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COMMUNICATION

The Freezing Characteristics of Garlic Bulbs (*Allium sativum* L.) Frozen Conventionally or with the Assistance of an Oscillating Weak Magnetic Field

Christian James · Baptiste Reitz · Stephen J. James

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Abstract Several novel freezing systems have been developed that claim to improve the quality of frozen foods by controlling ice crystal formation through enhancing super-cooling in the food prior to ice nucleation. One of these is the Cells Alive System (CAS) produced by ABI of Japan, which applies oscillating magnetic fields (OMF) during freezing. This short study was carried out to investigate what effect freezing under OMF conditions had on the degree of super-cooling and characteristics of the freezing curve of individual cloves within whole garlic bulbs when compared to freezing under the same conditions without OMF. Garlic (*Allium sativum* L.) was chosen as the test material since a previous study has shown it to significantly super-cool during conventional freezing. Overall, these results clearly indicate that (1) significant super-cooling occurred in garlic bulbs during freezing under some of the freezing conditions used in these trials; (2) freezing under the OMF conditions used in these experiments had little significant additional effect on the freezing characteristics, or degree of super-cooling, of garlic bulbs, in comparison with freezing under the same environment without OMF and (3) super-cooling is more likely to occur in garlic bulbs frozen from an initial ambient (21±1 °C) state than those frozen from an initial chilled (4±0.5 °C) state.

Keywords Crystallisation · Freezing · Garlic · Nucleation · Oscillating magnetic field · Super-cooling

C. James (✉) · B. Reitz · S. J. James
Food Refrigeration and Process Engineering Research Centre (FRPERC), The Grimsby Institute of Further & Higher Education (GIFHE), Nuns Corner, Grimsby, North East Lincolnshire DN34 5BQ, UK
e-mail: jamesc@grimsby.ac.uk

Introduction

It has been claimed that super-cooling during freezing may enhance the formation of small ice crystals during nucleation and that these may cause less damage than the large ice crystals formed during slow freezing and thus improve the quality of frozen foods. Various methods have been suggested to enhance super-cooling during freezing, such as high-pressure-assisted freezing (Otero and Sanz 2012) or oscillating magnetic fields (OMF) (Owada and Kurita 2001; Owada 2007). OMF are used by the Cells Alive System (CAS), a novel patented (Owada and Kurita 2001; Owada 2007) freezing process marketed by the Japanese company ABI (ABI Corporation Ltd., Chiba, Japan). CAS is not a refrigeration process itself, but is claimed to assist in improving existing freezing processes (both in terms of process speeds and product quality). The patent literature (Owada and Kurita 2001; Owada 2007) claims that OMF acts on polarised water molecules to delay the formation of ice crystals. Whether this is due to engendering of super-cooling or movement of the molecules during the ice formation process is unclear. However, the claimed consequence is that most of the ice crystals form at the same time, thus, restricting their size, resulting in less cellular damage during freezing. There is very little scientific published data on OMF-assisted freezing of foods (Fikiin 2003; James et al. 2012), although a number of papers have been published on OMF-assisted freezing of biological samples (such as teeth) using ABI equipment (Kaku et al. 2010, 2012; Abedini et al. 2011) and even on whole-organism survival of frozen small animals like *Drosophila* (Naito et al. 2012). The only published analyses on freezing of foods exposed to OMF are those of Suzuki et al. (2009) and Watanabe et al. (2011), whose results were negative.

The effects of electric and magnetic fields on freezing have been reviewed by Woo and Mujumdar (2010). There is evidence that water, being a diamagnetic material, can be magnetised in a magnetic field. However, Wowk (2012) in a recent critique questioned the claims made in recent papers using CAS, given the very small (<1 mT) field strengths used. In response to Wowk, Kobayashi and Kirschvink (2013), while agreeing that the 'papers and patents published by the ABI group postulate mechanisms of action that do not agree with basic biophysics', offered a plausible mechanism for the disruption of ice-crystal nucleation in super-cooled water by magnetically induced mechanical oscillation. This was based on the action of magnetic fields on ferromagnetic materials in biological tissues.

