBs, and $T_n = -8.24 \pm 4.73$ °C, $t_p = 127 \pm 18.12$ s, $t = 303.83 \pm 17.86$ s for maltodextrin solution without MNBs). This study suggested that the introduction of MNBs was a feasible method for enhancing ultrasound-assisted freezing process.

1. Introduction

Like drying (Delgado & Sun, 2002; Ma, Sun, Qu, & Pu, 2017; Pu & Sun, 2016, 2017; Qu, Sun, Cheng, & Pu, 2017; Sun, 1999; Sun & Woods, 1993; Yang, Sun, & Cheng, 2017) and cooling (Desmond, Kenny, Ward, & Sun, 2000; McDonald, Sun, & Kenny, 2001; Sun, 1997; Sun & Eames, 1996; Sun & Zheng, 2006; Wang & Sun, 2001, 2004), freezing (Cheng, Sun, & Pu, 2016; Kiani, Sun, Delgado, & Zhang, 2012; Kiani, Zhang, Delgado, & Sun, 2011; Ma et al., 2015; Pu, Sun, Ma, & Cheng, 2015; Xie, Sun, Xu, & Zhu, 2015; Xie, Sun, Zhu, & Pu, 2016) is a common technique used in thefood industry. Traditional freezing methods such as air blast or immersionfreezing could cause inferior quality of the frozen food products, novelfreezing methods have thus been developed (Cheng, Sun, Zhu & Zhang, 2017). Ultrasound-assisted immersion freezing has been proved to be effective in enhancing the freezing rate due to the cavitation effect, which occurs from the formation, growth, and violent collapse of bubbles (Delgado, Zheng, & Sun, 2009; Simal, Benedito, Sanchez, & Rossello, 1998; Xu, Zhang, Bhandari, Cheng, & Sun, 2015). The cavitation bubbles can promote the primary heterogeneous nucleation by acting as the ice nuclei, and also the secondary nucleation due to the instant high pressure and microturbulence created by the collapse of cavitation bubbles (James, Purnell, & James, 2015). The extreme pressure and microturbulence can break the ice crystals formed in the primary nucleation into smaller nuclei (Li & Sun, 2002). Based on this theory, some researchers used pre-existing bubbles to improve the cavitation intensity and found it effective for the enhancement of freezing rate. With the existence of visible bubbles (diameters of about 100 μm), the supercooled water can nucleate even at weak ultrasonic wave while solutions containing large bubbles need higher intensity for nucleation process acceleration (Hozumi, Saito, Okawa, & Matsui, 2002). One possible reason is that, large bubbles pulsate when the ultrasonic frequency corresponds to the radius of a certain bubble, then large losses of acoustic energy are caused, thus high intensity is needed to resist the attenuation (Chung, Lin, Pei, &

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[*] Corresponding author. School of Food Science and Engineering, South China University of Technology, Guangzhou 510641, PR China.
E-mail address: dawen.sun@ucd.ie (D.-W. Sun).
URLS: http://www.ucd.ie/refrig, http://www.ucd.ie/sun (D.-W. Sun).

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Hsu, 1992; Gülseren & Coupland, 2008). More recently, Hu, Sun, Gao, Zhang, Zeng, and Han (2013) studied the effect of pre-existing bubbles generated by an injector and showed that samples with pre-existing bubbles presented a quicker response to ultrasonic irradiation, and had shorter delay between the trigger of ultrasound and the occurrence of nucleation, indicating that ultrasound could be more effective in accelerating ice nucleation in samples with pre-existing bubbles. Results in the study of showed evidence that pre-existing bubbles could turn into cavitation bubbles similar to those generated by ultrasound.

In the past decade, bubbles at micro-nano scale, namely micro-nano bubbles (MNBs), have been a subject of intensive research (Liu, Kawagoe, Makino, & Oshita, 2013; Matsumoto & Tanaka, 2008; Uchida et al., 2011; Zhang, Inada, & Tezuka, 2003) due to their characteristics such as the increase of dissolution of gas in the liquid, the reduction in friction of liquid flow, the development of zeta potential and the generation of free-radicals. To make full use of the gas-liquid, there should be some mechanisms that explain the stabilization of the bubbles. One of the most significant properties of bubbles is that they tend to float upward with time and finally collapse on the liquid surface, driven by buoyancy. The upward floating rate (v_t) of bubble in the bulk liquid could be described by the equation below (Lambin, 1994):

$$vt = \frac{2(\rho - \rho')gr^2}{9\eta} \quad (1)$$

where ρ is the gas density in bubble, ρ' is the density of bulk liquid, g is the gravitational acceleration, r is the radius of bubble and η is the dynamic viscosity. It could thus be seen that the smaller the bubbles are, the lower the upward floating rate, prolonging the life-time of MNBs in liquid. In addition, the Young-Laplace equation reveals the phase equilibrium relationship of gas-liquid interface (Takahashi et al., 2003):

$$P = P_l + 2\frac{\sigma}{r} \quad (2)$$

where P is the gas pressure, P_l is the liquid pressure, σ is the surface tension, and r is the radius of the bubble. Theoretically, a smaller pressure difference on the interface contributes to the stability of the bubbles. According to Tolman (1949), the surface tension of droplet decreases significantly with decreasing size. That is, smaller bubbles with a few gas atoms will have lower surface tension and internal pressure. Furthermore, bubbles tend to shrink in water as the gases dissolve from the bubble into the bulk liquid. The amount of dissolved gas around the shrinking bubble will increase with rising inner pressure. As the dissolved gas condensed region gets thickened, the gas transfer will slow down from the bubble to the bulk liquid, explaining the stability of MNBs from another aspect (Takahashi et al., 2003). Moreover, the determinations of zeta potential reveal that the MNB aqueous is negatively charged and the electrical charged particles tend to repel each other, avoiding coalescence of MNBs (Takahashi, 2005; Ushikubo et al., 2010).