The aim of this short-targeted study was to investigate what effect freezing under CAS conditions, using an ABI-supplied CAS system, had on the degree of super-cooling and characteristics of the freezing curve of individual cloves within whole garlic bulbs when compared to freezing under the same conditions without CAS. Garlic (*Allium sativum* L.) was chosen as the test material since it has been shown to significantly super-cool in the previous work by the authors (James et al. 2009). All trials were carried out at an air temperature of ca. −20 °C and air velocity of 5 ms^{-1}. The relatively high air temperature (in terms of commercial freezing where temperatures below −30 °C are common) used in these trials was because preliminary studies had shown that super-cooling in garlic was more likely at slower freezing rates and warmer cooling media temperatures.

Materials and Methods

Samples

Fresh garlic bulbs (*Allium sativum* L.) were obtained from a local supermarket and stored in ambient (21±1 °C) conditions for no more than a week before use. Trials were carried out on bulbs from either an initial ambient (21±1 °C) or chilled (4±0.5 °C) state. Bulbs frozen from a chilled state were chilled for 24 h prior to freezing in a catering refrigerator running at 4±0.5 °C. A total of 24 garlic bulbs were used throughout the trials. The mean (SD) height, width and mass of the garlic bulbs used were 48.3 (6.0) mm, 50.6 (3.2) mm and 40.4 (4.7) g, respectively. The mean water content (measured using an AMB 310 moisture balance, Adam Equipment Co. Ltd., UK) of the garlic was 63.7 % (SD 3.7, n=10), this value is similar to that reported in a previous study by the authors (James et al. 2009).

Freezing Trials

An experimental batch air blast-freezer, with and without CAS being applied was used. The freezer had been designed and constructed in consultation with ABI (ABI Corporation Ltd., Chiba, Japan) and the magnetic coils and control system supplied and commissioned by ABI. An air temperature of −20±1 °C with an air velocity 5 ms^{-1} across the garlic bulbs was used with the following CAS settings of: off, 0, 50 and 100 %. The magnetic field strength measured beside the product using a gaussmeter (GM 07, Magnetic Instruments Ltd., Falmouth, UK) at these settings were 0, 418, 155 and 98 μT, respectively.

Wire T-type (copper-constantan) thermocouples (1 mm diameter) were used to measure temperatures in the geometric centre of individual cloves forming a whole garlic bulb. Temperatures were recorded every 10 s using a datalogger (Eltek Type 1000, Grant Instruments (Cambridge) Ltd., UK) until temperatures in the cloves were reading below −18 °C. A total of three replicate experiments were carried out for each condition.

Freezing Curve Analysis

The super-cooling point (nucleation temperature) was interpreted from the freezing curves as the minimum temperature of the liquid phase and the initial freezing point, the maximum value after the adiabatic enthalpy jump.

Statistical Analysis

Statistical analyses were carried out using Excel (Microsoft Corporation, Microsoft Excel for Mac 2011, version 14.4.3). A Fisher's exact test was used to determine whether the occurrence of super-cooling in the groups was statistically different. An unpaired Student's t test was used to determine any difference in super-cooling point and super-cooling time in the groups. For $p<0.05$, the compared data sets were deemed significantly different within 95 % confidence.

Results and Discussion

Representative freezing curves for garlic samples are shown in Fig. 1 for the different treatments. These clearly show super-cooling occurring under a number of the conditions. Significant multiple secondary phase changes are also clearly shown in many of the freezing curves. These can be attributed to solute crystallisation, which is known to occur in foods as well as solutions (Rahman et al. 2002) and indicate that garlic contains multiple solutes with different eutectic points. This characteristic may have an influence on garlic's super-cooling properties and requires further investigation.

Overall summaries of the results for the five freezing treatments are shown in Tables 1, 2, 3 and 4. The super-cooling point, nucleation point or 'metastable limit

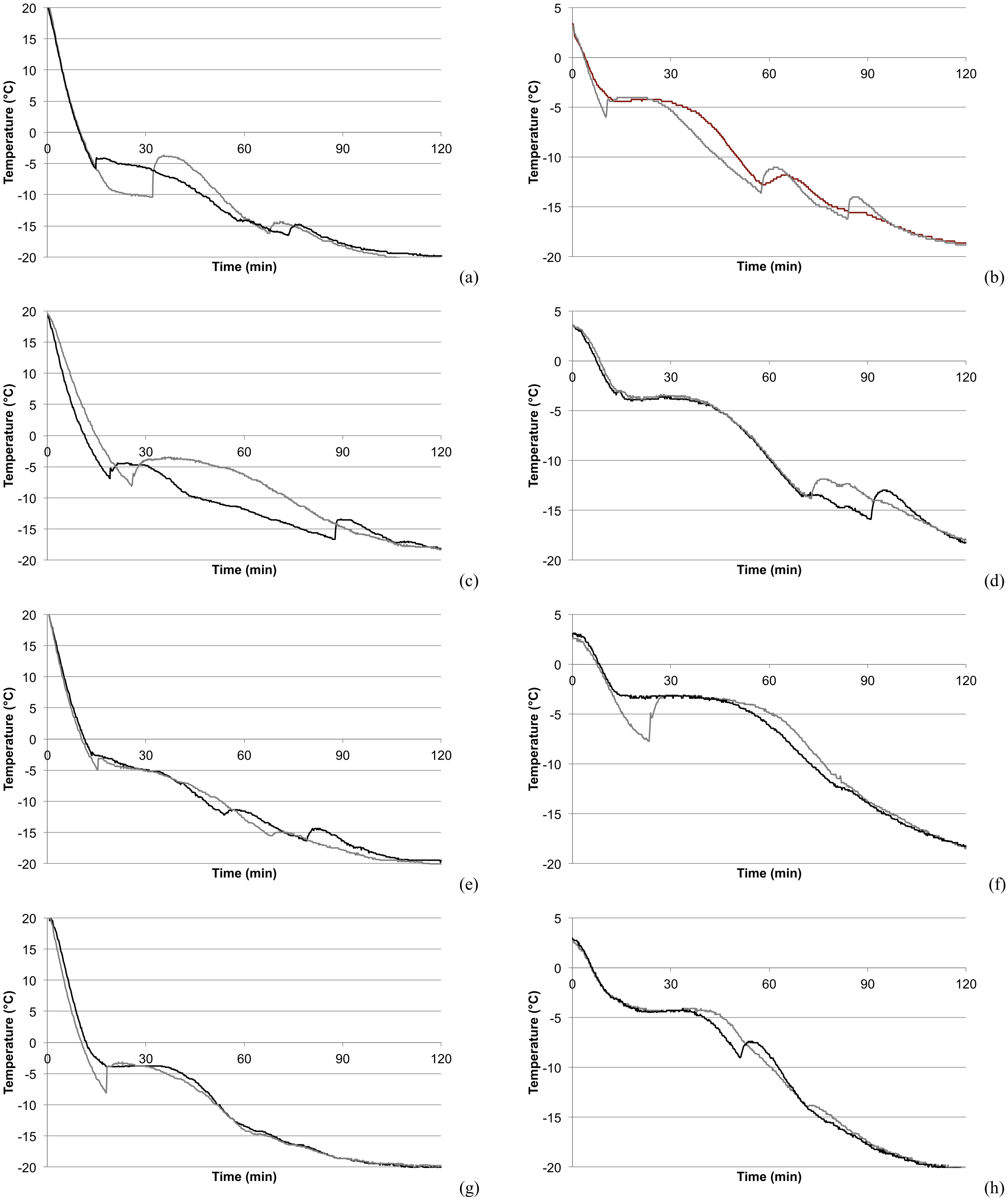

Fig. 1 Representative freezing curves (example curves where super-cooling did or did not occur) of individual garlic cloves in whole garlic bulbs, frozen in a batch air blast-freezer (−20±1 °C, 5 ms^{-1}): **a** from an ambient (21±1 °C) state without CAS, **b** from a chilled (4±0.5 °C) state without CAS, **c** from an ambient (21±1 °C) state with a setting of 0 % CAS, **d** from a chilled (4±0.5 °C) state with a setting of 0 % CAS, **e** from an ambient (21±1 °C) state with a setting of 50 % CAS, **f** from a chilled (4±0.5 °C) state with a setting of 50 % CAS, **g** from an ambient (21±1 °C) state with a setting of 100 % CAS and **h** from a chilled (4±0.5 °C) state with a setting of 100 % CAS

Table 1 Occurrence and degree of super-cooling in individual garlic cloves in whole garlic bulbs frozen from an ambient (21±1 °C) or chilled (4±0.5 °C) initial state in a batch air blast-freezer, without CAS (−20±1 °C, 5 ms^{-1})

	Ambient (21±1 °C)				Chilled (4±0.5 °C)			
	1	2	3	Overall	1	2	3	Overall
% of cloves within a whole garlic bulb that super-cooled	88 (7/8)	57 (4/7)	63 (5/8)	70 (16/23)	0 (0/5)	25 (2/8)	20 (1/5)	17 (3/18)
Super-cooling temperature (°C)[a]								
Mean	−8.0	−4.9	−6.8	−6.9	–	−5.4	−5.3	−5.4
SD	2.8	1.1	3.2	2.8	–	0.8	–	0.6
Min	−3.7	−3.2	−3.7	−3.2	–	−4.8	–	−4.8
Max	−11.4	−5.6	−11.0	−11.4	–	−6.0	–	−6.0
Degree of super-cooling (°C)[a]								
Mean	3.7	1.7	3.4	3.1	–	1.5	1.9	1.6
SD	2.6	0.8	2.0	2.2	–	0.7	–	0.6
Min	0.9	0.6	0.9	0.6	–	1.0	–	1.0
Max	6.6	2.4	5.8	6.6	–	2.0	–	2.0