As for the imposing ways commonly used at present for ultrasound-assisted freezing, there are mainly two regulation modes, namely duty cycle (for example, 3 s - on and 7 s - off) (Kiani, Zhang, Delgado, & Sun, 2013; Li & Sun, 2002; Sun & Li, 2003) and one-shot mode (for example, trigger the ultrasound when the supercooling degree reaches 1 °C and then hold for 3 s). The freezing process can generally be divided into several periods or stages, *i.e.*, chilling period, phase change period and tempering period, or liquid-state supercooled stage, phase-transition stage and solid-state temperature decrease stage, and a certain ultrasonic condition is used during the phase change period (Hu, Liu, Li, Li, & Hou, 2013; Xin, Zhang, & Adhikari, 2014). Based on the previous findings, it is reasonable to assume that MNBs combined with ultrasound has a promotion effect on ice nucleation, which should be further examined. In addition, studies up-to-now still show that the effects of MNBs and ultrasound on ice crystallization process especially the crystal growth period are not clear. Thus the ice crystallization process can generally be divided into such two periods, *i.e.*, ice nucleation and crystal growth.

Therefore, this study aimed to investigate the effects of MNBs in combination with ultrasound on liquid freezing process. The specific objectives were focused on 1) whether the MNBs have a promotion effect on ultrasound-assisted freezing process, including elevating the nucleation temperature, shortening the lagging time, phase transition time and total freezing time, and 2) whether the combination of MNBs with ultrasound is effective in accelerating both non-Newtonian fluid (5% maltodextrin solution) and Newtonian fluid (5% sucrose solution). It is hoped that results from the current study should shed more light on underlying mechanisms of ultrasound-assisted freezing process, and promote the early adoption of the technology by the food industry.

2. Materials and methods

2.1. Solutions

The sucrose or maltodextrin solution was a mixture of deionised water and sucrose (Guangdong Guanghua Sci-Tech Co. Ltd., Guangzhou, China) or maltodextrin (Shanghai Juyuan Bio-Tech Co. Ltd., Shanghai, China) in the ratio of 95% and 5% by mass, respectively. The solutions were degassed by heating using an electric stove, which remained boiling for 2 min to remove any dissolved gas. Then the degassed solutions or the samples were kept at a constant temperature of 20 °C (± 0.5 °C) in an air-conditioned room until further experiments.

A micro-bubble generator (XZCP-K, Xiazhichun Tec Co. Ltd., Yunnan, China) was used to produce the micro-nano bubbles based on the method reported by Liu et al. (2013). As depicted in Fig. 1, the gas and liquid sample were drawn into the pump and then transported into a mixing tank at a high pressure of 0.35–0.45 MPa to mix the gas and liquid sample adequately. When the gas-supersaturated liquid reached the spew nozzle, a sudden depressurization caused the nucleation of the micro-nano bubbles. The whole system was set up in the air-conditioned room with a controlled temperature (20 ± 0.5 °C).

2.2. Freezing equipment and experiment

2.2.1. Freezing equipment

Fig. 2 shows the set-up of the experimental freezing equipment consisting of a cooling system, an ultrasound bath and a real-time temperature monitoring system. The cooling system comprised of a refrigerator (Model LS-20 kW, Beijing BKP Tec Co. Ltd., Beijing, China) and a coolant circulation system driven by pumps. A mixture of polyethylene glycol (Guangzhou Gongyi Chemistry Technology Co, Ltd.,

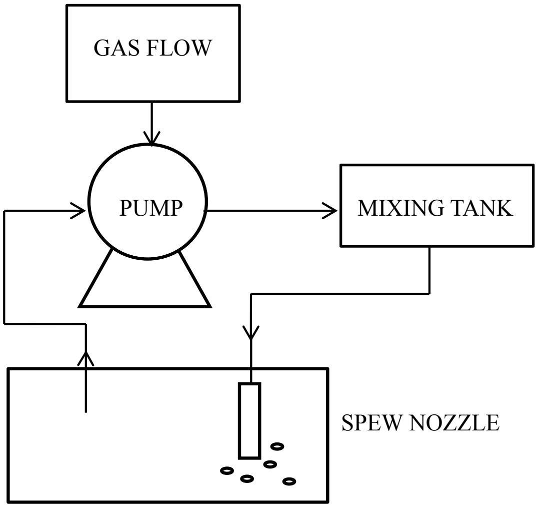

Fig. 1. Schematic diagram of the generation system of MNBs.