Time before nucleation, i.e. end of super-cooled state (min)[a]								
Mean	1434.3	640	1190	1159.4	–	695	700	696.7
SD	481.6	119.7	323.2	480.6	–	77.8	–	55.1
Min	950	530	900	530.0	–	640	–	640
Max	2190	810	1680	2190	–	750	–	750

[a] In garlic cloves in which super-cooling occurred

temperature' (the point at which ice crystal nucleation is initiated), of individual garlic cloves in whole garlic cloves was found to be between −1.9 and −12.3 °C. This was in agreement with a previous study by the authors (James et al. 2009). Significant super-cooling prior to nucleation was seen in nearly all the freezing curves of individual cloves in whole

Table 2 Occurrence and degree of super-cooling in individual garlic cloves in whole garlic bulbs frozen from an ambient (21±1 °C) or chilled (4±0.5 °C) initial state in a batch air blast-freezer, with 0 % CAS setting (−20±1 °C, 5 ms^{-1})

	Ambient (21±1 °C)				Chilled (4±0.5 °C)			
	1	2	3	Overall	1	2	3	Overall
% of cloves within a whole garlic bulb that super-cooled	75 (6/8)	50 (4/8)	67 (4/6)	64 (14/22)	63 (5/8)	13 (5/8)	0 (0/7)	26 (6/23)
Super-cooling temperature (°C)[a]								
Mean	−7.5	−6.1	−6.1	−6.7	−8.5	−3.5	–	−7.7
SD	1.2	1.4	2.5	1.7	2.7	–	–	3.2
Min	−6.1	−4.6	−3.3	−3.3	−5.1	–	–	−3.5
Max	−9.0	−7.4	−8.6	−9.0	−11.8	–	–	−11.8
Degree of super-cooling (°C)[a]								
Mean	3.1	1.6	3.1	2.7	1.0	0.5	–	1.0
SD	1.5	1.1	1.9	1.6	0.3	–	–	0.3
Min	1.3	0.2	1.2	0.2	0.7	–	–	0.5
Max	4.7	2.6	5.7	5.7	1.5	–	–	1.5
Time before nucleation, i.e. end of super-cooled state (min)[a]								
Mean	1323.3	1552.5	965	1277.9	2060	720	–	1836.7
SD	351.5	322.4	64.5	364.4	868.2	–	–	949.9
Min	900	1850	870	870	600	–	–	600
Max	1900	1160	1000	1900	2670	–	–	2670

[a] In garlic cloves in which super-cooling occurred

Table 3 Occurrence and degree of super-cooling in individual garlic cloves in whole garlic bulbs frozen from an ambient (21±1 °C) or chilled (4±0.5 °C) initial sate in a batch air blast-freezer, with 50 % CAS setting (−20±1 °C, 5 ms^{-1})

	Ambient (21±1 °C)				Chilled (4±0.5 °C)			
	1	2	3	Overall	1	2	3	Overall
% of cloves within a whole garlic bulb that super-cooled	43 (3/7)	75 (6/8)	43 (3/7)	55 (12/22)	0 (0/6)	13 (1/8)	0 (0/5)	5 (1/19)
Super-cooling temperature (°C)[a]								
Mean	−4.8	−9.3	−9.0	−8.1	–	−7.7	–	−7.7
SD	2.3	1.4	2.2	2.6	–	–	–	
Min	−2.5	−7.1	−7.6	−2.5	–	–	–	
Max	−7.0	−11.4	−11.5	−11.5	–	–	–	
Degree of super-cooling (°C)[a]								
Mean	1.8	5.1	4.0	4.0	–	4.5	–	4.5
SD	1.2	1.9	2.0	2.1	–	–	–	
Min	0.6	1.8	2.8	0.6	–	–	–	
Max	2.9	7.3	6.3	7.3	–	–	–	
Time before nucleation, i.e. end of super-cooled state (min)[a]								
Mean	1043.3	2758.3	1516.7	2019.2	–	1470	–	1470
SD	146.4	1161.0	584	1142.4	–	–	–	
Min	910	1770	1020	910	–	–	–	
Max	1200	4550	2160	4550	–	–	–	

[a] In garlic cloves in which super-cooling occurred

garlic bulbs frozen under the different conditions in the batch air blast-freezer (Tables 1, 2, 3 and 4). In all cases, super-cooling occurred more often in cloves that were frozen from an initial ambient state than in those frozen from an initial chilled state (Table 5), this difference was statistically different for all freezing conditions. When super-cooling occurred, the

Table 4 Occurrence and degree of super-cooling in individual garlic cloves in whole garlic bulbs frozen from an ambient (21±1 °C) or chilled (4±0.5 °C) initial sate in a batch air blast-freezer, with 100 % CAS setting (−20±1 °C, 5 ms^{-1})

	Ambient (21±1 °C)				Chilled (4±0.5 °C)			
	1	2	3	Overall	1	2	3	Overall
% of cloves within a whole garlic bulb that super-cooled	75 (6/8)	75 (6/8)	38 (3/8)	63 (15/24)	0 (0/7)	29 (2/7)	0 (0/7)	10 (2/21)
Super-cooling temperature (°C)[a]								
Mean	−3.4	−5.7	−7.9	−5.2	–	−4.1	–	−4.1
SD	1.9	3.9	1.8	3.2	–	0.8	–	0.8
Min	−1.9	−2.0	−6.1	−1.9	–	−3.5	–	−3.5
Max	−7.1	−12.3	−9.7	−12.3	–	−4.7	–	−4.7
Degree of super-cooling (°C)[a]								
Mean	1.0	2.7	4.8	2.5	–	0.9	–	0.9
SD	1.2	2.5	1.9	2.3	–	0.5	–	0.5
Min	0.2	0.5	2.7	0.2	–	0.5	–	0.5
Max	3.4	7.2	6.3	7.2	–	1.2	–	1.2
Time before nucleation, i.e. end of super-cooled state (min)[a]								
Mean	875	1093.3	1210	1029.3	–	440	–	440
SD	178.4	282.5	330.5	272.8	–	155.6	–	155.6
Min	600	860	990	600	–	330	–	330
Max	1140	1630	1590	1630	–	550	–	550

[a] In garlic cloves in which super-cooling occurred

Table 5 Comparison of the occurrence of super-cooling in individual garlic cloves in whole frozen garlic bulbs frozen under a range of conditions at −20 °C, and mean super-cooling temperature and time before nucleation in garlic cloves in which super-cooling occurred

	Setting	Initial temperature of garlic bulb	
		Ambient (21±1 °C)	Chilled (4±0.5 °C)
Overall % of cloves that super-cooled	No CAS (conventional)	70a	17b
	0 % CAS	64a	26b
	50 % CAS	55a	5b
	100 % CAS	63a	10b
Mean (SD) super-cooling temperature (°C)[a]	No CAS (conventional)	−6.9 (2.8)a	−5.4 (0.6)a
	0 % CAS	−6.7 (1.7)a	−7.7 (3.2)a
	50 % CAS	−8.1 (2.6)a	−7.7 (−)
	100 % CAS	−5.2 (3.2)a	−4.2 (0.8)a
Mean (SD) time before nucleation, i.e. end of super-cooled state (min)[a]	No CAS (conventional)	1434 (481)ac	697 (55)c
	0 % CAS	1278 (364)af	1837 (950)df
	50 % CAS	2019 (1142)bg	1470 (−)
	100 % CAS	1029 (273)a	440 (156)ceg

[a] In garlic cloves in which super-cooling occurred; different letters in the same and across columns indicate a significant difference ($p<0.05$)

mean nucleation point temperature was between −4.2 °C (SD 0.8 °C) and −8.1 °C (SD 2.6 °C), depending on the freezing conditions. The application of a weak OMF during freezing appeared to have no statistically significant effect ($p>0.05$) on either the occurrence of super-cooling (Table 5), degree of super-cooling (Table 5) or stability of super-cooling. The lowest occurrence of super-cooling was found at a 50 % CAS setting, but this was not found to be significantly different.

Few studies have investigated the effect of different initial product temperatures on super-cooling. One of the few that have, Martins et al. (2011), reported that it is possible to obtain nucleation temperatures as low as −3.8 °C in the centre of a strawberry, if low initial temperatures (0 to 4 °C), low air temperatures (−45.0 to −32.5 °C) and high air velocities (5.5 to 10.0 ms^{-1}) are used during freezing. These results contradict the findings of our work (Table 5), which show that super-cooling in cloves within whole garlic bulbs is more likely to occur if the initial product temperature is high (ambient) rather than low (chilled). Further, as yet unpublished, studies by the authors on super-cooling in strawberries have also shown the same relationship as that reported here on garlic.

Overall, the results of our study (and similar studies by Suzuki et al. (2009) and Watanabe et al. (2011)) do not support the patent claims (Owada and Kurita 2001; Owada 2007) that OMF-assisted freezing enhances super-cooling in foods during freezing. In the authors' opinion, this does not, as yet, invalidate ABI's CAS system as a method of enhancing the overall freezing of foods; however it does suggest that weak OMF may not affect all foods and that any effect will depend on a complex combination of food, freezing rate and magnetic field frequency. Similar observations have been made in recently published studies using ABI equipment to freeze human tissues (Nakagawa et al. 2012).

Conclusions

Overall, the results of this short-targeted study clearly indicate that (1) significant super-cooling occurred in garlic bulbs during freezing under some of the freezing conditions used in these trials; (2) freezing under the OMF conditions used in these experiments had little significant additional effect on the freezing characteristics, or degree of super-cooling, of garlic bulbs in comparison with freezing under the same environment without OMF and (3) super-cooling is more likely to occur in garlic bulbs frozen from an initial ambient (21±1 °C) state than those frozen from an initial chilled (4±0.5 °C) state.

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